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The Powder Diffraction Intensities of Graphite for X-rays and Neutrons

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Measurements are reported of the powder diffraction intensities of graphite for both X-rays and neutrons, with due allowance for crystallite orientation, thermal vibrations and the rhombohedral modification. The neutron intensities agree with those calculated from the Bernal structure to within 5%, thus showing that discrepancies in X-ray intensities must be mainly due to the inadequacy of the James & Brindley *f* curve. Comparison with the curve given by McWeeny suggests a certain, but only small, asymmetry of electron distribution. The neutron intensities, although confirming the Bernal method of layer stacking, cannot decide for or against Lukesh's proposed slight distortion of the carbon hexagons.

Introduction

A number of workers have given data on the X-ray powder diffraction intensities of graphite and from them have drawn conclusions concerning the structure. Hofman & Wilm (1936) gave detailed results for Ceylon graphite and, interpreting these in terms of the Bernal (1924) structure and the James & Brindley (1931) atomic scattering curve for carbon, concluded that the measured intensities of the *hkil* lines (excluding the $000l$ lines) were too weak and that the *hki*0 lines were too weak when $h = k$ but not otherwise. These conclusions led them to postulate that even in Ceylon graphite there is a considerable number of randomly oriented layers in the stacks of parallel carbon planes. With less crystalline graphites Hofmann & Wilm made similar measurements and deduced an increasing proportion of random layers. However, if this explanation of the observed intensities were true it would be expected that $10\bar{1}1$, like $20\bar{2}1$ and $12\bar{3}1$, would have a measured intensity well below the calculated value, but this is not found.

An independent set of measurements for a well-crystallized graphite was given much later by Lipson & Stokes (1942) in their paper which proposed the existence of the rhombohedral form of graphite. These authors explained the observed intensity relations, which might be roughly described as showing a falling away of intensity with Bragg angle θ, as due to the effect of thermal vibrations. The inadequacy of this explanation was pointed aut by Franklin (1950) and confirmed by the writer (Bacon, 1950*a*) who showed that the thermal vibrations were both too small and too anisotropic for Lipson & Stokes's interpretation to be correct. Moreover, when measurement is extended to reflexions from planes such as $12\bar{3}0$ and $12\bar{3}1$, which have smaller *d* values, very marked inconsistencies appear.

In addition to the different interpretations of the above authors there are found to be appreciable divergences in the two sets of measured intensities when these are examined in detail: for example the ratios of the $11\bar{2}0$ and 0006 intensities differ by a factor of two in the two cases. It is clear, therefore, that more precise intensity data are required for any fuller investigation of the relation between observed and calculated intensities. In seeking to obtain this, particular attention is paid, in the experimental work to be described, to making due allowance for the effects of preferential crystallite orientation and thermal vibrations. In calculating the theoretical intensities with which these new experimental data are to be compared it is clear that two main assumptions have to be made, and both of these assumptions have been questioned. First, the truth of the Bernal structure of graphite has to be considered. Lukesh & Pauling (1949) have suggested an alternative, orthorhombic, method of stacking graphite layers, giving equal co-ordination to all atoms, in order to account for the apparent enhancement of the $10\bar{1}0:11\bar{2}0$ intensity ratio. In addition, these same authors (Lukesh, 1950) postulated rather smaller changes within the carbon layers to account for observed twinning relations in pseudo-single crystals. Secondly, the use of the James–Brindley *f* curve has to be justified. Indeed Franklin (1950), from absolute measurements with poorly crystallized carbons, has concluded that this is not justifiable and has postulated that the electron distribution about the carbon atoms is far from spherically symmetrical, the *L* electrons being in fact concentrated about the centres of the C–C bonds. Subsequently, McWeeny (1951), recalculating the *f* curves of the light elements using more recent wave-mechanical methods, concludes that even in the absence of asymmetry due to bonding effects the expected *f* curve will be markedly different from the James–Brindley curve for values of $\sin \theta/\lambda$ less than 0·4 Å^{-1}.

It is in considering the above two main assumptions, concerned respectively with inter- and intra-atomic arrangements, that the value of supplementing the

X-ray intensity data with corresponding information from neutron diffraction becomes apparent. The process of neutron scattering by a carbon atom is a nuclear phenomenon in contrast to the electronic scattering of X-rays. The diffracted intensities will therefore depend on the nuclear positions (i.e. on the truth of the Bernal structure), but not on the electronic configuration. Moreover, absolute measurement of the intensities can be made quite easily. It will, in fact, be found that the neutron data provide significant evidence for the interpretation of the X-ray measurements.

Intensity measurements by X-ray diffraction

The sample of graphite chosen for the measurements was a highly crystalline specimen of electric-furnace graphite, produced by decomposition of carborundum. This sample occurred in the form of a soft block, of a very low density of about 0·6 g.cm.$^{-3}$, and transmission measurements using thin sections gave 0002 diffraction rings displaying no detectable preferential orientation. Moreover, the proportion of rhombohedral modification was only 4% (Bacon, 1950*b*).

Approximately cylindrical specimens, of diameter about 0·5 mm., were cut from the solid with a razor blade and examined in a standard 19 cm. camera using filtered Cu $K\alpha$ radiation. In order to confirm that there were no orientation errors, specimens were cut not only along the apparent grain of the material but also, with more difficulty, across it. The specimens were very fragile and the surfaces of the block were coated with collodion during the cutting. In the course of the measurements it became clear, from inconsistencies in the intensity ratios found for different specimens, that a certain amount of orientation had been produced during the process of preparing the specimens. The degree of orientation was much less than that found in specimens prepared by other methods such as extrusion, rolling, or filling a capillary tube with powder (as remarked upon by Nelson & Riley, 1945) but was large enough to make correction for it essential.

Correction for preferential orientation

In specimens of this sort the orientation takes the form of a tendency for the layer planes of the graphite crystallites to lie parallel to the length of the specimen. It can be described in terms of an orientation function $I(\varphi)$ defined such that $I(\varphi).dw$ is the fraction of the material for which the c axes lie within a solid angle dw about a line inclined at any particular angle φ to the length of the specimen. The form of this function can be found from the intensity distribution around the 0002 diffraction ring on a transmission photograph and it is then possible to calculate the intensity enhancement, relative to the *hki*0 reflexions, which would be expected for any plane. The result of such calculation is shown in Fig. 1, where the enhancement is plotted against the orientation, as specified, arbitrarily, by the ratio of the minimum and maximum intensities found on the 0002 ring of the vertically-mounted cylindrical specimen. As would be expected the enhancement ratio is largest for the 000*l* planes and falls to unity when the diffraction ring is of uniform intensity.

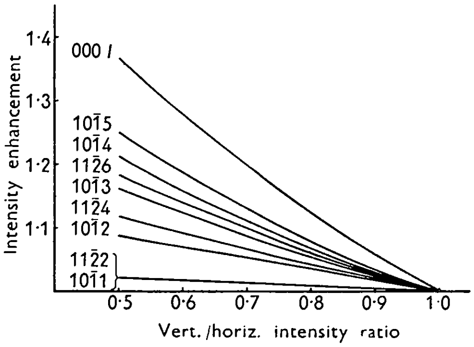

Fig. 1. The variation of intensity enhancement with degree of preferential orientation, as represented by the asymmetry of the diffraction ring on a transmission photograph.

By means of the curves given in Fig. 1 the experimental intensities for eight different specimens were corrected for orientation. The transmission photographs were taken by using a horizontal-slit collimator and scanning the specimen vertically, in order to include the same material as was irradiated for the powder photograph while at the same time obtaining a diffraction ring of uniform width. Table 1 shows the results obtained in the case of the (0002) reflexion, the intensities being expressed for convenience as the ratios of the experimental values to those calculated for the James–Brindley *f* curve and the Bernal structure, normalized to a value of unity for ($11\bar{2}0$).

In addition to the above method of correction of the intensity values of the individual specimens, the measured values were also plotted graphically against the values of the vertical/horizontal intensity ratio found on the transmission photographs of the individual specimens. The resulting curves, shown in Fig. 2 for 0002, 0004 and $11\bar{2}6$, were then extrapolated to the value unity on the axis of abscissae. Table 2 lists both the 'mean' and 'extrapolated' values

Table 1. *Orientation correction*; (0002) *reflexion for X-rays*

Specimen No.	1	2	3	4	5	6	7	8
Vert./horiz. ratio	0·6	0·74	0·75	0·81	0·93	0·93	0·95	0·98
Measured intensity enhancement	2·02	1·81	1·78	1·70	1·63	1·52	1·63	1·57
Enhancement corrected for orientation	1·54	1·54	1·53	1·52	1·57	1·47	1·58	1·56

Mean corrected intensity enhancement: 1·54.

Table 2. *X-ray intensity enhancements for zero preferential orientation*

Reflexion	0002	0004	0006	0008	11$\bar{2}$4	11$\bar{2}$6	10$\bar{1}$2	10$\bar{1}$3	10$\bar{1}$5
Mean value	1·54	1·44	0·96	0·71	0·83	0·64	1·09	1·08	0·73
Extrapolated value	1·53	1·42	0·93	0·72	0·84	0·66	1·10	1·12	0·67

for those of the reflexions for which the effect of orientation was sufficiently large to merit correction. The agreement between the two sets of values is considered to be good enough to accept their mean as an accurate value of the intensity enhancement at zero preferential orientation and to confirm the analysis of the effect of orientation on the intensities.

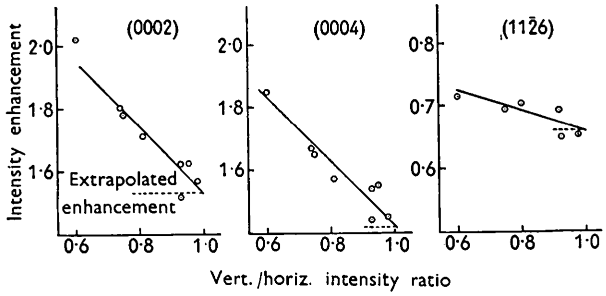

Fig. 2. Correction of experimental intensities for preferential orientation.

Correction for thermal vibrations

Magnus (1923) has calculated from specific-heat measurements the values of 2280° K. and 760° K. respectively for the Debye temperatures Θ_x and Θ_z applicable to vibrations in and perpendicular to the graphite layer planes. These values have been compared with deductions made from X-ray intensity measurements on identical specimens at room temperature and at a number of temperatures in the region of 500° C. These showed that the components of thermal vibration are a maximum along the c axis and fall off approximately as $\cos \alpha$ to a negligible value in the plane of the carbon layers, where α is the inclination to the c axis. This conclusion, which led to an estimate of 560° K. for Θ_z, depends very largely on the intensities of 11$\bar{2}$4 and 11$\bar{2}$6, planes whose normals are inclined at 54° and 42° respectively to the c axis. Unfortunately, the higher-angle 000l lines, namely 0006 and 0008, are too weak at the higher temperature to permit a very accurate direct determination of Θ_z; however a series of measurements of 0004 did suggest that the true value of Θ_z was higher than that deduced from the $\cos \alpha$ relation and a mean value of 700° K. was obtained.

From the foregoing results it was concluded that correction of the room-temperature intensity data for thermal vibrations could be best made by using the expression

$$\log_{10} (I/I_0) = -(0{\cdot}23 \cos^2 \alpha + 0{\cdot}05 \sin^2 \alpha) \sin^2 \theta$$

for planes close to the horizontal or vertical, but the empirical relation

$$\log_{10} (I/I_0) = -0{\cdot}35 \cos^2 \alpha . \sin^2 \theta$$

for the intermediate planes. The factor 0·05 is that deduced from the value of $\Theta_x = 2280°$ K. determined from specific-heat measurements, the variation of the X-ray intensities being too insignificant for Θ_x to be deduced from the latter. The root-mean-square error in the factors 0·23 and 0·35 in the above equations is ±0·05 so that in the cases of 0004, 0006 and 0008 the probable errors in the correction for thermal vibrations are greater than the likely errors in the experimental intensity measurements at room temperature.

Calculation shows that the variation of absorption

Table 3. *X-ray intensities for highly crystalline graphite*

Line	Experimental intensity relative to J–B calculation (corrected for orientation)	Intensity corrected for temperature (renormalized to 11$\bar{2}$0)	Experimental f value in electron units (amplitude)	McWeeny's f value corrected for 0·12 concentrated electrons
0002	1·53	1·51	4·60±0·04	4·58
10$\bar{1}$0	1·61	1·56	3·31±0·05	3·25
10$\bar{1}$1	1·68	1·65	3·27±0·04	3·11
10$\bar{1}$2	1·08	1·10	2·45±0·04	2·79
0004	1·43	1·51	2·70±0·07	2·62
10$\bar{1}$3	1·09	1·17	2·28±0·05	2·37
10$\bar{1}$4	0·68	0·78	1·71±0·07	2·08
11$\bar{2}$0	1	1	1·87	1·87
11$\bar{2}$2	0·93	0·97	1·79±0·02	1·77
10$\bar{1}$5	0·70	0·86	1·68±0·06	1·87
0006	0·96	1·17	1·94±0·11	1·89
20$\bar{2}$1	0·69	0·70	1·47±0·03	1·44
11$\bar{2}$4	0·83	0·95	1·66±0·05	1·60
0008	0·71	1·05	1·59±0·14	1·66
11$\bar{2}$6	0·65	0·91	1·47±0·05	1·49
12$\bar{3}$0	1·06	1·12	1·62±0·06	1·58
12$\bar{3}$1	0·92	1·00	1·53±0·04	1·57

correction from end to end of the film is only 0·5%; this correction was accordingly neglected.

Experimental results

Table 3 summarises the experimental results, showing, for all the lines which could be measured adequately, the intensity enhancement relative to the James & Brindley f curve and Bernal structure calculation and, also, the apparent f value in electron units. The f values are normalized to give the James & Brindley value of 1·87 for $11\bar{2}0$ and are shown together with the estimated experimental error.

The theoretical values shown in the last column of Table 3 will be considered subsequently. For the present we draw attention to the values given in the third column of the table. The fact that some of these values, in particular the lower-angle lines and $20\bar{2}1$, differ markedly from unity must be interpreted as due to divergences from the James & Brindley curve or the Bernal structure.

Before pursuing this interpretation further by discussing the corresponding data obtained by neutron diffraction, a few remarks will be made on a similar series of X-ray intensity measurements made with a more poorly crystallized material for which p, the probability of layer displacement, was 0·2. The results can be summarised as being in agreement with those for the highly crystallized sample, provided that in the case of broad lines such as $11\bar{2}4$, $11\bar{2}6$ and $12\bar{3}1$ correction is made for the effect of photometry over only a finite range, as discussed by Wilson (1942). This correction is made using the formula for line shape appropriate to a stack of carbon planes in which the distribution of disoriented layers is random, which has already been justified for this particular graphite (Bacon, 1951). In the case of the $11\bar{2}6$ line, for example, there is a correction of 50% even when integration is carried out over a distance of ±10 mm. on the film. For completeness it is also remarked here that these intensity measurements do not, therefore, support the writer's suggestion (Bacon, 1950*c*) that the apparent displacement of *hki*0 maxima might be due to the effect of the superposition of a displaced diffraction peak from a proportion of separate turbostratic material; these displacements have already been accounted for in an alternative manner (Bacon & Franklin, 1951).

Intensity measurements by neutron diffraction

The measurements to be discussed were made with the double-crystal spectrometer described by Bacon, Smith & Whitehead (1950), the diffraction patterns being plotted directly by connecting the output of a neutron counting ratemeter to a pen recorder. The first results, already reported briefly (Bacon, 1950*a*), were made with a solid slab of artificial graphite. Although this material (referred to above) was poorly crystallized ($p = 0{\cdot}2$) it was used in this early work on account of its relatively high density and low orientation. Any attempt to produce a sample of equal density with well crystallized material would have resulted in very high orientation, thus making the results very dependent on precise correction for this. With the poorer crystallized sample, however, the smaller orientation correction could be determined adequately by X-rays and allowed for on the basis of the curves given in Fig. 1, as discussed in the previous section. The neutron counting rates and resolution in these first records, of which a sample is shown as Fig. 3(i), were sufficient to determine the intensities only of 0002, ($10\bar{1}0+10\bar{1}1$) and ($11\bar{2}0+11\bar{2}2$), the two lines in the last two pairs being unresolved. The values obtained, expressed as the mean ratio of experimental to calculated intensity for eight independent recordings, are given in Table 4 together with the root-mean-square error.

Table 4. *Experimental neutron diffraction intensities for graphite with* $p=0{\cdot}2$

Line	Normalized integrated intensity relative to calculated
0002	1·02±0·02
$10\bar{1}0+10\bar{1}1$	1·05±0·04
$11\bar{2}0+11\bar{2}2$	1·00

As expressed in Table 4 the intensities are normalized to unity for the pair of lines ($11\bar{2}0+11\bar{2}2$) but it was found by comparison of the integrated intensity of the (0002) line with that found for the (111), (220) and (311) lines of diamond, in the manner described by Wollan & Shull (1948), that the intensities are in fact absolute values within the experimental accuracy of 5%. These preliminary results therefore provide strong support for the Bernal structure.

With improvements in the neutron diffraction apparatus, in particular the use of enriched boron in the BF_3 counter and a lead crystal (kindly provided by Dr C. G. Shull of Oak Ridge, U.S.A.) as monochromator, an increase of counting rate by a factor of about six times was achieved. With the sacrifice of some of this to gain improved resolution, a much more satisfactory diffraction pattern was obtained, as illustrated in Fig. 3(ii). Not only are $11\bar{2}0$ and $11\bar{2}2$ practically completely resolved but 0004 is well defined and $10\bar{1}2$ and $10\bar{1}3$ are clearly evident. In fact, the definition of $10\bar{1}2$ and $10\bar{1}3$ is now limited by diffraction broadening as much as by geometrical resolution.

Consideration of Fig. 3(ii) suggested that under the improved conditions a satisfactory pattern would be obtained with the low-density highly-crystalline graphite used for the X-ray measurements. This offered the advantages of negligible diffraction broadening, a known very low rhombohedral content and very low orientation. In fact, by using a cylindrical specimen bathed in the neutron beam, rather than the more conventional parallel-side block arranged for transmission, it was possible to eliminate the effect of

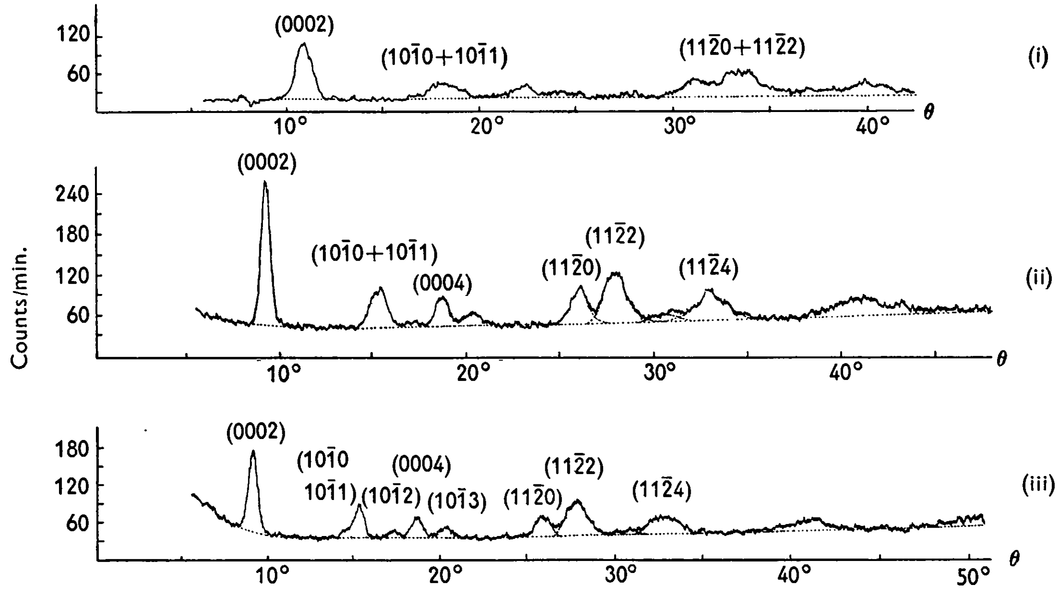

Fig. 3. Neutron diffraction patterns. (i) Initial results for graphite block, $p = 0{\cdot}2$, in transmission orientation; $\lambda = 1{\cdot}25$ Å. (ii) Improved results for same specimen; $\lambda = 1{\cdot}08$ Å. (iii) Cylindrical specimen of highly crystalline graphite bathed in neutron beam; $\lambda = 1{\cdot}08$ Å.

orientation instead of measuring and correcting for it. It can be shown that when the preferred orientation consists of a tendency for the basal planes to lie parallel to an axis the enhancements I_{11} and I_x, for parallel and cross-cut specimens respectively, are related by the equation

$$\tfrac{1}{3}(I_{11}+2I_x) = 1\,.$$

Thus if I_{11} and I_x can be measured with the same specimen the orientation effect can be eliminated. Initially a specimen of the solid material was cut in the form of a cylinder about $\frac{5}{8}$ in. in diameter and $1\frac{1}{4}$ in. in length, with the axis along the grain. Ten independent diffraction patterns were taken with the specimen bathed in the neutron beam. Subsequently it was cut into two portions and reassembled with the two grain directions horizontal and mutually perpendicular, followed by slightly trimming to a roughly cylindrical form. As in the case of the preparation of the X-ray samples, some surface orientation will be produced during this cutting. However, this now constitutes only a very small fraction of the total volume of material and the effect on the intensities will be negligible. The cylindrical specimens were rotated at about 1 rev./min., this being necessary in the case of the cross-grain specimen in order to give effectively circular symmetry about the vertical axis; it is this same requirement which made it necessary to use a cylindrical specimen rather than a parallel-sided block.

Fig. 3 (iii) shows a typical record obtained in this way and Table 5 summarises the results obtained. In order to allow for small day to day variations in pile power during the course of the ten recordings of each specimen the measured intensities of each pattern were normalized by making the sum of the integrated intensities of all the lines listed equal to 1000 units. Attention is drawn to the smallness of the differences between I_{11} and I_x, indicating the very small orientation which existed in this particular variety of soft graphite block.

The calculated intensities given in Table 5 are those determined from the Bernal structure and have been corrected for thermal vibrations using the factors

Table 5. *Highly crystalline graphite, cylindrical samples bathed in the neutron beam*

Line	Experimental intensities			Calculated Intensities (normalized to sum 1000)	Intensity ratio exp./calc.
	I_{11}	I_x	$\frac{1}{3}(I_{11}+2I_x)$		
0002	258±7	235±3	243±6	241	1·01±0·03
$10\bar{1}0+10\bar{1}1$	117±5	127±3	124±5	122	1·02±0·04
$10\bar{1}2$	24±2	25±2	25±3	26	0·96±0·11
0004	66±2	58±2	61±3	58	1·05±0·05
$10\bar{1}3$	54±2	51±2	52±3	56	0·94±0·05
$11\bar{2}0$	97±4	109±2	105±4	106	0·99±0·04
$11\bar{2}2$	226±5	236±3	233±5	233	1·00±0·02
$11\bar{2}4$	160±5	160±5	160±7	161	1·00±0·04

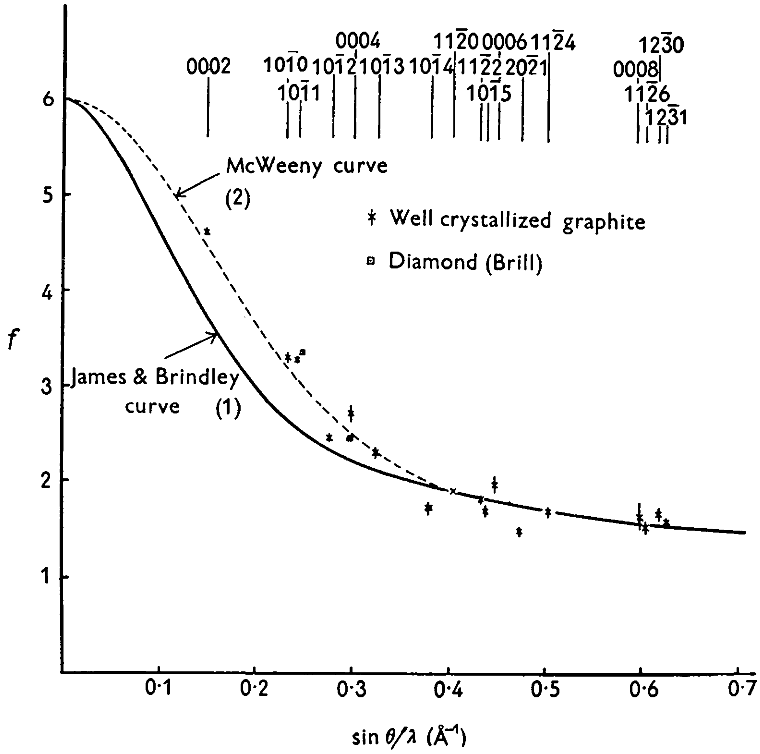

Fig. 4. Comparison of experimental *f* values with theoretical curves given by James & Brindley and by McWeeny.

obtained from the X-ray measurements. The variation of absorption correction with Bragg angle θ can be shown to be negligible. In the case of the lines $11\bar{2}2$ and $11\bar{2}4$, small corrections were made for the neighbouring pairs of weak lines $10\bar{1}5$, 0006 and $20\bar{2}2$, $20\bar{2}3$, respectively, which are inevitable included in the measured areas on the still relatively poorly resolved neutron diffraction records.

Bearing in mind that it has already been shown that the 0002 intensity for graphite is in absolute agreement with calculation to within 5%, it is considered that the values listed in the last column of Table 5 afford very strong evidence in support of the Bernal structure of graphite. In particular, they demonstrate that the alternative method of layer stacking suggested by Lukesh & Pauling (1949) cannot be correct since this would require rougly twofold changes in certain intensities. Whether they are adequate to distinguish between the ideal Bernal structure and one having slightly distorted, orthorhombic, layers will be considered in the subsequent discussion.

Discussion

It follows from the neutron diffraction results that essentially the whole of the discrepancy between the experimental X-ray intensities and the calculation based on the James–Brindley *f* curve and the Bernal structure appears to be due to the incorrectness of the *f* curve. The experimental *f* values which were given in column 4 of Table 3 are shown, with the estimated errors, in relation to the James–Brindley curve in Fig. 4 (Curve 1). Apart from the $000l$ reflexions and $20\bar{2}1$, the agreement is reasonably good for values of $\sin\theta/\lambda$ greater than 0·4. Rather similar results have been reported by Brill (1950) for the case of diamond. Brill finds good agreement at and above the value 0·4 but for the reflexions (111) and (220), which have values of $\sin\theta/\lambda$ lower than this, the intensities are well above the calculated curve. These two points are marked in Fig. 4, where it is seen that the enhancement is of the same order as for the reflexions from graphite.

Franklin (1950), in considering the enhancement of the (10) band from single carbon layers, has postulated that the three sp^2 electrons of the carbon atom are concentrated at the centres of the C–C bonds rather than being distributed uniformly about the atom centres. However, it appears that if sufficient concentration is assumed to account for the observed enhancement of the $10\bar{1}0$ line in graphite then large undesired changes are found in other lines—in particular $11\bar{2}0$ and $12\bar{3}0$. It appears that any large concentration of electron density cannot be reconciled with the experimental results, although, as will be suggested later, a small concentration may indeed occur.

McWeeny (1951) has recently recalculated the atomic *f* curve for carbon using analytical approximations to atomic wave functions given by Duncanson &

Coulson (1944). This new f curve is shown as Curve 2 in Fig. 4. It will be noticed that when $\sin\theta/\lambda$ is greater than 0·4, i.e. in the region where the experimental points lie on the James–Brindley curve, McWeeny's curve is very little different; on the other hand when $\sin\theta/\lambda < 0{\cdot}4$ McWeeny's curve is a very much better approximation to the experimental results, including those for diamond. McWeeny's analysis, as so far reported, does not allow for any bonding effects between atoms and it would be expected that the detailed discrepancies remaining between the experimental points and Curve 2 can be explained by such effects. It can be shown in an approximate manner that these need not be very large. A very slight concentration of electrons at the C–C bond centres would account for the significant weakness of $20\bar{2}0$ and $20\bar{2}1$, which are very sensitive to this; the concentration necessary is very much less than Franklin's original hypothesis would require and is, in fact, only about 0·04 electrons per bond per atom. If this concentration is assumed then a good deal of the noticeable discrepancy in the $000l$ reflexions also disappears, although there is no very great effect on other reflexions. The final column in Table 3 gives McWeeny's f values after an empirical correction is made in this way by taking a fraction 0·98, i.e. $(1-0{\cdot}12/6)$, of McWeeny's value with the addition of the amplitude given by the concentrated 0·12 electrons, making due allowance for the phases of the individual contributions. Comparison with the previous column of Table 3 shows that these corrected values are within the limits given for the experimentally determined amplitudes in the case of eleven of the sixteen lines measured. The five remaining lines are $10\bar{1}1$, $10\bar{1}2$, $10\bar{1}3$, $10\bar{1}4$ and $10\bar{1}5$ for which the extreme experimental amplitudes differ by $+4$, -10, -2, -15 and -7% respectively from those calculated. Of these, the discrepancy in $10\bar{1}2$ seems most significant since it is a quite strong well resolved line for well crystallized graphite, whereas $10\bar{1}4$ and $10\bar{1}5$ are weak lines and the latter is not perfectly resolved. It remains to be seen whether any future refinement of the wave-mechanical calculation to allow for bonding effects will support this low intensity found experimentally for $10\bar{1}2$.

Finally it remains to consider the neutron diffraction results a little further in the light of Lukesh's (1950) suggestion of distorted hexagons in the carbon layer planes, giving rise to a new unit cell which comprises fifteen of the normal orthohexagonal cells. It is presumed that the atoms in this large cell are displaced slightly from their normal positions in such a way as to replace the 120° hexagon angles by values of, say, $121\frac{2}{3}$ and $119\frac{1}{6}$°, to account for the reported prevalence of $2\frac{1}{2}$° twinning. It is these slight displacements which result in the production of a repeat unit of increased size, giving rise to weak satellite spots. Lukesh has pointed out that these extra reflexions would not be distinguished on powder photographs since not only are they very weak (a few per cent of the main reflexions) but also they occur at positions where they overlap other diffraction lines. To produce angular changes of the above magnitude between atoms 1·42 Å apart would require movements of the order of 0·03 Å. The consequent intensity changes will be greatest for the $hki0$ lines and if, over the large unit cell, the movements were effectively random they would be estimated to cause intensity reductions of about 2% and 5% for $11\bar{2}0$ and $12\bar{3}0$ respectively. Changes of this magnitude are less than the experimental errors of both the neutron and X-ray measurements which have been considered.

Conclusion

It is therefore concluded that the neutron diffraction powder intensities, while demonstrating that the Bernal structure of graphite is, at least, very nearly correct, are not able to decide for or against Lukesh's proposed slight distortion of the carbon hexagons. It seems that evidence for the atomic displacements within the large unit cell can come only from X-ray single-crystal intensity measurements. It is also concluded that McWeeny's theoretical f curve accounts for most of the apparent discrepancies in the X-ray intensities, but some smaller inconsistencies outside the experimental error do indeed remain. Of these the low value of $10\bar{1}2$ seems most significant and it remains to be seen whether this can be accounted for by bonding effects. It is unfortunate that this is a reflexion for which the neutron diffraction results are hardly conclusive; it could still be represented that the reason for this discrepancy may be either inter- or intra-atomic. Future improvement in the resolution of the neutron diffraction pattern could give a decisive answer.

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The Crystal Structure of Ammonium Trioxalatochromate (III), $(NH_4)_3[Cr(C_2O_4)_3].2H_2O$

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The crystal structure of $(NH_4)_3[Cr(C_2O_4)_3].2H_2O$ is triclinic $P\bar{1}$, with two formula units in a cell of dimensions $a=7{\cdot}79$, $b=10{\cdot}90$, $c=10{\cdot}73$ Å, $\alpha=98°\ 10'$, $\beta=112°\ 36'$, $\gamma=67°\ 22'$. By evaluating the functions $\sigma(x, y)$, $\sigma(y, z)$ and $\sigma(x, z)$, projections of the structure on three crystallographic planes were obtained.

The 72 independant parameters of the 24 atoms comprising a formula unit are given, and the configuration of the two stereo isomeric complex ions $[Cr(C_2O_4)_3]$ in a unit cell is described. Each of the three oxalato groups in a complex ion is planar, the inner oxygen atoms of such groups forming a slightly distorted octahedron round the central chromium atom.

The ammonium ions and the water molecules form the main bonds in the structure. Two of the three ammonium ions approach each other to within a distance of 3·06 Å. This distance is considerably shorter than the other ammonium–ammonium distances, which are found to be 3·72 and 3·83 Å.

It is shown that this ammonium and the corresponding potassium structure are isotype if, for any one of these structures, the complex ions together with their associated cations are rotated through 180° about the central chromium atoms. It is further illustrated that such a rotation results in the novel feature that a $P(0, v, \frac{1}{2}c)$ Harker section then gives direct evidence as to whether similar unknown structures belong to the potassium or to the ammonium scheme of packing.

1. Introduction

The crystal structure of the corresponding potassium salt has been previously described by the authors (Niekerk & Schoening, 1952). It was pointed out in this publication that the presence of four comparatively heavy atoms in a formula unit, together with the fact that the crystal was treated throughout as belonging to the pseudo space group $C2/c$, severely restricted the accuracy with which interatomic distances for the complex ion $[Cr(C_2O_4)_3]$, could be determined by using the double Fourier series method. These difficulties do not appear in the corresponding ammonium salt. Furthermore, a preliminary investigation of these two salts (Niekerk & Schoening, 1951*b*) showed that they are not isomorphous as was previously reported by Wyrouboff (1900) and by Rammelsberg (1854). The potassium salt is monoclinic whereas the ammonium salt is triclinic, although its apparent monoclinic symmetry is very pronounced. The present investigation was therefore undertaken with the aim of obtaining more accurate interatomic distances for the complex ion, and if possible to determine why and how the two structures differ.

2. Crystal data and space group

The crystals were prepared by Mr du Plessis of the Pretoria University following the method described by Werner (1912*a*, *b*). The crystals are triclinic, dark blue in colour, and generally crystallize in the form of fairly thick plates. The primitive triclinic unit cell, as determined from oscillation and Weissenberg photographs, was found to be

$$a = 7{\cdot}79,\ b = 10{\cdot}90,\ c = 10{\cdot}73\ \text{Å}\,,$$
$$\alpha = 98°\ 10',\ \beta = 112°\ 36',\ \gamma = 67°\ 22'\,.$$

The space group can be either $P1$ or $P\bar{1}$. If, from chemical consideration and by analogy to the corresponding potassium salt, two stereo isomeric complex ions are assumed in the unit cell, the space group is then fixed as $P\bar{1}$. Density measurements and the