Acta Cryst. (1955). **8**, 187

The X-ray Anomalous Reflexions from Diamond

BY J. A. HOERNI* AND W. A. WOOSTER

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(*Received* 20 *March* 1954 *and in revised form* 1 *November* 1954)

The anomalous X-ray reflexions from diamond have been investigated quantitatively using a photographic method. This investigation is restricted to the anomalies which correspond in reciprocal space to 'spikes' passing through certain reciprocal-lattice points, parallel to $\langle 100 \rangle$. It is found that the scattering density varies along the spikes according to the inverse 2·2 power of the distance from the associated reciprocal-lattice point. The 'spike magnitude' defined in the text is proportional to the scattering density of the spike at unit distance from the reciprocal-lattice point divided by the square of the corresponding structure amplitude. It is found that for spikes parallel to [100], the spike magnitudes only depend on the index h of the reciprocal-lattice points. Their relative values are < 5, 100, 75, 5 and 30 for $h = 0$, 1, 2, 3 and 4 respectively. Similar relations exist between the spikes parallel to [010] and [001], and the indices k and l. A theory to explain some of these results is advanced, based on the assumption that diamond has a domain texture and that each domain has a special atomic property associated with one of the three directions [100], [010], [001]. If the unique axis of a given domain is [100] then any one lattice plane parallel to (100) is populated by atoms of identical scattering power. The scattering power of the atoms in the various lattice planes varies in a random manner from one plane to another. A consequence of this theory is that not all of the carbon atoms in diamond are tetrahedrally symmetric.

1. Introduction

The extra X-ray reflexions from diamond are of two kinds. One is dependent upon temperature and may be identified with the thermal diffuse reflexion. The other is unique to diamond, is structure sensitive (being entirely absent in some crystals), is largely independent of temperature, and is described in reciprocal space in the following way. Through each reciprocal-lattice point there may be one, two or three reciprocal spikes which give rise to X-ray reflexions when they cut the reflecting sphere. These spikes are parallel to the axes $\langle 100 \rangle$. The boundary of a section of a spike normal to its length is as sharply defined as the boundary of a reciprocal-lattice point. Both of these types of reflexion have been described by a number of authors (Raman & Nilakantan, 1940; Lonsdale & Smith, 1941; Lonsdale, 1942; Guinier, 1944; Grenville-Wells, 1951; Hoerni, 1952; Hoerni & Wooster, 1952*a*). The spike-reflexions have not so far received an adequate quantitative experimental study nor a complete explanation. The density of the spike falls off with increasing distance from the reciprocal-lattice point and is centrosymmetrical with respect to that point. The present experimental investigation relates to the following matters: (i) the law of variation of the scattering density along a given spike, (ii) the relative densities of different spikes, (iii) the absolute spike-density for a given crystal, (iv) some measurements on different crystals.

2. Experimental method

Laue photographs were used throughout in this work and were mainly taken on a Weissenberg goniometer having a camera radius of 10·0 cm. and a translation–rotation ratio of 3 mm. per deg. The goniometer was provided with an electric clock mechanism which, every fifteen minutes, caused the crystal to perform one oscillation of a few degrees and to return to its original setting. During this oscillation the crystal passed through the setting corresponding to the Bragg reflexion of the reciprocal-lattice point to which the spike belonged. Also during the oscillation, an absorbing screen was automatically inserted in the path of the incident X-rays so as to cut down the intensity of the Bragg spot and make it comparable in density with the spike spot. A series of such photographs with Laue settings of the crystal progressively removed from the Bragg setting is shown in Fig. 1(*a*).

During an exposure lasting several hours the traverse across the Bragg setting was made a sufficient number of times to ensure that no serious error arose in comparing spike- and Bragg-reflexions due to variations in the intensity of the incident X-rays. If the measured intensity in the film is I and the maximum intensity of the Bragg spot is I_{Bm}, then we can obtain a 'reduced intensity', I', from the equation

$$I' = \frac{I}{I_{Bm}} \frac{n}{T},$$

where n is the number of times the crystal traverses the Bragg setting and T is the time during which the spike is being recorded.

---

* Present address: Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

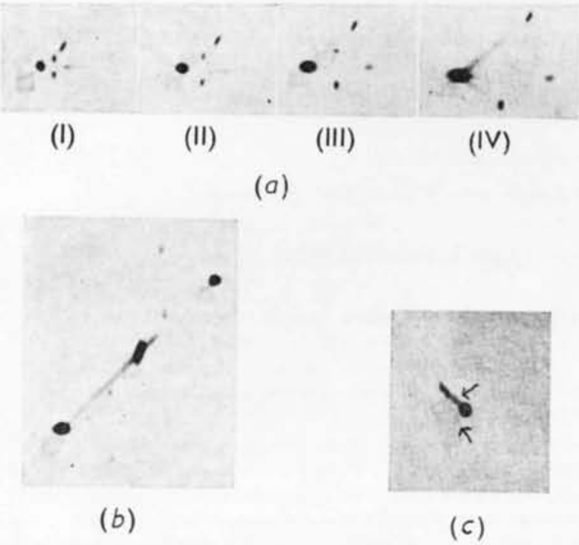

Fig. 1. (*a*) Four Laue photographs with the angle between the Bragg setting and the actual setting increasing (i)–(iv). The dense spot is the Laue spot, the three spots on a triangle are the spike spots and the top right-hand spot is the Weissenberg spot.

(*b*) Double Laue photograph. The outer dark spots are Laue reflexions, the central dark spot is the Bragg reflexion and faint spike spots can also be seen.

(*c*) Photograph of the faint spike spots associated with 222.

A double Laue photograph (Fig. 1(*b*)) was sometimes taken to examine the spikes at equal distances on opposite sides of the reciprocal-lattice point. For this purpose it was arranged that the Bragg setting occurred just at the middle of the traverse of the camera carriage on the Weissenberg goniometer. Contacts were arranged so that the motor stopped at the right- and at the left-hand sides of the traverse. In this way two Laue photographs were recorded on the same film and could readily be compared.

Although much of the work was done by comparing the spike with the associated Bragg spot, a number of spikes were compared with one another directly on the same film. By a fortunate accident it is possible, using copper radiation, to compare simultaneously the spikes through the reciprocal-lattice points 111, 113 and 202 (together with 022). To reduce the spike spots of 111 to an intensity comparable with that of the others it is necessary to place a nickel sheet over the film where the 111 spikes are going to occur. The intensity of the Bragg spots is not required in comparing spikes by this method.

The radiation used for most of this work was Cu $K\alpha$ but for the study of the spikes of 224, Cu $K\beta$ was used and for those of 333, Mo $K\alpha$. Ilford Industrial G film was found satisfactory in spite of the large grain size. The linearity of the response to X-rays was tested by means of a rotating sectored wheel, and no significant departure from linearity was observed over the whole range of densities used. The photometric determinations were performed on a hand-operated Dobson microphotometer. The crystals used were nearly spherical diamonds of diameter not greater than 0·5 mm.

3. Experimental observations

(i) *The variation of the scattering density along any spike*

As the distance between the Ewald sphere and the reciprocal-lattice point increases, the spike spots are produced further from the Laue spot (Fig. 1(*a*)). If the quantity R denotes the distance of the reciprocal-lattice point from the point where the spike cuts the Ewald sphere, (Hoerni & Wooster, 1952*b*, hereafter denoted I), then our problem may be stated as that of finding the variation of spike density as R increases. It was shown by Hoerni & Wooster (1953) (hereafter denoted II) that the relevant experimental quantity in the study of the density of a spike is the flux $J = \int I dS$, i.e. the intensity integrated over the whole area of the spike spot. The inclination of a given spike to the Ewald sphere does not change appreciably as R increases over the range investigated. Further, the area of a spike spot remains practically constant over this range of R. It is therefore sufficient for our purpose to measure the reduced maximum density I'_m for various values of R. When $\log I'_m$ is plotted against $\log R$, for 111, 113 and 220 spikes, we obtain the result shown in Fig. 2. In many of the photographs the axis parallel to the axis of oscillation was $[1\bar{1}0]$. There therefore occurred one equatorial [001], and two transverse [100], [010] spikes for (111). The spikes through 220 were parallel only to [100] and [010] and were therefore transverse, and the same is true for the 113 spikes. It will be seen that the lines through the points in Fig. 2 are substantially parallel. If we write the purely empirical relation

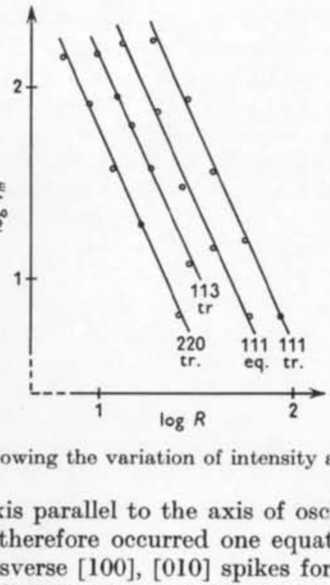

Fig. 2. Lines showing the variation of intensity along a spike.

$$I'_m \propto \beta / R^n$$

to express this result, the value of n is 2·2±0·1. For convenience the constant β is put equal to $(1/a)^n$, where a is the side of the unit cell of the Bravais lattice.

(ii) *The relative densities of different spikes*

Definition of the spike-density.—The flux of a spike spot, J, will be given by

$$J = J_0 \left(\frac{e^2}{mc^2}\right)^2 \frac{1+\cos^2 2\theta}{2} \frac{1}{\cos \nu} |F^0_{hkl}|^2 e^{-2M} \left(\frac{1}{Ra}\right)^{2\cdot 2} \Phi |\gamma|^2, \tag{1}$$

where

J_0 = flux of incident radiation,

$\left(\frac{e^2}{mc^2}\right)^2 \frac{1+\cos^2 2\theta}{2}$ = scattering by a free electron,

$1/\cos \nu$ = Lorentz correction (to be discussed below) when the spike makes an angle ν with the direction of the corresponding beam of diffuse X-rays,

F^0_{hkl} = structure amplitude at absolute zero,

e^{-2M} = temperature correction for intensity of reflection hkl,

Φ = shape and absorption factor of the crystal,

$|\gamma|^2$ = 'spike magnitude', a quantity characteristic of the scattering power associated with a spike. A superscript to γ refers to the direction of the spike and a subscript to its associated reciprocal lattice point.

R and a have the meaning already given.

The 'Lorentz factor for diffuse reflexions' was discussed in II, where it was shown that if we suppose the area of cross-section of the spike to be constant, then the diffracted flux is proportional to the area of the Ewald sphere intercepted by the spike. This is clearly proportional to $1/\cos \nu$. An experimental test of the truth of this relation was made by taking three photographs in which the crystal was rotated about the line joining reciprocal point 111 to the origin. In this way the only important variable was ν and it was found that constancy in the 'spike magnitude' could only be obtained by inserting the term $1/\cos \nu$.

The term involving the structure amplitude $|F^0_{hkl}|^2$ has been used throughout because all the observations on the spikes, with the exception of those on the 111 spikes, have been made near to the reciprocal-lattice point. On theoretical grounds (James, 1948), the F value to be used should be that at the point in reciprocal space where the spike cuts the reflecting sphere. This was tested on the 111 spikes and found to be supported by experiment. However, the inaccuracy of the measurements was generally greater than the possible variation in F value, and the value at the reciprocal-lattice point itself was therefore used.

The absolute value of Φ would be difficult to calculate for crystals of an arbitrary shape; the crystals investigated were nearly spherical and the calculation is possible (Evans & Ekstein, 1952). It was found that the factors Φ and e^{-2M} vary in opposite senses by nearly the same amount so that within the experimental accuracy, their product in equation (1) is constant over the whole range of values of θ. The last factor, $|\gamma|^2$, is independent of all variables affecting the blackness of the spike spot on the film and is characteristic of the spike under study.

4. Notes on the observations on individual spikes

Many observations on various spikes have been made using about a dozen crystals, and no instance has been found in which the intensities of the spikes departed from what would be expected on the basis of full cubic symmetry. Thus the three spikes through 111 are equivalent, as are also the two spikes through 220 etc. The spikes are in all cases centrosymmetrical about the corresponding reciprocal-lattice point within a range of $1/5a$ from that point. The distribution of the spikes for a crystal having the $[1\bar{1}0]$ axis perpendicular to the plane of the diagram is shown in Fig. 3. The full lines represent spikes lying in the plane of the diagram (equatorial spikes) and the broken lines represent spikes inclined at 45° to the plane of the diagram (transverse spikes). Any given spike can be made to cut the reflecting sphere on the left-hand or on the right-hand side of the incident beam. The positions of the reflecting sphere relative to the spike in these two settings are denoted by the arcs '*a*' and '*b*' in Fig. 3.

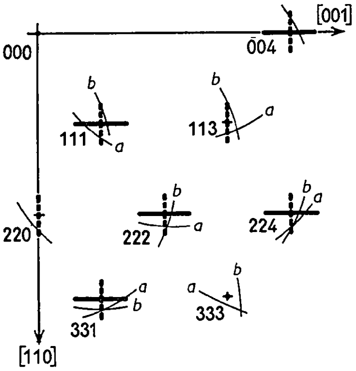

Fig. 3. Central section through the reciprocal lattice parallel to the plane $1\bar{1}0$. Full lines through reciprocal points indicate equatorial spikes and broken lines transverse spikes inclined at 45° to the plane of the diagram. Arcs a and b correspond to traces of the reflecting sphere when the spike intersects it on the left- and right-hand sides respectively of the incident X-ray beam.

220 *spikes*

There are two spikes passing through 220 parallel to [100] and [010] respectively and from a photograph showing spikes of 111 and 113 on the equator we derive $|\gamma^{\mathrm{tr.}}_{2\dot{0}2}|^2$ for the transverse spike of 202, namely,

$$|\gamma^{\mathrm{tr.}}_{2\dot{0}2}|^2 / |\gamma^{\mathrm{tr.}}_{1\dot{1}1}|^2 = 0{\cdot}77 \, .$$

An over-exposed photograph was taken to reveal a possible spike parallel to [001], but none was found.

113 *spikes*

There are two spikes passing through 113 parallel to [100] and [010] respectively. From the same photograph as that used for 202 spikes we obtain

$$|\gamma^{\text{tr.}}_{113}|^2/|\gamma^{\text{tr.}}_{111}|^2 = 1\cdot04\,.$$

An over-exposed photograph with the crystal set in the particularly favourable position '*b*' failed to reveal a spike parallel to [001].

222 *spikes*

According to the simple crystal structure of diamond, the reflexion 222 is 'forbidden'. It occurs, however, to a greater or lesser extent in all crystals. Although no spike spots related to 222 have previously been reported, we have obtained them after a relatively long exposure of 12 hr. The reflecting sphere was close to the reciprocal-lattice point in the setting '*a*' (Fig. 3) and the faint transverse spike is shown in Fig. 1(*c*). One of the two transverse spikes is masked by a white-radiation streak connecting the Laue and the Bragg spots. The following relation was found

$$|\gamma^{\text{tr.}}_{222}|^2/|\gamma^{\text{tr.}}_{111}|^2 = 0\cdot8\pm0\cdot2\,.$$

In arriving at this value it was assumed after Brill *et al.* (1939) that

$$|F_{111}|^2/|F_{222}|^2 = 285\,.$$

The equatorial spike of 222 would not be observed with the '*a*' setting but there is no reason to doubt its existence.

400 *spike*

The study of the 400 spike is difficult. Using filtered radiation two very faint transverse spike spots were observed, but it was not possible to study an equatorial spike because it would have been masked by a Laue spot. Using crystal-reflected radiation a faint spike spot was observed, at a distance from the Bragg spot great enough to ensure that the spike spot was not partly due to a residual Laue reflexion. The value of $|\gamma^{\text{eq.}}_{004}|^2$ was found to be roughly equal to $|\gamma^{\text{eq.}}_{224}|^2$ (see below).

331 *spike*

By comparison on one photograph of the spike parallel to [001] of the reciprocal-lattice point 331 with the spikes parallel to [100] and [001] of the point $20\bar{2}$ the ratio was obtained, namely

$$|\gamma^{\text{eq.}}_{331}|^2/|\gamma^{\text{tr.}}_{20\bar{2}}|^2 = 1\cdot36\,.$$

Very weak 331 transverse spikes, at least fifteen times weaker than the 331 equatorial spike, were also observed.

224 *spikes*

The 224 reflexion was observed with Cu $K\beta$ radiation (unfiltered) and spike spots were obtained on the same photograph from 224 and $\bar{1}\bar{1}1$. From the transverse spikes for 224 and $\bar{1}\bar{1}1$ the following ratio was obtained

$$|\gamma^{\text{tr.}}_{224}|^2/|\gamma^{\text{tr.}}_{\bar{1}\bar{1}1}|^2 = 0\cdot78\,.$$

A weak equatorial 224 spike spot gave the ratio

$$|\gamma^{\text{eq.}}_{224}|^2/|\gamma^{\text{tr.}}_{224}|^2 \doteqdot 0\cdot4\,,$$

the accuracy being no better than 20% because of the weakness of the spot in relation to the background.

Other spikes

Mo $K\alpha$ radiation was used but only weak transverse 115 spikes could be observed. Quantitative measurements could not be made because of the heavy background due to Compton scattering and the smallness of the spots.

Finally, observations at very small scattering angles were made with a view to observing any possible spikes through the origin of the reciprocal lattice, but none was found.

5. Comparison of spike magnitudes, $|\gamma|^2$, for various spikes

The relative values of $|\gamma|^2$, obtained from the comparisons of the spikes appearing together, are shown in Table 1. For convenience the value of $|\gamma^{\text{tr.}}_{113}|^2$ has been taken as 100. The accuracy of these measurements is about ±10% except where an indication of a lower accuracy has been given.

Table 1. *Relative values of* $|\gamma^2|$

Indices of reciprocal-lattice point	Zone indices of spike [100]	 [010]	 [001]
000	*a*	*a*	*a*
111	96	96	96
220	76	76	*a*
113	100	100	*a*
222	≈ 75	≈ 75	≈ 75
004	< 5	< 5	≈ 30
331	7	7	104
224	75	75	30
115	*p*	*p*	*a*
333	*a*	*a*	*a*

a = absent; *p* = present.

The data contained in Table 1 may be summarized in the following way. When the *h* index of any reflexion *hkl* has a given value, no matter what the values of *k* and *l* may be, the value of $|\gamma^{[100]}_{hkl}|^2$ is fixed. Thus, when *h* has the values 0, 1, 2, 3 and 4, the values of $|\gamma|^2$ are, within the limits of accuracy stated, equal to < 5, 100, 75, 5 and 30 respectively. Similar relations hold for the *k* and *l* indices with regard to $|\gamma^{[010]}_{hkl}|^2$ and $|\gamma^{[001]}_{hkl}|^2$ respectively. Another formulation of this result is 'In any given reciprocal plane parallel to a face (100) the spikes perpendicular to that reciprocal plane which pass through the various points lying in the plane, have the same spike magnitude $|\gamma|^2$'.

6. The absolute spike magnitude of one spike

The crystal chosen for this measurement showed strong spike spots, so that it can be assumed that the following absolute measurements set an upper limit to the spike magnitudes. The absolute measurement has been made by comparing a spike spot with the accompanying thermal diffuse spot. The theoretical expression of the intensity of a thermal diffuse spot in the neighbourhood of the reciprocal-lattice point (Ramachandran & Wooster, 1951*a*, *b*) depends on the elastic constants of the crystal; these have been determined (Bhagavantam & Bhimasenachar, 1944; Prince & Wooster, 1953). The thermal diffuse spot can thus be used to calibrate the absolute intensity of the incident monochromatic component of the beam in terms of film blackening. The $\bar{3}11$ (non-equatorial) reflexion obtained with the [001] axis of the crystal parallel to the axis of the camera was used. The spikes recorded were parallel to [010] and [001] and the former was compared with two points of the thermal spot corresponding to the directions parallel to [110] and $[11\bar{1}]$. The average value obtained from the two observations was

$$|\gamma^{[010]}_{\bar{3}11}|^2 = 0{\cdot}87 \pm 0{\cdot}05 \times 10^{-6}.$$

To express this result in simple form, let us assume that the incident beam is completely intercepted by an external face of the crystal parallel to $(\bar{3}11)$. Then the ratio of the flux of the spike spot to the incident flux for a distance of $1/10a$ from the reciprocal-lattice point would be

$$J/J_0 = 1{\cdot}15 \times 10^{-6}.$$

In addition to the observations already recorded, further measurements were made on two other clear and superficially similar crystals. The measurements included

(*a*) The determination of the law of variation of the spike density associated with 111. This was found in each case to be the same, namely, $R^{-2\cdot2\pm0\cdot1}$.

(*b*) The study of the relative intensities of corresponding spike-spots.

(*c*) The absolute spike magnitude for one spike. The results for (*b*) and (*c*) are given in Table 2.

Table 2

Crystal	$I^{\text{tr.}}_{111}$	$I^{\text{tr.}}_{113}$	$I^{\text{tr.}}_{202}$	$\lvert\gamma^{[010]}_{\bar{3}11}\rvert^2$
1	1·00	0·72	0·69	$0{\cdot}87 \times 10^{-6}$
2	1·00	0·70	0·76	$0{\cdot}55 \times 10^{-6}$
3	1·00	0·62	0·68	$0{\cdot}072 \times 10^{-6}$

Within the accuracy of these measurements the differences between the relative intensities of the 111, 113 and 202 spike spots are not significant. Qualitative studies of a number of other crystals also gave no indication of any variation in the relative intensities of the spike spots.

THEORETICAL INTERPRETATION

7. General considerations

Since the spikes are directed only along directions parallel to the axes ⟨100⟩, the perturbations of the crystal lattice must be restricted to planes of atoms parallel to (100), or to (010), or to (001). For an infinite lattice this follows in a direct way from the usual theory of the reciprocal equivalent of a perturbation of a crystal lattice (Wilson, 1949). For a small finite portion of the lattice it might be supposed that disc-like crystallites having their planes extended parallel to faces of the form {100} might give spikes along the axes ⟨100⟩. For such disc-like crystallites the intensity of the extensions of the reciprocal-lattice points would be proportional to the square of the structure amplitudes of the corresponding reciprocal-lattice points. The values of $|\gamma|^2$ given in Table 1 would thus be all equal, which is in disagreement with our observations.

To explain how such perturbations occur in one and the same piece of crystal parallel to all three planes of the form {100}, Guinier (1944, 1945) and Olmer (1949) advanced a domain theory. They supposed that in regions having linear dimensions at least some thousands of times greater than the length of the unit cell the anomalous planes were all parallel to only one of the three planes {100}. In the whole crystal roughly equal numbers of domains were supposed to have their anomalous planes parallel to (100), (010) and (001) respectively. This hypothesis is adopted in this paper.

A perturbation in a given domain can take two forms. It may be due to a displacement of atoms from their normal positions, or it may be due to a variation in the atomic scattering factor f of the atoms. By means of a Fourier analysis each type of perturbation can be resolved into a superposition of harmonic components. The spikes can be regarded as made up of a large number of subsidiary scattering points, each of which corresponds to a certain harmonic. In the case where the atoms undergo *small* displacements from their normal positions, the intensity ε of a given point of a spike associated with the reciprocal-lattice point $\mathbf{b}_{hkl}$, is related to the amplitude $\boldsymbol{\xi}$ of the corresponding harmonic component by the expression (James, 1948)

$$\varepsilon \propto |F_{hkl}|^2(\boldsymbol{\xi}\cdot\mathbf{b}_{hkl})^2.$$

It will be seen that this expression does not correspond with the experimental facts relating to the spikes of diamond, since for different spikes ε does not increase as b^2_{hkl} but falls to nearly zero and then rises again. For this reason the hypothesis that displacements of the atoms are responsible for the spikes cannot be sustained. However, if it could be assumed that so large a displacement of planes parallel to (100) as one-third of the unit cell side could occur, then the absence of spikes for the reciprocal plane having $h = 3$ could be explained. The method due to Wilson (1942, 1949), which he applied to the study of diffuse reflexions from cobalt, can be used for such a calculation. For diamond there would be no spikes associated with indices $0, \pm 3, \pm 6, \ldots$ but other spikes would have a constant spike magnitude, which again is contrary to experiment. This hypothesis of a shift of $a/3$ is therefore rejected. Thus all forms of displacement wave, including the travelling waves postulated by Banerjee (1947), are incapable of explaining the relative values of the spike magnitudes. An example of ε being proportional to b_{hkl}^2 has been observed by Daniel & Lipson (1943, 1944) using the alloy Cu_4FeNi_3, in which there is a sinusoidal variation of the spacing between the cubic planes. Table 1 shows that this is not the case for diamond. A comparison of the extra spots with the accompanying thermal diffuse spots is also instructive. The latter obey the relation, $\varepsilon \propto b_{hkl}^2$ and become conspicuous for reciprocal-lattice points of high indices where no spikes appear, as can be readily seen on comparing the photographs taken with molybdenum and copper characteristic radiation respectively.

The alternative type of disturbance, namely, that associated with varying f curves for different atoms, has been treated by Wilson (1949) for the simple case of a harmonic variation, namely

$$f(\mathbf{b}, x) = f_0(\mathbf{b})(1+2\Gamma \cos 2\pi K x)\,. \qquad (2)$$

Here $f_0(\mathbf{b})$ is the unperturbed atomic scattering factor and 2Γ and K are the amplitude and inverse wave-length of the harmonic variation. The intensity ratio between a Bragg reflexion and the two satellites caused by (2) is proportional to Γ^2 and is independant of the indices hkl. In order to interpret the spikes of diamond in terms of a variation in the f curves of the carbon atoms, it is necessary to generalize (2) in two ways. First, the harmonic term has to be replaced by an arbitrary function

$$1+\sum_n \Gamma_n \exp 2\pi i K_n x:$$

if the crystal domain is supposed to be a cube of edges Na and if cyclic boundary conditions are assumed the possible values of K_n are n/Na (n integral). Second, the experimental values of the spike magnitudes imply that the amplitude of variation in the f curve must also be a function of b_x. Formula (2) then becomes

$$f(\mathbf{b}, x) = f_0(\mathbf{b})(1+\gamma(b_x)\Sigma \Gamma_n \exp 2\pi i K_n x)\,. \qquad (3)$$

From (3) the following intensity of scattering I is obtained:

$$I \propto |F_{hkl}|^2 G_h G_k G_l + |F_{hkl}|^2 G_k G_l |\gamma(b_x)|^2 \sum_n |\Gamma_n|^2 (G_{h+n/N}+G_{h-n/N})\,, \qquad (4)$$

where

$$G_h = \sin^2 \pi N h / \sin^2 \pi h, \ldots, \quad \text{etc.}\,.$$

The first term in equation (4) represents the Bragg reflexion and the second term the spike parallel to [100]. The spike has a smooth variation of intensity and the summation in equation (4) may be replaced by an expression $N|\Gamma(R)|^2$, where R is the distance in reciprocal space from the nearest reciprocal-lattice point. As described in § 3(i), $|\Gamma(R)|^2$ is experimentally given by

$$|\Gamma(R)|^2 = 1/(aR)^{2\cdot 2}.$$

Thus (4) may be re-written as follows:

$$I \propto |F_{hkl}|^2 G_h G_k G_l + N|F_{hkl}|^2 |\gamma(b_x)|^2 |\Gamma(R)|^2 G_k G_l\,. \qquad (5)$$

To make equation (5) correspond with the experimental formula (1) we see that $|\gamma(b_x)|^2$ must take values proportional to the experimentally determined spike magnitude $|\gamma_{hkl}|^2$.

8. Physical interpretation of the theory

Two factors influence the value of the atomic scattering factor applicable to a given point on a spike, namely $\gamma(b_x)$ and $\Gamma(R)$. We shall deal with these in turn.

The interpretation of $\gamma(b_x)$

The usual f curve for carbon (James & Brindley, 1931; McWeeny, 1951) is shown by the full line in Fig. 4. The type of departure from this curve for the direction [100] which is shown by the atoms lying in the anomalous 100 planes is shown by the broken curve. The difference between the two curves gives a value proportional to $f_0(b_x).\gamma(b_x)$ at any value of b_x.

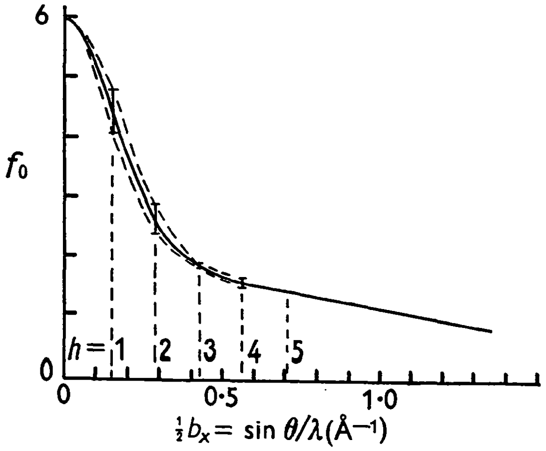

Fig. 4. The full line represents, for the direction [100], the usual atomic f curve for carbon and the broken curve shows the kind of variation from this postulated by the theory.

Thus in passing along a line in the Bravais lattice parallel to [100] the f curves for the successive atoms vary between certain limits. If we suppose that this variation in f value is due to deformation of the electron orbits without change in the total number of electrons associated with any one atom, certain of the values of $|\gamma_{hkl}|^2$ are readily determined. For zero angle of scattering the effective number of electrons must be six for all the atoms. In this case $|\gamma_{0kl}|^2$ should be zero, as is in fact observed. For angles of scattering corresponding to $b_x > 1{\cdot}1$ only the 1s electrons can be effective in scattering, and as they are so little affected by the position or distortion of the surrounding atoms, the effective f value will again be the same for all atoms. The values of $|\gamma_{hkl}|^2$ should thus be zero for the corresponding values of h, as is in fact the case. At the point corresponding to $b_x = 3/a$ the value of $|\gamma_{3kl}|^2$ is found to be nearly zero and therefore the broken curve coincides with the full curve at this point. The differences between the ordinates of the full and broken curves, divided by f_0, for the points on the axis of abscissae corresponding to $h = 1$, 2, 3 and 4 are proportional to the square roots of the values given above, namely, 100, 75, 5 and 30.

Information on the perturbation may be obtained by calculating the difference, $\sigma(\mathbf{r})$, between the electronic densities of a perturbed and an unperturbed atom. By inverting equation (3) we find that σ is given in arbitrary units by

$$\sigma(\mathbf{r}) = \int f_0(\mathbf{b})\gamma(b_x) \exp\left[-2\pi i \mathbf{b}\mathbf{r}\right] dv_b\,.$$

Applying the Convolution Theorem to this Fourier integral, we obtain

$$\sigma(\mathbf{r}) = \sigma(x, y, z) = \iiint_{-\infty}^{+\infty} \varrho_0(x-u,\, y-v,\, z-w)\omega(u)\delta(v)\delta(w)\,du\,dv\,dw\,, \quad (6)$$

where the unperturbed density ϱ_0 is the transform of f_0, $\omega(u)$ is the one-dimensional transform of $\gamma(b_x)$ and the δ are Dirac functions.

Equation (6) reduces to

$$\sigma(x, y, z) = \int_{-\infty}^{+\infty} \varrho_0(x-u, y, z)\omega(u)\,du \approx \omega(x) \int_{-\infty}^{+\infty} \varrho_0(u, y, z)\,du \quad (7)$$

since ϱ_0 is large only for $u \approx x$.

The last integral in (7) represents the projection of the electronic density of a carbon atom on the y–z plane, so that σ is mostly concentrated on the [100] axis passing through the centre of the atom. The function $\omega(x)$ describes the radial dependence of σ along the same axis. It cannot be determined uniquely since the phase variation of γ is unknown. Corresponding to the two possible real curves for $\gamma(b_x)$ shown in Fig. 5(a) the curves (i) and (ii) for $\omega(x)$ have been drawn in Fig. 5(b). (We have here $\omega(x) = -\omega(-x)$ since the total number of electrons is conserved.) Curve (i) seems reasonable since it corresponds to a transfer of peripheral electrons from one side of the atom to the other, just in the range of the valence electrons.

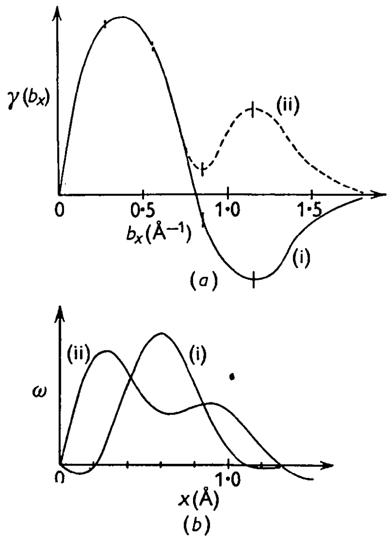

Fig. 5. (a) The curves are drawn through points having ordinates proportional to $\gamma(b_x)$ and abscissae proportional to b_x. If the first two values be taken positive the remainder may be positive (line (ii)) or negative (line (i)).

(b) Fourier transforms along [100] of $\gamma(b_x)$, (Fig. 5(a)) for the alternative assignation of the signs of $\gamma(b_x)$ denoted (i) and (ii) respectively. The more probable curve, (i), corresponds to a charge concentration along [100] at a distance of 0·6 Å from the centre of the carbon atom.

The function $\Gamma(R)$

According to equation (3) the product $\gamma(b_x)f_0(\mathbf{b})$ is proportional to the variation of the f value and the coefficient of proportionality is given by the sum $\Sigma\Gamma_n \exp\left[2\pi i K_n x\right]$ or by the function $\Gamma(R)$. Since only $|\Gamma(R)|^2$ can be experimentally determined, the phases of the Γ_n in equation (3) are unknown, and it is not possible to deduce the form of the function $\Sigma\Gamma_n \exp\left[2\pi i K_n x\right]$. However, the amplitude $|\Gamma_n|$ of an individual Fourier term, or more precisely the product $|\gamma(b_x)||\Gamma_n|$, may be found from absolute intensity measurements at a given point on a spike. This is of little use and does not enable us to determine, for instance, the maximum departure from the normal f curve. It would be valuable to find $\overline{|\Delta f/f_0|^2}$, i.e. the r.m.s. difference between the broken f curve and the full f_0 curve of Fig. 4. Unfortunately this cannot be done because the empirical law expressed by β/R^n is not valid near to the reciprocal-lattice point, where the true law of variation is unknown.

9. Conclusion

The theory given above requires (a) a domain structure of the diamond crystal, (b) within any one domain a number of abnormal planes of atoms parallel to only one of the three planes of the form $\{100\}$. The abnormality must consist in the atoms having a scattering power slightly greater or slightly less than normal. Any change in the f values of atoms must be due to distortions of the valence orbitals. The diamonds which show spikes are among the more nearly perfect crystals and any irregularity in the geometrical position of the centres of the atoms must be small. The only possibility remaining is that in a domain which gives spikes parallel to the axis $[100]$ the distribution of the $2sp^3$ orbitals relative to the (100) planes is not the same for all (100) planes.

Although the deviation from cubic symmetry would probably be small, such a deviation must occur for those carbon atoms lying in the anomalous planes. The three directions $\langle 100\rangle$ are not equivalent for these planes and the symmetry must therefore be lower than cubic. A further consequence of this is that the four tetrahedrally directed bonds would no longer be quite equivalent.

The experimental data and the theory of the abnormal character of certain diamonds discussed in this paper are based solely upon information derived from X-ray diffraction. A full understanding of the nature of these diamonds must be based on a study which includes other physical properties. Grenville-Wells (1952) has shown that there is no close correlation between the spikes and the ultra-violet and infra-red absorption, fluorescence, birefringence, and counting efficiency for certain types of radiation. Although there does not appear to be a sharp distinction between the types of diamond denoted I and II by Robertson, Fox & Martin (1934), yet the spikes are usually found in the type I diamonds. Attempts have been made by the authors to modify the spikes occurring in a given diamond by various physical treatments. These attempts have not resulted in any appreciable change of the spikes. Although a connexion between the occurrence of spikes and at least some other physical properties of the diamonds showing them might be expected to exist, further work is needed to show exactly what relations do exist.

One of us (J. H.) is indebted to the Swiss Commission for Post-doctoral Studies in Mathematics and Physics, for the award of a scholarship. We wish to thank Dr H. J. Grenville-Wells and Mr P. Grodzinski for the loan of a number of diamonds.

References

Banerjee, K. (1947). Presidential Address, 34th Indian Science Congress, Delhi.

Bhagavantam, S. & Bhimasenachar, J. (1944). *Nature, Lond.* **154**, 546.

Brill, R., Grimm, H. G., Hermann, C. & Peters, C. (1939). *Ann. Phys., Lpz.* **34**, 393.

Daniel, V. & Lipson, H. (1943). *Proc. Roy. Soc.* A, **181**, 368.

Daniel, V. & Lipson, H. (1944). *Proc. Roy. Soc.* A, **182**, 378.

Evans, H. T., Jr. & Ekstein, M. G. (1952). *Acta Cryst.* **5**, 540.

Grenville-Wells, H. J. (1951). Thesis, London.

Grenville-Wells, H. J. (1952). *Proc. Phys. Soc.* B, **65**, 313.

Guinier, A. (1944). *Bull. Soc. franç. Minér.* **67**, 382.

Guinier, A. (1945). *Proc. Phys. Soc.* **57**, 310.

Hoerni, J. (1952). Thesis, Cambridge.

Hoerni, J. & Wooster, W. A. (1952*a*). *Experientia*, **8**, 297.

Hoerni, J. & Wooster, W. A. (1952*b*). *Acta Cryst.* **5**, 626.

Hoerni, J. & Wooster, W. A. (1953). *Acta Cryst.* **6**, 543.

James, R. W. & Brindley, G. W. (1931). *Phil. Mag.* (7), **12**, 81.

James, R. W. (1948). *The Optical Principles of the Diffraction of X-rays.* London: Bell.

Lonsdale, K. (1942). *Proc. Roy. Soc.* A, **179**, 315.

Lonsdale, K. & Smith, H. (1941). *Proc. Roy. Soc.* A, **179**, 8.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Olmer, Ph. (1949). *Bull. Soc. franç. Minér.* **72**, 591.

Prince, E. & Wooster, W. A. (1953). *Acta Cryst.* **6**, 450.

Ramachandran, G. N. & Wooster, W. A. (1951*a*). *Acta Cryst.* **4**, 335.

Ramachandran, G. N. & Wooster, W. A. (1951*b*). *Acta Cryst.* **4**, 431.

Raman, C. V. & Nilakantan, P. (1940). *Proc. Ind. Acad. Sci.* A, **11**, 389.

Robertson, R., Fox, J. J. & Martin, A. E. (1934). *Phil. Trans.* A, **232**, 463.

Wilson, A. J. C. (1942). *Proc. Roy. Soc.* A, **180**, 277.

Wilson, A. J. C. (1949). *X-ray Optics.* London: Methuen.