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Diffuse X-ray Scattering from Neutron-Irradiated Graphite

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The theory of Cochran & Kartha has been used to calculate the intensity of diffuse X-ray scattering from neutron-irradiated graphite. The results are compared with the powder patterns reported by Bacon & Warren. It seems that the displacement, due to the interstitial atom, of atoms directly above or below it decreases at a slower rate with increasing distance (from the interstitial atom) than that given by the inverse-square law.

Introduction

The effect of isotropic-elastic-distortion centres in a crystal on the scattering of X-rays has been calculated by Huang (1947) and by Cochran (1956) for small atomic displacements. The theory was extended by Cochran & Kartha (1956*a*) to the case where atoms are displaced by comparatively large amounts from their mean positions; this theory was applied by them (Cochran & Kartha, 1956*b*) to calculate the effect, on the X-ray diffraction pattern, of a random distribution of interstitial atoms and vacancies in a single crystal of copper. In this paper their theory has been applied to calculate the diffuse X-ray scattering from neutron-irradiated graphite, in which case the interstitial carbon atoms are expected to cause an anisotropic elastic distortion of the lattice. The results are compared with the powder patterns of neutron-irradiated graphite reported by Bacon & Warren (1956).

Postulated model and the intensity formula

Bacon & Warren (1956) have set up a model of the damaged structure, involving two parameters α and ε, where α is the probability that an occasional interlayer spacing is increased by the amount ε. In the present analysis, the displacement u of an atom in the perfect structure due to an interstitial carbon atom is taken as $A\exp(-Br^2)$; A is the displacement of an atom in the same layer and directly above or below the interstitial atom, r is the distance of the atom from the one directly above or below the interstitial atom and B is a constant (Fig. 1). The displacements of atoms are assumed to be normal to the layers and the interstitial atoms to be distributed at random in the crystal.

The intensity $J_2(\mathbf{S})$ of diffuse scattering at a point defined by the vector $\mathbf{S}$ in reciprocal space is given by (Cochran & Kartha, 1956*a*)

$$J_2(\mathbf{S})=N\exp(-2M)\,|T_\delta(\mathbf{S})|^2\,, \tag{1}$$

where N is the number of defects, $T_\delta(\mathbf{S})$ the transform of each defect and $M=2\pi^2\overline{u^2}S^2$, $\overline{u^2}$ being the mean square displacement of an atom due to the combined effect of all the interstitial atoms. The defect is defined as consisting of positive atoms at positions where they have moved on putting the interstitial atom, and negative atoms at the positions in the perfect structure.

Taking the origin midway between the layers (at the centre of symmetry), the unit cell of graphite has the following four equivalent positions:

$$0,0,\tfrac{1}{4};\quad \tfrac{1}{3},\tfrac{2}{3},\tfrac{1}{4};\quad 0,0,\tfrac{\bar{1}}{4};\quad \tfrac{\bar{1}}{3},\tfrac{\bar{2}}{3},\tfrac{\bar{1}}{4}\,. \tag{2}$$

The first two equivalent points belong to the layer on one side of the centre of symmetry and the last two belong to the layer on the other side. In calculating the transform of the defect, the contribution of each such pair of layers is first obtained and then the contributions of the different pairs are added. The coordinates of atoms in the nth pair of layers in the perfect structure are:

$$\pm\,|n_1\mathbf{a},\ n_2\mathbf{b},\ (n+\tfrac{1}{4})\,\mathbf{c};\quad (n_1+\tfrac{1}{3})\,\mathbf{a},\ (n_2+\tfrac{2}{3})\,\mathbf{b},\ (n+\tfrac{1}{4})\,\mathbf{c}|\,, \tag{3}$$

where n, n_1, n_2 are integers (positive, negative and zero) and a, b, c are axes of the unit cell. The corresponding coordinates after putting the interstitial atom would be

$$\pm\,|n_1\mathbf{a},\ n_2\mathbf{b},\ \{n+\tfrac{1}{4}+(A_n/c)\exp(-Br^2)\}\,.\,\mathbf{c};\quad (n_1+\tfrac{1}{3})\,\mathbf{a},\ (n_2+\tfrac{2}{3})\,\mathbf{b},\ \{n+\tfrac{1}{4}+(A_n/c)\exp(-Br^2)\}\,.\,\mathbf{c}|\,. \tag{4}$$

A_n is the value of A for the nth pairs of layers. In the above, it is assumed that the structure remains centrosymmetrical after the insertion of the interstitial atom.

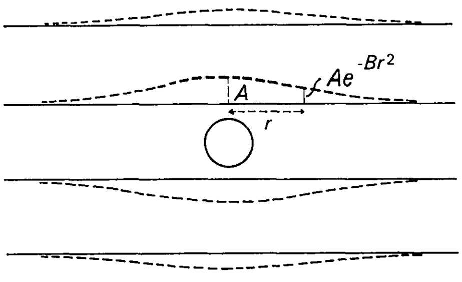

Fig. 1. The graphite layers around the interstitial atom. The dashed lines show the layers after distortion; the atomic displacement at a distance r from an atom directly above the interstitial is shown in the figure for the layer adjacent to the interstitial.

This is not quite true since the expected position of the interstitial atom is not at the centre of symmetry. It is further assumed that the values of A_n are the same for atoms with equivalent points $\pm(0,0,\frac{1}{4})$ and $\pm(\frac{1}{3},\frac{2}{3},\frac{1}{4})$. These approximations are, however, not expected to alter the results qualitatively.

The expression $t_n(\mathbf{S})$ for the contribution to $T_\delta(\mathbf{S})$ of the nth pair of layers would then be (Cochran, 1956)

$$t_n(\mathbf{S}) = 2f \sum_{n_1=-\infty}^{+\infty} \sum_{n_2=-\infty}^{+\infty} [-\cos 2\pi(\mathbf{r}+\mathbf{r}_c).\mathbf{S} - \cos 2\pi(\mathbf{r}+\mathbf{r}_o+\mathbf{r}_c).\mathbf{S} + \cos\{2\pi(\mathbf{r}+\mathbf{r}_c).\mathbf{S}+P\} + \cos\{2\pi(\mathbf{r}+\mathbf{r}_o+\mathbf{r}_c).\mathbf{S}+P\}], \ldots \quad (5)$$

where $\mathbf{r}=n_1\mathbf{a}+n_2\mathbf{b}$; $\mathbf{r}_o=\frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b}$; $\mathbf{r}_c=(n+\frac{1}{4})\mathbf{c}$; $P=\dfrac{2\pi A_n \mathbf{c}.\mathbf{S}}{\mathrm{c}} e^{-Br^2}=p_n e^{-Br^2}$, and f is the atomic scattering factor for carbon atom.

Expanding $\cos P$ and $\sin P$ into power series and applying Ewald's transformation to replace summations by integrals (Ekstein, 1945), the expression for $t_n(\mathbf{S})$ becomes

$$t_n(\mathbf{S}) = \frac{2f}{A_r}\Big[-p_n(S_1+S_2)\sum_H \int_0^R 2\pi r e^{-Br^2} J_0(2\pi rg)\,dr - \tfrac{1}{2}p_n^2(C_1+C_2)\sum_H \int_0^R 2\pi r e^{-2Br^2} J_0(2\pi rg)\,dr + \tfrac{1}{6}p_n^3(S_1+S_2)\sum_H \int_0^R 2\pi r e^{-3Br^2} J_0(2\pi rg)\,dr + \tfrac{1}{24}p_n^4(C_1+C_2)\sum_H \int_0^R 2\pi r e^{-4Br^2} J_0(2\pi rg)\,dr - \ldots\Big]. \quad (6)$$

In the above, A_r is the area of the projection of the unit cell along the c axis, $S_1=\sin 2\pi(n+\frac{1}{4})\mathbf{c}.\mathbf{S}$, $C_1=\cos 2\pi(n+\frac{1}{4})\mathbf{c}.\mathbf{S}$, $S_2=\sin 2\pi\{(\frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b}).\mathbf{S}+(n+\frac{1}{4})\mathbf{c}.\mathbf{S}\}$, $C_2=\cos 2\pi\{(\frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b}).\mathbf{S}+(n+\frac{1}{4})\mathbf{c}.\mathbf{S}\}$, R is the radius of the crystal cross-section normal to the c axis, $\mathbf{H}$ is a reciprocal lattice vector (to a reciprocal lattice point) and g is the projection of $(\mathbf{S}-\mathbf{H})$ on the (0001) reciprocal plane; the summations include all reciprocal lattice points. R can be taken as infinite and using the formula (Watson, 1958)

$$\int_0^\infty J_0(at)\exp(-p^2t^2)\,t\,dt = \frac{1}{2p^2}\exp\left(-\frac{a^2}{4p^2}\right), \quad (7)$$

we get

$$t_n(\mathbf{S}) = \frac{2\pi f}{A_r B}\Big[-p_n(S_1+S_2)\exp\left(-\frac{\pi^2g^2}{B}\right) - \tfrac{1}{4}p_n^2(C_1+C_2)\exp\left(-\frac{\pi^2g^2}{2B}\right) + \tfrac{1}{18}p_n^3(S_1+S_2) \times \exp\left(-\frac{\pi^2g^2}{3B}\right) + \tfrac{1}{96}p_n^4(C_1+C_2)\exp\left(-\frac{\pi^2g^2}{4B}\right) - \ldots\Big]. \quad (8)$$

In the above expression, only one term of the summation corresponding to the reciprocal lattice point, nearest to the point defined by $\mathbf{S}$ is retained. This seems to be justified unless the influence of the interstitial atom on the layers is very localized, which corresponds to a large value of B.

Results and discussion

The expression (8) suggests that the diffuse intensity, in general, decreases as one moves away from the lines parallel to $\mathbf{c}^*$ through each reciprocal-lattice point; the rate of decrease would depend on the magnitude of B. For small B, the diffuse intensity would drop down to inappreciable value as one moves slightly away from the lines parallel to $\mathbf{c}^*$ through each reciprocal-lattice point. This situation approximates to one-dimensional disorder and implies that the influence of the interstitial atoms is to move the layers normal to the c axis, leaving them undistorted. On the other hand, if the influence of the interstitial atom on the layers is localized, *i.e.* if B is large, the diffuse intensity will spread out from the lines parallel to $\mathbf{c}^*$ through each reciprocal lattice point. By studying the spread of the diffuse spot (after taking into account the thermal diffuse scattering) near a reciprocal lattice point in a plane normal to the $\mathbf{c}^*$ reciprocal axis, it may be possible to get a rough estimate of the lateral extent of the region of increased spacing around an interstitial atom.

The expression for $t_n(\mathbf{S})$ at the reciprocal point $(0, 0, 0, l+\omega)$, where l is an integer is given by

$$t_n(0,0,0,l+\omega) = \frac{4\pi f}{A_r B}\Big[-\frac{2\pi(l+\omega)A_n}{\mathrm{c}}\sin 2\pi \times (n+\tfrac{1}{4})(l+\omega) - \frac{\{2\pi(l+\omega)A_n\}^2}{4\mathrm{c}^2}\cos 2\pi(l+\omega)(n+\tfrac{1}{4}) + \frac{\{2\pi(l+\omega)A_n\}^3}{18\mathrm{c}^3}\sin 2\pi(n+\tfrac{1}{4})(l+\omega) + \frac{\{2\pi(l+\omega)A_n\}^4}{96\mathrm{c}^4}\cos 2\pi(n+\tfrac{1}{4})(l+\omega) - \ldots\Big]. \quad (9)$$

The diffuse intensity at $(0, 0, 0, l+\omega)$ will then be given by

$$\mathscr{I}(0,0,0,l+\omega) = N\exp\left\{-4\pi^2\overline{u^2}\left(\frac{l+\omega}{c}\right)^2\right\} \left|\sum_{-\infty}^{+\infty} t_n(0,0,0,l+\omega)\right|^2. \quad (10)$$

This expression has been used to calculate the diffuse intensity near the 0002 reciprocal lattice point along the c^* axis. The intensity curve is shown in Fig. 2. To obtain this curve, contributions of layers with n up to ± 10 have been taken. For $n=0$, *i.e.* for the layers adjacent to the interstitial atom, a value of A_n (=0·93 Å) was chosen so that the distance between the interstitial atom and the one directly above it may, after distortion, be equal to 2·75 Å, which is the closest distance observed between non-bonded carbon atoms in overcrowded organic molecules like di-*p*-xylylene (Lonsdale, Milledge & Rao, 1960). For the other layers, A_n was taken as inversely proportional to the square of the normal distance of the corresponding layer from the interstitial atom, the constant of proportionality (= 15·6) being such as to make the distance between the first and the second layers from the interstitial (and directly above it) about 3·05 Å after distortion; the distance between adjacent layers in the perfect structure is taken as 3·4 Å. An earlier value of the constant of proportionality, 7·8, which made the distance between the first and the second layers from the interstitial about 2·8 Å appeared to give too much intensity near the 0003 point. A value of 0·78 Å has been used for the root mean square displacement, $\sqrt{\overline{u^2}}$, of atoms. This is the value estimated for a damaged graphite sample showing 9·1% lattice expansion parallel to the *c* axis (Bacon & Warren, 1956), using the analogy with thermal diffuse scattering. The analogy is, as mentioned by Bacon & Warren, not justified; however, it may be expected to give a value of the right order.

The shapes and positions of the 0002 and 0004 lines for two samples of highly oriented graphite after neutron irradiation are given by Bacon & Warren (1956). For the sample showing 3·1% expansion along the *c* axis, the diffuse background around the 0002 line is faint but for the one showing 9·1% expansion, the diffuse background is quite pronounced and is asymmetric about the Bragg peak; the peak of the diffuse background shifts towards higher angles. The calculated curve of diffuse scattering (Fig. 2) shows the peak towards higher angles but the width of the peak as well as the amount of shift from the Bragg peak is larger than the experimental value. Secondly, the calculated curve shows a weaker diffuse peak on the low angle side of the Bragg peak as well. This probably implies that the constant A_n decreases more slowly with increase of interstitial-layer distance than is indicated by the inverse-square law. With a slower rate, both the diffuse peaks will come closer to the reciprocal lattice point and, with the Bragg peak superposed, give one broad maximum shifted towards the high angle side. This will also have the effect of decreasing the width and the amount of shift of the diffuse peak from the Bragg position, and bringing them closer to the experimental values. It may, however, be mentioned that for proper comparison between observed and calculated values, the curve of Fig. 2 should be compared with the intensity near 0002 along **c*** from measurements on a single crystal.

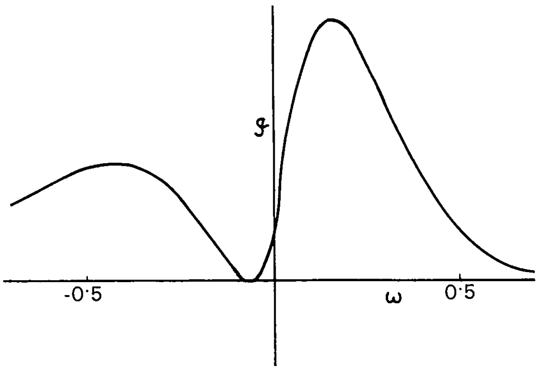

Fig. 2. The calculated intensity (arbitrary scale) near 0002 along the c^* axis.

This analysis neglects the contribution of interstitial atoms themselves, vacancies and the influence of atomic displacements parallel to the layers as well as of any regularity in the positioning of interstitial atoms. In view of this and the arbitrarily assumed model, the results must be only of qualitative significance.

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References

Bacon, G. E. & Warren, B. E. (1956). *Acta Cryst.* **9**, 1029.
Cochran, W. (1956). *Acta Cryst.* **9**, 259.
Cochran, W. & Kartha, G. (1956*a*). *Acta Cryst.* **9**, 941.
Cochran, W. & Kartha, G. (1956*b*). *Acta Cryst.* **9**, 944.
Ekstein, H. (1945). *Phys. Rev.* **68**, 120.
Lonsdale, K., Milledge, H. J. & Rao, K. V. K. (1960). *Proc. Roy. Soc.* A, **255**, 82.
Huang, K. (1947). *Proc. Roy. Soc.* A, **190**, 102.
Watson, G. N. (1958). *Theory of Bessel Functions*, p. 393. Cambridge Univ. Press.