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Trigonal Symmetry in Electron Diffraction Patterns from Faulted Graphite

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Electron-diffraction patterns both with hexagonal and trigonal symmetry were obtained from graphite. The trigonal patterns are shown to arise from a stacking fault on the basal plane. This observation is a consequence of the dependence of the pattern symmetry on the symmetry of the whole crystal, not only the symmetry of the unit cell.

Introduction

The possibility of measuring the unit-cell symmetry of a crystal by convergent-beam electron diffraction has been treated both theoretically and experimentally (*e.g.* Gjønnes & Moodie, 1965; Goodman & Lehmpfuhl, 1964, 1968). However, the symmetry observed in the diffraction pattern depends on the symmetry possessed by the scattering crystal as a whole, which need not be that of its unit cell. Evidence of this in the case of graphite is reported here and shown to be due to stacking faults on [0001].

Pyrolytic graphite* having a high degree of perfection was examined in a convergent-beam electron diffraction camera (as described by Cockayne, Goodman, Mills & Moodie, 1967) at 79 kV. The specimens consisted of large sheets of graphite having a constant thickness. The [0001] zone convergent-beam patterns were of two types, one with 6-fold symmetry and the other with 3-fold symmetry (Figs. 1 and 2). Sufficient translation of the crystal changed the pattern symmetry from one type to the other, the transition point coinciding with a region of distorted crystal as shown by the Kossel line pattern. This, coupled with the symmetry change, suggested that a region of stacking faulted crystal corresponded to the observed 3-fold symmetry and this hypothesis was tested by computation and against the symmetries predicted by dynamical theory. Hoerni (1950) observed similar patterns but the true symmetry of the 3-fold pattern was obscured.

Diffraction pattern symmetry

In recent years the means to analyse various elements of diffraction symmetry in dynamic electron diffraction experiments have been developed (Gjønnes & Moodie, 1965; Goodman & Lehmpfuhl, 1968; Pogany & Turner, 1968). These means and an extention of them can be used to deduce the diffraction symmetry to be expected from graphite, both when perfect and containing a stacking fault.

(*a*) *Symmetry of graphite*

Owing to the problem of obtaining perfect crystals, the exact structure of graphite is not yet known. Two possilities are reported differing in whether or not the atom layers are puckered. For plane layers the atoms lie in (*b*) and (*c*) of the space group† $P6_3/mmc$ (Bernal, 1924). If the layers are puckered the atoms lie in 2(*a*) and 2(*b*) of the space group $P6_3mc$, which differs only by the lack of mirror plane perpendicular to the sixfold screw axis. Bernal, on the basis of rough intensity measurements, deduced that any puckering would produce atomic deviations of less than $\pm 0{\cdot}2$ Å from planarity. It will become evident that the uncertainty of the existence of this mirror plane does not affect any conclusions arrived at.

(*b*) *Diffraction symmetry of perfect graphite*

In perfect hexagonal graphite (*AB* stacking) there are three mirror planes parallel to the three $(11\bar{2}0)$-type planes. As shown by Goodman & Lehmpfuhl (1968), for zero layer interactions, these result in three lines of reflexion in the zone axis pattern along the reciprocal lattice directions $[10\bar{1}0]^*$, $[01\bar{1}0]^*$ and $[1\bar{1}00]^*$. These directions are along the lines marked *C* in Fig. 3. In addition, axial glide planes exist at right angles to the mirror planes and these result in three more lines of reflexion along the pattern directions $[11\bar{2}0]^*$, $[1\bar{2}10]^*$ and $[2\bar{1}\bar{1}0]^*$ labelled *H* in Fig. 3. Goodman & Lehmpfuhl confined their discussion to zero-layer interactions. However, their results also apply in this instance to upper-layer interactions, as it can be shown, using arguments similar to those of Gjønnes & Moodie (1965), that a mirror or glide plane perpendicular to the faces of a parallel-sided crystal will always result in mirror lines appearing in the normal incidence pattern.

Consequently the zone-axis diffraction pattern should contain six lines of reflexion spaced at 30° intervals as confirmed by Fig. 1.

* Kindly supplied by Professor P. L. Walker Jr, Pennsylvania State University, U.S.A.

† Bernal gives the incorrect space group $P6_3/mcm$.

(*c*) *Diffraction symmetry from faulted graphite*

The effect of a stacking fault in graphite is to introduce into the crystal a section of rhombohedral structure (*ABC* stacking) having a space group $R\bar{3}m$ (Lipson & Stokes, 1942).

It is instructive to consider the symmetry of a completely rhombohedral crystal as the symmetry of a faulted crystal can be no greater. The projected structure has six mirror planes at 30° intervals, hence zero-layer interactions will result in a centrosymmetric zone-axis pattern with six mirror lines. Upper layer interactions will destroy three of the mirror lines at 60° intervals, those marked *H* in Fig. 3, and thus the centrosymmetry of the pattern, as the three-dimensional symmetry ($R\bar{3}m$) has only 3 separate glide or mirror directions. However, the effect of upper layers will be weak in a perfect rhombohedral crystal as the normal axis is 10 Å in length. It is not clear whether a hexagonal crystal with one fault will show a strong trigonal pattern or not. One might propose by simple scattering power arguments that the trigonality would be weak when the fault plane was close to the surface of the crystal, but the strength of the effect at intermediate depths is not obvious. As a result it was decided to make dynamical calculations to test directly the sensitivity of the zone-axis pattern to the presence of a stacking fault.

Calculations

The calculations were performed using the multi-slice technique of Goodman & Moodie (1965) which is based on the theory of Cowley & Moodie (1957). This method can be made as precise or, by sacrificing some precision, as rapid as possible, depending on requirements. In addition, the introduction of a stacking fault is trivial, as is shown later. The validity of the technique is well proven both theoretically (Moodie, 1972) and by agreement with experiment (Goodman & Lehmpfuhl, 1967) and the departure of a practical calculation from the exact theoretical result can be easily tested by a method due to Moodie (1965).

For the purpose of calculation, the crystal was divided into slices 13·4 Å in thickness (4 carbon atom layers stacked *ABAB*), which is considerably thicker than that used when precision is important, and 61 beams symmetrically disposed about the 0001 axis were included. These conditions were estimated by using the technique referred to above and by comparison with precise calculations, to result in a relative accuracy of approximately 3% between the calculated intensities of diffracted beams. However, the accuracy of representation of the symmetry operators was always that of the computer manipulations (~ 1 in 10^{12}).

To facilitate comparison with experiment the calculation was carried out at 160 different directions in one half of the incident cone, constituting a semicircular area of each convergent-beam disc. The assumption of three trigonally related mirror lines in the diffraction pattern of index $[10\bar{1}0]^*$, $[01\bar{1}0]^*$ and $[1\bar{1}00]^*$ then allowed the reconstruction of the remainder of each disc without further calculation. These mirror lines (*C* in Fig. 3) result from mirror planes common to both the hexagonal and rhombohedral forms and so are unaffected by stacking faults. The calculations were made at points at intervals of radius/10 to form a rectangular grid over the disc. This grid proved to be too coarse, resulting in an apparent lack of perfect 6- or 3-fold symmetry (*e.g.* Figs. 4 and 5). However, check calculations at hexagonally related points in the disc showed the appropriate perfect symmetry and that all the discrepancies of symmetry were introduced by the processing of the output and not in the calculation.

The multi-slice calculation evaluates the wave-function at the exit face of a crystal slice in terms of that at its entrance face, using the result as the input wave-function for the next slice. A shift in origin of this input wave-function at the slice corresponding to the depth of the stacking fault is all that is required to introduce a fault whose plane is parallel to the entrance and exit surfaces of the crystal. The shift used was $\frac{1}{3}$, $-\frac{1}{3}$ (Amelinckx & Delavignette, 1960).

(*a*) *Results*

The crystal thickness was measured at ~ 520 Å from the fine structure spacing of a high-order reflexion and 61 beam calculations made for both unfaulted and faulted cases. The agreement with experiment can be clearly seen by the comparison made in Figs. 4 and 5.

The sensitivity of the pattern to fault depth was demonstrated by results of another calculation. These showed the trigonality to decrease as the fault plane approaches the surface of the crystal. However, there

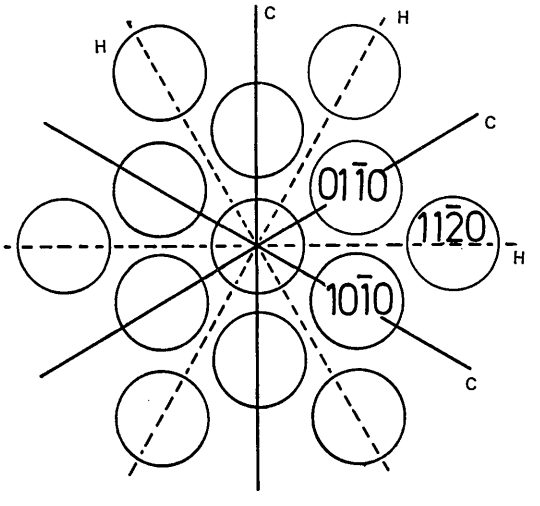

Fig. 3. Lines of mirror symmetry in the diffraction pattern of graphite as deduced from dynamical theory. *C*, lines common to both hexagonal and rhombohedral forms. *H*, lines from the hexagonal form only.

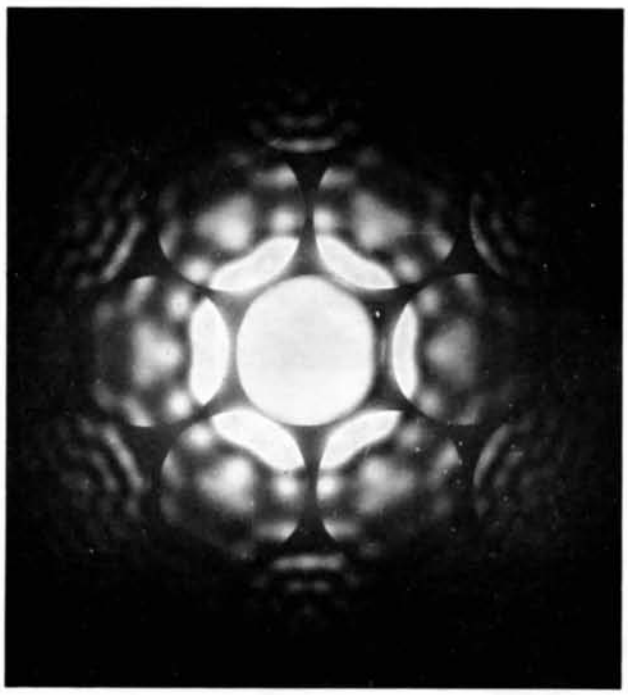

Fig. 1 A zone-axis convergent-beam diffraction pattern from graphite showing 6-fold rotational symmetry. Thickness approximately 520 Å.

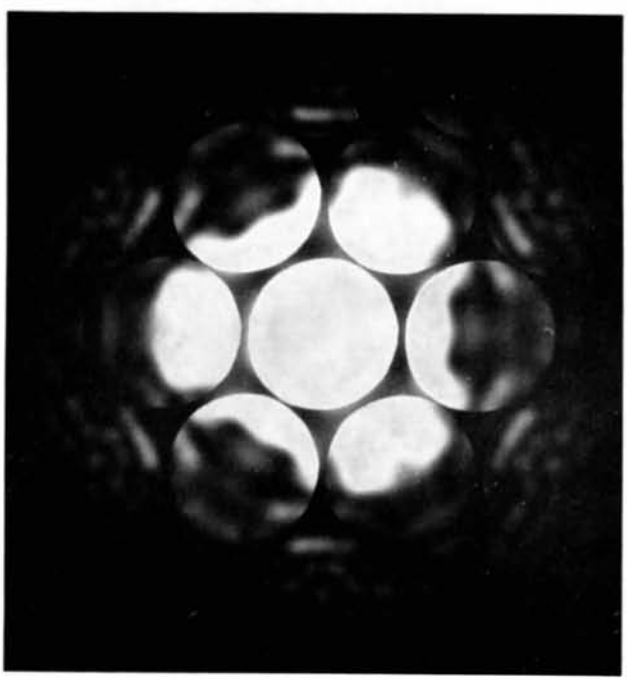

Fig. 2. A zone-axis pattern from a crystal region adjacent to that used for Fig. 1 showing 3-fold symmetry.

[*To face p.* 90

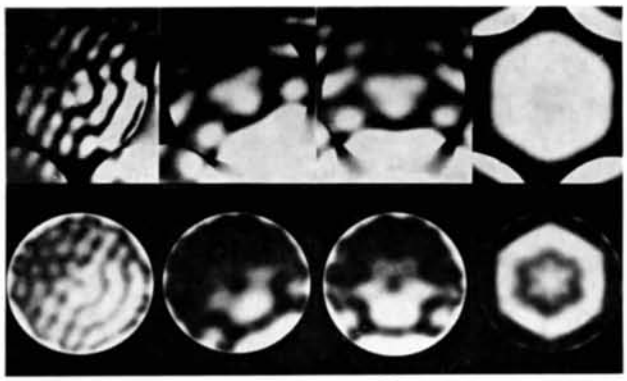

Fig. 4. Computed angular distributions for various orders from an unfaulted graphite crystal 520 Å thick (lower row) compared with the appropriate distributions from Fig. 1 (upper row).

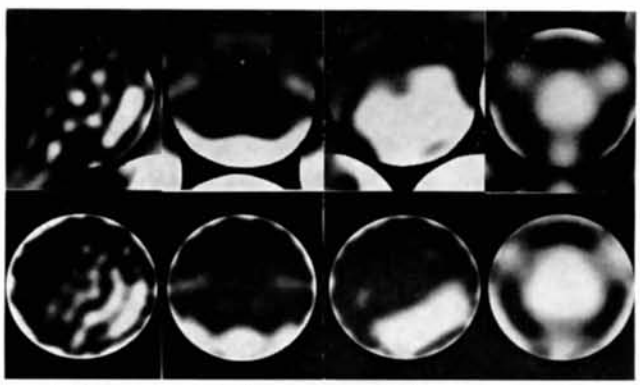

Fig. 5. Similar to Fig. 4, except that the calculation included a fault at 260 Å and the comparison is made with distributions from Fig. 2.

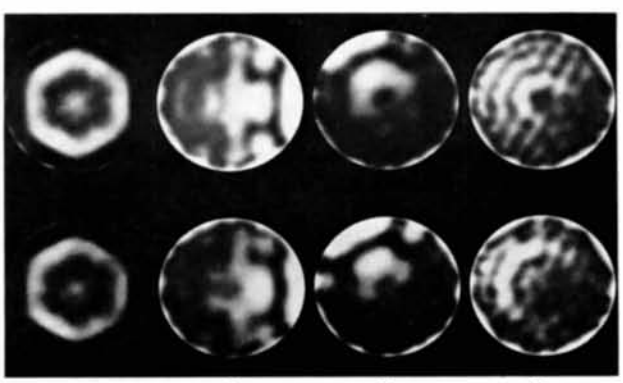

Fig. 6. Comparison of computed distributions for crystals 550 Å thick. Upper row: a fault 26 Å from the entrance face; lower row: a fault 26 Å from the exit face.

should be sufficient effect to reveal a fault 6 Å from the surface of a 500 Å thick crystal.

The reflexions fall into two groups, one in which the distributions depend strongly on the position of the fault plane and the other in which they are relatively intensitive. Reflexions having indices of the form $h-k=3n$ are, excluding the central beam, members of this latter group.

It is interesting to consider the relation between the pattern from a crystal of thickness h with a fault at a depth t and that of a second crystal of the same thickness but with a fault at a depth $(h-t)$. Since the second crystal can be transformed into the first by a rotation about the fault displacement vector, one can at once apply the reciprocity theorem* to the central beam distributions to show that they should be equal. Such a result was predicted by Howie & Whelan (1961) and the computed distributions in Fig. 6 show the equality. The case of the diffracted beams is different. The calculated distributions (Fig. 6) show a similarity which can be discussed quantitatively and will be described in a forthcoming publication (Johnson & Moodie, 1972).

Only the zone-axis pattern has been used to establish the presence and depth of a stacking fault. Other orientations may be superior for the purpose, notably those simultaneously exciting two equivalent adjacent reflexions of the set $h-k\neq 3n$, *e.g.* $40\bar{4}0$ and $04\bar{4}0$. Having obtained a method for the selection of unfaulted crystals it is now possible to make accurate measurements of the Fourier coefficients by the convergent-beam method, thus establishing the precise structure of graphite and providing data for comparison with theory. Finally, accurate measurement of fault depth will be of interest in connexion with the determination of stacking fault energy from the separation of partial dislocations, as the separation is dependent on the depth of the fault plane (Spence, 1962; Siems, Delavignette & Amelinckx, 1962).

* Applications of this theorem to dislocations are given by Pogany & Turner (1968).

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