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Dislocations and Twinning in Graphite

- by -

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SUMMARY

The twin composition plane in graphite is a 20° tilt boundary between lattices which are rotated, relatively, about an axis in the basal plane. Previous work has led to the proposition that some special type of structure must necessarily exist in the neighbourhood of the boundary which violates the normal hexagon arrangement of the carbon atoms. It is demonstrated that a tilt boundary of the required form can be explained as an array of partial dislocations, such a boundary being possible in either the hexagonal or the rhombohedral form. A boundary of this type is mobile, and can, by its movement, introduce or eliminate stacking faults and thus change the volume of rhombohedral graphite present in the normal hexagonal lattice. Such effects have been reported previously. The true twinning plane in this model is not the composition plane, which is the plane $\{1\bar{1}01\}$ referred to the structural (not the morphological) axes, but the plane $\{11\bar{2}1\}$.

The graphite structure consists of parallel layers of aromatic carbon rings, the C-C spacing in the rings being 1.42 Å, the hexagon width α 2.456 Å and the layer spacing c 3.348 Å.

The standard work on the twinning features in graphite is that of Palache (1941), which identifies the twin composition plane as $\{11\bar{2}1\}$ with respect to the morphological axes. We shall throughout this note use the hexagonal structural axes (see Fig. 1) in which system the indices of the composition plane become $\{1\bar{1}01\}$. The angle of tilt between the twins was determined by Palache as $20^{\circ}36'$, which is very close to $\tan^{-1}\alpha/2c$, ($20^{\circ}9'$ using the above values) and equivalent to the insertion of one hexagon width in every other basal plane. We shall use the value $20^{\circ}9'$ throughout in the following discussion. The true twinning plane (as distinct from this twin composition plane) is not established: this may, or may not, be $\{1\bar{1}01\}$. The theory advanced by Platt (1957) for the structure of the twin boundary results in the twinning plane and the composition plane being the same. To produce this result, quite special structures must be created in every other atomic plane of the type illustrated in Fig. 2, which Platt refers to as 8-4-8 structures. It is, in fact, unnecessary to adopt such a special arrangement to explain the observed structure as this may be interpreted more satisfactorily in dislocation terms.

Graphite may exist in either the hexagonal, ABABAB... stacking sequence, or in the rhombohedral ABCABC... stacking sequence. Consider first the hexagons drawn in Fig. 3(a) which shows the relative positions of the A, B and C planes. The C position may be achieved from the B position by a translation along, say, XY. A partial dislocation with a Burgers vector XY, that is $\sqrt{3}\,\alpha/2$ [1000], can therefore constitute a boundary between hexagon sheets in the B and C positions. Such a dislocation can, of course, be either positive or negative: the hexagons in the region of the partial dislocation may be either compressed or extended, the overall lateral strain being $\alpha/2$, which is the shift involved in the translation illustrated in Fig. 3. In Fig. 3(b) a line of hexagon nets is shown in the transition region between the B and C stacking positions from which it will be evident that, in this case, an extension of $\alpha/2$ has been introduced (as well as a shear, of course). For simplicity the distortion is shown relative to an undistorted A layer; in fact the strain is distributed symmetrically over both layers, but the relative strain is the same as that shown. Let us suppose the B-C line of hexagons to be cut at OO', and the strain released. This results in the arrangement of Fig. 3(c). Suppose now that the hexagons of both layers are rotated about OO', so that the gap PQ, of width $\alpha/2$, is closed by the rotation. The angle of tilt required to achieve this is $\tan^{-1}\alpha/2c$, or $20^{\circ}9'$. Thus a boundary is formed which is equivalent to the insertion (or removal) of an extra half-hexagon on each successive plane (or a full hexagon width on every alternate plane). The operation of the dislocations, $\sqrt{3}\alpha/2$ [1000] and $\sqrt{3}\alpha/2$ [00$\bar{1}$0], in sequence on successive planes is obviously equivalent to the perfect dislocation α [10$\bar{1}$0] on alternate planes in the hexagonal stacking.

The structure which will satisfy the observed tilt angle is drawn in detail in Fig. 4, for the case of both hexagonal graphite (above the dotted line) and rhombohedral graphite (below the dotted line), and again the A plane has been taken, for convenience, as an undistorted reference plane. In each case a partial dislocation of the type discussed is introduced into the intermediate layer of hexagons (wavy lines), as evidenced by the difference in position between extreme left and right, but with the strain removed by an operation of the type illustrated in Fig. 3(b) and (c), the gap created being shown in black. For both the hexagonal and rhombohedral cases, the tilt required to close such gaps in the planes is the same, namely $20^{\circ}9'$. In each case the original type of structure can be preserved: hexagonal ABABAB... twins to hexagonal ACACAC... and rhombohedral ABCABC.... can twin to rhombohedral BACBAC... In Fig. 4 the rhombohedral transformation illustrated shows ABC... twinning to ACB... and the exact sequence obviously depends on the direction of the Burger's vector, as any plane (say A) may be transformed to either of the other two possibilities (B or C) by a similar vector of different direction. Stacking faults can therefore exist. If, then, the lattice is rotated as described above, the structure will now fit along the cut planes when the angle of rotation is $20^{\circ}9'$. This is illustrated diagrammatically by the diagram at the foot of Fig. 4. Thus a sequence of partial dislocations can give a tilt boundary of the observed angle. The twin boundary in such a structure is thus an array of partial dislocations, forming a tilt boundary, and is evidently mobile, which is consistent with experimental observations (Laves and Baskin 1956).

Once this possibility is recognized, a number of characteristics of the graphite structure become resolvable. It follows that twinning in the hexagonal structure does not necessarily involve any transformation to the rhombohedral form (as was deduced by Laves and Baskin from x-ray measurements), although rhombohedral stacking faults could be perpetuated through the twinned structure, or even created. Apart from the twinning question, such partial dislocations can obviously constitute the boundaries of stacking faults, and thus the gliding of these dislocations under stress can increase (or diminish) the amount of rhombohedral graphite. This necessary association of gliding with rhombohedral development has already been noted by Laves and Baskin.

The dislocation structure of the twin composition plane imposes certain restrictions on the possible junctions of such boundaries. For example, as in Fig. 5(a), two boundaries may conform if their common vector lies along the third possible boundary line. One such boundary may terminate either on another or at a straight-forward dislocation boundary which is not of the twinning type; see Fig. 5(b). Three boundaries may also conform, but the sign of the tilt is important. In some cases, instead of three twin lamellae meeting, one of these may be split into two of opposite tilt (Fig. 5(c)). In any case, because of the tilting condition, there will always be very special restraints in the neighbourhood of nodes and at the ends of lamellae and the adaptation of graphite in this respect presumably depends on the readiness with which partial dislocations may be formed. This derives from the relatively weak interplanar (van der Waals) bonding in graphite.

It is not at once evident why the composition plane observed is $\{11\bar{2}1\}$ rather than $\{1\bar{1}01\}$, as the creation of the latter requires the same type of transformation: in this case the insertion of a hexagon length into every other plane (see Fig. 4) leading to a tilt angle across the $\{1\bar{1}01\}$ plane of $\tan^{-1} 2a/3c$, or $22^{\circ}57'$. One of the differences between these two possible planes is that, for a tilt of a given sign, there is only one possible partial for each layer plane in the $\{1\bar{1}01\}$ case, whereas in the case of $\{11\bar{2}1\}$ there may be two possibilities. Thus suppose the positions of a given plane in the original structure and the twinned structure to be symbolized by B-C: this is the case, for example, in the second plane drawn in Fig. 4. Rhombohedral stacking sequences of the following type are possible across $\{11\bar{2}1\}$: B-C, C-A, A-B,... or B-C, C-B, A-C ... Using similar notation for the (theoretical) case of the $\{1\bar{1}01\}$ composition plane, these alternatives do not arise. The sequence must be B-C, C-A, A-B. In the simple hexagonal twinned lattice, A-A, B-C, A-A,... there is no distinction, as one possibility only exists for both cases. For A-B, B-C, A-B, however, which is also pure hexagonal stacking in each twin, another possibility arises in the $\{11\bar{2}1\}$ case, namely A-B, B-A, A-B. This is again a structure which could not conform with a $\{1\bar{1}01\}$ tilt boundary. Particularly where stacking faults exist, then, the $\{11\bar{2}1\}$ boundary is much less restrictive in the necessary conditions it imposes, and would appear to be much more likely to form in lattices containing a distribution of stacking faults. No cases of the observation of a $\{1\bar{1}01\}$ composition plane appear to have been reported, although it may be possible to produce such twins in thin flakes of very perfect graphite.

The point of this discussion is, then, that the principal twinning characteristics of graphite can be explained in dislocation terms, and that, on this basis, the true twinning plane (as distinct from the twin composition plane) is $\{11\bar{2}1\}$ in the structural (not the morphological) system of axes. An experimental confirmation of this proposition would be valuable.

References

Laves, F., and Baskin, Y., 1956, Z.Kristallogr., 107, 22.
Palache, C., 1941, Amer. Min., 26, 709.
Platt, J. R., 1957, Z.Kristallogr., 109, 3.

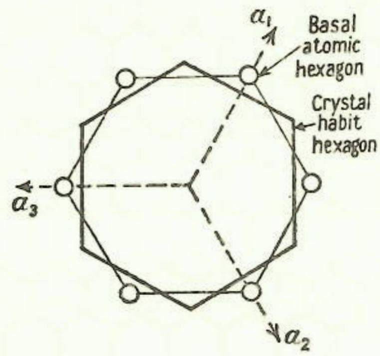

Figure 1. The relation between the structural and the morphological hexagons. The twin composition plane is $\{1\bar{1}01\}$ with respect to the $a_1a_2a_3$ and c axes.

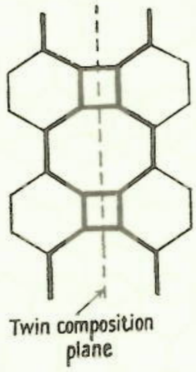

Figure 2. The boundary structure proposed by Platt.

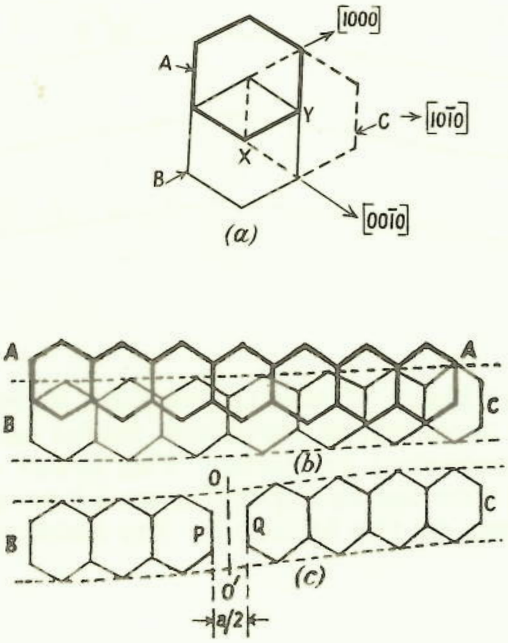

Figure 3. (*a*) The relative positions of hexagons in the A, B and C planes. (*b*) The distortion introduced into a row of hexagons in the neighbourhood of a partial dislocation, taking the A layer as a rigid reference network. (In fact, both layers are sheared similarly, of course.) (*c*) The B–C row of hexagons showing the gap, of width $a/2$, closed by the lattice rotation of 20° 9′.

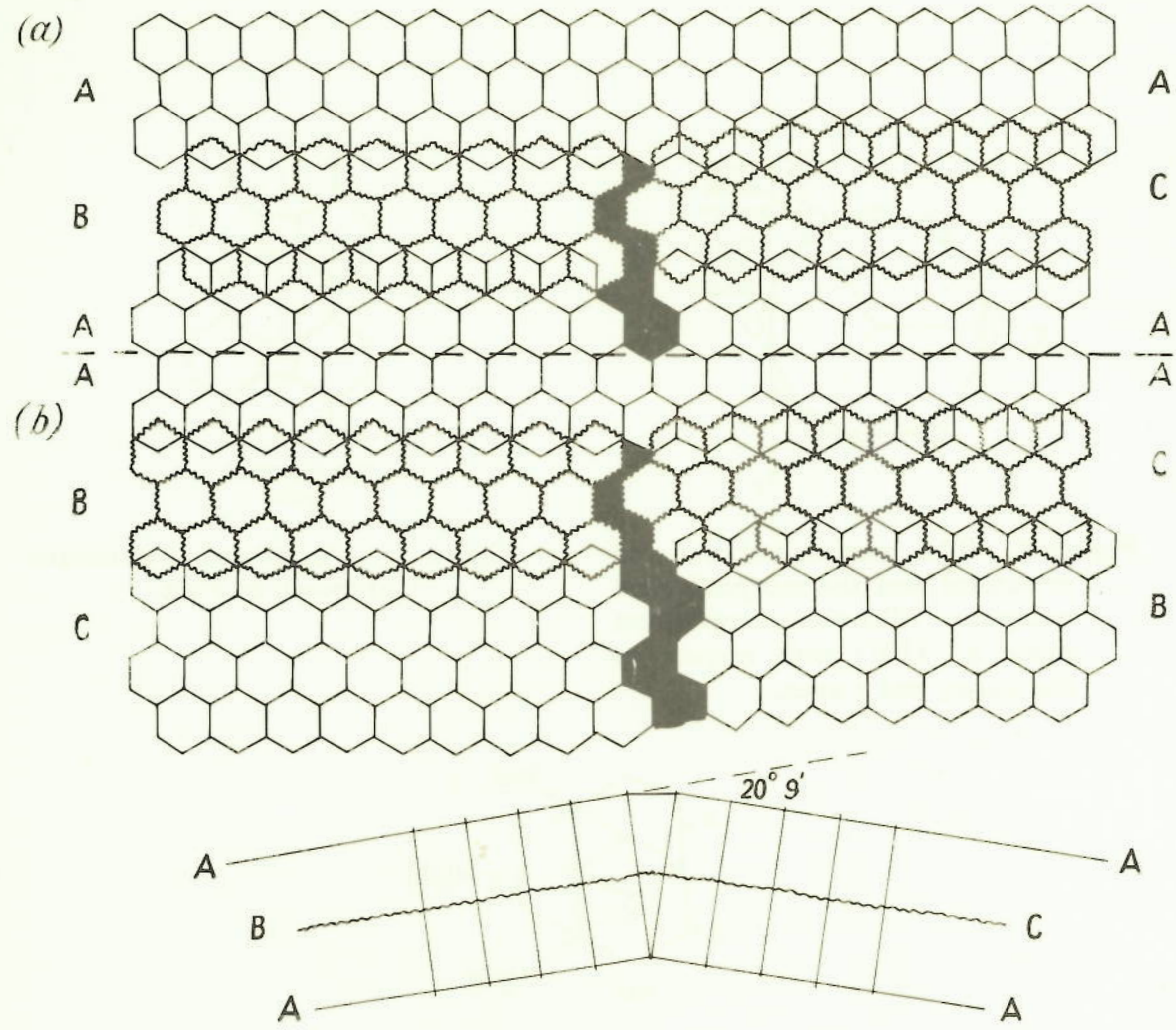

Figure 4. Successive layer planes in graphite showing the twin boundary dislocation structure for(a) hexagonal and (b) rhombohedral graphite. The lower diagram demonstrates (for the hexagonal case) how a rotation of $20^{o}9'$ closes up the lattice in the required way.

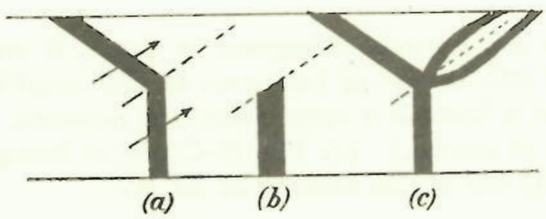

Figure 5. Possible twinning forms : (*a*) two lamellae with common boundary vectors, (*b*) a single lamella terminating at a dislocation boundary, and (*c*) the possible split into two lamellae of opposite tilt.