Acta Cryst. (1955). **8**, 49

On the Relations Between Structure and Morphology of Crystals. I

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(*Received* 4 *October* 1954)

An attempt is made to find relations between crystal structure and crystal morphology on an energy basis. It is concluded that the morphology of a crystal is governed by chains of strong bonds running through the structure. The effective period of such a chain of strong bonds is called a periodic bond chain vector (P.B.C. vector). The faces of a crystal are divided into three classes: (*a*) flat faces or *F*-faces, each of which is parallel to at least two P.B.C. vectors; (*b*) stepped or *S*-faces, each of which is parallel to at least one P.B.C. vector; (*c*) kinked faces or *K*-faces which are not parallel to any P.B.C. vector. *F*-faces are the most important faces; *S*-faces are of medium importance and *K*-faces are very rare or do not occur at all. Two examples are given, concerning the morphology of diamond and urotropine respectively.

Introduction

As soon as crystals became the subject of thorough investigation, attempts were made to correlate morphological development with internal structure. Up to now only geometrical characteristics of the structure had been taken into account (Bravais, Friedel, Fedorov, Niggli, Donnay), but, as crystal growth is a physical process, energy quantities will probably play a more important role than geometrical quantities like row densities and mesh areas.

Criticism of this kind has already been made by Wells (1946*a*, *b*, *c*) and by Buerger (1947), but these authors did not give a method by which the influence of energy factors could be taken into account in a practical way.

In this paper we present some theoretical considerations, which make it possible to correlate crystal morphology and crystal structure, starting from qualitative considerations on bond energies (see also Hartman & Perdok (1952) for a preliminary note and Hartman (1953) for details).

Outline of the main ideas

(*a*) The influence of strong bonds in the structure on the shape of a crystal is strikingly demonstrated by fibrous crystals like asbestos, where chains of strong bonds run parallel to the fibre axis. Niggli (1923), however, showed that even in crystals lacking such extreme properties, a main zone axis is parallel to a *Hauptbindungsrichtung* in the structure, as far as external influences can be excluded. It will be shown, however, that these *Hauptbindungsrichtungen* have to be replaced by the directions of chains of strong bonds.

(*b*) Gibbs (1906) showed thermodynamically that in the case of a crystal in equilibrium with its surroundings the condition that $\Sigma\sigma_i F_i$ is a minimum applies. Here σ_i is the specific surface free energy of the *i*th face and F_i the area of this face.

Wulff (1901), later Liebmann (1914) and more recently von Laue (1943) showed the Gibbs condition to be equivalent to the statement that a point can be located in the crystal (the Wulff point) from which the distances to the different crystal faces are proportional to the specific surface free energies, or, in other words, that the surface area of a crystal face —and consequently its morphological importance— decreases in general with increasing surface free energy.

The Gibbs condition, however, has never been applied to practical morphological problems because, apart from the fact that crystal growth is not a reversible process, no method is known by which the surface free energies of an actual crystal can be measured or calculated. Therefore we have to find an energy quantity associated with the crystal faces that is more accessible.

A considerable simplification of the problem is obtained by replacing the surface free energies by the surface energies, as defined by Born (1923) in his lattice theory; this means that only bond energies are taken into account.

Instead of this surface energy, however, we take the 'attachment energy', which is defined as the bond energy released when one building unit is attached to the surface of a crystal face. Now we assume that the time needed for the formation of a bond decreases with increasing bond energy. Therefore, the displacement velocity of a crystal face increases with increasing attachment energy; consequently the attachment energy will be representative for its morphological importance because a crystal face will disappear the sooner during crystal growth the faster it moves away from the growth centre. Though our assumption cannot be supported by strict thermodynamical and kinetical evidence, we found that the attachment energies, provided that these can be calculated, represent the morphological importance much better than the mesh areas (see Part II to appear later).

(*c*) Consider a two-dimensional crystal bounded by (10) and (01), each unit cell of which contains one building unit (Fig. 1(*a*)). Suppose there are two types of bonds: *a* in the direction [10] and *b* in the direction [01]; the bond energy of *a* is larger than that of *b*. Now the attachment energy on (10) is *a*, that on (01) is *b*, so that (10) has a greater displacement velocity than (01). Consequently the crystal will be elongated into the direction [10], i.e. the direction of the stronger bond.

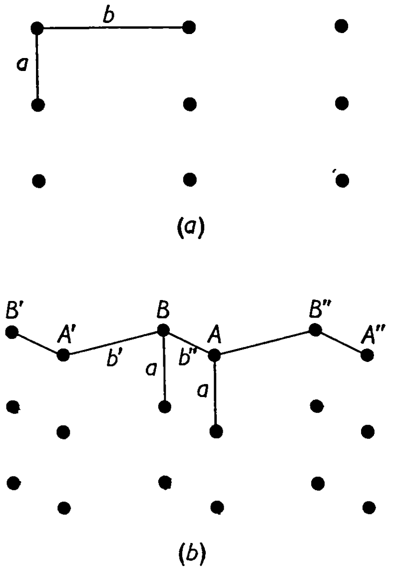

Fig. 1. (*a*) Two-dimensional crystal in which bond *a* is stronger than bond *b*. The crystal will be elongated in the direction of bond *a*.
(*b*) Two-dimensional crystal in which bonds *a* and *b''* are of the same strength, while bond *b'* is much weaker. The strong bond *b''* has no influence on the shape of the crystal, because it is the stronger bond in the chain –*b'*–*b''*–*b'*–*b''*–. The shape of the crystal is determined by the bonds *a* and *b'*. The crystal will be elongated in the direction of bond *a*.

Suppose now, that in a second case each cell has two building units, *A* and *B* (Fig. 1(*b*)), and that they are bound by a strong bond, the bond between *A* and *B''* being weak. We denote this weak bond by *b'* and the strong bond between *A* and *B* by *b''*; the bonds *a* between like building units *A* and like building units *B* in the [10] direction are assumed to have both the same strength as *b''*.

The growth in the direction [01] is now governed by two bonds *b'* and *b''*, of which the weaker determines the displacement velocity, so that the crystal will have smaller dimensions in the [01] than in the [10] direction. This means that the influence of the strong bond *b''* is reduced by its combination with *b'*.

From these examples three conclusions can be drawn:

(1) For a crystal to grow in the direction of a strong bond, these bonds must form an uninterrupted chain through the structure.
(2) If a bond chain contains bonds of different type, its influence on the shape of the crystal is determined by the weakest bond present in the chain.
(3) Important zone directions must be parallel to bond chains containing strong bonds only.

Obviously these chains are periodical in pattern: each period connects a building unit to a structurally equivalent one. In complicated structures each period may consist of several links or 'partial bond vectors' (representing the distance between centres of building units in length and direction). In general, the effective zone direction can be found as the direction of the sum vector of all the partial bond vectors; hence it is parallel to the translation relating two equivalent building units. This sum vector we call a *periodic bond chain vector* (P.B.C. vector). Sometimes the length of a P.B.C. vector is a submultiple of the translation distance, owing to pseudo-halvings, pseudo-thirdings etc.

Our working hypothesis is, then, that the P.B.C. *vectors give the clue to the understanding of the morphological development of a crystal*; important zones are parallel to P.B.C. vectors, and correspond to chains that contain only strong bonds. As soon as a chain of otherwise strong bonds contains one weak bond, it loses its morphological importance. Prominent faces are parallel to at least two high-energy bond chains.

(*d*) The use of the term 'strong bond' needs some further explanation. In general a strong bond is understood as a bond requiring a large amount of energy to be broken, or releasing a large amount of energy when it is formed. But we must be aware of the fact that not every strong bond in a crystal structure has necessarily released its energy in the crystallization process. This is quite obvious in the case of molecular structures; the strong, generally covalent, bonds between the atoms in the molecule have been formed before crystallization could take place and consequently do not have any influence on the morphology of the crystal. A similar effect may be observed in other types of structures; sometimes certain strong bonds may already have been formed in the liquid phase (precondensation), causing a difference in morphological development according to whether the crystal has grown from the melt or from the vapour. A strong bond can also lose its significance through the influence of the solvent. Molecules of the solvent may be adsorbed at the surface of a crystal face so that the formation of a new bond in the structure must be preceded by the breaking of the 'adsorption bond'. In this way the net amount of energy released in the crystallization process may be lowered to such an extent that the effect is discernible in the morphological development.

Therefore, it may be emphasized that we have to define a strong bond as a bond releasing a high amount of energy *in the crystallization process.*

(*e*) To obtain a general morphological picture of a crystal species we have to divide the crystal faces into three classes depending on their positions with respect to the P.B.C. vectors: *class F, or flat faces,* containing two or more coplanar P.B.C. vectors, *class S, or stepped faces,* containing one P.B.C. vector and *class K, or kinked faces,* containing no P.B.C. vector (for the terminology cf. Burton & Cabrera (1949); the name 'flat face' does not imply that all building units should be exactly coplanar: the coplanarity refers only to the P.B.C. vectors).

A glance at Fig. 2 will explain the difference between these classes. Suppose there are three P.B.C. vectors: vector $A\|[100]$, vector $B\|[010]$, and vector $C\|[001]$. These P.B.C. vectors define six F-faces, namely (001) and $(00\bar{1})$ defined by A and B; (010) and $(0\bar{1}0)$ defined by A and C; (100) and $(\bar{1}00)$ defined by B and C. Any face parallel to only one of the vectors A, B or C is an S-face. In Fig. 2 three of these are shown: (011), (101) and (110). Faces which are not parallel to any of the vectors are K-faces, one of which, namely (111), is shown in Fig. 2.

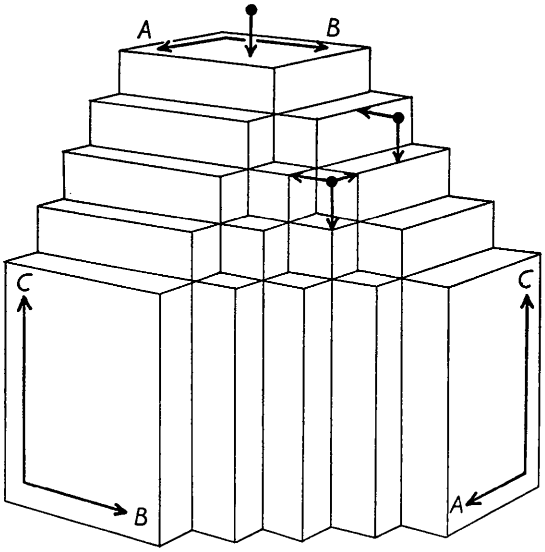

Fig. 2. Hypothetical crystal with three P. B. C. vectors: $A\|[100]$, $B\|[010]$ and $C\|[001]$. The figure shows the F-faces (100), (010) and (001); the S-faces (110), (101) and (011); and the K-face (111).

Another feature can be read off from the figure: the attachment of a building unit to the surface of an F-face involves the release of only a relatively small amount of energy, namely the bond energy in forming bonds of those P.B.C. vectors which do not lie in this F-face. The attachment of a building unit to the edge of a step of an S-face involves the formation of at least one strong bond more than in the case of an F-face. The attachment of a building unit into a kink involves the formation of at least one strong bond more than in the case of an S-face.

Hence the displacement velocities of K-faces are greater than those of S-faces, and the displacement velocities of the F-faces are the smallest. *Consequently the F-faces will become the larger (final growth) faces, and the K-faces are often not observed or belong to the very rare forms. All the other faces are S-faces.*

(*f*) Up to now we have considered only the morphological importance in connexion with the chance of disappearance of the crystal faces in the growth process. But it can be shown that a chance of appearance has also to be taken into account. For that purpose the very beginning of the crystallization process has to be considered.

When crystal growth is starting from a small germ there is in general a notable degree of supersaturation. The supply of material is then so abundant that any building unit, once attached to the surface of the germ, is already overgrown by a subsequent layer before it can diffuse back into the disordered phase. In this stage all kinds of zones with the directions $mp+nq+$ etc. (p, q, etc. being P.B.C. vectors) grow out with about the same velocity—the attachment energy is not yet the determining factor—so that the germ develops into a 'seed' with an approach to an isometric shape. As time proceeds and the external conditions come closer to 'equilibrium' conditions, the attachment energy begins to direct the growth process; the seed will develop more and more, so that its 'faces' (which might be represented by only one mesh) become real crystal faces with a noticeable extension.

If from now on the conditions of growth remain constant, no new faces can be formed which were not present originally on the seed. It is obvious that a higher index face cannot appear at all, as long as the diameter of the 'seed' is so small that there is no room for one mesh on its surface. Therefore, the greater the dimensions of the mesh corresponding to a crystal face, the smaller is the chance that it will appear, and consequently the less is its morphological importance. At this point the geometry of the lattice enters also into our considerations, which are otherwise confined to energy. The chance of appearance is of interest in comparing the relative importance of S-faces within one zone and will be treated more fully in Part II of this paper.

(*g*) Statistical methods sometimes enable us to arrange the crystal forms according to their importance (see, for example, Niggli (1923) and Parker (1923)). In agreement with the conclusions given above, the forms found in the beginning of such a list prove to be F-forms, the rest being S-forms, while K-forms close the list or do not occur at all. This general picture of the morphology was found to be correct in all cases examined so far. In Part II we will treat some minerals in greater detail and show that the theoretical morphological aspect, obtained by calculating the attachment energies, is in very good agreement with the experimental data.

Examples

(1) *Significance of periodic bond chains, illustrated in the case of diamond*

The three minerals diamond, arsenolite and senarmontite crystallize in the same type of structure. In diamond the building units are atoms, linked together by covalent bonds. The building units of the other minerals are molecules and the bonds between them are mainly of the van der Waals type. Both types of bonds decrease very rapidly in strength with increasing distance. Hence only the bond between building units at (0, 0, 0) and ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), and structural equivalents, need to be considered. Two of these bonds form the P.B.C. vector [$\frac{1}{2}$, $\frac{1}{2}$, 0]. The most prominent form of the three minerals is the octahedron. The faces of this form are, indeed, parallel to three P.B.C. vectors.

Niggli (1941) showed that the explanation on the basis of structure geometry encounters difficulties. Indeed here Niggli's conception of 'row density' cannot be used as a criterion for the importance of a zone. Some rows are covered with matter in such a way that a relatively short distance is followed by a distance three times as long. The question arises whether the shortest distance or the mean distance is determinative for the importance of a zone. According to the first criterion (shortest distance) the zone [111] would be more important than [110] (and presumably the dodecahedron more important than the octahedron). The second criterion (mean distance) indicates the zone [110] as more important than [111], in agreement with observations. These difficulties arise because the bonds between the atoms are not considered. The row [111] contains the shortest distance which corresponds at the same time to the strongest bond, but the three-times longer distance does not correspond to any bond at all.

(2) *Relative importance of F-, S- and K-faces, illustrated in the case of urotropine*

Urotropine crystallizes in a molecular structure in which the centres of the molecules lie in the nodes of a cubic body-centred structure. Two bonds can be distinguished: bond *a* between atoms in (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and bond *b* between atoms in (0, 0, 0) and (1, 0, 0). The latter bond is slightly longer so that it will be less strong than bond *a*. Every bond constitutes a P.B.C. vector and hence only the P.B.C. vectors [$\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$] and [1, 0, 0], and their symmetrical equivalents, have to be taken into account. The faces of the forms {110} and {100} are parallel to three and two, respectively, of these P.B.C. vectors, and hence these are *F*-faces. Experiments on the growth of urotropine crystals from their vapour (Stranski & Honigmann, 1950) proved the growth form to be {110}. The equilibrium forms, obtained by tempering at room temperature, are {110}, {100} and {211}, the latter two forms being rather small. According to the theory of Stranski {111} should also be present, when {211} is present. In our terms the observations can be understood because {211} is an *S*-form, whereas {111} is a *K*-form as it is not parallel to any of the P.B.C. vectors. Hence {111} has a greater displacement velocity than {211} and is therefore more apt to disappear.

The authors are very much indebted to Prof. Dr P. Terpstra, head of the Crystallographic Institute, for his encouraging interest and criticism, to Prof. Dr J. D. H. Donnay and Dr G. Donnay for stimulating discussions during the first stage of the work, and to Prof. Dr E. H. Wiebenga for his critical remarks on some thermodynamical questions.

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