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RELATIONS BETWEEN MORPHOLOGY AND STRUCTURE OF CRYSTALS

1. - The morphology shown by a crystal is the result of its growth history. The growth rates of crystal faces depend on internal and external factors. The two internal factors are: crystal structure and defects. Among the external factors that influence the growth rate the following are the most important ones: conditions of temperature and pressure, supersaturation, impurities present in the disordered phase or adsorbed on the surface of the crystal (including solvent and co-solutes) and the symmetry of the environment.

In the following paragraphs we shall mainly discuss the internal factors.

2. - To elucidate the general relation between morphology and structure we consider the growth of a two-dimensional crystal or a growth layer on a crystal face. We suppose that the layer is bounded by straight edges. The problem why these edges happen to be straight is not considered here. The problem with which we are faced is: which of all possible edges have the highest probabilities to appear as straight edges? In fig. 1 a two-dimensional crystal is drawn in which one of the edges has a kink. The growth of this crystal occurs by accretion of new building units. The building units A and C have the same interaction energy (the same bonds) with the crystal, so they have the same probability to be attached to the crystal. The building unit at B, however, will have a higher probability to be attached to the crystal, if it has at least one strong bond more to the crystal. When this is the case, the kink sites will fill up preferably, and the edge will remain straight. Evidently the condition that the edge remains straight is,

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that parallel to the edge there must be in the crystal structure an *uninterrupted chain of strong bonds that are formed during the crystallization process*. Such a chain has been called a Periodic Bond Chain (PBC) (Hartman and Perdok, 1952, 1955). As a consequence, layer growth will be possible when there is at least one PBC more in the layer, in a different direction.

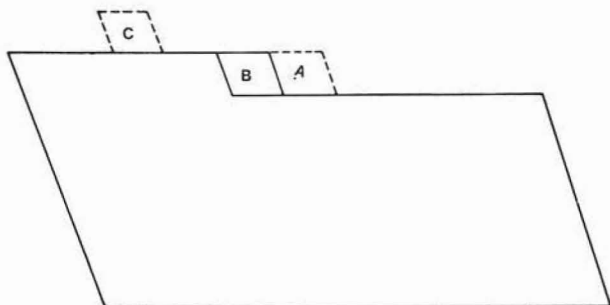


Fig. 1. — Two-dimensional crystal or polygonized growth layer with building units.

Consider now the growth of a three-dimensional crystal. Fig. 2 shows a schematic projection of a crystal structure. Each circle represents a PBC which is perpendicular to the plane of drawing. The horizontal face shows a layer growing on it. This layer growth is due to the fact that neighbouring PBC's are bonded by means of strong bonds. The deposition of a PBC next to the edge (A) is more probable than the deposition of a PBC elsewhere on the surface (C), just because of the presence of these strong bonds. Should there be no such bonds, then the probability for the deposition of a new PBC is the same at A, B or C, and the face will therefore not grow according to a layer mechanism. Following this reasoning we can distinguish three categories of crystal faces:

- F faces* (flat faces) which contain at least two PBC's in an elementary layer d_{hkl} ;
- S faces* (stepped faces) which contain only one PBC in a layer d_{hkl} ;
- K faces* (kinked faces) which contain no PBC in a layer d_{hkl} (which value must be given to d_{hkl} will be discussed in paragraph 4).

The three categories of faces are represented in fig. 3, where it is supposed that there are three PBC's parallel to the crystallographic axes a , b and c . Therefore (100) , (010) and (001) are F faces, while faces $(hk0)$, $(h0l)$ and $(0kl)$ are S faces and (hkl) are kinked faces, supposing that h , k and l are not zero.

Fig. 3 also indicates the three different mechanisms of crystallization: F faces have a layer growth mechanism, either by two-dimensional nucleation or by a screw dislocation mechanism. S faces need only one-dimensional nucleation and they tend to have a preferential

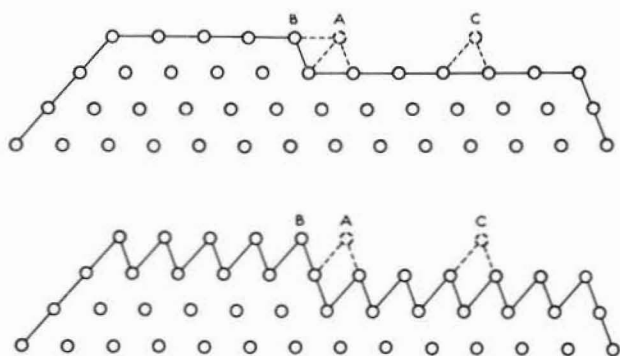


Fig. 2. — Three-dimensional crystal structure projected along a PBC $[uvw]$. Each circle represents a PBC seen end on. When neighbouring chains A and B are bonded by strong bonds, layer growth occurs and the face is an F face. When chains A and B are not bonded, the face is an S face and no layer growth occurs.

growth in one direction. K faces need no nucleation at all, so they grow very rapidly and do not normally occur on crystals. The F faces grow slowly and these are the most important ones. They determine the habit. S faces have an intermediate position. When growth occurs under conditions of slight supersaturation and no other external factors are interfering, a crystal is bounded by F faces only. The assumption made here is that the concentration of defects, particularly dislocations is about the same for all faces.

3. - The considerations in the foregoing paragraph give a qualitative understanding of the morphology associated with a certain crystal structure. A more quantitative approach is possible only when there exists a method to calculate growth rates of various faces. At present this is not possible. However, all correlations between structure and

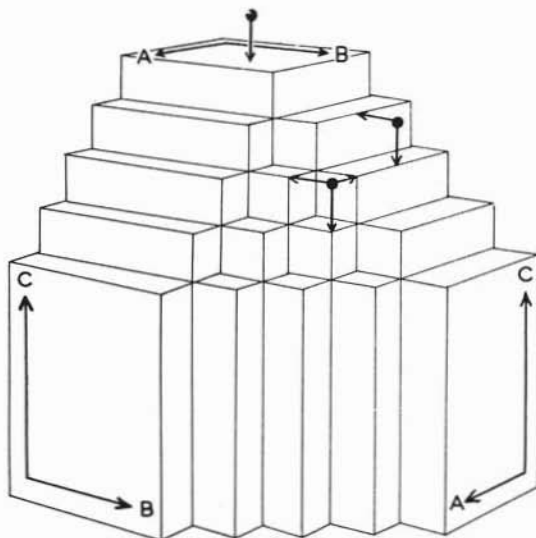


Fig. 3. — Hypothetical crystal with three PBC's: A // [100], B // [010] and C // [001]. F faces are: (100), (010) and (001); S faces are: (110), (101) and (011), while (111) is a K face. The attachment energy for (001) is one bond, for (011) two bonds and for (111) three bonds.

morphological data support the hypothesis that a crystal face is the more important (that is: occurs more frequently and has a greater surface area on the crystal) the smaller is the *attachment energy* E_{att} . This quantity is defined as the energy released per molecule when one layer d_{hkl} (a *slice*) is attached to the face. A low E_{att} means a low growth rate. As shown by Bennema (1972) current crystal growth theories are not in conflict with this hypothesis.

For the morphology it is sufficient to know the relative attachment energies of the crystal faces. Various approximations can be used. The simplest one is the broken bond approximation, in which the num-

ber of broken bonds is counted across the interface crystal-vacuum. This is probably a good approximation for covalent bonds. For ionic bonds lattice sums for the Coulomb interaction must be used and here the Madelung method is particularly useful (Madelung, 1918; Kleber, 1939; Hartman, 1956).

It should be emphasized here that the term « strong bond » means every bond between a crystallizing particle (atom, ion or molecule) and other particles in the first coordination sphere. Sometimes the boundary of the first coordination sphere is not at once clear, when the atom or ion has a large radius as e.g. K in sanidine. In most cases, however, one finds a clear hiatus in a list of increasing distances of anions surrounding a large cation. All bonds smaller than the hiatus are then considered to be strong bonds.

Another problem sometimes arises as to the nature of the crystallizing particles. For complex anions like SO_4^{--} , NO_3^- , HCO_3^- , or for complex cations like $\text{Mg}(\text{H}_2\text{O})_6^{++}$ (as e.g. in picromerite $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) there is no problem: the internal bonds in these complex ions existed before the crystallization process started. Doubts may arise whether e.g. all SiO_4 groups in the neso-silicates are present as such in the disordered phase.

4. - The foregoing paragraphs described the relation of morphology to structure in terms of bonding. A far simpler relation has been formulated in terms of lattice dimensions and structure symmetry. According to the *law of Bravais-Friedel* (Friedel, 1907) the morphological importance of a crystal face decreases with decreasing d_{hkl} , taking into account the lattice modes. Considering the cubic lattices three types of morphology should exist:

P-lattice: (100), (110), (111), ...

I-lattice: (110), (200), (211), ...

F-lattice: (111), (200), (220), ...

Donnay and Harker (1937) showed, that glide planes and screw axes also have their influence. They formulated their law as a law of observation without trying to give an explanation. The physical basis of their amendments to the law of Bravais-Friedel is that the surface, and therefore the surface energy, is repeated after a distance d_{hkl} . A good example is provided by pyrite, of which the most important

forms are $\{100\}$, $\{111\}$ and $\{210\}$. This is at variance with the three types of morphology derived from the lattices. Taking into account the glide plane a in the space group $Pa\bar{3}$, the order of decreasing d_{hkl} values becomes: (111) , (200) , (210) , ..., in excellent agreement with the observations. In many cases the Donnay-Harker law is well obeyed as shown by Shafranovskiy (1957) and in table 1 for orthorhombic sulphur (Hartman, 1953), where the forms are listed according to their persistences (the percentage of different combinations of crystal forms on which the form has been observed; cf. Niggli, 1923). The forms $\{114\}$ and $\{221\}$ do not appear on the Donnay-Harker column, while $\{121\}$ and $\{137\}$ do not appear in the persistence list. The order is of course not the same, but the rank correlation coefficient is very high.

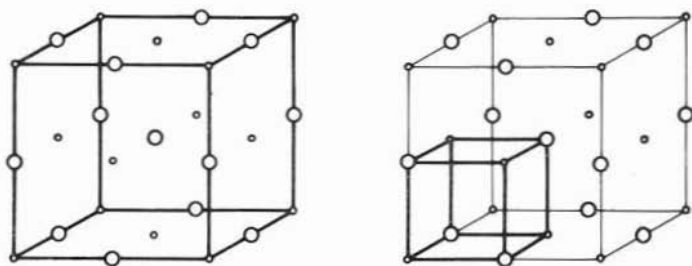


Fig. 4. — Unit cells of the NaCl structure type. Left: the face centered structural unit cell; right: the primitive morphological unit cell.

An extension to the Donnay-Harker law was given by Donnay and Donnay (1961). They considered the effect that certain atoms or centres of molecules with fortuitous values of their coordinates might have on the morphologically effective interplanar distance. The physical interpretation of the effect lies again in the periodicity of the surface energy, or better, the pseudo-periodicity. For example, consider the NaCl structure with space group $Fm\bar{3}m$. The largest interplanar distance is d_{111} , so the octahedron would be the most important form. However, in the structure, layers parallel to (111) of Na^+ ions alternate with layers of Cl^- ions with an interlayer distance d_{222} . The surface energy of (111) bounded by Cl^- ions is almost the same as when the face is bounded by Na^+ ions. In an electrostatic point charge

model these energies are even exactly the same. For NaCl, the full consequence is that for the crystal growth process the small cube in fig. 4 can be considered as the unit cell. Hence there may be a difference between the *structural lattice* and the *morphological lattice*. Another example is given by crystals of dibiphenylene ethylene. In this structure the disc-shaped molecules form piles along the *c* axis.

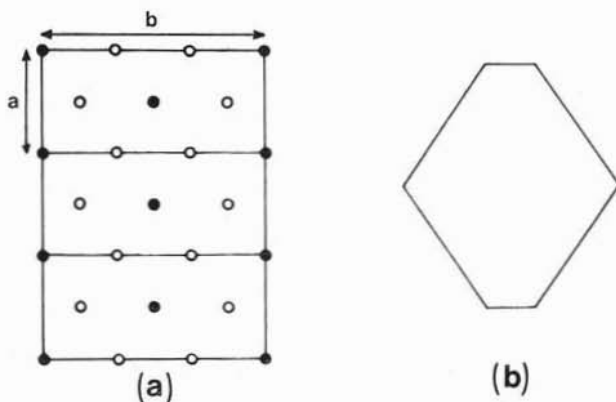


Fig. 5. — Projection of the dibiphenylene ethylene crystal structure along [001]. Each circle represents a pile of disc-shaped molecules in the *c* axis direction. In (a) three unit cells are shown; filled circles and open circles represent each a set of equivalent molecules. In (b) the cross-section of the needle-like crystals is shown.

There are two sets of equivalent molecules, the centres of which are at $(0, 0, 0)$ and at $(1/2, 1/6, 0.434)$. The fortuitous values near to $1/2$ and $1/6$ lead to a pseudo unit cell with $b' = b/3$ and a pseudo-centering (see fig. 5). From the unit cell dimensions and space group (Fenimore, 1948) the order of decreasing d_{hkl} values is:

$$(020), (110), (130), (200), (111), \dots$$

Introducing the pseudo-translations, the order becomes:

$$(130), (200), \dots$$

in agreement with the observations (needles bounded by large (130) and smaller (100) faces). The effect of pseudo-symmetry has been discussed in various cases: for columbite (Donnay and Donnay, 1961;

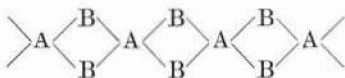
Hartman, 1967), for brookite (Hartman, 1965) and for SnI_4 (Hartman, 1968).

For the PBC method outlined in paragraph 3, the repeat distance of the surface configuration (or the surface energy) is of importance. Therefore the d_{hkl} values eventually are submultiples of the interplanar spacings caused by screw axes, glide planes or pseudo-symmetry (Hartman, 1963).

5. - Because of the periodicity of the crystal structure the PBC's must have the same composition as the crystal. Simple PBC's are found in simple structures with a high symmetry. Straight chains of the type:



are found along the cube edge of the NaCl structure type and along the cube body diagonal for the CsCl structure type. More complicated PBC's, but still easily recognizable, of the type:



occur in the fluorite structure along the $\langle 110 \rangle$ directions and in the rutile structure along the c axis.

A needle-like habit may occur when there is one prominent PBC. Examples are SiS_2 , which has a PBC of the AB_2 type just discussed along the needle axis. In this PBC the bonds between Si and S are covalent. Neighbouring PBC's are bonded by weak Van der Waals contacts between the sulphur atoms. Another example is the mineral stibnite. Along the c axis there are Sb_4S_6 chains which are laterally bonded by longer and weaker bonds than occur in the c axis chains.

The other extreme habit, plate-like, occurs when there are two or more prominent PBC's parallel to the plate. Examples are the CdI_2 structure in which there are layers parallel to (0001) consisting of a layer of Cd atoms between two layers of I atoms. Within such a slice there are three PBC's of the AB_2 type as found in fluorite along $\langle 110 \rangle$. Neighbouring slices are bonded weakly by Van der Waals forces mainly. Another example is the mica structure where all strong bonds are found within the tetrahedral-octahedral-tetrahedral layers.

The bonds between these slices are formed by the K-O bonds which are much weaker than the Si-O, Al-O and Mg-O bonds.

More complicated PBC's are found in more complex structures. The Si-O chains in pyroxenes are well known. In order to find the

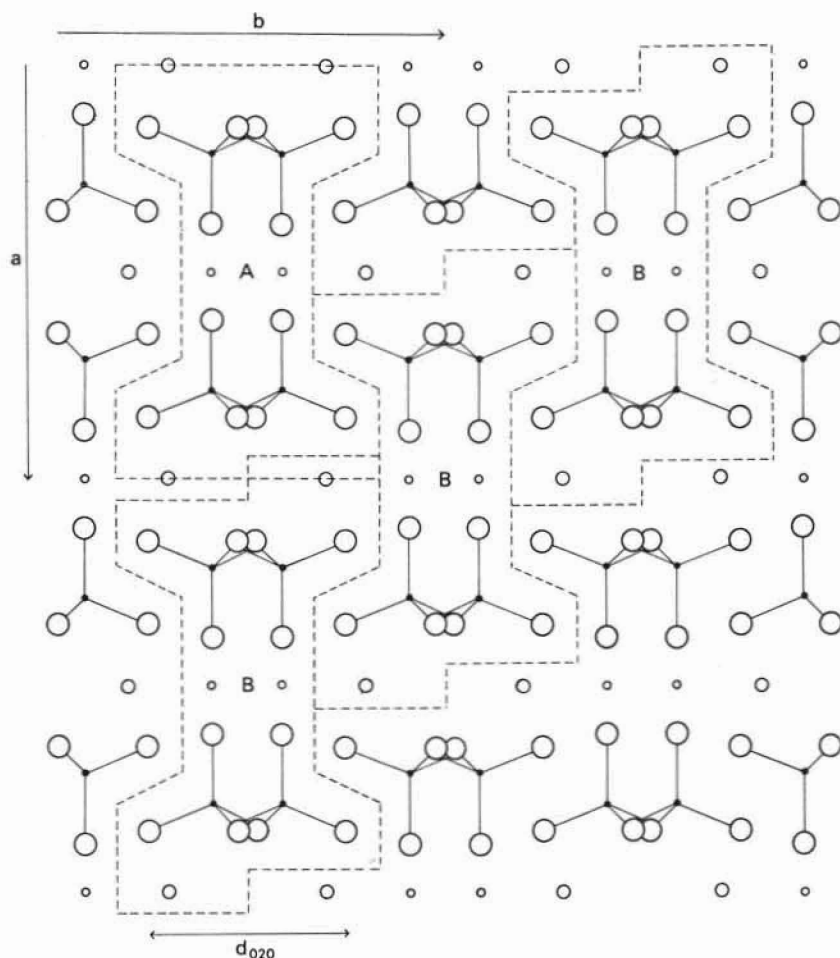


Fig. 6. — Schematized projection of the diopside structure along $[001]$. Large circles: oxygen; intermediate circles: Ca; small circles: Mg; dots: Si. Only Si-O bonds are drawn. A PBC $[001]$ has either the configuration «A» or «B». A slice d_{110} contains a succession of PBC's B, a slice d_{020} is composed of PBC's A or B.

PBC along the c axis (see fig. 6 which gives a projection along this axis) we have to join two of these Si_2O_6 chains by means of strong Mg-O bonds. To obtain the composition $\text{Ca}_2\text{Mg}_2\text{Si}_4\text{O}_{12}$ two Ca atoms must be joined to the $\text{Mg}_2\text{Si}_4\text{O}_{12}$ core of the PBC. It is not at once clear which Ca atoms have to be taken. One possibility is the PBC «A» where the Ca atoms are supposed to be statistically divided between neighbouring PBC's. A sequence of parallel PBC's of type «A» in the direction of the a axis determines a slice d_{020} , so (010) is an F face. Another possibility is shown in the PBC «B», where to both sides of the core a Ca atom is joined. When these PBC's are translated in the direction $[\frac{1}{2} \bar{1} \frac{1}{2} 0]$, the slice d_{110} is obtained. Hence {110} is an F form. Note that the [100] translation applied to the «B» type PBC produces exactly the same slice d_{020} as with the «A» type.

So from this analysis it may be concluded that {010} and {110} are F forms. This implies that there are other PBC's presumably in the directions [100], [101], $\langle \frac{1}{2} \frac{1}{2} 0 \rangle$, and $\langle \frac{1}{2} \frac{1}{2} 1 \rangle$. The surface of (110) in fig. 6 seems somewhat ragged. A smoother surface is obtained when the Si-O chains are joined first by the Ca atoms, leaving the Mg atoms at the outside. In this case, however, we have many unsaturated Mg-O bonds, which are stronger than the Ca-O bonds, and this might well give rise to a higher E_{att} . A final decision can be made only after the calculation of E_{att} for both cases.

Similar arguments can be applied to the amphibole structure. Here again (010) and (110) are found as F faces.

The elongated habit of sillimanite, andalusite and epidote can be explained by a PBC containing Al-O octahedral chains. For simplicity only the structure of sillimanite will be discussed. In fig. 7 four unit cells are drawn in a projection along the c axis. In this direction we find zigzag chains of the AB type with composition SiAlO_2 . A combination of two of these latter chains with one Al_2O_4 chain gives a complex chain $\text{Al}_4\text{Si}_2\text{O}_8$, which is not the stoichiometric composition. In order to arrive at this, the remaining oxygen atoms have to be divided among the two complex chains within one unit cell. Presumably this will be the oxygen atom linked to the silicon atom. There appear to be two possibilities to construct the complex chains of com-

position $\text{Al}_4\text{Si}_2\text{O}_{10}$, which are PBC's. These have been indicated in fig. 7 as A and B. A sequence of parallel PBC's «A» constitute the slice d_{200} of the F face (100). In the same way a sequence of parallel PBC's «B» constitutes a slice d_{020} . A slice $d_{1\bar{1}0}$ or d_{110} is formed when PBC's «A» are put into a sequence through the operation of

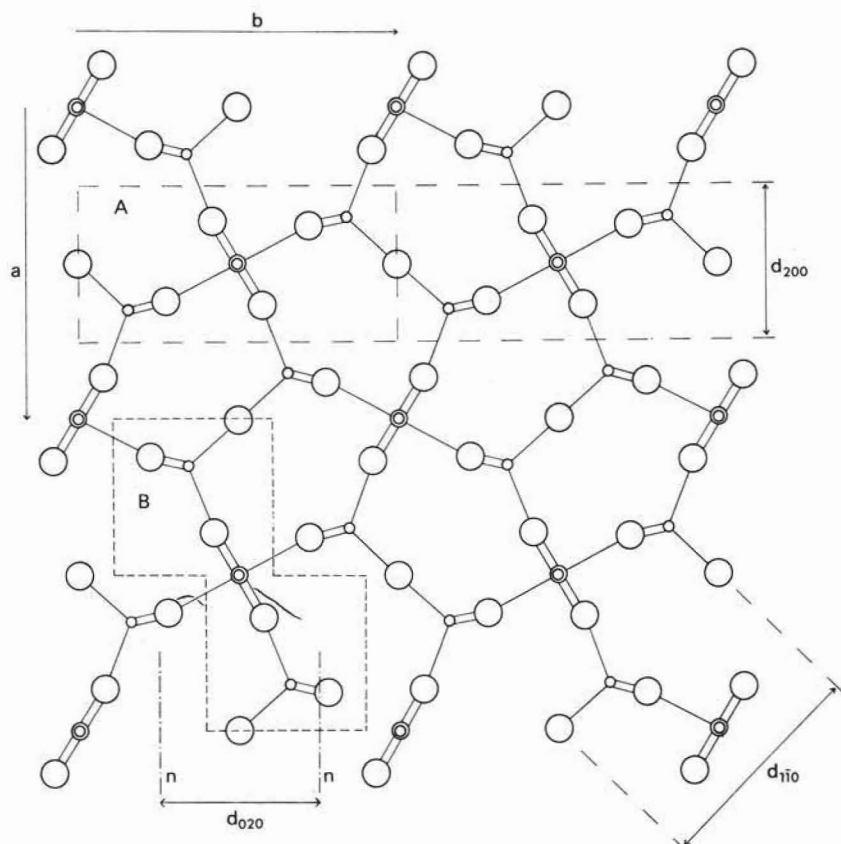


Fig. 7. — Schematized projection of the sillimanite structure along [001]. Four unit cells are shown. Large circles: two superimposed oxygen atoms; intermediate double circles: two superimposed Al atoms; small circles: Si atom and Al atom, superimposed. PBC's [001] are either of type «A» or of type «B». A slice d_{200} contains type A PBC's only. A slice d_{020} contains type B PBC's only. For a slice $d_{1\bar{1}0}$ (not drawn) either type A or type B may be used.

the glide plane n parallel to (010) . Because of the restriction imposed by the space group on the d_{hkl} values, it is not possible to use PBC «A» for a slice d_{020} . From this projection we can conclude that there are three F forms in the zone of the c axis: $\{100\}$, $\{010\}$ and $\{110\}$. The other PBC's must therefore be sought in directions $[010]$, $\langle 011 \rangle$, $[100]$, $\langle 101 \rangle$, and $\langle 111 \rangle$. Note that the PBC's as well as the slices are centro-symmetric and therefore have no electrostatic dipole moment perpendicular to their directions.

6. - The face development of a certain zone parallel to a PBC is not always in agreement with the Donnay-Harker law, or the extended law. This is due to the fact that sometimes the S face with the highest interplanar spacing between two F faces is, in reality, not an S face, but a K face. This is possible when the d_{hkl} value for this S face is halved, so that the layer $d_{2h, 2k, 2l}$ does not contain a PBC. Two examples will be considered.

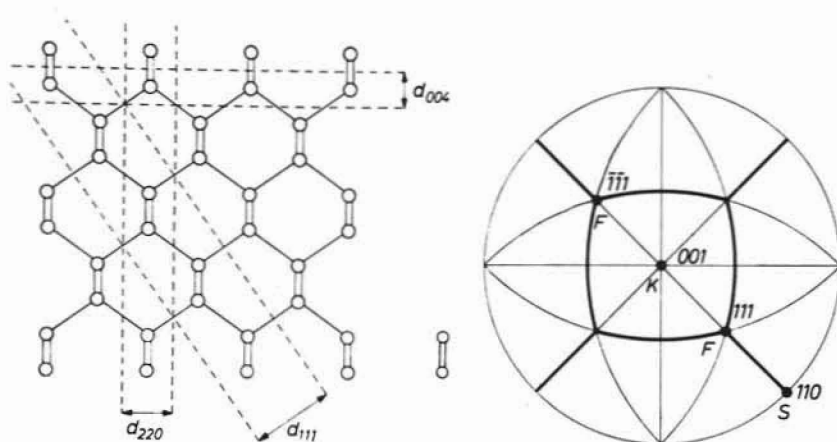


Fig. 8. — Left: projection of the diamond crystal structure along $[1\bar{1}0]$. Each circle represents a carbon atom. All C-C bonds are drawn. Zigzag C-C chains in the direction $[1\bar{1}0]$ constitute a PBC. These are bonded in the slice d_{111} , not bonded in d_{220} , while d_{00c} does not contain a PBC. Hence (111) is an F face, (110) an S face and (001) a K face. Right: In this stereographic projection the parts of the zones (110) that contain S faces are heavily drawn; on the other parts all faces have more or less K character.

Fig. 8 shows a projection of the diamond structure along $[\bar{1}\bar{1}0]$. The zigzag C-C-C chain in this direction constitutes a PBC. Neighbouring PBC's are bonded in a slice d_{111} , so the octahedron is an F face. Because of the space group $Fd\bar{3}m$ the periods for the faces (110)

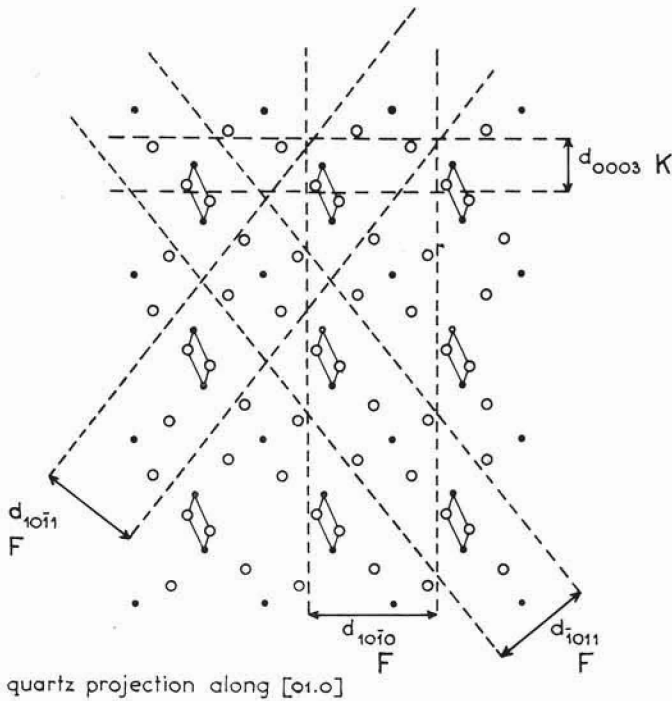


Fig. 9. — Projection of the quartz crystal structure along the b axis. Nine unit cells are shown. Dots: Si, circles: O. Only bonds in the core of the PBC are drawn. Note that the slice d_{003} is too thin to contain a PBC.

and (001) are d_{220} and d_{004} , respectively. In a layer d_{220} the PBC's are not bonded, so (110) is an S face. The layer d_{004} , however, contains only one carbon atom per primitive mesh area, so it is too thin to accommodate a PBC and according to the definition it must be a K face. Now every face between (111) and $(\bar{1}\bar{1}1)$ contains in its outer surface a portion which is parallel to (001) , so in fact all these faces have more or less K character. Therefore the occurrence of (hhl) faces

with $h > 1$ will be more probable than with $h < 1$, a conclusion reached first by Wolff (1962).

The same applies to quartz. It can be shown (Hartman, 1959) that the prism $(10\bar{1}0)$ and the two rhombohedra $(10\bar{1}1)$ and $(\bar{1}011)$ are F faces. Fig. 9 shows a projection along the b axis and the core of the PBC in this direction is shown. It consists of a chain Si-O-Si-O. This chain does not occur in the layer d_{0003} of the basal plane, the thirding being caused by the screw axis present in the space group $P\bar{3}_12$. Therefore the basis (0001) is a K face, and all faces between $(10\bar{1}1)$ and $(\bar{1}011)$ have more or less K character and should have lower persistencies than the steep rhombohedra between the prism and the F rhombohedra. This is in agreement with fig. 10 (Niggli, 1926) where the observed development is shown schematically.

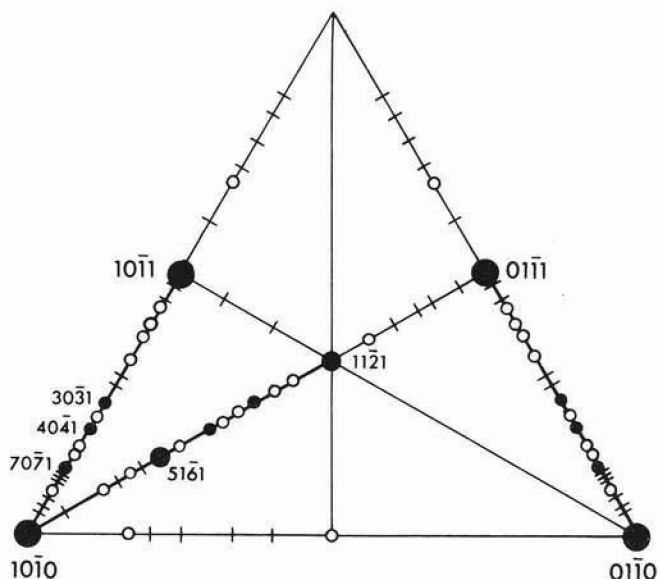


Fig. 10. — Schematic representation of the morphology of quartz (after Niggli). Note the frequent occurrence of faces between $(10\bar{1}0)$ and $(10\bar{1}1)$ and again between $(01\bar{1}1)$ and $(01\bar{1}0)$, while very few faces occur between the basal plane (0001) and the rhombohedra. This difference is caused by the fact that the latter faces have more or less K character, while the others are true S faces (cf. fig. 9).

TABLE 1. — *Crystal forms of orthorhombic sulphur.*

In column a the forms are arranged according to decreasing persistences P given in column b; in column c they are arranged according to decreasing d_{hkl} values, where the effect of glide planes and screw axes of the space group Fddd is taken into account; column d gives the multiple indices.

a	b	c	d
111	98	111	111
113	87	001	004
011	78	113	113
001	77	011	022
110	64	101	202
115	63	115	115
010	54	110	220
101	53	131	131
112	50	133	133
133	49	013	026
013	44	112	224
131	40	311	311
135	33	103	206
100	33	010	040
103	31	117	117
117	27	313	313
331	24	135	135
114	22	315	315
311	19	331	331
119	17	121	242
315	17	137	137
313	15	100	400
221	10	119	119

7. - One of the presuppositions of all theories concerning the relation between morphology and structure is that the crystal growth process is the same for symmetry-equivalent faces. This brings us to the other internal factor: the dislocation density. When there are screw dislocations in one direction only, whiskers may be formed. Not all needle-like crystals are whiskers. We have seen already that sometimes the crystal structure leads to a needle-like habit, but whiskers

are to be considered as a kind of abnormal growth. This implies that apart from the whisker habit there exists another quite different habit formed under other crystallization conditions, where the dislocation density is almost the same in every direction.

One of the consequences of the screw dislocation mechanism of crystal growth is the occurrence of growth spirals (see the contribution by Prof. Bedarida in this volume). Sometimes these spirals are polygonized, that is, the edges are straight and parallel to certain crystallographic directions. When there are no specific interactions with the ambient phase that would lead to a habit change, these straight edges will be parallel to PBC's in the growing face. However, when the solvent or some impurity is preferentially adsorbed along certain edges, these or other edges may become straight portions of the growth front. For example, the growth fronts on the (001) face of NaCl usually show straight portions along the PBC's $\langle 100 \rangle$. When the solution contains a certain amount of urea, insufficient to produce (111) faces, the edges nevertheless are parallel to the $\langle 110 \rangle$ directions, which do not represent PBC's of the NaCl structure.

8. - *Conclusion.* The relations between crystal structure and morphology can be described partly in terms of geometrical quantities, namely the d_{hkl} values, when submultiples due to the action of glide planes, screw axes and pseudo-symmetry features are taken into account. A deeper insight is obtained by considering the strong bonds formed during the crystallization process. This leads to the concept of a PBC and to a classification of crystal forms in three categories, F, S and K, which have different growth mechanisms. Growth forms usually will be bounded by F faces, and when the observations are not in agreement with the deductions from the crystal structure there must be an external influence. Some special features, such as the non-uniform face development of a zone parallel to a PBC can be understood from the crystal structure alone. The morphology as treated here is of a statistical nature. For individual crystals different dislocation densities for different faces and non-spherical symmetry of the surrounding medium will cause distortions from the ideal development. A further evaluation of the relative importance of F faces can be obtained by the calculation of the attachment energy E_{att} . Work on this topic is in progress.

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Answers from P. Hartman to discussion remarks.*Remark Ferraris.*

The periodicity of a crystal structure, i.e. relative lattice dimensions and space group, may be determined from morphology by the application of the geometrical laws. The general procedure is: (cf. various papers by Donnay and collaborators in *Amer. Miner.* after 1937) first find the type of Bravais lattice from the general forms $\{hkl\}$; then find glide planes and screw axes from $\{hkO\}$, $\{hOl\}$ etc. The point group should be known. Sometimes there remains a discrepancy between the periodicity and space group found from morphology and

the results from X-ray diffraction. In that case there is a pseudo-symmetry that may lead to the approximate location of centers of crystallizing particles, e.g. molecules (cf. Hartman, *Acta Cryst. A* 24 (1968) 359).

Remark Rigault.

The proposed relation probably has a limited validity, because the formula is a measure for a kind of mean angle between the bonds and the plane (hkl) without taking into consideration the mutual spatial relation of the bonds, namely the uninterrupted chains. Therefore no distinction in categories of faces can be made. Moreover, a large d_{hkl} value implies the existence of several bonds making large angles with the plane (hkl). This might indicate that the expression $(\sum_i p_i \vec{r}_i \times \vec{r}^*)$ is not very sensitive for changes in h, k and l. In that case the expression varies mainly as d_{hkl} .

Remark Giacovazzo.

The criterion of choosing the shortest bonds is general, insofar that bonds outside the first coordination sphere have little influence on the crystal growth process, because this process can be considered as a consecutive chemical reaction. For example, in aluminosilicates the strong bonds are to be found in the Si-O and Al-O tetrahedra and in the Al-O octahedra. It has no sense to consider bonds beyond these coordinations.

In complex structures first a list of strong bonds should be made, then projections along various lattice directions should be prepared. Two ways are now possible: (1) Find the cores of PBC's in a projection and see how these cores are connected laterally by strong bonds within slices d_{hkl} ; then complete the PBC to a stoichiometric composition. (2) Try to find in a projection slices of F faces and make sure that at the intersection of two slices there is a PBC.

In practice both ways are used simultaneously.

Remark Cristofolini.

For a certain crystal face and a certain growth front parallel to a PBC, the « building unit » is the analogon to Kossel's « repeatable step ». It is the group of atoms contained in one period of the PBC.

The boundary between two consecutive building units in a PBC is the place where the energy necessary to cut the PBC is lowest. The form of the building unit may be different for different growth fronts and for different faces, so there is in general no simple relation between unit cell and building unit.

Remark Riva di Sanseverino.

There is no experimental evidence for the existence of building units in the sense of complete stoichiometric assemblages of atoms, ions and molecules. Consideration of the crystal structure may suggest certain separate particles or groups of atoms, which can be corroborated in some cases by the physico-chemical properties of the solution or the gas phase.

It is hard to decide whether polyhydronium ions are present as such in a solution or not. If these ions were found to lie always within slices d_{hkl} of F faces, this might be an argument in favour to their existence in solutions.

Remark Rossi and Valera.

Dendrites usually occur when the supersaturation is relatively high. In that case the supersaturation varies locally across a face, being larger at the edges and corners. Growth therefore starts preferably at the corners and when the rate of formation of new layers competes with the spreading of the layers, dendrites are formed.

Their direction is often parallel to a lattice row near to the line joining corner and center of a crystal. For example, for NaCl (with PBC's $\langle 100 \rangle$), dendrites are parallel to $\langle 111 \rangle$. For NH_4Cl (PBC's $\langle 111 \rangle$) dendrites are parallel to $\langle 100 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$, depending on the supersaturation (cf. M. Kahlweit, *J. Crystal Growth* 7 (1970) 74). A general interpretation in terms of the PBC theory has not yet been given, but it seems that the first dendrites to appear on increasing the supersaturation are along short lattice periods that are not parallel to a PBC.