CRYSTAL FACES: STRUCTURE AND GROWTH[1]

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ABSTRACT

Hartman, P. 1982 Crystal faces: structure and growth – Geol. Mijnbouw 61: 313-320.

A review is given on current theories about the growth mechanisms of a crystal face. The growth depends on internal factors (crystal structure and defects) and on external factors (supersaturation, temperature and presence of impurities). Three categories of faces are distinguished, depending on the number of periodic bond chains (PBCs) present in a slice d_{hkl}. Only F (flat) faces containing two or more PBCs can grow according to a layer mechanism. They grow slowly and are important. Other faces grow continuously and fast. Impurities adsorbed on the crystal usually retard, but sometimes accelerate the growth and may even provoke the apparition of other faces. Beyond the roughening temperature T_R the flat surface structure of an F face transforms into a rough surface and the growth occurs continuously and is faster. T_R becomes lower when the interaction between crystal and fluid increases. The growth rate of an F face increases when the attachment energy of a new layer is higher. This allows to define a theoretical habit as exemplified for fluorite, quartz, olivine, feldspar, dolomite and calcite.

INTRODUCTION

All mineral crystals once have nucleated and grown to their present size and shape. Often minerals can be recognized merely by their crystal habit, when the crystals are bounded by planar faces. Yet, for one and the same mineral the habit can vary from one deposit to another. Evidently there are two types of factors that determine the shape or habit of a crystal:

– internal factors, such as crystal structure and defects;
– external factors, such as supersaturation or undercooling, temperature, and the presence of material that does not belong to the crystal and that will be designated by the general term 'impurity'. It encompasses trace elements, major foreign elements as well as the solvent.

In order to understand why a certain mineral crystal has acquired a certain habit, one has to consider the process of crystal growth. The present knowledge about crystal growth mechanisms was mainly developed in the domains of physical chemistry and of experimental and theoretical physics. Great progress has been made in the last decades, not in the least due to the impetus given by the demands of various industries on single crystals with specific physical properties.

It is the purpose of this paper to first present a brief survey on crystal growth mechanisms, followed by the application on mineral structures. Then the role of impurities and the influence of temperature and crystallization fluid on the structure of a crystal face and on its growth is discussed. Finally a few results are presented.

CRYSTAL GROWTH

All crystal growth theories are essentially based on a block model of a crystal. Each block (Fig. 1) is surrounded by six others and the cohesion of the crystal is accounted for by assuming bonds between these blocks. One block could be a unit cell. A planar crystal face is thought to grow layer after layer. A growing layer is a terrace that ends at a ledge or step. From the surrounding medium blocks (A) arrive on the terrace and, while being adsorbed, move around because of their kinetic energy until they desorb again, or are caught at the step. The step is not straight, but contains kinks (K), where blocks have left the step because of their excessive

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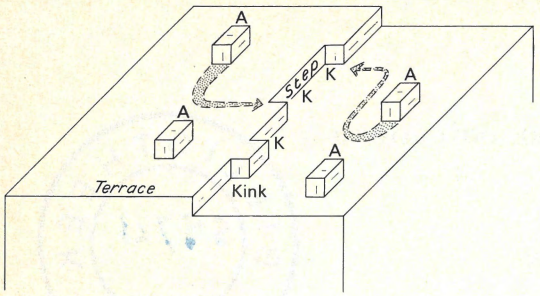

Fig. 1
Block model showing a growing layer on a crystal face. Adsorbed blocks (A) diffuse on the terrace until they are caught at kinks (K) in the step, or desorb again.

thermal energy. Growth occurs by filling in the kinks. When the crystal is in thermodynamic equilibrium with its surroundings (melt, solution or vapour), the flow of blocks towards the kinks equals the flow of blocks from kink sites onto the terrace. When the first flow is the larger one, the crystal grows; if it is the smaller one, the crystal melts, dissolves, or evaporates.

When the layer is completed, a nucleation process among the adsorbed blocks A is necessary to start the growth of the next layer. This so-called two-dimensional nucleation process of crystal growth was developed by KOSSEL (1927) and by STRANSKI (1928). The latter took theories about nucleation by VOLMER & WEBER (1926) into account in his subsequent work with KAISCHEW (STRANSKI & KAISCHEW, 1934; KAISCHEW & STRANSKI, 1934a, b).

It was assumed that a two-dimensional nucleus is formed only after completion of a layer. HILLIG (1966) developed a theory in which several nuclei are formed on a terrace. This model, now known as the polynucleation or birth-and-spread model, was studied in detail by LEWIS (1974).

In 1949 BURTON & CABRERA showed that the two-dimensional nucleation mechanism leads to measurable growth rates only if the supersaturation is about 25%. But it was known from experiments that crystals could grow at a supersaturation well below 1%. FRANK (1949) pointed out that crystals are not ideal and that a screw dislocation ending at a crystal face would circumvent the need for a nucleation process. Fig. 2 shows a crystal with a screw dislocation. The

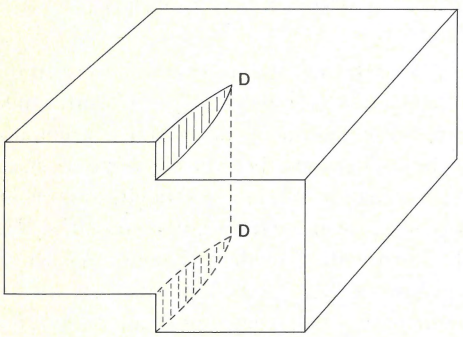

Fig. 2
Block model of a crystal with a screw dislocation DD ending at a face.

right front half is shifted with respect to the left front half over one block height. As a result a screw dislocation DD is created. The exposed step can grow now, turning around the point D. Successive stages are shown schematically in Fig. 3, where the face is seen from above. Its surface now carries a step in the form of a spiral. Since 1949 these predicted so-called growth spirals have indeed been observed, using phase-contrast microscopy. For a review see SUNAGAWA (1977, 1981).

APPLICATION TO MINERAL STRUCTURES

The PBC theory

The question arises which of the many faces that one can imagine on a crystal can grow according to one of the layer growth mechanisms described in the foregoing paragraph. Let us first consider a two-dimensional layer bounded by straight edges (Fig. 4). There is a kink at B and a next block could attach either at A or at C. The probability for adsorption at A and C is the same, but the chance for detachment at B, however, is smaller than at C if there exists a strong bond between the blocks A and B. In that case the straight edge is thus parallel to an uninterrupted chain of strong bonds called a Periodic Bond Chain (PBC). The same holds for the other straight edge, so the layer is determined by two PBCs in different directions. Because of the periodicity of the crystal structure every PBC must have a stoichiometric composition, namely that of the primitive cell. In three dimensions the PBC concept leads to three categories of crystal faces (Fig. 5):

- F faces (F = flat): the growth layer, a slice of thickness d_{hkl} contains two or more PBCs;
- S faces (S = stepped): a slice of thickness d_{hkl} contains only one PBC;
- K faces (K = kinked): a slice of thickness d_{hkl} does not contain any PBC.

The slice thickness d_{hkl} is the repeat distance, normal to the face (hkl) of the specific surface energy, taking into account submultiples due to centered lattices or to glide planes and screw axes perpendicular to the face.

Only F faces can grow according to a layer mechanism. S and K faces grow continuously and rather rapidly, because of the high number of kinks. Typical values are of the order of 10^7 kinks per mm^2 for an F face, 10^{11} for an S face and 10^{12} for a K face. Thus, if the growth rate would be determined entirely by the flow of blocks from solution or vapour directly into the kinks, it would be very small for F faces as compared to S and K faces. Surface diffusion on the terrace considerably increases the flow towards the kinks, but even then the growth rate of an F face is still much smaller than that of S or K faces. Hence, the habit of a crystal will be determined by the relative growth rates of the F faces.

The strong bonds have been defined as bonds formed during crystallization in the first coordination sphere of the

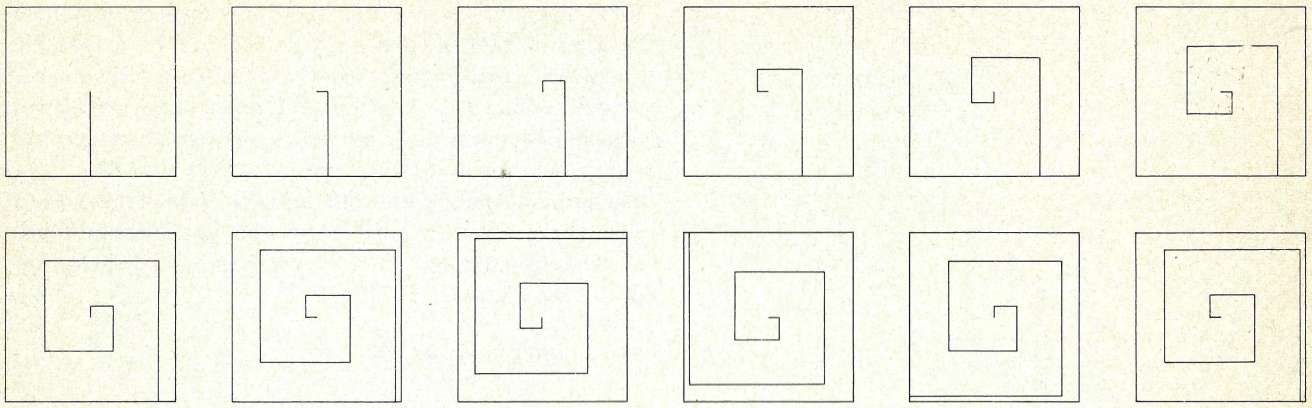

Fig. 3
Crystal face with a screw dislocation emerging in the centre, seen from above. The separate figures show schematically the development of a growth spiral.

particles (atoms, ions, or molecules). For example, growth of calcite involves the formation of bonds between Ca^{2+} and CO_3^{2-} ions. Growth of forsterite occurs by formation of bonds between Mg^{2+} and SiO_4^{4-} particles, because the Si-O bonds exist already in the melt (Cf. VIRGO ET AL., 1980; DE JONG ET AL., 1981).

The PBC theory described thus far was originally developed by HARTMAN & PERDOK (1952, 1955). To derive PBCs and F faces from a crystal structure they started to make a list of all strong bonds within a primitive cell. Then projections of crystal structures along lattice translations [uvw] were prepared. The procedure is then as follows: a PBC in the direction [uvw] may be found with the aid of the strong bonds listing. The next step is to search for bonds between neighbouring PBCs. These define slices of F faces. This procedure is repeated for other directions [uvw]. The number of PBCs is restricted because of the finite number of bonds in a cell. Similarly the number of F faces is restricted. For further details see HARTMAN (1973, 1979).

Because human errors are inherent to such a visual method, computer methods have been devised, such as described by TASSONI ET AL. (1978), KÜPPERS (1982) and STROM (1980, 1981). The latter method also starts with a list of strong bonds and finds direct chains in all possible directions. A direct chain is defined as a chain that would be interrupted when anyone of the bonds would be deleted. A complete PBC is then obtained by adding missing atoms to the direct chain.

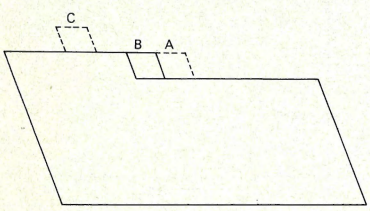

Fig. 4
A two-dimensional growth layer with block B in kink position. The probability that a block desorbs again is lower for A than for C when there is a strong bond between A and B.

Examples

1. The simplest PBC consists of one bond only. It occurs in metals with a cubic closest packing, such as Cu, Ag, Au or Pt. In copper each atom is surrounded by twelve identical atoms and the PBCs are of the kind . . . Cu-Cu . . . in the directions $<\frac{11}{22}0>$. These PBCs define the octahedron {111} and the cube {001} as F forms.
2. PBCs consisting of two bonds only are found in a few simple structures. In halite there are straight PBCs . . . Na-Cl-Na . . . along the cube edges, defining the cube {001} as F form. In diamond there are zigzag . . . C-C-C . . . PBCs in the directions $<\frac{11}{22}0>$, defining the octahedron {111} as F form. The cube is not an F form, because the space group Fd3m requires a slice with thickness d_{004}. This slice contains only one C atom per primitive cell and hence is too thin to contain a PBC. In sphalerite the tetrahedra {111} and $\{1\bar{1}1\}$ are determined as F forms by the zigzag . . . Zn-S-Zn . . . PBCs in the $<\frac{11}{22}0>$ directions.
3. Several structures contain PBCs of the form A_B^BA.

Fig. 6 shows a projection along $[1\bar{1}0]$ of the crystal structure of fluorite (HARTMAN, 1974). In this structure there are PBCs

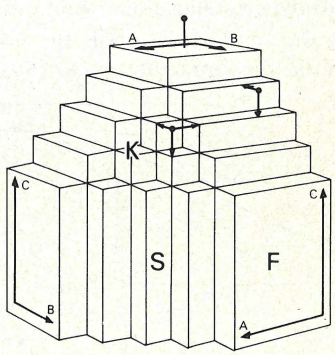

Fig. 5
Hypothetic crystal with three PBCs A, B and C parallel to the crystallographic axes a, b and c, respectively. (100), (010) and (001) are F (flat) faces. (110), (101) and (011) are S (stepped) faces. (111) is a K (kinked) face.

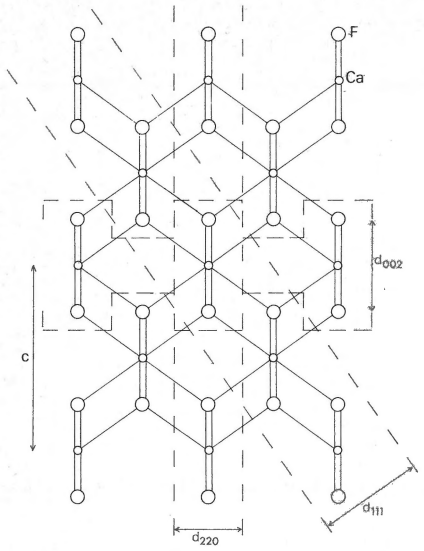

Fig. 6
Projection of the fluorite crystal structure along [1$\bar{1}$0]. Small circles: Ca; large circles: F. Strong bonds between Ca and F are drawn. There is a PBC of composition CaF_2 perpendicular to the plane of drawing. The PBCs are bonded to their neighbours in a slice d_{111}, but not in the slices d_{220} and d_{002}. Hence (111) is an F face, the others are S faces.

Ca^F_FCa along the cube face diagonals $<\frac{1}{2}\frac{1}{2}0>$. It is seen that the PBCs along [1$\bar{1}$0] are bonded to their neighbours in a slice d_{111}, defining the octahedron as an F form. In the slice d_{220} the PBCs are not bonded by strong bonds, so the rhombic dodecahedron {110} is an S face. Similarly, the PBCs are not bonded in a slice d_{002}, meaning that the cube is not an F face. Consequently, fluorite should crystallize in octahedra. This is at variance with the observation that most natural fluorite has a cubic {001} habit. The conclusion can be two-fold: either the theory is wrong, or external factors have a prevailing influence on almost all fluorite crystallized in nature. The latter conclusion is the correct one, as follows from the fact that fluorite crystallizes in octahedra from its vapour or from various fluxes (LECKEBUSCH & RECKER, 1972). Octahedral habits are also known of several other minerals with the same crystal structure type, such as cerianite, CeO_2 and thorianite ThO_2. LECKEBUSCH & RECKER (1972) clearly showed that the habit varies with the crystallization conditions.

PBCs having the same structure as the CaF_2 chains are found in the rutile type structure (HARTMAN, 1968; FELIUS 1976) along the c axis and as the Al_2O_4 chain in sillimanite (HARTMAN, 1979) and andalusite parallel to the c axis and in the epidote type structures parallel to the b axis. This chain is usually described as a chain of AlO_6 octahedra, whereby two octahedra share an edge. In the sillimanite structure there are also direct chains of the type . . . Al-O-Si-O-Al . . . of composition $AlSiO_2$ parallel to the c axis. Two of these direct chains form, together with the Al_2O_4 chain and loose O atoms, a rather complicated PBC of composition $Al_4Si_2O_{10}$ (for details see HARTMAN, 1979).

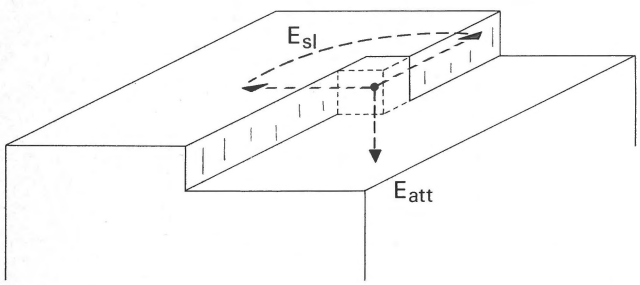

Fig. 7.
A block in kink position is bonded to the terrace with the attachment energy E_{att} and to the growing layer with the slice energy E_{sl}. Their sum is the lattice energy E_{cr}.

The attachment energy

A block is attached to the terrace by the so called attachment energy E_{att} (Fig. 7). When it is moved into a kink it is attached to the end of a chain and to the side of a step. The energy released in this process is called the slice energy E_{sl}. The sum is a constant, the crystal or lattice energy E_{cr}:

$$E_{att} + E_{sl} = E_{cr} \quad (1)$$

Arguments have been presented by HARTMAN & BENNEMA (1980) to show that the growth rate R of a face is an increasing function of E_{att}. The general trend is shown in Fig. 8. A rough approximation is to put R proportional to E_{att}. Results based on this approximation will be presented in the last paragraph. To obtain a qualitative idea, consider two structures where strong covalent bonds and weak Van der Waals bonds are both present. In antimonite, Sb_2S_3, the structure consists of covalently bonded atoms arranged in chains (PBCs) parallel to the c axis. Between these PBCs only weak Van der Waals bonding occurs. Therefore E_{att} of all faces (hk0) is very small, and they thus grow very slowly. All other faces cut the strong bonds, have a large E_{att} and grow fast. Hence the c-elongated habit of antimonite.

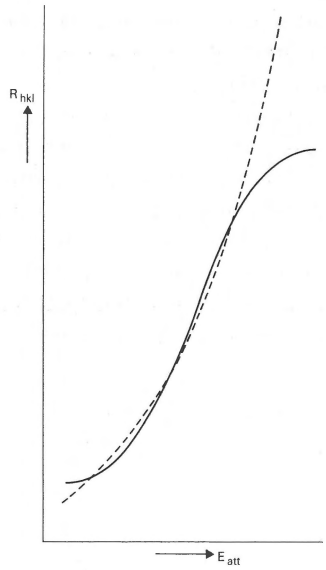

Fig. 8
The growth rate R of a crystal face as a function of the attachment energy E_{att}. Drawn line: spiral growth; dashed line: polynucleation growth.

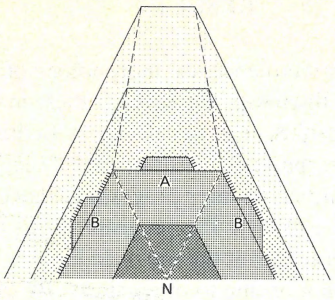

Fig. 9
Development of a crystal when during growth an impurity is adsorbed preferentially on face B and on the corresponding step on face A. The growth of A is accelerated, that of B is retarded, leading to a habit change. Starting from the nucleus N, four consecutive stages at equal time intervals are shown by different shadings.

The reverse effect is found in molybdenite, MoS_2, where the bonding within the layers (0001) is covalent, while between the layers it is of the weak Van der Waals type. Thus the attachment energy of (0001) is low, of all other faces it is high, which explains the platy (0001) habit.

In silicates the Si-O bond is presumably the strongest bond. Taking this into consideration it is at once clear why chain silicates like pyroxenes and amphiboles have a habit that is elongated along the Si-O chain direction. Similarly, phyllosilicates must have a platy habit.

THE ROLE OF IMPURITIES

One of the main factors causing habit change is the presence of impurities in the fluid. For example, when calcite crystallizes from an aqueous solution, all particles (ions or molecules) other than Ca^{2+}, CO_3^{2-} and $CaCO_3^0$ are to be considered as impurities.

Impurities can affect the crystal growth process by their adsorption on the surface of the growing crystal. The effect will be the greater the more tightly the impurity particles are adsorbed. Three ways of adsorption can be distinguished:

A. Adsorption at kink sites. This is the most efficient way of decreasing growth and dissolution rates, known as kink poisoning. It often leads ultimately to the formation of abnormal shapes such as dendrites (SEARS, 1960).

B. Adsorption at the step (but not in the kink). As shown by BLISNAKOV (1958) this will enhance the step growth rate. This occurs because the adsorption diminishes the specific edge energy and this in turn accelerates the spreading of the layers. Very often this effect is superseded by the third way:

C. Adsorption on the terrace. In this case the moving step is retarded because the impurities have to be swept away (CABRERA & VERMILYEA, 1958). Some impurities may be incorporated into the growing layer and these particles are definitely taken up by the crystal when the next layer buries them.

Fig. 9 shows a case where, at a certain stage during growth, an impurity is adsorbed preferentially on B and therefore also on steps on A. Consequently A will grow faster and B slower, leading to a habit change.

Sometimes K faces become slow-growing faces because a layer of adsorbed particles is formed on such a face. When the adsorbed layer has an epitactic relationship to the face, one can imagine the formation of temporary PBCs going from the crystal face into the adsorption layer and back again into the crystal. This would formally explain the observation of growth layers on K faces obtained through habit change (HARTMAN & KERN, 1964).

THE ROUGHENING TEMPERATURE

Temperature is an important factor not only in geology, but also in crystal growth technology. Many single crystals are grown by cooling a melt, a flux, a solution or a vapour. From theoretical work on the structure of the interface crystal-fluid (or-vapour) it has become evident in the last decade that the interface undergoes a drastic change at a certain temperature T_R, the roughening temperature (cf. BENNEMA & VAN DER EERDEN, 1977; GILMER, 1977; GILMER & JACKSON, 1977; VAN LEEUWEN, 1977; MÜLLER-KRUMBHAAR, 1977).

Consider again Fig. 1 and assume that the crystal is in thermodynamic equilibrium with its surroundings. At increasing temperature the flow of blocks from kink positions onto the terrace will increase. Blocks diffusing on the terrace will evaporate or dissolve sooner. This will increase the flow from the crystal, and to restore equilibrium the vapour pressure or the concentration in solution must be increased to make the

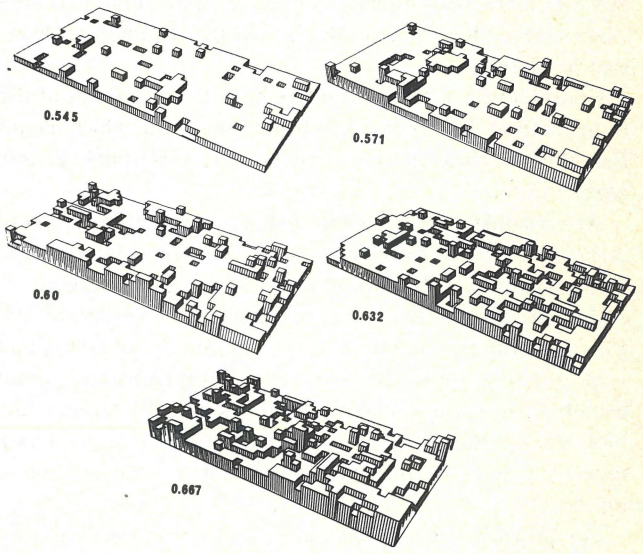

Fig. 10
Computer simulation of the surface structure of a crystal face at various temperatures that increase from the top left to the bottom figure. At low temperature the surface and adsorbed blocks are clearly distinguished. At the highest temperature the original surface cannot be localized anymore, the surface has become rough and growth occurs continuously, instead of layer after layer. (Gilmer & Jackson, 1977).

flow towards the kinks larger. All these processes result in an increase of adsorbed blocks on the terrace. Above a certain temperature the number of adsorbed blocks is so high that the original surface cannot be located anymore. The interface crystal-fluid or -vapour has become rough on the scale of the unit cell. Fig. 10 shows a computer simulation of a crystal surface under conditions of increasing temperature (GILMER & JACKSON, 1977). The transition to the rough state is rather sharp, is called the roughening transition, and occurs at the roughening temperature T_R. Such a rough surface cannot grow according to a layer mechanism, it grows continuously, much like a K face. Hence there is no reason why the face would stay flat. It may become curved as well, because the macroscopic shape of the face is now mainly determined by the curved planes of equal supersaturation or by the curved isothermal planes around the growing crystal.

It has been shown by VAN DER EERDEN (1976) that T_R increases when the so called α – factor increases. This factor was defined by JACKSON (1958) as

$$\alpha = \xi L / RT \qquad (2)$$

where L is the heat of melting, R the gasconstant and T the absolute temperature, while ξ is a crystallographic factor that can be written as (BENNEMA & GILMER, 1973)

$$\xi = E_{sl} / E_{cr} \qquad (3)$$

Associating L with the energy required to transform a solid block in kink position into a fluid block, one can define g (HARTMAN & BENNEMA, 1980) by

$$L = g E_{cr} \qquad (4)$$

and so

$$\alpha = g E_{sl} / R T \qquad (5)$$

Since T_R increases with increasing α, it follows that T_R is high when (a) E_{sl} is high and thus E_{att} is low, and (b) when g is high, that is, close to 1.

Consider now a grain boundary between two grains of the same mineral. In this case L = 0 and thus g = 0, which means that the interface at the grain boundary is rough at any temperature.

At crystallization from the melt L, and therefore g, are rather small. Only faces with high E_{sl}, the most important F faces, may have a T_R beyond the crystallization temperature and remain flat. Other faces are rough and generally curved. This was noticed already by BECKE (1913). KRETZ (1966) and VERNON (1968) found that pyroxene, hornblende and garnet usually form grain boundaries with their {110} faces, while biotite and phlogopite are bounded by {001} faces. These faces are indeed the most important F faces of these minerals.

For K faces E_{sl} is very low, so T_R is also very low, implying that under almost all practical circumstances K faces grow above their roughening temperature, even when g is close to 1. The same will hold for S faces.

The less dense the non-crystalline phase, the larger the factor g. Its value increases from melt to concentrated solution, to dilute solutions and finally to vapour, where g is close to 1. In the same order crystals tend to be bounded more and more by planar F faces.

RESULTS

In this section the theoretical morphology of a few minerals will be briefly discussed. To arrive at these morphologies the attachment energies must be calculated. In the examples only the electrostatic part will be considered. Using the MADELUNG (1918) method, a computer program ENERGY was written by WOENSDREGT (1971). The program allows to calculate the electrostatic potential at the site of an ion due to the slice that contains that ion or due to other slices. By calculating these potentials subsequently for all ions in a primitive cell one obtains E_{sl} and E_{att}. In the following examples the growth rate of a face is supposed to be proportional to its E_{att}.

Quartz

The theoretical morphology of quartz has been described by HARTMAN (1978). Three F forms are found: the prism $\{10\bar{1}0\}$ and the rhomohedra $\{10\bar{1}1\}$ (major), and $\{01\bar{1}1\}$ (minor). Fig. 11 shows the theoretical habit assuming Si^{4+} and O^{2-} ions. Note that the basal plane {0001} does not occur. In a slice d_{0003} (thirding because of the three-fold screw axis) no PBC occurs, so it is a K face. This fact is used in the industrial hydrothermal growth of quartz, where the seeds are plates perpendicular to the c axis, the direction of 'easy growth'.

Olivine

The theoretical morphology of forsterite has been derived by 'T HART (1978a, b). It was assumed that the crystallizing particles are Mg^{2+} and SiO_4^{4-} ions. Fig. 12 shows the calculated theoretical morphology based on a charge distribution in the silicate ion with Si^{2+} and $O^{1.5-}$, which is closer to reality than fully ionized ions (BORN, 1964). The habit closely agrees with the observed morphology of synthetic Co_2SiO_4 ('T HART & WESSICKEN, 1977).

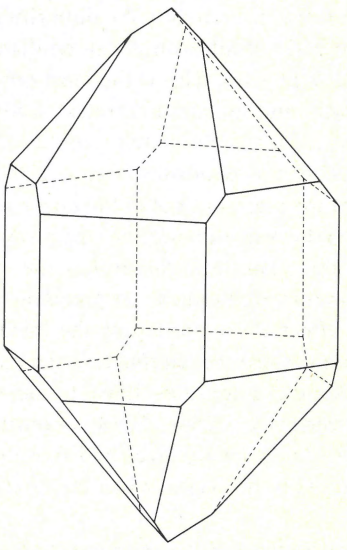

Fig. 11
Theoretical morphology of quartz based on an ionic structure.

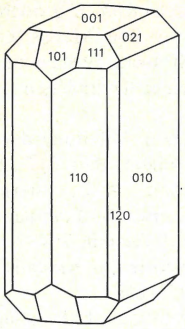

Fig. 12
Theoretical habit of forsterite based on the assumption that the crystallizing particles are Mg^{2+} and SiO_4^{4-} ions and that the charge distribution in the silicate anion is Si^{2+} and $O^{1.5-}$. ('t Hart, 1978b).

Feldspar

The theoretical morphology of feldspar has been derived for sanidine by WOENSDREGT (1983a, b). The structure is considered to consist of ions K^+, Si^{4+}, Al^{3+} and O^{2-}. When only the tetrahedral network is considered {110}, {001}, {010}, {$\bar{2}$01} and {$\bar{1}$11} are found as F forms. When also K-O bonds are taken into account six other F forms are added. Fig. 13a shows the theoretical habit of the growth form, while Fig. 13b represents the thermodynamic equilibrium form, obtained by plotting from a point normals to all F faces and making their lengths proportional to the specific surface energy. Transitions between the growth habit and the equilibrium habit might occur in nature when crystals are subjected for a long time to cycles of slight dissolution and slight growth. It is difficult to present one observed habit, because the habit of K-feldspars is rather variable. WOENSDREGT (1983a) distinguishes four different types: the prismatic Adularia habit with {$\bar{1}$01}, the prismatic Karlsbad habit with {$\bar{2}$01} and {001}, the a axis prismatic Baveno habit and the tabular Finisterre habit. It is clear that external factors must play a role.

Calcite and dolomite

Fig. 14 shows very schematically a cleavage rhombohedron of dolomite. The white blocks represent carbonate ions, the grey

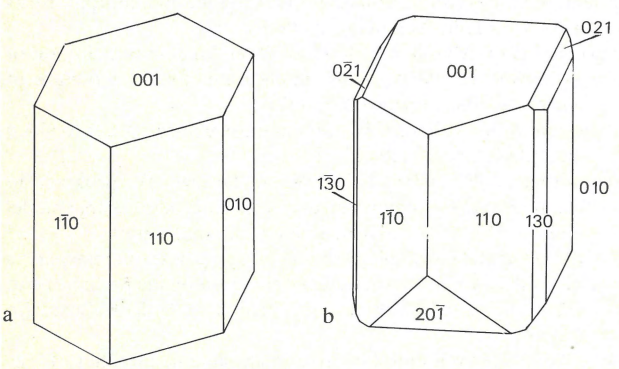

Fig. 13
Theoretical habit of feldspar (sanidine) based on an ionic structure. a: growth form; b: thermodynamic equilibrium form. (Woensdregt, 1983b).

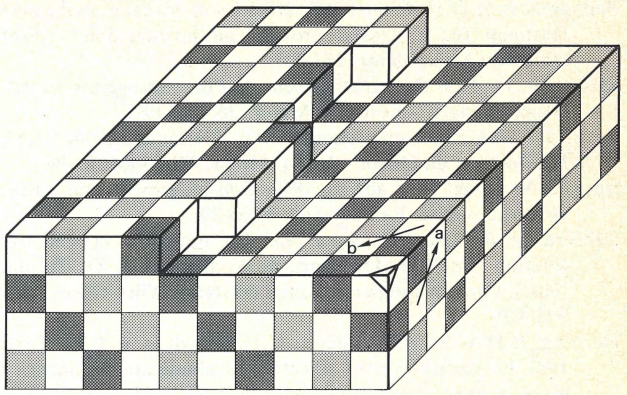

Fig. 14
Growth layer on the cleavage rhombohedron (10$\bar{1}$1) of dolomite. White blocks: CO_3^{2-}; dark grey blocks: Ca^{2+}; light grey blocks: Mg^{2+}. The crystallographic a and b axes and the three-fold axis are indicated. The edges of the rhombohedron are parallel to PBCs (Hartman, 1982).

blocks Mg^{2+} and Ca^{2+} ions. Along the edge of the rhombohedron a PBC . . . Ca^{2+}-CO_3^{2-}-Mg^{2+}-CO_3^{2-}-Ca^{2+} . . . exists and the cleavage rhombohedron {10$\bar{1}$1} is the main, if not the only form. Its attachment energy is far less than that of any other face of calcite or dolomite, so the theoretical habit is just this rhombohedron.

However, calcite is known for its great variability in habit, which therefore must be due to external factors. A review has been given by FOLK (1974) who points out that Mg^{2+} and SO_4^{2-} ions modify the habit. Strong adsorption of either of these ions at kink sites would hamper the growth of the rhombohedron and favour the occurrence of K faces. The K faces with the highest kink density are {0001} and {02$\bar{2}$1} (morphological indexing). Of these the {02$\bar{2}$1} faces have the highest electrostatic potential so the impurity ions are adsorbed strongest on these faces. This would explain the occurrence of steep rhombohedra. There is, however, another fact not considered by FOLK. KIROV ET AL. (1972) found experimentally that steep rhombohedra are also formed when the concentration ratio $[Ca^{2+}]/[CO_3^{2-}]$ is high. When it is low {0001} plates are produced, which fits well with the observation that these occur in nature floating on the water surface (FOLK, 1974). Explanations of these phenomena based on a growth model of calcite in which subsequently layers of carbonate ions and calcium ions are deposited (FOLK, 1974) are incorrect, since every habit change has to be related to a disturbance of the normal growth of the F form {10$\bar{1}$1}. Further work on these phenomena is in progress.

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