Crystal structure and crystal growth: I. The influence of internal structure on morphology

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Abstract

A new model of the relationship between crystal structure and morphology has been developed which uses the symmetry concepts of the Donnay-Harker method, as well as bonding concepts developed by Buerger and Jackson. For each face, one computes the *template fraction*, which is the fraction of the total bond energy attaching a new layer to the substrate. The layer is assumed to have thickness d, the interplanar spacing. New layers will be nucleated more rapidly on faces with higher template fraction, hence these faces will tend to grow themselves out of existence. The bonds defining the template fraction on each face are those which cross the *surface of least bonding,* which is considered to be the exposed surface. Prediction of the exposed surface configuration is an important by-product of the new model. Calculations are made by computer methods, and in addition to template energy, the *surface* or *cleavage energy* and other types of attachment energy may be routinely determined. Although only approximate bond energies have been used so far, examples suggest that the new model is more effective than either the Donnay-Harker or Hartman-Perdok (PBC) methods of rationalizing crystal morphology.

Introduction

The use of external morphology as a clue to the internal structure of crystals is no longer an active branch of crystallography, except for determining the presence or absence of a center of symmetry (but see the interesting paper by Schneer, 1970). However, attempting to determine the influence of internal structure on crystal morphology is still useful, for the following reasons: (1) Any model for predicting morphology logically includes or relies on a model for crystal growth, and thus such predictions can provide tests for crystal growth theories. (2) The observed morphology of crystals has been shown by experiment to be influenced by several factors besides internal structure, such as the composition and nature of the growth medium and the rate of crystallization (*e.g.* Buckley, 1951; Kern, 1955, 1968; Kleber, 1957). The presence of dislocations is also expected to influence the growth rate and thus the development of various forms. If the influence of internal structure could be accounted for, it might be possible to make inferences about the external factors which were operative during growth of particular geological specimens. (3) An important aspect of morphological and crystal-growth models in general is the prediction of

surface structure of crystals on an atomic level. Knowledge of the atomic structure of crystal faces, and of the processes which take place on them, has important applications in geology in the study of sector zoning, the distribution of minor and trace elements, and other problems involving crystal growth. Such knowledge is also useful in electronics and chemical technology, in such fields as semiconductors, catalysis, *etc.* There are experimental techniques which can give direct information on surface structure (Estrup, 1975), but so far these have been applied only to structurally simple substances.

This paper describes a new model of the influence of internal structure on crystal growth and morphology. The model uses the symmetry concepts developed by Bravais and Donnay and Harker, but also takes explicit account of the atomic arrangement and bonding, by means of a quantity called the *template fraction*, which is the fraction of the total bond energy in a growth layer attaching that layer to the substrate. Furthermore, the method involves prediction of the atomic configuration on the surface of each face; it is postulated that an exposed surface will usually be a *surface of least bonding*. In Part II (Dowty, 1976) predictions of surface structure are applied to the problem of sector zoning in minerals.

Previous investigations

Most important ideas on the relation between internal structure and morphology have been reviewed by Buckley (1951) and Hartman (1973). The two methods which have been used most often to try to predict or rationalize crystal morphology are the reticular density method of Bravais, as extended by Donnay and Harker (referred to as the DH method) and the periodic-bond-chain (PBC) method of Hartman and Perdok.

Donnay-Harker method

This method extends previous work by Bravais and Friedel. According to the "Law of Bravais," the importance of a face is proportional to the reticular density, or concentration of lattice points on the face (including those due to centering in nonprimitive lattices). Ranking the faces in decreasing order of their reticular density is the same as ranking them in increasing order of their reticular area, or decreasing order of their interplanar spacing d, as used in X-ray crystallography. Donnay and Harker (1937) proposed modifications taking account of the space-group symmetry, so that all equipoints, instead of just lattice points, are considered. Thus, in the calculation of d, only those Miller indices are used which satisfy the requirements for nonextinction of X-ray reflections, as given in Volume I of the *International Tables for X-ray Crystallography*. A physical interpretation of the DH law was given by Buerger (1947; see below). The implications of pseudosymmetry have been discussed by Donnay and Donnay (1961).

The DH method is easy to carry out, and in its purest form (neglecting pseudosymmetry) is completely objective. However, it can only be an approximation because it takes no direct account of atomic arrangement or bonding. Also, it does not distinguish between growth morphology and cleavage, and it is not applicable to the prediction of surface structure.

PBC method

The periodic-bond-chain method of Hartman and Perdok (1955a,b,c; Hartman, 1973) extends the ideas about strong bonding directions developed by Niggli (1920; 1926a) and Parker (1923, 1930), and also uses the concept of *attachment energy* developed by Kossel (1927) and Stranski (1928).

One first identifies infinite chains of atoms connected by relatively strong bonds only, *i.e.* the periodic bond chains. An interesting empirical approach to the location of PBC's has been described by Wolff and Gualtieri (1962). The most important faces morphologically are supposed to be the flat or F faces, which contain two or more PBC's. Stepped or S faces, containing only one PBC, occur less often, and kinked or K faces, containing no PBC's, occur only rarely or not at all. For the F faces, which are presumed to grow relatively slowly by means of two-dimensional growth layers or steps, the location of the PBC's defines the surface of the growing face, and one may identify a *slice*, whose thickness is the minimum thickness of the growth step. This thickness is d, the crystallographic repeat distance perpendicular to the face, which is determined by the DH rules. The F faces are ranked relative to each other by calculating the *attachment energy* across the interface between the established face and the newly-added slice; this is the average bond energy holding atoms to the surface. S and K faces are supposed to grow more rapidly than F faces because individual atoms are presumably attached to them by more than one bond; thus they present ready-made niches or kinks for the building units to fit into, and supposedly do not require the construction of growth steps or slices.

The PBC method not only takes explicit account of atomic arrangement and bonding, but also predicts surface structure. However, it is also an approximation, and has several theoretical and practical shortcomings: (1) The chains are supposed to have stoichiometric composition, which in crystals with even moderately complex structures leads to complicated chains with various kinks and excrescences. As the complexity of the chains increases, and the directions of the bond vectors within them become more variable, the relations which originally led to the division of the faces into F, S, and K types are obscured, and it is no longer a matter of individual atoms fitting into locations with greater or lesser numbers of bonds. (2) For even moderately complex structures, the PBC method can be extremely difficult to apply, requiring the consultation of projections and structure models. It is difficult to avoid subjectivity and error in the classification of a given face as an F, S, or K face, as shown by the example of barite (below). (3) If the PBC method is correct, it is difficult to see why the DH method should be successful in so many cases (several examples are given below). The PBC method does not systematically consider the symmetry of the crystal, except to determine slice thickness, and to predict the relative importance of S faces in a single zone (Hartman, 1958).

Crystal growth models—the surface of least bonding and the template fraction

When dealing with the growth of crystals with complex structures, it is expedient to consider new material as being added in the form of blocks, rather than individual atoms; some modern kinetic models of crystal growth use this approach (see review by Bennema and Gilmer, 1973). Except for the simplest faces of the simplest crystals, these blocks must usually be regarded as a mathematical fiction. In this paper, such blocks will be taken to be the smallest units which can be repeated by translation parallel to a given face, to give a layer with the stoichiometric composition of the crystal. The minimum height of such a layer on a face is d, as computed by the DH method, since this is the minimum repeat distance perpendicular to the face. The two minimum repeat distances in the plane of the face will be the vectors between lattice points, which also define the Bravais reticular area. Thus a block has thickness d and area of attachment to the substrate equal to the Bravais reticular area (neglecting any microscopic convolutions of the actual surface). The blocks thus defined will have different shapes on different forms. If the unit cell is primitive and no screw axes or glide planes are present, the blocks will have the volume of the unit cell. Otherwise, they will have volume $1/n$ of the unit cell when the DH rules call for using the multiple indices $n(hkl)$ to determine d.

It seems that the rapidity of growth on a given face depends largely on the rapidity with which the block for that face attaches itself to the surface, which has generally been considered to be dependent on the energy of attachment. On slowly-growing faces the block will usually fit into the "half-crystal" configuration (Kossell, 1927) as in position 1 in Figure 1a. Because three surfaces are available for attachment, the attachment energy will be high and the block

rapidly and firmly attached at roughly the same rate for all faces. However, if the growth is by two-dimensional nucleation, the stages which will largely determine the relative growth rates of faces will be the starting of new layers, as in position 2, Figure 1a, and secondarily the starting of new rows (position 3), because these stages are necessarily slower (Buerger, 1947). Thus the critical factor would seem to be the energy with which the block is bonded directly to the face or substrate. The situation is somewhat different if spiral or other dislocations are present, but again, the attachment energy directly to the substrate seems to be critical (Bennema and Gilmer, 1973). An actual two-dimensional nucleus in most cases probably has a volume greater than an individual block, but it is a reasonable hypotheses that *the number of blocks which go to make up a nucleus will be about the same on all faces.*

Because the blocks are not, in general, actual discrete units, some additional concepts are required. First, we need to specify the particular level in the crystal structure across which the attachment of new material takes place. This is equivalent to specifying the atomic structure of the exposed surface of the face, if we neglect temporary surface distortion and adsorption. It is a fundamental postulate of this paper that such an exposed surface will be a *surface of least bonding,* which is that surface parallel to a given face across which the total potential bond energy is at a minimum. Such a surface is not necessarily strictly planar but must possess the translational symmetry of the lattice.

Second, it might be asked why we consider only the energy of attachment to the preexisting surface, when the entire block may have to be built up from atoms or molecules. The answer is that the rapidity with which the blocks or nuclei are built up will depend on the presence of an appropriate template. The pre-
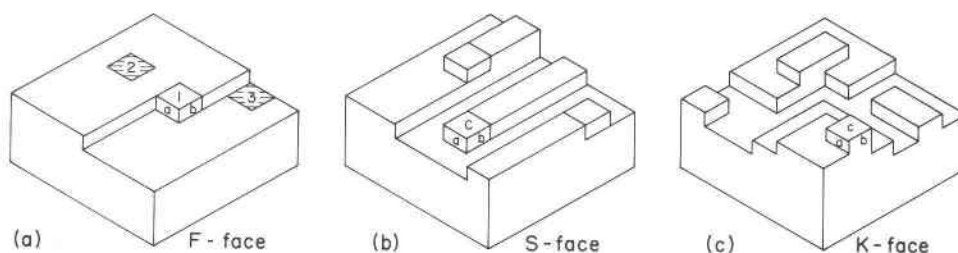

FIG. 1. Growth on different types of faces (schematic). (a) On the flat face, the template fraction for the main face is much smaller than that for the secondary faces a and b. The side face a has larger template fraction than b, yielding rows approximately perpendicular to a. (b) On the stepped face, the template fraction of the main face c is in between that of a and b, leading to the starting of new rows before layers are completed. (c) On the kinked face, the template fraction of the main face is larger than either a or b.

existing face or substrate will act as a template for a new block, and the greater the fraction of the total bonds in the block which are directed to the template, the more rapidly the block will be assembled. The *template fraction* is therefore defined as *the fraction of the total bond energy in a growth layer or slice which attaches that layer to the substrate.* This is somewhat similar in practice to the anisotropy factor of Jackson (1958) and others, although the anisotropy factor was defined in a more limited context. If we consider only layers of thickness d, the template fraction is the fraction of the total bond energy in a single block holding that block to the substrate, across the surface of least bonding.

The larger the template fraction for a particular face, the more rapid growth will be on that face, and the ranking of the forms according to their increasing template fractions is thus expected to approximate their decreasing importance as growth forms. It may easily be seen, as explained by Buerger (1947), how such a model reduces to that of Donnay and Harker; if it is assumed that the bond energy per unit area is approximately the same for all faces, the template fraction is directly proportional to the reticular area. This model actually follows Buerger's interpretation of the DH method in some respects, but by considering the templating properties of the substrate, rather than the attachment energy of molecules, the model is hopefully made applicable to ionic and other nonmolecular structures. Although for simplicity only layers of height d or a multiple of d have been considered in this paper, it may be that layers sometimes have smaller thickness. This seems particularly likely when there exists a pseudospacing that is a submultiple of the true interplanar spacing. By considering such factors, it may be possible to account for the effects of pseudosymmetry on morphology, as discussed by Donnay and Donnay (1961) for example.

Problems arise if some of the bonds are already formed in the growth medium. This may not only change the template fraction, which is properly speaking only concerned with the bonds that are formed during crystallization, but may also influence the surface configuration, and thus the surface of least bonding. In principle, such prestructuring may be dealt with, if the structure of the growth medium is known, as discussed by Hartman and Perdok (1955b); preformed bonds are simply ignored when computing the template fraction, and they are not allowed to be intersected by the surface of least bonding. In practice, great difficulties may be encountered

if there is much prestructuring, and in the extreme case of crystals composed solely of large molecules, the template fraction method would be completely inappropriate; one might use in this case an approach based more closely on Buerger's (1947) analysis.

Only the faces or forms near the head of the template fraction list are expected to grow by the layer mechanism, and thus only these will be identified on mature crystals. These are the F faces of Burton and Cabrera (1949) and Hartman and Perdok (1955), or the "smooth" faces of Jackson (1958). The more-rapidly-growing rough faces of Jackson or the S and K faces of Hartman and Perdok will either grow themselves out of existence or be so poorly defined as to escape identification as discrete faces. One could redefine S and K faces structurally on the basis of the template fractions of possible sub-faces (side faces of growth steps or units) versus that of the main face, as illustrated in Figure 1. However, according to the widely-accepted model of Jackson (1958), the actual mode of growth depends not only on the template fraction (anisotropy factor in his equations) but also the absolute value of bonding energy and the temperature. Thus it is not possible to establish *a priori* cut-off values of template fraction for classifying faces as F or smooth versus S, K or rough.

Hartman and Perdok (1955a,b,c; Hartman, 1973) also use a type of attachment energy to predict the relative importance of F faces, but they compute it in a different way. Instead of taking the total of bond strengths crossing the surface of least bonding on a block basis, they average the energy on an atomic or molecular basis, using only the atoms in the slice of thickness d, and neglecting the atoms which do not bond directly to the substrate. The reason for leaving the nonbonding atoms out of the averaging is not clear, since these latter atoms are part of the structure as well as the ones which are included in the averaging. At any rate, many examples (some are given below) have shown that the averaged per-atom or per-molecule attachment energy does not give as good an account of the morphology as the total per-block template fraction.

Predicting cleavage

As assumed by others (*e.g.* Wells, 1946), a reasonable hypothesis is that if cleavages are developed in a crystal, they will be those planes across which the bonding energy per unit area or the *cleavage energy* is at a minimum. This cleavage energy is identical to the surface energy as defined by Born (1923). Naturally, the cleavage will occur on a surface of least bonding.

The relative ranking of the faces on the basis of cleavage energy is in general not the same as the ranking on the basis of template energy. Thus it may be seen how the cleavages of a crystal may not always be the most important growth faces. However, the faces with lowest cleavage energy tend to be those with low indices, and are usually near the head of the morphological list.

The prediction of cleavage provides an important check on the method of calculation, because the cleavages of a crystal are generally well known, and they may be presumed to depend on internal structure, but not on growth variables such as composition of the medium or rate of growth. It will be assumed that a cleavage is correctly predicted if the plane in question has lower cleavage energy than all other planes which are not cleavages.

The equilibrium shape of a crystal

Gibbs (1878; in his collected works, 1961) defined a specific surface free energy for the faces of crystals, and proposed that the crystal would have equilibrium shape when the total free energy is minimized, the contribution of each face being its specific free energy multiplied by its area. Curie (1885) made an equivalent formulation, using the capillary constant instead of free energy. Wulff (1901) assumed that the growth velocity of a face would be proportional to the capillary constant. Born and Stern (1919) equated the capillary constant with the surface energy as defined by Born (1923), which is the same as the cleavage energy defined in this paper.

Most later work has tended to discount the effect of surface free energy on growth forms of large crystals for several reasons (*e.g.* Buckley, 1951, Ch. 3,4). Indeed, the surface or cleavage energy as measured by the methods of this paper is not at all a good predictor of growth morphology. A few faces with relatively low indices usually have low surface energies, but otherwise the values tend to group about some mean value of bonding density for the crystal, and do not increase greatly with increasing indices. In some simple crystals with high symmetry, such as NaCl, it is possible to identify only one or a few low-index forms which constitute the equilibrium shape, by means of the Wulff construction (Wulff, 1901). However, when the structure is complex and the symmetry is low, it may be necessary to consider forms with rather high indices. The Gibbs-Curie equilibrium shape of such crystals may be rather complex, perhaps in some cases approaching a sphere with only a few small faces.

It would be a misconception to assume that the typical growth shape of a crystal is the thermodynamic equilibrium shape, or that under ideal conditions (very slow growth) the crystal tends toward this shape. The growth shape of crystals above a certain size is evidently dominated by kinetic factors. It appears that large faces are developed during growth because they can become at times distinctly out of equilibrium with the growth medium, due to their proportionately larger kinetic barriers. That is, with respect to the faces which disappear, the larger faces grow at a slower rate at a given degree of supersaturation (although the relative growth rates of the different faces may change with different degrees of supersaturation). Thus in a thermodynamic sense it might be more fitting to call the typical growth shape of most crystals the "anti-equilibrium shape."

Computation methods

Computerized methods have been developed for locating the surface of least bonding, and for evaluating template fractions, cleavage energies and Hartman-Perdok attachment energies. At present the evaluation of these quantities is only approximate, but the computing method is rapid, and provides an essentially objective approach to predicting morphology. The procedure is conveniently divided into three steps, and three separate FORTRAN computer programs are currently used for the complete operation.[1]

Step 1 (Program MORPH)

The reticular area for each possible face is computed according to the DH rules, and the faces are ranked in increasing order of reticular area. This gives the predicted DH morphological aspect (Donnay and Harker, 1937) for the crystal, and serves to identify objectively the most likely faces on which to carry out more detailed work.

Step 2 (Program BOND)

A complete and unique set of interatomic bonds for the unit cell is identified, and a bond strength is assigned to each one. The procedure for identifying bonds and assigning strengths is basically that of a normal bond-length computing routine. At present, only bonds between first-nearest neighbor atoms, called hereafter *first-order bonds,* are routinely used; in the case of ionic structures, only cation–anion bonds are used. It is not difficult, however, to include

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[1] Copies of these programs are available from the author.

a limited number of higher-order bonds. A bond table or matrix is constructed, with entries for specific atoms, usually cations and anions. The number of atoms used as entries for the table is at least as great as that in the unit cell, and usually greater. If a bond exists between two atoms, the corresponding element in the table is the bond energy; if no bond exists, that element is zero.

The assignment of bond strengths or energies is critical in complex crystals, and several methods have been tried. For ionic crystals, one can use simple point-charge coulomb energies, as did Hartman and Perdok (1955c) and others. However, use of formal valences as charges has been found to be unsatisfactory for silicates, giving too little strength to the Si–O bonds for example. A different method is presently used for complex oxides and silicates although this too has been found to be inadequate in some cases (see Part II; Dowty, 1976). The lattice energy of the simple oxide of each cation is calculated from standard thermodynamic data (Kubaschewski and Evans 1967; Moore, 1970) using the Born-Haber cycle, and bond energies are computed assuming that all lattice energy is in the first-order bonds. It is then considered that oxygen has the same charge in all the oxides (the exact value is irrelevant, since oxygen is usually the principal anion in the crystals of interest, and only relative values are needed), and a relative "effective valence" or charge for each cation is derived. Hydroxyls and halogens, where they occur, can be assumed to have half the charge of oxygen. These charges are used in coulomb calculations for the crystal of interest. This method of approximation hopefully takes account of both a "normal" contribution from covalent resonance, and those bond strength variations in the crystal of interest which are reflected in the interatomic distances. Some "effective valences" are given in Table 1.

Step 3 (Program PLANE)

This step identifies the surface of least bonding and measures total bond strengths for each rational face
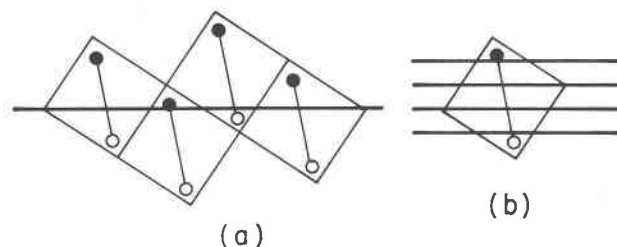

FIG. 2. Two dimensional illustration of the intersection of several unit cells by a rational plane; (a) the real case; (b) mathematically equivalent case of several planes intersecting a single unit cell.

selected in Step 1. The height of each atom from a plane or planes parallel to the rational face is computed, and the atoms are then ranked in order of this height coordinate. Except for faces with the simple indices (100), (010), (001), etc., a given rational plane intersects several unit cells at different levels (Fig. 2a). Instead of considering several unit cells, however, a mathematically equivalent procedure is to consider several equidistant planes cutting the same unit cell (Fig. 2b), which is in practice much simpler. The number of planes is at least as large as the sum of the indices. The height coordinate of each atom must then be determined with respect to each plane, and a given atom appears as many times in the final sorted list as there are separate planes. Fortunately, it is not necessary to take account of cell parameters or actual interatomic distances in this step; the atomic locations may be specified by their fractional coordinates only, and the cell may be considered to be a cube with edge length one.

In order to find the surface of least bonding, the set of parallel planes is in effect caused to move through the structure atom by atom, and the total bond strength which crosses the entire set is computed at each step. They are moved through a distance equal to their separation, which would be the interplanar spacing d if computed in the actual unit cell. This is done in practice by considering successively the atoms in the master sorted list, then going through the bond table and identifying all the atoms which lie above the given atom and are bonded to it or any other atoms with the same or smaller height coordinates. The location of the set of planes which gives the minimum total bond energy is specified in terms of the atoms above and below the planes.

The template fraction, the cleavage energy and the Hartman-Perdok (HP) attachment energy are routinely computed on the same pass through the unit cell. Minimizing the HP attachment energy some-

TABLE 1. Effective valences of some ions (normalized to Si^{4+} = 4.00)

Si^{4+}	4.00	Ca^{2+}	1.52
Ti^{4+}	3.17	Fe^{2+}	1.50
Cr^{3+}	2.34	Mg^{2+}	1.42
Fe^{3+}	2.24	Na^{+}	0.84
Al^{3+}	2.22	K^{+}	0.83

times gives a different location for the surface of least bonding than the template fraction and cleavage energy (which necessarily give the same location). There is an ambiguity in computing the template fraction in some cases. If we consider that actual growth layers can have thickness greater than d, the number of bonds attaching the layer to the substrate may be greater than if we consider the layers to have thickness d only; this is illustrated in Figure 3. A given bond in the unit cell may be considered only once in computing the template fraction for a slice of thickness d (Fig. 3a), but may be counted several times for a layer of indefinite thickness (Fig. 3b). In view of the fact that some growth layers have actually been observed by light optics, the template fractions for the examples given in this paper have been computed assuming a layer of indefinite thickness. The difference only appears when d is smaller than the bond lengths, and thus high-index faces are usually the only ones affected. It still seems reasonable that, barring pseudosymmetry, the actual thickness of layers parallel to different faces will be at least roughly proportional to d. The cleavage energy is necessarily computed using *all* possible bonds as in Figure 3b.

Limitations of the method

Two important limitations of this method should be mentioned at the outset. First, the bounding surface is restricted to a plane. This limitation is less serious than might be supposed, since the atom locations are specified in terms of their centers, and a plane dividing atoms by means of their centers may correspond to a quite undulatory surface with respect to the atoms as a whole. However, errors can be expected, especially in dealing with molecules or compound ions. The PBC method does not in principle have this limitation; but note that in the example of barite (below) the results are identical. Some other cases, in which the approximation fails, are discussed in Part

II (Dowty, 1976). It has been found necessary to consult crystal structure projections in some cases to check for non-planarity of the surface of least bonding. A fourth FORTRAN computer program (PROJ) has been written to plot to scale the projection of the atoms and bonds determined in Step 2. The projection direction can be made parallel to the zone axis defined by any two faces.

The second limitation is that only first-order bonds are taken into account, whereas in ionic crystals electrostatic interactions may be expected to operate over fairly great distances; lattice energy calculations generally do not converge unless many unit cells are included in the sums. This probably will not lead to mistakes in the location of the plane of least bonding for a given face very often, but will certainly cause errors in the quantitative evaluation of relative template fractions and attachment and surface energies for different faces.

The PBC method also uses a first-order bonding approximation for locating the exposed surface of the crystal on F faces. Once this is found, however, there is sometimes a convenient way of approximating complete electrostatic potentials, using the chains as units, rather than individual atoms (see Hartman, 1956). Unfortunately, this method is applicable with ease only to very simple chains, and quickly becomes impracticable as the structural complexity increases. For the present method, an atom-by-atom direct sum of electrostatic interactions or some similar approximation would probably be most suitable. Such a computation is not in principle difficult, using machine methods, but would require a rather different procedure from that described above, and considerably more computing time. In effect, one complete lattice energy sum would have to be carried out for each face, even if the location of the surface of least bonding were initially determined by the first-order approximation.
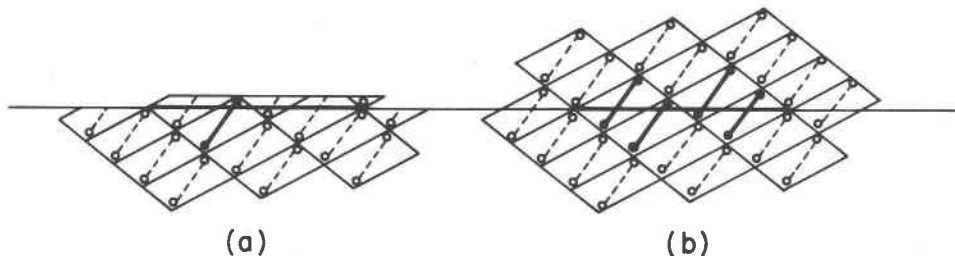

FIG. 3. Two-dimensional illustration of computation of template, attachment or surface energies. (a) A layer of thickness d only is considered. (b) A layer of indefinite thickness is considered. A single reticular unit is shown by the heavy line. In case (a) one bond crosses this area and in case (b) four bonds cross the area.

Examples

Structural data for the following examples have been obtained from Wyckoff (1968) where not otherwise noted. It is naturally almost impossible to separate completely the influence of external factors from that of internal structure on the morphology of individual specimens. In the absence of data from carefully controlled laboratory growth, it is still possible to eliminate much of the influence of external factors on the morphology of minerals by using the *persistence values* of Niggli (1920). Niggli (1926a,b) and Parker (1930) tabulate several persistence value studies, and Niggli (1926b) gives subjective evaluations of the morphology of all important minerals. The crystal drawings of Goldschmidt (1923) may also be used to evaluate morphology qualitatively, and to derive persistence values if necessary.

NaCl structure

Buckley (1951) summarizes the results of many experiments on NaCl itself. The forms disappear from a growing spherical seed in the order {110}, {210}, {111}, and the cube {100} is normally the only form remaining after long growth. These results apply to a number of methods of growth, and do not seem to be reflecting the effects of adsorption, according to Buckley. Niggli's (1926b) ranking of the importance of the forms in natural crystals of halite is first {100}, usually the only form present, then {111}, {110}, and {210}.

The unmodified DH rules incorrectly predict that the octahedron {111} should be the most important form; the forms are listed in DH order in Table 2. Donnay and Harker (1937) suggested that if the Na and Cl atoms are considered to be the same, the lattice becomes primitive rather than face-centered, and the first form is {100}. However, the second predicted form for a primitive cubic lattic is {110} and not {111}. According to the PBC method, {100} is the only *F* form; {110} and {210} are *S* forms; and {111} is a *K* form, since the only PBC's in the structure are parallel to [100], [010], and [001]. The atom-by-atom treatment of Stranski (1928) apparently demonstrated that {111} is less stable than {110} and presumably would be less important morphologically. The template energy method ranks the forms in the order {100}, {111}, {110}, {113}, {210}. This is not perfect, especially as regards the form {113} which is never observed, but it is in better agreement with the observations than any method previously proposed. The cleavage is correctly predicted to be {100}. Of course,

TABLE 2. Predicted morphology of NaCl

	Form	S^2	T	CL	HP'
1)	111	3	0.50(2)	1.73	3.0
2)	200	4	0.33(1)	1.00	1.0
3)	220	8	0.67(3)	1.41	2.0
4)	311	11	0.83(4)	1.51	2.0
5)	133	19	1.17(6)	1.61	2.5
6)	420	20	1.00(5)	1.34	2.0
7)	422	24	1.33(8)	1.63	2.0
8)	511	27	1.17(7)	1.35	3.0
9)	531	35	1.50(10)	1.52	2.5
10)	244	36	1.67(12)	1.67	3.0

Form - Ranked in Donnay-Harker order, with the indices as used by this method.
S^2 - Square of the relative reticular area.
T - Template fraction, with ranking in parentheses.
CL - Cleavage energy, divided by that of the first-ranked form.
HP' - Hartman-Perdok attachment energy, as average number of first-order Na-Cl bonds per atom.

the template fractions and cleavage energies in Table 2 are approximations, since they consider only first-order bonds. Born and Stern (1919) found that the surface energy of {110} is 2.706 times that of {100} on the basis of a complete electrostatic calculation. This differs considerably from the value $\sqrt{2}$ obtained from the first-order approximation; complete electrostatic template and surface energy calculations for all faces should be carried out.

Some oxides with the NaCl structure (*e.g.* MgO, MnO, CdO) commonly crystallize in octahedra although they have cubic cleavage. Presumably this is attributable to adsorption of foreign atoms, or to prestructuring in the growth medium (*e.g.* Hartman and Perdok, 1955b).

For several other simple crystals with face-centered lattices, such as fluorite, sphalerite, and diamond, the methods of this paper are not very successful. For example, the first-order bonds in sphalerite are the same as those in diamond, but the cleavage is {110} in sphalerite and {111} in diamond. As pointed out by Hartman (1959b), the difference apparently must be attributed to the partial ionic character of bonds in sphalerite. These crystals will be discussed in detail when more complete electrostatic computations of bond energies have been carried out.

Barite

This is one of the original examples given by Hartman and Perdok (1955c) for the PBC method. A comparison of results for the various methods is given in Table 3. It was assumed, following Hartman

TABLE 3. Observed and predicted morphology of barite

	Form	DH	HP	HP'	T	CL
1)	001*	6	0.388F	0.39	0.41(2)	1.03(2)
2)	210*	7	.396F	.39	.42(4)	1.00(1)
3)	101	1	.435F	.43	.29(1)	1.12(4)
4)	011	3	.945K	.53	.43(5)	1.29
5)	010*	12	.557F	.55	.59(10)	1.12(5)
6)	211	9	.472F	.47	.50(9)	1.08(3)
7)	100	2	.521F	.51	.41(3)	1.27
8)	410	26	S	.50	.81(19)	1.16
9)	102	8	S	.46	.49(7)	1.15
10)	111	4	S	.52	.46(6)	1.26
11)	213	28	S	.64	.91(26)	1.25
12)	230	38	S	–	–	–
13)	201	5	S	.53	.49(8)	1.30
14)	214	47	S	–	–	–
15)	212	13	S	.57	.71(13)	1.22
16)	310	81	S	–	–	–
17)	110	16	S	.52	.71(16)	1.15

Form – Listed in order of the persistence values of Braun (1932). Cleavage denoted by *.

DH – Ranking according to the unmodified Donnay-Harker law.

HP – Attachment energy and face type of Hartman and Perdok (1955c).

HP' – Attachment energy computed in this study by method of Hartman and Perdok.

T – Template fraction with ranking in parentheses.

CL – Cleavage energy divided by that of the first-ranked form, with ranking in parentheses.

and Perdok, that the sulfate ion can be represented as a point charge, and the formal valences were used. Both the PBC method and the template energy method seem to improve on the basic DH results. Donnay and Donnay (1962) have also made improved predictions of the morphology of barite, by considering only the centers of charges, rather than individual ions. Two of the three cleavages are correctly predicted by the cleavage energy; the third is ranked fifth in the list. Of course with respect to both cleavage and morphology, too perfect an agreement should not be expected, since sulfate ions were regarded as point charges and only first-order bonds were used. Note the lack of large differences in the cleavage or surface energies; no forms as far down as thirtieth in the list have relative cleavage energies higher than 1.4. Except for one form, {011}, the first-order attachment energies computed by the method of Hartman and Perdok have been reproduced by the present method (the small differences are due to round-off error). This shows that the use of planes in the present method probably has not caused any important errors. Note that some of the forms classified as S forms by Hartman and Perdok have lower HP attachment energies than some of the F forms, which seems to be contrary to the postulates of the Hartman-Perdok classification.

Although Hartman and Perdok (1955c) originally classified the form {011} as an F form, they computed the high attachment energy value of 0.945, and subsequently reclassified it as a K form, since according to them it is made up of parts of adjacent F faces. They attributed the anomalously high position of this form in the observed list to retardation of growth by adsorption of foreign ions. However, the present calculations reveal that they did not compute the attachment energy across a surface of least bonding. The attachment energy computed by their method across the surface of least bonding is 0.53, which is not particularly anomalous, and the form is certainly not out of place in the template fraction list; it is predicted to be fifth, and its real importance is fourth. The location of the two different planes is shown in the projection of Figure 4.

Rutile

The DH method ranks {100} first (Table 4) with slightly over half the reticular area of the next form, {110}. However, the cleavage is {110}, and this form is probably more important as a growth form. A recent PBC treatment (Woensdregt and Felius, cited by Hartman, 1973) classifies only {110} and {101} as F forms, although {100} and {111} are also important growth forms (Niggli, 1926b). Note also that the HP attachment energy in Table 4 for {101} ranks this form in sixth place. The form {221} is anomalously in third place in the HP attachment energy list.

The first-order template fraction gives equal rank to {110} and {100}, but by virtue of its larger reticular area, {110} has by a considerable margin the smallest cleavage energy. This would certainly be the thermodynamic equilibrium prism form, but the equilibrium terminating forms are hard to predict.

The following examples are minerals which show sector zoning, as discussed in Part II (Dowty, 1976). As might be expected, in these relatively complex structures the template fraction method often gives results which are very similar to those of the DH method.

Diopside-augite

Structural data (for diopside) were obtained from Clark et al. (1969). The DH method ranks the forms

BARITE [100] PROJECTION
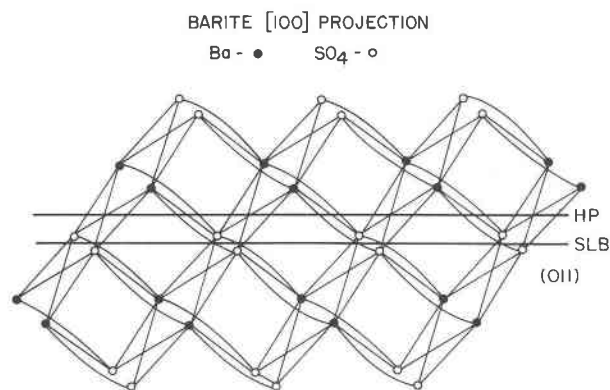
Ba - ●   SO₄ - ○

Fig. 4. Projection down [100] of the structure of barite. The (011) surface chosen by Hartman and Perdok (1955c) is denoted HP; the surface of least bonding is denoted SLB.

of diopside or augite in the order {110}, {100}, {010}, {11$\bar{1}$}. The template fraction method ranks them in the order {110}, {010}, {11$\bar{1}$}, {100}, and correctly ranks {110} first in the cleavage list. The four forms listed do in fact appear to be the most important forms on augite, although Niggli (1926b) also mentions {130}. Except for this face, which is ranked fourteenth, both the DH and template energy methods agree reasonably well with the order of the forms as listed by Niggli down to about fifteenth place. The first five forms in the ranking according to the HP attachment energy are {010}, {22$\bar{1}$}, {110}, {021} and {10$\bar{1}$}, in very poor agreement with the observed morphology.

Staurolite

Structural data were obtained from Smith (1968). The forms are ranked in the order {010}, {110}, {001}, by both the DH and template fraction methods, and these forms are ranked 1,2,4 by the HP attachment energy. These are the first three forms listed by Niggli (1926b) as important; staurolite does not commonly show many forms. The form {101}, the only other form mentioned by Niggli, is anomalously far down the list by all three methods. The indistinct {010} cleavage is correctly predicted by the cleavage energy calculations.

Quartz

The three forms which are almost always present are the hexagonal prism m {10$\bar{1}$0}, the positive rhombohedron r {10$\bar{1}$1}, and the negative rhombohedron z {01$\bar{1}$1}; the positive rhombohedron is usually larger than the negative one. These are the first forms in both the DH and template fraction lists (which rank the two rhombohedra equally), and they were classi-

fied as F faces by Hartman (1959c), using the PBC method. The next most important forms, although usually small, are s {$\bar{2}$111} and x {51$\bar{6}$1} (indices are for a morphologically right-handed crystal). The form {$\bar{2}$111} takes fifth place in the DH list and in the template energy list ranks equivalently with several other forms after the first three; m, r, and z have just half the template fraction of this next group. However {51$\bar{6}$1} is an anomaly by any method of prediction; evidently its prominence is attributable to retardation of growth because of adsorption of foreign ions or molecules (Hartman, 1959a). Indeed, synthetic crystals show high concentrations of foreign ions in {51$\bar{6}$1} sectors (*e.g.* Cohen, 1960).

Andalusite

The DH and template energy methods are not completely successful in predicting the morphology of andalusite. The most important forms by far are {110}, {001}, and {011}, with {101} occasionally present (Niggli, 1926b). The DH methods ranks {110}, {011}, and {101} as the first three forms, but {001} is in eleventh place. The template fraction method ranks the forms in the order {101}, {110}, {111}, with {001}

Table 4. Observed and predicted morphology of rutile

	Form	DH	T	CL	HP
1	110*	2	0.16(1)	1.00(1)	4.03(1)
	100	1	0.16(2)	1.40(3)	4.03(2)
	111	4	0.42(5)	1.70	4.09(4)
	101	3	0.33(3)	1.55	4.11(6)
2	210	5	0.41(4)	1.58	5.08(12)
	310	8	0.67(9)	1.80	5.71(22)
	320	13	0.58(7)	1.37(2)	5.08(13)
	410	16	0.91(18)	1.90	6.80(25)
3	231	15	0.67(10)	1.45(4)	4.90(11)
	221	9	0.58(8)	1.54(5)	4.08(3)
	313	36	–	–	–
	311	12	0.67(11)	1.62	4.76(8)
	334	–	–	–	–
	323	40	–	–	–
	301	10	0.67(12)	1.69	5.43(14)

Form – Listed by groups after Niggli (1926b). 1. main forms. 2. secondary prism forms. 3. secondary non-prism forms.

DH – Ranking according to the unmodified Donnay-Harker Law.

T – Template fraction, with ranking in parentheses.

CL – Cleavage energy, divided by that of the first ranked form, with ranking in parentheses.

HP' – Attachment energy according to the method of Hartman and Perdok (in $e^2/\overset{\circ}{A}$. Charges: Ti = +4, 0 = -2)

eighth, and incorrectly ranks {101} first in the cleavage list, instead of {110}. The HP attachment energy ranks the forms in the order {101}, {001}, {100}, {111}, {011}, {110}, *etc.* which is an improvement with respect to {001} but much worse with respect to the other forms.

Bookite

The three most important forms are {100}, {210}, and {111} (Niggli, 1926b; Arnold, 1929), which are the first three forms in both the DH and template fraction lists. The agreement after these first forms is not exact, but generally the common forms are near the head of the list. The cleavage energy correctly predicts the indistinct {210} cleavage. The HP attachment energy ranks {100} and {210} first and second, but {111} is at least eleventh.

Plagioclase

Most igneous plagioclase probably crystallizes with the high-albite structure, the parameters for which (Smith, 1974) have been used in this example. According to Niggli (1926b) the most important forms are {001}, {110}, {1$\bar{1}$0}, {010}, and {10$\bar{1}$}. The first four forms are the first four in the ranking according to the DH method, the template fraction and the HP attachment energy. The form {10$\bar{1}$} is anomalously low in all the lists. The cleavage energy incorrectly ranks {110} and {1$\bar{1}$0}, which are only poor cleavages, ahead of {001} and {010}, which are perfect and good cleavages, respectively.

Epidote

Structural data were obtained from Dollase (1971). Epidote shows a great many forms. The most important zone is [010], on which the principal forms are {001}, {100}, {10$\bar{1}$}, {10$\bar{2}$}, and {20$\bar{1}$} (Niggli, 1926b). The DH method ranks these forms 1, 2, 3, 5, and 9, and the template fraction method ranks them 1, 2, 3, 4, and 7, correctly assigning first rank in cleavage energy to {001}, although {100} is essentially equal. The HP attachment energy ranks these forms 2, 1, 3, 10, and 17. In almost all cases the important faces in each zone as described by Niggli (1926b) rank high in both the DH and template energy lists, which do not differ greatly from each other. Except for the first few forms, the difference in template energy between successive forms is usually small, which accounts for the large number of forms observed.

Conclusions

Many examples including those given in this paper show that the template fraction method is at least as successful in general as any other systematic method yet proposed for predicting morphology. Of course, we can only hope to isolate the contribution of internal structure by this approach, and factors such as composition of the medium, supersaturation, and the presence of dislocations have not yet been directly accounted for. The restriction to first-order bonds, the necessity of using a mathematical plane in the calculations, and the uncertainty of bond strengths all tend to make the predictions in any particular case less than certain, even if the basic hypothesis is accepted and external factors are not important. Methods of overcoming these limitations are being investigated.

What is perhaps of more immediate practical importance than the ability to predict morphology is the ability to predict surface structure in complex crystals, and the procedure developed in this study is probably applicable to this independently of any particular model of the relationship between structure and morphology.

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