THE RELATIVE IMPORTANCE OF THE SEVERAL
FACES OF A CRYSTAL

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ABSTRACT

A number of rules have been proposed to correlate the relative importance of the several faces of a crystal with the geometrical features of the crystal lattice. Chief of these are the rule of simplest indices, Bravais' rule, and Donnay-Harker's rule. The latter has had considerable success in formulating the relative importance of the faces of a crystal, but it is completely empirical, as are all the other rules. This paper suggests a rational basis for the rule. It is shown that if the crystal grows by the accretion of molecular chunks which are equivalent by an operation with a translation component, then Bravais' rule can be derived from crude surface energy considerations. These considerations also explain the stability of crystal faces and predict that crystals should form without faces when they grow from media of equal surface tension. The same theory accounts for the known deviations from Bravais' rule by ionic crystals.

INTRODUCTION

The faces displayed by a crystal represent a boundary between the crystal and the medium which deposited the crystal. Thus it should be obvious that the character of the collection of faces displayed by a crystal is determined by both the crystal and the depositing medium, or, more generally, by the crystal and its environment.

There is plenty of experimental evidence that the relative sizes of the several faces of a crystal can be influenced by the environment depositing the crystal. Buckley¹ and Bunn² have been active in this field and have provided rival structural explanations for the mechanism of the influence of impurities in the depositing solution on the variation of crystal habit. It is also known that temperature, pressure, and rapidity of growth (i.e., other aspects of the general environment of growth) produce variations in crystal habit. While the nature of the external influences other

than impurities have not been extensively discussed, it is not difficult to advance reasonable explanations for them.

It has also been recognized that the crystal itself has an influence on its habit, and, in a crude empirical way, the general characteristics of the influence are known. Yet those crystallographers interested in this aspect of morphology have been content with the empirical relation and have not attempted to give any rational explanation of it. It is the chief purpose of this paper to suggest such an explanation.

**Attempts to Formulate the Influence of the Crystal**

Attempts to formulate the characteristics of the crystal's influence on its own form development arose early in the history of crystallography. All such attempts were empirical formulations which sought to relate the form development to some aspect of the lattice geometry (as distinct from structure or bonding).

Perhaps the crudest approximation is the rule that faces with simplest indices are the best developed and that the importance of the faces decreases with increasing complexity of the indices. This approximation dates from Hauy's time and has even been called the "Law of Hauy." There are other formulations which are essentially equivalent to this rule. Thus, Barker's *Principle of Simplest Indices* provides that the important faces of a crystal can be assigned simple indices, and this implies, in turn, that importance in development of a face is related to the simplicity of the indices. Again, Goldschmidt's *Law of Complication* which recently achieved some popularity in America, implies this relation. The simplest-indices rule has obvious shortcomings. For example, it requires all isometric crystals to have identical form development, and it requires all crystals to have form developments which are related to one another by homogeneous deformations, which is obviously contrary to observation.

A much better approximation was discovered by Bravais. Bravais' rule states that the relative importance (implying both frequency of occurrence and area) of the development of the faces of a crystal is in the

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same order as their reticular density (or, what is the equivalent, in the same order as their interplanar spacing).

An alternative form of Bravais' rule is attributed to Fedorov. This is that the habit of a crystal is approximately that of the shape of a cell of its polar (reciprocal) lattice. This can be easily shown to follow directly from Bravais' rule, but it is less comprehensive in that it merely gives the order of development of the three important pinacoidal enclosing forms.

As Bravais' rule came into vogue in America, Goldschmidt's "Law of Complication" waned. The protagonists of Bravais' rule enthusiastically proclaimed it "The Law of Bravais" and gave the impression that it was a law of nature on the same plane as one of the laws of thermodynamics. This generality of the "law" was supported by analyses of the form developments of certain individual crystals favorable to the rule.

That the "Law" of Bravais was not quite as perfect as its proponents claimed was suspected as the numerous exceptional crystals turned up. A much better approximation was then discovered which explained many of the exceptions. This was announced as a new "law" of nature by Donnay and Harker, who pointed out that many more crystals came into conformity with the requirements of Bravais' rule if "interplanar spacings" are interpreted to mean not only the spacings of the lattice but also to include modifications of spacings as required by those space group operations which contain translation components. This required a recognition of the same extinction conditions that occur in x-ray diffraction by crystals.

It might be pointed out here that an interesting relation exists between form development, as required by the Bravais-Donnay-Harker rule, and the powder photograph of the crystal. The order of importance of the crystal faces is exactly that of the order of appearance of the corresponding lines on the powder photograph (proceeding from \( \theta = 0 \) to \( \theta = 90^\circ \)), provided that no orders of a line other than the first are considered. This proviso merely takes account of the fact that one form is represented by one line, since orders of a face have no meaning.

It is important to recognize that the Bravais-Donnay-Harker rule is strictly empirical and represents an attempt to find something about the crystal which is related to the comparative development of crystal faces. It is undesirable to accept the rule as a "law," particularly in view of the embarrassing history of the designation "law" in connection with crystal form development. As a generalization it rests on the sum total of the individual cases investigated, and among these there are some serious

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exceptions. Furthermore, in the cases which support the rule, there is not necessarily complete agreement between the relative reticular density sequence and the order-of-importance sequence. Nevertheless, it must be recognized that there is a strong tendency for many crystals to conform in at least a general way to the requirements of the rule. What is the explanation of the agreement?

**PINACOID DEVELOPMENT FOR A SIMPLE CRYSTAL**

To get a preliminary picture of the possible significance of the Bravais rule, consider the growth of a simple crystal. The crystal is assumed to be simple in that,

1. the crystal is triclinic,
2. the crystal is built up of discrete molecules, and
3. there is one molecule per unit cell.

The growth process consists of the locating of one molecule at each point of the triclinic lattice. For further simplification, suppose that the molecule has the shape of the parallelepiped unit cell. Growth then consists of the addition of blocks to the solid structure.

No assumptions are made about the specific character of the bonding between molecules in the crystal other than that ionic bonding is temporarily excluded (for reasons which will develop subsequently) and that the latent bond strength density is, on the average, uniformly distributed about the surface of the molecule. When a molecule lands on the crystal surface so as to continue the crystal structure, then the energy of the bond between molecule and crystal is (to first approximation) proportional to the area of the surface joining the molecule to the crystal. If several sites on the crystal are available to molecules, the preferred site (neglecting differential thermal effects) is the one with maximum bond strength. With the simplifying assumptions of this section, this is the site which offers the greatest area of attachment between crystal and molecule.

Consider, first, the growth process of three pinacoids, which represent, in simplified form, a series of three planes of different reticular density. Except when a new layer starts, the general conditions of the three pinacoids is shown in Fig. 1. New molecules add themselves to each layer by falling into a corner of the step on the growing surface. The corner on each of these pinacoids exposes an identical area to a molecule about to take its place in a corner. This area is the sum of the areas of the three

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pinacoidal bases of the unit cell and is a measure of the first coordination of the molecule arriving at the surface. It is easily demonstrated that a molecule landing on any growing rational plane whatever (provided, as above, that the molecule is not starting a new layer) lands in a corner of the same character and achieves a first coordination measured by the area of the same three pinacoidal bases of the cell. This can be generalized for molecules of more general shape than that of a unit cell parallelepiped,

![Fig. 1](image1.png)  ![Fig. 2](image2.png)

with the result that it can be said that any molecule landing on a rational plane in such a way as to continue the general growth of that growing plane, does so in such a way as to achieve a first coordination measured by half the external surface of the molecule. Thus, in the growth of any rational plane, there is no differential in the immediate coordination of the system crystal-molecule and therefore, from the point of view of the energy realized by the coordination of the molecule and the plane, no plane of the crystal has an advantage over any other. Therefore if molecules rain evenly on all surfaces of a crystal, equal volumes might be expected to be added to each pinacoid (or other plane) in a given time, and consequently the planes might be expected to advance at an even rate.

But consider the situation as a layer starts: Fig. 2 shows a molecule in place on each of the three pinacoids of the simple crystal. It is evident that the surfaces of attachment are the pinacoidal bases of the cell taken one at a time. Since the volume of the cell is any base times its corresponding interplanar spacing, the area of any base is inversely propor-
tional to its spacing. Thus the surfaces of attachment of the first molecules are in the inverse order of the interplanar spacings of the pinacoids to which they attach themselves. The most likely attachment of the three possible ones is that which has the greatest coordination of attachment, namely the molecule which rests on the pinacoid of least interplanar spacing. It might thus be expected that the probability of starting a new layer is highest for the pinacoid of least spacing. Since the bottleneck of starting a new layer continually recurs, the pinacoid of least spacing must be the pinacoid of most rapid growth. It is well known that the most rapidly growing faces tend to eliminate themselves. Consequently the pinacoid of least spacing tends to be the least well developed.

The reasoning given above evidently accounts for Fedorov's rule, which, freely interpreted and expressed in the language of the Bravais' rule, states that a crystal tends to have a habit development such that the decreasing importance of the pinacoids is in the order of decreasing spacing.

COORDINATION AND SURFACE ENERGY

The simplified analysis just given does not lend itself easily to generalization, chiefly because coordination other than that due to the immediate coordination is difficult to evaluate. Fortunately it is easy to reformulate coordination in terms of surface energy. It should be evident that surface energy is caused by the lack of saturation of all bonds in the crystal due to the free surface. The chief contribution to this bond energy comes from bonds at the surface, and thus from surface coordination, but secondary coordinations are also involved. Thus, surface energy and total realized coordination energy across the free surface are complementary.

Returning, now, to the simple case discussed in the last section, the situation can be summarized as follows: If several sites are available to a molecule, the preferred site is that which permits the molecule to attain the greatest immediate coordination. Evidently this statement ought to be corrected so that its last part reads, "which permits the molecule to attain the greatest total coordination." In view of the complementary nature of realized coordination and surface energy, this can also be stated in the following terms: If several sites are available to a molecule, the preferred site is the one for which the molecule achieves the greatest decrease in its surface energy. Furthermore, growth is least rapid for the plane which requires, for the starting of each new layer, the attachment of a molecule in the position which leads the molecule to retain the most surface energy (which is the complementary way of saying that the molecule achieves the least total coordination or least bonding energy).
RELATIVE IMPORTANCE OF CRYSTAL FACES

SURFACE ENERGY AND BRAVAIS' RULE

Bravais' rule is usually stated in such a way as to involve the "importance" of the development of a face. An equivalent, but somewhat more convenient form of the rule for the present requirements is that the faces of a crystal have growth velocities in the inverse order of their interplanar spacings. If this is true, and if the analysis of the last section is also true, this implies that the residual surface energies of the attached molecules which start new layers are in the inverse order of the interplanar spacings of the faces to which they are attached. That this is at least roughly correct can be appreciated from Fig. 3, where a crystal is represented as being made up of parallelepiped cells. (If ellipsoids are substituted for these parallelepipeds, the following feature still holds.) It will be observed that the molecules shown shaded, which start the new layers, project above the general levels of the planes by an amount equal to the interplanar spacing, \( d_{hkl} \). When a molecule starts a new layer, it thus constitutes an excrescence on the layer, the height of which is roughly a measure of the residual surface energy of the molecule which starts the new layer.

This analysis is quite crude, but it appears to be essentially correct for the simple case taken for study. In this case, the Bravais' rule appears to operate because the residual surface energy of the added molecule is a function of the way the molecule fits into the surface, and this, in turn, is a function of \( d_{hkl} \).

That this crude analysis is essentially correct can be appreciated by considering the contours of potential in the neighborhood of a location on
a simple crystal surface. In Fig. 4, the full line $AB$ may be taken to represent a contour in the energy field of a plane with indices (11). At $B$, the main contribution comes from molecule $a$. For a plane of index (12), a molecule $b$ is also part of the surface, and it also contributes a potential at $B$ of a magnitude comparable with that contributed by molecule $a$. For this second plane, therefore, point $B$ has a greater energy than it had for the first plane. Plane (12), therefore, offers a molecule which starts a

![Fig. 4](image)

new layer by adding itself above $a$ a greater drop in energy than does plane (11). The presence of molecule $b$ thus increases the realized coordination (or decreases the residual surface energy) of the molecule which starts a new layer.

**THE STABILITY OF FACES**

The crude analysis just given for the differing rates of growth of the faces of a crystal can also be applied in answering the question as to why high-index faces do not accept molecules in such a way as to become low-index faces. For example, Fig. 5 shows a surface with intercepts 1, 3.

![Fig. 5](image)

When the plane grows, molecule $a$ is first added to the surface, temporarily changing the slope of that region of the surface to intercepts 1, 2. Why does not another molecule, $d$, then add itself to the surface next to $a$, thus changing the intercepts of the surface to 1, 1, and so on, until the crystal consists of pinacoids only? It will be observed, however, that if both molecules $a$ and $d$ are added to the surface, the surface ex-
crescence due to $a$ plus $d$ is twice as high as that due to $a$ alone, and hence
molecules added to the surface after $a$ arrives preferably attach them-
selves at neighboring positions similar to $a$, such as $b$ and $c$. Thus, a plane
rejects molecules which attempt to add themselves in positions which
would change the index of the plane to one of less complexity.

A very similar analysis shows that a plane rejects molecules which at-
tempt to add themselves in positions which would change the index of
the plane to one of greater complexity. Thus a plane tends to avoid
variations in its slope because of surface energy barriers. In this way a
crystal plane, once started, is stable, and maintains its slope, and there-
fore its identity.

**Crystals Without Faces**

Crystals without faces would be anomalous to some crystallographers,
yet they are not only possible but normal under certain circumstances.
From the last section it is evident that the stability of a face is a function
of surface energy. Furthermore, the very existence of crystal faces de-
pends on surface energy. Therefore, if a crystal is grown in a medium
whose surface tension is equal to its own, no faces can develop.

This condition is exactly realized when a crystal grows in an aggregate
of identical crystals, as in the case of recrystallization. Under such cir-
cumstances, no crystal form development is to be expected, and Harker
and Parker\(^{12}\) have shown that the shapes actually assumed by crystals
grown by recrystallization tend to be polyhedra bounded by dihedral
angles of 120° whose orientations are independent of any vectorial
properties of the crystal.

The condition is nearly realized when a close-packed crystal forms from
a melt of the pure metal. In this case, the melt is nearly close-packed, and
the forces on an atom at a metal-melt interface are nearly alike on both
sides, thus causing the interfacial tension to nearly vanish. For this
reason, copper crystals and zinc crystals formed from pure melts have
typically rounded forms. On the other hand, when a metal crystal and its
melt differ considerably in density, as in the case of bismuth, then the
interfacial tension between crystal and melt is considerable. Under these
circumstances crystals with well-developed faces form from a pure melt.

**The Donnay-Harker Rule**

In the development given above, it was assumed that the crystal was
characterized by molecules which were translationally equivalent. The

\(^{12}\) Harker, David, and Parker, Earl R., Grain shape and grain growth: *Trans. Amer.
residual surface energy of the molecule was due to the projection of this molecule above the general level of the nearly smooth surface. It is evident that the same general state of affairs will hold if the molecules are equivalent by other operations having a translation component, namely screw axes and glide planes. Under such circumstances, some planes related by the translation-bearing operation (for example, in symmetry $P\overline{6}$, planes $(h0l)$ with $l$ odd) have submultiple spacings, and therefore have lower excrescences when molecules add themselves to the surfaces. Consequently the surface energy conditions of molecules added to these planes are equivalent to those of planes with corresponding submultiple spacings. These planes tend to eliminate themselves by rapid growth as compared with other planes. Thus the Donnay-Harker rule also follows from surface energy considerations.

**Deviations from the Bravais-Donnay-Harker Rule**

Notable deviations from the generalized Bravais rule have been found. These include certain individual nonconforming planes in certain crystals and also crystals which do not conform at all. Such exceptions should be a warning that the effect is not referred to the appropriate variable. Specifically, it suggests that the variable in the crystal’s effect on its own habit is not as simple as interplanar spacings based on either planes rational with respect to lattice translations or rational with respect to translation-bearing symmetry operations in general. A general explanation of certain deviations from Bravais’ rule is therefore that the planes of growth need not always be rational. When this is the case, there is no need for the habit of a crystal to conform with Bravais’ rule.

In the following sections, some of the causes of deviation from Bravais’ rule are discussed.

**Deviations Due to Growth from Ionic Solution.**—Among the crystals which do not conform to the Bravais’ rule at all are the class of crystals which are notably ionic. Since the ionic crystals which have been studied for conformity with the rule have been grown from solutions which ionize the solute, it is evident that molecules cannot possibly be deposited on the surface of the crystal from such solutions. Rather the solutions must deposit particles which are of two kinds, namely the two oppositely charged ions, and these are not equivalent by any symmetry operation of the crystal. For this reason the excrescences on the surface of the crystal caused by adding the particle to the surface, as the plane grows, is smaller.

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than it would be if the entire motif were added. It is thus no longer possible to measure the size of the projection by \( d_{hkl} \), and consequently the crystal does not conform to Bravais' rule.

As outlined above, the Bravais rule works because the crystal builds up by the addition of translationally equivalent units, and this requires that the new layers added are always rational lattice planes. When the entire motif is not deposited as a unit, then the crystal cannot be built up by the addition of layers which are rational planes, for some layers must be interleaved between rational layers. Such interleaved layers can be fictitiously described as rational provided a fictitious translation-bearing operation is assumed between them. This fictitious operation also brings some positive and negative ions into coincidence with one another. Therefore, if a subcell is chosen from the lattice which is composed of such fictitious translations (three which bring positive and negative ions into coincidence) the crystal comes into fictitious conformity with Bravais' rule.

Deviations Due to Growth by Accretion of Molecules Which Are Not Crystallographically Equivalent.—In discussing the rational basis for Bravais' rule with Dr. J. D. H. Donnay about four years ago, the writer pointed out that the form development of superstructures ought to follow that required by Bravais' rule for the basic structure rather than that required for the superstructure itself. Dr. Donnay tested this prediction by studying the form development of orthorhombic low-chalcocite, which was known to the writer to be related as a superstructure to hexagonal high-chalcocite. In a private communication to the writer, Dr. Donnay reported that the morphology of high-chalcocite did indeed follow that of the simpler structure upon which it is based.

This general behavior is to be expected on the basis of the theory of form development presented in this paper. Suppose, for example, that a crystal is composed of two kinds of chemically equivalent molecules which are located in the crystal in non-equivalent sites. Unless a polymerization has taken place in the solution from which the crystal is grown, the growth of the faces of the crystal can be expected to take place by addition of the individual molecules to the faces. This means that motif fractions rather than translation-equivalent motifs land on the crystal faces during growth. Now Bravais' rule can be rationalized along the lines discussed in this paper only if growth is by motif units which are equivalent by an operation with a translation component, a feature which does not obtain in the case under consideration. Consequently Bravais'
rule cannot be expected to hold in this case. Of course the reason for this
is that the surface energy due to the excrescence can be measured by
\( d_{hkl} \) only if the added molecular units are translation-equivalent. When
the unit added is a motif fraction, the excrescence due to the addition of
the molecule is less than it would be if the entire motif were added and its
height follows a different rule. Indeed it follows, at least roughly, the rule
that its height is approximately that which it would be if all molecules
were translation-equivalent, and this is so only if the structure is referred
to the cell and symmetry of the basic structure.

In a rough way, the discussion just given applies to cases where two
chemically non-identical molecules, which do not associate in solution,
add themselves to the surface of a growing crystal. The crystals in these
two cases correspond with distortion structures and substitution structures
respectively in the theory of derivative crystal structures. Provided asso-
ciation does not take place in the solution, crystals with derivative
structures can be expected to display a form development which deviates
from the Bravais-Donnay-Harker rule in the direction of the habit to be
expected from the basic structure.

*Deviations Due to Molecular Asymmetry.*—In the rationalization of
Bravais’ rule it was assumed that the molecule was at least as sym-
metrical as the cell of the lattice. When this is not so, then it does not
follow that the surface energy of the attached molecule is measurable
simply by \( d_{hkl} \). Thus, in the accretion of polar molecules to the surfaces of
polar crystals, one should not expect the same rate of growth for all faces
of identical spacing. For example, if the crystal lacks a center, one would
not expect the same rate of growth for \( hkl \) and \( hkl \), in spite of the fact that
\( d_{hkl} \) and \( d_{hkl} \) are identical. The reason, of course, is difference in surface
energy.

*Deviations Due to Non-uniform Bond Density.*—One of the simplifying
assumptions which were made was that the added molecule has a uniform
distribution of bond density. When this is the case, the coordination
energy realized when the molecule adds itself to the crystal is a purely
geometrical function of the manner of attachment of the molecule to the
crystal. If, however, some aspect of the molecule’s surface is characterized
by a concentration of strong bonds, the preferred mode of attachment of
the molecule is no longer a simple function of geometry, but is influenced
by the location and strength of the strong bonds. The coordination energy
realized when the molecule attaches itself is therefore no longer a simple
function of \( d_{hkl} \), and it cannot be expected that Bravais’ rule will be
strictly obeyed. The deviation from Bravais’ rule to be expected in such

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cases is in the direction of the reduction of importance of faces parallel to the surface of strong bond concentration in the molecule starting a new layer, and an increase in importance of faces parallel to the surface of low bond concentration in the molecule starting the new layer.

**Variation of Habit Due to Impurities**

It is not the function of this paper to discuss in any detail the influence of the environment on the form development of the crystal. Nevertheless it is desirable to draw attention at this point to the fact that the influence of impurities on form development can be considered from the viewpoint just adopted for considering the influence of the “normal” molecules on the habit of their crystal. If impurities are present, then both the impurity particles (which may be molecules or ions) and normal molecules may compete for positions of high coordination on the crystal surfaces. Since impurity and “normal” molecules are different, a site of high coordination for one particle is not necessarily identical with a site of high coordination for the other. Nevertheless, realized coordination energy, or its complement, surface energy, is the feature which governs the preference of sites in each case. This should be the guiding principle in seeking to predict which faces have their growths most retarded by the adsorption of impurity particles.

The influence of the impurity is more complex than that of the normal particle, however, for the impurity particle may be included as a particle in a layer being formed. Its effect on slowing down the growth of the particular face may not be felt until the next layer is about to cover the impurity in the first layer. When this occurs, it may be impossible for the second layer to continue its growth until the foreign particle has been removed by energy competition and replaced by a normal particle. A new second layer may fortuitously start elsewhere on the first layer before this can occur.

**Conclusion**

Those who have hitherto interested themselves in the influence of the crystal on its own form development have followed a purely empirical course and have arrived at a correlation of form development with lattice geometry. In this paper there has been an attempt to rationalize these empirical findings along lines of simple energy considerations.

Such considerations lend rational support to the Bravais’ rule and its generalization. On the other hand, they throw emphasis on another aspect of crystal growth. Whereas Bravais’ rule emphasizes purely the lattice geometry of the growing crystal, energy considerations make it plain that emphasis should be focussed on the characteristics of the particles which
arrive at the crystal surfaces during the growth process. When there is a simple relation between the characteristics of the arriving particles and the lattice geometry the whole growth effect can be formulated in terms of lattice geometry alone. When the arriving particles have characteristics other than mere geometrical shape to be taken into consideration, then the habit effect cannot be made functional upon lattice geometry only, and deviations can be expected from Bravais' rule.

Thus one of the most fundamental factors in determining crystal habit is the characteristics of the particles which arrive at the crystal surfaces, including both their geometry and physics of bonding. When the particle which would normally be added to the crystal to continue its structure must compete with "impurity" particles, then the corresponding characteristics of the impurity particles constitute another fundamental factor in determining habit. Both lattice geometry and bonding characteristics of the crystal constitute a third factor. Only in special cases can all three factors be formulated as a function of lattice geometry alone.