

On the Relations Between Structure and Morphology of Crystals. II

BY P. HARTMAN AND W. G. PERDOK

Kristallografisch Instituut der Rijksuniversiteit, Melkweg 1, Groningen, Netherlands

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The characteristic features of *S*-faces (stepped faces, i.e. faces parallel to one periodic bond chain only) are further developed. After giving some definitions, a discussion follows of the factors determining the morphological importance of *S*-faces. The conclusion is drawn that the development of *S*-faces in a particular zone can be represented by an addition scheme of indices and that an *S*-face is the more important, the greater the relative strength of the bonds in the periodic bond chain to which it is parallel.

An outline is given of the way in which the morphology of an actual crystal can be derived from the structure. This is illustrated in the case of cubic closest packing. The result is that the octahedron is the most important form, followed by the cube, provided crystallization takes place from the vapour. Crystallization from the melt involves the consideration of pre-condensation effects. In this case the influence of the strongest bond on the morphology diminishes and weaker bonds become more important. This leads to a preponderance of the cube, a relation actually observed with copper.

Introduction

(a) In Part I (Hartman & Perdok, 1955) the forms of a crystal were divided into three classes with decreasing morphological importance: *F*-, *S*- and *K*-forms.* Niggli (1923) introduced a method of obtaining quantitative data on the morphological importance. He defined the *Fundortpersistenz* (*F*-values) and the *Kombinationspersistenz* (*P*-values), as the percentage of 'localities in which', or 'combinations on which' the form has been observed. The drawback of this method is that crystals showing rare forms enter with the same weight into the statistics as crystals showing common forms only, in spite of the fact that the latter are far more abundant. As a consequence, the lower *F*- and *P*-values are much less reliable than the higher values. Therefore special attention is here paid to the forms with high *F*- and *P*-values, these forms being *F*-forms in most cases. The relative importance of *F*-forms is determined by the attachment energy (see Part I). With the *S*-forms several influences have to be taken into account. Before discussing these influences some definitions have to be given.

(b) Let us consider *S*-faces in one particular zone. In our view the surface of an *S*-face must consist of parts of adjacent *F*-faces. In Fig. 1 two *F*-faces (F_1 and F_2) and an *S*-face (BB'') are projected parallel to their zone axis. The actual profile of the *S*-face is $BAB'A'B''$; one step BAB' consists of two flat parts BA and AB' , parallel to F_2 and F_1 respectively. Therefore we can say that an *S*-face consists of alternating strips of adjacent *F*-faces. The smallest possible strip

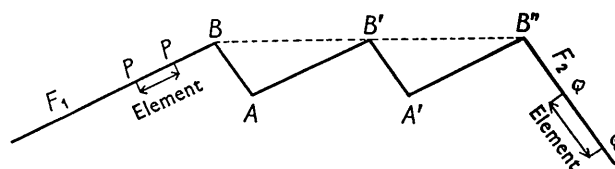


Fig. 1. Profile of two *F*-faces and one *S*-face. F_1 and F_2 are *F*-faces; their zone axis $[F_1F_2]$ is normal to the plane of the drawing. BB'' is an *S*-face showing actually the profile $BAB'A'B''$. AB' and AB are parts of the adjacent *F*-faces F_1 and F_2 , respectively; they are called *flat parts*. A is the *step edge*. $BB' = B'B''$ is the *profile period*. The flat part AB consists of one element of the face F_2 and the flat part AB' consists of three elements of the face F_1 . PP is the *element period* of F_1 in the zone $[F_1F_2]$ and QQ is the *element period* of F_2 in the zone $[F_1F_2]$.

of an *F*-face we call an 'element of the *F*-face'. In Fig. 1 the flat part AB represents one element of the *F*-face F_2 and the flat part AB' represents three elements of the *F*-face F_1 . The distance BB' we call the 'profile period' of the *S*-face. The distances PP and QQ we call the 'element periods' of the *F*-faces.

Morphology of *S*-faces

The factors determining the importance of an *S*-face are related to its chance of appearance and its chance of disappearance. (We do not use the word 'chance' in its exact thermodynamical sense.)

(1) As pointed out in Part I, a face can appear only in the first stage of crystal growth. It must occupy an area of at least one mesh on the seed, so that the chance of appearance of an *S*-face decreases with increasing mesh area. For *S*-faces of one and the same zone the chance of appearance decreases with increasing profile period. Hence, if the element periods

* *F*: Flat faces, containing two or more coplanar periodic bond chain (P.B.C.) vectors.

S: Stepped faces, containing one P.B.C. vector.

K: Kinked faces, containing no P.B.C. vector.

of the F -faces do not differ much in length, an addition scheme of indices like that of Goldschmidt will be determinative for the chance of appearance (cf. Niggli, 1941, p. 541).

As an example we consider the zone [001] of a crystal with the F -faces (100) and (010). Suppose that one element of (100) and of (010) each, determine (100) as an S -face. A following S -face can be found by taking two elements of an F -face and one element of the other F -face. In this way the faces (210) and (120) are obtained. The profile periods of these faces are in general longer than the profile periods of (110), so that it is more probable that (110) appears on the seed, than (210) or (120). The addition scheme of indices reads:

(100)		(110)		(010) F -faces
			 S_1 -face
	(210)		(120) S_2 -faces
(310)	(320)	(230)	(130) S_3 -faces

There are in general $2^{n-1} S_n$ -faces. For small n we may say that the chance of appearance depends on the level (n) in the addition scheme of indices. If, however, the element periods of the F -faces differ much in length, then the profile period of, say, (310) may be smaller than that of (120). In such a case the addition scheme becomes 'asymmetric' as it were, and then it becomes a Baumhauer series, rather than a Goldschmidt normal series (cf. Donnay, 1937).

(2) The chance of disappearance depends on the relative displacement velocities of the faces. If we assume that every building unit landing on the flat part of a step migrates on it, and moves to the edge, where it is captured, then the displacement velocity is determined by the attachment energy of a building unit to the edge of a step. This means that S -faces of one and the same zone all have the same displacement velocity. If a building unit is supposed to be captured on the flat part also, then the average attachment energy of a building unit to a step (including flat part and edge) determines the displacement velocity, so that S -faces with long flat parts would have the smallest velocities; therefore the S_1 -face would be the most unimportant of all.

In a large number of cases we have found that S_1 -faces are more important than S_n -faces of higher order n in the same zone. Therefore we are forced to suppose that for S -faces in one and the same zone the profile period is the determining factor for their importance.

(3) The relative importance of S -faces belonging to different zones depends not only on the profile period but also on the bond energies in the different periodic bond chains. As to this last factor, two possibilities arise, either of which may be responsible for the importance of S -faces: (1) the attachment energy of a building unit to the edge of a step; (2) the strength of the weakest bond in the periodic bond chain parallel to the zone.

As yet, our observations do not permit us to distin-

guish between these two possibilities, because in most cases a higher attachment energy (possibility (1)) is caused by weaker bonds in the chain (possibility (2)). Therefore, in general, we can say that S -faces with smaller attachment energies would be more important. In the majority of cases this has been found to be correct. Moreover, it appeared that S -faces of second and higher order seldom have a P - or F -value higher than 10, and, if so, they occur almost exclusively in the zones with the smallest attachment energies for the S -faces, which again shows the decisive role played by high-energy periodic bond chains.

Some general rules for practical applications

Up to now we have defined an F -face as being a face parallel to at least two P. B. C. vectors. The converse, however, is not true: not every face parallel to two P. B. C. vectors is an F -face. For it often occurs that one of the chains is a zigzag chain, and that the face is perpendicular to the plane in which this zigzag chain lies. It may happen, then, that the surface of the so-called F -face actually consists of two elements of neighbouring F -faces, so that it has to be considered as an S -face (an example will be given in Part III). Sometimes it may even become a K -face. This phenomenon occurs quite often and reduces the number of genuine F -faces considerably. A consequence of this is that the number of periodic bond chains is also limited. When the period of a chain consists of periods of other chains, it may be neglected, because the combination of such a chain with another chain will not give an F -face, but an S -face. The general way to derive the morphology of a crystal from its structure runs, then, as follows:

(1) The strong bonds are found by means of chemical considerations.

(2) Chains of strong bonds are sought, these chains being submitted to the following conditions: (a) it must be possible to divide the whole structure into a fabric of chains with stoichiometric composition which do not have any bond in common; (b) the chain should not entirely consist of periods of other chains. The period of a chain is in general the structural period, but sometimes it may be one half of the latter, owing to pseudo-centring.

(3) The F -faces can be obtained, for example, by drawing in a stereogram the zone circles corresponding to the P. B. C. vectors; the points of intersection of these zone circles represent stereographic poles of possible F -faces. In general not all faces found in this way are genuine F -faces; some of them may be S - or even K -faces. Since an F -face grows in layers, the following conditions should be fulfilled: (a) it must be possible to divide the whole structure into slices which do not have any atom in common and which have stoichiometric composition; (b) the slice should not entirely consist of elements of other F -faces, because in this case the face would be an S -face.

(4) The *S*-faces can be obtained by combining the elements of the *F*-faces. The element periods (*PP* and *QQ* in Fig. 1) are determined by the periodicity of the bonds in the slice of the *F*-face. In practice, however, the elements are not characterized by the element periods but by a P.B.C. vector *Z*, lying in the element, of which the element period is the projection, i.e. $PP = Z \sin \alpha$, where α is the angle between the vector *Z* and the zone axis under consideration.

Morphology of cubic closest packing

As an example the metals crystallizing in the cubic closest packing may be taken. As yet little is known quantitatively about the metallic bond, but it is generally assumed that the bond energy is a rapidly decreasing function of the distance.

(1) Bonds

For the moment we will confine ourselves to nearest neighbour-neighbour interaction. Then there is only one type of bond, namely that between atoms in $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$, and its symmetrical equivalents.

(2) P.B.C. vectors

The bond is periodically repeated and hence there is only one kind of P.B.C. vector, which consists of this one bond. The vector may be denoted by $[\frac{1}{2}, \frac{1}{2}, 0]$ and its corresponding bond energy may be *a*.

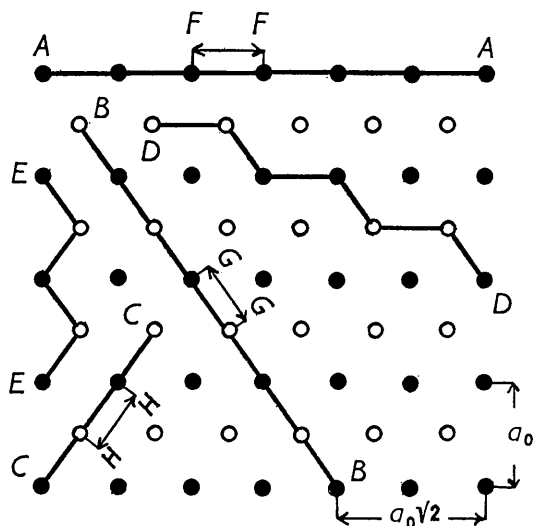


Fig. 2. Projection of the cubic closest packing on $[1\bar{1}0]$. Each small circle and each dot represents a periodic bond chain parallel to $[1\bar{1}0]$. *A-A* is a slice of the *F*-face (001); *B-B* is a slice of the *F*-face (111); *C-C* is a slice of the *F*-face ($1\bar{1}\bar{1}$); *D-D* is the profile of the *S*₁-face (113) and *E-E* is the profile of the *S*₁-face (110). *F-F*, *G-G* and *H-H* are elements of (001), (111) and ($1\bar{1}\bar{1}$), respectively.

- : atoms at heights 0 and 1 above the plane of the paper.
- : atoms at height $\frac{1}{2}$ above the plane of the paper.
- : bond *a*.

(3) *F*-forms

The P.B.C. vector $[\frac{1}{2}, \frac{1}{2}, 0]$ and its symmetrical equivalents define the *F*-forms {111} and {100}. In Fig. 2 slices of these faces are shown. An atom attaching to the surface of (111) forms three bonds with it so that the attachment energy is $3a$. An atom attaching to the surface of (100) forms four bonds with it, so that the attachment energy is $4a$. Hence the octahedron is more important than the cube since it has the lower attachment energy. As a matter of fact, Forty & Frank (1953) obtained crystals of silver from the vapour which were bounded by {111} and {100}, the octahedron distinctly predominating.

(4) *S*-forms

In the zone $[1\bar{1}0]$ we find the *F*-faces (001), (111) and ($1\bar{1}\bar{1}$). Slices of these faces are shown in Fig. 2. The profile of the *S*₁-face between the two *F*-faces (001) and (111) consists of alternating elements of these *F*-faces. An element of (001) is characterized by the P.B.C. vector $[\frac{1}{2}, \frac{1}{2}, 0]$; an element of (111) is characterized by the P.B.C. vector $[\frac{1}{2}, 0, \frac{1}{2}]$. These two vectors have as their sum-vector $[1, \frac{1}{2}, \frac{1}{2}]$, which defines the face (113) in the zone $[1\bar{1}0]$ under consideration; hence (113) is the *S*₁-face. Therefore the addition scheme of indices becomes (cf. Niggli, 1941, p. 541):

(002)	(111)	<i>F</i> -faces
	(113)	<i>S</i> ₁ -face
(115)	(224)	<i>S</i> ₂ -faces

In this scheme the indices of the face (001) have to be doubled in order to obtain (113) as the first *S*-face.

In the same way it can be shown that the *S*₁-face between (111) and ($1\bar{1}\bar{1}$) is (110). The corresponding addition scheme of indices is:

(111)	($1\bar{1}\bar{1}$)	<i>F</i> -faces
	(220)	<i>S</i> ₁ -face
(331)	(33 $\bar{1}$)	<i>S</i> ₂ -faces

The profile period of (110) (a_0) is smaller than the profile period of (113) ($\frac{1}{2}a_0/22$) and therefore the form {110} is more important. For the order of importance we find now: {111}, {100}, {110}, {113}, . . . , which is the same as the order predicted by the law of Donnay & Harker (1937).

(5) More detailed picture

In order to get an idea of the behaviour of other faces, we suppose that the interaction energy of two copper atoms depends on their distance according to the formula $E_r = E(r/r_0)^{-6}$. *E* is the interaction energy between the atoms in $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and r_0 their distance. If bonds with an energy smaller than $0.01 E$ are neglected, then we find the bonds given in Table 1.

The bonds *b* and *c* are much weaker than *a*, hence they have a minor influence on the morphology, except in the case that bond *a* is less significant for the crystallization, e.g. when the bond has been formed

Table 1. *Bonds in the structure of copper*

Bond	Between atoms in	r (Å)	Energy
<i>a</i>	(0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0)	2.55	1.00 <i>E</i>
<i>b</i>	(0, 0, 0) and (1, 0, 0)	3.61	0.12 <i>E</i>
<i>c</i>	(0, 0, 0) and (1, $\frac{1}{2}$, $\frac{1}{2}$)	4.42	0.04 <i>E</i>

already in the disordered state (cf. Part I, § (d)). In molten copper near the solidifying point a considerable short-range order can be assumed. The strong bonds *a* are then already formed to a great extent (pre-condensation) and hence the process of crystallization is mainly determined by the weaker bonds. For the morphology this means that the *F*-forms defined by these become more prominent. To describe this process the bonds *a* should be credited with a smaller energy.

The bonds *b* and *c* constitute each a complete P.B.C. vector. Hence they introduce the *F*-forms {110}, {113}, {210} and {531}. Table 2 shows the

Table 2. *Attachment energies of F- and S-forms*

Form	Bonds formed when one atom attaches to the surface	Energy of attachment	Energy of attachment, when bond <i>a</i> is neglected
{111}	$3a + 3b + 9c$	3.72	0.72
{100}	$4a + b + 12c$	4.60	0.60
{110}	$5a + 2b + 10c$	5.64	0.64
{113}	$5a + 3b + 10c$	5.76	0.76
{210}	$6a + 2b + 10c$	6.64	0.64
{531}	$6a + 3b + 10c$	6.76	0.76
<i>S</i> -face in zone [110]	$5a + 3b + 12c$	5.84	0.84
<i>S</i> -face in zone [100]	$6a + 2b + 12c$	6.72	0.72
<i>S</i> -face in zone [211]	$6a + 3b + 11c$	6.80	0.80

attachment energies in two extreme cases: crystallization from the vapour in which no pre-condensation occurs, and crystallization under such circumstances that the influence of bond *a* can be neglected (as presumably in the melt).

If we compare the order of importance for the various cases with that predicted by the law of Donnay & Harker and with the equilibrium form predicted by Stranski & Kaischew (1931), we obtain the results in Table 3. It appears that with increasing pre-condensation the cube becomes more important than the octahedron, which is even preceded by {110} and {210}. Now in fact it has been observed that copper crystallizes from its melt in cubes, while from the vapour octahedra are generated (Groth, 1906–19). The metals silver and gold crystallize from their melts in octahedra. This may be due to the greater screening capacity of these atoms, so that the bonds *b* and *c* are still weaker (cf. the similar case of zinc and cadmium, Stranski, 1949).

Table 3. *Forms, listed in the order of decreasing morphological importance, according to various assumptions*

Attachment energy with bond <i>a</i>	Attachment energy without bond <i>a</i>	Equilibrium form, Stranski & Kaischew	Law of Donnay & Harker
{111}	{100}	{111}	{111}
{100}	{110}	{100}	{100}
{110}	{210}	{110}	{110}
{113}	{111}	{113}	{113}
<i>S</i> -forms in zone [110]	<i>S</i> -forms in zone [100]	{210}	{331}
		{531}	{210}
			{112}
			etc.
{210}	{113}		
<i>S</i> -forms in zone [100]	{531}		
{531}	<i>S</i> -forms in zone [211]		
<i>S</i> -forms in zone [211]	<i>S</i> -forms in zone [110]		

Recently Shafranovskii & Malkova (1950) found that forms {*hk*0} have an unexpectedly high frequency on naturally occurring crystals of copper, silver and gold. Some of them are more frequent than {113}. It follows from Table 2 that this can easily occur when the bond *a* is ineffective in the crystallization process.

(6) Conclusion

The morphology, as deduced from the structure, is in agreement with observations on crystals when grown from the vapour. The prominence of the octahedron and the cube can be traced back to the influence of nearest neighbour interaction energy.

Unlike purely geometrical theories, the one presented here affords an explanation of the effect of pre-condensation on morphology.

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