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The Equilibrium Forms of Crystals

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The face development of the equilibrium form of a crystal is discussed. The most important faces are *F* faces.

For non-ionic crystals it is found that the equilibrium form may also exhibit *S* and *K* faces. The surface energy of *S* and *K* faces is expressed in terms of the surface energies of neighbouring *F* faces plus a correction term.

The size of each of these *S* and *K* faces is determined by the magnitude of this correction term. For the *S* faces in a certain zone this correction term is expressed in terms of the interaction energies of periodic bond chains parallel to the zone axis. The *S* faces appear on the equilibrium form as strips. The breadth of each *S* face is proportional to a certain negative power of its mesh area. As a consequence the morphological importance of an *S* face is a rapidly decreasing function of its mesh area. This relation includes the law of Donnay & Harker for separate zones.

The *K* faces are much smaller than the *S* faces and unimportant. For ionic crystals the law of Donnay & Harker may fail even for a separate zone. In this connexion the angular dependence of the interaction energy of two parallel ionic chains is discussed.

Introduction

It is a well known fact that in a crystallization crop very small crystals often show more faces than larger ones. These small crystals are formed at the end of the crystallization process after the larger ones have crystallized. The supersaturation is very low then and often the crop has undergone some slow temperature fluctuations, which have their greatest effect on tiny crystals. The small crystals are therefore closer to the equilibrium form than the larger ones, which show what is usually called the growth form. The difference between these two forms is well illustrated by the work of Stranski & Honigmann (1950) on urotropine.

The equilibrium form of a crystal is thermodynamically described by the Gibbs condition that $\Sigma \sigma_i F_i$ is a minimum, where σ_i is the specific surface free energy of the i'th face and F_i is its area. When the various quantities σ_i are known, the equilibrium form can be derived by means of the Wulff construction (1901). From a certain point as origin (the Wulff point) the normals on the faces are drawn. The lengths of these normals are taken proportional to the appropriate σ_i values and a plane is drawn through the end of each normal and perpendicular to it. The polyhedron enclosed by these planes represents the equilibrium form.

The faces exhibited by this equilibrium form have low surface free energies and most of them belong to the class of the *F* faces (Hartman & Perdok, 1955*a*). In all cases studied so far it has been found that the growth form, when grown in pure solution, or from the vapour, and under low degrees of supersaturation, exhibits *F* faces only. The question arises whether an equilibrium form can show *S* and *K* faces also. In the following sections it will be shown that this is sometimes possible and that as a consequence new light is thrown upon the understanding of the law of Donnay & Harker (1937).

The specific surface free energy of an S_1 face between two *F* faces

Suppose the (100) and (010) faces of a triclinic crystal are *F* faces and (110) is the S_1 face in between. The profile of this latter face is drawn in Fig. 1; it consists of alternating elements of the *F* faces (Hartman & Perdok, 1955*b*). This suggests that the surface free energy per mesh area of the S_1 face can be represented by the sum of the surface free energies per mesh area of the *F* faces plus a small correction term:

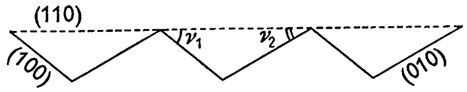


Fig. 1. Surface profile of the *S* face (110); it consists of alternating elements of the *F* faces (100) and (010).

$$A_{110}\sigma_{110} = A_{100}\sigma_{100} + A_{010}\sigma_{010} + A_{110}\Delta\sigma_{110} \,. \quad (1)$$

Here A_{110}, etc. represent the mesh areas of the faces (110) etc. Now if $\nu_1 = (100):(110)$ and $\nu_2 = (010):(110)$, we have:

$$A_{100} = A_{110} \sin \nu_2 / \sin (\nu_1 + \nu_2),$$

and

$$A_{010} = A_{110} \sin \nu_1 / \sin (\nu_1 + \nu_2)$$

so that (1) becomes:

$$\sigma_{110} = \sigma_{100} \sin \nu_2 / \sin (\nu_1 + \nu_2) + \sigma_{010} \sin \nu_1 / \sin (\nu_1 + \nu_2) + \Delta\sigma_{110} \,. \quad (2)$$

It will be shown now that the S_1 face appears on the crystal only when $\Delta\sigma_{110} < 0$. In Fig. 2 we put $OA = \sigma_{100}$ and $OB = \sigma_{010}$. The line OC is the normal on (110). TC is the position of (110) when it just touches the edge between (100) and (010). Now:

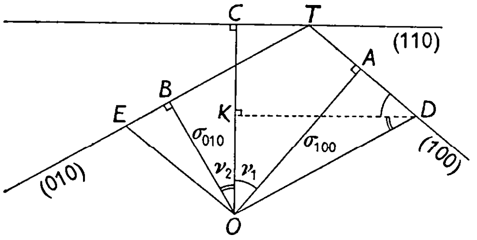


Fig. 2. Cross-section perpendicular to the c axis of a crystal. $OA = \sigma_{100}$, the specific surface free energy of (100). Similarly $OB = \sigma_{010}$. The face (110) does not appear on the crystal; it just touches the edge of (100) and (010) at T. In that case $OC = \sigma_{110}$.

$$OC = OK + KC,$$
$$OK = OD \sin \nu_2 \text{ and } OD = \sigma_{100}/\sin(\nu_1+\nu_2),$$
$$KC = DT \sin \nu_1 \text{ and } DT = OE = \sigma_{010}/\sin(\nu_1+\nu_2),$$

so that

$$OC = \sigma_{100} \sin \nu_2/\sin(\nu_1+\nu_2) + \sigma_{010} \sin \nu_1/\sin(\nu_1+\nu_2). \quad (3)$$

It follows from (2) and (3) that $OC = \sigma_{110}$ when $\Delta\sigma_{110} = 0$. (A similar result has been obtained by Yamada (1923) in a different way.) From Fig. 2 it is evident that the face (110) can appear between (100) and (010) only if $\sigma_{110} < OC$, or if $\Delta\sigma_{110} < 0$.

It should be emphasized here that this result is quite general. It applies to any face between two other faces. We took the example of an S_1 face between two F faces in view of the treatment in further sections.

To find an expression for $\Delta\sigma_{110}$ we consider Fig. 3.

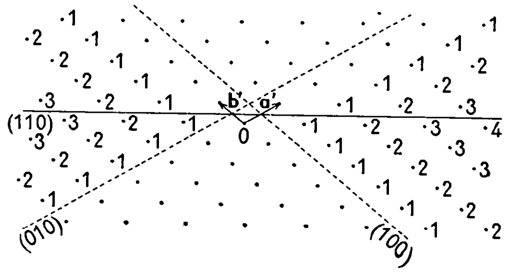


Fig. 3. Projection of a triclinic structure along the c axis. Each dot represents a periodic bond chain [001] seen end on. The numbers near the dots indicate the coefficients c_{uv} that differ from zero.

Each dot represents a periodic bond chain [001] seen end on. When the temperature is 0° K. the free energy is equal to the energy. In this case the surface free energy can be described by the sum of the interaction energies of the chains. To obtain the specific surface energy of (100) the crystal is divided into two parts along a plane parallel to (100). The part at the right-hand side of the dashed line, marked (100) in Fig. 3, is then removed to infinity. The energy per mesh area necessary for this removal is

$$2A_{100}\sigma_{100} = -\sum_{u=1}^{\infty}\sum_{v=-\infty}^{+\infty} uE(u,v)\,,$$

where $E(u,v)$ is the interaction energy of the chain at the origin O with the chain at a distance $\mathbf{r}(u,v) = u\mathbf{a}'+v\mathbf{b}'$; in the present case a' and b' are the projections of the a and b axes on a plane perpendicular to [001], so that $a' = a \sin\beta$ and $b' = b \sin\alpha$. Similarly:

$$2A_{010}\sigma_{010} = -\sum_{u=-\infty}^{+\infty}\sum_{v=1}^{\infty} vE(u,v)$$

and

$$2A_{110}\sigma_{110} = -\sum_{u=-\infty}^{+\infty}\sum_{m=1}^{\infty} mE(u,m-u), \text{ where } m = u+v\,.$$

According to (1) the correction term becomes

$$2A_{110}\Delta\sigma_{110} = -\sum_{u=-\infty}^{+\infty}\sum_{m=1}^{\infty} mE(u,m-u) + \sum_{u=1}^{\infty}\sum_{v=-\infty}^{+\infty} uE(u,v) + \sum_{u=-\infty}^{+\infty}\sum_{v=1}^{\infty} vE(u,v)\,. \quad (4)$$

We write this equation in the form

$$2A_{110}\Delta\sigma_{110} = \sum_{u=-\infty}^{+\infty}\sum_{v=-\infty}^{+\infty} c_{uv}E(u,v)\,. \quad (5)$$

For each pair of (u,v) values the coefficients c_{uv} have been calculated and put in Fig. 3 near the corresponding chain. It is easy to see that c_{uv} conforms to the following scheme:

$$\begin{array}{lllll}
u \geqq 0 \text{ and } v \geqq 0: & c_{uv} = & 0; & & \\
u \leqq 0 \text{ and } v \leqq 0: & c_{uv} = & 0; & & \\
u > 0 \text{ and } v < 0: & c_{uv} = & u, & \text{if} & |u| \leqq |v|\,, \\
 & c_{uv} = & -v, & \text{if} & |u| > |v|; \\
u < 0 \text{ and } v > 0: & c_{uv} = & v, & \text{if} & |u| \geqq |v|\,, \\
 & c_{uv} = & -u, & \text{if} & |u| < |v|\,.
\end{array}$$

In many cases $E(u,v)$ is a continuously decreasing function of $\mathbf{r}(u,v)$, so that $E(1,\bar{1})$ will be much larger than other terms $E(u,v)$ in (5). When, moreover, we take into account that $E(u,v) = E(\bar{u},\bar{v})$, an approximate expression for $\Delta\sigma_{110}$ can be derived from (5):

$$\Delta\sigma_{110} \approx E(1,\bar{1})/A_{110}\,. \quad (6)$$

The morphological development of a zone

Suppose now that both (100) and (110) are present on the equilibrium form. What are then the conditions that the S_2 face (210) appears between the other two faces? The surface free energy per mesh area of (210) can be represented by

$$A_{210}\sigma_{210} = A_{100}\sigma_{100}+A_{110}\sigma_{110}+A_{210}\Delta\sigma_{210}\,. \quad (7)$$

A reasoning similar to that used in the foregoing section to derive (6) was applied to the present case and led to the following approximate expression for $\Delta\sigma_{210}$:

$$\Delta\sigma_{210} \approx E(1,\bar{2})/A_{210}\,.$$

Evidently the general approximate expression for the specific surface energy correction is

$$\Delta\sigma_{hk0} \approx E(k,\bar{h})/A_{hk0}\,. \quad (8)$$

One remark must be made here: equation (8) holds only when each face ($hk0$) appears between two other faces (h_1k_10) and (h_2k_20) such that $h_1+h_2 = h$ and $k_1+k_2 = k$. This leads to an addition scheme of indices (cf. Hartman & Perdok, 1955*b*):

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

Thus, e.g. (320) should appear between (110) and (210); (530) between (320) and (210); and so on.

For each face ($hk0$) that is present on a crystal, the breadth b_{hk0} is proportional to $\Delta\sigma_{hk0}$. The relation to the lattice dimensions is

$$b_{hk0} = \Delta\sigma_{hk0}r(k,\bar{h})/d_{hk0}\,. \quad (9)$$

Here d_{hk0} is the interplanar spacing of the face ($hk0$); $r(k,\bar{h})$ is the length of the vector $\mathbf{r}(k,\bar{h}) = k\mathbf{a}'-h\mathbf{b}'$ (cf. Fig. 3). For a certain zone this length is proportional to A_{hk0}. The interaction energy of two chains $E(k,\bar{h})$ can often be put proportional to the $(-n)$th power of $r(k,\bar{h})$. Then, in view of (8) and (9), the following proportionality exists:

$$b_{hk0} \sim A_{hk0}^{-(n-1)}\,. \quad (10)$$

If n is large enough, say $n > 3$, b_{hk0} soon fades out for higher values of h and k. The appearance of (210) and (120) in a zone (where (110) is present already), decreases b_{110} somewhat. Likewise b_{210} will be decreased a little when (310) appears between (210) and (100). But if $b_{110} \gg b_{210} \gg b_{310}$ the ratio b_{210}/b_{110} will hardly change, so that formula (10) still holds good, when a number of S faces appears on the equilibrium form.

A crystal approaches the equilibrium form when it is subjected to small temperature fluctuations. During the period of increasing temperature its edges and corners are rounded off, and the S faces have a chance to appear when the temperature decreases. Faces with a large breadth b_{hk0} are more likely to be produced than faces with a small breadth. Moreover, the former are also more likely to be observed than the latter. Hence, the frequency of observation is more or less proportional to b_{hk0}. Therefore, according to formula (10), it is a continuously decreasing function of the mesh area A_{hk0}. When the exponent n in (10) is equal to 2, and when a strict proportionality is assumed between the frequency of observation and b_{hk0}, we obtain the law of Donnay & Harker (1937) for a separate zone (cf. also Donnay, 1938).

Sometimes this law fails to account for the whole morphology of a crystal species (Hartman & Perdok, 1956), but in these cases the law often still holds good for the development of separate zones. But it sometimes even fails to account for the development of a zone. Evidently this must occur when the proportionality (10) fails. This is the case when the interaction energy $E(u,v)$ either (*a*) depends not only on the distance between the chains, but also on their mutual orientation; or (*b*) when this energy is not a continuously decreasing function of this distance.

These deviations occur with ionic chains and will be treated in the next section.

The angular dependence of the interaction between ionic chains

Let us consider the interaction energy of the ionic chains in Fig. 4(*a*). The chains are seen end on. Cylindrical coordinates (z, r, θ) are used. The chain direction is taken as the z axis. The electrostatic

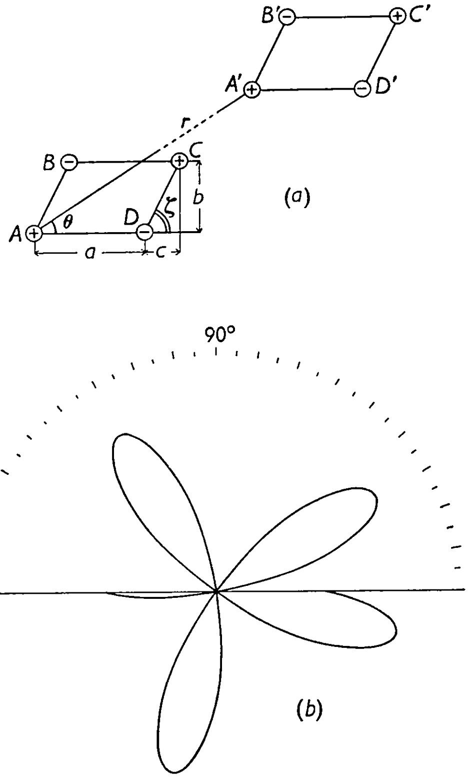


Fig. 4. (*a*) Two ionic chains, a distance r apart, are projected along the chain direction. (*b*) Graphical representation in polar coordinates of the interaction energy of the ionic chains in (*a*), when θ varies from 0° to 180°. Maximum attraction occurs at 76·5° and 166·5°; maximum repulsion at 31·5° and 121·5°.

potential at A' due to the row of equally charged ions through A is, according to Madelung (1918),

$$\varphi_{AA'} = \frac{4e}{p}\left[\sum_{l=1}^{\infty} K_0(2\pi l r_{AA'}/p) \cos\{2\pi l(z_A - z_{A'})/p\}\right] - \frac{2e}{p}\ln(r_{AA'}/2p) + C\,. \qquad (11)$$

Here p is the chain period, K_0 is the Hankel cylinder function of order zero, e is the electronic charge and C is an infinite constant.

The total electrostatic interaction energy between the two chains is

$$E = \Sigma\Sigma e_i e_j \varphi_{ij}\,, \qquad (12)$$

where i ranges from A to D and j from A' to D' (see Fig. 4(a)). When r is large enough, say $r > 2p$, the terms containing K_0 are negligibly small. The interaction energy of the chains is then equal to

$$E(r_{AA'}, \theta) = (2e^2/p)\ln(r^2_{AB'}r^2_{AD'}r^2_{BA'}r^2_{CB'}/r^4_{AA'}r_{AC'}r_{BD'}r_{CA'}r_{DB'})\,.$$

When a, b, and c are small compared with $r_{AA'}$, each term $\ln r_{ij}$ can be expanded into a power series of $r^{-n}_{AA'}$. Neglecting higher powers than $r^{-4}_{AA'}$, we find

$$E(r_{AA'}, \theta) = -12e^2p^{-1}r^{-4}_{AA'}a^2\{(b^2-c^2)\cos 4\theta - 2bc\sin 4\theta\}\,. \qquad (13)$$

Extrema of this function occur at

$$\tan 4\theta_m = -2bc/(b^2-c^2)\,,$$

from which

$$\tan 2\theta_m = b/c\,,$$

or

$$\theta_m = \tfrac{1}{2}\zeta \pm \tfrac{1}{4}n\pi\,. \qquad (14)$$

The absolute value of each extremum is:

$$|E_m| = 12e^2p^{-1}r^{-4}_{AA'}a^2(b^2+c^2)\,. \qquad (15)$$

The interaction energy changes sign at

$$\tan 4\theta_0 = (b^2-c^2)/2bc\,,$$

from which

$$\theta_0 = \tfrac{1}{2}\zeta \pm (2n+1)\pi/8\,. \qquad (16)$$

To illustrate the dependency on θ, a graph is drawn in Fig. 4(b) of the function

$$\varrho = -\{(b^2-c^2)\cos 4\theta - 2bc\sin 4\theta\}\,,$$

the θ-dependent part in (13), where we took $b = 2$ and $c = 1$ in arbitrary units. Within 180° two directions of maximum attraction occur, and two others of maximum repulsion. According to the particular character of F faces, the chains in a crystal structure are arranged in such a way that the directions of maximum attraction are more or less parallel to the F faces. But as a consequence the directions of maximum repulsion are more or less parallel to the S_1 faces. Hence, in general, $E(1, \bar{1})$ will be positive, so that according to (6) $\Delta\sigma_{110} > 0$ and the face (110) does not appear on the equilibrium form.

Would it be possible then for a different S face, e.g. (310), to appear instead of (110) on the equilibrium form? It will be shown that this does not happen either. When a face (310) is supposed to appear between (100) and (010) we can write its surface free energy in a form similar to (1):

$$A_{310}\sigma_{310} = 3A_{100}\sigma_{100} + A_{010}\sigma_{010} + A_{310}\Delta'\sigma_{310}\,. \qquad (17)$$

On the other hand, when (310) appears between (100) and (210), this energy is

$$A_{310}\sigma_{310} = A_{100}\sigma_{100} + A_{210}\sigma_{210} + A_{310}\Delta\sigma_{310}\,. \qquad (18)$$

From (1), (7), (17) and (18) we find

$$\Delta'\sigma_{310} = \Delta\sigma_{310} + A_{210}\Delta\sigma_{210}/A_{310} + A_{110}\Delta\sigma_{110}/A_{310}\,. \qquad (19)$$

If we suppose that $|E(1, \bar{1})| \gg |E(1, \bar{2})| \gg |E(1, \bar{3})|$, the approximations (6) and (8) may be used, so that

$$\Delta'\sigma_{310} \approx E(1, \bar{1})/A_{310}\,. \qquad (20)$$

Hence also the surface energy correction $\Delta'\sigma_{310}$ is positive and the face (310) does not appear on the equilibrium form. We thus arrive at the conclusion, which is a generalization and no doubt will have exceptions, that the equilibrium form of an ionic crystal shows no S faces. When the surface energy of the S faces is lowered through adsorption, some of these may well appear on the crystal. This problem will be discussed in a later publication.

It may be mentioned here that the interaction between chains of neutral atoms or of molecules varies little with the angle. Most of the interaction energy will be van der Waals energy, so that $E(1, \bar{1})$ will always be negative. In most cases $|E(1, \bar{1})| \gg |E(1, \bar{2})|$ and also $|E(1, \bar{1})| \gg |E(2, \bar{1})|$, so that we arrive at a second generalized conclusion, namely that the equilibrium form of a non-ionic crystal may show S_1 faces. It evidently depends on the value of $\Delta\sigma_{110}$ whether the breadth is large enough to make the face observable.

The development of *K* faces

For the development of K faces on an equilibrium form, similar arguments apply as with S faces. Their appearance is, however, more restricted, as will be shown now.

Suppose a crystal has three P.B.C. vectors [100], [010] and [001]. Then (111) is a K face and its surface free energy can be expressed as

$$A_{111}\sigma_{111} = A_{100}\sigma_{100} + A_{010}\sigma_{010} + A_{001}\sigma_{001} + A_{111}\Delta\sigma_{111}\,. \qquad (21)$$

Here $\Delta\sigma_{111} = 0$ when the face (111) just touches the vertex of the pyramid formed by (100), (010) and (001). This is easily proved when (111) is considered as a face in the zone $[1\bar{1}0]$ between (001) and (110). If (111) is bound to touch the edge made by (001) and (110), then

$$A_{111}\sigma_{111} = A_{001}\sigma_{001}+A_{110}\sigma_{110} \,.$$

If, moreover, (111) should touch the above mentioned vertex, (110) must have degenerated to a line. In that case

$$A_{110}\sigma_{110} = A_{100}\sigma_{100}+A_{010}\sigma_{010} \,,$$

which proves, in connexion with the foregoing equation, that

$$\Delta\sigma_{111} = 0 \,.$$

The quantity $\Delta\sigma_{111}$ must be expressed in terms of the interaction energy $E(u, v, w)$ between the contents of two primitive unit cells the centers of which are a distance $\mathbf{r}(u, v, w) = u\mathbf{a}+v\mathbf{b}+w\mathbf{c}$ apart. Then

$$2A_{100}\sigma_{100} = -\sum_{u=1}^{\infty}\sum_{v=-\infty}^{+\infty}\sum_{w=-\infty}^{+\infty} uE(u, v, w) \,,$$

and similarly

$$2A_{010}\sigma_{010} = -\sum_{u=-\infty}^{+\infty}\sum_{v=1}^{\infty}\sum_{w=-\infty}^{+\infty} vE(u, v, w) \,,$$

$$2A_{001}\sigma_{001} = -\sum_{u=-\infty}^{+\infty}\sum_{v=-\infty}^{+\infty}\sum_{w=1}^{\infty} wE(u, v, w) \,.$$

Now

$$2A_{111}\sigma_{111} = -\sum_{q=1}^{\infty}\sum_{v=-\infty}^{+\infty}\sum_{w=-\infty}^{+\infty} qE(u, v, w) \,,$$

where $q = u+v+w$, so that, in view of (21),

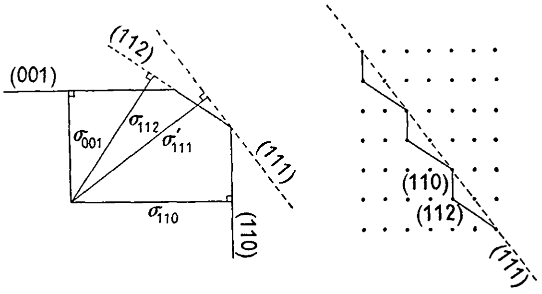
$$\begin{aligned} 2A_{111}\Delta\sigma_{111} = &-\sum_{q=1}^{\infty}\sum_{v=-\infty}^{+\infty}\sum_{w=-\infty}^{+\infty} qE(u, v, w) \\ &+\sum_{u=1}^{\infty}\sum_{v=-\infty}^{+\infty}\sum_{w=-\infty}^{+\infty} uE(u, v, w) \\ &+\sum_{u=-\infty}^{+\infty}\sum_{v=1}^{\infty}\sum_{w=-\infty}^{+\infty} vE(u, v, w) \\ &+\sum_{u=-\infty}^{+\infty}\sum_{v=-\infty}^{+\infty}\sum_{w=1}^{\infty} wE(u, v, w) \,. \end{aligned} \tag{22}$$

If $E(u, v, w)$ is negative and proportional to $|r(u, v, w)|^{-n}$ in most cases $E(1, \bar{1}, 0)$, $E(1, 0, \bar{1})$ and $E(0, 1, \bar{1})$ are the largest terms in (22).

Taking into account that $E(u, v, w) = E(\bar{u}, \bar{v}, \bar{w})$, we find the approximation

$$\Delta\sigma_{111} \approx \{E(1, \bar{1}, 0)+E(1, 0, \bar{1})+E(0, 1, \bar{1})\}/A_{111} \,. \tag{23}$$

The question arises whether such a K face can appear at all on the equilibrium form, since the faces (110), (101) and (011) will appear also. The energy $E(1, \bar{1}, 0)$ forms the greater part in the energy $E(1, \bar{1})$ in (6) that determines the quantity $\Delta\sigma_{110}$. And because $E(1, \bar{1}, 0)$ was supposed to be negative (110) must be present on the crystal and so are (101) and (011). The face (111) appears only when σ_{111} is smaller than the value σ_{111}' belonging to the plane that touches the corner made by the three faces (110), (101) and (011) (see Fig. 5(*a*)). The edge of the latter two faces may be considered as a face (112) the area of which is just zero. As can be seen from Fig. 5(*b*), one mesh of (110) plus one mesh of (112) correspond to two meshes of (111), so that



(*a*) (*b*)

Fig. 5. (*a*) Cross-section of a crystal perpendicular to $[1\bar{1}0]$. The face (111) just touches the vertex made by (100), (101) and (011). The face (112) just touches the edge between (101) and (011). (*b*) Projection of crystal lattice along $[1\bar{1}0]$.

$$2A_{111}\sigma_{111}' = A_{112}\sigma_{112}+A_{110}\sigma_{110};$$

further, we have

$$A_{112}\sigma_{112} = A_{101}\sigma_{101}+A_{011}\sigma_{011} \,,$$

from which we find

$$\begin{aligned} A_{111}\sigma_{111}' = &\,A_{100}\sigma_{100}+A_{010}\sigma_{010}+A_{001}\sigma_{001} \\ &+\tfrac{1}{2}(A_{110}\Delta\sigma_{110}+A_{101}\Delta\sigma_{101}+A_{011}\Delta\sigma_{011}) \,. \end{aligned} \tag{24}$$

Taking into account only the first (and largest) terms in the expressions for $\Delta\sigma_{110}$ etc., we find

$$\begin{aligned} A_{111}\sigma_{111}' \approx &\,A_{100}\sigma_{100}+A_{010}\sigma_{010}+A_{001}\sigma_{001} \\ &-\tfrac{1}{2}\{E(1, \bar{1}, 0)+E(1, 0, \bar{1})+E(0, 1, \bar{1})\} \,, \end{aligned} \tag{25}$$

while, according to (21) and (23),

$$\begin{aligned} A_{111}\sigma_{111} \approx &\,A_{100}\sigma_{100}+A_{010}\sigma_{010}+A_{001}\sigma_{001} \\ &-\{E(1, \bar{1}, 0)+E(1, 0, \bar{1})+E(0, 1, \bar{1})\} \,. \end{aligned} \tag{26}$$

Hence the face (111) will show even between (110), (101) and (011). Its area is of the order of the breadths of the neighbouring S faces, so that it is rather small.

By a similar reasoning it could be shown that the face (112) will appear between (102), (012) and (111) if these faces are present on the crystal.

With ionic crystals some of the energies $E(1, \bar{1}, 0)$ etc., or all of them, may be positive. In that case it evidently depends on the sign of the sum

$\{E(1, \bar{1}, 0)+E(1, 0, \bar{1})+E(0, 1, \bar{1})\}$ whether (111) will be present on the equilibrium form. In general this expression will be positive, so that (111) does not appear.

The general aspect of the equilibrium form and the law of Donnay & Harker

From the foregoing section we obtain the following general picture. The large faces on the equilibrium form are those with small σ values. They belong to the class of the F faces. The exhibition of other faces depends on the type of bonding. We saw that with ionic crystals in general no S faces and no K faces will be present on the equilibrium form.

With non-ionic crystals the edges that are parallel to P.B.C. vectors are replaced by a set of S faces. Each of these faces has the form of a trapezium extended in the direction of its parallel sides. Where two or more S faces touch each other, K faces may be formed which have the appearance of small polygons.

The real equilibrium form of a crystal is hard to obtain. It is approximated best by a 'tempered' crystal, that is a crystal which has been subject to small temperature fluctuations. During the period of decreasing temperature this crystal grows, though very slowly and very little. The K faces, which have the highest growth rate and are smallest, have the greatest chance to disappear.

This implies that in general S faces are more prominent than K faces.

Moreover, when a crystal is measured, S faces are more likely to be observed than K faces, since S faces are seen as streaks or lines, while K faces appear as spots or points.

Approximate equilibrium forms may be found in nature among the euhedral minerals. Many of them crystallized very slowly and have undergone temperature fluctuations, so that the conditions during crystallization were near to equilibrium conditions. Many of the relations in the foregoing sections are strictly valid only at the absolute zero. However, it appears that these relations hold also at higher temperatures, so that the changes brought about by these higher temperatures are presumably small. The influence of adsorption is certainly not to be neglected. Sometimes, however, statistical data may give a picture of the morphology that is not too seriously affected by this influence. In such cases, where the influence of the structure dominates, we may expect that a comparison of the available statistical data with the form list according to the law of Donnay & Harker will reveal the following difference: When both lists are cut off at the same number of forms the Donnay–Harker list will show more K forms and fewer S forms than the list of observed forms. This difference has actually been found. Details will be reported later.

Conclusion

Although the calculation or the experimental determination of the surface energies of F faces is rather difficult, it is all the same possible to derive the zone development on the equilibrium forms. The general relation (10) includes the law of Donnay & Harker for separate zones, thereby giving this law of observation a theoretical background.

The angular dependence of the interaction energy of ionic chains can sometimes disturb the relation (10) and cause a zone development different from the usual type.

As with the growth forms (cf. Hartman & Perdok, 1955*a*) K faces are unimportant.

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