

ON THE VALIDITY OF THE DONNAY-HARKER LAW*

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ABSTRACT

A physical explanation of the Donnay-Harker law and its extension is given based on the assumptions that the specific surface energy of a crystal is approximately isotropic and that the growth rate R_{hkl} of a crystal face is roughly proportional to its attachment energy. This leads to a formulation of the Donnay-Harker law in the form that R_{hkl} is proportional to $1/d_{hkl}^m$, where m is larger than 1. It is argued that the Donnay-Harker law and its extension are valid in the majority of cases and consistent with certain modifications of habit in response to external changes, for instance with the three lattices of calcite that can be distinguished under various conditions of growth. Finally it is shown that the extended Donnay-Harker law is strictly valid for the naphthalene structure.

SOMMAIRE

On donne une explication physique de la loi de Donnay et Harker et de sa généralisation, explication fondée sur deux postulats: (1) l'énergie de surface spécifique d'un cristal est à peu près isotrope; (2) la vitesse de croissance R_{hkl} d'une face cristalline est *grosso modo* proportionnelle à son énergie d'attachement. On est ainsi conduit à énoncer la loi de Donnay et Harker sous cette forme: R_{hkl} est proportionnelle à $1/d_{hkl}^m$, où m est plus grand que 1. On montre, avec arguments à l'appui, que la loi de Donnay et Harker et sa généralisation sont valides dans la plupart des cas et sont même compatibles avec certains changements de faciès dûs au changement des conditions externes, par exemple, avec les trois réseaux de la calcite qu'on peut distinguer suivant les conditions de croissance. On montre finalement la stricte validité de l'extension de la loi de Donnay et Harker pour la structure de naphthalène.

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BRIEF HISTORICAL DEVELOPMENT OF THE EXTENDED LAW OF BRAVAIS

In 1849 Bravais put forward the hypothesis

* Dedicated to Professor Dr. J.D.H. Donnay on the occasion of his 75th anniversary

that, in general, a crystal face was the more important the higher its reticular density, although he was aware of the possible influence of external factors (Bravais 1866). Friedel (1907) made an extensive investigation of the validity of this hypothesis and concluded that it was valid in so many cases that it could be considered a law of observation, independent of any speculation. Yet, several inexplicable exceptions persisted. Niggli (1919) was the first to notice the influence of glide planes and screw axes on the reticular density. He applied his ideas to the determination of the space group of pyrite from morphological data. As {210} is more important than {110} he concluded that there must be a glide plane a in the space group, leading to the symmetry $Pa3$. The forms, in order of importance, would then be {111}, {200}, {210}, . . ., in excellent agreement with observation. However, this work remained largely unknown and so it occurred that in 1937 Donnay & Harker rediscovered the influence of glide planes and screw axes on the reticular density. They showed that many of the exceptions noted by Friedel could be explained and, moreover, that some space-group determinations could be made on the basis of morphological data. A review was given by Donnay in 1946.

An extension of the Donnay-Harker law was given by J.D.H. and G. Donnay in 1961, in which they showed how a pseudo-cell can occur if the coordinates of certain atoms have fortuitous values. This will be discussed below. At present the extended Donnay-Harker law can be formulated as follows: the smaller the growth rate of a crystal face, the larger its parameter d_{hkl} . It should be noted that Donnay & Harker (1937) formulated the law as follows: the morphological importance of a crystal face is inversely proportional to its reticular area. Strictly speaking this is incorrect in a mathematical sense because the morphological importance was not expressed quantitatively. In this paper we shall use the term *proportional* in its mathematical sense and so the extended Donnay-Harker law was reformulated above in qualitative terms. The parameter d_{hkl} is defined as the period in which the surface energy is

repeated exactly (owing to lattice type, screw axes or glide planes) or almost exactly (owing to fortuitous values of the coordinates of atoms that play a special role in the growth process). In the latter case the parameter d_{hkl} eventually can be a submultiple of the value following from the unit-cell dimensions and the space group.

A PHYSICAL EXPLANATION OF THE DONNAY-HARKER LAW

In order to find an explanation of the law one could consider the results of current crystal-growth theories. In these theories the growth of the more important crystal faces is a process in which layer after layer is deposited, by two-dimensional nucleation or by spiral growth owing to the presence of a screw dislocation (e.g., Elwell & Scheel 1975). If one considers the formulae derived for the linear growth rate R_{hkl} of a face (hkl), measured along the face normal and expressed in units length \cdot time $^{-1}$, then indeed R_{hkl} appears to depend on d_{hkl} . Unfortunately, in all cases the expressions are such that R_{hkl} increases when d_{hkl} increases. Consequently a physical explanation of the law must not be sought in the parameter d_{hkl} itself, but in other parameters.

To this end we consider the specific surface energy γ . By plotting all values γ_{hkl} along the normals of the faces (hkl) we obtain the so-called γ plot. From the work of Herring (1951), Wolff & Gualtieri (1962) and Bennema (1973) we can conclude that this γ plot is a rather complex surface whose shape can be described as framboidal, *i.e.*, like raspberries, with shallow protrusions and acute depressions. The specific surface energy is clearly anisotropic, but calculations of these energies show that the maximum and minimum values do not differ more than by a factor of 1.5. Such calculations have been carried out for metals by Drechsler & Müller (1968) and for anthracene by Kitai-gorodski & Ahmed (1972). Now the specific surface energy of a face can be related to d_{hkl} in the following way.

Let us call E_i the interaction energy per molecule of a slice d_{hkl} in a crystal with a slice i , the slices being numbered consecutively from 0 to i . Then the total energy to split the crystal parallel to the face (hkl) along the boundary of the slices 0 and 1 is $\sum iE_i$. The factor i here arises as follows. Consider the term E_3 , the interaction between slice number 0, in the upper part, and slice number 3, in the lower part. The same interaction is found between the second slice of the upper part and the second of the

lower, and again between the third of the upper and the first of the lower. Hence the energy term E_3 appears three times in the summation. To find the specific surface energy we must know the number of molecules within a slice per unit area of the surface. If the primitive unit cell of volume V_p contains Z molecules, the area per molecule is $V_p/(Z d_{hkl})$ and the number of molecules per unit area is $Z d_{hkl} V_p$. In splitting the crystal we obtain two surfaces, so the specific surface energy γ becomes

$$\gamma = Z d_{hkl} \sum i E_i / 2 V_p \quad (1)$$

Now we define the attachment energy E_{att} as the energy released per molecule when one slice d_{hkl} crystallizes on the face (hkl). So, $E_{att} = \sum E_i$ (Hartman 1973), which is almost equal to the surface energy per molecule if terms other than E_1 can be neglected. This is commonly the case for the more important crystal forms, so that E_{att} is a good approximation of $\sum i E_i$. Hence

$$\gamma \approx Z d_{hkl} E_{att} / 2 V_p \quad (2)$$

As γ does not vary much with orientation, we assume as a first approximation that it is isotropic. Then it follows from eq. (2) that E_{att} is proportional to $1/d_{hkl}$. Now it is generally assumed that the growth rate R_{hkl} increases when E_{att} increases. As was shown by Bennema & Gilmer (1973) this qualitative relation between R_{hkl} and E_{att} can be justified by crystal-growth theories. The quantitative relation between R_{hkl} and E_{att} is being investigated, but the results so far obtained indicate that a simple proportionality between R_{hkl} and E_{att} is indeed a reasonable approximation. Then, by virtue of eq. (2), R_{hkl} is in first approximation proportional to $1/d_{hkl}$. This is only in apparent conflict with the fact mentioned above that R_{hkl} increases with d_{hkl} according to crystal-growth theories, because the influence of E_{att} on R_{hkl} far outweighs that of d_{hkl} itself. In a second approximation we should include the anisotropy of γ , the values of γ being somewhat lower for the most important faces and somewhat higher for unimportant ones. This means that γ is a slightly increasing function of $1/d_{hkl}$, which, for convenience, we write as $1/d_{hkl}^m$, where the exponent m is larger than 1 but probably does not exceed 2. Then, according to eq. (2), E_{att} is proportional to $1/d_{hkl}^m$. Assuming again the proportionality between R_{hkl} and E_{att} , this means that R_{hkl} is also proportional to $1/d_{hkl}^m$.

As early as 1947 Buerger presented an explanation of the Bravais law, considering crystal

growth as a stacking of identical blocks. He assumed that the energy of the bond between a block and a crystal face is proportional to the area of the surface joining the block to the crystal. In our terms his starting point was that E_{att} is proportional to $1/d_{hkl}$. As pointed out by Dowty (1976) this implies that the bond energy per unit area is approximately the same for all faces, which is just our starting point. The derivation given in the present paper is advantageous because γ is a quantity accessible to both theoretical and experimental work, the latter in the form of the observation of equilibrium forms, and because it is quite general, not depending from the start on the properties of a model. Models enter implicitly in the reasoning where R_{hkl} is related to E_{att} on the basis of crystal-growth theories. The link with the growth rate is made both by Buerger (1947) and Dowty (1976) by considering the start of a new layer; for this, according to Dowty, 'the critical factor would seem to be the energy with which the block is bonded directly to the face', which is in our terms E_{att} . This is an oversimplification of the problem, but as stated above, the assumption that R_{hkl} increases with E_{att} is reasonable, although they made this assumption on incorrect grounds. They consider growth rate to depend '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' (Dowty 1976). This suggests that a block attaches itself faster to the face when E_{att} is higher, but this is not true. The probability of blocks landing on the surface is the same for all surfaces, but it is the probability of *detachment* of a block that is low when E_{att} is high. Therefore, the block will stay longer on the surface and thus will have a greater probability of becoming incorporated into the growing layer or into the two-dimensional nucleus.

THE VALIDITY OF THE DONNAY-HARKER LAW AND OF ITS EXTENSION

It follows from the foregoing paragraph that the Donnay-Harker law and its extension are valid if (1) γ is approximately isotropic, (2) E_1 is the main term of $\sum_i E_i$, and (3) R_{hkl} is proportional to E_{att} . The first condition can be expected to hold reasonably well for metals and for organic crystals where van der Waals interaction predominates. For ionic crystals the anisotropy in γ is presumably larger. Leaving out of consideration extreme anisotropy such as occurs for example in mica, the anisotropy

is restricted to one or two crystal forms having a decidedly lower value than the other forms (*cf.*, 't Hart 1978). Often this does not invalidate the law. The second condition means that the law can be expected not to hold for faces with small d_{hkl} values, but these are absent or rare.

The third condition is a reasonable approximation. The conclusion must be that in the majority of cases the law is valid. Any exception must therefore have a special explanation, which often is to be found in the effect of external factors on crystal habit. We leave aside the fact that the law cannot explain the occurrence of one merohedral form in preference to another with exactly the same d_{hkl} value.

To show the effect of external factors we consider first the NaCl structure. In the case of growth from aqueous solution the crystals are cubes. In the growth process the Na^+ and Cl^- ions can be considered as point charges which have exactly the same attachment energies to the {100} faces. This means that for the growth process they are indistinguishable and therefore identical. Hence, the lattice is determined by the cube having the shortest Na-Cl distance as cell edge. The symmetry of this model is $Pm\bar{3}m$ and the main form according to the Donnay-Harker law is {100}. However, at high supersaturations the habit changes to octahedral (Kern 1953). A probable explanation is that growth rate is so high that dehydration processes of the ions play a role, and because the hydration energy of Na^+ is larger than that of Cl^- , the ions can be distinguished in the growth process. Thus the symmetry for the crystal-growth process is the same as that of the structural cell, $Fm\bar{3}m$, leading to {111} as the most important form.

A similar argument holds for calcite, for which three lattices have been considered by Friedel (1926) and by Donnay *et al.* (1934). First there is the X-ray cell, $R\bar{3}c$, containing 2CaCO_3 , which operates in the growth process when the Ca^{2+} ion and the two differently oriented CO_3^{2-} ions can be distinguished. The second cell is obtained when the two CO_3^{2-} ions are not distinguished. This cell has the edge $\frac{1}{2}[11\bar{1}]$, space group $R\bar{3}m$ (indexing based on the smallest rhombohedral unit cell), and contains 1CaCO_3 . In fact it means a body-centring of the structural unit cell. The third cell is based on the cleavage rhombohedron. Its edge is $\frac{1}{4}[3\bar{1}\bar{1}]$, space group $R\bar{3}m$, and it contains $\frac{1}{2}\text{CaCO}_3$. This cell determines the growth process if the Ca^{2+} and CO_3^{2-} ions can be considered as point charges and therefore as identical. Table 1 shows the form sequences with their frequencies as determined by Palache (1943). The usual form in which calcite crystal-

TABLE 1. CRYSTAL FORMS OF CALCITE WITH THEIR FREQUENCIES OF OCCURRENCE, ARRANGED IN DECREASING ORDER OF d_{hkl}

differently oriented carbonate ions distinguished cell edge [100] hkl freq. h.k.l (morph.)		differently oriented carbonate ions not distinguished cell edge $\frac{1}{2}[11\bar{1}]$ hkl freq. h.k.l (morph.)		calcium and carbonate ions considered as point charges cell edge $\frac{1}{2}[3\bar{1}\bar{1}]$ hkl freq. h.k.l (morph.)	
110	xx 02 $\bar{2}$ 1	110	xx 02 $\bar{2}$ 1	211	xx 10 $\bar{1}$ 1
211	xx 10 $\bar{1}$ 1	211	xx 10 $\bar{1}$ 1	10 $\bar{1}$	xx 11 $\bar{2}$ 0
222	xx 000 $\bar{1}$	222	xx 000 $\bar{1}$	220	xx 02 $\bar{2}$ 1
101	xx 11 $\bar{2}$ 0	101	xx 11 $\bar{2}$ 0	332	xx 01 $\bar{1}$ 2
210	x 4483	200	xx 4041	310	xx 2131
200	xx 4041	(220)		(422)	
(20)		332	xx 01 $\bar{1}$ 2	21 $\bar{1}$	xx 10 $\bar{1}$ 0
332	xx 01 $\bar{1}$ 2	321	x 22 $\bar{2}$ 3	444	xx 000 $\bar{1}$
321	x 2243	211	x 2461	431	4 1232
20 $\bar{1}$	8 8.4.1 $\bar{2}$.1	433	0 20 $\bar{2}$ 5	(20 $\bar{2}$)	
211	x 2461	310	xx 2131	543	x 11 $\bar{2}$ 3
433	0 20 $\bar{2}$ 5	(422)		32 $\bar{1}$	xx 1341
310	xx 2131	21 $\bar{1}$	xx 10 $\bar{1}$ 0	400	xx 4041
(422)		(444)		521	x 3142
432	0 4489	442	x 04 $\bar{4}$ 5	655	4 10 $\bar{1}$ 4
320	xx 4.8.1 $\bar{2}$.5	431	4 12 $\bar{3}$ 2	552	x 01 $\bar{1}$ 1
21 $\bar{1}$	xx 10 $\bar{1}$ 0	411	6 20 $\bar{2}$ 1	41 $\bar{1}$	xx 32 $\bar{5}$ 1
		(330)			
		(20 $\bar{2}$)			
		543	x 11 $\bar{2}$ 3		
1 = 2n	for hhl	h + k + l = 2n		h + k + l = 4n	

xx very common forms, recorded from more than 25 localities
 x common forms, recorded from 10 to 25 localities

lizes from aqueous solutions under low supersaturation is the cleavage rhombohedron {211}, which ranks first in the third column. Here Ca^{2+} and CO_3^{2-} behave largely as point charges. When, under high supersaturation or in the presence of impurities they can be distinguished, the main form should be the steep rhombohedron {110}. Indeed, Kirov *et al.* (1972) found that calcite crystallizes in steep rhombohedra {110} when growth takes place from a solution containing an excess of Ca^{2+} ions, whereas with an excess of CO_3^{2-} ions the basal plane {111} predominates. At high supersaturations and without one of the ions being in excess, the rhombohedron {100} becomes dominant. Kirov *et al.* correctly point out that a combination of {110} and {111} of calcite correspond to {111} of NaCl and that these forms might be expected when one of the ions is present in excess. In that case the kinetics are governed by the incorporation of the ions present in low concentration. Comparison of the first and second columns reveals that the exact orientation of the CO_3^{2-} ion does not have a large effect. Among the 15 forms listed the first column has 9 very common forms, of which 4 are at the beginning of the list. For the second column these numbers are 8(6), for the third 10(7), which stresses again the importance of the sublattice.

THE EXTENDED DONNAY-HARKER LAW

Donnay & Donnay (1961) discussed this

extension by referring to the columbite structure. Hartman (1968a) has shown that the SnI_4 structure is a quantitative example of this extension. He showed that two consecutive planes (100), a distance d_{400} apart, both cut the same number of I-I contacts, although the relative orientation of the molecules at both cuts is entirely different one from the other. As the surface energy can be quantified by counting the number of cut I-I contacts, its repeat period is indeed d_{400} .

The naphthalene structure was considered by Hartman & Perdok (1956) as an exception to the Donnay-Harker law, which predicts the sequences: {001}, {111}, {011}, {110}, {20 $\bar{1}$ }, ... Of these forms {011} has never been observed. The structure, in space group $P2_1/a$, consists of two molecules per unit cell with their centres at the positions of two centres of symmetry, namely (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0). A fact not noticed by Hartman & Perdok (1956) is that each interaction between two molecules at (0, 0, 0) and at ($\frac{1}{2}$ + u , $\frac{1}{2}$ + v , w) also exists between the latter molecule and the one at (1 + 2u, 1 + 2v, 2w). So the bond assemblage in the sense of Donnay & Donnay (1961) is strictly centred, and we have to apply the extra extinctions of a C lattice, which explains the absence of {011}.

Violations of the Donnay-Harker law commonly allow the location of centres of molecules, as was shown by Hartman (1968b) and later more elegantly by Hazell (1971). Moreover, they also can give an indication that the observed habit is the result of a habit change by external factors. Let us recall the well-known fact that fluorite almost always crystallizes in cubes whereas the octahedron is the most important form both from the space group $Fm\bar{3}m$ and from the calculation of attachment energies (Hartman 1974). This indicates that the cubes reflect external factors.

CONCLUSIONS

The law of Donnay-Harker and its extension by Donnay & Donnay can be understood by assuming a low anisotropy of the specific surface energy and by assuming a proportionality between the growth rate of a face and its attachment energy. The lattice to which the law has to be applied need not be the structural lattice but can be a sublattice determined by the crystal-growth process. Application of the Donnay-Harker law to the structural unit cell can give information about coordinates of atoms or centres of molecules, or about the influence of external factors on the morphology.

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