AN INTERPRETATION OF THE LAW OF DONNAY AND HARKER

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ABSTRACT

A physical interpretation of the law of Donnay and Harker is given in terms of bonds between building units in a crystal structure. The following conclusions could be drawn:

(*a*) The law of Donnay and Harker is well obeyed, when the crystal structure is complicated, i.e. when the building units are uniformly distributed throughout the unit cell and occupy several general positions.

When the structure is relatively simple, three conditions must be fulfilled:

(1) The centers of the building units must lie in a general position or in such special positions which do not introduce extra extinctions;
(2) Only one general or special position must be occupied;
(3) The bond energy must decrease with increasing bond length, the latter term being defined as the distance between centers of building units.

(*b*) When these conditions are not fulfilled, a pseudo-lattice may sometimes be found to express the observed morphology better than does the structural lattice. This pseudo-lattice is always determined by the bonds in the structure.

(*c*) It may occur that no lattice or pseudo-lattice can be found to give a sequence of forms in agreement with the observed morphology. This can be traced back to the influence of one or more of the following structural features:

(1) Building units of one kind in special positions;
(2) Like building units in different positions;
(3) Different kinds of building units;
(4) Different kinds of bonds (e.g. strong repulsive energies in ionic structures);
(5) Particularly non-spherical shape of molecules.

(*d*) The relations between morphology and structure are of a more fundamental nature than the relations between morphology and space group. The presented physical interpretation of the law of Donnay and Harker accounts not only for the validity of this law, but also for its exceptions.

INTRODUCTION

The law of Donnay and Harker, which is a generalization of the law of Bravais, states (Donnay and Harker, 1937):

> "The morphological importance of a crystal face is inversely proportional to its reticular area S if the lattice is of the hexahedral mode (no centering) and the space group is devoid of screw axes and glide planes. The effect of lattice centering, screw axes and glide planes is corrected for if the face indices are replaced, in the S formula, by the "multiple indices" of the lowest order of x-ray reflection compatible with the space group symmetry."

This law has been presented as a law of observation; Donnay and Harker gave examples in which the law is obeyed, but showed also that sometimes anomalies do occur, which in some cases can be removed by referring the morphology to a pseudo-lattice.

The present authors have shown (Hartman and Perdok, 1955*a*, *b*) that the consideration of bond energies in the structure gives a better agreement with the observed morphological aspect than do the reticular areas of the lattice. Nevertheless there are many cases of striking agreement between the Donnay-Harker reticular densities and the observed morphological importance, and we have to explain why the geometrical parameters (space group and cell dimensions) of the lattice can rule a physical process like crystal growth to such an extent. We will give here a physical interpretation of the Donnay-Harker law, and show:

(*a*) In which cases we may expect a good agreement,
(*b*) Under which conditions a pseudo-lattice will be found,
(*c*) Why sometimes the Donnay-Harker law is not obeyed at all.

EXTERNAL AND INTERNAL FACTORS

The morphology of a crystal is determined by external and internal factors. External factors are e.g. the influences of solvent and cosolutes. The contribution of these factors may be reduced, when statistical methods are applied which derive one "genotype" from a large number of "phaenotypes" as observed e.g. on a widely spread mineral (Niggli, 1941, p. 450) or on laboratory products under different conditions. Internal factors deal with the structure: its geometry (cell dimensions, symmetry, atomic coordinates) and its physics (type and strength of bonds). The fact that the geometrical law of Donnay and Harker is often obeyed indicates that the factors which rule the morphology converge, so to say, into the lattice. This creates the impression that the lattice rules the morphology and that its influence outweighs the influence of other factors.

PHYSICAL INTERPRETATION OF THE LAW

It follows from the statement of the law that the morphological extinctions correspond with the *x*-ray extinctions for atoms in the general position. For a physical interpretation we have to consider "building units" rather than atoms. These building units are particles that exist already in the disordered phase and therefore they may be ions and molecules as well as atoms. The geometrical position of an ion or molecule is then taken as the center of gravity of the positions of the constituent atoms and it will be referred to as the "center" of the building unit.

Imagine a structure with building units occupying only the equivalent sites of one general position. Suppose further that the energies of the bonds between the building units decrease with increasing bond lengths. According to our theory that face will be the more important one, for which the attachment energy is smaller. The attachment energy is the bond energy released when one building unit is attached to the surface of a crystal face. We consider the F-faces only. The whole structure can be divided into slices parallel to these F-faces. Only the bonds between two neighboring slices contribute to the attachment energy. Evidently the attachment energy is small when:

(*a*) The bonds are weak,
(*b*) There is only one bond per building unit (see Fig. 1).

In case (*b*) the bond is in general nearly perpendicular to the slice, because the chance that the building unit is attached to the slice with a second bond increases when the first bond deviates more and more from the direction of the normal to the slice.

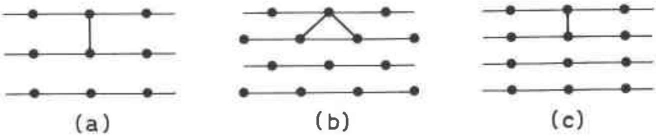

FIG. 1. The effect of bond length and number of bonds per building unit on the distance between slices. Dots represent centers of building units. Only bonds going from one building unit of the upper slice to the next slice are shown. (*a*) One relatively long bond is (nearly) perpendicular to the slices. (*b*) One building unit is attached with two bonds to a lower slice. (*c*) One building unit is attached with one shorter bond to a lower slice.

The attachment energy can increase in two ways:

(1) The bonds become stronger,
(2) There are more bonds per building unit.

In both cases the distance between the slices decreases (Fig. 1). In case (1) because a stronger bond corresponds to a shorter bond length and in case (2) because the bonds can no longer be perpendicular to the slice.

Hence it can be concluded that a face is the more important, the larger the distance between the slices (as this corresponds to a lower attachment energy) and therefore the greater $d_{(hkl)}$.

It may be emphasized that this statement holds for any space group, because we consider the real reticular areas of a structure with building units in the general position. The S-formula used by Donnay and Harker gives reticular areas in a primitive lattice. The procedure of multiplying the indices in the S-formula is essentially to find real reticular areas, by taking into account the effect of lattice centerings and of symmetry operations that have a translation component.

For a physical interpretation of the law the following conditions must be fulfilled:

(1) The centers of the building units must lie in a general position or in such special positions which do not introduce extra extinctions;
(2) Only one general or special position must be occupied;
(3) The bond energy must decrease with increasing bond length, the latter term being defined as the distance between centers of building units.

We may expect that under these conditions the law of Donnay and Harker will hold. In the following lines we shall discuss cases where these conditions are not fulfilled.

EXAMPLES OF EXCEPTIONS TO THE LAW

(1) The first condition is not fulfilled when building units are situated in special positions that introduce extra extinctions in addition to those of the general position.

An example is provided by the *naphthalene* structure, first discussed by Wells (1946). In the morphological setting the space group symbol is $P2_1/a$ (with the b-axis along the twofold axis). The dimensions of the cell are: $a=8.23$ Å, $b=6.00$ Å, $c=8.66$ Å, and $\beta=122°55'$. The crystals are plates $\{001\}$, bounded by $\{110\}$ and $\{20\bar{1}\}$. The latter two forms are of about equal importance; sometimes $\{\bar{1}11\}$ appears. The law of Donnay and Harker gives the sequence:

$$\{001\},\ \{\bar{1}11\},\ \{011\},\ \{110\},\ \{20\bar{1}\},\ \cdots$$

In this case the law is not well obeyed: in the third place it gives $\{011\}$, a form never observed. Now the centers of the molecules lie in (000), which special position introduces in the space group $P2_1/a$ the condition that $h+k=2n$ for (hkl). Therefore (011) should be (022), so that it does no longer appear among the most important forms. The extinction condition $h+k=2n$ for (hkl) indicates a pseudo-centering of (001); consequently the structure should have a pseudo-lattice $C2/m$. This is indeed the case. The forms $\{110\}$ and $\{20\bar{1}\}$ do not, however, appear in the second and third rank.

Still worse is the agreement in the case of *p-benzoquinone* (Wells, 1946), which substance exhibits the same morphology as naphthalene. The cell dimensions are: $a=7.03$ Å, $b=6.79$ Å, $c=5.77$ Å and $\beta=101.0°$. Here the Donnay-Harker sequence (referred to the pseudo-lattice $C2/m$) is:

$$\{001\},\ \{110\},\ \{\bar{1}11\},\ \{111\},\ \{200\},\ \{020\},\ \{20\bar{1}\},\ \cdots$$

Here $\{20\bar{1}\}$ ranks 7th instead of 3rd. Attention may be called to the fact that only the coordinates of the *centers* of the molecules are considered and not those of the atoms, because only complete molecules are the building units of the structure. In this connection, it may be remarked that (contrary to the views of Wells (1946) a physical interpretation of the law does not require coplanarity of atoms.

The morphology of naphthalene can be related to its structure by applying the concept of periodic bond chains.* A schematic picture of the naphthalene type of structure is drawn in Figs. 2 and 3.† The bonds between the molecules are of the Van der Waals type. Because the bond energy decreases rapidly with increasing distance, only nearest neighbor interaction has to be considered. Four bonds can be found and because of the special positions of the molecules, every P.B.C. vector corresponds with only one bond (Table 1).

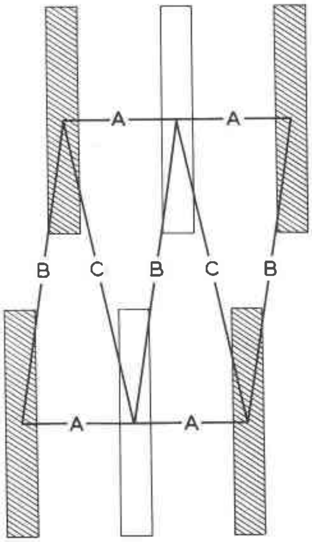

FIG. 2. Schematic picture of the naphthalene type of structure projected on (010). Molecules are represented by rectangles, the centers of the shaded ones being at heights 0 and 1, the others at height $\frac{1}{2}$. The heavy lines indicated by letters represent *P.B.C.* vectors. Note that there is no *P.B.C.* vector in the direction $[\bar{\tfrac{1}{2}}\tfrac{1}{2}1]$.

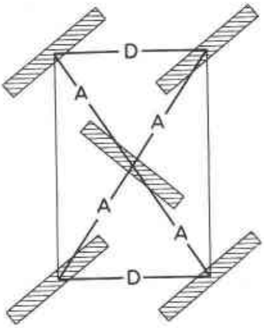

FIG. 3. Schematic picture of the naphthalene type of structure projected parallel to [001]. For significance of rectangles, lines and letters see Fig. 2.

The four P.B.C. vectors define the *F*-forms:‡ {001}, {110}, $\{20\bar{1}\}$, $\{\bar{1}11\}$ and {100}. The relative importance of these *F*-forms is deter-

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* The treatment in Hartman, 1953, does not consider the attachment energy.

† In order to show the bonds more clearly, the molecules in Figs. 2, 3, and 5 are not drawn on the same scale, nor do the dimensions of the unit cell refer to any particular substance.

‡ An *F*-form has faces containing at least two P.B.C. vectors.

TABLE 1. P.B.C. VECTORS IN THE STRUCTURE OF NAPHTHALENE

P.B.C. vector	Between molecules the centers of which lie in:	Energy
A $[\frac{1}{2}\frac{1}{2}0]$	$(000)-(\frac{1}{2}\frac{1}{2}0)$	a
B $[001]$	$(000)-(001)$	b
C $[\frac{1}{2}\frac{1}{2}1]$	$(000)-(\frac{1}{2}\frac{1}{2}1)$	c
D $[010]$	$(000)-(010)$	d

mined by the attachment energies. A Van der Waals bond between two molecules is the stronger, the more numerous are the places of contact. From the structure it follows that these places of contact between two molecules forming bond a and d are more numerous than those between the molecules forming bond b and c. Therefore the former bonds are the stronger ones. Table 2 gives the attachment energies. If we assume that $a=d$ and $b=c$, then the most important form is $\{001\}$. Next come $\{110\}$ and $\{20\bar{1}\}$, which are about equally important, and then $\{\bar{1}11\}$ and $\{100\}$ follow. This result is in good agreement with the observed morphology, mentioned at the beginning of this section. The same morphology can be deduced for substances having a similar structure (e.g., anthracene, diphenyl, p-benzoquinone, pyrene, durene; cf. Hartman, 1953).

(2) There are two cases in which the second condition is not fulfilled.

(*a*) The building units are all alike, but they occupy more than one position.

An example can be found in the structure of *dibiphenylene-ethylene* (Fenimore, 1948). The space group is *Pcan* and the dimensions of the unit cell are: $a=17.22$ Å, $b=36.9$ Å and $c=8.23$ Å. The molecules are nearly planar; they are parallel to the a-axis and make an angle of about $35\frac{1}{2}°$ with the face (001). The centers of the molecules lie in (000) and in $(\frac{1}{2}, \frac{1}{6}, 0.434)$, so that there are twelve molecules per unit cell. In the direction of the c-axis, the molecules lie close together with their planes approximately parallel. Hence the Van der Waals bond in the direction of the c-axis is very much stronger than in other directions, so that the

TABLE 2. ATTACHMENT ENERGIES OF THE F-FORMS OF NAPHTHALENE

F-form	Attachment energy
$\{001\}$	$b+2c$
$\{110\}$	$a+c+d$
$\{20\bar{1}\}$	$2a+b$
$\{\bar{1}11\}$	$a+b+c+d$
$\{100\}$	$2a+2c$

substance must crystallize in needles parallel to the *c*-axis, which was in fact observed by Fenimore. The needles were bounded by {130} dominant and {100} small. Figure 4 gives a projection of the structure on (001). Each pile of molecules in the direction of the *c*-axis is represented by a small circle. It can be seen from this projection that the strongest periodic bond chains run in the directions ⟨310⟩ and ⟨010⟩, which fact accounts for the development of the forms {130} and {100}.

The sequence of the law of Donnay and Harker is:

{020}, {110}, {130}, {200}, {111}, {121}, · · ·

Donnay and Fenimore (1948) pointed out that the structure consists of (001)-centered pseudo-cells with a *b*-axis equal to one third of the structural period. For this pseudo-cell the order given by the law of Donnay and Harker is:

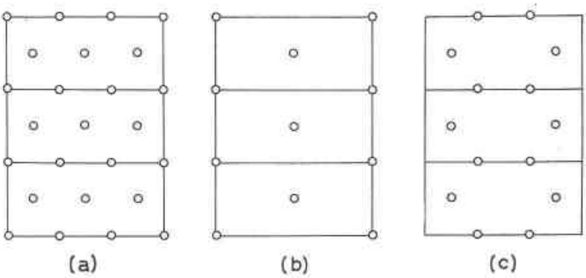

FIG. 4. Projection of the structure of dibiphenylene ethylene on (001). Only the centers of the molecules are shown. Each figure represents three unit cells. *(a)* complete structure; *(b)* molecules in special position; *(c)* molecules in general position.

{130}, {200}, · · ·

Thus we see that the acceptance of a pseudo-cell is necessary in order to have the law of Donnay and Harker obeyed, just because of the interaction of two crystallographically different kinds of molecules. *It may be emphasized that the shape of the pseudo-cell is determined by the bonds between the molecules.*

(*b*) There is more than one kind of building units.

A beautiful example of the difficulties which can arise here, has been discussed by Wells (1946), namely *cuprite* Cu_2O. The Cu atoms form an *F*-lattice, the O atoms an *I*-lattice, while the space group is *Pn*3*m*.

The sequences considered by Wells (1946) are:

space group *Pn*3*m*:	{011}, {111}, {001}, {112}, {122}, · · ·
Cu atoms only	{111}, {001}, {011}, {113}, {133}, · · ·
O atoms only	{011}, {001}, {112}, {013}, {111}, · · ·

The most important form is the octahedron (Kleber & Schroeder, 1935); the theoretical order derived from attachment energies (Hartman & Perdok, 1955*d*): {111}, {011}, {001}, correctly expresses this fact.

Another example is *chalcopyrite*, discussed by Garrido (1949). The S atoms are situated in position (*d*) $(x, \frac{1}{4}, \frac{1}{8})$ with $x=\frac{1}{4}$. This special position introduces additional extinctions, namely: $h+k+l=2n$ and $2k+l=4n$ for (hkl); $k=2n$ and $l=2n$ for $(0kl)$; $h=2n$ and $k=2n$ for $(hk0)$. The sequence obtained when only S atoms are considered is even somewhat better than the sequence given by the pseudosymmetry $F\bar{4}3m$ (Table 3).

TABLE 3. ORDER OF IMPORTANCE OF FORMS OF CHALCOPYRITE ACCORDING TO THE LAW OF DONNAY AND HARKER AND ACCORDING TO TWO MODIFICATIONS. THE COEFFICIENTS INDICATING THE IMPORTANCE HAVE BEEN TAKEN FROM GARRIDO (1949)

Space group $I\bar{4}3d$		Pseudosymmetry $F\bar{4}3m$		Considering S atoms only	
order	imp.	order	imp.	order	imp.
{011}	6	{112}	7	{112}	7
{112}	7	{010}	4	{010}	4
{013}	4	{001}	6	{001}	6
{010}	4	{110}	5	{011}	6
{001}	6	{012}	5	{110}	5
{121}		{132}		{012}	5
{123}		{116}	3	{132}	
{015}		{332}		{116}	3
{110}	5	{136}		{013}	4
{012}	5	{120}			
		{011}	6		

The cause of this peculiarity can be found when the periodic bond chains are considered. The strongest bonds in chalcopyrite are those between the S atoms and the nearest metal atoms. There are two kinds of periodic bond chains, namely in the directions ⟨110⟩ and ⟨201⟩, consequently the dominant form is {112}. In these chains a sulfur atom is bound to a nearest sulfur atom through a metal atom, so that the structure can be considered to consist of sulfur-sulfur "pseudo-bonds." The law of Donnay and Harker is therefore best obeyed when only S atoms are considered.

(3) (*a*) In ionic structures a smaller distance does not always correspond to a stronger bond.

An example can be found in the development of the zone [001] of *barite* (Hartman & Perdok, 1955*c*).

The observed order of importance is:

(210), (200), (020), (220), (410), · · ·

The law of Donnay and Harker gives the sequence:

(200), (210), (020), (220), (410), · · ·

The anomaly of the first two forms can be understood when the periodic bond chains are considered. In the direction [120] lies a chain the period of which is [$\frac{1}{2}$10]; the chain in the direction of the *b*-axis has the shorter period [010]. The potential energy of an ion in the former chain is higher than that in the latter chain, although its period is longer. This is caused by the fact that the chain in the direction [120] is relatively straight, whereas the other chain is of the zigzag type, so that the repulsion between ions of like charges is greater.

(*b*) The third condition can also be violated when the shape of the molecules differs considerably from that of a sphere. An example is *p-diphenylbenzene,* which has a structure similar to that of naphthalene. The cell dimensions are: $a = 8.08$ Å, $b = 5.60$ Å, $c = 13.59$ Å and $\beta = 91°55'$. This compound crystallizes in tablets {001}, {110}, on which the form {201} has sometimes been observed. In contradistinction to the morphology of naphthalene, the form {20$\bar{1}$} never appears. This is caused by the fact that the longest dimension of the molecules lies in the acute angle β (Fig. 5), while in naphthalene it is found in the obtuse angle β.

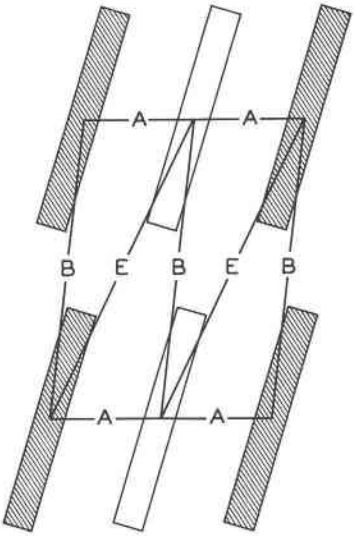

FIG. 5. Schematic picture of the p-diphenylbenzene type of structure, in which the molecules slope backward in the acute angle β. Projection on (010). For significance of rectangles, lines and letters see Fig. 2. Note that in this case there is a *P.B.C.* vector $E[\bar{\frac{1}{2}}\frac{1}{2}1]$ instead of $C[\frac{1}{2}\frac{1}{2}1]$.

The result is that $[\bar{\frac{1}{2}}\frac{1}{2}1]$ becomes a *P.B.C.* vector instead of $[\frac{1}{2}\frac{1}{2}1]$, although it is the longer of the two. Hence the form $\{201\}$ is an *F*-form, whereas the form $\{20\bar{1}\}$ is an *S*-form and therefore unimportant. The sequence given by the law of Donnay and Harker is:

$$(001),\ (011),\ (110),\ (\bar{1}11),\ (111),\ (012),\ (200),\ (20\bar{1}),\ (\bar{1}12),\ (201),\ (112),\ \cdots$$

The rank of the observed form $\{201\}$ is 10; it should be 3.

COMPLICATED STRUCTURES

The crystals that do not obey the law of Donnay and Harker usually have relatively simple structures. For crystals with complicated structures, one may expect the law of Donnay and Harker to be generally followed, although this seems to be in contradiction with the second condition. In such crystal structures several general positions are occupied by building units and if the structure is not fibrous or micaceous, the building units are about "uniformly" distributed in the unit cell. All building units are surrounded by a number of shorter and longer bonds. The longer bonds will, on the average, point more or less into the directions of the normals to the planes with the larger lattice spacings d_{hkl}. The shorter bonds are, on the average, more or less parallel to these planes. Because in general the bond strength is a decreasing function of the bond length, the longer bonds will be at the same time the weaker bonds, so that the attachment energies will be smaller for planes with greater d_{hkl} values, which are therefore the more important ones.

SPACE GROUP DETERMINATIONS

Donnay and collaborators have used the morphological extinctions for space group determinations (Donnay, 1946). It may be inferred from the above considerations that often a lattice can be found in agreement with the law. This lattice, however, is not necessarily identical with the structural lattice. In the case of naphthalene the morphological aspect leads to the space group $C2/m$, which in reality is the symmetry of the pseudo-lattice inherent in the structure. The symmetry of the structural lattice is obscured by the special position of the molecules. For a pseudo-lattice to be detected by suitable application of the law, coplanarity of atoms or centers of building units is not required (see dibiphenylene-ethylene). Morphological extinctions do not entirely correspond with x-ray extinctions. This is an advantage for the application of the law of Donnay and Harker in the first stages of a structure determination (Donnay and Fenimore, 1948), but at the same time it puts a limitation on the method. An advantage, because it can give information as to whether the structure possesses a pseudo-lattice. A limitation, because one is never certain whether a certain morphological extinction is caused by a symmetry element or by a building unit in a special position, until the morphological results are compared with the x-ray results.

CONCLUSIONS

It has been shown (Hartman and Perdok, 1955*a*) that for each structure a set of periodic bond chains gives the clue to the morphology. When this set of periodic bond chains is the same as the set that can be derived from a hypothetical structure with building units in the sites of one general position in the same unit cell, then the law of Donnay and Harker correctly expresses the morphology.

When a pseudo-lattice expresses the law better than does the structural lattice, this pseudo-lattice is determined by the set of periodic bond chains. These chains run in the directions of the axes of the pseudo-cell (P-lattice), or the face diagonals (A-, B-, C- or F-lattices), or the body diagonals (I-lattice).

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