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Approximate Location of Centres of Molecules from Morphological and Unit-cell data

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Centres of molecules can sometimes be located approximately from morphology, unit-cell dimensions, number of molecules per unit cell and space group. This is possible when the observed morphology is not in accordance with the morphology predicted from the law of Donnay and Harker applied to the known unit-cell dimensions and space group. Additional information about the centers can be obtained by the periodic-bond-chain method.

Introduction

In the course of a crystal-structure determination any information about particular structural features may be helpful. In this paper it will be shown how sometimes the centres of molecules can be located from the following data: morphology, cleavage, unit-cell dimensions, number of molecules per unit cell and space group.

The method is based on the application of a reversed Donnay-Harker law and of the periodic-bond-chain method. For several molecular compounds approximate coordinates of the centres of molecules are predicted and compared with the coordinates known from crystal structure determinations.

Before entering into the details of the method the use of some terms and symbols will be discussed.

(a) *Centres of molecules*. The crystal structure is considered as a packing of molecules. The proposed method gives essentially some information about the packing, not in detail, but rather the coordination of one molecule by its neighbours. For convenience the molecules are indicated by the coordinates x_m , y_m and z_m of their geometrical centres, because these are most easily computed by giving each atom the same weight. In the examples the hydrogen atoms are ignored.

(b) *Sublattice and pseudolattice*. The method gives idealized coordinates of the centres of molecules. Sometimes the points that occupy these idealized positions have a lattice which differs from the real lattice by having shorter periods, namely submultiples (for instance, by centring a face or by halving an axis). The lattice belonging to the points that occupy the *idealized* positions is called a *sublattice**. The *actual* centres of molecules have a *pseudolattice* with a certain *pseudosymmetry*. In some cases (see example 3) *partial pseudosymmetry* occurs, that is, the particular pseudosymmetry is valid for a certain projection only and not for the three-dimensional structure.

(c) The symbol d_{hkl} stands for the interplanar spacing of planes (hkl), which are not necessarily lattice planes. Whenever h , k and l have a common factor, this arises either from the space group extinction, or from extra extinctions that find their origin in the idealized positions of centres of molecules.

(d) The symbol $[uvw]$ not only indicates a zone axis or a lattice row, but also the length of its period. For example, in a lattice of type C the distance between the points (0,0,0) and ($\frac{1}{2}, \frac{1}{2}, 0$) is indicated by $[\frac{1}{2}\frac{1}{2}0]$ or by $\frac{1}{2}[110]$.

* The relation between a sublattice and a lattice is therefore the same as that between a lattice and a superlattice.

Outline of the method

A. Arguments from the Donnay–Harker law

According to the Donnay–Harker law there can be assigned to each crystalline compound a space lattice and a space group in such a way that the importance of a crystal form $\{hkl\}$ decreases with decreasing interplanar distance d_{hkl} , taking into account space group extinctions (Donnay & Harker, 1937).

The space lattice and space group derived from the morphology need not be the same as those found from X-ray diffraction. This discrepancy will manifest itself quite clearly when we consider the order of decreasing d_{hkl} values for the real structural lattice and space group. When a form $\{hkl\}$ with a large d_{hkl} value is not present on the crystals, whereas other forms with smaller interplanar spacings have indeed been observed, it can be concluded that the morphologically effective interplanar distance of $\{hkl\}$ is a submultiple of d_{hkl} , for instance half that value. In this way the anomaly can be removed by introducing an extra (morphological) extinction. Physically this means that two surfaces, differing in height by $\frac{1}{2}d_{hkl}$, have equal surface energies, or nearly so. If we suppose further that the interaction energy of two molecules decreases with increasing distance between their centres, irrespective of their mutual orientation, then we may also suppose that these centres are repeated at levels a distance $\frac{1}{2}d_{hkl}$ apart. This gives a relation between the coordinates. The distance from a point $P(x, y, z)$ to a lattice plane (hkl) going through the origin is equal to $(hx + ky + lz)d_{hkl}$. When the effective interplanar spacing becomes d_{hkl}/n , two equivalent atoms $A(x_1, y_1, z_1)$ and $B(x_2, y_2, z_2)$ lie in planes a distance d_{hkl}/n apart, so that

$$(x_2 - x_1)h + (y_2 - y_1)k + (z_2 - z_1)l = 1/n. \quad (1)$$

Since A and B are related to each other through symmetry operations, three equations of this type suffice to determine x_1 , y_1 and z_1 .

Several causes may lead to the anomalies obtained when the Donnay–Harker law is applied in reverse direction, that is, from the structure (cell dimensions and space group) towards the morphology:

(1) Growth units (molecules in a molecular structure) may occupy special positions in the space group, thereby introducing extra extinctions as was shown by Hartman & Perdok (1956) for naphthalene.

(2) Fortuitous values of certain coordinates may lead to extra extinction as was shown by Donnay & Donnay (1961*a, b*) for columbite, FeNb_2O_6 . It may be remarked here that these extra extinctions are not necessarily observed as extinctions or as a weakening of X-ray or neutron reflexions. This is due to the fact that differences of orientation of molecules exert little or no influence on the morphology, but much, in general, on the X-ray intensities. Presumably the morphological extinctions will be found as weakening of X-ray reflexions in the following cases:

- (i) The molecules have more or less a spherical shape.
- (ii) The molecules are flat or rod-shaped, but almost parallel to each other.
- (iii) The centre of the molecule is occupied by a heavy atom.

(3) A physical interpretation of the Donnay–Harker law can be formulated in this way, that the strength of a bond between growth units decreases when their distance is larger (Hartman & Perdok, 1956) (see also part *B* of this section). However, when a molecule has an extreme form, very long or very flat, or when it is somewhat elongated, with polar groups liable to hydrogen bond formation at its ends, a shorter distance does not of necessity imply a stronger bond, and thus the Donnay–Harker law may be violated.

(4) The normal habit can be changed by specific solvents or by impurities. For organic molecules Lindenberg (1956) found that the solvent effect is noticeable when the molecules from crystal and solvent have some common active groups.

When we can exclude the two last-named causes, it is seen that the two first-named may give us information about fortuitous values of the coordinates of molecule centres.

B. Arguments from the periodic-bond-chain method

The application of the periodic bond chain theory of crystal morphology (Hartman & Perdok, 1955; Hartman, 1963) may furnish more restrictions on the coordinates, or give information about the relative strengths of bonds.

According to this theory the morphology of a crystal is determined by a set of periodic bond chains (*PBC*'s) running through the crystal structure. The crystal faces are divided into three categories by considering the number of *PBC*'s contained in a layer of thickness d_{hkl} (taking into account all extinctions arising from the space group and the fortuitous positions of the crystallizing units). When this layer contains no *PBC* the face is called a *K face*; when it contains one *PBC* only, the face is called an *S face* and when it contains two or more *PBC*'s the face is called an *F face* and the layer d_{hkl} is called a *slice*.

The *F faces* are the most important ones. They grow slice after slice by two-dimensional nucleation or by a screw dislocation mechanism. The *S* and *K faces* are unimportant. In nearly all cases the observed faces should be *F faces*. Within the category of the *F faces* the importance increases with increasing bonding energy per molecule in a slice. If we assume that the interaction energy between two molecules in the crystal is larger when the distance between their centres is smaller, we find that in general an *F face* is the more important the denser the packing in the slice, and thus the larger the thickness d_{hkl} of the slice.

C. Information about the centres of molecules

From the unit-cell dimensions and space group a list of (hkl) planes with decreasing d_{hkl} values is derived.

The observed forms are marked with an asterisk. Then the extra extinctions are considered and from the number of molecules per unit cell possible coordinates for the molecule centres are calculated by applying equation (1). Whenever a choice remains to be made, possible *PBC*'s are sought that correspond to the observed morphology. With the aid of these *PBC*'s the molecules are further located if possible.

Finally, when all three coordinates are found the *F* character of the observed faces is checked. In some examples of various complexity it will be shown what results can be obtained.

Examples

(1) *p*-Chloroaniline

The data are: $a=8.665$, $b=7.397$, $c=9.281$ Å; space group *Pnma*; $Z=4$; only $\{111\}$ observed (Palm, 1966).

The list of decreasing d_{hkl} runs:

101, 011, *111, 002, 200, 102, 201, 210, 020, ...

Since $Z=4$, the molecules must lie in the symmetry plane, so $y_m = \frac{1}{4}$. From this list we conclude that the interplanar distances of (101) and (011) are d_{202} and

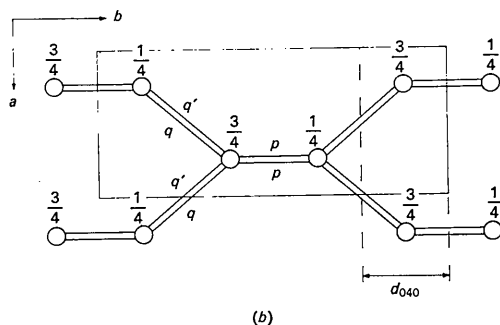
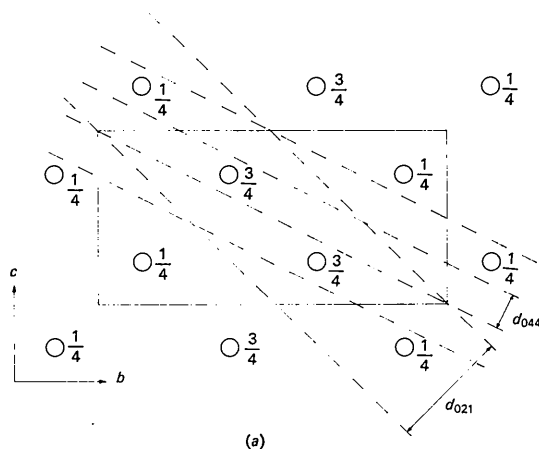


Fig. 1. (a) Centres of papaine molecules projected along $[100]$. In this zone the most prominent face is (021), a slice of which is shown. The interplanar distance of (011) is d_{044} . (b) Here the projection is along $[001]$. Each molecule is surrounded by six other molecules forming two bonds *p*, two bonds *q* and two bonds *q'*. Molecules within a layer d_{040} are not linked together by these bonds.

d_{022} respectively. Equivalent points are at $(x, \frac{1}{4}, z)$ and $(x + \frac{1}{2}, \frac{1}{4}, \frac{1}{2} - z)$, and therefore application of equation (1) to the halving of d_{011} leads to:

$$\frac{1}{2} - 2z_m = \frac{1}{2}, \quad \text{whence } z_m = 0.$$

From the equivalent points $(x, \frac{1}{4}, z)$ and $(1 - x, \frac{3}{4}, 1 - z)$ the halving of d_{101} leads to:

$$(1 - 2x_m) + (1 - 2z_m) = \frac{1}{2},$$

whence $x_m + z_m = \frac{3}{4}$, and $x_m = \frac{3}{4}$. Therefore the centres of the molecules should be at $(\frac{3}{4}, \frac{1}{4}, 0)$.

From the crystal structure determination the average of the positions of the C, N and Cl atoms is: $x_m = 0.7499$ and $z_m = 0.9932$, which agrees well with the predictions. It may be noticed that the position $(\frac{3}{4}, \frac{1}{4}, 0)$ in this space group, taken by itself, forms a face-centred sublattice, which explains immediately the occurrence of $\{111\}$ as principal form.

(2) α -(NSOCl)₃

The data are: $a=7.552$, $b=11.540$, $c=10.078$ Å; space group *Pnma*; $Z=4$; tabular $\{010\}$ with $\{101\}$ or prismatic $\parallel b$ axis (Wiegers, 1963; Hazell, Wiegers & Vos, 1966).

Since $Z=4$ the molecule probably has a symmetry plane of its own, and thus $y_m = \frac{1}{4}$.

The list of decreasing d_{hkl} runs:

011, *101, *020, 111, 002, ...

As the interplanar distance of (011) is halved, we find, just as in the foregoing example, that $z_m = 0$.

The forms $\{101\}$ and $\{010\}$ suggest that the main periodic bond chains have the directions $\langle 101 \rangle$ and $\langle 010 \rangle$. The former is produced by the glide plane (001) which brings $(x, \frac{1}{4}, 0)$ to $(x + \frac{1}{2}, \frac{1}{4}, \frac{1}{2})$. The *PBC* $[010]$ is strongest when the molecules at $(x, \frac{1}{4}, 0)$ and $(-x, \frac{3}{4}, 0)$ are as close together as possible, which gives $x_m = 0$.

The centres calculated from the crystal structure analysis are at $x_m = -0.0747$ and $z_m = -0.0647$. The position $(0, \frac{1}{4}, 0)$ taken by itself forms a *B*-face-centred sublattice.

(3) Papaine

The data are: $a=45.0$, $b=104.3$, $c=50.8$ Å; space group $P2_12_12_1$; $Z=4$; needles $\{110\}$ terminated by $\{0kl\}$, most probably $\{021\}$ (Drenth & Jansonijs, 1966).

The list of decreasing d_{hkl} runs:

020, 011, *110, *021, 120, 101, 111, 040, ...

The effective interplanar distance of (010) should be d_{040} . The general position is at $y, \frac{1}{2} - y, y + \frac{1}{2}$ and $1 - y$, which gives $y_m = \frac{1}{8}$.

The needle habit indicates that indeed $\{110\}$ is the most important form, so the effective interplanar spacing of (011) must be a submultiple of d_{011} , while the $\{0kl\}$ form is most certainly $\{021\}$.

The suggestion that the effective interplanar distance of (011) should be d_{022} does not lead to acceptable

results. Therefore the arguments of the *PBC* method are considered.

The forms $\{110\}$ and $\{021\}$ can be generated by the *PBC*'s $[001]$ and $\langle 112 \rangle$. The latter *PBC* suggests that the (001) plane is pseudo-centred. This can only be the case when the centres at (x, y, z) and $(1-x, y+\frac{1}{2}, \frac{1}{2}-z)$ have the same z , that is $z_m = \frac{1}{4}$. The submultiple of d_{011} is then d_{044} and slices of (021) are easily discernible in the projection along $[100]$ [Fig. 1(a)]. A further consequence of the pseudocentring of (001) is that also x_m must be equal to $\frac{1}{4}$.

The centres were found to lie at $(0.29, 0.18, 0.22)$ instead of the ideal $(\frac{1}{4}, \frac{1}{8}, \frac{1}{4})$.

It is interesting to note here the partial pseudosymmetry of the packing of the molecules in the projections along $[100]$ and $[010]$. The unit cell is pseudo-face-centred in (001) , which introduces the extra extinction condition $h+k=2n$ for all (hkl) . The $[100]$ projection (Fig. 1) has a pseudo unit cell with $c'=c$ and $b'=\frac{1}{2}b$, with centring. For the pseudocell $k'+l'=2n$ and for the real cell $k+2l=4n$ for all $(0kl)$. This pseudosymmetry is valid for the projection only, and not for the three-dimensional structure. Hence the Donnay-Harker law is violated and the morphology should be interpreted by means of the second extension of the law of Bravais by Donnay & Donnay (1961*a, b*).

The $[010]$ projection has a pseudocell with $c'=\frac{1}{2}c$ and $a'=\frac{1}{2}a$, and thus for the real cell $h=2n$ and $l=2n$ for all $(h0l)$. If we take into account these accidental extinctions, the list of decreasing effective d_{hkl} would be:

$$*110, *021, 111, 040, \dots$$

in agreement with observation.

It will be shown now that the observed morphology is in accordance with the morphology derived from the packing of the molecules. The shortest bonds in the idealized structure are given in Fig. 1(b). Each molecule is surrounded by six others in the form of a three-sided prism, making two bonds p (36.4 \AA), two bonds q (42.8 \AA) and two bonds q' (also 42.8 \AA). The strong *PBC* $[001]$ is formed by bonds p only, while the weaker *PBC* $[112]$ is formed by a succession of bonds $-q-p-q'-p-q-$. Because of the needle habit p must be stronger than q or q' . The *PBC*'s $\langle 112 \rangle$ and $[001]$ not only determine the F faces $\{110\}$ and $\{021\}$, but also $\{201\}$.

However, the position $(\frac{1}{4}, \frac{1}{8}, \frac{1}{4})$ introduces the condition $h+l=2n$ for $h0l$, which leads to a halving of d_{201} . Since a *PBC* $[112]$ contains per period all four molecules, or in other words since there is only one *PBC* $[112]$ per unit cell, a layer d_{402} cannot contain a *PBC*. Hence $\{201\}$ is not an F face, but a K face. The bonds q and q' also form the *PBC*'s $[100]$ and $\langle 101 \rangle$ which, together with the *PBC*'s $[001]$ and $\langle 112 \rangle$ determine in addition $\{010\}$, $\{131\}$, $\{1\bar{3}1\}$, $\{111\}$ and $\{1\bar{1}1\}$ as possible F faces. Figs. 1(a) and (b) show that in a layer d_{040} no *PBC* occurs; hence $\{010\}$ is a K form. A projection along $[\bar{1}01]$ showed that in a layer d_{131} neighbouring *PBC*'s are not bonded, and therefore $\{131\}$

and $\{1\bar{3}1\}$ are S forms. The same projection indicated $\{111\}$ and $\{1\bar{1}1\}$ faces as the only F faces in the zone $\langle 101 \rangle$. Thus the position $(\frac{1}{4}, \frac{1}{8}, \frac{1}{4})$ leads to the F forms $\{110\}$, $\{021\}$, $\{111\}$ and $\{1\bar{1}1\}$ of which the latter two have not been observed.

(4) Ribonuclease, modification I

The data are: $a=44.48$, $b=75.74$, $c=37.71 \text{ \AA}$; space group $P2_12_12_1$; $Z=4$; plates $\{010\}$ with $\{101\}$ and $\{011\}$; excellent cleavage $\{100\}$ (Harker, King, Pignataro, Adelman & Furnas, 1957; King, 1965).

The list of decreasing d_{hkl} runs:

$$110, *020, *011, 120, *101, 111, 021, 121, (*200, 130, \dots$$

An effective interplanar distance d_{220} and d_{240} is suggested from this list. It follows that either $x_m=0, y_m=0$ or $x_m=\frac{1}{4}, y_m=\frac{1}{4}$. We choose the first set, because the other set would lead to the same structural scheme, the difference being the position with respect to the twofold screw axes.

The morphology suggests the following prominent *PBC*'s: $\langle 101 \rangle$ and $\langle 111 \rangle$. The latter will be favoured if the molecules at $(0, 0, z)$, $(\frac{1}{2}, \frac{1}{2}, 1-z)$ and $(1, 1, z+1)$ are strongly bonded. This occurs most probably when the distances are equal, therefore $z_m = \frac{1}{4}$. The centres were found to lie at $(0.00, 0.00, 0.25)$, in good agreement with the derived position. All centres of molecules lie at the nodes of a B -centred pseudolattice with $a'=a$, $b'=\frac{1}{2}b$ and $c'=c$. For this structure the list of decreasing d_{hkl} (indices referred to real cell) runs:

$$*020, *101, 121, (*200, 220, 040, 002, *022, 141, \dots$$

We see that the most prominent forms occur in the first and second places, but $\{011\}$ is too far down the list. This must be due to the fact that bond strengths do not decrease with increasing distance between molecules. Possible bonds are given below, together with the distance between the idealized centres of molecules.

p , with distance $\frac{1}{2}[101]=29.16 \text{ \AA}$	
q ,	$[001]=37.71$
r ,	$\frac{1}{2}[010]=37.87$
s ,	$[100]=44.48$
t ,	$\frac{1}{2}[111]=47.79$

From their lengths, we should expect the bond strength to decrease from p to t .

For explaining the occurrence of $\{010\}$, $\{101\}$ and $\{011\}$ the bonds p , s and t are sufficient and therefore

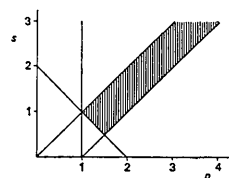


Fig. 2. Inequalities of energies of bonds p and s between ribonuclease molecules when the energy of bond t is arbitrarily put equal to 1. Possible energies occur in the grey region.

q and r are probably very weak. The corresponding PBC 's $\langle 101 \rangle$, $[100]$ and $\langle 111 \rangle$ define the following F faces: $\{010\}$, $\{101\}$, $\{121\}$, $\{1\bar{2}1\}$ and $\{011\}$.

The energy per molecule within a slice d_{hkl} is:

$$\begin{aligned} &\text{for } d_{020}: 2p + s \\ &\text{for } d_{101}: p + 2t \\ &\text{for } d_{121}: p + t \\ &\text{for } d_{022}: s + 2t. \end{aligned}$$

If we suppose that this energy is a measure of the importance of a face, we obtain:

$$\begin{aligned} \{010\} &> \{101\}, \text{ whence } p + s > 2t \\ \{010\} &> \{011\}, \text{ whence } p > t \\ \{101\} &> \{011\}, \text{ whence } p > s \\ \{011\} &> \{121\}, \text{ whence } s + t > p. \end{aligned}$$

The solution of these inequalities is given in Fig. 2, where the shaded area gives the possible values of p and s , when $t = 1$.

From the morphology we are led to the conclusion that the bond p is the strongest one, followed by s and t (where s is probably the stronger one), while q and r are very weak.

(5) Ribonuclease, modification II

The data are: $a = 30.28$, $b = 38.39$, $c = 53.16$ Å and $\beta = 105.83^\circ$; space group $P2_1$; $Z = 2$; tabular $\{100\}$, with $\{011\}$, $\{0\bar{1}1\}$ and $\{001\}$ (Harker *et al.*, 1957; King, 1965).

The list of decreasing d_{hkl} runs:

$$*001, *011, *100, 10\bar{1}, 002, 110, \dots$$

Although the observed forms appear ahead in the list, there is one discrepancy: the crystals are tabular on $\{100\}$ instead of $\{001\}$. This suggests that the effective interplanar spacing of (001) should be d_{002} , from which we find $z_m = \frac{1}{4}$. Putting $y_m = 0$, the centres of the molecules are at $(x_m, 0, \frac{1}{4})$ and $(\bar{x}_m, \frac{1}{2}, \frac{3}{4})$.

Little can be said about x_m . In any case x_m cannot be equal to $\frac{1}{4}$, since then the effective interplanar distance of (100) would be d_{200} , which is far too small for the most important form. The anomaly of d_{011} coming before d_{100} in the list of decreasing d_{hkl} cannot be removed, and therefore no further information about x_m can be obtained.

The morphology can be explained by the occurrence of three PBC 's: $[010]$, $\langle 011 \rangle$ and $[100]$, which determine the F faces $\{100\}$, $\{001\}$, $\{011\}$ and $\{0\bar{1}1\}$, all of which have been observed. A further investigation showed that this set of PBC 's is not incompatible with values of x_m between 0 and $\frac{1}{4}$. Hence x_m cannot be restricted any further.

From the crystal structure it was found that $x_m = 0.17$ and $z_m = 0.74$ of which the latter value agrees well with our prediction ($\frac{3}{4}$).

(6) α -Bromoisotutin

The data are: $a = 8.449$, $c = 36.607$ Å; space group $P3_12$; $Z = 6$; only form observed: rhombohedron $\{10\bar{1}1\}$ (Craven, 1964).

The list of decreasing d_{hkl} runs:

$$0003, 10\bar{1}0, *10\bar{1}1, 10\bar{1}2, 10\bar{1}3, 0006, \\ 10\bar{1}4, 10\bar{1}5, 10\bar{1}6, 10\bar{1}7, 11\bar{2}0, \dots$$

The absence of the basal plane suggests that the effective interplanar spacing is d_{0006} , which leads to $z_m = 1/12$ since there are 6 molecules per unit cell. The absence of the prism $\{10\bar{1}0\}$ suggests an interplanar

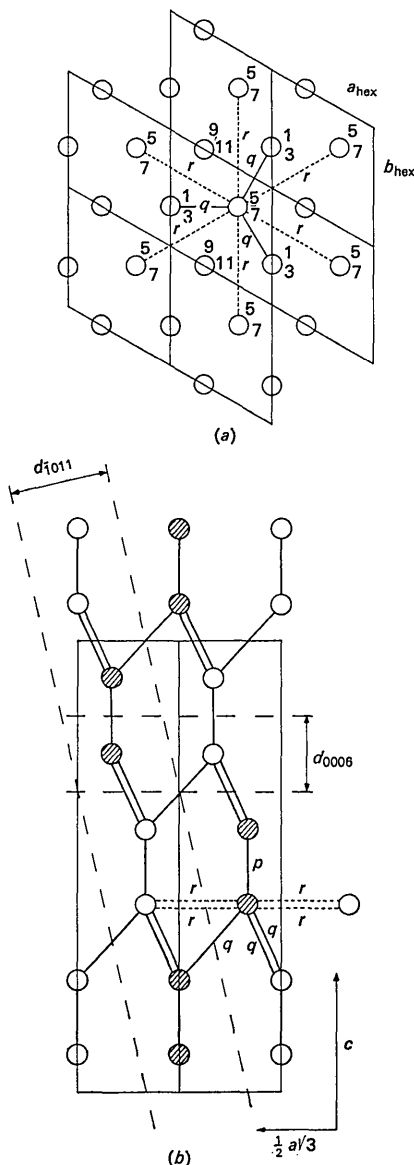


Fig. 3. (a) Centres of α -bromoisotutin molecules projected along the c axis. Heights of the centres are given in twelfth parts of the c axis. The molecule at $5/12$ has a bond p with the molecule that lies vertically above it at $7/12$; it has a bond q with three molecules at $3/12$ and it has a bond r with six molecules at $5/12$. (b) The same centres projected along the b axis. The shaded ones are at height $\frac{1}{2}$, the others at heights 0 and 1. A slice d_{0006} is indicated. The molecules in this slice are bonded by bonds r only. A slice d_{1011} of the rhombohedron is seen to contain bonds p and q only.

spacing of either $d_{20\bar{2}0}$ or $d_{30\bar{3}0}$. Because of the threefold axis we choose $d_{30\bar{3}0}$ as the most probable one.

Positions associated with one threefold axis and lying within the unit cell are (x, y, z) , $(1-y, 1+x-y, z+\frac{1}{3})$, $(y-x, 1-x, z+\frac{2}{3})$. From equation (1) we find:

$$(1-y_m)-(x_m)=\frac{1}{3} \text{ and } (y_m-x_m)-(1-y_m)=\frac{1}{3},$$

from which $x_m=0$ and $y_m=\frac{2}{3}$.

The average of 22 atoms is: $x_m=0.0899$, $y_m=0.6715$ and $z_m=0.07611$, whereas the predicted values are: $x_m=0$, $y_m=0.6667$ and $z_m=0.08333$.

The idealized position $(0, \frac{2}{3}, 1/12)$ and its equivalents form a rhombohedral sublattice with $a_{rh}=(\frac{1}{3})[1\bar{1}01]=13.141 \text{ \AA}$ and $\alpha_{rh}=37^\circ 30'$. Each molecule is surrounded by ten molecules (see Fig. 3), one at a distance 6.101 \AA (bond p), three at a distance 7.811 \AA (bond q) and six at a distance 8.449 \AA (bond r).

These last six bonds occur in a slice d_{0006} . However, the form $\{0001\}$ has not been observed and therefore the bonds r will be weak, so we are left with one bond p and three bonds q for each molecule. One bond p and one bond q constitute together a *PBC*, the period of which is equal to the edge of the rhombohedral subcell. The rhombohedron determined by these bonds is $\{\bar{1}011\}$ and not $\{10\bar{1}1\}$ as described by Craven (1964). A slice d_{1011} is shown in Fig. 3(b).

It may be remarked that the molecular packing can be considered as a distorted diamond or arsenolite structure.

Conclusion

The foregoing examples show that sometimes the observed morphology is not in accordance with the morphology predicted from cell dimensions and space

group by a reversed application of the law of Donnay and Harker. In these cases it is possible to locate approximately the centres of molecules.

Further information on the position of these centres can be obtained by applying the *PBC* method. It gives information either about one or two of the coordinates of the centres, or about bond strengths, and it further corroborates the location of the centre.

In this way such structural features as complete or partial pseudosymmetry are easily revealed. This may be a useful clue in arriving at a trial model of the structure in the early stages of a structure analysis.

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Diffraction of X-rays by the Faulted Cylindrical Lattice of Chrysotile

I. Numerical Computation of Diffraction Profiles

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The current theory of the diffraction of X-rays by a cylindrical lattice is supplemented, and the influence of some misfit boundaries discussed. The numerical computation of diffraction profiles of some reflexions was carried out, and the influence of the curvature, wall thickness, incompleteness and the presence of several types of misfit boundaries determined.

Introduction

The theoretical aspects of the diffraction of X-rays by a cylindrical lattice of chrysotile were studied very

thoroughly by Jagodzinski & Kunze (1954*a,b,c*) and by Whittaker (1955*a,c*), who derived formulae for the diffracted intensity by the ideal complete cylindrical lattice, and discussed the influence of azimuthal misfits. Kunze (1956*a,b*) derived formulae for the diffracted intensity by the ideal incomplete cylindrical lattice.

The object of this paper is to give a more complete analysis of the form of diffraction profiles, based on

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