Summary

It has been demonstrated that the increase in beam path due to changing refractive indices causes a substantial deviation from classical Bragg conditions at very small angles. The effect becomes more pronounced as the density difference between lamellar types increases and as the relative thickness of the two types approach each other. Below a critical angle θ_c diffraction is replaced by total reflection of the X-ray beam.

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The Approximate Location of Centres of Molecules from Morphological Data

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Hartman has shown how the centres of molecules may sometimes be located when the observed morphology is not that predicted by the Donnay–Harker law and how further information may be obtained by the periodic-bond-chain method. The method outlined here shows how the two methods may be combined, either by using structure-factor charts, or by a series summation analogous to a Fourier summation.

Introduction

Hartman (1968) has shown how it is possible to locate the centres of molecules for crystals which do not obey the Donnay & Harker (1937) law. He has also shown how additional information can be obtained about the centres by the periodic-bond-chain method.

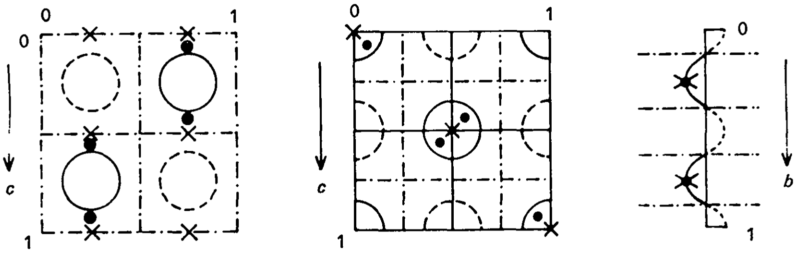
The Donnay–Harker rule for crystal morphology leads to the expectation that the prominence of crystal forms should be in the order of the reticular densities (lattice points per unit area) of the corresponding planes. That is in the order of decreasing d_{hkl}, planes which correspond to space group absences being omitted from the list.

Hartman supposes that if a low order form $\{hkl\}$ is absent this is because the interplanar spacing is d_{hkl}/n where n is probably 2. If the centres of the molecules are at x_1, y_1, z_1, and x_2, y_2, z_2 then

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

If x_1, y_1, z_1, and x_2, y_2, z_2 are related by symmetry it is possible to substitute the expressions for the equivalent positions and to solve equation (1).

One method of solving the equation is to regard the structure as being composed of point atoms at the centroids of the molecules and to use structure factor graphs for the planes corresponding to the absent forms to find the possible positions for the centroids.



011 101 020

Fig. 1. α-$(NSOCl)_3$. Structure factor graphs for 011, 101, and 020. The nodes are shown by alternate dots and dashes. Positions of the centres of the molecules are shown by crosses, the experimental values thus ●.

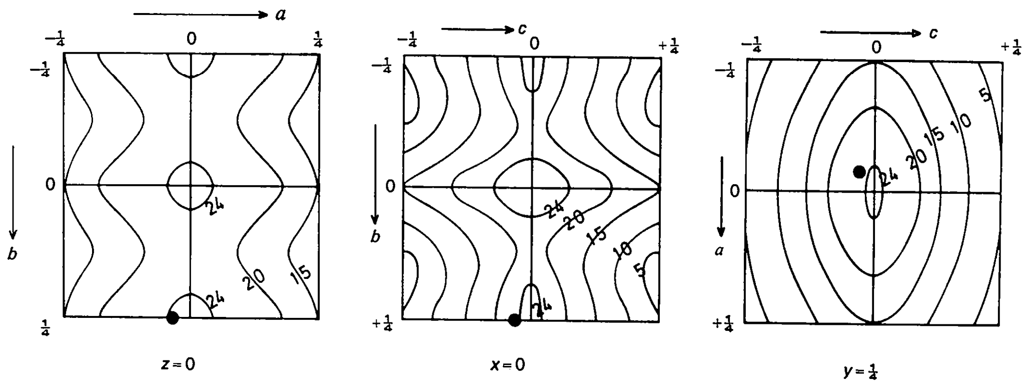


Fig. 2. α-$(NSOCl)_3$. $C(x,y,z)\times 10$, sections are shown for $x=0$, $y=\frac{1}{4}$, and $z=0$. The positions of the centres are shown thus ●.

This procedure may also be used to obtain information from prominent forms. The centroid should lie close to a node if a form is absent and to a maximum or a minimum if a form is prominent.

Example α-(NSOCl)₃

The data are $a=7{\cdot}55$, $b=11{\cdot}54$, $c=10{\cdot}08$ Å; space group *Pnma*; $Z=4$; tabular $\{010\}$ with $\{101\}$ or prismatic parallel to the b axis (Wiegers, 1963; Hazell, Wiegers & Vos, 1966). The possible forms are (listed in order of decreasing d_{hkl}): 011, *101, *020, 111, 002, ...

The forms present are indicated by asterisks. Structure factor graphs for 020, 011, and 101 are shown in Fig. 1. As $Z=4$ and the molecule does not possess a centre of symmetry then the molecule must lie at $y=\frac{1}{4}$. From the 011 graph it is seen that if y is to be $\frac{1}{4}$ and the centre to lie on a node then z must be 0 (or $\frac{1}{2}$). If 101 is to be non-zero then $x=0$ (or $\frac{1}{2}$). The centre therefore is at 0, $\frac{1}{4}$, 0; other solutions *e.g.* $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{2}$ can be obtained but are only the original one with a change of origin.

The values of x, y, z obtained from the crystal-structure determinations are: $x=-0{\cdot}0747$, $y=\frac{1}{4}$, $z=-0{\cdot}0647$.

Summation method

The information from the various forms can be combined by calculating a three-dimensional series analogous to that used for electron density, the maxima of which are to give the possible positions for the centres of the molecules. This we can do by calculating

$$C(xyz)=\sum_h\sum_k\sum_l \{I(hkl)P_1|\exp\{-2\pi i(hx+ky+lz)\}| + P_2(1-|\exp\{-2\pi i(hx+ky+lz)\}|) \quad (2)$$

where $P_1=1$ and $P_2=0$ if a form is present, and $P_1=0$ and $P_2=1$ if a form is absent. $I(hkl)$ may be taken as a constant over the range in which the summation is carried out and zero elsewhere. A better way would be to let $I(hkl)$ represent, in some way, the prominence of a form.

Example α-(NSOCl)₃

The function $C(x,y,z)$ was calculated for α-$(NSOCl)_3$ using the first three forms, giving the three-dimensional map of which the three sections at $x=0$, $y=\frac{1}{4}$, and $z=0$ are drawn in Fig. 2. The symmetry is such that there are mirror planes at $x=\frac{1}{4}$, $y=\frac{1}{4}$, and at $z=\frac{1}{4}$. The ambiguity of choice between 0,0,0 and 0,$\frac{1}{4}$,0 is clearly seen; indeed were it not for the additional information that the molecule could have a mirror plane but not a centre of symmetry one would probably have chosen 0,0,0.

α-$(NSOCl)_3$ was chosen as an example where the orientation of the molecule was easily determined (from a Patterson projection) but where the determination of the positions of the molecules was not so easy by conventional methods.

Conclusion

Useful information concerning the centres of molecules can sometimes be obtained from the morphology. The use of structure factor graphs and Fourier-like series can be used to combine the ideas of the reverse Donnay–Harker law and of the periodic-bond-chain method.

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