Determination of Phases by the Conditions of Non-Crystallographic symmetry

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If a molecule is either repeated more than once within the same crystallographic asymmetric unit, or if more than one crystal form is available, then the phase problem can be reduced to finding the set of unknown phases (α's) which gives the largest value of R in the expression

$$R = \sum_i \sum_j A_{ij} \cos (\alpha_i + \alpha_j + \varphi_{ij})$$

The coefficients A_{ij} and angles φ_{ij} are simple functions of the structure amplitudes and overall dimensions of the molecule relative to a chosen origin. The matrix $[A_{ij}]$ is populated mainly along its diagonal. A general technique for finding the phases from the expression R is given. It is applied to a two-dimensional case where there are two identical five-atom molecules in plane group $p1$.

1. Introduction

Sayre (1952) has given the crystallographic interpretation of a theorem of Shannon (1949), which has been considered from a more general standpoint by Brillouin (1956). The theorem indicates that if the intensities $|F|^2$ could be measured at points corresponding to the reciprocal lattice of the doubled cell, direct structure determination could be accomplished. A situation approaching this arises when two identical molecules (or 'sub-units') are contained in the crystallographic asymmetric unit; and a similar situation arises when the identical structure may be crystallized in two different unit cells. In each case, for the determination of a structure of given volume, the number of observable intensities is doubled.

In an earlier paper (Rossmann & Blow, 1962, referred to as R. & B.) we have described how the relative angular orientations of the sub-units may be determined. We now wish to show how the condition that the sub-units shall have identical structure provides information about the phases. The method will be illustrated by a two-dimensional example in which two sub-units of five atoms exist in a unit cell of plane group $p1$ (Fig. 1).
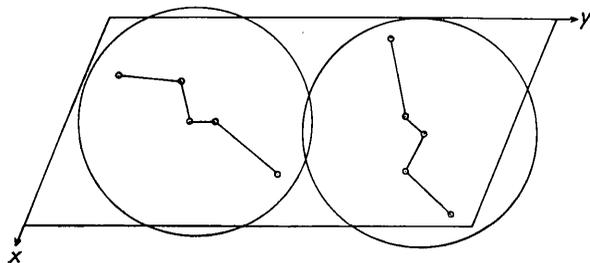
In order to solve this problem, it is necessary to be able to define the operation which, by rotation and translation, brings one sub-unit into coincidence with the other, and to have a rough idea of how the sub-units are arranged in the unit cell. The rotational parameters can be derived by the methods of R. & B. In some cases the translational parameters can then be found by comparing the original and rotated Patterson functions, (this has been done successfully for insulin, unpublished), while, for instance, in plane group $p1$ the translation is trivial, since the origin may be chosen to lie on the rotation axis. Whether the arrangement of sub-units is then uniquely determined will depend on the physical information available about their size and shape. For the purposes of this communication, we shall assume that this problem can be solved.

The 'rotation function' described in R. & B. was applied to a model structure, with the result shown
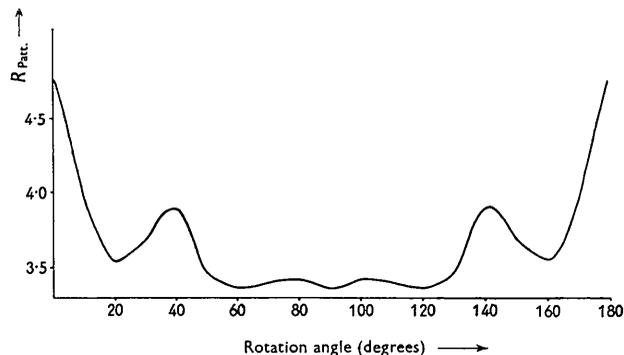

Fig. 2. Rotation function (2 Å resolution), $R_{\mathrm{Patt.}}$, which measures the different overlap of the Patterson with a rotated version of itself. The relative orientation of the two five atom molecules is shown to be $-140°$, $-40°$, $+40°$ or $+140°$. (The calculation was done by Mr D. Davies, to whom we are indebted.)

Fig. 1. Ten atom structure showing two identical five atom molecules contained within the 11 Å radius circles and related by a rotation of $-140°$.

in Fig. 2. The effect of the ambiguity between rotations of $\pm 40°$ and $\pm 140°$ will be discussed later.

The next step is to specify two areas U, U', which are related by the correct rotation and translation parameters, and which contain the two molecules. Their precise shape is of no great importance, and in the model structure circular areas were chosen, as indicated in Fig. 1, which together cover an area $2U = 90\%$ the area V of the unit cell.

2. Equalization of sub-units

We now wish to apply the condition that the electron density at any point within one circle shall equal the electron density at an appropriately related point in the other circle. This condition is to be used to obtain information about the phases.

Let

$$E = \int_U [\varrho(\mathbf{x}) - \varrho(\mathbf{x}')]^2 dx , \tag{1}$$

where

$$\mathbf{x}' = [\mathbf{C}]\mathbf{x} + \mathbf{d} . \tag{2}$$

$\mathbf{x}'$ is the point in U' which is to be identified with $\mathbf{x}$ in U, by the rotation $[\mathbf{C}]$ and the translation $\mathbf{d}$. E will become a minimum, tending to zero, when electron densities of the two sub-units are equalized. Then

$$E = \int_U [\varrho^2(\mathbf{x}) + \varrho^2(\mathbf{x}')] dx - 2 \int_U \varrho(\mathbf{x}) \cdot \varrho'\mathbf{x}') dx . \tag{3}$$

If we make the assumption that *all* the density of the cell lies in either U or U', then the first integral becomes equal to

$$(1/V^2) \sum_h F^2(\mathbf{h}) ,$$

while the second integral has already been defined (in R. & B.) as the 'rotation function' of the electron density. If some density lies outside U and U' the value of the first integral is changed, but it is readily shown (by considering a structure which is identical to the real structure within U, but has no density outside) that the condition for minimizing E is to a good approximation the same as for maximizing the second integral R. We shall now consider the variation of R as a function of the phase angles.

It is shown in R. & B. that if

$$R = \int_U \varrho(\mathbf{x}) \cdot \varrho(\mathbf{x}') dx$$

then

$$R = (U/V^3) \sum_h \sum_p |F_h||F_p|G_{hp}$$
$$\times \cos (\alpha_h + \alpha_p + \Omega_{hp} - 2\pi \mathbf{p} \cdot \mathbf{d}) . \tag{4}$$

In this equation $|F_h|$ and α_h are the magnitude and phase of the structure factor associated with $\mathbf{h}$; $\mathbf{d}$ is the translation vector in equation (2) and G_{hp} and Ω_{hp} are the magnitude and phase of the diffraction

function of the volume U for the reciprocal lattice vector $\mathbf{h} + [\tilde{\mathbf{C}}]\mathbf{p}$:

$$G_{hp} \exp [i\Omega_{hp}] = (V/U) \int_U \exp \{-2\pi i(\mathbf{h} + [\tilde{\mathbf{C}}]\mathbf{p}) \cdot \mathbf{x}\} dx .$$

G_{hp} has large values only if the reciprocal space vector $\mathbf{h}$ is brought close to $-\mathbf{p}$ by the rotation expressed by $[\mathbf{C}]$ in equation (2), and Ω_{hp} is zero if the volume U is centrosymmetric about the origin. The expression (4) has the disadvantage that it is in general not symmetrical about the two variables $\mathbf{h}$ and $\mathbf{p}$; it can be cast into a symmetrical form by writing

$$R = \sum_i \sum_j A_{ij} \cos (\alpha_i + \alpha_j + \phi_{ij}) \tag{5}$$

where

$$A_{ij} \exp [i\phi_{ij}] = (U/2V^3)[|F_i||F_j|G_{ij}$$
$$\times \exp \{i(-2\pi \mathbf{j} \cdot \mathbf{d} + \Omega_{i,j})\}$$
$$+ |F_j||F_i|G_{ji} \exp \{i(-2\pi \mathbf{i} \cdot \mathbf{d} + \Omega_{j,i})\}]$$
$$= A_{ji} \exp [i\phi_{ji}] . \tag{6}$$

The significance of the two contributions in (6), with respect to proper and improper rotations, is discussed in Appendix I.

In order to equalize the sub-units, E must be made zero, which means finding a set of phases α_i which gives R its largest possible value. This clearly implies that for many of the terms with large A_{ij} the angle $(\alpha_i + \alpha_j + \phi_{ij})$ must be close to 0 (or $2n\pi$). Since the ϕ_{ij} can be calculated from the known parameters, each term of the summation thus represents a probable *phase relationship* between α_i and α_j, whose importance depends on the magnitude of A_{ij}. Since R is a maximum,

$$\partial R/\partial \alpha_i = -2 \sum_j A_{ij} \sin (\alpha_i + \alpha_j + \phi_{ij}) = 0 . \tag{7}$$

This condition, satisfied by the same phase relationships, is necessary but not sufficient, since R when plotted as a function of the α's has many maxima, most of which are small.

3. Some properties of the equations (7)

The set of equations (7) may conveniently be thought of as a matrix with elements A_{ij}, each with an attached phase $(\alpha_i + \alpha_j + \phi_{ij})$. Any one equation (7) is represented by one row of the matrix, and by (6) the matrix is symmetrical. This matrix does not have the significance of a matrix in the usual linear algebra; equations (7) are non-linear, and form a set of simultaneous transcendental equations, for which no *direct* method of solution exists. Before describing the approach to solution which has been adopted, we shall consider some features of this matrix.

(i) *Matrix populated along the diagonal*

It is convenient to assign a number i to each structure factor in order of increasing Bragg angle. Associated

with each reflexion i is its reciprocal-lattice vector $\mathbf{s}_i$. A_{ij} can only be large if $\mathbf{s}_i$ and $-\mathbf{s}_j$ (or $\mathbf{s}_j$ and $-\mathbf{s}_i$) are such that one is brought close to the other by the given rotation [C]. Whatever the rotation, this can only happen if the terms have a similar Bragg angle. Thus if the terms are set in order of increasing Bragg angle, all large A_{ij} are near the diagonal of the matrix.

(ii) All phases may be changed by π

One may note that

$$\cos\left[\alpha_i+\alpha_j+\phi_{ij}\right] = \cos\left[(\alpha_i+\pi)+(\alpha_j+\pi)+\phi_{ij}\right],$$

so that if a set of phases α_i satisfies (7) or maximizes (5), the set $(\alpha_i+\pi)$ will do so equally well. The effect on an electron density map of changing all phases by π is to reverse the sign of the electron density. There is one phase, α_0 (for the (000) reflexion), which it is physically unreasonable to reverse. (There is a close analogy to Babinet's principle in Fraunhofer diffraction.) This allows us to distinguish between the two possible sets.

(iii) Terms on the diagonal

In cases of higher symmetry, or with a rotation of 180°, it may happen that a vector $\mathbf{s}_i$ is rotated to $-\mathbf{s}_i$ or to a symmetry-related position. Under these conditions the relevant term in (7),

$$A_{ii}\sin\left(\alpha_i+\alpha_i+\phi_{ii}\right),$$

may dominate in the ith row, indicating the phase relationship $2\alpha_i \simeq 2n\pi-\phi_{ii}$.

If we define α_i by the limits $0 \leq \alpha_i < 2\pi$, then $\alpha_i = (\pi-\frac{1}{2}\phi_{ii})$ or $(2\pi-\frac{1}{2}\phi_{ii})$. We now have, instead of the usual type of phase relationship, an indication of phase, with an ambiguity. This ambiguity will be resolved by the effect of the off-diagonal terms in the row.

(iv) Relationship with the 'shrinkage stage' methods of Bragg & Perutz (1952)

As previously indicated, important phase relationships will only arise when $\mathbf{s}_i$ and $\mathbf{s}_j$ both correspond to a similar Bragg angle. Bragg & Perutz (1952) examined a series of haemoglobin crystals in which the unit cell lengths a, b, and $c\sin\beta$ were scarcely altered, but β varied between 84° and 143°. The corresponding $h0l$ reciprocal-lattice points were all arranged along lines of constant h, but the different shrinkage stages allowed these lines to be sampled at many more points than would be possible with a single-crystal form. By comparing intensities at adjacent points, they were able to determine where the sign of the molecular transform changed, applying the principle that it could not change too rapidly. This is exactly analogous to the procedure by which (5) and (7) indicate phase relationships between points with similar Bragg angles. The chief differences are

(a) that the criterion of equalizing sub-units (1) is more stringent than the 'principle of minimum wave-length' (Bragg and Perutz, 1952);

(b) that by considering a rotation of the three-dimensional reciprocal lattice, phase relationships are generated through the lattice in a more general way.

4. Solution of the phase requirements

It is shown in Appendix II that the ith row of the matrix has a magnitude

$$S_i \equiv \sum_j A_{ij} \cos\left(\alpha_i+\alpha_j+\phi_{ij}\right) = F_i^2/V^2. \tag{8}$$

For convenience, define $\Theta_{ij}=\alpha_i+\alpha_j+\phi_{ij}$. If it is assumed that the angles Θ_{ij} are independent of each other, each term in the summation over j is like one step of a random walk, with the limitation that the sum of steps in a row is S_i.

Let us fix our attention on one term, A_{ij}. If it is assumed that all the other steps in the ith row, $A_{ik}(k \neq j)$, are in random directions, the probability that their resultant lies between $\mathbf{Q}$ and $\mathbf{Q}+d\mathbf{Q}$ can be calculated by the Markoff method (see Chandrasekhar, 1943). The length of each step, A_{ik}, is known, but the probability function is unsuitable for rapid calculation. A much simpler form is obtained by assuming that the length of each step is governed by a Gaussian probability distribution whose mean-square length is A_{ik}. We then have

$$P(\mathbf{Q})d\mathbf{Q} \propto \exp\left\{-|\mathbf{Q}|^2 \sum_{k\neq j} A_{ik}^2\right\} d\mathbf{Q}.$$

However, we know that on taking the final step of length A_{ij} in a direction Θ_{ij} with S_i, we must reach the end of the vector $\mathbf{S}_i$. Hence

$$|\mathbf{Q}|^2 = A_{ij}^2+S_i^2-2A_{ij}S_i\cos\Theta_{ij},$$

and thus it can be shown that

$$P_{ij}(\Theta)d\Theta \propto \exp\left\{-(4A_{ij}S_i/\sum_{k\neq j}A_{ik}^2)\sin^2\tfrac{1}{2}\Theta\right\}d\Theta. \tag{9}$$

Let us first consider the case when $j=i$ for the term under consideration, A_{ii}. Expression (9) gives the probability distribution for Θ_{ii} based on this diagonal term. Here $\Theta_{ii}=2\alpha_i+\phi_{ii}$. Thus if $p_{ij}(\alpha)d\alpha$ is the probability, according to the jth term of the ith row, that α_i lies between α and $\alpha+d\alpha$, then

$$p_{ii}(\alpha) \propto \exp\left\{-(4A_{ii}S_i/\sum_{k\neq i}A_{ik}^2)\sin^2(\alpha-\tfrac{1}{2}\phi_{ii})\right\}. \tag{10}$$

In the general case, $i \neq j$, expression (9) gives us the probability distribution for $\alpha_i+\alpha_j=\Theta_{ij}-\phi_{ij}$. Thus if some probability function $P_j(\alpha)$ is available for phase angle j, then this ij term indicates a probability distribution for α_i as follows:

$$p_{ij}(\alpha) = \int_{\Theta=0}^{2\pi} P_{ij}(\Theta)P_j(\Theta-\alpha-\phi_{ij})d\Theta. \tag{11}$$

The integration over Θ is introduced as all values of Θ have a finite probability. Thus

$$p_{ij}(\alpha) \propto \int_0^{2\pi} P_{ij}(\Theta) \exp \left\{ -(4A_{ij}S_i/\sum_{k \neq j} A_{ik}^2) \right.$$
$$\left. \sin^2 ((\Theta - \alpha_j - \phi_{ij})/2) \right\} d\Theta . \quad (12)$$

In practice there are several significant terms A_{ij}, affecting α_i, each giving a different distribution $p_{ij}(\alpha)$. It is to be expected that these distributions will be similar, or, if they are different, then it is hoped that only those distributions with small A_{ij} will differ grossly. Nevertheless it is important to take into account all terms in a single row. We may consider the final distribution for $P_i(\alpha)$ as the joint distribution of all separate distributions from each term in an equation.

$$\therefore P_i(\alpha) = \prod_j \{\prod p_{ij}(\alpha)\}$$

or, from (11)

$$P_i(\alpha) = \prod_m \left\{ \prod_j \left[\int_0^{2\pi} P_{ij}(\Theta) P_j(\Theta - \alpha - \phi_{ij}) d\Theta \right] \right\}. \quad (13)\dagger$$

Let us now consider the total process of determining the phase probability distributions, starting only with a knowledge of the coefficients A_{ij} and phases ϕ_{ij}. We may write down immediately that $\alpha_0 = 0$ with a probability of unity. We as yet know nothing at all about any other phase, and express our present ignorance by setting the probabilities of all values of phase α_i as equal. We then apply (10) to the diagonal term of each row $(j = i)$ and take $p_{ii}(\alpha)$ as our first estimate of $P_i(\alpha)$. This form of $P_i(\alpha)$ can now be used in (12) with all ij terms, which are then combined by (13) to give improved versions of $P_i(\alpha)$. Because of the ambiguity of $p_{ii}(\alpha)$, indicating two phases $180°$ apart as equally probable, all these probability distributions will have two peaks $180°$ apart, except where an interaction with α_0 exists. Where such an interaction does exist, a preliminary indication of phase will be given.

The new joint probability distributions $P_i(\alpha)$ are used in a second cycle of refinement, and the initial distributions are discarded. In the second cycle, phase indications will be obtained for those phases which interact with equations whose phases were previously determined because of their strong A_{io} terms. The iterative process can be repeated until the phases so determined give values of E (equation (3)) approaching zero, the phase indications spreading further from the origin of reciprocal space with each cycle of refinement.

Consider now the case of an equation with a dominant diagonal term A_{ii}. The value of R (equation (4)) will be little changed whether $\alpha_i = \pi - \frac{1}{2}\phi_{ii}$ or $2\pi - \frac{1}{2}\phi_{ii}$,

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† The phase probability distribution of all m symmetry related phases can be multiplied together, provided one takes care of their relative phases as required by any particular space group.

that is to say the probabilities $P_i(\alpha = \pi - \frac{1}{2}\phi_{ii})$ and $P_i(\alpha = 2\pi - \frac{1}{2}\phi_{ii})$ are almost equal. The simplest approach would be to use the phase with the greater probability, but should that not be correct, the error introduced into the Fourier summation would be large. Blow & Crick (1959) and Dickerson, Kendrew & Strandberg (1961) show that the best approach to the formally identical problem of combining the information from different isomorphous replacement derivatives is to use the centroid of the phase probability distribution as Fourier coefficients, ξ, in an electron-density calculation.

That is

$$\xi_i = |F_i| \int_0^{2\pi} P_i(\alpha) \exp [i\alpha] d\alpha \bigg/ \int_0^{2\pi} P_i(\alpha) d\alpha . \quad (14)$$

5. A worked example

A two-dimensional structure (Fig. 1), in plane group $p1$, in a cell with $a = 21·6$, $b = 42·0$ Å, $\gamma = 111·5°$, containing two independent, but identical molecules each with five equal atoms was chosen as a trial for the proposed method. In order to limit the amount of computation, calculations were restricted to the 35 reflexions of lowest Bragg angle. The calculated structure amplitudes for these reflexions, corresponding to 6·2 Å resolution, were used as 'observed' data from which to deduce the phase angles. A Fourier synthesis using these structure amplitudes with the 'correct' calculated phases is shown in Fig. 3.
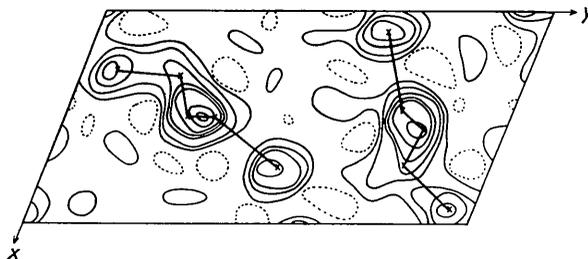

Fig. 3. Electron density map using only the innermost thirty five structure amplitudes (6·2 Å resolution) with structure factor calculated phases.

The equations in A_{ij} and ϕ_{ij} were now derived and solved by the method described in this paper. One iteration for thirty-five phases took 20 min. on the EDSAC 2. Rotations of both $-140°$ and $+40°$ were used, but the latter, incorrect rotation, did not refine to a low value of E (Table 1). Rotations of $+140°$ and $-40°$, represent enantiomorphic solutions.

The first refinement (seven cycles) using the correct rotation of $-140°$ led to a recognizable structure (Fig. 4). The phases are given in Table 2. The second refinement process used $|G_{hp}|$ instead of G_{hp} in the calculation of the coefficients A_{ij}. This can be shown to be rather like the physical criterion of minimizing

$$E' = \int_U [\varrho^2(\mathbf{x}) - \varrho^2(\mathbf{x}')]^2 d\mathbf{x} ,$$

or maximizing

$$R' = \int_U \varrho^2(\mathbf{x}) \cdot \varrho^2(\mathbf{x}') d\mathbf{x} . \tag{15}$$

Table 1. *Values of the functions E and R*

Rotation	Structure	$2R \times 10^4$	$E \times 10^4$
$+40°$	'correct' phases	1·41	1·51
	deduced phases 1	1·99	0·93
$-140°$	'correct' phases	2·69	0·23
	deduced phases 2	2·62	0·30
	deduced phases 3	2·76	0·16

The 'correct' phases refer to the phases given by conventional structure factor calculations, from the assumed atomic positions.

Deduced phases 1 were found by refining the G criterion (maximization of R, equation (4)) using the rotation of $+40°$, which represents an extraneous solution of the rotation function.

Deduced phases 2 were found by refining the G criterion (maximization of R, equation (4)) using rotation of $-140°$, which represents the correct solution of the rotation function.

Deduced phases 3 were found by refining the $|G|$ criterion (maximization of R', equation (15)) using rotation of $-140°$.

Table 2. *Comparison of 'correct' structure factor calculated phases and those found on refinement of the G and $|G|$ criteria, corresponding to the 'deduced 2' and 'deduced 3' phase angles*

i	Indices (h, k)	α_i^0 (correct)	α_i^0 (deduced 2)	α_i^0 (deduced 3)	$|F_i|$
0	0 0	0	0	0	60
1	0 1	300	304	308	6
2	−1 1	321	287	306	21
3	1 0	181	178	182	17
4	0 2	195	222	213	17
5	−1 2	22	21	22	41
6	1 1	192	305	214	11
7	−1 3	288	316	286	22
8	0 3	233	153	148	3
9	1 2	39	226	32	10
10	−2 1	152	88	156	13
11	−2 2	221	195	209	18
12	−1 4	217	7	229	26
13	2 0	350	57	1	7
14	−2 3	345	243	339	23
15	0 4	51	271	64	20
16	1 3	36	177	347	6
17	2 1	310	28	7	14
18	−2 4	52	221	50	8
19	−1 5	13	71	83	12
20	0 5	20	298	255	1
21	2 2	228	240	212	24
22	1 4	262	170	237	28
23	−2 5	290	5	326	14
24	−3 2	36	339	357	22
25	−3 3	186	85	161	8
26	−3 1	95	39	33	20
27	−1 6	48	193	95	15
28	−3 4	274	173	189	15
29	2 3	342	263	271	16
30	−2 6	254	308	286	32
31	3 0	167	282	212	8
32	1 5	174	237	272	14
33	0 6	275	241	246	11
34	−3 5	51	26	24	8
35	3 1	320	242	202	25

This criterion led to a structure more nearly like the correct structure (Fig. 5). The phases given by the sixth cycle of refinement, are shown in Table 2.
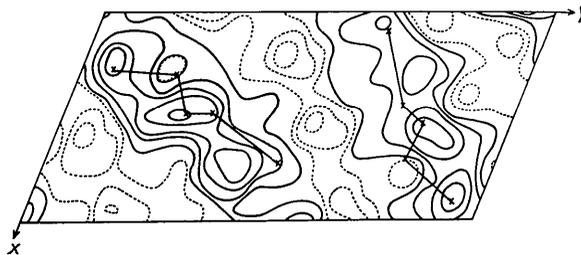
Fig. 4. Electron density map using the innermost thirty five structure amplitudes with phases deduced by maximizing R (equation (4)).
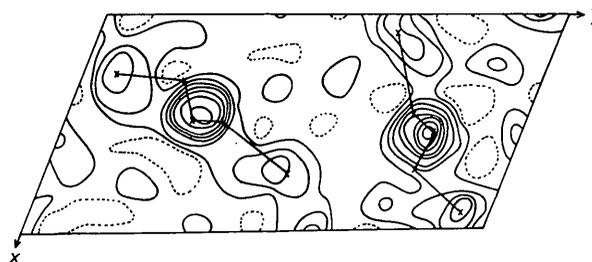
Fig. 5. Electron density map using the same structure amplitude but phases deduced on the basis of maximizing R', (equation (15)).

It may be noted from Table 2 that the phase determination deteriorates with increasing i. Indeed an electron-density map including only those terms for which $i \le 23$ is substantially better than shown in Fig. 5. In these phase probability calculations only the interactions between the 35 innermost reflections were considered. As the largest A_{ij} elements must lie on or near the diagonal of the matrix, the effect of neglecting A_{ij} terms with $j > 35$ becomes more serious as i increases. In our example a significant number of terms have been neglected in a large proportion of the equations and the effect is serious. It becomes less important as the number of unknown phases becomes larger. A measure of the seriousness of the effect is the ratio of the surface area to volume of the 'sphere of reflection' used to terminate the data.

APPENDIX I

The effect of proper rotations

Let

$$\phi_{hp} = [-2\pi \mathbf{p} \cdot \mathbf{d} + \Omega_{hp}]$$
$$= -2\pi[\mathbf{p} \cdot \mathbf{d} + (\mathbf{h} + \mathbf{h}') \cdot \mathbf{S}]$$

(see R. & B.)

where $\mathbf{h}' = [\tilde{\mathbf{C}}] \cdot \mathbf{p}$, and $\mathbf{S}$ is the position vector of the centre of the volume U over which the integration

was performed, and for which $G_{hp} \exp[i\Omega_{hp}]$ represents the diffraction function.

$$\therefore \phi_{hp} = -2\pi[\mathbf{p}.\mathbf{d}+\mathbf{h}.\mathbf{S}+\{[\tilde{\mathbf{C}}].\mathbf{p}\}.\mathbf{S}]$$
$$= -2\pi[\mathbf{h}.\mathbf{S}+\mathbf{p}\{[\mathbf{C}].\mathbf{S}+\mathbf{d}\}]$$
$$= -2\pi[\mathbf{h}.\mathbf{S}+\mathbf{p}.\mathbf{S}']$$

where $\mathbf{S}'$ is the position vector of the centre of the volume U'. That is $\mathbf{S}'=[\mathbf{C}].\mathbf{S}+\mathbf{d}$.

Now if the rotation is proper we may take $\mathbf{S}=\mathbf{S}'$ and integrate over the volume of both sub-units, for it is irrelevant where the boundary between these is drawn. Thus for a proper rotation

$$\phi_{hp} = -2\pi[(\mathbf{h}+\mathbf{p}).\mathbf{S}] = \phi_{ph},$$

but for an improper rotation

$$\phi_{hp} = -2\pi[\mathbf{h}.\mathbf{S}+\mathbf{p}.\mathbf{S}'] \neq \phi_{ph}.$$

APPENDIX II

The magnitude, S_i, of the sum of the terms in a row of the matrix $A_{ij} \cos(\alpha_i+\alpha_j+\phi_{ij})$

By definition of a structure factor

$$|F(h)| \exp[-i\alpha_h] = V\int_V \varrho(\mathbf{x}) \exp[-2\pi i\mathbf{h}.\mathbf{x}]dx$$

where V is the volume of the unit cell. If there is no density outside the volumes U and U', and within V, then it follows that

$$|F(\mathbf{h})| \exp[-i\alpha_h]$$
$$= V\left\{\int_U \varrho(\mathbf{x}) \exp[-2\pi i\mathbf{h}.\mathbf{x}]dx \right.$$
$$\left. + \int_{U'} \varrho(\mathbf{x}) \exp[-2\pi i\mathbf{h}.\mathbf{x}]dx\right\},$$
$$= V\left\{\int_U \varrho(\mathbf{x}) \exp[-2\pi i\mathbf{h}.\mathbf{x}]dx \right.$$
$$\left. + \int_U \varrho(\mathbf{x}') \exp[-2\pi i\mathbf{h}.\mathbf{x}']dx\right\},$$

since whenever $\mathbf{x}$ is in U, $\mathbf{x}'$ (given by equation (2)) is within U'. But since $\varrho(\mathbf{x})=\varrho(\mathbf{x}')$:

$$|F(\mathbf{h})| \exp[-i\alpha_h] = V\left\{\int_U \varrho(\mathbf{x}') \exp[-2\pi i\mathbf{h}.\mathbf{x}]dx \right.$$
$$\left. + \int_U \varrho(\mathbf{x}) \exp[-2\pi i\mathbf{h}.\mathbf{x}']dx\right\}.$$

Substituting a Fourier summation for $\varrho(\mathbf{x})$; that is, writing

$$\varrho(\mathbf{x}) = (1/V)\sum_p |F_p| \exp[i(\alpha_p-2\pi\mathbf{p}.\mathbf{x})],$$

we have

$$|F(\mathbf{h})| \exp[-i\alpha_h]$$
$$= \int_U \left\{\sum_p |F(\mathbf{p})| \exp[i(\alpha_p-2\pi\mathbf{p}.\mathbf{x}')]\right\} \exp[-2i\mathbf{h}.\mathbf{x}]dx$$
$$+ \int_U \left\{\sum_p |F(\mathbf{p})| \exp[i(\alpha_p-2\pi\mathbf{p}.\mathbf{x})]\right\}$$
$$\times \exp[-2\pi\mathbf{h}.\mathbf{x}']dx.$$

Making use of (2) to write $\mathbf{x}'$ in terms of $\mathbf{x}$

$$|F(\mathbf{h})| = \sum_p |F(\mathbf{p})| \exp[i(\alpha_p+\alpha_h)]$$
$$\times \left\{\exp[-2\pi i\mathbf{p}.\mathbf{d}]\int_U \exp[-2\pi i(\mathbf{h}.\mathbf{x}+\mathbf{p}.[\mathbf{C}].\mathbf{x})]dx \right.$$
$$\left. + \exp[-2\pi i\mathbf{h}.\mathbf{d}]\int_U \exp[-2\pi i(\mathbf{p}.\mathbf{x}+\mathbf{h}.[\mathbf{C}].\mathbf{x})]dx\right\}.$$

Since $\mathbf{p}.[\mathbf{C}].\mathbf{x}=[\tilde{\mathbf{C}}]\mathbf{p}.\mathbf{x}$, the first integral becomes

$$\int_U \exp[-2\pi i(\mathbf{h}+[\tilde{\mathbf{C}}]\mathbf{p})\mathbf{x}]dx = (U/V)G_{hp} \exp[i\Omega_{hp}],$$

by definition.

Making a similar substitution for the second integral leads to

$$|F(\mathbf{h})| = (U/V)\sum_p |F(\mathbf{p})| \exp[i(\alpha_p+\alpha_h)]$$
$$\times \{\exp[-2\pi i\mathbf{p}.\mathbf{d}]G_{hp} \exp[i\Omega_{hp}]$$
$$+ \exp[-2\pi i\mathbf{h}.\mathbf{d}]G_{ph} \exp[i\Omega_{ph}\}$$
$$|F(\mathbf{h})|^2 = (U/V)\sum_p |F(\mathbf{p})||F(\mathbf{h})| \exp[i(\alpha_p+\alpha_h)]$$
$$\times \{\exp[-2\pi i\mathbf{p}.\mathbf{d}]G_{hp} \exp[i\Omega_{hp}]$$
$$+ \exp[-2\pi i\mathbf{h}.\mathbf{d}]G_{ph} \exp[i\Omega_{ph}]\}.$$

This may be compared with (6), $\mathbf{h}$ being replaced by $\mathbf{i}$ and $\mathbf{p}$ by $\mathbf{j}$. It is evident that

$$|F(\mathbf{i})|^2 = 2V^2 \sum_j A_{ij} \exp[i(\alpha_i+\alpha_j+\phi_{ij})].$$

Using Friedel's Law

$$|F(\mathbf{i})|^2 = 2V^2 \sum_j A_{ij} \cos(\alpha_i+\alpha_j+\phi_{ij}) = 2VUS_i.$$

So that
$$S_i = (1/2V^2)|F(\mathbf{i})|^2.$$

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Crystal Structures with a Chabazite Framework. II. Hydrated Ca-chabazite* at Room Temperature

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The crystal structure of hydrated Ca-chabazite (composition $Ca_{1.95}Al_{3.9}Si_{8.1}O_{24} . 13(?)H_2O$) was studied from $\{hk0\}$ data of the rhombohedral cell ($R\bar{3}m(?)$: $a = 9.42$ Å, $\alpha = 94° 28'$). The atomic coordinates of the Si, Al and oxygen atoms of the framework were refined without difficulty assuming space group $R\bar{3}m$. Great difficulty was found in locating the calcium atoms and water molecules, and the proposed distribution, although giving $R = 0.11$, is uncertain: consequently, three-dimensional analyses at both low and room temperatures are being considered. However it is certain that, during hydration, the distribution of Ca atoms changes markedly, and the framework changes shape. The non-framework peaks in the F_o-synthesis can be interpreted on the basis of thirteen water molecules and two calcium atoms per unit cell. There are twelve peaks for the calcium atoms and it was postulated that there are six different types of unit cells projected onto the pseudo-rhombohedral F_o-synthesis. It is thought that the arrangement of the Si and Al atoms results in asymmetric electric fields which cause the water molecules, and especially the calcium ions, to move away from positions of rhombohedral symmetry. Ordering of the Si and Al atoms, together with twinning, best explains the X-ray and optical observations: however, other possibilities cannot be ruled out definitely. The calcium atoms have four water molecules as nearest neighbours, which may be regarded as an incomplete sphere of hydration.

Introduction

In part I (Smith, 1962) of this series, a general introduction to the program of studies on chabazite was given, together with a detailed account of the structure of dehydrated-Ca-chabazite. The more complex study of hydrated-Ca-chabazite falls into three parts: (*a*) determination of the Si,Al–O framework from two-dimensional data, and discovery that at least some of the calcium atoms and water molecules appear to be statistically distributed in projection, (*b*) determination of a possible configuration of calcium atoms and water molecules on the basis of a symmetry lower than rhombohedral, (*c*) study of chabazite by three-dimensional data at room temperature and below − 100 °C. Because considerable time will elapse before part (*c*) can be completed, and because the conclusions

reached in parts (*a*) and (*b*) are important, an account of the preliminary results is given here, even though uncertainties remain.

Experimental

Optical examination of the chabazite showed the presence only of rhombohedral faces. However, the crystals displayed complex optical phenomena in polarized light. The extinction was variable in parallel light, showing the presence of domains separated from each other by boundaries in which the extinction changed abruptly. However, there were large continuous changes of extinction in each domain, and the domain boundaries, although tending to be planar, were curved in an irregular manner. Examination in convergent light yielded confused figures because of the summation of effects from several domains; the least confused figures indicated a moderate optic axial angle (near 50°) with a positive sign. Similar

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