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## The Use of Non-Crystallographic Symmetry for Phase Determination

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When a crystal contains more than one identical molecule or sub-unit in the crystallographic asymmetric unit, the structure factors must satisfy a set of complex linear equations. Given a set of structure amplitudes for a structure with the postulated non-crystallographic symmetry, the particular nature of the eigenvalue spectrum of the matrix of the equations provides a formal basis for an iterative procedure for generating the phases of the structure factors from the equations. The method has been tested on a number of model structures. An estimate is given of how strong the non-crystallographic symmetry constraints must be in order to generate a unique set of phases.

### Introduction

In a previous paper (Crowther, 1967) it was shown that the structure-factor equations, which may be constructed when a crystal contains more than one identical molecule or sub-unit within the crystallographic asymmetric unit (Main & Rossmann, 1966), can be written in the form

$$\mathbf{HF} = \mathbf{F} \quad (1)$$

Here  $\mathbf{F}$  is a vector whose elements are the complex structure factors out to the resolution to which we are working and  $\mathbf{H}$  is a hermitian matrix ( $H_{rs} = H_{sr}^*$ , where the asterisk denotes complex conjugate) describing the relative geometry of the sub-units. The elements of  $\mathbf{H}$  are expressed in terms of the rotations and translations relating the various sub-units, which we assume are known, so that the elements of  $\mathbf{H}$  can be evaluated numerically for any given arrangement of sub-units.

Any eigenvector of the matrix  $\mathbf{H}$  corresponding to a unit eigenvalue is a possible solution of (1) and conversely the number of independent solutions of (1) is

equal to the number of unit eigenvalues of the matrix  $\mathbf{H}$ . The Fourier transform of the particular set of structure factors constituting an eigenvector of  $\mathbf{H}$  will be called an eigendensity. Eigenvectors and eigendensities corresponding to unit eigenvalues will be termed 'allowed'. Any structure with the postulated non-crystallographic symmetry may, to the resolution to which we are working, be expressed as a linear combination of the allowed eigendensities and correspondingly its transform may be expressed as a linear combination of the allowed eigenvectors. The allowed eigendensities form a more appropriate set of functions in which to expand a density with non-crystallographic symmetry than the more normally used Fourier terms.

Turning now to structure determination, let us take an unknown structure with known non-crystallographic symmetry. The question we pose is whether, given a set of measured structure amplitudes, it is possible to use the constraints introduced by non-crystallographic symmetry to solve the structure. For simplicity we take the space group to be  $P1$  and let us suppose that  $(2N+1)$  reflexions are to be included,

that is  $N$  independent reflexions plus the  $N$  Friedel related reflexions plus the  $F_0$  term. At this resolution the matrix  $\mathbf{H}$  will have  $m$  allowed eigenvectors,  $(\mathbf{u}_1 \dots \mathbf{u}_m)$ , where  $m < N$ . The transform,  $\mathbf{F}$ , of the structure must be expressible as a linear combination of the allowed eigenvectors in the form

$$\mathbf{F} = \sum_{j=1}^m \mu_j \mathbf{u}_j \quad (2)$$

where the  $\mu_j$  are real (Crowther, 1967). The  $N$  unknown phases may be eliminated from (2) to give a set of  $(N+1)$  simultaneous quadratic equations for the  $m$  unknowns  $\mu_j$  which involve only the measured intensities, namely

$$|F_h|^2 = \sum_{j=1}^m \sum_{k=1}^m \mu_j \mu_k u_{jh}^* u_{kh}, \quad h=0, 1, \dots, N \quad (3)$$

where  $u_{jh}$  is the  $h$  component of the eigenvector  $\mathbf{u}_j$ . A plot of the number,  $m$ , of unit eigenvalues as ordinate against the number,  $N$ , of independent reflexions included, when the equations are truncated at different resolutions, gives a straight line, whose gradient is the fractional decrease in the number of parameters needed to describe the system.

If the gradient of the  $(m, N)$  plot were less than unity, the problem should in general be determined, since the number of unknowns is then less than the number of equations. In order for there to be a *unique* solution however, it will be shown that the gradient of the  $(m, N)$  plot must be considerably less than unity. In the Appendix it is shown that for space group  $P1$  the gradient of the  $(m, N)$  plot is less than  $(2U/V)$ , where  $U$  is the volume of a sub-unit and  $V$  is the volume of the unit cell. The gradient of the  $(m, N)$  plot therefore decreases and the strength of constraint increases as the number of sub-units in the asymmetric unit increases.

Although the above formulation (3) enables a quantitative measure of the constraints introduced by the non-crystallographic symmetry to be given, it is not very useful for structure determination, since there is no simple method of solving a large set of simultaneous quadratic equations. In any case the coefficients  $u_{jh}^* u_{kh}$  in (3) become difficult to compute when the number of reflexions included is large. Accordingly a different approach has been used, though still based on the eigenvalue analysis described above. The method, which is iterative, attempts to determine structure factor phases, rather than the coefficients,  $\mu_j$ , in the expansion of the transform in terms of the allowed eigenvectors.

### An iterative method of phase determination

We assume that the iterative phase determination has been initiated in the way described below. Let us suppose that at some stage of phase determination we have an approximate set of phases which, when combined with the observed structure amplitudes, gives a structure factor vector which will be denoted by  $\mathbf{F}^{(r)}$ .

Since the phases are approximate, the transform of  $\mathbf{F}^{(r)}$  will not in general have the required non-crystallographic symmetry.  $\mathbf{F}^{(r)}$  will not be a solution of equations (1) and will therefore contain components of non-allowed eigenvectors. We may write

$$\mathbf{F}^{(r)} = \sum_{j=1}^m \mu_j^{(r)} \mathbf{u}_j + \sum_{j=m+1}^{2N+1} \mu_j^{(r)} \mathbf{u}_j,$$

where the summation is split into two parts corresponding to the allowed and non-allowed components respectively. In the Appendix to Crowther (1967) it was proved that the eigenvalues of matrix  $\mathbf{H}$  satisfy the condition  $0 \leq \lambda_j \leq 1$ . A better solution of the equations may therefore be produced by multiplying  $\mathbf{F}^{(r)}$  by matrix  $\mathbf{H}$  giving

$$\begin{aligned} \mathbf{G}^{(r+1)} &= \mathbf{H}\mathbf{F}^{(r)} \\ &= \sum_{j=1}^m \mu_j^{(r)} \mathbf{u}_j + \sum_{j=m+1}^{2N+1} \mu_j^{(r)} \lambda_j \mathbf{u}_j. \end{aligned} \quad (4)$$

Multiplication by matrix  $\mathbf{H}$  leaves the allowed components, which have eigenvalue unity, unchanged but reduces the contribution from each non-allowed component by a factor equal to the corresponding eigenvalue. In particular, contributions from eigenvectors with eigenvalue zero will be completely removed. The importance of having an eigenvalue spectrum lying between 0 and 1 is now apparent.

The moduli of the elements of the resulting vector  $\mathbf{G}^{(r+1)}$  will not now be equal to the observed structure amplitudes, so that the modulus of each element must be individually rescaled. This operation may be written as:

$$\mathbf{F}^{(r+1)} = \mathbf{S}^{(r+1)} \mathbf{G}^{(r+1)} \quad (5)$$

where  $\mathbf{S}^{(r+1)}$  is the diagonal rescaling matrix. Combining (4) and (5) we may eliminate  $\mathbf{G}^{(r+1)}$  and write

$$\mathbf{F}^{(r+1)} = \mathbf{S}^{(r+1)} \mathbf{H}\mathbf{F}^{(r)}. \quad (6)$$

Equation (6) forms the basis for the iterative phasing procedure. Each step of the iteration consists of multiplying the current approximation vector by the matrix  $\mathbf{H}$  and then rescaling each structure amplitude to its observed value. It is important to note that, although the iterative process is based on the underlying eigenvalue and eigenvector analysis of the matrix  $\mathbf{H}$ , it is not necessary to know the eigenvalues or eigenvectors explicitly.

For computational purposes the elements of the diagonal rescaling matrix are given by:

$$S_{hh}^{(r+1)} = |F_h| / |G_h^{(r+1)}|.$$

However if we wish to investigate the iteration analytically, we find that the setting up of the rescaling matrix is essentially a non-linear operation, since the elements are given by:

$$S_{hh}^{(r+1)} = |F_h| \left\{ \sum_{j=1}^{2N+1} \sum_{k=1}^{2N+1} \mu_j^{(r)} \mu_k^{(r)} \lambda_j \lambda_k u_{jh}^* u_{kh} \right\}^{-1/2}.$$

Thus rescaling reintroduces or reinforces non-allowed components, so that the next approximation to the solution still has the form:

$$\mathbf{F}^{(r+1)} = \sum_{j=1}^m \mu_j^{(r+1)} \mathbf{u}_j + \sum_{j=m+1}^{2N+1} \mu_j^{(r+1)} \mathbf{u}_j .$$

A necessary condition for convergence of an iterative process of the type defined by (6) would be that the contribution from the non-allowed components should be smaller at the  $(r+1)$ th stage than at the  $r$ th stage. The contribution from the non-allowed components can be simply expressed, since it follows from the orthonormality of the eigenvectors that at any stage of the iteration the complete set of  $\mu_j$  must satisfy:

$$\sum_{j=1}^{2N+1} (\mu_j^{(r)})^2 = \sum_{j=1}^{2N+1} (\mu_j^{(r+1)})^2 = \sum_{h=-N}^N |F_h|^2 .$$

Thus a necessary condition for convergence is:

$$\sum_{j=m+1}^{2N+1} (\mu_j^{(r+1)})^2 < \sum_{j=m+1}^{2N+1} (\mu_j^{(r)})^2 .$$

A sufficient condition for convergence would be that

$$\sum_{j=m+1}^{2N+1} (\mu_j^{(r)})^2 \rightarrow 0 \quad \text{as } r \rightarrow \infty .$$

Because of the analytical form of the rescaling matrix any attempt to demonstrate convergence by these means quickly leads to intractable algebra, even if a number of simplifying assumptions are made. It is hoped though that the non-allowed contributions reintroduced by the rescaling will be smaller than the non-allowed contributions removed by multiplying by the matrix  $\mathbf{H}$ , so that the iterative process will converge. The examples discussed below show this to be the case.

An alternative way of considering the phasing procedure is in terms of a complex vector space. The allowed eigenvectors of  $\mathbf{H}$  define a subspace of dimension  $m$  in a space of dimension  $(2N+1)$ . The phasing procedure attempts to find a vector  $\mathbf{F}$  lying in the allowed subspace, the moduli of whose elements are equal to the observed structure amplitudes. Successive applications of the matrix  $\mathbf{H}$  have the effect of projecting into the allowed subspace the vector  $\mathbf{F}^{(r)}$  representing an approximate solution. Strictly speaking the condition that  $\mathbf{F}$  lies in a subspace is not quite precise since we have shown that  $\mathbf{F}$  must be a real linear combination of the allowed eigenvectors, whereas the general subspace condition admits of complex linear combinations of the allowed eigenvectors. Granted, however, that the initial approximation is chosen to satisfy the Friedel relation, all subsequent iterates will also satisfy it, since the Friedel character is preserved under transformations of the type considered. Clearly the strength of the geometrical constraint imposed on  $\mathbf{F}$  increases as the relative dimension of the allowed subspace decreases. This relative dimensionality of the allowed subspace is simply one half the gradient of the appropriate  $(m, N)$  plot.

We have considered so far the convergence of the phasing process to a solution; we have not considered the uniqueness of this solution. Is it possible for there to be more than one structure which has the given structure amplitudes and which satisfies the particular non-crystallographic symmetry? This is analogous to asking about the existence of homometric structures (Patterson, 1944), though the discussion of these is generally restricted to the case of point atoms, whereas our analysis of non-crystallographic symmetry has not been so restricted. When the density is not restricted to point atoms and the structure amplitudes are in any case subject to error, the question has to be phrased in much vaguer terms; namely do there exist significantly different structures which have the postulated non-crystallographic symmetry and whose structure amplitudes do not differ significantly from the observed values? It will be shown in the next section that for a particular one-dimensional example containing three sub-units there are at least three solutions. A general answer to the uniqueness question can not yet be given. Clearly the more restricted the allowed subspace the more likely the solution is to be unique. However, the restrictedness of the subspace may not be a sufficient criterion for uniqueness, since for given non-crystallographic symmetry it is possible that some permitted sets of structure amplitudes will lead to a unique solution whereas others will not.

#### Mode of application of the iterative phasing procedure

At the start of the iterative phase determination the only phase which is known is that of the  $F_0$  term, which we assume to be real and positive. The phase determination may proceed in one of two ways. In the first way the initial approximation vector  $\mathbf{F}^{(0)}$  has its elements set equal to the corresponding structure amplitudes, all the phases being zero, and we operate from the beginning on a structure factor vector containing all reflexions. The second way is more like the procedure of Main & Rossmann (1966). At first the approximation vector contains only those reflexions close to the origin of reciprocal space, since these are the ones which interact most strongly with the known  $F_0$  term; as before, their phases are initially set to zero. After refining the phases of these reflexions, a new band of reflexions is included and their phases refined, while holding the existing phase estimates fixed. After this partial refinement of the newly introduced reflexions, all reflexions so far included are allowed to refine together. The procedure continues in this way, phase information being gradually extended outwards from the origin of reciprocal space.

In the first method we are working in a space of fixed dimension equal to the total number  $(2N_0+1)$  of reflexions included in the structure determination and the initial approximation lies a long way from the solution point. In the second method we are working in a series of subspaces, the dimensions of which even-

tually increase to  $(2N_0 + 1)$  and where after refinement at any stage we have an approximation to the solution which fits the currently included reflexions as well as possible. The dimension of the allowed subspace into which we are projecting will also increase, but the linearity of the  $(m, N)$  plot means that the ratio of the dimension of the currently allowed subspace to the dimension of the subspace spanned by the currently included reflexions remains constant.

Clearly the paths traced by the successive approximation vectors  $F^{(r)}$  are likely to be very different, since in the first method they can lie anywhere in the complete space of dimension  $(2N_0 + 1)$  whereas in the second method they are constrained to lie in a series of subspaces spanned by the reflexions currently included in the refinement. It is possible therefore, if there is more than one solution to a particular problem, that application of these different phasing methods will demonstrate its existence.

The speed of refinement may be followed by observing the mean phase change,  $\overline{\delta\theta}$ , between successive iterates. The discrepancy,  $R$ , between the observed amplitudes and the calculated amplitudes of an iterate before rescaling gives a measure of how far we are from a solution. They are defined formally by:

$$\overline{\delta\theta} = \frac{1}{(2N+1)} \sum_{h=-N}^N |\arg F_h^{(r+1)} - \arg F_h^{(r)}|,$$

$$R = \left( \sum_{h=-N}^N ||F_h| - |G_h^{(r)}|| \right) / \left( \sum_{h=-N}^N |F_h| \right).$$

The choice of origin for the crystal is determined by the way in which the envelopes around the sub-units are specified. Phases generated during the refinement are referred to the origin chosen for specifying the sub-unit geometry. The enantiomorphy of the final structure will also be fixed by the sub-unit geometry, provided the arrangement of sub-units within the unit cell is enantiomorphic. For suppose we have a problem with matrix  $\mathbf{H}$  and solution vector  $\mathbf{F}$  so that

$$\mathbf{F} = \mathbf{H}\mathbf{F}. \quad (7)$$

The structure factor vector  $\mathbf{F}^*$  representing the structure of opposite hand will not in general satisfy these equations. Taking the complex conjugate of (7) we have

$$\mathbf{F}^* = \mathbf{H}^*\mathbf{F}^*.$$

Hence  $\mathbf{F}^*$  is a solution of (7) if and only if  $\mathbf{H}^* = \mathbf{H}$  which implies that  $\mathbf{H}$  is real. This means either that the arrangement of envelopes and the structure are centrosymmetric, so that the question of enantiomorphy does not arise, or that the envelopes themselves are centrosymmetric while the structure is not. In the latter case it is clear that a centrosymmetric geometrical constraint can only determine the real parts of structure factors, while the imaginary parts and therefore the enantiomorphy remain undefined. The one further ambiguity, that of distinguishing the positive from the corresponding negative electron density solution, both

of which satisfy the phase equations, is overcome by specifying that the  $F_0$  term must be positive. This seems in general sufficient to ensure that the iterative phasing procedure generates the positive rather than the corresponding negative density solution (Rossmann & Blow, 1963).

### Application to some one-dimensional examples

It seemed simplest initially to apply the phasing technique to some one-dimensional examples. In particular it was thought to be interesting to try the three sub-unit example published by Main & Rossmann (1966). The fractional sub-unit size is 0.29 with sub-unit centres at 0.2, 0.5 and 0.83; amplitudes and phases of reflexions are given out to  $h=44$ . The  $(m, N)$  plot for this arrange-

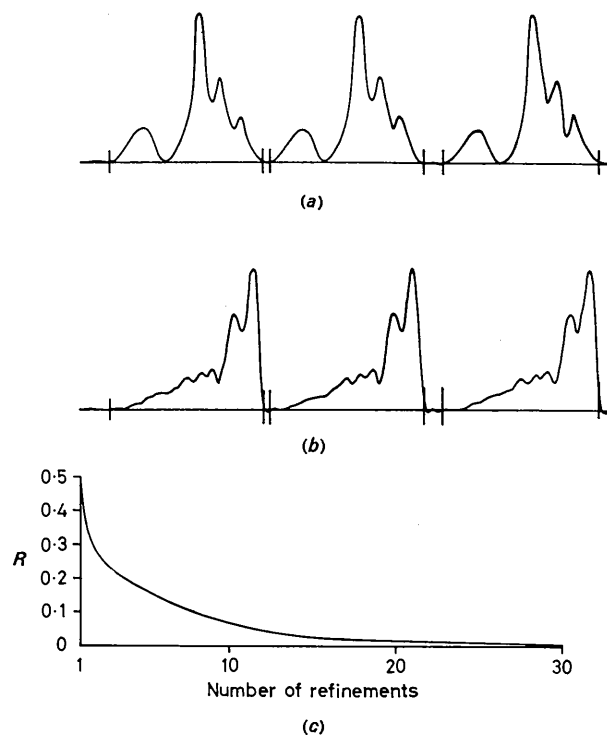


Fig. 1. Phase determination for a one-dimensional example containing three sub-units (Main & Rossmann, 1966). (a) postulated structure; (b) structure generated by the first phasing procedure; (c) behaviour of the  $R$  value during refinement.

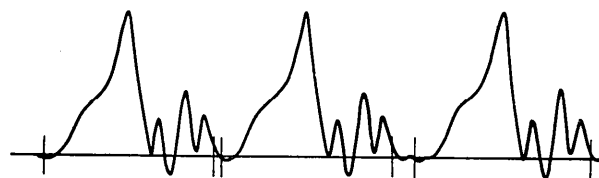


Fig. 2. Phase determination for a one-dimensional example containing three sub-units (Main & Rossmann, 1966): the structure generated by the second phasing procedure.

ment of sub-units has gradient 0.56, so that the problem appears to be well overdetermined. The structure calculated from the given amplitudes and phases is shown in Fig. 1(a). The first phasing technique, that is, repeated projection of the vector containing the 45 available independent structure amplitudes, converged well and after 30 iterations the value of  $R$  had fallen to 0.008. However the calculated phases were very different from the postulated ones and the structure obtained from the calculated phases and given amplitudes is shown in Fig. 1(b). The behaviour of  $R$  during the refinement is given in Fig. 1(c). Application of the second phasing procedure, in which phase information is extended outwards from the origin, gives yet another structure with  $R < 0.01$  as shown in Fig. 2. Clearly then, the solution to this problem is not unique, since we have generated three structures having the given non-crystallographic symmetry and structure amplitudes. The solution point corresponding to the postulated structure does not seem to be accessible to the projection methods used. However the iterative methods do converge and the suggestion that the different projection methods might generate different solutions, when more than one exists, seems justified.

An example containing four sub-units was tried next, with sub-unit size 0.21 and sub-unit centres at 0, 0.22, 0.46 and 0.72, reflexions out to  $h=45$  being included. The gradient of the  $(m, N)$  plot is 0.40. The postulated structure is shown in Fig. 3(a). Application of the second phasing method gave good results out to  $h=34$ , at which point the mean phase error was  $23^\circ$ . Beyond this the structure amplitudes are small and phasing breaks down. The structure obtained from the calculated phases [Fig. 3(b)] is very similar to the postulated structure. Application of the first phasing method also converged but did not give the postulated structure.

This rather brief discussion of some one-dimensional examples shows that the phasing method does converge. The fact that the answers are not unique is the fault of the problems, not of the phasing method. Ac-

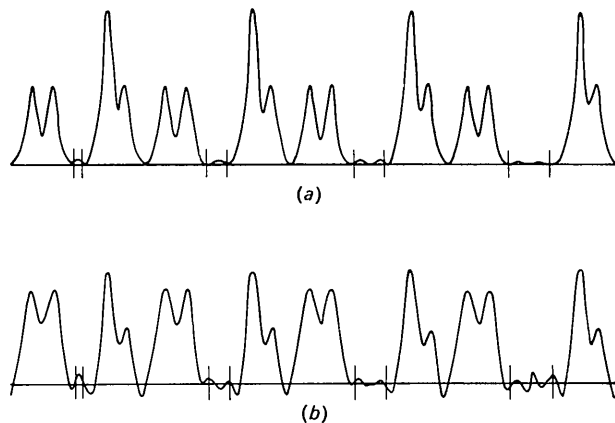


Fig. 3. Phase determination for a one-dimensional example containing four sub-units: (a) postulated structure; (b) structure generated by the second phasing procedure.

cordingly it was decided to study some two-dimensional problems to see whether the constraints introduced by non-crystallographic symmetry would be strong enough to ensure unique solutions.

### Some two-dimensional examples

Application of the phasing procedures to a two-dimensional example containing two sub-units failed to give good results, despite the fact that the gradient of the corresponding  $(m, N)$  plot was 0.36. However the methods did give good results with a three sub-unit example and this will be discussed next.

The model structure was based on the molecule 1,3,5-triamino-2,4,6-trinitrobenzene (Cady & Larson, 1965). The structure of this molecule is shown in Fig. 4, the hydrogen atoms of the amino groups being omitted. The envelope enclosing the reference sub-unit is shown as a dotted rectangle, this shape being chosen for ease of calculation of the matrix  $\mathbf{H}$ . The other two sub-units are generated by threefold rotation of the reference sub-unit about the centre of the cell. The gradient of the  $(m, N)$  plot for this arrangement of rectangular sub-units is 0.18. Fig. 5 is a histogram showing the distribution of eigenvalues when the innermost 69 reflexions are included. (Note that this includes only 35 independent reflexions.) It can be seen that the majority of the eigenvalues (50 out of 69) are less than 0.05, so that the application of the matrix  $\mathbf{H}$  will effectively remove a large part of the non-allowed components from the current approximation vector.

The molecule was placed in a square cell of side 9 Å and structure factors were calculated to a resolution of 1.0 Å, with the assumption that all 18 atoms were identical. The result of the Fourier synthesis using these model structure factors is shown in Fig. 6.

The second phasing method was applied to the structure amplitudes. Reflexions were included by bands of 0.10 in  $(2 \sin \theta/\lambda)$ , a new band of reflexions being added when the mean phase change produced by a refinement of the phases already included fell below  $0.1^\circ$ . The phasing procedure converged well and when refinement was terminated the mean phase error, excluding structure factors with very small amplitudes, whose phases are poorly determined, was  $22^\circ$ . The  $R$  value at this point was 14%. A Fourier synthesis using the generated phases and postulated structure amplitudes, gave the result shown in Fig. 7. The chief difference between the calculated structure and the postulated one lies in the relative weights of the atoms rather than their positions. The variation of the mean phase error with  $(2 \sin \theta/\lambda)$  at various stages of refinement is shown in Fig. 8. These plots have a very similar form to those given by Main (1967). In both examples the phase error, which is a rapidly increasing function of  $(2 \sin \theta/\lambda)$  when reflexions out to  $(2 \sin \theta/\lambda) = 0.8$  are included, falls dramatically when reflexions out to 1 Å are included; at this stage only the last band of reflexions to be introduced had bad phase errors.

Application of the first phasing procedure gave very similar results to those already described. The behaviour during refinement of the mean phase error and  $R$  value are shown in Fig. 9. After 150 projections of the complete vector, the mean phase change between projections had fallen to less than  $0.1^\circ$ , at which point the  $R$  value was 13% and the mean phase error  $26^\circ$ . Refinement was continuing but very slowly.

These results suggest that in this case the constraints introduced by the non-crystallographic symmetry are sufficiently strong to generate a reasonably good set of phases. If we regard the problem as one of generating a set of phases to minimize the value of the  $R$  value, we may say that the  $R$  value has a single very shallow minimum; that is, the solution is unique but poorly defined. The absolute difference in  $R$  values produced by substitution of the postulated structure factors into the equations and by refinement is only 1%. These two sets of phases have nevertheless a mean difference of approximately  $20^\circ$ , although the corresponding structures are very similar. The four sub-unit example considered by Main (1967) clearly had a much sharper minimum, which is to be expected since the maximum gradient of the  $(m, N)$  plot for his example, as predicted by the fraction  $(2U/V)$ , is 0.08 and the actual gradient will be even smaller. The gradient of the  $(m, N)$  plot for our example was 0.18.

#### Extension of the theory to two crystal forms

All discussion has been limited to the case where the independent sub-units occur within a single crystal form. Is it possible to extend the theory to the case where a given sub-unit occurs in more than one crystal form, as done by Main & Rossmann (1966)? The problem is of course that the introduction of a new crystal form produces information at a new set of sampling points, rather than simply increasing the information available at the existing lattice points. Suppose we have two crystal forms with structure factor vectors  $F_1$  and  $F_2$ , where, when working to a given

resolution, these vectors lie in two spaces of different dimension. The vectors satisfy equations of the form

$$H_{11}F_1 = F_1 \quad (8)$$

$$H_{22}F_2 = F_2 \quad (9)$$

Either or both of the crystal forms may contain only a single sub-unit in the asymmetric unit, in which case the corresponding equations arise from exclusion of density only (Main & Woolfson, 1963) and not from non-crystallographic symmetry. Constraints arising from exclusion are of the same form as those coming from non-crystallographic symmetry but are much weaker. If the two crystal forms contain identical sub-units, their transforms must in addition satisfy connecting relations of the form

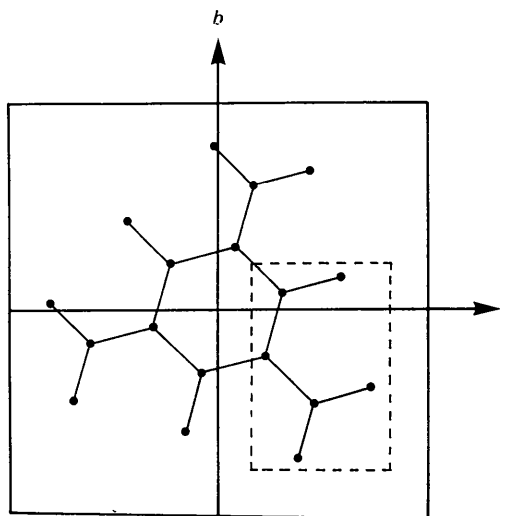


Fig. 4. Model structure based on 1,3,5-triamino-2,4,6-trinitrobenzene. The choice of reference sub-unit is indicated by the dotted rectangle. Other sub-units are generated by threefold rotation about the origin.

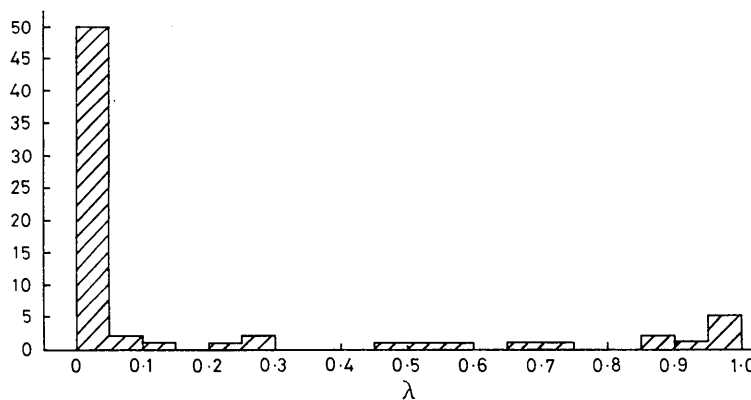


Fig. 5. Histogram showing the distribution of eigenvalues for the arrangement of sub-units given in Fig. 4. The innermost 69 reflexions are included.

$$\begin{aligned} \mathbf{H}_{12}\mathbf{F}_2 &= \mathbf{F}_1 \\ \mathbf{H}_{21}\mathbf{F}_1 &= \mathbf{F}_2 \end{aligned} \quad (10)$$

where  $\mathbf{H}_{12}, \mathbf{H}_{21}$  are rectangular matrices representing mappings from a space of one dimension into another space of different dimension. The meaning of equation (10) is that if we take a structure satisfying the postu-

lated non-crystallographic symmetry of crystal 1 and operate on its transform,  $\mathbf{F}_1$ , with the matrix  $\mathbf{H}_{21}$ , we generate a new vector  $\mathbf{F}_2$  referring to crystal 2. The transform of this vector has sub-units which are identical in structure to the sub-units in crystal 1 but which are arranged according to the non-crystallographic symmetry postulated for crystal 2.

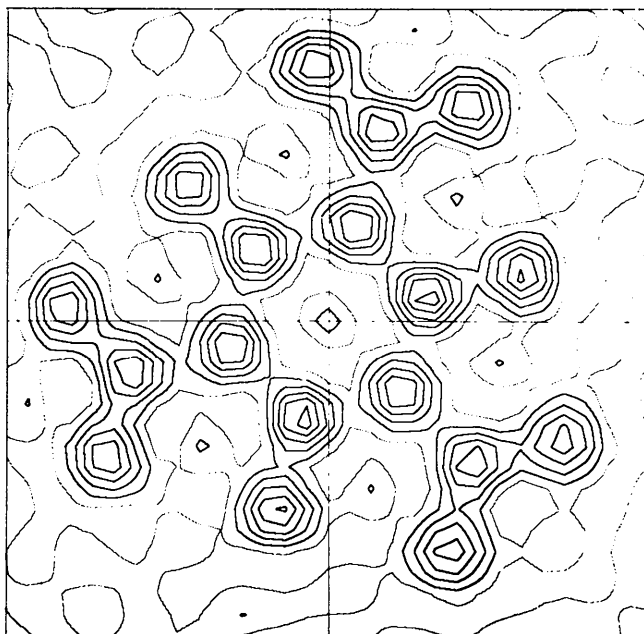


Fig. 6. Fourier synthesis using structure factors computed from the model structure.

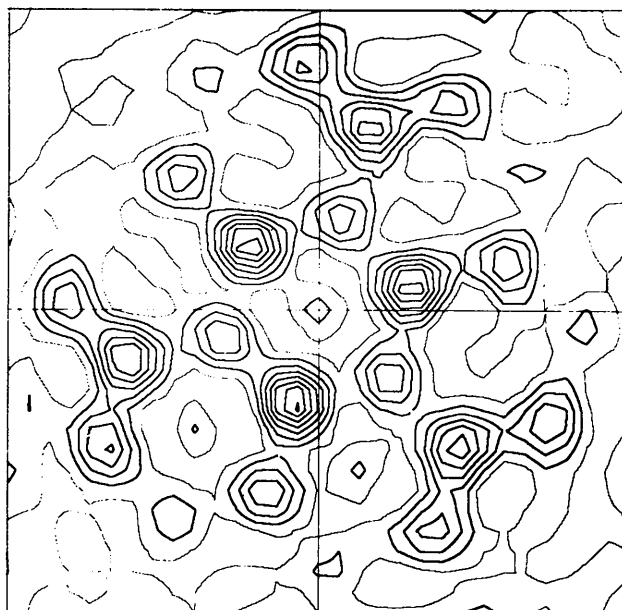


Fig. 7. Fourier synthesis using postulated structure amplitudes and phases generated by the second phasing procedure.

By considering the algebraic form of the connecting equations, which are set up in a similar way to those for a single crystal form with non-crystallographic symmetry (Crowther, 1967), it can be shown that the matrices  $\mathbf{H}_{12}, \mathbf{H}_{21}$  of the two sets of connecting equations are related in a rather simple way. In particular it is possible to write the two sets of connecting equations in terms of a single matrix  $\mathbf{M}$  in the form

$$\mathbf{M}\mathbf{F}_2 = k_2\mathbf{F}_1 \quad (11)$$

$$\mathbf{M}^+\mathbf{F}_1 = k_1\mathbf{F}_2 \quad (12)$$

where  $\mathbf{M}^+$  denotes the complex conjugate of the transpose of  $\mathbf{M}$  and  $k_1, k_2$  are constants depending on the unit-cell sizes of the two crystals and on the numbers of sub-units in the two asymmetric units. In addition the matrices  $\mathbf{M}, \mathbf{M}^+$  can be defined in such a way that they satisfy further relations. To show that this is plausible multiply equation (12) by  $\mathbf{M}$  and substitute from equation (11) to give

$$\mathbf{M}\mathbf{M}^+\mathbf{F}_1 = k_1k_2\mathbf{F}_1.$$

Comparing this with (8) we see that it should be possible to make

$$\frac{1}{(k_1k_2)}\mathbf{M}\mathbf{M}^+ = \mathbf{H}_{11}. \quad (13)$$

Thus if we perform a mapping  $\mathbf{M}^+$  from the first space to the second and then a reverse mapping  $\mathbf{M}$  from the second back to the first, the product of these cross mappings is a mapping in the first space, which expresses the constraints arising from the non-crystallographic symmetry in the first crystal. In a similar way we may show

$$\frac{1}{(k_1k_2)}\mathbf{M}^+\mathbf{M} = \mathbf{H}_{22}. \quad (14)$$

The relations imply that if we find vectors  $\mathbf{F}_1, \mathbf{F}_2$  which satisfy (11) and (12), they will also automatically satisfy (8) and (9). When we include only a finite number of reflexions from the two crystals, the matrix products  $\mathbf{M}\mathbf{M}^+, \mathbf{M}^+\mathbf{M}$  will suffer truncation effects which make (13) and (14) only approximately true. However only those reflexions lying on the edge of the region of reciprocal space being considered will be significantly affected.

We now wish to know whether there is a method of using (11) and (12) for structure determination. Since (11) and (12) define mappings between spaces of different dimension, it is not possible to apply the eigenvalue analysis directly. However by adding respectively  $k_1\mathbf{F}_1, k_2\mathbf{F}_2$  to equations (11) and (12) we obtain

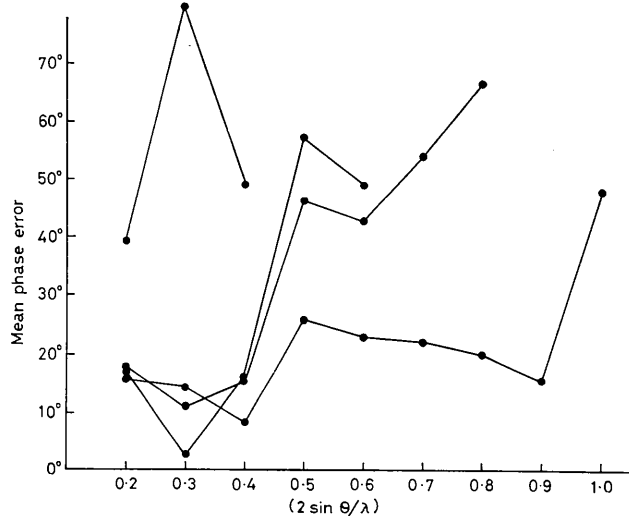


Fig. 8. Distribution of the mean phase error at various stages of refinement during the second phasing procedure.

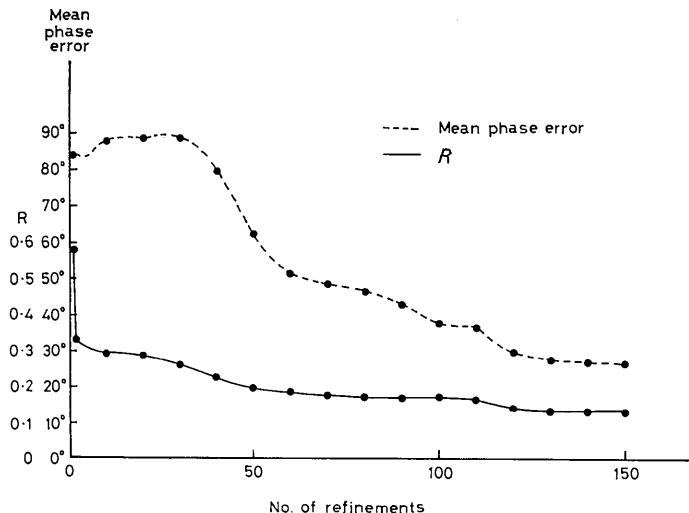


Fig. 9. Behaviour of the mean phase error and  $R$  value during phase determination by the first phasing procedure.



$$k_1\mathbf{F}_1 + \mathbf{M}\mathbf{F}_2 = (k_1 + k_2)\mathbf{F}_1, \quad (15)$$

$$\mathbf{M}^+\mathbf{F}_1 + k_2\mathbf{F}_2 = (k_1 + k_2)\mathbf{F}_2. \quad (16)$$

These may be written in partitioned matrix form as

$$\begin{pmatrix} k_1\mathbf{I} & \mathbf{M} \\ \mathbf{M}^+ & k_2\mathbf{I} \end{pmatrix} \begin{pmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{pmatrix} = (k_1 + k_2) \begin{pmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{pmatrix}$$

where  $\mathbf{I}$  is the identity matrix. Putting

$$\hat{\mathbf{H}} = \frac{1}{(k_1 + k_2)} \begin{pmatrix} k_1\mathbf{I} & \mathbf{M} \\ \mathbf{M}^+ & k_2\mathbf{I} \end{pmatrix}, \quad \hat{\mathbf{F}} = \begin{pmatrix} \mathbf{F}_1 \\ \mathbf{F}_2 \end{pmatrix}$$

this becomes

$$\hat{\mathbf{H}}\hat{\mathbf{F}} = \hat{\mathbf{F}}. \quad (17)$$

Thus we can represent the two sets of equations (11) and (12) by a single set of equations in a compound space of dimension equal to the sum of the dimensions of the separate transform spaces. The matrix  $\hat{\mathbf{H}}$  is hermitian and can be shown to have an eigenvalue spectrum satisfying  $0 \leq \lambda_j \leq 1$ . Equations (20) describing the non-crystallographic symmetry constraints in the two crystal case therefore have an identical form to those arising from non-crystallographic symmetry in a single form.

The strength of constraints introduced by having two crystal forms can now be measured by the gradient of the  $(m, N)$  plot for the matrix  $\hat{\mathbf{H}}$  in just the same way as for the single crystal case, except that now the number of unit eigenvalues is plotted against the sum of the number of independent reflexions included for each crystal. Similarly (20) can be used as a basis for an iterative phasing procedure, of the same type as that described for a single crystal, except that now between applications of matrix  $\hat{\mathbf{H}}$  the two parts of the vector  $\hat{\mathbf{F}}$  must be scaled to the structure amplitudes appropriate for the two crystal forms. In practice, because of the special form of  $\hat{\mathbf{H}}$ , it is convenient to rewrite (17) for the iteration as:

$$\mathbf{G}_1^{(r+1)} = (\mathbf{M}\mathbf{F}_2^{(r)} + k_1\mathbf{F}_1^{(r)})/(k_1 + k_2)$$

$$\mathbf{G}_2^{(r+1)} = (\mathbf{M}^+\mathbf{F}_1^{(r)} + k_2\mathbf{F}_2^{(r)})/(k_1 + k_2),$$

where  $\mathbf{G}_1^{(r+1)}, \mathbf{G}_2^{(r+1)}$  are to be rescaled to the structure amplitudes appropriate for the two crystals. A computer program written to perform the iteration need only store the matrix  $\mathbf{M}$ , which has far fewer elements than  $\hat{\mathbf{H}}$ .

### Summary

The results described in this paper, taken in conjunction with those of Main (1967), are encouraging. They suggest that although the presence of two identical sub-units in the asymmetric unit is not a sufficiently strong constraint to generate reliable phase information, the presence of three or four such sub-units can provide reliable phase information. In particular the gradient of the  $(m, N)$  plot, which gives a measure of the strength of the constraints introduced by the non-

crystallographic symmetry, must be less than about 0.2 and preferably even smaller.

## APPENDIX

### The gradient of the $(m, N)$ plot

Although in any given case the gradient of the  $(m, N)$  plot can be found by computing the eigenvalue spectrum of the matrix  $\mathbf{H}$  when it is truncated at different resolutions, it would be useful if an estimate could be made without going through this tedious computation. The argument given in Crowther (1967), which predicts that the gradient is  $1/n$  in the case where the asymmetric unit contains  $n$  sub-units, is incorrect and should be replaced by the following.

Let us take  $n$  equal sub-units of size  $U$  in a one-dimensional unit cell of size  $V$ , so that the sub-units occupy a fraction  $(nU/V)$  of the unit cell and let us consider reflexions out to  $h = N$  say. The Fourier terms corresponding to these reflexions form, to this resolution, a complete set of functions in the mathematical sense. There are  $(2N + 1)$  such terms, namely  $F_0, A_1, B_1, \dots, A_N, B_N$ . We may take independent linear combinations of these terms to form eigendensities, of which a fraction  $(nU/V)$  will have density only within the sub-units, while the remaining fraction  $(1 - nU/V)$  will have density only in the gaps between the sub-units. This means that we can construct  $(nU/V)(2N + 1)$  independent densities which vanish outside the sub-units. By considering the symmetry of these functions, it is clear that only  $1/n$  of them can be chosen to give equal densities within the sub-units; that is, only a fraction  $1/n$  of them correspond to allowed eigendensities. We therefore have the relation:

$$m = \frac{1}{n} \binom{nU}{V} (2N + 1)$$

or

$$m \simeq \left( \frac{2U}{V} \right) N.$$

We therefore predict that the gradients of the various  $(m, N)$  plots for different numbers of sub-units, shown in Crowther (1967), (Fig. 4), should be given by  $(2U/V)$ . Table 1 shows this prediction to be very good.

Table 1. Agreement between observed and predicted gradients of  $(m, N)$  plots for some one-dimensional examples

Number of sub-units	Predicted gradient $(2U/V)$	Observed gradient
2	0.71	0.70
3	0.58	0.56
4	0.42	0.40

In two- and three-dimensional examples the agreement between predicted and observed gradients is not nearly so good. This is for the following reason. We have divided the original set of functions into a set

complete on the sub-units and a set complete on the gaps, both sets vanishing on the sub-unit boundaries. Clearly the original set of functions can give non-zero densities on the sub-unit boundaries. In one dimension, where the boundaries are points, this distinction is not important. In two- and three-dimensions where the boundaries become respectively closed curves and surfaces, the effect is significant and means that the observed gradient of the  $(m, N)$  plots for two- and three-dimensional examples is always less than  $(2U/V)$ .

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### The Crystal Structure of Tris(cyclopentadienyl)samarium (III).\*

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The crystal structure of tris(cyclopentadienyl)samarium (III),  $\text{Sm}(\text{C}_5\text{H}_5)_3$ , has been determined by analysis of three-dimensional X-ray diffraction data. The crystals are orthorhombic, space group  $Pbcm$ , with eight chemical formula units per unit cell. Cell dimensions are:  $a = 14.23$ ,  $b = 17.40$  and  $c = 9.73$  Å. The heavy atom positions were deduced from Patterson projections, and cyclopentadienyl rings were found from difference syntheses. The final  $R$  value for the 1266 observed reflexions is 12.5%. The eight  $\text{Sm}(\text{C}_5\text{H}_5)_3$  in the unit cell are divided into two symmetrically independent, and structurally different groups ( $A$  and  $B$ ). The  $A$  and  $B$  groups form close-packed infinite chains along the  $c$  axis and the  $A$  and  $B$  chains alternate in layers parallel to (100) with an average spacing of  $\frac{1}{2}a$ . In either group, the samarium atom could be described as having a distorted tetrahedral environment and approximately three pairs of electrons are responsible for the bonding between the metal atom and the cyclopentadienyl rings. Both types of structures are disordered, and a plausible mechanism for the disorder is discussed.

#### Introduction

This paper deals with the crystal structure determination of tris(cyclopentadienyl)samarium(III),  $\text{Sm}(\text{C}_5\text{H}_5)_3$ . The present work is the second of a series on the study of metal-cyclopentadienyls (Wong, Yen, & Lee, 1965), and  $\text{Sm}(\text{C}_5\text{H}_5)_3$  is the first rare earth tris(cyclopentadienyl) complex ever to be studied.

This compound has been reported as having a pure electrostatic type of bonding (Birmingham & Wilkinson, 1956). However, in view of the much darker colour of the compound in its crystalline state (orange red) as compared with the samarium ion (light yellow), and the low sublimation temperature ( $\sim 160^\circ\text{C}$  in vacuum), we suspect that the bonding may be somewhat covalent. Also, there exists almost no structural information concerning bonding between rare earth metal

and organo-carbon atoms. For the above reasons, we feel that careful structural study of this compound is of interest.

#### Experimental

The air and moisture sensitive compound was synthesized in this laboratory according to Birmingham & Wilkinson (1956). The single crystals used were grown by sublimation at  $\sim 160^\circ\text{C}$  under reduced pressure in thin-walled Pyrex capillaries. Laue photographs showed it to be of  $mmm$  symmetry; zero-layer Weissenberg photographs taken along the three principal axes, with  $\text{Mo } K\alpha$  radiation, showed the following systematic absences:  $h00$  for  $h$  odd,  $0kl$  for  $k$  odd and  $h0l$  for  $l$  odd, which would make the space groups  $Pbcm$  or  $Pbc2_1$ , most probable. However, in either case the extinction condition  $h00$  for  $h$  odd had to be considered as incidental. The centrosymmetric space group  $Pbcm$  was tentatively chosen, and it was later shown to be correct. For data collection, the equi-inclination, multiple-film Weissenberg technique was used with Zr-filtered  $\text{Mo } K\alpha$  radiation. Copper foils were inserted be-

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