Acta Cryst. (1959). **12**, 957

Syntheses for the Deconvolution of the Patterson Function. Part I. General Principles

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(*Received* 19 *March* 1959)

The paper deals with a series of Fourier syntheses which have been worked out for 'developing' a structure when information is available about a part of the structure, i.e., when some of the atomic positions are known. The syntheses are of two classes, which have been named the alpha and beta classes. In the former class, a suitable combination of the measured intensities, namely $|F(H)|^2$, with the intensities due to the known group of atoms alone, say $|F_P(H)|^2$, is multiplied by $F_P(H)$, the structure factor of the known atoms, and these are used as coefficients in a Fourier synthesis. In the beta class, the same combination is divided by $F_P^*(H)$ and then used as coefficients in the Fourier synthesis. In both classes of syntheses, there is a concentration of electron density at the positions of the unknown atoms. In each class, four different types of syntheses have been suggested according to the nature of the available data, e.g., if only a single crystal is available, or if an isomorphous pair is available, or if some atoms in the single crystal exhibit anomalous dispersion and so on.

The unwanted background is least in the case of isomorphous and anomalous syntheses, of which the latter is the more powerful one. The syntheses are particularly useful with non-centrosymmetric crystals, although, if the known group of atoms have a centre of symmetry, then the syntheses also exhibit an artificial inversion centre. The general theory is discussed in this paper, while the detailed proofs are given in Part II.

1. Introduction

As is well known, it is possible to obtain the Patterson diagram of a crystal structure by performing a Fourier synthesis, using the measured intensities ($|F(hkl)|^2$) as coefficients. This diagram gives the autocorrelation function of the electron-density distribution in the crystal, and contains peaks at positions corresponding to the interatomic vectors between the atoms in the crystal, i.e.,

$$\mathbf{p}_k=\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j \quad (i, j=1 \text{ to } N)\,, \tag{1}$$

where N is the total number of atoms in the unit cell. It is also obvious that, if no further information about the structure is available, other than the measured values of $|F|^2$, then the Patterson contains all the information that is contained in the measured data. This follows because if F is the Fourier transform of the structure (ϱ say), then ϱ is obtained by inverting this transform, by using the data on F. Since only $|F|^2$ are measured, its Fourier transform would give, in real space, all the information about the structure which is contained in the measured data.

This argument may be made clearer by taking the usual representation of the electron-density distribution in an actual crystal, namely in terms of individual atoms. If the scattering powers of these atoms ($j=1$ to N) are denoted by f_j, then, as is well known,

$$|F(hkl)|^2=\left|\sum_1^N f_j \exp 2\pi i(hx_j+ky_j+lz_j)\right|^2 \tag{2}$$

$$=\sum_{i=1}^N \sum_{j=1}^N f_i f_j \cos 2\pi(hu_{ij}+kv_{ij}+lw_{ij})\,, \tag{3}$$

where

$$(u_{ij}, v_{ij}, w_{ij})=\mathbf{r}_{ij}\,.$$

It is obvious from the form of this function that no information about the individual atomic coordinates x_j, y_j, z_j is contained in the Patterson, but only that about the interatomic vectors u_{ij}, v_{ij}, w_{ij}.

Thus, in principle, the determination of the actual structure from the X-ray data (which for all practical purposes is equivalent to the determination of the atomic coordinates x_j, y_j, z_j) is equivalent to the deduction of the atomic coordinates from the interatomic vectors, by making use of auxiliary data, other than the intensities. The need for using auxiliary data must be particularly emphasized for it is often stated in the literature on the subject that a structure has been solved purely from the intensities, using say, inequality methods, or probability methods etc. In all these cases, the auxiliary data which have been fed in are not explicit. The inequality method is not very useful if the number of atoms in the unit cell is large and the atoms are all alike. If, on the other hand, the number is small, or if a small number of atoms are heavy, then their interactions are distinguishable in the Patterson diagram, and this could form as good a starting point for solving the structure as the inequality methods. Thus, a careful study of the auxiliary information which is fed in for structure analysis should be of great help in developing general methods for the analysis of crystal structures.

A general survey of this type is reserved for a later paper. In this paper, it is proposed to study the effect of one type of such auxiliary information, namely the knowledge of a part of the structure. This often happens during the process of structure analysis. Thus, in the heavy atom technique, the positions of the heavy atoms can be found out and in the isomorphous replacement technique, the configuration of the group of replaceable atoms is also generally determinable. If the crystal is centrosymmetric, this information helps to obtain the signs of a number of reflections. In the non-centrosymmetric case, no such definite information is available, although it may lead to a limitation of the phase angle. It is the purpose of this paper to discuss what are the best types of syntheses which can be employed making use of the partial information about the structure. It is found that any such partial information about the atomic positions can be fed in to obtain a better picture of the structure than what was available before. In other words, it should be possible to 'develop' a structure from the partial knowledge, making use of the intensity data.

It is, perhaps, of interest to mention that the present study arose from a systematic discussion of the Difference-Patterson (D.P.) technique (Kartha & Ramachandran, 1955) from the Fourier-synthesis point of view. Buerger (1950) has shown that, in principle, a vector set (Patterson) can be solved for the fundamental set (namely the structure). Thus, the structure is there right in the Patterson; it has only to be extracted out. The D.P. is one of the methods of doing this. It was shown that by using the superposition method, it is possible to solve the D.P. for the structure uniquely, except in the case of a non-centrosymmetric structure in which the set of replaceable atoms has centre of symmetry, when there is a duplication of the structure by an artificial centre of symmetry. The attempt to interpret these results from the point of view of Fourier synthesis led to the various syntheses to be discussed in this paper.*

In the last section of the paper, a method is also suggested for obtaining the structure from the Patterson alone without having even partial information about any of the atomic positions, but using the knowledge about the number and nature of the atoms in the structure. This method is likely to succeed best when all the atoms are alike, a case which is not amenable to the other techniques to be discussed in this paper in which the 'heaviness' of a group of atoms is made use of.

In order that the treatment may be readily followed by the non-theorists, Part I will not deal with the most general form of the theory. Instead, the special cases of isomorphous structures and structures containing anomalous scatterers will be discussed, which show how the two classes of syntheses, designated as the alpha and beta class arise in a natural way. A brief summary of the main results obtained in the investigation and of the properties of the proposed new syntheses are also included in this paper. The proof of these, together with other theoretical considerations are reserved for Part II. All the formulae are derived for a non-centrosymmetric crystal in this paper. The modifications, if any, required for centrosymmetric structures are indicated in the succeeding parts.

2. Statement of the problem and main results

We suppose that the positions of a (small) number P out of a total of N atoms in the unit cell are known, so that the number of unknown atoms is $Q=N-P$. The subscripts N_j, P_j and Q_j will denote one of the atoms of the category N, P and Q respectively and in each case, the summation over j will be over the appropriate number. Thus, the structure factor F_N of the whole crystal for a reflection denoted by the index $\mathbf{H}$ (which stands for the triplet h, k, l and also represents the corresponding reciprocal vector), is

$$F_N(\mathbf{H})=\sum_{j=1}^{N} f_{Nj} \exp 2\pi i \mathbf{H}.\mathbf{r}_{Nj}=|F_N| \exp i\alpha_N \quad (4)$$

and the structure factor of the P-atoms is

$$F_P(\mathbf{H})=\sum_{j=1}^{P} f_{Pj} \exp 2\pi i \mathbf{H}.\mathbf{r}_{Pj}=|F_P| \exp i\alpha_P\ . \quad (5)$$

In general, we know $|F_N|^2$, the intensities of the reflections given by the whole crystal, and also F_P, the structure factor of the P-atoms both in magnitude and phase, since the positions of these atoms are assumed to be known. In addition, f_{Qj} the atomic scattering factors of the other atoms are also known.

Making use of these data, two classes of Fourier syntheses have been worked out for developing the structure. The first, called the α-class, has as coefficients the product of $|F_N|^2$ with F_P in the general case, and the second, called the β-class makes use of the quotient of $|F_N|^2$ by F_P^* (where F_P^* is the complex conjugate of F_P) in the general case. The two syntheses thus make use of the coefficients

$$\alpha_{\text{gen}}=|F_N|^2|F_P| \exp i\alpha_P \quad (6)$$

and

$$\beta_{\text{gen}}=(|F_N|^2/|F_P|) \exp i\alpha_P\ . \quad (7)$$

We shall use the equality symbol, as in the above equations, to denote the Fourier synthesis in which

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* It was interesting that the D.P. can be solved by geometrical methods (e.g. by vector shift methods), while the Fourier method seemed to fail because of ambiguity in phase determination. This was pointed out to the senior author by Prof. P. P. Ewald, commenting on the paper on the Difference-Patterson. This comment of Prof. Ewald was the germ from which this whole investigation has grown and we should like to record our indebtedness to him for his pregnant remark. It turns out that the 'double-phased' Fourier synthesis does reveal the structure in the non-centric case, as shown in section 3.

Table 1. *Coefficients to be used in the different α- and β-syntheses and list of peaks occurring in each.*

Negative peaks are indicated by a bar over their symbols

The set 4·1 are the required peaks

Type of synthesis	Coefficient	Peaks
α_{gen}	$\lvert F_N\rvert^2\lvert F_P\rvert \exp i\alpha_P$	1·1, 1·2, 2·1, 2·2, 3·1, 3·2, 4·1, 4·2
α_{mod}	$(\lvert F_N\rvert^2-\lvert F_P\rvert^2-\sum_j f^2_{Qj})\lvert F_P\rvert \exp i\alpha_P$	2·2, 3·1, 3·2, 4·1, 4·2
α_{is}	$(\delta\lvert F_N\rvert^2-\delta\lvert F_P\rvert^2)\lvert F_P\rvert \exp i\alpha_P$	3·1, 3·2, 4·1, 4·2
α_{an}	$[\frac{1}{2}\varDelta\lvert F_N\rvert^2-(F'_PF''^*_P+F'^*_PF''_P)]\lvert F''_P\rvert \exp i\alpha''_P$	$\bar{3}\cdot\bar{1}$, $\bar{3}\cdot\bar{2}$, 4·1, 4·2
β_{gen}	$\alpha_{\text{gen}}/\lvert F_P\rvert^2$	1·1, $\bar{1}\cdot\bar{2}$, 2·1, 2·2, 3·1, 3·2, 4·1
β_{mod}	$\alpha_{\text{mod}}/\lvert F_P\rvert^2$	2·2, 3·1, 3·2, 4·1
β_{is}	$\alpha_{\text{is}}/\lvert F_P\rvert^2$	3·1, 3·2, 4·1
β_{an}	$\alpha_{\text{an}}/\lvert F''_P\rvert^2$	$\bar{3}\cdot\bar{1}$, $\bar{3}\cdot\bar{2}$, 4·1

the quantities on the right hand side are used as coefficients. Thus, equation (6) represents the Fourier summation

$$\alpha_{\text{gen}}=\sum_{\mathbf{H}}\lvert F_N(\mathbf{H})\rvert^2\lvert F_P(\mathbf{H})\rvert \exp[-i2\pi\mathbf{H}.\mathbf{r}+i\alpha_P(\mathbf{H})]. \tag{8}$$

It can be shown that both the α- and β-class of syntheses tend to deconvolute the Patterson function and yield the structure, although against a background of unwanted peaks. The ratio of the heights of the wanted to the unwanted peaks is of the order of P, the number of known atoms, and the background in the case of β-syntheses is always much less than for the α-class. In either case, the background can be considerably reduced by modifying the coefficient of the synthesis from that given above for the general case. Thus even in the absence of any other information, one knows

$$\sum_{j=1}^{Q} f^2_{Qj}$$

in addition to F_P. Thus, one may calculate the modified α-synthesis

$$\alpha_{\text{mod}}=[\lvert F_N\rvert^2-\lvert F_P\rvert^2-\sum_j f^2_{Qj}]\lvert F_P\rvert \exp i\alpha_P \tag{9}$$

and the modified β-synthesis

$$\beta_{\text{mod}}=\frac{[\lvert F_N\rvert^2-\lvert F_P\rvert^2-\sum_j f^2_{Qj}]}{\lvert F_P\rvert}\exp i\alpha_P\,, \tag{10}$$

in which there would be no peaks in the positions of the known atoms P, and the background would also be reduced.

Further reduction is possible in the special cases when the group of P known atoms are the replaceable atoms of a pair of isomorphous crystals, or when they constitute a group of anomalous scatterers. The corresponding syntheses are, with isomorphous crystals,

$$\alpha_{\text{is}}=[\delta\lvert F_N\rvert^2-\delta\lvert F_P\rvert^2]\,\lvert F_P\rvert \exp i\alpha_P \tag{11}$$

$$\beta_{\text{is}}=\alpha_{\text{is}}/\lvert F_P\rvert^2 \tag{12}$$

where

$$\delta\lvert F_N\rvert^2=\lvert F^{(1)}_N\rvert^2-\lvert F^{(2)}_N\rvert^2,\;\;\delta\lvert F_P\rvert^2=\lvert F^{(1)}_P\rvert^2-\lvert F^{(2)}_P\rvert^2 \tag{13a}$$

and

$$F_P=F^{(1)}_P-F^{(2)}_P,\;\;\alpha_P=\alpha^{(1)}_P=\alpha^{(2)}_P. \tag{13b}$$

The superscripts (1) and (2) stand for the two isomorphous crystals. It will be noticed that $\delta\lvert F_N\rvert^2$ is known from experiment and $\delta\lvert F_P\rvert^2$ and F_P are calculable from the known positions of the replaceable atoms.

With a crystal containing anomalous scatterers, if

$$\varDelta\lvert F(\mathbf{H})\rvert^2=\lvert F(\mathbf{H})\rvert^2-\lvert F(-\mathbf{H})\rvert^2,$$

namely the intensity difference between a pair of inverse reflections, and if F'_P, F''_P are the structure amplitudes of the P-atoms contributed by the real (f'_{Pj}) and imaginary ($i\varDelta f''_{Pj}$) components of the atomic scattering factors f_{Pj}, then we can form the anomalous α-synthesis:

$$\alpha_{\text{an}}=[\tfrac{1}{2}\varDelta\lvert F_N\rvert^2-(F'_PF''^*_P+F'^*_PF''_P)]\lvert F''_P\rvert \exp i\alpha''_P \tag{14}$$

and the anomalous β-synthesis:

$$\beta_{\text{an}}=\alpha_{\text{an}}/\lvert F''_P\rvert^2. \tag{15}$$

It may be mentioned that the second term within the square bracket in equations (14) and (15) vanishes when the anomalous scatterers (P-atoms) are all of one type of atom. The two syntheses then become identical with the $\alpha^{\circ}_{\text{an}}$- and $\beta^{\circ}_{\text{an}}$-syntheses discussed in section 4.

Table 2. *Positions of the peaks occurring in the various syntheses*

The designation follows that in Part II

For the relative weights and number of peaks in the α- and β-class, see Tables 1 and 2 of Part II

Designation	Position	Description
1.1	$\mathbf{r}_{Pj}$	Known
1.2	$\mathbf{r}_{Pi}-\mathbf{r}_{Pj}+\mathbf{r}_{Pk}\;\;(i\neq j)$	Unwanted
2.1	$\mathbf{r}_{Pj}$	Known
2.2	$\mathbf{r}_{Qi}-\mathbf{r}_{Qj}+\mathbf{r}_{Pk}\;\;(i\neq j)$	Unwanted
3.1	$2\mathbf{r}_{Pi}-\mathbf{r}_{Qk}$	Unwanted
3.2	$\mathbf{r}_{Pi}+\mathbf{r}_{Pj}-\mathbf{r}_{Qk}\;\;(i\neq j)$	Unwanted
4.1	$\mathbf{r}_{Qj}$	Wanted
4.2	$\mathbf{r}_{Pi}-\mathbf{r}_{Pj}+\mathbf{r}_{Qk}\;\;(i\neq j)$	Unwanted

The various syntheses are summarized in Tables 1 and 2. Table 1 contains the coefficients to be employed and the positions of the wanted and unwanted peaks in each case. The peaks are denoted by numbers, from (**1.1**) to (**4.2**) in this table, and the corresponding coordinates, the number and weight of the peaks are given in Table 2.

The relative advantages of the different syntheses will be considered in detail later. Here, we may mention that, as one goes down Table 1, the background will be noticed to get progressively reduced both in the α- and β-class of syntheses. In the syntheses using data from anomalous scatterers, the background becomes partly negative in the α- and wholely negative in the β-class. In general, the background is less in the β-syntheses than in the α-class of syntheses.

Although the various syntheses have been derived in a systematic manner in the present investigation, it should be mentioned that some of the β-syntheses, namely β_{gen} and two syntheses closely similar to β_{mod} and β_{is} have been previously mentioned by Rogers (1951). The authors were not aware of this paper during the development of the work reported here and they are grateful to Prof. A. J. C. Wilson for drawing their attention to it.

We shall now consider the genesis of the two classes of syntheses, α and β.

3. Significance of the α- and β-classes of syntheses

The essential properties of the α- and β-syntheses are best understood with reference to a pair of isomorphous crystals. Suppose there are N atoms in the unit cell of both the crystals, P of which in one are replaced by P other atoms in the other. Let $f_{Pj}^{(1)}$ and $f_{Pj}^{(2)}$ be the atomic scattering factors of the two types of atoms and let $F_N^{(1)}$ and $F_N^{(2)}$ represent the structure amplitudes of the two crystals. If, as before, we denote by Q the rest of the atoms, which occur in the same positions in both the crystals, then

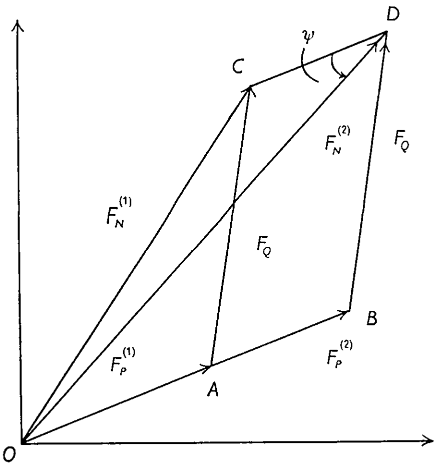

Fig. 1. Relation between structure amplitude vectors with isomorphous crystals

$$F_N^{(1)}=F_P^{(1)}+F_Q, \quad F_N^{(2)}=F_P^{(2)}+F_Q \tag{16}$$

where

$$F_N^{(1),(2)}=\Sigma f_{Pj}^{(1),(2)} \exp 2\pi i \mathbf{r}_{Pj}.\mathbf{H}\,. \tag{17}$$

The relationships between these vectors are shown in Fig. 1 in which their phases are also marked. It is in general possible to find the positions of the replaceable atoms (P), e.g. by an analysis of the Difference-Patterson (Kartha & Ramachandran, 1955). Consequently, both the magnitude and phase of $F_P^{(1)}$ and $F_P^{(2)}$ and consequently of their difference

$$F_P=F_P^{(1)}-F_P^{(2)}=|F_P| \exp i\alpha_P \tag{18}$$

can be calculated. From experiment, the magnitudes of $|F_N^{(1)}|$ and $|F_N^{(2)}|$ are known. Consequently, the triangle OCD of Fig. 1 is fully known and can be solved. If we denote the angle at D by ψ, then the phase of $F_N^{(2)}$ is $\alpha_N^{(2)}=\alpha_P\pm\psi$. The ambiguity occurs because of the well known reason that only $\cos\psi$ is determined by the conditions of the problem, being

$$\cos\psi=\{|F_N^{(1)}|^2-|F_N^{(2)}|^2-|F_P|^2\}/\{2|F_P||F_N|\}\,. \tag{19}$$

This ambiguity cannot be resolved with a single pair of isomorphous crystals. However, let us examine what can be done without any other auxiliary data. Recasting equation (19), we may write it in the form

$$|F_N^{(1)}|^2-|F_N^{(2)}|^2-|F_P|^2=2|F_P||F_N^{(2)}| \cos\psi \tag{20a}$$

where

$$\psi=\alpha_N^{(2)}-\alpha_P\,. \tag{20b}$$

The quantity on the left hand side of equation (20a) may be obtained purely from experiment, once the positions of the P-atoms are known. Consider, therefore, the significance of the right hand side. Writing the cosine in terms of exponential functions, we have

$$\begin{aligned}2|F_P||F_N^{(2)}| \cos\psi\\ &=|F_N^{(2)}| \exp[i\alpha_N^{(2)}]|F_P| \exp[-i\alpha_P]\\ &\quad+|F_N^{(2)}| \exp[-i\alpha_N^{(2)}]|F_P| \exp[i\alpha_P]\\ &=F_N^{(2)}F_P^*+F_N^{(2)*}F_P\,,\end{aligned} \tag{21}$$

where F^* stands for the complex conjugate of F, i.e., the structure factor of a structure which is the inverse of the original one.

It may be readily shown (e.g. by the methods worked out in Part II) that, if one performs a Fourier synthesis using as coefficients the quantities given in equation (21) then the synthesis will contain peaks at $\mathbf{r}_{Ni}-\mathbf{r}_{Pj}$ and at $-(\mathbf{r}_{Ni}-\mathbf{r}_{Pj})$ with strengths $f_{Ni}f_{Pj}$ respectively. Thus, this diagram will contain many fewer peaks than the Patterson diagram, although it is still in the nature of a vector diagram. However, the structure N may be obtained from it by the following two methods:

(a) *Multiplicative technique.—The α-synthesis*

Consider the Fourier synthesis in which one uses the following coefficients, instead of those in equations (20) or (21)

$$\begin{aligned}\alpha^{\circ}_{\text{is}} &= (|F_N^{(1)}|^2-|F_N^{(2)}|^2-|F_P|^2)F_P\\ &= 2|F_P|^2|F_N^{(2)}| \exp{[i\alpha_P]} \cos\psi\,. \qquad (22)\end{aligned}$$

The notation $\alpha^{\circ}_{\text{is}}$ is used to distinguish it from α_{is} in equation (11). The right hand side of equation (22) may be put in the form

$$F_N^{(2)}|F_P|^2+F_N^{(2)*}F_P^2\,.$$

Taking the first of the two terms in the above expression, it is seen to lead to a modulation† of the structure to be determined (viz. $N^{(2)}$) by the Patterson of the replaceable P-atoms. It can be shown (as is proved in Part II) that this contains strong peaks at the atomic positions of the required structure N, besides a number of other peaks, whose strengths individually are only $(1/P)$ times that of the required peaks. So also, the second term leads only to a number of dispersed spurious peaks. The essential point is that there is a P-fold concentration (or superposition) of peaks at the required positions (viz. of the N atoms) but not elsewhere.

It is interesting to consider the physical significance of the synthesis $\alpha^{\circ}_{\text{is}}$ using the coefficients in equation (22). First of all consider the synthesis

$$\sum_{\mathbf{H}} (|F_N^{(1)}|^2-|F_N^{(2)}|^2-|F_P|^2) \exp -2\pi i\mathbf{H}.\mathbf{r}\,. \qquad (23)$$

If only $(|F_N^{(1)}|^2-|F_N^{(2)}|^2)$ is used, then this is the Difference-Patterson, which contains peaks only at the positions corresponding to P–P and P–Q types of vectors. On the other hand, $|F_P|^2$ alone leads to the Patterson of the P-atoms, i.e., to the P–P vectors, but their peak strengths are less than in the D–P. So, if this is subtracted from the D–P, we are left with the P–Q in addition to the P–P vectors of diminished strength.

Now, the coefficients in the above expression are multiplied by F_P in equation (22). We may write F_P in the form‡

$$F_P = \sum_j f_j \exp 2\pi i\mathbf{H}.\mathbf{r}_j\,.$$

Taking one of the two terms on the right hand side (say with $j=1$) and multiplying into (23) we get

$$\sum_{\mathbf{H}} (|F_N^{(1)}|^2-|F_N^{(2)}|^2-|F_P|^2)f_1 \exp -2\pi i\mathbf{H}.(\mathbf{r}-\mathbf{r}_1)\,.$$

The effect is readily seen to be equivalent to multiplying the values of the synthesis (23) by f_1 and shifting by the vector $\mathbf{r}_1$. Thus, the effect of multiplying each term of the synthesis (23) by F_P and thus obtaining (22) is equivalent to performing the following geometrical operation on the diagram containing the P–P and P–Q vectors: Multiply the value of the function at all points in the diagram by f_1 and shift by $\mathbf{r}_1$, by f_2 and shift by $\mathbf{r}_2$ etc. and add the resultant values at each point.

This is clearly the so-called 'weighted sum function'. It has been shown in the paper on Difference-Patterson (Kartha & Ramachandran, 1955) that the above geometric operation can lead to the structure from the D–P.

Exactly the same interpretation may be given to all the four α-syntheses—viz., they are all weighted sum functions. Only the original diagrams on which they operate are different in each case. In the case of α_{gen}, it is the complete Patterson; with α_{mod}, the P–P vectors are removed; and so on.

(b) *Division technique.—The β-synthesis*

There is another way in which the expression (21) can be modified to obtain a synthesis leading to the structure N; this is by dividing each term by F_P^*. Thus, one uses as coefficients

$$\begin{aligned}\beta^{\circ}_{\text{is}} &= \frac{(|F_N^{(1)}|^2-|F_N^{(2)}|^2-|F_P|^2)}{|F_P|} \exp{[i\alpha_P]}\\ &= 2|F_N^{(2)}| \cos\psi \exp{[i\alpha_P]}\,. \qquad (24)\end{aligned}$$

The right hand side now takes the form (omitting superscript 2)

$$\begin{aligned}|F_N| \exp{[i\alpha_N]}+|F_N| \exp{[-i\alpha_N]} \exp{[i2\alpha_P]}\\ = F_N+F_N^* \exp{[i2\alpha_P]}\,. \qquad (25)\end{aligned}$$

The first term leads straightway to the required structure N. The second term leads to a modulation of the inverse of the required structure by the so-called 'phase-squared' structure of the replaceable atoms P. The effect of this is discussed in detail in Part II, but here we may mention that it leads to a distribution of minor peaks, but does not lead to a concentration, if the replaceable atoms form a non-centrosymmetric group. Once again, the ratio of the peak heights at the required positions and elsewhere is of the order of P:1.

It may be wondered why division by F_P^* succeeds in the same way as multiplication by F_P in resolving the Patterson, or vector diagram of a structure. The answer is obtained by a study of a Fourier synthesis using $(1/F_P^*)$ as coefficient. This is considered in detail in the Appendix to Part II, where it is shown that it has large peaks exactly at the positions corresponding to the original P-atoms (i.e. at $\mathbf{r}_{Pj}$), with some extra minor peaks. Thus, the synthesis with $(1/F_P^*)$ leads to peaks at the same positions as the synthesis with F_P as coefficients. It is no wonder that multiplying the Patterson coefficients by either of these leads to very similar results.

In fact, it may be shown (which is proved also in the Appendix to Part II) that a synthesis with $\exp i\alpha_P$ as coefficient has properties similar to the above two syntheses, viz. with F_P and $1/F_P^*$. So, the simple phase factor $\exp i\alpha_P$ should itself serve as a deconvoluting agent. Using this a third class of synthesis, called the γ-class, has been worked out. The discussion of this is reserved for a later paper.

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† For an exact definition of this term, see Part II.

‡ The subscript P is omitted in this paragraph.

So also, a Fourier synthesis with the modulus of the structure factor ($|F_N|$) as coefficient leads to a diagram with its main peaks at the same positions as in the Patterson (for a proof see Appendix to Part II). Now, this may be combined with F_P, $1/F_P^*$ or $\exp i\alpha_P$ to get three other classes of syntheses, which are called the α', β', and γ' classes. These also tend to deconvolute the Patterson. The usual heavy atom phased synthesis $|F_N| \exp i\alpha_P$ is the same as the γ'_{gen}-synthesis. These again will be considered in detail in a later paper.

If the replaceable atoms form a centrosymmetric group, but the crystal as a whole does not have a centre of symmetry, then, with respect to this inversion centre as origin, $\alpha_P=0$ or π and $2\alpha_P=0$ or 2π. Hence (25) becomes

$$=F_N+F_N^*$$

and the synthesis leads to the structure plus its inverse about the centre of symmetry of the replaceable atoms. It is easy to show that a similar result occurs with the other α-synthesis also. Here again, there is a concentration at the positions corresponding to the structure *and its inverse* about the centre of symmetry of the replaceable atoms, but in addition, there is a background of minor peaks. It is interesting to recall that this result was predicted by Kartha & Ramachandran (1955) from a study of the technique of obtaining the structure from the Difference-Patterson by vector shift methods.

The discussion in this section is mainly for the purpose of illustrating the properties of the α- and β-class of syntheses. Actually when isomorphous crystals are available, it would be more advantageous to use as coefficients for the Fourier series the terms α_{is} and β_{is} of equations (11) and (12) rather than the terms given in (22) and (24), for it would result in still further reduced background and in the elimination of the peaks at the positions of the known atoms P. The syntheses which are suggested for actual application under various conditions are given in Tables 1 and 2, and the proofs of the results are contained in Part II. The main attempt in this section has been to show the need for multiplication and division by F_P or F_P^* for deconvoluting the Patterson, or the Difference-Patterson, as the case may be.

4. Syntheses with anomalous dispersion data

Suppose that P of the N atoms in a crystal have a complex scattering factor for the radiation under study, while for the remaining Q atoms the scattering factor is real. The P-atoms will in general be heavy atoms in such a case and their positions $\mathbf{r}_{Pj}$ could be deduced from a study of the Patterson diagram. Obviously, the crystal would exhibit Bijvoet inequality ($\Delta|F(\mathbf{H})|^2$, the difference in intensity between the reflections of indices $\mathbf{H}$ and $-\mathbf{H}$). From a study of the Bijvoet inequality, and making use of the known positions of the P-atoms, it is possible to determine the phases of the reflections, but for an ambiguity (see e.g. Ramachandran & Raman, 1956; Raman, 1958, 1959). If the P-atoms form a centro-symmetric group, the effect of this ambiguity is readily understood. If one chooses the centre of symmetry of the P-atoms as origin, the two possible values of the phase, say $\alpha_N^{(1)}$ and $\alpha_N^{(2)}$, are related by the equation

$$\alpha_N^{(1)}+\alpha_N^{(2)}=\pi\ .$$

In consequence, if one performs a Fourier synthesis using both the phases (the so-called sine synthesis), then one obtains in addition to positive peaks at the correct atomic positions, negative peaks of equal magnitude at positions related to these by inversion at the origin (Raman, 1958). The difference from the effect of the ambiguity in the isomorphous series case is to be noted—the peaks at the inverse positions are positive in the latter case, while they are negative here.

However, if the P-atoms form a non-centric group, then the ambiguity takes the form

$$\alpha_N^{(1)}+\alpha_N^{(2)}=\pi+2\alpha_P^\circ\ ,$$

where α_P° is the phase of the contribution from the real part of the scattering power from the P-atoms. In this case, no simple meaning can be attached to the synthesis making use of both the possible values. The situation is exactly analogous to the isomorphous replacement method, in which, when the replaceable atoms form a non-centric group, the Fourier synthesis performed using the two possible values of the phase does not have simple interpretation. On the other hand, both the alpha and the beta types of syntheses can lead to the structure as shown above. In the same way, in the anomalous case also, one may either multiply or divide the Bijvoet inequality by F_P'' and use these coefficients for Fourier syntheses. Here F_P'' is the contribution from the imaginary component of the scattering of the P-atoms. It is found convenient to use in addition a coefficient $\frac{1}{2}$ in this case, so that the coefficients to be used in the alpha-anomalous and the beta-anomalous syntheses are respectively

$$\alpha_{\text{an}}^\circ=\tfrac{1}{2}\Delta|F|^2F_P''=\tfrac{1}{2}\Delta|F|^2|F_P''|\ \exp i\alpha_P''\ , \qquad (27)$$

$$\beta_{\text{an}}^\circ=\alpha_{\text{an}}^\circ/|F_P''|^2=(\tfrac{1}{2}\Delta|F|^2/|F_P''|)\exp i\alpha_P''\ . \qquad (28)$$

There will be a concentration of peaks at the required atomic positions in both cases, together with a spread out background of peaks, which is partially negative in the alpha synthesis and completely negative in the beta case. As in the isomorphous series case, the best syntheses using the anomalous dispersion data do not employ the coefficients α_{an}° and β_{an}° of equations (27) and (28), but α_{an} and β_{an} of equations (14) and (15) which slightly differ from these and lead to the elimination of the peaks at the known atomic positions $\mathbf{r}_{Pj}$. The details are reserved for Part II.

5. Relative merits of the different syntheses

In view of the negative background the β_{an} synthesis is superior to all the others. However, it can be calculated only when the crystal contains a set of anomalous scatterers. One may not always meet with such happy examples. In general, it will be possible to calculate only the β_{mod} synthesis. The success of this synthesis will obviously depend on the nature of the P-group. In the choice of the P-group, two factors have to be taken into account. The first is the ratio of the strength of the wanted to the unwanted peaks and the second is the number of unwanted peaks. A large ratio can be secured only if either P is large or if f_{Pj} is large compared to the f_{Qj}. Increase of P results in the undesirable increase of the number of unwanted peaks. The number is small only if P is small or if it is very large, nearly $=N$, the total number of atoms. The latter is impractical and so the optimum P-group is a small number of atoms having large scattering factors, i.e. heavy atoms.

It is also preferable that the syntheses are calculated in three dimensions rather than in two dimensions. The reason is that the chances of the unwanted peaks coming together and forming a peak of strength comparable to a real structure peak are much less in three dimensions than in projections.

An important fact to be taken into account in the calculation of the β-syntheses is that terms with very small values of $|F_P|$ might lead to difficulties. It is obvious that if $|F_P|=0$, the corresponding β-coefficient tends to infinity, so that the synthesis also becomes infinite. However, when $|F_P|=0$, the phase α_P is completely indeterminate, and if one averages over all possible values of α_P the contribution becomes zero. Consequently, such terms must be omitted in the evaluation of β-syntheses, and the synthesis will never become infinite. However, if $|F_P|$ is small, but not zero, the corresponding coefficients will be very large and will dominate the synthesis. It is preferable to avoid this by omitting such terms also, and including only those terms for which $|F_P|$ is greater than a specified value, say, one fifth or one-tenth the root mean square value for the particular range of the Bragg angle.

The above discussion holds essentially for a non-centrosymmetric crystal. The case of a centrosymmetric crystal can be readily deduced from these, but this is reserved for a subsequent paper. Obviously, in this case, neither the α_{an} nor the β_{an} synthesis is possible. So also, if the crystal (N-atoms) is non-centrosymmetric, while the known group of P-atoms is centrosymmetric some modifications are needed. This is considered in detail in Part II.

In conclusion, it is worthwhile comparing the syntheses proposed here with other deconvolutory functions proposed so far (Beevers & Robertson (1950); Clastre & Gay (1950); Garrido (1950); Buerger (1951); McLachlan (1951)). Most of these functions require that certain mechanical operations must be performed on the Patterson function, so that they are cumbersome to evaluate. The functions presented here are in the form of Fourier syntheses and their evaluation is quite easy, particularly if computors of the type of X-RAC are available. However, all the syntheses considered here, except for α_{gen} and β_{gen}, require that the data be reduced to absolute scale. This difficulty is there, however, even in the determination of phase by the isomorphous crystal method.

6. Solution of the structure straight from the Patterson diagram

As already mentioned, the solution of a crystal structure containing all identical atoms presents special difficulties, since it is not easy to locate the atomic positions of a part of the structure initially. It occurred to the authors that in such cases (and in fact even more generally) it may be worthwhile refining the Patterson diagram itself, without making any attempt to obtain the phases. As was mentioned in section 1, the intensity data as such do not contain any information other than the interatomic vectors, and so it would be worthwhile obtaining these vectors as accurately as possible directly from the intensities. Thus, suppose that $\mathbf{p}_k=\mathbf{r}_i-\mathbf{r}_j$ are the interatomic vectors, then

$$|F(\mathbf{H})|^2=\sum_{i=1}^{N}\sum_{j=1}^{N} f_i f_j \exp 2\pi i\mathbf{H}.(\mathbf{r}_i-\mathbf{r}_j)$$

$$=\sum_{k=1}^{N^2}\varphi_k \exp 2\pi i\mathbf{H}.\mathbf{p}_k \tag{29}$$

where

$$\varphi_k=f_i f_j\,. \tag{30}$$

In view of the centrosymmetric disposition of the vectors this takes the form

$$|F(\mathbf{H})|^2=\varphi_0+2\sum_{k=1}^{\frac{1}{2}N(N-1)}\varphi_k\cos 2\pi\mathbf{H}.\mathbf{p}_k \tag{31}$$

where

$$\varphi_0=\sum_{i=1}^{N} f_i^2\,. \tag{32}$$

When all the atoms are alike, it should be possible to estimate from the magnitudes of the peaks in the Patterson the number of interactions contained in each peak. This should be particularly simple with the three-dimensional Patterson. One can then resolve and refine the positions of the superposed peaks by the method of least squares. The experience gained in this laboratory during the last few years with the least squares technique suggests that if the number of vectors $\mathbf{p}_k$ occurring within a peak and their relative strengths (which in our case are equal) are known, then they can be resolved by this method.

Thus, by locating the peaks in the Patterson and refining them by the least squares technique, one can obtain a complete set of interatomic vectors $\mathbf{p}_k$.

Although this involves a lot of labour, the solution thereafter is simple, for the deconvolution of the Patterson (or the autocorrelation function of the structure) is straightforward, using vector shift methods (Buerger, 1951). In fact, if a single peak is present in the Patterson, then even a single shift of the origin to this peak is sufficient to extract the structure, for the coincident peaks would give the structure straightway, but for a duplication by inversion at the mid-point of the shift vector. (A detailed theory of the superposition methods will be presented elsewhere). Chance coincidences can be eliminated by making more than one vector shift, and the same thing holds for the extra coincidences which occur when shifting to a double peak. In any case, if the peak positions are accurately known, then these operations can be made algebraically, and techniques can be developed for mechanising them.

The essential point is that, in this technique, one deals directly with the intensity data and considers them as the structure amplitudes of the 'Patterson structure' (see Part II). One then uses the usual methods of Fourier and least squares refinements for obtaining the 'peaks' $\mathbf{p}_k$ in this structure. The number and relative heights of these peaks are known beforehand. Thereafter, using the relation that $\mathbf{p}_k=\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$, the Patterson structure is analyzed for the crystal structure. This last part is facilitated by making use of vector shift methods. This approach eliminates all need for phase determination by trial and error or other auxiliary techniques. It makes use only of the information regarding the contents of the unit cell, namely, the number and types of atoms occurring in the repeating unit, and the intensity data.

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Syntheses for the Deconvolution of the Patterson Function. Part II. Detailed Theory for Non-Centrosymmetric Crystals

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(*Received* 19 *March* 1959)

This part contains the more detailed mathematical portion of theory discussed in Part I. First, the significance of various syntheses using as coefficients F, $|F|^2$, F^2, $|F|$, $\exp[i\alpha]$, $\exp[2i\alpha]$, $1/F$, $|F|\exp[i(\pi-\alpha)]$ and also products of the type F_1F_2, where F_1 and F_2 are the structure amplitudes of two portions of a structure, is discussed. It is then used to work out the positions and strengths of the peaks in the different types of alpha and beta syntheses. The new syntheses are also compared with the known types of syntheses, such as the 'heavy atom-phased synthesis'. The main theoretical results have been verified by detailed numerical computation made with a hypothetical non-centric structure containing 6 atoms.

1. Introduction

In Part I, the general principles involved in the alpha- and the beta-types of syntheses were discussed, and it was shown how it is possible to obtain more information about a crystal structure, if a part of it (viz. the positions of some of the atoms) is known, making use of intensity data alone. In the alpha type of syntheses, a suitable function of the measured intensity is *multiplied* by the structure factor of the known atoms for the same reflection and the resulting quantity is used as the coefficient in a Fourier synthesis. In the beta syntheses, on the other hand, a function of the measured intensity is *divided* by the complex conjugate of the structure factor of the known atoms and then used as a coefficient in the Fourier syntheses. In this paper, the detailed theory of these syntheses is worked out and the proofs of the various statements made in Part I are given. The theoretical results have been verified by means of numerical