

Crystal Structure Determinations by the Fourier-Transformation of the Minimum Function

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The Fourier integral of the Buerger minimum function is used for the calculation of the phases of the structure amplitudes. This method was applied to the crystal structure determination of bafertisite, $\text{BaFe}_2\text{TiO}[\text{Si}_2\text{O}_7](\text{OH})_2$, the synthetic silicate $\text{Na}_2\text{Mn}_2[\text{Si}_2\text{O}_7]$, and vinogradovite $\text{Na}_2\text{Ti}_4[\text{Si}_2\text{O}_6]_2 \cdot [\text{Si}_4\text{O}_{10}] \cdot \text{O}_4 \cdot n\text{H}_2\text{O}$. Some possible methods of automatic search for the displacement vectors necessary for the construction of the minimum function were examined.

An effective method of interpreting the Patterson function has been proposed by Wrinch (1939) and developed by Butuzov (1949), Sanadze & Zhdanov (1950), Clastre & Gay (1950*a,b*), Garrido (1950), Beever & Robertson (1950), Belov & Mokeyeva (1951), Kitaygorodsky (1951, 1952), Vainstein (1952*a,b*; 1954) and others. Buerger (1959) has turned this method into a convenient tool for crystal structure determination. To locate the coincident peaks on superimposed Patterson maps (displaced relative to each other) Buerger has proposed special image-seeking functions, maxima of which correspond to the atomic positions in the structure. The most effective is the minimum function

$$M_n(\mathbf{r}) = \min \{P(\mathbf{r} - \mathbf{r}_1); P(\mathbf{r} - \mathbf{r}_2); \dots P(\mathbf{r} - \mathbf{r}_n)\}. \quad (1)$$

Even this function often has some additional (false) maxima which impede the analysis.

There are two reasons for the appearance of false maxima. The first of these is that overlapping peaks on the Patterson map are always taken into consideration. The second reason is the existence of some geometrical relationships between the atomic coordinates in the structure. This results in the appearance of false maxima on the Buerger image-seeking functions even if the Patterson function has no overlapped peaks.

The simplest example of such a relationship in a structure is an arrangement of three atoms in a line when the distance between atoms h and p equals one half of that between p and m (Fig. 1). This relationship can be described by the expression $3\mathbf{r}_p = 2\mathbf{r}_h + \mathbf{r}_m$ and results in the appearance of false peaks on the image-seeking functions if \mathbf{r}_{hp} and \mathbf{r}_{mp} are used as the displacement vectors. The appearance of false peaks is conditioned by the following general relationship between the atomic coordinates of the nonsymmetric part of the structure:

$$\mathbf{r}_p + \mathbf{r}_n + \mathbf{r}_k = \mathbf{r}_m + \mathbf{r}_l + \mathbf{r}_h \quad (2)$$

This relationship gives the possibility of getting 9 differences between the vectors on either side of the equation. The use of any of these differences results in the appearance of two centrosymmetric pairs of false peaks. If one uses $\pm \frac{1}{2}(\mathbf{r}_p - \mathbf{r}_h)$ as the displacement vector, the false peaks will occur at the points $\pm [\mathbf{r}_l - \mathbf{r}_k - \frac{1}{2}(\mathbf{r}_p - \mathbf{r}_h)]$ and $\pm [\mathbf{r}_l - \mathbf{r}_n - \frac{1}{2}(\mathbf{r}_p - \mathbf{r}_h)]$. Hence the following condition holds: a false peak will appear on the image-seeking functions if a displacement vector equals the difference between two arbitrary Patterson vectors which take no part in the building up of the image of the structure. Strictly speaking one should take into consideration the periodicity of the struc-

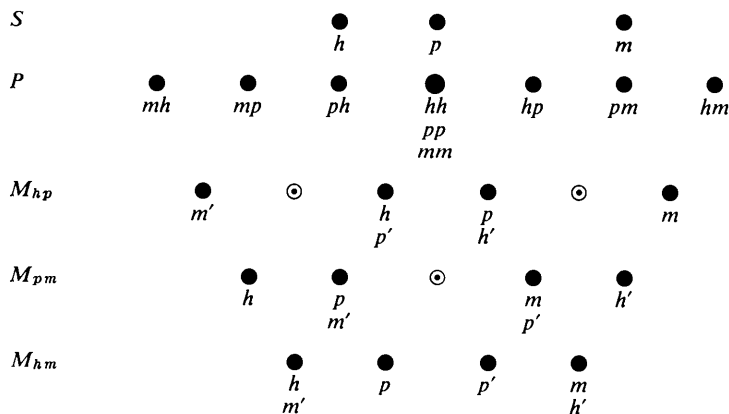


Fig. 1. The simplest case of the appearance of false peaks in the image-seeking function. S , structure consisting of three atoms. P , Patterson function. M_{ij} , seeking function; i, j indicate the displacement vector. \odot , false peaks.

ture and write, instead of (2):

$$\mathbf{r}_{h\beta\gamma} = \mathbf{r}_{kl} - \mathbf{r}_{mn} + \mathbf{R}_{\alpha\beta\gamma} \quad (3)$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, $\mathbf{R}_{\alpha\beta\gamma} = \alpha\mathbf{e}_a + \beta\mathbf{e}_b + \gamma\mathbf{e}_c$, \mathbf{e}_i are the unit vectors of the crystallographic axes, and α, β, γ are integers. It should be stressed that if (3) holds, the false peaks on the image-seeking functions will appear even if no peaks overlap in the Patterson map.

To detect false maxima one can calculate the image-seeking function of higher rank using, for example, the crystal symmetry and some additional crystal chemistry data. Another way enables one to construct automatically the first approximation of the electron density distribution in the crystal from the image-seeking function. These functions are used to calculate phases of structure amplitudes (Simonov & Vainstein, 1959; Simonov, 1961, 1965a). Under these circumstances there is no necessity to identify peaks of the image-seeking function with the atoms of the structure. Image-seeking functions give an approximation to the electron density distribution $\varrho(\mathbf{r})$. Therefore the Fourier integral of such a function gives a corresponding approximation to the Fourier-coefficients of the electron distribution:

$$\tilde{F}_{\mathbf{H}} = q \int M_n(\mathbf{r}) \exp [2\pi i \mathbf{H}\mathbf{r}] d\mathbf{v} \quad (4)$$

The phases of $\tilde{F}_{\mathbf{H}}$ were assigned to the $|F_{\text{obs}}|$ to obtain the first approximation of the electron density distribution. This approximation will be called a superpositional synthesis. The effectiveness of this method of obtaining the phases of the structure amplitudes (using the Fourier integral of the Buerger minimum function) has been demonstrated by some crystal structure determinations.

Such a calculation of the relative phases of the structure amplitudes allows one to take into consideration the positions of all the peaks appearing on $M_n(\mathbf{r})$ without using any *a priori* structure models. The influence of the false peaks of $M_n(\mathbf{r})$ on $\varrho(\mathbf{r})$ is partly eliminated by the fact that $\varrho(\mathbf{r})$ is calculated using $|F_{\text{obs}}|$'s. It is well known that taking full account of symmetry allows the rank of $M_n(\mathbf{r})$ to be raised and thus enables an additional refinement of the function to be made which reduces the false peaks. The described method of obtaining phases enables one to take into consideration the symmetry of a structure in reciprocal space through the values of $\tilde{F}_{\mathbf{H}}$, rather than through the symmetry in real space of the $M_n(\mathbf{r})$ function. Consider a centrosymmetric orthorhombic crystal. Using the vector between atoms connected by an inversion centre one can construct the function $M_2(\mathbf{r})$. The independent part of this function is defined in one half of the unit cell. Then the Fourier integral gives different values for F_{hkl} , $F_{\bar{h}kl}$, $F_{h\bar{k}l}$, and $F_{h\bar{k}\bar{l}}$. As the symmetry of a space group results in a definite relationship between F_{hkl} , $F_{\bar{h}kl}$, $F_{h\bar{k}l}$, and $F_{h\bar{k}\bar{l}}$ one can obtain the most probable signs of the structure amplitudes by use of the above mentioned relationship and $|\tilde{F}_{\mathbf{H}}|$ values.

Before using $M_n(\mathbf{r})$ to obtain the phases it seems useful to modify this function in such a way as to make it closer to the $\varrho(\mathbf{r})$ distribution. If the $M_2(\mathbf{r})$ function is constructed on the base of a centrosymmetrical vector one can modify it by the addition of the sum $\sum_{\mathbf{H}} f_{z_0} \cos 2\pi \mathbf{H}\mathbf{r}_0 \times \exp [-2\pi i \mathbf{H}\mathbf{r}]$ which doubles the

value of the centrosymmetrical peak and makes its weight equal to the weights of all the other structural peaks (Simonov, 1961). Rao (1967) has proposed taking $M_n(\mathbf{r})=0$ at all points where $M_n(\mathbf{r}) \leq 0$. This cuts off the negative background of the function making it closer to the $\varrho(\mathbf{r})$ and so gives an improvement in the set of phases obtained with the help of $M_n(\mathbf{r})$.

The programs for the calculation of the phases of the structure amplitudes were worked out at the Computer Centre of the Moscow State University (Simonov & Shchedrin, 1961; Shchedrin, Tovbis & Simonov, 1966). Utilizing these programs some structure determinations were carried out with the help of the above mentioned method. The method was first applied to the structure determination of bafertesite $\text{BaFe}_2\text{TiO}[\text{Si}_2\text{O}_7](\text{OH})_2$. The structure was solved with the help of two-dimensional projections (Simonov, 1965a). In this case the presence of the very heavy Ba atoms was so helpful that the full power of the method was not demonstrated. The second successful structure determination by this method was carried out on the synthetic silicate $\text{Na}_2\text{Mn}_2[\text{Si}_2\text{O}_7]$ ($a=8.757$, $b=13.294$, $c=5.744$ Å; $\beta=90^\circ 10'$; $P2_1/n$; $Z=4$). In this structure there are two crystallographically independent Mn atoms. Their positions were determined from the three-dimensional Patterson function. The centrosymmetrical peaks Mn-Mn were used to obtain two functions $M_2(\mathbf{r})$. Fourier integrals of these functions allowed one to obtain two approximate electron density distributions $\varrho_1(\mathbf{r})$ and $\varrho_2(\mathbf{r})$. In the calculation of these superpositional syntheses we considered only the centre of symmetry from all the symmetry elements of the space group $P2_1/n$. The next step was to obtain $\varrho(\mathbf{r}) = \min \{\varrho_1(\mathbf{r}); \varrho_2(\mathbf{r})\}$ and lastly the final $\varrho(\mathbf{r})$ minimum-function map was found by means of the comparison of $\varrho(\mathbf{r})$ with itself according to the symmetry of the group $P2_1/n$. Sections of the final three-dimensional superpositional synthesis are shown in Fig. 2. Basic atomic positions were obtained by the least-squares method. The synthesis in Fig. 2 enabled the positions of all the atoms of the structure to be found except those of the oxygen O(4). The relative weights of the peaks are satisfactory and false peaks are virtually absent.

Vinogradovite, $\text{Na}_4\text{Ti}_4[\text{Si}_2\text{O}_6]_2 \cdot [\text{Si}_4\text{O}_{10}] \cdot \text{O}_4 \cdot n\text{H}_2\text{O}$ ($a=5.218$, $b=8.692$, $c=24.605$; $\beta=99^\circ 50'$; $A2/a$; $Z=2$), was the next structure solved by means of three-dimensional superpositional syntheses. As only 20% of the electrons are associated with Ti atoms in this structure it was not practical to use Ti as a heavy atom. Still, the analysis of the three-dimensional

Patterson distribution allowed the location of the Ti atom which occupies a general position in the unit cell. The centrosymmetrical vector Ti-Ti was used as the base for getting $M_2(\mathbf{r})$. The three-dimensional set of structure amplitudes was calculated using the Fourier integral of $M_2(\mathbf{r})$. Taking into account the previously determined signs the superpositional synthesis was calculated and refined, taking into account the symmetry elements of the group $A2/a$. The final superpositional synthesis appeared so convincing that we were able to correct the tentative chemical formula of the mineral proposed by Semenov, Bomschedt-Kupletskaia, Moleva & Sludskaya (1956) to $\text{Na}_5\text{Ti}_4\text{AlSi}_6\text{O}_{24} \cdot 3\text{H}_2\text{O}$. The superpositional synthesis of vinogradovite and atomic positions after least-squares refinement are shown in Fig. 3.

The above mentioned structure investigations have shown the expediency of using the Fourier integral of the minimum-function to calculate the phases of structure amplitudes. One should consider the possibility of applying this method to structures without a centre of symmetry. It is sufficient to obtain $M_n(\mathbf{r})$ which is an approximation to the asymmetrical distribution of electron density. Then using the Fourier integral one

can get the real and imaginary parts of the structure amplitudes. Thus, as soon as one finds the displacement vectors which separate the structure from the Patterson distribution, and hence obtain $M_n(\mathbf{r})$, it becomes possible to get the superpositional synthesis which gives a better approximation to the electron density distribution in a crystal than does the $M_n(\mathbf{r})$ function.

The most important decision in the use of the superposition methods is the choice of vectors for obtaining the image-seeking function. In centrosymmetric cases it is desirable to displace Patterson maps by the vectors between atoms connected by an inversion centre. Even then the symmetric Patterson peaks have weights half as big as peaks due to similar atoms not involved in the displacement vector. In practice one often encounters difficulties in locating single centrosymmetric maxima which are indistinguishable in the general Patterson background, even for structures of moderate complexity. There are some approaches to get over this difficulty and to derive an algorithm for seeking displacement vectors. We shall consider three of them.

I. M. Gelfand has proposed an original method of seeking the global minimum of a function of many variables. Based on this method Vainstein, Gelfand, Kayushina & Fedorov (1963) and Gelfand, Vul, Ginzburg & Fedorov (1966) worked out an algorithm for the determination of molecular crystal structures. The structure search is carried out by minimization of functional $S = R + \alpha D$ where $R = \sum_{\mathbf{H}} ||F_{\text{obs}}| - |F_{\text{calc}}||$ and D

is the function of permissible distances. $D \approx 0$ if intermolecular contacts are satisfactory, and α is a normalizing coefficient. Being formulated in such a way the problem is solved in a space whose dimension equals the number of generalized parameters which describe the structure. The minimization of R can be used in searching for displacement vectors which are necessary for the $M_n(\mathbf{r})$ calculation. Here the $|F|$ values obtained according to (4) will play the part of $|F_{\text{calc}}|$. To calculate $M_3(\mathbf{r})$ it is quite sufficient to locate two displacement vectors. To do this one has to solve the problem of minimizing R in six-dimensional space. The principle of maximum superposition (Sarma & Srinivasan, 1962) can be taken as the basis of the second approach to the working out of the algorithm for the displacement-vectors search. For non-centrosymmetric structures, and in cases where the presence of the inversion centre is in question, the procedure of automatic seeking of displacement vectors consists of the following stages:

- (1) Selection of two arbitrary peaks on the Patterson diagram, peaks in general positions being preferred.
- (2) Construction of two $M_2(\mathbf{r})$ functions using these peaks. If the multiplicity of the chosen peaks is n_1 and n_2 then on $^1M_2(\mathbf{r})$ and $^2M_2(\mathbf{r})$ there will separate n_1 and n_2 displaced structure images and the same quantity of inverted images.

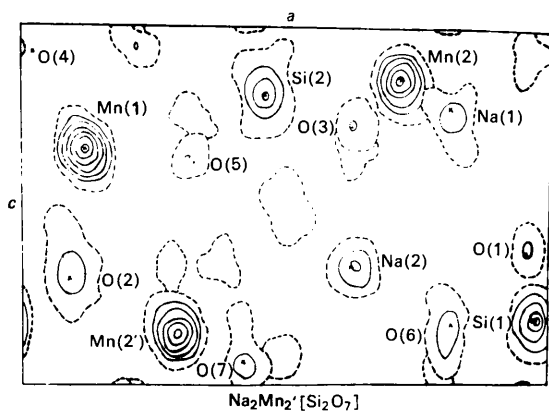


Fig. 2. The set of sections of the three dimensional superposition synthesis of $\text{Na}_2\text{Mn}_2[\text{Si}_2\text{O}_7]$. \times the basic atomic position after the least-squares refinement.

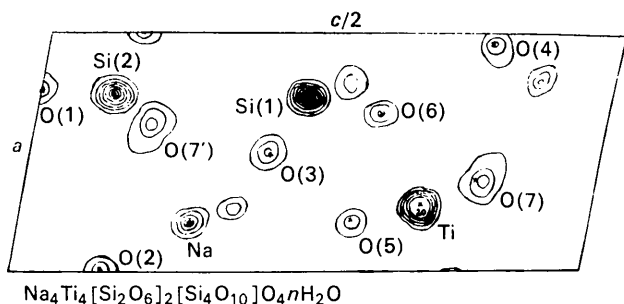


Fig. 3. The set of sections of the three dimensional superposition synthesis of vinogradovite. \times the basic atomic positions after the least-squares refinement.

(3) ${}^1M_2(\mathbf{r})$ and ${}^2M_2(\mathbf{r})$ are superimposed, being parallel to each other. The function $M(\mathbf{r})$ is calculated, the vector \mathbf{t} which determines the parallel displacement of ${}^1M_2(\mathbf{r})$ and ${}^2M_2(\mathbf{r})$ being the parameter for the calculation of

$${}^4M_4(\mathbf{r}) = \min \{ {}^1M_2(\mathbf{r} + \frac{1}{2}\mathbf{t}); {}^2M_2(\mathbf{r} - \frac{1}{2}\mathbf{t}) \}. \quad (5)$$

The sought value of \mathbf{t} , equal to \mathbf{t}_0 , is obtained from the condition: $I_{t_0} = \max \int {}^4M_4(\mathbf{r}) d\mathbf{v}$. The meaning of this condition is simple: I_t increases when a large number of peaks coincide on ${}^1M_2(\mathbf{r} + \frac{1}{2}\mathbf{t})$ and ${}^2M_2(\mathbf{r} + \frac{1}{2}\mathbf{t})$ i.e. one or several structure images superimpose. If on ${}^4M_4(\mathbf{r})$ the number of peaks is much larger than the number of the atoms which have to be located, then this indicates that there is probably more than one image in the function. Then an additional cycle of the search for maximum superposition is needed but this time one must use $M_4(\mathbf{r})$ function copies. The greater the multiplicity of the first chosen Patterson peaks, the more cycles of the maximum-superposition search may be needed. If the presence of an inversion centre was known then there is no need to use two independent functions $M_2(\mathbf{r})$ for the maximum-superposition search. It is sufficient to construct $M_2(\mathbf{r})$ by one arbitrary Patterson vector and to seek maximum superposition when displacing two copies of the same function (Simonov, 1965b).

One more approach to the solution of finding displacement vectors for superposition was made by Germain & Woolfson (1966). The authors constructed $M_2(\mathbf{r})$ by an arbitrary Patterson vector. Depending on the multiplicity of the peak used several structure images, displaced relative to each other, will be present in the function. Now one can take the Fourier coefficients for $M_2(\mathbf{r})$ according to (4), raise them to the second power and calculate a new Patterson function using $|\bar{F}_H|^2$. In this new Patterson function the most powerful peaks will correspond to the vectors connecting different displaced structure images on $M_2(\mathbf{r})$.

The characteristic feature of the algorithms under consideration is that they allow one to carry out automatically (on a computer) the whole of the processes making up the superposition method of crystal structure analysis. This would consist of five successive stages: 1. Construction of the Patterson function. 2. Automatic seeking of the displacement vectors. 3. The construction of the image-seeking function $M_n(\mathbf{r})$. 4.

Fourier transformation of $M_n(\mathbf{r})$ thus obtaining the phases of structure amplitudes. 5. Calculation of a first approximation to the electron density distribution.

I am much obliged to Professor N. V. Belov, my teacher and a strict judge of my works, who drew my attention to superposition methods. The working out of the basic algorithms and its computer realization would have been impossible without the personal contact and cooperation of B. M. Shchedrin and A. B. Tovbis to whom I should like to express my gratitude.

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