

The Intensities and Fourier Transforms of Difference Reflections

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The intensities of 'difference reflections' of crystals with supercells or of crystals with a modulated structure are formulated using 'generalized atomic scattering factors'. The Fourier transform of the structure factors of a single set of difference reflections is the sum of the convolutions of the point functions representing average atomic positions, with the transforms of the generalized atomic scattering factors. The Patterson function of one set of difference reflections is the sum of the convolutions of the point functions representing average interatomic vectors, with the convolutions of the transforms of the generalized atomic scattering factors. These results are applied in a subsequent paper to Patterson maps based on the satellite reflections of a plagioclase feldspar.

1. Introduction

There are many crystals with a structure consisting of a supercell containing smaller subcells having similar arrangements of atoms. In such a case, the diffraction pattern consists of a set of relatively strong reflections and of one or several sets of relatively weak 'difference reflections'. The main reflections carry information about the 'average' structure; the difference reflections carry information about the structural differences between the individual subcells.

A well known group of crystals having a superstructure of this type is the feldspars. In anorthite, for example, there are three sets of difference reflections (*b*, *c*, and *d*) in addition to the set of main (*a*) reflections. Another interesting and relatively important example is the plagioclases, where there are two groups of satellite reflections (*e* and *f*) besides the main reflections. [For a survey of feldspar structures, see Smith & Ribbe (1969).]

In the present paper, attention is directed to properties of the Fourier transforms based on intensities or amplitudes of different sets of difference reflections, especially if the supercell is a modulated structure. A practical application of these results is demonstrated in a companion paper immediately following this one. The companion paper describes and interprets Patterson maps based on satellite reflection of a plagioclase feldspar.

2. The structure factor

Let us suppose that a supercell is composed of $m = N_1 N_2 N_3$ almost identical subcells. The unit subcell is described by vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$; the unit-cell edges of the supercell are $N_1 \mathbf{a}$, $N_2 \mathbf{b}$ and $N_3 \mathbf{c}$, where N_1 , N_2 and N_3 are integers. The position and occupancies of a certain atomic site in individual subcells are similar but not identical. The position vector of the p th atom

in the s th subcell is $\xi_p + \Delta_{ps}$, where ξ_p is the average position vector of the p th atom. Similarly, if f_p is the average atomic scattering factor associated with the p th position, then the atomic scattering factor of the p th atom in the s th subcell can be expressed as $f_p(1 + \varepsilon_{ps})$.

If the supercell has n subcells, there are n sets of reflections: $n - 1$ of them are sets of difference reflections and one set comprises the main reflections. If the reciprocal cell is based on \mathbf{a}^* , \mathbf{b}^* and \mathbf{c}^* (vectors reciprocal to subcell edges), the indices of the main reflections are integers and the indices of the difference reflections are fractional. The reciprocal lattice vectors corresponding to the main reflections are $\mathbf{B}_H = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$; for the a th set difference reflections, the reciprocal vectors are $\mathbf{B}_H^a = \mathbf{B}_H + \boldsymbol{\beta}^a$, where $\boldsymbol{\beta}^a = \frac{m_1}{N_1} \mathbf{a}^* + \frac{m_2}{N_2} \mathbf{b}^* + \frac{m_3}{N_3} \mathbf{c}^*$ and m_1, m_2, m_3 is a set of three integers satisfying $0 \leq m_1 < N_1$, $0 \leq m_2 < N_2$ and $0 \leq m_3 < N_3$ (Fig. 1).

The structure factor of a difference reflection belonging to the a th set characterized by reciprocal vector $\mathbf{B}_H^a = \mathbf{B}_H + \boldsymbol{\beta}^a$ is

$$F_H^a = \sum_p \left[\sum_s (1 + \varepsilon_{ps}) \exp(2\pi i \Delta_{ps} \cdot \mathbf{B}_H^a) \times \exp(2\pi i \mathbf{r}_s \cdot \mathbf{B}_H^a) \right] f_p \exp(2\pi i \xi_p \cdot \mathbf{B}_H^a), \quad (1)$$

where the first summation extends over all atoms in one subcell and the second summation is over all subcells in the unit cell. Vector \mathbf{r}_s is the position vector of the origin of the s th subcell in the supercell, $\mathbf{r}_s = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$, where n_1 , n_2 and n_3 are integers and $\exp(2\pi i \mathbf{r}_s \cdot \mathbf{B}_H^a) = \exp(2\pi i \mathbf{r}_s \cdot \boldsymbol{\beta}^a) = \Phi_s^a$.

The term $\frac{f_p}{m} \sum_s (1 + \varepsilon_{ps}) \exp(2\pi i \Delta_{ps} \cdot \mathbf{B}_H^a) \Phi_s^a = \Psi_p^a$ has the same meaning that the usual atomic scattering factor has in the expression for the structure factor of a cell without a superstructure; therefore, we will call

it the generalized atomic scattering factor. It depends on differences in atomic positions (vectors Δ_{ps}) and on differences in electron density (related to ε_{ps}) among individual subcells. If these differences vanish, the term becomes zero for the difference reflections (because $\sum_s \Phi_s^a = 0$), and it degenerates into f_p for the main reflections. Furthermore, it is different for different sets of difference reflections because of the factors Φ_s^a .

3. Fourier transforms of structure factors of difference reflections

The Fourier transform of structure factors of difference reflections belonging to the a th set is

$${}^a q(\boldsymbol{\eta}) = \frac{m}{V} \sum_H^a \sum_p \Psi_p^a \exp(2\pi i(\boldsymbol{\xi}_p - \boldsymbol{\eta}) \cdot \mathbf{B}_H^a), \quad (2)$$

where the first summation extends over all reflections of the a th set, Ψ_p^a is the generalized atomic scattering factor as defined in the last section and V is the volume of a subcell.

Using the convolution theorem, equation (2) becomes

$${}^a q(\boldsymbol{\eta}) = \sum_p R_p^a * P_p^a, \quad (3)$$

where

$$R_p^a = \frac{1}{V} \sum_H^a \Psi_p^a \exp(-2\pi i \boldsymbol{\eta} \cdot \mathbf{B}_H^a)$$

and

$$P_p^a = m \sum_H^a \exp(2\pi i(\boldsymbol{\xi}_p - \boldsymbol{\eta}) \cdot \mathbf{B}_H^a).$$

R_p^a is the Fourier transform of the generalized atomic scattering factor. It has, therefore, the same meaning that the atomic electron density has in a usual Fourier map. In the limiting case where displacements and substitutions vanish, it transforms into an electron density distribution function for the main reflections, and it is zero for the difference reflections. Function P_p^a can be expressed as the distribution of point functions δ :

$$P_p^a = \sum_s \delta(\boldsymbol{\xi}_p - \boldsymbol{\eta} + \mathbf{r}_s) \Phi_s^{a*}, \quad (4)$$

where $\boldsymbol{\xi}_p$ are confined to a single subcell, vectors \mathbf{r}_s are position vectors of the origins of individual subcells and phase factors Φ_s^{a*} are the complex conjugates of phase factors introduced in § 2.

Let us return to R_p^a , the Fourier transform of the generalized atomic factor Ψ_p^a . By inserting

$$\Psi_p^a = \frac{f_p}{n} \sum_s (1 + \varepsilon_{ps}) \exp(2\pi i \Delta_{ps} \cdot \mathbf{B}_H^a) \Phi_s^a$$

into

$$R_p^a = \frac{1}{V} \int \Psi_p^a(\boldsymbol{\eta}) \exp(-2\pi i \boldsymbol{\eta} \cdot \mathbf{B}_H^a) dV_H,$$

we obtain

$$R_p^a = \frac{1}{nV} \sum_s \Phi_s^a (1 + \varepsilon_{ps}) q_p(\boldsymbol{\eta} - \Delta_{ps}), \quad (5)$$

where q_p is the electron distribution function of the p th atom.

Let us now examine a hypothetical, two-dimensional example of a structure consisting of four subcells, each having two atoms. Atom A has the same position in each subcell; atom B has an average position given by the vector $\boldsymbol{\xi}_B$, but its position in individual subcells is $\boldsymbol{\xi}_B + \Delta_j$, where j is 1, 2, 3 or 4 (see Fig. 2). The generalized atomic scattering factor for atom A is $\frac{1}{4} f_A \sum_s \Phi_s^a$

which reduces to $\frac{1}{4} f_A$ for the main reflections and to zero for the difference reflections. The generalized atomic scattering factor for atom B is

$$\frac{1}{4} f_B \sum_j \Phi_j^a \exp(2\pi i \Delta_j \cdot \mathbf{B}_H^a).$$

In this example the main reflections have integer indices h and k (based on reciprocal vectors \mathbf{a}^* , \mathbf{b}^* of the subcell); the difference reflections have indices $h+m/4$ and k , where m is an integer $1 \leq m < 3$ and h and k are also integers. Each value of m characterizes one set of difference reflections. In Fig. 3 we show schematically the transforms of generalized atomic factors Ψ_B^m for all three sets of difference reflections. In Fig. 3 each circle represents a displaced atom, labeled by a corresponding multiplier, $\frac{1}{4} \Phi_s^m$.

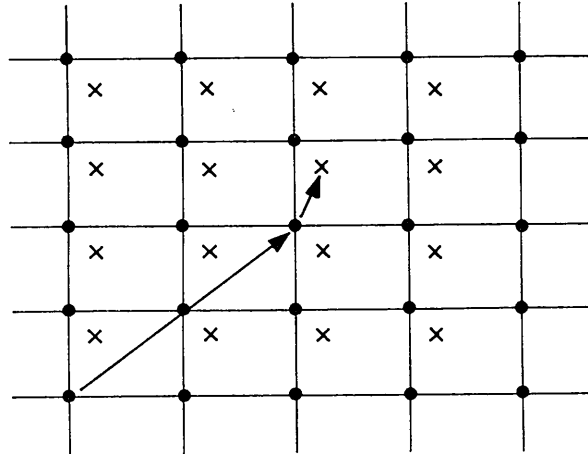


Fig. 1. A two-dimensional example, $N_1=3$, $N_2=4$; crosses indicate difference reflections corresponding to a set characterized by $\boldsymbol{\beta} = \frac{3}{4}\mathbf{a} + \frac{1}{4}\mathbf{b}$.

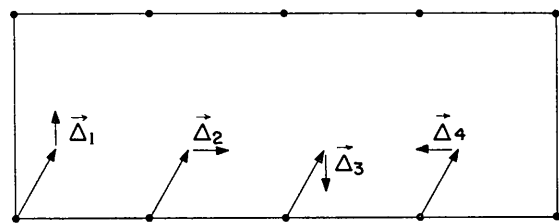


Fig. 2. A two-dimensional example, $N_1=4$, $N_2=1$. Each subcell contains two atoms: atom A in the origin of each subcell, atom B at the end of position vectors $\boldsymbol{\xi}_B + \Delta_i$ ($i=1, 2, 3, 4$).

Fig. 4 shows schematic images of the transforms of the structure factors corresponding to individual sets of reflections. The transform based on structure factors of the main reflections, the 'average structure', is shown in Fig. 4(a). Transforms of structure factors corresponding to different sets of difference reflections are shown in Fig. 4(b), (c) and (d). The transform based on all structure factors is the sum of all partial transforms, and it represents the original structure.

In summary: the Fourier transform of the structure factors of a single set of difference reflections is the sum of the convolutions of the point functions (representing average atomic positions) with the transforms of the generalized atomic factors (carrying information about the differences among the subcells). In other words, in the map based on a single set of difference reflections, transforms of generalized atomic factors [given by equation (5)] rather than atomic electron density functions are centered at end points of average atomic position vectors.

4. Patterson function based on difference reflections

The Patterson function is defined as the Fourier transform of the squares of the absolute values of structure factors. Therefore, for difference reflections belonging to the a th set, we have

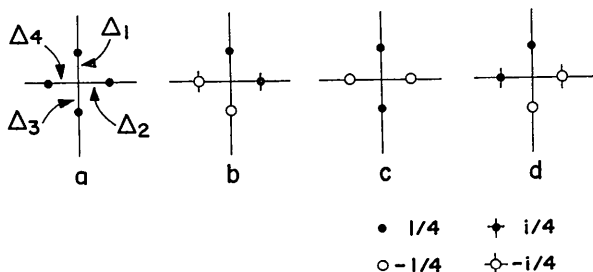


Fig. 3. Schematic representation of Fourier transforms of generalized atomic factor Ψ_b . (a) A transforms corresponding to main reflections; (b), (c), (d) Transforms corresponding to difference reflections characterized by $m=1, 2, 3$. \bullet \circ \oplus \otimes schematically represent atomic distributions multiplied by factors $\frac{1}{4}$, $-\frac{1}{4}$, $i/4$, $-i/4$ respectively.

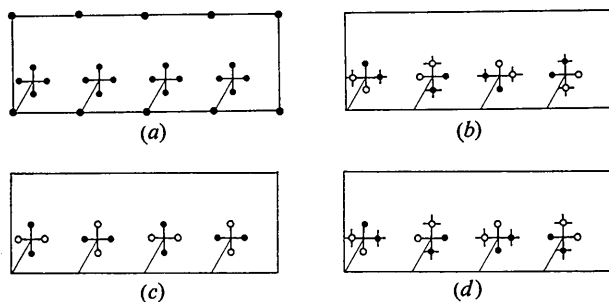


Fig. 4. Schematic representation of a Fourier transform of structure factors corresponding to main reflections (a) and to individual sets of difference reflections (b, c, d).

$$U^a(\boldsymbol{\eta}) = \frac{m^2}{V} \sum_H \sum_{pq}^a \Psi_p^a \Psi_q^{a*} \exp(2\pi i(\xi_p - \xi_q - \boldsymbol{\eta}) \cdot \mathbf{B}_H^a). \quad (6)$$

As with equation (3) in the previous section, equation (6) can be transformed into a sum of convolutions:

$$U^a(\boldsymbol{\eta}) = V \sum_{pq} R_{pq}^{\prime a} P_{pq}^{\prime a}.$$

Here, function $R_{pq}^{\prime a}$ is

$$R_{pq}^{\prime a} = \frac{1}{V^2} \sum_H^a \Psi_p^a \Psi_q^{a*} \exp(-2\pi i \boldsymbol{\eta} \cdot \mathbf{B}_H^a)$$

and function $P_{pq}^{\prime a}$ is

$$P_{pq}^{\prime a} = m^2 \sum_H^a \exp(2\pi i(\xi_p - \xi_q - \boldsymbol{\eta}) \cdot \mathbf{B}_H^a).$$

Further, $R_{pq}^{\prime a}$ can be expressed as a convolution,

$$R_{pq}^{\prime a} = \frac{1}{V^2} R_p^a * R_q^{a*},$$

and expanded as

$$R_{pq}^{\prime a} = \frac{1}{m^2 V^2} \sum_{rs} \Phi_r^a \Phi_s^{a*} (1 + \varepsilon_{pr}) (1 + \varepsilon_{qs}) \varrho'_{pq}(\boldsymbol{\eta} + \Delta_{pr} - \Delta_{qs}), \quad (9)$$

where ϱ'_{pq} is the convolution of atomic electron density functions ϱ_p and ϱ_q . Here, function $R_{pq}^{\prime a}$ has the same meaning as the convolution of atomic electron distribution functions for ordinary Patterson maps. If ε and Δ approach zero (for either atom p or q , or both), functions $R_{pq}^{\prime a}$ vanish for all sets of difference reflections.

Function $P_{pq}^{\prime a}$ can, in turn, be expressed as a sum of point functions:

$$P_{pq}^{\prime a} = m \sum_t \delta(\xi_p - \xi_q - \boldsymbol{\eta} + \mathbf{r}_t) \cdot \Phi_t^{a*}. \quad (10)$$

Before examining the Patterson function of the example discussed in § 3, let us summarize the results. The Patterson function of the a th set of difference reflections is the sum of the convolutions of the point functions (representing average interatomic vectors) with the convolutions of the transforms of the generalized atomic scattering factors. Therefore, peaks in the Patterson function based on a single set of difference reflections are centered in the usual way at the end points of the average interatomic vectors, but they are convolutions of transforms of generalized atomic scattering factors (carrying information about displacements and substitutions distinguishing individual atomic positions in different subcells), rather than convolutions of electron density functions.

To be more specific, let us now examine the Patterson function of the two-dimensional example from § 3. Functions $R_{pq}^{\prime a}$ are shown schematically in Fig. 5. Corresponding Patterson functions are shown schematically in Fig. 6. Fig. 6(a) represents the Patterson function based on the main reflections – the 'average Patterson'; Fig. 6(b), (c) and (d) shows Patterson functions based on individual sets of difference reflections.

The sum of all four partial Patterson functions is the Patterson function of the supercell, as expected (Fig. 7).

5. Modulated structures

One special case of difference reflections is the satellite reflections of a modulated structure [see Guinier (1963) and Korekawa (1967)]. The intensity of satellite reflections can be calculated easily in the usual way (for additional discussion of the material presented in this section, see the Appendix); an attempt is made here to show that the formulation using generalized atomic factors, described in previous sections, can also be applied in the case of this superstructure, making it very simple to calculate Fourier transforms of satellite intensities or amplitudes.

Let us suppose that the axes of a supercell are chosen in such a way that

$$\mathbf{a}_s = N_{11}\mathbf{a} + N_{12}\mathbf{b} + N_{13}\mathbf{c},$$

$$\mathbf{b}_s = N_{21}\mathbf{a} + N_{22}\mathbf{b} + N_{23}\mathbf{c}$$

and

$$\mathbf{c}_s = N_{31}\mathbf{a} + N_{32}\mathbf{b} + N_{33}\mathbf{c},$$

where N_{ij} are integers. Furthermore, let us assume that the displacements of atoms from average positions and their occupancies are determined by plane modulation waves with the wave vector perpendicular to face A of the supercell (there can be one or more wavelengths of the modulation wave in the supercell). If the wave vector of this wave is \mathbf{B}_T the displacement of the i th atom in the s th subcell is

$$\Delta_{js} = \Delta_j \cos 2\pi(\mathbf{r}_s \cdot \mathbf{B}_T + \alpha_j)$$

where Δ_j is the vector indicating maximum displacement of atom j and α_j is the phase of the wave describing its displacement. Similarly, for occupancies ε_{js} we have

$$\varepsilon_{js} = \varepsilon_j \cos 2\pi(\mathbf{r}_s \cdot \mathbf{B}_T + \alpha'_j).$$

If we accept the result derived in the Appendix (that for a structure modulated by a simple harmonic wave, satellites are located at $\mathbf{B}_H \pm \mathbf{B}_T$ in reciprocal space) we obtain:

$$\Phi_s^a = \exp(2\pi i \mathbf{r}_s \cdot \mathbf{B}_T)$$

and

$$\Psi_j = \frac{f_j}{m} \sum_s [1 + \varepsilon_j \cos 2\pi(\mathbf{r}_s \cdot \mathbf{B}_T + \alpha'_j)] \\ \times \exp[2\pi i(\Delta_j \cdot \mathbf{B}_H \cos 2\pi(\mathbf{r}_s \cdot \mathbf{B}_T + \alpha_j) + \mathbf{r}_s \cdot \mathbf{B}_T)].$$

If we expand the exponential functions and realize that $\sum_s \exp(2\pi i \mathbf{r}_s \cdot \mathbf{B}_T) = 0$, we finally obtain:

$$\Psi_j = \frac{1}{2} \varepsilon_j \exp(\mp 2\pi i \alpha'_j) + \pi i \Delta_j \cdot \mathbf{B}_H^a \exp(\mp 2\pi i \alpha_j) \quad (11)$$

which is identical to expression (12) in the Appendix.

To calculate the Patterson function based on satellite intensities we use a procedure similar to that discussed in § 4. First, it is necessary to calculate functions R_{pq}^a , a convolution of Fourier transforms of generalized

atomic scattering factors φ_p and φ_q . These functions are then convoluted by sets of point functions given by equation (9), representing average interatomic vectors. The resulting Patterson function has the same properties as the more general Patterson function described in § 4. Unless all phases α_j and α'_j are equal, R_{pq}^a is complex. This means that the real and imaginary parts of the Patterson function can be calculated for each set of satellite reflections. This will be considered in more detail in the paper on plagioclase satellites immediately following this article.

Let us examine properties of R_{pq}^a calculated for a rather special model. It may be assumed that the displacements of modulation waves for atoms p and q are parallel and of equal length, and that the convoluted atomic distribution function q' is a Gaussian function $\exp(-0.1\xi^2)$. The phase difference between modulation waves for atoms p and q varies from 0 to π . The number of subcells in the direction parallel with the wave vector of the modulation wave is 13; the absolute value of displacement is 3 units. In this case, transform R_{pq}^a was not calculated from equation (11) but from the more exact equation (9). The results are shown in Fig. 8. A similar calculation was performed with a modulation wave consisting not of a single cosine wave but of an approximately square modulation wave (Fig. 9):

$$\cos 2\pi(\mathbf{r}_s \cdot \mathbf{B}_T + \alpha_j) - \frac{1}{3} \cos 2\pi(3\mathbf{r}_s \cdot \mathbf{B}_T + \alpha_j) \\ + \frac{1}{5} \cos 2\pi(5\mathbf{r}_s \cdot \mathbf{B}_T + \alpha_j) \\ - \frac{1}{7} \cos 2\pi(7\mathbf{r}_s \cdot \mathbf{B}_T + \alpha_j) + \frac{1}{9} \cos 2\pi(9\mathbf{r}_s \cdot \mathbf{B}_T + \alpha_j).$$

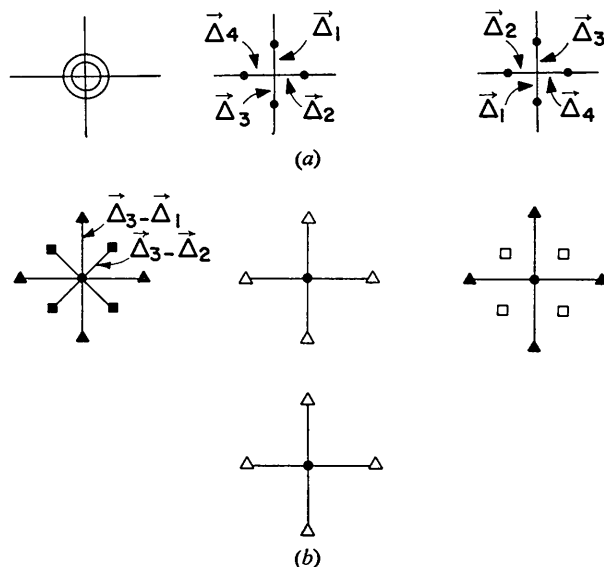


Fig. 5. Schematic representation of functions R_{pq}^a based on our two-dimensional example. Transforms $R_{AA}^0, R_{AB}^0, R_{BA}^0$ are shown in (a); transforms corresponding to reflections with $m=0, 1, 2$ and 3 are shown in (b). $\bullet, \circ, \blacksquare, \square, \blacktriangle, \triangle$ and Δ schematically represent q' functions multiplied by $\frac{1}{2}, -\frac{1}{2}, \frac{1}{6}, -\frac{1}{6}, \frac{1}{6}, -\frac{1}{6}$.

It is interesting to note that the form of the transform changed only slightly. This means that from an examination of the Patterson function of satellite intensities it is possible to infer reasonably reliable information concerning the 'short-range characteristics' of the modulation (directions and amplitudes of displacements and their phases), but we cannot expect to be able to differentiate between similar forms of modulation waves.

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APPENDIX

Let us calculate $A_H(\mathbf{X})$, the amplitude of a wave diffracted by the unit cell of a modulated structure. The origin of this unit cell is at \mathbf{X} ; the position of the j th atom with respect to the origin of its unit cell is

$$\xi_j = \xi_{oj} + \Delta_j \cos 2\pi((\mathbf{X} + \xi_{oj}) \cdot \mathbf{B}_T + \alpha_j),$$

and it is associated with an atomic scattering factor

$$f_j = f_j^0 (1 + \epsilon_j \cos 2\pi(\mathbf{X} + \xi_{oj}) \cdot \mathbf{B}_T + \alpha_j')$$

where ξ_{oj} is the average position vector of atom j , \mathbf{B}_T is the wave vector of the modulation wave; phases α_j and α_j' are phases of the modulation of the atomic position of j th atom and of its scattering factor respectively. The average atomic scattering factor of the j th atom is f_j^0 . Therefore,

$$A_H(\mathbf{X}) = \sum_j f_j \exp [2\pi i(\mathbf{X} + \xi_j) \cdot \mathbf{B}'_H],$$

where \mathbf{B}'_H is a reciprocal-space vector.

By inserting for f_j and ξ_j and recognizing that Δ_j is much smaller than ξ_{oj} , we can approximate

$$A_H(\mathbf{X}) = \sum_j f_j^0 (1 + \epsilon_j \cos 2\pi[(\mathbf{X} + \xi_{oj}) \cdot \mathbf{B}_T + \alpha_j]) \times \{1 + 2\pi i \mathbf{B}'_H \cdot \Delta_j \cos 2\pi[(\mathbf{X} + \xi_{oj}) \cdot \mathbf{B}_T + \alpha_j]\} \times \exp [2\pi i(\mathbf{X} + \xi_{oj}) \cdot \mathbf{B}'_H].$$

Neglecting a cross product containing ϵ_j and $|\Delta_j|$, we have

$$A_H(\mathbf{X}) = \exp (2\pi i \mathbf{X} \cdot \mathbf{B}'_H) \cdot \sum_j f_j^0 \exp (2\pi i \xi_{oj} \cdot \mathbf{B}'_H)$$

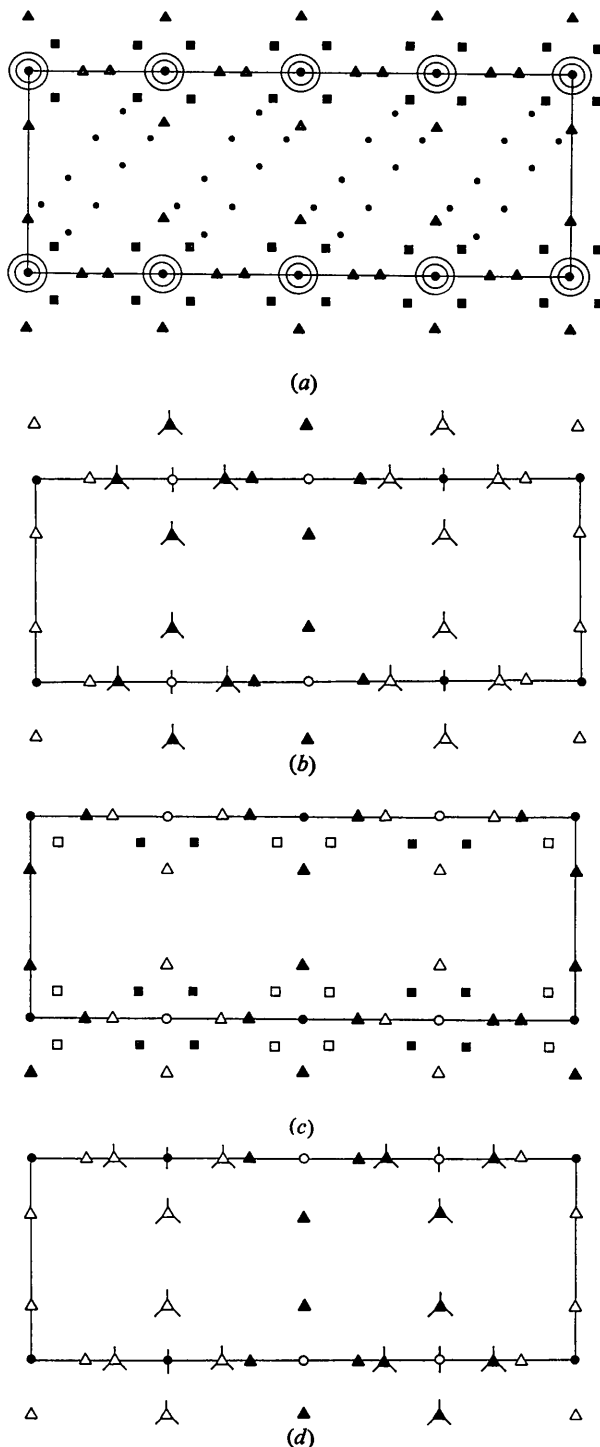


Fig. 6. Schematic representation of Fourier transforms of intensities corresponding to main reflections (a), and to individual sets of difference reflections (b,c,d). ●, ○, ⊕, ⊗, ■, □, ▲, △, ⤴ and ⤵ represent g' functions multiplied by 1, -1, i , $-i$, $\frac{1}{2}$, $-\frac{1}{2}$, $\frac{1}{4}$, $-\frac{1}{4}$, $\frac{1}{4}i$, $-\frac{1}{4}i$.

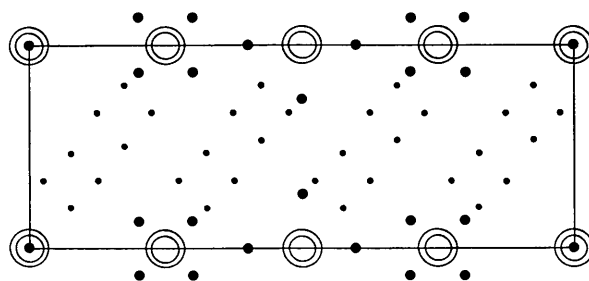


Fig. 7. Sum of functions from Fig. 6(a), (b), (c), (d), giving a schematic representation of a Patterson function based on all intensities. ○, ● and • represent convolutions Q_{AA} , Q_{AB} , Q_{BB} , respectively.

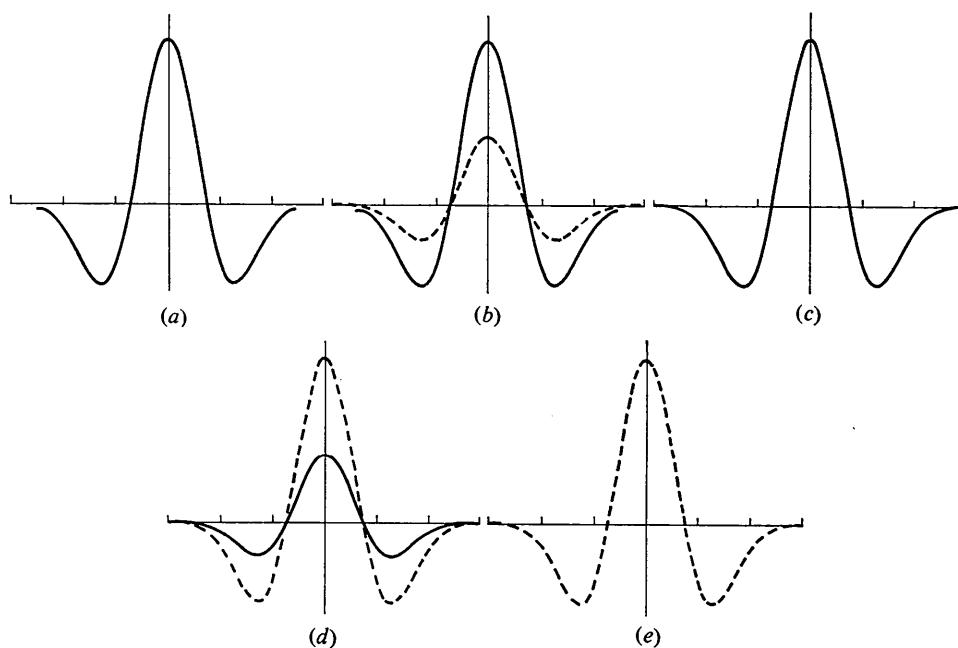


Fig. 8. R_{pq}^s for a modulated structure. Atoms p and q are displaced in the x direction by a simple cosine wave; amplitude, 3 units; phase difference between waves acting upon atoms p and q is $0, \frac{1}{4}\pi, \frac{1}{2}\pi, \frac{3}{4}\pi, \pi$; (a), (b), (c), (d), (e) respectively. Real part of R_{pq}^s , solid line; imaginary part of R_{pq}^s , broken line. For phase difference 0 , imaginary part vanishes; for phase difference π , real part vanishes; for phase difference $\frac{1}{2}\pi$, both parts are numerically equal.

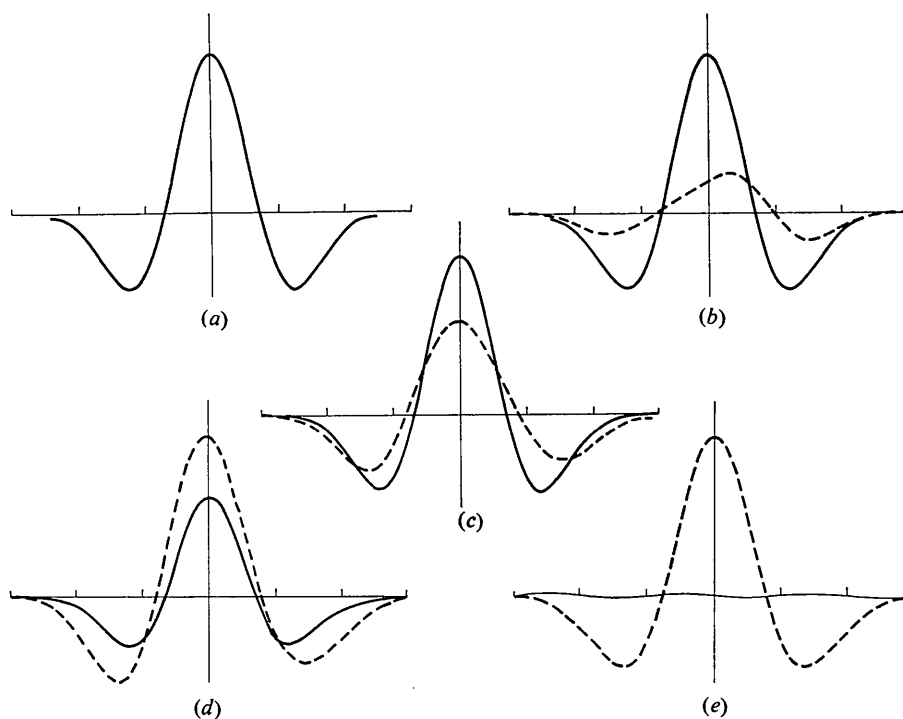


Fig. 9. R_{pq}^s for a modulated structure. Atoms p and q are displaced in the x direction by an approximately square wave represented by 5 cosine terms. Total amplitude of displacement, 3 units; phase difference between waves modulating atoms p and q is the same as in the example in Fig. 8. Real part of R_{pq}^s , solid line; imaginary part of R_{pq}^s , broken line. For phase difference 0 , imaginary part vanishes; for phase difference π , real part vanishes.

$$\begin{aligned}
& + \exp [2\pi i \mathbf{X} \cdot (\mathbf{B}'_H + \mathbf{B}_T)] \sum_j f_j \{ \frac{1}{2} \varepsilon_j \exp (2\pi i \alpha'_j) \\
& + \pi i \mathbf{B}'_H \cdot \Delta_j \exp (2\pi i \alpha_j) \cdot \exp [2\pi i \xi_{oj} \cdot (\mathbf{B}'_H + \mathbf{B}_T)] \} \\
& + \exp [2\pi i \mathbf{X} \cdot (\mathbf{B}'_H - \mathbf{B}_T)] \sum_j f_j \{ \frac{1}{2} \varepsilon_j \exp (-2\pi i \alpha'_j) \\
& + \pi i \mathbf{B}'_H \cdot \Delta_j \exp (-2\pi i \alpha_j) \\
& \times \exp [2\pi i \xi_{oj} \cdot (\mathbf{B}'_H - \mathbf{B}_T)] \} .
\end{aligned}$$

Summing further over the unit cells, the first term leads to sharp main reflections, the second and third terms lead to sharp satellite reflections located at $\mathbf{B}_H \pm \mathbf{B}_T$, where \mathbf{B}_H is a reciprocal lattice vector based on the reciprocal-cell edges of the subcell. The generalized atomic scattering factor is

$$f_j(\frac{1}{2}\varepsilon_j \exp(-2\pi i \alpha'_j) + \pi i \Delta_j \cdot \mathbf{B}'_H \exp(-2\pi i \alpha_j)) \quad (12)$$

for reflections at $\mathbf{B}_H + \mathbf{B}_T$. For reflections at $\mathbf{B}_H - \mathbf{B}_T$ signs change in the exponent of the phase factors of the generalized atomic scattering factor.

Glossary of some more frequently used symbols

a, b, c Base vectors of the subcell.
a*, b*, c* Base vectors of the reciprocal lattice based on the subcell.

Δ_{ps} Displacement vector of the p th atom in the s th subcell from its average position ξ_p .
 f_p^f Average atomic scattering factor of the p th atom.
 ε_{ps} Fractional increment of the atomic scattering factor of the p th atom in the s th cell.
 \mathbf{B}_H Reciprocal lattice vector of a main reflection.
 \mathbf{B}'_H Reciprocal lattice vector of a difference reflection of the a th set.
 β^a Difference between \mathbf{B}'_H and \mathbf{B}_H .
 Φ_s^a Phase factor of the contribution from the s th subcell to a difference reflection of the a th set.
 \mathcal{V}_p^a Generalized atomic scattering factor for difference reflections of the a th set.
 ${}^a\varrho(\boldsymbol{\eta})$ Fourier transform of structure factors of reflections belonging to the a th set.
 $U^a(\boldsymbol{\eta})$ Patterson function based on intensities of reflections of the a th set.

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Patterson Function of Plagioclase Satellites

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The real and imaginary parts of Patterson functions based on 'e' and 'f' satellites were calculated. In 'e' satellite maps, Patterson interactions involving cations are most prominent and permit relatively simple calculation of the amplitudes and phases of 26 displacement modulation waves. The deformation of the silicate chain, which is apparently one of the major features of the plagioclase superstructure, is shown in detail. The interpretation of the 'f' satellite Patterson function is less straightforward, but it shows clearly that the associated displacements are of very small amplitude, directed along [025] and that they do not involve Na/Ca cations.

1. Introduction

In two earlier papers (Toman & Frueh, 1971; Toman & Frueh, 1972 henceforth referred to as TF1 and TF2) the nature of the plagioclase superstructure was examined by studying the statistical distribution of the intensities of satellite reflections. The chemical composition of the sample examined in these two

papers corresponds to a plagioclase with 55% anorthite, and the results formulated there can be condensed as follows:

(a) The intensity distributions of 'e' satellites (for terminology see Bown & Gay, 1958, or TF1) and of 'f' satellites are qualitatively very different, suggesting that the 'e' and 'f' satellites are related to entirely different aspects of the superstructure.