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A Direct Sign-determining Method Based upon Fourier Series

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New functions $G(\mathbf{H}, \xi)$ and $K(\mathbf{H}, \xi)$ derived by application of Fourier series with the coefficients depending upon unitary structure factors $U(\mathbf{H})$ are introduced and a method for their use for sign determination is suggested. For all ξ within the interval $\xi_{\text{min.}} < \xi < \frac{1}{4}$, where $\xi_{\text{min.}}$ is a structure dependent parameter, the conditions $G(\mathbf{H}, \xi) = 0$ and $K(\mathbf{H}, \xi) = 0$ are satisfied only then when the correct signs are alloted to the coefficients. The method was successfully applied to a hypothetical centrosymmetric structure for which the signs of $U(h00)$ for all h from 1 to 16 were determined. A generalization of the functions which enables to include gradually all $|U(hkl)|$ into the computation is also suggested.

1. Introduction

The phase determination from the diffraction intensity data is the main problem in solving crystal structures. The recent search for a direct method for the determination of phases was greatly stimulated by Harker & Kasper's paper (1948) on the use of inequalities existing between structure factors. During the last decade several methods have been developed by means of which the phases of structure factors can be found directly. All these methods which are based either on inequality relations, probability theory, statistics or the Patterson function have been published in this Journal and so are known to the X-ray crystallographers.

Meanwhile, only a few papers published deal with the application of Fourier series for direct sign determination; Gillis (1948) in deriving one of his inequalities was first to use the $|\cos^3 2\pi x|$ function developed in a series of cosine terms only. Recently, Hughes (1957) used general Fourier series in deriving a set of inequalities which in certain cases, were more convenient.

In the present paper a new method for the direct sign determination for centrosymmetric structures is described. The method is based on the use of functions derived by expanding the expression for the structure factor in a Fourier series.

2. One-dimensional case

Analogous to the expression for the unitary structure factor

$$U_c(h) = 2\sum_{i=1}^{N/2} n_i \cos 2\pi h x_i \qquad (2\cdot1)$$

in the one-dimensional centrosymmetric case, we introduce the expression:

$$U_s(h) = 2\sum_{i=1}^{N/2} n_i \sin 2\pi h x_i \qquad (2\cdot2)$$

with the usual symbols and notation.

A centrosymmetric structure can always be defined in such a way that:

$$0 \le |x_i| \le \tfrac{1}{2}\,. \qquad (2\cdot3)$$

If the condition

$$0 \le |x_i| \le \tfrac{1}{4} \qquad (2\cdot4)$$

were satisfied it would be possible to expand each cosine term with h odd in a Fourier cosine series with the fundamental period $2L = \frac{1}{2}$:

$$n_i \cos 2\pi h x_i = n_i a_0(h) + \sum_{n=1}^{\infty} n_i a_n(h) \cos 2\pi 2 n x_i \qquad (2\cdot5)$$

where $a_0(h)$ and $a_n(h)$ depend only upon the values of h and n (Appendix (i), (1), (2)).

For the purpose of using equation (2·5) under condition (2·3) we introduce a new parameter ξ such that:

$$0 \le |x_i - \xi| \le \tfrac{1}{4}\,. \qquad (2\cdot6)$$

Then equation (2·5) can be written:

$$n_i \cos 2\pi h(x_i - \xi) - [n_i a_0(h) + \sum_{n=1}^{\infty} n_i a_n(h) \cos 2\pi 2n(x_i - \xi)] = 0\,. \qquad (2\cdot7)$$

By summation over all x_i we obtain the equation:

$$2\sum_{i=1}^{N/2} n_i \cos 2\pi h(x_i - \xi) - \left\{a_0(h) + \sum_{n=1}^{\infty} a_n(h)\left[2\sum_{i=1}^{N/2} n_i \cos 2\pi 2n(x_i - \xi)\right]\right\} = 0\,, \qquad (2\cdot8)$$

the validity of which now is given by the condition:

$$0 \le |x_i(\text{max.}) - \xi| \le \tfrac{1}{4} \qquad (2\cdot9)$$

which means that for all values of ξ within the interval

$$\xi_{\text{min.}} < \xi \le \tfrac{1}{4} \qquad (2\cdot10)$$

equation (2·8) must be satisfied. Thus

$$\xi_{\text{min.}} = x_i(\text{max.}) - \tfrac{1}{4}\,.$$

Now we shall consider the left side of equation (2·8) as a function $G(h, \xi)$. It follows that, for given parameters (h, x_i), $G(h, \xi) = 0$ only if the values of ξ are within the limits defined in (2·10).

If we substitute the sum of cosines and sines in equation (2·8) by the expressions (2·1) and (2·2) respectively, we have

$$\begin{aligned} G(h, \xi) = {} & U_c(h) \cos 2\pi h\xi \\ & - [a_0(h) + \sum_n a_n(h) U_c(2n) \cos 2\pi 2n\xi] \\ & + U_s(h) \sin 2\pi h\xi - [\sum_n a_n(h) U_s(2n) \sin 2\pi 2n\xi] \quad (2·11) \end{aligned}$$

where $G(h, \xi) = 0$ for

$$\xi_{\text{min.}} \le \xi \le \tfrac{1}{4}\,.$$

The function $G(h, \xi)$ is best represented graphically when plotted against ξ with an $\xi_{\text{min.}}$ arbitrarily chosen, since the value of $\xi_{\text{min.}}$ changes from structure to structure (Fig. 1).

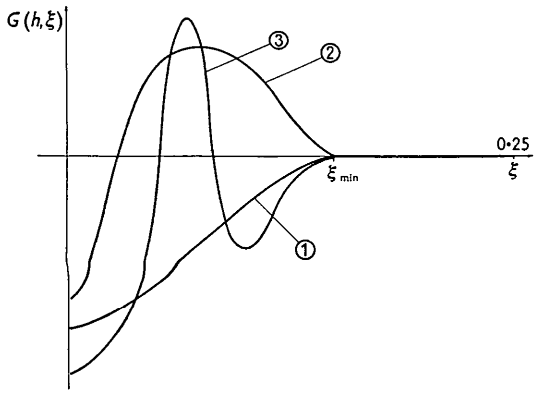

Fig. 1. General shape of the function $G(h, \xi)$ for $h = 1(1)$, $h = 3(2)$ and $h = 5(3)$. As $G(h, \xi)$ depends upon the unitary structure factors, $\xi_{\text{min.}}$ and the shape of the curve change from structure to structure.

The shape of the curve depends upon both the moduli and the signs of the coefficients $U_c(h)$, $U_c(2n)$, $U_s(h)$ and $U_s(2n)$. If only the moduli are known we can allot a sign to each of these coefficients arbitrarily. Obviously, we should try several sets of signs, but only that set may be considered as correct for which $G(h, \xi) = 0$ for all ξ satisfying condition (2·10). Moreover, the value of $\xi_{\text{min.}}$ for a given odd h will be valid for any other odd h, which yields an additional condition for $\xi_{\text{min.}}$ and a further check for the reliability of the chosen set of signs. Herewith the fundamental idea of the method is explained.

The coefficients $U_s(h)$ and $U_s(2n)$ cannot be determined from the experiment. This obstacle is easily removed by using Fourier series involving only cosine terms in the interval $(0, \tfrac{1}{2})$:

$$U_s(h) = b_0(h) + \sum_n b_n(h) U_c(n) \qquad (2·12)$$

(Appendix (ii), (3)–(6)). Herewith the use of the function $G(h, \xi)$ is limited only to those structures for which $|x_i(\text{max.})| < \tfrac{1}{2}$. A suggestion for the use of $G(h, \xi)$ in the case when $x_i(\text{max.}) = \tfrac{1}{2}$ is given in Appendix (iv).

An additional relation between the structure factors can be obtained in a similar way by expanding $\cos^2 2\pi hx$ and $-\cos^2 2\pi hx$ in a Fourier cosine series in the interval $[0, \tfrac{1}{4}]$ and $[\tfrac{1}{4}, \tfrac{1}{2}]$ respectively, with the fundamental period $2L = 1$ (Appendix (iii), (7)). Thus we introduce another function $K(h, \xi)$ defined as:

$$\begin{aligned} K(h, \xi) = {} & 1 + U_c(2h) \cos 2\pi 2h\xi \\ & - 2[\sum_n a_{2n+1}(h) U_c(2n+1) \cos 2\pi(2n+1)\xi] \\ & + U_s(2h) \sin 2\pi 2h\xi \\ & - 2[\sum_n a_{2n+1}(h) U_s(2n+1) \sin 2\pi(2n+1)\xi] \quad (2·13) \end{aligned}$$

where $K(h, \xi) = 0$ for all values of ξ which satisfy condition (2·10).

The function $G(h, \xi)$ involves even structure factors as coefficients of the cosine terms except one which is odd. On the contrary the values of the even coefficients of the sine terms depend upon the odd structure factors. For the function $K(h, \xi)$ the inverse relation holds. The function $G(h, \xi)$ should be more convenient for determining the signs of the even structure factors and $K(h, \xi)$ for the odd ones, as will be demonstrated in detail in § 4.

3. Generalization of $G(h, \xi)$ and $K(h, \xi)$ for the three-dimensional case

The reflexions hkl are divided into groups with indices ph, pk, pl where p is an integer defining the group. By appropriate transformation of the axes for each hkl, the indices ph, pk, pl can be transformed into ph', 0, 0 and the functions $G(h, \xi)$ and $K(h, \xi)$ may be applied in the same way as in the one-dimensional case. Using the reciprocal-lattice notation, we have for each $H(hkl)$ in the pth group $\mathbf{H} = p\mathbf{H}_0$ where $\mathbf{H}_0$ is the vector belonging to the lowest reflexion. Using the same notation the expressions (2·1) and (2·2) can be rewritten

$$U_c(\mathbf{H}) = 2 \sum_{i=1}^{N/2} n_i \cos 2\pi \mathbf{H}.\mathbf{r}_i \qquad (3·1)$$

$$U_s(\mathbf{H}) = 2 \sum_{i=1}^{N/2} n_i \sin 2\pi \mathbf{H}.\mathbf{r}_i \qquad (3·2)$$

respectively. Similarly, we introduce a new parameter defined by $\xi' = \mathbf{H}_0.\xi$, where the value of $\xi'_{\text{min.}}$ depends upon $\mathbf{H}_0$. For the sake of simplicity and analogy with the preceding paragraph, ξ will be further written instead of ξ' and $\xi_{\text{min.}}$ instead of $\xi'_{\text{min.}}$. For the same reason $G(\mathbf{H}, \xi')$ and $K(\mathbf{H}, \xi')$ will be replaced by $G(\mathbf{H}, \xi)$ and $K(\mathbf{H}, \xi)$ respectively.

The functions $G(\mathbf{H}, \xi)$ and $K(\mathbf{H}, \xi)$ may therefore be written in the form

$$G(\mathbf{H}, \xi) = U_c(\mathbf{H}) \cos 2\pi p\xi - \left[a_0(p) + \sum_{n=1}^{\infty} a_n(p) U_c(2n\mathbf{H}_0) \cos 2\pi 2n\xi\right] + U_s(\mathbf{H}) \sin 2\pi p\xi - \left[\sum_{n=1}^{\infty} a_n(p) U_s(2n\mathbf{H}_0) \sin 2\pi 2n\xi\right] \quad (3{\cdot}3)$$

$$K(\mathbf{H}, \xi) = 1 + U_c(2\mathbf{H}) \cos 2\pi 2p\xi - 2\left\{\sum_{n=1}^{\infty} a_{2n+1}(p) U_c[(2n+1)\mathbf{H}] \cos 2\pi(2n+1)\xi\right\} + U_s(2\mathbf{H}) \sin 2\pi 2p\xi - 2\left\{\sum_{n=1}^{\infty} a_{2n+1}(p) U_s[(2n+1)\mathbf{H}] \sin 2\pi(2n+1)\xi\right\} \quad (3{\cdot}4)$$

where p is now an odd integer.

Each of the functions $G(\mathbf{H}, \xi)$ and $K(\mathbf{H}, \xi)$ is identical with a sum of Fourier series $G_i(\mathbf{H}, \xi)$ and $K_i(\mathbf{H}, \xi)$ respectively, the sum being taken over all atoms in the unit cell, so that we may write:

$$G(\mathbf{H}, \xi) = 2\sum_{i=1}^{N/2} G_i(\mathbf{H}, \xi) \quad (3{\cdot}5)$$

$$K(\mathbf{H}, \xi) = 2\sum_{i=1}^{N/2} K_i(\mathbf{H}, \xi)\,. \quad (3{\cdot}6)$$

Multiplying each $G_i(\mathbf{H}, \xi)$ as well as $K_i(\mathbf{H}, \xi)$ by $\cos 2\pi \mathbf{H}_1 . \mathbf{r}_i$ and $\sin 2\pi \mathbf{H}_1 . \mathbf{r}_i$ respectively, we obtain new functions G_c, K_c, G_s and K_s of the form:

$$G_c(\mathbf{H}, \mathbf{H}_1, \xi) = 2\sum_{i=1}^{N/2} G_i(\mathbf{H}, \xi) \cos 2\pi \mathbf{H}_1 . \mathbf{r}_i \quad (3{\cdot}7)$$

$$K_c(\mathbf{H}, \mathbf{H}_1, \xi) = 2\sum_{i=1}^{N/2} K_i(\mathbf{H}, \xi) \cos 2\pi \mathbf{H}_1 . \mathbf{r}_i \quad (3{\cdot}8)$$

$$G_s(\mathbf{H}, \mathbf{H}_1, \xi) = 2\sum_{i=1}^{N/2} G_i(\mathbf{H}, \xi) \sin 2\pi \mathbf{H}_1 . \mathbf{r}_i \quad (3{\cdot}9)$$

$$K_s(\mathbf{H}, \mathbf{H}_1, \xi) = 2\sum_{i=1}^{N/2} K_i(\mathbf{H}, \xi) \sin 2\pi \mathbf{H}_1 . \mathbf{r}_i \quad (3{\cdot}10)$$

where $\mathbf{H}_1$ is not necessarily different from $\mathbf{H}$. The value of $\xi_{\text{min.}}$ which belongs to these functions will be either equal to, or less than the value of $\xi_{\text{min.}}$ belonging to the function $G(\mathbf{H}, \xi)$ and $K(\mathbf{H}, \xi)$, no matter which $\mathbf{H}_1$ has been chosen. It is evident that the functions (3·7)–(3·10) depend upon $(\mathbf{H}+\mathbf{H}_1)$, $(\mathbf{H}-\mathbf{H}_1)$, $(2n\mathbf{H}_0+\mathbf{H}_1)$, $(2n\mathbf{H}_0-\mathbf{H}_1)$, $[(2n+1)\mathbf{H}_0+\mathbf{H}_1]$ and $[(2n+1)\mathbf{H}_0-\mathbf{H}_1]$.

For the purpose of expanding the expressions (3·7)–(3·10) in series similar to those given by (3·3) and (3·4), we introduce new symbols by writing

$$U_{cc}(\mathbf{H}_1, \mathbf{H}_2) = 2\sum_{i=1}^{N/2} (n_i \cos 2\pi \mathbf{H}_1 . \mathbf{r}_i)(\cos 2\pi \mathbf{H}_2 . \mathbf{r}_i) \quad (3{\cdot}11)$$

$$U_{cs}(\mathbf{H}_1, \mathbf{H}_2) = 2\sum_{i=1}^{N/2} (n_i \cos 2\pi \mathbf{H}_1 . \mathbf{r}_i)(\sin 2\pi \mathbf{H}_2 . \mathbf{r}_i) \quad (3{\cdot}12)$$

$$U_{sc}(\mathbf{H}_1, \mathbf{H}_2) = 2\sum_{i=1}^{N/2} (n_i \sin 2\pi \mathbf{H}_1 . \mathbf{r}_i)(\cos 2\pi \mathbf{H}_2 . \mathbf{r}_i) \quad (3{\cdot}13)$$

$$U_{ss}(\mathbf{H}_1, \mathbf{H}_2) = 2\sum_{i=1}^{N/2} (n_i \sin 2\pi \mathbf{H}_1 . \mathbf{r}_i)(\sin 2\pi \mathbf{H}_2 . \mathbf{r}_i)\,. \quad (3{\cdot}14)$$

Using the formulae (2·1) and (2·2) we may write these expressions in the form

$$U_{cc}(\mathbf{H}_1, \mathbf{H}_2) = \tfrac{1}{2}[U_c(\mathbf{H}_1+\mathbf{H}_2) + U_c(\mathbf{H}_1-\mathbf{H}_2)] \quad (3{\cdot}15)$$

$$U_{cs}(\mathbf{H}_1, \mathbf{H}_2) = \tfrac{1}{2}[U_s(\mathbf{H}_1+\mathbf{H}_2) - U_s(\mathbf{H}_1-\mathbf{H}_2)] \quad (3{\cdot}16)$$

$$U_{sc}(\mathbf{H}_1, \mathbf{H}_2) = \tfrac{1}{2}[U_s(\mathbf{H}_1+\mathbf{H}_2) + U_s(\mathbf{H}_1-\mathbf{H}_2)] \quad (3{\cdot}17)$$

$$U_{ss}(\mathbf{H}_1, \mathbf{H}_2) = \tfrac{1}{2}[-U_c(\mathbf{H}_1+\mathbf{H}_2) + U_c(\mathbf{H}_1-\mathbf{H}_2)]\,. \quad (3{\cdot}18)$$

We have now for the functions (3·7)–(3·10) the following expressions:

$$G_c(\mathbf{H}, \mathbf{H}_1, \xi) = U_{cc}(\mathbf{H}, \mathbf{H}_1) \cos 2\pi p\xi + U_{sc}(\mathbf{H}, \mathbf{H}_1) \sin 2\pi p\xi - a_0(p) U_c(\mathbf{H}_1) - \left[\sum_{n=1}^{\infty} a_n(p) U_{cc}(2n\mathbf{H}_0, \mathbf{H}_1) \cos 2\pi 2n\xi\right] - \left[\sum_{n=1}^{\infty} a_n(p) U_{sc}(2n\mathbf{H}_0, \mathbf{H}_1) \sin 2\pi 2n\xi\right] \quad (3{\cdot}19)$$

$$K_c(\mathbf{H}, \mathbf{H}_1, \xi) = U_c(\mathbf{H}_1) + U_{cc}(2\mathbf{H}, \mathbf{H}_1) \cos 2\pi 2p\xi + U_{sc}(2\mathbf{H}, \mathbf{H}_1) \sin 2\pi 2p\xi - 2\left\{\sum_{n=1}^{\infty} a_{2n+1}(p) U_{cc}[(2n+1)\mathbf{H}_0, \mathbf{H}_1] \cos 2\pi(2n+1)\xi\right\} - 2\left\{\sum_{n=1}^{\infty} a_{2n+1}(p) U_{sc}[(2n+1)\mathbf{H}_0, \mathbf{H}_1] \sin 2\pi(2n+1)\xi\right\} \quad (3{\cdot}20)$$

$$G_s(\mathbf{H}, \mathbf{H}_1, \xi) = U_{cs}(\mathbf{H}, \mathbf{H}_1) \cos 2\pi p\xi + U_{ss}(\mathbf{H}, \mathbf{H}_1) \sin 2\pi p\xi - a_0(p) U_s(\mathbf{H}_1) - \left[\sum_{n=1}^{\infty} a_n(p) U_{cs}(2n\mathbf{H}_0, \mathbf{H}_1) \cos 2\pi 2n\xi\right] - \left[\sum_{n=1}^{\infty} a_n(p) U_{ss}(2n\mathbf{H}_0, \mathbf{H}_1) \sin 2\pi 2n\xi\right] \quad (3{\cdot}21)$$

$$K_s(\mathbf{H}, \mathbf{H}_1, \xi) = U_s(\mathbf{H}_1) + U_{cs}(2\mathbf{H}, \mathbf{H}_1) \cos 2\pi 2p\xi + U_{ss}(2\mathbf{H}, \mathbf{H}_1) \sin 2\pi 2p\xi - 2\left\{\sum_{n=1}^{\infty} a_{2n+1}(p) U_{cs}[(2n+1)\mathbf{H}_0, \mathbf{H}_1] \cos 2\pi(2n+1)\xi\right\} - 2\left\{\sum_{n=1}^{\infty} a_{2n+1}(p) U_{ss}[(2n+1)\mathbf{H}_0, \mathbf{H}_1] \sin 2\pi(2n+1)\xi\right\}. \quad (3{\cdot}22)$$

By variation of $\mathbf{H}_1$ all hkl can be included in the computation. If a convenient value of $\mathbf{H}$ was chosen, one will obtain a $\xi_{\text{min.}}$ with a value considerably smaller than $\frac{1}{4}$. The value of $\xi_{\text{min.}}$ depends upon the atomic coordinates (x_i, y_i, z_i), i.e. it varies from structure to structure.

A further generalization of the expressions (3·7)–(3·10) might be useful by the introduction of more $\mathbf{H}_j$ terms. In this case we have:

$$G_{\substack{ccc\\sss}}(\mathbf{H}, \mathbf{H}_1, \mathbf{H}_2, \mathbf{H}_3, \ldots, \xi) = 2\sum_{i=1}^{N/2} G_i(\mathbf{H}, \xi) \times \begin{matrix}(\cos 2\pi\mathbf{H}_1.\mathbf{r}_i)\,(\cos 2\pi\mathbf{H}_2.\mathbf{r}_i)\,(\cos 2\pi\mathbf{H}_3.\mathbf{r}_i)\ldots\\(\sin 2\pi\mathbf{H}_1.\mathbf{r}_i)\,(\sin 2\pi\mathbf{H}_2.\mathbf{r}_i)\,(\sin 2\pi\mathbf{H}_3.\mathbf{r}_i)\ldots\end{matrix} \quad (3{\cdot}23)$$

$$K_{\substack{ccc\\sss}}(\mathbf{H}, \mathbf{H}_1, \mathbf{H}_2, \mathbf{H}_3, \ldots, \xi) = 2\sum_{i=1}^{N/2} K_i(H, \xi) \times \begin{matrix}(\cos 2\pi\mathbf{H}_1.\mathbf{r}_i)\,(\cos 2\pi\mathbf{H}_2.\mathbf{r}_i)\,(\cos 2\pi\mathbf{H}_3.\mathbf{r}_i)\ldots\\(\sin 2\pi\mathbf{H}_1.\mathbf{r}_i)\,(\sin 2\pi\mathbf{H}_2.\mathbf{r}_i)\,(\sin 2\pi\mathbf{H}_3.\mathbf{r}_i)\ldots\end{matrix} \quad (3{\cdot}24)$$

4. Application and discussion

The functions $G(h, \xi)$ and $K(h, \xi)$ may be conveniently applied for sign determination in the following way:

The search for the correct set of signs begins with the set which satisfies condition (2·10). At first, we have to remember that this condition is satisfied for only one set of signs S_{2n} belonging to even amplitudes $U_c(2n)$, but that two sets of signs S_{2n+1} and $-S_{2n+1}$ can be alternatively allotted to the odd amplitudes $U_c(2n+1)$. This is due to the alternative imposed by the choice of the origin, since we can define the structure by means of the parameters x_i as well as $\frac{1}{2}+x_i$. It will be convenient therefore to omit all odd terms $U_c(2n+1)$ and to carry out the computation with a reduced function $G_r(h, \xi)$ which includes the even terms $U_c(2n)$ only. This means that an arbitrary symmetry centre was introduced in the points $x=\frac{1}{4}, \frac{3}{4}$ so that to each atom in x_i an arbitrary atom $\frac{1}{2}-x_i$ was added. For this reason, two sets of signs S_{2n} and $(-1)^n S_{2n}$ are possible, according to the choice of origin at $x=0$ or $x=\frac{1}{4}$. Which of the two sets is correct has to be determined by means of the function $K(h, \xi)$. The set of signs obtained by means of $G_r(1, \xi)$ is to be applied in considering the next odd function $G_r(3, \xi)$, by which the next even amplitude $U_c(2n)$ is introduced and the procedure continued.*

The method was examined in this laboratory on a hypothetical centrosymmetric structure defined, without the knowledge of the author, by five identical points atoms with the x-coordinates given in Table 1. The unitary structure factors $U_c(h)$ were calculated for h from 1 to 16, but only the moduli $|U_c(h)|$ were given to the author for sign determination by means of the suggested method.

Table 1. *Atomic parameters of the hypothetical structure*

x_1	0·06	x_4	0·30
x_2	0·20	x_5	0·40
x_3	0·24		

The functions G and K were multiplied by a factor 200π for the sake of convenience in the computation which was carried out by means of Beevers & Lipson strips.

The terms of the series included in the computation on $G(h, \xi)$ and $K(h, \xi)$ depended upon h and $U(n)$. So for example the coefficients of the series in $G(h, \xi)$ are of the value:

$$a_n = \frac{4h}{\pi(h^2-4n^2)} \sin 2\pi h/4 . \cos 2\pi n/2$$

(Appendix (i), (2)). It is seen that those terms of the series with the coefficients a_n where the difference (h^2-4n^2) is as small as possible will most contribute to the sum of the series. By increasing h, the higher terms of the series will also be included. By analogy the same is true for $K(h, \xi)$. Absolute values of unitary structure factors exert also a great influence upon the convergence of the series. In the product by a_n they give the criterion to judge whether they will be included in the computation or not.

The reduced function $G_r(1, \xi)$ was given by the formula

$$\begin{aligned} 200\pi G_r(1, \xi) &\\ = -400 - 800/3\,U_c(2)\cos 2\pi 2\xi + 800/15\,U_c(4)\cos 2\pi 4\xi &\\ -800/35\,U_c(6)\cos 2\pi 6\xi + - \ldots + 628\,U_s(1)\sin 2\pi\xi\,. \end{aligned}$$

In the first approximation the remaining terms were omitted from the computation.

Substituting the values for $U_c(h)$ for $h=2, 4, 6$ from Table 4 we have

$$\begin{aligned} 200\pi G_r(1, \xi) = -400 - 83\,.\,S_2 \cos 2\pi 2\xi &\\ +9\,.\,S_4 \cos 2\pi 4\xi - 8\,.\,S_6 \cos 2\pi 6\xi &\\ -[-400+83\,.\,S_2+9\,.\,S_4+8\,.\,S_6] \sin 2\pi\xi\,. \end{aligned}$$

In order to find out the correct set of the three signs S_2, S_4, S_6 we have to compute $2^3=8$ different for $200\pi G_r(1, \xi)$. The result is shown graphically in Fig. 2. It is clearly seen that only set No. VI (Table 2) in

Table 2. *Variation of signs of the structure factors $U(2)$, $U(4)$ and $U(6)$*

	S_2	S_4	S_6		S_2	S_4	S_6
I	+1	+1	+1	V	+1	−1	−1
II	+1	+1	−1	VI	−1	+1	−1
III	+1	−1	+1	VII	−1	−1	+1
IV	−1	+1	+1	VIII	−1	−1	−1

* In practice, the function $G(h, \xi)$ will not have the constant value zero throughout the interval $\xi_{\min.} \leqq \xi \leqq \frac{1}{4}$ but will fluctuate between small positive and negative values decreasing to $G(h, \xi)=0$ for $\xi=\frac{1}{4}$. This fluctuation is caused by the approximation of the series by a limited number of terms and may be source of an uncertainty in the choice of the signs. It is necessary, therefore, to consider the subsequent functions $G(h, \xi)$ with h odd in order to find out the correct set of signs and so to eliminate the ambiguous ones. It might happen that even after that trial we cannot decide between two sets; that will be so when the values of $U_c(h)$ are very near to zero. On such an occasion we have to decide which set of signs is most probable.

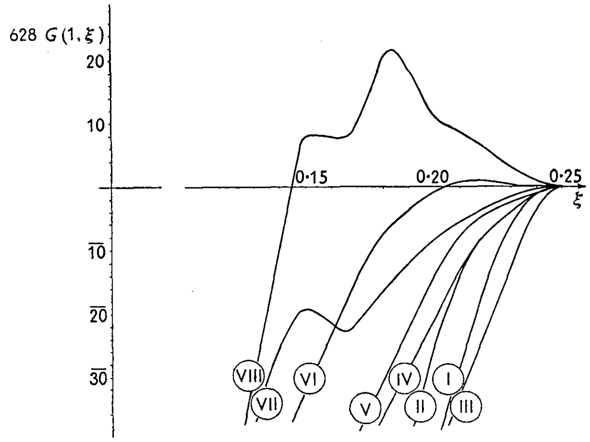

Fig. 2. Curves of the functions $G(1, \xi)$ for eight possible variations of the signs S_2, S_4, S_6 for the hypothetic structure. Variation No. 6 is correct.

which $S_2=-1$, $S_4=+1$, $S_6=-1$ satisfies the condition (2·11) where $\xi_{\min.}$ has the value $\xi_{\min.}=0{\cdot}20$. For all the other seven variations of signs the function $200\pi G_r(1, \xi)$ 'detaches' itself considerably from the abcissa even very near the point $\xi=\frac{1}{4}$ and remains different from zero for all ξ which is $\xi<\frac{1}{4}$.

Now, we have to use the function $G_r(3, \xi)$ with the signs for $U_c(2)$, $U_c(4)$, $U_c(6)$ just obtained and try to find out the correct signs for $U_c(8)$ and $U_c(10)$. We can easily establish that $G_r(3, \xi)=0$ for all ξ for which $0{\cdot}20 \leq \xi \leq \frac{1}{4}$, when the above signs S_h for $h=2$, 4, 6 are inserted and when $S_8=-1$ and $S_{10}=+1$. The use of the subsequent functions $G_r(5, \xi)$, $G_r(7, \xi)$ and $G_r(11, \xi)$ confirmed the previous choice of signs and gave the signs for the amplitudes for higher h. (Fig. 3 and Table 3).

Table 3. *Subsequent determination of the signs S_{2n} by means of $G(h, \xi)$*

	S_2	S_4	S_6	S_8	S_{10}	S_{12}	S_{14}	S_{16}
$G(1, \xi)$	−1	+1	−1					
$G(3, \xi)$	−1	+1	−1	−1	+1			
$G(5, \xi)$	−1	+1	−1	−1	+1			
$G(7, \xi)$	−1	+1	−1	−1	+1	−1		
$G(11, \xi)$	−1	+1	−1	−1	+1	−1	−1	+1

Thus, all possible variations of signs for the even amplitudes were reduced to two sets of signs S_{2n} and $S_{2n}(-1)^n$. Only the result for such a small amplitude as $|U_c(14)|=0{\cdot}06$ could not be considered as reliable. Nevertheless the sign $S_{14}=-1$ seemed more probable.

Function $K(h, \xi)$ involves, except $U(2h)$, only odd structure factors $U_c(2n+1)$ and $U_s(2n+1)$. Meanwhile, all $U_s(2n+1)$ involve even terms $U_c(2n)$ only, for which the signs have just been determined and given by the two alternative sets. It was shown by the computation, which had been carried out for $K(1, \xi)$, and

Table 4. *Calculated S_c and determined S_d signs of the hypothetical structure*

h	$\|U_c(h)\|$	S_c	S_d	h	$\|U_c(h)\|$	S_c	S_d
1	0·04	+1	+1	9	0·25	−1	−1
2	0·32	−1	−1	10	0·28	+1	+1
3	0·11	+1	+1	11	0·40	−1	−1
4	0·17	+1	+1	12	0·15	−1	−1
5	0·20	+1	+1	13	0·25	+1	+1
6	0·35	−1	−1	14	0·06	−1	−1
7	0·20	−1	−1	15	0·20	+1	+1
8	0·29	−1	−1	16	0·26	+1	+1

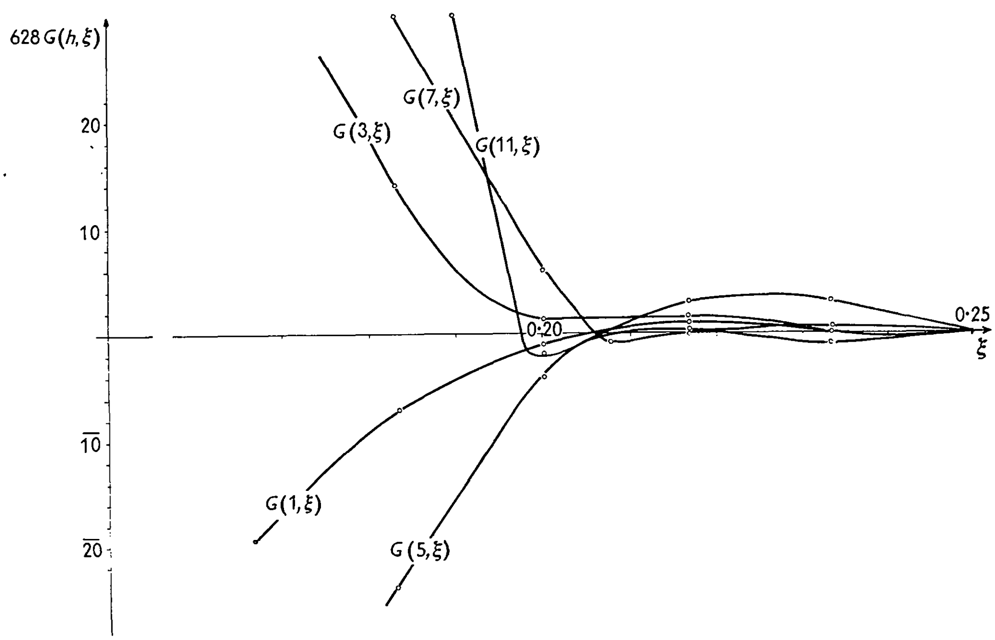

Fig. 3. Curves of the function $G(h, \xi)$ for $h=1$, 3, 5, 7, 11 by means of which the correct signs S_{2n} for the hypothetical structure were determined.

$K(3, \xi)$, $K(5, \xi)$, $K(7, \xi)$ and $K(9, \xi)$ in the same way as for $G_r(h, \xi)$, that condition (2·10) could be satisfied only when the signs S_{2n} had been used for even $U_c(h)$; on the other hand, by using the signs $S_{2n}(-1)^n$ contradictory results were always obtained. Similarly the sign for $|U_c(1)|=0{\cdot}04$ could not be determined with certainty, but it was supposed that $S_1=+1$ is more probable.

Table 4 gives the values of the structure amplitudes $|U_c(h)|$ for h from 1 to 16, appertaining to the signs S_h as well as to signs S_d obtained by the method described. It follows that the agreement is complete.

5. Appendix

(i). The function $\cos 2\pi hx$ within the interval $0 \le |x| \le \frac{1}{4}$ for h odd can be expanded in a Fourier cosine series with the coefficients

$$a_0(h) = \frac{2}{\pi h} \sin 2\pi h/4 \tag{1}$$

$$a_n(h) = \frac{4h}{\pi(h^2-4n^2)} \sin 2\pi h/4 . \cos 2\pi n/2 . \tag{2}$$

(ii) The function $\sin 2\pi hx$ within the interval $0 \le |x| \le \frac{1}{2}$ can be expanded in a Fourier cosine series with the coefficients

$$b_0(h) = \frac{1}{\pi h}[1-(-1)^h] \tag{3}$$

$$b_n(h) = \frac{2h}{\pi(h^2-n^2)}[1-(-1)^{h+n}] . \tag{4}$$

In the Fourier series

$$\sin 2\pi hx = b_0(h) + \sum_n b_n(h) \cos 2\pi nx \tag{5}$$

let the parameter x acquire all values x_i. Then, by summation over all i, we can express $U_s(h)$ by means of $U_c(n)$ in such a way that

$$U_s(h) = \frac{1}{\pi}\left\{\frac{1-(-1)^h}{h} + 2\sum_n \frac{h[1-(-1)^{h+n}]}{h^2-n^2} U_c(n)\right\} . \tag{6}$$

(iii). The function $\cos^2 2\pi hx$ within $0<x<\frac{1}{4}$ and the function $-\cos^2 2\pi hx$ within $\frac{1}{4}<x<\frac{1}{2}$ for every odd h can be expanded in a Fourier series with the coefficients

$$A_0 = 0 \tag{7}$$

$$A_n = \frac{8h^2}{\pi(2n-1)[4h^2-(2n-1)^2]} \cdot \sin 2\pi(2n-1)/4 . \tag{8}$$

(iv) The use of series (2·12) is stipulated by the condition $x_i(\text{max.})<\frac{1}{2}$. In the case of $x_i(\text{max.})=\frac{1}{2}$ for any variation of signs, the function $G(h, \xi)$ will attain the value of zero only for $\xi=\frac{1}{4}$. Such a behaviour of the function $G(h, \xi)$ will be discovered during the calculation. In this case the introduction of 'difference structure factors' $U_{cd}(h)$ defined by

$$U_{cd}(h) = S_h|U_c(h)| - n_i \cos 2\pi h/2 \tag{9}$$

is suggested, so that the whole procedure is to be repeated using these factors.

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