$H^+$ ions formed from the $H_2O$ molecules which have contributed $O^{2-}$ ions to the complex ion.

The X-ray work on this structure was carried out in Uppsala, where I was assisted by Mr Bengt Lindqvist, whom I should like to thank for his valuable aid. The Swedish Natural Science Research Council supported the investigation financially, and their support is gratefully acknowledged. The computation work took place at Pennsylvania State College, and I wish to thank Prof. Ray Pepinsky for his generous invitation to me to visit his Institute and to work with his X-RAC computer.*

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# Fourier Strips at a 3° Interval

BY C. A. BEEVERS

*Dewar Crystallographic Laboratory, University of Edinburgh, Scotland*

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The production of a new set of Fourier strips to an interval of 3° is described and the uses are outlined. It is thought that this set will be of considerable service in structure-factor calculation as well as in the computation of electron-density and Patterson maps, and in the calculation of molecular Fourier transforms.

## 1. Introduction

The printed 'strips' of numbers for the evaluation of the Fourier series used in X-ray analysis were introduced by Lipson & Beevers in 1934, when a set of strips to an interval of 6° was produced. Some 75 copies of the original set were distributed to workers in many parts of the world, and they have been widely used both for the Fourier-series summation of electron densities, and for the Patterson syntheses which are being increasingly employed in the study of complex structures. They have also been used for Fourier analysis in other applications, e.g. by Ross (1943).

The original strips tabulated the values of $A\cos nh\theta$ and $A\sin nh\theta$, where $\theta$ is 6°, and $n$ takes the values 0 (1) 15 along the strip, and where $A$ has the values 0 (1) 100 on different strips. In this set the negative values of $A$ are on the reverse side of the corresponding positive-value strips. Strips having the same value of $h$ are placed in order of $A$ in one compartment of a box with sloping sides, and the different compartments of this box contain strips of the different values of $h$ from 0 to 20.

As was pointed out in one of the early papers (Lipson & Beevers, 1936), the interval $\theta = 6°$ is considered adequate for the Fourier synthesis of crystals having their greatest projection edge less than 15 Å. Modern X-ray analysis is, however, frequently concerned with projection edges considerably greater than this, at least in one direction, and therefore a finer interval of division is necessary. Furthermore, the 6° strips are inaccurate for structure-factor calculations, although a structure factor can always be reduced to summations of terms of the type $A \begin{matrix}\cos\\ \sin\end{matrix} nh\theta$. For this use of the strips the atomic parameters would be taken to be $h\theta$, and the contribution of the atom to the different orders would be obtained by going to different values of $n$ along the strip. With $\theta = 6°$, however, the coordinate $h\theta$ would be hopelessly inaccurate for the higher orders (larger $n$), and furthermore the limit of 20 to the value of $h$ would restrict the atom to the first third of the unit cell. These considerations limit the application of the 6° strips to structure-factor calculations.

The present paper describes the design of a further set of Fourier strips at an interval $\theta=3°$. It is thought that this set will not only permit the strip method to be used for Fourier synthesis of unit cells up to 30 Å projection edge, but will also provide a wide field of application to structure-factor calculation (see Beevers & Lipson, 1952).

The Fourier-strip method requires the addition of

the numbers on the selected batch of strips to be carried out either mentally or by the use of an auxiliary adding machine. Various means have been devised to avoid this large amount of adding. Among these methods are:

(*a*) Hollerith machines using punched cards. These methods are apt to be rather cumbersome, and are not particularly fast or cheap, although they are accurate and comprehensive. Many sets of the data have to be carried on the Hollerith cards since a large number of additions must be run through at one time, and this necessitates a very large pack of cards.

(*b*) Electrical analogue machines of the Hägg–Laurent type (Hägg & Laurent, 1946). Machines of this type which will work to a high accuracy are difficult to make, but if a slightly lower accuracy is permitted an inexpensive machine can be made which will operate very well (Stern, 1950). One advantage of the Hägg–Laurent type of machine is that it can be made to carry out the summations over the full unit cell, i.e. $n\theta$ up to 360°, whilst the strip methods, in order to keep the strips to a manageable length, require the separation of the functions having the different symmetries at $n\theta = 90°$ and 180°.

(*c*) Electronic machines of the X-RAC type and also fast digital computers. These can undoubtedly be made to any requirements of accuracy and speed. They are, however, very expensive both to build and to maintain, and for this reason are not likely to replace the need for a cheap and individual method.

Robertson (1948*a*, *b*) has also described an extension of his previously described procedure. This uses a set of strips containing the values of $A \cos\theta$ only, but to three figures. The multiples $nh$ of $n$ are selected either by using a set of stencils, or a mechanical sorting device. These methods have several disadvantages compared with the strip method described in the present paper. They are necessarily slower and considerably more awkward in use. Several sets of the strips are needed in case the same amplitude is required more than once. Their only advantage lies in the three-figure accuracy, and this is very seldom required in the author's experience. Indeed the chief applicability of strip methods is in the carrying out of rough preliminary calculations, many of which are usually required in a structure determination. However, if three-figure working is needed it can be obtained in the present set of strips by the selection of two strips for amplitudes greater than 100.

It is therefore thought that the Fourier-strip method still has advantages of cheapness, convenience, availability and adaptability which make the production of a 3° set of strips worth while. This conclusion was reached by the X-ray Analysis Group of the Institute of Physics in 1947 when the writer was asked to produce a new set of strips to a 3° interval. This task has now been completed, and more than 120 sets of the new strips have been supplied to many different laboratories.

## 2. Design of the strips

The present set of strips contains the values of $A \cos nh\theta$ and $A \sin nh\theta$, where $A$ has the range of values 1 (1) 100 (100) 900, i.e. 1 to 100 in steps of 1 and 100 to 900 in steps of 100, together with the corresponding negative numbers. The wave-number $h$ of the strip, has values 0 (1) 30 and is constant on one strip, whilst $n$ goes from 0 to 30 in steps of 1 along one strip, even values of $n$ being on one side and odd values of $n$ on the other. For values of $n$ in the range 30–60, the same strips can be used, but reading from right to left and making appropriate changes of the sign of the amplitude $A$. Similarly the range of $n$ can be extended to cover 60–90 and 90–120, $n = 120$ being of course the full range of the argument $n3°$. The rules governing the changes of sign and the direction in which the strip must be read are easily seen to be as given in Table 1.

Table 1

| | Cosine | | Sine | |
|---|---|---|---|---|
| $n$ | $h$ even | $h$ odd | $h$ even | $h$ odd |
| 0–30 | + | + | + | + |
| 60–30 | + | − | − | + |
| 60–90 | + | − | + | − |
| 120–90 | + | + | − | − |

The range of $h$ can be extended similarly by the interchange of $h$ and $n$ in Table 1. In this case, however, since successive values of $n$ are on the same strip, we need to control the signs of the odd and even places along the strip independently. This is aided in the present set by the placing of odd and even positions on obverse and reverse sides. In this way a set of strips is obtained which represents every possible value of both $n$ and $h$, by merely changing signs in an appropriate way. The even-place sides of the strips are denoted by CE (cosine even places) and SE (sine even places), whilst the odd-place sides are denoted by CO (cosine odd places) and SO (sine odd places). The even sides give a set of Fourier strips identical with the original 6° set.

The first entry on each strip is the amplitude $A$ which, as already stated, covers the range $-100$ to $+100$ in steps of 1 and then goes up to $\pm 900$ in steps of 100. If the amplitudes can be reduced to within the range $\pm 100$ the strips can be added mentally with a good speed, keeping a careful watch for the many cancellations or near cancellations which occur in a set of arbitrary positive and negative numbers. Amplitudes greater than 100 must be obtained by drawing two strips, and if there are many such double strips in a summation the work of addition will probably be found most speedy with the use of a machine. The maximum amplitude possible from two strips, viz. $\pm 1{,}000$, is considered to be sufficiently accurate for any crystal-structure calculations, and it is probable that the majority of computations can

be carried out within the range $\pm 100$. For more precise information on the subject of accuracy see Cochran (1948). In all but final syntheses it is possible to get surprisingly good results using quite small input amplitudes and it is possible to save much time in this way.

We therefore require sine strips for values of $h$ from 1 to 30, and cosine strips from 0 to 30 (sine strips for $h$ zero being zero throughout), i.e. 61 strips of each amplitude and sign. The total number of positive amplitudes is 100 (1 to 100) plus 8 (200 to 900 in steps of 100), thus giving a total number of amplitudes equal to 216. The total number of strips in a set is thus $61 \times 216 = 13{,}176$; each strip containing 16 entries on its 'even' side and 15 on its 'odd' side. Each strip also carries at its left-hand side letters and numbers for its identification, and a cross total in brackets at the right.

### 3. Production of the strips

We have produced 130 sets of these 13,176 strips and are now (1952) engaged in a further issue of 140 sets. Suppose the strips arranged with successive amplitudes below one another, then there are only 31 different columns of numbers of each sign. This arises since $nh$ is integral so that there are only 31 positive values of sine and cosine $nh\theta$, and 31 negative values, namely the values of $\pm$(sin 0°, sin 3°, sin 6°, etc.). Sufficient copies of these columns were duplicated and the copies were arranged so as to give the tables required. As the complete columns were too long for convenient handling they were divided into six parts, $\pm A =$ 1 (1) 36, 37 (1) 72, and 73 (1) 100 (100) 900, each part thus being a column of 36 numbers. The total of every line of the tables was then obtained by the use of an adding machine. The complete set of tables was typed on to stencils and duplicated on to thin card by Roneo machines (later by an Ellams flat-bed duplicator). The odd- and even-place tables were printed back to back, great care being taken with the up-and-down registration.

The cutting of the tables into strips is accomplished using a Merrett-type guillotine fitted with adjustable stops, and with a device for catching the cut strips in order. Care is necessary to guard against occasional variations in the spacings of the rows of figures, but with practice it is easy to obtain a packet of strips of uniform width. Adjacent strips are cut from the same card and will therefore be of identical length, and this ensures that in use the packet can be slightly bent and 'flipped' through one at a time for the rapid selection of the correct amplitude. The strips are stored in boxes with sloping sides very similar to those used in the original set. There are 31 compartments in each box, one box being used for cosine and one for sine strips. Each compartment corresponds to one value of $h$. In use it is of some help if the edges of cards of amplitudes $\pm 10$, 20, 30 etc. are coloured to facilitate the ready selection of amplitudes. The strips of zero amplitude are omitted altogether from the set, as are the sine strips with $h$ zero. Also the sides corresponding to $\cos h = 30$, $n$ odd, and $\sin h = 30$, $n$ even, are zero and are left blank.

The box of strips which is being used can be conveniently placed on the table with its length directed away from the worker, the smaller $h$ values being towards him. Selection of the strips may be made with the left hand, the right hand being used to keep the place in the list of required amplitudes. After withdrawal, the strips chosen should be carefully checked before adding. If addition is done mentally each column should be added twice. If machine addition is being used the cross totals given in brackets at the right-hand end of the strips may be used, the total of the cross totals should of course be equal to the cross total of the totals.

### 4. Uses of the Fourier strips

The use of the strips for Fourier synthesis is well known. In the general case the formula for a two dimensional summation is:

$$\varrho(x, y) = \frac{1}{S} \sum_h \sum_k F(hk) \exp\left[-2\pi i(hx+ky)\right]$$

$$= \frac{1}{S} \sum_h \sum_k \{A(hk) \cos 2\pi(hx+ky) + B(hk) \sin 2\pi(hx+ky)\}$$

where $x$ and $y$ are the variable coordinates covering the cell, $S$ is the area of the projection, and $A$ and $B$ are the two parts of the structure factor, i.e.

$$A = |F| \cos \alpha, \; B = |F| \sin \alpha ,$$

$\alpha$ being the phase angle of the reflexion. The variation of the signs and magnitudes of the $A$'s and $B$'s with changes of sign of $h$ and $k$ can be utilized to reduce the limits of summation of $h$ and $k$. This process and, if necessary, an expansion of the cos or sin $2\pi(hx+ky)$ terms reduces the summation to a number of summations of the form

$$\sum_0^H \sum_0^K A(hk) \cos 2\pi hx . \cos 2\pi ky ,$$

or to similar terms involving sines, where $H$ and $K$ are the upper limits of $h$ and $k$. For the detailed reductions for all space groups see Lonsdale (1936). These summations are evaluated by the use of the strips in two stages. If $K$ is smaller than $H$, the $A(hk)$'s for constant $k$ are first collected and the sums

$$S(k) = \sum_0^H A(hk) \begin{matrix}\cos \\ \sin\end{matrix} 2\pi hx$$

are formed for each value of $k$ and $x$. These are next used as coefficients in the second-stage summations

$$\sum_0^K S(k) \begin{matrix}\cos \\ \sin\end{matrix} 2\pi ky ,$$

which have to be carried out for each value of $x$. The necessary ranges of $x$ and $y$ must be considered and also the interval in these coordinates at which the summation is to be done. In the earlier papers the rule suggested for the choice of interval was that if $H$ and $K$ are sufficiently small they should be multiplied by factors to bring the product as near as possible to 20. This factor can then be regarded as multiplying $\theta$, the interval of subdivision, and brings the latter up to a suitable value. The range of the strips is, of course, correspondingly increased. If $H$ or $K$ is less than 20 the strips need only to be added on the even sides, but if the maximum index $H$ or $K$ is greater than 20 then both even and odd sides should be added. In all such summations care must be taken to allow for the case where the number of $A(hk)$'s or $B(hk)$'s is reduced when $h = 0$ or $k = 0$ (see the Introduction to Lonsdale, 1936).

The 3° strips are also of considerable value in the calculation of structure factors, especially in the earlier stages of an analysis. In these stages it is convenient to keep the atoms to within 60ths or 120ths, when the strips can be used directly to give the values of the sums of terms like $\begin{matrix}\cos\\ \sin\end{matrix} 2\pi hx \,.\, \begin{matrix}\cos\\ \sin\end{matrix} 2\pi ky$. A strip can be selected to give first of all the values of $\cos 2\pi hx$ or $\sin 2\pi hx$, and these values can be used as the amplitudes of a $\cos 2\pi ky$ or $\sin 2\pi ky$ strip, which will give the answer for successive values of $k$. The strips for the various atoms can be laid beneath each other for convenience in adding. The accuracy obtainable by thus 'forcing' the atoms on to the nearest 6° or 3° is limited, and more accurate procedures are discussed by Sayre (1951) and by Beevers & Lipson (1952).

The calculation of molecular transforms also has its value in crystal-structure work, and this application of the strips has been described by Whittaker (1948).

I am indebted to the X-ray Analysis Group of the Institute of Physics for encouragement in starting this work and for some financial assistance, to Dr T. H. Goodwin for the supply of the cross-totals of the strips, and to my wife for much assistance in the work of cutting.

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# The Use of Fourier Strips for Calculating Structure Factors

BY C. A. BEEVERS

*Dewar Crystallographic Laboratory, University of Edinburgh, Scotland*

AND H. LIPSON

*Physics Department, College of Technology, Manchester, England*

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A method is described for using Fourier strips directly for the calculation of structure factors. The accuracy of the method is discussed, and some examples are given of the procedure involved.

## 1. Introduction

Much more attention seems to have been paid to the systematic calculation of electron densities in crystals than to the calculation of structure factors; the former operation is more easily dealt with, since it is concerned with precisely located points in the unit cell, whereas structure factors depend upon arbitrary positions. Nevertheless, when methods of evaluating electron densities had been satisfactorily worked out, the similarity of the electron-density equation

$$\varrho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) \exp\left[-2\pi i(hx+ky+lz)\right]$$

and the structure-factor equation

$$F(hkl) = \sum_n f_n \exp\left[2\pi i(hx_n+ky_n+lz_n)\right]$$

suggested to several workers (e.g. Robertson, 1936; Sayre, 1951) that these methods could be used for both operations.

There are, however, some difficulties associated with