that one is occupied by zinc; another, with the parameters (0·75, 0·80, 0·30), corresponds to the interstitial ions. Each of these latter forms three bonds to water molecules of mean length 2·15±0·05 Å, and three to oxygen ions 1·95±0·05 Å, and is thus identical with the Zn ion. Since the oxygens are already bonded to $Mn^{4+}$, however, a redistribution of the manganese valency electrons is necessary to preserve the balance of charge, and $\delta$ additional divalent ions between the oxygen and water sheets will give rise to an equal number in the $Mn^{4+}$ layer. This type of electrical defect, here localized in the vicinity of the interstitial ions, is better known in the tungsten bronzes. It has been demonstrated for psilomelane (Wadsley, 1953*a*) and is believed to be common to many complex manganese oxides.

The octahedron coordinated to an additional ion shares an edge with a Zn octahedron and a face with the Mn octahedron immediately below. Chalcophanite specimens with appreciable values of $\delta$ probably represent a partial transition to another structural type. In order to avoid face sharing, a considerable regrouping of the Mn sheet must be made for a stoichiometric compound ($\delta = 1$) to have a stable configuration, and the prediction of this proposes many difficulties.

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# A Stencil Method for Computing Structure Factors

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A method of using the Donnay tables for the systematic computation of structure factors is described. The advantages of the method are that it is rapid, that the required apparatus is simple to construct, and that it makes use of existing tables. In addition, a complete record of the contribution of each atom to every structure factor is obtained.

## Introduction

There is a need for a simple rapid method for calculating structure factors systematically, comparable with those available for summing Fourier series. The method proposed by Beevers & Lipson (1952) is a step in this direction, but its use is limited to the stages in a structure determination at which the atomic parameters can be expressed to the nearest 1/120th of the cell edge; the modification suggested for finer subdivision makes the method much more cumbersome. Strips with finer subdivision would be too extensive to produce *en masse*. Strips with fixed amplitude are quite practicable (Alexander, 1953), but require repetitive multiplication, a process that necessitates a calculating machine and is bound to slow down the calculations to some extent.

It occurred to the authors that it might be practicable to keep the apparatus within reasonable bounds by using stencils of the type employed in certain methods of Fourier synthesis (Patterson & Tunnell, 1942; Robertson, 1948). It was further discovered that cosine tables of the type required already existed in the form of those published by Donnay & Ham-

| (+) | (−) | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 500 | (420)$^{0}$ | 420 | 420 | 420 | 420 | 420 | 420 | 420 | 419 | 419 | 419 | 490 | 990 |
| 10 | 510 | 419 | 419 | (419)$^{1}$ | 419 | 418 | 418 | 418 | 418 | 417 | 417 | 417 | 480 | 980 |
| 20 | 520 | 417 | 416 | 416 | 416 | (415)$^{2}$ | 415 | 414 | 414 | 414 | 413 | 413 | 470 | 970 |
| 30 | 530 | 413 | 412 | 412 | 411 | 410 | 410 | (409)$^{3}$ | 409 | 408 | 407 | 407 | 460 | 960 |
| 40 | 540 | 407 | 406 | 405 | 405 | 404 | 403 | 403 | 402 | (401)$^{4}$ | 400 | 399 | 450 | 950 |
| | | | | | | | | | | | | | | |
| 50 | 550 | 399 | 399 | 398 | 397 | 396 | 395 | 394 | 393 | 392 | 391 | 391 | 440 | 940 |
| 60 | 560 | (391)$^{5}$ | 390 | 389 | 388 | 386 | 385 | 384 | 383 | 382 | 381 | 380 | 430 | 930 |
| 70 | 570 | 380 | 379 | (378)$^{6}$ | 377 | 375 | 374 | 373 | 372 | 371 | 369 | 368 | 420 | 920 |
| 80 | 580 | 368 | 367 | 365 | 364 | (363)$^{7}$ | 362 | 360 | 359 | 357 | 356 | 355 | 410 | 910 |
| 90 | 590 | 355 | 353 | 352 | 350 | 349 | 347 | (346)$^{8}$ | 344 | 343 | 341 | 340 | 400 | 900 |

Fig. 1. Section of page of Donnay tables corresponding to $ky = 0{\cdot}181$ ($\cos 2\pi ky = 0{\cdot}420$). The values of $x$ at the left and right of the diagram can be disregarded. Successive holes expose values, which are correct to two significant figures, of the product $\cos 2\pi hx . \cos 2\pi(0{\cdot}181)$.

burger (1948). These will be referred to as the Donnay tables.

## Basis of the method

The Donnay tables give values of $A \cos 2\pi x$ for different amplitudes $A$; on each page, $x$ varies from 0 to 0·250 in intervals of 0·001 and on the separate pages $A$ varies from 10 to 1000 in intervals of 10.

Stencils are used to extract the required values of $\cos 2\pi hx$ or $\sin 2\pi hx$. For example, if $x = 0{\cdot}012$, a stencil is made to expose the table at positions corresponding to successive values of $hx$, namely 0·000, 0·012, 0·024, etc. For cosine determination the hole corresponding to $h = 0$ is placed at $x = 0{\cdot}000$ (Fig. 1) and for sine values the stencil is reversed, the same hole being placed at $x = 0{\cdot}250$. For higher values of $x$ the stencils become more complicated and, of course, changes of sign must be indicated; these may be indicated directly on the stencils, but it is found preferable to list the signs at the side, since then the same stencil can be used for four different values of parameter ($x$, $-x$, $\frac{1}{2}+x$, $\frac{1}{2}-x$) for both cosines and sines. A typical stencil is shown in Fig. 2. To complete a set of structure factors of the type $\Sigma \cos 2\pi hx \cos 2\pi ky$, each atom is considered in turn. The amplitude $A$ of the Donnay tables is made equal to $\cos 2\pi ky$ (to two significant figures) for a particular value of $k$, and the successive values of $\cos 2\pi hx \cos 2\pi ky$ are then read off, again to two significant figures, by means of the stencil for the particular value of $x$. The next value of $\cos 2\pi ky$ is ascertained, the appropriate page of the Donnay tables selected, and the process repeated. When the entries have been completed the totals are found.

For structure factors of the type $\cos 2\pi(hx+ky)$, the expression may be expanded into the form

$$\cos 2\pi hx \cos 2\pi ky - \sin 2\pi hx \sin 2\pi ky\ .$$

This expansion does not double the work because the two sums obtained can be used to obtain both $F(hk0)$ and $F(\bar{h}k0)$.

Variations of this procedure are possible and may occur to others who may use the method. For example, it has been decided to produce separate stencils for odd and even indices because very often the formulae are different and only alternate values are required from a stencil. This will not double the number of stencils; the same one can be used for $x$ and $\frac{1}{4}\pm x$, with appropriate orientation of the stencil and adjustment of the signs.

## Practical details

So far the method has been used only with circles drawn on tracing paper. Successive values of $hx$ were obtained from a calculating machine, and the signs were checked from the tables produced by Buerger (1941). The stencils are almost self-checking: practi-

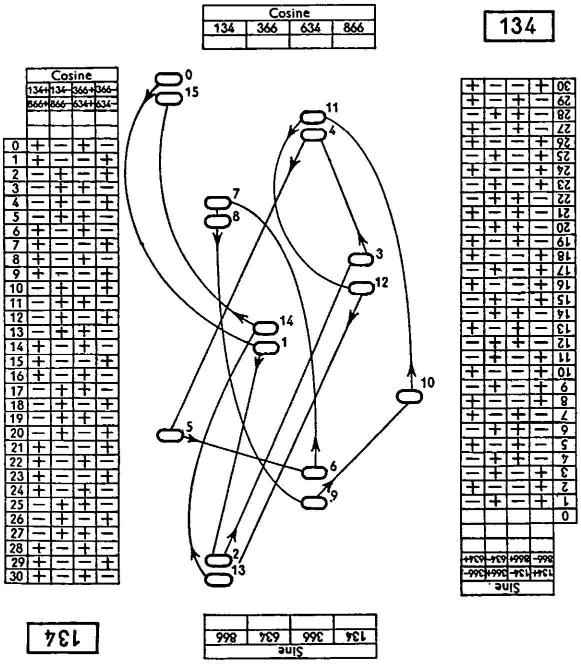

Fig. 2. Stencil for $x = 0{\cdot}134$, with $h$ varying from 0 to 15. The four columns of signs on the left are those of $\cos 2\pi hx \cos 2\pi ky$ under the following conditions:

(i) $x$ and $-x$ with $\cos 2\pi ky$ positive,
(ii) $x$ and $-x$ with $\cos 2\pi ky$ negative,
(iii) $\frac{1}{2}-x$ and $\frac{1}{2}+x$ with $\cos 2\pi ky$ positive,
(iv) $\frac{1}{2}-x$ and $\frac{1}{2}+x$ with $\cos 2\pi ky$ negative.

The equivalent tables for $\sin 2\pi hx$ are inverted on the right.

cally all of them have some pattern (Fig. 2) departures from which are easily recognized.

It is proposed to mount the Donnay tables on stiff card of the same type as that from which the stencils are to be cut. With the present arrangement it is possible to obtain the contribution of a single atom to 100 reflexions in about 20 min.; with stiff card and a board with proper locating pins, this rate should be somewhat increased.

The initial values of $\cos 2\pi ky$ can be obtained very conveniently from the tables produced by Buerger (1941). If these are not available then the preliminary tables may be prepared by laying the appropriate stencils over the page of the Donnay tables with $A = 1000$.

The additions can be performed mentally since only two-figure accuracy is involved. (Three-figure accuracy could be obtained only by increasing the size of the Donnay tables to 1000 pages—a formidable but not impossible task.) The authors have found a small Contex machine useful; its essential purpose is addition only, but for this it is much quicker than other machines. Positive and negative quantities are kept separate and the difference between the two is obtained mentally.

## Advantages of the method

It is not claimed that the method can compete with methods involving the use of punched-card or electronic devices. It is intended as a simple device for general laboratory use, and as such it has some definite advantages over existing methods:

1. It makes use of existing tables.
2. It is portable; for a given problem all that is needed is the Donnay tables and stencils equal in number to the number of parameters concerned in the projection.
3. It is cheap enough for several copies to be available in one laboratory.
4. It leaves the worker with a complete record of the calculations.

This last point is important. A complete record allows a detailed examination of the changes that occur in the structure factors as slight changes of parameter are made; one can isolate the effect of a single atom, and so have available the type of evidence that was much used in early structure determinations, but which is now largely ignored.

The method has been used in several investigations in this laboratory and is becoming increasingly popular.

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