The Determination of Parameters in Crystal Structures by means of Fourier Series.

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1. *Introduction.*

The Fourier representation of the results of X-ray analysis was first suggested by W. H. Bragg.* It was developed independently by Duane, and used by Havighurst and Compton† to give striking representations of the distribution of scattering matter in crystals. Duane and Havighurst were first in applying the method to the much more accurate X-ray measurements available in 1925, and in showing how useful it could be.

Duane used a formula derived by Epstein and Ehrenfest.‡ They showed that the intensity of an X-ray reflexion from a plane $(h\,k\,l)$ of a crystal is proportional to the square of the coefficient of a term in the Fourier series, representing the density $\rho\,(x, y, z)$ of the diffracting material in the crystal as a function of x, y, z. The general term may be written

$$\mathrm{A}\,(h\,k\,l)\sin\,(2\pi hx/a - \delta_h)\sin\,(2\pi k/b - \delta_k)\sin\,(2\pi lz/c - \delta_l)$$

Duane reversed the line of thought, and showed that it is possible to deduce the density in the crystal from the measured intensities of X-ray reflexion. The X-ray measurements give the values of $(\mathrm{A}\,(h\,k\,l)\,)^2$ but not the phase angles δ_h, δ_k, δ_l. This difficulty, Duane showed, could be surmounted in certain simple cases.

Havighurst§ used this triple Fourier series to determine the density of scattering matter in such crystals as rock-salt, NaCl. The calculations are lengthy, and Havighurst confined himself to evaluating the series along certain lines (cube edges or face-diagonals). Later, he used the same series for the determination of crystal parameters and analysed by its aid the mercurous halides which have structures with two parameters.

Compton made the further step of correlating the coefficients $\mathrm{A}\,(h\,k\,l)$ with

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* 'Phil. Trans.,' A, vol. 215, p. 253 (1915).

† Duane, 'Proc. Nat. Acad. Washington,' vol. 11, p. 489 (1925); Havighurst, *ibid.*, vol. 11, p. 502 (1925); Compton, "X-rays and Electrons," p. 151.

‡ 'Proc. Nat. Acad. Sci.,' vol. 10, p. 133 (1924).

§ 'J. Amer. Chem. Soc.,' vol. 48, p. 2113 (1926).

the absolute value F (*h k l*) of the structure factor. F (*h k l*) is the ratio of the wave amplitude scattered in a given direction by all atoms in the unit cell, to that which would be scattered according to the classical formula by a single electron under the same conditions. Using the values of F, and adding to the series a suitable constant term, Compton showed that the series represents the "electron density" at any point in the crystal. He used a simple Fourier series to express the distribution of scattering matter in sheets parallel to a given plane; for this the values of F for the different orders of reflexion by parallel planes are alone required. He also developed a formula for the radial distribution of scattering matter in an atom; for this a knowledge of the atomic scattering curve (F curve) is necessary.

The first Fourier representations of distribution of scattering matter by Havighurst and Compton were based on measurements of the quantity F (*h k l*) by Bragg, James and Bosanquet.* Compton's formula for the sheet distribution of scattering matter has been used to check the results of crystal analysis (beryl, topaz and alum)† and to measure the thermal agitation of atoms.‡

It is interesting to note that the formula of Duane is implicitly developed in a paper by Ewald in 1921 on the reciprocal lattice, referred to more fully below. It was formulated by A. B. Porter for a corresponding optical problem in 1905, and W. H. Bragg's treatment in 1915 is based on Porter's equations. Porter based his work on Abbe's diffraction theory of microscopic vision. The correlation of the intensities of spectra with coefficients in the terms of a Fourier series is indeed a well-known optical principle due originally to Abbe fifty years ago, and used by him to discuss the resolving power of microscopes; it is now becoming clear that it has its most far-reaching and perfect expression in the interpretation of X-ray diffraction.

2. *The Double Fourier Series.*

In Havighurst's calculations, although a triple Fourier series in x, y, z is used, the density is only calculated for a series of points along a chosen line in the crystal. In Compton's calculations the density in sheets parallel to a plane, or the radial density distribution, is measured. In both cases the density is in effect expressed as a function of one variable (distance along a line, perpendicular to a plane, or along an atomic radius), though theoretically the

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* 'Phil. Mag.,' vol. 41, p. 304 (1921), and vol. 42, p. 1 (1921).

† Beryl—Bragg and West, 'Roy. Soc. Proc.,' vol. 111, p. 691 (1926); Topaz—Alston and West, 'Z. Kryst.,' vol. 69, p. 149 (1928); Alum—Cork, 'Phil. Mag.,' vol. 4, p. 688 (1927).

‡ James and Firth, 'Roy. Soc. Proc.,' A, vol. 117, p. 62 (1927).

formula may be used for a complete expression of the density throughout the crystal. The difficulty of dealing with all three variables is one of calculation, as, in order to get a passably accurate expression for the density, hundreds of terms must be evaluated and summed for every point x, y, z.

The present paper describes evaluations of the series which are more extensive than those previously carried out, in that the density is *calculated for values of two variables*. The values of F $(h\,k\,l)$ are measured for all crystal reflexions around a given zone; for instance, if the zone is the a axis of the crystal, the values of F $(0\,k\,l)$ are used. A Fourier series is formed in which these values appear as coefficients, the variables being the co-ordinates y and z. Values of y and z are taken at convenient intervals, and the Fourier series is summed for every pair of co-ordinates. The result is a series of figures in rows and columns which indicate the distribution of scattering matter in the unit cell, as projected on the face (100). The direction of projection is parallel to the a axis.

The calculations can be made quite rapidly. In the cases described below, the required range of each co-ordinate is divided into 24 intervals in one direction and 12 in the other, and the Fourier series of about 40 terms is summed for 288 points.* This is done for the a, b and c axes as zone axes in turn, leading to projections of the unit cell upon its faces (100), (010) and (001). The projections (shown as contoured diagrams in figs. 1a, 2a and 3a) indicate clearly the spatial distribution of scattering matter throughout the unit cell when they are considered in combination. They enable the atomic parameters to be measured, and the number of electrons in each atom to be counted. It is the object of the present paper to describe this analysis, and to compare its results with those obtained by other ways of analysing a crystal.

In order to form the Fourier series which represents the density distribution, it is necessary to know both the amplitudes and the phase constants of all the terms. X-ray measurement determines the former, but not the latter, for it is concerned with intensities which depend on the square of the amplitude coefficients alone. If, however, the crystal has centres of symmetry, and the

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* A comparison shows that the amount of calculation required for projection on a plane is much less than that required for a complete survey of density throughout the unit cell. Suppose that F $(h\,k\,l)$ values for the general planes were used, which represented reflexion up to as high an angle as those taken into account in the present calculations for planes around each zone. The number of terms in the Fourier series representing the density at a point then proves to be between 200 and 300 instead of 40, and the series would have to be summed for 48 times as many points.

origin of co-ordinates is taken to be at one of these centres, the equations assume a much more simple form.

It will be assumed that the crystal has a centre of symmetry at the origin, and that the formula for the projection on the face (100) is required. The axes of the unit cell are of lengths a, b, c, and make angles α, β, γ with each other, so that $bc \sin \alpha$ is the total area of the face on which projection is made. Let $\rho(y, z)$ be the density of scattering matter per unit area of the projection at the point y, z. It may then be shown that

$$\rho(y, z) = (1/bc \sin \alpha) \,.\, \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \mathrm{F}(0\,k\,l) \cos 2\pi (ky/b + lz/c). \qquad (1)$$

In this formula, there are no phase-constants, but $\mathrm{F}(0\,k\,l)$ must be given the correct sign. It is positive or negative, according to whether the scattering matter in the unit cell diffracts a wave in the same or the opposite phase to that scattered by an electron at the origin. All positive and negative values of k and l are taken into account (*i.e.*, although $\mathrm{F}(0\,k\,l)$ is identical with $\mathrm{F}(0\,\bar{k}\,\bar{l})$ the corresponding terms are counted as separate contributions to the series).

In the special case where $k = 0$, $l = 0$, the value of $\mathrm{F}(0\,0\,0)$ must be taken to be Z, the total number of electrons in the unit cell. The corresponding member of the Fourier series is a constant. When integrating $\rho(y, z)$ over the face (100), all terms vanish, except the term involving $\mathrm{F}(0\,0\,0)$. Thus

$$\int_{-b/2}^{+b/2} \int_{-c/2}^{+c/2} \rho(y, z)\, dy\, dz \sin \alpha = \mathrm{F}(0\,0\,0) = \mathrm{Z}. \qquad (2)$$

Formula (1) is an extension, to two dimensions, of the formula derived by Compton for the distribution of scattering matter in sheets, and holds for a cell of any shape provided that it has a symmetry centre. It may be proved by forming the expression for $\mathrm{F}(0\,k\,l)$

$$\mathrm{F}(0\,k\,l) = \int_{-b/2}^{+b/2} \int_{-c/2}^{+c/2} \rho(y, z)\, dy\, dz \sin \alpha \cos 2\pi (ky/b + lz/c). \qquad (3)$$

When a series $\Sigma\Sigma\, \mathrm{A}(q, r) \cos 2\pi (qy/b + rz/c)$ is substituted for $\rho(y, z)$ all terms vanish on integration except those for which $q = k$, $r = l$ and $q = -k$, $r = -l$. Remembering that $\mathrm{F}(0\,k\,l) = \mathrm{F}(0\,\bar{k}\,\bar{l})$, this shows that the coefficient $\mathrm{A}(k, l)$ of the series is equal to $\mathrm{F}(0\,k\,l)/bc \sin \alpha$.

It will readily be seen that formula (1) gives the projection of scattering matter in the unit cell, in a direction parallel to any zone axis, on any crystal plane. The zone axis is taken as one axis of reference, and two other axes of reference are chosen in the plane. A set of indices $(h\,k\,l)$ becomes a set such as $(0\,\mathrm{K}\,\mathrm{L})$ referred to the new axes, and $\mathrm{F}\,(h\,k\,l)$ must now be labelled $\mathrm{F}\,(0\,\mathrm{K}\,\mathrm{L})$. Formula (1) then applies.

The formula quoted above is a special case of the general formula for the density at the point x, y, z in a crystal cell of any shape and symmetry. The reflexion from the plane $(h\,k\,l)$ must now be characterised by both an amplitude and a phase constant. Following Ewald (*loc. cit.*) $\mathrm{F}\,(h\,k\,l)$ may be expressed as a complex quantity

$$\begin{aligned}\mathrm{F}\,(h\,k\,l) &= |\,\mathrm{F}\,(h\,k\,l)\,|\,e^{\iota\theta\,(h\,k\,l)},\\ &= \frac{\mathrm{V}}{abc}\int_{-a/2}^{+a/2}\int_{-b/2}^{+b/2}\int_{-c/2}^{+c/2}\rho\,(x,\,y,\,z)\,e^{2\pi i\,(hx/a+ky/b+lz/c)}\,dx\,dy\,dz. \qquad (4)\end{aligned}$$

V is the volume of the unit cell, and a, b, c are the lengths of its edges.

If we assume a series for $(x,\,y,\,z)$ of the form

$$\rho\,(x,\,y,\,z) = \sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\mathrm{A}\,(pqr)\cos\,(2\pi\,(px/a + qy/b + rz/c) + \alpha\,(pqr)\,),$$

a formal solution is given by

$$\mathrm{A}\,(h\,k\,l) = |\,\mathrm{F}\,(h\,k\,l)\,|\,.\,\frac{1}{\mathrm{V}}.$$

$$\alpha\,(\,h\,k\,l) = -\,\theta\,(h\,k\,l).$$

The series for $(x,\,y,\,z)$ is thus

$$\rho\,(x,y,z) = \frac{1}{\mathrm{V}}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}|\,\mathrm{F}\,(h\,k\,l)\,|\cos\,(2\pi\,(hx/a+ky/b+lz/c)-\theta\,(h\,k\,l)\,). \qquad (5)$$

As before, $\mathrm{F}\,(0\;0\;0)$ is equal to Z, the total number of electrons in the unit cell. In this general case $|\,\mathrm{F}\,(h\,k\,l)\,| = |\,\mathrm{F}\,(\bar{h}\,\bar{k}\,\bar{l})\,|$ and $\theta\,(h\,k\,l) = -\,\theta\,(\bar{h}\,\bar{k}\,\bar{l})$. All terms except the constant term in the series occur in identical pairs, but it is convenient to keep the series in this form for the sake of symmetry of expression.

3. *Application of the Double Fourier Series.*

The Fourier series is applied in this paper to a crystal which has already been analysed by other methods.* The crystal is diopside, $\mathrm{CaMg}\,(\mathrm{SiO}_3)_2$, the structure of which depends on 14 parameters. Extensive measurements of $\mathrm{F}\,(0\,k\,l)$, $\mathrm{F}\,(h\,0\,l)$, $\mathrm{F}\,(h\,k\,0)$ are available and are quoted in the paper referred to above. All 14 parameters had been determined by Warren and Bragg, and it is therefore of interest to see how closely the former values agree with the

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* Warren and Bragg, ' Z. Krist.,' vol. 69, p. 167 (1928).

parameters deduced from the projections of density on the cell faces. The average difference, in this quite complex crystal, proves to be only 0·5 per cent. Other interesting points arise from a consideration of the projections, which are dealt with below.

The main point which it is desired to emphasise, is one discussed by West and the author* in a recent paper on the analysis of complex crystals. If absolute measurements of X-ray diffraction are available, the analysis of complex crystals is far more simple and certain than it is when merely comparative or qualitative estimates of diffraction are made. The paper on the structure of diopside was intended to be an illustration of the use of these measurements. The 14 parameters of the crystal can be deduced by using the absolute measurements without making any assumptions as to the probable arrangement of the atoms. In the present paper, the values of the parameters are derived in a quite different way, and the agreement in the results shows that the crystal has been analysed correctly.

The two methods of analysis are not independent, for the former analysis was used to give the correct sign to each coefficient $F(hkl)$. If the sign could be determined otherwise, the complete analysis could be made by the Fourier series. This point is briefly discussed in section 9 of the paper by Bragg and West. In the previous analysis of diopside, atomic scattering curves (F curves) for the atoms were used, and values of the parameters were found which made the observed and calculated values of $F(hkl)$ agree, signs being of course disregarded. For convenience, we may denote by $|F(hkl)|$ the quantity we can deduce from X-ray measurements of intensity, and by $F(hkl)$ the coefficient of the Fourier series. When the analysis of the structure was completed it was possible to give the right sign to each coefficient, *i.e.*, to determine $F(hkl)$. In the present analysis, therefore, the magnitudes of the Fourier coefficients depend only on X-ray measurement, but their signs are found by a previous analysis. It will be realised, however, that there is in general very little doubt about the sign of each coefficient, once an approximate analysis of the crystal has been made. It is determined in most cases by the positions of the heavier atoms of calcium, magnesium, and silicon, and quite approximate estimates of their parameters will suffice. The sign is only doubtful when F is very small, and in that case it does not matter.

As was emphasised by Duane, any given set of X-ray results may be explained even in the case of a centrosymmetrical crystal by as many different arrangements of scattering matter as there are permutations of signs in the Fourier

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* Bragg and West, 'Z. Krist.,' vol. 69, p. 118 (1928).

coefficients. The test for the correct solution is that it is reasonable, or that it indicates a distribution of scattering matter which outlines atoms such as we know to exist in the crystal. In the former analysis, the existence of four molecules of $CaMg\,(SiO_3)_2$ in the unit cell was assumed from the start, and these atoms were moved about until the experimental results were explained. In the present analysis we show in effect that a certain set of signs given to the measured values of $|F\,(h\,k\,l)|$ leads to a distribution of density which (*a*) gives consistent projections on all three cell faces ; (*b*) gives the correct number of atoms in the unit cell ; (*c*) gives the correct number of electrons to each atom. The evidence for the correctness of the solution is set forth, using the Fourier series, in a new form which is perhaps more attractive and easy to grasp.

It must be realised, however, that the analysis by assigning parameters to atoms which make observed and calculated results agree, and the analysis by finding a suitable set of signs for Fourier terms, fundamentally depend upon precisely the same criteria for their success. We assume as one criterion, for instance, that the calcium atom contains about 18 electrons with a spatial distribution which we have been able to estimate. In the first type of analysis this yields an F curve for the scattering by calcium, and such F curves are used in comparing calculated and observed results. In an analysis entirely conducted by the Fourier method, signs would be adjusted till the series outlined a recognisable calcium atom, again with the number of electrons and spatial distribution which we expect. Every step in the one type of analysis may be paralleled by a similar step in the other.

4. *Tabulation of Experimental Results for Diopside.*

The crystal diopside is monoclinic, with $a = 9\cdot71$ Å, $b = 8\cdot89$ Å, $c = 5\cdot24$ Å, $\beta = 74^\circ\ 10'$. The unit cell contains four molecules of $CaMg\,(SiO_3)_2$, hence the total number Z of electrons in the unit cell is 432. The space group is $C_{2h}{}^6$ $(2Ci - 6)$.

The projections dealt with in this paper are upon the three faces (100), (010) and (001) of the unit cell. Sets of values of $F\,(0\,k\,l)$, $F\,(h\,0\,l)$, $F\,(h\,k\,0)$ are required which are as extensive as possible. These values, taken from the paper on diopside, may be put in the form of tables such as those below.

In Table I, for example, l varies along the rows and k along the columns. Owing to the conditions imposed by the space group, only even values of k appear, and also $F\,(0\,0\,l)$ is zero when l is odd. The complete table would show negative values of k as well as of l. This is unnecessary because $F\,(0\,k\,l) = F\,(0\,\bar{k}\,\bar{l})$; we may say that every table has a centre of symmetry at the value

432 corresponding to F (0 0 0). Negative values of F are denoted by a bar above the figure. As mentioned above, the magnitudes of F are in every case determined by experimental measurement. The sign of each coefficient is determined by a previous analysis of the crystal, which need only be assumed to be approximately correct.

Table I.—Values of F (0 k l).

When $k = 0$, l is even. k is always even. When l is odd, $F(0\,k\,l) = -F(0\,k\,\bar{l})$.

Index k ↓ \ Index l→	$\bar{8}$	$\bar{7}$	$\bar{6}$	$\bar{5}$	$\bar{4}$	$\bar{3}$	$\bar{2}$	$\bar{1}$	0	1	2	3	4	5	6	7	8
0	38	—	29	—	136	—	$\overline{175}$	—	432	—	$\overline{175}$	—	136	—	$\overline{29}$	—	38
2	0	0	0	0	0	0	75	$\overline{44}$	19	44	75	0	0	0	0	0	0
4		26	33	$\overline{26}$	0	50	72	$\overline{82}$	0	82	72	$\overline{50}$	0	26	33	$\overline{26}$	
6			0	29	0	$\overline{44}$	88	50	94	$\overline{50}$	88	44	0	$\overline{29}$	0		
8				0	0	0	28	25	0	$\overline{25}$	28	0	0	0			
10								66									
12								29									

Table II.—Values of F (h 0 l).

For all reflexions, h and l are even.

Index h ↓ \ Index l→	$\bar{8}$	$\bar{6}$	$\bar{4}$	$\bar{2}$	0	2	4	6	8
0	38	$\overline{29}$	136	$\overline{175}$	432	$\overline{175}$	136	$\overline{29}$	38
2	0	0	19	$\overline{88}$	0	46	0	$\overline{36}$	0
4	0	$\overline{72}$	90	$\overline{128}$	15	$\overline{80}$	77	$\overline{49}$	0
6		0	0	0	100	$\overline{82}$	59	$\overline{30}$	
8			33	$\overline{51}$	76	$\overline{32}$	0		
10				$\overline{63}$	56	$\overline{44}$			
12					0				

Table III.—Values of F $(h\,k\,0)$.

For all reflexions, $h + k$ is even. $F(h\,k\,0) = F(h\,\bar{k}\,0)$.

Index k ↓ / Index h →	0	1	2	3	4	5	6	7	8
0	432		0		15		100		76
1		0		76		$\overline{63}$		41	
2	19		$\overline{51}$		$\overline{23}$		$\overline{19}$		$\overline{32}$
3		13		50		37		0	
4	0		16		$\overline{50}$		0		
5		$\overline{84}$		$\overline{55}$		0		$\overline{96}$	
6	$\overline{94}$		31		29		0		
7		0		0		40			
8	0		$\overline{17}$						

In order to get a perfect representation of the scattering power in the crystal, it would be necessary to measure all values of F up to indices so high that the values become vanishingly small. It will be clear from the tables that the experimental results fall far short of the ideal. All values of F have been measured up to a glancing angle represented by $\sin\theta = 0\cdot45$ for planes $(0\,k\,l)$ and $(h\,0\,l)$, and $\sin\theta = 0\cdot30$ for the planes $(h\,k\,0)$, using rhodium Kα radiation for which $\lambda = 0\cdot615$ Å. Hence the Fourier representation will be in all cases imperfect, and particularly so for the projection on the c face where values of F $(h\,k\,0)$ are used.

5. *Ewald's Reciprocal Lattice.*

The figures in these tables may be given an interesting interpretation by the elegant method of the "Reciprocal Lattice*" which we owe to Ewald.† Every set of parallel planes of a crystal is represented by a point in the reciprocal lattice. The line joining this point to the origin of the reciprocal lattice is at right angles to the crystal planes, and its distance from the origin is inversely proportional to their spacing. Since there is a definite structure-factor for each set of planes, a corresponding figure or "weight" can be attached to the point of the reciprocal lattice. The structure factors for first, second and

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[*] It will be realised that each point in the reciprocal lattice corresponds to a simple sinusoidal distribution of density in the crystal, and that the complete representation of a given set of parallel crystal planes is an extended row of points.

[†] 'Z. Krist.,' vol. 56, p. 129 (1921).

high orders of X-ray reflexion become a set of figures attached to points in a row at equal intervals, the first order being nearest the origin. The assemblage of points corresponding to reflexion by all planes of the crystal builds up a space lattice, the reciprocal lattice.

We may consider the " weights " attached to the points of reciprocal lattice as being, in our notation, the values F $(h\,k\,l)$. In general F $(h\,k\,l)$ is a complex quantity, according to Ewald, representing both the amplitude and phase of the scattered wave. In the particular case considered here, it is real but positive or negative. The indices h, k, l give the co-ordinates of the point with reference to the axes of the reciprocal lattice. We attach a weight F (0 0 0) to the origin equal to Z, the number of electrons in the unit cell of the crystal.

If this convention be adopted, it will be seen that the figures in Tables I, II and III represent *plane sections, through the origin, of Ewald's reciprocal lattice.* The origin of the lattice is always at the figure 432. The Fourier representation may therefore be summed up as follows. Any plane of the reciprocal lattice passing through the origin has a two-dimensional array of figures. These are the coefficients of a Fourier series, which gives the projection of the scattering matter in the crystalline cell on a plane. The direction of projection is that of the zone axis corresponding to the plane section of the reciprocal lattice. The orientation of the crystal plane on which projection takes place is obviously immaterial. Any convenient plane inclined to the zone axis, and any axes of reference in that plane, can be chosen. The indices $(h\,k\,l)$ must, of course, be transformed into indices $(h'\,k'\,l')$ to correspond to the new axes which have been chosen. This merely means that having chosen our axes of reference in the crystal plane, we must choose a corresponding frame of reference for the network of points in the central section of the reciprocal lattice.

It is interesting to note that the whole development of the Fourier representation is implicitly contained in the paper by Ewald referred to above. He develops it, however, only in respect to a set of scattering points in the crystal, and not to a continuous distribution of scattering matter.

6. *Summation of the Fourier Series.*

The Fourier series for projections on (100), (010) and (001) faces of the unit cell are summed in Tables IV, V and VI. The figures in these tables correspond to series

$$S(y, z) = \Sigma\,\Sigma\,F(0\,k\,l)\cos 2\pi(ky/b + lz/c)$$
$$S(x, z) = \Sigma\,\Sigma\,F(h\,0\,l)\cos 2\pi(hx/a + lz/c)$$
$$S(x, y) = \Sigma\,\Sigma\,F(h\,k\,0)\cos 2\pi(hx/a + ky/b).$$

To make the tables more compact, the actual sums of the series are divided by 10. The density per unit area at any point in a projection is given by

$$S(y, z)/bc \sin\alpha, \qquad S(x, z)/ac \sin\beta, \qquad S(x, y)/ab \sin\gamma.$$

(Since the crystal in the present example is monoclinic, $\sin\alpha = \sin\gamma = 1$.) Thus in order to derive the density per unit area from the figures in the tables, they must be multiplied by 10 and divided by the area of the face on which projection is being made.

The origin is taken to be at the centre of the unit cell. This origin is marked in each table, and the range of the figures in the *a*, *b* or *c* direction is indicated. It is not necessary to calculate the density all over the cell face as it repeats by symmetry. Since an atom in the general position becomes eight atoms in the unit cell, owing to the symmetry elements, it follows that it is only necessary to plot the density distribution over one-eighth of the surface of each face. The continuation of these sets of figures over the whole of each face will be clear if they are considered in conjunction with the contoured diagrams of figs. 1A, 2A, 3A.

Table IV.—Projection on Face (100).

$S(y, z) \times 10^{-1}$.

↑	163	122	58	29	2	$\bar{6}$	3	$\bar{6}$	2	29	58	122	163
	129	83	40	24	6	$\bar{4}$	33	$\bar{4}$	6	24	40	83	129
	65	30	17	25	30	42	76	42	30	25	17	30	65
	28	9	24	52	75	134	191	134	75	52	24	9	28
	22	22	48	83	112	214	285	214	112	83	48	22	22
	17	29	51	69	91	212	289	212	91	69	51	29	17
	2	13	21	24	33	143	210	143	33	24	21	13	2
	0	4	0	$\bar{5}$	$\bar{6}$	67	111	67	$\bar{6}$	$\bar{5}$	0	4	0
	12	11	0	1	6	29	49	29	6	1	0	11	12
	24	16	4	22	35	25	25	25	35	22	4	16	24
	29	16	3	37	68	44	36	44	68	37	3	16	29
$\frac{b}{2}$	31	13	0	42	78	76	79	76	78	42	0	13	31
	33	8	$\bar{6}$	31	70	112	137	112	70	31	$\bar{6}$	8	33
	31	5	$\bar{8}$	20	54	142	193	142	54	20	$\bar{8}$	5	31
	29	4	$\bar{5}$	15	40	156	224	156	40	15	$\bar{5}$	4	29
	24	4	2	12	27	139	213	139	27	12	2	4	24
	12	$\bar{1}$	2	7	12	93	159	93	12	7	2	$\bar{1}$	12
	$\bar{1}$	$\overline{12}$	$\bar{2}$	$\bar{1}$	$\bar{2}$	45	97	45	$\bar{2}$	$\bar{1}$	$\bar{2}$	$\overline{12}$	$\bar{1}$
	2	$\bar{5}$	7	12	15	37	74	37	15	12	7	$\bar{5}$	2
	17	13	21	33	45	66	95	66	45	33	21	13	17
	22	18	16	31	50	86	111	86	50	31	16	18	22
	28	21	$\bar{2}$	6	23	68	91	68	23	6	$\bar{2}$	21	28
	65	50	3	$\bar{5}$	$\bar{4}$	34	52	34	$\bar{4}$	$\bar{5}$	3	50	65
	129	99	38	12	$\bar{6}$	10	19	10	$\bar{6}$	12	38	99	129
↓	(163)	122	58	29	2	$\bar{6}$	3	$\bar{6}$	2	29	58	122	163

Origin← $\frac{c}{2}$ →

Table V.—Projection on Face (010).

S $(x, z) \times 10^{-1}$.

364	291	138	33	20	48	55	48	76	127	162	159	150	159	162	127	76	48	55	48	20	33	138	291	364
330	242	121	25	14	39	36	34	71	131	167	160	136	128	125	101	70	63	74	64	23	21	117	264	330
249	206	76	8	8	19	24	20	54	115	146	128	91	78	74	68	72	77	94	78	29	9	82	192	249
150	106	24	$\overline{13}$	3	27	17	9	40	95	109	82	52	28	32	45	57	87	109	97	34	$\bar{3}$	31	114	150
73	36	$\overline{14}$	$\overline{24}$	16	26	20	5	18	59	67	40	7	0	14	36	63	98	127	87	50	$\bar{5}$	1	52	73
32	5	$\overline{30}$	$\overline{26}$	8	30	20	19	17	38	40	15	$\overline{10}$	$\bar{7}$	14	40	66	104	130	117	59	8	$\bar{2}$	24	32
17	$\bar{4}$	$\overline{25}$	$\overline{21}$	6	18	14	8	13	25	13	1	$\overline{13}$	$\bar{4}$	18	41	65	94	110	100	57	10	3	20	17
18	4	$\overline{14}$	$\overline{16}$	$\bar{5}$	1	4	8	16	16	4	$\bar{7}$	$\overline{12}$	2	16	34	53	71	82	70	46	16	14	23	18
21	10	$\bar{3}$	$\overline{11}$	$\overline{16}$	$\overline{16}$	$\bar{8}$	11	25	14	2	$\bar{8}$	$\bar{7}$	2	21	21	36	51	56	46	27	16	18	24	21
18	14	3	$\bar{5}$	$\overline{12}$	$\bar{7}$	11	33	35	34	6	2	2	4	5	13	28	43	35	32	17	13	14	20	18
21	16	14	0	2	14	34	61	56	36	10	12	12	12	6	19	30	56	54	37	22	26	14	14	21
12	14	17	21	19	33	50	78	68	43	21	18	22	18	15	27	55	74	66	40	28	33	17	10	12
(2)	8	19	25	29	45	73	87	71	39	21	24	28	24	21	39	71	87	73	45	29	25	19	8	2

$\frac{c}{4}$

Origin ← $\frac{a}{2}$ →

Table VI.—Projection on Face (001).

S $(x, y) \times 10^{-1}$.

122	87	22	$\overline{15}$	5	50	80	80	67	47	30	11	6	11	6	47	67	80	80	50	5	$\overline{15}$	22	67	122
54	31	0	$\bar{3}$	31	68	79	65	49	43	37	22	10	8	27	51	81	95	85	40	$\bar{5}$	$\bar{7}$	68	157	216
17	5	$\bar{4}$	12	48	76	70	44	34	35	39	26	11	4	19	45	78	94	82	38	$\bar{5}$	8	100	217	273
14	1	$\overline{12}$	$\overline{11}$	32	57	47	20	10	14	24	14	2	$\bar{6}$	2	20	46	58	55	25	$\bar{4}$	15	102	207	258
40	21	$\bar{8}$	$\overline{16}$	6	25	21	1	$\bar{6}$	$\bar{5}$	6	5	3	5	6	9	10	15	19	12	$\overline{12}$	$\bar{2}$	58	137	174
85	56	3	$\overline{25}$	$\overline{11}$	18	29	15	0	$\overline{11}$	$\bar{6}$	5	28	47	55	31	4	$\overline{11}$	$\bar{5}$	2	$\bar{1}$	$\bar{3}$	21	60	83
151	116	46	4	15	52	74	62	31	6	1	25	75	121	135	96	37	$\bar{2}$	$\bar{4}$	12	17	6	6	14	23
189	154	78	36	51	91	115	101	56	19	7	36	103	170	197	155	80	23	13	29	37	22	5	4	5
171	140	78	44	60	102	119	97	54	9	$\bar{9}$	17	87	163	203	173	102	39	21	30	32	16	0	$\bar{4}$	$\bar{1}$
118	96	50	30	46	75	82	61	28	$\bar{4}$	$\overline{18}$	$\bar{7}$	44	111	156	150	104	57	36	31	18	0	$\bar{8}$	0	$\overline{10}$
66	51	23	13	28	46	42	27	18	7	$\bar{6}$	$\overline{11}$	5	47	94	113	104	85	66	44	14	$\bar{9}$	$\overline{11}$	5	20
37	26	12	11	21	26	16	10	21	30	26	2	$\bar{8}$	14	58	98	117	122	108	78	33	1	0	26	43
(25)	20	12	13	20	22	11	9	28	47	45	16	$\bar{8}$	7	44	93	126	139	129	94	42	7	10	40	59

$\frac{b}{4}$

Origin ← $\frac{a}{2}$ →

The positions of the atoms are revealed by the figures. A heavy atom makes the figures rise to an obvious maximum. A light atom (oxygen) is sometimes so close to a heavier neighbour in a projection that its position is not shown by a separate maximum value.

Some of the figures are negative, indicated by a bar above them. In a case of X-ray diffraction such as this, where anomalous scattering does not occur, negative scattering matter has no significance. The density should be positive everywhere, approaching a zero value in the regions between the atoms. The appearance of negative values may be partly due to errors in measurements of F, but even if these were perfect, negative values are to be expected because the Fourier series is not complete. Additional values of F for higher indices would make the figures correspond more closely to the ideal values.

The diagrams in figs. 1A, 2A and 3A were made by plotting the figures giving the density distribution in their positions on each face of the unit cell, and then drawing contour lines through points of equal density. The contours are drawn at intervals of 40, corresponding to intervals of 400 in the actual values of

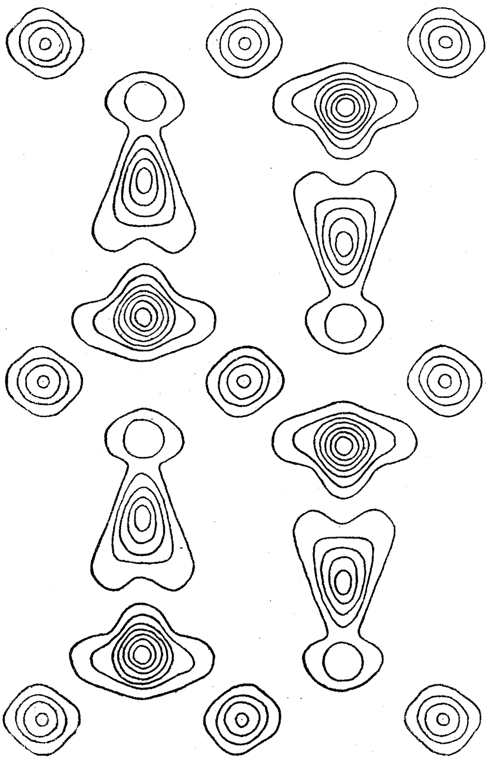

FIG. 1A.

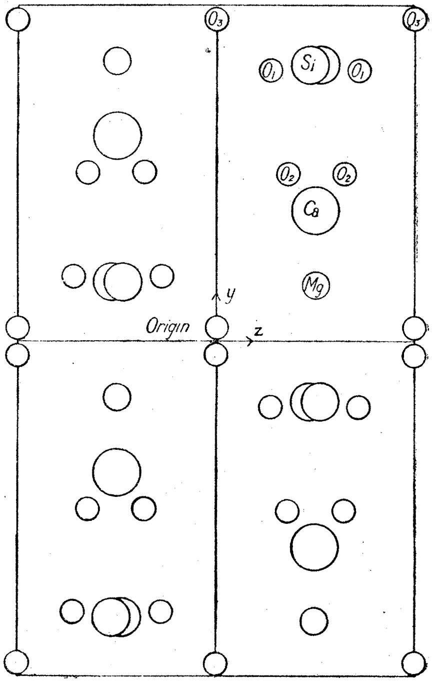

FIG. 1B.

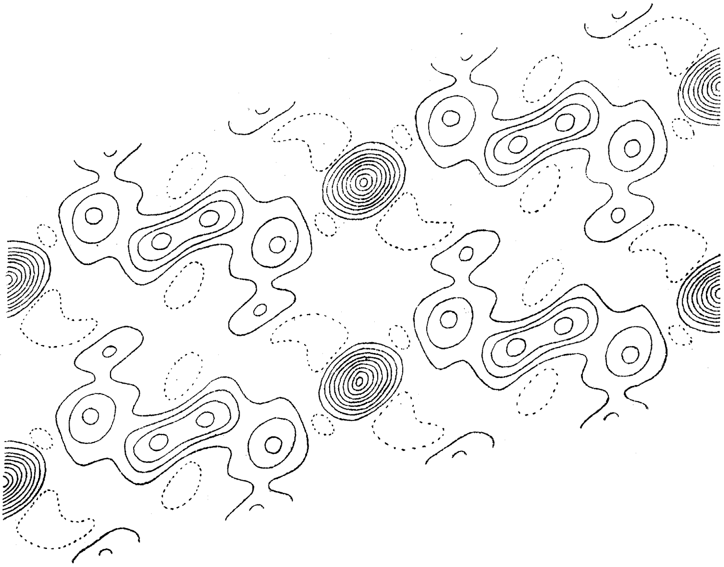

FIG. 2A.

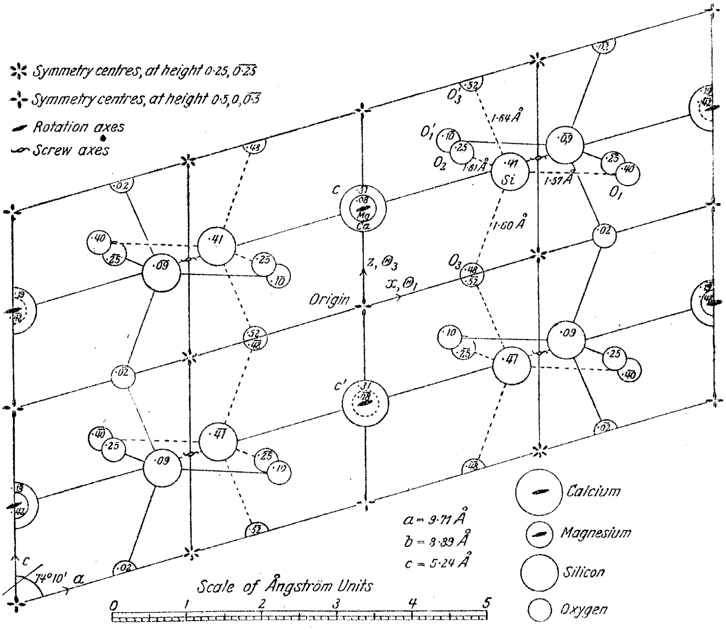

FIG. 2B.

S (y, z), etc. The positions of the atoms as found in the previous paper on diopside are shown in figs. 1B, 2B, 3B, and the two sets of figures are seen to correspond very closely. In the projection on (010) the areas enclosing

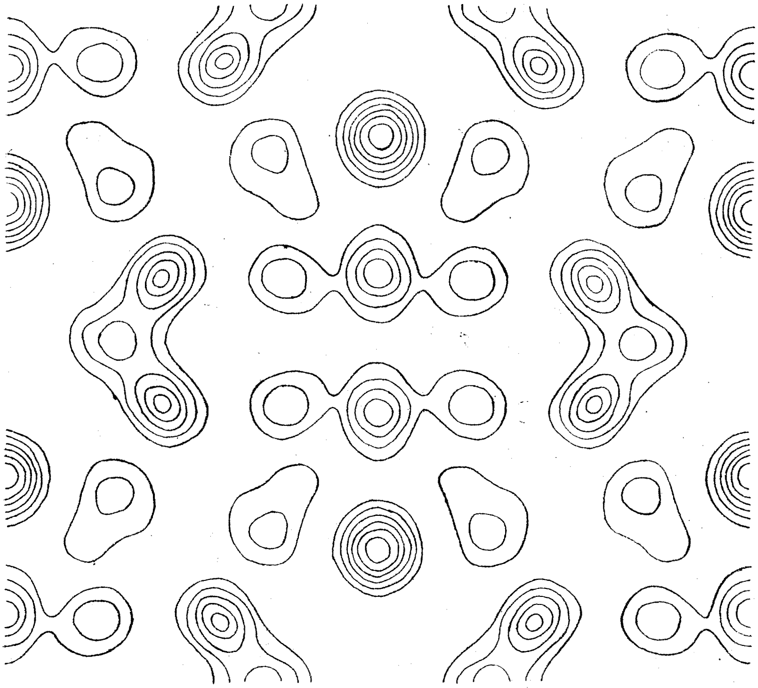

Fig. 3a.

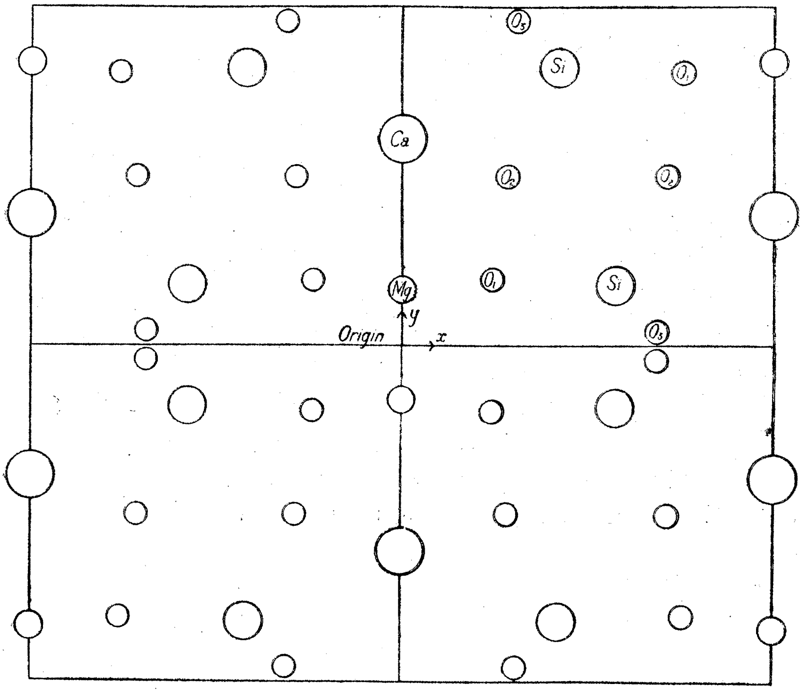

Fig. 3b.

negative values are marked by dotted lines, these lines being the contours of zero level where $S(x, z) = 0$. The zero contours are not marked in the other projections. The first continuous contour line around each atom or group passes through all points where S is 400, the next through points where it is 800, and so forth.

7. *The Number of Electrons in the Atoms, and their Identification.*

The density in the space between the atoms is in general quite small. Since this is the case, it is possible to draw an approximate boundary around each atom or group of atoms in a projection and to calculate the total number of electrons in that area. We may take, as an instance, the projection on (010), and count the number of electrons in the most obvious rounded mass shown in that projection, where the contour lines rise to a peak of 364 (3640). The figures S are plotted at intervals $a/24$, $c/24$. The density per unit area is equal to

$$S(x, z)/ac \sin \beta$$

and this density may be taken to be the average density over a cell with sides $a/24$, $c/24$. This little cell of area $ac \sin \beta/24^2$ contributes an amount

$$(S(x, z)/ac \sin \beta) \,.\, (ac \sin \beta/24^2) = S(x, z)/2304.$$

Thus the total number of electrons in the whole mass of scattering matter is given by

$$\Sigma\, S(x, z)/2304,$$

where $\Sigma\, S(x, z)$ is 10 times the sum of all the numbers in Table V which outline the atom or group in question. Although the boundary enclosing these numbers is somewhat indefinite, trial shows that it does not matter much where it is drawn because the density between the atoms is so small. In the case considered, the number of electrons proves to be 28·3, corresponding to a superimposed calcium atom and magnesium atom (18 + 10). The remaining atoms in the projection (010) are so superimposed that it is difficult to disentangle them, but all atoms stand out clearly in one projection or another. The following table shows the electron-count in all cases where it is possible. There are three kinds of oxygen atom, O_1, O_2 and O_3.

Projection on (100).

Atoms.		No. of electrons.
Ca + $2O_2$	......	35·3
Si + O_1	......	20·1
Mg	......	13·3
O_3	......	8·0

Projection on (010).

Atoms.		No. of electrons.
Ca + Mg	......	28·3
O_3	......	7·7 approx.

Projection on (001).

Atoms.		No. of electrons.
Ca	......	16·6
Mg	......	12·6
Si + O_3	......	19·8
O_2	......	9·6
O_1	......	8·0

Two points of interest may be noted. The average number of electrons in the oxygen atoms is distinctly less than 10, being in fact 8·3. It is thus much nearer to the value 8 for a non-ionised atom than to the value 10 for O^{-2}. The average number for Si + O is equal to 20, so that according to these figures the number of electrons in the silicon atom is 11·7, and in the oxygen atom is 8·3. The estimate of 9·6 electrons for O_2 in the (001) projection is at variance with these estimates, and the discrepancy shows that too much reliance must not be placed upon them. Nevertheless it is interesting to see that the figures do not correspond to ions Si^{+4}, O^{-2} each with 10 electrons. They suggest, on the other hand, that both the oxygen atoms and the silicon atoms are only partially ionised. As against this, if the estimates given above for the numbers of electrons in all the atoms of the projection on (001) are added, the sum for the molecule $CaMg(SiO_3)_2$ is 104 which does not check with the correct number 108. Some electrons have been missed in the count, and the missing electrons may belong to the diffuse oxygen atoms. It is indeed difficult to make estimates for the oxygen atoms, since their boundaries are not precise and the incomplete Fourier series leads to irregular variations of the density between the atoms. For instance, it is possible to see in the figures of Table VI at the point $a/2$, 0, a small mass of scattering matter which cannot be associated with any atom, and is a kind of optical " ghost."

The other point of interest is the division of electrons between calcium and magnesium. The total number is found to be 28, corresponding to the figures 18 + 10 which we would expect. The magnesium atom, however, appears to have more than its due share of these electrons. The material is reported to contain 1·12 per cent. of FeO, and if this iron replaces magnesium it would raise the average number of electrons in the Mg position from 10 to 10·5. The number of magnesium in the projections is, however, between 12 and 13 whereas calcium appears to have about 16 electrons instead of 18. The possibility that calcium and magnesium interchange their positions to a certain extent is suggested. In view of the complexity of the crystal, and the difficulty of allowing for extinction in correcting some of the observed intensities, it would be misleading to stress any of these figures unduly.

It is quite clear that the atoms can be successfully identified by counting the electrons in them.

8. *The Parameters of the Structure.*

The position of an atom as shown in a projection may either be taken to be the point where the density shows a maximum, or to be the centre of gravity of the whole mass of scattering matter. For the oxygen atoms the latter has been determined, but this can only be done when the atom stands out clearly separated from its neighbours. In some cases overlapping is so extensive that no precise co-ordinates can be found. An interesting special case is shown in the projection on (100) fig. 1*a*. Two oxygen atoms overlap at the centre of the figure, forming a single rounded mass. These oxygen atoms are derived from each other by inversion at the centre. It is clear that their co-ordinates in both *b* and *c* directions are very nearly equal to zero, but it is impossible to find their precise values. The information derived from the various projections is tabulated below.

Table VII.

Projection.	(100).			(010).			(001).		
	θ_1.	θ_2.	θ_3.	θ_1.	θ_2.	θ_3.	θ_1.	θ_2.	θ_3.
		°	°	°		°	°	°	
Ca	—	−107	90	0	—	90	0	−108	—
Mg	—	30	90	0	—	90	0	34	—
Si	—	146	(90)	78	—	85	74	147	—
O_1	—	(148)	(50)	137	—	55	135	151	—
O_2	—	(100)	(115)	43	—	125	51	91	—
O_3	—	(180)	(0)	52	—	0	52	(180)	—

The figures in brackets are approximate because of overlapping of atoms. The values for O_1 and O_2 in the (010) projection are bracketed because the position of the centre of gravity of the pair can be placed at the co-ordinates given in the table although these two atoms cannot be resolved.

The parameters deduced from all three projections are combined below, and are compared with the parameters deduced by the analysis in a previous paper.

Table VIII.

	Parameters determined by Fourier analysis.			Values given in previous paper on diopside.		
	θ_1.	θ_2.	θ_3.	θ_1.	θ_2.	θ_3.
	°	°	°	°	°	s
Ca	0	−107·5	90	0	−110	90
Mg	0	32	90	0	30	90
Si	76	146·5	85	76	148	85
O_1	135	151	(50)	136	145	50
O_2	51	91	(115)	51	90	115
O_3	52	(180)	0	56	173	0

Even when the results of the three projections are combined, certain co-ordinates of the oxygen atoms remain doubtful. They might be obtained by taking, for instance, the calcium atom as outlined in the (001) projection and subtracting it from the group Ca + 2O in the (100) projection, so as to leave the oxygen atoms clearly defined, but the figures are perhaps not sufficiently accurate to make such a process sure. It seems better to give in the table definite values only in those cases where they can be read directly from the projections.

The parameters are given in degrees, in accordance with the notation in the previous paper. The average difference between the two sets of values, for all figures except those in brackets, is 1·6°. If the parameters are expressed as fractions *u*, *v*, *w* of the axial lengths *a*, *b*, *c*, this corresponds to an average difference of 0·005 in these fractions. For a crystal with 14 parameters this is a small difference, and the agreement is evidence of the effectiveness of quantitative measurements in analysing complex structures.

Table IX.

	Parameters determined by Fourier analysis.			Values given in previous paper on diopside.		
	u.	*v.*	*w.*	*u.*	*v.*	*w.*
Ca	0	−0·299	0·25	0	−0·306	0·25
Mg	0	0·089	0·25	0	0·083	0·25
Si	0·211	0·407	0·236	0·211	0·411	0·236
O_1	0·375	0·419	(0·14)	0·378	0·402	0·139
O_2	0·142	0·253	(0·32)	0·142	0·250	0·320
O_3	0·145	(0·50)	0·00	0·155	0·480	0·00

9. *Analysis by Fourier Series.*

The diopside crystal was first analysed by making calculated and observed values of $|F(h\,k\,l)|$ agree. This determined the sign of $F(h\,k\,l)$ and it was possible to form the Fourier representation of the distribution of scattering matter. It is interesting to see whether any of the labour of finding suitable parameters could have been shortened by employing the Fourier analysis at an earlier stage.

This appears to be the case. Consider the projection on (010) where calcium and magnesium atoms are superimposed, fig. 2A. In Table II it will be seen that $F(h\,0\,l)$ is positive when $\pm\,l$ is 0, 4, 8 and negative when $\pm\,l$ is 2, 6. This means that the sign of $F(h\,0\,l)$ is determined by the position of the calcium and magnesium atoms, so that all terms in the Fourier series

$$\Sigma\,\Sigma\,F(h\,0\,l)\cos 2\pi(hx/a + lz/c)$$

are positive at the point $x = 0$, $z = c/4$, where these atoms are situated. The sole exception is F (202). It so happens that for this spectrum alone oxygen and silicon contributions to F (202) more than neutralise those of calcium and magnesium.

If therefore some hint had been obtained at an early stage of the analysis that the calcium and magnesium atoms were superimposed in this projection, and that they determined the sign of $F(h\,0\,l)$, it would then have been possible to use the Fourier series to find the projection on (001) and so the x and z co-ordinates of all the atoms. This would have been done without the labour of trying different values for the parameters, and seeing which gave the best agreement between calculated and observed values of $F(h\,0\,l)$.

There is no such simple rule for the signs of $F(0\,k\,l)$ and $F(h\,k\,0)$, and it is necessary to analyse the crystal in order to determine these signs. However a study of the contribution of the various atoms to these F values shows that, in every case except F (022), the sign is determined by the calcium, magnesium, and silicon atoms. Therefore a knowledge of the positions of these heavy atoms would make it possible to form the Fourier series, and so to fix the oxygen atoms. This would be of great advantage in analysis, because the determination of the oxygen parameters is a troublesome matter owing to their small scattering power.

To sum up, a preliminary analysis of the crystal which gives approximate positions of the heavy atoms, suffices to fix the signs of the coefficients F. The Fourier series may thus be formed, and the positions of all the atoms accurately read off on the projections.

It is interesting to re-interpret the ordinary process of analysis by the conceptions of the Fourier series. In particular, a study of the effect of extinction is very illuminating. Extinction affects the most powerful reflexions, and allowance for it is an uncertain matter. When comparing calculated and observed values of F, the discrepancies for the powerful reflexions are very obvious, and might seem to cast doubt on the success of the analysis. In our analyses of complex crystals by quantitative measurements we have always held, however, that this doubt is not justified, and that the agreement for a large number of reflexions of high order is ample evidence for the correctness of the solution. When now the Fourier series is formed, it is clear that the effect of allowance for extinction on the calculated distribution of scattering matter is very small. For instance, in the (010) projection of diopside, the position of the superimposed calcium and magnesium atoms is shown by a peak rising to 3640. The strongest reflexion is (002) and F (002) is taken to have a value of 175. It may be in error by 30 units owing to incorrect allowance for extinction, but clearly this will hardly affect the peak of 3640. The density is determined by a large number of F values not affected by extinction, and the few reflexions at low angles which are so affected are relatively unimportant.

If the form of the Fourier series

$$\Sigma\,\Sigma\,\mathrm{F}\,(0\,k\,l)\cos 2\pi\,(hx/a + lz/c)$$

be considered, it will be seen that each term represents a series of periodic undulations of density, parallel to a line whose slope is determined by the indices k, l. The higher the indices k and l, the shorter is the wave-length. We may thus distinguish the effect on the projection of the different terms. Those with low indices group the density into certain masses which begin to outline the atoms. The terms with high indices trim the outlines, and give precision to the atoms. The number of electrons in each atom is determined by the terms with low indices. Since these are affected by allowance for extinction, the numbers of electrons counted in section 7 must be accepted with reserve. On the other hand, the precise positions of the atoms are almost entirely determined by the terms with high indices. Hence the values of the parameters may be relied on to be correct.

This is merely another way of regarding the familiar consideration that reflexions with low indices must be measured accurately if we are to tell whether the atoms are ionised or not, and that reflexions with high indices serve to fix the positions of the atoms with precision.

Summary.

The representation of the scattering matter in a crystal by Fourier series, first used by W. H. Bragg and later developed by Duane, Havighurst and Compton, is applied here to the determination of the parameters in a complex crystal.

A series is used which gives the projection of the scattering matter in the unit cell on each of its faces in turn. For instance, when projection is made on the face (100) of the cell, the formula for the density $\rho(y, z)$ of the scattering matter at a point y, z is as follows :—

$$\rho(y, z) = (1/bc \sin \alpha) \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \mathrm{F}(0\,k\,l) \cos 2\pi (ky/b + lz/c).$$

In this formula, $\mathrm{F}(0\,k\,l)$ is the value of the structure factor for the reflexion $(0\,k\,l)$ measured in absolute units. The formula applies to a cell of any shape, provided that it has a centre of symmetry. $\mathrm{F}(0\,0\,0)$ is taken to be the number of electrons in the unit cell.

This series is evaluated for the crystal diopside $\mathrm{CaMg(SiO_3)_2}$. The signs of the coefficients $\mathrm{F}(0\,k\,l)$ had been fixed by a previous analysis of the crystal. The projections are shown as contoured diagrams in figs. 1A, 2A and 3A. The positions of the atoms agree very closely with those given by the previous analysis, figs. 1B, 2B and 3B, made by finding values for the parameters which gave agreement between calculated and observed values of F. A comparison of the two sets of 14 parameters is shown in Table IX.

It is possible to count the numbers of atomic electrons in the projections. They are approximately as follows :—Ca 16·5, Mg 12·5, Si 11·5, O 8·5–9. It is interesting to note that the oxygen does not appear to be an ion O^{-2} with 10 electrons.

The groups of F values used for any projection may be conveniently described as the weights attached to a network of points on a central section of Ewald's reciprocal lattice.

The employment of Fourier series in analysing complex crystals is discussed, and it is concluded that it may be used in conjunction with an analysis of the usual type made by assigning parameters to the atoms, and may considerably shorten the labour of analysis. The series is particularly of value in discovering the positions of the lighter atoms and in leading directly to precise values of the parameters.

In a recent paper by Mr. West and the author in the 'Zeitschrift für Krystallographie,' entitled "A Technique for the X-ray Examination of Crystal Structures with many Parameters," examples were given to show that the use of absolute measurements of X-ray diffraction enabled these complex crystal structures to be solved with directness and accuracy. The use of the same measurements in the method of Fourier series affords further evidence in support of the effectiveness of such absolute measurements.

It is with great pleasure that I acknowledge my indebtedness to my father, Sir William Bragg, for suggestions which materially contributed to the work described in this paper. At the time when I was following up the connection between our usual methods of analysis and the analysis by Fourier series, a connection briefly treated in the paper by Mr. West and myself, my father showed me some results which he had obtained by using relative values of the first few terms of two- and three-dimensional Fourier series to indicate the general distribution of scattering matter in certain organic compounds. It was largely as a result of his suggestions that I was encouraged to make all the computations for these two-dimensional series, using the extensive absolute measurements which we had made on certain crystals.