molecular cell, and the other two are each twice the simple cell edge so that the cell contains 16 molecules.

The second part of this paper deals with the crystallographic variations in the perovskite group and other ABO_3 structure types, presenting them diagrammatically for orderly consideration. Plotting temperature along a third co-ordinate is suggested as an aid in comparing polymorphic transformations in related compounds and mixed crystals. Such a diagram invites prediction of properties as yet unmeasured and may serve to indicate fields of special interest for investigation.

The writer wishes to express her gratitude especially to Philip W. Anderson, W. L. Bond, Alan N. Holden and J. J. Lander for discussions that were helpful in the preparation of this paper and to B. T. Matthias and J. P. Remeika for providing the crystals on which the work was done.

References

BARTH, T. F. W. (1925). *Norsk geol. Tidsskr.* **8**, 201.

EWALD, P. P. & HERMANN, C. (1931). *Strukturbericht* 1913–28. Leipzig: Akademische Verlagsgesellschaft.

GOLDSCHMIDT, V. M. (1926). *Skr. norske VidenskAkad.*, Matem.-Naturvid. Kl., no. 2.

GOLDSCHMIDT, V. M., BARTH, T. & LUNDE, G. (1925). *Skr. norske VidenskAkad.*, Matem.-Naturvid. Kl., no. 7.

*HOFFMAN, A. (1935). *Z. phys. Chem.* B, **28**, 65.

HULM, J. K. (1950). *Proc. Phys. Soc. Lond.* A, **63**, 1184.

JONKER, G. H. & SANTEN, J. H. VAN (1947). *Chem. Weekbl.* **43**, 672.

JONKER, G. H. & SANTEN, J. H. VAN (1950). *Physica, 's Grav.*, **16**, 337.

LANDER, J. J. (1949). *J. Chem. Phys.* **17**, 892.

LAPITSKII, A. V. (1946). *J. Gen. Chem., Moscow*, **16**, 917.

MATTHIAS, B. T. (1949). *Phys. Rev.* **75**, 1771.

*MEGAW, H. D. (1946). *Proc. Phys. Soc. Lond.* **58**, 133.

*NÁRAY-SZABÓ, ST. v. (1943*a*). *Naturwissenschaften*, **31**, 202.

NÁRAY-SZABÓ, ST. v. (1943*b*). *Naturwissenschaften*, **31**, 466.

*POSNJAK, E. & BARTH, T. F. W. (1934). *Z. Krystallogr.* **88**, 271.

QUILL, L. L. (1932). *Z. anorg. Chem.* **208**, 257.

ROOKSBY, H. P. (1945). *Nature, Lond.*, **155**, 484.

*WYCKOFF, R. W. G. (1948). *Crystal Structures.* New York: Interscience Publishers.

*ZACHARIASEN, W. H. (1928). *Skr. norske VidenskAkad.*, Matem.-Naturvid. Kl., no. 4.

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* Sources of data for Figs. 7 and 8.

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The Calculation of Structure Factors by Fourier Summation

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A method is described by which the structure factors of a proposed crystal can be calculated by sampling of the proposed unit cell followed by harmonic (Fourier) rather than non-harmonic summation. It is suggested that rapid computing devices may be used more advantageously with this than with the present methods, and that the advantage would be particularly great for structures with many atoms or with non-spherical atoms. The nature of the inherent error is discussed and a method for eliminating it is presented; an example of the use of the method is given, with a comparison of the results with those obtained by the ordinary method; and strips for 'hypothetical' two-dimensional carbon, nitrogen and oxygen atoms are given.

1. Introduction

The reduction of structure-factor calculation to Fourier-series summation would make it possible to perform the two principal types of computation in X-ray crystal-structure analysis by a single method which is particularly suited to such rapid computing devices as the electronic Fourier-summation computer X-RAC (Pepinsky, 1947) and Hollerith or IBM punched-card machines (Cox & Jeffrey, 1949; Donohue & Schomaker, 1949; Grems & Kasper, 1949; Cox, Gross & Jeffrey, 1949). The purpose of this paper is to show how this reduction can be effected, and to point out the nature of the inherent error and a procedure by which it can be eliminated.

The Fourier transform of the unit cell of a crystal is a continuous function in reciprocal space which constitutes a complete description of the X-ray scattering properties of the unit cell, standing in exactly the same relation to the unit cell as the familiar atomic scattering function does to a single atom. It includes a description of the scattering properties of the crystal which results when the unit cell is repeated on the crystal lattice, for the structure factors of the crystal are merely the values which the unit-cell transform assumes at the points of the crystal reciprocal lattice. For this reason, as is well known, the ordinary calculation of structure factors can be replaced by Fourier transformation of the unit cell.

What remains to be shown is how Fourier transformation can in turn be replaced by the much easier process of Fourier summation. It is pointed out in §2 that, with a certain qualification to be noted immediately below, Fourier transformation can be replaced by the process of sampling the unit cell on a lattice (that is, producing the array of numbers which are the values assumed by the continuous electron-density function of the unit cell at the points of the sampling lattice), and then summing the Fourier series which has as coefficients the numbers obtained from the sampling; for this process will yield the same continuous periodic function in reciprocal space as would be produced by putting down the Fourier transform of the unit cell over and over again with its origin successively at each of the points of the lattice reciprocal to the sampling lattice. The qualification to be noted is that some method must be found for avoiding the effect of the overlapping which arises from the periodicity of the Fourier sum. In §4 it is shown that this effect can, indeed, be rendered harmless by starting with a unit cell composed of *hypothetical atoms*, atoms whose scattering has been made zero beyond a certain distance in reciprocal space. The final sections are devoted to an actual example of the use of the method and to a convenient method for producing any required hypothetical atom.

2. The fundamental relationship

Let the lattice vectors of a crystal be $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$, so that the lattice points of the crystal are

$$\mathbf{n}=n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3 \quad (n_1, n_2, n_3 \text{ integers}),$$

and let

$$\mathbf{x}=x_1\mathbf{a}_1+x_2\mathbf{a}_2+x_3\mathbf{a}_3$$

be the variable position vector in crystal space. Let $d(\mathbf{x})$ be the electron-density function of the proposed unit cell. Now let the reciprocal-lattice vectors of the crystal be $\mathbf{A}_1, \mathbf{A}_2, \mathbf{A}_3$ (defined in terms of the $\mathbf{a}$'s in the usual way), the reciprocal-lattice points be

$$\mathbf{N}=N_1\mathbf{A}_1+N_2\mathbf{A}_2+N_3\mathbf{A}_3 \quad (N_1, N_2, N_3 \text{ integers}),$$

and the variable position vector in reciprocal space be

$$\mathbf{X}=X_1\mathbf{A}_1+X_2\mathbf{A}_2+X_3\mathbf{A}_3.$$

Then, as was pointed out in §1, the Fourier transform

$$D(\mathbf{X})\equiv\int d(\mathbf{x})e^{-i2\pi\mathbf{X}\cdot\mathbf{x}}d\tau \qquad (1)$$

of the proposed unit cell takes on, at the crystal reciprocal-lattice points $\mathbf{X}=\mathbf{N}$, values $D(\mathbf{N})$ which are the Fourier coefficients, or structure factors, of the proposed crystal. For this reason, the calculation of structure factors can be replaced by Fourier transformation.

Now let the numbers $d(\mathbf{n}')$ be the values assumed by the electron-density function $d(\mathbf{x})$ at the points of a sampling lattice

$$\mathbf{n}'=n_1'\mathbf{a}_1'+n_2'\mathbf{a}_2'+n_3'\mathbf{a}_3' \quad (n_1', n_2', n_3' \text{ integers}).$$

Then the Fourier sum

$$(\mathbf{a}_1'\mathbf{a}_2'\mathbf{a}_3')\sum_{\mathbf{n}'} d(\mathbf{n}')\,e^{-i2\pi\mathbf{n}'\cdot\mathbf{X}} \qquad (2)$$

will yield $D(\mathbf{X})$ repeated in reciprocal space at each point of the lattice

$$\mathbf{N}'=N_1'\mathbf{A}_1'+N_2'\mathbf{A}_2'+N_3'\mathbf{A}_3' \quad (N_1', N_2', N_3' \text{ integers})$$

which is the reciprocal of the sampling lattice $\mathbf{n}'$. Fig. 1 illustrates this relationship schematically for two different sampling lattices $\mathbf{n}'$. (This relationship follows from the fact, referred to above, that the Fourier coefficients of a periodic function are the values sampled from the transform of any of its unit cells by the lattice reciprocal to its own lattice.)

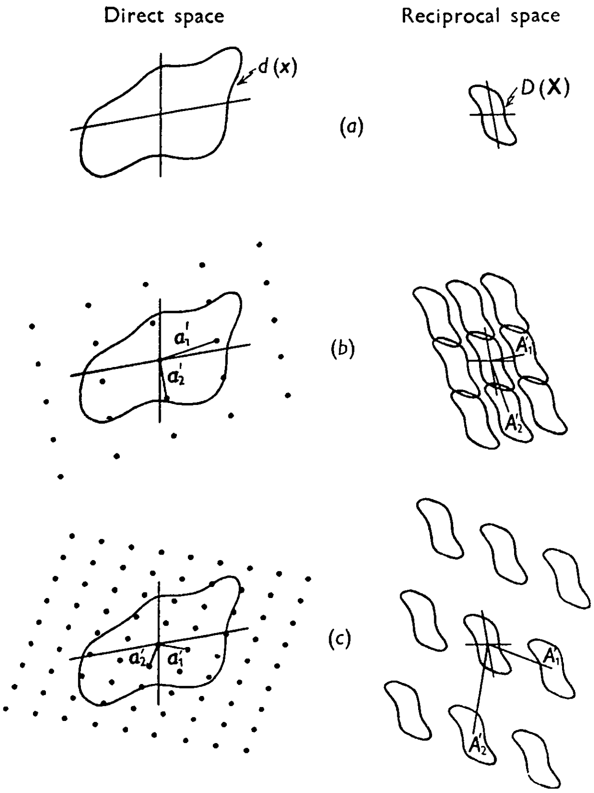

Fig. 1. Schematic diagram to illustrate the effect of sampling and Fourier summation. (*a*) A function $d(\mathbf{x})$ and its Fourier transform $D(\mathbf{X})$. (*b*) and (*c*) The function $d(\mathbf{x})$ sampled on two different lattices $\mathbf{n}'$ and the corresponding repetition of $D(\mathbf{X})$ on the lattices $\mathbf{N}'$. Note the overlapping in (*b*) and (*c*), more severe in the former.

3. Overlapping

Because this fundamental relationship is strictly, as distinct from approximately, true, the only errors introduced in replacing Fourier transformation by sampling and Fourier summation are those due to the overlapping caused by the periodicity of the result. The overlapping can be reduced by increasing the fineness of the sampling lattice $\mathbf{n}'$, and hence the coarseness of the repetition lattice $\mathbf{N}'$, but this procedure is costly because it rapidly increases the number of terms appearing in (2). Nor, strictly speaking, can this procedure entirely avoid overlapping in the crystal-structure problem, because the proposed unit cell is finite in extent and therefore its transform is infinite in extent. Consequently, it would appear to be impossible to avoid some slight overlapping, no matter how fine a sampling lattice were used.

4. The method of hypothetical atoms*

A way out of the difficulty of overlap can, however, be found by making use of the fact that in X-ray analysis there is no use in calculating the structure factors of a proposed crystal at distances from the origin of reciprocal space greater than $2/\lambda$, for with X-rays of wave-length λ no structure factors beyond that limit can be observed. It is quite proper, therefore, to calculate the structure factors of crystals in which the atoms have been replaced by *hypothetical atoms* whose scattering factors coincide with those of the corresponding real atoms out to a distance $2/\lambda$ in reciprocal space and are zero thereafter. Such crystals will possess structure factors which vanish outside the sphere of radius $2/\lambda$ and which are identical with those of the real crystal inside that sphere; accordingly, the transforms of the proposed unit cells of such hypothetical crystals take on, at the reciprocal-lattice points $\mathbf{N}$, values which are zero† for $|\mathbf{N}| > 2/\lambda$, and which are the desired values for $|\mathbf{N}| < 2/\lambda$. Consequently, the overlapping can cause no errors if (1) the proposed unit cell is composed only of atoms whose transforms are cut off at $2/\lambda$, (2) the sampling lattice $\mathbf{n}'$ is a sublattice of the crystal lattice $\mathbf{n}$, and (3) the repetition lattice $\mathbf{N}'$ is coarse enough to prevent overlapping of spheres of radius $2/\lambda$.

The last of these conditions is clearly the same as requiring that the points of the repetition lattice $\mathbf{N}'$ be at least $4/\lambda$ apart, i.e. that the points of the sampling lattice $\mathbf{n}'$ must be not more than $\frac{1}{4}\lambda$ apart. For copper radiation, with $\lambda = 1{\cdot}54$ A., this minimum required fineness of sampling is $1{\cdot}54/4 \doteqdot 0{\cdot}385$ A. A Fourier summing device which can accept terms whose indices run from -30 to $+30$, say, would therefore be capable, in the case of copper radiation, of dealing with unit cells not larger than $60 \times 0{\cdot}385 \doteqdot 23$ A. on an edge.

The method can be used in three dimensions* to calculate all structure factors within the limiting sphere, or in two dimensions or one dimension to obtain a principal plane or principal line of structure factors. In the first case the coefficients for the Fourier sum will be obtained with the use of the full three-dimensional hypothetical atoms, and in the other two cases with the projections of these atoms on a plane or line. A method for calculating the appearance of hypothetical atoms, either in three dimensions or in projection, is given in §6.

5. Example: lumisterol nitro-iodo-benzoate

Lumisterol nitro-iodo-benzoate occurs in crystals of space group $P2_1$, with

$$a = 10{\cdot}55,\quad b = 7{\cdot}63,\quad c = 20{\cdot}57\,\text{A.},\quad \beta = 93{\cdot}5^\circ,$$

and with two molecules of $C_{35}H_{46}O_4NI$ in each unit cell. There are some 1150 $F(h0l)$'s, all of which are real, within the limiting sphere for copper radiation. Of these only half are independent quantities, because $F(\bar{h}0\bar{l}) = F(h0l)$. All of these 575 independent structure factors have been calculated for a proposed structure by the present method, using Beevers–Lipson strips and a desk calculator as the Fourier summing device.

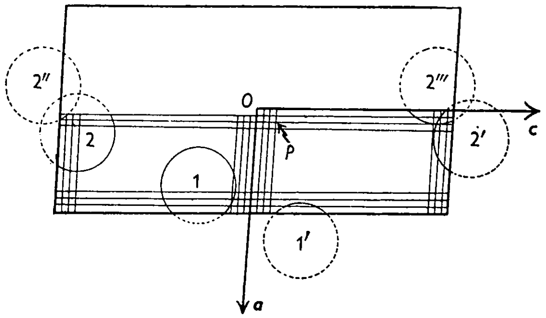

Fig. 2. The region for the proposed unit cell of lumisterol nitro-iodo-benzoate. The sampling lattice $\mathbf{n}'$, which divides the cell into 30ths along $\mathbf{a}$ and 60ths along $\mathbf{c}$, is partly indicated by the lighter lines. The value sampled from the proposed unit cell at the point P will enter the summation with indices 2, 3. An atom in the position indicated by circle 1 falls partly outside the region; the portion lost (indicated by the broken line) is reinserted by the corresponding part of the symmetry-related circle 1′. Similarly, atom 2 is totally sampled by use of 2′, 2″ and 2‴.

The first step was to draw out, on a scale of 4 cm. = 1 A., the region to which the proposed unit cell $d(\mathbf{x})$ would be confined (see Fig. 2). Because the origin is a centre of symmetry for this choice of $d(\mathbf{x})$, $D(\mathbf{X})$ will be real and hence easy to compute.

Next the sampling sublattice $\mathbf{n}'$ was drawn in. Since $20{\cdot}57/0{\cdot}385 \doteqdot 54$ and $10{\cdot}55/0{\cdot}385 \doteqdot 28$, the proposed unit cell might have been sampled at 28ths along a and 54ths along c, and overlapping just avoided. But because the

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[*] An alternative method is to use atoms with a large temperature factor. The disadvantages are (*a*) that the structure factors so calculated cannot be compared directly with the observed structure factors, and (*b*) that the far-out structure factors so calculated are so small that they are rendered very uncertain by rounding-off errors. The advantage is that the atoms will have no diffraction rings and will accordingly be of smaller effective radius than the hypothetical atoms, so that sampling each atom will not take so long.

[†] Note that they will not be zero for general points $|\mathbf{X}| > 2/\lambda$, but only for reciprocal lattice points $|\mathbf{N}| > 2/\lambda$. Hence condition (2) below.

[*] Cochran (private communication) has used an ingenious device to overcome the difficulty of sampling in three dimensions. He calculates the $F(hkl_0)$ structure factors by two-dimensional sampling and Fourier summing of the projection, not of $d(\mathbf{x})$, but of $d(\mathbf{x}) \cos 2\pi l_0 z$.

Beevers–Lipson strips have the property of yielding the values of a Fourier sum only at intervals of 1/120 or 1/60 or 1/40 or 1/30 or 1/24 or... of the cell edge of the repetition lattice, and because it is desirable to have these evaluated points coincide with the reciprocal-lattice points $\mathbf{N}$ of the crystal itself so that no interpolation is required, $\mathbf{n}'$ was chosen to sample at 30ths along a and 60ths along c. This ensured that evaluating the Fourier sum at 30ths by 60ths would yield the array of structure factors directly.

Projections on a plane of the hypothetical atoms corresponding to C, CH, CH_2, CH_3, N, O and I were next calculated by the method given in § 6 and were prepared on strips of transparent material as in Fig. 3. Table 1 gives the figures necessary to construct these strips. Then each atom in turn was pivoted by means of a pin at the point on the drawing proposed as its centre and swung about so that its contribution to the electron density at each point $\mathbf{n}'$ could be read off and written down next to that point. When this had been done for all the atoms the entries for each point $\mathbf{n}'$ were added together, and the resulting set of numbers was the array of coefficients used in the Fourier summation.* (In order to reduce rounding-off errors, the strips were made to show true electron density multiplied by 10. Midway through the summation all figures were divided by 10 to compensate for this.) Notice that, because $d(\mathbf{x})$ has a centre of symmetry at the origin, the sampling had to be carried out only for the lower half of the region.

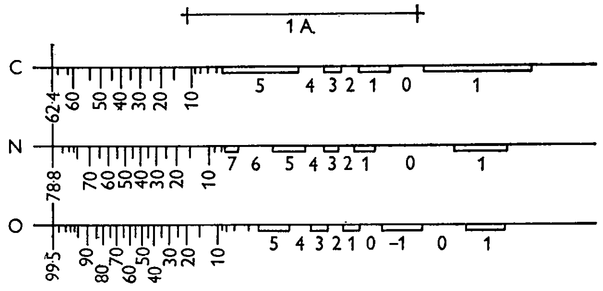

Fig. 3. Strips used for inserting the hypothetical carbon, nitrogen and oxygen atoms. The figures give electrons/square Ångström unit multiplied by 10. For a fuller explanation, see Fig. 4.

In carrying out the sampling, several points must be carefully attended to if the numbers produced are indeed to be the sampled values of a function possessing the full symmetry of a unit cell of the crystal and capable, when repeated on the crystal lattice, of representing the proposed electron distribution of the crystal: (*a*) Each atom in the asymmetric unit must be *completely* sampled, any contribution falling outside the lower half of the region being put in again at the points dictated by the symmetry elements. Fig. 2 gives an illustration of this. Contributions at a boundary of the region will have to be entered both where they immediately occur and at other symmetry-related portions of the boundary. (*b*) The values finally employed at the boundaries and corners of the region must be the sampled values divided by the number of unit cells meeting at those boundaries or corners; otherwise, $d(\mathbf{x})$ will not correctly represent the crystal when repeated on the crystal lattice.

Table 1. *Table for constructing the hypothetical atoms of Fig.* 3

	Radial distance in Ångström units for		
10 e.A.$^{-2}$	C	N	O
95	—	—	0·11
90	—	—	0·15
85	—	—	0·19
80	—	—	0·22
75	—	0·11	0·25
70	—	0·16	0·28
65	—	0·20	0·31
60	0·09	0·24	0·34
55	0·16	0·28	0·36
50	0·21	0·32	0·39
45	0·26	0·35	0·42
40	0·30	0·38	0·44
35	0·34	0·42	0·47
30	0·38	0·45	0·51
25	0·43	0·50	0·55
20	0·48	0·54	0·58
15	0·53	0·60	0·64
10	0·61	0·68	0·72
9	0·63	0·71	0·74
8	0·65	0·74	0·76
7·5	—	0·75	—
7	0·68	—	0·79
6·5	—	0·81	—
6	0·72	—	0·86
5·5	0·74	0·96	0·90
4·5	1·07	1·10	1·03
3·5	1·19	1·18	1·13
2·5	1·26	1·25	1·20
1·5	1·34	1·36	1·27
0·5	1·48	1·41	1·34
−0·5	—	—	1·44
−0·5	—	—	1·61
0·5	1·62	1·75	1·80
0·5	2·09	1·98	1·97

For other space groups the above remarks still apply. Furthermore, it should be noted that in any space group the actual sampling need be carried out only over the asymmetric unit of the pattern, the ordinary Fourier expression then reducing to the well-known special form for the space group in question. For any space groups in which the unit cell does not possess a centre of symmetry at the origin, two summations will have to be performed to give the real and imaginary parts of the transform, the first using the centrosymmetrical array of coefficients

$$\tfrac{1}{2}[d(\mathbf{n})+d(-\mathbf{n}')],$$

and the second the anti-centrosymmetrical array

$$\tfrac{1}{2}[d(\mathbf{n}')-d(-\mathbf{n}')].$$

It should also be noted that equation (2) possesses a negative exponential, whereas the Fourier expression

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* This array of numbers is, in the terminology of the (F_o-F_c) synthesis (Cochran, to be published), the F_c synthesis. These numbers need only be subtracted from the F_o synthesis, when that has been calculated, to yield directly the (F_o-F_c) synthesis.

used for calculating electron-density maps has a positive exponential. This fact will necessitate a slight alteration in the details of summing in non-centrosymmetrical cases only.

Finally, the Fourier summation was carried out in the ordinary way. The results of the summation had now to be multiplied by $2|\mathbf{a}_1' \times \mathbf{a}_2'| = 2 \times$ (area of a unit parallelogram of the sampling lattice) $= 2 \times$ (area of unit cell)/$(60 \times 30) \doteqdot 0{\cdot}24067$. (The factor 2 arose from the customary halving of the sum in the course of summation.) For example, the uncorrected value for $F(0, 0)$ was 2881; upon multiplication by 0·24067 this became 693, which may be compared with the true value for $F(0, 0)$ of 696.

Table 2 lists the $F(50l)$'s as calculated by this and by the usual method. The disagreement factor for this line is 6%.

The times required for the several operations were as follows. Preparation of the sampling lattice: 1 hr. Preparation of the strips representing hypothetical atoms: 1 hr. for each type of atom. (These strips do not, of course, have in general to be redone for other calculations.) Sampling and adding to obtain coefficients: 15 min. per atom in the asymmetric unit. Thus the total investment of time before the summation was begun was, for the present example, about 16 hr. The time required for the summation, using Beevers–Lipson strips, was about 36 hr., giving a total of about 52 hr. for the entire process. It is estimated that by the usual method the total time required by the same person would have been about 125 hr.

6. Calculation of the appearance of hypothetical atoms

In order to calculate the appearance of a hypothetical atom, a necessary preliminary to the sampling procedure, it is first necessary to know the scattering factor, or Fourier transform, of the real atom which it is to replace. It may include any effects of temperature, non-sphericity, etc., which are desired. This transform, when terminated abruptly at the desired distance from the origin, is the transform of the hypothetical atom. The remaining problem is to effect the transformation to real space. This can be performed for spherical atoms by the well-known forms to which the Fourier transformation reduces in the spherically symmetric case (James, 1948; Cruickshank, 1949). However, sampling and Fourier summation provide a more rapid method and one which is not restricted to spherical atoms. In this case it is impossible totally to avoid overlapping, but if the sampling lattice $\mathbf{N}'$ is sufficiently fine (for example, intervals of 0·1 A.$^{-1}$) the hypothetical atoms will be well separated (10 A. for the figures just given) and overlap will be negligible. The function to be sampled is the entire terminated scattering factor, or the appropriate plane or line section through the origin, according as it is the three-dimensional hypothetical atom, or its projection on a plane or a line, that is desired. If the atom is spherical, the Fourier sum need be evaluated only along one radial line.

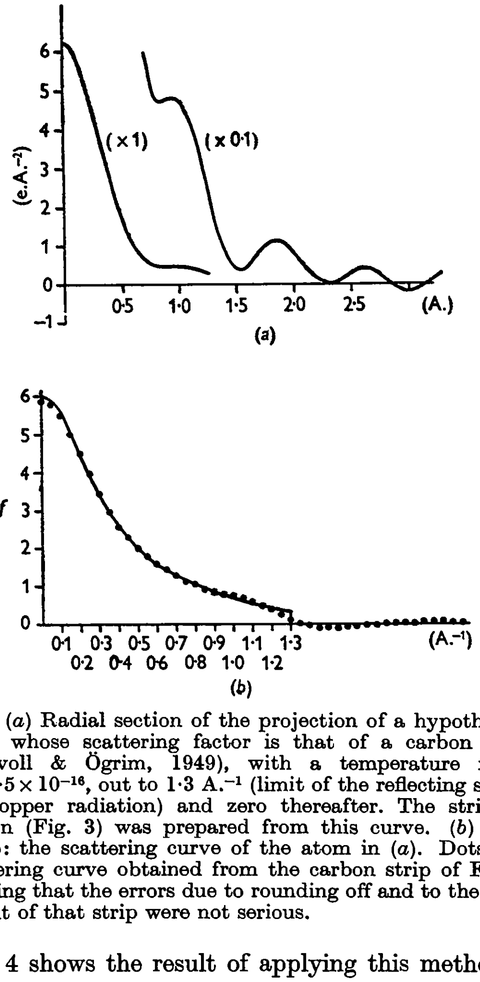

Fig. 4. (*a*) Radial section of the projection of a hypothetical atom whose scattering factor is that of a carbon atom (Viervoll & Ögrim, 1949), with a temperature factor $B = 3{\cdot}5 \times 10^{-16}$, out to 1·3 A.$^{-1}$ (limit of the reflecting sphere for copper radiation) and zero thereafter. The strip for carbon (Fig. 3) was prepared from this curve. (*b*) Solid curve: the scattering curve of the atom in (*a*). Dots: the scattering curve obtained from the carbon strip of Fig. 3, showing that the errors due to rounding off and to the finite extent of that strip were not serious.

Fig. 4 shows the result of applying this method in two dimensions to the carbon atom. The scattering curve was that given by Viervoll & Ögrim (1949), with

Table 2. *Comparison of sampling and ordinary methods for* $F(50l)$

$l=$	$\overline{23}$	$\overline{22}$	$\overline{21}$	$\overline{20}$	$\overline{19}$	$\overline{18}$	$\overline{17}$	$\overline{16}$	$\overline{15}$	$\overline{14}$	$\overline{13}$	$\overline{12}$	$\overline{11}$	$\overline{10}$	$\overline{9}$	$\overline{8}$
Sampling	$\overline{5}$	$\overline{15}$	$\overline{24}$	$\overline{14}$	0	$\overline{7}$	$\overline{7}$	4	16	5	20	40	53	44	56	25
Ordinary	$\overline{5}$	$\overline{15}$	$\overline{23}$	$\overline{12}$	$\overline{1}$	$\overline{6}$	$\overline{5}$	6	16	6	22	42	53	47	54	24
$l=$	$\overline{7}$	$\overline{6}$	$\overline{5}$	$\overline{4}$	$\overline{3}$	$\overline{2}$	$\overline{1}$	0	1	2	3	4	5	6	7	8
Sampling	53	39	64	21	$\overline{16}$	$\overline{2}$	$\overline{6}$	$\overline{46}$	$\overline{61}$	$\overline{11}$	$\overline{13}$	$\overline{69}$	$\overline{72}$	$\overline{34}$	$\overline{40}$	$\overline{30}$
Ordinary	53	39	60	20	$\overline{19}$	$\overline{4}$	$\overline{7}$	$\overline{50}$	$\overline{63}$	$\overline{13}$	$\overline{11}$	$\overline{70}$	$\overline{70}$	$\overline{35}$	$\overline{39}$	$\overline{29}$
$l=$	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	
Sampling	$\overline{33}$	$\overline{7}$	$\overline{6}$	5	14	6	36	16	24	17	23	17	17	5	9	
Ordinary	$\overline{33}$	$\overline{6}$	$\overline{5}$	8	13	5	35	19	25	19	20	18	15	5	10	

a temperature factor $B = 3{\cdot}5 \times 10^{-16}$, terminated at $2/(1{\cdot}54 \times 10^{-8}) \doteqdot 1{\cdot}3$ A.$^{-1}$. The sampling was done on a square lattice $0{\cdot}1$ A.$^{-1}$ on an edge. It will be seen that the diffraction rings fall to a density less than $0{\cdot}1$ e.A.$^{-2}$ at distances from the centre of the atom greater than about 2 A. For the lumisterol calculation the hypothetical atoms were simply not produced beyond that point. That this termination introduced no serious error may be seen from Fig. 4(*b*), in which the scattering curve calculated from the hypothetical atom actually employed agrees closely with the desired scattering curve.

The author here wishes to express his thanks particularly to Dr H. Lipson, to whom the general method is due, to Dr Raymond Pepinsky, at whose laboratory and with whose encouragement the first part of this work was done, to Mrs D. Crowfoot Hodgkin for her interest and many valuable suggestions, and to the Rockefeller Foundation for a grant of research funds.

References

Cox, E. G., Gross, L. & Jeffrey, G. A. (1949). *Acta Cryst.* **2**, 351.
Cox, E. G. & Jeffrey, G. A. (1949). *Acta Cryst.* **2**, 341.
Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65.
Donohue, J. & Schomaker, V. (1949). *Acta Cryst.* **2**, 344.
Grems, M. D. & Kasper, J. S. (1949). *Acta Cryst.* **2**, 347.
James, R. W. (1948). *The Optical Principles of the Diffraction of X-Rays.* London: Bell.
Pepinsky, R. (1947). *J. Appl. Phys.* **18**, 601.
Viervoll, H. & Ögrim, O. (1949). *Acta Cryst.* **2**, 277.

Acta Cryst. (1951). **4**, 367

Sur la Convergence et l'Erreur dans les Structures Non-Centrosymétriques

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Some conclusions obtained by Cruickshank are confirmed by a more direct method: (1) The method of successive applications of the Fourier transform is convergent for non-centrosymmetric structures. (2) Under identical conditions, the error in atomic positions is twice as great for non-centrosymmetric as for centrosymmetric structures.

Introduction

L'une des méthodes le plus couramment employées dans la détermination des structures cristallines, est l'application réitérée des transformations de Fourier. A partir d'un ensemble de coordonnées voisines des positions atomiques correctes, on détermine les angles des phases, avec ces angles et les $|F_{\text{observés}}|$ on calcule une transformée de Fourier, qui indique des modifications des positions atomiques. Avec ces coordonnées on répète la même opération, et ainsi de suite, jusqu'à obtenir des positions qui ne sont pas modifiées par la transformation de Fourier: à ce point, on considère qu'on a atteint la limite de convergence de la méthode, et qu'on a obtenu les coordonnées définitives.

Pour démontrer que le processus converge vers les coordonnées correctes, il faut prouver qu'il existe une région autour de chaque atome, à l'intérieur de laquelle les pics des transformées de Fourier successives se déplacent uniformément vers la position vraie.

Dans la plupart des nombreuses communications parues récemment, traitant des erreurs dans les déterminations des structures cristallines, on admet implicitement cette convergence, en supposant que l'on connaisse les modules et les arguments des facteurs de structure, aux erreurs expérimentales près. Booth (1946) propose de tenir compte des modifications $\Delta\alpha$ des angles des phases en introduisant dans les séries différentielles un terme correctif; Cruickshank (1950), en établissant une relation entre ce terme et les modifications des coordonnées atomiques, a pu démontrer que la méthode donne une limite de convergence, dans le cas des structures non-centrosymétriques.

Nous avons repris la démonstration d'une manière plus directe (Cruickshank utilise les séries différentielles de Booth et des calculs statistiques), et nous avons traité le cas des structures avec ou sans centre de symétrie. Les deux cas seront traités séparément.

Structures non-centrosymétriques

Supposons une structure formée par i atomes; $|F|$ et α sont les modules et les arguments des facteurs de structure correspondant aux positions correctes des atomes $\mathbf{r}_i$; $\mathbf{s}$ est le vecteur de diffusion $|s| = 2\sin\theta/\lambda$, $\mathbf{r}$ est le vecteur de position. $|F|$ et α sont des fonctions de $\mathbf{s}$.

Avec la portion d'espace réciproque contenue dans une sphère de rayon $|S_0|$ on peut définir une fonction

$$\rho(\mathbf{r}) = \int_{|s|<|S_0|} |F| \cos[2\pi(\mathbf{r} \times \mathbf{s}) - \alpha]\, dv \qquad (1)$$