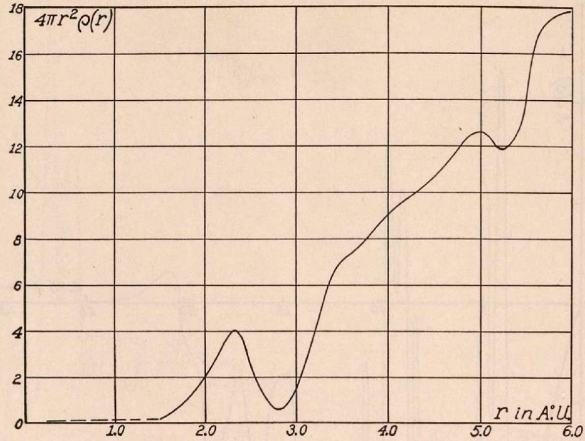

FIG. 3. Radial density distribution in rhombic sulphur, giving the number of atoms per A at any distance from a given atom.

to suggest a structure of long chains, the ring solution is the more probable. This result is in good agreement with the chemist's picture of a closed ring S_8 molecule in rhombic sulphur.

The results obtained here for sulphur serve as a good illustration of the use of the Fourier integral method of analysis. Without knowing or determining the crystal structure of the material, one obtains by a perfectly straightforward mechanical operation the relation of each atom to its neighbors. The value of such information for its own interest, or for its usefulness in a complete structure determination is evident.[11]

[11] Based upon this verification of the ring molecule the structure of rhombic sulphur has since been worked out. The results will be reported elsewhere.

A Fourier Series Method for the Determination of the Components of Interatomic Distances in Crystals*

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(Received June 18, 1934)

A method for the direct determination of the components of interatomic distances in crystals has been developed from a consideration of the properties of the Fourier series whose coefficients are the squares of the F-coefficients for the crystal reflections. Valuable structural information is thus obtained without making any assumptions as to the phase to be allotted to the F-coefficients. The practical application of the method is illustrated by a discussion of the structures of potassium dihydrogen phosphate and hexachlorobenzene.

1. INTRODUCTION

IN any crystal, the density of scattering power for x-rays (electron density) can be represented by a three-dimensional Fourier series of the form[1]

$$\rho(xyz)=\sum_{hkl=-\infty}^{\infty}\sum\sum\alpha(hkl)e^{2\pi i(hx/a+ky/b+lz/c)}. \quad (1)$$

* Presented in part at the Washington Meeting of the American Physical Society, Phys. Rev. **45**, 763A (1934).

[1] For literature references and notation see W. L. Bragg, Proc. Roy. Soc. **A123**, 537 (1929); also A. L. Patterson, Zeits. f. Krist. **76**, 177 (1930).

If this density is real, as is usually the case, we have, in addition,

$$\alpha(h, k, l)=\alpha^*(-h, -k, -l), \qquad (1a)$$

where α^* is the conjugate complex of α. It is a well-known result that the values of $F(hkl)$ obtained from absolute measurements of integrated intensity of x-ray reflection are connected with the coefficients $\alpha(hkl)$ of the series (1) by the relation

$$F(hkl)=|\alpha(hkl)|. \qquad (2)$$

The problem of x-ray crystal analysis is the determination of the appropriate phases for the quantities $\alpha(hkl)$. This involves the use of our knowledge of the atomic scattering powers of the atoms of which the crystal is composed. These atoms are allotted positions in the unit cell in accordance with the space group requirements. Each of these positions, except in very special cases, involves one or more parameters in its specification. In general, a crystal structure investigation will involve the determination of a large number of such parameters and their calculation in most cases can only be carried out by a process of trial and error.

In this paper a method is presented which enables the principal interatomic distances to be directly determined. The directions in which these distances lie can also be obtained. No assumptions are involved in the deduction of these results and they are independent of the space group determination.

These interatomic distances place very definite limits on the values which the unknown parameters can assume. The labor involved in their determination is thus very considerably reduced.

2. One-Dimensional Problem

It is simpler to discuss the one-dimensional problem first. Consider the distribution of electron density normal to a crystallographic plane whose spacing is d. This density can be expressed in the form

$$\rho(x)=\sum_{-\infty}^{\infty}\alpha(n)e^{2\pi inx/a}; \quad \alpha(n)=\alpha^*(-n). \qquad (3)$$

Let the curve of Fig. 1 represent any such distribution function. Consider an element dx at a distance x from the origin. The distribution

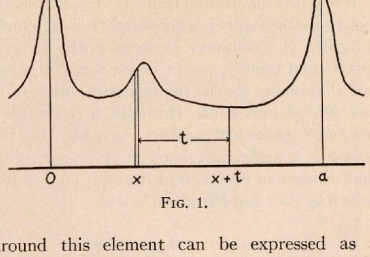

FIG. 1.

around this element can be expressed as a function of a parameter t in the form $\rho(x+t)$. Suppose we weight this distribution by the quantity $\rho(x)dx$, the amount of scattering matter in the element dx, and compute the weighted average distribution about any element dx when x is allowed to assume all values within the period. This average distribution $A(t)$ is given by

$$A(t)=d^{-1}\int_0^d \rho(x)\rho(x+t)dx. \qquad (4)$$

This integral is well known in the modern theory of the Fourier series as the "Faltung" of $\rho(x)$ and can immediately be evaluated by substituting (3) in (4), i.e.,

$$A(t)=\sum|\alpha(n)|^2e^{2\pi int/d}. \qquad (5)$$

This series can obviously be computed directly from the measured intensities of reflection from the various orders of the plane and it will be of great value to crystal analysis if we can obtain a simple physical interpretation of its meaning. This is readily done for the integral form, as follows.

We see that the principal contributions to $A(t)$ will be made when both $\rho(x)$ and $\rho(x+t)$ have large values. Thus if there is a peak in the curve $A(t)$ for a value $t=t_1$, it means simply that there are two peaks in the curve $\rho(x)$ at a distance t_1 apart. This simple qualitative result has a direct interpretation in crystal analysis. If we find a peak in the curve $A(t)$ for a given plane at a distance t_1 from the origin, we know that somewhere in the distribution normal to the plane there are planes of atoms at a distance t_1 apart.[2]

[2] The result obtained here is an extension of the application to crystals of the theory of scattering of x-rays in liquids reported by Gingrich and Warren at the Washington meeting of the American Physical Society and arose in a discussion of that work. Phys. Rev. **46**, 368 (1934).

While this qualitative result is very simple, its exact mathematical expression is extremely difficult. The distances between peaks are not reproduced exactly except in the simplest cases and that makes a strict mathematical interpretation almost impossible. However, a trial with a few simple series will convince the reader that the accuracy is sufficiently good to give very useful approximations for these distances. This is also shown by the examples given below.

3. Three-Dimensional Series

The result of the preceding paragraph can be extended immediately to three dimensions. We evaluate the integral

$$A(uvw)=(abc)^{-1}\int_0^a\int_0^b\int_0^c \rho(xyz) \times\rho(x+u, y+v, z+w)dxdydz$$
$$=\sum\sum\sum |\alpha(hkl)|^2 e^{2\pi i(hu/a+kv/b+lw/c)}$$
$$=\sum\sum\sum F^2(hkl)e^{2\pi i(hu/a+kv/b+lw/c)}. \quad (6)$$

By a direct extension of the above argument, we can show that if we find a maximum of $A(uvw)$ at some point $(u_1v_1w_1)$, then there are two maxima (atoms) in the distribution $\rho(xyz)$ whose distance apart is given by the vector whose components are $(u_1v_1w_1)$.

4. Two-Dimensional Series

In the practical application of this method to the analysis of crystals, the two-dimensional series promises to be the most fruitful. It is much easier to compute and much easier to represent than the three-dimensional series; and it is much less confused and more easily interpreted than the one-dimensional series. We consider a distribution of the type

$$A(uv)=\sum_{hk=-\infty}^{\infty}\sum F^2(hk0)e^{2\pi i(hu/a+kv/b)} \quad (7)$$

and discuss the components of the interatomic distances which lie in the plane under consideration.

5. Examples of the Method

The practical application of the method is best discussed in the light of known structures. Two such examples have been chosen. Potassium dihydrogen phosphate, which has been very thoroughly investigated by West[3] provides an example of a simple inorganic substance with several atoms in fixed positions and one set of atoms in a general position involving three parameters. A complete set of absolute measurements of intensity is available for the two principal zones of the crystal. The second example is hexachlorobenzene,[4] a relatively simple organic structure whose atoms are all in general positions. For this crystal, Lonsdale has obtained a satisfactory set of relative intensities for the zone [010] from which a picture is obtained of the projection on the (010) face. No original data have been obtained for either of these crystals. The present paper merely involves a rediscussion of the published data, making use of the new method of analysis.

(a) Potassium dihydrogen phosphate

This substance crystallizes in the space group $V_d^{12}(I\bar{4}2d)$. The unit cell, whose dimensions are $a=b=7.43$A; $c=6.97$A, contains four molecules KH_2PO_4. The positions of the potassium and phosphorus atoms are fixed by symmetry conditions. Qualitative consideration of the complexity of the spectra indicates that the sixteen oxygen atoms occupy the sixteen-fold general position[5] requiring three parameters for its specification. We shall confine ourselves here to the application of the new method to the determination of the x and y parameters of the oxygen atoms.

We compute[6] the series

$$\sum\sum F^2(hk0)e^{2\pi i(hu/a+kv/b)},$$

making use of the observed absolute F values published by West. The result of this computation is shown in the form of a contour map in Fig. 2(*b*). From the positions of the eight peaks surrounding the origin and our knowledge of the space group, we can immediately determine the oxygen parameters in this plane. The maxima

[3] J. West, Zeits. f. Krist. **74**, 306 (1930).
[4] K. Lonsdale, Proc. Roy. Soc. **A133**, 536 (1931).
[5] R. W. G. Wyckoff, *Analytical Expression of the Results of the Theory of Space Groups*, Washington, 1930.
[6] The method of Beevers and Lipson (Phil. Mag. **17**, 855 (1934)) is very convenient.

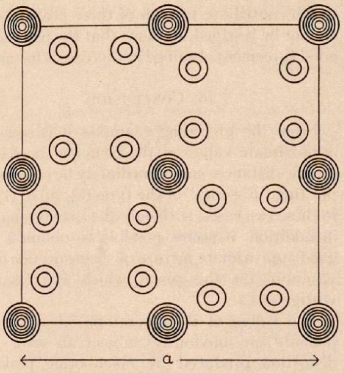

FIG. 2a.

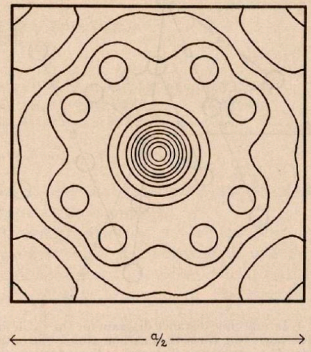

FIG. 2b.

FIG. 2. Potassium dihydrogen phosphate. (a) Electron density projected on (001), J. West.[3] (b) Contour map of the $F^2(hk0)$ series.

occur for the values[7] $\theta_1 = 29.6°$ and $\theta_2 = 51.4.°$ These are to be compared with the values obtained by West, i.e., $\theta_1 = 29°$, $\theta_2 = 52°$.

(b) Hexachlorobenzene

The space group in this case is $C_{2h}{}^5(P2_1/c)$. There are two molecules C_6Cl_6 in a cell of dimensions $a = 8.07$A, $b = 3.84$A, $c = 16.61$A, $\beta = 116°25'$. All the atoms are in twofold general positions,[5] the molecules having central symmetry.

In this case we compute the series

$$\sum\sum F^2(h0l)e^{2\pi i(hu/a+lw/c)},$$

using the relative F values observed by Lonsdale. The contour map (Fig. 3) shows the result of this computation. If we assume that peaks of the type A, B and C are due mainly to Cl–Cl distances and make use of the space group data we are led without further assumptions to a slightly irregular hexagon of chlorines arranged with respect to the axes as shown in Fig. 4. To explain other principal peaks we are led to an inner hexagon of carbons. The components of the various interatomic distances are given in Table

[7] $\theta_1 = 360u/a$, etc.

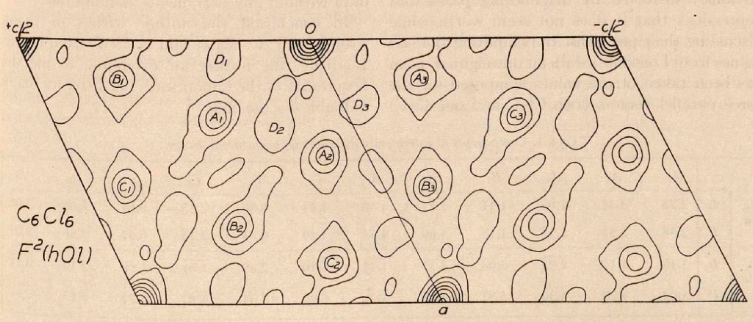

FIG. 3. Hexachlorobenzene. Contour map of the $F^2(h0l)$ series.