Fourier Integral Analysis of X-Ray Powder Patterns

B. E. WARREN AND N. S. GINGRICH, *Eastman Laboratory of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts*

(Received June 18, 1934)

A method is developed for the harmonic analysis of x-ray powder patterns. From the experimental scattering curve one obtains directly a radial distribution function giving the number of atoms to be found at any distance from a given atom. As an illustration, the method is applied to the pattern of rhombic sulphur. A radial distribution curve is obtained which indicates that each atom has two nearest neighbors at a distance of about 2.3A. The result is in good agreement with the chemist's picture of an S_8 ring molecule.

INTRODUCTION

THE determination of the radial distribution of atoms surrounding any given atom, by application of Fourier integral analysis to the experimental x-ray diffraction patterns of liquids, was suggested by Zernike and Prins.[1] The method has been successfully used by Debye and Menke[2] in the study of liquid mercury. It suggests itself immediately that the method should be equally applicable to the x-ray powder patterns of crystalline materials and that, by this method of analysis, the same kind of information should be obtained, namely the radial distribution of atoms about any one atom.

The treatment of x-ray diffraction in crystals by means of a Fourier series representation of the density of scattering matter is well known.[3, 4] However, the applicability of the method to a complex crystal has been rather limited because of the fact that one can determine from the intensities of reflection only the magnitudes of the coefficients in the Fourier series. The *phases* are usually unknown and hence the method is not generally applicable. An important feature of the present method of treatment is found in the fact that the coefficients are given in terms of the observed *intensities*, not the amplitudes, and hence there is no ambiguity as to phase. Needless to say since the new method does not require as much diffraction information, it will not yield as much structural information. Instead of determining a complete crystal structure, the new method gives simply the distribution of atoms about any one atom.

[1] Zernike and Prins, Zeits. f. Physik **41**, 184 (1927).
[2] Debye and Menke, *Ergeb. der Tech. Röntgenkunde* II.
[3] A. H. Compton, *X-rays and Electrons.*
[4] W. H. Bragg and W. L. Bragg, *The Crystalline State.*

THEORY

For simplicity in presentation we shall assume a crystal containing only one kind of atom, and then later give the corresponding result for the general case. From an array of atoms which takes all orientations in space, the intensity of scattered radiation is given as a function of the angle of scattering by the relation[5]

$$I(s)=I_0\frac{e^4}{m^2c^4R^2}\left(\frac{1+\cos^2 2\theta}{2}\right)\sum_p\sum_q f_p f_q\frac{\sin sr_{pq}}{sr_{pq}}. \quad (1)$$

$s=4\pi\sin\theta/\lambda$, f_p is the atomic scattering factor for atom p and r_{pq} is the distance from atom p to atom q. For a crystal containing only one kind of atom (1) becomes

$$I(s)=\psi(s)N\sum_p \sin sr_p/sr_p, \quad (2)$$

where N is the effective number of atoms in the sample and

$$\psi(s)=I_0\frac{e^4}{m^2c^4R^2}f^2\left(\frac{1+\cos^2 2\theta}{2}\right).$$

Representing the distribution of atoms about any one atom by a density function $\rho(r)$ such that $4\pi r^2\rho(r)dr$ is the number of atoms between r and $r+dr$ from the atom under consideration, Eq. (2) becomes

$$I(s)=N\psi(s)\left\{1+\int_0^\infty 4\pi r^2\rho(r)\frac{\sin sr}{sr}dr\right\}. \quad (3)$$

Let

$$i(s)=(I(s)/N\psi(s))-1$$

$$si(s)=4\pi\int_0^\infty r\rho(r)\sin sr\,dr. \quad (4)$$

[5] P. Debye, Ann. d. Physik **46**, 809 (1915).

By the Fourier integral theorem this can be written

$$r\rho(r)=(2\pi^2)^{-1}\int_0^\infty si(s)\sin sr\,ds. \quad (5)$$

The integration over the scattered intensity $I(s)$ is from zero to large angles and hence includes the diffraction maximum at zero angle (000 order) which is not experimentally observable. Replace $I(s)$ by $I'(s)+I(s)$ where $I'(s)$ is the intensity distribution in the 000 order beam and $I(s)$ is the observable intensity curve.

$$2\pi^2r\rho(r)=\int_0^\infty \frac{sI'(s)}{N\psi(s)}\sin srds + \int_0^\infty s\left\{\frac{I(s)-N\psi(s)}{N\psi(s)}\right\}\sin sr\,ds. \quad (6)$$

The first integral has the same value for either an amorphous or crystalline material and is readily evaluated either from consideration of a spherical sample of continuously distributed scattering matter or by a modification of the usual method of calculating the integrated reflection from a powdered crystal.

$$\int_0^\infty \frac{s^2I'(s)}{N\psi(s)}ds=2\pi^2r\rho_0,$$

where ρ_0 is the average density of the sample in atoms per cc. Our relation takes the final form

$$4\pi r^2\rho(r)=4\pi r^2\rho_0+(2r/\pi)\int_0^\infty si(s)\sin sr\,ds. \quad (7)$$

The $si(s)$ curve is readily constructed from the experimental scattering curve and the operation involved in Eq. (7) is then best carried out with a harmonic analyzer. The final result is a curve of $4\pi r^2\rho(r)$ as a function of r. It might be pointed out that the result is obtained by a purely mechanical, straightforward operation and that it is not even necessary to index the lines of the powder pattern or to have fitted the lines to a quadratic form.

The integral in Eq. (7) can also be expressed in terms of the integrated reflections of the lines in the powder pattern. The relation then becomes a series, with a term for each line in the powder pattern.[6] However, since the number of lines in a powder pattern is usually rather large, the evaluation of the series becomes altogether too laborious; and for practical purposes the evaluation of (7) with a harmonic analyzer is the most satisfactory method.

In the general case, one has a crystal containing several kinds of atoms with scattering factors which do not have the same dependence upon $\sin\theta$. In this case the problem must be set up in terms of the electron density in the crystal rather than the atom density. Eq. (7) then takes the more general form

$$\int_M \rho_m d\sigma_m 4\pi r^2\rho(r)=4\pi r^2\rho_0\sum_M Z_m + (2r/\pi)\int_0^\infty s\{(I/N\psi(s))-\sum_M f_m{}^2\}\sin sr\,ds, \quad (8)$$

where N is the number of molecules in the sample, Σ_M indicates summation over the atoms per molecule, ρ_m and $\rho(r)$ are electron densities in electrons per cc, and $\psi(s)$ is the intensity per electron. In this case one obtains a distribution curve giving the weighted average density of electrons at distance r from a point, each value being weighted by the electron density at the individual point. The positions of the peaks indicate distances which are slightly larger than the interatomic distances and the areas under the peaks give directly the number of pairs of atoms, having that particular distance of separation, multiplied by the product of the atomic numbers.

Application to Rhombic Sulphur

The method of harmonic analysis has been successfully applied to the powder pattern of rhombic sulphur, the crystalline structure of which had not hitherto been determined. The powdered material was mounted on a thread with dilute collodion and the cylindrical sample placed in a powder diffraction camera of radius 4.75 cm. Since there must be no extraneous background blackening, it is very necessary to use a strictly monochromatic x-ray beam. This was obtained by reflecting the $K\alpha$ line of Mo from a rocksalt crystal placed in front of the camera. With the tube running at 20 m.a. and 35 kv peak an exposure of 25 hours was sufficient.

From the microphotometer record of the film, an intensity curve was derived in the usual way.

[6] N. Gingrich and B. Warren, Phys. Rev. **45**, 762 (1934).

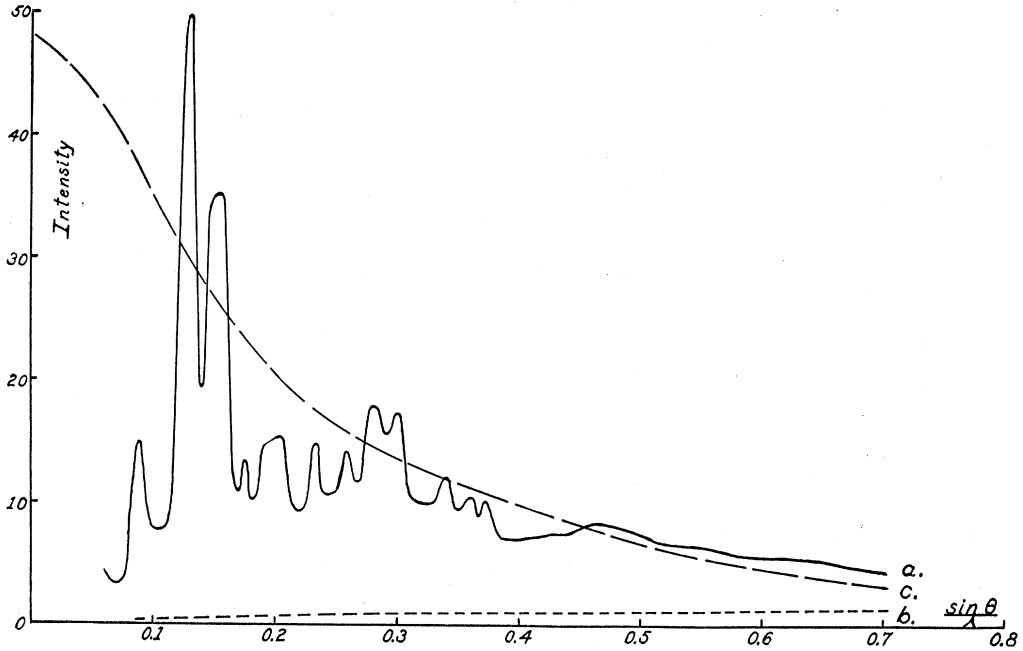

FIG. 1. (*a*) Experimental scattering curve for rhombic sulphur corrected for absorption. (*b*) Modified scattering. (*c*) Independent unmodified scattering $N\psi(s)$.

The experimental intensity curve, corrected for absorption in the cylindrical sample,[7] is given in Fig. 1*a*, the intensity being expressed in arbitrary units.

As seen from Eq. (3), at large angles of scattering $I(s)$ approaches $N\psi(s)$ and hence at sufficiently large values of sin θ the experimental curve is given by the modified and *independent* unmodified scattering of N atoms.

Independent, unmodified

$$I = N\psi(s).$$

Modified[8]

$$I = N\sum_M \{Z_m - \sum (f_n)^2\} I_0 \frac{e^4}{m^2c^4R^2}\left(\frac{1+\cos^2 2\theta}{2}\right).$$

Assuming that the scattering can be taken as independent at sin $\theta/\lambda = 0.7$ the fractional parts of unmodified and modified scattering are calculated. Since $I = I_{\text{unmod.}} + I_{\text{mod.}}$ this determines the ordinates at sin $\theta/\lambda = 0.7$ for both the modified and independent unmodified curves. Both of these curves are readily calculated as a function of the angle, from the tables of scattering factors[9] and, having fixed the scale of ordinates at one point, the two curves are readily plotted on the same scale as $I(s)$. The unmodified part of the experimental scattering curve is then obtained by subtracting 1*b* from 1*a*. The difference divided by 1*c* gives the quotient $I(s)_{\text{coh.}}/N\psi(s)$ from which the curve $si(s)$ is constructed. Although the assumption of independent scattering at large angle is only an approximation, it is nevertheless a sufficiently good one, and affords a very simple method of putting the $si(s)$ curve upon a quantitative basis.

The curve $si(s)$ obtained in this way is plotted against s (Fig. 2) and the integration involved in Eq. (7) carried out on a Coradi harmonic analyzer. The coefficients, which the analyzer delivers for the different harmonics, give directly the values of the integral for various values of r. The scale of abscissae used in Fig. 2 corresponds to 0.4A per harmonic. It might be pointed out that although the $si(s)$ curve has been put upon an absolute basis by several approximations, any errors which have crept in will only result in displacing the curve up or down or in tilting it somewhat. Since these are long period variations,

[7] F. C. Blake, Rev. Mod. Phys. **5**, 180 (1933).
[8] E. O. Wollan, Rev. Mod. Phys. **4**, 233 (1932).
[9] James and Brindley, Phil. Mag. **12**, 81 (1931).

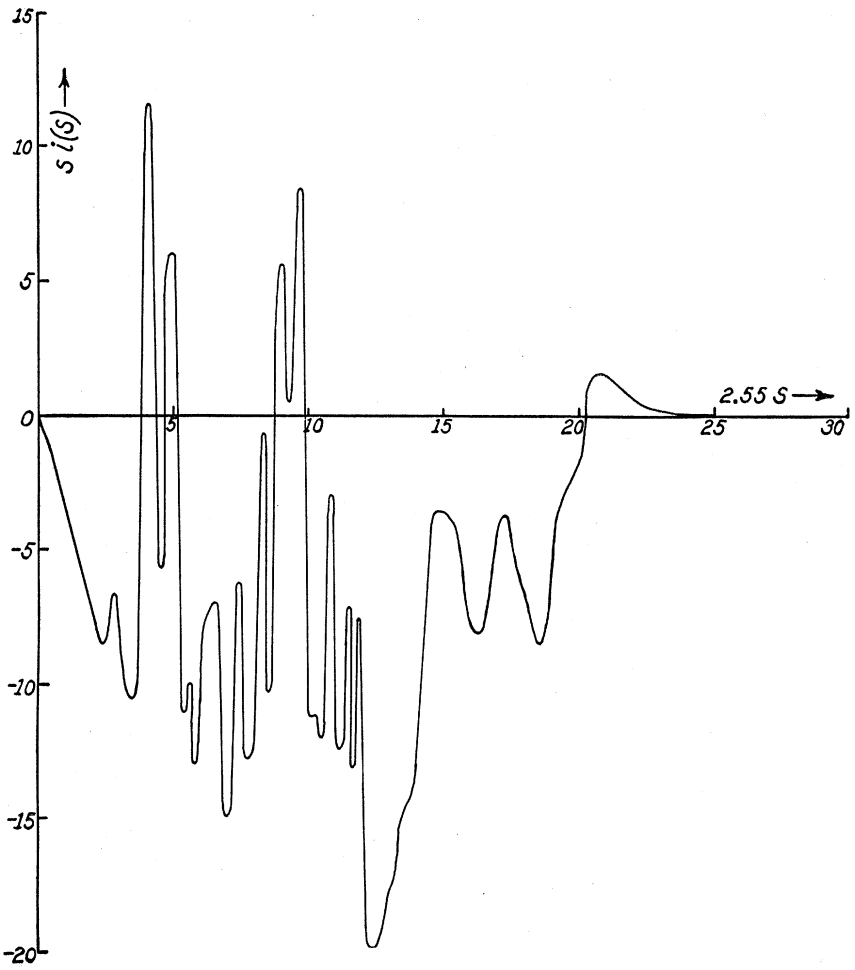

FIG. 2. Curve $si(s)$ against s for rhombic sulphur.

they will affect appreciably only the first one or two harmonics but not the higher ones. Hence only the first two or three points on the $4\pi r^2\rho(r)$ curve will be in error and this does not greatly matter, since this part of the curve is known to have zero ordinate.

The integration involved in Eq. (7) was carried out on the harmonic analyzer for the first 15 harmonics, thus giving points on the r-scale from 0 to 6.0A. The curve obtained is shown in Fig. 3. From the curve one gets directly the concentration of atoms at any distance from a given atom and furthermore, since the work has been carried through on a quantitative basis, the areas under the peaks give directly the number of atoms in that range of distances.

The interpretation of the curve is quite simple. At small distance from an atom there are of course no other atoms. At a distance of about 2.35A there is a peak with area 2.3 atoms. This is interpreted as meaning 2 atoms at a distance slightly less than 2.35A. Beyond these two nearest neighbors, the next nearest atoms are at a distance of 3.25A or more. The *S–S* distance 2.35A is slightly larger than the distance 2.2A obtained from the Trithionate group[10] but this is not unexpected since the slight overlapping of the next nearest neighbors, which causes a peak area of 2.3 atoms rather than 2.0, will also shift the peak slightly toward larger distances. In order that each atom should have two nearest neighbors, the structure must contain long chains or chains closed into rings and, since there is nothing about the physical properties of sulphur

[10] W. H. Zachariasen, J. Chem. Phys. **2**, 109 (1934).

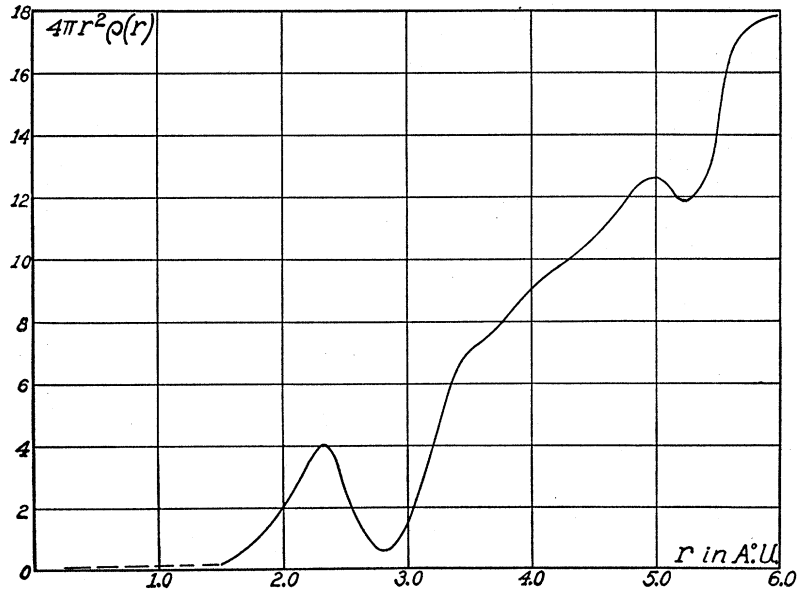

FIG. 3. Radial density distribution in rhombic sulphur, giving the number of atoms per A at any distance from a given atom.

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*

A. L. PATTERSON, *George Eastman Research Laboratories, Massachusetts Institute of Technology*

(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]

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

* 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).