

$2k+l=4n+1$ or $4n+3$ are useful in fixing the oxygen parameters. Here the bismuth and arsenic contributions are of opposite signs, and the oxygen effect is appreciable in many cases, for instance in pairs such as $211(w-)$, $\bar{2}11(w)$; $213(m)$, $\bar{2}13(w)$ which were observed on Weissenberg photographs.

No attempt was made to determine the oxygen parameters directly from intensities; rather, the intensity data were used to verify assumptions based on predicated atomic distances and configuration. The configuration of the arsenate ion is well known to be tetrahedral. Since the arsenic atoms lie in fourfold inversion axes, the aspect of the tetrahedron is fixed by symmetry. If reasonable assumptions are made concerning its size, it is only necessary to rotate the tetrahedron about the axis, and to find the position which best agrees with the indicative intensities. The As-O distance in the arsenate anion has been reported as 1.73 Å. in YAsO_4 and as 1.66 Å. in BAsO_4 (*Strukturbericht*, 3). A value independent of parameter determinations may be obtained by comparison of the cell volumes of arsenates with respect to isomorphous phosphates of the same cation; for instance, AlPO_4 and AlAsO_4 ; BPO_4 and BAsO_4 . This indicates that the arsenate group is about 3.5% larger than the phosphate group. Since the P-O distance in the phosphate group has been accurately determined as 1.56 Å., the As-O distance in the arsenate ion may safely be taken as 1.63 Å.

From these considerations it has been possible to derive satisfactory parameters for the oxygen, though no high degree of accuracy can be claimed. The results, expressed in fractions of the unit cell, are:

$$x=0.213, \quad y=0.149, \quad z=0.080.$$

Table 1 gives the data for the first half of the powder pattern showing the comparison between visually

estimated intensities and intensity numbers calculated on the basis of the proposed structure. These numbers (which have been reduced by a convenient factor) were obtained from the expression, $I \sim \text{L.P. } pF^2$, where L.P. is the appropriate Lorentz polarization factor, p is the multiplicity and $F^2 = A^2 + B^2$.

Interatomic distances and structure

The O-As distances in the arsenate group have been assumed to be 1.63 Å. For the most reasonable position of this group with reference to the bismuth positions, the bismuth is found to have a co-ordination ring of eight oxygen atoms. Four are at 2.49 Å., four others at 2.59 Å. All other oxygen atoms are more than 4 Å. away. The average oxygen distance to nearest neighbor oxygen atoms is 2.85 Å., the individual distances being 2.60, 2.75, 3.02 and 3.02 Å.

Tetragonal bismuth arsenate has the scheelite structure (CaWO_4). Other crystals which have this structure are the periodates of sodium, potassium, ammonium and rubidium; the perrhenates of silver, sodium, ammonium and rubidium; the molybdates of lead, strontium, calcium and barium. No other arsenate is known to have this structure. Bismuth vanadate is reported to have an orthorhombic cell which is of a deformed scheelite type.

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Evaluation of Fourier Transforms by a Fourier Synthesis Method

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A convenient numerical method is developed for evaluating the Fourier transforms of arbitrary functions by the use of Beavers-Lipson strips. A detailed procedure is worked out for the determination of the radial distribution curve of an amorphous material from the X-ray diffraction intensity curve, but the method is generally applicable provided that the transformed function is continuous and approaches zero sufficiently rapidly. For the purpose considered, strips giving values of $A \sin 2\pi nx$ at intervals of $\frac{1}{120}$ in x to two-figure accuracy and extending up to the 45th harmonic are shown to be suitable. The accuracy of the method has been tested by evaluating the transforms of the first three odd Hermite functions with satisfactory results.

Introduction

In the study of amorphous materials by X-ray diffraction the experimental data are obtained in the form

of a curve relating the intensity of diffracted radiation to the Bragg angle of diffraction, θ . This can be converted into a radial distribution function of the electron

density in the material by means of a Fourier sine transform which is of the form, omitting constant multipliers,

$$\phi(r) = \int_0^{\infty} f(s) \sin 2\pi r s ds,$$

where $s = (2 \sin \theta) / \lambda$, r represents distance in the structure, and $f(s)$ is an experimentally determined function of s related to the distribution of intensity in the diffraction pattern. The method of evaluating this transform described in the literature (Katzoff, 1934) is to plot graphs of $f(s) \sin 2\pi r s$ for each value of r at which it is desired to evaluate $\phi(r)$, and to determine the area of each graph either by weighing, counting squares or with a planimeter. The construction of the graphs for all the values of r required is an extremely laborious process, and in order to diminish this work the use of a Coradi Harmonic Analyser has been suggested, but such instruments are neither generally available nor ideally adapted to the purpose. More recently a photoelectric Fourier transformer has been described (Born, 1945) which will perform the transformation and present the curve of $\phi(r)$ on the screen of a cathode-ray oscillograph, the data being inserted in the form of a mask cut to the shape of the function $f(s)$. This apparatus is, however, unlikely to be available in the average laboratory, and a simple and reasonably rapid method is very desirable.

Similar problems arise in connexion with the response of electrical transmission systems to arbitrary input signals, and a number of graphical methods adapted to this purpose have been described by Cunningham (1947). The third method he describes lends itself readily to modification into a direct numerical method, using strips of the type of those described by Beevers & Lipson (1936*a, b*) and widely used in crystal-structure analysis.

Theoretical

In order to obtain a detailed procedure suitable to the problem in hand, the following theoretical treatment is convenient.

Let θ = the Bragg angle,

λ = wave-length of radiation in A.,

$s = (2 \sin \theta) / \lambda$,

r = distance within the structure of the specimen material in A.,

$\rho(r)$ = the excess density function in the structure,

I_s = the intensity diffracted at the Bragg angle θ ,

P_s = the polarization factor at this value of θ ;

then it may be shown that

$$\frac{I_s}{P_s} = K \int_0^{\infty} r \rho(r) \frac{\sin 2\pi r s}{s} dr,$$

where K is a constant involving the geometry of the apparatus and the intensity of the primary beam. Hence putting

$$s I_s / P_s = f(s),$$

we have $f(s) = K \int_0^{\infty} r \rho(r) \sin 2\pi r s dr$.

In practice the function $r \rho(r)$ may be regarded as effectively zero for $r >$ some value, say r_a . Hence we may replace the upper limit of the integral by r_a :

$$f(s) = K \int_0^{r_a} r \rho(r) \sin 2\pi r s dr.$$

Also $r \rho(r) = 0$ when $r = 0$, and is not defined for $r < 0$. Hence $r \rho(r)$ may be expanded as a Fourier half-range sine series which will be uniformly convergent in the range $0 \leq r \leq r_a$, since $r \rho(r)$ is continuous in this range, i.e.

$$r \rho(r) = \sum_{n=0}^{\infty} A_n \sin n\pi \frac{r}{r_a} \quad (0 \leq r \leq r_a).$$

Therefore

$$\begin{aligned} f(s) &= K \int_0^{r_a} \sum_{n=0}^{\infty} A_n \sin n\pi \frac{r}{r_a} \sin 2\pi r s dr \\ &= K \sum_{n=0}^{\infty} A_n \int_0^{r_a} \sin n\pi \frac{r}{r_a} \sin 2\pi r s dr \\ &= \frac{1}{2} K \sum_{n=0}^{\infty} A_n \int_0^{r_a} \{ \cos \pi(n/r_a - 2s)r - \cos \pi(n/r_a + 2s)r \} dr \\ &= \frac{1}{2} K \sum_{n=0}^{\infty} A_n \left[\frac{r_a \sin \pi(n/r_a - 2s)r}{\pi(n - 2sr_a)} - \frac{r_a \sin \pi(n/r_a + 2s)r}{\pi(n + 2sr_a)} \right]_{0}^{r_a} \\ &= \frac{K r_a}{2\pi} \sum_{n=0}^{\infty} A_n \left(\frac{\sin \pi(n - 2sr_a)}{n - 2sr_a} - \frac{\sin \pi(n + 2sr_a)}{n + 2sr_a} \right). \end{aligned}$$

For integral values of $2sr_a$ every term in the summation is zero except that for which $2sr_a = n$, and then

$$\begin{aligned} f\left(\frac{n}{2r_a}\right) &= \text{Lt}_{2sr_a \rightarrow n} \frac{K r_a A_n \sin \pi(n - 2sr_a)}{2\pi(n - 2sr_a)} \\ &= \frac{1}{2} K r_a A_n. \end{aligned}$$

Therefore $A_n = 2f(n/2r_a) / K r_a$.

Hence the desired function $r \rho(r)$ may be synthesized by summing the series $\sum_{n=0}^{\infty} A_n \sin n\pi \frac{r}{r_a}$, which we may approximate by termination after a suitable number of terms.

Practical details

In order to establish a satisfactory method it is necessary to take account of the following considerations:

(a) The range of s over which $f(s)$ is observed.

(b) The number of ordinates on the $f(s)$ curve which are required in order to represent its form satisfactorily.

(c) The value of r_a beyond which $r\rho(r)$ may be considered essentially zero.

(d) The number of ordinates on the $r\rho(r)$ curve which are required to represent its form satisfactorily.

Thus, if the diffraction pattern is recorded as far as $\theta=45^\circ$, $f(s)$ will be known over the range $0 < s < 0.92$ for Cu $K\alpha$ radiation. Amorphous diffraction patterns are usually diffuse enough for $f(s)$ to be adequately represented by ordinates at intervals of $s=0.02$. Then if we adopt the usual technique of fitting the experimental intensity curve to the calculated incoherent scattering curve at the maximum value of s observed, viz. 0.92 in this case, we shall have 45 non-zero ordinates. The Fourier series for $r\rho(r)$ will therefore be terminated after the 45th term, and also we have

$$1/2r_a = 0.02.$$

$$\text{Therefore } r_a = 25 \text{ \AA.},$$

which is a reasonable value for r_a . About two or three points per Ångström unit need to be evaluated on the $r\rho(r)$ curve in order to give sufficient certainty in drawing the curve, and convenient points at which to sum the series are therefore at intervals of $r/r_a = \frac{1}{60}$.

In view of these considerations a suitable set of strips will go up to the 45th harmonic and will give values of $A_n \sin(n\pi r/r_a)$ at intervals of $r/r_a = \frac{1}{60}$ in circular measure, i.e. 3° . This involves 30 values of each strip. Summation of the strips then gives the desired function directly from 0 to 12.5 Å., and the portion from 12.5 to 25 Å. is obtained by changing the sign of the odd harmonics, i.e. the even and odd harmonics are summed separately and added for the first half of the range and subtracted for the second half, writing down the results in reverse order.

It was expected that strips giving integral values of A_n from 1 to 99 and values of $A_n \sin(n\pi r/r_a)$ to the nearest integer would provide sufficient accuracy, and this is confirmed by the tests described below. As high values of A_n never occur for large values of n , since $f(s)$ is small at large s , the work involved in preparing the strips was reduced by limiting the value of A_n to $A_n=1$ to 50 for $n=17$ to 25, $A_n=1$ to 20 for $n=26$ to 32, and $A_n=1$ to 10 for $n=33$ to 45. A_n was also limited to the range 1 to 50 for $n=2$ to 6. Negative values of A_n were not included, as the ordinates of the $f(s)$ curve are always positive. They would be an added convenience if it were desired to transform an assumed structure to give a calculated intensity curve, but this can always be done by adding separately the terms with positive and negative coefficients.

Tests of the method

The method was tested by applying it to the first three odd Hermite functions

$$\phi_1(x) = 2x \exp[-\frac{1}{2}x^2],$$

$$\phi_3(x) = 4x(2x^2 - 3) \exp[-\frac{1}{2}x^2],$$

$$\phi_5(x) = 8x(4x^4 - 20x^2 + 15) \exp[-\frac{1}{2}x^2],$$

which have the property that apart from a constant factor they are identical with their respective Fourier sine transforms (Titchmarsh, 1937, p. 76). The functions were calculated, plotted and transformed using 15 harmonics only, as the use of the full 45 harmonics gave an undesirable compression in the abscissae of the transform. The results were then scaled to agree with the original curve at the peaks. In Fig. 1 the Hermite

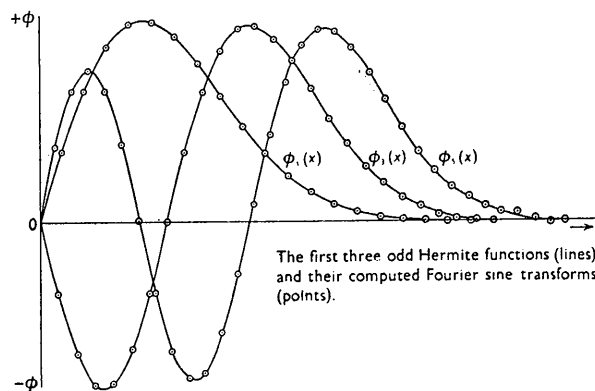


Fig. 1.

functions are shown by the full lines, and the circles show the values obtained for the transforms using the strip synthesis. Agreement is within 1-2% of the peak height. Using the full 45 harmonics for the transformation of $\phi_1(x)$, it was found that the errors are reduced by about half. The method is therefore quite satisfactory for the purpose for which it is developed.

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