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False Detail in Three-Dimensional Fourier Representations of Crystal Structures

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An investigation is made of the diffraction rings to be expected in a three-dimensional Fourier representation of a crystal structure when the Fourier series terminates while the coefficients are appreciable. The method followed is an extension of that used by Bragg and West in discussing the analogous problem for two-dimensional projections. The diffraction rings for one-, two- and three-dimensional representations are compared.

The maxima representing heavy atoms in a two-dimensional Fourier projection of a crystal structure are often surrounded by one or more nearly circular regions of negative density, the origin of which is well understood. They are diffraction rings, closely analogous to those which surround the image of a star viewed with a telescope of small aperture, and are due to the fact that in summing the Fourier series from which the projection is obtained it has been terminated while its coefficients are still appreciable. We may think of the spectra that can be given by the crystal, the amplitudes of which give the coefficients of the series, as associated with the points of the reciprocal lattice. For a two-dimensional projection, the reciprocal-lattice points concerned are those lying in a plane passing through the origin and perpendicular to a zone axis of the crystal. Terms corresponding to all points in the plane up to a certain distance from the origin are included in the summation, and we may think of the circle drawn on the plane, having the origin as centre, and including these points, as defining an equivalent optical aperture for the projection, which is, formally, an optical image. The problem has been discussed from this point of view by Bragg & West (1930), who calculated, with certain approximations, the form of the rings for a crystal consisting of point atoms, and found that their results agreed fairly closely, as regards the positions of the maxima and minima, with the rings obtained by making a projection of a fictitious rock-salt crystal, in which the atoms scattered as Hartree atoms at rest. Three-dimensional Fourier series are being increasingly used in crystal analysis, and it seems desirable to consider the analogous problem when the volume density is determined by means of such a series for points in a plane passing through the centre of the atom.

Let $\mathbf{b}_m$ be the vector from the origin to the reciprocal-lattice point m, and let $F(m)$ be the structure amplitude of the spectrum corresponding to this point. The electron density at a point in the structure at a vector distance $\mathbf{r}$ from the origin is given by

$$\rho(\mathbf{r})=\frac{1}{V}\sum_m F(m)\,e^{-2\pi i(\mathbf{r}\,.\,\mathbf{b}_m)}, \qquad (1)$$

where V is the volume of unit cell of the structure, and the summation is to be taken over all the reciprocal-lattice points m.

We now assume the lattice to be primitive, and to consist of atoms at rest, which scatter as points, so that the structure factor for each spectrum is the same, and equal to $F(0)$. Equation (1) in this case becomes

$$\rho(\mathbf{r})=\frac{1}{V}F(0)\sum_m e^{-2\pi i(\mathbf{r}\,.\,\mathbf{b}_m)}. \qquad (2)$$

Let us now suppose the unit cell to become larger and larger so that the reciprocal-lattice cell, the volume of which is $1/V$, becomes smaller and smaller. If the volume of the cell becomes large enough, we may suppose the reciprocal-lattice points to be continuously distributed with density V, and may replace the summations of (2) by an integration throughout the relevant volume of the reciprocal-lattice space. We then approach the case of the image of a single scattering point.

Let R, Fig. 1, be a reciprocal-lattice point fixed by the spherical polar co-ordinates (b, θ, ϕ) and let OP be a fixed vector $\mathbf{r}$, lying in the equatorial plane. Let dv be an element of volume in the neighbourhood of R. The reciprocal-lattice points in this element of volume, together with those in an equal element at R' at the opposite end of the diameter from R, contribute to the integral for $\rho(\mathbf{r})$ an amount

$$2F(0)\cos 2\pi(\mathbf{r}\,.\,\mathbf{b})\,dv,$$

and the value of $\rho(\mathbf{r})$ at the extremity of the vector $\mathbf{r}$ is obtained by integrating this expression throughout the relevant volume of the reciprocal-lattice space, treating $\mathbf{b}$ as a vector continuously variable in length and direction. Let χ be the angle between the vectors $\mathbf{r}$ and $\mathbf{b}$. Then the scalar product $\mathbf{b}\,.\,\mathbf{r}$ is equal to $br\cos\chi$, which, from the right-angled spherical triangle AQR, Fig. 1, is equal to $br\sin\theta\cos\phi$. As the element of volume dv, we take $b^2\sin\theta\,d\theta\,d\phi\,db$, and the expression for $\rho(r)$ then becomes

$$\rho(r)=2F(0)\int_0^{2\pi}\int_0^{\frac{1}{2}\pi}\int_0^{B} b^2\sin\theta \times\cos 2\pi(rb\sin\theta\,\cos\phi)\,db\,d\theta\,d\phi, \qquad (3)$$

in which it is assumed that the relevant reciprocal-lattice points are all those lying within a sphere of radius B. Equation (3), when integrated, gives the volume density in the Fourier representation of the structure at a point at a radial distance r from a scattering point. It is evident that the density distribution about the point is spherically symmetrical.

The integrations may be handled in the following manner:

If $J_0(x)$ is the Bessel function of zero order,

$$\int_0^{2\pi} \cos(x\cos\phi)\,d\phi = 2\pi J_0(x). \tag{4}$$

Integration of (3) with respect to ϕ therefore gives

$$\rho(r) = 4\pi F(0)\int_0^B \int_0^{\frac{1}{2}\pi} b^2 \sin\theta J_0(2\pi r b\sin\theta)\,d\theta\,db. \tag{5}$$

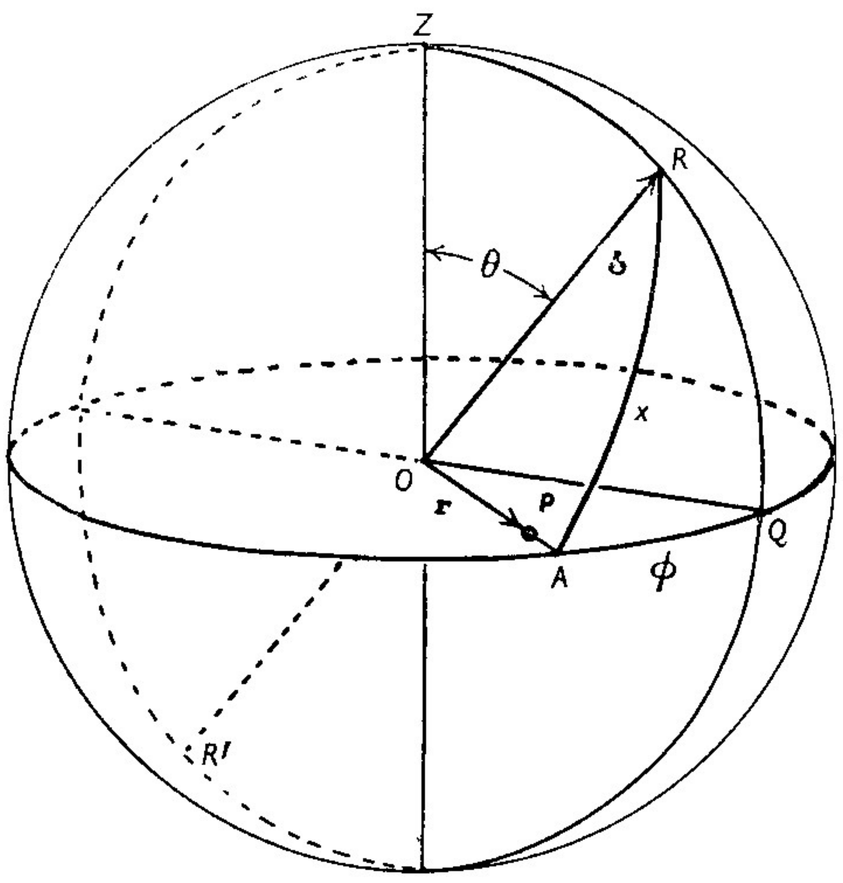

Fig. 1. Definition of co-ordinates in reciprocal space.

Using the expansion

$$J_0(x) = 1 - 2^{-2}x^2 + (2.4)^{-2}x^4 - (2.4.6)^{-2}x^6 + \ldots,$$

we may express the integrand of (5) as a series, which may be integrated term by term, first with respect to b and then with respect to θ. This leads quite directly to

$$\rho(r) = 4\pi B^3 F(0)\left[\frac{2}{3!} - \frac{4m^2}{5!} + \frac{6m^4}{7!} - \frac{8m^6}{9!} + \ldots\right] \tag{6}$$

$$= 4\pi B^3 F(0)\ (\sin m - m\cos m)/m^3, \tag{7}$$

where $m = 2\pi Br$. If we put

$$\Phi(m) = 3\,(\sin m - m\cos m)/m^3,$$

the expression for the density becomes

$$\rho(r) = \tfrac{4}{3}\pi B^3\, F(0)\Phi(m). \tag{8}$$

The first factor in (8) is the volume of the reciprocal-lattice space within which the points of the lattice used in the integration lie, and the density is of course proportional to this when all the spectra have equal amplitude. The distribution of density about the image points is given by the function $\Phi(m)$. The Fourier series gives a three-dimensional image of the points in the crystal lattice. Each image point is surrounded by a series of concentric 'diffraction spheres', the radial distribution in which is given by (8) if the approximation is valid by which the summation of the Fourier series is replaced by an integration.

The function $\Phi(m)$ occurs in the theory of diffraction by a uniform spherical distribution of scattering matter. The scattering factor f of a sphere of scattering matter of uniform density unity and of radius R is given by

$$f = \tfrac{4}{3}\pi R^3\Phi(\mu R), \tag{9}$$

where $\mu = (4\pi\sin\theta)/\lambda$. This may easily be verified by integrating the well-known expression for the scattering factor of a spherical shell, $4\pi r^2\,(\sin\mu r)/\mu r$, with respect to r (see also Debye, 1927).

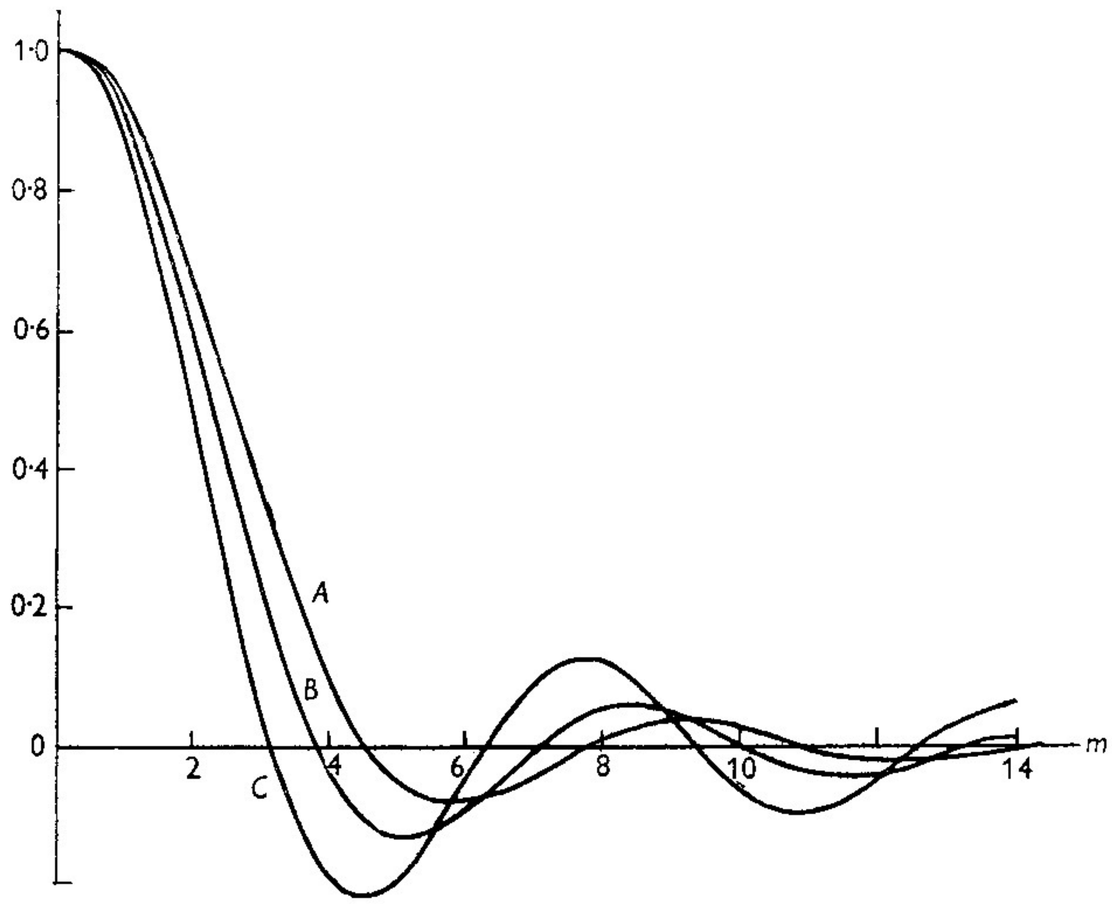

Fig. 2. Curves of (A), $3(\sin m - m\cos m)/m^3$; (B), $2J_1(m)/m$; (C), $(\sin m)/m$.

The variation of $\Phi(m)$ is shown by curve A of Fig. 2. The roots of the function occur for $m = 1{\cdot}430\pi$, $2{\cdot}459\pi$, $3{\cdot}471\pi$, $4{\cdot}477\pi$, $5{\cdot}482\pi$,.... Its value is unity for $m = 0$, and the value at the first minimum, which occurs at $m = 5{\cdot}763$, is $-0{\cdot}0850$. Table 1 gives some values of the function.

If d_0 is the spacing corresponding to the highest order spectra used in making the projection, and θ the corresponding glancing angle,

$$B = 2(\sin\theta)/\lambda = 1/d_0.$$

Table 1. *Values of* $\Phi(m) = 3(\sin m - m\cos m)/m^3$

m	$\phi(m)$	m	$\phi(m)$
0	1	7	−0·040
1	0·904	8	0·013
2	0·653	9	0·035
3	0·346	10	0·024
4	0·087	11	−0·002
5	−0·052	12	−0·019
6	−0·084	13	−0·016

The corresponding radius of the diffraction sphere of positive density is given by

$$2\pi r/d_0 = 2\pi rB = 1{\cdot}430\pi, \quad \text{or} \quad r = 0{\cdot}715d_0.$$

We may compare these results with those obtained for the two-dimensional projection. In this case the appropriate Fourier series for point atoms is

$$\sigma(\mathbf{r}) = (1/A)\, F(0) \sum_m \cos 2\pi(\mathbf{r}.\mathbf{b}_m), \qquad (10)$$

where the summation now extends only over the reciprocal-lattice points lying in a plane, the area of the mesh of which is A. The limiting integral form of the series for a very large mesh is now

$$\sigma(r) = 2F(0) \int_0^{\pi} \int_0^{B} b \cos(2\pi r b \cos\phi)\, db\, d\phi$$

$$= 2F(0) \int_0^{B} b\, J_0(2\pi r b)\, db, \qquad (11)$$

by (4). Using the relation

$$\int_0^t x J_0(x) = t J_1(t),$$

we can at once write (11) in the form

$$\sigma(r) = B^2 F(0)\, 2J_1(m)/m, \qquad (12)$$

where again $m = 2\pi B r$, the result obtained by Bragg & West. The variation of $2J_1(m)/m$ with m is shown in curve B, Fig. 2. It is the well-known Fraunhofer diffraction function for a circular aperture. The radius of the positive diffraction disk is in this case equal to $0{\cdot}61 d_0$, and is slightly less than for the three-dimensional case. On the other hand, the negative trough surrounding the first maximum is considerably more marked, $-0{\cdot}132$ instead of $-0{\cdot}085$.

For completeness, we may include the one-dimensional series, the use of which was first suggested by Bragg (1915). This series is

$$S(r) = (1/a) \sum_n F(n)\, e^{-2\pi i(r b_n)},$$

where b_n is the distance of the nth reciprocal-lattice point in a row from the origin, corresponding to the nth order spectrum from a set of crystal planes of spacing a. $S(r)\, dr$ gives the total diffracting matter in the unit cell between two planes parallel to the crystal planes considered, and at distances r and $r+dr$ from the origin. Treating this series in the same way as the others, we obtain for the case of point atoms widely spaced

$$S(r) = 2BF(0)\, (\sin m)/m. \qquad (13)$$

The function $(\sin m)/m$ is plotted in Fig. 2, curve C, for comparison with other curves. The false detail in one-, two- and three-dimensional Fourier representations of point atoms, when reciprocal-lattice points up to a distance B from the origin are considered, is thus given by the Fraunhofer diffraction function for a slit of width $2B$, a circular aperture of radius B, and a sphere of radius B, respectively.

Discussion of results

In the above treatment, only point atoms at rest have been considered, and it would not therefore at first sight appear to apply at all closely to actual atoms. In the heavier atoms, however, a considerable fraction of the average electron population lies at distances from the atomic centre smaller than the wave-length of the radiations commonly used in crystal analysis. To these electrons, the treatment given should apply fairly well, and, indeed, the work of Bragg & West quoted above shows that even for comparatively light atoms such as chlorine there is fair correspondence between the diffraction rings observed in the projections of the artificial crystal, with the series terminated at moderate values of B, and the calculated diffraction pattern. In any actual crystal the outer electrons of the atom, and the thermal motion, by reducing the intensities of the high-order spectra, tend to smear out the rings; but well-marked rings do occur in two-dimensional projections from crystals containing heavy atoms, and the example of iron pyrites has been discussed by Parker & Whitehouse (1932).

The treatment given above shows that false detail due to diffraction is also to be expected in three-dimensional representations. The regions of negative density are, however, considerably shallower, relative to the height of the main maximum, than in the two-dimensional case, and the effects will be less marked, and might become inappreciable owing to the smearing-out tendencies that must always be present. In a recent example of a three-dimensional analysis of a crystal containing a heavy atom, that of *p*-chloriodoxybenzene by Archer (1948) in this laboratory, no appreciable diffraction rings were observed round the peaks due to the iodine atoms, but the theory given above suggests that it would be unsafe to conclude from this single example that the effect can be neglected in three-dimensional analyses.

In conclusion, I should like to thank Dr S. Skewes of the University of Cape Town, who pointed out to me the form of the sum of the series in equation (6).

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