

ANNALES ACADEMIAE SCIENTIARUM FENNICAE

Series A

VI. PHYSICA

241

**SPHERICAL HARMONIC EXPANSIONS IN X-RAY
DIFFRACTION ANALYSIS**

BY

K. KURKI-SUONIO and V. MEISALO

Department of Physics
University of Helsinki
Helsinki, Finland

HELSINKI 1967
SUOMALAINEN TIEDEAKATEMIA

Abstract

It is desirable to represent the electron densities and scattering factors of atoms in terms of harmonics adapted to the symmetry. As a consequence of the invariance of the harmonics under the Fourier transformation, every term in such an expansion of the atomic factor corresponds to an electron density with the same angular dependence. Theoretical considerations suggest that a few terms will be sufficient for a good approximation, and there is a certain connection between this series and the angular momenta of the electronic wave functions. It is shown how the radial coefficients of such expansions can be derived for the atoms of a crystal from experimental structure amplitudes. Explicit formulas are given up to the 10th order for calculation of the cubic-harmonic expansions for an atom in a tetrahedral or cubic crystalline field. As an example, the nonsphericity of the ions of KBr is studied using the data of MEISALO and INKINEN (*Acta Cryst.* 22, 58 (1967)); both ions are seen to have essentially the symmetry of the cubic harmonic K_4 .

Mathematical basis

The spherical harmonics

$$(1) \quad Y_l^m(\theta, \varphi) = P_l^{|m|}(\cos \theta) e^{im\varphi} ; l = 0, 1, 2, \dots ; m = 0, \pm 1, \dots, \pm l,$$

with the associated Legendre functions

$$P_l^m(z) = \frac{1}{2^l l!} (1-z^2)^{m/2} \frac{d^{l+m}}{dz^{l+m}} (z^2-1)^l$$

give certainly the most convenient description of nearly spherical structures, such as the electron distributions or scattering factors of single atoms. The spherical harmonics form a complete orthogonal set of functions in the full solid angle. Therefore any density function $\rho(\mathbf{r})$ can be expressed as a series

$$(2) \quad \rho(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm}(r) Y_l^m(\theta, \varphi)$$

and is uniquely determined by the set of radial functions $a_{lm}(r)$. Even for a bonded atom $\rho(\mathbf{r})$ is nearly spherical (varies slowly with the angular variables) and the first few functions a_{lm} will be sufficient for a good description.

In a crystal, local symmetry determines the symmetry of the atom. In each order l there is a definite number of linearly independent harmonics

$$(3) \quad K_l^\alpha(\theta, \varphi) = \sum_{m=-l}^l c_{lm\alpha} Y_l^m(\theta, \varphi)$$

with this particular symmetry. They can be chosen to be orthogonal. The expansion (2) for the atom concerned must possess this same symmetry in each order, and it can therefore be written in the form

$$(4) \quad \varrho(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{\alpha} b_{l\alpha}(r) K_l^\alpha(\theta, \varphi)$$

A high symmetry will strongly reduce the number of terms. The full cubic symmetry is certainly the most favourable case. The functions (3) are then the α -type cubic harmonics of VON DER LAGE and BETHE [36] and the expansion (4) contains up to the 10th order only five terms, see eqs. (13) below.

The X-ray scattering factor of $\varrho(\mathbf{r})$ is simply the Fourier transform

$$(5) \quad f(\mathbf{b}) = \int \varrho(\mathbf{r}) e^{2\pi i \mathbf{b} \cdot \mathbf{r}} d^3r.$$

The spherical harmonics are invariant in this transformation. To be more specific, let $Y_l(\theta, \varphi)$ be any harmonic of order l , *i.e.* any linear combination of the functions (1) with a definite l , and $g(r)$ an arbitrary radial function. Then we have

$$(6) \quad \int g(r) Y_l(\theta, \varphi) e^{2\pi i \mathbf{b} \cdot \mathbf{r}} d^3r = 4\pi i^l G(b) Y_l(u, v),$$

where b, u, v are the spherical coordinates of the vector \mathbf{b} in the reciprocal space, and the radial transform $G(b)$ is

$$(7) \quad G(b) = \int_0^{\infty} g(r) j_l(2\pi br) r^2 dr,$$

where j_l is the spherical Bessel function of order l . Therefore the terms of the expansion (4) behave in the transformation as independent entities, each keeping its angular dependence. Thus, the corresponding scattering factor is

$$(8) \quad f(b) = 4\pi \sum_{l=0}^{\infty} i^l \sum_{\alpha} B_{l\alpha}(b) K_l^\alpha(u, v) \quad \text{with} \quad B_{l\alpha}(b) = \int b_{l\alpha}(r) j_l(2\pi br) r^2 dr,$$

where each term is the transform or scattering factor of the corresponding term in (4).

If the harmonics (3) are known, there will be no difficulties, in principle, in working out the expansions (4) or (8). One can apply the conventional methods for orthogonal expansions. Also, there are several methods for

finding the functions K_l . ALTMANN and CRACKNELL [2] have given general group-theoretical methods for obtaining them in any particular symmetry. MUELLER and PRIESTLEY [33] have developed a simpler procedure for cubic cases. Their general formulas are given in spherical coordinates and they note that the formulas obviously would be very complicated in cartesian coordinates. In applications, where only the first few orders are needed, one has no use of the general formulas and the cartesian representation will be more practical — at least more perspicuous in many cases. Then the question is how to find the harmonic polynomials

$$K_l^\alpha(x,y,z) = r^l K_l^\alpha(\theta,\varphi) .$$

For cubic symmetries these are given in the lowest few orders by Von der LAGE and BETHE [36] and with some more general considerations by BETTS, BHATIA and WYMAN [5]. Actually one can find them for any order through a simple procedure. In most cases one can directly write down all homogeneous polynomials of the correct symmetry, and the corresponding harmonic polynomials of this symmetry can then be constructed from them by the method of Gauss, see *e.g.* HEINE [18].

This representation, or some closely related ones, have been used in several cases. KONOBEVSKIJ and MAMEDOV [21, 22, 23] as well as WEISS *et al.* [12, 39, 40, 41] use symmetric polynomials for the description of aspherical atoms with the motivation that they are simple functions with the correct symmetry. Another equivalent representation in terms of angular variables is used by FREEMAN, WEISS and WATSON in their studies of d - and f -electrons [14, 15, 16, 37, 42]. Although the cubic harmonics, either in angular variables or in terms of harmonic polynomials, do occur in these papers and in some others [*e.g.* 6, 35], there seems to be no clear tendency to their systematic use. At least no advantage is taken of their simple transformation properties, which certainly are a most prominent advantage and suggest very strongly their use whenever the electron densities or scattering factors of nonspherical single atoms are considered.

Physical preliminaries

The use of the harmonic expansions (4) and (8) seems to be reasonable also from a physical point of view. The quantal state of an atom is commonly expressed in terms of one-electron wave functions of the form

$$(9) \quad \Psi = \psi(r,\theta,\varphi) \chi = R(r) Y_m^l(\theta,\varphi) \chi ,$$

where χ is the spin function. In principle the state is an infinite series of Slater determinants of these functions, but for most purposes one or a

few terms give a sufficient approximation. Since BETHE's classical work [4], the effect of a crystalline field on the one-electron wave functions has been qualitatively well known, and this formalism is still used whenever the problems are handled in terms of single atoms. In the one-electron representation the electron density is always a sum of the form

$$(10) \quad \varrho(\mathbf{r}) = \sum a_{ij} \psi_i^* \psi_j = \sum \varrho_{ij}(\mathbf{r}) .$$

The fact that $\hat{\varrho}(\mathbf{r})$ is a one-particle operator assures that only products of two orbitals ψ_j occur. The sum (10) can always be changed into the form of the expansion (2) or (4), since, as is well known, any product of two spherical harmonics can be expressed as a finite sum

$$(11) \quad Y_l^{m*} Y_{l'}^{m'} = \sum_{\lambda=|m'-m|}^{l+l'} C_{\lambda}(l m l' m') Y_{\lambda}^{m'-m}$$

where the coefficients are integrals of products of three Legendre functions

$$(12) \quad C_{\lambda}(l m l' m') = \frac{2\lambda+1}{2} \frac{(\lambda-|m'-m|)!}{(\lambda+|m'-m|)!} \int_{-1}^1 P_l^{m'}(x) P_{l'}^{m'}(x) P_{\lambda}^{|m'-m|}(x) dx ,$$

cf. [4, 14, 42]. These coefficients are well known from the theory of angular momentum.¹⁾

The highest order that may occur in the expansion (4) is twice the highest value of l in the one electron wave functions (9) used. The representation of the state by a finite sum of Slater determinants leads therefore to a finite number of terms in the expansions (4) or (8) of the corresponding electron density or atomic factor. The situation is still more simplified by symmetry considerations. For instance, we know that a closed shell has a spherical electron density, so it contributes only to the first term of the expansions. Therefore the number of terms depends only on the valence electrons, provided that the closed shells are not deformed by the crystalline field.

For instance, if the state of the valence electrons is a mixture of s - and p -states, then only terms up to the second order may occur in the expansions (4) and (8). In the most general case this may involve, in addition to the spherical term, three first order terms with the angular factors x, y, z and five second-order terms, with angular dependence $\frac{1}{2}(3z^2-1), xz, yz, xy, x^2-y^2$ (x, y, z understood to be the direction cosines). McWEENY [29, 30] and DAWSON [11] have considered single configurations where the valence electrons are in different p -states or sp -hybrid states. For instance, the

¹⁾ Note, however, that the phases of our Y_l^m are not the CONDON and SHORTLEY [9] phases commonly used in angular momentum theory.

contribution to $\varrho(\mathbf{r})$ of a hybrid orbital $\varphi_v = \varphi(s) + \lambda\varphi(p_z)$ will be of the form

$$\begin{aligned}\varrho_v(\mathbf{r}) &= \varrho_{ss}(r) + \lambda\varrho_{sp}(r)Y_1^0 + \lambda^2\varrho_{pp}(r)(Y_1^0)^2 \\ &= \varrho_{ss}(r) + \frac{1}{3}\lambda^2\varrho_{pp}(r) + \lambda\varrho_{sp}(r)Y_1^0 + \frac{2}{3}\lambda^2\varrho_{pp}(r)Y_2^0.\end{aligned}$$

In case of axial symmetry we are in this way led to the formulas

$$\varrho(\mathbf{r}) = \varrho_0(r) + \varrho_1(r)Y_1^0 + \varrho_2(r)Y_2^0, \quad f(\mathbf{b}) = f_0(b) + f_1(b)Y_1^0 + f_2(b)Y_2^0$$

for the electron density and the scattering factor of the atom. Since $Y_1^0 = z = \cos\theta$ and $Y_2^0 = \frac{1}{2}(3z^2 - 1)$ we have a simple relation to the expression $f = f_{||}\cos^2\theta + f_{\perp}\sin^2\theta + f_a\cos\theta$ used by McWEENY and DAWSON. We have $f_0 = \frac{1}{3}(f_{||} + 2f_{\perp})$, $f_1 = f_a$ and $f_2 = \frac{2}{3}(f_{||} - f_{\perp})$. For some other symmetries DAWSON derives the formula $f = f_1^{|}|x^2 + f_2^{|}|y^2 + f_3^{|}|z^2 + f_az$, which can be written as the harmonic expansion

$$f = f_0 + f_1z + f_2^{\alpha}\frac{1}{2}(3z^2 - 1) + f_2^{\beta}(x^2 - y^2)$$

with

$$f_0 = \frac{1}{3}(f_1^{|}| + f_2^{|}| + f_3^{|}|), \quad f_1 = f_a, \quad f_2^{\alpha} = \frac{1}{3}(2f_3^{|}| - f_1^{|}| - f_2^{|}|), \quad f_2^{\beta} = \frac{1}{2}(f_1^{|}| - f_2^{|}|).$$

WEISS and FREEMAN [42] give an extensive discussion of the d - and f -electrons in cubic and tetrahedral fields. Their expressions, given in terms of symmetric polynomials, can also be very easily related to the harmonic expansion. For the first few α - and β -type cubic harmonics of Von der LAGE and BETHE [36] we shall use the expressions

$$\begin{aligned}(13) \quad K_0 &= 1 \\ K_3 &= xyz \\ K_4 &= x^4 + y^4 + z^4 - \frac{3}{5} \\ K_6 &= x^6 + y^6 + z^6 - \frac{15}{11}K_4 - \frac{3}{7} \\ K_7 &= xyz(x^4 + y^4 + z^4 - \frac{5}{11}) \\ K_8 &= x^8 + y^8 + z^8 - \frac{28}{15}K_6 - \frac{210}{143}K_4 - \frac{1}{3} \\ K_9 &= xyz(x^6 + y^6 + z^6) - \frac{21}{17}K_7 - \frac{35}{143}K_3 \\ K_{10} &= x^{10} + y^{10} + z^{10} - \frac{45}{19}K_8 - \frac{42}{17}K_6 - \frac{210}{143}K_4 - \frac{3}{11},\end{aligned}$$

where again x, y, z are the direction cosines. If there are f -states but no states with higher angular momenta involved, we need these functions only up to the 6th order, and we have the expressions

$$(14) \quad \begin{aligned}\varrho &= \varrho_0(r) + \varrho_3(r)K_3 + \varrho_4(r)K_4 + \varrho_6(r)K_6 \\ f &= f_0(b) + f_3(b)K_3 + f_4(b)K_4 + f_6(b)K_6\end{aligned}$$

with

$$f_n(b) = 4\pi i^n \int_0^\infty \varrho_n(r) j_n(2\pi br) r^2 dr$$

according to (7), for the tetrahedral electron density and the atomic factor with f -electrons involved. In a cubic case the odd terms vanish and only three terms are left. If only d -electrons are present, the 6th order must be dropped. We also see immediately the well-known fact that the p -electrons give only a spherical contribution in these symmetries.

If theoretical wave functions of different possible bond configurations exist and if the radial functions ϱ_n or f_n can be studied experimentally, it might be possible to get some estimates of the populations of different valence electron states. In fact, there has been considerable interest in obtaining such results about the d -electrons from X-ray and neutron diffraction [*e.g.* 1, 13, 34, 37, 41]. In the following, a calculation method is proposed for extracting the radial functions f_n and ϱ_n of an atom from experimental structure amplitudes of a crystal.

Evaluation of the radial functions from structure amplitudes

To use the representation discussed above, one should be able to derive from experiments the radial coefficients $\varrho_n(r)$ or $f_n(b)$ of different harmonics for the crystal atoms. The X-ray structure amplitudes $F_{\mathbf{b}_j}$ of a crystal, contain all the information about the average electron density

$$(15) \quad \varrho(\mathbf{r}) = \frac{1}{V} \sum F_{\mathbf{b}_j} e^{-2\pi i \mathbf{b}_j \cdot \mathbf{r}} .$$

Since the nonsphericity of atoms concerns only the outer electrons, practically all information about it is contained in the lower-order reflections which can be measured. The only question is whether the experimental accuracy is sufficient to reveal it. There is, however, an increasing number of cases where the deformation is shown to be detectable. The most obvious demonstrations are the occurrence of »forbidden reflections» and the differences of coincident reflections [*e.g.* 8, 13, 20, 21, 23, 25, 28, 41]. The measurements of these exceptional features give valuable information about the nature of the nonsphericity. This information is, however, restricted to certain points in the reciprocal space and does not exhaust the information contained in the experimental structure amplitudes.

The Fourier series (15) contains all experimental information. In a careful analysis one may be able to see nonsphericities of the atoms in the

density maps [e.g. 10, 34, 38]. The termination effects, however, make it very difficult to draw definite conclusions in this way. An alternative approach is to calculate the atomic factors from the experiments, as is done in the works of the present authors and their collaborators [e.g. 19, 24, 26, 31, 32]. In this method the termination effects are much simpler in character, and more definitive statements about the significance of the asphericity can be obtained. However, these calculations have no connection with the harmonic analysis.

It is easy to transform the Fourier series into a harmonic expansion. We merely apply the well-known spherical-wave expansion

$$(16) \quad e^{-2\pi i \mathbf{b}_j \cdot \mathbf{r}} = \sum_{n=0}^{\infty} (2n+1)(-i)^n \left[\sum_{m=-n}^n \frac{(n-|m|)!}{(n+|m|)!} Y_n^m(u_j, v_j) Y_n^{-m}(\theta, \varphi) \right] j_n(2\pi b_j r),$$

where the spherical coordinates of the vector \mathbf{b}_j are denoted by b_j, u_j, v_j corresponding to r, θ, φ for the vector \mathbf{r} . If this substitution is made in (15) we get an expansion of the type (2)

$$(17) \quad \varrho(\mathbf{r}) = \sum \varrho_{nm}(r) Y_n^m(\theta, \varphi),$$

where

$$(18) \quad \varrho_{nm}(r) = \frac{1}{V} (2n+1)(-i)^n \frac{(n-|m|)!}{(n+|m|)!} \sum_j F_{\mathbf{b}_j} Y_n^{-m}(u_j, v_j) j_n(2\pi b_j r)$$

This leads to the »spherical Fourier method» of АТОЖИ [3]. Symmetry considerations will essentially simplify these expressions, leading to expansions of the type (4), as АТОЖИ has shown explicitly in one special case.

If the origin is at the center of an atom, this expansion will converge rapidly in the region of that atom, just because the atom is nearly spherical. The higher terms will be needed only if we want to describe the neighbouring atoms, too.

In practice, each coefficient (18) is a finite sum, since the series is terminated at the cutoff value of $b = 2 \sin \theta / \lambda$. Here again we meet the usual difficulties arising from the termination effects. The use of difference series will, of course, improve the situation, but the difficulties are the same in principle. The uncertainty of the residual term is spread all over the \mathbf{r} -space and makes it difficult to see which features are significant and which are not. Therefore we prefer to keep the analysis in the reciprocal space and want to make the conclusions from the atomic factors rather than from the density maps. This procedure has the advantage that the termination effects have very little influence on the atomic factors except near the cutoff. They express the information in the reciprocal space, where the residual term is

locally separated from the experimental information. The significance of different features can be seen much more easy. Therefore we want to take a step forward from the series (17) and calculate from it the atomic factor as the scattering factor of a sphere. The radius R of the sphere must, of course, be chosen so that the atom is separated from its surroundings as completely as possible.

In this way we get for the atomic factor the expansion

$$(19) \quad f_T(\mathbf{b}) = \int_{\mathbf{r}} \varrho(\mathbf{r}) e^{2\pi i \mathbf{b} \cdot \mathbf{r}} d^3r = \sum f_{nm}(b) Y_n^m(u, v)$$

where according to (7)

$$f_{nm}(b) = 4\pi i^n \int_0^R \varrho_{nm}(r) j_n(2\pi br) r^2 dr .$$

Further from (18), we get

$$(20) \quad f_{nm}(b) = \frac{4\pi}{V} (2n+1) \frac{(n-|m|)!}{(n+|m|)!} \sum_j F_{\mathbf{b}_j} Y_n^{-m}(u_j, v_j) I_n(2\pi b, 2\pi b_j; R)$$

with $I_n(x, y; R) = \int_0^R j_n(xr) j_n(yr) r^2 dr$. This integration can be performed explicitly (*cf.* LUKE [27]) and it gives

$$(21) \quad I_n(x, y; R) = \begin{cases} \frac{R^2}{x^2 - y^2} [x j_{n+1}(xR) j_n(yR) - y j_n(xR) j_{n+1}(yR)] & \text{for } x \neq y \\ \frac{R^3}{2} [j_n^2(xR) - j_{n+1}(xR) j_{n-1}(xR)] & \text{for } x = y \end{cases}$$

We see by comparison of (20) and (18) that all symmetry considerations concern the expansions of $\varrho(\mathbf{r})$ and $f_T(\mathbf{b})$ in a completely similar manner. The task involved in their calculation is therefore essentially the same. The series for f_T has now the advantage of keeping the analysis in reciprocal space, and it can be expected that uncertainties due to termination are mainly concentrated on the cutoff limit. Therefore it ought to be possible to see in much closer detail the significance of different features in the results. For instance, one will be able to see the significance of the radial coefficients in different orders, whether there is any experimental evidence for their existence or not. This again may be valuable for discussion of the occurrence of different angular momenta in the valence electron wave functions.

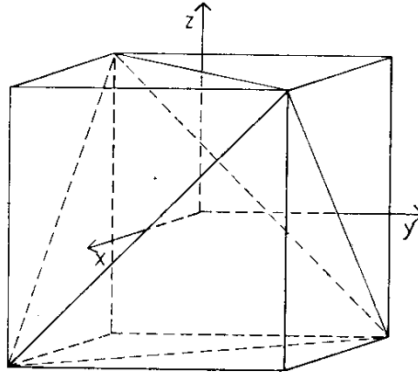


Fig. 1. The choice of the coordinate axes in the case of tetrahedral symmetry.

Tetrahedral and cubic symmetries with a special application to KBr

Let the atom considered have tetrahedral (or cubic) symmetry. This means that the electron density of the entire crystal has tetrahedral symmetry with respect to the position of this atom. The cubic symmetry is a special case of the tetrahedral one, realized when the antisymmetric ($\rho(-\mathbf{r}) = -\rho(\mathbf{r})$) component of the density function vanishes.

In this symmetry there is just one natural choice of the coordinate axes, see Fig. 1. If the structure amplitudes F_{hkl} are labelled with respect to this coordinate system, we get the simple rules:

1. F_{hkl} is independent of the order of indices.
2. $F_{\bar{h}\bar{k}\bar{l}} = F_{hkl}^*$.

In this way we are led to the well-known multiplicities p_{hkl} of the reflections from the crystal, with a maximum of 48 when all indices hkl are different and nonzero.

We can perform in (18) or (20) the summation over identical reflections; we get the result

$$\sum_{\text{identical reflections}} F_{\mathbf{b}_j} Y_n^m(u_j, v_j) = \begin{cases} p_{hkl} \text{ } \overset{\text{Re}}{\underset{i\text{Im}}{\int}} \int Y_n^m(hkl) \{F_{\mathbf{b}_j}\} & \text{for } n = 2\nu, m = 4\mu \\ 0 & \text{for } n = 2\nu + 1, m = 4\mu + 2 \\ & \text{in other cases,} \end{cases}$$

where $\overset{\text{Re}}{\underset{i\text{Im}}{\int}} \int Y_n^m$ is the symmetrized spherical harmonic

$$(22) \quad \overset{\text{Re}}{\underset{i\text{Im}}{\int}} \int Y_n^m(hkl) = \begin{cases} 1 & \text{for } n \text{ even} \\ \frac{1}{3} [Y_n^m(hkl) + Y_n^m(klh) + Y_n^m(lhk)] & \text{for } n \text{ odd} \end{cases}$$

expressed in terms of the direction cosines hkl of the vector \mathbf{b}_j . Because of the symmetry of ρ and f we can also replace Y_n^m in the series (17) and (19) by the symmetrized $\overset{\text{Re}}{\underset{i\text{Im}}{\int}} \int Y_n^m$, and we get their expansions into the form

$$\varrho(\mathbf{r}) = \Sigma \varrho_{nm}(r) \mathcal{Y}_n^m(x y z), \quad f_{\mathbf{T}}(\mathbf{b}) = \Sigma f_{nm}(b) \mathcal{Y}_n^m(h k l)$$

with

$$\varrho_{nm} = \frac{1}{V} (2n+1) (-1)^{\nu} \frac{(n-|m|)!}{(n+|m|)!} \sum_{\mathbf{b}_j} p_{hkl} \operatorname{Re}_{\operatorname{Im}} \{F_{\mathbf{b}_j}\} \mathcal{Y}_n^{-m}(h_j k_j l_j) j_n(2\pi b_j r)$$

and

$$f_{nm} = \frac{4\pi}{V} (2n+1) \frac{(n-|m|)!}{(n+|m|)!} \sum_{\mathbf{b}_j} p_{hkl} \operatorname{Re}_{\operatorname{Im}} \{F_{\mathbf{b}_j}\} \mathcal{Y}_n^{-m}(h_j k_j l_j) I_n(2\pi b, 2\pi b_j; R)$$

where Re must be chosen for $n = 2\nu$, $m = 4\mu$ and Im for $n = 2\nu + 1$, $m = 4\mu + 2$.

In the lowest few orders we have ¹⁾

$$\mathcal{Y}_0^0 = 1$$

$$\mathcal{Y}_2^0 = 0$$

$$\mathcal{Y}_3^{\pm 2} = \pm i \frac{6 \cdot 5!!}{3} K_3$$

$$\mathcal{Y}_4^0 = \frac{7!!}{3 \cdot 4!} K_4, \quad \mathcal{Y}_4^{\pm 4} = -\frac{5 \cdot 7!!}{3} K_4$$

$$\mathcal{Y}_5^{\pm 2} = 0$$

$$\mathcal{Y}_6^0 = \frac{11!!}{3 \cdot 6!} K_6, \quad \mathcal{Y}_6^{\pm 4} = -\frac{7 \cdot 11!!}{3 \cdot 2!} K_6$$

$$\mathcal{Y}_7^{\pm 2} = \pm i \frac{2 \cdot 13!!}{3 \cdot 5!} K_7, \quad \mathcal{Y}_7^{\pm 6} = \pm i \frac{22 \cdot 13!!}{3} K_7$$

$$\mathcal{Y}_8^0 = \frac{15!!}{3 \cdot 8!} K_8, \quad \mathcal{Y}_8^{\pm 4} = \frac{15!!}{3 \cdot 4!} K_8, \quad \mathcal{Y}_8^{\pm 8} = \frac{65 \cdot 15!!}{3} K_8$$

$$\mathcal{Y}_9^{\pm 2} = \pm i \frac{2 \cdot 17!!}{3 \cdot 7!} K_9, \quad \mathcal{Y}_9^{\pm 6} = \mp i \frac{26 \cdot 17!!}{3 \cdot 3!} K_9$$

$$\mathcal{Y}_{10}^0 = \frac{19!!}{3 \cdot 10!} K_{10}, \quad \mathcal{Y}_{10}^{\pm 4} = -\frac{11 \cdot 19!!}{15 \cdot 6!} K_{10}, \quad \mathcal{Y}_{10}^{\pm 8} = -\frac{187 \cdot 19!!}{15 \cdot 2!} K_{10}$$

where the notation of (13) is used.

In these orders the summation over m can be done immediately and we obtain

$$(23) \quad \varrho(\mathbf{r}) = \Sigma \varrho_n(r) K_n(xyz), \quad f(\mathbf{b}) = \Sigma f_n(b) K_n(hkl)$$

¹⁾ $n!! = n(n-2) \dots (2 \text{ or } 1)$.

with

$$(24) \quad \varrho_n(r) = \frac{(-1)^v}{V} C_n \sum_{\mathbf{b}_j} p_{\mathbf{b}_j} \operatorname{Re}\{F_{\mathbf{b}_j}\} K_n(h_j k_j l_j) j_n(2\pi b_j r),$$

$$(25) \quad f_n(b) = \frac{4\pi}{V} C_n \sum_{\mathbf{b}_j} p_{\mathbf{b}_j} \operatorname{Re}\{F_{\mathbf{b}_j}\} K_n(h_j k_j l_j) I_n(2\pi b, 2\pi b_j; R)$$

with

$$\begin{aligned} C_0 &= 1, & C_3 &= 7 \cdot \frac{108}{5} \left(\frac{5!!}{3 \cdot 3!} \right)^2 = 105, \\ C_4 &= 9 \cdot \frac{12}{7} \left(\frac{7!!}{3 \cdot 4!} \right)^2 = 32.8125, & C_6 &= 13 \cdot 8 \left(\frac{11!!}{3 \cdot 6!} \right)^2 = 2408.656, \\ C_7 &= 15 \cdot \frac{112}{13} \left(\frac{13!!}{3 \cdot 7!} \right)^2 = 10322.813, & C_8 &= 17 \cdot \frac{64}{33} \left(\frac{15!!}{3 \cdot 8!} \right)^2 = 9258.691, \\ C_9 &= 19 \cdot \frac{1536}{55} \left(\frac{17!!}{3 \cdot 9!} \right)^2 = 531654.635, & C_{10} &= 21 \cdot \frac{384}{65} \left(\frac{19!!}{3 \cdot 10!} \right)^2 = 448736.96. \end{aligned}$$

To give an example we applied this method to KBr using the experimental structure amplitudes measured by MEISALO and INKINEN [31]. The radial coefficients (24) and (25) of the difference series corresponding to (22) are shown in Figs. 2 and 3 for both K^+ and Br^- . The ionic radii used in the calculation of $f_n(b)$ were 1.57 Å for K^+ and 1.73 Å for Br^- , as given in ref. [31]. These curves are normalized in such a way that they present directly the contribution of each component to $\varrho(\mathbf{r})$ or $f(\mathbf{b})$ in the direction where it is largest, *i.e.* in [100] direction for the 4th and 8th order and in [111] direction for the 6th and 10th order.

To judge the significance of the different harmonic components we have to take account of several considerations. The use of difference series is equivalent to the use of a theoretical residual term. The possible termination errors of Figs. 2 and 3 will be therefore due to the difference between the true residual term and the theoretical one. As concluded qualitatively, the termination error will have essential influence on the f_n curves only near the cutoff b of the experimental values, contrary to the situation in \mathbf{r} -space. Thus, their significance is mainly determined by the experimental inaccuracies. The error bars in Fig. 3 show the customary standard deviations calculated from the errors δF_n given in ref. [31]. The uncertainty of the scale factor has not been included in the limits. Its effect is mainly confined to the spherical component f_0 . The errors due to division of the intensities of coincident and overlapping reflections in the ratio of the theoretical intensities may also be significant, especially at those values of b where

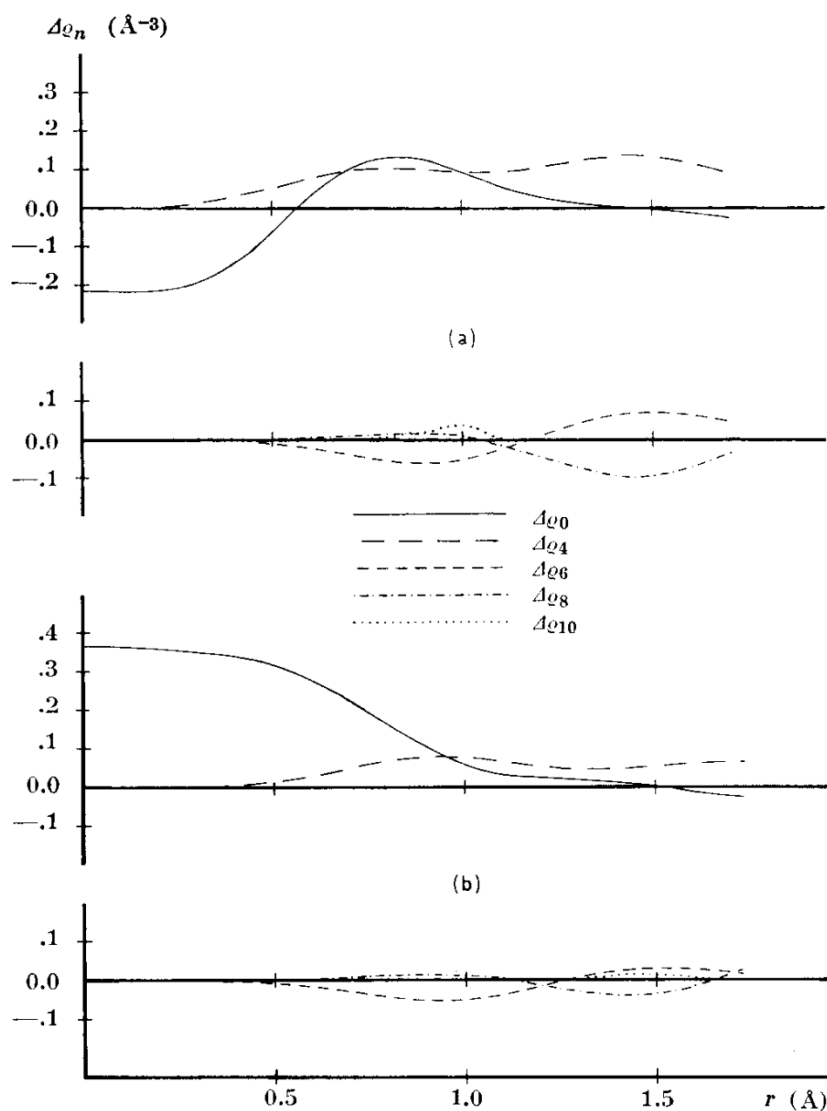


Fig. 2. The radial coefficients of the cubic harmonic expansion of Δq , (a) for K^+ and (b) for Br^- in KBr.

such clusters occur. This may cause the apparently significant values of the higher-order components in the case of K^+ . A closer examination of the properties of the series (21) will show in more detail their behaviour in different circumstances, *e.g.* when different kinds of systematic errors are present, and the nature of termination errors.

As is natural, the term f_4 is the only clearly significant nonspherical component in our example. It is therefore solely responsible for the properties of the Δf_T curves, which led to the conclusions of ref. [31]. It can also be easily checked that f_0 and f_4 do give Δf curves nearly identical to those found by direct calculation (Figs. 3 and 4 of ref. [31]); if the contributions of the higher components f_6, f_8 and f_{10} are added, those curves are reproduced very accurately. This, of course, is only a check on the correctness of the present calculation.

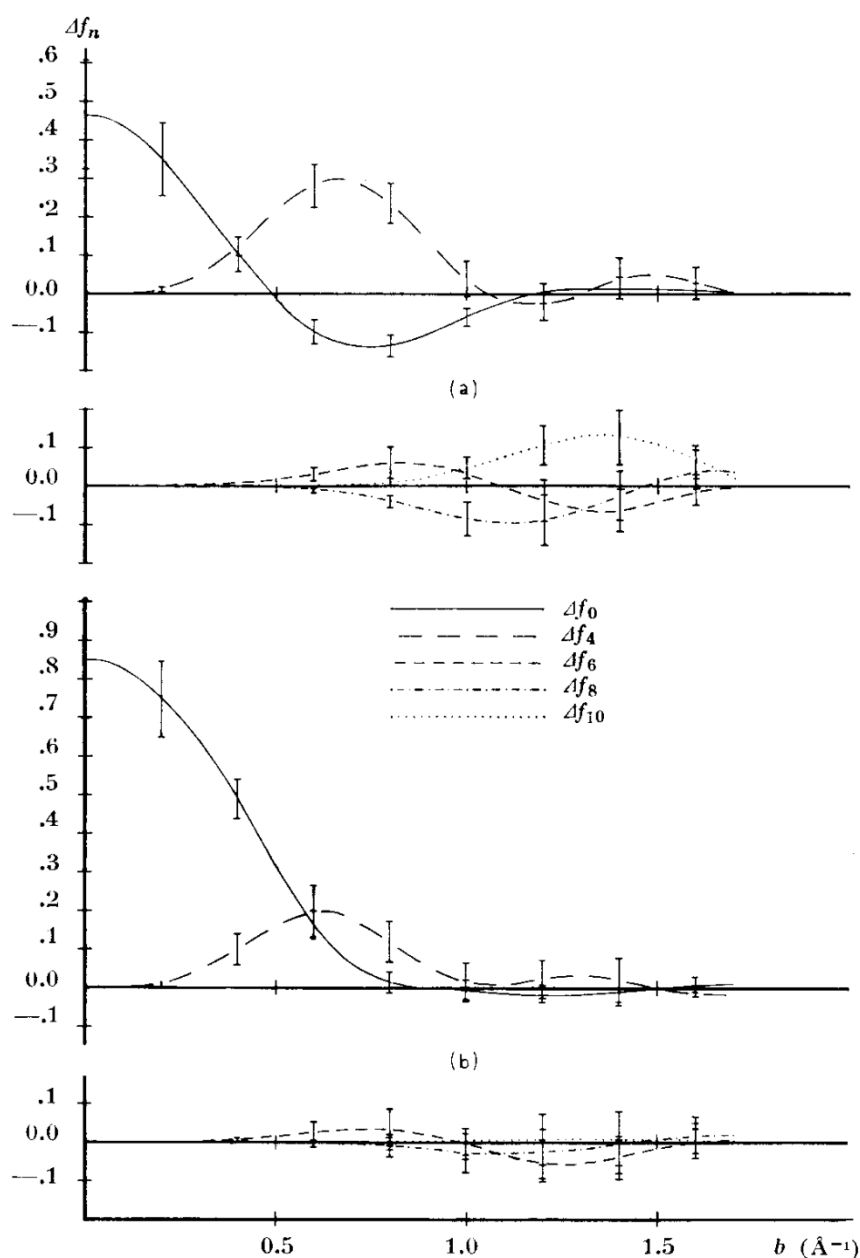


Fig. 3. The radial coefficients of the cubic harmonic expansion of Δf , (a) for K^+ and (b) for Br^- in KBr .

The harmonic representation is no doubt preferable to the Δf curve representation as it shows the entire behaviour of the atomic factor in all directions at once. It also defines accurately what we have earlier called the average trend of the atomic factor curves in a way which is equivalent to the spherically symmetric form factors of BROWN and WILKINSON [7] derived from a projection of the Fourier series. Of course, the main advantage is still the simple behaviour in the Fourier transformation, which means that $f_n(b)$ represents the scattering factor of that component of the electron density which is represented by $\rho_n(r)$ in real space, both having the same

angular dependence. Thus, a concrete interpretation of the results in terms of the electron density is always immediately available.

The programs for calculation of the radial coefficients (24) and (25) from the quantities F_b or ΔF_b and δF_b were written by the authors in ALGOL. In the present form they cover only the cubic symmetry, but a simple modification will make them applicable to tetrahedral cases, too. Also, there will be no difficulties in writing similar programs for other symmetries when needed. The spherical Bessel functions are calculated in programs by a special procedure modified from a procedure of GAUTSCHI [17] for calculation of ordinary Bessel functions. The calculations were performed with the ELLIOTT 803 computer at the Department of Nuclear Physics of the University of Helsinki and partly with the ELLIOTT 503 of the Finnish State Computer Center.

Acknowledgements

We are indebted to Dr. P. Lipas for reading the manuscript and the National Research Council for Sciences, Finland for financial support.

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Printed June 1967