A Generalized Debye Scattering Equation

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The Debye scattering equation for amorphous material and the Laue scattering equation for crystalline material follow from different assumptions on the orientation distribution of the interatomic distance vector $\boldsymbol{r}_{\mu,\nu}$. A generalization of these assumptions leads to a new scattering equation which is presented here.

1. Theory

Consider the interatomic distance vector $\boldsymbol{r}_{\mu,\nu} = \boldsymbol{r}_\mu - \boldsymbol{r}_\nu$ between the atoms μ and ν in an assembly of N atoms. Let the angles θ, ϕ describe the orientation of $\boldsymbol{r}_{\mu,\nu}$ in a spherical coordinate system $\mathcal{S}$. Then the function $g_{\mu,\nu}(\phi,\theta)$ gives the probability of finding $\boldsymbol{r}_{\mu,\nu}$ in orientation (ϕ,θ). In the derivation of the Debye scattering equation one assumes that $\boldsymbol{r}_{\mu,\nu}$ is distributed with equal probability in space. In case of amorphous material this argument may be true, but only for $\boldsymbol{r}_{\mu,\nu}$ several times greater than the distances between nearest neighbours. Atom μ is surrounded by nearest neighbours whose distribution in space depends on the chemical bonds in that vicinity. Since a local structural order exists around atom μ, $g_{\mu,\nu}(\phi,\theta)$ will take on sharp maxima for certain directions (ϕ,θ). We conclude that the Debye scattering equation must be modified in order to describe local order.

Let $\boldsymbol{s}(\alpha,\beta,\Theta)$ denote the scattering vector, where the angles α, β describe the orientation of $\boldsymbol{s}(\alpha,\beta,\Theta)$ in $\mathcal{S}$. Then the diffracted intensity $I(\Theta)$ is given by (with f_μ as atomic scattering factor of atom μ)

$$\begin{aligned} I(\Theta) &= \sum_{\mu=1}^{N}\sum_{\nu=1}^{N} f_\mu f_\nu^* \frac{n_{\mu,\nu}}{d_{\mu,\nu}},\\ n_{\mu,\nu} &:= \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} \exp(2\pi i\,\boldsymbol{s}(\alpha,\beta,\Theta)\cdot\boldsymbol{r}_{\mu,\nu}(\phi,\theta)) \\ &\qquad \cdot\ g_{\mu,\nu}(\phi,\theta)\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi,\\ d_{\mu,\nu} &:= \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} g_{\mu,\nu}(\phi,\theta)\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi. \end{aligned} \tag{1}$$

For $g_{\mu,\nu}(\phi,\theta) = 1$ the Debye scattering equation follows from (1). Using spherical harmonic functions $Y_l^m(\phi,\theta)$, one can expand $g_{\mu,\nu}(\phi,\theta)$ according to

$$g_{\mu,\nu}(\phi,\theta) = \sum_{l=0}^{L}\sum_{m=-l}^{l} a_l^m(\mu,\nu) Y_l^m(\phi,\theta), \tag{2}$$

where the coefficients $a_l^m(\mu,\nu)$ depend on the summation indices l, m and on the atomic pair (μ,ν) (see Appendix A1). The $a_l^m(\mu,\nu)$ will be called structure coefficients subsequently. L is the degree of expansion, see below. Inserting (2) into (1) results in (see Appendix A2)

$$\begin{aligned} I(\Theta) &= \sum_{\mu=1}^{N} f_\mu^2 + 8\pi \sum_{\mu=1}^{N-1}\sum_{\nu=\mu+1}^{N} f_\mu f_\nu^* \\ &\quad\cdot \sum_{l=0}^{L}\sum_{m=-l}^{l} \frac{a_l^m(\mu,\nu) i^l j_l(k(\Theta) r_{\mu,\nu}) Y_l^m(\alpha,\beta)}{Z(\mu,\nu)}, \end{aligned} \tag{3}$$

where j_l is the spherical Bessel function of order l, taken for the product $k(\Theta) r_{\mu,\nu}$ ($k = 4\pi\sin(\Theta)/\lambda$), and $Z(\mu,\nu)$ is a normalization constant. Equation (3) is the new scattering formula, allowing for modelling the local order via the coefficients $a_l^m(\mu,\nu)$ (Appendix A3). The Debye scattering formula follows from (3) for $a_0^0(\mu,\nu) = \sqrt{4\pi}$ and all other coefficients are zero (Appendix A4).

2. Intensity calculation

The Debye scattering equation is used for the calculation of scattered intensities from amorphous samples and from nanocrystalline materials [1, 2]. If a

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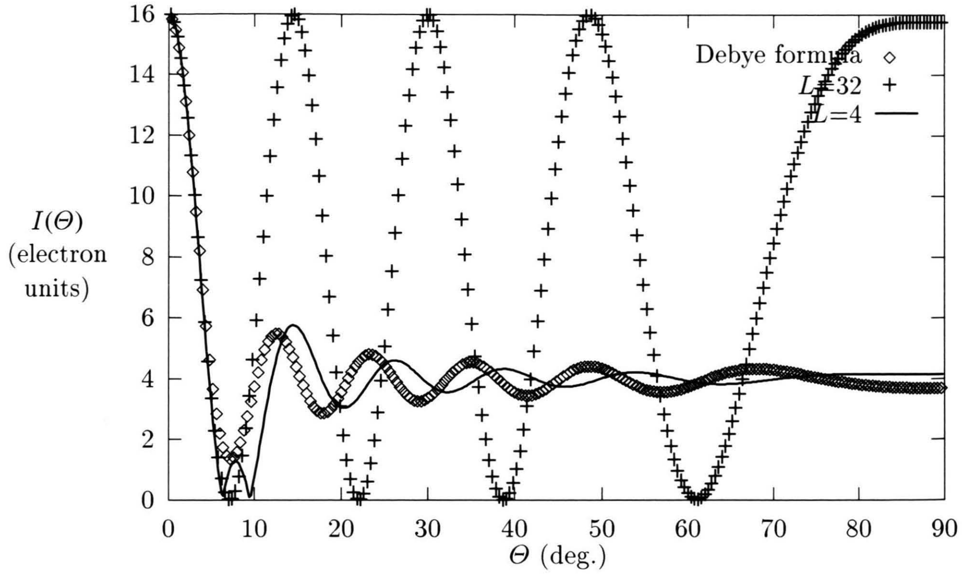

Fig. 1. Scattering curves according the Debye formula and (3) for a tetrahedron with $r_{\mu,\nu} = \sqrt{8}$, $\lambda = 1$, $\alpha = \beta = 0$.

structural model for local order with a finite number N of atoms is given, then the coordinates $\phi_{\mu,\nu}, \theta_{\mu,\nu}$ for each $\boldsymbol{r}_{\mu,\nu}$ are known and

$$g_{\mu,\nu}(\phi,\theta) = \delta(\phi_{\mu,\nu} - \phi)\delta(\theta_{\mu,\nu} - \theta). \tag{4}$$

With (4) one can calculate the $a_l^m(\mu,\nu)$ from

$$a_l^m(\mu,\nu) = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} Y_l^{m\,*}(\phi,\theta)\delta(\phi_{\mu,\nu} - \phi) \cdot \delta(\theta_{\mu,\nu} - \theta)\sin\theta \,\mathrm{d}\theta\mathrm{d}\phi = Y_l^{m\,*}(\phi_{\mu,\nu},\theta_{\mu,\nu}). \tag{5}$$

Consider the tetrahedron (with $N = 4$) as a simple example for local structural order. Tetrahedral arrangements of atoms are quite frequently found in amorphous materials. As an illustration, Fig. 1 compares three intensity curves for a single tetrahedron. The curves were calculated by the Debye scattering equation (drawn using ◇) and by (3) with $L = 4$ (drawn using –) and with $L = 32$ (drawn using +). For simplicity, $f_\mu(\Theta) = f = 1.0$ was set. Obviously, the degree of expansion L is decisive. With $L = 32$ the scattering curve from (3) coincides exactly with the curve calculated from (14), which is the general scattering equation for an assembly of N atoms. For $L = N^2 = 16$, the curve from (3) (not drawn in Fig. 1) deviates from the exact result only at the highest scattering angles. With true scattering factors f_μ, both curves coincide already for $L = N^2 = 16$, because of the intensity damping by f_μ at higher Θ.

The Debye formula was not derived for a definite atomic arrangement, but for all possible orientations with respect to $\mathcal{S}$. The remarkable difference between the curves of the Debye formula and those of (3) is therefore no surprise, but this comparison gives an idea for the description of atomic assemblies by the (proper) choice of the expansion degree L. The Debye formula is the lowest possible expansion with $L = 1$. In terms of diffraction, amorphous or partial amorphous structures are described by $1 \leq L \leq N^2$.

The structural unit of amorphous SiO_2 may serve as a second example. Four O atoms are located at the corners of a tetrahedron, one Si atom sits in the center. The scattering curve (with $\lambda = 1, r_{\mathrm{O-Si}} = \sqrt{3}, r_{\mathrm{O-O}} = \sqrt{8}, L = N^2 = 25$) for such a single tetrahedron is given in Figure 2.

The example above concerned the scattering from just one single structural unit. Now a structural unit in various orientations has to be discussed. The atomic positions of the structural unit change with its orientation. Then the question arises how to describe the coordinates of the interatomic distance vector $\boldsymbol{r}_{\mu,\nu}$ and

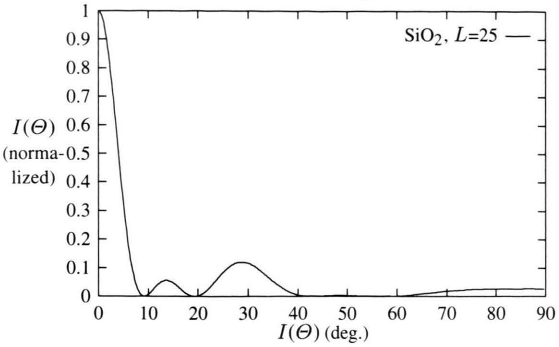

Fig. 2. Scattering curve according (3) for a SiO$_2$ tetrahedron $r_{\text{O-Si}} = \sqrt{3}$, $r_{\text{O-O}} = \sqrt{8}$, $\lambda = 1$, $\alpha = \beta = 0$.

how to establish $g_{\mu,\nu}(\phi,\theta)$ from the coordinates. The simple relation (4) is valid only for a single structural unit in fixed orientation. A description is proposed which generalizes (4), by intervals $\Delta\phi$ and $\Delta\Theta$ and by constant probabilities for $\boldsymbol{r}_{\mu,\nu}$ within these intervals. Thus (with $\omega = \phi$ or θ)

$$\Delta(\omega_{\mu,\nu} - \omega) = \begin{cases} 1 \text{ if } \omega^a_{\mu,\nu} \le \omega_{\mu,\nu} \le \omega^b_{\mu,\nu}, \\ 0 \text{ else,} \end{cases} \tag{6}$$

where ω^a and ω^b are the lower and upper limits of the interval. With (6), $g_{\mu,\nu}(\phi,\theta)$ may be defined as

$$g_{\mu,\nu}(\phi,\theta) = \Delta(\theta_{\mu,\nu} - \theta)\Delta(\phi_{\mu,\nu} - \phi). \tag{7}$$

From (7) finally the $a_l^m(\mu,\nu)$ follow according to (5). Unfortunately, with (7) the integral in (5) can not be solved analytically, but either numerically or analytically under simplifying assumptions.

3. Structure determination

For structure evaluation from measured intensity curves $I(\Theta)$, any scattering formula has to be inverted. In the case of the Debye scattering equation and amorphous or liquid samples the Fourier inversion as described by Warren [3] or Wagner [4] is widely used. To invert the scattering equation (3) it is neccessary to determine the structure coefficients $a_l^m(\mu,\nu)$ and the distances $\boldsymbol{r}_{\mu,\nu}$. Each intensity value $I(\Theta)$ gives one equation of the form (3), where the $a_l^m(\mu,\nu)$ and the $r_{\mu,\nu}$ (in the spherical Bessel function) are unknown (Appendix A5). Unfortunately, (3) represents a non-linear equation system, but under certain circumstances only the $a_l^m(\mu,\nu)$ or the $r_{\mu,\nu}$ need to be found.

In particular, a simpler problem is generated if the structural unit and its distances $r_{\mu,\nu}$ are known in advance. In this case only the $a_l^m(\mu,\nu)$ must be determined and the equation system becomes linear. In the example of SiO$_2$, such an approach could be useful to discriminate between different amorphous or partially amorphous phases. Solving a linear equation system is easier than to perform a Fourier inversion, but the drawback in the present application is the rapidly growing number of unknowns $a_l^m(\mu,\nu)$ with growing N (Appendix A6).

The corresponding equation system takes on the form

$$I(\Theta) - \sum_{\mu=1}^{N} f_\mu^2 = \sum_{\mu=1}^{N-1} \sum_{\nu=\mu+1}^{N} \sum_{l=0}^{L} \sum_{m=-l}^{l} c(\mu,\nu,l,m,\alpha,\beta,\Theta) a_l^m(\mu,\nu), \tag{8}$$

where

$$c(\mu,\nu,l,m,\alpha,\beta,\Theta) = \frac{8\pi f_\mu f_\nu^* i^l j_l(k(\Theta) r_{\mu,\nu}) Y_l^m(\alpha,\beta)}{Z(\mu,\nu)} \tag{9}$$

are elements of the two-dimensional coefficient matrix C (Appendix A7). If two or more interatomic distances are equal, $r_{\mu,\nu} = r_{\mu',\nu'}$ and if the corresponding atoms have equal scattering factors f, then because of (9) the corresponding two columns of C become equal. As a consequence, one must set $a_l^m(\mu,\nu) = a_l^m(\mu',\nu')$ in order to avoid an underdetermined problem (Appendix A8).

The tetrahedron may serve as example again. The theoretical intensity calculated in the preceeding section was taken as input for the calculation of the $\bar{a}_l^m(\mu,\nu)$ according to (8) (Appendix A9). The resulting values for the $\bar{a}_l^m(\mu,\nu)$ are given in Table 1 together with the values for the $a_l^m(\mu,\nu)$ which were calculated from (5) (Appendix A10). For $\mu > 1$ and $\nu = 1 \ldots N$, the $\bar{a}_l^m(\mu,\nu)$ are identical to $\bar{a}_l^m(1,\nu)$. As a consistency check, one can re-calculate $I(\Theta)$ using the $a_l^m(\mu,\nu)$ and obtain precisely an identical intensity distribution. In the same way, the errors $\Delta\bar{a}_l^m(\mu,\nu)$ for the solution can be calculated from

Table 1. The structure coefficients $a_l^m(\mu,\nu)$ and the x-ray structure coefficients $\bar{a}_l^m(\mu,\nu)$ for a tetrahedron.

μ	ν	l	m	$a_l^m(\mu,\nu)$	$\bar{a}_l^m(\mu,\nu)$	μ	ν	l	m	$a_l^m(\mu,\nu)$	$\bar{a}_l^m(\mu,\nu)$
1	1	0	0	0.282095	0.282095	1	2	0	0	0.282095	0.272495
1	1	1	-1	0.0	0.0	1	2	1	-1	0.0	0.0
1	1	1	0	0.488603	0.488602	1	2	1	0	0.34549	0.0
1	1	1	1	0.0	0.0	1	2	1	1	0.244301	0.0
1	1	2	-2	0.0	0.0	1	2	2	-2	-0.193137	0.0
1	1	2	-1	0.0	0.0	1	2	2	-1	0.0	0.0
1	1	2	0	0.630783	0.630783	1	2	2	0	0.157696	-0.017001
1	1	2	1	0.0	0.0	1	2	2	1	0.386274	0.0
1	1	2	2	0.0	0.0	1	2	2	2	0.0	0.0
1	1	3	-3	0.0	0.0	1	2	3	-3	0.0	0.0
1	1	3	-2	0.0	0.0	1	2	3	-2	-0.361326	0.0
1	1	3	-1	0.0	0.0	1	2	3	-1	0.0	0.0
1	1	3	0	0.746353	0.746353	1	2	3	0	-0.131938	0.0
1	1	3	1	0.0	0.0	1	2	3	1	0.342784	0.0
1	1	3	2	0.0	0.0	1	2	3	2	0.0	0.0
1	1	3	3	0.0	0.0	1	2	3	3	-0.147511	0.0
1	1	4	-4	0.0	0.0	1	2	4	-4	0.110633	0.0
1	1	4	-3	0.0	0.0	1	2	4	-3	0.0	0.0
1	1	4	-2	0.0	0.0	1	2	4	-2	-0.418154	0.0
1	1	4	-1	0.0	0.0	1	2	4	-1	0.0	0.0
1	1	4	0	0.846284	0.846284	1	2	4	0	-0.343803	-0.097315
1	1	4	1	0.0	0.0	1	2	4	1	0.118272	0.0
1	1	4	2	0.0	0.0	1	2	4	2	0.0	0.0
1	1	4	3	0.0	0.0	1	2	4	3	-0.312918	0.0
1	1	4	4	0.0	0.0	1	2	4	4	0.0	0.0

Coefficients for $\mu > 1$, $\nu > 2$ omitted for brevity.

(8) if an error estimate $\Delta I(\Theta)$ for the measured intensity is provided.

Once the $a_l^m(\mu,\nu)$ and from them $g_{\mu,\nu}(\theta,\phi)$ have been found, the corresponding structural unit has to be identified. From inspection of the graphs of $g_{\mu,\nu}(\theta,\phi)$ or from comparison with tabulated $a_l^m(\mu,\nu)$ one has to conclude on the structural unit and to extract the $\theta_{\mu,\nu}$,$\phi_{\mu,\nu}$. In general, several structural units together with their particular orientations will result in similar $g_{\mu,\nu}(\theta,\phi)$. The interpretation of $g_{\mu,\nu}(\theta,\phi)$ has to include structural information from other experiments to come to clear conclusions. This drawback applies in the same manner to the interpretation of $\rho(r)$.

In other cases, the geometric type of the structural unit may be known (i. e. the $a_l^m(\mu,\nu)$), but the actual distances within may still be missing. Then the $r_{\mu,\nu}$ have to be found which lead to the solution of a nonlinear equation system according to (3). The solution of a nonlinear equation system relies on iterative methods and on reliable starting values for the unknowns, but under certain mathematical conditions the iteration will end up with the (mathematically) true solution. We did not elaborate a mathematical proof for the problem under consideration but carried out successfully some numerical experiments (Appendix A11). Table 2 gives starting values and final values after 180 iterations for the $r_{\mu,\nu}$ of the tetrahedron. The exact solution is $r_{\mu,\nu} = r = 2.8284$. The errors $\Delta r_{\mu,\nu}$ can be estimated from the dependence of the solution on $I(\Theta) \pm \Delta I(\Theta)$.

Table 2. Iterative calculation of interatomic distances $r_{\mu\nu}$ for a tetrahedron.

Starting value	Final value	Exact solution
3.3941	2.8281	2.8284
1.9799	2.8246	2.8284
3.9598	2.8285	2.8284
1.9799	2.8286	2.8284
3.9598	2.8303	2.8284
3.9598	2.8309	2.8284

In the general case, both $a_l^m(\mu,\nu)$ and $r_{\mu,\nu}$ are unkown. Then the unkowns must be found from (3) which again corresponds to the solution of a nonlinear equation system. Since the number of unknowns is now $U + N^2 - N$ (see (16)) the amount of calculations is prohibitively high unless a computer with parallel processing is used.

4. Discussion

The advantage in this new appproach is of methodical nature. Apart from counting statistics and experimental difficulties like Compton scattering, the solution of equation system (8) is mathematically unequivocal. Working with the orientation distribution function $g_{\mu,\nu}(\phi,\theta)$ instead of the radial distribution function $\rho(r)$ is a new approach to the interpretation of amorphous structures. This approach allows to understand the amorphous structure as result of variations in the arrangement of structural units rather than as a variation of distances between nearest neighbours (Appendix A12).

5. Appendix

(A1) The definition (2) of a distribution function for any atom pair (μ,ν) within the atom assembly describes the most general case, where $g_{\mu,\nu}$ for the pair (μ,ν) is thought to be independent of $g_{\mu'\nu'}$ for the pair (μ',ν'). Actually, some geometrical relations between the vectors $\boldsymbol{r}_{\mu,\nu}$ will exist within the atom assembly. Then between $g_{\mu,\nu}$ and $g_{\mu'\nu'}$ and therefore also between the structure coefficients $a_l^m(\mu,\nu)$ and $a_l^m(\mu',\nu')$ corresponding algebraic relations exist. These relations reduce the actual number of structure coefficients, which is very important for the practical use of (2). The most simple of these relation is $a_l^m(\mu,\nu) = (-1)^l a_l^m(\nu,\mu)$.

(**A2**) The exponential function can be written as a double sum over spherical harmonic functions Y_l^m [5]. Now, $k(\Theta) = 4\pi\sin(\Theta)/\lambda$ is the absolute value of the vector $\boldsymbol{k}(\alpha,\beta,\Theta) = 2\pi\boldsymbol{s}(\alpha,\beta,\Theta)$, and $r_{\mu,\nu}$ is the absolute value of the vector $\boldsymbol{r}_{\mu,\nu}(\phi,\theta)$. Furthermore, $Y_l^{m\,*}$ is the conjugate complex of Y_l^m, i is the imaginary unit and j_l is the spherical Bessel function, then

$$\exp(i\,\boldsymbol{k}(\alpha,\beta,\Theta)\cdot\boldsymbol{r}_{\mu,\nu}(\phi,\theta)) = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l j_l(k(\Theta)r_{\mu,\nu})Y_l^{m\,*}(\phi,\theta)Y_l^m(\alpha,\beta). \tag{10}$$

For the Y_l^m an orthonormalization condition exists

$$\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi} Y_l^{m\,*}(\phi,\theta)Y_{l'}^{m'}(\phi,\theta)\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi = \delta_{ll'}\delta_{mm'}. \tag{11}$$

The terms for $\mu = \nu$ in (1) can be grouped independently, because for $r_{\mu,\mu} = 0$ the phase factor equals 1. Inserting (2) into (1) and using the expansion (10) gives

$$\begin{aligned} I(\Theta) = \sum_{\mu=1}^{N} f_\mu^2 + 4\pi\sum_{\mu=1}^{N}\sum_{\nu=1,\neq\mu}^{N} f_\mu f_\nu^* \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\sum_{l=0}^{L}\sum_{m=-l}^{l} a_l^m(\mu,\nu)Y_l^m(\phi,\theta)\sum_{l'=0}^{\infty}\sum_{m'=-l'}^{l'} i^{l'} j_{l'}(k(\Theta)r_{\mu,\nu}) \\ \cdot\, Y_{l'}^{m'\,*}(\phi,\theta)Y_{l'}^{m'}(\alpha,\beta)\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi\left(\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\sum_{l=0}^{L}\sum_{m=-l}^{l} a_l^m(\mu,\nu)Y_l^m(\phi,\theta)\sin\theta\,\mathrm{d}\theta\mathrm{d}\phi\right)^{-1}. \end{aligned} \tag{12}$$

A reduction in the summations over μ and ν comes from the symmetry $a_l^m(\mu,\nu) = (-1)^l a_l^m(\mu,\nu)$. Then the summation over ν needs to go from $\mu+1$ to N only, since all coefficients $a_l^m(\nu,\mu)$ are accounted for by $2a_l^m(\mu,\nu)$. In that respect it is of advantage that $j_l(k(\Theta)r_{\mu,\nu}) = j_l(k(\Theta)r_{\nu,\mu})$, since $r_{\mu,\nu} = r_{\nu,\mu}$.

The product between the two double sums produces products of the form $Y_l^{m\,*}(\phi,\theta)Y_{l'}^{m'}(\phi,\theta)$. Because of (11), all terms with $l \neq l'$ and $m \neq m'$ vanish. The denominator gives a normalization constant $Z(\mu,\nu)$. If the atomic positions can be described by δ–functions, as in the tetrahedron or other polyhedra, then $Z(\mu,\nu) = Z = 1$. Finally one receives (3) from (12).

Most mathematical textbooks give the spherical harmonics as complex quantities. They are, however, also defined for R^3. We use (with P_l^m as the associated Legendre function)

$$Y_l^m = \begin{cases} (-1)^m\sqrt{\dfrac{2l+1}{4\pi}\dfrac{(l-m)!}{(l+m)!}}P_l^m(\cos(\theta))\cos(m\phi) & \text{for } m \geq 0, \\ \sqrt{\dfrac{2l+1}{4\pi}\dfrac{(l-\|m\|)!}{(l+\|m\|)!}}P_l^{\|m\|}(\cos(\theta))\sin(\|m\|\phi) & \text{for } m < 0. \end{cases} \tag{13}$$

(**A3**) If the degree of expansion is $L = \infty$, then (3) is exact. For the actual usage of (3), L must be finite and as small as possible. If a single structural unit is considered in a fixed orientation, then the intensity calculated from (3) can be compared with the intensity obtained from the exact formula

$$I(\Theta) = \sum_{\mu=1}^{N}\sum_{\nu=1}^{N} f_\mu f_\nu^* \exp(2\pi i\boldsymbol{r}_{\mu,\nu}\cdot\boldsymbol{s}_{\mu,\nu}(\Theta)). \tag{14}$$

For the assemblies of N atoms studied in this work it was sufficient to put $L = N^2$.

(A4) With $Y_0^0 = 1/\sqrt{4\pi}$ and $j_0 = \sin(kr)/(kr)$ one has from (3)

$$\frac{4\pi \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} f_\mu f_\nu^* \sqrt{4\pi} \frac{\sin k(\Theta) r_{\mu,\nu}}{k(\Theta) r_{\mu,\nu}} \frac{1}{\sqrt{4\pi}}}{\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \sqrt{4\pi} \frac{1}{\sqrt{4\pi}} \sin\theta d\theta d\phi}$$

$$= \frac{4\pi \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} f_\mu f_\nu^* \frac{\sin k(\Theta) r_{\mu,\nu}}{k(\Theta) r_{\mu,\nu}}}{4\pi} \tag{15}$$

$$= \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} f_\mu f_\nu^* \frac{\sin k(\Theta) r_{\mu,\nu}}{k(\Theta) r_{\mu,\nu}}.$$

(A5) In the usual Fourier inversion procedure just one diffractogram $I(\Theta_i)$ $(i = 1, i_{end})$ is recorded at arbitrary orientation of the sample. Since the coordinates α, β of the scattering vector $\mathbf{s}$ enter into (3), the possibility of variation in α, β appears, in order to yield as many equations as possible for structure determination. The orientation of $\mathbf{s}$ has to be taken into account for an at least partial crystalline sample. In principle, (3) is applicable even to a single crystal.

(A6) The number U of geometric coefficients $a_l^m(\mu, \nu)$ neccessary for N distinct atomic positions is in the general case

$$U = \frac{N^2 - N}{2} \sum_{l=0}^{N} (2l + 1). \tag{16}$$

(A7) $C = [c(i, j)]$ with $i = 1, i_{end}$ and $j = 1, j_{end}$. i_{end} is the number of intensity values $I(\Theta_i)$ taken at Bragg angles Θ_i with $\mathbf{s}$ in orientation α, β with respect to $\mathcal{S}$. The index j counts the four loops over $\mu = 1, N - 1$; $\nu = \mu + 1, N$; $l = 0, L$ and $m = -l, l$.

(A8) The coefficients $\bar{a}_l^{\,m}(\mu, \nu)$ which follow as solution of (8) therefore may be different from the structure coefficients $a_l^m(\mu, \nu)$ calculated from (5) and may be called x-ray structure coefficients. The sign $^-$ indicates that the $\bar{a}_l^{\,m}(\mu, \nu)$ are found from the inversion of the scattering equation.

If all interatomic distances are equal and if all atoms are of the same element, then (8) becomes

$$I(\Theta) - Nf^2 = 4\pi(N^2 - N)f^2 \sum_{l=0}^{L} i^l j_l(k(\Theta)r) \cdot \sum_{m=-l}^{l} Y_l^m(\alpha, \beta)\, \bar{a}_l^{\,m}. \tag{17}$$

(A9) From (5) with $\mu = \nu$ one has

$$a_l^m(\mu, \mu) = Y_l^{m*}(0, 0) \tag{18}$$

for any atom μ. Equation (18) reduces the number of unknowns by N, see (A6).

(A10) For the tetrahedron with $N = 4$ atoms one has to find the spherical coordinates ϕ, θ of $N^2 = 16$ interatomic distances $r_{\mu,\nu}$. If the cartesian coordinates of the for atoms are (1,1,1), (1,-1,-1), (-1,1,-1), (-1,-1,1) then their spherical coordinates follow from

$$\phi = \begin{cases} \frac{\pi}{2} - \arctan\frac{x}{y} & \text{for } y \geq 0, \\ \frac{3\pi}{2} - \arctan\frac{x}{y} & \text{for } y < 0, \end{cases} \tag{19}$$

$$\theta = \arccos\frac{z}{\sqrt{x^2 + y^2 + z^2}}, \tag{20}$$

$$r = \sqrt{x^2 + y^2 + z^2}. \tag{21}$$

(A11) For the numerical solution we used a Newtonian method described in G. Engeln-Müllges und F. Reuter, Numerikalgorithmen, VDI-Verlag, Düsseldorf, 1996.

(A12) The radial distribution function $\rho(r)$ gives the probability for the distance r between nearest neighbours in the atomic arrangment. In our understanding, we do not expect large variations in r for nearest neighbours, but sharp, distinct values for r because of the chemical bonds between the atoms. Variations in r for large values are only the geometric consequence from variations in the orientation of fundamental structural units. In fact, if one looks at pictures for visualization of an amorphous structure (e. g. for B_2O_3, As_2S_3 [6]) one sees that r is not changed for nearest neighbours.

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