Calculation of Powder-Pattern Intensity Distributions

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If spherical crystals are assumed, and a Patterson function which is averaged over all orientations is used, it is possible to obtain a simple expression for the intensity distribution in a powder pattern. Unlike the Debye equation, which is useful only for extremely small crystals, the present equation is practical no matter how large the crystals. As two examples, powder patterns are calculated for crystals containing 67 atoms and 536 atoms.

1. Introduction

For powder patterns, the peak areas are given by the well known expressions for the integrated intensity. For some purposes, such as comparing the intensity from an amorphous sample with that from a corresponding sample of small crystals, it is the intensity distribution in which we are interested. To obtain the intensity distribution, we sometimes make use of the Debye equation as given by equation (10.3) of Warren (1969).

\[
\begin{align*}
I_{\text{eu}} &= \sum_m \sum_n f_m f_n \sin 2\pi sr(mn),
\end{align*}
\]

where \(I_{\text{eu}}\) is the intensity in electron units from one crystal assumed to take all orientations, \(s = 2 \sin \theta / \lambda\), \(r(mn)\) is the distance between atoms \(m\) and \(n\), and the summation is over all atoms in the crystal. Although completely general, the equation is practical only for extremely small crystals, since for larger crystals the number of terms in the summation becomes much too great.

It is of interest to obtain an expression for the intensity distribution which can be used when the crystals are not extremely small. With the single restriction that the crystals are assumed to be spherical in shape, it is possible to obtain a simple expression.

2. The intensity derivation

In terms of electron densities, the intensity in electron units from one crystal is given by

\[
I_{\text{eu}} = \int g(xyz) \exp[2\pi is \cdot t] dv
\]

where \(g(xyz)\) is the electron density at position \(xyz\) in the crystal. To correspond to a powder pattern, we take an average in which the vector \(s\) is allowed to take all orientations:

\[
\langle \exp[-2\pi is \cdot r] \rangle = \frac{\sin 2\pi sr}{2\pi sr}.
\]

Let \(x' = x + u, y' = y + v, z' = z + w\). Introducing \(\gamma\) to allow for the axes not being orthogonal, \(dv = \gamma dx dy dz\). If \(V\) is the volume of the unit cell, \(V = \gamma abc\). With these changes equation (1) becomes

\[
I_{\text{eu}} = \int \int g(xyz) g(x' + u, y' + v, z' + w)
\]

\[
\times \frac{\sin 2\pi sr}{2\pi sr} \gamma dx dy dz dv'.
\]

We now introduce the Patterson function, which is given by equations (9.20) and (9.21) of Warren (1969):

\[
\int_0^a \int_0^b \int_0^c g(xyz) g(x + u, y + v, z + w) \gamma dx dy dz = \frac{1}{V} \sum_{hkl} \frac{F^2(hkl)}{\gamma} \exp[-2\pi i H \cdot r],
\]

where \(H = hb_1 + kb_2 + lb_3\), \(r = u a_1 + v b_2 + w c_3\).

In equation (2) there is an integration with respect to \(\gamma dx dy dz\) over the whole volume of the crystal. The integration in equation (3) covers only the volume of one unit cell. Hence for equation (3) to be used, there must be an additional multiplication by the number of unit cells for which there is another cell within the crystal at displacement \(r\). With \(N\) as the number of unit cells in the crystal, and \(g(r)\) as the fraction of the cells having a neighbor within the crystal at displacement \(r\), equation (2) can be written

\[
I_{\text{eu}} = \int \frac{1}{V} \sum_{hkl} \frac{F^2(hkl)}{\gamma} \exp[-2\pi i H \cdot r]
\]

\[
\times \frac{\sin 2\pi sr}{2\pi sr} N g(r) dv'.
\]
The integration by $dv'$ involves a summation over all displacement vectors $r$. In a spherical crystal, $r$ occurs in all orientations with equal probability, and we can use appropriate averages:

$$\langle \exp[-2\pi i \mathbf{H} \cdot \mathbf{r}] \rangle = \frac{\sin 2\pi H R}{2\pi H R}.$$ 

Let vectors of length $r$ be drawn in all orientations from each unit cell, and let $q(r)$ be the fraction of the vectors terminating within the crystal. With $dv' = 4\pi r^2 dr$, equation (4) becomes

$$I_{eu} = \left\{ \frac{1}{V} \sum_{hkl} F^2(hkl) \times \frac{\sin 2\pi H R}{2\pi H R} \frac{\sin 2\pi sr}{2\pi sr} Nq(r)4\pi r^2 dr \right\}.$$ (5)

Expressing the product $\sin 2\pi H R \sin 2\pi sr$ in terms of cosines, we obtain

$$I_{eu} = \frac{N}{2\pi V} \sum_{hkl} F^2(hkl) \times \int_0^{2\pi} q(r) \left\{ \cos 2\pi(s-H)r - \cos 2\pi(s+H)r \right\} dr.$$ (6)

In the Appendix it is shown that

$$q(r) = 1 - \frac{3r}{4R} + \frac{r^3}{16R^3}.$$ (7)

The integrals in equation (6) are of the form

$$\int_0^{2\pi} q(r) \cos (br) dr = \frac{3R}{4} Z(bR),$$ (8)

where

$$Z(x) = \frac{1}{x^2} \left[ 1 + \left( \frac{\sin x}{x} \right)^2 - 2 \frac{\sin 2x}{2x} \right].$$ (9)

Some important properties of $Z(x)$ and a partial tabulation of the function are given in Table 1.

In equation (6) we introduce a multiplicity $m(hkl)$ and add a prime to the summation to indicate that we use only one member in each $hkl$ group. We introduce equation (8) in equation (6) and to express the intensity in terms of the variable $\sin 0$, we make the replacements $s = 2\sin \theta/A$ and $AH(hkl) = 2\sin \theta_{hkl}$. Multiplying by $M$, the number of crystals in the sample, we have an expression for the intensity from the sample:

$$I_{eu} = \frac{3MNA^3}{32\pi V} \left( \frac{R}{A} \right) \frac{1}{\sin \theta} \times \sum_{hkl} \frac{m(hkl)F^2(hkl)}{\sin \theta_{hkl}} \left\{ Z\left( \frac{4\pi R}{A} \sin \theta - \sin \theta_{hkl} \right) \right\}. \quad (10)$$

In general, the term $Z\left( \frac{4\pi R}{A} \sin \theta + \sin \theta_{hkl} \right)$ can be neglected; it is important only for small values of $\sin \theta$. Each $hkl$ contributes a peak centered at $\sin \theta = \sin \theta_{hkl}$ and the larger the crystal the more rapidly the contribution drops off on either side.

3. The integrated intensity

It is of interest to calculate the integrated intensity from equation (10) for comparison with the expression obtained in the usual way. If $D$ is the distance from the sample to the receiving surface, the power per unit length of diffraction circle is given by

$$P_{eu} = \int I_{eu}(1)Dd(2\theta).$$ (11)

From $x = (4\pi R/\lambda)(\sin \theta - \sin \theta_{hkl})$ we have

$$d(2\theta) = \frac{\lambda}{2\pi R \cos \theta} dx.$$ 

With $I_{eu}$ from equation (10) for a single $hkl$ peak, and under the assumption that the crystals are large enough for the differences between $\sin \theta$ and $\sin \theta_{hkl}$ to be disregarded, equation (11) becomes

$$P_{eu} = \frac{3MNA^3}{32\pi V} \left( \frac{R}{A} \right) \frac{mF^2}{\sin^2 \theta \sin \theta_{hkl}} \frac{\lambda}{2\pi R \cos \theta} \int_{-\infty}^{+\infty} Z(x) dx.$$ 

Since

$$\int_{-\infty}^{+\infty} Z(x) dx = 4\pi/3,$$

we obtain

$$P_{eu} = \frac{3MNA^3}{8\pi V} \frac{mF^2}{\sin \theta \sin 2\theta}.$$ (12)

<table>
<thead>
<tr>
<th>Table 1. The function $Z(x) \times 10^4$</th>
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<td>$x$</td>
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The power per unit length of diffraction circle, obtained in the usual way, is given by equation (4.11) of Warren (1969):

\[ P' = \frac{I_0}{16\pi R} \left( \frac{e^4}{m^2 c^2} \right) V A^3 m F^2 \frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta} \]

To change to the notation of this paper, we replace \( R \) by \( D \), replace \( V \) by \( MN v_a \), replace \( v_a \) by \( V \) and divide by \( \lambda \) to change to electron units. The result is identical to equation (12).

4. The peak breadth

The breadth at half maximum intensity of the powder pattern peaks produced by equation (10) is determined by the function \( Z(x) \) where \( x = \frac{4\pi R}{\lambda} (\sin \theta - \sin \theta_{\text{nlk}}) \). For \( x = 0 \), \( Z(x) = 1 \) and for \( x = -1.738 \), \( Z(x) = 0.500 \). Hence

\[ 1.738 = \frac{4\pi R}{\lambda} \cos \theta (\theta(1/2) - \theta(hkl)) \]

On a 20 scale, the full breadth in radians at half maximum intensity is

\[ B = 4[\theta(1/2) - \theta(hkl)] \]

from which

\[ B = \frac{1.738A}{\pi R \cos \theta} \]

If a sphere is represented as a set of parallel columns, the average column length, weighted with respect to the volume of the column is given by \( L = 3R/2 \). In terms of the average column length

\[ B = \frac{0.832A}{L \cos \theta} \] (13)

Equation (13) is quite similar to the particle-size broadening equations obtained by other methods.

5. Simplified example

To illustrate the application of equation (10) we consider the simplified example of cubic crystals containing only one kind of atom. Calling \( n \) the number of atoms per unit cell, we consider the three cases:

- SC \( n = 1 \) all \( hkl \)
- BCC \( n = 2 \) only \( h + k + l = \text{even} \)
- FCC \( n = 4 \) only \( hkl \) unmixed.

For all three cases \( F^2 = nF^2 \), \( V = a^3 \), the number of atoms in the sample is \( MNn \), and the intensity per atom is \( I_eu/MNn \). Equation (10) is readily reduced to an expression for the intensity per atom divided by \( f^2 \):

\[ \frac{I_eu}{MNnf^2} = \frac{3}{32\pi} \left( \frac{\Lambda}{a} \right)^3 \frac{R}{\lambda} \frac{n}{\sin \theta} \times \sum_{hkl} \frac{m(hkl)}{\sin \theta_{hkl}} \left( \frac{4\pi R}{\lambda} \left[ \sin \theta - \sin \theta_{hkl} \right] ight) 
- Z \left( \frac{4\pi R}{\lambda} \left[ \sin \theta + \sin \theta_{hkl} \right] \right) \]

where

\[ \sin \theta_{hkl} = \left( \frac{\lambda}{2a} \right) (h^2 + k^2 + l^2)^{1/2} \]

The number of atoms in a spherical crystal is \((4\pi/3)(R/a)^3n\). For a numerical example we choose the case BCC, \( n = 2 \); with \( (a/\lambda) = 2.5 \). The curves are computed for two sizes; \((R/a) = 2.0\) with 67 atoms per crystal, and \((R/a) = 4.0\) with 536 atoms per crystal. The intensity curves are shown by Fig. 1. The first example with 67 atoms per crystal is in a size range corresponding to the extreme upper limit for use of the Debye equation and the lower limit for the present method to be applicable. Small shoulders are seen at the base of the first peaks. These are due to small oscillation in the \( Z(x) \) function.

6. Conclusions

For extremely small crystals where a representation in terms of unit cells is meaningless, the intensity calculation should be carried out by means of the Debye equation. For other than extremely small crystals, the intensity calculation is readily carried out by the use of equations (10) or (14), and the amount of work involved is the same no matter how large the crystal. The equations which have been developed here are exact only for spherical crystals, and for this case it is

![Fig. 1. The powder pattern intensity per atom divided by \( f^2 \) for BCC spherical crystals with 2 atoms per cell, with \( (a/\lambda) = 2.5 \). Dashed curve \((R/a) = 2.0\) with 67 atoms per crystal. Solid curve \((R/a) = 4.0\) with 536 atoms per crystal.](image-url)
obviously unnecessary to consider the orientation of the crystalline axes within the sphere. For crystals which are approximately spherical, the equations could still be used as an approximation.

APPENDIX

Derivation of \( q(r) \)

For a spherical crystal of radius \( R \), let \( q(xyz, r) \) be the fraction of the surface of a sphere of radius \( r \) which is within the crystal, the sphere being centered at a position \( xyz \) which is within the crystal and at a distance \( p \) from the crystal center. We consider first the case that \( r < R \).

For \( p < R - r \) \( q(xyz, r) = 1 \);

for \( p > R - r \) \( q(xyz, r) = \frac{R^2 - (p-r)^2}{4pr} \).

Averaging over all positions \( xyz \) gives

\[
q(r) = \frac{3}{4\pi R^3} \int_0^{R-r} 4\pi p^2 \, dp + \int_{R-r}^R \frac{R^2 - (p-r)^2}{4pr} \, 4\pi p^2 \, dp
\]

\[
q(r) = 1 - \frac{3r}{4R} + \frac{r^3}{16R^3}.
\]

For the case \( R < r < 2R \), the same result is obtained. Hence equation (7) covers the whole range from \( r = 0 \) to \( r = 2R \). For \( r = 2R \), \( q(r) = 0 \).

Reference