Calculation of the X-ray Powder Reflection Profiles of Very Small Needle-Like Crystals. 
I. Principles of the Method

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Abstract

The aim of this paper is to develop a calculation method which allows the theoretical profiles of X-ray powder reflections to be obtained in the case of very small needle-like crystallites. This method takes into account not only the shape transform of the crystallite but also the variation of the structure factor. The study is limited to the case where the cross section of the needles contains two of the principal crystallographic axes and the third axis is along the crystallite direction of elongation. An example of the application of this method is given for a microcrystallized fibrous silicate known as sepiolite.

I. Introduction

The main types of information that can be obtained from a powder diagram are the values of the reticular distances and the average sizes of the crystallites. This latter determination is based on the hypothesis that the profile of a diffraction peak depends only on the size (or the distribution of sizes) of the scattering domains. In particular, it is supposed in this case that the structure factor of the considered reflection stays constant over all the domain where these reflections exist.

In fact, there are a number of systems where the scattering domains are too small for this approximation to be justified. The reflection profiles in the powder diagram depend not only on the form and dimensions of the crystallites but also on the variation of the structure factor. In this case, the direct methods using the Fourier transform of the reflection profiles are not applicable for the determination of the coherent domain characteristics. The principle of analysis of the powder diagram therefore necessitates the comparison of the experimental reflection profiles with the calculated ones by an integration method (which takes into account simultaneously the variation of the structure factor and the shape function of the diffracting domains).

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II. Theoretical principles

A finite three-dimensional crystal can be mathematically expressed as

$$
\varrho (x, y, z) * \left\{ \left[ \sum_{p} \sum_{q} \sum_{r} \delta(r_0 - pa_1 - qa_2 - ra_3) \right] g(x, y, z) \right\},
$$

(1)

where * represents the convolution operation, \(g(x, y, z)\) is the electron density function defining the unit motif, \(\sum_{p} \sum_{q} \sum_{r} \delta(r_0 - pa_1 - qa_2 - ra_3)\) represents the infinite number of Dirac deltas defining the direct lattice, \(r_0\) is any vector of the direct space, \(p, q, r\) are integers, \(a_1, a_2, a_3\) are the translation vectors defining the direct lattice, and \(g(x, y, z)\) is the shape function of the diffracting domain (as defined by Ewald, 1940).

The function which gives the amplitude of the X-rays scattered by such a finite three-dimensional crystallite is the Fourier transform of (1):

$$
\Phi(s) = \frac{F(s)}{\Omega} \left\{ \left[ \sum_{h} \sum_{k} \sum_{l} \delta(s - hA_1 - kA_2 - lA_3) \right] \right\} * D(s_1, s_2, s_3),
$$

(2)

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where \( s \) is the scattering vector ((\(|s| = 2 \sin \theta / \lambda\)) and \( s_1, s_2, s_3 \) are the lengths of its projections along the reciprocal-lattice axes, \( F(s) \) is the Fourier transform of \( \varphi(x, y, z) \) (structure factor), \( \Omega \) is the volume of the unit cell in direct space, \( \sum \sum \delta(s - hA_1 - kA_2 - lA_3) \) defines the reciprocal lattice with the translation vectors \( A_1, A_2, A_3 \), \( h, k, l \) are integers (Miller indices) and \( D(s_1, s_2, s_3) \) represents the Fourier transform of the shape function (shape transform).

It is known that (Guinier, 1964; Wilson, 1949), for well-ordered crystals, the function \( \Phi(s) \) has appreciable values only in the neighbourhood of the geometrical nodes \( h, k, l \). Around each of these nodes, the volume where the function \( D \) is non-negligible is sufficiently small so that within it the structure factor stays practically constant and equal to \( F_{hkl} \).

The intensity diffracted by such a crystallite around the node \( hkl \) (that is around the end of the vector \( s = hA_1 + kA_2 + lA_3 \)) is then written as

\[
i_{hkl}(u, v, w) = \frac{\Phi \Phi^*}{\sigma}  \frac{1}{\sigma} F_{hkl}^* F_{hkl} D(u, v, w) D^*(u, v, w) ,
\]

where \( \sigma \) is the volume of the scattering domain and \( u, v, w \) are related to the components of the scattering vector by

\[
|s_1| = hA_1 + u, \quad |s_2| = kA_2 + v, \quad |s_3| = lA_3 + w.
\]

The shape transform must be normalized to the volume of the scattering domains and therefore the intensity expression becomes

\[
i_{hkl}(u, v, w) = \frac{1}{\Omega} |F_{hkl}|^2 |S(u, v, w)|^2
\]

with

\[
|S(u, v, w)|^2 = |D(u, v, w)|^2 / \sigma.
\]

If the overall distribution of the sizes of the crystallites in the powder is expressed by a function \( \zeta_N \), the intensity of a powder reflection \( hkl \) is then given by

\[
i(s) = \frac{1}{4\pi \Omega s^2} |F_{hkl}|^2 \sum_{\Delta A} \zeta_N |S_N(u, v, w)|^2 dA ,
\]

where \( s \) is the modulus of the scattering vector and \( dA \) is the element of the surface common to the sphere of radius \( s \) and to the node.

This equation shows that it is possible to obtain directly the distribution of the sizes and forms of the crystallites from the intensity distribution \( I(s) \) (Bertaut, 1950).

III. The case of very small crystallites with needle-like shapes

The case which will be considered is that of needle-shaped crystallites for which the length (for example parallel to the \( a_3 \) axis) comprises a great number of unit-cell repetitions, while the cross section (parallel to the \( a_1, a_2 \) plane) contains a small number \( n \) of unit cells \( (n < 10) \).

In this case, it can be verified that the shape transform of a crystallite, \( D(s_1, s_2, s_3) \), has non-negligible values along \( s_3 \) only in the interval \( \Delta s_3 \) which is small enough to admit the structure factor \( F(s_1, s_2, s_3) \) as constant in this interval, whereas the large extension of the shape transform \( D(s_1, s_2, s_3) \) in the \( (s_1, s_2) \) plane needs to take into account the variation of \( F \) with \( s_1 \) and \( s_2 \).

From (2), the amplitude diffracted by such a needle about a geometrical node \( hkl \) should be written as

\[
\Phi_{hkl}(u, v, w) = (1/\Omega) F_r(s_1, s_2) S(u, v, w).
\]

The intensity of a powder reflection can thus be expressed as

\[
I(s) = \frac{1}{4\pi \Omega s^2} \int |F_r(s_1, s_2)|^2 |S(u, v, w)|^2 dA .
\]

We shall develop the calculation method of this integral for two types of reflections: for the ‘basal’ reflections contained in the reciprocal plane perpendicular to the direction of elongation of the needles, the integration method may be simplified; for the arbitrary \( hkl \) reflections, it is necessary to employ a more complicated integration method.
(1) Calculation procedure for the 'basal' reflections

Let us reconsider the example of a crystallite elongated along \( a_3 \) with its cross section parallel to the \((a_1, a_2)\) plane. In this case, the intensity of each reflection is localized within a platelet-shaped domain which is extended in the \((A_1, A_2)\) plane with a small thickness along \( A_3 \) (see Fig. 1).

In this case, the 'basal' reflections for which the powder profiles will be calculated are indexed \( hkl \).

Let \( s_0 \) be the radius vector of the center of any \( hkl \) node and \( s \) any vector within the same domain. Let us call \( s_p \) the projection of \( s \) in the \((A_1, A_2)\) plane, \( \varphi \) the angle between \( s_p \) and \( s_0 \) (Fig. 2) and \( \psi \) the angle between \( s \) and \( s_p \). The integral in (7) can be simplified as follows.

Let \( O' \) be the center of the \( hkl \) node. Let us define from \( O' \) a new axis system \((X, Y, Z)\) in which \( O'X \) and \( O'Y \) are respectively parallel and perpendicular to \( s_0 \), \( O'Z \) is along \( A_3 \).

The position of a point with respect to the new coordinates will be \((X, Y, Z)\) with

\[
\begin{align*}
X &= s_p \cos \varphi - s_0 = s \cos \psi \cos \varphi - s_0, \\
Y &= s_p \sin \varphi = s \cos \psi \sin \varphi, \\
Z &= s \sin \psi .
\end{align*}
\]

As the thickness along \( Z \) of the plate-like domain is very small, the \( \psi \) angle is small and we can write

\[
\begin{align*}
X &\approx s \cos \varphi - s_0, \\
Y &\approx s \sin \varphi .
\end{align*}
\]

In addition, the vertical curvature of the surface common to the sphere of radius \( s \) and to the plate-like domain can be neglected.

Therefore, the sphere of radius \( s \) can be replaced by a cylinder with the same radius and with the generating line parallel to \( A_3 \).

In this case, the surface element becomes \( dA = sd\varphi dZ \); \(|S(u, v, w)|^2\) becomes \(|S(X, Y, Z)|^2\); \(|F(s_1, s_2)|^2\) becomes a function \( |F_{hkl}(X, Y)|^2 \), variable with \( X \) and \( Y \) around the value \( |F_{hkl}|^2 \) at the center of the \( hkl \) node [then, because of (9), \( F_{hkl}(X, Y) \) varies only with \( s \) and \( \varphi \)], and (7) becomes

\[
I(s) \approx \frac{1}{4\pi s^2} \int_Z \int_\varphi |F_{hkl}(X, Y)|^2 |S(X, Y, Z)|^2 d\varphi dZ .
\]

The square of the shape-transform function can be decomposed to

\[
\]

Then the intensity for a basal \( hkl \) reflection finally becomes

\[
I(s) = \frac{1}{4\pi s^2} \int_\varphi |F_{hkl}(X, Y)|^2 |S(X, Y)|^2 d\varphi \times \int_Z |S(Z)|^2 dZ .
\]

The calculation of the \(|S(X, Y)|^2\) function is given for the case of identical parallelepiped-shape needles with rectangular cross sections. The square of the shape-transform function is (Guinier, 1964)

\[
|S|^2 = \frac{\sin^2 \pi l_{a1} X \sin^2 \pi l_{a2} Y \sin^2 \pi l_{a3} Z}{l_{a1} \pi^2 X^2 \ l_{a2} \pi^2 Y^2 \ l_{a3} \pi^2 Z^2},
\]

where \( l_{a1}, l_{a2}, \text{ and } l_{a3} \) are the dimensions of the needle.

Table 1. Flowchart

```
START

INPUT DATA
FROM CARDS
a, b, c, \( \alpha, \beta, \gamma \), \( s_{\text{min}}, s_{\text{max}} \), etc.

DEFINITION OF THE
REFLECTING DOMAIN

DEFINITION OF THE
ORIENTATION OF THE
REFLECTING DOMAIN

INTERSECTION OF THE REFLECTING
DOMAIN WITH THE INTEGRATION
SPHERE OF RADIUS \( s \)

FINDING THE COORDINATES
OF POINTS WITH THIS \( s \),
AND WITHIN THE COHERENT DOMAIN

CALCULATION OF \( F^2 \)
FOR THESE POINTS

CALCULATION OF \( S^2 \)
FOR THESE POINTS

CALCULATION OF THE INTEGRAL

\( S = S + \Delta S \)

\( S > s_{\text{max}} \)  YES

\( S \leq s_{\text{max}} \)  NO

OUTPUT
\( S \text{ vs } I_{\text{obs}}(s) \)
```
But it is more realistic to consider in the sample a size distribution of the needles. In this case, the function $|S|^2$ is better represented (Ergun, 1970; Rousseaux, 1975; Rousseaux & Tchoubar, 1975; Khattak & Cox, 1977) by a product of three Cauchy-type functions:

$$
|S|^2 = \frac{l_{a1}}{(1 + \pi X l_{a1})^2} \frac{l_{a2}}{(1 + \pi Y l_{a2})^2} \frac{l_{a3}}{(1 + \pi Z l_{a3})^2},
$$

where $l_{a1}$, $l_{a2}$, $l_{a3}$ are the mean sizes of the needles along each direction.

The flowchart of the program which allows the computation of the profiles of the $hkl0$ reflection, with (11) and (13), is given in Table 1.

(2) Calculation procedure for any $hkl$ reflection

In Fig. 1, the intersection of the sphere of radius $s$ with any $hkl$ domain can be seen. In this general case, equations (8) become

$$
X = s \cos \psi \cos \varphi - s_0,
Y = s \cos \psi \sin \varphi,
Z = s \sin \psi - s_0 \sin \psi_0,
$$

where $\psi$ is the angle between $s$ and $s_m$ and $\psi_0$ is the angle between $s_0$ and its projection $s_{p0}$ on the $(A_1, A_2)$ plane. The surface element $dA$ is

$$
dA = s^2 \cos \psi d\psi d\varphi = s d\varphi dZ.
$$

Then (7), giving now the intensity of the $hkl$ reflection, takes the form

$$
I(s) = \frac{1}{4\pi \Omega s} \int \int \int |F_{hkl}(X, Y)|^2 |S(X, Y, Z)|^2 \cos \psi d\psi d\varphi
$$

which from (12) or (13) can be written

$$
I(s) = \frac{1}{4\pi \Omega s} \int \int \cos \psi |S(Z)|^2
$$

$$
\times \left[ \int |F_{hkl}(X, Y)|^2 |S(X, Y)|^2 d\varphi \right] d\psi.
$$
IV. Application to Eskisehir sepiolite fibers

Sepiolite is a magnesium silicate of the clay mineral group with an ideal chemical formula for the half unit cell of $\text{Si}_{12}\text{Mg}_8\text{O}_{32}.n\text{H}_2\text{O}$. Its structure can be schematized by a quincunx arrangement of talc-type layers separated by parallel channels of about $7 \times 13$ Å (Fig. 3). The space group as given by Brauner & Preisinger (1956) is orthogonal $Pn cn$ with lattice parameters $a = 13.4$, $b = 26.9$, $c = 5.24$ Å. Eskisehir sepiolite is the most poorly crystallized member of the sepiolite family.

Electron microscopy shows (a) the fibrous nature of the crystallites with average lengths of about 500 Å (Rautureau & Yücel, 1976) (Fig. 4); (b) the very small development of the crystallites in the cross-sectional plane of the fibers (Fig. 5).

Since the $hk0$ reflections were investigated in the first place, the shape functions to be used in the profile calculations are deduced from the high-resolution electron micrographs.

The experimental X-ray diagram is given on an absolute scale (electron units per unit cell). We do this by equalizing, at large scattering angles, the experimental curve to the theoretically calculated 'total gas curve' for the sample (Pons et al., 1980).

The results of the calculations are given in Fig. 6. Curve (b) shows a calculated profile of the 110 reflection when only the particle shape is taken into account by using (12) (the structure factor is assumed constant within the plate-like domain). In curve (c), the variation of the structure factor is now introduced. Curve (d) corresponds to the same case as (c) where (12) is replaced by (13).

As can be seen, the agreement between the calculated and experimental diagrams is much better and more meaningful when both the variation of the structure factor and a distribution of particle sizes are taken into account.

References