Recording and Calculation of \(hk\) Rod Intensities in Case of Diffraction by Highly Oriented Powders of Lamellar Samples

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Abstract

The aim of this paper is to describe a technique for recording the intensity distribution along definite crystallographic directions by using a classical \(\theta,2\theta\) powder goniometer. This method was developed for application to highly oriented powders. In the calculation of simulated spectra, the partial misorientation of the particles is considered. The reflection intensities and profiles are compared for different shapes of the misorientation function \(N(\alpha)\).

Introduction

Fine dispersed minerals are usually investigated by powder diffraction methods. Theoretical works have been developed to account for the intensities produced by perfectly isotropic powders (Warren, 1941; Wilson, 1949; Brindley & Merin, 1951; Ruland, 1967). For platelike particles, it is generally impossible to obtain ideally random samples. The particles have a tendency to partial orientation which changes the relative intensities and modifies the profiles. In calculating intensities, the orientation function has been considered by Guentert & Cvicevich (1964), Rutland & Tompa (1968), de Courville, Tchoubar & Tchoubar (1979), and Plançon (1980).

In the powder diffraction technique, one has the disadvantage of overlapping of intensities. This difficulty can be overcome by using highly oriented powders with axial texture. Overlapping can be avoided by scanning along the directions passing through the origin of reciprocal space with the aid of a powder goniometer (Krinari, 1975). Another technique employs a two- or three-circle spectrometer for scanning along the generating line of an \((hk)\) cylinder (Ellenson, Semmingsen, Guerard, Onn & Fischer, 1977; Hastings, Ellenson & Fischer, 1979).*

We describe: (i) an experimental technique for intensity recordings which consist in scanning along \((hk)\)-cylinder-generating lines by using a classical powder goniometer without \(\theta,2\theta\) coupling; and (ii) the method of calculation of simulated spectra which will be compared with the experimental ones. This calculation includes the experimentally determined orientation functions.

This method, allowing one to resolve quantitatively order–disorder problems, is convenient not only for lamellar particles but also for fibrous systems.

1. Experimental

The reciprocal space of a layer crystal consists of \((hk)\) rods perpendicular to the \((a,b)\) plane of the layer (Fig. 1). Their cross section depends on the area of the layer. In this cross section, the intensity varies with the shape transform of the layer, while along the

*Because of the axial texture the different \(hk\) rods which are located at the same distance from the origin overlap and generate \((hk)\) cylinders. So the scanning provides the intensity along an \((hk)\)-cylinder-generating line.

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rod the intensity distribution depends on the nature of
the layers and on their stacking mode (Hendricks &
Teller, 1942; Mérié, 1949; Jagodzinski, 1949; Kakinoki &
Komura, 1952, 1954a, b; Cowley, 1976a, b; Drits &
Sakharov, 1976; Plançon & Tchoubar, 1977; Plançon, 1981;
Sakharov, Naoumov & Drits, 1982).
For a crystal with large dimensions and no mosaic disorder, the $hk$ rods become infinitely thin.

I.1. Geometrical conditions required for recording the intensity along an $hk$ rod
The experiments are performed in transmission geometry. Let us consider a single crystal with large
dimensions and no mosaic spread. The recording of
the intensity $i_{hk}(Z)$ at height $Z$ along the $hk$ rod is
obtained by setting the sample and the counter as in
Fig. 2. The normal to the sample $n_s$ and the $hk$ rod lie
in the plane normal to the goniometer axis. The
rotation angles $\theta_s$ and $\theta_c$ for the sample and the
counter are related by

$$s = |s| = (s_0^2 + Z^2)^{1/2}$$
$$\phi = \arctan(Z/s_0)$$
$$\theta_s = 2 \arcsin(\lambda s/2)$$
$$\theta_c = \theta_s/2 - \phi$$

where $s_0 = |s_0|$ is the distance of the $hk$ rod from the
origin of the reciprocal space; $s$ is the scattering vector;
$\lambda$ is the wavelength; and $\theta_c$ and $\theta_s$ are positive when
measured anticlockwise.

These geometrical conditions are valid for an
oriented powder, but in that case $n_s$ would be defined
with respect to the ‘mean’ plane of the sample.

I.2. Experimental determination of the orientation function
A general procedure has been described by Taylor
& Norrish (1966) for powders of highly oriented
particles. The orientation of the particles in the sample
has a revolution symmetry around $n_s$ and can be
defined by a function $N(\alpha)$ which is proportional to
the number per unit solid angle of particles with
normals making an angle $\alpha$ with $n_s$.

To determine the $N(\alpha)$ function, one measures the
integrated intensity of an $I_{001}$ reflection as the sample
rotates around the goniometer axis by an angle $\alpha$ and
the counter remains fixed at the angle $\theta_c = 2\theta_{001}$. The
starting position $\alpha = 0^\circ$ corresponds to the
symmetrical-reflection geometry ($n_s\parallel s$, Fig. 3).

The entire sample is irradiated by the X-ray beam.
In order to neglect the sample absorption effect, it is
necessary to select the most convenient wavelength
and to reduce the sample dimensions. Generally, it
is a rectangular flake ($L \times l \times e$) with $l<1$ mm and
e $<0.5$ mm. The magnitude of $L$ does not affect the
determination. Under these conditions, $I_{001}(\alpha)$ varies
like $N(\alpha)$. The normalization of $N(\alpha)$ is given by:

$$N(\alpha) = I_{001}(\alpha) \int_0^\infty I_{001}(\alpha) 2\pi \sin \alpha \, d\alpha. \hspace{1cm} (1)$$

II. Calculation of the intensities diffracted by highly
oriented samples
The recording of intensity is made with step scanning.
For each step, the sample and the counter are fixed in
the asymmetrical-transmission geometry described in
§ 1.1. Owing to the misorientation, the experimental data correspond to a partial integration of the intensity inside the \( h k \) rods. This integration along an \( (h k) \)-cylinder-generating line is given by (Plançon, 1980)

\[
I_{hk}(s) = \frac{1}{s} \frac{1}{\Omega_\sigma} \sum_{hk} \left[ \int N_e(s, \varphi) i_{hk}(Z) T(X) \, d\varphi \right],
\]

(2)

where

\[
\sum_{hk} \text{ means the summation on all } h k \text{ rods which go over into an } (hk) \text{ cylinder;}
\]

\( \varphi = (S, S_0) \);

\( X \) and \( Z \) coordinates perpendicular to and along the rod axis are \( s \cos \varphi - s_0 \) and \( s \sin \varphi \) respectively (Fig. 4);

\( i_{hk}(Z) \) represents the intensity along the \( (hk) \) rod.

This function depends only on the structure of the elementary particles (nature and stacking of layers); \( T(X) \) is defined from the size and shape of the coherent domain of the layers. For domains having an isometric shape like a square or a hexagon, the shape function is well approximated by a circle (Brindley & Merig, 1951). \( T(X) \) then becomes dependent only on the circle radius. For the anisometric domains, a good approximation is obtained by a rectangular shape \( L \times l \) (Rousseaux & Tchoubar, 1975). In that case, \( T(X) \) depends on the length \( L \) and width \( l \);

\( \Omega_\sigma \) is the unit cell area and \( \sigma \) the coherent domain area;

\( N_e(s, \varphi) \) is given by the expression (Plançon, 1980)

\[
N_e(s, \varphi) = \frac{1}{2\pi} \int_0^{2\pi} N(\varphi) \, d\psi,
\]

(3)

where \( N(\varphi) \) is defined by (1).

The three angles \( \alpha, \psi, \varphi \) are related by

\[
\alpha = \arccos[-\sin \Delta \theta \sin \varphi + \cos \Delta \theta \cos \varphi \cos \psi],
\]

where \( \Delta \theta = \theta_c - \theta_v/2 \) represents the deviation of the sample position with respect to the symmetrical \( \theta, 2\theta \) transmission position.

One can notice from (2) that the limits of integration will increase with the half-width at half-maximum (HWHM) of the function \( N(\varphi) \) and change for each value of \( s \).

Since for each value of \( s \) there corresponds a value \( Z_m = (s^2 - s_0^2)^{1/2} \), it is possible to draw the calculated profiles with respect to \( Z_m \).

An illustration of intensity calculations is given for the graphite intercalation compound \( \text{KC}_8 \) (Rousseaux, Plançon, Tchoubar, Guerard & Lagrange, 1981). This compound is obtained by inserting K layers between carbon layers in a highly oriented pyrolytic graphite (HOPG) sample (Moore, Ubbelhode & Young, 1964). HOPG samples have a well defined c direction (mosaicity 0-5°) but a random orientation in a and b directions. After the intercalation process, the mosaicity broadens to 3°. In this compound the reciprocal rods \( 02, 11, 11, 02, 11 \) and \( 11 \) are located at the same distance from the reciprocal-space origin. For a film it is only possible to access to the \( I_{02,11}(Z) \) intensity corresponding to the summation of these different rods. This intensity is represented in Fig. 5.

To illustrate the role of \( N(\varphi) \), one considers a set of triangular functions which are normalized according to (1). The maxima of these curves are respectively 2450, 390 and 16 for HWHM values 0-4, 1 and 5°. Fig. 6 gives the diffracted intensities calculated for: (i) full line, HWHM = 5°; and (ii) dotted line, HWHM = 1°. It can be concluded that a small misorientation...
decreases drastically the measured intensities. This effect is enhanced with HWHM = 0.4° for which the ratio \( \frac{(1101)_{0.4}}{(1101)_{5}} \) reaches 8.1. Therefore, the narrower \( N(z) \) is, the more convenient is the method.

Furthermore, we get only the relative intensities in the experiments. Fig. 7 shows this relative evolution of the peaks (heights and widths) for the three triangular functions \( N(z) \). The curves have been normalized with respect to the first peak. We observe that a small misorientation leads to an evident decrease of the intensity as \( s \) increases. In addition, the broadening of the peaks expands with the HWHM value.

Moreover the rôle of the shape of the function \( N(z) \) has been studied. A calculation has been performed for a rectangular function with HWHM = 1°. It is concluded that the absolute intensities of the spectra are modified as follows: \( I_{\text{Rect}}/I_{\text{Tria}} \approx 1.7 \), while to a first approximation the relative intensities of the reflections and their profiles are not changed. Then a slight mistake in the determination of the experimental orientation-function shape has little weight in the fitting of experimental data with calculated ones.

### Conclusion

This paper gives a method which allows the structural study of highly orientable powders (like films). This method takes into account the actual orientation function of the crystallites and minimizes the overlapping of reflections. Then it is possible to compare accurately the experimental spectrum profiles with simulated curves, especially to perform order-disorder studies. It only requires a classical powder goniometer without \( 2\theta \) coupling and allows experiments in any controlled atmosphere, temperature or pressure.

We applied this technique successfully to the study of pyrographite intercalation compounds (\( \text{KC}_8 \) and \( \text{FeCl}_3 \)).

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### References