

## 2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

The method is of doubtful use for structure determination or quantitative analysis. The wide range of wavelengths, continually varying absorption and profile widths, and other factors create a major difficulty in deriving accurate values of the relative intensities.

Conventional energy-dispersive diffraction methods using white X-rays and a solid-state detector are described in Chapter 2.5 and Section 5.2.7.

## 2.3.3. Specimen factors, angle, intensity, and profile-shape measurement

The basic experimental procedure in powder diffraction is the measurement of intensity as a function of scattering angle. The profile shapes and  $2\theta$  angles are derived from the observed intensities and hence the counting statistical accuracy has an important role. There is a wide range of precision requirements depending on the application and many factors are involved: instrument factors, counting statistics, profile shape, and particle-size statistics of the specimen. *The quality of the specimen preparation is often the most important factor in determining the precision of powder diffraction data.*

D. K. Smith and colleagues (see, for example, Borg & Smith, 1969; see also Yvon, Jeitschko & Parthé, 1977) developed a method for calculating theoretical powder patterns from well determined single-crystal structures and have made available a Fortran program (Smith, Nichols & Zolensky, 1983). This has important uses in powder diffraction studies because it provides reference data with correct  $I$ 's and  $d$ 's, free of sample defects, preferred orientation, statistical errors, and other factors. The data can be displayed as recorded patterns by using plot parameters corresponding to the experimental conditions (Subsection 2.3.3.9). Calculated patterns have been used in a large variety of studies such as identification standards, computing intermediate members of an isomorphous series, testing structure models, ordered and disordered structures, and others. Many experiments can be performed with simulated patterns to plan and guide research. The method must be used with some care because it is based on the small single crystal used in the crystal-structure determination and the large powder samples of minerals and ceramics, for example, may have a different composition. Errors in the structure analysis are magnified because the powder intensities are based on the squares of the structure factors.

The Lorentz and polarization factors for diffractometry geometry have been discussed by Ladell (1961) and Pike & Ladell (1961).

Smith & Snyder (1979) have developed a criterion for rating the quality of powder patterns; see also de Wolff (1968a).

## 2.3.3.1. Specimen factors

Ideally, the specimen should contain a large number of small equal-sized randomly oriented particles. The surface must be flat and smooth to avoid microabsorption effects, *i.e.* particle interferences which reduce the intensities of the incident and reflected beams and can lead to significant errors (Cline & Snyder, 1983). The specimen should be homogeneous, particularly if it is a mixture or if a standard has been added. Low packing density and specimen-surface displacement (§2.3.1.1.6) may cause significant errors. It is recommended that the powder and the prepared specimen be examined with a low-power binocular optical microscope. Smith & Barrett (1979), Jenkins, Fawcett, Smith, Visser, Morris & Frevel (1986), and Bish & Reynolds (1989) have surveyed methods of specimen preparation

and they include bibliographies on special handling problems. Powder diffraction standards for angle and intensity calibration are described in Section 5.2.9.

## 2.3.3.1.1. Preferred orientation

Preferred orientation changes the relative intensities from those obtained with a randomly oriented powder sample. It occurs in materials that have good cleavage or a morphology that is platy, acicular or any special shape in which the particles tend to orient themselves in specimen preparation. The micas and clay minerals are examples of materials that exhibit very strong preferred orientation. When they are prepared as reflection specimens, the basal reflections dominate the pattern. It is common in prepared thin films where preferred orientation occurs frequently or may be purposely induced to enhance certain optical, electrical, or magnetic properties for electronic devices. By comparison of the relative intensities with the random powder pattern, the degree of preferred orientation can be observed.

Powder reflections take place from crystallites oriented in different ways in the instrument geometries as shown in Fig. 2.3.1.2. In reflection specimen geometry with  $\theta$ - $2\theta$  scanning, reflections can occur only from lattice planes parallel to the surface and in the transmission mode they must be normal to the surface. In the Seemann-Bohlin and fixed specimen with  $2\theta$  scanning methods, the orientation varies from parallel to about  $45^\circ$  inclination to the surface. The effect of preferred orientation can be seen in diffraction patterns obtained by using the same specimen in the different geometries.

The effect is illustrated in Fig. 2.3.3.1 for *m*-chlorobenzoic acid,  $C_7H_5ClO_2$ , with reflection and transmission patterns and the pattern calculated from the crystal structure. The degree of preferred orientation is shown by comparing the peak intensities of four reflections in the three patterns:

( <i>hkl</i> )	(120)	(200)	(040)	(121)
Reflection	9.8	0.6	1.6	2.5
Transmission	5.2	0.5	0.7	9.3
Calculated	3.0	6.6	4.0	9.1

Care is required to make certain the differences are not caused by a few fortuitously oriented large particles.

Various methods have been used to minimize preferred orientation in the specimen preparation (Calvert, Sirianni, Gainsford & Hubbard, 1983; Smith & Barrett, 1979; Jenkins *et al.*, 1986; Bish & Reynolds, 1989). These include using small particles, loading the powder from the back or side of the specimen holder, and cutting shallow grooves to roughen the surface. The powder has also been sifted directly on the surface of a microscope slide or single-crystal plate that has been wetted with the binder or petroleum jelly. Another method is to mix the powder with an inert amorphous powder such as Lindemann glass or rice starch, or add gum arabic, which after setting can be reground to obtain irregular particles. Any additive reduces the intensity and the peak-to-background ratio of the pattern. A promising method that requires a considerable amount of powder is to mix it with a binder and to use spray drying to encapsulate the particles into small spheres which are then used to prepare the specimen (Smith, Snyder & Brownell, 1979).

Preferred orientation would not cause a serious problem in routine identification providing the reference standard had a similar preferred orientation and both patterns were obtained with the same diffractometer geometry. However, when accurate values of the relative intensities are required, as in crystal-

### 2.3. POWDER AND RELATED TECHNIQUES: X-RAY TECHNIQUES

structure refinement and quantitative analysis, it may be the major factor limiting the precision.

In practice, it is very difficult to prepare specimens that have a completely random orientation. Even materials that do not have good cleavage or special morphological forms, such as quartz and silicon, show small deviations from a completely random orientation. These show up as errors in the structure refinement and a correction factor is required.

An empirical correction factor determined by the acute angle  $\varphi$  between the preferred-orientation plane and the diffracting plane ( $hkl$ )

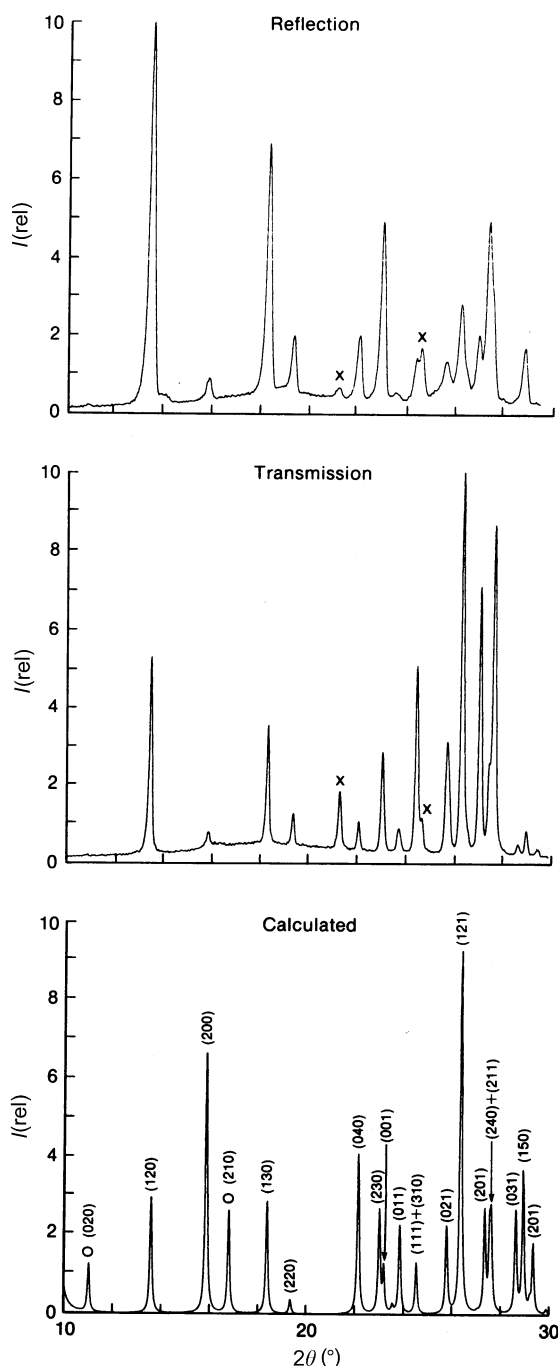


Fig. 2.3.3.1. Differences in relative intensities due to preferred orientation as seen in synchrotron X-ray patterns of *m*-chlorobenzoic acid obtained with a specimen in reflection and transmission compared with calculated pattern. Peaks marked  $\times$  are impurities,  $O$  absent in experimental patterns.

Table 2.3.3.1. Preferred-orientation data for silicon

$hkl$	$R(\text{Bragg})$ (%)	GP
1 1 1	1.86	-0.11
2 2 0	2.02	-0.11
3 1 1	2.01	0.17
4 0 0*	0.86	-0.15
3 3 1	1.73	-0.19
4 2 2	2.43	0.04
5 1 1	1.36	0.19
5 3 1	2.44	-0.08
4 4 2	1.69	-0.19
6 2 0	1.25	0.29
5 3 3	2.40	-0.04

\* Selected preferred orientation plane.

Table 2.3.3.2.  $R(\text{Bragg})$  values obtained with different preferred-orientation formulae

	$R(\text{Bragg})$		
	Si	SiO <sub>2</sub>	Mg <sub>2</sub> GeO <sub>4</sub>
No corrections	3.50	2.57	12.5
Gaussian	1.65	1.60	5.71
Exponential	0.75	1.83	5.30
March/Dollase	0.75	1.64	4.87
Preferred-orientation plane	100	211	100

$$I(\text{corr.}) = I(hkl)P(hkl)\varphi \quad (2.3.3.1)$$

can be used (Will *et al.*, 1988). Three functions have been used to represent  $P(hkl)\varphi$  and the term GP is the variable refined:

$$P(hkl)\varphi = \exp(-GP\varphi^2) \quad (2.3.3.2)$$

(Rietveld, 1969) for transmission specimens;

$$P(hkl)\varphi = \exp[GP(\pi/2 - \varphi^2)] \quad (2.3.3.3)$$

for reflection specimens; and

$$P(hkl)\varphi = (GP^2 \cos^2 \varphi + \sin^2 \varphi/GP)^{-3/2} \quad (2.3.3.4)$$

(Dollase, 1986).

These functions are quite similar for small amounts of non-randomness. The preferred-orientation plane is selected by trial and error. For example, a modified fast routine of the powder least-squares refinement program with only seven cycles of refinement on each plane for the first dozen allowed Miller indices can be used to find the plane that gives the lowest  $R(\text{Bragg})$  value as shown in Table 2.3.3.1. All three functions improve the  $R(\text{Bragg})$  value as shown in Table 2.3.3.2 but the evidence is not conclusive as to which is the best. More research is required in this area. Several specimens made of the same material may show different preferred-orientation planes, and in some cases the preferred-orientation plane never occurred in the crystal morphology. A more complicated method examines the polar-axis density distribution using a cubic harmonic expansion to describe the crystallite orientation of a rotating sample (Järvinen, Merisalo, Pesonen & Inkinen, 1970; Ahtee, Nurmela, Suortti & Järvinen, 1989; Järvinen, 1993).