## 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 $(hkl)$
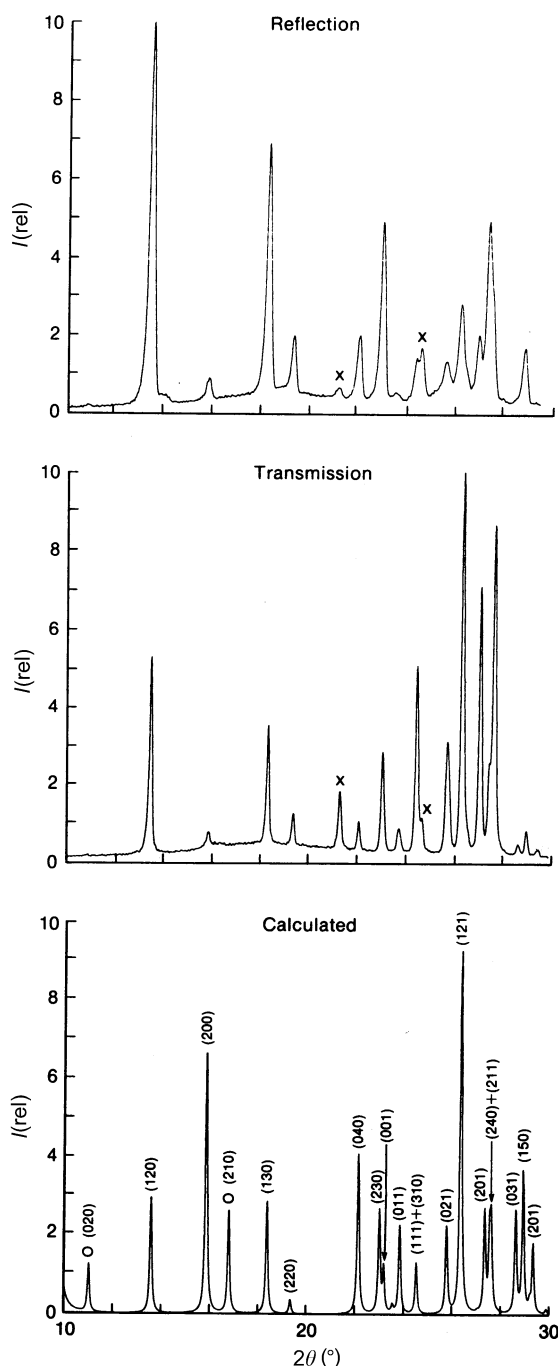


Fig. 2.3.3.1. Differences in relative intensities due to preferred orientation as seen in synchrotron X-ray patterns of *m*-chlorobenzoic acid obtained with a specimen in reflection and transmission compared with calculated pattern. Peaks marked × are impurities, *O* absent in experimental patterns.

Table 2.3.3.1. *Preferred-orientation data for silicon*

| $h\ k\ l$ | $R$(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(Bragg) values obtained with different preferred-orientation formulae*

| | $R$(Bragg) | | |
|---|---|---|---|
| | Si | SiO$_2$ | Mg$_2$GeO$_4$ |
| 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 |

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

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:

$$P(hkl)\varphi = \exp(-\text{GP}\varphi^2) \qquad (2.3.3.2)$$

(Rietveld, 1969) for transmission specimens;

$$P(hkl)\varphi = \exp[\text{GP}(\pi/2 - \varphi^2)] \qquad (2.3.3.3)$$

for reflection specimens; and

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

(Dollase, 1986).

These functions are quite similar for small amounts of nonrandomness. 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 $R$(Bragg) value as shown in Table 2.3.3.1. All three functions improve the $R$(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).

**references**