

3.2. THE PHYSICS OF DIFFRACTION FROM POWDERS

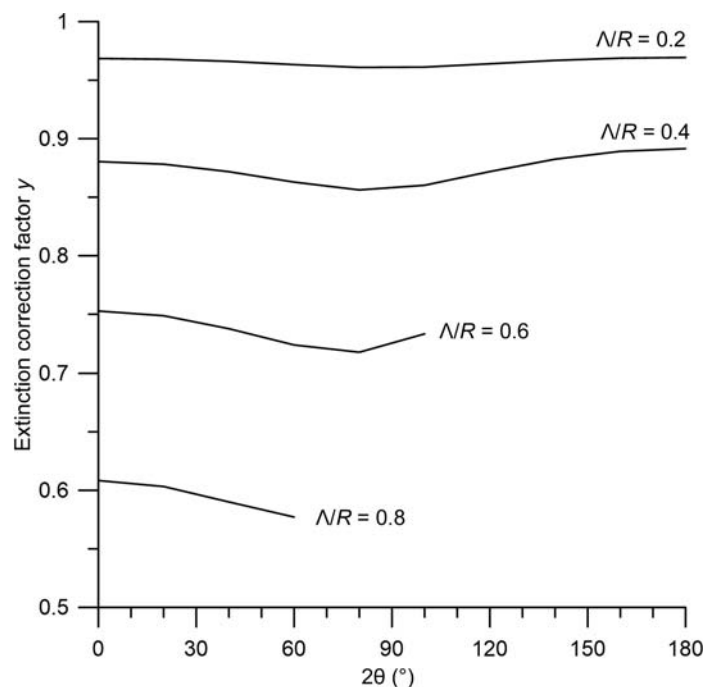


Figure 3.2.6
Extinction correction for spherical particles according to Thorkildsen & Larsen (1998).

as the kinematic approximation. This is a consequence of the Born approximation, whereby the diffracted intensity from one grain is proportional to the number of atoms within it. However, as the size of the crystallite grows, so will the intensity of the diffracted wave within it. The diffracted radiation will be re-diffracted back into the incident beam, leading to a measured integrated intensity less than the kinematic value, by a ratio $y(\mathbf{G}) = I_{\text{obs}}(\mathbf{G})/I_{\text{kinematic}}(\mathbf{G})$, which depends on the particular Bragg reflection \mathbf{G} . This is the phenomenon of primary extinction, which can be understood within the framework of the dynamical theory of diffraction. The following discussion ignores absorption.

The relevant physical parameter is the extinction length Λ . For X-rays,

$$\Lambda(\mathbf{G}) = \frac{V}{r_e \lambda P |A_{\mathbf{G}}|},$$

where V is the unit-cell volume, $r_e = 2.82 \times 10^{-15}$ m, $A_{\mathbf{G}}$ is the structure factor, and P is the polarization factor: 1 or $\cos^2 2\theta$ for S or P polarization, respectively. For neutrons,

$$\Lambda(\mathbf{G}) = \frac{V}{\lambda |A_{\mathbf{G}}^{(n)}|}.$$

As an example, the 111 reflection of Si has an extinction length of 7.2 μm for 1.54 \AA X-rays and 50 μm for 1.59 \AA neutrons. Intensities from the kinematic theory are correct in the limit that the coherent grain size is much less than Λ . Note that extinction is most significant for the strongest reflections in a powder-diffraction pattern.

There are no exact calculations of extinction available for sample geometries applicable to powder samples, but Thorkildsen and Larsen have obtained a rigorous series solution for spherical particles of radius R in powers of Λ/R (Thorkildsen & Larsen, 1998). To lowest order,

$$y = 1 - (R/\Lambda)^2 f_1(\theta), \text{ where}$$

$$f_1(\theta) = \frac{8}{5\pi \sin 2\theta} (1 + \pi\theta - 4\theta^2 - \cos 4\theta - \theta \sin 4\theta)$$

for $0 \leq \theta \leq \pi/4$

$$= \frac{4}{5\pi \sin 2\theta} (2 - \pi^2 + 6\pi\theta - 8\theta^2 - 2 \cos 4\theta + \pi \sin 4\theta - 2\theta \sin 4\theta)$$

for $\pi/4 \leq \theta \leq \pi/2$.

This first term gives y accurate to 3% for $R/\Lambda \leq 0.4$. Fig. 3.2.6 shows their calculated result up to fifth order.

3.2.4. The Debye scattering equation

The Debye scattering equation is an alternative method to compute the diffraction pattern of a collection of solid grains, which does not rely on a requirement of crystalline periodicity (Debye, 1915). Consequently, it is useful for cases where the grains of the sample are not fragments of idealized crystals, such as are frequently observed in nanoparticles. For a collection of identical grains, each containing N atoms having individual scattering amplitude b_j , $1 \leq j \leq N$, the orientation-average cross section per grain is given by

$$\left\langle \frac{d\sigma}{d\Omega} \right\rangle_{\text{orientation}} = \sum_j b_j^2 + \sum_j \sum_{k \neq j} b_j b_k \frac{\sin(2\pi q r_{jk})}{2\pi q r_{jk}},$$

where r_{jk} is the distance between atoms j and k , and the scattering vector $q = 2 \sin \theta / \lambda$. For neutrons, b_j is the scattering length; in the case of multiple isotopes of a given atomic species, one may use the coherent scattering length to obtain the coherent elastic cross section. For X-rays, $b_j = r_e f_j(\sin \theta / \lambda)$, the classical electron radius times the atomic scattering factor, and the cross section must be multiplied by the polarization factor as described in Section 3.2.2.1. This topic is treated in much greater detail in Chapters 3.6, 5.6 and 5.7 of this volume.

3.2.5. Summary

Although a powder-diffraction experiment is simple experimentally, considerable physics goes into determining the actual experimental data. Any user attempting to extract the maximum information from the diffraction data (especially through a Rietveld refinement) ultimately needs to understand all of the factors that affect the experimental data. This chapter provides a succinct summary of the major factors that contribute to the experimental data. Many of these factors are explored in more detail in other chapters of this volume.

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