

3.2. THE PHYSICS OF DIFFRACTION FROM POWDERS

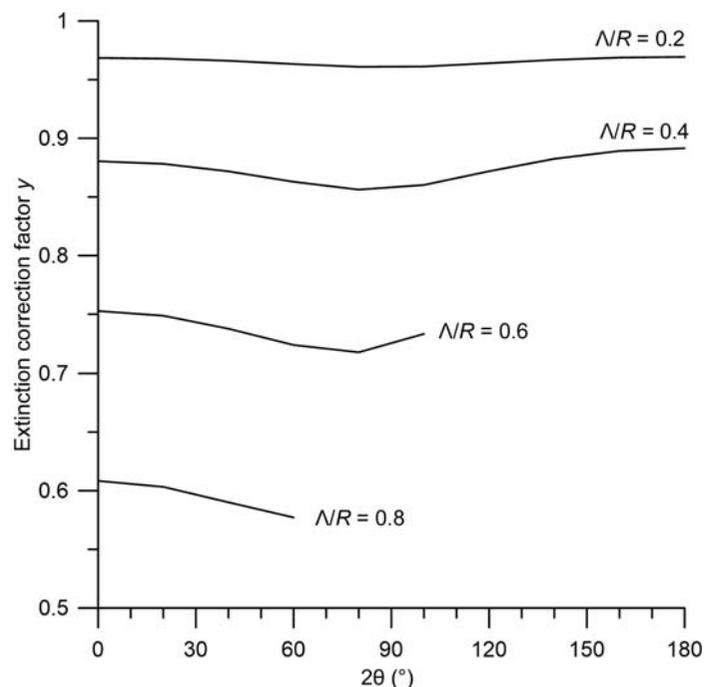


Figure 3.2.6
Extinction correction for spherical particles according to Thorkildsen & Larsen (1998).

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

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

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.

References

- Bindzus, N., Straasø, T., Wahlberg, N., Becker, J., Bjerg, L., Lock, N., Dippel, A.-C. & Iversen, B. B. (2014). *Experimental determination of core electron deformation in diamond*. *Acta Cryst.* **A70**, 39–48.
- Brindley, G. W. (1945). *The effect of grain or particle size on x-ray reflections from mixed powders and alloys, considered in relation to the quantitative determination of crystalline substances by x-ray methods*. *Philos. Mag.* **36**, 347–369.
- Caglioti, G., Paoletti, A. T. & Ricci, F. P. (1958). *Choice of collimators for a crystal spectrometer for neutron diffraction*. *Nucl. Instrum. Methods*, **3**, 223–228.
- Caglioti, G., Paoletti, A. & Ricci, F. P. (1960). *On resolution and luminosity of a neutron diffraction spectrometer for single crystal analysis*. *Nucl. Instrum. Methods*, **9**, 195–198.
- Cheary, R. W. & Coelho, A. (1992). *A fundamental parameters approach to X-ray line-profile fitting*. *J. Appl. Cryst.* **25**, 109–121.

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- Cheary, R. W. & Coelho, A. A. (1998). *Axial divergence in a conventional X-ray powder diffractometer. I. Theoretical foundations*. *J. Appl. Cryst.* **31**, 851–861.
- Coppens, P. (1997). *X-ray charge densities and chemical bonding*. Oxford: International Union of Crystallography/Oxford University Press.
- Debye, P. (1915). *Zerstreuung von Röntgenstrahlen*. *Ann. Phys.* **351**, 809–823.
- Dollase, W. A. (1986). *Correction of intensities for preferred orientation in powder diffraction: application of the March model*. *J. Appl. Cryst.* **19**, 267–272.
- Gozzo, F., De Caro, L., Giannini, C., Guagliardi, A., Schmitt, B. & Prodi, A. (2006). *The instrumental resolution function of synchrotron radiation powder diffractometers in the presence of focusing optics*. *J. Appl. Cryst.* **39**, 347–357.
- Hermann, H. & Ermrich, M. (1987). *Microabsorption of X-ray intensity in randomly packed powder specimens*. *Acta Cryst.* **A43**, 401–405.
- Hewat, A. W. (1979). *Absorption corrections for neutron diffraction*. *Acta Cryst.* **A35**, 248.
- Ida, T. (2010). *Efficiency in the calculation of absorption corrections for cylinders*. *J. Appl. Cryst.* **43**, 1124–1125.
- Järvinen, M. (1993). *Application of symmetrized harmonics expansion to correction of the preferred orientation effect*. *J. Appl. Cryst.* **26**, 525–531.
- Kaduk, J. A. & Reid, J. (2011). *Typical values of Rietveld instrument profile coefficients*. *Powder Diffr.* **26**, 88–93.
- Krivoglaz, M. A. (1969). *Theory of X-ray and thermal-neutron scattering by real crystals*. New York: Plenum Press. (Translated from the Russian by S. Moss.)
- Langford, J. I. & Wilson, A. J. C. (1978). *Scherrer after sixty years: a survey and some new results in the determination of crystallite size*. *J. Appl. Cryst.* **11**, 102–113.
- Larson, A. C. & Von Dreele, R. B. (2004). *General Structure Analysis System (GSAS)*. Los Alamos National Laboratory Report LAUR 86–748. Los Alamos, USA.
- Loopstra, B. O. & Rietveld, H. M. (1969). *The structure of some alkaline-earth uranates*. *Acta Cryst.* **B25**, 787–791.
- March, A. (1932). *Mathematische Theorie der Regelung nach der Korngestalt bei affiner Deformation*. *Z. Kristallogr.* **81**, 285–297.
- Marshall, W. & Lovesey, S. W. (1971). *Theory of Thermal Neutron Scattering*. Oxford: Clarendon.
- Masson, O., Dooryhée, E. & Fitch, A. N. (2003). *Instrument line-profile synthesis in high-resolution synchrotron powder diffraction*. *J. Appl. Cryst.* **36**, 286–294.
- Patterson, A. L. (1939). *The Scherrer formula for X-ray particle size determination*. *Phys. Rev.* **56**, 978–982.
- Popa, N. C. (1998). *The (hkl) dependence of diffraction-line broadening caused by strain and size for all Laue groups in Rietveld refinement*. *J. Appl. Cryst.* **31**, 176–180.
- Riello, P., Fagherazzi, G., Clemente, D. & Canton, P. (1995). *X-ray Rietveld analysis with a physically based background*. *J. Appl. Cryst.* **28**, 115–120.
- Rietveld, H. M. (1969). *A profile refinement method for nuclear and magnetic structures*. *J. Appl. Cryst.* **2**, 65–71.
- Rodríguez-Carvajal, J. (1993). *Recent advances in magnetic structure determination by neutron powder diffraction*. *Phys. B Condens. Matter*, **192**, 55–69.
- Rodríguez-Carvajal, J. (2001). *Recent developments of the program FULLPROF*. *IUCr Commission on Powder Diffraction Newsletter*, **26**, 12–19.
- Sabine, T. M. (1987). *The N-crystal spectrometer*. *J. Appl. Cryst.* **20**, 23–27.
- Scherrer, P. (1918). *Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen*. *Nachr. Ges. Wiss. Göttingen*, pp. 98–100.
- Smith, D. K. (2001). *Particle statistics and whole-pattern methods in quantitative X-ray powder diffraction analysis*. *Powder Diffr.* **16**, 186–191.
- Soller, W. (1924). *A new precision X-ray spectrometer*. *Phys. Rev.* **24**, 158–167.
- Stephens, P. W. (1999). *Phenomenological model of anisotropic peak broadening in powder diffraction*. *J. Appl. Cryst.* **32**, 281–289.
- Suortti, P. (1972). *Effects of porosity and surface roughness on the X-ray intensity reflected from a powder specimen*. *J. Appl. Cryst.* **5**, 325–331.
- Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *Rietveld refinement of Debye–Scherrer synchrotron X-ray data from Al₂O₃*. *J. Appl. Cryst.* **20**, 79–83.
- Thorkildsen, G. & Larsen, H. B. (1998). *Primary extinction in cylinders and spheres*. *Acta Cryst.* **A54**, 172–185.