

## MODERN XRD METHODS IN MINERALOGY

**Robert E. Dinnebier and Karen Friese**

*Max-Planck-Institute for Solid State Research, Stuttgart, Germany*

**Keywords:** powder diffraction, single crystal diffraction, synchrotron radiation, neutron radiation, diffractometer, structure determination, structure refinement.

### Contents

1. Introduction
2. The Diffraction of X-rays
  - 2.1. The Laue Equations
  - 2.2. The Bragg Equation
  - 2.3. The Ewald Sphere
3. The Generation of the Primary Beam
  - 3.1. Filters and Monochromators
  - 3.2. Detectors
4. Single Crystal Methods
  - 4.1. The Rotation Method
  - 4.2. The Weissenberg Camera
  - 4.3. The Precession Camera
  - 4.4. The Automatic Single Crystal Diffractometer
5. Powder Diffraction
  - 5.1. The Characteristics of a Powder Diffraction Pattern
  - 5.2. Measurement of a Powder Pattern
6. The Position of a Bragg Reflection
7. The Intensity of a Bragg Reflection
  - 7.1. The Atomic Form Factor
  - 7.2. The Structure Factor
  - 7.3. Intensity Corrections
8. The Profile of a Bragg Reflection
  - 8.1. The (Pseudo-)Voigt Function
  - 8.2. Asymmetry Caused by Axial Divergence
  - 8.3. Sample Broadening
9. Crystal Structure Solution
  - 9.1. The Patterson Function
  - 9.2. Direct Methods
  - 9.3. Specialized Methods for Powder Diffraction
10. Crystal Structure Refinement
  - 10.1. Difference Fourier Synthesis
  - 10.2. Powder Pattern Profile Fitting
11. Powder Diffraction in Non-ambient Conditions
  - 11.1. Micro-Reactor
  - 11.2. High Pressure Powder Diffraction
  - 11.3. Energy-Dependent Powder Diffraction
12. Texture, Stress, and Microdiffraction
  - 12.1. Texture

12.2. Stress

12.3. Microdiffraction

Glossary

Bibliography

Biographical Sketch

## Summary

This article describes the basics of crystal structure determination and refinement from X-ray diffraction data, with a focus on applications in mineralogy.

## 1. Introduction

Since the performance of the first X-ray diffraction experiments on a single crystal in 1912, X-ray crystallography has been of major importance in natural sciences and especially in mineralogy. X-ray diffraction provided the ideal means to understand structures of minerals (and other crystalline matter) on an atomic scale. It thus established relationships between the crystal structure and the physical and chemical properties of the material under investigation. In other cases it related the crystal structure to the special thermodynamical conditions under which a mineral (or a rock) was formed, and therefore provided important information for petrology and geology. In particular the powder diffraction method allowed the unambiguous identification of minerals and—with the introduction of quantitative phase analysis—also the quantification of the different phases of a mixture, for example, a rock.

The structure determination of minerals exhibits several typical difficulties. Often the chemical composition is quite variable, requiring a distinct contrast in scattering power of the different elements to allow for successful identification. Two (or more) chemical elements can occupy the same crystallographic site. This frequently leads to different degrees of long- and short-range ordering, which often implies the existence of very weak intensities or diffuse scattering, making X-ray crystallography on minerals far more challenging than crystallography on synthetic materials. This is especially true for the wide range of aluminosilicates, which include most of the rock-forming minerals.

With the availability of neutron and synchrotron radiation sources, new fields of research were developed. The entirely different dependence of the scattering power on the order number of the elements for neutron than for X-ray diffraction makes it possible to distinguish between neighboring elements in the periodic table. Furthermore, neutron diffraction provides the means to determine magnetic structures. On the other hand, the high brilliance, low divergence, and wavelength tunability of synchrotron radiation are of crucial importance for the detection of weak intensities, the measurement of crystals with very large unit cells, and allow use to be made of the effect of anomalous dispersion. In any case, the strongest impact is observed in the field of powder diffraction, where the two new sources enhance the resolution of a powder diffraction pattern by more than an order of magnitude compared with laboratory sources. Consequently, more complicated crystal structures can be solved with increasing accuracy by the powder method. Additionally the higher resolution makes it possible to extract detailed microstructural information on, for example, lattice strain or

domain size.

This compact review of modern X-ray crystallography in mineralogy gives a basic introduction to the different methods and their applications. Both single-crystal and X-ray powder diffraction procedures are included, with an emphasis on modern powder diffraction using synchrotron radiation. Wherever possible the focus is on applications directly related to mineralogical problems.

Because of the restricted space for literature references only the most helpful sources used for the preparation of this review have been cited.

## **2. The Diffraction of X-Rays**

In 1912 Friedrich, Knipping, and von Laue performed the first diffraction experiment using single crystals of copper sulfate and zinc sulfite. Based on these experiments Max von Laue developed his theory of X-ray diffraction. At the same time W.L. Bragg and W.H. Bragg performed their diffraction experiments, and in turn used an alternative, though equivalent, way of explaining the observed diffraction phenomena. Up to now what have become known as the “Laue conditions” and “Bragg equation” have formed the basis of X-ray diffraction of crystalline material, and it is therefore inevitable to start any monograph on X-ray crystallography with a short resume of the investigations carried out by these scientists.

Like visible light, an X-ray beam is an electromagnetic wave characterized by an electric field vector  $E$  that is perpendicular to the direction of propagation, and a magnetic field vector  $H$  that in turn is perpendicular both to  $E$  and the direction of propagation. Yet the wavelength of an X-ray beam is considerably shorter than that of an optical wave: the spectra of visible light comprise the range from 4000 to 7000 Å, while X-rays have typically wavelengths between 0.1 to 10 Å. Because X-ray wavelengths are comparable to the interatomic distances within a crystalline material, one observes characteristic interactions between the X-rays and the ordered array of electrons in the crystal structure. These interactions make X-rays the most important source for the investigation of crystal structures. The nature of these interactions and the basic laws of diffraction will be explained in this article.

If electromagnetic X-ray waves encounter an object, they are scattered by the electrons of the object. The field of the X-rays forces the electrons within the material to oscillate, and the electrons are in turn the starting point of secondary waves of the same frequency and wavelength as the primary waves. These waves are superimposed on each other, and if constructive interference occurs, it give rise to the different diffraction phenomena, which are generally strong if the distances within the object are comparable to the wavelength of the incoming beam. In addition the periodic nature of the atomic arrangement within a crystal gives rise to special diffraction phenomena, which are in many ways comparable to the diffraction of visible light by a refraction lattice.

### **2.1. The Laue Equations**

To understand diffraction in a three-dimensional crystal it is helpful to concentrate on

the one-dimensional case first. Figure 1 shows a one-dimensional lattice consisting of a row of point-like scattering centers which are separated by a periodic distance  $a$ . If a plane wave hits such a row of points, every scatterer gives rise to a new secondary wave which propagates in a spherical manner. The individual scattered waves are superimposed on, and generally extinguish, each other. Only along the common tangents will the spherical waves oscillate with identical phases, and therefore interfere in a constructive way, forming a common *diffracted* wave. It can be seen in the figure that the planes of common tangents exist in various directions, which define the different diffraction orders.

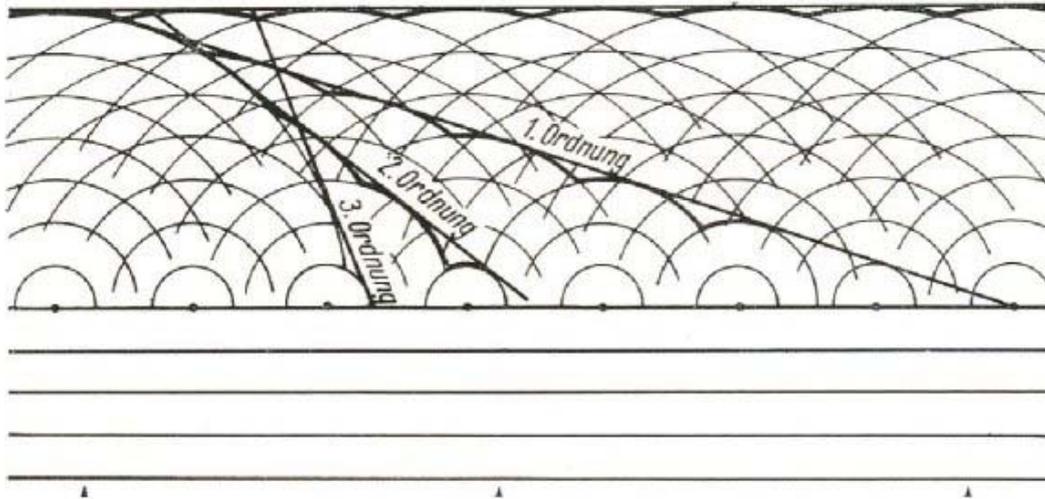


Figure 1. Diffraction of a plane wave by a row of point-like scatterers

The diffracted waves of all orders have the same wavelength as the incoming primary beam. If one completes the figure in the third direction perpendicular to the plane of paper, it becomes evident that the resulting wavefront moves along a cone.

Figure 2 shows the same conditions, but now the direction of the primary beam forms an arbitrary angle  $\varphi_a^0$  with the diffracting array of points. The cone-like wavefront of the first order is shown. The diffracted beams that are perpendicular to this wavefront in turn form a cone with an opening angle of  $2\varphi_a$ . The phase difference between two waves that have been diffracted by neighboring points is—in the case of the first diffraction order—exactly equal to the wavelength  $\lambda$ . Following the figure one can see that the phase difference is given by:

$$s - t = a \cos \varphi_a - a \cos \varphi_a^0 = a(\cos \varphi_a - \cos \varphi_a^0) = \lambda \quad (1)$$

and for the second order

$$s - t = a \cos \varphi_a - a \cos \varphi_a^0 = a(\cos \varphi_a - \cos \varphi_a^0) = 2\lambda \quad (2)$$

or generally

$$s - t = a \cos \varphi_a - a \cos \varphi_a^0 = a(\cos \varphi_a - \cos \varphi_a^0) = h\lambda \quad (3)$$

where  $h$  is an integer. Considering now a three-dimensional lattice, it is evident that every lattice direction requires a similar condition. For the lattice vectors in the direction of the three lattice parameters  $a$ ,  $b$ ,  $c$ , these conditions are:

$$\begin{aligned} a(\cos \varphi_a - \cos \varphi_a^0) &= h\lambda \\ b(\cos \varphi_b - \cos \varphi_b^0) &= k\lambda \\ c(\cos \varphi_c - \cos \varphi_c^0) &= l\lambda \end{aligned} \quad (4)$$

These equations are called the Laue equations.  $\varphi_a^0$ ,  $\varphi_b^0$  and  $\varphi_c^0$  are the angles between the incoming primary beam and the three basis vectors while  $\varphi_a$ ,  $\varphi_b$  and  $\varphi_c$  are the angles between the basis vectors and the diffracted secondary beam;  $h$ ,  $k$ , and  $l$  are integers. The equations for all other lattice directions are linear combinations from the above three, and accordingly no further conditions have to be defined.

Diffraction from a three-dimensional lattice can only exist if the conditions (Eq. 1) are simultaneously fulfilled for all three directions. Whenever the condition is fulfilled for the direction of a basis vector, a cone of diffracted beams is formed, which opens in the direction of the corresponding vector. For two of these cones that open in different directions, a common beam only exists in the direction of their mutual intersection. In Figure 3, for example, the cone formed around the vector  $a$  and the second cone formed around the vector  $b$  have a common beam in the direction of  $k$ .

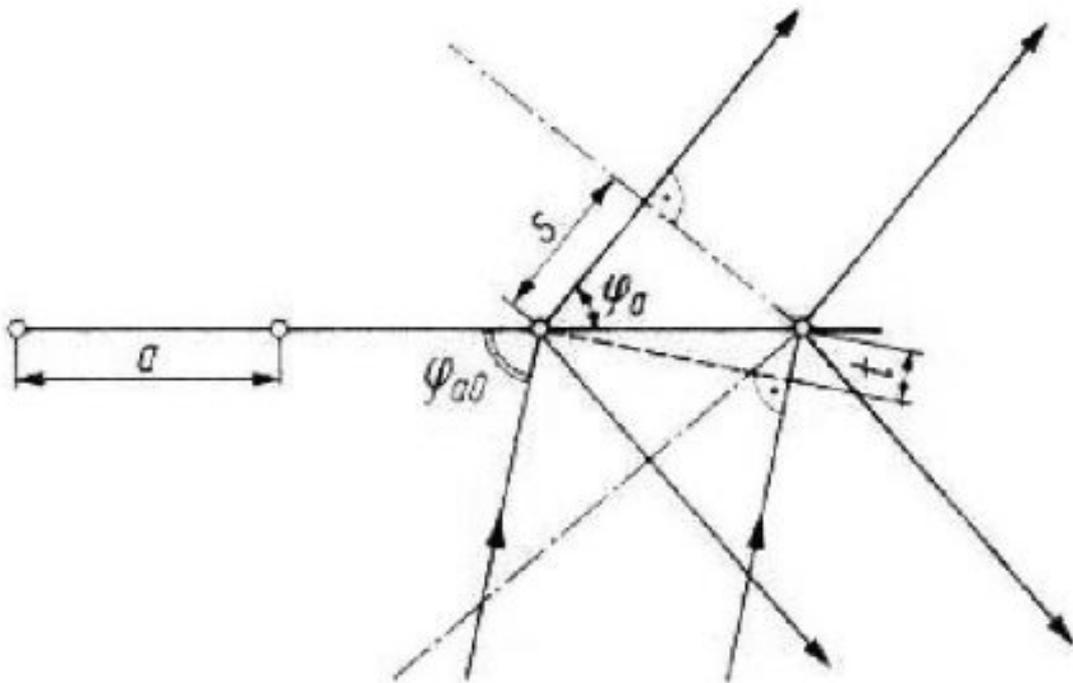


Figure 2. Diffraction of a plane wave by a row of point-like scatterers

A third cone that opens around the vector  $c$  does not intersect with the former two, and does not contain the direction  $k$ . This proves that not all the three Laue conditions are fulfilled at the same time, and consequently there is no constructive interference between the three beams. If well-defined relationships exist between the lattice vectors, the primary beam direction, and the wavelength  $\lambda$ , a common direction  $k$  for the three cones of diffracted beams is observed. Only then are the three Laue equations simultaneously fulfilled, and constructive interference of the diffracted waves occurs.

## 2.2. The Bragg Equation

An alternative description for the diffraction of X-rays by a lattice plane was suggested by W.L. Bragg in 1912, and is known as the Bragg equation:

$$n \cdot \lambda = 2 \cdot d \cdot \sin(\Theta) \tag{5}$$

with  $\lambda$  as the wavelengths of the X-rays,  $d$  as the interplanar spacing of parallel lattice planes, and  $2\Theta$  as the diffraction angle. Figure 4 illustrates this relationship.

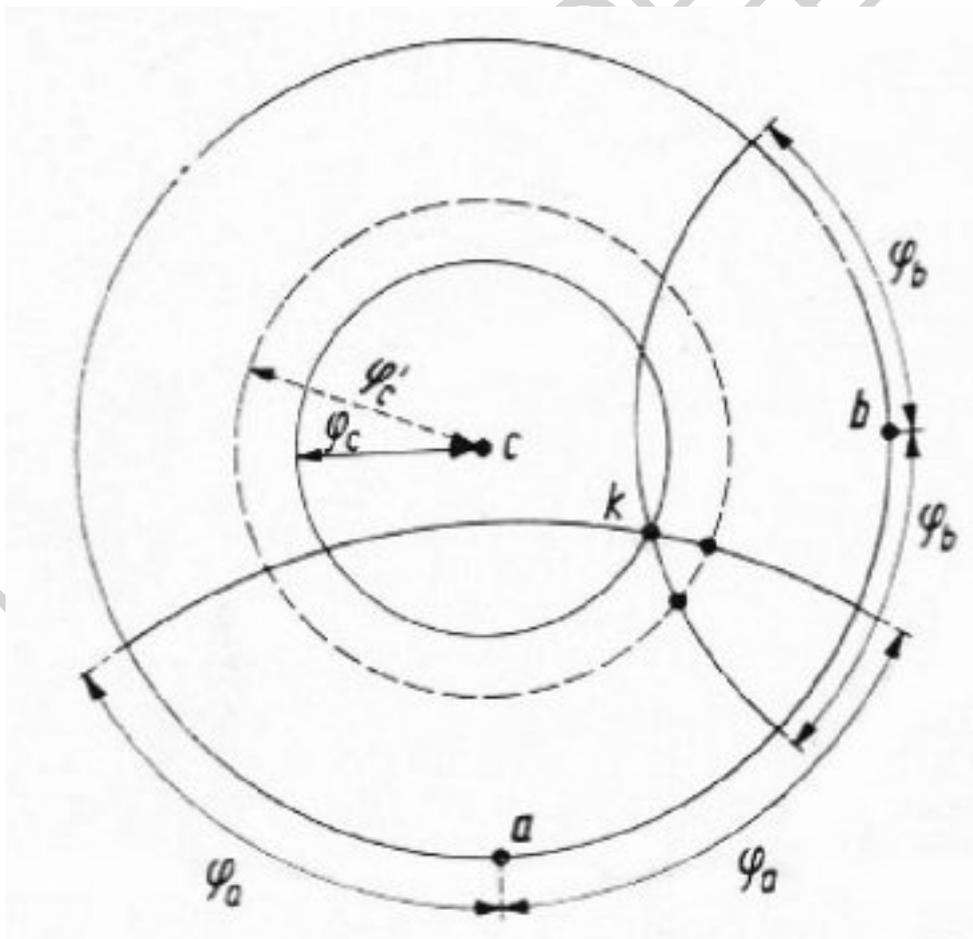


Figure 3. Representation of the Laue conditions for the diffraction by a crystal lattice

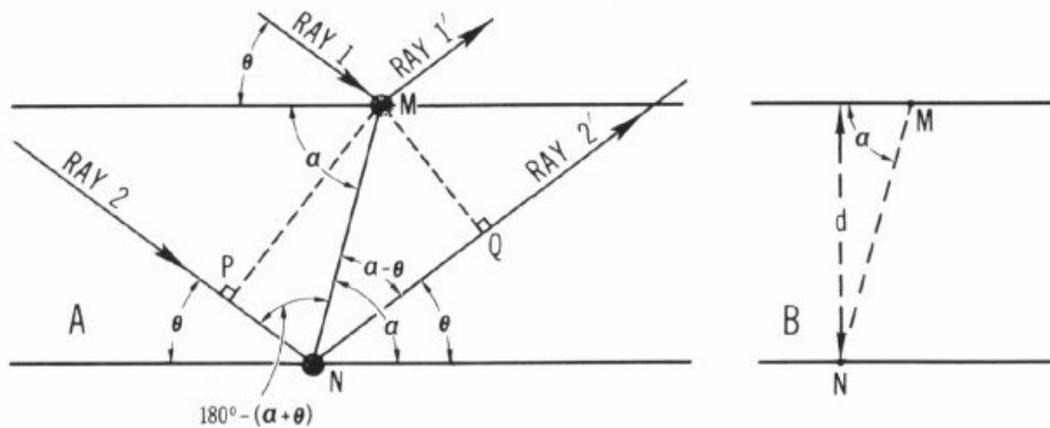


Figure 4. Bragg diffraction on two consecutive lattice planes

As mentioned above, the X-rays will be diffracted by the electrons of the atoms, which act as scattering centers by sending out spherical waves. Eq. 5 defines in which directions ( $2\Theta$ ), at a fixed value of  $\lambda$  and  $d$ , constructive interference of the scattered waves is possible.

This is exactly the case if the extra distance traveled by ray 2 in Figure 4 is a multiple ( $n$ ) of the wavelength. For simplicity, the number  $n$  may be included in the indexing of the set of lattice planes ( $(222) = 2 \cdot (111)$ ) and consequently in the  $d$  spacing.

Several relationships in crystallography directly follow from the Bragg equation (Eq. 5). It can be shown for instance that a constant error in  $2\Theta$  has a much stronger impact on the error in  $d$  spacing at low scattering angles than it has at high angles. Another consequence of the Bragg equation is that the resolution augments with increasing scattering angles. Relationships for strain and for the size of coherently scattering domains can also be derived.

### 2.3. The Ewald Sphere

The so-called Ewald construction or Ewald sphere is a useful tool to examine whether the diffraction condition for a reciprocal lattice point (see Section 6) is fulfilled or not, and is widely used in crystallography. Therefore the principle will be briefly outlined here.

We imagine a sphere of radius  $1/\lambda$  with the primary beam passing through the diameter IO (see Figure 5). The origin of the reciprocal lattice coincides with the point O. If the vector  $r_H^*$  lies on the surface of the sphere, the corresponding lattice planes  $hkl$  lie parallel to IP and form an angle  $\theta$  with the primary beam. The necessary condition to fulfill the Bragg equation is that the lattice point defined by the vector  $r_H^*$  (which corresponds to the lattice planes  $hkl$ ) must lie on the surface of the sphere with radius  $1/\lambda$ , which is called the Ewald sphere.

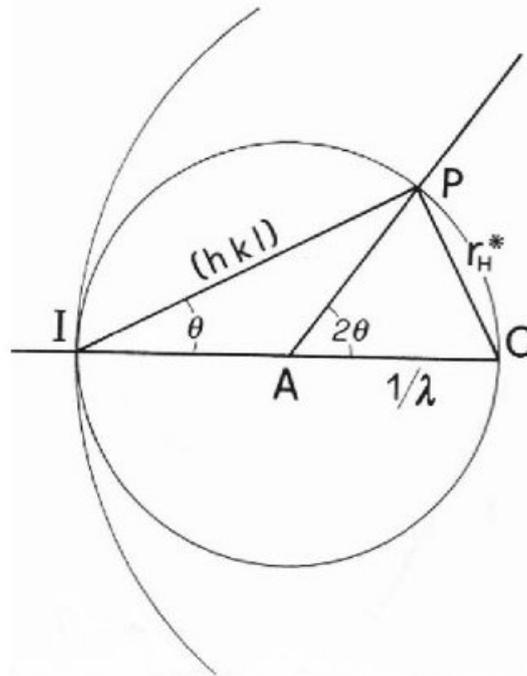


Figure 5. The Ewald sphere and the limiting sphere (in two dimensions)

For X-rays and neutrons with wavelengths from 0.5 to 2 Å the Ewald sphere has an appreciable curvature with respect to the lattice planes. If a monochromatic primary beam and a crystal in arbitrary orientation are used, generally none of the reciprocal lattice points touches the surface of the Ewald sphere (excluding the origin of reciprocal space). Therefore, the different experimental techniques described below all try to bring as many reciprocal lattice points as possible onto the surface of the sphere (that is, into diffraction position).

If  $r_H^* > 2/\lambda$  it is not possible to observe the corresponding reflection H. This condition defines the “limiting sphere” with the center O and the radius  $2/\lambda$ . Only lattice points within the limiting sphere can be brought into diffraction position. (This has consequences for the choice of the wavelength in a given experimental setup.) On the other hand if  $\lambda > 2a_{\max}$  (where  $a_{\max}$  is the largest period of the unit cell) then the diameter of the Ewald sphere is smaller than  $r_{\min}^*$  (the smallest period of the reciprocal lattice) and no lattice node can intercept the surface of the Ewald sphere.

-  
-  
-

TO ACCESS ALL THE **65 PAGES** OF THIS CHAPTER,  
 Visit: <http://www.eolss.net/Eolss-sampleAllChapter.aspx>

## Bibliography

- Bish D.L. and Post J.E. (1989). Modern powder diffraction. *Reviews in Mineralogy* **20**, 369 pp. Washington, D.C.: Mineralogical Society of America. [First review on modern powder diffraction methods.]
- Bloss F.D. (1971). *Crystallography and Crystal Chemistry*, 545 pp. New York: Holt, Rinehart, and Winston. [General introduction in crystallography and crystal chemistry.]
- Brechbuehl K.A. and Jakob R.T. (2000). *Tiny Grains of Vivianite in the Skin of the Oetzi Mummy*. 49<sup>th</sup> Annual (2000) Denver X-ray conference, July 31 – August 4, 2000, Denver, Colorado, collected abstracts #D056 [Unusual application of powder diffraction.]
- David W.I.F. (ed.) (2002). *Structure Determination by Powder Diffraction*, 337 pp. Oxford: Oxford University Press. [Book about state of the art structure determination from powder diffraction data.]
- Giacovazzo C., Monaco H.L., Viterbo D., Scordari F., Gilli G., Zanotti G., and Catti M. (1992). *Fundamentals of Crystallography. IUCr Texts on Crystallography 2.* (ed. C. Giacovazzo), 825 pp.. Oxford: Oxford University Press. [One of the basic and most complete introductions to crystallography.]
- International Union of Crystallography. (1983). *International Tables for Crystallography, Volumes I–IV*, Dordrecht, Netherlands and Boston, MA: D. Reidel. [Standard tables for crystallographic data.]
- Kern A. (1992). *Präzisionspulverdiffraktometrie: Ein Vergleich Verschiedener Methoden. Diplomarbeit*, Heidelberger Geowissenschaftliche Abhandlungen, Issue 58, 175 pp. [Thesis on high-precision laboratory X-ray powder diffraction.]
- Kleber W. (1983). *Einführung in die Kristallographie*, 392 pp. Berlin: VEB Verlag Technik Berlin. [Comprehensive introduction to crystallography in German.]
- Klug H.P. and Alexander L.E. (1974). *X-Ray Diffraction Procedures, Second Edition*, 996 pp. New York: Wiley. [Comprehensive book on the basics of powder diffraction.]
- Krischner H. (1980). *Einführung in die Röntgenfeinstrukturanalyse*. 171 pp. Braunschweig and Wiesbaden: Verlag Friedr. Vieweg & Sohn. [Introduction to X-ray powder diffraction.]
- McLachlan D. (1957). *X-ray Crystal Structure*, 416 pp. New York, Toronto, London: McGraw-Hill. [Comprehensive introduction to crystal structure analysis with stress on film methods and diffractometry.]
- Neder R.B. and Proffen T. (1996). *Journal of Applied Crystallography* **29**, 727–735, *Teaching diffraction with the aid of computer simulations*. [see title.]
- Schuster M. (2001). *Dünnschichtanalytik mit Röntgenmethoden*, 18pp, *Report of Siemens AG*, Munich: Siemens AG. [Introduction to stress and texture analysis using diffraction methods.]
- Stutzman P.E. and Leigh S. (2000). Compositional Analysis of NIST Reference Material Clinker 8486. *Cement Microscopy (Proceedings of Cement Microscopy, 22nd NIST International Conference Proceedings, April 29–May 4, 2000, Montreal, Canada)*, pp. 22–38. NIST. [Application of powder diffraction to quantitative phase analysis.]

## Biographical Sketches

**Robert Ernst Dinnebier** was born in Mannheim, Germany, in 1964. From 1984–1989 he studied mineralogy at the University of Heidelberg. In 1993 he was awarded a Ph.D. His thesis concerned the development of a program system for measurement and evaluation of powder diffraction data; Computer-automation of powder diffractometers and Rietveld refinement.

From 1993–1995 he undertook postdoctoral research at the National Synchrotron Light Source at Brookhaven National Laboratory in connection with the Department of Physics at SUNY Stony Brook. His fields of interest are *ab initio* structure determination using Synchrotron powder diffraction data, especially of organometallics and fullerenes; phase analysis, anomalous dispersion, and software development towards routine conversion of powder pattern into crystal structures.

From 1995–2000 he did his habilitation at the Laboratory of Crystallography at Bayreuth University with a thesis on “The *ab initio* structure determination of molecular solids from powder diffraction data”.

From 2001 onwards he has been group leader of the scientific service group diffraction at the Max Planck Institute for Solid State Research at Stuttgart, and a lecturer in crystallography at the University of Stuttgart.

Currently he is chairman of the sub-committee “Synchrotron Radiation” of the International Center for Diffraction Data (ICDD), Philadelphia (USA), of the Powder Diffraction Group of the German Society of Crystallography (DGK), and of the Commission on Powder Diffraction (CPD) of the International Union of Crystallography (IUCr).

**Karen Friese** was born in Hamburg, Germany, in 1964. She studied mineralogy at the University of Hamburg from 1984–1990. She was awarded a Ph.D. in 1996. Her thesis was entitled: *In<sub>(1+x)</sub>Ga<sub>(1-y)</sub>Se<sub>2</sub>: ein Kompositkristall mit zylindersymmetrischer Störwelle.*

From 1997–2001 she was engaged in postdoctoral research in the study of structural phase transitions at the University of the Basque Country, Bilbao, Spain. Since 2001 she has been working as a scientist at the Max Planck Institute for Solid State Research (Stuttgart). Her research field is non-routine crystal structure analysis.