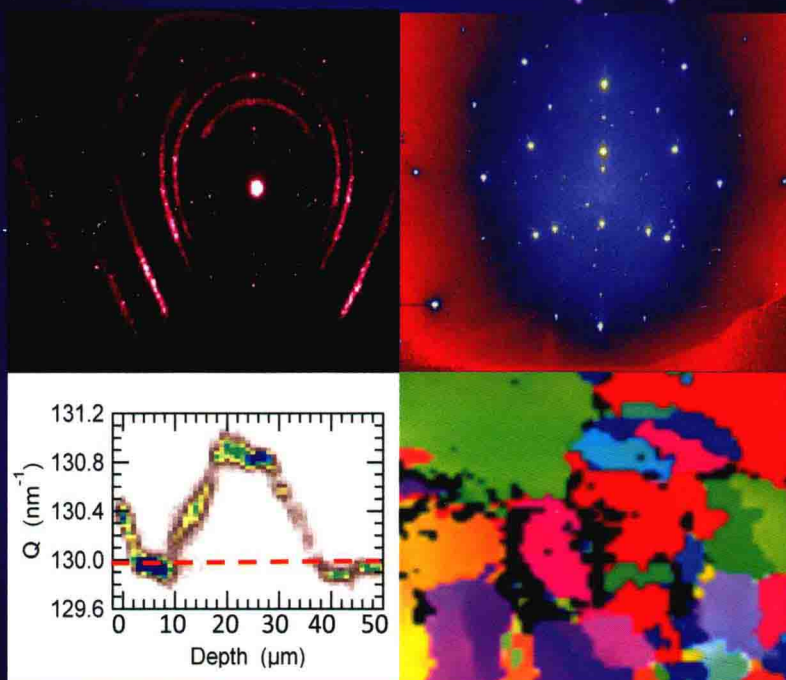


STRAIN AND DISLOCATION GRADIENTS FROM DIFFRACTION

Spatially-Resolved Local Structure and Defects



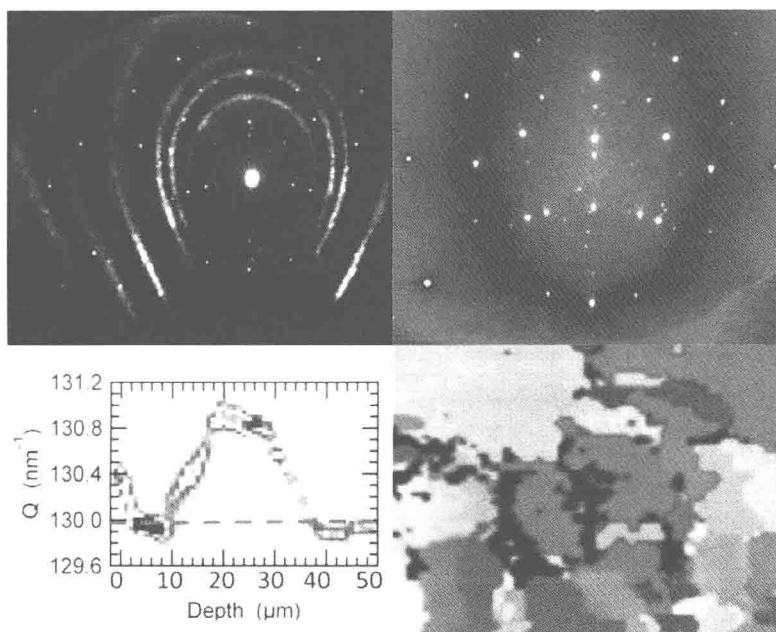
Editors

Rozaliya Barabash • Gene Ice

Imperial College Press

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Preface

Strain and Dislocation Gradients from Diffraction

The prediction and subsequent 1912 discovery by Friedrich and Knipping of what came to be known as Laue diffraction set in motion a scientific revolution that continues to this day. Not only did Laue diffraction provide conclusive evidence of the wave nature of X-rays, but it also settled the issue of crystal structure and gave a powerful new tool for investigating the unit cells that comprise the building blocks of crystals. Beyond the average unit cell, X-ray diffraction rapidly evolved to become the definitive tool for the study of imperfections in crystals. Indeed, diffraction changed the status of crystallography from a descriptive discipline to a highly precise science with access to the underlying internal structure of crystals, their defects and thus their structure/property relationships.

To acknowledge the importance of the diffraction discovery, the United Nations Education, Science and Culture Organization (UNESCO) declared 2014 the International Year of Crystallography. During the last 100 years, diffraction methods based on X-ray, neutron, electron and Mössbauer beams have evolved into the most powerful probes of materials. The development of ultra-brilliant third-generation synchrotron X-ray sources, together with advances in X-ray optics, has created intense X-ray micro-beams, which provide new opportunities for in-depth understanding of materials' behavior.

This book highlights diffraction studies of mesoscale strain gradients and dislocation distributions in crystals, which lie at the heart of emerging research programs around the world. While diffraction techniques to study materials at nano- and macroscale are mature, the “meso” scale of ~ 0.01 – $10\mu\text{m}$ remains elusive both for experimental characterization and for theoretical modeling; experimental studies are complicated by the need for three-dimensional (3D) spatially resolved diffraction measurements below the sample surface, while modeling efforts are complicated by the

interactions of defects at a scale too fine to approximate by continuum methods. Key to this emerging area of research are the defect distributions that control materials properties.

In order to understand diffraction caused by different defects, and hence to map defect distributions, it is necessary to understand the origin of the distortions created by defects and the corresponding changes in the reciprocal space of the non-ideal crystals. Chapter 1 describes defect classifications based on their displacement fields and provides a connection between different dislocation arrangements, including geometrically necessary and statistically stored dislocations and other common defects and the corresponding changes in the reciprocal space and diffraction patterns.

The following chapters of the book provide overviews of microdiffraction techniques developed during the last decade to extract information about strain gradients and dislocation distributions. X-ray microdiffraction is a particularly exciting probe of crystalline structure, orientation and strain. X-ray microdiffraction is non-destructive with good strain resolution, competitive or superior spatial resolution in thick samples and the ability to probe below the sample surface. Several mutually complementary microdiffraction techniques using white/pink and/or monochromatic radiation are now in use. These include:

- The polychromatic X-ray microdiffraction (PXM) or micro-Laue diffraction combined with differential aperture microscopy (DAXM) for depth-resolved 3D X-ray microscopy. This approach was developed by Oak Ridge National Laboratory with partners at the Advanced Photon Source, Howard University and elsewhere (Chapters 1, 2 and 10). This technique utilizes reflection geometry and is best suited to probe strains and dislocation gradients in polycrystalline and/or multiphase materials with crystalline feature (e.g. grain) sizes of several micrometers.
- Variations of PXM are also used at the Advanced Light Source (Chapter 4) and European Synchrotron Radiation Facility (Chapter 5) with distinct hardware and data processing software.
- High-energy transmission Laue microdiffraction has been demonstrated by researchers at Oxford University (Chapter 3). They developed two different approaches: Laue orientation tomography (LOT) and high-energy DAXM.
- Three-dimensional high-energy X-ray diffraction microscopy with monochromatic radiation is a powerful method developed by the

group at Risø DTU National Laboratory for Sustainable Energy (Chapters 6–9). This method is faster than point-probe methods that enable studies not only in 3D but also in the fourth dimension: time. It is based on two principles: the use of highly penetrating hard X-rays from a synchrotron source and the application of “tomographic” reconstruction algorithms for the analysis of the diffraction data.

- The example of depth-resolved measurements with energy-variable X-ray diffraction is described in Chapter 11. The method is based on the analysis of X-ray diffraction peaks measured at varying X-ray energies; the latter being controllably changed in small steps that probe surfaces in reciprocal space. By increasing energy and, correspondingly, the X-ray penetration length, progressively deeper materials’ layers are probed.
- The application of microdiffraction to high-pressure studies of materials is described in Chapter 13. It shows how microdiffraction can probe the microstructural response under extreme conditions.
- Finally, X-ray microdiffraction techniques are put into context by a description of state-of-the-art electron back-scattering diffraction (EBSD) methods (Chapter 12) which are often used for surface characterization and the determination of lattice orientation, phase and overall texture. As X-ray and electron methods evolve, the kinds of science they can address are beginning to overlap and their complementary capabilities offer the promise of future breakthroughs in our understanding of materials.

As editors we wish to express gratitude to all the contributors who made this project happen and to the Materials Sciences and Engineering Division of the U.S. Department of Energy’s Basic Energy Sciences for their continuing support. We hope that this book will promote further progress both in technique development in the new applications of the techniques described herein to advance our understanding of defects distribution and their influence on materials behavior.

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Editor Biographies

Dr. Rozaliya Barabash works at the X-ray scattering and microscopy group at the Oak Ridge National Laboratory. Prior to joining this research group, Rozaliya worked as an associate professor in the department of physics and engineering at the National Technical University of Ukraine, Kiev. In Kiev, she studied, under the mentorship of Professor M.A. Krivoglaz, diffuse scattering from different inhomogeneously distributed and correlated defects in two- and three-dimensional crystals. Her areas of expertise are diffraction theory and the application of X-ray and neutron scattering to condensed matter physics, shock-induced deformation, crystallography, nanomaterials, thin films, interfaces, structure of metals and ceramics, understanding the atomic arrangements of atoms, early stages of phase separation in complex materials, scattering by surface layers with concentration and strain gradient, and phase transformations. She spent several months between 1997 and 1998 as a visiting professor at the Institut für Metallkunde, Bergacademie, Freiberg, and one year as a visiting scientist at the Max Planck Institute in Stuttgart between 1999 and 2000. She has authored over 150 technical publications, two books and twelve book chapters, and has edited two books and nine journal issues.

Dr. Gene Ice is director of the materials science and technology division at the Oak Ridge National Laboratory (ORNL) and has more than 30 years' experience of pioneering new synchrotron radiation optics and methods for materials characterization. Gene joined the former metals and ceramics division in 1979. His early work on X-ray optics lead to the co-invention of dynamically bent sagittal-focusing crystal optics, which are now deployed at synchrotron facilities around the world. After ten years of designing and then operating the ORNL materials science beam line at the National Synchrotron Light Source, Gene began research to develop polychromatic microdiffraction methods for materials characterization.

This research ultimately led to the construction of the world's first dedicated polychromatic microdiffraction facility with submicron resolution in three dimensions. He became the leader of the X-ray scattering and microscopy group in 1995, an ORNL corporate fellow in 2003 and a division director in 2010. In addition to other honors, Gene is a fellow of the American Physical Society, a fellow of ASM International, a main editor of the *Journal of Synchrotron Radiation* and has won two R&D100 awards for X-ray optics. He has authored more than 230 refereed papers, 15 book chapters, two US patents and has been invited to give numerous talks on five continents.

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Chapter 1

Diffraction Analysis of Defects: State of the Art

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Materials' properties are largely determined by the self-organization and collective behavior of defects. A number of X-ray methods including Laue microdiffraction, rocking curve measurements and reciprocal space mapping can be used to characterize mesoscale dislocation structures and elastic strain. This chapter describes how dislocations and other common defects cause local strain field fluctuations and alter the structure factors of the cells in which they occur, as well as in neighboring cells. These changes alter the diffraction conditions in reciprocal space, and result in characteristic features in the diffracted intensity. These diffraction features can be used to model the local strain and dislocation structure of advanced materials. Different dislocation arrangements are considered such as: randomly distributed statistically stored dislocations (SSDs) and geometrically necessary dislocations (GNDs); dislocation loops; dislocation dipoles; dislocation boundaries including incidental dislocation boundaries (IDBs) and geometrically necessary boundaries (GNBs). The impact of twins is also discussed.

1.1. Defect Classification in the Kinematic Approximation

Defects break the long-range symmetry of a crystal lattice and displace atoms from their ideal positions. To understand how defects impact on diffraction, it is necessary to address four questions:

1. How do defects distort the lattice?
2. Are the defects ordered and/or correlated?

3. Do they change the structure factors of their unit cells and surrounding unit cells?
4. Do they interact with external fields?

As is well known, the scattering from atoms of an ideal perfect crystal add constructively under the Bragg–Laue conditions, which results in δ -function-like intensity maxima localized at reciprocal lattice sites of the crystal. Real crystals always contain defects, which perturb the ideal periodic arrangement of the atoms and change local structure factors. The qualitative nature of diffracted intensity depends on whether it is possible to relate the atomic positions to an average lattice. If the defects cause atomic displacements, which are localized in the immediate vicinity of the defects, then it is possible to relate a single periodic lattice to the crystal; typically, if the mean square fluctuations of the atomic displacements remain finite and do not exceed the interatomic distance, then it is possible to relate an average periodic lattice to the crystal with defects. These defects are called “defects of the first kind” (Krivoglaz, 1969, 1996).

Some defects distort the lattice in a manner that makes it impossible to reference atomic positions to a single periodic lattice. However, it is often still possible to relate slightly different periodic lattices to relatively large parts of the crystal (for example, subgrains, dislocation cells, etc.). Such defects are called “defects of the second kind” (Krivoglaz, 1969, 1996).

For the analysis of the diffraction, an Ewald sphere representation is usually used (Fig. 1.1). In this representation, \mathbf{k}_2 and \mathbf{k}_1 are the wave vectors along the diffracted and incident beam. In the kinematic approximation, complex scattering amplitudes from the electron probability density are integrated with the corresponding phases to determine the scattering intensity, $I(\mathbf{Q})$, for diffraction vector or momentum transfer, \mathbf{Q} . In electronic units, intensity of scattering by a monochromatic beam is described by the equation (Krivoglaz, 1969, 1996):

$$I(\mathbf{Q}) = \left| \int \rho(\mathbf{r}) e^{i\mathbf{Q} \cdot \mathbf{r}} d\mathbf{r} \right|^2, \quad \text{where } \mathbf{Q} = \mathbf{k}_2 - \mathbf{k}_1 \quad (1.1)$$

Here, $\rho(\mathbf{r})$ is a total electron probability density at position vector \mathbf{r} . Integration in Eq. 1.1 is performed over the whole scattering volume. For an infinite ideal crystal, the intensity distribution as a function of momentum

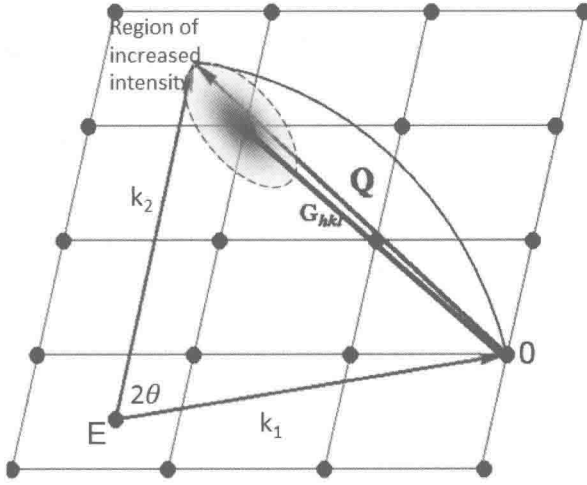


Fig. 1.1. Ewald representation of the diffraction experiment: \mathbf{G}_{hkl} is a reciprocal lattice vector, \mathbf{Q} is a diffraction vector or momentum transfer and 2θ is a scattering angle between the incident \mathbf{k}_1 and scattered \mathbf{k}_2 radiation wave vectors with wavelength λ . The origin of the reference reciprocal lattice frame, 0, is located at the end of the incident \mathbf{k}_1 vector. The origin of the Ewald sphere with a radius $|\mathbf{k}_1| = |\mathbf{k}_2| = 2\pi/\lambda$ is positioned at E. The ends of the momentum transfer, \mathbf{Q} , and wave vectors \mathbf{k}_1 and \mathbf{k}_2 , must be on the surface of the Ewald sphere. If $\mathbf{Q} = \mathbf{G}_{hkl}$, the Ewald sphere passes through one more reciprocal lattice site and Bragg–Laue diffraction will occur in the direction of the \mathbf{k}_2 vector. If the condition $\mathbf{Q} \neq \mathbf{G}_{hkl}$ is not satisfied, as shown in the figure, the Bragg–Laue diffraction will not occur for this reflection, instead the diffuse scattering will originate from the region of increased intensity around the (hkl) reciprocal lattice point.

transfer will consist of the δ -function-like peaks positioned at the reciprocal lattice sites.

For crystalline materials, it is convenient to write Eq. 1.1 in terms of the scattering from unit cells that fill the real-space crystal lattice with repeated structures. The complex scattering amplitudes from each unit cell — called the structure factor, F — are summed to determine the total scattering from the crystal.

$$I(\mathbf{Q}) = \left[\sum_s e^{i\mathbf{Q} \cdot \mathbf{R}_s^0} F \right]^2 \quad \text{where } F = \sum_{\gamma} f_{\gamma} e^{i\mathbf{Q} \cdot \mathbf{r}_{\gamma}} \quad (1.2)$$

Here, the index s labels the unit cell sites with positions \mathbf{R}_s^0 ; γ are the atoms in each unit cell with relative positions \mathbf{r}_{γ} ; F is the structure factor; and f_n is the atomic scattering factor of the n th atom of a unit cell.

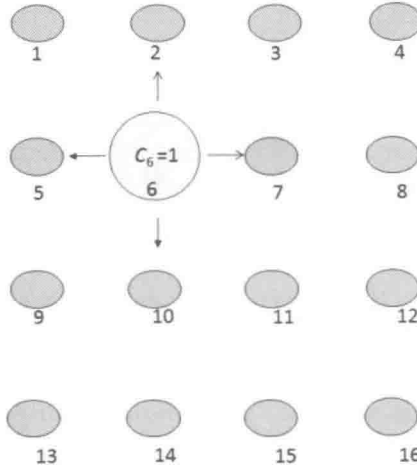


Fig. 1.2. Sketch of crystal lattice plane with one point defect in the position $t = 6$. Only $c_6 = 1$, for all other lattice sites $c_t = 0$.

Defects typically redistribute the scattering intensity expected from a perfect crystal. Defects displace surrounding atoms (unit cells) and change the scattering factor of the unit cells in which they are embedded. To describe the distribution of defects, we adopt the random numbers c_t (Krivoglaz, 1969, 1996) such that:

$$\begin{aligned} c_t &= 1, \text{ for a defect at position } t. \\ c_t &= 0, \text{ for positions without defects.} \end{aligned} \quad (1.3)$$

In the example given in Fig. 1.2, only $c_6 = 1$ and at all other lattice sites, $c_t = 0$. In the ideal crystal the lattice site positions without any defects are characterized by the position vector \vec{R}_s^0 , and positions of defects by the vector \vec{R}_t . Each unit cell will be identified by its number, s . If the unit cell consists of several atoms then the position of atoms inside the unit cell will be numbered by the index, γ . The defect positioned on the lattice site, t , creates a partial displacement, \mathbf{u}_{st} , and partial rotation, \mathbf{m}_{st} , of the s th unit cell. The total displacement, \mathbf{u}_s , and/or rotation, \mathbf{m}_s , of the s th unit cell are determined from the sum of all displacements/rotations due to all the defects:

$$\mathbf{u}_s = \sum_t c_t \mathbf{u}_{st}, \quad \text{and} \quad \mathbf{m}_s = \sum_t c_t \mathbf{m}_{st} \quad (1.4)$$

Similarly, the structure factor, F_s , for sth unit cell in the presence of defects can be written as:

$$F_s = F + \sum_t c_t \varphi_{st} \quad (1.5)$$

Here, F is an average structure factor of the crystal without defects, and φ_{st} is a partial structure factor change of the sth cell caused by a defect in the t location.

As briefly aforementioned, in the kinematic approximation a qualitative classification of defects with respect to their impact on diffraction has been suggested by Krivoglaz (1969, 1996). All structural defects can be formally classified into two kinds depending on the exponent value of the corresponding structural Debye–Waller factor (DWF), $\text{Exp}[-2M]$. If the exponent, M , is finite then the defects are of the first kind. If $M \rightarrow \infty$ then they are defects of the second kind (Fig. 1.3).

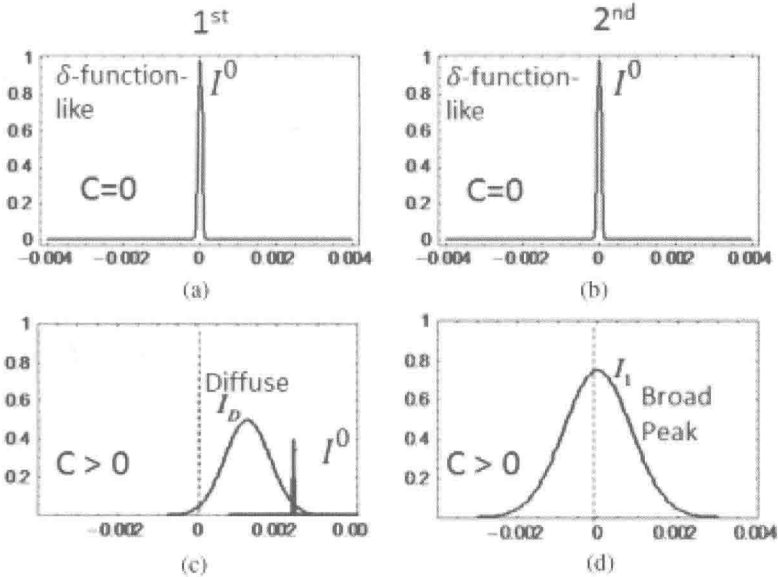


Fig. 1.3. Impact of the first and second defect kinds on diffraction: (a, b) δ -function-like shape of the intensity positioned in the reciprocal lattice site; (c) peaks of diffuse scattering and shifted weak δ -function-like maximum caused by defects of the first kind; and (d) broad peak formed in the crystals by defects of the second kind.

1. Defects of the first kind do not change the δ -function-like shape of the intensity distribution, I^0 , of regular Bragg reflections. They can shift the intensity peak position, change the integral intensity of the peak due to the change in average structure factor and introduce diffuse scattering. The peak intensity is multiplied by a structural DWF. Examples of such defects are point defects, small dislocation loops and precipitates.
2. Defects of the second kind cause asymmetric broadening of the peak; their intensity distribution does not have a δ -function-like shape even for an infinite crystal. Examples of such defects are dislocations, disclinations/disconnections, disclination dipoles, stacking faults, twins, boundaries, long cylinder-like chains of impurities, etc.

Generalizing Eq. 1.2 to include displacement/rotations of the unit cells and changes in the structure factors, the diffracted intensity can be written as:

$$I = |F|^2 \sum_{s,s'} e^{i\mathbf{Q}(\mathbf{R}_s^0 - \mathbf{R}_{s'}^0)} e^{-T} \quad (1.6)$$

where T is a correlation function. In crystals without defects the correlation function $T = 0$. The correlation function is distinct for different kinds of defects.

In many diffraction experiments the diffracted intensity is also averaged along certain directions or surfaces. For example, the Debye pattern from a polycrystalline material averages over the textured crystal orientations of the polycrystalline grains that intercept the beam (Krivoglaz, 1969, 1996; Warren, 1990). Single-crystal Laue patterns integrate intensity along the radial direction of the diffraction vector, \mathbf{Q} (Barabash *et al.*, 2003a; Ice and Barabash, 2007). The integrated intensity in a rocking curve averages along one of the directions transverse to reciprocal lattice vector, \mathbf{G}_{hkl} (Ice and Barabash, 2007).

Usually, the intensity in the radial (along the diffraction vector, \mathbf{Q}) and transverse (perpendicular to the diffraction vector) directions in reciprocal space have distinct responses to distortions caused by crystal defects. The transverse plane is most sensitive to orientation changes of the unit cells. This is why diffraction measurements in the transverse plane give information about the so-called “orientation space.” The intensity