JEROLD M. SCHULTZ

DIFFRACTION
for
MATERIALS SCIENTISTS

PRENTICE-HALL INTERNATIONAL SERIES
in the PHYSICAL and CHEMICAL ENGINEERING SCIENCES

**Demonstrates the universality and utility
of the scattering method in solving
structural problems in materials science**

Diffraction for Materials Scientists

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To the students of MET 801, who keep me honest

Preface

The thrust of *Diffraction for Materials Scientists* is to convince the reader (student) of the universality and utility of the scattering method in solving structural problems in materials science. This textbook is aimed at teaching the fundamentals of scattering theory and the broad scope of applications in solving real problems. Consistent with this thrust, many of the details of the practice of diffraction experimentation have been omitted. It is intended that *Diffraction for Materials Scientists* be augmented by additional notes dealing with experimental practice; this is how the text has been used by the author.

The core of this text is the first chapter. There the underlying physical concepts and the mathematical tools of kinematic scattering theory are introduced. The remainder of the text could be thought of as the extension of those principles to general areas of application. (The exception to this scheme is Chapter 4, which deals with dynamical concepts.) An attempt has been made to make it clear that each application is a straightforward extension of the central theoretical framework.

The connection between theory and practice is made in two ways. Examples of the results of scattering investigations arc used throughout the text, and numerous student problems are provided at the ends of chapters. Some of the problems are of a "drill" variety, while others require extension of the textual material.

Two departures from the approaches used by other authors demand comment. The first relates to the introduction of classical crystallography. The materials scientist is sometimes involved in establishing details of crystal structure, and consequently requires the crystallography background necessary to that purpose. It is the author's feeling that the introduction of classical crystallography early in a text can divert the student's attention and can distort the student's understanding of the position of symmetry relations in diffraction analysis. With this in mind, the concepts of classical crystallography have been deferred to the fifth chapter (of seven). There, the concepts are introduced very specifically as a vehicle for simplifying the work of crystal structure analysis, via characterization of redundancies of atomic position in the unit cell. By this point in the text, the student is comfortable with general diffraction theory and modes of its application and can handle this new set of concepts.

The second departure of the approach regards Chapter 4, on the dynamical theory. It was tempting to maintain textual continuity by omitting emphasis on dynamical concepts. However, the materials scientist is very often involved in questions of image formation in transmission electron microscopy and x-ray topography. It thus seemed important to deal with the mechanics of dynamical theory. The general aim of that material is toward the understanding of image formation. Concepts of primary and secondary extinction and of natural line breadth are made subservient to this aim.

The author is indebted to the many authors and publishers for permitting the republication of their illustrations; acknowledgments are presented in the figure captions. In addition, a large debt is owed to all of the students who had to deal with this book in manuscript form.

JEROLD SCHULTZ

Newark, Delaware

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Diffraction Fundamentals 1

1.1 INTRODUCTION

The scattering of waves of submicron wavelength by matter provides a set of the most incredibly useful and versatile tools available to the materials scientist. A partial list of some of the types of information available from diffraction studies follows

- Determination of crystal structures
- Determination of liquid structures
- Identification of (crystalline) unknowns
- Orientation of single crystals
- Particle-size or grain-size analysis
- Measurement of stacking fault probabilities
- Internal (residual) strain measurement
- Determination of the matrix of elastic constants
- Determination of the Debye temperature
- Detection and measurement of ordering in alloys
- Measurement of degree of crystallinity in polymers
- Detailed composition determination in solid solutions
- Pole figure analysis
- Direct visual observation of lattice defects and local lattice strains
- Determination of dislocation Burgers' vectors

With the exception of the last two entries in the list, all of the above uses are based on a rather simple set of concepts which constitute the *kinematic* *theory of diffraction.* The last two entries depend on a refined treatment, the *dynamical theory.* This latter is more physically correct for all diffraction problems, but degenerates to kinematic results for all but relatively rather perfect crystals.

This text attempts to guide the reader through a unified approach to structure problems. Beginning with the first chapter, we set down the basic concepts and mathematics of the kinematic theory. For the most part, the remainder of the text becomes a compendium of specific applications of the basic theory. Thus, while the excitement lies ahead, it behooves the reader to pay particular attention to detail over the earliest portion of this text. The reader should have seen, by the time we have looked at a few applications, that the theory is an at least potentially rigorous one and one which possesses much power when properly understood. He or she should understand also by that time that great experimental imagination is needed to be able to produce truly meaningful results, even in so well-developed a science. That is, to utilize anything approaching the full power of the diffraction method, the investigator must have a thorough grasp of its implications and also of some of the barriers toward its utilization. The basic goal of this text is to foster such awareness.

1.2 GENERAL THEORY OF DIFFRACTION

The work of diffraction analysis proceeds in the following way. Consider in Fig. 1.1 a beam of radiation of wavelength λ incident on some "black box" body whose internal structure is unknown. Using a film or some type of radiation detector, the intensity of scattered radiation $I(\mathbf{s})$ is measured as a function of scattering angle 2θ. As we shall see, the vector $\mathbf{s}$, where $s = 2(\sin\theta)/\lambda$ is a more convenient variable than 2θ. The results of the scattering experiment may appear in different ways, as shown in Fig. 1.2, depending on the experimental conditions.

From the details of such patterns it is possible to reconstruct the structure of the scattering medium. The reason for this is as follows. Consider Fig. 1.3. A plane wave enters the medium and is then scattered spherically by each

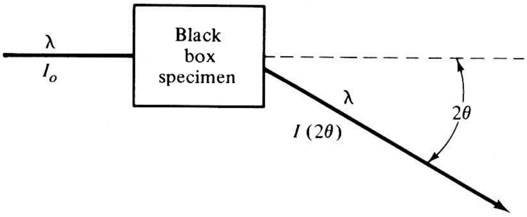
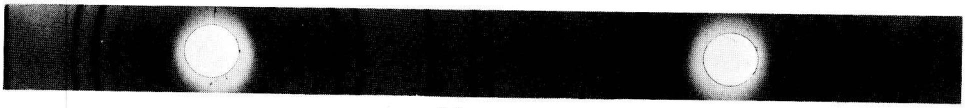
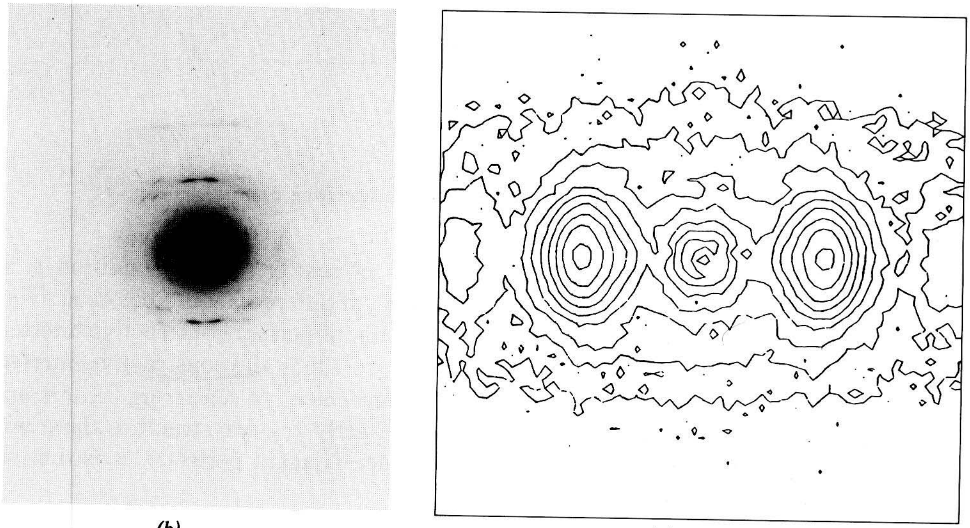


Figure 1.1. Representative experiment. An incident beam of wavelength λ and intensity I_o is scattered by the specimen. A ray elastically scattered in a direction 2θ from the direction of incidence, with intensity $I(2\theta)$, is shown.



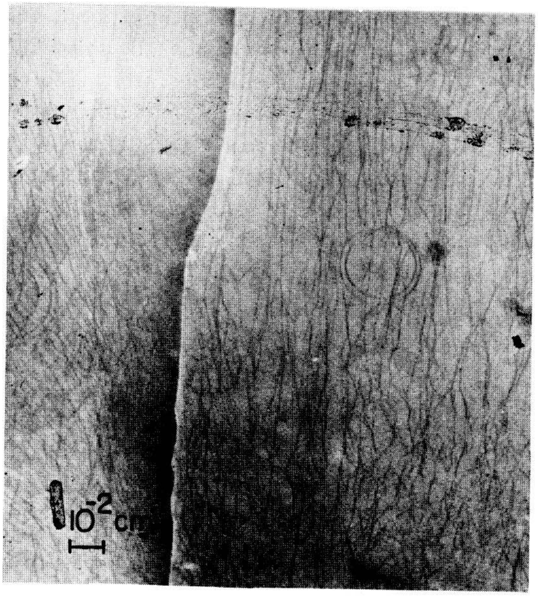
(a)



(b)

(c)

Figure 1.2. Examples of diffraction results: *(a)* Debye-Scherrer x-ray pattern from a copper powder (taken using CuK$_\alpha$ radiation); *(b)* electron diffraction pattern from a highly oriented poly(ethylene terephthalate) film (taken at 265°C, using 100-kV electrons); *(c)* small-angle x-ray scattering intensity contour plot from an "elastic hard film" of polypropylene (taken using the ORNL 10-meter SAXS instrument, using CuK$_\alpha$ radiation); and *(d)* enlargement of a $10\bar{1}3$ back-reflection diffraction spot from a zinc crystal (using FeK$_\alpha$ radiation). Dislocation lines and rings are clearly visible in *(d)*.



(d)

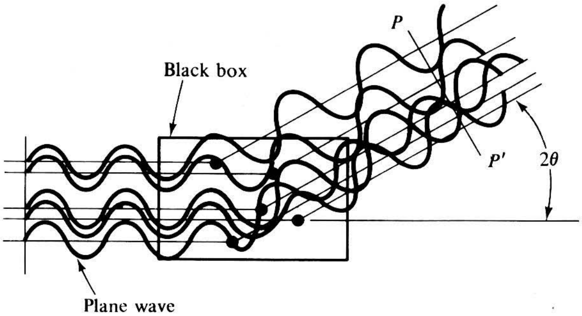


Figure 1.3. Interference effects developed by scattering from several centers.

scattering center. For a particular direction of scattering, the condition is as shown. Each scattered ray has traversed a path of different length before arriving at some common plane PP'. Thus the condition of perfect constructive interference has been destroyed. However, the degree to which the constructive interference has been destroyed depends upon the placement of scattering centers and on the scattering angle 2θ. In fact, for a perfectly regular structure there will be some angles $2\theta_{hkl}$ at which the interference is again perfectly constructive. These are the well-known Bragg angles

$$n\lambda = 2d_{hkl} \sin \theta_{hkl} \tag{1.1}$$

For imperfect crystals or amorphous materials, perfect constructive interference is an impossibility. Hence, the sharp diffraction spikes cannot be observed.

The general theory of scattering follows directly from this rudimentary introduction. Let us think of an incident wave of wavelength λ and unit propagation vector $\hat{\mathbf{s}}_o$. The wave scattered at angle 2θ will maintain its wavelength (coherent scattering) and will have its propagation direction characterized by the unit vector $\hat{\mathbf{s}}$. Let the vector distances of the several scattering centers be represented by a set $\mathbf{r}_i$ with origin anywhere within the "black box." The condition is now as indicated in Fig. 1.4.

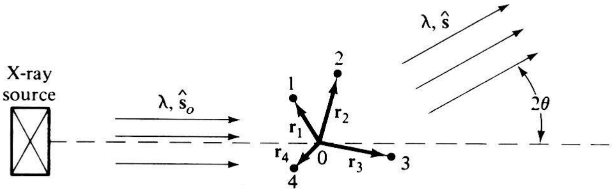


Figure 1.4. Schematic scattering experiment, to define vector quantities. $\hat{\mathbf{s}}_o$ and $\hat{\mathbf{s}}$ are unit vectors in the incident and scattered directions. The $\mathbf{s}_j$ are the vector distances from the origin to the jth scatterers.

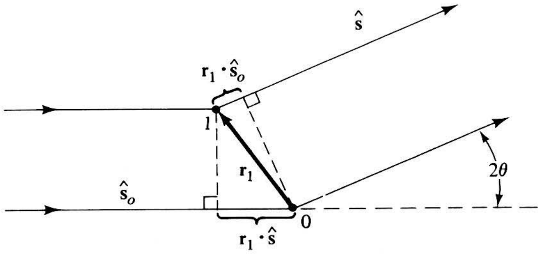


Figure 1.5. Path length difference geometry.

Consider the scattering by centers 1 and 2. Let the incident amplitude be

$$A = A_I \sin\left(\omega t - 2\pi \frac{x}{\lambda}\right) \tag{1.2}$$

Here A_I is the amplitude of scattering by one isolated scatterer. If the distance from the source, through O, to the detector (at scattering angle 2θ) is R_O, then the amplitudes of the two rays through centers 1 and 2 are, respectively

$$A_1 = A_I \sin\left\{\omega t - 2\pi \frac{R_O + \mathbf{r}_1 \cdot (\hat{\mathbf{s}} - \hat{\mathbf{s}}_O)}{\lambda}\right\} \tag{1.3}$$

$$A_2 = A_I \sin\left\{\omega t - 2\pi \frac{R_O + \mathbf{r}_2 \cdot (\hat{\mathbf{s}} - \hat{\mathbf{s}}_O)}{\lambda}\right\} \tag{1.4}$$

The construction leading to this result is shown in Fig. 1.5.

It is convenient at this point to introduce the scattering vector $\mathbf{s} = \frac{\hat{\mathbf{s}} - \hat{\mathbf{s}}_O}{\lambda}$. The construction for $\mathbf{s}$ is sketched in Fig. 1.6. Clearly

$$s = |\mathbf{s}| = \frac{2 \sin\theta}{\lambda} \tag{1.5}$$

(In the case of scattering by atomic planes within a crystal, $\mathbf{s}$ is normal to the diffracting plane.)

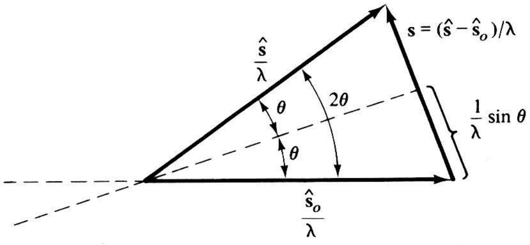


Figure 1.6. Geometrical representation of the scattering vector s.

The total amplitude is thus written

$$A = A_I \sum_i \sin\left[\left(\omega t - 2\pi\frac{R_O}{\lambda}\right) - 2\pi\mathbf{r}_i \cdot \mathbf{s}\right] \tag{1.6}$$

This simplifies a great deal. A result from the classical theory of electromagnetic waves tells us that the intensity of scattering is just the square of the amplitude (see Appendix A). Thus,

$$\begin{aligned} I(\mathbf{s}) = A_I^2 &\left\{ \sum_i \sin\left[\left(\omega t - 2\pi\frac{R_O}{\lambda}\right) - 2\pi\mathbf{r}_i \cdot \mathbf{s}\right]\right\} \\ &\left\{ \sum_j \sin\left[\left(\omega t - 2\pi\frac{R_O}{\lambda}\right) - 2\pi\mathbf{r}_j \cdot \mathbf{s}\right]\right\} \end{aligned} \tag{1.7}$$

This is of the form

$$I(\mathbf{s}) = A_I^2 \sum_i \sin\,(a + b_i) \sum_j \sin\,(a + b_j) \tag{1.8}$$

Using the identity

$$\sin\,(a + b) = \cos\,a \sin\,b + \sin\,a \cos\,b \tag{1.9}$$

the intensity formula expands to become

$$\begin{aligned} I(\mathbf{s}) = A_I^2 &\left(\sin^2 a \sum_i \sum_j \cos\,b_i \cos\,b_j + \cos^2 a \sum_i \sum_j \sin\,b_i \sin\,b_j\right) \\ &+ A_I^2 \sin\,a \cos\,a \left(\sum_i \sum_j \cos\,b_i \sin\,b_j + \sum_i \sum_j \sin\,b_i \cos\,b_j\right) \end{aligned} \tag{1.10}$$

Experimentally we average over many periods of the wave. That is, we take an average over time. Thus, we replace $\sin^2 a$ by its time average, $\cos^2 a$ by its time average, etc. These averages are

$$\begin{aligned} \overline{\sin^2 a} &= ½ \\ \overline{\cos^2 a} &= ½ \\ \overline{\sin\,a \cos\,a} &= 0 \end{aligned} \tag{1.11}$$

and we have for our experimental intensity

$$\begin{aligned} I(\mathbf{s}) &= \frac{A_I^2}{2}\left(\sum_i \sum_j \cos\,b_i \cos\,b_j + \sum_i \sum_j \sin\,b_i \sin\,b_j\right) \\ &= I_I\left(\sum_i \sum_j \cos\,b_i \cos\,b_j + \sum_i \sum_j \sin\,b_i \sin\,b_j\right) \end{aligned} \tag{1.12}$$

where $I_I = (A_I^2)/2$ is the mean squared, or measurable, intensity of the primary beam.