INTRODUCTION TO DIFFRACTION IN MATERIALS SCIENCE AND ENGINEERING

AARON D. KRAWITZ

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PREFACE

This book aims to convey an understanding of the arrangement of atoms in crystalline solids and to introduce diffraction, a primary method used by materials scientists and engineers for the study of such arrangements.

The field of materials science and engineering has been particularly active in exploiting diffraction as an analytical tool. This is because the field is concerned with the relation of the structure of materials to their properties. Since diffraction is a means of determining crystal structures, it can be used to characterize new structures, as well as to determine the presence and amount of known structures—qualitative and quantitative phase analysis. Materials scientists are also interested in the effect that changes in structure, such as texture, ordering, interstitial impurities, plastic deformation, residual stress, and very small crystallites or grains have on material behavior. Diffraction lends itself well to the study of all these.

Diffraction utilizes electromagnetic (X-rays) or particle waves (neutrons, electrons). These have typically had wavelengths of 1-2 Å, the scale of atomic spacings in materials (except for the much shorter wavelengths that are utilized in electron microscopes, in conjunction with imaging capabilities). However, synchrotron X-rays of a few tenths of an Angstrom and cold neutrons of 3-5 Angstroms have become more accessible. This accessibility is changing the way we use these tools in our studies of materials. Increasingly, industrial, governmental and academic engineers and scientists will be able to go to national or international centers to perform experiments. You do not have to be a professional diffraction specialist to utilize the world's best facilities. Governments have invested a lot of money in facilities whose success is judged in part by the number of users they attract and help. This change in the materials science landscape will take several years to fully permeate the scientific and engineering community. A major goal of this text is to help expand these user communities.

Neutrons are treated for three reasons. One is that comparative methods of study have long been used in the humanities and it seems to me that a comparative approach using X-rays and neutrons should also be pedagogically useful. Comparative studies offer insights hard to obtain in other ways. They facilitate critical thinking. Another is that, although trained with X-rays, I have primarily used neutrons for more than

20 years to measure residual stresses in engineering materials. I have come to believe in their value to materials scientists and engineers. However, probably the most important reason is that user access to reactor and pulsed neutron sources at national facilities is greater than ever before and exciting new opportunities for materials scientists and engineers have emerged and are now emerging.

The book begins with a treatment of crystallography (Chapter 1). I believe that a grasp of the basic principles of the arrangements of atoms in space is necessary for the understanding of materials. The properties of materials are so dependent on their crystal structure that an adequate grounding in the subject should be, in my view, a fundamental part of a materials science curriculum. In my experience, a first diffraction course is an excellent place in the curriculum for exposure to the principles of crystallography. The approach here is fairly practical. A primary objective is the ability to use the International Tables for Crystallography. This requires an ability to understand crystal structure in terms of the concepts of symmetry, point groups, lattices, unit cells, crystal systems, space groups and equipoints. The geometrical representation of crystals, including the notation for planes and directions in lattices and a number of geometrical relationships concerning interplanar spacings, interplanar angles, and cell volumes is then considered (Chapter 2). This is done using the concept of reciprocal space. Basic reciprocal lattice concepts are useful both for crystallographic calculations and for understanding diffraction.

Aspects of X-rays and neutrons of relevance to materials scientists in the context of diffraction applications are discussed in Chapters 3 and 4, respectively. Although the use of conventional X-rays is overwhelmingly greater than synchrotron X-rays or neutrons, the subsequent topics essentially apply to both X-ray and neutron diffraction. It is, of course, possible to simply skip the neutron chapter, as well as subsequent references to neutron diffraction.

The diffraction process and diffraction from single crystals and powders are covered in Chapters 5 and 6, respectively. The basic ideas needed to employ diffraction in the study and characterization of materials is presented, and a number of structure factors are worked out (Chapter 5). Discussions of intensity and the effect of absorption and thermal vibration (temperature) on intensity are introduced in this section. Diffraction experiments lend themselves to modeling in advance, and the issues discussed herein are important for the modeling of experiments.

Chapter 7 deals with "two-dimensional recording" of diffraction patterns. For many years the primary means of recording diffraction information for X-rays was film, and several ingenious cameras were devised to record three-dimensional diffraction patterns on two-dimensional surfaces (film). With the advent of electronic detectors and computers, the use of cameras has drastically decreased. However, an interesting thing has occurred. Although actual film recording has become rare, two-dimensional recording has reemerged due to developments in detectors. Large area detectors are being employed and, in the case of neutrons, substantial coverage around samples is becoming a reality. Thus, film recording has become relevant again. Of the three "film" methods dealt with here, powder and Laue cameras are of particular relevance in materials science. The rotation method is included largely for its pedagogical value.

The applications begin with qualitative and quantitative phase analysis (Chapter 8). The discussion of qualitative phase analysis emphasizes use of the Powder Diffraction File. Chemical identification by X-ray fluorescence is also (briefly) included. Quantitative phase analysis deals with the use of intensities to obtain amounts of phases present in multiphase mixtures. Chapter 9 attempts to provide an appreciation for more complex structures, those containing atoms at variable positions. It is through these that the power of diffraction to elucidate complex structures hopefully becomes apparent. The view of structures as built up by filling equipoints is emphasized, first through trigonometric structure factors and then with the Rietveld profile refinement method. This text does not deal with Fourier methods. The chapter features a fairly elaborate example utilizing trigonometric structure factors. The information in this chapter will enable variable position structure factors to be calculated from scratch or through existing programs. Residual stress measurements are discussed in Chapter 10. The elements of making residual stress measurements are discussed thoroughly enough to enable their design and interpretation. The use of neutrons to make stress measurements has developed rapidly since 1980 and a number of dedicated instruments are now available. Chapter 11 offers elementary treatments of texture, line broadening due to small scattering units, and long-range order. They are intended to give a feeling for the physical origins of the diffraction effects.

This text is intended as a one semester, first course exposure to diffraction usage in materials science and engineering, or a book for self-study. It aims to provide a sound basis for students and practitioners who desire (or are required to have) an understanding of the possibilities of diffraction in materials science. My university has, through its Campus Writing Program, developed a model program for using writing to develop critical thinking skills. This initiative, part of a national movement called Writing Across the Curriculum, has proven effective in delivering a more comprehensive treatment of course subject matter in all disciplines. I have embraced these ideas in my teaching and have tried to incorporate them in this text through the examples and the critical thinking questions that are part of the exercises at the ends of chapters. These are not really writing assignments but pose more open-ended questions which should extend the students' thinking. I thank the staff of the Campus Writing Program at MU for exposing me to these ideas, Dr. Martha Townsend, Dr. Martha Patton, and Jo Ann Vogt.

This book is ultimately based on ideas I was exposed to as a student of Professor J. B. Cohen at Northwestern University. He has been my primary influence in pursuing diffraction applications as the basis of my career. I am proud to acknowledge my debt to him and deeply saddened by his untimely death during the preparation of this manuscript. My last communication with him was to obtain permission to use the GeSe structure as a case study in Chapter 9. It was our final lab project in my first diffraction course with him more than 30 years ago.

Prof. R. Andrew Winholtz tested the text in an earlier version and has made numerous suggestions throughout the writing process. My former MS student Dr. Brent Butler provided X-ray data used for some of the figures. Dr. Hans Priesmeyer supplied the wonderful neutron radiograph of a rose in a lead cask. Mr. L. Ross, generously provided fluorescence information and plots. Dr. W. B. Yelon kindly provided Rietveld data. Russ Brown, David Nickolaus, and Dan Coats prepared most of the figures. Jon Paggett also provided valuable assistance. My department Chair, Prof. Robert Tzou, was very supportive throughout the project. I would also like to acknowledge Dr. Michael T. Hutchings with whom I co-edited what is still the only volume on neutron stress measurements. He was the driving force for the NATO Advanced Workshop in 1991 that did so much to develop the field. I would like to acknowledge my other teachers in the Dept. of Materials Science and Engineering at Northwestern, who did so much for me. My former and present colleagues at the MU Research Reactor Center, Drs. R. M. Brugger, K. Herwig, B. Heuser, H. Kaiser, D. F. R. Mildner, M. Popovici, J. J. Rhyne, F. K. Ross, S. A. Werner, and W. B. Yelon also contributed through numerous discussions over the years. Many departmental and campus colleagues and friends have also been supportive and I thank them.

Finally, I want to express my gratitude to my neutron stress colleagues with whom I have talked diffraction for 20 years.

This book would not have been completed without the support of my wife, Nikki, and my son, Adam.

Columbia, Missouri Aaron Krawitz
January, 2001

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1

CRYSTALLOGRAPHY

INTRODUCTION

A materials scientist should understand the nature of materials. This includes the periodic distribution of atoms in space characteristic of most crystalline solids—the crystal structure. Many physical attributes may be traced to the crystal structure. This includes the deformability of face-centered cubic metals, the use of graphite as a lubricant, the double-helix structure of DNA, and the mechanism of conduction in ionic conductors, to name a few. Although an elementary understanding of diffraction can be obtained with only a superficial appreciation of the nature of the structure of crystalline materials, a real understanding of materials—and many diffraction methods—requires more.

It turns out that any shape, symbol, design, or object can be reproduced periodically to create a regular array that fills all space. This involves use of the symmetry operations of rotation, reflection, and inversion, as well as translation. This can be illustrated in two-dimensions using an irregular shape, a bent leg for example, as shown in Figure 1.1. Not only can the shape fill an infinite plane, it can be arranged in different ways, such as in a square array, Figure 1.1(*a*), or a slanted or oblique array, Figure 1.1(*b*). More complex arrays can be created using the same shape or **asymmetric unit**. The array in Figure 1.1(*c*) has a rotational feature. At certain locations, marked on Figure 1.2(*a*) with ovals, a 180° rotation will cause the whole pattern to come back into registry. In Figure 1.1(*d*), another type of symmetric relationship is shown. In this case certain lines, indicated on Figure 1.2(*b*), act as mirrors; that is, the whole figure can be reflected through them and come back into registry. In general, reflection of an asymmetric unit through a mirror plane changes it from a right-handed unit to a left-handed one.

Having determined that the shape repeated in Figure 1.1 is a leg, and that the repeated patterns it forms can contain symmetrical elements, what is the smallest

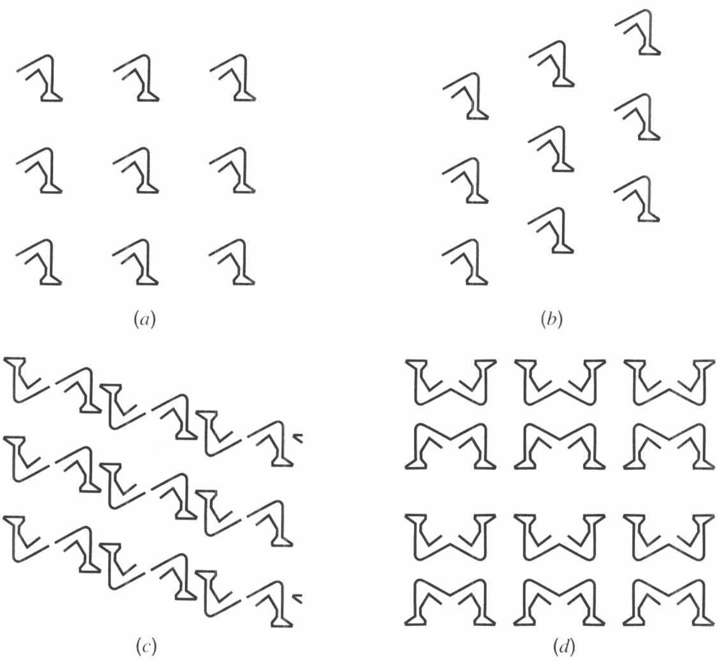

FIGURE 1.1. Four different arrays in a plane using an asymmetric "leg." (*a*) Square array; (*b*) oblique array; (*c*) oblique array with 2-fold rotational symmetry; (*d*) rectangular array with mirror plane symmetry.

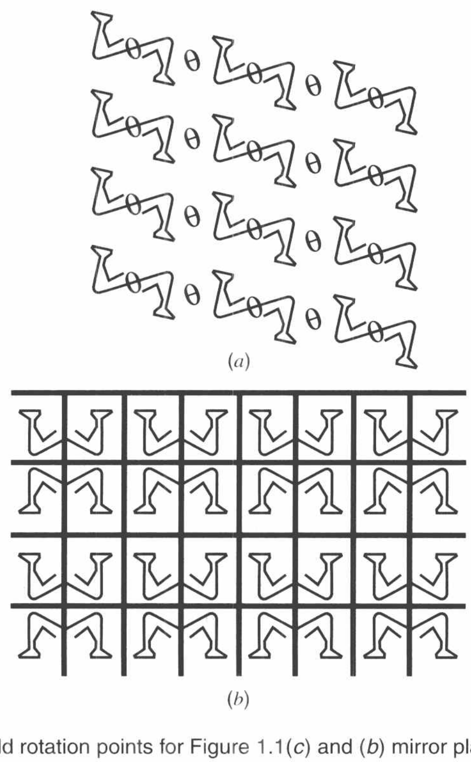

FIGURE 1.2. Two-fold rotation points for Figure 1.1(*c*) and (*b*) mirror planes in Figure 1.1(*d*).

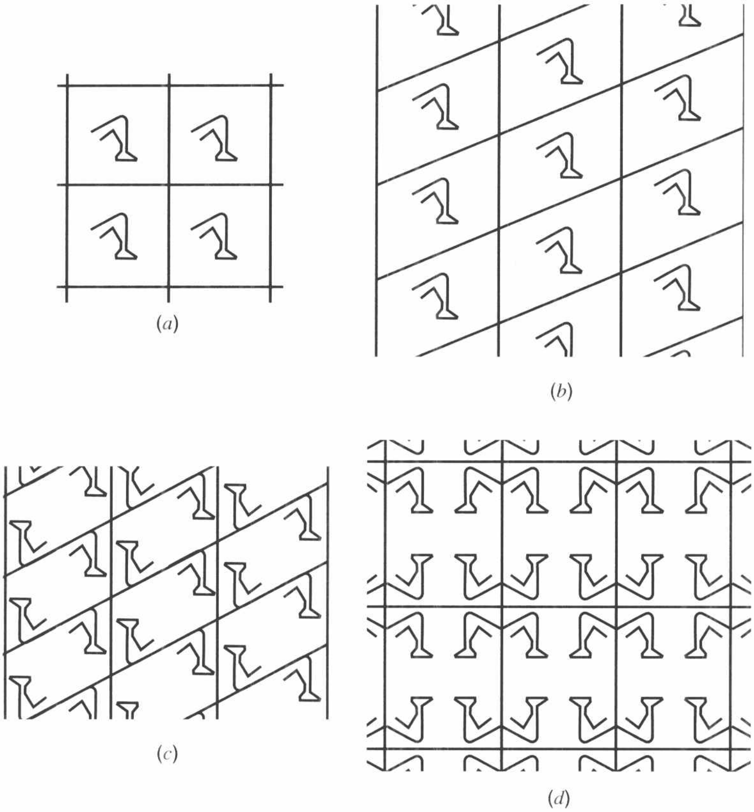

FIGURE 1.3. Unit cells for Figure 1.1: (*a*) square; (*b*) oblique; (*c*) oblique; (*d*) rectangular.

portion of the pattern that will contain both the asymmetric unit and the symmetry elements? In Figure 1.3 these portions are indicated for each of the four patterns presented in Figure 1.1. They contain all the information necessary to generate an infinite array of the pattern. They are called unit cells and fill space by being translated, that is, shifted parallel to the edges of the cell by distances equal to the lengths of the cell edges, and reproduced.

A repeating pattern has three defining aspects: the shape of the unit cell, the symmetry within it, and the translation of the unit cell to fill space. The smallest cell that can be translated must have a shape that is compatible with the symmetry within it. The symmetry within the cell is defined with respect to specific points and operations. The set of such symmetry operations is called a **point group** because it leaves at least one point in space unmoved. Each point group contains a unique combination of symmetry elements. There are a finite set of symmetries with respect to a point in space: 2 in one dimension, 10 in two dimensions, and 32 in three dimensions. In Figure 1.1, three such point groups were shown. Figure 1.1(*a*) and (*b*) contains no internal symmetry; put differently, the least amount of symmetry is no symmetry, yet an infinite planar array can still be created. The only difference between Figure 1.1(*a*) and (*b*) is that the shape of the unit cell changed. In Figure 1.1(*c*) twofold rotation is introduced in the unit cell, while in Figure 1.1(*d*) mirror planes are introduced. Example 1.1 demonstrates how more than one set of symmetries can exist in a pattern.

Example 1.1 *Symmetry of a Soccer Field*

An asymmetric unit consisting of some straight lines and arcs is shown in Figure E1.1(*a*). If a vertical mirror plane is placed on the right-hand side of the unit and a horizontal mirror plane on the bottom, a soccer field pattern, which has mirror symmetry, will be generated, as shown in Figure E1.1(*b*). In addition, if a point is placed at the center of the field and the pattern is rotated 180°, it will return to registry. This is called 2-fold rotational symmetry. This soccer field pattern possesses the same symmetry as in Figure 1.1(*d*), which also has a 2-fold rotation axes at the intersections of mirror planes.

(a)

(b)

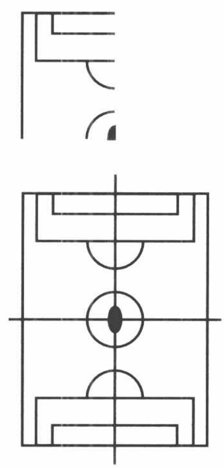

FIGURE E1.1. (*a*) Asymmetric unit used, with mirror symmetry, to generate (*b*) a soccer field.

There is also a finite set of basic cell types: one in one dimension, four in two dimensions, and seven in three dimensions. These cell types are compatible with the possible point groups. Figure 1.1 includes a square cell (*a*), a parallelogram or oblique cell (*b*), and a rectangular cell (*c*) and (*d*). Thus, Figure 1.1 includes three of the four cell types possible in two dimensions.

In three dimensions the 32 point groups and 7 basic cell shapes can be combined to produce 230 distinct three-dimensionally periodic arrays in space, called **space groups**. When atoms are associated with these space groups, they are called **crystal structures**. The evolution of these crystal structures will now be presented.