X-RAY CRYSTAL STRUCTURE

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Library of Congress Catalog Card Number: 57-6404

THE MAPLE PRESS COMPANY, YORK, PA.

Preface

Many books have been written in a *popular* style to emphasize the importance of x-ray crystallography and to create interest in the wonderful findings of the workers in the field. A few books have been written with *rigor* for the benefit of the most advanced scholars. In between the extremes of *popular* and *rigorous* there is a gap. As a consequence of this gap, a very large proportion of the x-ray crystallographers actively engaged in the field in America today are working out structures successfully only because they have bridged the gap by having read a necessarily large number of those papers in the scientific journals which serve as signposts for the theory and the proper procedure. It is the purpose of the present text to furnish a common source in which the student may find condensed the teachings of the pioneers in crystallography. Although the lone investigator is borne in mind throughout the book, it has been hoped that the book may also be of use as a university text in a two-quarter course in structure analysis. Much of this book has been used as lecture material over a six-year period at the University of Utah (1947–1953) and, in the form of mimeographed lecture notes, has been under constant revision from the beginning. The first four chapters pertain to crystallography preparatory to the last five chapters on structure.

Thanks for advice and encouragement during the early writing of the text are due Dean Carl J. Christensen, Dr. John R. Lewis, and Dr. Hugh Hamilton of the University of Utah; and facilities for the final completion of the manuscript were furnished by Dr. Thomas C. Poulter of the Stanford Research Institute to whom I am grateful. Unusual effort and skill in drawing and typing by Alice Morey Bailey contributed to the early progress. Other contributors were Mrs. J. Fredrickson, Hazel Christopher, and Mrs. Laurie Chamberlain to whom I am appreciative. Mrs. Fredolyn McLachlan kindly gave invaluable aid in proofreading. I am especially grateful for the critical reading and criticisms of Dr. George E. Duvall and Dr. Bruno J. Zwolinski.

Thanks are also due to many workers who have allowed the reproduction of diagrams and photographs from their works, and acknowledgment is made in each case in the text. It is impossible to overemphasize the assistance obtained from the writings of such men as R. W. James, A. H. Compton, and many others, and again an attempt is made throughout the text to give them credit.

Dan McLachlan, Jr.

Contents

Chapter 1

CRYSTALS

1-1. Introduction

The history of crystallography is divisible into two parts: (1) before 1912 and (2) after 1912. Prior to 1912, crystals were studied by optical methods almost exclusively. By means of optical goniometers and microscopes, thousands of crystals, particularly minerals and some organic compounds, had been investigated. From the great quantity of data thus obtained, a number of laws were deduced in the field of crystallography. The rules of symmetry were established and the 32 crystal classes identified and defined. The concept of Miller indices was developed. The existence of six crystal systems was recognized. The principle of nodes or centers was developed, and the 14 Bravais lattices were enumerated. The art of pictorial representation by means of projections and other geometrical devices was well advanced, and nomenclature was growing faster than it was being unified. With the polarizing microscope, crystals could be classified into uniaxial and biaxial types, and indicatrices could be drawn or computed. With this knowledge, the optical tools of crystallography were used for identification in industry and mining as well as for academic purposes in promoting the science.

With the first successful diffraction of x-rays in 1912, crystallographers began investigations of crystals on an atomic basis. X-rays furnished means for studying the manner in which atoms are held together in the systematic configurations which account for the symmetry and beauty of crystals. It was recognized almost immediately that the atoms in the crystal are arranged in repeating imaginary cells similar to eggs in an egg crate; only there may be many atoms in one cell. It was found that each cell exhibits the same symmetry as the

entire crystal. The theory of point groups (giving rise to the 32 crystal classes) could be applied to the individual cells. While gross properties were previously used to identify symmetry, now symmetry could be based on the configuration of atoms in each cell.

By studying the arrangement of diffraction spots on a photographic film and by placing particular attention on the systematic absence of spots where they would otherwise be expected to occur, crystals were further classified beyond the 32 classes. There are 230 space groups among crystals, all identifiable by the occurrence of absences or extinctions.

By measuring the position and distances between diffraction spots on the x-ray film, interplanar distances can be computed. Hence the crystallographer is not confined in his study to the external planes or growth faces of a crystal; he can now consider internal planes. With a broader concept of crystallographic planes, Miller indices took on a broader meaning. The dimensions of the cell could be measured. Knowing density, Avogadro's number, and atomic weight, the atomic content of the cell can be computed.

Early in the x-ray studies, attention was directed toward the varying intensities of the diffraction spots. With the introduction of Fourier series as a mathematical tool, crystallographers learned to incorporate the measured intensities of the spots into computation of the positions of atoms in unit cells. This is the objective and ultimate goal of present-day crystallography; and the overcoming of the many difficulties in its achievement has occupied the time of some of the most inventive and most analytical thinkers since 1927.

Some of the achievements of past workers are listed below in the order in which they were encountered. The further improvement of methods (as well as the development of new methods) furnishes fields of research for years to come.

1. The production of an intense monochromatic collimated beam of x-rays.
2. Acquiring a crystal either from nature or by growth in the laboratory.
3. The development of cameras for recording diffraction maxima in such a configuration that they can be identified and assigned the appropriate Miller indices.
4. The measurement of intensities by photographic means or by ionization chambers, Geiger counters, or scintillation counters.
5. The correction of intensities for polarization, divergence of beam, temperature, absorption of crystal, and the speed of rotation of the crystal.

6. The development of facilities and machines for hastening the computations of the theoretical structure factors and electron densities.
7. Devising theories and means for finding the phases of the Fourier coefficients.

While the above items outline broadly the achievements in developing x-ray diffraction as a tool in crystallography, the list of achievements in the successful applications of x-rays in the study of the structure of matter is much longer. Contributions to the fields of textiles and fibers, drugs, metals, minerals, foods, and living tissues are beyond the scope of this text. While this book is largely devoted to the use of x-rays in structure determination, this first chapter discusses the general properties of crystals.

1-2. The Crystal Systems or Primitive Lattices

The two most pronounced properties of crystals which distinguish them from all other forms of matter are: (1) the properties of crystals

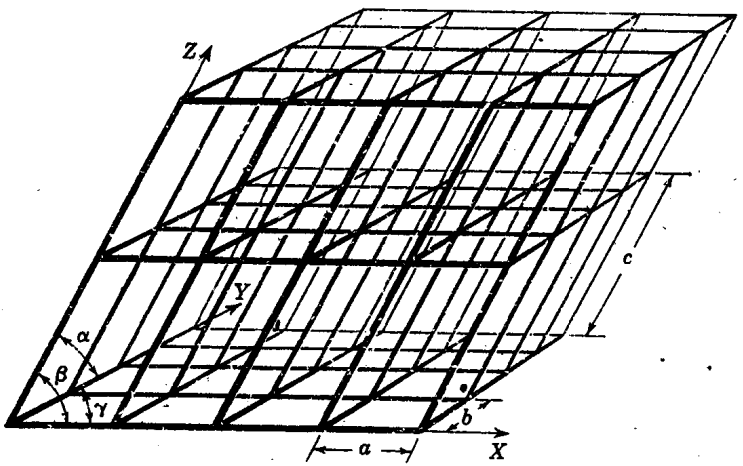

FIG. 1-1. The general (triclinic) space lattice showing the unit cell dimensions a, b, c and the angles α, β, and γ. It is becoming standard practice among crystallographers, however, to make α, β, and γ represent the obtuse angles.

are a function of the direction along which the properties are measured and (2) the atomic configuration is repetitive in three dimensions. The directions are usually referred to three crystallographic axes, x, y, and z. The volume of the repeating pattern is called a unit cell.

The concept of a repetitive unit cell immediately brings up the question as to how many shapes can be used to fill space with identical

cells so that there are no voids and no overlaps. The answer is that there are six such primary shapes or crystal lattices.

The edges of the unit cell have the dimensions a along x, b along y, and c along z. A face of a cell which has the edges a and b as two of its boundaries is called a C face, one bounded by a and c is a B face, and, by b and c, an A face.

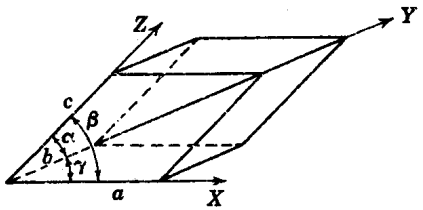

FIG. 1-2. The triclinic cell.

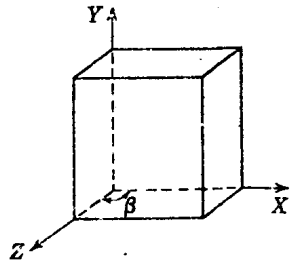

FIG. 1-3. The monoclinic cell.

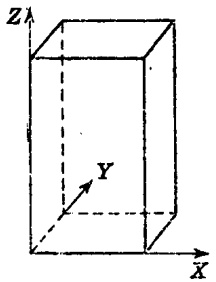

FIG. 1-4. The orthorhombic cell.

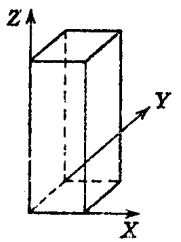

FIG. 1-5. The tetragonal cell.

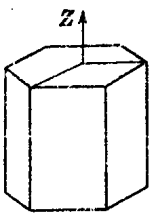

FIG. 1-6. The hexagonal cell.

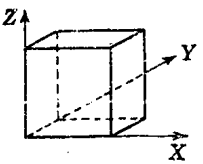

FIG. 1-7. The cubic cell.

In three dimensions there is one general lattice, and the others are special cases of the general one. The general lattice is the triclinic lattice shown in Fig. 1-1. It is produced by the intersection of three parallel sets of planes in such a manner that the distances between the points of intersection have general dimensions a, b, and c. The lines connecting these intersections are considered the unit cell edges, and the angles between them have general values α, β, and γ.

The special lattices result from special values of a, b, c, α, β, or γ. For example, one very special case is the cube, in which $a = b = c$ and

$\alpha = \beta = \gamma = 90°$. The special lattices obtained in this way, as well as the general lattice, are shown in Table 1-1.

Table 1-1

1. Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
2. Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90°, \beta \neq 90°$
3. Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
4. Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
5. Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
6. Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$

The six lattices enumerated in this table are shown in Figs. 1-2 to 1-7. The angle between the b and c edges is designated α, between a and c edges β, and between the a and b edges γ.

1-3. Atomic Positions

If one can name all the atoms in a crystal according to the accepted symbols in the periodic table and tell where each atom is located in the crystal, then the crystal structure is known. Since all crystals are repetitive in content and atomic configuration, the task is reduced to that of naming and locating only the atoms in one unit cell. The location of the ith atom in a unit cell is determined by measuring its position with respect to the three crystallographic directions x, y, and z and expressed as $x_iy_iz_i$. The positions from which the distances are measured are called centers. In the primitive lattices, the centers are the corners of the unit cells and the directions are the edges.

1-4. Bravais Lattices

The discovery that cells have centers other than those at the unit cell corners was made by Bravais. This discovery resulted in 14 lattices instead of the original six. These 14 lattices are often called Bravais lattices because of his discovery of them by optical means. The 14 Bravais lattices are shown in Figs. 1-2a to 1-7a. The symbols

Table 1-2

No centers except corners	P
Centered on A face	A
Centered on B face	B
Centered on C face	C
Centered on all faces	F
Body-centered	I
Rhombohedral	R
Hexagonal	H

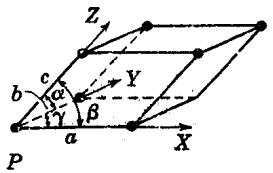

FIG. 1-2*a*. The triclinic lattice is always primitive, *P*.

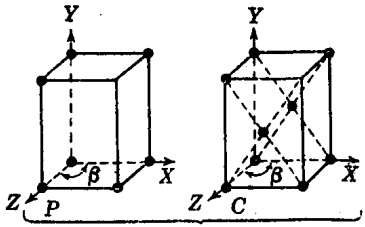

FIG. 1-3*a*. The monoclinic lattice may be primitive, *P*, or centered, *C*, i.e., centered on the *ab* face. (Note that in this lattice only the *y* axis is vertical. This long-established practice may some day be abandoned.)

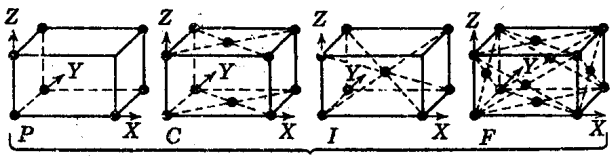

FIG. 1-4*a*. The orthorhombic lattices are the primitive, *P*, the centered, *C*, the body-centered, *I*, and the face-centered, *F* (centered on all faces).

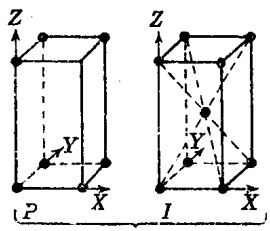

FIG. 1-5*a*. The tetragonal lattice may be primitive, *P*, or body-centered, *I*.

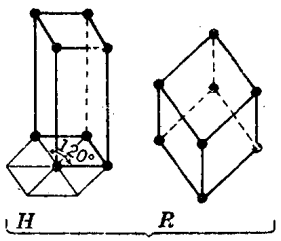

FIG. 1-6*a*. The hexagonal system is divided into the hexagonal division, *H*, and the rhombohedral division, *R*.

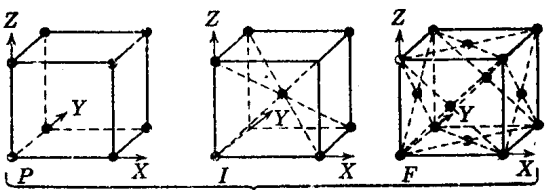

FIG. 1-7*a*. The cubic system may be primitive, *P*, body-centered, *I*, or face-centered, *F*.

shown in Table 1-2 are used to designate the various kinds of primitive and nonprimitive cells.

1-5. Miller Indices

One consequence of the fact that a crystal is a repeating pattern of unit cells fitting together, each containing atoms in identical configurations, is that the atoms appear to be located in a laminar manner along parallel planes. That atoms may appear to be so aligned is analogous to the numerous lines upon which the trees in an orchard appear to be arranged. The directions of the planes of alignment through the crystal are indicated by the Miller indices.

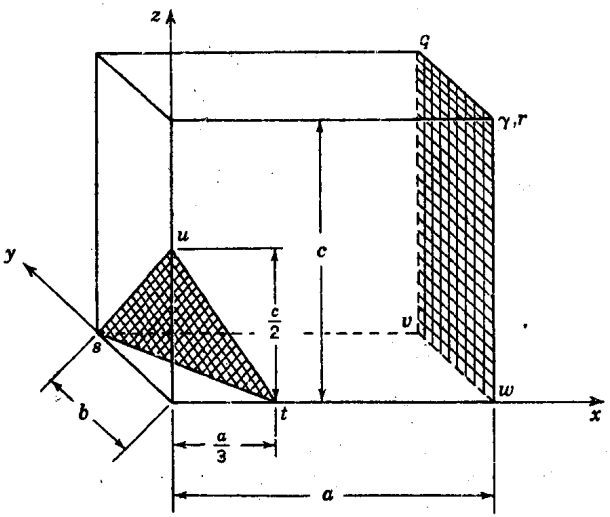

FIG. 1-8. Showing the position of the (312) plane and the (100) plane in the unit cell.

Miller indices[1]* can be described as follows. Any natural crystal can be considered as having three axes designated as the x, y, and z axes. Three reference distances a, b, and c can be set off along each of these axes. While optical methods can furnish only the ratios $a:b:c$ of these axes, x-rays furnish their actual length. Any naturally grown face of a crystal is so oriented that its intercepts on the x, y, and z axes cut a, b, and c at integral fractions of their lengths. In Fig. 1-8 is a unit cell having dimensions a, b, and c in the x, y, and z directions, respectively, with a plane cutting the x axis at t, the y axis at s, and the z axis at u. This plane has been so oriented that a has been cut at $\frac{1}{3}$, b at unity, and c at $\frac{1}{2}$. The Miller indices are defined as the reciprocal of these fractions and, therefore, the Miller indices of this plane are

*Superscript numbers refer to the references at the ends of the chapters.

(312). The plane *wvqr* of Fig. 1-8, for example, cuts a at unity, b at ∞, and c at ∞, and has the Miller indices (100). Thus, the direction of any plane or family of planes can be uniquely defined in terms of the Miller indices. A tetragonal crystal with its external faces labeled according to the Miller indices is shown in Fig. 1-12.

1-6. Families of Planes

Whereas Fig. 1-8 showed only one plane having the Miller indices (312), there are many planes having this same direction. To show this, Fig. 1-9 has drawn within a unit cell the plane $s't'u'$ having Miller indices (824). As the figure shows, there are innumerable planes within a very large crystal having this same direction. All are spaced

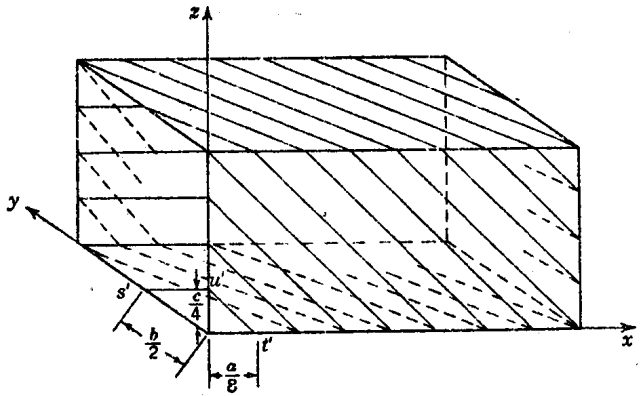

FIG. 1-9. Showing all the planes belonging to the (824) family of planes. They are all parallel, equally spaced, and commensurate with the unit cell dimensions.

so that their intercepts on the x axis are spaced at $a/8$, on the y axis $b/2$, and on the z axis $c/4$. Such a set of planes is called a *family of planes*. Each plane may or may not be populated with atoms. Of great significance in x-ray work is the perpendicular distance d_{hkl} between the planes, which is to be discussed later.

1-7. Orientation within the Crystal

In x-ray work a person may desire to take a crystal which the optical crystallographer has classified as far as he can go (i.e., to the 32 classes) and rotate it about a given set of crystallographic axes in one of the single-crystal x-ray cameras. In "setting up the crystal" one must know the orientation of the axes with respect to the external shape of the crystal. For example, in Fig. 1-10 the left-hand figure has the unit cell edges parallel with some of the prominent faces of the crystal so that the face M is perpendicular to x and parallel to the y and z axes;