

Preface

A little over five years have passed since the first edition of this book appeared in print. Seems like an instant but also eternity, especially considering numerous developments in the hardware and software that have made it from the laboratory test beds into the real world of powder diffraction. This prompted a revision, which had to be beyond cosmetic limits. The book was, and remains focused on standard laboratory powder diffractometry. It is still meant to be used as a text for teaching students about the capabilities and limitations of the powder diffraction method. We also hope that it goes beyond a simple text, and therefore, is useful as a reference to practitioners of the technique.

The original book had seven long chapters that may have made its use as a text inconvenient. So the second edition is broken down into 25 shorter chapters. The first fifteen are concerned with the fundamentals of powder diffraction, which makes it much more logical, considering a typical 16-week long semester. The last ten chapters are concerned with practical examples of structure solution and refinement, which were preserved from the first edition and expanded by another example – solving the crystal structure of Tylenol[®].

Major revisions include an expanded discussion of nonconventional crystallographic symmetry in Chap. 5, a short description of two new types of detectors that are becoming common in laboratory powder diffractometry – real-time multiple strip and multi wire detectors in Chap. 6, a brief introduction to the total scattering analysis in Chap. 10, a short section in Chap. 11 describing nonambient powder diffractometry, an expanded discussion of quantitative phase analysis, including the basics of how to quantify amorphous component in Chap. 13, an update about the recent advancements in the *ab initio* indexing, together with an example of a difficult pseudo-symmetric case represented by $\text{Li}[\text{B}(\text{C}_2\text{O}_4)_2]$, and a major update of Chap. 15 dedicated to the fundamentals of Rietveld analysis, including a brief introduction of the mechanism of restraints, constraints, and rigid bodies. The collection of problems that may be used by instructors to assess students' progress and as self-exercises has also expanded. All problems related to the solution and refinement of crystal structures from powder diffraction data are assembled at the end of Chap. 25.

Considering all these additions, something had to go. A major deletion from the earlier paper version is the section on X-ray safety, which has been moved to the electronic part of the book. Readers familiar with the first edition know that the book included a CD with electronic figures, experimental data, and solutions of all problems. Over the years, both the publisher and we have had numerous inquiries from people who accidentally used the CD as a coaster, clay pigeon, or simply sat on it before making a backup copy. While each and every request about sending a copy of the CD was fulfilled, we thought that it makes more sense to have the electronic files available online. The files are hosted by Springer (<http://www.springer.com/978-0-387-09578-3>) and they are made available to everyone who has the book. The files include color figures, powder diffraction data, examples, web links, and solutions to all the problems found throughout the book. Files with the solutions of the problems are only available to instructors, who must register with the publisher.

Finally, we would like to thank everyone who provided critique and feedback. Most important, we thank the readers who opted to buy our book with their hard-earned money thus providing enough votes for the publisher to consider this second, revised edition. It is our hope that this edition is met with even better acceptance by our readers of students, practitioners, and instructors of the truly basic materials characterization technique, which is the powder diffraction method.

Ames, Iowa, October 2008
College Park, Maryland, October 2008

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Preface to the First Edition

Without a doubt, crystals such as diamonds, emeralds and rubies, whose beauty has been exposed by jewelry-makers for centuries, are enjoyed by everybody for their perfect shapes and astonishing range of colors. Far fewer people take pleasure in the internal harmony – atomic structure – which defines shapes and other properties of crystals but remains invisible to the naked eye. Ordered atomic structures are present in a variety of common materials, for example, metals, sand, rocks or ice, in addition to the easily recognizable precious stones. The former usually consist of many tiny crystals and therefore, are called polycrystals, for example metals and ice, or powders, such as sand and snow. Besides external shapes and internal structures, the beauty of crystals can be appreciated from an infinite number of distinct diffraction patterns they form upon interaction with certain types of waves, for example, X-rays. Similarly, the beauty of the sea is largely defined by a continuously changing but distinctive patterns formed by waves on the water's surface.

Diffraction patterns from powders are recorded as numerical functions of a single independent variable, the Bragg angle, and they are striking in their fundamental simplicity. Yet, a well-executed experiment encompasses an extraordinarily rich variety of structural information, which is encoded in a material- and instrument-specific distribution of the intensity of coherently scattered monochromatic waves whose wavelengths are commensurate with lattice spacing. The utility of the powder diffraction method – one of the most essential tools in the structural characterization of materials – has been tested for over 90 years of successful use in both academia and industry. A broad range of general-purpose and specialized powder diffractometers are commonly available today, and just about every research project that involves polycrystalline solids inevitably begins with collecting a powder diffraction pattern. The pattern is then examined to establish or verify phase composition, purity, and the structure of the newly prepared material. In fact, at least a basic identification by employing powder diffraction data as a fingerprint of a substance, coupled with search-and-match among hundreds of thousands of known powder diffraction patterns stored in various databases, is an unwritten mandate for every serious work that involves crystalline matter.

Throughout the long history of the technique, its emphasis underwent several evolutionary and revolutionary transformations. Remarkably, the new developments have neither taken away, nor diminished the value of earlier applications of the powder diffraction method; on the contrary, they enhanced and made them more precise and dependable. A noteworthy example is phase identification from powder-diffraction data, which dates back to the late 1930s (Hanawalt, Rinn, and Frevel). Over the years, this application evolved into the Powder Diffraction File[™] containing reliable patterns of some 300,000 crystalline materials in a readily searchable database format (Powder Diffraction File is maintained and distributed by the International Centre for Diffraction Data, <http://www.icdd.com>).

As it often happens in science and engineering, certain innovations may go unnoticed for some time but when a critical mass is reached or exceeded, they stimulate unprecedented growth and expansion, never thought possible in the past. Both the significance and applications of the powder diffraction method have been drastically affected by several directly related as well as seemingly unrelated developments that have occurred in the recent past. First was the widespread transition from analogue (X-ray film) to digital (point, line, and area detectors) recording of scattered intensity, which resulted in the improved precision and resolution of the data. Second was the groundbreaking work by Rietveld, Young and many others, who showed that full profile powder diffraction data may be directly employed in structure refinement and solution. Third was the availability of personal computers, which not only function as instrument controllers, but also provide the much needed and readily available computing power. Computers thus enable the processing of large arrays of data collected in an average powder diffraction experiment. Fourth was the invention and rapid evolution of the internet, which puts a variety of excellent, thoroughly tested computer codes at everyone's fingertips, thanks to the visionary efforts of many bright and dedicated crystallographers.

Collectively, these major developments resulted in the revolutionary changes and opened new horizons for the powder diffraction technique. Not so long ago, if you wanted to establish the crystal structure of a material at the atomic resolution, virtually the only reliable choice was to grow an appropriate quality single crystal. Only then could one proceed with the collection of diffraction data from the crystal followed by a suitable data processing to solve the structure and refine relevant structural parameters. A common misconception among the majority of crystallographers was that powder diffraction has a well-defined niche, which is limited to phase identification and precise determination of unit cell dimensions. Over the past ten to twenty years the playing field has changed dramatically, and the *ab initio* structure determination from powder diffraction data is now a reality. This raises the bar and offers no excuse for those who sidestep the opportunity to establish details of the distribution of atoms in the crystal lattice of every polycrystalline material, whose properties are under examination. Indeed, accurate structural knowledge obtained from polycrystals is now within reach. We believe that it will eventually lead to a much better understanding of structure-property relationships, which are critical for future advancements in materials science, chemistry, physics, natural sciences, and engineering.

Before a brief summary recounting the subject of this book, we are obliged to mention that our work was not conducted in a vacuum. Excellent texts describing the powder diffraction method have been written, published, and used by the generations of professors teaching the subject and by the generations of students learning the trade in the past. Traditional applications of the technique have been exceptionally well-covered by Klug and Alexander (1954), Azaroff and Buerger (1958), Lipson and Steeple (1970), Cullity (1956 and 1978), Jenkins and Snyder (1996), and Cullity and Stock (2001). There has never been a lack of reports describing the modern capabilities of powder diffraction, and they remain abundant in technical literature (*Journal of Applied Crystallography*, *Acta Crystallographica*, *Powder Diffraction*, *Rigaku Journal*, and others). A collective monograph, dedicated entirely to the Rietveld method, was edited by Young and published in 1993. A second collection of reviews, describing the state of the art in structure determination from powder diffraction data, appeared in 2002, and it was edited by David, Shankland, McCusker, and Baerlocher. These two outstanding and highly professional monographs are a part of the multiple-volume series sponsored by the International Union of Crystallography, and are solid indicators that the powder diffraction method has been indeed transformed into a powerful and precise, yet readily accessible, structure determination tool. We highly recommend all the books mentioned in this paragraph as additional reading to everyone, although the older editions are out of print.

Our primary motivation for this work was the absence of a suitable text that can be used by both the undergraduate and graduate students interested in pursuing in-depth knowledge and gaining practical experience in the application of the powder diffraction method to structure solution and refinement. Here, we place emphasis on powder diffraction data collected using conventional X-ray sources and general-purpose powder diffractometers, which remain primary tools for thousands of researchers and students in their daily experimental work. Brilliant synchrotron and powerful neutron sources, which are currently operational or in the process of becoming so around the world, are only briefly mentioned. Both may, and often do provide unique experimental data, which are out-of-reach for conventional powder diffraction especially when high pressure, high and low temperature, and other extreme environments are of concern. The truth, however, is that the beam time is precious, and both synchrotron and neutron sources are unlikely to become available to everyone on a daily basis. Moreover, diffraction fundamentals remain the same, regardless of the nature of the employed radiation and the brilliance of the source.

This book has spawned from our affection and lasting involvement with the technique, which began long ago in a different country, when both of us were working our way through the undergraduate and then graduate programs in Inorganic Chemistry at L'viv State University, one of the oldest and finest institutions of higher education in Ukraine. As we moved along, powder diffraction has always remained on top of our research and teaching engagements. The major emphasis of our research is to obtain a better understanding of the structure–property relationships of crystalline materials, and both of us teach graduate-level powder diffraction courses at our respective departments – Materials Science and Engineering at Iowa State University and Chemistry at the State University of New York (SUNY) at Binghamton.

Even before we started talking about this book, we were unanimous in our goals: the syllabi of two different courses were independently designed to be useful for any background, including materials science, solid-state chemistry, physics, mineralogy, and literally any other area of science and engineering, where structural information at the atomic resolution is in demand. This philosophy, we hope, resulted in a text that requires no prior knowledge of the subject. Readers are expected to have a general scientific and mathematical background of the order of the first two years of a typical liberal arts and sciences or engineering college.

The book is divided into seven chapters. The first chapter deals with essential concepts of crystallographic symmetry, which are intended to facilitate both the understanding and appreciation of crystal structures. This chapter will also prepare the reader for the realization of the capabilities and limitations of the powder diffraction method. It begins with the well-established notions of the three-dimensional periodicity of crystal lattices and conventional crystallographic symmetry. It ends with a brief introduction to the relatively young subject – the symmetry of aperiodic crystals. Properties and interactions of symmetry elements, including examination of both point and space groups, the concept of reciprocal space, which is employed to represent diffraction from crystalline solids, and the formal algebraic treatment of crystallographic symmetry are introduced and discussed to the extent needed in the context of the book.

The second chapter is dedicated to properties and sources of radiation suitable for powder diffraction analysis, and gives an overview of the kinematical theory of diffraction along with its consequences in structure determination. Here, readers learn that the diffraction pattern of a crystal is a transformation of an ordered atomic structure into a reciprocal space rather than a direct image of the former. Diffraction from crystalline matter, specifically from polycrystalline materials is described as a function of crystal symmetry, atomic structure, and conditions of the experiment. The chapter ends with a general introduction to numerical techniques enabling the restoration of the three-dimensional distribution of atoms in a lattice by the transformation of the diffraction pattern back into direct space.

The third chapter begins with a brief historical overview describing the powder diffraction method and explains the principles, similarities, and differences among the variety of powder diffractometers available today. Since ionizing radiation and highly penetrating and energetic particles are employed in powder diffraction, safety is always a primary concern. Basic safety issues are concisely spelled out using policies and procedures established at the US DOE's Ames Laboratory as a practical example. Sample preparation and proper selection of experimental conditions are exceedingly important in the successful implementation of the technique. Therefore, the remainder of this chapter is dedicated to a variety of issues associated with specimen preparation, data collection, and analysis of most common systematic errors that have an impact on every powder diffraction experiment.

Beginning from chapter four, key issues that arise during the interpretation of powder diffraction data, eventually leading to structure determination, are considered in detail and illustrated by a variety of practical examples. This chapter describes preliminary processing of experimental data, which is critical in both

qualitative and quantitative phase analyses. In addition to a brief overview of phase identification techniques and quantitative analysis, readers will learn how to determine both the integrated intensities and angles of the observed Bragg peaks with the highest achievable precision.

Chapter five deals with the first major hurdle, which is encountered in powder diffraction analysis: unavoidably, the determination of any crystal structure starts from finding the shape, symmetry, and dimensions of the unit cell of the crystal lattice. In powder diffraction, finding the true unit cell from first principles may present considerable difficulty because experimental data are a one-dimensional projection of the three-dimensional reciprocal lattice. This chapter, therefore, introduces the reader to a variety of numerical techniques that result in the determination of precise unit cell dimensions. The theoretical background is followed by multiple practical examples with varying complexity.

Chapter six is dedicated to the solution of materials' structures, that is, here we learn how to find the distribution of atoms in the unit cell and create a complete or partial model of the crystal structure. The problem is generally far from trivial, and many structure solution cases in powder diffraction remain unique. Although structure determination from powder data is not a wide-open and straight highway, knowing where to enter, how to proceed, and where and when to exit is equally vital. Hence, in this chapter both direct and reciprocal space approaches and some practical applications of the theory of kinematical diffraction to solving crystal structures from powder data are explained and broadly illustrated. Practical examples start from simple, nearly transparent cases, and end with quite complex inorganic structures.

The solution of a crystal structure is considered complete only when multiple profile variables and crystallographic parameters of a model have been fully refined against the observed powder diffraction data. Thus, the last, the seventh chapter of this book describes the refinement technique, most commonly employed today, which is based on the idea suggested in the middle 1960s by Rietveld. Successful practical use of the Rietveld method, though directly related to the quality of powder diffraction data (the higher the quality, the more reliable the outcome), largely depends on the experience and the ability of the user to properly select a sequence in which various groups of parameters are refined. In this chapter, we introduce the basic theory of Rietveld's approach, followed by a series of hands-on examples that demonstrate the refinement of crystal structures with various degrees of completeness and complexity, models of which were partially or completely built in chapter six.

The book is supplemented by an electronic volume – compact disk – containing powder diffraction data collected from a variety of materials that are used as examples and in the problems offered at the end of every chapter. In addition, electronic versions of some 330 illustrations found throughout the book are also on the CD. Electronic illustrations, which we hope is useful to both instructors and students because electronic figures are in color, are located in a separate folder /Figures on the CD. Three additional folders named /Problems, /Examples and /Solutions contain experimental data, which are required for solving problems, as self-exercises, and our solutions to the problems, respectively. The disk is organized as a web page,

which makes it easy to navigate. All web links found in the book, are included on the CD and can be followed by simply clicking on them. Every link is current as of January 2003. The compact disk is accessible using both Mac's and PC's, and potential incompatibility problems have been avoided by using portable document, HTML, and ASCII formats.

Many people have contributed in a variety of ways in the making of this book. Our appreciation and respect goes to all authors of books, monographs, research articles, websites, and computer programs cited and used as examples throughout this text. We are indebted to our colleagues, Professor Karl Gschneidner, Jr. from Iowa State University, Professor Scott R.J. Oliver from SUNY at Binghamton, Professor Alexander Tishin from Moscow State University, Dr. Aaron Holm from Iowa State University, and Dr. Alexandra (Sasha) Pecharsky from Iowa State University, who read the entire manuscript and whose helpful advice and friendly criticism made this book better. It also underwent a common-sense test, thanks to Lubov Zavalij and Vitalij Pecharsky, Jr. Some of the experimental data and samples used as the examples have been provided by Dr. Lev Akselrud from L'viv State University, Dr. Oksana Zaharko from Paul Scherrer Institute, Dr. Iver Anderson, Dr. Matthew Kramer, and Dr. John Snyder (all from Ames Laboratory, Iowa State University), and we are grateful to all of them for their willingness to share the results of their unpublished work. Special thanks are in order to Professor Karl Gschneidner, Jr. (Iowa State University) and Professor M. Stanley Whittingham (SUNY at Binghamton), whose perpetual attention and encouragement during our work on this book have been invaluable. Finally yet significantly, we extend our gratitude to our spouses, Alexandra (Sasha) Pecharsky and Lubov Zavalij, and to our children, Vitalij Jr., Nadya, Christina, Solomia, and Martha, who handled our virtual absence for countless evenings and weekends with exceptional patience and understanding.

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Chapter 2

Finite Symmetry Elements and Crystallographic Point Groups

In addition to simple translations, which are important for understanding the concept of the lattice, other types of symmetry may be, and are present in the majority of real crystal structures. Here we begin with considering a single unit cell, because it is the unit cell that forms a fundamental building block of a three-dimensionally periodic, infinite lattice, and therefore, the vast array of crystalline materials.

2.1 Content of the Unit Cell

To completely describe the crystal structure, it is not enough to characterize only the geometry of the unit cell. One also needs to establish the distribution of atoms in the unit cell, and consequently, in the entire lattice. The latter is done by simply translating each point inside the unit cell using (1.1). Hence, the three noncoplanar vectors **a**, **b**, and **c** form a basis of the coordinate system with three noncoplanar axes *X*, *Y*, and *Z*, which is called the crystallographic coordinate system or the crystallographic basis. The coordinates of a point inside the unit cell, i.e., the coordinate triplets *x*, *y*, *z*, are expressed in fractions of the unit cell edge lengths, and therefore, they vary from 0 to 1 along the corresponding vectors (**a**, **b**, or **c**).¹ Thus, the coordinates of the origin of the unit cell are always 0, 0, 0 (*x* = 0, *y* = 0 and *z* = 0), and for the ends of **a**-, **b**-, and **c**-vectors, they are 1, 0, 0; 0, 1, 0 and 0, 0, 1, respectively. Again, using capital italic *X*, *Y*, and *Z*, we will always refer to crystallographic axes coinciding with **a**, **b**, and **c** directions, respectively, while small italic *x*, *y*, and *z* are used to specify the corresponding fractional coordinates along the *X*, *Y*, and *Z* axes.

An example of the unit cell in three dimensions and its content given in terms of coordinates of all atoms is shown in Fig. 2.1. Here, the centers of gravity of three atoms (“large,” “medium,” and “small” happy faces) have coordinates x_1, y_1, z_1 ; x_2, y_2, z_2 and x_3, y_3, z_3 , respectively. Strictly speaking, the content of the unit cell

¹ In order to emphasize that the coordinate triplets list fractional coordinates of atoms, in crystallographic literature these are often denoted as x/a , y/b , and z/c .

should be described by specifying other relevant atomic parameters in addition to the position of each atom in the unit cell. These include types of atoms (i.e., their chemical symbols or sequential numbers in a periodic table instead of “large,” “medium” and “small”), site occupancy, and individual displacement parameters. All these quantities are defined and explained later in the book, see Chap. 9.

2.2 Asymmetric Part of the Unit Cell

It is important to realize that the case shown in Fig. 2.1 is rarely observed in reality. Usually, unit cell contains more than one molecule or a group of atoms that are converted into each other by simple geometrical transformations, which are called *symmetry operations*. Overall, there may be as many as 192 transformations in some highly symmetric unit cells. A simple example is shown in Fig. 2.2, where each unit cell contains two molecules that are converted into one another by 180° rotation around imaginary lines, which are perpendicular to the plane of the figure. The location of one of these lines (*rotation axes*) is indicated using small filled ellipse. The original molecule, chosen arbitrarily, is white, while the derived, symmetrically related molecule is black.

The independent part of the unit cell (e.g., the upper right half of the unit cell separated by a dash-dotted line and hatched in Fig. 2.2) is called the asymmetric unit. It is the only part of the unit cell for which the specification of atomic positions and other atomic parameters are required. The entire content of the unit cell can be established from its asymmetric unit using the combination of symmetry operations present in the unit cell. Here, this operation is a rotation by 180° around the line perpendicular to the plane of the projection at the center of the unit cell. It is worth noting that the rotation axis shown in the upper left corner of Fig. 2.2 is not the only axis present in this crystal lattice – identical axes are found at the beginning and in the middle of every unit cell edge as shown in one of the neighboring cells.²

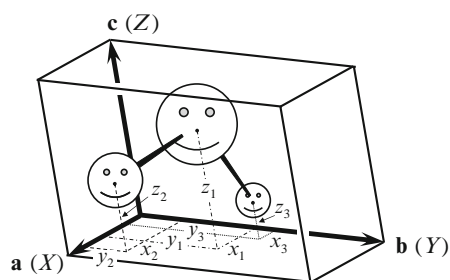


Fig. 2.1 Illustration of the content of the unit cell. The coordinates of the center of gravity of each atom are given as triplets, i.e., x_1, y_1, z_1 ; x_2, y_2, z_2 and x_3, y_3, z_3 .

² The appearance of additional rotation axes in each unit cell is the result of the simultaneous presence of both rotational and translational symmetry, which interact with one another (see Sects. 2.5 and 3.3, below).

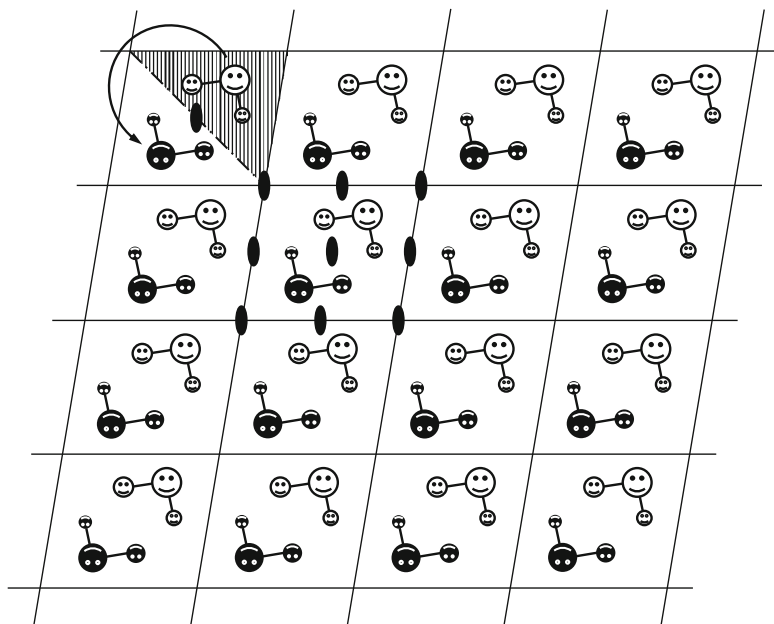


Fig. 2.2 Asymmetric unit (*hatched vertically*) contains an independent molecule, which is clear. Black molecules are related to clear molecules in each unit cell via rotation by 180° around the lines perpendicular to the plane of the projection at the center of each unit cell. The difference in color is used only to highlight symmetrical relationships, since the clear and the black molecules are indeed identical. All rotation axes intersecting every unit cell are shown in a neighboring cell.

Symmetry operations, therefore, can be visualized by means of certain symmetry elements represented by various graphical objects. There are four so-called simple symmetry elements: a point to visualize inversion, a line for rotation, a plane for reflection, and the already mentioned translation is also a simple symmetry element, which can be visualized as a vector. Simple symmetry elements may be combined with one another, producing complex symmetry elements that include roto-inversion axes, screw axes, and glide planes.

2.3 Symmetry Operations and Symmetry Elements

From the beginning, it is important to acknowledge that a symmetry operation is not the same as a symmetry element. The difference between the two can be defined as follows: a symmetry operation performs a certain symmetrical transformation and yields only one additional object, for example, an atom or a molecule, which is symmetrically equivalent to the original. On the other hand, a symmetry element is a graphical or a geometrical representation of one or more symmetry operations, such

as a mirror reflection in a plane, a rotation about an axis, or an inversion through a point. A much more comprehensive description of the term “symmetry element” exceeds the scope of this book.³

Without the presence of translations, a single crystallographic symmetry element may yield a total from one to six objects symmetrically equivalent to one another. For example, a rotation by 60° around an axis is a symmetry operation, whereas the sixfold rotation axis is a symmetry element which contains six rotational symmetry operations: by 60° , 120° , 180° , 240° , 300° , and 360° about the same axis. The latter is the same as rotation by 0° or any multiple of 360° . As a result, the sixfold rotation axis produces a total of six symmetrically equivalent objects counting the original. Note that the 360° rotation yields an object identical to the original and literally converts the object into itself. Hence, symmetry elements are used in visual description of symmetry operations, while symmetry operations are invaluable in the algebraic or mathematical representation of crystallographic symmetry, for example, in computing.

Four simple symmetry operations – rotation, inversion, reflection, and translation – are illustrated in Fig. 2.3. Their association with the corresponding geometrical objects and symmetry elements is summarized in Table 2.1. Complex symmetry elements are shown in Table 2.2. There are three new complex symmetry elements, which are listed in italics in this table:

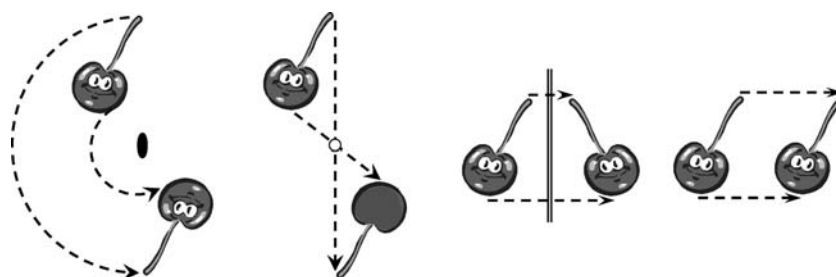


Fig. 2.3 Simple symmetry operations. From *left to right*: rotation, inversion, reflection, and translation.

³ It may be found in: P.M. de Wolff, Y. Billiet, J.D.H. Donnay, W. Fischer, R.B. Galiulin, A.M. Glazer, Marjorie Senechal, D.P. Schoemaker, H. Wondratchek, Th. Hahn, A.J.C. Wilson, and S.C. Abrahams, Definition of symmetry elements in space groups and point groups. Report of the International Union of Crystallography ad hoc committee on the nomenclature in symmetry, *Acta Cryst.* **A45**, 494 (1989); P.M. de Wolff, Y. Billiet, J.D.H. Donnay, W. Fischer, R.B. Galiulin, A.M. Glazer, Th. Hahn, M. Senechal, D.P. Schoemaker, H. Wondratchek, A.J.C. Wilson, and S.C. Abrahams, Symbols for symmetry elements and symmetry operations. Final report of the International Union of Crystallography ad hoc committee on the nomenclature in symmetry, *Acta Cryst.* **A48**, 727 (1992); H.D. Flack, H. Wondratchek, Th. Hahn, and S.C. Abrahams, Symmetry elements in space groups and point groups. Addenda to two IUCr reports on the nomenclature in symmetry, *Acta Cryst.* **A56**, 96 (2000).

Table 2.1 Simple symmetry operations and conforming symmetry elements.

Symmetry operation	Geometrical representation	Symmetry element
Rotation	Line (axis)	Rotation axis
Inversion	Point (center)	Center of inversion
Reflection	Plane	Mirror plane
Translation	Vector	Translation vector

Table 2.2 Derivation of complex symmetry elements.

Symmetry operation	Rotation	Inversion	Reflection	Translation
Rotation	–	<i>Roto-inversion axis</i> ^a	No ^b	<i>Screw axis</i>
Inversion	–	–	No ^b	No ^b
Reflection	–	–	–	<i>Glide plane</i>
Translation	–	–	–	–

^a The prefix “roto” is nearly always omitted and these axes are called “inversion axes.”

^b No new complex symmetry element is formed as a result of this combination.

- Roto-inversion axis (usually called inversion axis), which includes simultaneous rotation and inversion.⁴
- Screw axis, which includes simultaneous rotation and translation.
- Glide plane, which combines reflection and translation.

Symmetry operations and elements are sometimes classified by the way they transform an object as proper and improper. An improper symmetry operation inverts an object in a way that may be imaged by comparing the right and left hands: the right hand is an inverted image of the left hand, and if you have ever tried to put a right-handed leather glove on your left hand, you know that it is quite difficult, unless the glove has been turned inside out, or in other words, inverted. The inverted object is said to be enantiomorphous to the direct object and vice versa. Thus, symmetry operations and elements that involve inversion or reflection, including when they are present in complex symmetry elements, are improper. They are: center of inversion, inversion axes, mirror plane, and glide planes. On the contrary, proper symmetry elements include only operations that do not invert an object, such as rotation and translation. They are rotation axes, screw axes, and translation vectors. As is seen in Fig. 2.3 both the rotation and translation, which are proper symmetry operations, change the position of the object without inversion, whereas both the inversion and reflection, that is, improper symmetry operations, invert the object in addition to changing its location.

Another classification is based on the presence or absence of translation in a symmetry element or operation. Symmetry elements containing a translational component, such as a simple translation, screw axis, or glide plane, produce infinite numbers of symmetrically equivalent objects, and therefore, these may be called

⁴ Alternatively, roto-reflection axes combining simultaneous rotation and reflection may be used, however, each of them is identical in its action to one of the roto-inversion axes.



infinite symmetry elements. For example, the lattice is infinite because of the presence of translations. All other symmetry elements that do not contain translations always produce a finite number of objects, and they may be called finite symmetry elements. Center of inversion, mirror plane, rotation, and roto-inversion axes are all finite symmetry elements. Finite symmetry elements and operations are used to describe the symmetry of finite objects, for example, molecules, clusters, polyhedra, crystal forms, unit cell shape, and any noncrystallographic finite objects, for example, the human body. Both finite and infinite symmetry elements are necessary to describe the symmetry of infinite or continuous structures, such as a crystal structure, two-dimensional wall patterns, and others. We begin the analysis of crystallographic symmetry from simpler finite symmetry elements, followed by the consideration of more complex infinite symmetry elements.

2.4 Finite Symmetry Elements

Symbols of finite crystallographic symmetry elements and their graphical representations are listed in Table 2.3. The full name of a symmetry element is formed by adding “N-fold” to the words “rotation axis” or “inversion axis.” The numeral N generally corresponds to the total number of objects generated by the element,⁵ and it is also known as the order or the multiplicity of the symmetry element. Orders of axes are found in columns 2 and 4 in Table 2.3, for example, a threefold rotation axis or a fourfold inversion axis.

Note that the onefold inversion axis and the twofold inversion axis are identical in their action to the center of inversion and the mirror plane, respectively. Both the center of inversion and mirror plane are commonly used in crystallography, mostly

Table 2.3 Symbols of finite crystallographic symmetry elements.

Rotation angle, ϕ	Rotation axes		Roto-inversion axes	
	International symbol	Graphical symbol ^a	International symbol	Graphical symbol ^a
360°	1	none	$\bar{1}$ ^b	
180°	2		$\bar{2} = m^c$	
120°	3		$\bar{3} = 3 + \bar{1}$	
90°	4		$\bar{4}$	
60°	6		$\bar{6} = 3 + m \perp 3$	

^a When the symmetry element is perpendicular to the plane of the projection.

^b Identical to the center of inversion.

^c Identical to the mirror plane.

⁵ Except for the center of inversion, which results in two objects, and the threefold inversion axis, which produces six symmetrically equivalent objects. See (4.27) and (4.28) in Sect. 4.2.4 for an algebraic definition of the order of a symmetry element.

because they are described by simple geometrical elements: point or plane, respectively. The center of inversion is also often called the “center of symmetry.”

Further, as we see in Sects. 2.4.3 and 2.4.5, below, transformations performed by the threefold inversion and the sixfold inversion axes can be represented by two independent simple symmetry elements. In the case of the threefold inversion axis, $\bar{3}$, these are the threefold rotation axis and the center of inversion present independently, and in the case of the sixfold inversion axis, $\bar{6}$, the two independent symmetry elements are the mirror plane and the threefold rotation axis perpendicular to the plane, as denoted in Table 2.3. The remaining fourfold inversion axis, $\bar{4}$, is a unique symmetry element (Sect. 2.4.4), which cannot be represented by any pair of independently acting symmetry elements.

Numerals in the international symbols of the center of inversion and all inversion axes are conventionally marked with the bar on top⁶ and not with the dash or the minus sign in front of the numeral (see Table 2.3). The dash preceding the numeral (or the letter “b” following the numeral – shorthand for “bar”), however, is more convenient to use in computing for the input of symmetry data, for example, -1 (or 1b), -3 (3b), -4 (4b), and -6 (6b) rather than $\bar{1}$, $\bar{3}$, $\bar{4}$, and $\bar{6}$, respectively.

The columns labeled “Graphical symbol” in Table 2.3 correspond to graphical representations of symmetry elements when they are perpendicular to the plane of the projection. Other orientations of rotation and inversion axes are conventionally indicated using the same symbols to designate the order of the axis with properly oriented lines, as shown in Fig. 2.4. Horizontal and diagonal mirror planes are normally labeled using bold lines, as shown in Fig. 2.4, or using double lines in stereographic projections (see Table 2.3 and Sect. 2.8).

When we began our discussion of crystallographic symmetry, we used a happy face and a cherry to illustrate simple concepts of symmetry. These objects are inconvenient to use with complex symmetry elements. On the other hand, the commonly used empty circles with or without a comma inside to indicate enantiomorphous objects, for example, as in the International Tables for Crystallography,⁷ are not intuitive. For example, both inversion and reflection look quite similar. Therefore, we will use a trigonal pyramid, shown in Fig. 2.5. This figure illustrates two pyra-



Fig. 2.4 From left to right: horizontal twofold rotation axis (*top*) and its alternative symbol (*bottom*), diagonal threefold inversion axis inclined to the plane of the projection, horizontal fourfold rotation axis, horizontal, and diagonal mirror planes. *Horizontal* or *vertical lines* are commonly used to indicate axes located in the plane of the projection, and *diagonal lines* are used to indicate axes, which form an angle other than the right angle or zero with the plane of the projection.

⁶ As in the “Crystallography” true-type font for Windows developed by Len Barbour. The font file is available from <http://x-seed.net/freestuff.html>. This font has been used by the authors to typeset crystallographic symbols in the manuscript of this book.

⁷ International Tables for Crystallography, vol. A, Fifth revised edition, Theo Hahn, Ed., Published jointly with the International Union of Crystallography (IUCr) by Springer, Berlin (2002).

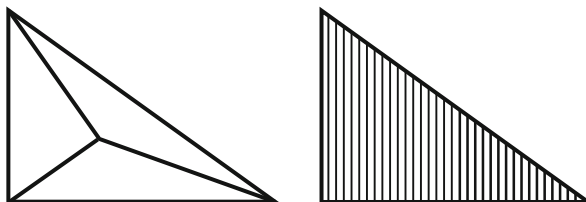


Fig. 2.5 Trigonal pyramid with its apex up (*left*) and down (*right*) relative to the plane of the paper. Hatching is used to emphasize enantiomorphous objects.

mids, one with its apex facing upward, where lines connect the visible apex with the base corners, and another with its apex facing downward, which has no visible lines. In addition, the pyramid with its apex down is hatched to accentuate the enantiomorphism of the two pyramids.

To review symmetry elements in detail we must find out more about rotational symmetry, since both the center of inversion and mirror plane can be represented as rotation plus inversion (see Table 2.3). The important properties of rotational symmetry are the direction of the axis and the rotation angle. It is almost intuitive that the rotation angle: (ϕ) can only be an integer fraction ($1/N$) of a full turn (360°), otherwise it can be substituted by a different rotation angle that is an integer fraction of the full turn, or it will result in the noncrystallographic rotational symmetry. Hence,

$$\phi = \frac{360^\circ}{N} \quad (2.1)$$

By comparing (2.1) with Table 2.3, it is easy to see that N , which is the order of the axis, is also the number of elementary rotations required to accomplish a full turn around the axis. In principle, N can be any integer number, for example, 1, 2, 3, 4, 5, 6, 7, 8... However, in periodic crystals only a few specific values are allowed for N due to the presence of translational symmetry. Only axes with $N=1, 2, 3, 4,$ or 6 are compatible with the periodic crystal lattice, that is, with translational symmetry in three dimensions. Other orders, such as 5, 7, 8, and higher will inevitably result in the loss of the conventional periodicity of the lattice, which is defined by (1.1). The not so distant discovery of fivefold and tenfold rotational symmetry continue to intrigue scientists even today, since it is quite clear that it is impossible to build a periodic crystalline lattice in two dimensions exclusively from pentagons, as depicted in Fig. 2.6, heptagons, octagons, etc. The situation shown in this figure may be rephrased as follows: "It is impossible to completely fill the area in two dimensions with pentagons without creating gaps."

It is worth noting that the structure in Fig. 2.6 not only looks ordered, but it is indeed perfectly ordered. Moreover, in recent decades, many crystals with fivefold symmetry have been found and their approximant structures have been determined with various degrees of accuracy. These crystals, however, do not have translational symmetry in three directions, which means that they do not have a finite unit cell

Fig. 2.6 Filling the area with shaded pentagons. White parallelograms represent voids in the two-dimensional pattern of pentagons.

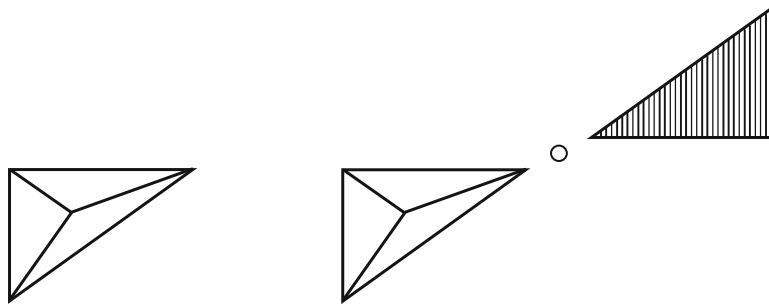
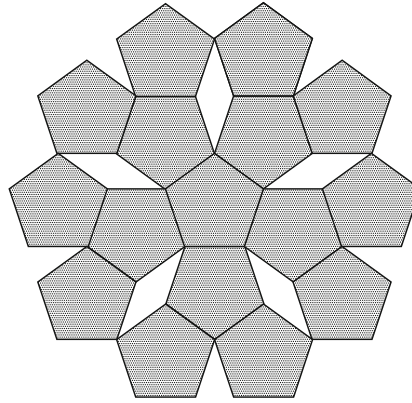


Fig. 2.7 Onefold rotation axis (*left*, unmarked since it can be located anywhere) and center of inversion (*right*).

and, therefore, they are called quasicrystals: quasi – because there is no translational symmetry, crystals – because they produce discrete, crystal-like diffraction patterns.

2.4.1 Onefold Rotation Axis and Center of Inversion

The onefold rotation axis, shown in Fig. 2.7 on the left, rotates an object by 360° , or in other words converts any object into itself, which is the same as if no symmetrical transformation had been performed. This is the only symmetry element which does not generate additional objects except the original.

The center of inversion (onefold inversion axis) inverts an object through a point as shown in Fig. 2.7, right. Thus, the clear pyramid with its apex up, which is the original object, is inverted through a point producing its symmetrical equivalent – the hatched (enantiomorphous) pyramid with its apex down. The latter is converted back into the original clear pyramid after the inversion through the same point. The center of inversion, therefore, generates one additional object, giving a total of two related objects.

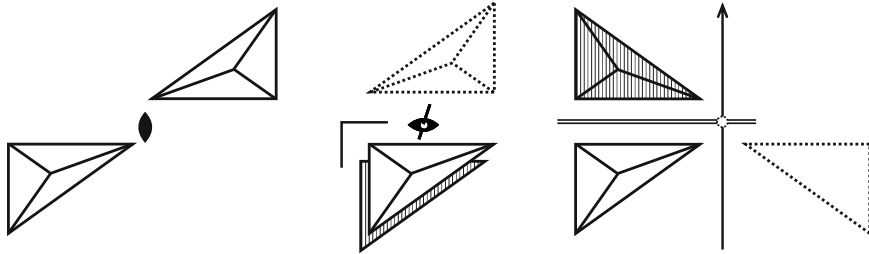


Fig. 2.8 Twofold rotation axis perpendicular to the plane of the projection (*left*), and mirror planes (*middle* and *right*). In the middle – the mirror plane nearly coincides with the plane of the projection (the equivalent twofold inversion axis is tilted by a few degrees away from the vertical) for clarity. On the right – the mirror plane is perpendicular to the plane of the projection. Also shown in the middle and on the right is how the twofold inversion axis, which is perpendicular to the mirror plane, yields the same result as the mirror plane.

2.4.2 Twofold Rotation Axis and Mirror Plane

The twofold rotation axis (Fig. 2.8, left) simply rotates an object around the axis by 180° , and this symmetry element results in two symmetrically equivalent objects: original plus transformed. Note that the 180° rotation of the new pyramid around the same axis converts it to the original pyramid. Hence, it is correct to state that the twofold rotation axis rotates the object by 0 (360°) and 180° .

The mirror plane (twofold inversion axis) reflects a clear pyramid in a plane to yield the hatched pyramid, as shown in Fig. 2.8, in the middle and on the right. Similar to the inversion center and the twofold rotation axis, the same mirror plane reflects the resulting (hatched) pyramid yielding the original (clear) pyramid. The equivalent symmetry element, that is, the twofold inversion axis first rotates an object (clear pyramid) by 180° around the axis, as shown by the dotted image of a pyramid with its apex up in the middle or apex down on the right of Fig. 2.8. The pyramid does not remain in this position because the twofold axis is combined with the center of inversion, and the pyramid is immediately (or simultaneously) inverted through the center of inversion located on the axis. The final locations are shown by the hatched pyramids in Fig. 2.8. The mirror plane is used to describe this combined operation rather than the twofold inversion axis because of its simplicity and a better graphical representation of the reflection operation versus the roto-inversion. Similar to the twofold rotation axis, the mirror plane results in two symmetrically equivalent objects.

2.4.3 Threefold Rotation Axis and Threefold Inversion Axis

The threefold rotation axis (Fig. 2.9, left) results in three symmetrically equivalent objects by rotating the original object around the axis by 0 (360°), 120° , and 240° .

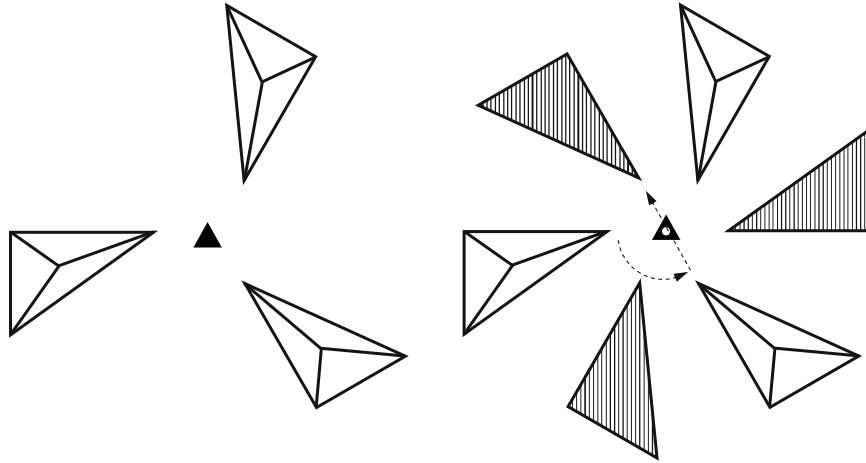


Fig. 2.9 Threefold rotation (*left*) and threefold inversion (*right*) axes perpendicular to the plane of the projection. The *dashed arrows* on the right schematically show the counterclockwise rotation by 120° and a simultaneous inversion through the center of symmetry located on the axis.

The threefold inversion axis (Fig. 2.9, right) produces six symmetrically equivalent objects. The original object, for example, any of the three clear pyramids with apex up, is transformed as follows: it is rotated by 120° counterclockwise and then immediately inverted from this intermediate position through the center of inversion located on the axis, as shown by the dashed arrows in Fig. 2.9. These operations result in a hatched pyramid with its apex down positioned 60° clockwise from the original pyramid. By applying the same transformation to this hatched pyramid, the third symmetrically equivalent object would be a clear pyramid next to the first hatched pyramid rotated by 60° clockwise. These transformations are carried out until the next obtained object repeats the original pyramid.

It is easy to see that the six symmetrically equivalent objects are related to one another by a threefold rotation axis (the three clear pyramids are connected by an independent threefold axis, and so are the three hatched pyramids) and by a center of inversion, which relates the pairs of opposite pyramids. Hence, the threefold inversion axis is not only the result of two simultaneous operations (3 then $\bar{1}$), but the same symmetrical relationships can be established as a result of two symmetry elements present independently. In other words, $\bar{3}$ is identical to 3 and $\bar{1}$.

2.4.4 Fourfold Rotation Axis and Fourfold Inversion Axis

The fourfold rotation axis (Fig. 2.10, left) results in four symmetrically equivalent objects by rotating the original object around the axis by 0 (360°), 90° , 180° , and 270° .

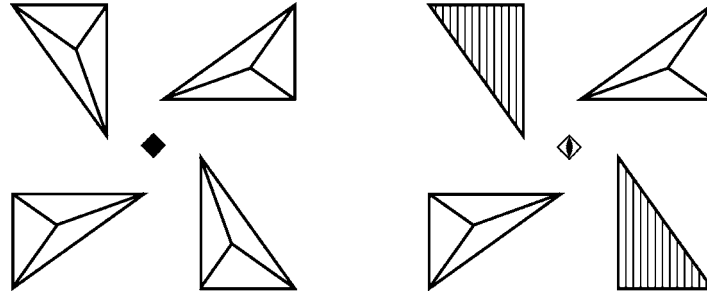


Fig. 2.10 Fourfold rotation (*left*) and fourfold inversion (*right*) axes perpendicular to the plane of the projection.

The fourfold inversion axis (Fig. 2.10, right) also produces four symmetrically equivalent objects. The original object, for example, any of the two clear pyramids with apex up, is rotated by 90° counterclockwise and then it is immediately inverted from this intermediate position through the center of inversion located on the axis. This transformation results in a hatched pyramid with its apex down in the position next to the original pyramid, but in the clockwise direction. By applying the same transformation to this hatched pyramid, the third symmetrically equivalent object would be a clear pyramid next to the hatched pyramid in the clockwise direction. The fourth object is obtained in the same fashion. Unlike in the case of the threefold inversion axis (see Sect. 2.4.3), this combination of four objects cannot be produced by applying the fourfold rotation axis and the center of inversion separately, and therefore, this is a unique symmetry element. In fact, the combination of four pyramids shown in Fig. 2.10 (right), does not have an independent fourfold symmetry axis, nor does it have the center of inversion! As can be seen from Fig. 2.10, both fourfold axes contain a twofold rotation axis (180° rotations) as a subelement.

2.4.5 Sixfold Rotation Axis and Sixfold Inversion Axis

The sixfold rotation axis (Fig. 2.11, left) results in six symmetrically equivalent objects by rotating the original object around the axis by 0 (360°), 60° , 120° , 180° , 240° , and 300° .

The sixfold inversion axis (Fig. 2.11, right) also produces six symmetrically equivalent objects. Similar to the threefold inversion axis, this symmetry element can be represented by two independent simple symmetry elements: the first one is the threefold rotation axis, which connects pyramids 1–3–5 and 2–4–6, and the second one is the mirror plane perpendicular to the threefold rotation axis, which connects pyramids 1–4, 2–5, and 3–6. As an exercise, try to obtain all six symmetrically equivalent pyramids starting from the pyramid 1 as the original object by applying 60° rotations followed by immediate inversions. Keep in mind that objects are not retained in the intermediate positions because the sixfold rotation and inversion act simultaneously.

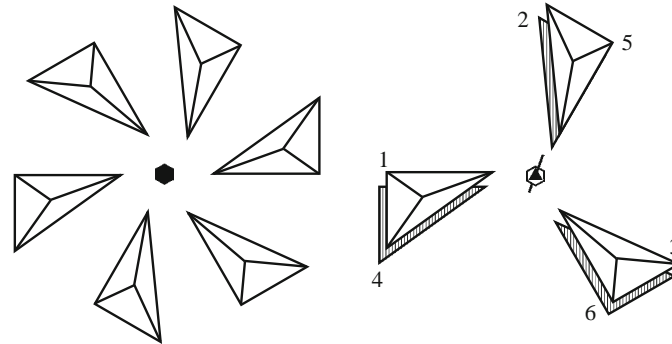


Fig. 2.11 Sixfold rotation (*left*) and sixfold inversion (*right*) axes. The sixfold inversion axis is tilted by a few degrees away from the vertical to visualize all six symmetrically equivalent pyramids. The numbers next to the pyramids represent the original object (1), and the first generated object (2), etc. The odd numbers are for the pyramids with their apexes up.

The sixfold rotation axis also contains one threefold and one twofold rotation axes, while the sixfold inversion axis contains a threefold rotation and a twofold inversion (mirror plane) axes as subelements. Thus, any N -fold symmetry axis with $N > 1$ always includes either rotation or inversion axes of lower order(s), which is (are) integer divisor(s) of N .

2.5 Interaction of Symmetry Elements

So far we have considered a total of ten different crystallographic symmetry elements, some of which were combinations of two simple symmetry elements, acting either simultaneously or consecutively. The majority of crystalline objects, for example, crystals and molecules, have more than one nonunity symmetry element.

Symmetry elements and operations interact with one another, producing new symmetry elements and symmetry operations, respectively. When applied to symmetry, an interaction means consecutive (and not simultaneous, as in the case of complex symmetry elements) application of symmetry elements. The appearance of new symmetry operations can be understood from a simple deduction, using the fact that a single symmetry operation produces only one new object:

- Assume that symmetry operation No. 1 converts object X into object X_1 .
- Assume that another symmetry operation, No. 2, converts object X_1 into object X_2 .
- Since object X_1 is symmetrically equivalent to object X , and object X_2 is symmetrically equivalent to object X_1 , then objects X and X_2 should also be related to one another.

The question is: what converts object X into object X_2 ? The only logical answer is: there should be an additional symmetry operation, No. 3, that converts object X into object X_2 .

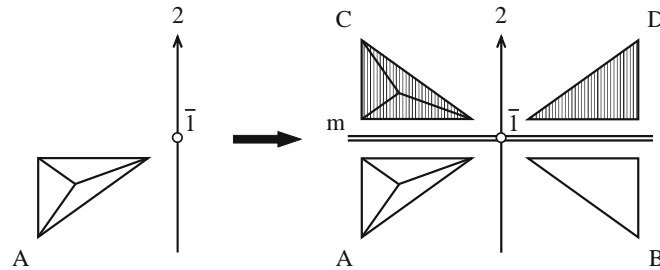


Fig. 2.12 Schematic illustrating the interaction of symmetry elements. A twofold rotation axis (2) and a center of inversion ($\bar{1}$) located on the axis (*left*) result in a mirror plane perpendicular to the axis intersecting it at the center of inversion (*right*). The important difference from Fig. 2.8 (*middle* and *right*), where neither the twofold axis nor the center of inversion are present independently, the combination of four pyramids (A, B, C, and D) here includes either of these symmetry elements.

Consider the schematic shown in Fig. 2.12 (left), and assume that initially we have only the twofold rotation axis, 2 , and the center of inversion, $\bar{1}$. Also assume that the center of inversion is located on the axis (if not, translational symmetry will result, see Sects. 3.1 and 3.2).

Beginning with the Pyramid A as the original object, and after rotating it around the axis by 180° we obtain Pyramid B, which is symmetrically equivalent to Pyramid A. Since we also have the center of inversion, it converts Pyramid A into Pyramid D, and Pyramid B into Pyramid C. It is easy to see from Fig. 2.12 (right) that Pyramid C is nothing else but the reflected image of Pyramid A and vice versa, and Pyramid D is the reflected copy of Pyramid B. Remembering that these mirror reflection relationships between A and C, and B and D were not present from the beginning, we conclude that a new symmetry element – a mirror plane, m – has emerged as the result of the sequential application of two symmetry elements to the original object (2 and $\bar{1}$).

The mirror plane is, therefore, a derivative of the twofold rotation axis and the center of inversion located on the axis. The derivative mirror plane is perpendicular to the axis, and intersects the axis in a way that the center of inversion also belongs to the plane. If we start from the same Pyramid A and apply the center of inversion first (this results in Pyramid D) and the twofold axis second (i.e., $A \rightarrow B$ and $D \rightarrow C$), the resulting combination of four symmetrically equivalent objects and the derivative mirror plane remain the same.

This example not only explains how the two symmetry elements interact, but it also serves as an illustration to a broader conclusion deduced at the beginning of this section: any two symmetry operations applied in sequence to the same object create a third symmetry operation, which applies to all symmetrically equivalent objects. Note that if the second operation is the inverse of the first, then the resulting third operation is unity (the onefold rotation axis, 1). For example, when a mirror plane, a center of inversion, or a twofold rotation axis are applied twice, all result in a onefold rotation axis.

The example considered in Fig. 2.12 can be also written in a form of an equation using the international notations of the corresponding symmetry elements (see Table 2.3):

$$2 \times \bar{1}(\text{on } 2) = \bar{1}(\text{on } 2) \times 2 = m(\perp 2 \text{ through } \bar{1}) \quad (2.2)$$

where “ \times ” designates the interaction between (successive application of) symmetry elements. The same example (Fig. 2.12) can be considered starting from any two of the three symmetry elements. As a result, the following equations are also valid:

$$2 \times m(\perp 2) = m(\perp 2) \times 2 = \bar{1}(\text{at } m \perp 2) \quad (2.3)$$

$$m \times \bar{1}(\text{on } m) = \bar{1}(\text{on } m) \times m = 2(\perp m \text{ through } \bar{1}) \quad (2.4)$$

2.5.1 Generalization of Interactions Between Finite Symmetry Elements

In the earlier examples (Fig. 2.12 and Table 2.5), the twofold rotation axis and the mirror plane are perpendicular to one another. However, symmetry elements may in general intersect at various angles (ϕ). When crystallographic symmetry elements are of concern, and since only one-, two-, three-, four- and sixfold rotation axes are allowed, only a few specific angles ϕ are possible. In most cases they are: 0° (e.g., when an axis belongs to a plane), 30° , 45° , 60° and 90° . The latter means that symmetry elements are mutually perpendicular. Furthermore, all symmetry elements should intersect along the same line or in one point, otherwise a translation and, therefore, an infinite symmetry results.

An example showing that multiple symmetry elements appear when a twofold rotation axis intersects with a mirror plane at a 45° angle is seen in Fig. 2.13. All eight pyramids can be obtained starting from a single pyramid by applying the two symmetry elements (i.e., the mirror plane and the twofold rotation axis), first to the

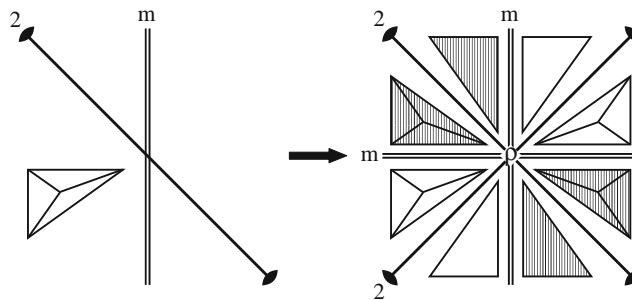


Fig. 2.13 Mirror plane (m) and twofold rotation axis (2) intersecting at 45° (*left*) result in additional symmetry elements: two mirror planes, twofold rotation axis and fourfold inversion axis (*right*).

Table 2.4 Typical interactions between finite symmetry elements.

First element	Second element	Derived element (major)	Comments, examples
$\bar{1}$	N-fold axis	m for even N N-fold inversion axis for odd N	$\bar{2} = m$ $\bar{3}$
2	2 at $\phi = 30^\circ, 45^\circ, 60^\circ,$ or 90°	N-fold rotation axis, $N = 180/\phi$	6, 4, 3, or 2 perpendicular to first and second axes
m	m at $\phi = 30^\circ, 45^\circ, 60^\circ,$ or 90°	Same as above	6, 4, 3, or 2-fold axis along the common line
m	2 at 90°	Center of inversion	$\bar{1}$ where m and 2 intersect
m	2 at $\phi = 30^\circ, 45^\circ, 60^\circ$	N-fold inversion axis, $N = 180/(90 - \phi)$	$\bar{3}, \bar{4}$ or $\bar{6}$ in m and perpendicular to 2
3 or $\bar{3}$	2, 4, or $\bar{4}$ at 54.74° ; 3 or $\bar{3}$ at 70.53°	Four intersecting 3 or $\bar{3}$ plus other symmetry elements	Symmetry of a cube or tetrahedron

original pyramid and, second to the pyramids that appear as a result of symmetrical transformations. As an exercise, try to obtain all eight pyramids beginning from a selected pyramid using only the mirror plane and the twofold axis that are shown in Fig. 2.13 (left). Hints: original pyramid (1), rotate it (2), reflect both (4), rotate all (6), and reflect all (8). Numbers in parenthesis indicate the total number of different pyramids that should be present in the figure after each symmetrical transformation.

So far, we have enough evidence that when two symmetry elements interact, they result in additional symmetry element(s). Moreover, when three symmetry elements interact, they will also produce derivative symmetry elements. For example, three mutually perpendicular mirror planes yield a center of inversion in a point, which is common for all three planes, plus three twofold rotation axes along the lines where any two planes intersect. However, all cases when more than two elements interact with one another can be reduced to the interactions of pairs. The most typical interactions of the pairs of symmetry elements and their results are shown in Table 2.4.

2.5.2 Symmetry Groups

As established earlier, the interaction between a pair of symmetry elements (or symmetry operations) results in another symmetry element (or operation). The former may be new, or it may already be present in a given combination of symmetrically

Table 2.5 Symmetry elements resulting from all possible combinations of 1, $\bar{1}$, 2, and m when 2 is perpendicular to m, and $\bar{1}$ is located at the intersection of 2 and m.

Symmetry operation	1	$\bar{1}$	2	m
1	1	$\bar{1}$	2	m
$\bar{1}$	$\bar{1}$	1	m	2
2	2	m	1	$\bar{1}$
m	m	2	$\bar{1}$	1

equivalent objects. If no new symmetry element(s) appear, and when interactions between all pairs of the existing ones are examined, the generation of all symmetry elements is completed. The complete set of symmetry elements is called a symmetry group.

Table 2.5 illustrates the generation of a simple symmetry group using symmetry elements from Fig. 2.12. The only difference is that in Table 2.5, a onefold rotation axis has been added to the earlier considered twofold rotation axis, center of inversion, and mirror plane for completeness. It is easy to see that no new symmetry elements appear when interactions between all four symmetry elements have been taken into account.

Considering only finite symmetry elements and all valid combinations among them, a total of 32 crystallographic symmetry groups can be constructed. The 32 symmetry groups can be derived in a number of ways, one of which has been illustrated in Table 2.5, but this subject falls beyond the scope of this book. Nevertheless, the family of finite crystallographic symmetry groups, which are also known as the 32 point groups, is briefly discussed in Sect. 2.9.

2.6 Fundamentals of Group Theory

Since the interaction of two crystallographic symmetry elements results in a third crystallographic symmetry element, and the total number of them is finite, valid combinations of symmetry elements can be assembled into finite groups. As a result, mathematical theory of groups is fully applicable to crystallographic symmetry groups.

The definition of a group is quite simple: a group is a set of elements $G_1, G_2, \dots, G_N, \dots$, for which a binary combination law is defined, and which together satisfy the four fundamental properties: closure, associability, identity, and the inverse property. Binary combination law (a few examples are shown at the end of this section) describes how any two elements of a group interact (combine) with one other. When a group contains a finite number of elements (N), it represents a finite group, and when the number of elements in a group is infinite then the group is infinite. All crystallographic groups composed from finite symmetry elements are finite, that is, they contain a limited number of symmetry elements.

The four properties of a group are: closure, associability, identity, and inversion. They can be defined as follows:

- *Closure* requires that the combination of any two elements, which belong to a group, is also an element of the same group:

$$G_i \times G_j = G_k$$

Note that here and below “ \times ” designates a generic binary combination law, and not multiplication. For example, applied to symmetry groups, the combination law (\times) is the interaction of symmetry elements; in other words, it is their sequential application, as has been described in Sect. 2.5. For groups containing numerical elements, the combination law can be defined as, for example, addition or multiplication. Every group must always be closed, even a group which contains an infinite number of elements.

- *Associability* requires that the associative law is valid, that is,

$$(G_i \times G_j) \times G_k = G_i \times (G_j \times G_k).$$

As established earlier, the associative law holds for symmetry groups. Returning to the example in Fig. 2.12, which includes the mirror plane, the twofold rotation axis, the center of inversion and onefold rotation axis (the latter symmetry element is not shown in the figure, and we did not discuss its presence explicitly, but it is always there), the resulting combination of symmetrically equivalent objects is the same, regardless of the order in which these four symmetry elements are applied. Another example to consider is a group formed by numerical elements with addition as the combination law. For this group, the associative law always holds because the result of adding three numbers is always identical, regardless of the order in which the sum was calculated.

- *Identity* requires that there is one and only one element, E (unity), in a group, such that

$$E \times G_i = G_i \times E = G_i$$

for every element of the group. Crystallographic symmetry groups have the identity element, which is the onefold rotation axis – it always converts an object into itself, and its interaction with any symmetry element produces the same symmetry element (e.g., see Table 2.5). Further, this is the only symmetry element which can be considered as unity. In a group formed by numerical elements with addition as the combination law, the unity element is 0, and if multiplication is chosen as the combination law, the unity element is 1.

- *Inversion* requires that each element in a group has one, and only one inverse element such that

$$G_i^{-1} \times G_i = G_i \times G_i^{-1} = E.$$

As far as symmetry groups are concerned, the inversion rule also holds since the inverse of any symmetry element is the same symmetry element applied twice, for example, as in the case of the center of inversion, mirror plane and twofold

rotation axis, or the same rotation applied in the opposite direction, as in the case of any rotation axis of the third order or higher. In a numerical group with addition as the combination law, the inverse element would be the element which has the sign opposite to the selected element, that is, $M + (-M) = (-M) + M = 0$ (unity), while when the combination law is multiplication, the inverse element is the inverse of the selected element, or $MM^{-1} = M^{-1}M = 1$ (unity).

It may be useful to illustrate how the rules defined here can be used to establish whether a certain combination of elements forms a group or not. The first two examples are noncrystallographic, while the third represents a simple crystallographic group.

1. Consider an integer number 1, and multiplication as the combination law. Since there are no limitations on the number of elements in a group, then a group may consist of a single element. Is this group closed? Yes, $1 \times 1 = 1$. Is the associative rule applicable? Yes, since $1 \times 1 = 1$ no matter in which order you multiply the two ones. Is there one and only one unity element? Yes, it is 1, since $1 \times 1 = 1$. Is there one and only one inverse element for each element of the group? Yes, because $1 \times 1 = 1$. Hence, this is a group. It is a finite group.
2. Consider all integer numbers ($\dots -3, -2, -1, 0, 1, 2, 3 \dots$) with addition as the combination law. Is this group closed? Yes, since a sum of any two integers is also an integer. How about associability? Yes, since the result of adding three integers is always identical, regardless of the order in which they were added to one another. Is there a single unity element? Yes, this group has one, and only one unity element, 0, since adding 0 to any integer results in the same integer. Is there one and only one inverse element for any of the elements in the group? Yes, for any positive M , the inverse is $-M$; for any negative M , the inverse is $+M$, since $M + (-M) = (-M) + M = 0$ (unity). Hence, this is a group. Since the number of elements in the group is infinite, this group is infinite.
3. Consider the combination of symmetry elements shown in Fig. 2.12. The combination law here has been defined as interaction of symmetry elements (or their consecutive application to the object). The group contains the following symmetry elements: 1, $\bar{1}$, 2 and m . Associability, identity, and inversion have been established earlier, when we were considering group rules. Is this group closed? Yes, it is closed as shown in Table 2.5. Therefore, these four symmetry elements form a group as well. This group is finite.

2.7 Crystal Systems

As described earlier, the number of finite crystallographic symmetry elements is limited to a total of ten. These symmetry elements can intersect with one another only at certain angles, and the number of these angles is also limited (e.g., see Table 2.4). The limited number of symmetry elements and the ways in which they may interact with each other leads to a limited number of the completed (i.e., closed)

Table 2.6 Seven crystal systems and the corresponding characteristic symmetry elements.

Crystal system	Characteristic symmetry element or combination of symmetry elements
Triclinic	No axes other than onefold rotation or onefold inversion
Monoclinic	Unique twofold axis and/or single mirror plane
Orthorhombic	Three mutually perpendicular twofold axes, either rotation or inversion
Trigonal	Unique threefold axis, either rotation or inversion
Tetragonal	Unique fourfold axis, either rotation or inversion
Hexagonal	Unique sixfold axis, either rotation or inversion
Cubic	Four threefold axes, either rotation or inversion, along four body diagonals of a cube

sets of symmetry elements – symmetry groups. When only finite crystallographic symmetry elements are considered, the symmetry groups are called point groups. The word “point” is used because symmetry elements in these groups have at least one common point and, as a result, they leave at least one point of an object unmoved.

The combination of crystallographic symmetry elements and their orientations with respect to one another in a group defines the crystallographic axes, that is, establishes the coordinate system used in crystallography. Although in general, a crystallographic coordinate system can be chosen arbitrarily (e.g., see Fig. 1.3), to keep things simple and standard, the axes are chosen with respect to the orientation of specific symmetry elements present in a group. Usually, the crystallographic axes are chosen to be parallel to rotation axes or perpendicular to mirror planes. This choice simplifies both the mathematical and geometrical descriptions of symmetry elements and, therefore, the symmetry of a crystal in general.

As a result, all possible three-dimensional crystallographic point groups have been divided into a total of seven crystal systems, based on the presence of a specific symmetry element, or a specific combination of symmetry elements present in the point group. The seven crystal systems are listed in Table 2.6.

2.8 Stereographic Projection

All symmetry elements that belong to any of the three-dimensional point groups can be easily depicted in two dimensions by using the so-called stereographic projections. The visualization is achieved similar to projections of northern or southern hemispheres of the globe in geography. Stereographic projections are constructed as follows:

- A sphere with a center that coincides with the point (if any) where all symmetry elements intersect (Fig. 2.14, left) is created. If there is no such common point,

then the selection of the center of the sphere is random, as long as it is located on one of the characteristic symmetry elements (see Table 2.6).

- This sphere is split by the equatorial plane into the upper and lower hemispheres.
- The lines corresponding to the intersections of mirror planes and the points corresponding to the intersections of rotation axes with the upper (“northern”) hemisphere are projected on the equatorial plane using the lower (“southern”) pole as the point of view.
- The projected lines and points are labeled using appropriate symbols (see Table 2.3 and Fig. 2.4).
- The presence of the center of inversion, if any, is shown by adding letter *C* to the center of the projection.

Figure 2.14 (right) shows an arbitrary stereographic projection of the point group symmetry formed by the following symmetry elements: twofold rotation axis, mirror plane and center of inversion (compare it with Fig. 2.12, which shows the same symmetry elements without the stereographic projection). The presence of onefold rotation axis is never indicated on the stereographic projection.

Arbitrary orientations are inconvenient because the same point-group symmetry results in an infinite number of possible stereographic projections. Thus, Fig. 2.15

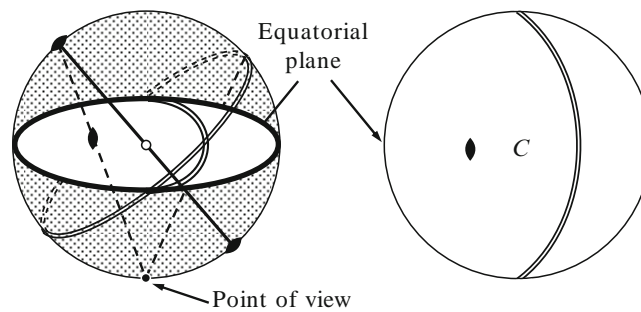


Fig. 2.14 The schematic of how to construct a stereographic projection. The location of the center of inversion is indicated using letter *C* in the middle of the stereographic projection.

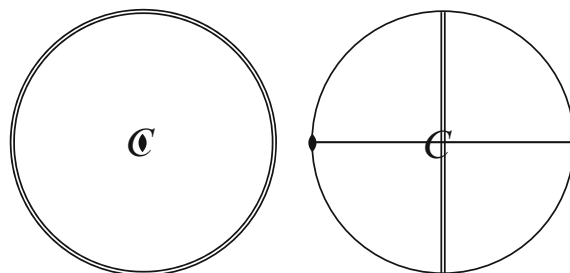


Fig. 2.15 The two conventional stereographic projections of the point group symmetry containing a twofold axis, mirror plane and center of inversion. The onefold rotation is not shown.

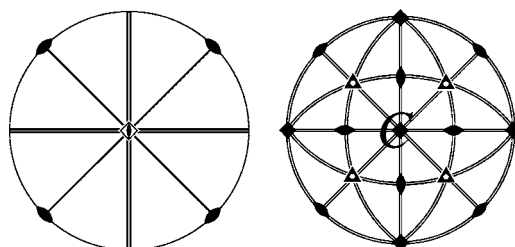


Fig. 2.16 Examples of the stereographic projections with tetragonal (*left*) and cubic (*right*) symmetry.

shows two different stereographic projections of the same point-group symmetry with the horizontal (left) and vertical (right) orientations of the plane, both of which are standard.

Figure 2.16 (left) is an example of the stereographic projection of a tetragonal point group symmetry containing symmetry elements discussed earlier (see Fig. 2.13). Figure 2.16 (right) shows the most complex cubic point group symmetry containing three mutually perpendicular fourfold rotation axes, four threefold rotation axes located along the body diagonals of a cube, six twofold rotation axes, nine mirror planes, and a center of inversion. More information about the stereographic projection can be found in the International Union of Crystallography (IUCr) teaching pamphlets⁸ and in the International Tables for Crystallography, Vol. A.

2.9 Crystallographic Point Groups

The total number of symmetry elements that form a crystallographic point group varies from one to as many as 24. However, since symmetry elements interact with one another, there is no need to use each and every symmetry element that belongs to a group in order to uniquely define and completely describe any of the crystallographic groups. The symbol of the point-group symmetry is constructed using the list of basic symmetry elements that is adequate to generate all derivative symmetry elements by applying the first property of the group (closure).

The orientation of each symmetry element with respect to the three major crystallographic axes is defined by its position in the sequence that forms the symbol of the point-group symmetry. The complete list of all 32 point groups is found in Table 2.7.

The columns labeled “first position,” “second position” and “third position” describe both the symmetry elements found in the appropriate position of the symbol and their orientation with respect to the crystallographic axes. When the corresponding symmetry element is a rotation axis, it is parallel to the specified

⁸ E.J.W. Whittaker, The stereographic projection, <http://www.iucr.org/iucr-top/comm/cteach/pamphlets/11/index.html>.

Table 2.7 Symbols of crystallographic point groups.

Crystal system	First position		Second position		Third position		Point group
	Element	Direction	Element	Direction	Element	Direction	
Triclinic	1 or $\bar{1}$	N/A	None		None		1, $\bar{1}$
Monoclinic	2, m or 2/m	Y	None		None		2, m, 2/m
Orthorhombic	2 or m	X	2 or m	Y	2 or m	X	222, mm2, mmm
Tetragonal	4, $\bar{4}$ or 4/m	Z	None or 2 or m	X	None or 2 or m	Base diagonal	4, $\bar{4}$, 4/m, 422, 4mm, $\bar{4}2m$, 4/mmm
Trigonal	3 or $\bar{3}$	Z	None or 2 or m	X	None		3, $\bar{3}$, 32, 3m, $\bar{3}m$
Hexagonal	6, $\bar{6}$ or 6/m	Z	None or 2 or m	X	None or 2 or m	Base diagonal	6, $\bar{6}$, 6/m, 622, 6mm, $\bar{6}2m$, 6/mmm
Cubic	2, m, 4 or $\bar{4}$	X	3 or $\bar{3}$	Body diagonal	None or 2 or m	Face diagonal	23, m3, 432, $\bar{4}3m$, m $\bar{3}$ m

Table 2.8 Crystallographic point groups arranged according to their merohedry.

Crystal system	N ^a	\bar{N} ^a	$N\perp m$ ^b	$N\perp 2$ ^b	$N m$	$\bar{N} m$	$N\perp m m$
Triclinic	1	$\bar{1}$					
Monoclinic	2	\bar{m}	2/m				
Orthorhombic				222	mm2		mmm
Tetragonal	4	$\bar{4}$	4/m	422	4mm	$\bar{4}m2$	4/mmm
Trigonal	3	$\bar{3}$		32	3m	$\bar{3}m$	
Hexagonal	6	$\bar{6}$	6/m	622	6mm	$\bar{6}m2$	6/mmm
Cubic	23		m$\bar{3}$	432		43m	m$\bar{3}$m

^a N and \bar{N} are major N-fold rotation and inversion axes, respectively.

^b m and two are mirror plane and twofold rotation axis, respectively, which are parallel (||) or perpendicular (\perp) to the major axis.

crystallographic direction but mirror planes are always perpendicular to the corresponding direction.⁹ When the crystal system has a unique axis, for example, 2 in the monoclinic crystal system, 4 in the tetragonal crystal system, and so on, and when there is a mirror plane that is perpendicular to the axis, this combination is always present in the point-group symbol. The axis is listed first and the plane is listed second with the two symbols separated by a slash (/). According to Table 2.7, the crystallographic point group shown in Fig. 2.15 is 2/m, and those in Fig. 2.16 are $\bar{4}m2$ (left) and m $\bar{3}m$ (right), respectively.

The list of crystallographic point groups appears not very logical, even when arranged according to the crystal systems, as has been done in Table 2.7. Therefore, in Table 2.8 the 32-point groups are arranged according to their merohedry, or in

⁹ In fact, since a mirror plane can be represented by a two-fold inversion axis, this is the same as the latter being parallel to the corresponding direction, see Fig. 2.8 (right).

other words, according to the presence of symmetry elements other than the major (or unique) axis.

Another classification of point groups is based on their action. Thus, centrosymmetric point groups, or groups containing a center of inversion are shown in Table 2.8 in bold, while the groups containing only rotational operation(s) and, therefore, not changing the enantiomorphism (all hands remain either left of right), are in *italic*. Point groups shown in rectangular boxes do not have the inversion center; however, they change the enantiomorphism. An empty cell in the table means that the generated point group is already present in a different place in Table 2.8, sometimes in a different crystal system.

2.10 Laue¹⁰ Classes

Radiation and particles, that is, X-rays, neutrons, and electrons interact with a crystal in a way that the resulting diffraction pattern is always centrosymmetric, regardless of whether an inversion center is present in the crystal or not. This leads to another classification of crystallographic point groups, called Laue classes. The Laue class defines the symmetry of the diffraction pattern produced by a single crystal, and can be easily inferred from a point group by adding the center of inversion (see Table 2.9).

For example, all three monoclinic point groups, that is, 2, m, and 2/m will result in 2/m symmetry after adding the center of inversion. In other words, the 2, m, and 2/m point groups belong to the Laue class 2/m, and any diffraction pattern obtained from any monoclinic structure will always have 2/m symmetry. The importance of this classification is easily appreciated from the fact that Laue classes, but not crys-

Table 2.9 The 11 Laue classes and six “powder” Laue classes.

Crystal system	Laue class	“Powder” Laue class	Point groups
Triclinic	$\bar{1}$	$\bar{1}$	1, $\bar{1}$
Monoclinic	2/m	2/m	2, m, 2/m
Orthorhombic	mmm	mmm	222, mm2, mmm
Tetragonal	4/m	4/mmm	4, $\bar{4}$, 4/m
	4/mmm	4/mmm	422, 4mm, $\bar{4}m2$, 4/mmm
Trigonal	$\bar{3}$	6/mmm	3, $\bar{3}$
	$\bar{3}m$	6/mmm	32, 3m, $\bar{3}m$
Hexagonal	6/m	6/mmm	6, $\bar{6}$, 6/m
	6/mmm	6/mmm	622, 6mm, $\bar{6}m2$, 6/mmm
Cubic	$m\bar{3}$	$m\bar{3}m$	23, $m\bar{3}$
	$m\bar{3}m$	$m\bar{3}m$	432, $\bar{4}3m$, $m\bar{3}m$

¹⁰ Max von Laue (1879–1960). German physicist who was the first to observe and explain the phenomenon of X-ray diffraction in 1912. Laue was awarded the Nobel Prize in Physics in 1914 “for his discovery of the diffraction of X-rays by crystals.” For more information about Max von Laue see <http://www.nobel.se/physics/laureates/1914/>.

Table 2.10 Lattice symmetry and unit cell shapes.

Crystal family	Unit cell symmetry	Unit cell shape/parameters
Triclinic	$\bar{1}$	$a \neq b \neq c; \alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic	2/m	$a \neq b \neq c; \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
Orthorhombic	mmm	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$
Tetragonal	4/mmm	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$
Hexagonal and Trigonal	6/mmm	$a = b \neq c; \alpha = \beta = 90^\circ, \gamma = 120^\circ$
Cubic	$m\bar{3}m$	$a = b = c; \alpha = \beta = \gamma = 90^\circ$

tallographic point groups, are distinguishable from diffraction data, which is caused by the presence of the center of inversion. All Laue classes (a total of 11) listed in Table 2.9 can be recognized from three-dimensional diffraction data when examining single crystals. However, conventional powder diffraction is fundamentally one-dimensional, because the diffracted intensity is measured as a function of one variable (Bragg¹¹ angle), which results in six identifiable “powder” Laue classes.

As seen in Table 2.9, there is one “powder” Laue class per crystal system, except for the trigonal and hexagonal crystal systems, which share the same “powder” Laue class, 6/mmm. In other words, not every Laue class can be distinguished from a simple visual analysis of powder diffraction data. This occurs because certain diffraction peaks with potentially different intensities (the property which enables us to differentiate between Laue classes 4/m and 4/mmm; $\bar{3}$, $\bar{3}m$, 6/m, and 6/mmm; $m\bar{3}$ and $m\bar{3}m$) completely overlap since they are observed at identical Bragg angles. Hence, only Laue classes that differ from one another in the shape of the unit cell (see Table 2.10), are ab initio discernible from powder diffraction data without a complete structural determination.

2.11 Selection of a Unit Cell and Bravais¹² Lattices

The symmetry group of a lattice always has the highest symmetry in the conforming crystal system. Taking into account that trigonal and hexagonal crystal systems are usually described in the same type of the lattice, seven crystal systems can be grouped into six crystal families, which are identical to the six “powder” Laue classes. Different types of lattices, or in general crystal systems, are identified by the presence of specific symmetry elements and their relative orientation. Furthermore, lattice symmetry is always the same as the symmetry of the unit cell shape

¹¹ Sir William Henry Bragg (1862–1942). British physicist and mathematician who together with his son William Lawrence Bragg (1890–1971) founded X-ray diffraction science in 1913–1914. Both were awarded the Nobel Prize in Physics in 1915 “for their services in the analysis of crystal structure by means of X-rays.” See <http://www.nobel.se/physics/laureates/1915/> for more details.

¹² Auguste Bravais (1811–1863). French crystallographer, who was the first to derive the 14 different lattices in 1848. A brief biography is found on Wikipedia at http://en.wikipedia.org/wiki/Auguste_Bravais.

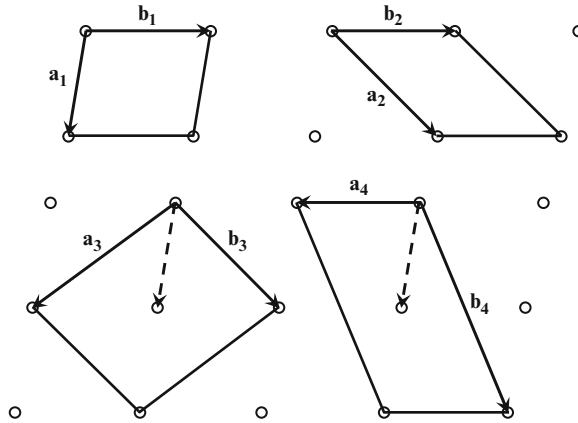


Fig. 2.17 Illustration of different ways to select a unit cell in the same two-dimensional lattice.

(except that the lattice has translational symmetry but the unit cell does not), which establishes unique relationships between the unit cell dimensions (a , b , c , α , β and γ) in each crystal family as shown in Table 2.10. Thus, the fundamental *rule number one* for the proper selection of the unit cell can be formulated as follows: symmetry of the unit cell should be identical to the symmetry of the lattice, excluding translations.

We have already briefly mentioned that in general, the choice of the unit cell is not unique (e.g., see Fig. 1.3). The uncertainty in the selection of the unit cell is further illustrated in Fig. 2.17, where the unit cell in the same two-dimensional lattice has been chosen in four different ways.

The four unit cells shown in Fig. 2.17 have the same symmetry (a twofold rotation axis, which is perpendicular to the plane of the projection and passes through the center of each unit cell), but they have different shapes and areas (volumes in three dimensions). Further, the two unit cells located at the top of Fig. 2.17 do not contain lattice points inside the unit cell, while each of the remaining two has an additional lattice point in the middle. We note that all unit cells depicted in Fig. 2.17 satisfy the rule for the monoclinic crystal system established in Table 2.10. It is quite obvious, that more unit cells can be selected in Fig. 2.17, and an infinite number of choices are possible in the infinite lattice, all in agreement with Table 2.10.

Without adopting certain conventions, different unit cell dimensions might, and most definitely would be assigned to the same material based on preferences of different researchers. Therefore, long ago the following rules (Table 2.11) were established to designate a standard choice of the unit cell, dependent on the crystal system. This set of rules explains both the unit cell shape and relationships between the unit cell parameters listed in Table 2.10 (i.e., rule number one), and can be considered as *rule number two* in the proper selection of the unit cell.

Applying the rules established in Table 2.11 to two of the four unit cells shown at the top of Fig. 2.17, the cell based on vectors \mathbf{a}_1 and \mathbf{b}_1 is the standard choice. The unit cell based on vectors \mathbf{a}_2 and \mathbf{b}_2 has the angle between the vectors much farther

Table 2.11 Rules for selecting the unit cell in different crystal systems.

Crystal family	Standard unit cell choice	Alternative unit cell choice
Triclinic	Angles between crystallographic axes should be as close to 90° as possible but greater than or equal to 90°	Angle(s) less than or equal to 90° are allowed
Monoclinic	Y -axis is chosen parallel to the unique twofold rotation axis (or perpendicular to the mirror plane) and angle β should be greater than but as close to 90° as possible	Same as the standard choice, but Z -axis in place of Y , and angle γ in place of β are allowed
Orthorhombic	Crystallographic axes are chosen parallel to the three mutually perpendicular twofold rotation axes (or perpendicular to mirror planes)	None
Tetragonal	Z -axis is always parallel to the unique fourfold rotation (inversion) axis. X - and Y -axes form a 90° angle with the Z -axis and with each other	None
Hexagonal and trigonal	Z -axis is always parallel to three- or sixfold rotation (inversion) axis. X - and Y -axes form a 90° angle with the Z -axis and a 120° angle with each other	In a trigonal symmetry, ^a threefold axis is chosen along the body diagonal of the primitive unit cell, then $a = b = c$ and $\alpha = \beta = \gamma \neq 90^\circ$
Cubic	Crystallographic axes are always parallel to the three mutually perpendicular two- or fourfold rotation axes, while the four threefold rotation (inversion) axes are parallel to three body diagonals of a cube	None

^aInstead of a rhombohedrally centered trigonal unit cell shown in Fig. 2.20, below.

from 90° than the first one. The remaining two cells contain additional lattice points in the middle. This type of the unit cell is called *centered*, while the unit cell without a point in the middle is *primitive*. In general, a primitive unit cell is preferred over a centered one, otherwise it is possible to select a unit cell with any number of points inside, and ultimately it can be made as large as the entire crystal. However, because rule number one requires that the unit cell has the same symmetry as the entire lattice except translational symmetry, it is not always possible to select a primitive unit cell, and so centered unit cells are used.

The *third rule* used to select a standard unit cell is the requirement of the minimum volume (or the minimum number of lattice points inside the unit cell). All things considered, the following unit cells are customarily used in crystallography.

- Primitive, that is, noncentered unit cell. A primitive unit cell is shown schematically in Fig. 2.18 (left). It always contains a single lattice point per unit cell (lattice points are located in eight corners of the parallelepiped, but each corner is shared by eight neighboring unit cells in three dimensions).
- Base-centered unit cell (Fig. 2.18, right) contains additional lattice points in the middle of the two opposite faces (as indicated by the vector pointing toward the

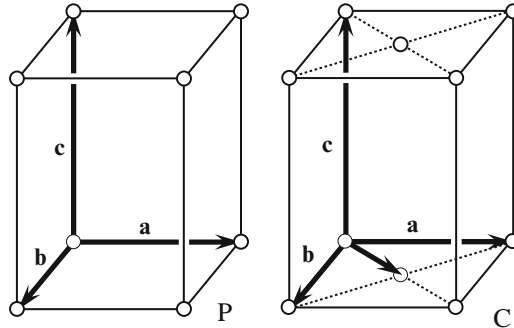


Fig. 2.18 Primitive unit cell (*left*) and base-centered unit cell (*right*).

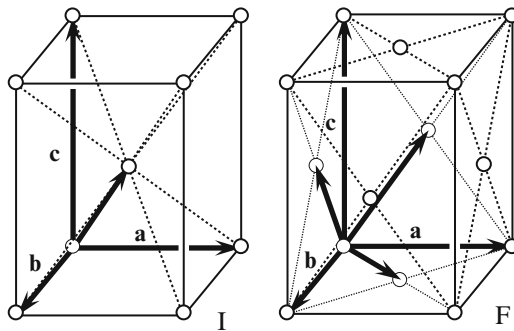


Fig. 2.19 Body-centered unit cell (*left*) and face-centered unit cell (*right*).

middle of the base and by the dotted diagonals on both faces). This unit cell contains two lattice points, since each face is shared by two neighboring unit cells in three dimensions.

- Body-centered unit cell (Fig. 2.19, left) contains one additional lattice point in the middle of the body of the unit cell. Similar to a base-centered unit cell, the body-centered unit cell contains a total of two lattice points.
- Face-centered unit cell (Fig. 2.19, right) contains three additional lattice points located in the middle of each face, which results in a total of four lattice points in a single face-centered unit cell.
- Rhombohedral unit cell (Fig. 2.20) is a special unit cell that is allowed only in a trigonal crystal system. It contains two additional lattice points located at $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$ as shown by the ends of the two vectors inside the unit cell, which results in a total of three lattice points per unit cell.

Since every unit cell in the crystal lattice is identical to all others, it is said that the lattice can be primitive or centered. We already mentioned (1.1) that a crystallographic lattice is based on three noncoplanar translations (vectors), thus the presence of lattice centering introduces additional translations that are different from the three basis translations. Properties of various lattices are summarized in

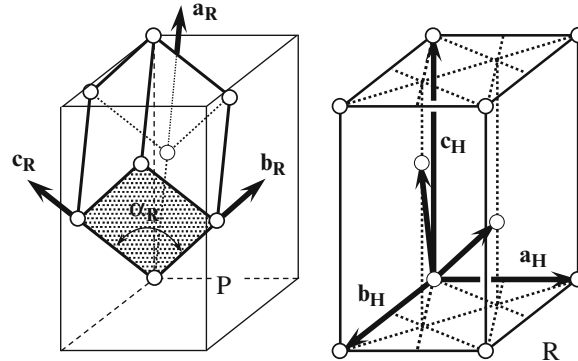


Fig. 2.20 Primitive (*left*) and hexagonal rhombohedral (*right*) unit cells.

Table 2.12 Possible lattice centering.

Centering of the lattice	Lattice points per unit cell	International symbol	Lattice translation(s) due to centering
Primitive	1	P	None
Base-centered	2	A	$\frac{1}{2}(\mathbf{b} + \mathbf{c})$
Base-centered	2	B	$\frac{1}{2}(\mathbf{a} + \mathbf{c})$
Base-centered	2	C	$\frac{1}{2}(\mathbf{a} + \mathbf{b})$
Body-centered	2	I	$\frac{1}{2}(\mathbf{a} + \mathbf{b} + \mathbf{c})$
Face-centered	4	F	$\frac{1}{2}(\mathbf{b} + \mathbf{c}); \frac{1}{2}(\mathbf{a} + \mathbf{c}); \frac{1}{2}(\mathbf{a} + \mathbf{b})$
Rhombohedral	3	R	$\frac{1}{3}\mathbf{a} + \frac{2}{3}\mathbf{b} + \frac{2}{3}\mathbf{c}; \frac{2}{3}\mathbf{a} + \frac{1}{3}\mathbf{b} + \frac{1}{3}\mathbf{c}$


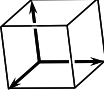
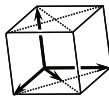
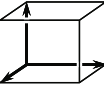
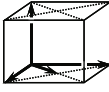
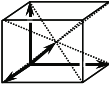
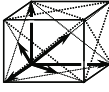
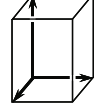
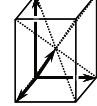
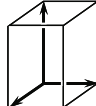
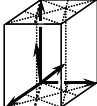
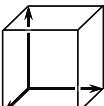
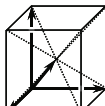
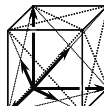
Table 2.12 along with the international symbols adopted to differentiate between different lattice types. In a base-centered lattice, there are three different possibilities to select a pair of opposite faces if the coordinate system is fixed, which is also reflected in Table 2.12.

The introduction of lattice centering makes the treatment of crystallographic symmetry much more elegant when compared to that where only primitive lattices are allowed. Considering six crystal families (Table 2.11) and five types of lattices (Table 2.12), where three base-centered lattices which are different only by the orientation of the centered faces with respect to a fixed set of basis vectors being taken as one, it is possible to show that only 14 different types of unit cells are required to describe all lattices using conventional crystallographic symmetry. These are listed in Table 2.13, and they are known as Bravais lattices.

Empty positions in Table 2.13 exist because the corresponding lattices can be reduced to a lattice with different centering and a smaller unit cell (rule number three), or they do not satisfy rules number one or two. For example:

- In the triclinic crystal system, any of the centered lattices can be reduced to a primitive lattice with the smaller volume of the unit cell (rule number three).
- In the monoclinic crystal system, the body-centered lattice can be converted into a base-centered lattice (C), which is standard. The face-centered lattice is reduced

Table 2.13 The 14 Bravais lattices.

Crystal system	P	C	I	F	R
Triclinic					
Monoclinic					
Orthorhombic					
Tetragonal					
Hexagonal, Trigonal					
Cubic					

to a base-centered lattice with half the volume of the unit cell (rule number three). Even though the base-centered lattice may be reduced to a primitive cell and further minimize the volume of the unit cell, this reduction is incompatible with rule number one since more complicated relationships between the unit cell parameters would result instead of the standard $\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$.

- In the tetragonal crystal system the base-centered lattice (C) is reduced to a primitive (P) one, whereas the face-centered lattice (F) is reduced to a body-centered (I) cell; both reductions result in half the volume of the corresponding unit cell (rule number three).

The latter example is illustrated in Fig. 2.21, where a tetragonal face-centered lattice is reduced to a tetragonal body-centered lattice, which has the same symmetry, but half the volume of the unit cell. The reduction is carried out using the transformations of basis vectors as shown in (2.5)–(2.7).

$$\mathbf{a}_I = \frac{1}{2}(\mathbf{a}_F - \mathbf{b}_F) \quad (2.5)$$

$$\mathbf{b}_I = \frac{1}{2}(\mathbf{a}_F + \mathbf{b}_F) \quad (2.6)$$

$$\mathbf{c}_I = \mathbf{c}_F \quad (2.7)$$

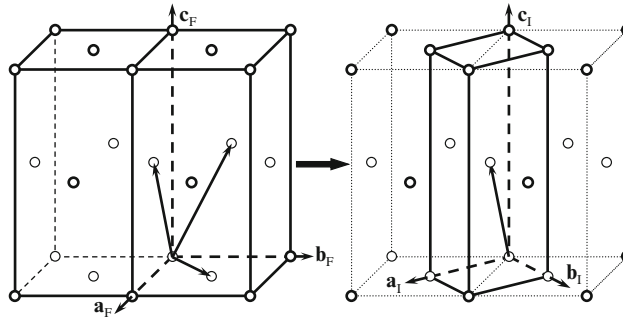


Fig. 2.21 The reduction of the tetragonal face-centered lattice (*left*) to the tetragonal body-centered lattice with half the volume of the unit cell (*right*). Small circles indicate lattice points.

The relationships between the unit cell dimensions and unit cell volumes of the original face-centered (V_F) and the reduced body-centered (V_I) lattices are:

$$a_I = b_I = \frac{a_F}{\sqrt{2}} = \frac{b_F}{\sqrt{2}}; \quad c_I = c_F \quad (2.8)$$

$$V_I = V_F/2 \quad (2.9)$$

2.12 Additional Reading

1. C. Giacovazzo, H.L. Monaco, G. Artioli, D. Viterbo, G. Ferraris, G. Gilli, G. Zanotti, and M. Catti, *Fundamentals of crystallography*. IUCr texts on crystallography 7, Second Edition, Oxford University Press, Oxford and New York (2002).
2. D. Schwarzenbach, *Crystallography*, Wiley, New York (1996).
3. C. Hammond, *The basics of crystallography and diffraction*. IUCr texts on crystallography 3. Oxford University Press, Oxford, New York (1997).
4. D.E. Sands, *Introduction to crystallography*, Dover Publications, Dover (1994).
5. D. Farmer, *Groups and symmetry*, Amer. Math. Soc., Providence, RI (1995).
6. *International Tables for Crystallography*, vol. A, Fifth Revised Edition, Theo Hahn, Ed., Published for the International Union of Crystallography by Springer, Berlin (2002).
7. *International Tables for Crystallography*. Brief teaching edition of volume A, Fifth Revised Edition. Theo Han, Ed., Published for the International Union of Crystallography by Springer, Berlin (2002).
8. IUCr Teaching pamphlets: <http://www.iucr.org/iucr-top/comm/cteach/pamphlets.html>

2.13 Problems

1. Consider two mirror planes that intersect at $\phi = 90^\circ$. Using geometrical representation of two planes establish which symmetry element(s) appear as the result

of this combination of mirror planes. What is(are) the location(s) of new symmetry element(s)? Name point-group symmetry formed by this combination of symmetry elements.

2. Consider two mirror planes that intersect at $\phi = 45^\circ$. Using geometrical representation of two planes establish which symmetry element(s) appear as the result of this combination of mirror planes. What is(are) the location(s) of new symmetry element(s)? Name point-group symmetry formed by this combination of symmetry elements.

3. Consider the following sequence of numbers: $1, 1/2, 1/3, 1/4, \dots, 1/N, \dots$. Is this a group assuming that the combination law is multiplication, division, addition or subtraction? If yes, identify the combination law in this group and establish whether this group is finite or infinite.

4. Consider the group created by three noncoplanar translations (vectors) using the combination law defined by (1.1). Which geometrical form can be chosen to illustrate this group? Is the group finite?

5. Determine both the crystal system and point group symmetry of a parallelepiped (a brick), which is shown schematically in Fig. 2.22 and in which $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90^\circ$?

6. Determine both the crystal system and point group symmetry of benzene molecule, C_6H_6 , which is shown in Fig. 2.23. Treat atoms as spheres, not as dimensionless points.

7. Determine both the crystal system and point-group symmetry of the ethylene molecule, C_2H_4 , shown schematically in Fig. 2.24. Using the projection on the left,

Fig. 2.22 Illustration of a parallelepiped (a brick) in which three independent edges have different lengths.

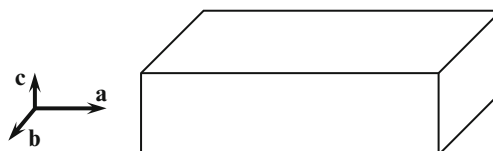


Fig. 2.23 The schematic of benzene molecule. Carbon atoms are white and hydrogen atoms are black.

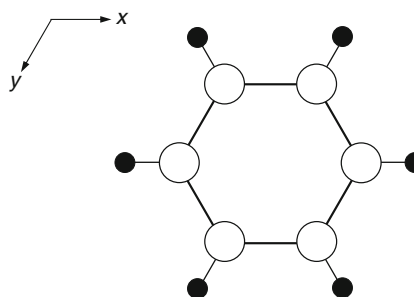
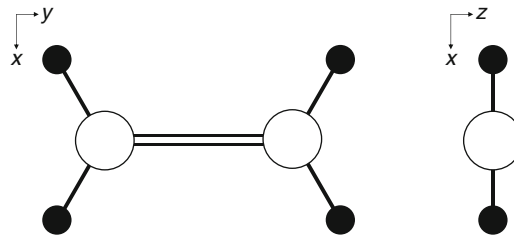


Fig. 2.24 The schematic of ethylene molecule. Carbon atoms are *white* and hydrogen atoms are *black*.



show all symmetry elements that you were able to identify in this molecule, include both the in-plane and out-of-plane symmetry elements. Treat atoms as spheres, not as dimensionless points.

8. Determine the point-group symmetry of the octahedron. How many, and which symmetry elements are present in this point-group symmetry?

9. The following relationships between lattice parameters: $a \neq b \neq c$, $\alpha \neq \beta \neq 90$ or 120° , and $\gamma = 90^\circ$ potentially define a “diclinic” crystal system (two angles $\neq 90^\circ$). Is this an eighth crystal system? Explain your answer.

10. The relationships $a = b \neq c$, $\alpha = \beta = 90^\circ$, and $\gamma \neq 90^\circ$ point to a monoclinic crystal system, except that $a = b$. What is the reduced (standard) Bravais lattice in this case? Provide equations that reduce this lattice to one of the 14 standard Bravais types.

11. Imagine that there is an “edge-centered” lattice (for example unit cell edges along Z contain lattice points at $\frac{1}{2}\mathbf{c}$). If this were true, the following lattice translation is present: $(0, 0, \frac{1}{2})$. Convert this lattice to one of the standard lattices.

12. Monoclinic crystal system has primitive and base-centered Bravais lattices (see Table 2.13, above). Using two-dimensional projections depicted in Fig. 2.25, show how a body-centered lattice and a face-centered monoclinic lattice (their unit cells are indicated with the dashed lines) can be reduced to a base-centered lattice. Write the corresponding vectorial relationships between the unit cell vectors of the original body-centered and face-centered lattices and the transformed base-centered lattices. What are the relationships between the unit cell volumes of the original body- and face-centered lattices and the resulting base-centered lattices?

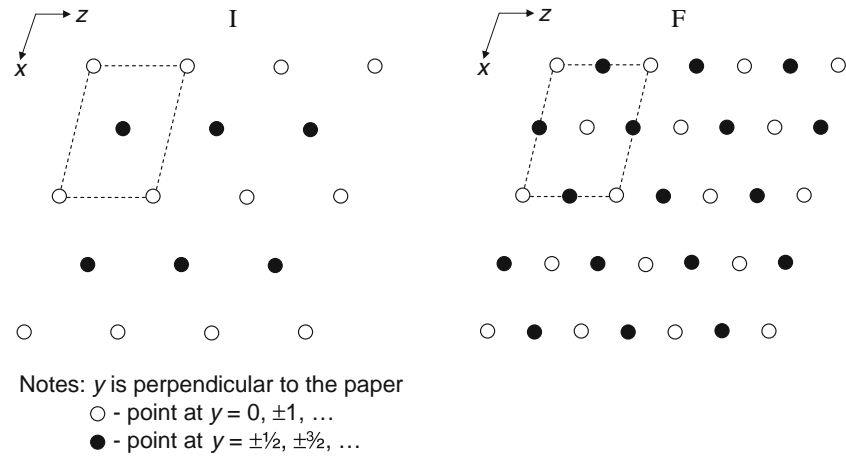


Fig. 2.25 Body centered (*left*) and face centered (*right*) monoclinic lattices projected along the Y -axis with the corresponding unit cells shown using the dashed lines.