
Preface to the Second English Edition

The second English edition is largely based on the third German edition of the Teubner Studienbuch "Kristallstrukturbestimmung," which appeared in 2002. In particular, Chapter 7, dealing with experimental methods, has been extensively rewritten. In view of the huge recent advances in the use of area detector systems for single-crystal data collection, their description has replaced much of the material on "classic" methods. Similarly, the practical example (Chapter 15) now describes area-collector methods more fully. Among many other cases, the sections on Rietveld refinement, macromolecular crystallography and uses of databases have been updated. I am grateful to my colleague R.O. Gould for continuing his excellent translation of the first edition, and for the friendly and careful collaboration in achieving many large and small improvements.

Werner Massa

Marburg, November 2003

Preface to the First German Edition

Crystal structure analysis using X-rays has undergone an expansion of avalanche proportions in the last twenty years, thanks to the development of rapid and automatic means of data collection and the enormous growth of the computer hardware and software for carrying out the necessary calculations. Because of its wide applicability and its precision, it has become one of the most important tools in both organic and inorganic chemical research. Despite the fact that crystallography plays a very minor role in most undergraduate study, many students have found that in the course of graduate or even undergraduate research, they need to undertake a crystal structure determination themselves, or at least to become competent to interpret crystallographic results. Thanks to ever improving program systems, the many complex steps of a structure analysis are certainly becoming less and less difficult for the beginner to master. Nonetheless, regarding the process simply as a "black box" is fraught with danger.

This book is aimed at those students of chemistry and related subjects who wish to take a look into the black box before they step into its territory, or who simply wish to learn more of the fundamentals, the opportunities and the risks of the method. In view of the well-known fact that the likelihood a book will actually be read is inversely proportional to its number of pages, fundamentals of the method are treated here as briefly and as intuitively as possible. It seems more important that chemists should have a grasp of the basic principles and their application to a problem, than that they be in a position to understand fully the complex mathematical formalisms employed by the computer programs.

On the other hand, some aspects of the subject, which bear directly on the quality of a structure determination, are worth fuller treatment. These include discussion of a number of significant errors and the recognition and treatment of disorder and

twinning. Most important crystallographic literature is available in English, but a few references in other languages, principally German, have been included.

This book is based in part on lectures and on a seminar at the University of Marburg. Consciously or unconsciously, many colleagues have made their contributions. I am particularly grateful to Professor D. Babel for many helpful suggestions and a critical reading of the manuscript. I thank Dr. K. Harms for proofreading the manuscript and Mr. C. Frommen for considerable assistance with the production of camera-ready copy using the \LaTeX program. Finally, I acknowledge the help of my wife Hedwig and my children for all their assistance and patience during the preparation of this book.

Werner Massa

Marburg, April 1994

Crystal Lattices

2.1

The Lattice

A “crystal” is a solid object in which a basic pattern of atoms is repeated over and over in all three dimensions. In order to describe the structure of a crystal, it is thus only necessary to know the simplest repeating “motif” and the lengths and directions of the three vectors which together describe its repetition in space (Fig. 2.1). The motif can be a molecule, as in Fig. 2.1, or the building block of a network structure. Normally, it consists of several such units, which may be converted into one another by symmetry operations (as in Fig. 2.2). The three vectors a , b , c which describe the translations of the motif in space are called the basis vectors. By their operation one

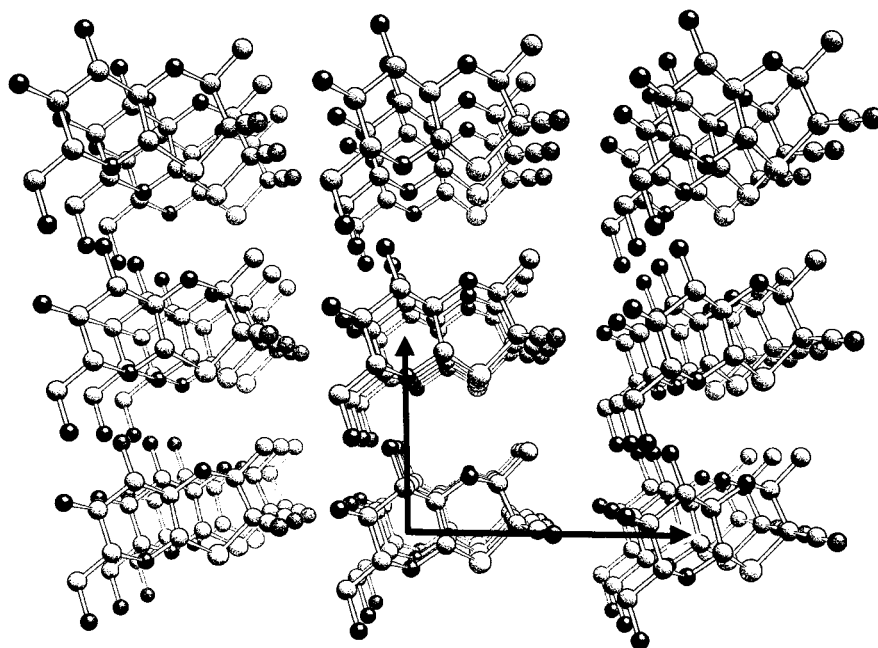


Fig. 2.1. Portion of the crystal of a simple molecular structure with the basis vectors shown. (The third vector is normal to the plane of the paper.)

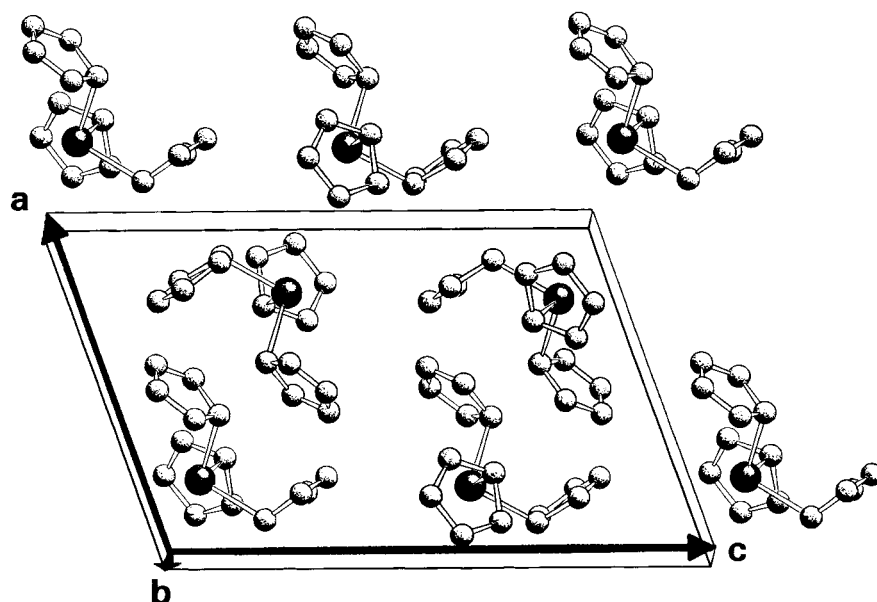


Fig. 2.2. A more complex structure in which the motif consists of four differently orientated molecules of $(C_5H_5)_3Sb$. The translation in the b -direction is not shown.

upon another, a lattice is generated. Any point in such a lattice may be described by a vector r ,

$$r = n_1 a + n_2 b + n_3 c \quad (2.1)$$

where n_1 , n_2 and n_3 are integers. It is important to keep in mind that the lattice is an abstract mathematical concept, the origin of which may be chosen more or less arbitrarily in a crystal structure. If it is chosen to lie on some particular atom, it follows that every point of the lattice will lie on an identical atom in an identical environment. It is, of course, equally valid to place the origin on an empty point in the structure.

Unfortunately, the word lattice has taken on a different meaning in common speech: when, for example, the phrase “rock-salt lattice” is used, what is meant is the “rock-salt structure type”.

2.1.1 The Unit Cell

The smallest repeating volume of the lattice is called the unit cell. It is characterized by three lattice constants a , b , c (the lengths of the basis vectors) and by the three angles α , β , γ which separate these vectors from one another. By definition, α is the angle between the basis vectors b and c , β between a and c , and γ between a and

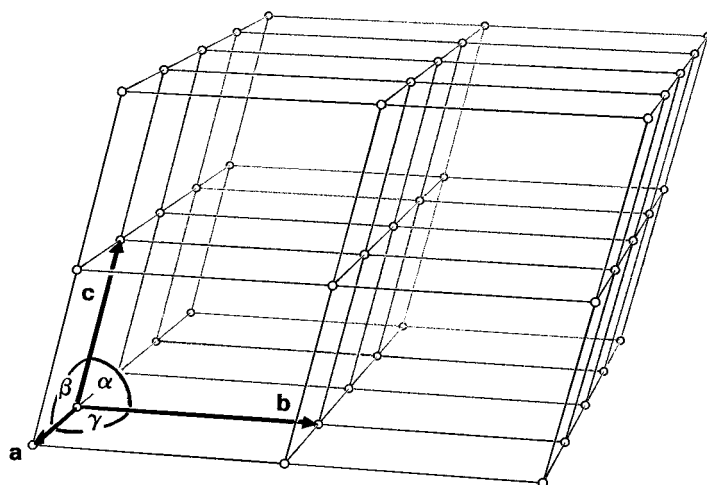


Fig. 2.3. Portion of a lattice.

b (Fig. 2.3). The lengths of the lattice constants for “normal” organic or inorganic structures, with the determination of which we are concerned here, is of the order of 3 to 40 Å. For protein structures they rise to 100 Å or more. A crystal structure is solved, if the types and locations of all the atoms in the unit cell are known; in general there will be between 1 and 1000 of these.

2.1.2 Atom Parameters

The positions of atoms are conveniently described in terms of the crystallographic axes defined by the three basis vectors: these are normally referred to as the **a**-, **b**- and **c**-axes. The lattice constants are then used as units, and the atomic positions are given in terms of fractional co-ordinates x , y , z , which describe fractions of the lattice constants a , b , and c respectively (Fig. 2.4). The coordinates of an atom at the center of the unit cell, for example, are simply written as $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

When a drawing is made using the published atom parameters for a structure, the lattice parameters and angles must be known. Then, “absolute” coordinates for

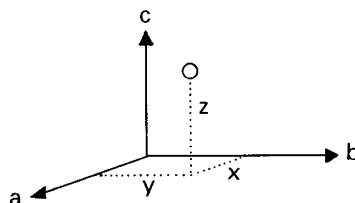


Fig. 2.4. Example of atomic parameters x, y, z in units of the basis vectors.

each atom xa, yb, zc give the appropriate distances along each of the crystallographic axes.

2.1.3

The Seven Crystal Systems

In addition to the three dimensional periodicity, a further very important property of nearly all crystals is their symmetry. This is treated more fully in Chapter 6; it is now only necessary to examine those aspects of symmetry which affect the lattice. For example, if there is a mirror plane in the crystal normal to the \mathbf{b} -axis, it follows that the \mathbf{a} - and \mathbf{c} -axes must lie in this plane, and hence be themselves perpendicular to the \mathbf{b} -axis. If a 3-fold rotation axis lies parallel to the \mathbf{c} -axis, this implies that the angle between \mathbf{a} and \mathbf{b} (γ) must be 120° . Full consideration of the possible symmetries for the lattice gives rise to seven possibilities, the seven crystal systems (Tab. 2.1). They are distinguished from one another by their shape — the geometry of the lattice that is required by the underlying symmetry elements.

Conventions: In order to describe crystal structures clearly and unambiguously, various rules have been adopted concerning the choice and naming of the unit-cell axes. In general, a “right-handed” system is chosen. This means that if the positive direction of \mathbf{a} is directed forward and that of \mathbf{b} to the left, then \mathbf{c} must point upwards. If one holds the thumb, the index finger and the middle finger of the right hand as a waiter might to support a tray, then these three fingers, starting with the thumb, give the directions of the \mathbf{a} , \mathbf{b} and \mathbf{c} -axes of a right-handed system. In the triclinic system, there are no restrictions on the choice of cell edges or angles, but in the monoclinic system, there is a “unique” axis — that one which is perpendicular to the other two. This unique axis is normally taken as the \mathbf{b} -axis, and the unrestricted angle is thus β (this is, rather inconsistently, called the second setting) and the \mathbf{a} - and \mathbf{c} -axes are chosen so that $\beta \geq 90^\circ$. At one time, the \mathbf{c} -axis was chosen as the unique axis (the “first” setting — the unrestricted angle is γ). The \mathbf{c} -axis is always chosen as the unique axis in *trigonal*, *hexagonal* and *tetragonal* crystals.

When the unit cell of an unknown crystal is determined experimentally, its metric symmetry gives an indication of the crystal system. However, it is the actual underlying symmetry elements, which may only be fully determined at a later stage of the investigations, which determine the crystal system. That the metric symmetry

Table 2.1. The seven crystal systems and the restrictions on their cell dimensions. See Fig. 2.3 for the definition of the angles.

Restriction in	cell edges	cell angles
triclinic	none	none
monoclinic	none	$\alpha = \gamma = 90^\circ$
orthorhombic	none	$\alpha = \beta = \gamma = 90^\circ$
tetragonal	$a = b$	$\alpha = \beta = \gamma = 90^\circ$
trigonal, hexagonal	$a = b$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

of a crystal correspond within experimental error to the restrictions of a particular crystal system is a necessary but not a sufficient condition for establishing it. Occasionally it happens, as with the cryolites, $\text{Na}_3\text{M}^{\text{III}}\text{F}_6$, that all cell angles are within less than a tenth of a degree of 90° , but the crystal is actually not orthorhombic, but only monoclinic. The β -angle is merely very near 90° by chance.

2.2 The Fourteen Bravais Lattices

In the description of a lattice, it was said that the smallest possible basis vectors should be chosen for the crystal. The smallest possible unit in this lattice, the unit cell, is then the smallest volume that is representative of the crystal as a whole. This is called a “*primitive cell*”. As is shown in Fig. 2.5, there are several ways in which this unit cell can be chosen.

All of the cells, shown here in two dimensional projection, are primitive and have the same volume. The choice of cell for the description of a crystal structure will be that by which the symmetry elements are best described. In other words, the cell which shows the highest possible symmetry. Usually, this implies the choice of orthogonal or hexagonal axial systems. The origin of the cell is located on an inversion center if that is possible. There are situations (Fig. 2.6) where all variants of a primitive unit cell are oblique, but that a larger cell, with 2, 3 or 4 times the volume, may be chosen which corresponds to a crystal system of higher symmetry. In order to be able to describe the symmetry elements conveniently, it is usually better to use the larger cells, even though they contain additional lattice points. Such cells are called centered and contain 2, 3 or 4 lattice points.

When lattices are described by these larger cells, to the six primitive lattices must be added eight centered lattices, which together are described as the fourteen Bravais lattices. Primitive lattices are given the symbol *P*. The symbol *A* is given to a one-face-centered or end-centered lattice, in which a second lattice point lies at the center of the *A*-face (that defined by the *b*- and *c*-axes), and *B* or *C* for a lattice centered

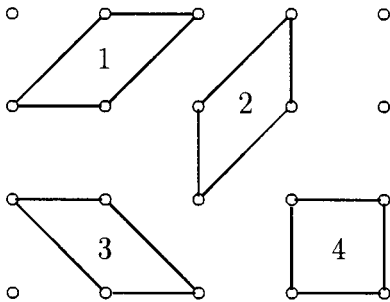


Fig. 2.5. Various choices of primitive unit cells in a lattice.

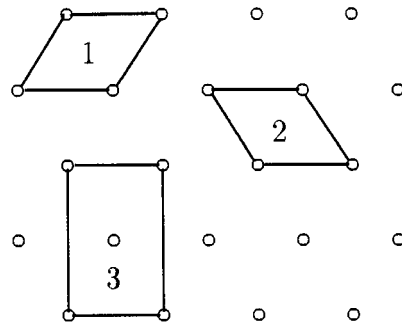


Fig. 2.6. The choice of cell 3 illustrates a centered lattice.

on the B or C face. In these cases, the cell volume is double that of the primitive cell. If the cell has lattice points at the centers of the A , B and C faces, it is called F (all face centered lattice), and has four times the volume of a primitive cell. A cell with a lattice point at its centre has double the volume of its primitive cell and is called a body centered lattice and given the symbol I (from the German *innenzentriert*). Nearly all metals crystallize in a cubic I or F lattice.

N.B. In the cubic $CsCl$ structure, a unit cell may be chosen with the Cs atoms at the corners and the Cl atom at the body centre. Despite what is written in many texts, this is a primitive cubic lattice. A body centered lattice requires that the origin and the body center of the cell be occupied by the same atoms or molecules having the same environment and the same orientation. In other words, shifting the origin of the cell to the body center must give a description of the structure indistinguishable from the original one.

2.2.1

The Hexagonal, Trigonal and Rhombohedral Systems

Both the *hexagonal* (with 6-fold symmetry) and the *trigonal* (with 3-fold symmetry) systems require a hexagonal axial system, ($a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$). They are conventionally described with the 6-fold axis of the lattice parallel to the c -axis. For this reason, many texts recognize only six crystal systems, and treat trigonal as a subset of hexagonal. The trigonal system does, however, have one unique feature, and that is the *rhombohedral* unit cell. In this case, the smallest primitive cell may be chosen with $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$. The unique axis, along which the 3-fold symmetry axis lies, is now one of the body diagonals of the cell. In order to make this more easily described mathematically, it is convenient to transform this cell to one which is centered at the points $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$, and is thus three times as large, but has the shape of the conventional hexagonal cell, with the c -direction as the unique axis. (Fig. 2.7).

This is called the *obverse* setting of a rhombohedral unit cell, and is the standard setting for the rhombohedral system. Rotating the a - and b -axes by 60° about c gives the alternative *reverse* setting. The lattice is now centered at the points $\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$ and $\frac{2}{3}, \frac{1}{3}, \frac{2}{3}$. Lattices which have *rhombohedral centering* are given the symbol R .

The full 14 Bravais lattices are given in Fig. 2.8. It can be seen that only some centerings are distinct in some crystal systems. For example, a B -centered monoclinic axial system (when b is the unique axis) is not given — any such cell may be better described as monoclinic P with half the volume (Fig. 2.9). Figure 2.10 shows that a monoclinic C -lattice may equally well be described as monoclinic I . It is most convenient here to choose whichever setting results in the smallest value for the monoclinic angle β .

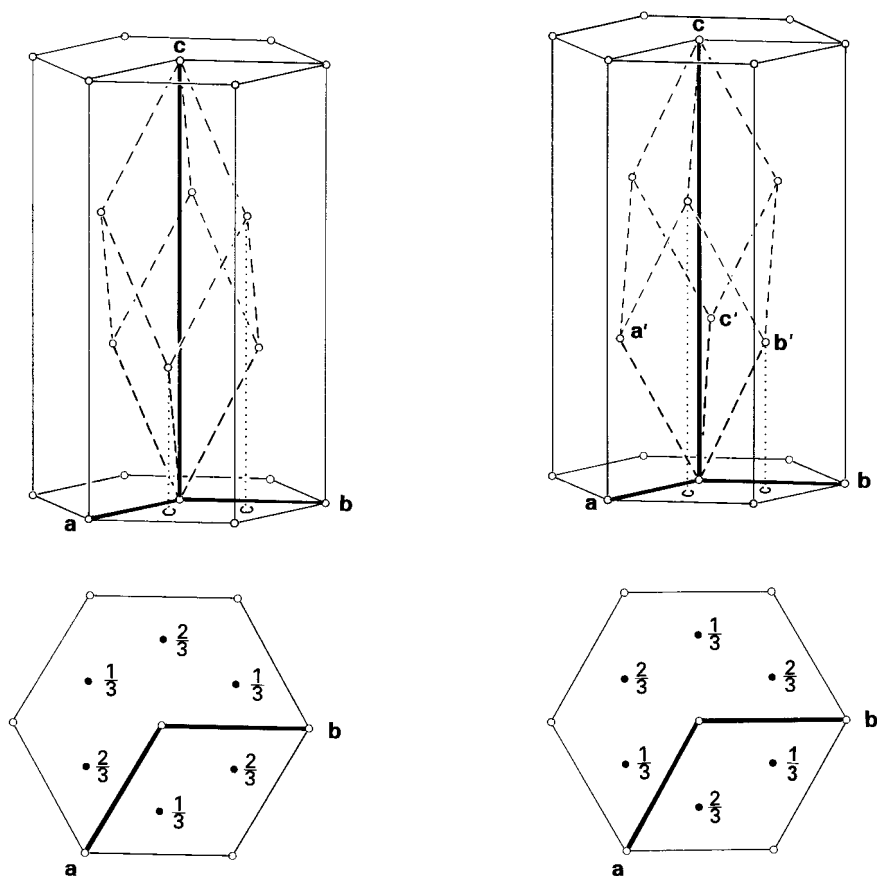


Fig. 2.7. A Rhombohedral unit cell in the *obverse* (left) and *reverse* (right) *hexagonal setting*.

2.2.2 The Reduced Cell

In order to discover whether an experimentally determined unit cell may in fact be transformed into a “better” cell of higher symmetry, algorithms have been developed to transform any cell into the so-called standard reduced form. This must fulfil the condition that $a \leq b \leq c$, and that α, β and γ are all either $\leq 90^\circ$ or $\geq 90^\circ$. For any crystal whatever, there is in principle only one cell which fulfils these conditions. One very important use of the reduced cell is in checking whether a particular structure has already been reported in the literature. Comparison of a reduced cell with those in data bases (see Chapter 13) should uncover any equivalent reduced cells, even if they were originally reported differently. Such a precaution should always be taken before embarking on intensity measurements (Chapter 7) for a “new” compound. A second very important use of the reduced cell is that it gives a clear guide to the

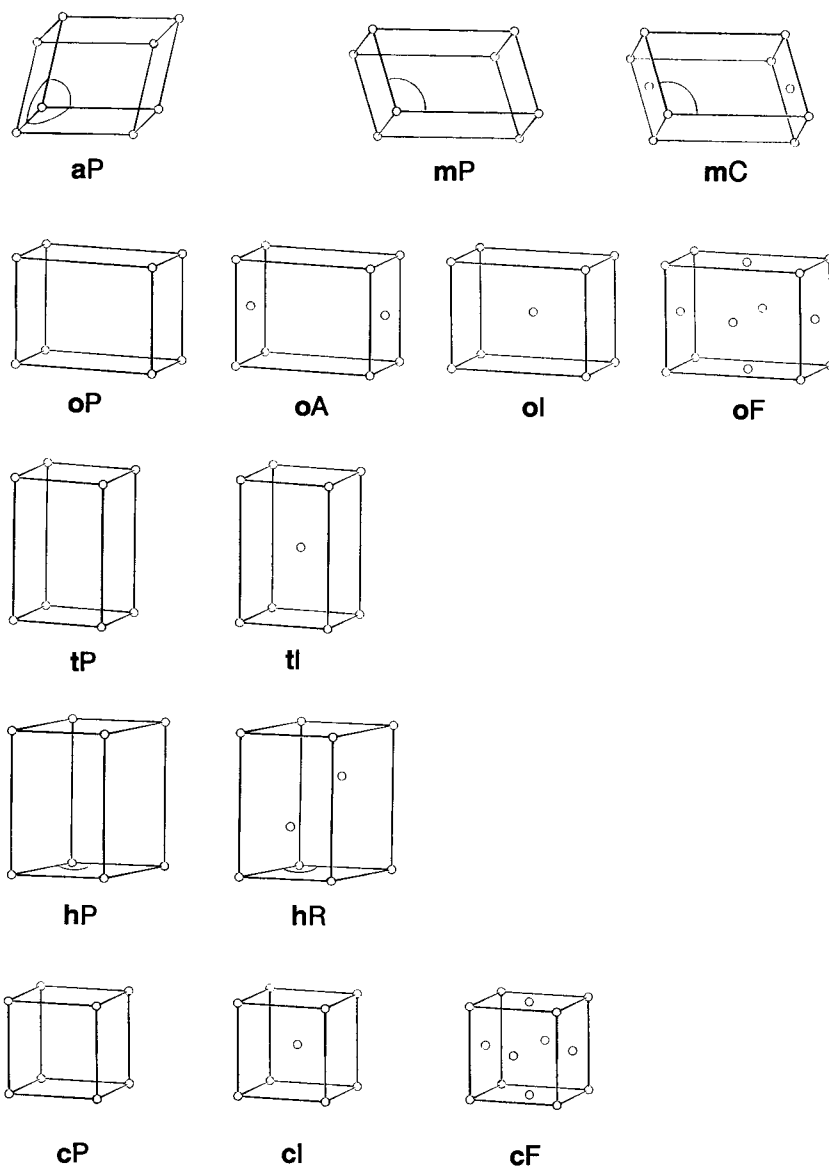


Fig. 2.8. The 14 Bravais lattices (Pearson's nomenclature). **aP** triclinic; **mP** monoclinic primitive; **mC** monoclinic C-centered (may be transformed to **mI**); **oP** orthorhombic primitive; **oA** orthorhombic A-centred (also, with different choice of axes, **oC**); **oI** orthorhombic body-centered; **oF** orthorhombic (all-)face centered; **tP** tetragonal primitive; **tI** tetragonal body-centered; **hP** trigonal or hexagonal primitive; **hR** rhombohedral, hexagonal setting; **cP** cubic primitive; **cI** cubic body-centered; **cF** cubic (all-)face centered.

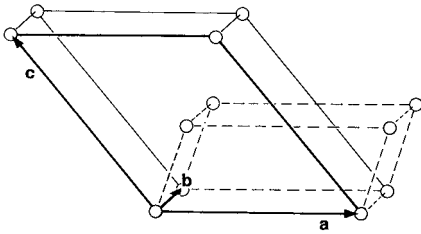


Fig. 2.9. Unnecessary monoclinic *B*-centering; correct *P*-cell outlined with dashes.

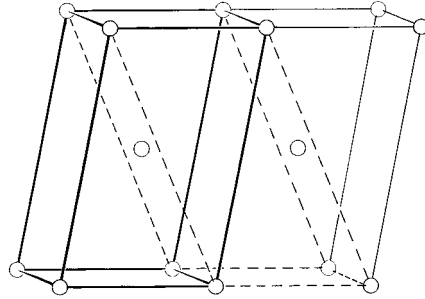


Fig. 2.10. Alternative monoclinic *C*- (dashed) and *I*-centering (full lines). In this case, *I* is preferred. View approximately normal to the *ac*-plane.

metric symmetry of the cell. This is usually expressed in terms of the Niggli-matrix (equation 2.2) which can indicate possible “correct” conventional cells. (International Tables for Crystallography, Vol. A, Chapter 9)¹ [12]

$$\text{Niggli-Matrix: } \begin{pmatrix} a^2 & b^2 & c^2 \\ bc \cos \alpha & ac \cos \beta & ab \cos \gamma \end{pmatrix} \quad (2.2)$$

The reduction of a cell and its subsequent transformation to the conventional cell can be carried out by programs such as LEPAGE [56] or usually using the supplied software of a single-crystal diffractometer. It will indicate the possible Bravais lattices for a crystal. At this point, only the metric symmetry of the crystal can be established. The actual symmetry may be lower, but cannot be higher. How a unit cell is established experimentally will be discussed in chapters 3, 4 and 7.

¹*International Tables of Crystallography* are a key resource for crystallographers. The latest edition currently consists of Volumes A, B, C, E, F (see www.iucr.org/iucr-top/it), from which Vol. A (space group symmetry) and C (mathematical, physical and chemical tables) are most important for practical work.