

Chapter 4

Crystallography

Atoms form bonds which attract them to one another. When you put many atoms together and they form bonds amongst themselves, are there any rules as to how they order themselves? Can we categorize all the possibilities of how the atoms order themselves? If we do, does it help to understand other properties of the materials that are formed?

4.1 The crystalline state

A fundamental property of the crystalline state is that it is possible to have different values of a physical property in different directions. This *anisotropy* can be seen clearly in a gypsum crystal ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, see Figure 4.1 if a face of the crystal is covered with a thin layer of wax and a heated metal tip is applied to it. The melting front of the wax layer will be ellipsoidal rather than circular. This indicates that the thermal conductivity is different in the two directions on the face of the crystal.

If the melting front had been circular, as it would be on a piece of glass, it would imply that the thermal conductivity is the same in all directions, called *isotropy*.

Anisotropy of physical properties is normal in crystals. It is, however, not universal, as there are some crystals whose properties are isotropic. The origin of a crystals anisotropy lies in the internal structure of the crystals. As shown in Figure 4.2, there are three states of matter that can be described.

A gas adapts both the volume and shape of its container and is statistically homogeneous. The gas molecules move rapidly in space and thus have



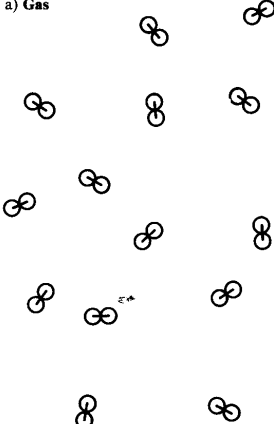
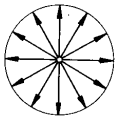
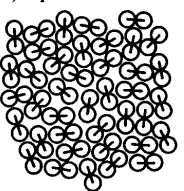
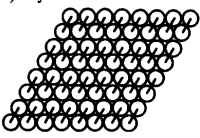
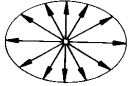
Figure 4.1: A crystal of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

high kinetic energy. The attractive forces between molecules are negligible in comparison to the kinetic energy. As the temperature is lowered, the kinetic energy decreases and at the boiling point the total kinetic energy will be equal to the energy of attraction among the molecules. Further cooling converts the gas into a liquid. The attractive forces cause the molecules to touch. However, they do not maintain fixed positions, so only small regions of order may be found. A liquid will take on the shape of its container, but will maintain a fixed volume. If a large enough volume is considered, the molecular arrangement will be statistically homogeneous.

At a low enough temperature the kinetic energy becomes so small that molecules become permanently attached to each other. A three-dimensional framework of attractive interactions forms among the molecules and the array becomes a solid - it crystallizes. The result of these permanent interactions is that the molecules have become regularly ordered. The distribution of molecules is no longer statistical, but is periodically homogeneous.

All matter tends to crystallize, if the temperature is sufficiently low. However, some materials can not make it into a three-dimensional periodic order rapidly enough as cooling occurs. When this happens a *glassy solid* is generated. Glasses have a higher energy content than the corresponding crystals and can best be considered as a frozen, viscous liquid. They are *amorphous*

or "form-less" bodies. It is possible to distinguish amorphous materials from crystals by studying their melting behavior. A crystal has a sharp melting temperature T_m , while an amorphous material has a temperature range where softening occurs. More directly, it is possible to detect three-dimensional ordering by seeing sharp interference phenomena (diffraction) from the interaction of x-rays with a crystal. Amorphous bodies, as they do not have underlying order, produce no such effect.

Representation of the state	Retention of shape	Retention of volume	Distribution of molecules	Physical properties
a) Gas  Boiling point	No	No	Statistically homogeneous ¹ Isotropic ² 	
b) Liquid  Melting point	Yes	No		
c) Crystal 	Yes	Yes	Periodically homogeneous ¹ Anisotropic ³ 	

¹ Equal physical properties in parallel directions \rightleftarrows
² Equal physical properties in all directions
³ Different physical properties in different directions

Figure 4.2: Schematic representation of the states of matter, (a) gas, (b) liquid, (c) crystal

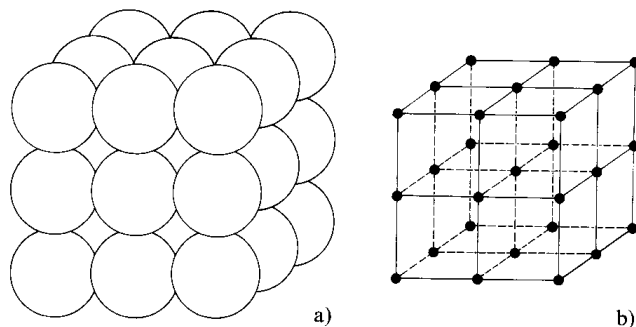


Figure 4.3: (a) The three-dimensional periodic arrangement of the atoms in a crystal of α polonium (b) and the space lattice of the crystal.

4.2 The lattice and its properties

If each atom in α -polonium is replaced by a point put at the center of mass of the atom, what remains is a *point* or *space lattice* (see Figure 4.3). A point or a space lattice is a three-dimensional periodic arrangement of points, and it is a pure mathematical concept. We will develop the concept of a lattice via the line lattice and the plane lattice.

4.2.1 Line and plane lattices

In Figure 4.4 we may consider moving from the point 0 along the vector \vec{a} to the point 1. By a similar movement of $2\vec{a}$, we will reach point 2, etc. By this movement, one point is brought into coincidence with another by using a repetition operation called a *lattice translation*, and a *line lattice* is generated. All points which may be brought into coincidence with one another by a lattice translation are called *identical points*, or *points equivalent by translation*. $|\vec{a}| = a_0$ is called the *lattice parameter*, and this constant alone completely defines the one-dimensional lattice.

If a lattice translation \vec{b} ($\vec{b} \neq \vec{a}$) is then allowed to operate on the line lattice, the result is the *plane lattice* shown in Figure 4.4. The vectors \vec{a} and \vec{b} define a *unit mesh*. The entire plane lattice may now be constructed from the knowledge of three lattice parameters, $|\vec{a}| = a_0$, $|\vec{b}| = b_0$ and γ , the included angle. If any point is moved by an arbitrary lattice translation, it will come into coincidence with another point.

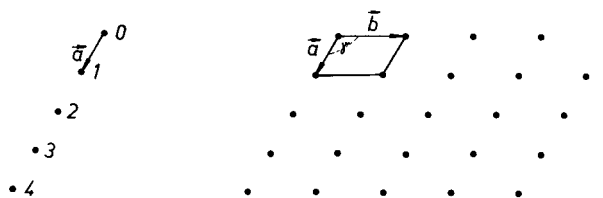


Figure 4.4: Line lattice with its lattice parameter $|\vec{a}| = a_0$, and the plane lattice with the unit mesh defined by the vectors \vec{a} and \vec{b} .

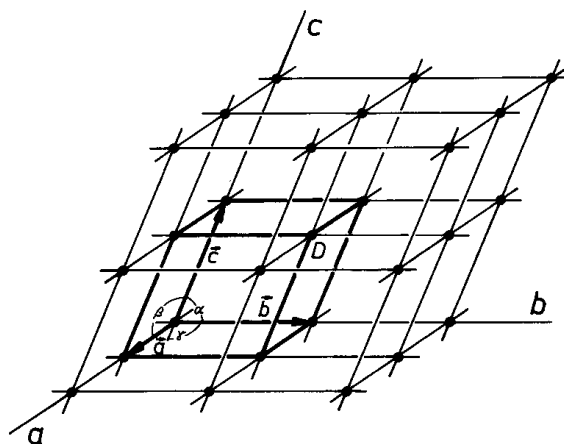


Figure 4.5: Space lattice with the unit cell defined by the vectors \vec{a} , \vec{b} and \vec{c} .

4.2.2 Space lattice

If yet another lattice translation \vec{c} is now introduced in a direction not coplanar with \vec{a} and \vec{b} , its action on the plane lattice generates the space lattice shown in Figure 4.5. According to the arrangement of the vectors \vec{a} , \vec{b} and \vec{c} , we may introduce an *axial system* with the *crystallographic axes* a , b , and c , normally chosen to be right-handed.

The vectors \vec{a} , \vec{b} and \vec{c} define a *unit cell*, which may be alternatively described by six lattice parameters: $|\vec{a}| = a_0$, $|\vec{b}| = b_0$, $|\vec{c}| = c_0$ and interaxial lattice angles α , β , and γ . The application of lattice translations to the unit cell will produce the entire space lattice. The unit cell thus completely defines the entire lattice.

Every unit cell has eight vertices and six faces. At all vertices there is an identical point. Can all of these points be considered part of the unit cell?

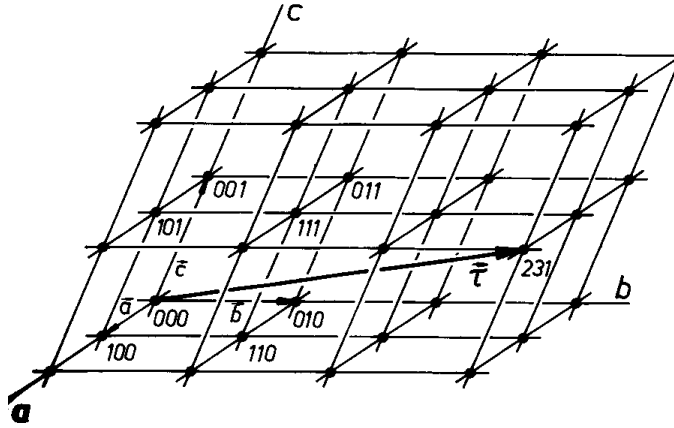


Figure 4.6: Designation of lattice points using the coordinates uvw that define the vector from the origin to the lattice point uvw , $\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}$. Also shown are the coordinates of the vertices of a unit cell.

The lattice point D in Figure 4.5 is not only part of the marked-out unit cell, but part of all eight cells which meet at that point. In other words, only one eighth of it may be attributed to the marked unit cell, and since $8 \times \frac{1}{8} = 1$, the unit cell contains only one lattice point. Such unit cells are called simple or *primitive*, and are given the symbol P.

4.3 Designations of points, lines and planes

4.3.1 The lattice point uvw

Every lattice point is uniquely defined with respect to the origin of the lattice by the vector $\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}$. The lengths of \vec{a} , \vec{b} and \vec{c} are simply the lattice parameters, so only the coordinates u , v and w need to be specified, and are normally written as a triples uvw . In Figure 4.6, the vector \vec{r} describes the point 231. The coordinates u , v and w normally are integers. When they have integral values, the points uvw are the coordinates of the points of a P-lattice.

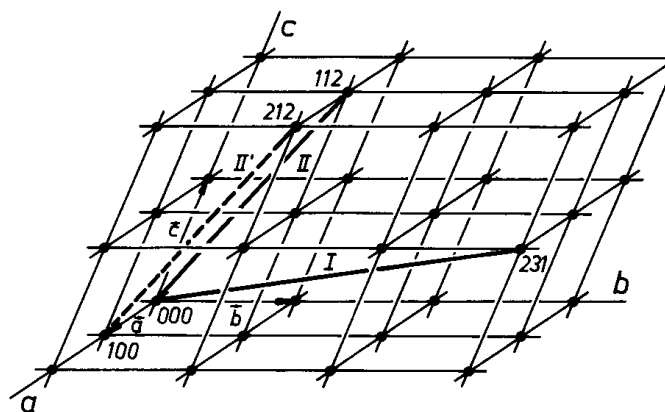


Figure 4.7: Designation of lattice lines using the coordinates $[uvw]$ that define the vector from the origin to the given point $\vec{r} = u\vec{a} + v\vec{b} + w\vec{c}$. ($I : [231]$, $II : [112]$)

4.3.2 Lattice lines $[uvw]$

A line may be specified mathematically in any coordinate system by two points. The lattice line I in Figure 4.7 contains the points 000 and 231. Since the lattice line passes through the origin, the other point on its own describes the direction of the line in the lattice, and the coordinates of this point thus define the line. for this purpose, they are placed in square brackets $[231]$, or in general $[uvw]$, to show that they represent the direction of a line.

The lattice line II' passes through the points 100 and 212. Line II is parallel to this line, and passes through the origin as well as the point 112 and consequently both lines may be referred to by the symbol $[112]$.

Figure 4.8 shows a projection of a space lattice along c onto the a, b -plane. The lattice line A intersects the points with coordinates 000, 210, 420, $\bar{2}\bar{1}0$. Note that minus signs are placed above the numbers to which they apply – this applies to all crystallographic triples. Each point on the line has different values of uvw , but the ratio $u : v : w$ remains constant. In this case, the smallest triple is used to define the lattice line. Lines parallel to \vec{a} or \vec{b} are thus identified as $[001]$ or $[010]$ respectively.

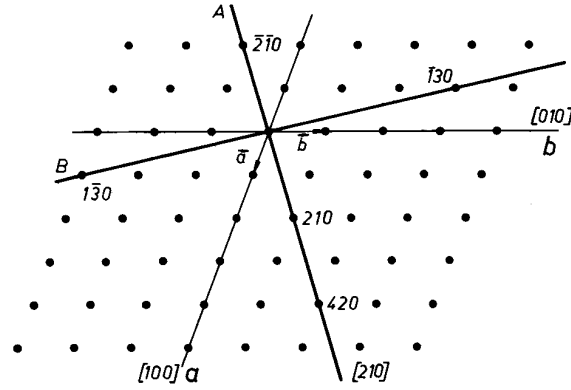


Figure 4.8: Projection of a space lattice along c onto the a , b -plane. The lattice line A is defined by the triple $[210]$, while B may be given as $[\bar{1}30]$ or $[1\bar{3}0]$.

4.3.3 Lattice planes (hkl)

Consider a plane in the lattice intersecting the axes a , b and c at the points $m00$, $0n0$ and $00p$. The coordinates of the three intercepts completely define the position of a lattice plane, see Figure 4.9. Normally, however, the reciprocals of these coordinates are used rather than the coordinates themselves to designate the plan: a -axis: $h = \frac{1}{m}$, b -axis: $k = \frac{1}{n}$, c -axis: $l = \frac{1}{p}$. The smallest integral values are chosen for the reciprocal intercepts, they are written as a triple (hkl) in round brackets, and called *Miller indices*. The lattice plane show in Figure 4.9 has the intercepts $m|n|p = 2|1|3$ the reciprocals of these are $\frac{1}{2}|\frac{1}{1}|\frac{1}{3}$, leading to Miller indices (362) . Note that the direction normal to the (362) plane is $[213]$, and that the designation (362) represents an infinite set of parallel planes.

Two lattice planes (h_1, k_1, l_1) and (h_2, k_2, l_2) intersect in a line $[uvw]$ (see Figure 4.10), which can be identified by the solution of the equations:

$$\begin{aligned} h_1u + k_1v + l_1w &= 0 \\ h_2u + k_2v + l_2w &= 0 \end{aligned}$$

There are two solutions, $[uvw]$ and $[\bar{u}\bar{v}\bar{w}]$. They represent the opposite directions of the same line. In this context $[uvw]$ is called a *zone axis*.

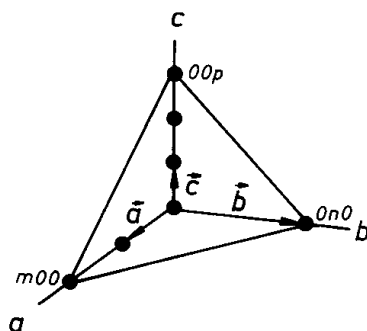


Figure 4.9: The intercepts on the axes of a lattice plane with the Miller indices (362).

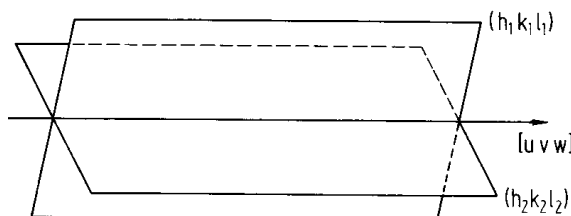


Figure 4.10: The lattice planes (h_1, k_1, l_1) and (h_2, k_2, l_2) intersect in the lattice line $[uvw]$.

4.4 Crystal structure

In order to progress from a lattice to a crystal, the points of the lattice must be occupied by atoms, ions or molecules. Because the points are all identical, the collections of objects occupying them must also be identical. In general, crystals are not built up as simply as the crystal of α -polonium in Figure 4.3.

Let us consider the construction of a crystal by means of a hypothetical example. Figure 4.11a shows a lattice with a rectangular unit cell projected on the a, b -plane. We now place the molecule ABC in the unit cell of the lattice in such a way that A lies at the origin and B and C within the chosen cell (Fig. 4.11b). The position of B or C with respect to the origin may be described by a vector \vec{r} in terms of the lattice translations $\vec{a}, \vec{b}, \vec{c}$:

$$\vec{r} = x\vec{a} + y\vec{b} + z\vec{c} \text{ (See Fig. 4.12)}$$

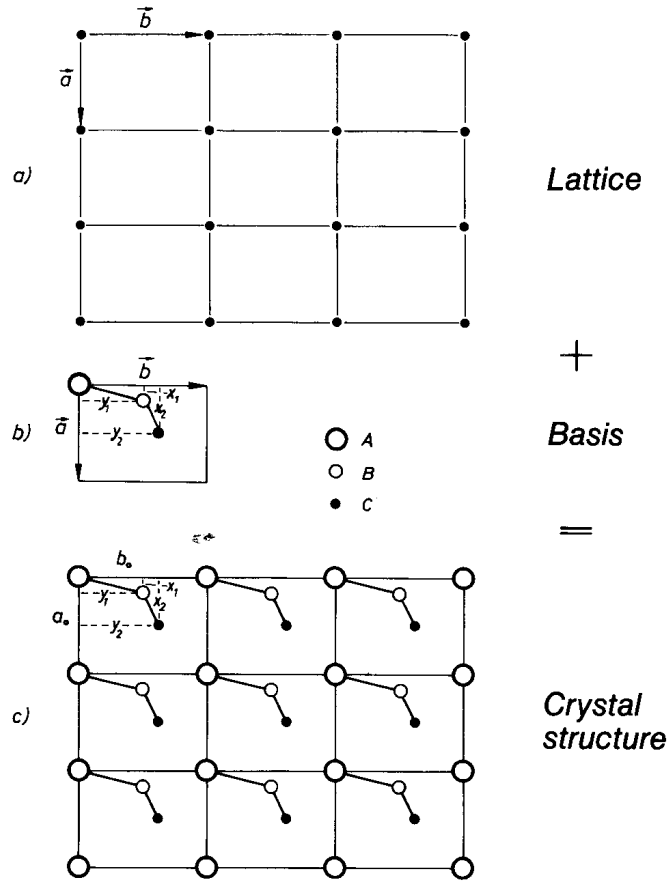


Figure 4.11: Interrelationship of the lattice (a), the basis or the arrangement of atoms in the unit cell (b) and the crystal structure (c), all shown as a projection on the a, b -plane.

The coordinates are yet another triple: x, y, z where $0 \leq x, y, z < 1$ for all positions within the unit cell. In our example, the atoms have the following coordinates: $A=0,0,0$; $B=x_1, y_1, z_1$; $C = x_2, y_2, z_2$. This arrangement of atoms within a unit cell is called a *basis*. Lattice translations reproduce the atoms throughout the entire lattice (Fig. 4.11c), or *lattice + basis = crystal structure*. It follows that not only the A-atoms, but also the B- and C-atoms lie on the points of congruent lattices, which differ from one another by the amount indicated in the basis. Every atom in a crystal structure is repeated throughout the crystal by the same lattice translations.

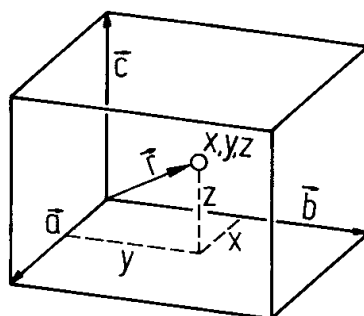


Figure 4.12: Description of a point in a unit cell by the coordinate-triple x, y, z defining the vector $\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$

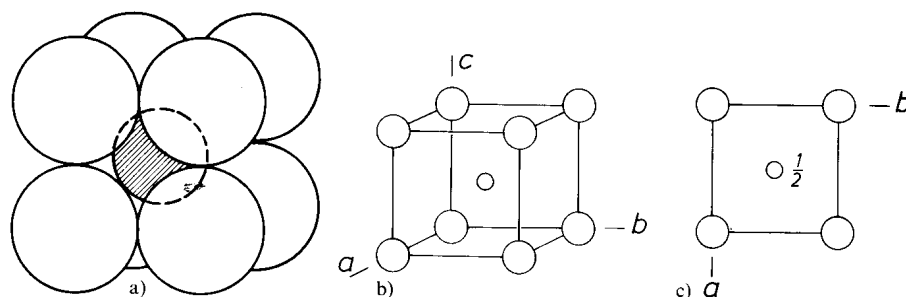


Figure 4.13: (a) The CsI structure shown in a perspective drawing taking account of the relative sizes of the ions, (b) with ions reduced to their centers of gravity and (c) as a parallel projection on the (001).

An example of a simple crystal structure is cesium iodide. The unit cell is a cube ($a_0 = b_0 = c_0 = 4.57\text{\AA}$, $\alpha = \beta = \gamma = 90^\circ$). The basis is $\text{I}^-:0,0,0$; $\text{Cs}^+:\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. In Figure 4.13 a unit cell is shown as a perspective picture with the relative sizes of the ions indicated. For more complex structures, this method of illustration is less useful, as it prevents the positions of atoms from being clearly seen. Consequently, it is more usual merely to indicate the centers of gravity of the atoms, as in Figure 4.13b. Figure 4.13c shows the same structure represented as a parallel projection on one cube face.

An important quantity for any structure is Z , the number of chemical formula units per unit cell. For CsI, $Z = 1$ as there is only one Cs^+ ion and one I^- ion per cell. Using only structural data, it is thus possible to calculate the density of materials.

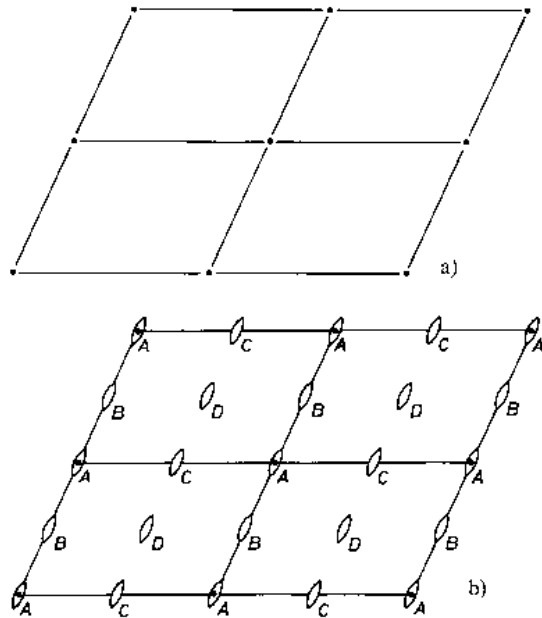


Figure 4.14: A general plane lattice (a) and its symmetry (b). Symmetry elements marked with the same letter are equivalent to one another.

4.5 Principles of symmetry

Up to now, the only repetition operation that we have used formally has been the lattice translation: the operation of three non-coplanar lattice translations on a point which gives rise to the space lattice.

In addition to lattice translations, there are other repetition operations, such as rotations and reflections. In these cases, an object is brought into a coincidence with itself by rotation about an axis or reflection in a plane. When a symmetry operation has a *locus*, that is a point, a line, or a plane that is left unchanged by the operation, this locus is referred to as the *symmetry element*. A mirror plane is the symmetry element of the symmetry operation of reflection, a rotation axis is the symmetry element of the rotation symmetry operation, and the inversion symmetry operation has a point as the symmetry element called the inversion center.

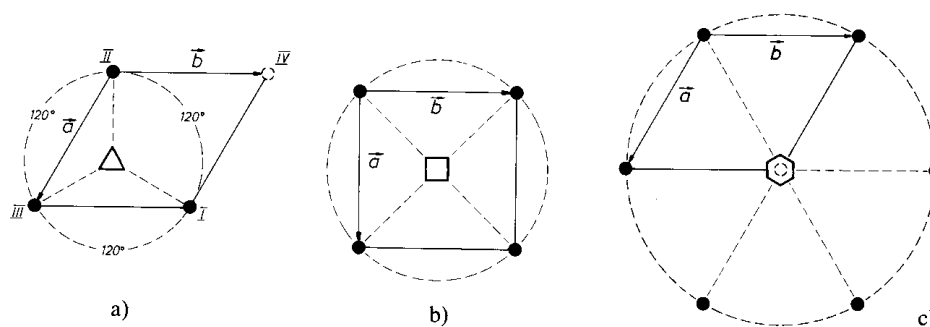


Figure 4.15: The arrays of points resulting from the operation on a point of (a) 3-fold, (b), 4-fold and (c) 6-fold axes normal to the plane of the paper can lead to lattice planes. \circ additional points produced by lattice translations.

4.5.1 Rotation axes

If you take a copy of the general plane lattice shown in Figure 4.14a and rotate the copy until it can lay directly over the original it will require a rotation of 180° . A further rotation of 180° , making a full 360° rotation, returns the copy of the lattice to its original position.

The order of a rotation axis is given by X where $X = \frac{360^\circ}{\epsilon}$, and ϵ is the minimum angle (in degrees) required to reach a position indistinguishable from the starting point. In the above case, $X = \frac{360^\circ}{180} = 2$, and the axis is called a *2-fold rotation axis*. The symbol for this operation is simply the digit 2. In a diagram, it is represented as \blacklozenge if it is normal to the plane of the paper, or as \rightarrow if it is parallel to it.

Whenever a 2-fold axis passes through a point, such as A in Figure 4.14b, a 2-fold axis must pass through all points equivalent by translation to A . 2-fold axes normal to the lattice plane will also pass through all points B , C and D which lie on the midpoint of a translation vector.

Objects are said to be *equivalent* to one another if they can be brought into coincidence by the application of a symmetry operation. If no symmetry operation except lattice translation is involved to bring them into coincidence, the objects are said to be *equivalent by translation* or *identical*. In Figure 4.14b, all rotation axes A are equivalent to one another, as are all axes B , C and D . On the other hand, the axes A are not equivalent to B , and so forth.

[a] *Threefold rotation axis: 3* (graphical symbol \blacktriangle). Figure 4.15a shows a 3-fold rotation axis normal to the plane of the paper. By its operation,

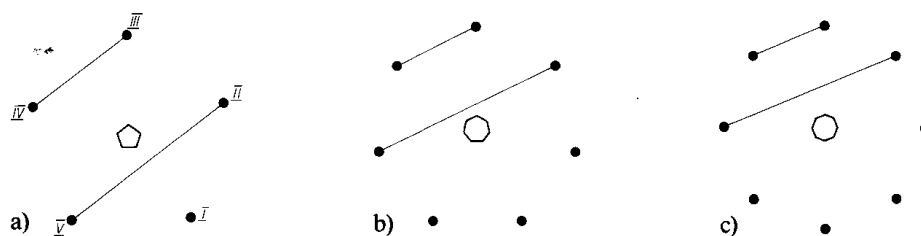


Figure 4.16: The arrays of points resulting from the operation on a point of (a) 5-fold, (b) 7-fold and (c) 8-fold axes do not fulfill the conditions for a lattice plane, in that parallel lines through equivalent points do not have equal spacings. These rotation symmetries cannot occur in lattices.

a rotation of 120° , point I comes into coincidence with point II , and, by a second rotation of 120° with point III . A further rotation of 120° returns it to its original location. A lattice translation moves point I to point IV , and the four points thus generated produce the unit mesh of a lattice plane. Thus, 3-fold axes are compatible with space lattices.

[b] *Fourfold rotation axis; 4* (graphical symbol \blacksquare). Fourfold axes are also compatible with space lattices. As shown in Figure 4.15b, the action of a 4-fold axis on a point results in a square of points which is also the unit mesh of a lattice plane.

[c] *Fivefold rotation axis: 5*. The operation of this axis on a point results in a regular pentagon of points, as shown in Figure 4.16a. The line through points III and IV is parallel to that through II and V . If these are to be lattice lines, the spacings of the two pairs of point must either be equal or have an integral ratio. Since this is clearly not the case, the point in Figure 4.16a do not constitute a lattice plane, and we may conclude that 5-fold axes are impossible in space lattices.

[d] *Sixfold rotation axis: 6* (graphical symbol \bullet). This operation, applied to a single point, results in a regular hexagon (Figure 4.15c). A lattice translation places a lattice point on the axis itself, and the resulting array meets the condition for a lattice plane. Inspection of Figure 4.15a and c will show that the lattices resulting from 6-fold and 3-fold axes are, in fact, equal.

[e] *Rotation axes of order higher than 6*. Figure 4.16b and c shows the effect of attempting to build up a lattice plane by applying 7-fold and 8-fold axes to a point. The results are analogous to those for the 5-fold axis described above. These arrays do not produce equal spacings of points in

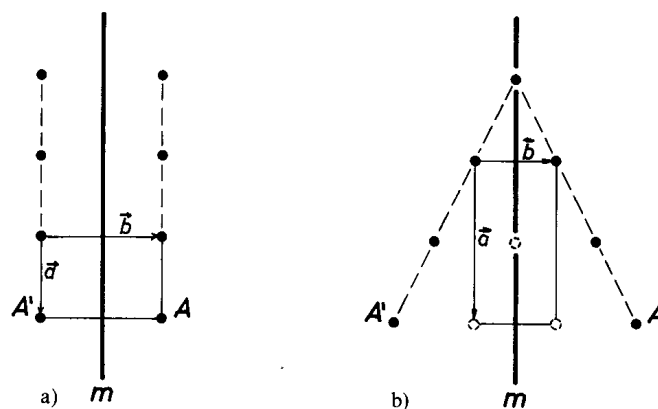


Figure 4.17: Operation of m on a lattice line: in (a) the lattice line is parallel to m . The resultant plane lattice is primitive with a rectangular unit cell. in (b), the lattice line is tilted with respect to m . The resultant plane lattice again has a rectangular unit cell, but is now centered. \circ additional points produced by lattice translations.

parallel lines and so cannot occur in lattices. The same result will occur for any rotation axis with $X > 6$.

In space lattices, and consequently in crystals, only 1-, 2-, 3-, 4- and 6-fold rotation axes can occur.

4.5.2 Mirror planes

The symmetry operation of reflection has a symmetry element called a plane of symmetry or a *mirror plane*. It is given the symbol m and the graphical symbol is a bold line for a plane perpendicular to the paper and a bold angle for a plane parallel to the paper. Any point or object on one side of the mirror plane is matched by the generation of an equivalent point or object on the other side at the same distance from the plane along a line normal to it.

Figure 4.17 shows the operation of a mirror plane on a lattice line A , generating another lattice line A' . Whether the line A is parallel to the mirror plane or not, the result is a rectangular unit mesh. The generation of the lattice plane in Figure 4.17b requires that a lattice point lies on m ; this lattice contains two point per unit mesh and is called centered. A primitive

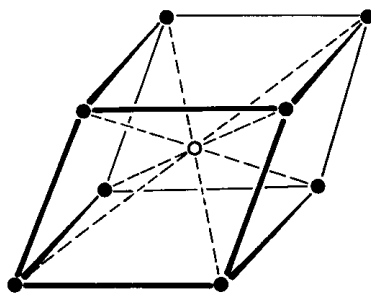


Figure 4.18: The unit cell of a general lattice, showing the inversion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. All lattices are centrosymmetric.

mesh is not chosen in this case since the rectangular cell (with the symmetry plane parallel to the edge) is easier to work with.

4.5.3 The inversion center

The symmetry operation called *inversion* relates pairs of points or objects which are equidistant from and on opposite sides of a central point (called an *inversion center*). The symbol for this operation is $\bar{1}$. Every space lattice has this operation (see Figure 4.18) and is thus *centrosymmetric*.

4.5.4 Compound symmetry operations

A compound symmetry operation is when two symmetry operations are performed in sequence as a single event. This produces a new symmetry operation but the individual operations of which it is composed are lost. Figure 4.19 shows such an operation which consists of a rotation of 90° about an axis followed by an inversion through a point on the axis. Successive applications of this compound operation move a point at 1 to 2,3,4 and back to 1. Note that the resulting array has neither an inversion center nor a 4-fold rotation axis.

Compound symmetry operations are summarized in Figure 4.20, where the names of the symmetry elements corresponding to the symmetry operations are given in round brackets. Neither reflection plus inversion nor translation plus inversion results in a new operation. Glide and screw operations are beyond the needs of the present discussion.

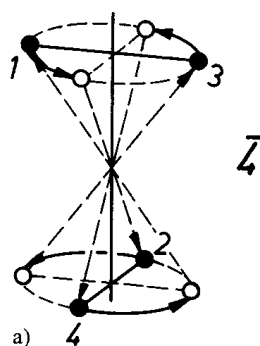


Figure 4.19: The compound symmetry operation of a 4-fold rotation and an inversion. The open circles represent auxiliary points occupied when only one part of the compound operation has been applied.

	Rotation	Reflection	Inversion	Translation
Rotation	×	Roto-reflection	Roto-inversion	Screw rotation
Reflection	(Roto-reflection axis)	×	2-fold rotation	Glide reflection
Inversion	(Roto-inversion axis)	(2-fold rotation axis)	×	Inversion
Translation	(Screw axis)	(Glide plane)	(Inversion centre)	×

Figure 4.20: Compound symmetry operations of simple operations. The corresponding symmetry elements are given in round brackets.

Rotoinversion axes

The compound symmetry operation of rotation and inversion is called *rotoinversion*. Its symmetry elements are the *rotoinversion axes*, with the general symbol \bar{X} . There are only five possible rotation axes $X : 1, 2, 3, 4, 6$, and five corresponding rotoinversion axes $\bar{X} : \bar{1}, \bar{2}, \bar{3}, \bar{4}$, and $\bar{6}$.

$\bar{1}$ implies a rotation of 360° followed by inversion through a point on the 1-fold rotoinversion axis (See Figure 4.21a). This operation is identical to inversion through an inversion center. For this reason, $\bar{1}$ is used as a symbol for the inversion center. As seen from Figure 4.21b, the operation $\bar{2}$ is identical with m , a mirror plane.

The rotoinversion operation $\bar{3}$ (graphical symbol \blacktriangle) is shown in Figure 4.21c. Successive applications of the operation $\bar{3}$ move a point to altogether six equivalent positions. In this case, both of the simple operations 3 and $\bar{1}$ are necessarily present.

Figure 4.19 shows the rotoinversion axis $\bar{4}$ (graphical symbol \blacksquare). As can be seen, $\bar{4}$ implies the presence of a parallel 2. The rotoinversion axis $\bar{6}$ (graphical symbol \blacklozenge) is shown in Figure 4.21d. There are six equivalent positions and $\bar{6}$ implies the presence of a parallel 3 and a perpendicular m .

Rotoreflexion axes

Like the rotoinversion axes, *rotoreflexion* axes S_1, S_2, S_3, S_4 , and S_6 may be defined. Rotoreflexion implies the compound operation of rotation and reflection in a plane normal to the axis. However, these axes represent nothing new, since it is easy to demonstrate the correspondence $S_1 = m$; $S_2 = \bar{1}$, $S_3 = \bar{6}$, $S_4 = \bar{4}$, and $S_6 = \bar{3}$.

The axes X and \bar{X} , including $\bar{1}$ and m , are called *point-symmetry elements*, since their operations always leave at least one point unmoved. For 1, this property applies to every point in space, for m to every point on the plane, from 2, 3, 4, 6, to every point on the axis, and for $\bar{1}, \bar{3}, \bar{4}, \bar{6}$ to a single point.

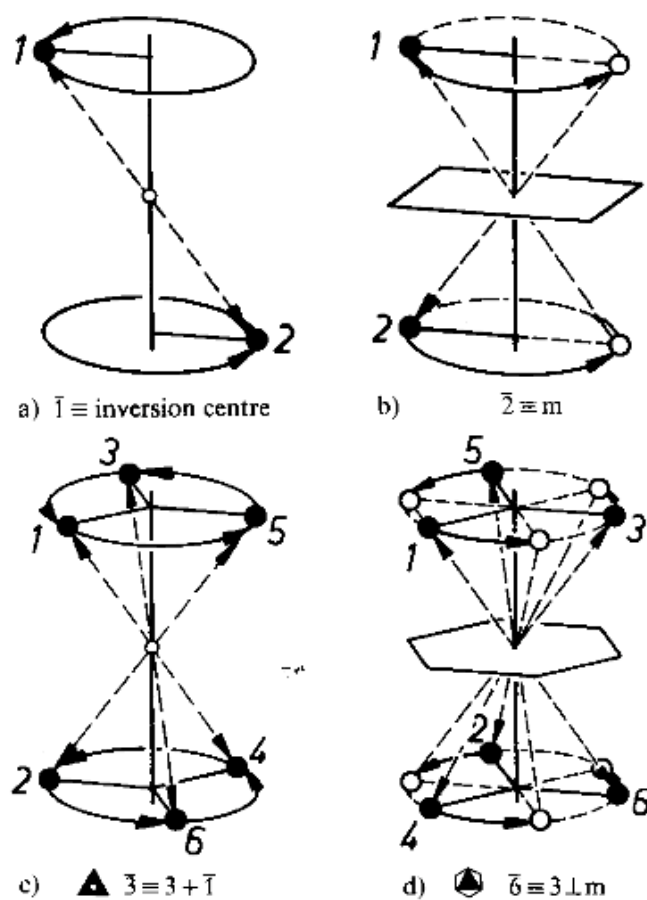


Figure 4.21: The operation of rotoinversion axes on a point 1: (a) $\bar{1}$ (b) $\bar{2} = m$ (c) $\bar{3} = 3 + \bar{1}$, (d) $\bar{6} = 3 \perp m$. For $\bar{4}$ see Fig 4.19. The *unfilled* circles represent auxiliary points which are not occupied when the two operations of which the compound operation is composed are not themselves present.

4.6 The 14 Bravais lattices

The general space lattice, with no restrictions on the shape of the unit cell, may be used to describe all crystals. In most cases, however, the lattices which occur are special in that they have special features, such as unit cell dimensions (lattice parameters) which are equal in two or three directions or angles between cell edges with particular values, such as 60° , 90° or 120° . The general lattice has no point symmetry elements except inversion centers. The presence of rotation axes and mirror planes will restrict the cell parameters in some way, and give special lattices. These special lattices give rise to simplifications in the description of physical properties, and are therefore fundamental in the description and categorization of materials. For instance, when lattice translations in two directions are equivalent, all physical properties are equal in these directions.

Before we consider special space lattices, it is useful to develop the concepts by consideration of general and special plane lattices.

The general (oblique) plane lattice

If we take a point 1, and operate on it with a 2-fold axis, we will generate an equivalent point 2 (Figure 4.22). The application of a lattice translation \vec{a} to point 1 generates an identical point 3, and the 2-fold axis then relates point 3 to point 4. We now have generated a unit mesh of the lattice. It has the shape of an oblique parallelogram, where $a_0 \neq b_0$ and $\gamma \neq 90^\circ$.

It is possible to vary a_0 , b_0 and γ in any way without losing the 2-fold axis. Thus this lattice is the most general plane lattice possible.

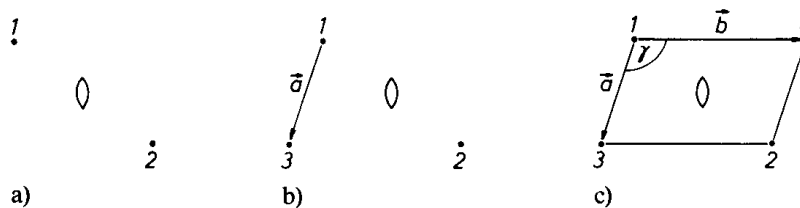


Figure 4.22: Development of the general plane lattice, with an oblique unit mesh.

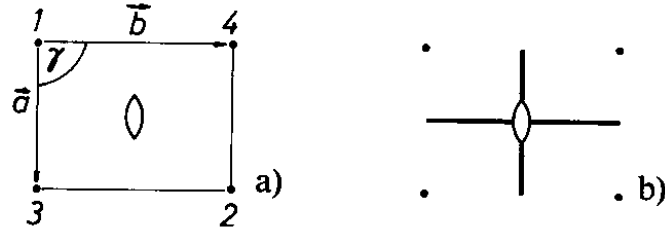


Figure 4.23: (a) Development of the special plane lattice with a rectangular unit mesh and (b) its symmetry.

Special plane lattices

1. Returning to Figure 4.22, point 3 could have been chosen so that the point 1, 2 and 3 described a right triangle, with the right angle at point 3 (see Figure 4.23). The operation of the 2-fold axis now results in a rectangular unit mesh, $a_0 \neq b_0$, $\gamma = 90^\circ$. The arrangement of the points is now "special", as further symmetry has been introduced, namely two mutually perpendicular mirror planes, parallel to the 2-fold axis.
2. A further possibility in Figure 4.22 would be to choose the location of point 3 so that point 1, 2 and 3 formed an isosceles triangle with the two equal edges meeting at point 3. The unit mesh of the resulting lattice is a rhombus: $a_0 = b_0$, $\gamma \neq 60^\circ, 90^\circ \text{ or } 120^\circ$, see Figure 4.24. By extension of the edges 1-4 and 1-3 a further unit translation on the other side of 1, an alternative choice of unit mesh arises. It is rectangular ($a'_0 \neq b'_0$, $\gamma = 90^\circ$), and is called centered because it has a point at its center identical to those at the vertices. Consideration of the symmetry of this cell shows that there are a pair of mirror planes, and several 2-fold axes.
3. Returning once more to figure 4.22, we choose the position of point 3 in such a way as to make the point 1, 2 and 3 describe an isosceles right triangle, with the right angle at 3. The resultant lattice now has a square unit mesh: $a_0 = b_0$, $\gamma = 90^\circ$. As shown in Figure 4.25, there are now a 4-fold axis and four mirror planes parallel to it in the cell.
4. Finally, let us choose the position of point 3 in Figure 4.22 such that the points 1, 2 and 3 make an equilateral triangle (see Figure 4.26). The

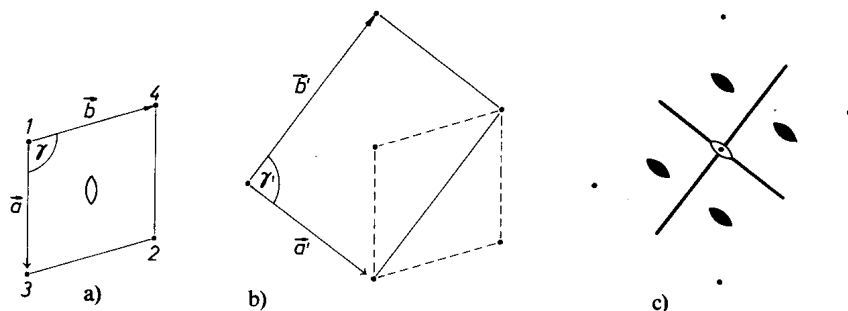


Figure 4.24: (a) Development of the special plane lattice with a rhombic unit mesh, and (b) its alternative description by a centered rectangular mesh. (c) Symmetry of the centered unit mesh.

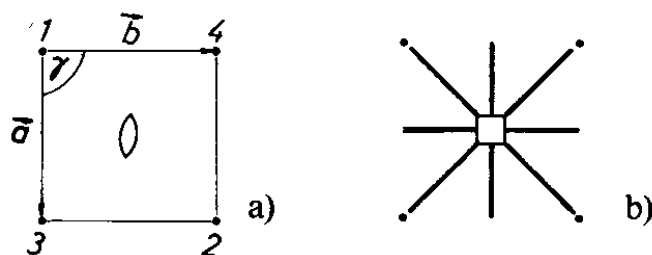


Figure 4.25: (a) Development of the special plane lattice with a square unit mesh, and (b) its symmetry.

unit mesh of the resulting hexagonal lattice is now a 120° rhombus, or $a_0 = b_0$, $\gamma = 120^\circ$. In addition to the 2-fold axis, there is now 3- and 6-fold axes as well as several mirror planes.

We have now developed all four of the possible special lattice planes (which were, in fact, introduced by considering possible rotations axes earlier) from the general plane lattice. These plane lattices are summarized in Figure 4.27 with their characteristic symmetry elements. The general lattice possesses a 2-fold axes only, but the special lattices all have further symmetry elements, which are shown on their diagrams in Figure 4.28a-d. It should be noted that only point symmetry elements are shown here. There are compound symmetry elements involving translation and glide planes (which we will not cover explicitly in this text) that are not shown.

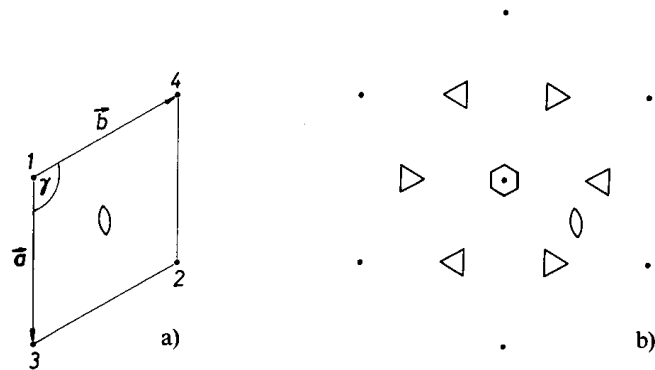


Figure 4.26: (a) Development of the special hexagonal plane lattice, and (b) its symmetry. The unit mesh is a 120° rhombus.

		Shape of unit mesh	Lattice parameters	Characteristic symmetry elements
General plane lattices		Parallelogram	$a_0 \neq b_0$ $\gamma \neq 90^\circ$	2
Special plane lattice	a	Rectangle (primitive)	$a_0 \neq b_0$ $\gamma = 90^\circ$	m
	b	Rectangle (centred)	$a_0 \neq b_0$ $\gamma = 90^\circ$	m
	c	Square	$a_0 = b_0$ $\gamma = 90^\circ$	4
	d	120° Rhombus	$a_0 = b_0$ $\gamma = 120^\circ$	6 (3)

Figure 4.27: Plane lattices

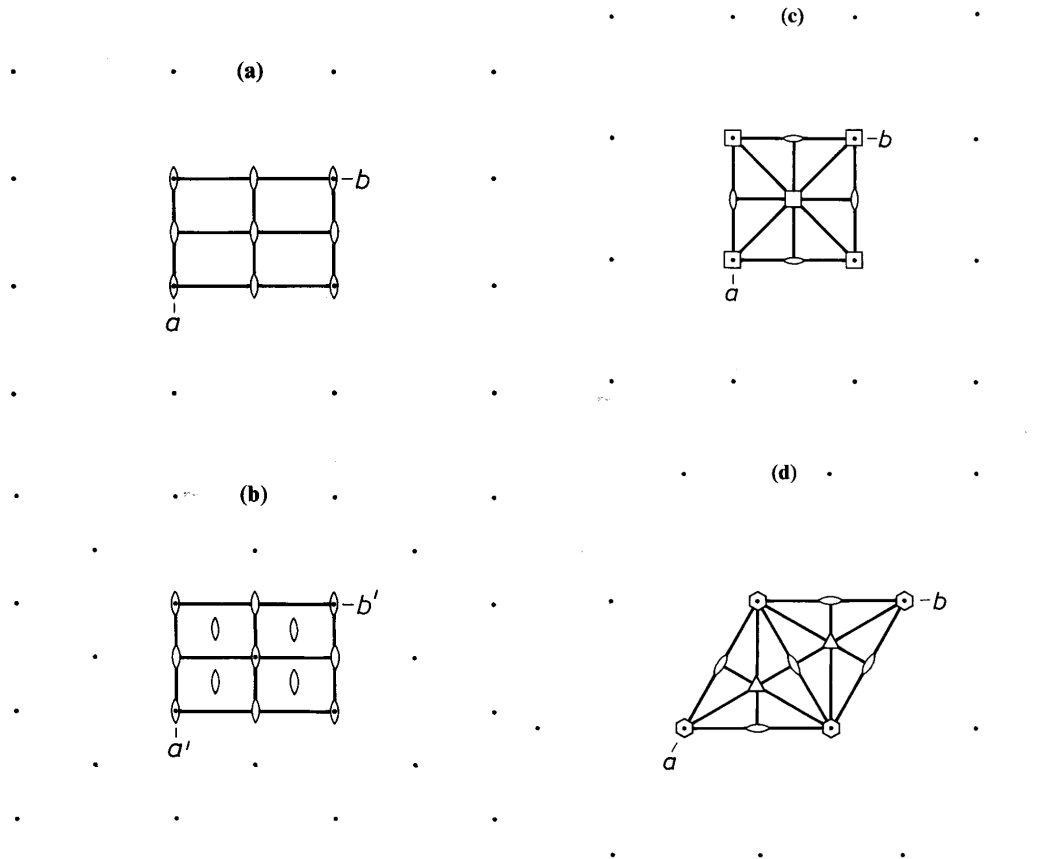


Figure 4.28: Symmetry elements of the special lattice planes with a primitive (a) and centered (b) rectangular unit mesh, and a square (c) and a hexagonal (120° rhombus) (d) unit mesh.

4.6.1 The primitive space lattices (P-lattices)

The relationships between lattices and symmetry elements in three dimensions are similar to those in two. From the general plane lattice, several special space lattices may be derived, in which congruent lattice planes are stacked above one another. If the symmetry of the lattice planes is not changed, the five spaced lattice with primitive unit cells (P-lattices) are produced. These are given in Figure 4.29.

Shape of unit mesh in stacked layers	Interplanar spacing	Lattice
Parallelogram ^a ($a_0 \neq c_0$)	b_0	Monoclinic P
Rectangle ($a_0 \neq b_0$)	c_0	Orthorhombic P
Square ($a_0 = b_0$)	$c_0 \neq (a_0 = b_0)$	Tetragonal P
Square ($a_0 = b_0$)	$c_0 = (a_0 = b_0)$	Cubic P
120°-Rhombus ($a_0 = b_0$)	c_0	Hexagonal P

Figure 4.29: P-lattices

Compare the stacking processes illustrated in Figures 4.30a-b, 4.31a-b, 4.32a-b, 4.33a-b, 4.34a-b. Notice that the centered rectangular plane lattice is not included because we are looking only at primitive lattices at present. The square lattice maybe stacked with either $c_0 \neq a_0 = b_0$ or $c_0 = a_0 = b_0$; the former develops the tetragonal P-lattice, the latter the cubic P-lattice. The cubic lattice is a special case of the tetragonal, since new, characteristic symmetry elements appear (three-fold rotation axes along the body diagonals of the unit cell). The generation of the general or triclinic P-lattice by stacking is shown in Figure 4.35a. All the primitive lattices are illustrated in Figure 4.36.

There is one important point to remember about primitive lattices: $Z=1$. This means there is only one formula unit per unit cell. It also means that this unit cell is the smallest unit cell that can be repeated to fill up space.

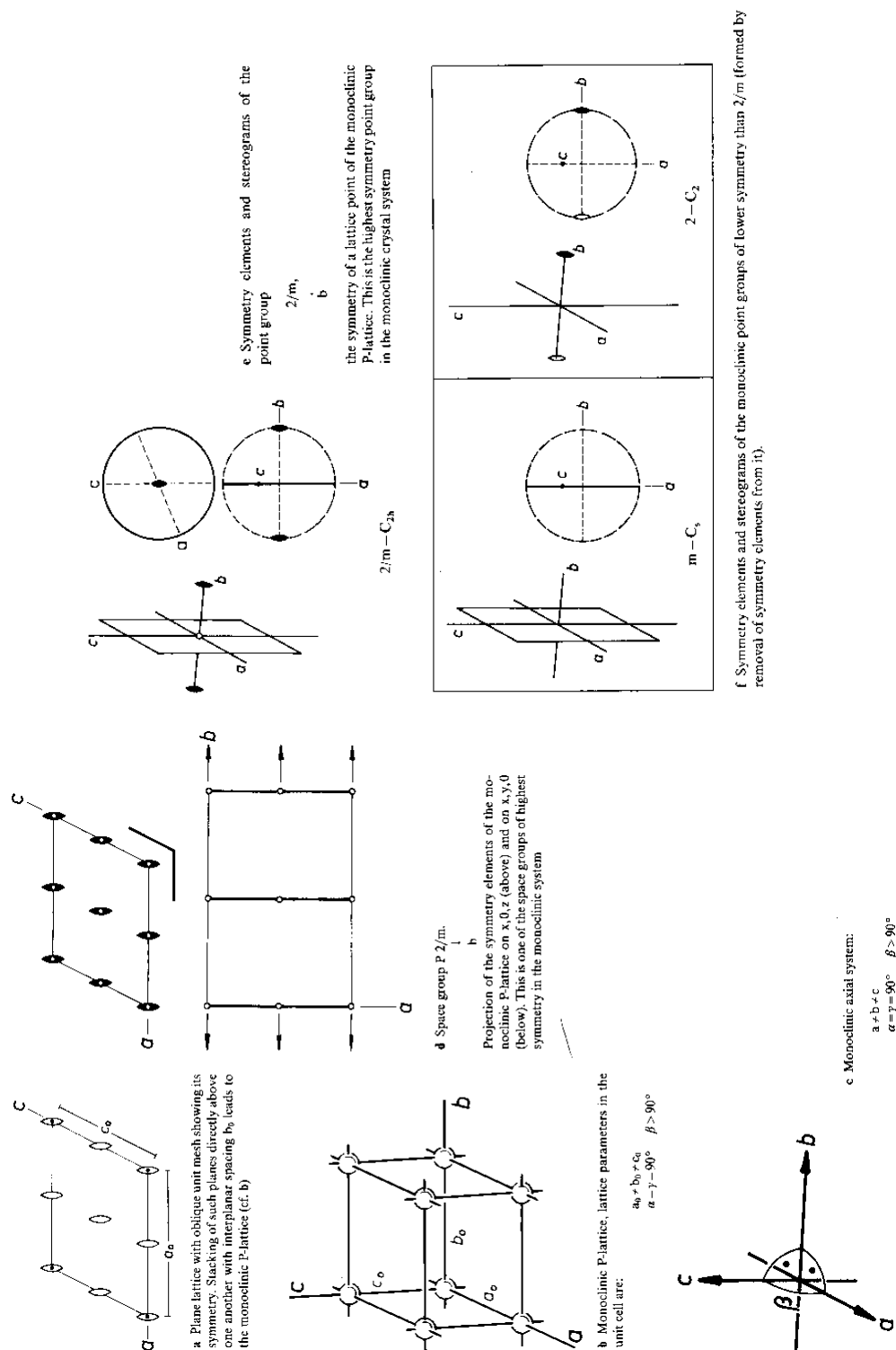


Figure 4.30: Monoclinic crystal system

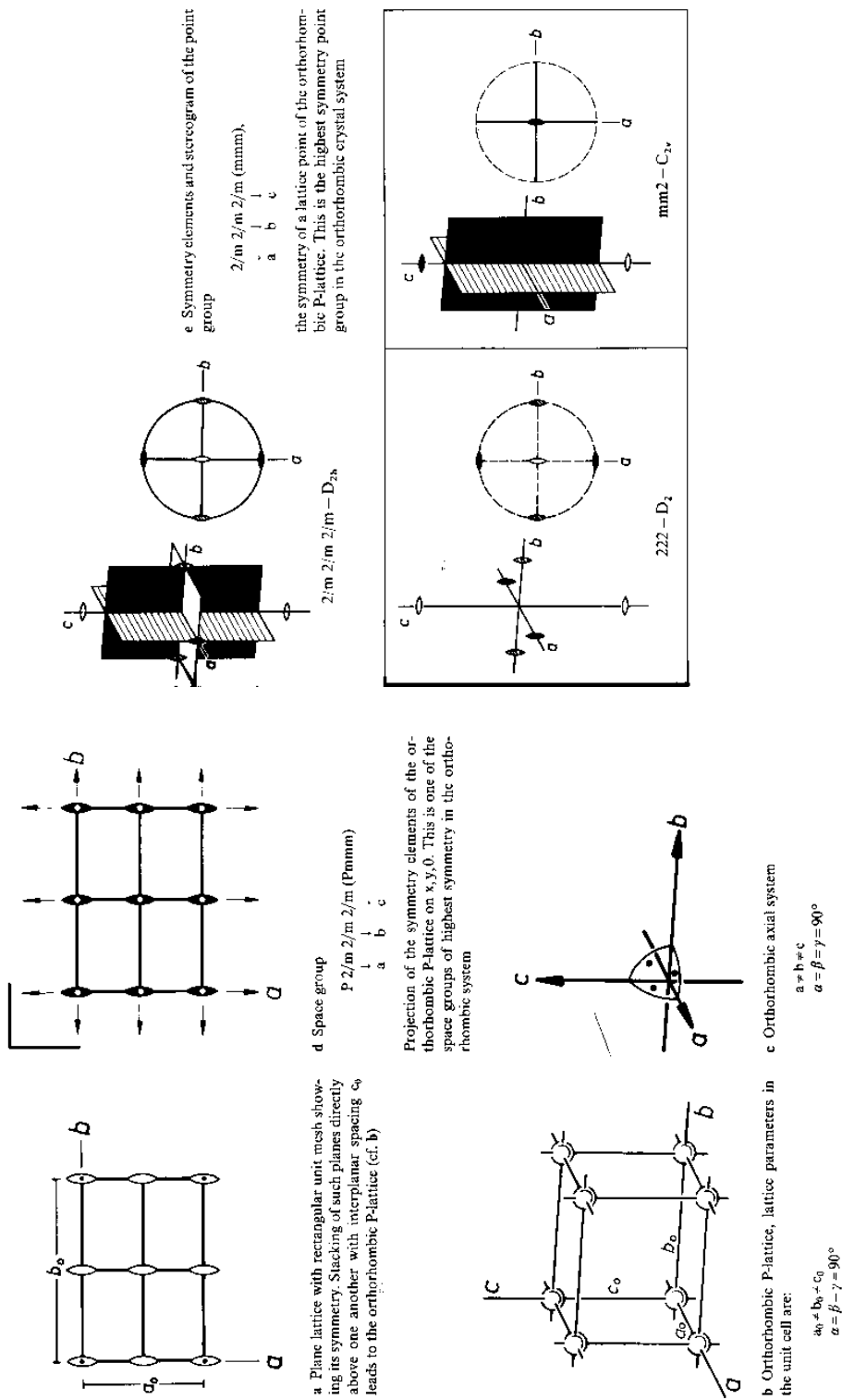


Figure 4.31: Orthogonal crystal system

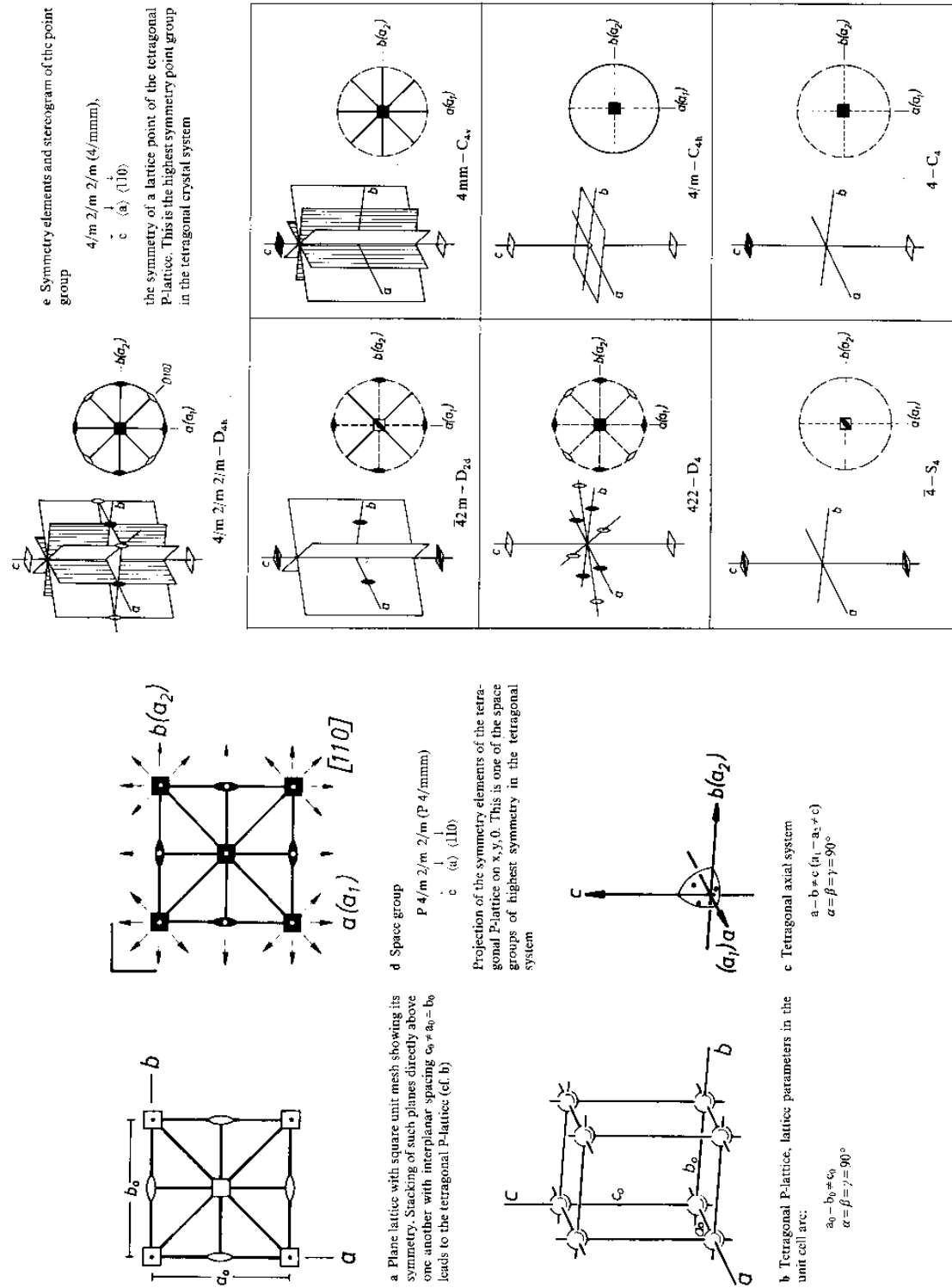


Figure 4.32: Tetragonal crystal system

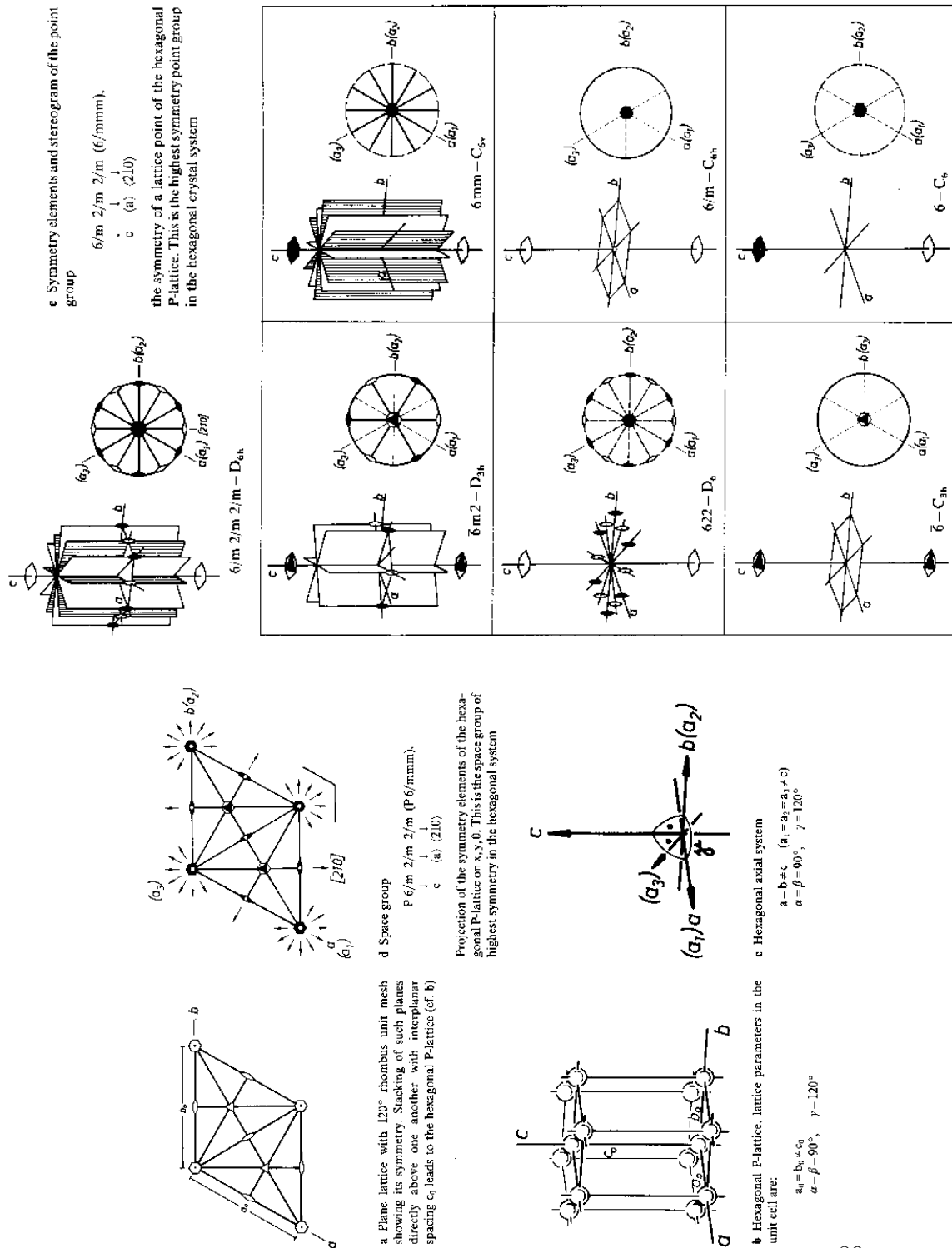


Figure 4.33: Hexagonal crystal system

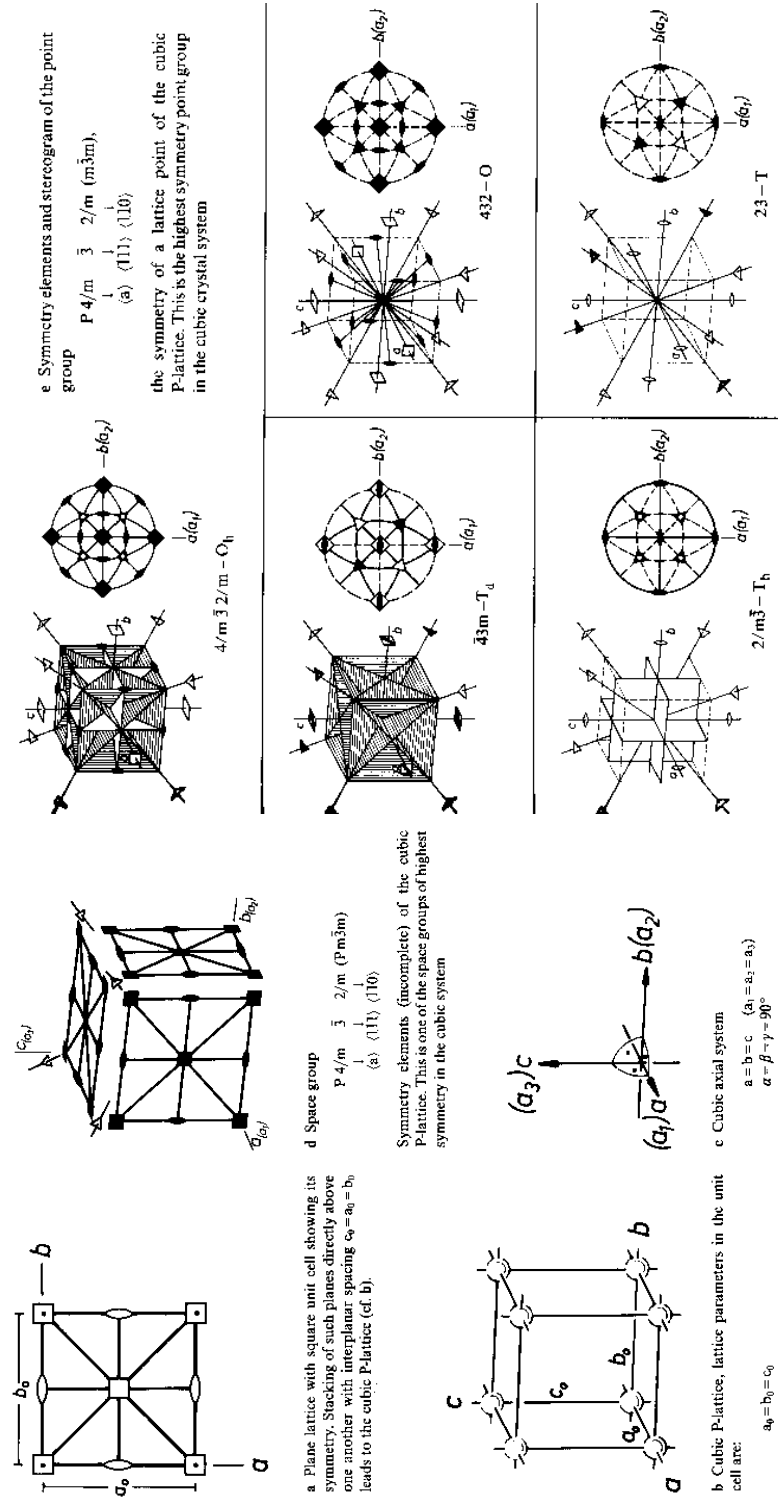


Figure 4.34: Cubic crystal system

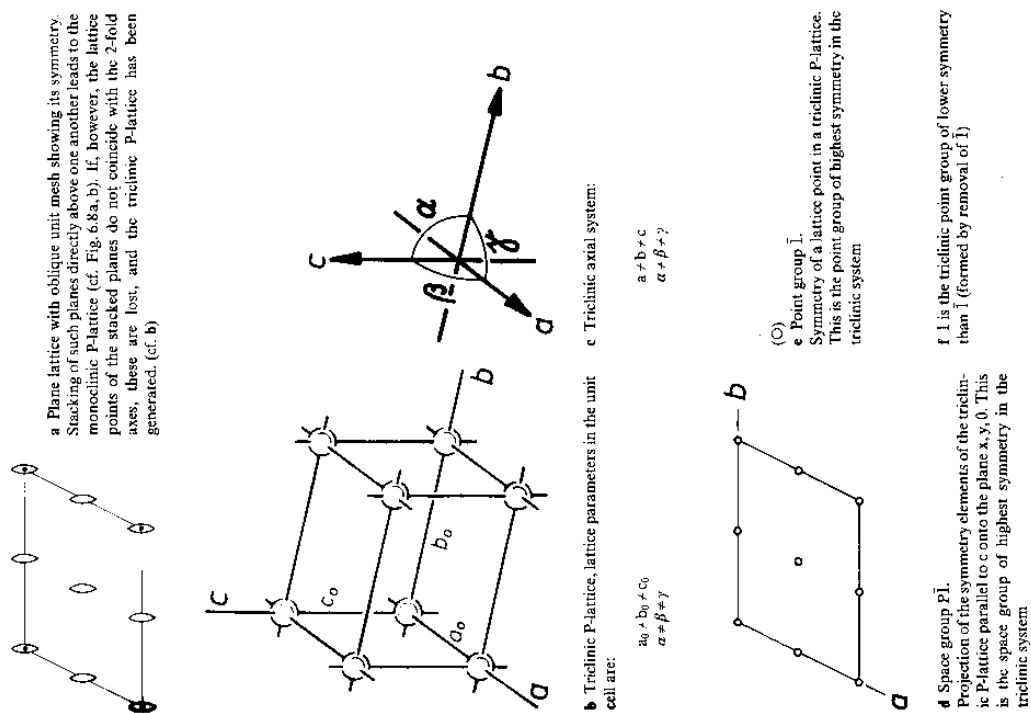


Figure 4.35: Triclinic crystal system

Table 6.3. The 14 Bravais Lattices

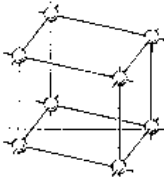

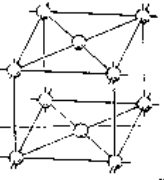
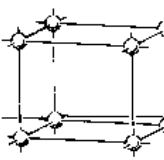
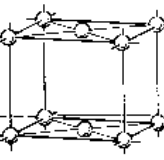
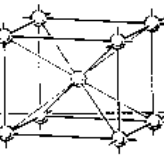
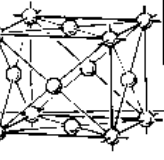
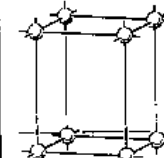
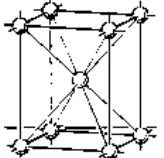
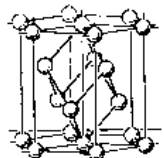
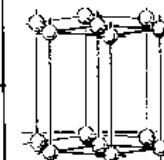
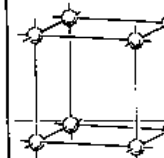
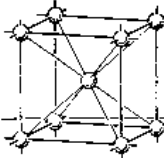
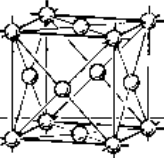
	P	C	I	F
Triclinic				
Monoclinic				
Orthorhombic				
Tetragonal				
Trigonal				
Hexagonal				
Cubic				

Figure 4.36: The 14 Bravais lattices

4.6.2 The symmetry of the Primitive lattices

Before considering the symmetry of the lattices, it is useful to learn two rules governing the generation of a symmetry element by the combination of two others. In the following two rules the presence of any two of the given symmetry elements implies the presence of the third:

Rule 1 *A rotation axis of even order ($X_e = 2, 4$ or 6), a mirror plane normal to X_e , and an inversion centre at the point of intersection of X_e and m (Figure 4.37).*

Rule 2 *Two mutually perpendicular mirror planes and a 2-fold axis along their line of intersection (Figure 4.38).*

Every lattice is centrosymmetric and has inversion centers on the lattice points and midway between any two of them. Thus, in a P-lattice, there are inversion centers at $0,0,0$; $\frac{1}{2},0,0$; $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$ and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$.

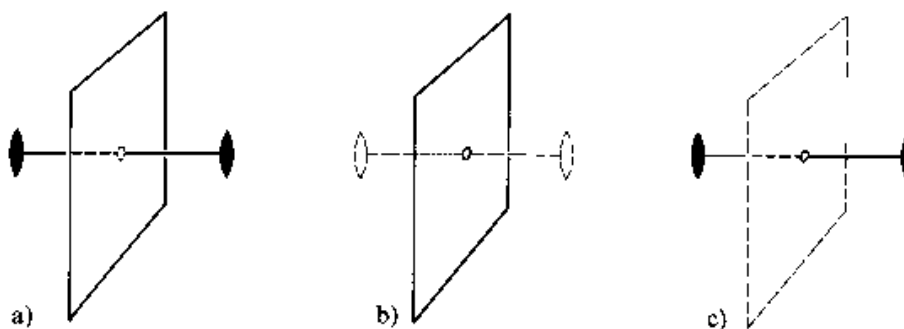


Figure 4.37: Symmetry Rule 1: (a) $2 \perp m \rightarrow \bar{1}$ (at the intersection of 2 and m); (b) $\bar{1}$ on $m \rightarrow 2$ (passing through $\bar{1}$ and normal to m); (c) $\bar{1}$ on 2 $\rightarrow m$ (passing through $\bar{1}$ and normal to 2).

Symmetry of the Triclinic P-Lattice. The only point symmetry elements of the triclinic lattice are inversion centers (Fig. 4.35) at the coordinates given above. A projection of the symmetry elements parallel to c onto $x, y, 0$ is shown in Figure 4.39. The z -coordinates implied for the inversion centers are 0 and $\frac{1}{2}$.

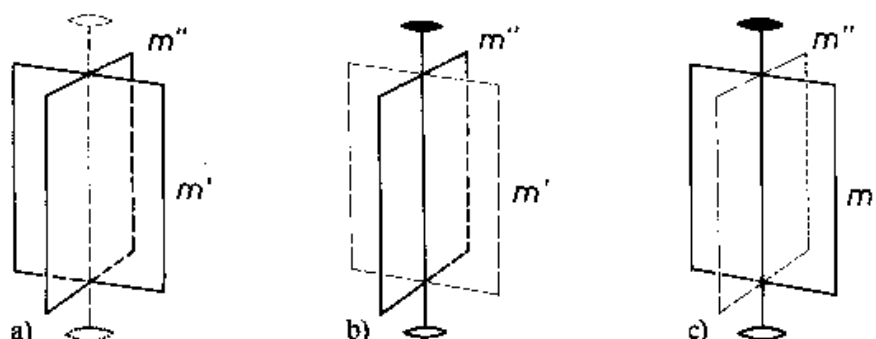


Figure 4.38: Symmetry Rule 2: (a) $m' \perp m'' \rightarrow 2$ (along the intersection of m' and m''); (b) 2 on $m'' \rightarrow m' \perp m''$ (with 2 as the line of intersection); (c) 2 on $m' \rightarrow m'' \perp m'$ (with 2 as the line of intersection).

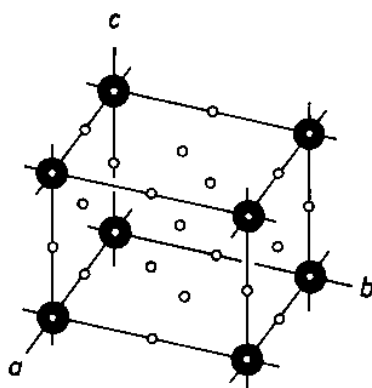


Figure 4.39: Triclinic P-lattice with the symmetry elements of space group $P \bar{1}$

Space Group : The complete set of symmetry operations in a lattice or a crystal structure, or a group of symmetry operations including lattice translations is called a space group

The space group of a primitive lattice which has only $\bar{1}$ is called $P \bar{1}$, and the conditions for its unit cell parameters are $a_0 \neq b_0 \neq c_0$; $\alpha \neq \beta \neq \gamma$.

Symmetry of the Monoclinic P-Lattice. The set of lattice planes from which we generated the monoclinic P-lattice (Fig. 4.30a) contain a set of 2-fold axes parallel to b . In addition, there are mirror planes normal to b

at $x, 0, z$ and $x, \frac{1}{2}, z$ as well as the inversion centers that were present in the triclinic case. The location of the mirror planes follows from our first rule: (2 and $\bar{1}$ generate $m \perp 2$ at $\bar{1}$.) The array of symmetry elements of the lattice is shown in Figure 4.30d in projections on the $x, 0, z$ and $x, y, 0$.¹ Since the 2 is normal to the m , this combination is given the symbol $2/m$, pronounced, "two over m ". It is not necessary to represent the inversion center, since $2/m$ implies $\bar{1}$, by Rule 1.

The space group of the monoclinic P-lattice is $P\ 2/m$, where it is conventional to choose the b -axis parallel to 2 and normal to m . The b -axis is called the *symmetry direction*.

Symmetry of the Orthorhombic P-Lattice. In addition to the symmetry of the stacked planes (Fig. 4.31a), the orthorhombic P-lattice (Fig. 4.31b) has mirror planes normal to c at $x, y, 0$ and $x, y, \frac{1}{2}$ and inversion centers (Fig. 4.31d). Further, the application of rule 1 ($m + \bar{1} \rightarrow 2 \perp m$) or rule 2 ($m \perp m \rightarrow 2$) generates 2-fold axes at $x, 0, 0$; $x, 0, \frac{1}{2}$; $x, \frac{1}{2}, 0$; $x, \frac{1}{2}, \frac{1}{2}$; $0, y, 0$; $0, y, \frac{1}{2}$; $\frac{1}{2}, y, 0$ and $\frac{1}{2}, y, \frac{1}{2}$.

This set of symmetry elements can be given a symbol. The symmetry elements are arranged in the order of the crystallographic axes: a, b, c . Each axis has a 2-fold rotation axis parallel to it and mirror planes normal to it. Thus, the symbol for this space group is: $P\ 2/m\ 2/m\ 2/m$, where the first symmetry element goes with axis a , the second with b and the third with c . The a, b and c axes are all called *symmetry directions*. Figure 4.40 gives a projection of all point symmetry elements of space group $P\ 2/m\ 2/m\ 2/m$, and separate projections showing those elements related to the symmetry directions a, b and c .

Symmetry of the Tetragonal P-Lattice. In addition to the symmetry of the stacked planes (Fig. 4.32a), the tetragonal P-lattice (Fig. 4.32b) has mirror planes $\perp c$ at $x, y, 0$ and $x, y, \frac{1}{2}$ and inversion centers (Fig. 4.32d). Further, the application of Rule 1 ($m + \bar{1} \rightarrow 2 \perp m$) or rule 2 ($m \perp m \rightarrow 2$) generates several 2-fold axes. It should be noted in passing that the projection of the symmetry elements for this space group in Figure 4.32d is incomplete, since there are also glide planes present. The same holds true for Figures 4.33, 4.34, which in addition contain screw axes. These symmetry elements are essentially irrelevant to our present purpose, and will not be considered further.

¹need to add footnote about the L shaped object in the figure that indicates a mirror plane in the plane of the page.

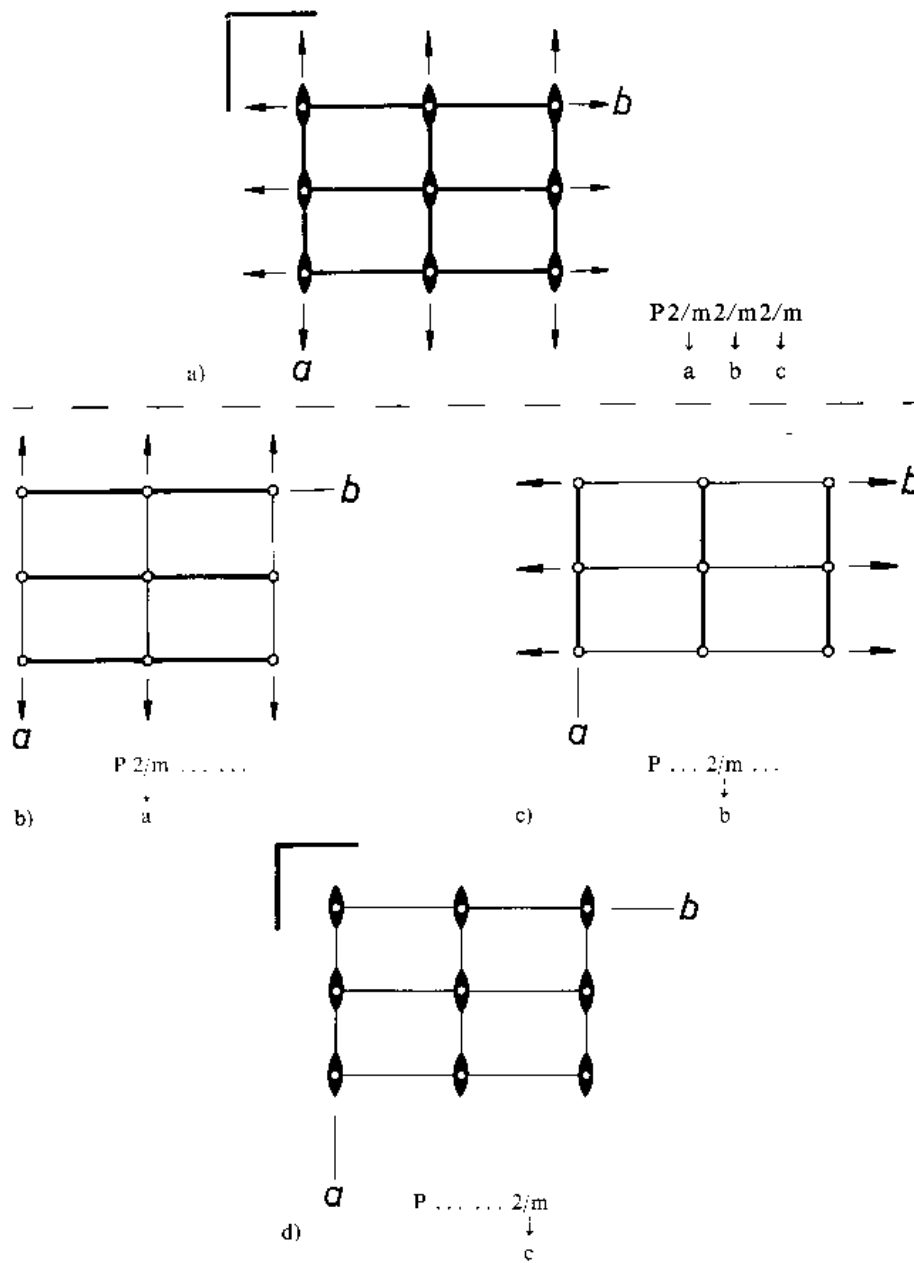


Figure 4.40: (a) Space group $P 2/m 2/m 2/m$. In the other diagrams, only the symmetry elements corresponding to the symmetry direction a, b, c are shown.

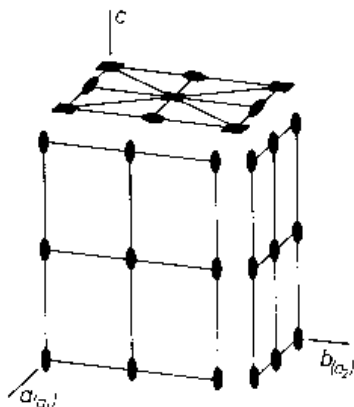


Figure 4.41: Symmetry elements of the space group $P 4/m 2/m 2/m$. The 2 along $\langle 110 \rangle$ and the inversion centers are not shown.

The unit cell of a tetragonal P-lattice has the shape of a tetragonal prism; it is bounded by two lattice planes with square unit meshes and four planes with rectangular meshes, the symmetries of which are shown in Figure 4.41.

The 4-fold axes have the effect of making a and b equivalent, and they are often denoted as a_1 and a_2 , as in Fig. 4.32d. Similarly, the direction $[110]$ and $[1\bar{1}0]$ are equivalent to one another. We must now introduce a further type of brackets, pointed brackets $\langle \rangle$. The symbol $\langle uvw \rangle$ denotes the lattice direction $[uvw]$ and all directions equivalent to it. Similarly, $\langle a \rangle$ denotes the a -axis and all equivalent axes. For the tetragonal lattice, $\langle 110 \rangle$ implies both $[110]$ and $[1\bar{1}0]$ directions, and $\langle a \rangle$ implies both the a - and b -axes.

In the space group symbol, the symmetry elements are given in the order; c , $\langle a \rangle$, diagonal of the $\langle a \rangle$ -axis (i.e. $\langle 110 \rangle$), all of which are called *symmetry directions*. Thus, equivalent symmetry operations are given only once. The space group symbol is thus $P 4/m 2/m 2/m$. Figure 4.42 gives a projection of all point symmetry elements of space group $P 4/m 2/m 2/m$, and separate projections showing those elements related to the symmetry directions c , $\langle a \rangle$ and $\langle 110 \rangle$.

Symmetry of the Hexagonal P-Lattice. In addition to the symmetry of the stacked planes, the hexagonal P-lattice, like the orthorhombic and tetragonal lattices, has mirror planes $\perp c$ at $x, y, 0$ and $x, y, \frac{1}{2}$, and inversion centers (Fig. 4.33d), so the application of Rule 1 ($m + \bar{1} \rightarrow 2 \perp m$) or rule 2 ($m \perp m \rightarrow 2$)

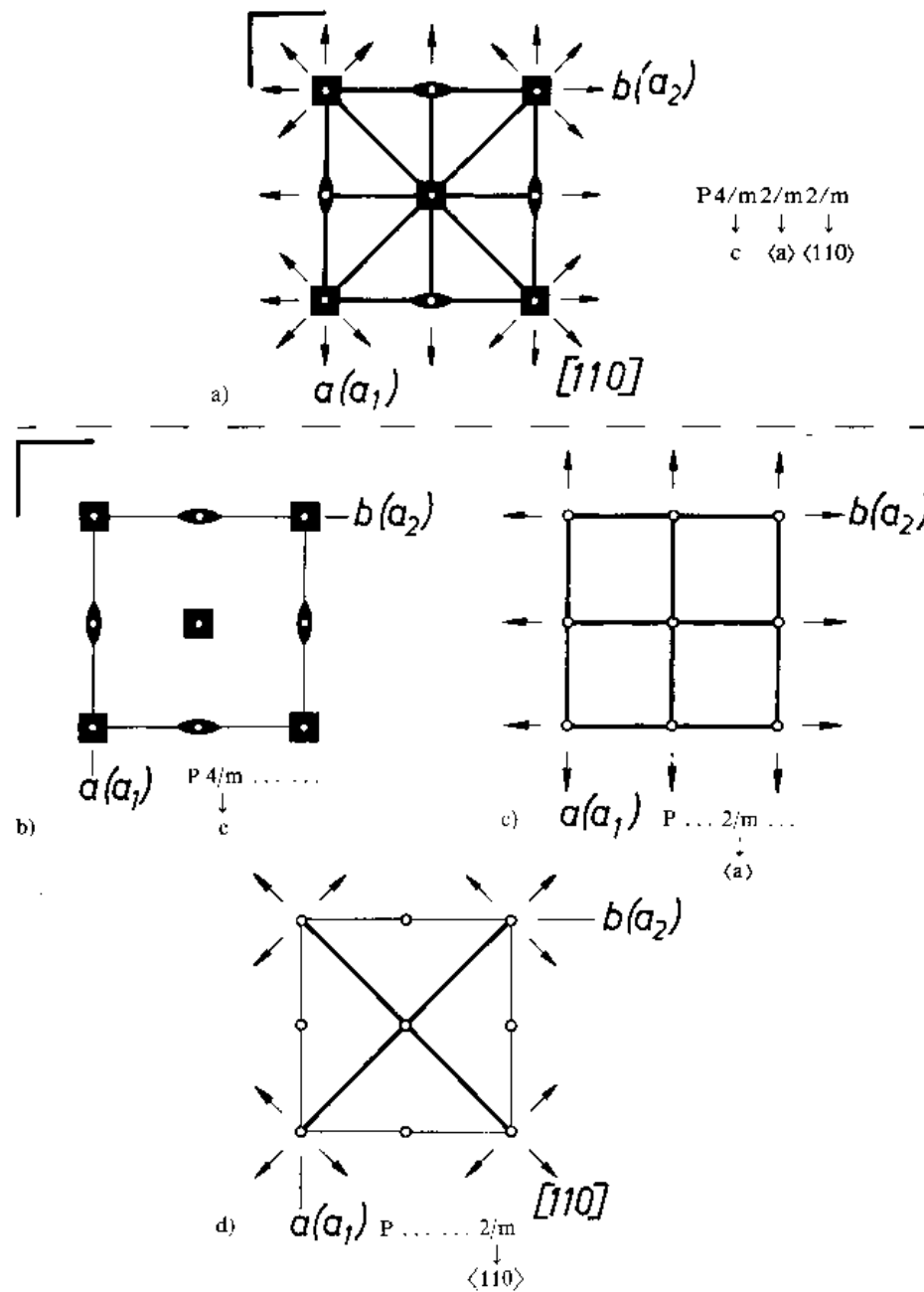


Figure 4.42: (a) Space group $P 4/m 2/m 2/m$. In the other diagrams, only the symmetry elements corresponding to the symmetry direction $\langle a \rangle$, $\langle a \rangle$, $\langle 110 \rangle$ are shown.

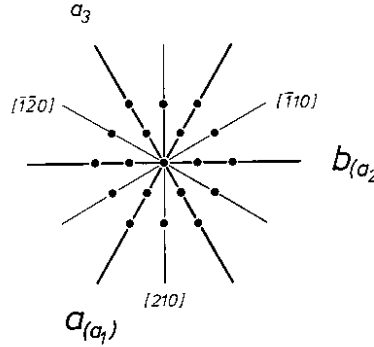


Figure 4.43: Hexagonal P-lattice projected along (001) emphasizing the symmetry directions $\langle a \rangle = a_1, a_2, a_3$ and $\langle 210 \rangle = [210], [\bar{1}, 1, 0]$ and $[\bar{1}\bar{2}0]$

generates several 2-fold axes.

Figure 4.43 shows the projection of a hexagonal P-lattice on (001). The 6-fold axis makes $a = b$ and a and b may also be written as a_1 and a_2 . Another direction, called the a_3 -axis, may then be added, making an angle of 120° with a_1 and a_2 , and equivalent to both of them. Thus, $\langle a \rangle$ now represents a_1, a_2, a_3 . The diagonals bisecting the $\langle a \rangle$ -axes are $[210]$, $[\bar{1}\bar{2}0]$ and $[\bar{1}10]$. As for the tetragonal lattice, the symmetry elements are arranged in the space group symbol in the order: c , $\langle a \rangle$, diagonal of the $\langle a \rangle$ -axis (i.e. $\langle 210 \rangle$), all of which are called *symmetry directions*.

The space group symbol is thus: $P 6/m 2/m 2/m$. Figure 4.44 gives a projection of all the point-symmetry elements of space group $P 6/m 2/m 2/m$, and separate diagrams showing those elements related to the symmetry directions c , $\langle a \rangle$ and $\langle 210 \rangle$.

Symmetry of the Cubic P-Lattice. The symmetry of the stacking planes is shown in Fig. 4.34a. The stacking results in a lattice with a cubic unit cell ($a_0 = b_0 = c_0$). This means that the lattice planes $0, y, z$ and $x, 0, z$ have the same symmetry as $x, y, 0$, see Fig. 4.34d. This equivalence of the planes generates four 3-fold axes along the body diagonals of the unit cell as well as inversion centers, so these axes are represented as $\bar{3}(\rightarrow 3 + \bar{1})$. Application of Rule 1 ($m + \bar{1} \rightarrow 2 \perp m$) or rule 2 ($m \perp m \rightarrow 2$) generates 2-fold axes parallel to $[110]$ and equivalent directions. (These 2-fold axes are not included in Fig 4.34d).

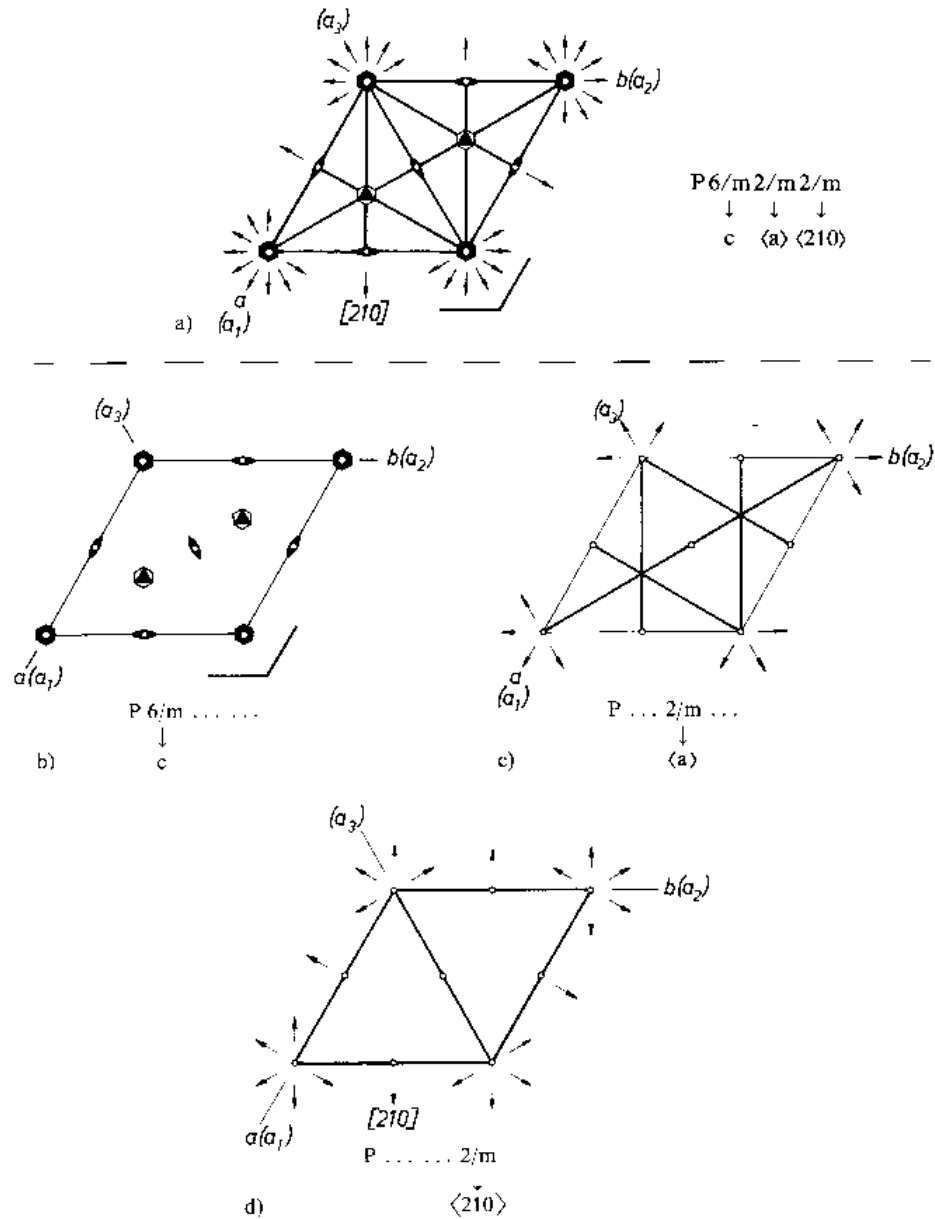


Figure 4.44: (a) Space group $P 6/m 2/m 2/m$. In the other diagrams, only the symmetry elements corresponding to the symmetry direction c , $\langle a \rangle$, $\langle 210 \rangle$ are shown.

In the space group symbol, the symmetry elements are given in the order: $\langle a \rangle$, $\langle 111 \rangle$ = body diagonals of the unit cell, $\langle 110 \rangle$ = face diagonals of the unit cell. The space group symbol for the cubic P-lattice is thus: $P 4/m \bar{3} 2/m$. Figure 4.45 gives a projection of all the point-symmetry elements of space group $P 4/m \bar{3} 2/m$, and separate diagrams showing those elements related to the symmetry directions $\langle a \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$.

4.6.3 The centered lattices

Consideration of the primitive lattices we have so far generated raises the question as to whether it is possible to import into the P-lattices one or more further lattice planes without destroying the symmetry. Let us first consider the monoclinic P-lattice.

Figure 4.46 shows the monoclinic P-lattice and its symmetry, $P 2/m$, projected onto $x, 0, z$. Each point of the lattice has $2/m$ symmetry, which implies the presence of an inversion center in the point. Insertion of new lattice planes parallel to (010) into the lattice is only possible if the lattice points fall on a position which also has symmetry $2/m$, i.e. on $0,0,0$; $\frac{1}{2},0,0$; $0,\frac{1}{2},0$; $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$ and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. These possibilities must each be considered.

- a) *Lattice Plane with Lattice Point at $\frac{1}{2}, \frac{1}{2}, 0$.* (Fig 4.47). These new lattice points center the a, b -face of the unit cell. This is called a C-face centered lattice, or more simply a C-Lattice.
- b) *Lattice Plane with Lattice Point at $0, \frac{1}{2}, \frac{1}{2}$.* (Fig 4.48). If the new plane centers the b, c -face, the result will be an A-face centered lattice. Since, however, in monoclinic cells, the a and c axes may lie anywhere in the mirror plane, they may be swapped, converting the A-lattice into a C-lattice.
- c) *Lattice Plane with Lattice Point at $\frac{1}{2}, 0, \frac{1}{2}$.* (Fig 4.49). The result is now a B-lattice, from which a smaller, primitive unit cell can be chosen (outlined in bold) that still has monoclinic symmetry.
- d) *Lattice Plane with Lattice Point at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.* (Fig 4.50). A lattice is formed, with a lattice point at the body center of the unit cell. This is called a body centered or I-lattice (from the German *innenzentriert*). As with the A-lattice, choice of different axes convert this to a monoclinic C-lattice.

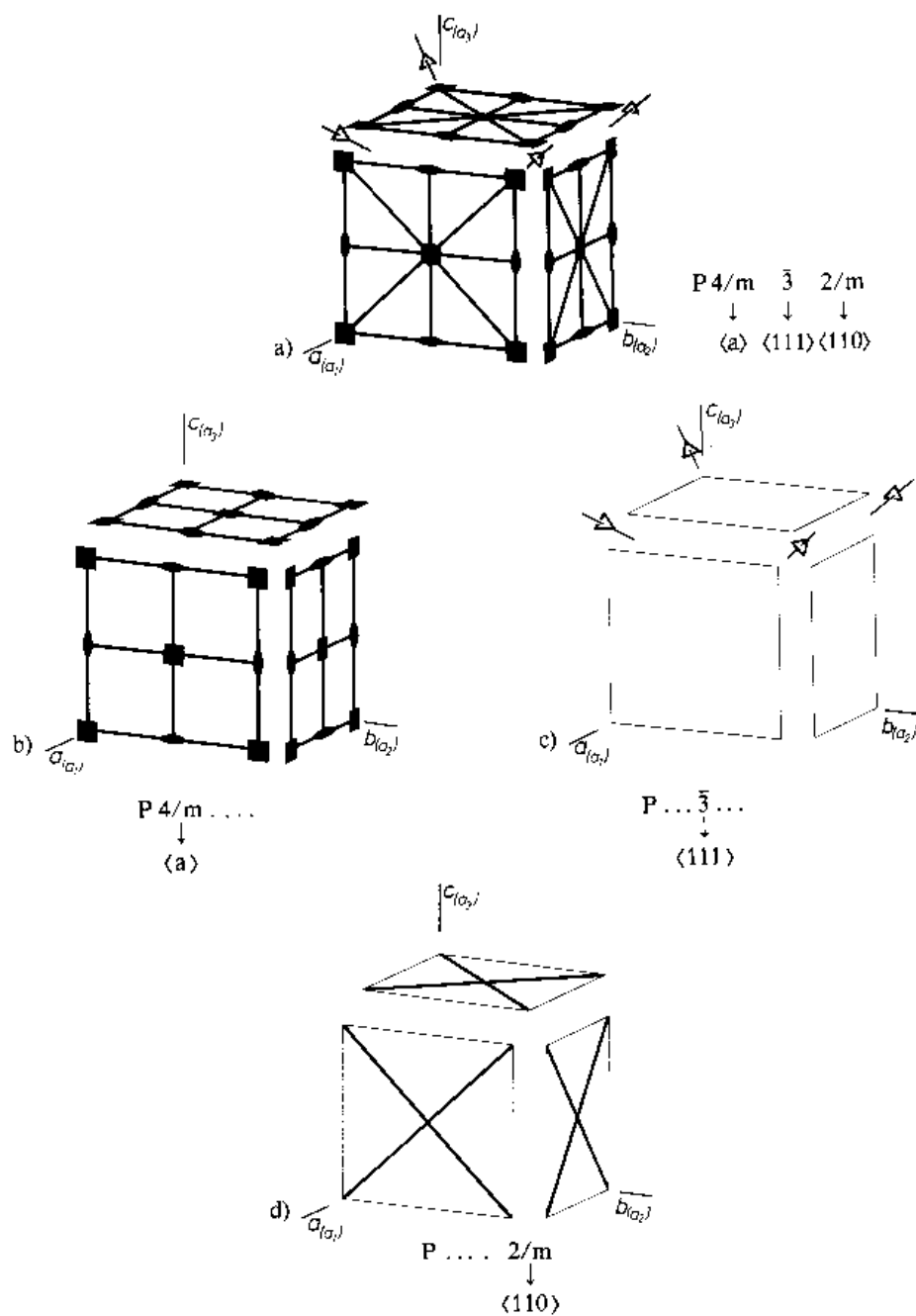


Figure 4.45: (a) Space group $P 4/m \bar{3} 2/m$. In the other diagrams, only the symmetry elements corresponding to the symmetry direction $\langle a \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ are shown.

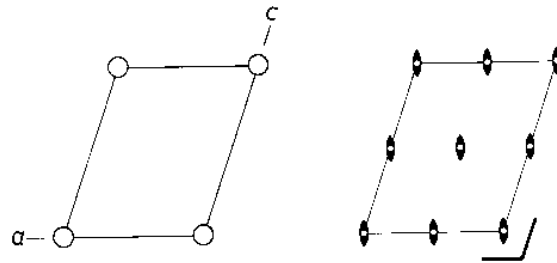


Figure 4.46: The monoclinic P-lattice and its symmetry elements projected onto $x, 0, z$ (\bigcirc represents a lattice point with $y = 0$)

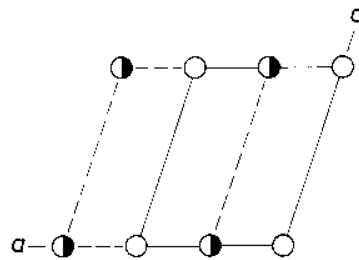


Figure 4.47: The monoclinic C-lattice and its symmetry elements projected onto $x, 0, z$ (the half-filled \bigcirc represents a lattice point with $y = \frac{1}{2}$)

- e) *Lattice Plane with Lattice Point at $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; $0, 0, \frac{1}{2}$.* In any of these cases, the result is simply to halve the cell; no new type of lattice is formed.
- f) It is also possible to introduce two lattice planes at the same time, for example, as in both a) and b), giving additional lattice points at $\frac{1}{2}, \frac{1}{2}, 0$ and $0, \frac{1}{2}, \frac{1}{2}$ (Fig 4.51a). Since it is necessary that all lattice points have the same environment, and parallel lattice lines the same period a further lattice point (shown with a dashed outline) must be added at $\frac{1}{2}, 0, \frac{1}{2}$. Thus, all the faces of the unit cell are now centered, giving an all-face centered or F-lattice.

A general principle following from this is that *a lattice centered on two faces cannot exist because the requirement that all lattice points are identical and parallel lattice lines have the same lattice period will convert it to an all-face centered lattice.*

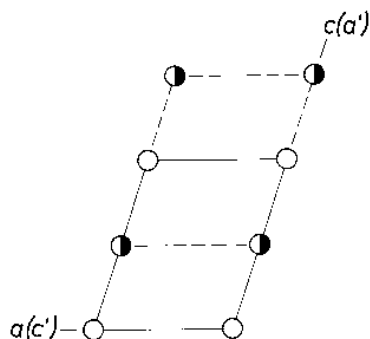


Figure 4.48: The monoclinic A-lattice (a_0, b_0, c_0) can, by interchanging a and c , be converted to a monoclinic C-lattice (a'_0, b'_0, c'_0)

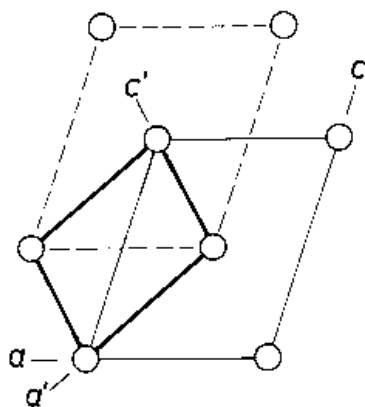


Figure 4.49: The monoclinic B-lattice (a_0, b_0, c_0) can be converted to a smaller monoclinic P-lattice (a'_0, b'_0, c'_0)

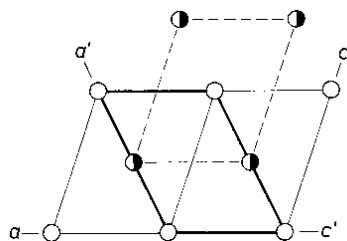


Figure 4.50: The monoclinic I-lattice (a_0, b_0, c_0) can be converted to a monoclinic C-lattice (a'_0, b'_0, c'_0)

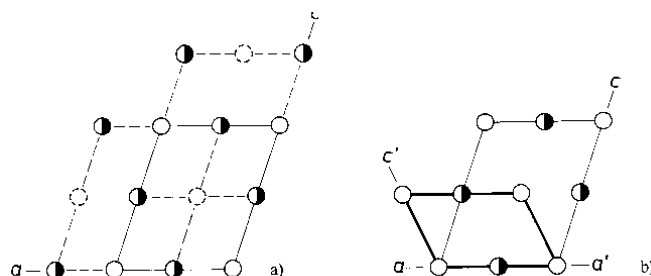


Figure 4.51: (a) The development of the monoclinic F-lattice. (b) The monoclinic F-lattice (a_0, b_0, c_0) can be converted to a monoclinic C-lattice (a'_0, b'_0, c'_0)

The monoclinic F-lattice can, in fact, be reduced to a C-lattice of half the volume, as is shown in Fig. 4.51.

We have now considered all the possibilities for introducing extra lattice planes into the monoclinic P-lattice, and have shown that all of these may be represented either as P- or C-lattices ($A, I, F \rightarrow C$; $B \rightarrow P$). (see Figure 4.36)

The orthorhombic lattice may be developed in the same way, giving rise to orthorhombic, A-, B-, C-, I- and F-lattices. The I- and F-lattices are now not reducible as they were in the monoclinic case. The A-, B- and C-lattices are alternative representations of the same lattice; the a -, b - and c -axes can always be chosen so as to generate a C-lattice. (see Figure 4.36).

Similar considerations to those in the monoclinic case lead from the tetragonal P-lattice to the tetragonal I-lattice, and from the cubic P-lattice to the cubic I- and F-lattices. (see Figure 4.36)

An examination of the hexagonal P-lattice will show that the only point with the same symmetry as $0,0,0$ is $0,0,\frac{1}{2}$. The addition of a lattice plane there will merely halve the size of the unit cell.

A six fold axis always contains a 3-fold axis. Staring from this fact, the plane lattice with a 120° rhombus as unit mesh contains a 3-fold axis at $0,0,z$; $\frac{1}{3}, \frac{2}{3}, z$ and $\frac{2}{3}, \frac{1}{3}, z$ (Fig. 4.52a). it is possible to add a second plane at a height of $\frac{1}{3}c_0$ with a lattice point on the 3-fold axis at $\frac{2}{3}, \frac{1}{3}, z$ and a third plane at a height of $\frac{2}{3}c_0$ with a lattice point on the 3-fold axis at $\frac{1}{3}, \frac{2}{3}, z$ (Fig.4.52b). The fourth plane will then come at a height of c_0 , directly above the first. this new arrangement of lattice points reduces the 6-fold axis to 3-fold and removes the mirror planes at $x,0,z$; $0,y,z$ and x,x,z as well as the 2-fold

axes parallel to the c -axis. The resulting lattice has the shape of a hexagonal lattice ($a_0 = b_0 \neq c_0$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) but contains three lattice points per unit cell $(0,0,0; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}; \frac{1}{3}, \frac{2}{3}, \frac{2}{3})$

It is possible, however, to describe this lattice by a primitive unit cell ($a'_0 = b'_0 = c'_0, \alpha' = \beta' = \gamma'$). If the first cell is used to describe the lattice, it is called a trigonal R-lattice, if the second is used, the lattice is called rhombohedral P (Fig. 4.52b). The unit cell of the rhombohedral P-lattice has indeed the shape of the rhombohedron, with six rhombi as faces. Special cases of the rhombohedral P-lattice are: (a) $\alpha' = 90^\circ$ gives the cubic P-lattice; (b) $\alpha' = 60^\circ$ gives the cubic F-lattice and (c) $\alpha' = 109.47^\circ$ give the cubic I-lattice.

Centered lattices are not primitive, therefore $Z > 1$. You *can* define a primitive cell for each of the centered cells. This primitive cell will have $Z = 1$, and be the smallest unit cell that will fill space. However, you will not be able to see the important symmetry that is associated with the unit cell clearly from the primitive cell. The reason we define centered, and other non-primitive unit cells, is to highlight the symmetry relationships in the lattice.

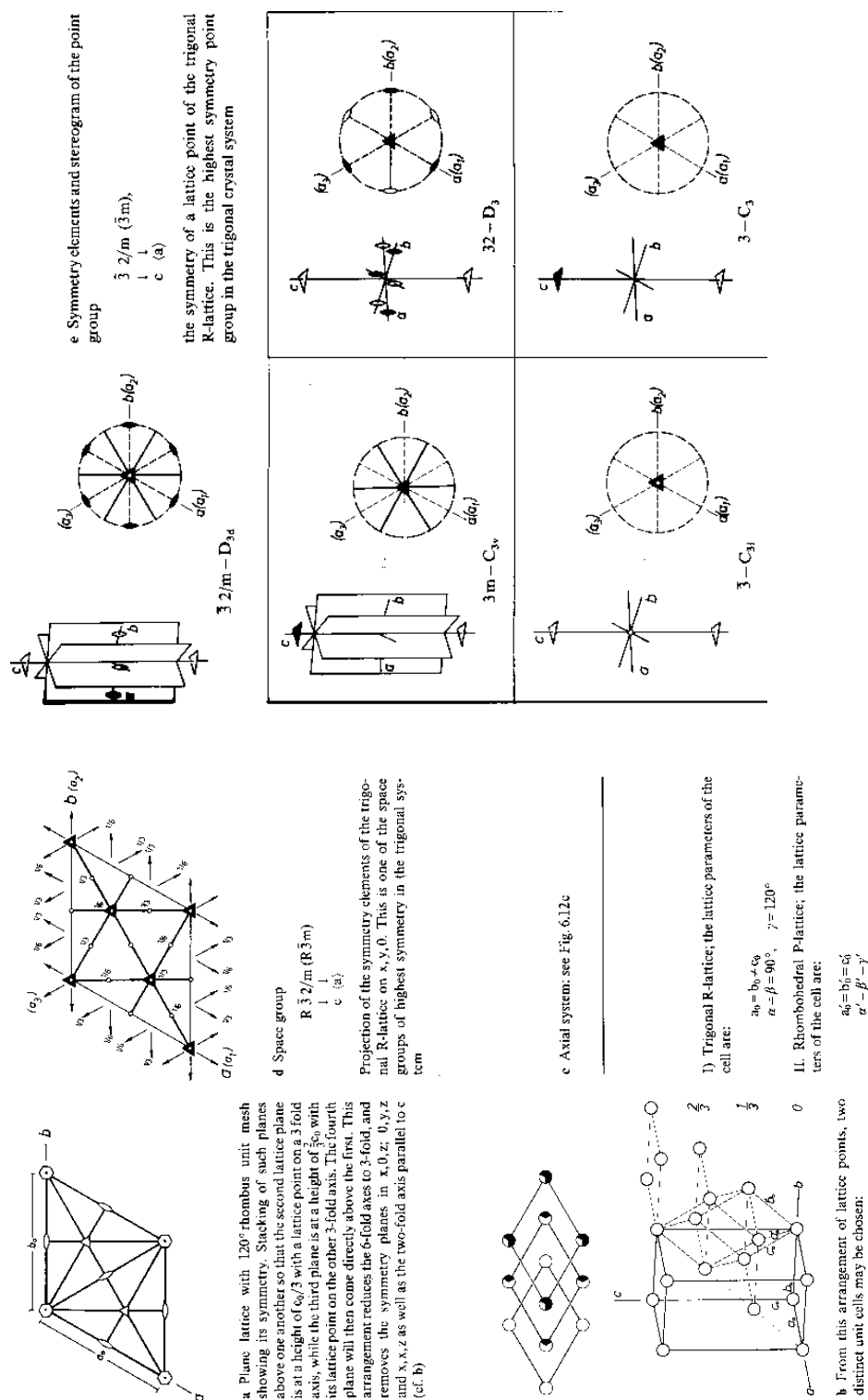


Figure 4.52: Trigonal crystal system

4.6.4 The symmetry of the centered lattices

With the exception of the trigonal R-lattice, the derivation above of the centered lattices always paid strict attention to retaining the full symmetry of the corresponding P-lattice. All the symmetry elements of the P-lattice remained, only the translation properties were altered. The centering does indeed introduce new symmetry elements, notably screw axes and glide planes (which we will not be covering). In spite of this, the symbols for the space groups of the centered lattices may easily be given, since the new symmetry elements do not appear in them.

Now it is not difficult to derive the symbol for the trigonal R-lattice from the reduced symmetry of the lattice planes. There are, in addition to the normal ones, further inversion centers, which, by Rule 1 ($m + \bar{1} \rightarrow 2 \perp m$), generate a set of 2-fold axes parallel to a_1, a_2, a_3 (Fig. 4.52d). The 3-fold axis becomes $\bar{3}$ since $3 + \bar{1} \rightarrow \bar{3}$. The order of the symmetry directions here is: $c, \langle a \rangle$, giving the symbol $R \bar{3} 2/m$.

The space group symbols of the 14 Bravais lattices are given in Figure 4.53 in the same order as in Figure 4.36. ***The Bravais lattices represent the 14 and only ways in which it is possible to fill space by a three-dimensional periodic array of points.*** All crystals are built up on one of these lattices. Earlier we defined a crystal structure as a lattice plus a basis. While the number of lattices is fixed at 14, there are infinitely many possible ways of arranging atoms in a cell. Any crystal structure, however, has only one Bravais lattice. The symmetry directions in the crystal systems are summarised in Figure 4.54. The axial restrictions that accompany the seven crystal systems of the 14 Bravais lattices are shown in Figure 4.55.

The number and coordinates of the lattice points in the unit cells of the Bravais lattices is given in Figure 4.56.

	P	C	I	F
Triclinic	$P\bar{1}$			
Monoclinic	$P2/m$	$C2/m$		
Orthorhombic	$P2/m2/m2/m$	$C2/m2/m2/m$	$I2/m2/m2/m$	$F2/m2/m2/m$
Tetragonal	$P4/m2/m2/m$		$I4/m2/m2/m$	
Trigonal	$P6/m2/m2/m$	$R\bar{3}2/m$		
Hexagonal				
Cubic	$P4/m\bar{3}2/m$		$I4/m\bar{3}2/m$	$F4/m\bar{3}2/m$

Figure 4.53: The space group symbols for the 14 Bravais lattices.

	Position in the international symbol		
	1st	2nd	3rd
Triclinic	–		
Monoclinic	b		
Orthorhombic	a	b	c
Tetragonal	c	$\langle a \rangle$	$\langle 110 \rangle$
Trigonal	c	$\langle a \rangle$	$-c$
Hexagonal	c	$\langle a \rangle$	$\langle 210 \rangle$
Cubic	$\langle a \rangle$	$\langle 111 \rangle$	$\langle 110 \rangle$

Figure 4.54: Symmetry directions in the seven crystal systems

Crystal system	Restrictions on the axial system	Figure	Equivalences of crystallographic axes caused by:
Triclinic	$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma^a$	6.7c	
Monoclinic	$a \neq b \neq c \quad \alpha = \gamma = 90^\circ, \quad \beta > 90^\circ$	6.8c	
Orthorhombic	$a \neq b \neq c \quad \alpha = \beta = \gamma = 90^\circ$	6.9c	
Tetragonal	$a = b \neq c \quad \alpha = \beta = \gamma = 90^\circ$ ($a_1 = a_2 \neq c$)	6.10c	$4, \bar{4}/c$
Trigonal ^b	$a = b \neq c \quad \alpha = \beta = 90^\circ, \quad \gamma = 120^\circ$ ($a_1 = a_2 \neq c$)	6.12c	$3/c$
Hexagonal		6.12c	$6, \bar{6}/c$
Cubic	$a = b = c \quad \alpha = \beta = \gamma = 90^\circ$ ($a_1 = a_2 = a_3$)	6.13c	$3//\langle 111 \rangle$

^a As usual, the signs = and \neq are to be read as *must be equivalent* and *need not be equivalent* respectively as a consequence of symmetry.

^b An alternative definition divides the hexagonal and trigonal systems differently, giving a hexagonal and a rhombohedral system. The rhombohedral system (see Fig. 6.11 b) has the restrictions on its axial system: $a' = b' = c'$; $\alpha' = \beta' = \gamma'$.

Figure 4.55: The seven crystal systems defined by their axial restrictions.

Lattice	No. of lattice points in unit cell	Coordinates of lattice points in unit cell
P	1	0,0,0
A	2	0,0,0; $0, \frac{1}{2}, \frac{1}{2}$
B	2	0,0,0; $\frac{1}{2}, 0, \frac{1}{2}$
C	2	0,0,0; $\frac{1}{2}, \frac{1}{2}, 0$
I	2	0,0,0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
R	3	0,0,0; $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$; $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$
F	4	0,0,0; $\frac{1}{2}, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$; $0, \frac{1}{2}, \frac{1}{2}$

Figure 4.56: Number and coordinates of the lattice points in the unit cells of the 14 Bravais lattices

4.7 The 230 space groups

The space group symbols for the 14 bravais lattices, given in Figure 4.53, do not in general enumerate all the symmetry elements of the space group. In particular, the space groups of centered lattices contain new symmetry operations. These are compound symmetry operations which arise through reflection and translation (a *glide plane* which are notated by a, b, c, n or d), as well as rotation and translation (a *screw axis*, which is notated X_y , where y can have a value between 1 and $X-1$, for instance 2_1 or 4_2). We will not cover these specifically, but we need to be aware that they are present in order to finish the categorization of crystals.

The space groups we determined for the 14 Bravais lattices represent the highest symmetry possible in a given crystal system. If we simply put a spherical object (an atom) at each lattice point in any of the crystal systems we will generate the highest possible symmetry for that crystal system. However, if we add a basis of two or more atoms to each lattice point, we may lower the symmetry that is possible for a given crystal system. The space groups of highest symmetry contain the symmetry elements of one or more space groups of lower symmetry, called subgroups. As an example we will start with the two monoclinic space groups of highest symmetry; $P 2/m$ and $C 2/m$. As long as we maintain either the 2-fold rotation (2) or the mirror plane (m), we will still have a monoclinic space group. If we lost both of those we would drop down in symmetry to the triclinic space group ($P \bar{1}$). So $2/m$ can be replaced by either 2 or m (and 2_1 and c when the screw axes and glide planes are included). This allows 13 possible monoclinic space groups, shown in Figure 4.57, as subgroups of $P 2/m$ and $C 2/m$.

When all possible lower symmetry subgroups are determined from the 14 high symmetry space groups that define the 14 Bravais lattices, there are a total of 230 possible space groups allowed. These are all listed in Figure 4.57.

So, where can atoms actually sit to maintain the symmetry of a space group? Figure 4.58 gives the symmetry elements for the space group $P mm2$. The application of the symmetry operations to a point x, y, z will generate the points x, \bar{y}, z ; \bar{x}, y, z ; \bar{x}, \bar{y}, z , as well as equivalent points such as $x, 1-y, z$; $1-x, y, z$ and $1-x, 1-y, z$. The number of equivalent points in the unit cell is called its multiplicity. In Figure 4.58a, the position is "4-fold", or said to have a multiplicity of 4. This position has no restrictions on its movement; it has three degrees of freedom, and, as long as it does not move onto a point symmetry element, it continues to have a multiplicity of 4. Such a position

Crystal system	Point group	Space groups			
triclinic	1 $\bar{1}$	P1 P $\bar{1}$			
monoclinic	2 m 2/m	P2 Pm P2/m P2 ₁ /c	P2 ₁ Pc P2 ₁ /m C2/c	C2 Cm C2/m	Cc P2/c
orthorhombic	222	P222 C222 ₁ I2 ₁ 2 ₁ 2 ₁	P222 ₁ C222	P2 ₁ 2 ₁ 2 F222	P2 ₁ 2 ₁ 2 ₁ I222
	mm2	Pmm2 Pca2 ₁ Pna2 ₁ Ccc2 Aba2 Iba2	Pmc2 ₁ Pnc2 Pnn2 Amm2 Fmm2 Ima2	Pcc2 Pmn2 ₁ Cmm2 Abm2 Fdd2	Pma2 Pba2 Cmc2 ₁ Ama2 Imm2
	mmm	Pmmm Pmma Pbam Pmmn Cmcm Cmma Immm	Pnnn Pnna Pccn Pbcn Cmca Ccca Ibam	Pccm Pmna Pbcm Pbca Cmmm Fmmm Ibca	Pban Pcca Pnnm Pnma Cccm Fddd Imma
tetragonal	4	P4 I4 P $\bar{4}$	P4 ₁ I4 ₁ I $\bar{4}$	P4 ₂	P4 ₃
	4/m	P4/m I4/m	P4 ₂ m I4 ₁ /a	P4/n	P4 ₂ /n
	422	P422 P4 ₂ 22 I422	P4 ₂ 2 P4 ₂ 2 ₁ 2 I4 ₁ 22	P4 ₁ 22 P4 ₃ 22	P4 ₁ 2 ₁ 2 P4 ₃ 2 ₁ 2
	4mm	P4mm P4cc I4mm	P4bm P4nc I4cm	P4 ₂ cm P4 ₂ mc I4 ₁ md	P4 ₂ nm P4 ₂ bc I4 ₁ cd
	42m	P42m P4 ₂ m2 I4m2	P42c P4c2 I4c2	P4 ₂ m P4b2 I42m	P4 ₂ c P4n2 I42d
	4/mmm	P4/mmm P4/mbm P4 ₂ /mmc P4 ₂ /mbc I4/mmm	P4/mcc P4/mnc P4 ₂ /mcm P4 ₂ /mnm I4/mcm	P4/nbm P4/nmm P4 ₂ /nbc P4 ₂ /nmc I4 ₁ /amd	P4/nnc P4/ncc P4 ₂ /nnm P4 ₂ /ncm I4 ₁ /acd
trigonal	3	P3 P $\bar{3}$	P3 ₁ R3	P3 ₂	R3
	32	P312 P3 ₂ 12	P321 P3 ₁ 21	P3 ₁ 12 R32	P3 ₁ 21 P31c
	3m	P3m1 R3m	P31m R3c	P3c1	
	3m	P31m R3m	P31c R3c	P3m1 P3c1	
hexagonal	6	P6 P6 ₄ P6	P6 ₁ P6 ₃	P6 ₅	P6 ₂
	6/m	P6/m	P6 ₃ /m		
	622	P622 P6 ₂ 22	P6 ₁ 22 P6 ₃ 22	P6 ₅ 22	P6 ₂ 22
	6mm	P6mm P6m2	P6cc P6c2	P6 ₃ cm P6 ₂ m	P6 ₃ mc P62c
	6/mmm	P6/mmm	P6/mcc	P6 ₃ /mcm	P6 ₃ /mmc
cubic	23	P23 I2 ₁ 3	F23	I23	P2 ₁ 3
	m3	Pm3 Im3	Pn3 Pa3	Fm3 Ia3	Fd3
	432	P432 I432	P4 ₃ 32 P4 ₃ 32	F432 P4 ₁ 32	F4 ₃ 2 I4 ₁ 32
	43m	P43m F43c	F43m I43d	I43m	P43n
	m3m	Pm3m Fm3m Im3m	Pn3n Fm3c Ia3d	Pm3n Fd3m	Pn3m Fd3c

Figure 4.57: The 230 space groups.

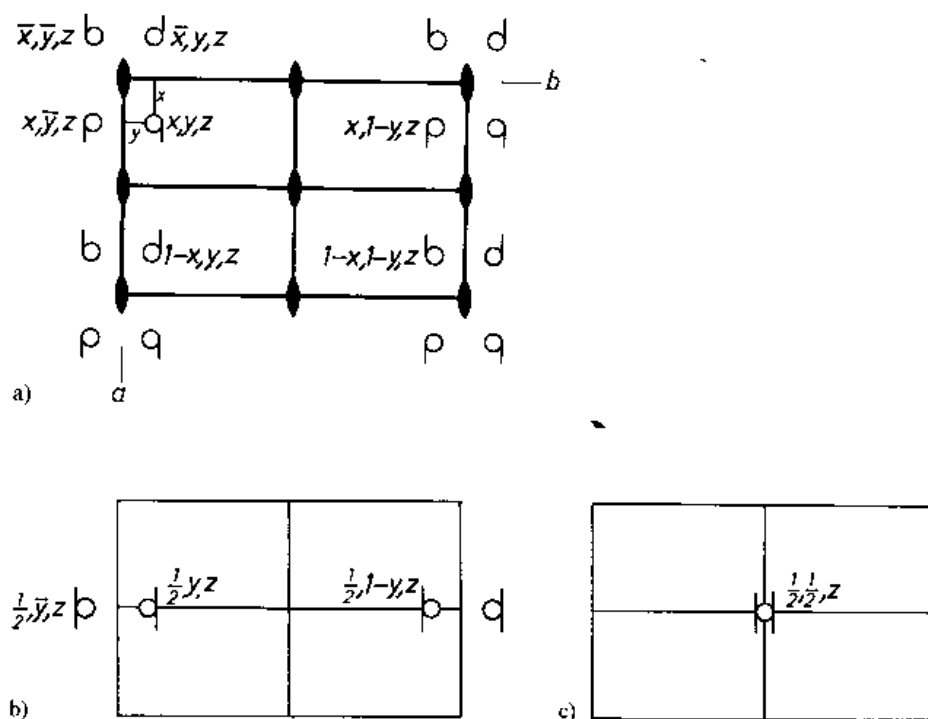


Figure 4.58: Symmetry elements of space group $P\,mm2$ in projection on $x, y, 0$. (a) the general position x, y, z . (b) the special position $\frac{1}{2}, y, z$. (c) The special position $\frac{1}{2}, \frac{1}{2}, z$.

is called a *general position*. A general position is a set of equivalent points with a site symmetry of 1. It is asymmetric, and this is indicated in Figure 4.58 by the tail on the circle.

If the point in the general site x, y, z is moved on to the mirror plane at $\frac{1}{2}, y, z$ the point $1-x, y, z$ comes into coincidence with it; the two points coalesce at the mirror plane to a single point $\frac{1}{2}, y, z$. At the same time, the points $x, 1-y, z$ and $1-x, 1-y, z$ coalesce to the single point $\frac{1}{2}, 1-y, z$ (fig. 4.58a,b). From the 4-fold general position, we have obtained a 2-fold *special position*. Special positions are not asymmetric; they possess site symmetry higher than 1, and in figure 4.58b, the site symmetry is m (it is on a mirror plane). This special position has two degrees of freedom. As long as the point remains on the mirror plane, its multiplicity is unchanged.

If a point on $\frac{1}{2}, y, z$ moves onto the 2-fold axis at $\frac{1}{2}, \frac{1}{2}, z$ the two points

$\frac{1}{2}, y, z$ and $\frac{1}{2}, 1 - y, z$ coalesce to $\frac{1}{2}, \frac{1}{2}, z$. This special position retains only a single degree of freedom. The point symmetry of the position rises to $mm2$, and the multiplicity falls to 1. Some space groups have special positions with no degrees of freedom, an important case of this being a point on an inversion center.

All space groups, and all their symmetries and special positions are listed in the *International Tables for Crystallography*.

4.7.1 Space group and crystal structure

In Section 4.4 we defined a crystal structure as a lattice plus a basis. It is thus possible to describe it as a geometrical arrangement of atoms. Figure 4.59 gives the lattice and the basis for the rutile (TiO_2) structure. The perspective drawings and the projection on the $x, y, 0$ are derived from these data.

Every crystal structure can be similarly described by its *space group and the occupation of general or special positions by atoms*. The crystal structure of rutile is in space group $P 4_2/mnm$ (see Figure 4.60 for the full space group description). The titanium atoms occupy the special position notated a , and the oxygen atoms occupy the special positions f with $x = 0.3$. Substituting 0.3 in for x in the coordinates for the O-atoms gives the specific coordinates listed for the basis. The description of a crystal structure in terms of the space group is much simpler than that in terms of the basis when positions of high multiplicity are involved. In addition, the space group shows clearly which atoms are related to one another by the symmetry elements of the space group. This relationship is particularly important for positions with one or more degrees of freedom. Any movement in x alters the relationship of all the related atoms; for example, an increase in x results in the movement of the O-atoms indicated by the arrows in Figure 4.59.

A		B		
Lattice	Basis	Space group	Positions of the atoms	
tetragonal P $a_0 = 4.59 \text{ \AA}$ $c_0 = 2.96 \text{ \AA}$	Ti: 0,0,0 $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	P $4_2/mnm$ $a_0 = 4.59 \text{ \AA}$ $c_0 = 2.96 \text{ \AA}$	a	Ti: 0,0,0 $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
	O: 0.3, 0.3, 0 0.8, 0.2, $\frac{1}{2}$ 0.2, 0.8, $\frac{1}{2}$ 0.7, 0.7, 0		f	O: x, x, 0 $\frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}$ $\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2}$ $\bar{x}, \bar{x}, 0$ x = 0.3

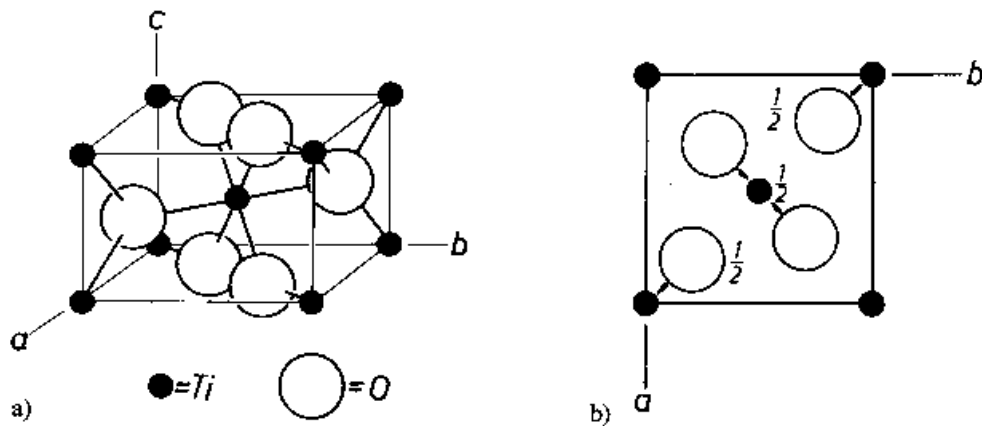


Figure 4.59: A description of the crystal structure of rutile TiO_2 (a) in perspective, and (b) in projection on the $x, y, 0$.

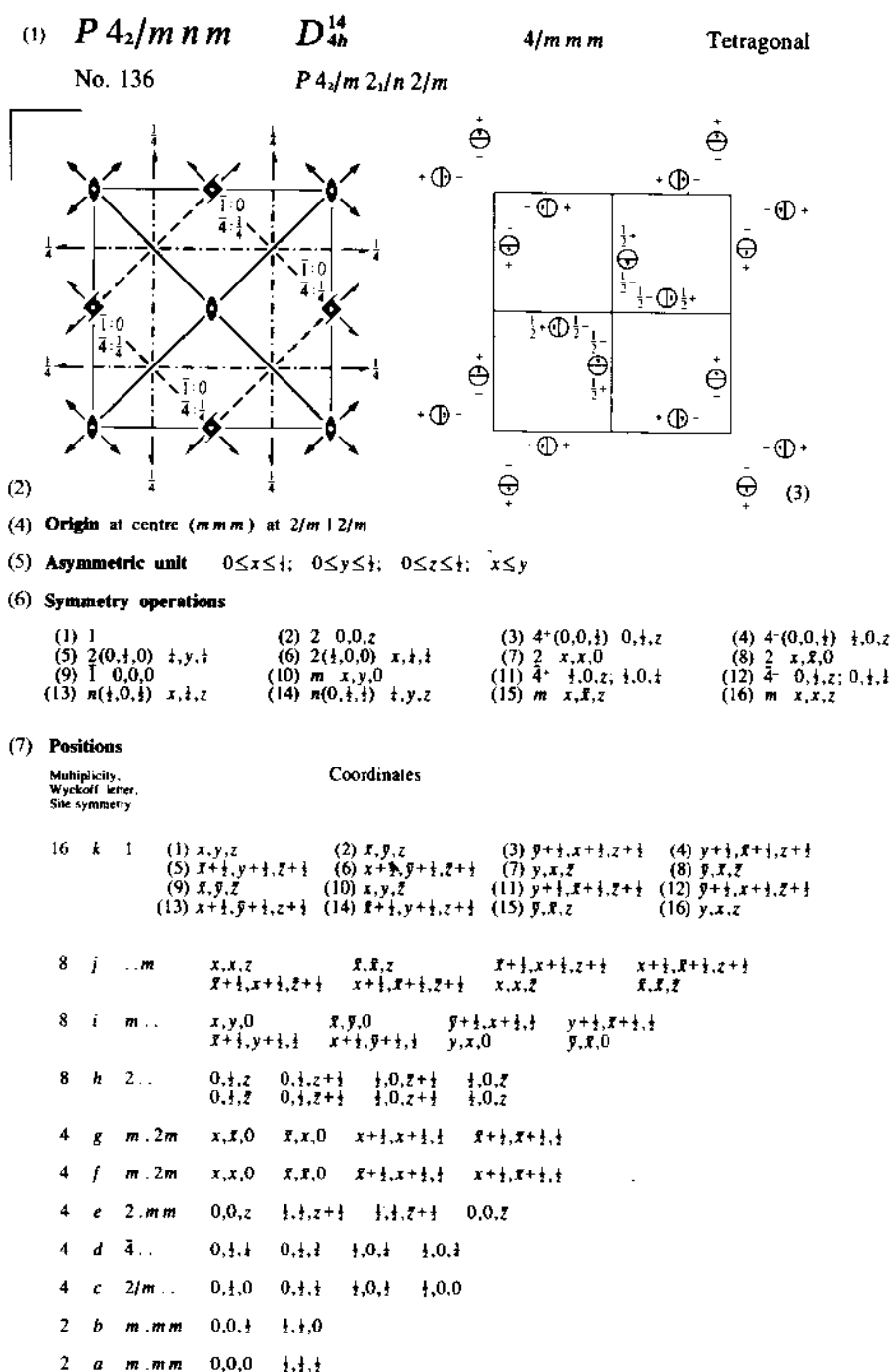


Figure 4.60: Space group $P 4_2/mnm$, from the International Tables for Crystallography.

4.7.2 Space groups and physical properties

Piezoelectricity

Some crystals, when subjected to pressure or tension in certain directions develop an electric charge; this property is called *piezoelectricity*. This effect is clearly seen in plates of quartz (space group $P 3_12$), cut normal to the a-axis and compressed or pulled along the a-axis. The a-axis in quartz has a polar 2-fold rotation axis. Polar axes are those which have distinct physical properties in the parallel and antiparallel directions. These directions must thus not be themselves related by symmetry. It follows that within the crystal there will be an asymmetric charge distribution along the polar axes. The opposite faces, normal to the polar axis, develop electric charges within a pressure is applied along the axis. The direction of this electric field is reversed when the pressure is replaced by tension.

Piezoelectricity is only observed in crystals which have polar axes. Polar directions only exist in space groups without a center of symmetry (non-centrosymmetric).

The piezoelectric effect is reversible. If an electric field is applied in the direction of the polar axis of a quartz plate, the crystal will undergo compression or expansion. The application of an alternating field will cause the crystal to vibrate. Piezoelectricity has many technical applications, including ultrasonic generators, amplifiers, microphones and quartz time-pieces.

Pyroelectricity

When a crystal of tourmaline is heated, the polar ends of the crystal develop electric charges. Heating causes the positive end of the x-axis to become positively charged relative to the negative end, and cooling has the opposite effect. This effect results from the fact that tourmaline has a permanent electric dipole. The charge which builds up is soon dissipated by conduction into the surroundings. Changes in temperature change the size of the electric dipole.

The dipole moment is a vector. Pyroelectricity can only arise when the space group has no symmetry operations which alter the direction of this dipole. The vector must remain unchanged by all the symmetry operations.

Knowledge of the symmetry allows one to quickly decide whether pyroelectricity or piezoelectricity are not possible for a given material. It, how-

ever, gives only a qualitative indication of the possible presence of pyroelectricity or piezoelectricity.