

Introduction to Crystallography, by H. K. D. H. Bhadeshia, in “Microstructural Characterisation, editor E. Metcalfe, The Institute of Metals, London, 1988, pp. 1–42.

Introduction to Crystallography

Amorphous solids are homogeneous and isotropic because there is no long range order or periodicity in their internal atomic arrangement. By contrast, the crystalline state is characterised by a regular arrangement of atoms over large distances. Crystals are therefore anisotropic – their properties vary with direction. For example, the interatomic spacing varies with orientation within the crystal, as does the elastic response to an applied stress.

Engineering materials are usually aggregates of many crystals of varying sizes and shapes; these *polycrystalline* materials have properties which depend on the nature of the individual crystals, but also on aggregate properties such as the size and shape distributions of the crystals, and the orientation relationships between the individual crystals. The randomness in the orientation of the crystals is a measure of *texture*, which has to be controlled in the manufacture of transformer steels, uranium fuel rods and beverage cans.

The crystallography of interfaces connecting adjacent crystals can determine the deformation behaviour of the polycrystalline aggregate; it can also influence the toughness through its effect on the degree of segregation of impurities to such interfaces.

The Lattice

Crystals have translational symmetry: it is possible to identify a regular set of points, known as the lattice points, each of which has an identical environment.

The set of these lattice points constitutes a three dimensional lattice. A *unit cell* may be defined within this lattice as a space-filling parallelepiped with origin at a lattice point, and with its edges defined by three non-coplanar *basis vectors* \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 , each of which represents translations between two lattice points. The entire lattice can then be generated by stacking unit cells in three dimensions. Any vector representing a translation between lattice points is called a *lattice vector*.

The unit cell defined above has lattice points located at its corners. Since these are shared with seven other unit cells, and since each cell has eight corners, there is only one lattice point per unit cell. Such a unit cell is *primitive* and has the lattice symbol P .

Non-primitive unit cells can have two or more lattice points, in which case, the additional lattice points will be located at positions other than the corners of the cell. A cell with lattice points located at the centres of all its faces has the lattice symbol F ; such a cell would contain four lattice points. Not all the faces of the cell need to have face-centering lattice points; when a cell containing two lattice points has the additional lattice point located at the centre of the face defined by \mathbf{a}_2 and \mathbf{a}_3 , the lattice symbol is A and the cell is said to be A -centred. B -centred and C -centred cells have the additional lattice point located on the face defined by \mathbf{a}_3 & \mathbf{a}_1

or \mathbf{a}_1 & \mathbf{a}_2 respectively. A unit cell with two lattice points can alternatively have the additional lattice point at the body-centre of the cell, in which case the lattice symbol is I . The lattice symbol R is for a trigonal cell; the cell is usually defined such that it contains three lattice points.

The basis vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 define the the unit cell; their magnitudes a_1 , a_2 and a_3 respectively, are the *lattice parameters* of the unit cell. The angles $\mathbf{a}_1 \wedge \mathbf{a}_2$, $\mathbf{a}_2 \wedge \mathbf{a}_3$ and $\mathbf{a}_3 \wedge \mathbf{a}_1$ are conventionally labelled γ , α and β respectively.

Note that our initial choice of the basis vectors was arbitrary since there are an infinite number of lattice vectors which could have been used in defining the unit cell. The preferred choice includes small basis vectors which are as equal as possible, provided the shape of the cell reflects the essential symmetry of the lattice.

The Bravais Lattices

The number of ways in which points can be arranged regularly in three dimensions, such that the stacking of unit cells fills space, is not limitless; Bravais showed in 1848 that all possible arrangements can be represented by just fourteen lattices.

The fourteen Bravais lattices can be categorised into seven *crystal systems* (cubic, tetragonal, orthorhombic, trigonal, hexagonal, monoclinic and triclinic, Table 1); the cubic system contains for example, the cubic- P , cubic- F and cubic- I lattices. Each crystal system can be characterised uniquely by a set of defining symmetry elements, which any crystal within that system must possess as a

System	Conventional unit cell	Defining symmetry
Triclinic	$\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3, \alpha \neq \beta \neq \gamma$	monad
Monoclinic	$\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3, \alpha = \gamma, \beta \geq 90^\circ$	1 diad
Orthorhombic	$\mathbf{a}_1 \neq \mathbf{a}_2 \neq \mathbf{a}_3, \alpha = \beta = \gamma = 90^\circ$	3 diads
Tetragonal	$\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3, \alpha = \beta = \gamma = 90^\circ$	1 tetrad
Trigonal	$\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	1 triad
Hexagonal	$\mathbf{a}_1 = \mathbf{a}_2 \neq \mathbf{a}_3, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	1 hexad
Cubic	$\mathbf{a}_1 = \mathbf{a}_2 = \mathbf{a}_3, \alpha = \beta = \gamma = 90^\circ$	4 triads

Table 1: The crystal systems.

minimum requirement (Table 1).

The Bravais lattices are illustrated in Fig. 1, each as a projection along the \mathbf{a}_3 axis. Projections like these are useful as simple representations of three-dimensional objects. The coordinate of any point with respect to the \mathbf{a}_3 axis is represented as a fraction of a_3 along the point of interest; points located at $0\mathbf{a}_3$ are unlabelled; translational symmetry requires that for each lattice point located at $0\mathbf{a}_3$, there must exist another at $1\mathbf{a}_3$.

Directions

Any vector \mathbf{u} can be represented as a linear combination of the basis vectors \mathbf{a}_i of the unit cell ($i = 1, 2, 3$):

$$\mathbf{u} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 \quad (1)$$

and the scalar quantities u_1 , u_2 and u_3 are the components of the vector \mathbf{u} with respect to the basis vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . Once the

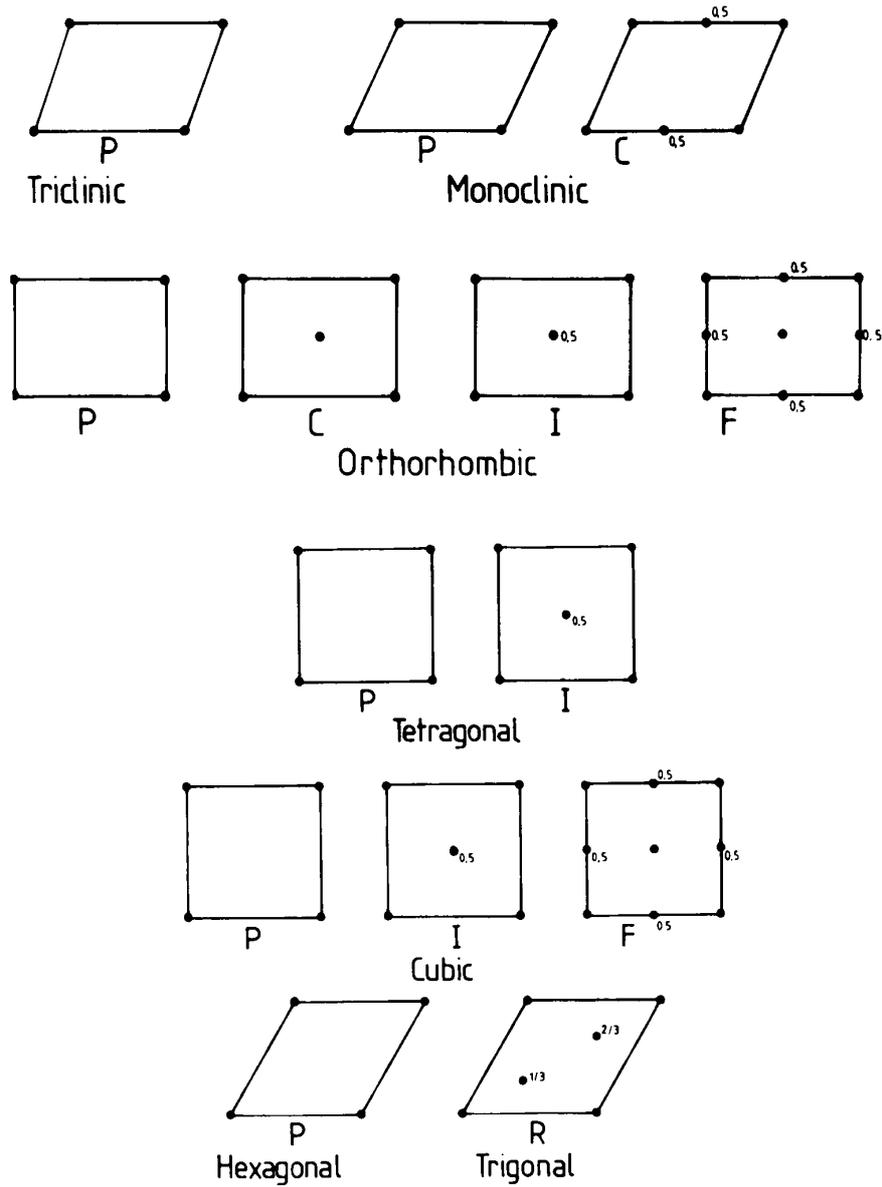


Fig. 1: Projections of the fourteen Bravais lattices along the a_3 axis. The numbers indicate the coordinates of lattice points relative to the a_3 axis; the unlabelled lattice points are by implication located at coordinates 0 and 1 with respect to the a_3 axis. Note that the P , F , I , C and R type cells contain 1, 4, 2, 2 and 3 lattice points per cell, respectively.

unit cell is defined, any direction \mathbf{u} within the lattice can be identified uniquely by its components $[u_1 \ u_2 \ u_3]$, and the components are called the Miller indices of that direction and are by convention enclosed in square brackets (Fig. 2).

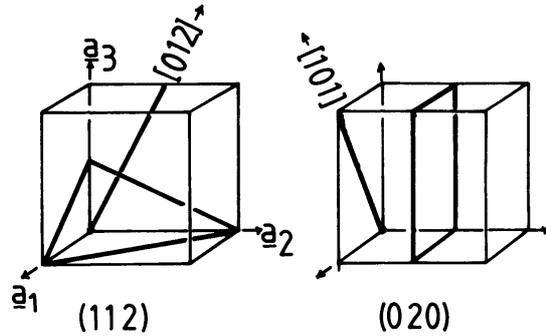


Fig. 2: Miller indices for directions and planes.

It is sometimes the case that the properties along two or more different directions are identical. These directions are said to be *equivalent* and the crystal is said to possess *symmetry*. For example, the $[1 \ 0 \ 0]$ direction for a cubic lattice is equivalent to the $[0 \ 1 \ 0]$, $[0 \ 0 \ 1]$, $[0 \ \bar{1} \ 0]$, $[0 \ 0 \ \bar{1}]$ and $[\bar{1} \ 0 \ 0]$ directions; the bar on top of the number implies that the index is negative.

The indices of directions of the same form are conventionally enclosed in special brackets, *e.g.* $\langle 1 \ 0 \ 0 \rangle$. The number of equivalent directions within the form is called the multiplicity of that direction, which in this case is 6.

Planes

If a plane intersects the \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 axes at distances x_1 , x_2 and x_3 respectively, relative to the origin, then the Miller indices of

that plane are given by $(h_1 \ h_2 \ h_3)$ where:

$$h_1 = \phi a_1/x_1, \quad h_2 = \phi a_2/x_2, \quad h_3 = \phi a_3/x_3.$$

ϕ is a scalar which clears the numbers h_i off fractions or common factors. Note that x_i are negative when measured in the $-\mathbf{a}_i$ directions. The intercept of the plane with an axis may occur at ∞ , in which case the plane is parallel to that axis and the corresponding Miller index will be zero (Fig. 2).

Miller indices for planes are by convention written using round brackets: $(h_1 \ h_2 \ h_3)$ with braces being used to indicate planes of the same form: $\{h_1 \ h_2 \ h_3\}$.

The Reciprocal Lattice

The reciprocal lattice is a special co-ordinate system. For a lattice represented by basis vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 , the corresponding reciprocal basis vectors are written \mathbf{a}_1^* , \mathbf{a}_2^* and \mathbf{a}_3^* , such that:

$$\mathbf{a}_1^* = (\mathbf{a}_2 \wedge \mathbf{a}_3)/(\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3) \quad (2a)$$

$$\mathbf{a}_2^* = (\mathbf{a}_3 \wedge \mathbf{a}_1)/(\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3) \quad (2b)$$

$$\mathbf{a}_3^* = (\mathbf{a}_1 \wedge \mathbf{a}_2)/(\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3) \quad (2c)$$

In equation 2a, the term $(\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3)$ represents the volume of the unit cell formed by \mathbf{a}_i , while the magnitude of the vector $(\mathbf{a}_2 \wedge \mathbf{a}_3)$ represents the area of the $(1 \ 0 \ 0)_A$ plane. Since $(\mathbf{a}_2 \wedge \mathbf{a}_3)$ points along the normal to the $(1 \ 0 \ 0)_A$ plane, it follows that \mathbf{a}_1^* also points along

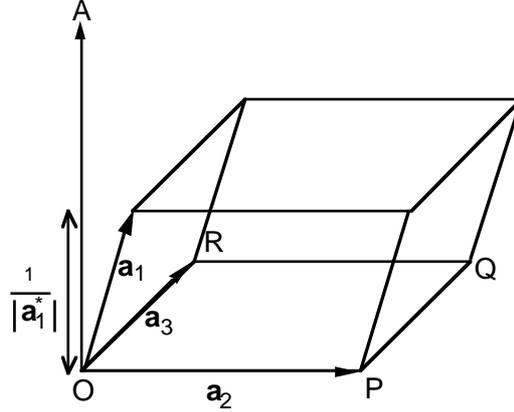


Fig. 3: The relationship between \mathbf{a}_1^* and \mathbf{a}_i . The vector \mathbf{a}_1^* lies along the direction \underline{OA} and the volume of the parallelepiped formed by the basis vectors \mathbf{a}_i is given by $\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3$, the area $OPQR$ being equal to $|\mathbf{a}_2 \wedge \mathbf{a}_3|$.

the normal to $(1\ 0\ 0)_A$ and that its magnitude $|\mathbf{a}_1^*|$ is the reciprocal of the spacing of the $(1\ 0\ 0)_A$ planes (Fig. 3).

The components of any vector referred to the reciprocal basis represent the Miller indices of a plane whose normal is along that vector, with the spacing of the plane given by the inverse of the magnitude of that vector. For example, the reciprocal lattice vector $\mathbf{u}^* = (1\ 2\ 3)$ is normal to planes with Miller indices $(1\ 2\ 3)$ and interplanar spacing $1/|\mathbf{u}^*|$.

We see from equation 3 that

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = 1 \quad \text{when } i = j, \quad \text{and} \quad \mathbf{a}_i \cdot \mathbf{a}_j^* = 0 \quad \text{when } i \neq j$$

or in other words,

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$$

δ_{ij} is the Kronecker delta, which has a value of unity when $i = j$ and is zero when $i \neq j$.

Example: Electrons in Metals

Metals are electrical conductors because some of the electrons are able to move freely, even though they move in a periodic array of positive metal ions. Electrons are waves, characterised by a wave number k

$$k = \pm \frac{2\pi}{\lambda}$$

where λ is the wavelength. The lattice does not affect the motion of these electrons except at critical values of k , where the lattice planes reflect the electrons[†]. For a square lattice, these critical values of k are given by

$$k = \pm \frac{n\pi}{a \sin \theta} \quad (3)$$

where a is the lattice parameter and θ is the direction of motion. The component of \mathbf{k} along the x axis is $k_x = k \sin \theta$ and since $\theta = 0$, it follows that reflection occurs when $k_x = \pm\pi/a$ and similarly when $k_y = \pm\pi/a$.

This can be represented in k -space, which is reciprocal space with a reciprocal lattice parameter of magnitude $2\pi/a$. In Fig. 4, electrons are reflected in the lattice whenever k falls on any point on the square $ABCD$. This square is known as the first Brillouin zone boundary.

[†] Reflection occurs when the Bragg law is satisfied, *i.e.* when $\mathbf{k} \cdot \mathbf{g} = 0.5g^2$, where \mathbf{g} is a reciprocal lattice vector representing the planes doing the reflecting.

Electron energy contours are frequently plotted in k -space. Inside a Brillouin zone, the energy of electrons can increase ‘smoothly’ with k ; there is then a discontinuity (an energy gap) at the zone boundary. This is followed by a second Brillouin zone ($n = 2$ in equation 3) and so on.

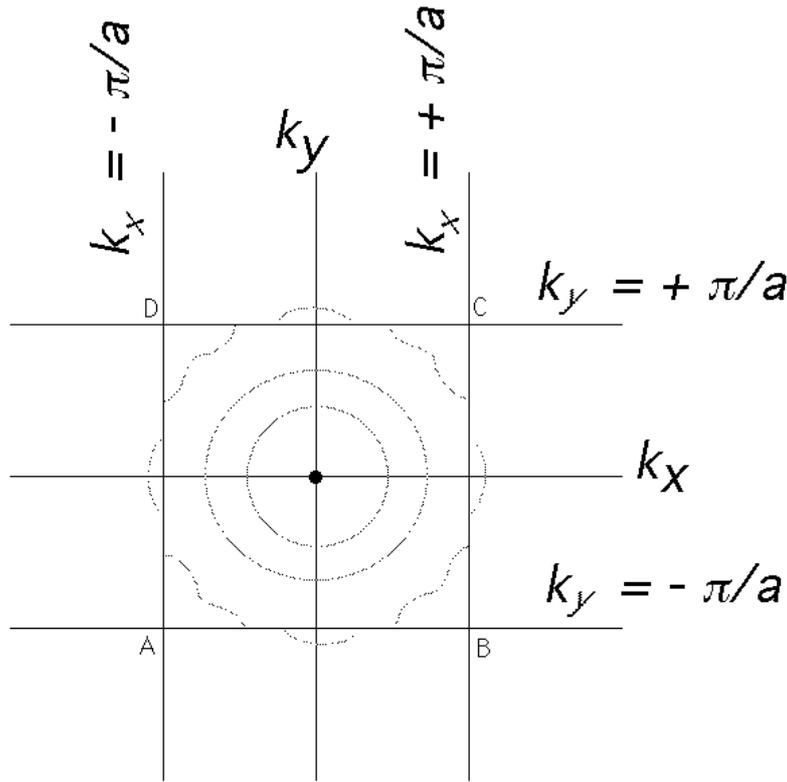


Fig. 4: The first Brillouin zone for a two-dimensional square lattice. Electron energy contours are also plotted. Note the discontinuity at the first Brillouin zone boundary. ■

Fig. 5 shows the shape of the first Brillouin zone for the face-centred cubic lattice, drawn in k -space. Reflections in this lattice occur first from the $\{1\ 1\ 1\}$ and $\{2\ 0\ 0\}$ planes, so the boundaries of the zone are parallel to this.

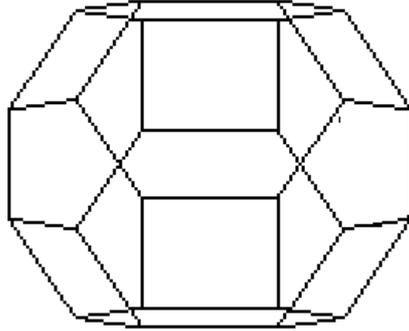


Fig. 5: The shape of the first Brillouin zone for a three-dimensional face centred-cubic lattice.

Symmetry

Although the properties of a crystal can be anisotropic, there may be different directions along which they are identical. These directions are said to be *equivalent* and the crystal is said to possess *symmetry*.

That a particular edge of a cube cannot be distinguished from any other is a measure of its symmetry; an orthorhombic parallelepiped has lower symmetry, since its edges can be distinguished by length.

Some symmetry operations are illustrated in Fig. 6; in essence, they transform a spatial arrangement into another which is indistinguishable from the original. The rotation of a cubic lattice through 90° about an axis along the edge of the unit cell is an example of a symmetry operation, since the lattice points of the final and original lattice coincide in space and cannot consequently be distinguished.

We have already encountered translational symmetry when defining the lattice; since the environment of each lattice point is identical, translation between lattice points has the effect of shifting the

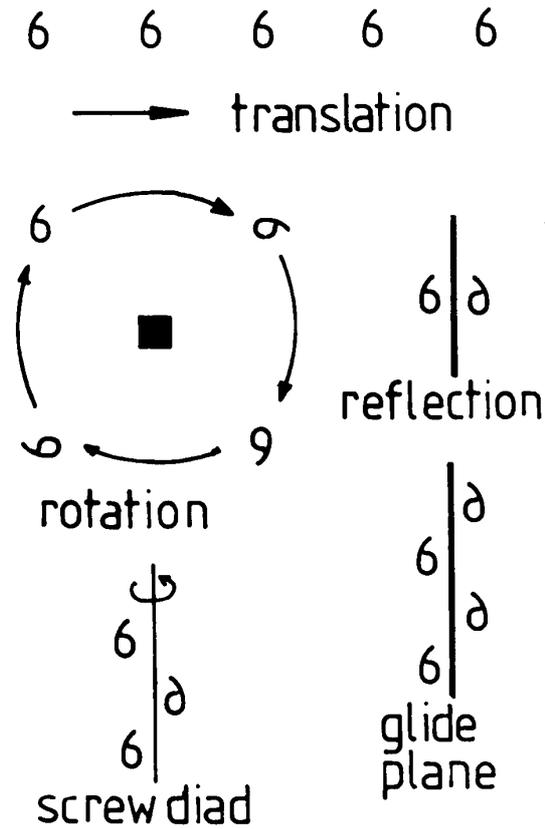


Fig. 6: An illustration of some symmetry operations.

origin.

Symmetry Operations

An object possesses an n -fold axis of rotational symmetry if it coincides with itself upon rotation about the axis through an angle $360^\circ/n$. The possible angles of rotation, which are consistent with the translational symmetry of the lattice, are 360° , 180° , 120° , 90° and 60° for values of n equal to 1, 2, 3, 4 and 6 respectively. A five-fold axis of rotation does not preserve the translational symmetry of the lattice and is forbidden. A one-fold axis of rotation is called a monad and the terms diad, triad, tetrad and hexad correspond

to $n = 2, 3, 4$ and 6 respectively.

All of the Bravais lattices have a *centre of symmetry*. An observer at the centre of symmetry sees no difference in arrangement between the directions $[u_1 \ u_2 \ u_3]$ and $[-u_1 \ -u_2 \ -u_3]$. The centre of symmetry is such that inversion through that point produces an identical arrangement but in the opposite sense. A *rotoinversion* axis of symmetry rotates a point through a specified angle and then inverts it through the centre of symmetry such that the arrangements before and after this combined operation are in coincidence. For example, a three-fold inversion axis involves a rotation through 120° combined with an inversion, the axis being labelled $\bar{3}$.

A rotation operation can also be combined with a translation parallel to that axis to generate a *screw axis* of symmetry. The magnitude of the translation is a fraction of the lattice repeat distance along the axis concerned. A 3_1 screw axis would rotate a point through 120° and translate it through a distance $t/3$, where t is the magnitude of the shortest lattice vector along the axis. A 3_2 operation involves a rotation through 120° followed by a translation through $2t/3$ along the axis. For a right-handed screw axis, the sense of rotation is anticlockwise when the translation is along the positive direction of the axis.

A plane of *mirror symmetry* implies arrangements which are mirror images. Our left and right hands are mirror images. The operation of a $\bar{2}$ axis produces a result which is equivalent to a reflection through a mirror plane normal to that axis.

The operation of a *glide plane* combines a reflection with a trans-

lation parallel to the plane, through a distance which is half the lattice repeat in the direction concerned. The translation may be parallel to a unit cell edge, in which case the glide is *axial*; the term *diagonal* glide refers to translation along a face or body diagonal of the unit cell. In the latter case, the translation is through a distance which is half the length of the diagonal concerned, except for *diamond* glide, where it is a quarter of the diagonal length.

Crystal Structure

Lattices are regular arrays of imaginary points in space. A real crystal has atoms associated with these points. The location of an atom of copper at each lattice point of a cubic- F lattice, generates the *crystal structure* of copper, with four copper atoms per unit cell (one per lattice point), representing the actual arrangement of copper atoms in space.

The atom of copper is said to be the *motif* associated with each lattice point:

$$\text{lattice} + \text{motif} = \text{crystal structure}$$

The motif need not consist of just one atom. Consider a motif consisting of a pair of carbon atoms, with coordinates $[0\ 0\ 0]$ and $[\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]$ relative to a lattice point. Placing this motif at each lattice point of the cubic- F lattice generates the diamond crystal structure (Fig. 7), with each unit cell containing 8 carbon atoms (2 carbon atoms per lattice point).

Some Crystal Structures

The cubic- F zinc sulphide (zinc blende) structure (Fig. 8) is

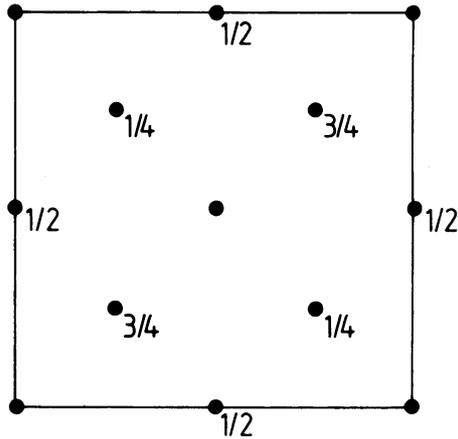


Fig. 7: Projection of the diamond crystal structure along the a_3 axis.

similar to that of diamond, except that the motif now consists of two different atoms with coordinates $[0\ 0\ 0]$ and $[\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]$. Gallium arsenide also has the zinc blende structure.

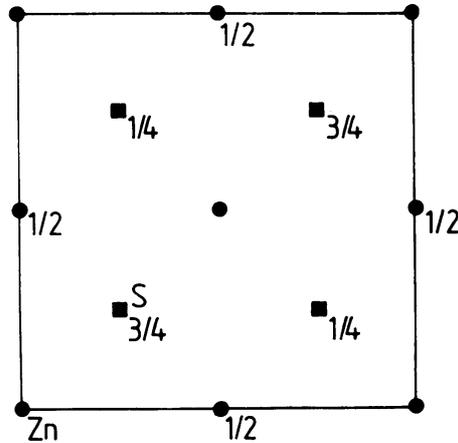


Fig. 8: Projection of the zinc blende crystal structure along the a_3 axis.

The sodium chloride structure (also adopted by CrN, HfC, TiO) can be generated by placing a motif consisting of a sodium atom at

$[0\ 0\ 0]$ and a chlorine atom at $[0\ 0\ \frac{1}{2}]$ at each lattice point of the cubic- F lattice (Fig. 9).

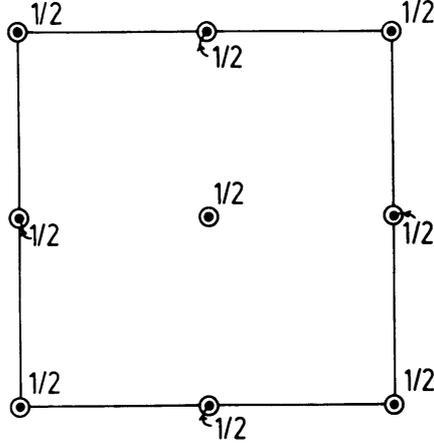


Fig. 9: Projection of the chloride crystal structure along the a_3 axis.

The fluorite structure of CaF_2 is obtained by placing a motif of a calcium atom at $[0\ 0\ 0]$ and two fluorine atoms at $[\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]$ at each lattice point of the cubic- F structure, so that the unit cell contains a total of four calcium atoms and eight fluorine atoms, each fluorine atom surrounded by a tetrahedron of calcium atoms, and each calcium atom by a cube of eight fluorine atoms (Fig. 10). The fluorite structure is adopted by many compounds such as CoSi_2 , UO_2 and Mg_2Si .

The crystal structure of the intermetallic compound Fe_3Al which contains 16 atoms per unit cell may be generated by placing a motif of an Al atom at $[0\ 0\ 0]$ and Fe atoms at $[0\ 0\ \frac{1}{2}]$, $[\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]$ and $[-\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}]$ at each lattice point of the cubic- F lattice.

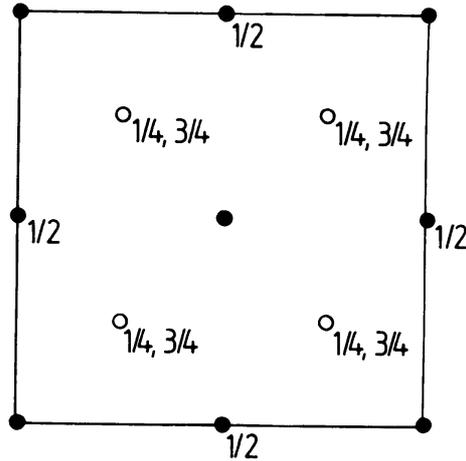


Fig. 10: Projection of the fluorite crystal structure along the a_3 axis.

Interstices

The atoms inside a unit cell do not fill all space. The empty space represents the interstices. It is often the case that these interstices can accommodate small impurity atoms. As an example, we shall consider the crystal structure of iron which at ambient temperature has the cubic-I lattice with an atom of iron at each lattice point. There are two kinds of interstitial sites capable of accommodating small atoms such as carbon or nitrogen. These are the tetrahedral and octahedral sites as illustrated in Fig. 11.

Crystallography and Crystal Defects

A plane of atoms can glide rigidly over its neighbour in process described as *slip* with the *slip system* defined by the plane and the direction of slip. This kind of deformation requires enormous stresses, far greater than those required to actually deform a crystal. This is because almost all crystals contain defects known as

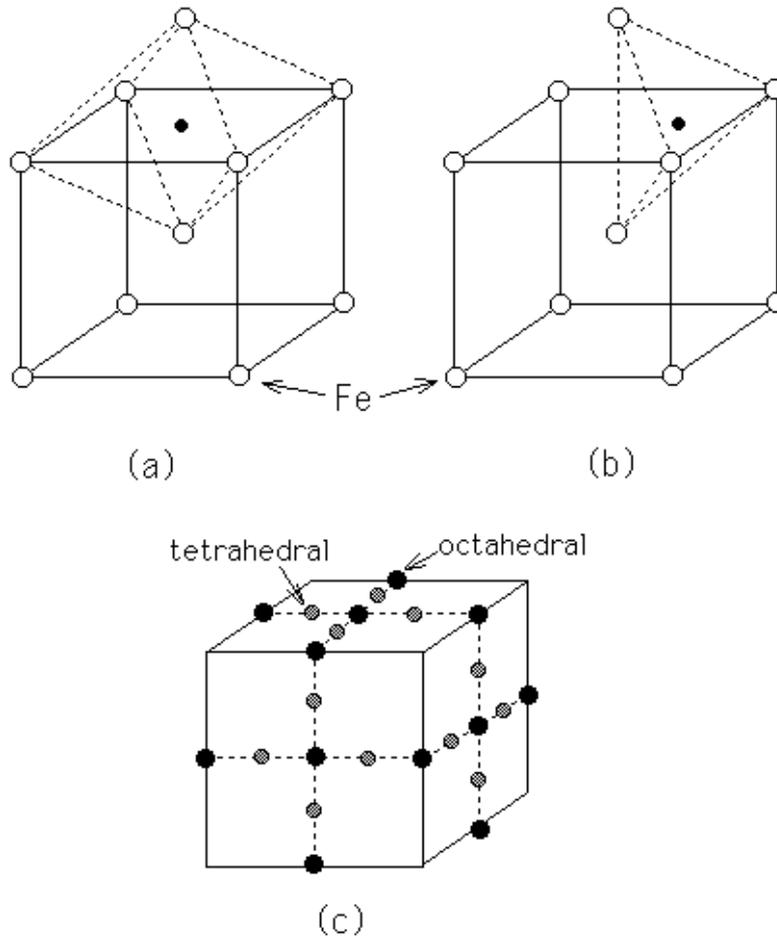


Fig. 11: The main interstices in the body-centred cubic structure of ferrite. (a) An octahedral interstice; (b) a tetrahedral interstice; (c) location of both kinds of interstices.

dislocations. A dislocation enables the planes to glide in a piece-wise manner rather than the rigid displacement of the entire plane. This greatly reduces the stress required to cause slip.

A good analogy to illustrate the role of a dislocation is to imagine the force required to pull an entire carpet along the floor. On the other hand, if a bump is introduced into the carpet, the force needed to move the bump along is much smaller. The amount and

direction of displacement produced by propagating the bump is, in the context of a dislocation, known as its Burgers vector.

Crystals may also contain point defects, which are imperfections of occupation. A vacancy is when an atom is missing from a site which should be occupied. An interstitial occurs when an atom is forced into a space within the crystal structure, where atoms are not normally located.

Polycrystalline materials contain many crystals; another common term for crystals in such materials is *grains*. Atoms in the grain boundary between crystals must in general be displaced from positions they would occupy in the undisturbed crystal. Therefore, grain boundaries are defects.