§1 – Crystal Structure

Solid state physics is a sub-field of Condensed Matter and Material Physics, which deals with the properties of solids.

Most of solid state physics deals with crystals and the properties of electrons within crystals. In fact, this course will exclusively consider crystals as representative of all matter.

1.1 Lattice Vectors

An ideal crystal is simply a form of infinite tessellation: a base pattern repeated over and over. The base pattern is a group of atoms called the **basis**. The simplest basis is a single atom, as in Cu, Fe etc.

A **lattice** is a regular, periodic array of points in space. It can be defined in 3-dimensions by three fundamental translational vectors $\vec{a_1}, \vec{a_2}, \vec{a_3}$ and must satisfy the condition that for some position $\vec{r}$ in the crystal, the atomic arrangement looks exactly the same when observed at a point $\vec{r}\,'$, where:

$$\vec{r}\,' = \vec{r} + u_1\vec{a_1} + u_2\vec{a_2} + u_3\vec{a_3} \tag{1.1}$$

The lattice comprises the points $\vec{r}\,'$ defined by equation (1.1) where u_i are some integers $-\infty \leq u_i \leq \infty$.
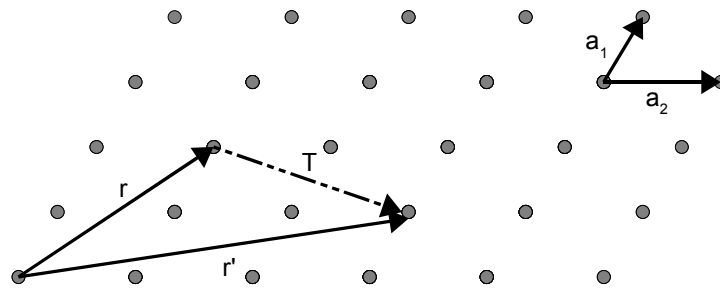
From this we can see that the crystal structure can be broken down as:

$$\text{lattice} + \text{basis} = \text{crystal structure} \tag{1.2}$$

We can perform a translation operation on a crystal by displacing it by an amount $\vec{T}$ where:

$$\vec{T} = u_1\vec{a_1} + u_2\vec{a_2} + u_3\vec{a_3} \tag{1.3}$$

Clearly, $\vec{r} + \vec{T} = \vec{r}\,'$ if equation (1.1) is satisfied, so we can see $\vec{T}$ as being the vector distance between two lattice points.

Figure 1.1: Section of a 2-dimensional monoatomic crystal. The
atomic arrangement at **r** and **r'** look the same to observers at
these points, since **T** is a integer number of the primitive
translation vectors **a**$_1$ and **a**$_2$ (**T** = -**a**$_1$ + 2**a**$_2$).

The *primitive translation vectors*, as shown in Fig. 1.1 define the smallest possible volume (or in this case area) of a cell that can be used as a base pattern for the crystal structure.

Such a cell is called a *primitive (unit) cell*. There is always **one** lattice point per unit cell. Generally lattice points are shared by several cells, with the sum of the fractions of lattice points equalling 1 (within one primitive cell).

In three dimensions, the volume of the primitive cell is given by:

$$V_c = \left| \vec{a}_1 \cdot \left(\vec{a}_2 \times \vec{a}_3 \right) \right|$$

(1.4)

The basis of a primitive cell is called the *primitive basis*. No basis contains fewer particles than the primitive basis.

Although the number of particles for a given crystal structure is always the same, the choice of primitive cell is not unique.

A unique and symmetric way of choosing the primitive cell is known as the *Wigner-Seitz cell* and is shown below in Fig. 1.2:
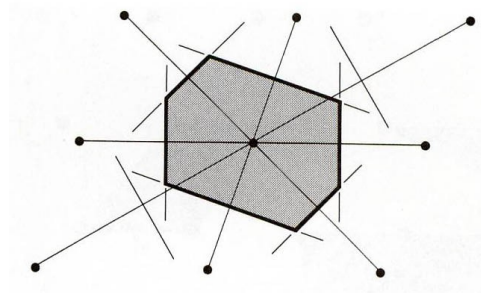
Figure 1.2: One way of choosing the primitive cell is as follows: 1) draw lines to connect a particular lattice point to all nearby lattice points; 2) at the midpoints and normal to the lines, draw additional lines and planes. The smallest volume enclosed in this process is the Wigner-Seitz primitive cell.

1.2   Types of Lattices

Crystals can be classified by the symmetry properties of the lattice.

Apart from translation, there are two types of lattice operations:

1. Reflection
2. Rotation

These are known as ***point operations***.

In two-dimensions, rotation about a lattice point preserves the translational properties for a rotation (in radians) of:

$$\theta = \frac{2\pi}{i}$$

(1.5)

Where $i \in \{1,2,3,4,6\}$. We can show (though it is not necessary here) that any other rotation will not preserve the lattice symmetry.

Note: There is no five-fold symmetry in a periodic lattice, as shown in Fig. 1.3. Mathematicians have shown that it is impossible to construct such a pattern from a single base pattern.

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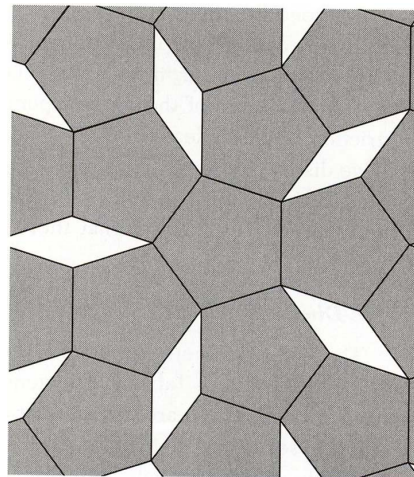
Figure 1.3: A fivefold axis of symmetry cannot exist in a periodic lattice, since it is impossible to fill the area of a plane with a connected array of pentagons. However, we can fill the area of a plane with two distinct designs. A crystal constructed from a non-random assembly of two unique designs is called a quasicrystal.

The most general type of two-dimensional lattice is an **oblique** lattice, which only preserves the lattice form under rotations of π or 2π. Although there are an infinite number of possible lattices, due to the limited possible point operations, there are clearly four distinct restrictions on the lattice (3 rotation, 1 reflection), leading to four **special lattice types**, which have higher degrees of symmetry than the oblique lattice. Along with the oblique lattice, there are **five** distinct lattices in 2-dimensions. These lattices are known as **Bravais lattices**. Figure 1.4 shows the five 2D Bravais lattices:
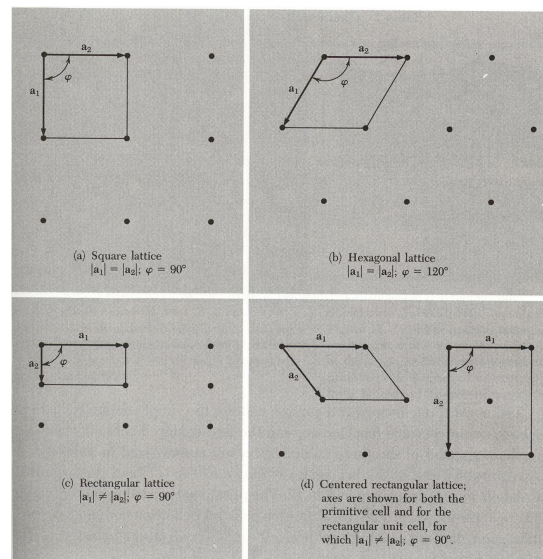

Figure 1.4: The five 2-dimensional Bravais lattice types.

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In three dimensions, there are **seven** crystal systems. The most general is the ***triclinic*** system. The other six are: ***monoclinic***, ***orthorhombic***, ***tetragonal***, ***cubic***, ***trigonal*** and ***hexagonal***. There are also **six** lattice centrings, shown below with there usual labels in brackets:

- ***Primitive-*** (or ***simple-***) ***centred*** (P): lattice points on the cell corners only;
- ***Body-centred*** (I): additional lattice point at centre of cell;
- ***Face-centred*** (F): additional lattice point at centre of each face;
- ***Single face-centred*** (***A-***, ***B-*** or ***C- centred***): additional lattice point at the centre of one face.

This would suggest that there might be 42 possible lattices. However, most of these are degenerate (i.e. they are equivalent to another lattice form). Bravais (1845) showed that there are, in fact, only **14** lattices in 3D, called Bravais lattices.
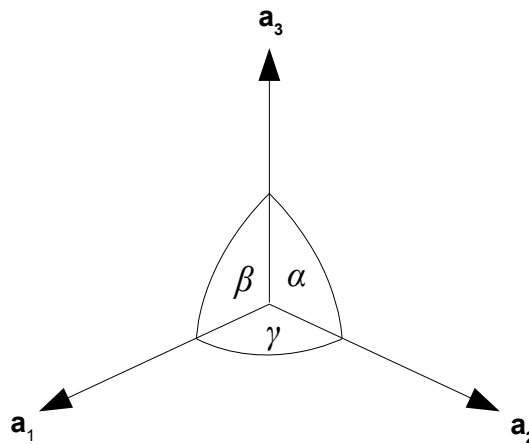
Figure 1.5: Diagram of conventional cell axes,
showing standard notation for angle labels.

Table 1.2.1 shows the main properties of the 3D crystal systems (number of lattices, conventional cell axes and vertex angles). The angles are as defined in Fig.1.5:

Table 1.2.1: The 14 Bravais Lattices in 3 Dimensions

System	Number of Lattices	Conventional Cell Axes and Angles
Triclinic	1	$a_1 \neq a_2 \neq a_3$ $\alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$ $\alpha = \gamma = \dfrac{\pi}{2} \neq \beta$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$ $\alpha = \beta = \gamma = \dfrac{\pi}{2}$
Tetragonal	2	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \gamma = \dfrac{\pi}{2}$
Cubic	3	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = \dfrac{\pi}{2}$
Trigonal	1	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma < \dfrac{2\pi}{3} \wedge \neq \dfrac{\pi}{2}$
Hexagonal	1	$a_1 = a_2 \neq a_3$ $\alpha = \beta = \dfrac{\pi}{2} ; \ \gamma = \dfrac{2\pi}{3}$

Note:

The notation a, b and c are often used to signify the lengths of the translational vectors.

a)   Important Lattices

The 3D Bravais lattices we are most concerned with are the cubic lattices.

As mentioned in table 1.2.1, there are three types of cubic lattices:

1.   *Simple cubic* (*sc*)

2.   *Body-centred cubic* (*bcc*)

3.   *Face-centred cubic* (*fcc*)

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Note:

Only the sc cubic crystal is a primitive cell. Fig. 1.6 and Fig. 1.7 show how to determine the primitive cells of bcc and fcc cubic crystals:
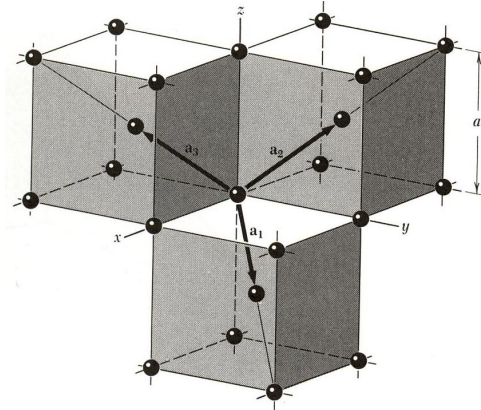
Figure 1.6: Primitive translational vectors of the body-centred cubic lattice. The primitive cell, on completion, is a rhombohedron. In terms of the cube edge *a*, the primitive translational vectors are given by:

$$\vec{a}_1 = \frac{1}{2}a(\hat{x}+\hat{y}-\hat{z}); \quad \vec{a}_2 = \frac{1}{2}a(-\hat{x}+\hat{y}+\hat{z}); \quad \vec{a}_3 = \frac{1}{2}a(\hat{x}-\hat{y}+\hat{z})$$
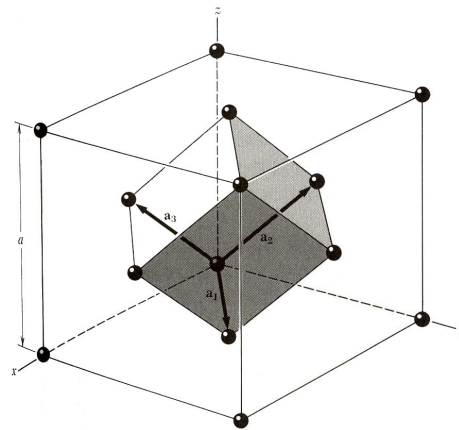
Figure 1.7: Rhombohedral primitive cell and primitive translational vectors of the face-centred cubic lattice. In terms of the cube edge a, the primitive translational vectors are:

$$\vec{a}_1 = \frac{1}{2}a(\hat{x}+\hat{y}); \quad \vec{a}_2 = \frac{1}{2}a(\hat{y}+\hat{z}); \quad \vec{a}_3 = \frac{1}{2}a(\hat{z}+\hat{x})$$

When considering cubic lattices, we would prefer to work in Cartesian coordinates, because they are mathematically simpler to use.

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Thus, we can define a ***conventional unit cell***, whose sides are a_0. These can be seen in Fig. 1.8:
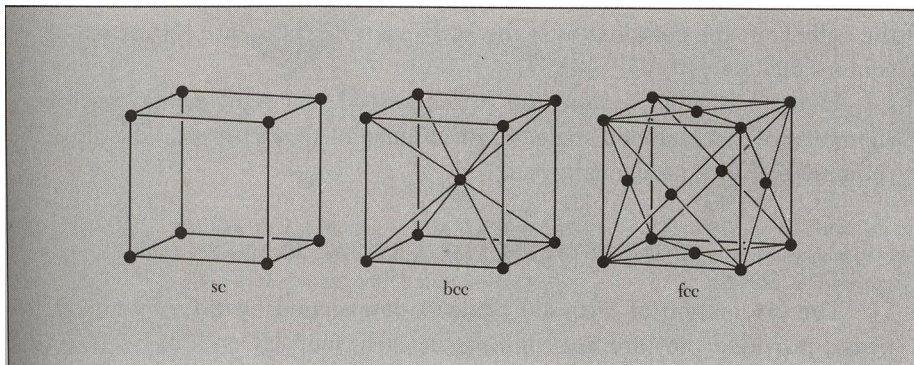

Figure 1.8: Conventional cells of the three cubic lattice types.

Note:

This is not the same as the primitive unit cell, which must always have just 1 lattice point. For a conventional cell, the number of lattice points are:

- Simple cubic – 1 lattice point (conventional cell = primitive cell);

- Body-centred cubic – 2 lattice points;

- Face-centred cubic – 4 lattice points.

1.3   Bases, Structures and Close-Packing

A basis may comprise a single atom, e.g. Cu, or it could consist of many atoms.

There are several key structures which arise from such bases.
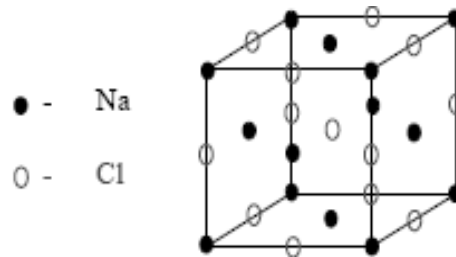
a)   Sodium-Chloride (rock-salt) structure

This consists of two inter-penetrating fcc lattices, decorated with a basis of Na at the origin and Cl at $\dfrac{\vec{a}}{2}$ (½,0,0).

The conventional cell has atoms at the points. Coordinates written this way imply fractions of the unit cell along each of the lattice vectors (not necessarily Cartesian).

Sodium (Na+): $\left\{\dfrac{1}{2},0,0\right\}; \quad \left\{0,\dfrac{1}{2},0\right\}; \quad \left\{0,0,\dfrac{1}{2}\right\}; \quad \left\{\dfrac{1}{2},\dfrac{1}{2},\dfrac{1}{2}\right\}$

Chloride (Cl⁻): $\left\{0,0,0\right\}; \quad \left\{\dfrac{1}{2},\dfrac{1}{2},0\right\}; \quad \left\{\dfrac{1}{2},0,\dfrac{1}{2}\right\}; \quad \left\{0,\dfrac{1}{2},\dfrac{1}{2}\right\}$
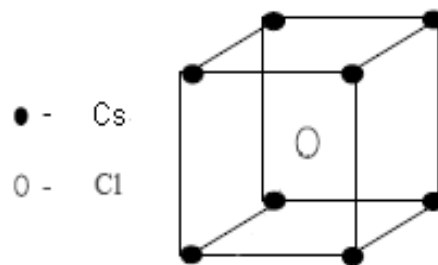
Figure 1.9: Conventional cell of the
Sodium Chloride structure

b) Caesium Chloride structure

This consists of two inter-penetrating sc lattices. The conventional cell looks like a bcc lattice, but the central atom is different from those at the vertices.

The structure is decorated with a basis of Cs at the origin, Cl at $\frac{1}{2}\left(\vec{a}+\vec{b}+\vec{c}\right)$.

Figure 1.10: Conventional cell of the
Caesium Chloride structure

c) Close-Packed Structures

If we assume that atoms are uniform spheres, we can define a close packed structure, in which the packing fraction, the ratio of the volume of the spheres to the volume of the cell structure is maximised.

In 2-dimensions, this is called circle packing and there is only one way to close-pack circles: the hexagonal lattice (in this case the packing fraction refers to the relative areas).

The packing fraction of the hexagonal lattice is $\eta=\dfrac{\pi\sqrt{3}}{6}\approx0.907$.

In 3-dimensions, close-packing is known as sphere packing and two close-packed structures exist. These close-packed structures are:

1. *Cubic close-packing* (*fcc*);

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2. *Hexagonal close-packing* (*hcp*).

These are produced by placing an additional layer of spheres on top of a hexagonal lattice. There are two possible locations to place a sphere, corresponding to the two close-packed structures.
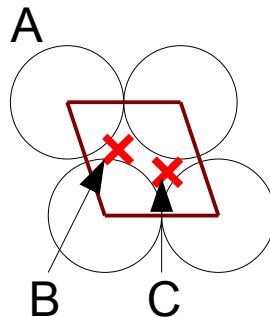
Figure 1.11: Diagram of sphere close-packing. In the second layer, a sphere can be placed at site B without loss of generality. In the third layer, either site A or C can be chosen.

Fig. 1.11 shows how close sphere packing is achieved. The sequence ABAB... corresponds to the hcp structure. The sequence ABCABC... corresponds to the fcc structure.

Both fcc and hcp structures have a packing fraction of $\eta = \dfrac{\pi}{3\sqrt{2}} \approx 0.7405$.

Kepler conjectured that these close-packed structures are the densest possible (for spheres).Gauss proved that they are the densest form of lattice and the general proof of the conjecture was completed in 1998.

We usually prefer to work with the conventional cells and their properties are summarised in table 1.3.1 below:

Table 1.3.1: Comparison of Close-Packed 3D Lattices

Name	Conventional Cell Axes	Conventional Angles	Spheres per Cell	Nearest Neighbours	Sequence
hcp	$a_1 = a_2$ $a_3 = 2\sqrt{\dfrac{2}{3}}$	$\alpha = \beta = \dfrac{\pi}{2}$ $\gamma = \dfrac{2\pi}{3}$	2	12	ABA
fcc	$a_1 = a_2 = a_3$	$\alpha = \beta = \gamma = \dfrac{\pi}{2}$	4	12	ABC

Structures of the Elements

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As mentioned previously, certain elements such as copper may have single-atom bases.

Wavefunctions are approximately spherical, so we would expect the close-packed sphere structures to be prevalent.

Indeed, hcp is the most common structure, with fcc coming second.

The simple cubic (sc) structure is very rare: only two examples are known in the natural elements, namely Polonium and one phase of Plutonium.

The hcp structure need not follow the maximum c/a ratio, since it is not constrained by symmetry.

Some elements form covalent bonds, such as O_2, N_2, I_2 etc. The basis of these is a binary molecule.

The group IV elements, except lead (*C*, *Si*, *Ge*, *Sn*) have a **diamond** structure.
The diamond structure is an fcc lattice decorated by a basis of two atoms: one at the origin, the other at $\frac{1}{4}\left(\vec{a}+\vec{b}+\vec{c}\right)$.

The diamond conventional cell looks like an fcc lattice, but extra lattice points are placed at:

$$\left\{\frac{1}{4},\frac{1}{4},\frac{1}{4}\right\}; \quad \left\{\frac{1}{4},\frac{3}{4},\frac{3}{4}\right\}; \quad \left\{\frac{3}{4},\frac{1}{4},\frac{3}{4}\right\}; \quad \left\{\frac{3}{4},\frac{3}{4},\frac{1}{4}\right\}$$

This arrangement gives a coordination number (number of nearest neighbours) of 4, with tetrahedral bonding. This is the ideal shape for the orbitals, resulting in an extremely strong, covalently bonded crystal.
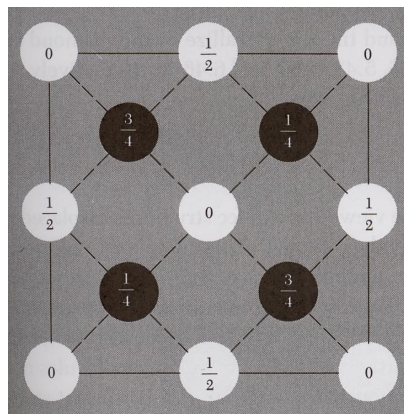
Figure 1.12: Atomic positions in the conventional cell of the diamond structure. The numbers signify the height of the lattice point in units of cube edge *a*. The white and black lattice points are on different fcc lattices, displaced by 1/4 *a* along the body diagonal.

Although we know that the basis is two atoms, there is no way to construct a primitive cell, as can be seen from Fig. 1.13.
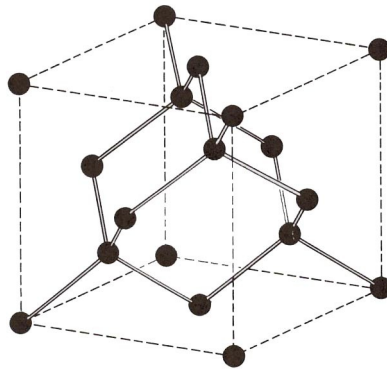
Figure 1.13: Conventional cell of the diamond
structure, showing the tetrahedral bond arrangement.

If the basis contains two chemically different atoms, then this type of lattice is called a ***zincblende*** structure.

Examples of a zincblende structure include *ZnSe*, *CdS*, *ZnS*, *GaAs* and so on.
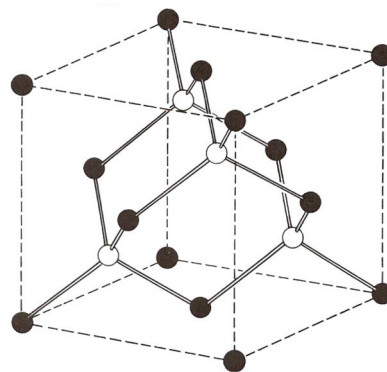
Figure 1.14: Conventional cell of the zincblende
crystal structure.

1.4   Point Defects

There are three main types of point imperfections or point defects in crystals:

1.   Vacant lattice sites

2.   Chemical impurities

3.   Additional atoms in non-regular lattice sites

a)   Lattice Vacancies

The simplest point imperfection is a ***lattice vacancy***, which is a missing atom/ion. This is commonly referred to as a ***Schottky defect***. These are often represented by a square.

In a perfect crystal, a Schottky defect can be achieved by transferring an atom from an interior lattice site to one on the surface of the crystal.

For a material in thermal equilibrium, there will always a certain number of Schottky defects because this disorder increases the entropy of the system.

In close-packed metals near the melting point, the number of lattice vacancies is of the order $10^{-3}-10^{-4}$. However, in some alloys, especially hard metal carbides such as *TiC*, the number of vacancies can be up to 50% of the available lattice sites.

Lattice vacancies are a thermodynamic effect and so the likelihood of a vacant site is probabilistic. In thermal equilibrium, the probability is: $P(n)=\exp\left(-\dfrac{E_V}{k_B T}\right)$

Where E_V is the energy required to move the atom from a lattice site inside the crystal to one on the surface.

If there are *N* atoms in a given crystal, then the number of vacancies *n* in thermal equilibrium is given by:

$$\frac{n}{N-n}=\exp\left(-\frac{E_V}{k_B T}\right)$$

(1.6)

If $n \ll N$, this simplifies to:

$$\frac{n}{N}\simeq\exp\left(-\frac{E_V}{k_B T}\right)$$

(1.7)

We can see from equation (1.7) that the equilibrium concentration of vacancies decreases with temperature.

Note:

The actual concentration of vacancies will be higher than the equilibrium concentration if the crystal is grown at a high temperature and cooled suddenly. The important thing to note is that when the crystal rapidly drops below the melting temperature, the defects are frozen into the material.

Another type of vacancy defect is called a ***Frenkel defect***, in which an atom moves from a lattice site to a non-regular lattice site. This is known as an ***interstitial position***.

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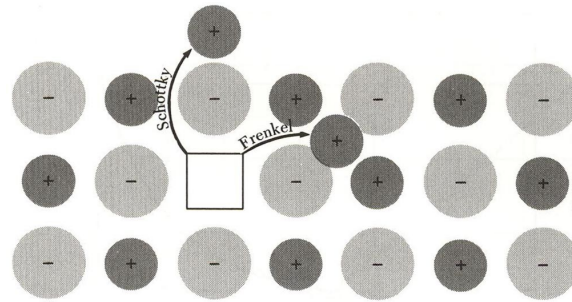
Figure 1.15: Schottky and Frenkel defects in an ionic crystal. The arrows indicate the displacement of the ions.
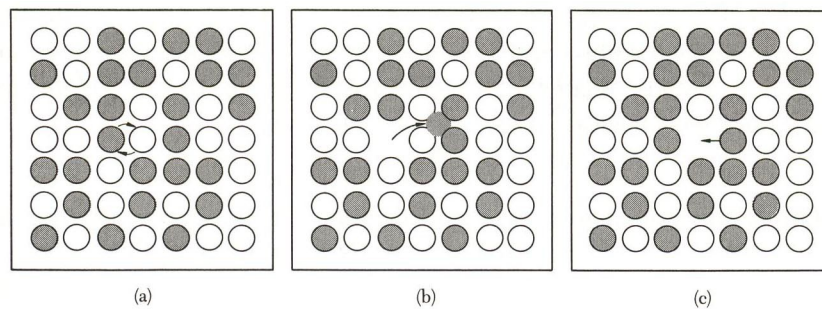
b) Diffusion

Diffusion can occur in one of three ways:

1. Interchange of atoms by rotation about a midpoint;
2. Migration of an atom through interstitial sites;
3. Atoms exchanging position with a vacant lattice site.

For this course, we are mainly concerned with Schottky defects, which are the most common lattice vacancies in pure alkali halides (e.g. *NaCl*).

Diffusion does occur, but we will mainly neglect it as it is a relatively slow process.

Figure 1.16: The three basic types of diffusion. (a) Interchange of atoms by rotation about a midpoint axis. More than two atoms may rotate together. (b) Atomic migration through interstitial sites. (c) Exchange of an atom with a vacant lattice site.

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c) Colour

Although pure alkali halide crystals are transparent in the visible spectrum, there are several ways that they can be coloured:

- by adding chemical impurities;

- by creating an excess of the metal ion;

- by bombardment from electrons, neutrons, *x*-rays, gamma-rays;

- by electrolysis.

A **colour defect** is a lattice defect that absorbs visible light. Ordinary lattice defects do not affect the visible colour of the crystal but they do affect the ultraviolet absorption. Point defects are also responsible for some of the electrical properties in semiconductor materials.

1.5 Dislocations

In the previous section, we were concerned with 0-dimensional point defects.

This section looks at 1-dimensional line defects, commonly referred to as **dislocations**.

These are mainly responsible for the mechanical properties of solids.

The **critical shear stress** σ_c is the elastic limit of shear displacement of atoms in the solid. For a perfect crystal, the theoretical critical shear stress is given by:

$$\sigma_c = G\frac{a}{2\pi d}$$

(1.8)

Where a is the interatomic spacing, d is the interplanar spacing and G is the shear modulus.

Even after taking into account various other factors which affect the shear stress, the observed (real) values are much lower than expected. This can only be due to imperfections which are sources of mechanical weakness: dislocations.

There are two main types of dislocation:

1. Edge dislocations;

2. Screw dislocations.

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a) Edge Dislocation
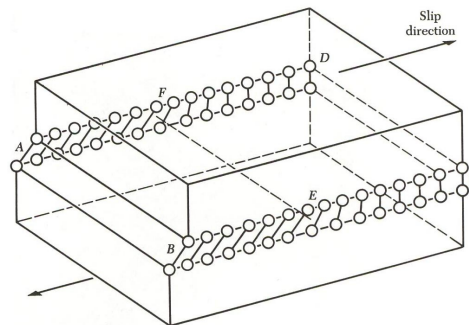
Figure 1.17: An edge dislocation EF in the plane ABCD. The
displacement in the slipped region ABEF is more than half a
lattice constant, whereas displacement of the unslipped region
FECD is less than half a lattice constant.

An edge dislocation is where part of the lattice has slipped along some slip plane. The boundary at which the slipped and unslipped regions meet is called the dislocation. The position of the dislocation is marked by the edge of the extra plane of atoms, seen in Fig. 1.18.
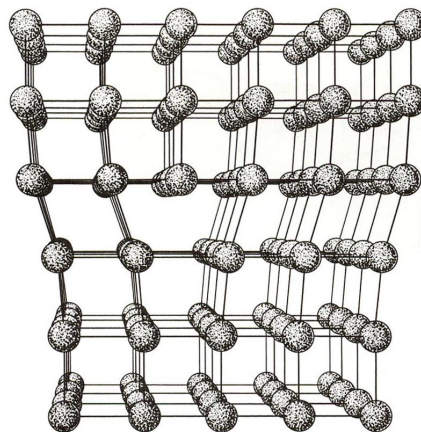
Figure 1.18: Structure of an edge dislocation. The
deformation can be thought of as caused by insertion of an
extra plane of atoms in the upper half of the crystal.

Simple edge dislocations extend indefinitely in the slip plane, which is **normal** to the slip direction.

Under a shearing force, the edge dislocation moves through the crystal. This motion, as shown in Fig. 1.19 is analogous to the movement of a ruck across a carpet. The ruck moves more easily than the entire carpet. When the atoms on one side of the slip plane move with respect to those on the other side, atoms at the slip plane experience repulsive terms from some neighbours and attractive forces from others. These forces approximately cancel, meaning that crystals with high levels of edge dislocations are highly plastic.
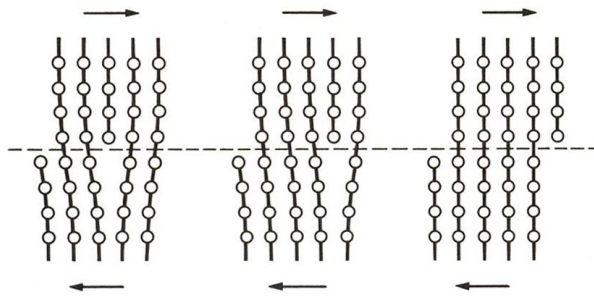
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Figure 1.19: Motion of a displacement under a
shear, tending to shift the upper surface of
the material to the right of the figure.

The passage of an edge dislocation through a crystal is equivalent to a slip displacement in one part
of the crystal.

b) Screw Dislocation

Again, the dislocation is the boundary between slipped and unslipped regions. However, unlike the
edge dislocation, the dislocation is **parallel** to the slip direction.
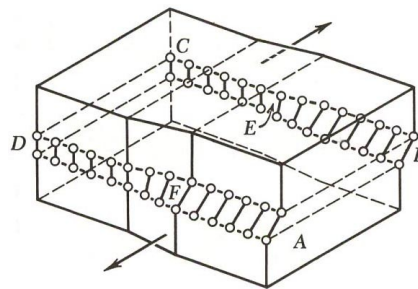
Figure 1.20: Depiction of a screw dislocation. The section
ABEF of the slip plane has slipped in the direction parallel to
the dislocation line EF. This can be seen as a helix of lattice
planes, such that we change planes by travelling completely
around the dislocation line.

This type of dislocation can be visualised by imagining cutting part way through the crystal with a
knife and shearing the crystal parallel to the cut, as seen in Fig. 1.21 below:
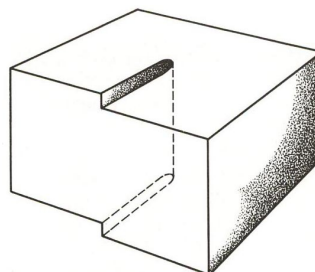
Figure 1.21: Another depiction of a screw
dislocation. The dislocation line is surrounded by
strained material.

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The effect of a screw dislocation is to transform successive atomic planes into the surface of a helix; this explains the name of this dislocation.
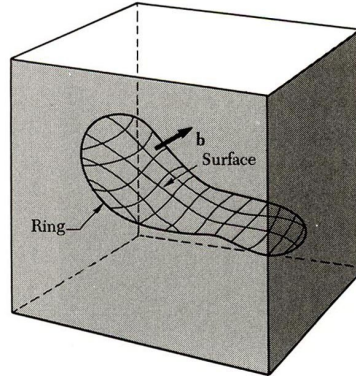
c) Burgers Vectors

Figure 1.22: Diagram showing a general dislocation ring in a medium (represented by the rectangular block). Here, **b** is the Burgers vector of the displacement.

More complicated dislocations can be constructed from combinations of edge and screw dislocations.

In general, we can form a dislocation pattern parametrised by some closed curve, or open curve ending on the surface on both sides, using the following process:

1. Make a cut along any simple surface bounded by the curve;

2. Displace the material on one side of this surface by some vector $\vec{b}$ relative to the other. This vector is called the ***Burgers vector***;

3. In regions where $\vec{b}$ is not parallel to the cut, the relative displacement either produces a gap in the half-surfaces, or causes them to overlap;

4. Finally, rejoin the material on both sides.

In order to maintain the crystallinity of the material, the Burgers vector must be equal to a lattice vector.

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Defects comprising purely edge or screw dislocations have Burgers vectors perpendicular (and lying in the slip plane) or parallel to the dislocation respectively.
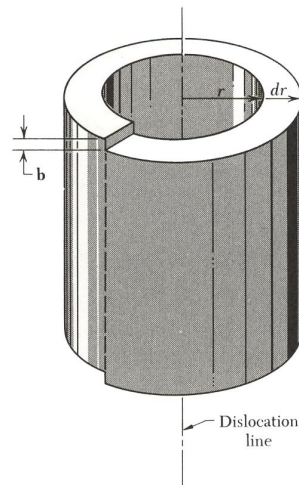
Figure 1.23: Shell of an elastically distorted material surrounding a screw dislocation with Burgers vector **b** perpendicular to the dislocation line.