Solid State Physics

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Abstract

These are a set of notes I have made, based on lectures given by M.Moore at the University of Manchester Jan-June '08. Please e-mail me with any comments/corrections: jap@watering.co.uk.

Contents

0.1 Introduction

We shall be focusing on just 4 of the many topics within this subject:

- Crystal structure;

- Lattice vibrations - phonons;

- Electrons in solids;

- Semi-conductors.

We shall use the 'standard model of solid state physics', which is the method by which we model electrons moving in some periodic potential, which is only due to the ionic core; we ignore inter-electron Coulomb interactions. We shall only talk about crystalline materials; ignoring amorphous solids, glasses etc.

1 Crystal Structures & Crystallography

- use to guess at the underlying atomic structure of a system.
A few definitions:

Structure   Array of atoms specified by a basis, plus a (Bravais) lattice.

Basis   Group of atoms (/ions/molecules) which is repeated.

Lattice   Pattern of repeats.

 For example, in 1D, we could use the basis of a diatomic molecule, such as HCl. We then specify a line of dots (the lattice sites), and structure (the shape of the HCl molecule). We then arrage the HCl along the lattice, where each lattice site is the same as every other; the HCl could be imagined as a small line, with two (different) blobs on its ends, and one blob is on a lattice point, and the next (same type of) blob on the next lattice point.

 In 3D, we say that the lattice is defined by primitive translation vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$; such that all points on it can be written as:
$$\boldsymbol{r} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$$

Where the n_i are arbitrary integers, including zero and negative numbers. Hence, the set of all possible points on the lattice is $\boldsymbol{r}$. We also have that the $\boldsymbol{a}_i$ have to be non-coplanar.
To define a basis, first we must define a 'primitive unit cell'. We have a cubic example in Fig (1). The volume of the box is given by the vector triple product:

$$V = |\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)|$$
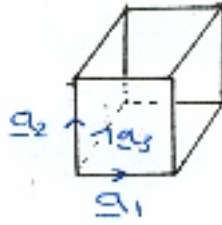
Figure 1: A cubic example of a primitive cell. The bottom LHS is the origin, with the $\boldsymbol{a}_i$ being measured with respect to it.

We specify the position of atom j within the primitive cell via:

$$\boldsymbol{r}_j = x_j \boldsymbol{a}_1 + y_j \boldsymbol{a}_2 + z_j \boldsymbol{a}_3 = (x_j, y_j, z_j)$$

Consider an atom A in the centre of the front-face. Hence, it is at:

$$(x_A, y_A, z_A) = (\tfrac{1}{2}, \tfrac{1}{2}, 0)$$

Similarly, consider an atom B in the middle of the RHS face, or an atom C in the very centre of the box:

$$(x_B, y_B, z_B) = (1, \tfrac{1}{2}, \tfrac{1}{2}) \qquad (x_C, y_C, z_C) = (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$$

Note, for a given lattice, more than one choice of unit cell is possible, as is shown in Fig (2). A
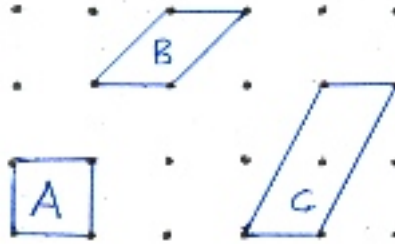
Figure 2: 2D square lattice. A, B are two choices of unit cell which have the smallest area, and are examples of primitive cells. Note, C is not a primitive cell.

primitive unit cell is the smallest possible, with only one lattice point per cell. In the above example, A contains 4 atoms per cell, but each corner is surrounded by 4 cells. Hence one lattice point per cell. However, unit cell C has 2 lattice points, and has an area twice that of A or B.

1.1 The Fundamental or Bravais Lattice

Lattices are characterised by their symmetry properties. One can always construct a unit cell with the same symmetries as the lattice; such as cell A in the above 2D square lattice. The unit

cells, stacked together, must fill all space, without leaving gaps (tessellation!). We can easily see by example that no Bravais lattice exists with 5-fold symmetry; see this by attemping to stack pentagons: there is always gaps left over.

Bravais lattices are the fundamental lattice types. They fill all space and are such that the enviroment of each lattice point is identical. An example of a non-Bravais lattice is a 'brick work construction'. Imagining a brick wall, where each lattice site is the vertex of a brick. Lattice sites on adjacent levels of the wall will not be in the same enviroment.

1.1.1   Two Dimensional Bravais Lattices

There are only 5 such lattices.

General Unit Cell   Consider the cell below in Fig (3).
We are able to form the *oblique lattice* if we have $a_1 \neq a_2$, and $\phi \neq 60°, 90°$.
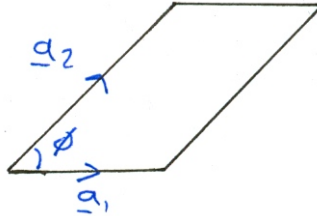
Figure 3: Oblique lattice. Also the form of the general 2D unit cell. We define $a_1 = |\mathbf{a}_1|, a_2 = |\mathbf{a}_2|$

Square Lattice   We use the above general cell, with $a_1 = a_2$, and $\phi = 90°$, to give us the *square lattice*. Note, it will have symmetries for rotations through $90°$.

Rectangular Lattice   We have a rectangular lattice if we have $a_1 \neq n_2$, but $\phi = 90°$. Now we only have symmetries for rotations through $180°$.

Triangle Lattice   Here, if we have $a_1 = a_2$ and $\phi = 60°$ or $120°$. This is also sometimes referred to as the hexagonal lattice.

Rhombic Lattice   This is for $a_1 = a_2$ and $\phi \neq 60, 90, 120°$. It is a centred rectangular structure, and is a non-primitive unit cell, as contains an internal lattice site. The rhombic lattice is non-primitive, as it can be seen that contains $4 \times \frac{1}{4} + 1 = 2$ lattice sites.

Oblique Lattice   This is the final one, and it is the one we used as a template to begin with.
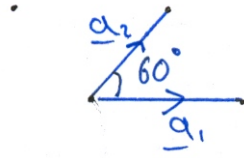
Figure 4: The triangular lattice.
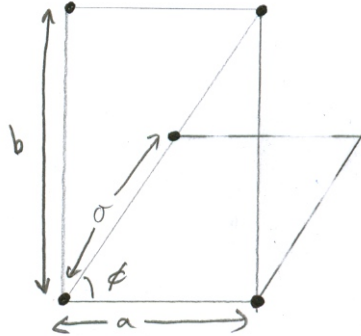
Figure 5: The rhombic lattice. Notice that the cell is not primitive, but a primitive cell can be constructed; the parallelogram squashed to the right. We define $\tan \phi = \frac{b}{a}$.

1.1.2   Three Dimensional Bravais Lattices

There are 14 of these in total, but we will only consider a few. The general one is the *triclinic lattice*. The general triclinic lattice is a unit cell, which is a parallelepiped with all sides different
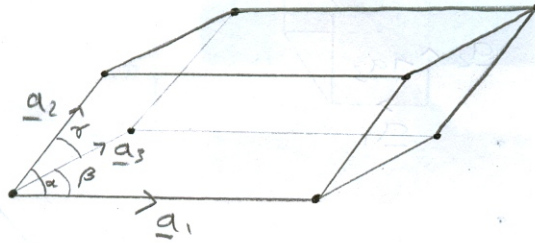
Figure 6: The triclinic lattice: the prototype for the general 3D Bravias lattice.

lengths, and all angle different from $90, 120°$. The remaining 13 lattices have some symmetry, such as relations between the sides or angles. We shall concentrate on 3:
Simple cubic (sc), body centred cubic (bcc) and face centred cubic (fcc).

Simple Cubic Lattice   Examples of such lattices is the Polonium crystal. Note, the simple cubic
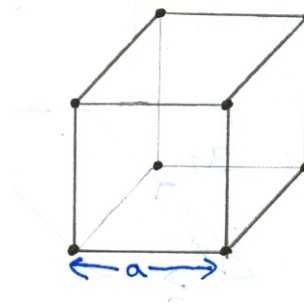
Figure 7: Simple cubic lattice, all sides have length a. An example of such a lattice is Polonium. In Polonium, $a = 3.34\text{Å}$

lattice is a primitive cell, as there are 8 corners, each of which is shared by 8 other cells.
The number of nearest neighbours can be seen to be 6.

 Packing fraction is the fraction of space filled by touching spheres at each lattice point. Visualise this by imagining each lattice site of be the centre of an atom, whose radius is $\frac{a}{2} \equiv r$. Hence, the packing fraction is:

$$\frac{\frac{4}{3}\pi r^3}{a^3} = \frac{4\pi}{3 \times 8} = \frac{\pi}{6} \approx 0.524$$

Hence, the packing fraction for all simple cubic lattices is 0.524, which we will see is quite small.

Body Centred Cubic   Examples of these are more numerous: Li, Na, Na, Fe. The bcc is a cube
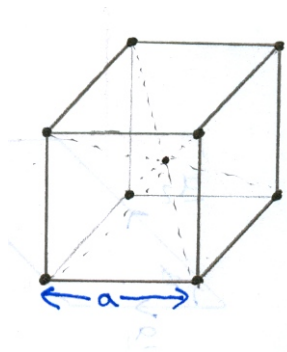
Figure 8: The conventional cell for the body centred cubic bcc. It has a lattice point in the centre of a cube. Note, it is not a primitive cell.

with lattice sites on its corners and centre. Hence, contains $8 \times \frac{1}{8} + 1 = 2$ lattice sites per unit cell. Hence, not a primitive unit cell. The primitive cell is possible to find, but is very hard to use & visualise.
The number of nearest neighbours can be computed from any lattice site; hence, using the centre atom, we see that there are 8. The nearest neighbour distance d is the same as the distance from

centre to corner; which, via trivial Pythagoras, is just:

$$2d = \sqrt{a^2 + a^2 + a^2} \quad \Rightarrow \quad d = \frac{\sqrt{3}}{2}a$$

The packing fraction (derived in example sheet) is 0.680. We state that the basis for the conventional unit cell is:

$$(0,0,0) \quad (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$$

Face Centred Cubic   This has lattice sites at each vertex, and one in the centre of each face. Examples of such structures are Sr, Ag, Cu, Ne.
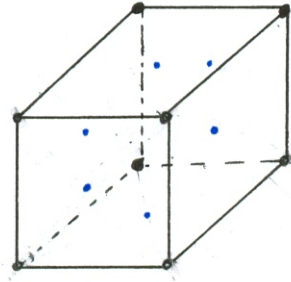
Figure 9: The conventional cell for the face centred cubic fcc. It has a lattice point on the centre of each face, as well as at each vertex. The Black points are on the vertices, blue on the faces. Each side has length a.

 If the nearest neighbour distance is d, it is just the distance from one vertex to the centre of its face:

$$d^2 = \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 \quad \Rightarrow \quad d = \frac{a}{\sqrt{2}}$$

The number of atoms in each conventional unit cell is given by:

$$8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 1 + 3 = 4$$

Where the 6 is the number of lattice sites on faces, each of which is shared by 2 other cells (the factor of $\frac{1}{2}$).
Although hard to visualise, the number of nearst neighbors is 12.
The packing fraction (again, on problem sheet) is 0.740.
The fcc actually has the highest packing fraction (hence giving it the name 'cubic close packed structure); a role that is shared only with the hexagonal close packed structure.
The basis is:

$$(0,0,0) \quad (0, \tfrac{1}{2}, \tfrac{1}{2}) \quad (\tfrac{1}{2}, 0, \tfrac{1}{2}) \quad (\tfrac{1}{2}, \tfrac{1}{2}, 0)$$

1.2   Miller Indices

These are indices for crystal planes: X-rays in X-ray crystallography are scattered by sets of parallel crystal planes.

Any plane is specified by 3 non-colinear points, such as the intercepts on the a_1, a_2, a_3 axes. That is, the translation vectors of the unit cell (or Bravais lattice).

So, to form the Miller indices:

- Take the reciprocal of the intercepts;

- Scale up so that they become integers.

So, for example, if we have a plane which intercepts the axes at $(2, 3, 2)$, its reciprocal is $(\frac{1}{2}, \frac{1}{3}, \frac{1}{2})$, and scaling (multiply by 6 in this case) results in $(3, 2, 3)$. These are the Miller indices.

If the intercept is negative, put a bar over the index. For example, for intercepts $(-3, 2, 2)$, we will have indices $(\bar{2}, 3, 3)$.

If the plane is parallel to an axis, its intercept will be at infinity, hence its index will be 0.

Planes with Miller indices (h, k, l) are parallel to those with (nh, nk, nl), for any integer n.

Using Fig (10) as a guide:
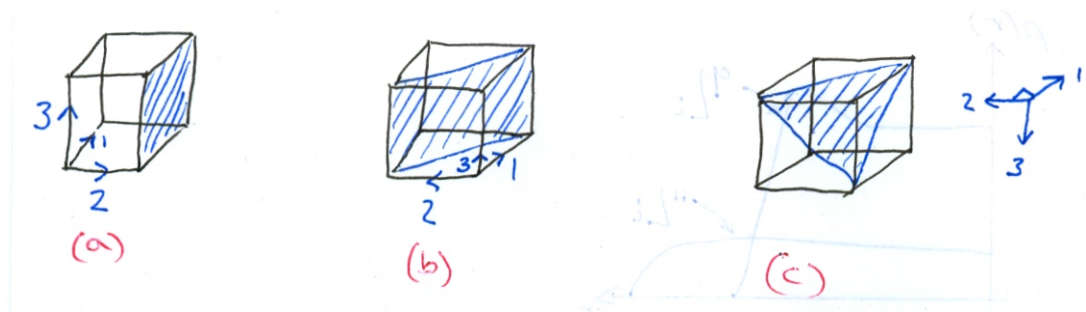
Figure 10: Planes through a unit cell. The axes are defined differently in each case. The axes for (c) are to the right, and are fixed on the front-right-face of the cube.

(a) has intercepts at $(\infty, 1, \infty)$ and therefore Miller indices $(0, 1, 0)$.
(b) has intercepts at $(1, 1, \infty)$, and indices $(1, 1, 0)$.
(c) has intercepts at $(1, 1, -1)$, and therefore indices $(1, 1, \bar{1})$.

1.2.1   Direction of a Vector

We use square brackets to denote vectors, and round brackets for Miller indices.

So, the indices are the smallest integers whose ratios are in the ratios of the components of the vector, reffered to the crystal axes. So, for example, if:

$$v = \frac{1}{3}a_1 + \frac{1}{3}a_2 + \frac{1}{6}a_3$$

Then it has indices $[2, 2, 1]$.

In general, direction $[h, k, l]$ is perpendicular to the plane of Miller indices (h, k, l).

1.3   Some Simple Crystal Structures

These are mainly non-elements.

1.3.1   CsCl - Cesium Chloride Structure

This is a bcc structure, where we can think of the vertices of the cube being Cl^- ions, and the centre point being a Cs^+ ion. However, if we switch everything round, its still the same structure. So, in each cell is:

$$8 \times \frac{1}{8} = 1Cl^-$$

And 1 Cs^+ ion per cell.

Hence, 1 molecule of CsCl per cell. Hence it is the primitive unit cell.

Each Cs^+ ion is surrounded by $8Cl^-$ ions (and vice-versa). Hence, we say that the *coordination number* is 8 (just the number of nearst neighbours).

The basis, as referred to a conventional simple cubic unit cell is:

$$Cl^- \; at \; (0, 0, 0) \quad Cs^+ \; at \; (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$$

1.3.2   NaCl - Sodium Chloride Structure

This is based upon the fcc, with Cl^- at the corners and cube faces. However, there are also Na^+ in the centre of the cube, and centre of all edges of the cube. This is hard to draw, so I wont!

The coordination number is 6.

In each conventional unit cell is:

$$Cl^- \;\; : \;\; 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$

$$Na^+ \;\; : \;\; 12 \times \frac{1}{4} + 1 = 4$$

Hence, 4 NaCl molecules in the conventional unit cell. Hence, not a primitive cell.

The basis, as referred to the simple cubic cell:

$$Cl^- \;\; : \;\; (0, 0, 0) \, (\tfrac{1}{2}, \tfrac{1}{2}, 0) \, (\tfrac{1}{2}, 0, \tfrac{1}{2}) \, (0, \tfrac{1}{2}, \tfrac{1}{2})$$
$$Na^+ \;\; : \;\; (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) \, (0, 0, \tfrac{1}{2}) \, (0, \tfrac{1}{2}, 0) \, (\tfrac{1}{2}, 0, 0)$$

The basis, as referred to the fcc lattice:

$$Cl^- : (0, 0, 0) \quad Na^+ : (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2})$$

1.3.3 Close Packing of Elements

We refer to the periodic table:
Columns 3-7 have various structures, but often not close packed, due to covalent bonding (such as in diamond).
The metals in 1-2, transition metals and inert gases are all only one of 3 structures: bcc (pf = 0.68), fcc (pf = 0.74) and hexagonal close packed (hcp) (pf = 0.74). Note, the latter two have the highest known packing fraction (pf).

 Packing of spheres:
First layer: Position A: hexagonal lattice.
Second layer: Position B or C. Suppose B.
Third layer: either A or C.
So, if:
ABABABABAB... then hcp
ABCABCABC... then fcc.

1.3.4 The Diamond Structure

Elements such as C, Si, Gr, Sn form these structures.
Carbon: fcc lattice with a basis:
$$(0,0,0) \ (\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4})$$
Which is repeated at each lattice site of the fcc lattice.
Each atom is surrounded by 4 nearest neighbours at the vertices of a regular tetrahedron.
A result of sp^3 directional covalent bonding (an unexplained term!)
This gives a very open structre, with pf = 0.34.

1.4 X-ray Diffraction

To see crystal structure, one needs to probe them with particles/photons whose wavelength is of the order the interatomic spacing. i.e.:
$$\lambda \approx 1\text{Å} = 1nm$$

We have the useful relation:
$$\lambda(\text{Å}) = \frac{12.4}{E(keV)}$$
So, we need energies of $10 - 50$keV: X-rays!

 There are problems: the intensity of scattering off atoms goes like Z^2; hence, if two species present, one such as hydrogen ($Z = 1$), and something higher, say $Z = 18$, then it will be very hard to 'see' the hydrogen.

 If we use neutrons as probes, then, via $E = \frac{p^2}{2m}$ and $p = \frac{h}{\lambda}$, we have:
$$\lambda(\text{Å}) = \frac{0.28}{[E(eV)]^{1/2}}$$

Thus, for $\lambda \approx 1\text{Å}$, we need $E \approx 0.08\text{eV}$. Which are thermal neutrons; and are very expensive to produce!

If we use electrons, then the results are hard to interpret, due to multiple scattering inside the substance; and are thus restricted to surface investigations.
Neutrons and X-rays scatter only once when inside the crystal, which makes the data easier to understand.

Whatever projectile is used, scattering occurs only at angles determined by Bragg's law:

1.4.1   Bragg's Law

Crystal acts like a diffraction grating, and the scattering angle is determined by which set of parallel plates the wave scatters from. We get constructive interference; i.e. a strong scattered beam only
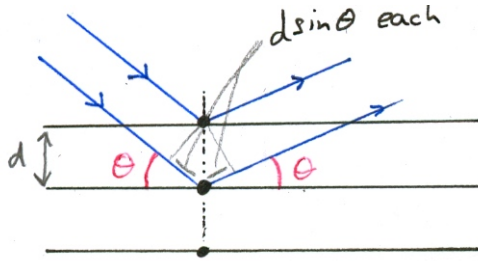
Figure 11: Bragg diffraction. Each plane is spaced by d. Each wave has an angle of incidence θ. The path difference between two outgoing waves is $2d\sin\theta$ - each contribution is the same, although the diagram dosent look like it!

is path difference between successive planes is an integer number of wavelengths. That is:

$$2d\sin\theta = n\lambda \qquad n = 1, 2, \ldots \tag{1.1}$$

This is known as *Bragg's law.*

For X-rays, the intensity of reflection from a given ste of planes increases with the density of electrons in the plane. Consider a simple cubic structure.

In general, for a plane with Miller indices (h, k, l), the planes are spaced by an amount:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{1.2}$$

Intensity of scattering off planes with low Miller indices is greater, as they have a higher density of atoms on them.

Thus, we get Bragg reflections at:

$$\sin\theta = \frac{n\lambda}{2a}\sqrt{h^2 + k^2 + l^2} < 1$$

Where a is the lattice spacing, and n the 'order' of reflection.
As h, k, l increase, the Bragg lines (or spots) get fainter; and disappear altogether if $\sin\theta > 1$.
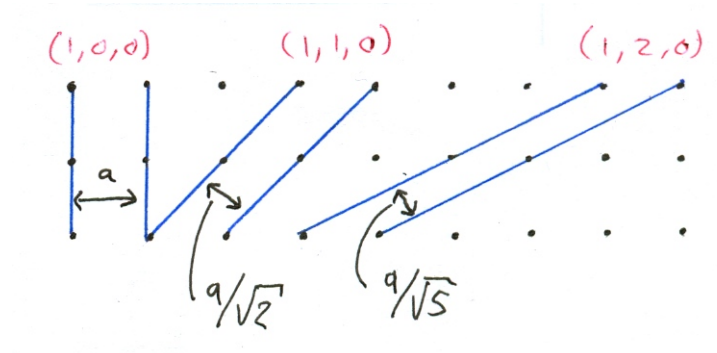
Figure 12: Planes in a simple cubic structure. Indicated are the Miller indices for each plane, as well as the plane spacing d.

1.4.2   Indexing of Lines

Suppose a relection takes place at θ_2, θ_1. Then:

$$\frac{\sin \theta_2}{\sin \theta_1} = \frac{\sqrt{h_2^2 + k_2^2 + l_2^2}}{\sqrt{h_1^2 + k_1^2 + l_1^2}}$$

Now, h, k, l are always integers; so, we (theoretically) play around with various combinations of them, untill we obtain the measured ratio. Hence, this allows us to determine the likely Miller indices of the plane producing the lines.

This process is known as *indexing*.

1.5   The Reciprocal Lattice

In solid state physics, we are often concerned with the scattering of waves (be they EM, acoustic, de Broglie matter waves) in a crystal lattice.

Bragg's law applies to any such wave, but the form $2d \sin \theta = n\lambda$ is not very convenient for practical applications. So, for such applications, we use it in terms of the reciprocal lattice vectors.

Consider the wavevector $\boldsymbol{k}$. Thus:

$$\boldsymbol{k} = k\hat{\boldsymbol{k}} = \frac{2\pi}{\lambda}\hat{\boldsymbol{k}}$$

Where $\hat{\boldsymbol{k}}$ is the unit vector along the wave direction. Vectors measured in this dimension (i.e. having units $[\mathrm{L}^{-1}]$) are called 'vectors in k-space'.

1.5.1   Definition of Reciprocal Lattice

Suppose:

$$\boldsymbol{R} = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3$$

Where the n_i are integers, or zero; and $\boldsymbol{a}_i$ are the basis generators, in the real space of the lattice.

Reciprocal lattice: set of points in k-space, such that:

$$e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = 1 \tag{1.3}$$

We define basis vectors $\boldsymbol{b}_j$ in k-space by:

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}$$

We define the reciprocal lattice in k-space, of the original lattice (original lattice basis: $\boldsymbol{a}_i$), as being given by:

$$\boldsymbol{G} = m_1\boldsymbol{b}_1 + m_2\boldsymbol{b}_2 + m_3\boldsymbol{b}_3 \tag{1.4}$$

So that $\boldsymbol{G}$ is any lattice point in the reciprocal lattice; where m_i are positive, negative and zero integers.

Suppose we had a 2D square reciprocal lattice; then:

$$|b_1| = |b_2| = \frac{2\pi}{a}$$

So that:

$$\boldsymbol{G} = m_1\boldsymbol{b}_1 + m_2\boldsymbol{b}_2$$

Then, to find the reciprocal lattice basis vectors, in terms of the real-space basis vectors, we consider:

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij} \qquad \boldsymbol{a}_1 = a\hat{\boldsymbol{i}} \quad \boldsymbol{a}_2 = a\hat{\boldsymbol{j}}$$

Hence, we can easily see that we must have:

$$\boldsymbol{b}_1 = \frac{2\pi}{a}\hat{\boldsymbol{i}} \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}\hat{\boldsymbol{j}}$$

Suppose instead that we had a rectangular lattice; then $\boldsymbol{a}_1 = a\hat{\boldsymbol{i}}$ and $\boldsymbol{a}_2 = b\hat{\boldsymbol{j}}$; then $\boldsymbol{b}_1 = \frac{2\pi}{a}\hat{\boldsymbol{i}}$ and $\boldsymbol{b}_2 = \frac{2\pi}{b}\hat{\boldsymbol{j}}$.

Consider the 1D case; where, in the space-lattice (i.e. not the reciprocal lattice), we have $\boldsymbol{a} = a\hat{\boldsymbol{i}}$; then the reciprocal basis vector is just $\boldsymbol{b} = \frac{2\pi}{a}\hat{\boldsymbol{i}}$. Hence, any point on the reciprocal lattice is specified by:

$$\boldsymbol{G} = m\frac{2\pi}{a}\hat{\boldsymbol{i}}$$

Where m is an integer.

So, we find the set of reciprocal lattice basis vectors by finding those which are orthogonal to the real-space lattice bases. In 3D this is a little more complicated, but can be done via:

$$\boldsymbol{b}_1 = \frac{2\pi}{V}\boldsymbol{a}_2 \times \boldsymbol{a}_3 \tag{1.5}$$

$$\boldsymbol{b}_2 = \frac{2\pi}{V}\boldsymbol{a}_3 \times \boldsymbol{a}_1 \tag{1.6}$$

$$\boldsymbol{b}_3 = \frac{2\pi}{V}\boldsymbol{a}_1 \times \boldsymbol{a}_2 \tag{1.7}$$

Notice, they are cyclic. We have that V is the volume of the parallelepiped defined by the vectors $\boldsymbol{a}_i$. That is:

$$V = |\boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3)| \tag{1.8}$$

So, to see if our generating expressions above do produce $\boldsymbol{b}_i$ such that they are orthogonal to $\boldsymbol{a}_j$, we just need to do the check:

$$\boldsymbol{b}_1 \cdot \boldsymbol{a}_1 = \frac{2\pi}{V} \boldsymbol{a}_1 \cdot (\boldsymbol{a}_2 \times \boldsymbol{a}_3) = 2\pi$$

And one can check for all other combinations.

1.5.2 Examples

Simple Cubic   Here, we have the following real-space vectors:

$$\boldsymbol{a}_1 = a\hat{\boldsymbol{i}} \qquad \boldsymbol{a}_2 = a\hat{\boldsymbol{j}} \qquad \boldsymbol{a}_3 = a\hat{\boldsymbol{k}}$$

And we can easily see that the reciprocal lattice vectors are just:

$$\boldsymbol{b}_1 = \frac{2\pi}{a}\hat{\boldsymbol{i}} \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}\hat{\boldsymbol{j}} \qquad \boldsymbol{b}_3 = \frac{2\pi}{a}\hat{\boldsymbol{k}}$$

So, we see that both the real and reciprocal lattice basis vectors are simple cubic; with the reciprocal unit cell having side length $\frac{2\pi}{a}$.

Face Centred Cubic   Here, the generators or the primitive unit cell are:

$$\boldsymbol{a}_1 = \tfrac{a}{2}(\hat{\boldsymbol{j}} + \hat{\boldsymbol{k}}) \qquad \boldsymbol{a}_2 = \tfrac{a}{2}(\hat{\boldsymbol{k}} + \hat{\boldsymbol{i}}) \qquad \boldsymbol{a}_3 = \tfrac{a}{2}(\hat{\boldsymbol{i}} + \hat{\boldsymbol{j}})$$

We can get that the reciprocal vectors are given by:

$$\boldsymbol{b}_1 = \tfrac{2\pi}{a}(\hat{\boldsymbol{j}} + \hat{\boldsymbol{k}} - \hat{\boldsymbol{i}}) \qquad \boldsymbol{b}_2 = \tfrac{2\pi}{a}(\hat{\boldsymbol{k}} + \hat{\boldsymbol{i}} - \hat{\boldsymbol{j}}) \qquad \boldsymbol{b}_3 = \tfrac{2\pi}{a}(\hat{\boldsymbol{i}} + \hat{\boldsymbol{j}} - \hat{\boldsymbol{k}})$$

Which are actually the primitive basis vectors of the bcc conventional unit cell; with side length $\frac{4\pi}{a}$.

Body Centred Cubic   As we just saw, the reciprocals of the fcc were the bcc; hence, the reciprocals of the bcc are the fcc.
The reciprocal lattice of the bcc is fcc, with conventional cell side $\frac{4\pi}{a}$.

1.5.3 Theorems

Theorem 1   Every reciprocal lattice vector is normal to a lattice plane of the crystal lattice.

Proof:

$$\boldsymbol{G} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$$

Will be normal to the plane through 3 points, $n_1\boldsymbol{a}_1, n_2\boldsymbol{a}_2, n_3\boldsymbol{a}_3$, if $\boldsymbol{G}$ is normal to any vector in the plane. That is, if all:

$$n_1\boldsymbol{a}_1 - n_2\boldsymbol{a}_2$$
$$n_1\boldsymbol{a}_1 - n_3\boldsymbol{a}_3$$
$$n_2\boldsymbol{a}_2 - n_3\boldsymbol{a}_3$$

Lie in the plane. So, for normality:

$$\boldsymbol{G} \cdot (n_1\boldsymbol{a}_1 - n_2\boldsymbol{a}_2) = 0$$
$$\boldsymbol{G} \cdot (n_1\boldsymbol{a}_1 - n_3\boldsymbol{a}_3) = 0$$
$$\boldsymbol{G} \cdot (n_2\boldsymbol{a}_2 - n_3\boldsymbol{a}_3) = 0$$

Noting orthogonality of $\boldsymbol{a}_i$ and $\boldsymbol{b}_j$; we see that this is just:

$$2\pi(hn_1 - kn_2) = 0$$
$$2\pi(hn_1 - ln_3) = 0$$
$$2\pi(kn_2 - ln_3) = 0$$

Hence, we see that:

$$n_1 \propto \frac{1}{h} \qquad n_2 \propto \frac{1}{k} \qquad n_3 \propto \frac{1}{l}$$

But, the Miller indices of the crystal plane through the points $n_1\boldsymbol{a}_1, n_2\boldsymbol{a}_2, n_3\boldsymbol{a}_3$ are the h, k, l above (upto a muliplicative factor). Thus, we see that any vector $\boldsymbol{G}$ in the reciprocal lattice is normal to the plane of the crystal lattice with Miller indices h, k, l.

Theorem 2   The spacing d os the planes with Miller indices h, k, l of the crystal lattice, is equal to:

$$d = \frac{2\pi}{|\boldsymbol{G}(h, k, l)|}$$

Proof:

 Consider a plane (h, k, l); with normal unit vector $\hat{\boldsymbol{G}}$ to the plane. Consider a point $\boldsymbol{R}$ on the plane, as measured from some origin. Where the origin is on a lattice site of a plane parallel to (h, k, l).
Let d be the distance between two parallel planes:

$$d = \boldsymbol{R} \cdot \hat{\boldsymbol{G}}$$

Now:

$$\hat{\boldsymbol{G}} = \frac{\boldsymbol{G}(h, k, l)}{|\boldsymbol{G}(h, k, l)|}$$

Now, as $\boldsymbol{R}$ is a vector of the Bravais lattice, we also have the relation:

$$e^{i\boldsymbol{G} \cdot \boldsymbol{R}} = 1$$

Hence, we immediately see that $\boldsymbol{G} \cdot \boldsymbol{R} = 2\pi n$. Thus, putting this all together, we see that:

$$d = \frac{2\pi n}{|\boldsymbol{G}(h,k,l)|} \tag{1.9}$$

And, for the shortest distance, $n = 1$.
Recall, for the simple cubic lattice, we have:

$$\boldsymbol{G} = \frac{2\pi}{a}(h\hat{\boldsymbol{i}} + k\hat{\boldsymbol{j}} + l\hat{\boldsymbol{k}})$$

Thus, for $n = 1$:

$$d = \frac{2\pi}{|\boldsymbol{G}(h,k,l)|} = 2\pi \frac{a}{2\pi\sqrt{h^2 + k^2 + l^2}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

A result we had before.

1.5.4   Bragg's Law
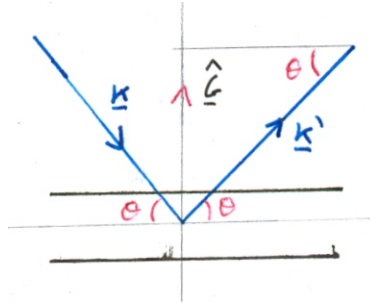
Figure 13: Bragg diffraction, showing the vector $\hat{G}$, normal to the plane.

From the geometry, if scattering takes place of a plane with Miller indices h, k, l, and unit vector normal $\hat{\boldsymbol{G}}(h, k, l)$, we see that:

$$\boldsymbol{k} - \boldsymbol{k}' = A\hat{\boldsymbol{G}}$$

Where A is some constant. But, $|k| = |k'| = k = \frac{2\pi}{\lambda}$, as the scattering is elastic; but, also from the geometry of the figure:

$$2k \sin \theta = A$$

And, Bragg's law is $2d \sin \theta = n\lambda$; thus:

$$A = \frac{2kn\lambda}{2d} = \frac{2\pi n}{d} = |\boldsymbol{G}|$$

Hence:

$$\boldsymbol{k} - \boldsymbol{k}' = \boldsymbol{G} \tag{1.10}$$

Where we have that the difference between the incoming and outgoing wave is the reciprocal lattice vector.

For strong reflection, incoming and ougoing wavs must have wavevectors which differ by a reciprocal lattice vetor.

1.5.5   The Ewald Construction

The probability of exactly satisfying $\boldsymbol{k} - \boldsymbol{k}' = \boldsymbol{G}$ is small, for fixed $\boldsymbol{k}$. To see this:

 Put the tip of $\boldsymbol{k}$ on a reciprocal lattice point, and describe a circle/sphere with the tip of $\boldsymbol{k}'$.
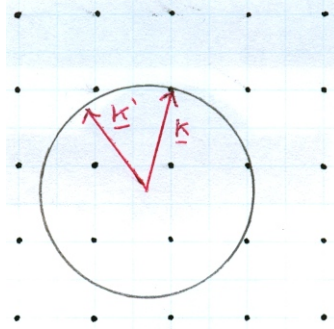
Figure 14: Showing how the 2D version of the Ewald sphere is constructed. The vector $\boldsymbol{k}$ has a fixed origin, and fixed tip, on a lattice point. The vector $\boldsymbol{k}'$ then sweeps out a circle - both vectors have the same length. Strong reflection only then occurs if the circle exactly cuts a lattice point; which is only once or twice in this diagram. Hence, low probability.

 We can ensure Bragg points are obtained by various techniques:

The Laue Method   Here, we improve the possibility of strong diffraction by using a range of wavelengths:

$$\lambda_1 \to \lambda_2 \qquad k_1 \to k_2$$

So, the Ewald sphere looks different here:
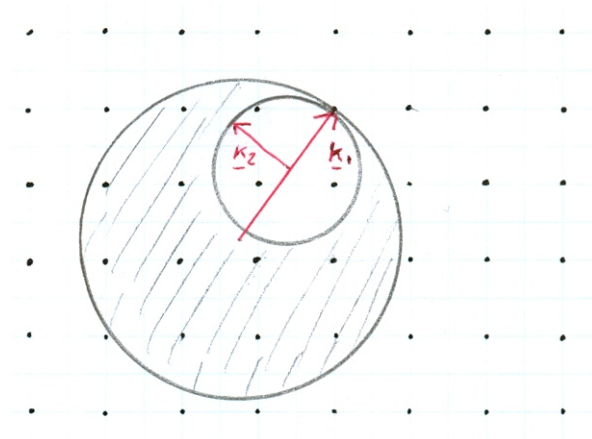
Figure 15: The Laue method. All lattice points within shaded region are 'seen' by method.

All reciprocal lattice vectors within the shaded region provide diffraction maxima: i.e. the allowed $\boldsymbol{G}$ vectors.

The Laue method is actually carried out by firing 'white' X-rays (multi-chromatic) at a single crystal, and observing the diffraction pattern which will result on the screen. There will be a big blob in the middle, from the through-beam. The spots seen have the same symmetry as the crystal.

Powder Method This is a cylinder of film, with a hole poked through in the wall, for (mono-chromatic) X-rays to go through, with a rod of specimen in the centre.

The mono-chromatic X-rays are produced by bombardment, e.g. of Ca, and removing a K-shell electron $\lambda = 1.54\text{Å}$.

The sample is polycrystalline, or powder, made from grains, glued together.

This method determines values of the Bragg angle θ, for fixed λ.

The polycrystalline sample contains so many crystals that there is a chance that one of them will be orientated to give the reflection at an angle θ.

So, when the experiment is finished, the cylinder is exposed, cut open; and there will be lines in the film.

1.6   The Effect of A Basis

Most crystal structure are Bravais lattices with a basis: Consider a basis of atoms $1, 2, \ldots, n$; located
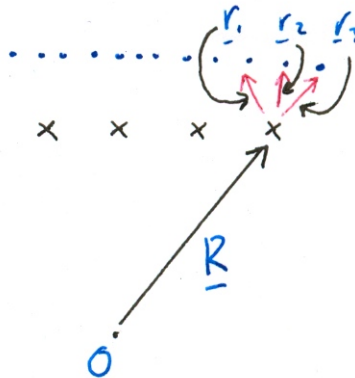
Figure 16: The Bravais lattice (crosses), with a basis (dots). Bravais lattice sites are at $\boldsymbol{R}$, and each basis point at $\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3$ (say), from each Bravais lattice point.

at positions measured from a Bravais lattice site: $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n$.

The phase of a wave scattered from atom i, relative to that of the wave scattered from the nearest Bravais point, in a reflection in which $\boldsymbol{k} - \boldsymbol{k}' = \boldsymbol{G}$ is $\boldsymbol{G} \cdot \boldsymbol{r}_i$. Similarly, the phase shift caused by

scattering from the jth atom is $\boldsymbol{G}\cdot\boldsymbol{r}_j$. This group of atoms will produce waces which, in the direction $\boldsymbol{k}'$, have additonal factors:

$$e^{i\boldsymbol{G}\cdot\boldsymbol{r}_1} + e^{i\boldsymbol{G}\cdot\boldsymbol{r}_2} + \ldots + e^{i\boldsymbol{G}\cdot\boldsymbol{r}_n}$$

If all the atoms at $\boldsymbol{r}_1,\ldots,\boldsymbol{r}_n$ scatter X-rays with the same efficency. So, the total wave amplitude from reflection, from all the basis atoms is multiplied by:

$$S(\boldsymbol{G}) = \sum_{j=1}^{n} e^{i\boldsymbol{G}\cdot\boldsymbol{r}_j}$$

Which we call the *geometric structure factor*.

The intensity of the reflected wave in direction $\boldsymbol{k}'$ is multiplied by $|S(\boldsymbol{G})|^2$. Thus, S is a measure of destructive interference between waves scattered from basis atoms.
For different atoms in the basis, which scatter X-rays with differing efficiencies:

$$S(\boldsymbol{G}) = \sum_{j=1}^{n} f_j(\boldsymbol{G})e^{i\boldsymbol{G}\cdot\boldsymbol{r}_j} \tag{1.11}$$

Where $f_j(\boldsymbol{G})$ is the *atomic form factor*, which is determined by the density of electrons:

$$f_j(\boldsymbol{G}) \propto \int d^3\boldsymbol{r}\, n(\boldsymbol{r})e^{i\boldsymbol{G}\cdot\boldsymbol{r}}$$

For $\boldsymbol{G} = 0$, we have that the atomic form factor is just propotional to the total number of electrons Z. Let us consider some examples:

bcc Lattice   We have that the bcc lattice as a simple cubic lattice, with a basis of 2 atoms:

$$\boldsymbol{r}_1 = (0,0,0) \qquad \boldsymbol{r}_2 = (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2})a$$

That is, the above $\boldsymbol{r}_i$ are the basis, relative to the simple cubic lattice. The basis vectors for $\boldsymbol{G}$, in the simple cubic lattice are:

$$\boldsymbol{b}_1 = \frac{2\pi}{a}\hat{\boldsymbol{i}} \qquad \boldsymbol{b}_2 = \frac{2\pi}{a}\hat{\boldsymbol{j}} \qquad \boldsymbol{b}_3 = \frac{2\pi}{a}\hat{\boldsymbol{k}}$$

So that:

$$\boldsymbol{G} = h\hat{\boldsymbol{b}}_1 + k\hat{\boldsymbol{b}}_2 + l\hat{\boldsymbol{b}}_3$$

Where h,k,l are positive, negative, or zero, integers. So, we have that:

$$S(\boldsymbol{G}) = \sum_{j=1}^{2} e^{i\boldsymbol{G}\cdot\boldsymbol{r}_j}$$

Which gives:

$$S(\boldsymbol{G}) = 1 + e^{i\pi(h+k+l)}$$

Notice, we can see two types of cases, noting that $e^{in\pi} = 1$ if n even, and -1 if n odd. Thus:

$$S(\boldsymbol{G}) = \begin{cases} 2 & h+k+l \quad even \\ 0 & h+k+l \quad odd \end{cases}$$

Hence, in a bcc lattice, destructive interference causes odd-spots to disappear. So, the $(1,0,0)$ reflection disappears, for example. To see this, consider that the waves from planes 1, 3 pick up phase difference of π, and the inteference from plane 2 destructively cancels 1, 3.

fcc Lattice   Here, the basis is:

$$\boldsymbol{r}_1 = (0,0,0)a \quad \boldsymbol{r}_2 = (\tfrac{1}{2}, \tfrac{1}{2}, 0)a \quad \boldsymbol{r}_3 = (\tfrac{1}{2}, 0, \tfrac{1}{2})a \quad \boldsymbol{r}_4 = (0, \tfrac{1}{2}, \tfrac{1}{2})a$$

And we have that:

$$\boldsymbol{G} = \frac{2\pi}{a}(h\hat{\boldsymbol{i}} + k\hat{\boldsymbol{j}} + l\hat{\boldsymbol{k}})$$

Hence:

$$
\begin{aligned}
S(\boldsymbol{G}) &= \sum_{j=1}^{4} e^{i\boldsymbol{G}\cdot\boldsymbol{r}_j} \\
&= 1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)} \\
&= \begin{cases} 4 & h,k,l \quad even, \ or \ odd \\ 0 & h,k,l \qquad else \end{cases}
\end{aligned}
$$

Diamond Lattice   We use a Bravais lattice being an fcc lattice, with a basis:

$$\boldsymbol{r}_1 = (0,0,0) \quad \boldsymbol{r}_2 = (\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4})$$

The reciprocal lattice ot the fcc, is the bcc:

$$\boldsymbol{b}_1 = \frac{2\pi}{a}(\hat{\boldsymbol{j}} + \hat{\boldsymbol{k}} - \hat{\boldsymbol{i}}) \quad \boldsymbol{b}_2 = \frac{2\pi}{a}(\hat{\boldsymbol{k}} + \hat{\boldsymbol{i}} - \hat{\boldsymbol{j}}) \quad \boldsymbol{b}_3 = \frac{2\pi}{a}(\hat{\boldsymbol{i}} + \hat{\boldsymbol{j}} - \hat{\boldsymbol{k}})$$

So that:

$$\boldsymbol{G} = (h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3)$$

Hence:

$$
\begin{aligned}
S(\boldsymbol{G}) &= \sum_{j=1}^{2} e^{i\boldsymbol{G}\cdot\boldsymbol{r}_j} \\
&= 1 + e^{-i\frac{\pi}{2}(h+k+l)} \\
&= \begin{cases} 2 & h+k+l \quad 2\times even & (a) \\ 1 \pm i & h+k+l \qquad odd & (b) \\ 0 & h+k+l \quad 2 \times odd & (c) \end{cases}
\end{aligned}
$$

The relative intensities of the middle case, over the first:

$$\frac{(b)}{(c)} = \frac{|1 \pm i|^2}{2^2} = \frac{1}{2}$$

1.7   Brillouin Zones

The primitive cell of the reciprocal lattice maybe be taken to be the parallelepiped denoted by $\boldsymbol{b}_1, \boldsymbol{b}_2, \boldsymbol{b}_3$. The parallelepiped contains one reciprocal lattice point. Each corner is shared with 8 parallelepipeds: thus, $8 \times \frac{1}{8} = 1$ lattice point per parallelepiped.
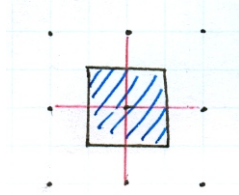
Figure 17: The Brillouin zone. Take a lattice point (in reciprocal lattice space), draw lines to its nearest neighbours. Bisect these lines, and the area that is enclosed is the (first) Brillouin zone.

It is often useful to take the primitive cell as the smallest volume bounded by planes normal to the G vectors of the nearest neighbours.

It is just another way of dividing up reciprocal space, into identical cells which fill it uniformly. Each cell contains one lattice site at the centre of the cell. It is the *first Brillouin zone*.
The same construction in the direct (real) lattice is called the *Wigner Seitz cell*.

The first Brillouin zone is the set of points that can be reached from the origin, without crossing any Bragg plane. The second Brillouin zone is the set of points that can be reached from the first zone by crossing only one Bragg plane.
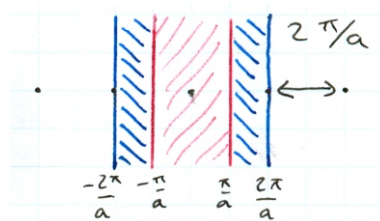
Figure 18: The first and second Brillouin zones, for a 1D reciprocal lattice. The sites are spaced by $\frac{2\pi}{a}$. The first zone is the red area (inner), and second zone is the (disconnected, outer) blue area.
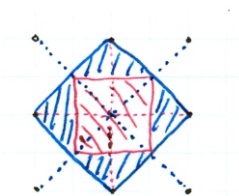
Figure 19: The first and second Brillouin zones for a 2D reciprocal (square) lattice. Notice how each is generated, and that the second zone is disconnected,

1.8   Lattice Defects

So far, we have only considered perfect crystals, which is ok for chemically pure, infinite crystals. Real crystals have defects; and we consider 4 main types.

1.8.1   Chemical Impurities

The colours in diamond, for example, are due to impurities. The electrical conductivity of many semi-conductors is due entirely to impurities.

1.8.2   Point Defects

Considering a few types:

Schottky Defects   If we remove a lattice point to the surface, we get a vacant site. We can do this via thermal excitation. The ratio of the number of defects is:

$$\frac{n}{N} \propto e^{-\epsilon/k_B T}$$

Where ϵ is the energy needed to form a defect, and is typically of the order 1eV. So, if $T = 1000$K, then $\frac{n}{N} \approx 10^{-5}$.

Frenkel Defect   If we move a lattice site to somewhere else within the structure. So, we move to an 'interstitial' site site. Here, we have:

$$\frac{n}{N} \propto e^{-\epsilon/2k_B T}$$

Where ϵ here is the energy needed to form the defect.

 Point defects are important in understanding diffusion in solids, and ionic conductivity of salts (such as LiH).

1.8.3   Dislocations

These are 'linear' faults, where we essentially hammer in a new plane of lattice sites to an existing lattice.

2   Phonons

Phonons are the basis of our understanding of the thermal properties of insulators; such as specific heat & thermal conductivity. In metals however, there are electronic contributions as well.

They are basically the *quanta of elastic waves in the solid.* Compare with photons being the quanta of EM radiation. Acoustic phonons at long wavelengths are sound waves.

At finite temperatures, the atoms of the crystal vibrate due to their thermal energy. We can treat such vibrations classically (as a set of harmonic oscillators), or quantum mechanically (as a phonon gas - like we did the photon gas & blackbody radiation). Quantum effects are always important for phonons, except at high temperatures.

2.1 Elastic Waves

Let us consider the motion of entire planes of atoms. Such as [1, 0, 0] (the cube edge), [1, 1, 0] (the face diagonal), [1, 1, 1] (the body diagonal). Let us consider the [1, 0, 0] plane. Consider three lines of lattice sites: $s-1, s, s+1$. Each lattice site, on each line, is displaced by u_i, from its equilibrium position. That is, $s-1$ is displaced by u_{s-1}. So, we can use an SHM description, as we also suppose that the displacements are small; and that forces depend linearly on displacement. Let us also only

Figure 20: The vibrations of 3 lines of planes of lattice points. Notice that each point (on a line) moves from its equilibrium by a different amount (between lines), but the same amount on a line.

consider only the nearest neighbour interaction. So, the model to have in mind is a line of masses, with springs between each. Let us write the equation of motion:

$$m\frac{d^2 u_s}{dt^2} = c(u_{s+1} - u_s) + c(u_{s-1} - u_s) = c(u_{s+1} + u_{s-1} - 2u_s)$$

Where c is related to the second differential of the potential energy. Now, we have solutions of the form:

$$u_s(t) = e^{-i\omega t}$$

Now, let us find the normal modes of the lattice; all atoms in a normal mode vibrate with the same frequency. So, inserting this solution into our equation of motion easily results in:

$$-m\omega^2 u_s = c(u_{s+1} + u_{s-1} - 2u_s)$$

Where we have cancelled off the exponential factors. Now, let us make an 'ansatz':

$$u_s \propto e^{iksa} u \tag{2.1}$$

Then, we have:

$$-m\omega^2 u = c(e^{ika} + e^{-ika} - 2)u$$

Let us only consider the non-trivial solution (that is, $u \neq 0$). The above easily becomes:

$$-m\omega^2 u = 2cu(\cos ka - 1)$$

Rearranging:

$$\omega^2 = \frac{2c}{m}(1 - \cos ka)$$

Let us use the trig identity:

$$1 - \cos x = 2\sin^2 \tfrac{1}{2}x$$

Thus, we have:

$$\omega^2 = \frac{4c}{m}\sin^2 \tfrac{1}{2}ka$$

Which is a dispersion relation:

$$\omega(k) = \sqrt{\frac{4c}{m}}|\sin \tfrac{1}{2}ka| \tag{2.2}$$

Where we will generally leave off the modulus-sign. Notice that in the dispersion plot, we see the
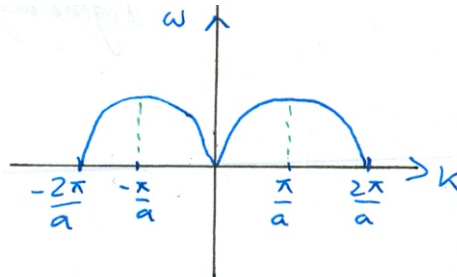

Figure 21: The dispersion curve. Notice that $-\frac{\pi}{a} < k < \frac{\pi}{a}$ is the first Brillouin zone.

first Brillouin zone. Now, any other k' may be written:

$$k' = k + \frac{2\pi n}{a}$$

Where k is within the first Brillouin zone. That is, $-\frac{\pi}{a} < k < \frac{\pi}{a}$. Hence:

$$\omega^2(k') = \frac{4c}{m}\sin^2(\tfrac{1}{2}ka + \pi n)$$

But this is just the same as $\omega^2(k)$, due to the periodicity of the function. Also:

$$
\begin{aligned}
u_s(k') &= ue^{ik'sa} \\
&= ue^{i(k+\frac{2\pi n}{a})sa} \\
&= ue^{iksa}e^{i2\pi ns} \\
&= ue^{iksa} \\
&= u_s(k)
\end{aligned}
$$

So, lattice vibrations corresponding to k' are identical to those corresponding to k. Hence, the first Brillouin zone contains all possible motions. The group velocity is just:

$$
\begin{aligned}
v_g &= \frac{d\omega}{dk} \\
&= 2\sqrt{\frac{c}{m}}\frac{1}{2}a\cos\tfrac{1}{2}ka \\
&= \sqrt{\frac{ca^2}{m}}\cos\tfrac{1}{2}ka
\end{aligned}
$$

Thus, we have computed the group velocity; the velocity of wavepackets, that of energy transmission.

There are some special cases:

- At the Brillouin zone boundary, where $k = \pm\frac{\pi}{a}$. Then, we see that $v_g = 0$. Hence, motion corresponds to standing waves: no wave transmission. Such waves have wavelength $\lambda = 2a$. Hence, the Bragg relation $2a\sin\theta = n\lambda$ becomes just $\sin\theta = 1$; because normal to the plane and $n = 1$.

- Consider also the long-wave limit. We have that $\lambda >> a$; and thus that $ka << 1$. Hence, the $\sin x \to x$. Thus, the dispersion relation is just $\omega(k) \approx \left(\frac{ca^2}{m}\right)^{1/2}k$. Hence, its group velocity is just a constant $v_g = v$. The velocity of sound, which is of the order $10^4 ms^{-1}$, but will vary from solid to solid. The dispersion relation obviously becomes better approximated by this as $k \to 0$. Bear in mind that $k = \frac{2\pi}{\lambda}$.

2.2   Diatomic Lattice

Suppose we have a diatomic crystal, such as CsCl; which is a body-centred cubic lattice, with Cs^+ on the vertices, and Cl^- in the centre. Now, suppose we have a wave propogating in the [1, 0, 0] direction: along the front face. So, the plane of vibration will contain alternating masses: m_2, m_1, m_2, m_1, m_2 which have displacements $v_{s-1}, u_s, v_s, u_{s+1}v_{s+1}$. Hence, the equation of motion, for atom m_1, in plane s is:

$$
m_1\frac{d^2u_s}{dt^2} = c(v_s - u_s) + c(v_{s-1} - u_s)
$$

That is, just:

$$
m_1\frac{d^2u_s}{dt^2} = c(v_s + v_{s-1} - 2u_s)
$$

Equivalently:

$$m_2 \frac{d^2 v_s}{dt^2} = c(u_{s+1} + u_s - 2v_s)$$

Now, we look for solutions of the form:

$$u_s = u e^{iksa - i\omega t} \qquad v_s = v e^{iksa - i\omega t}$$

Hence, putting into the equations reveals:

$$
\begin{aligned}
-\omega^2 m_i u &= cv(1 + e^{-ika}) - 2cu \\
-\omega^2 m_2 v &= cu(e^{ika} + 1) - 2cv
\end{aligned}
$$

Solving each, we find, in order:

$$
\begin{aligned}
\frac{u}{v} &= \frac{c(1 + e^{-ika})}{2c - \omega^2 m_1} \\
\frac{u}{v} &= \frac{2c - \omega^2 m_2}{c(1 + e^{ika})}
\end{aligned}
$$

Now, if we equate these two expressions, and solve, we get to the following:

$$\omega^4 m_1 m_2 - 2c\omega^2(m_1 + m_2) + 4c^2 \sin^2 \tfrac{1}{2}ka = 0$$

This may easily be solved, to give:

$$\omega^2 = \frac{c(m_1 + m_2)}{m_1 m_2}\left[1 \pm \sqrt{1 - \frac{4m_1 m_2}{(m_1 + m_2)^2}\sin^2 \tfrac{1}{2}ka}\right]$$

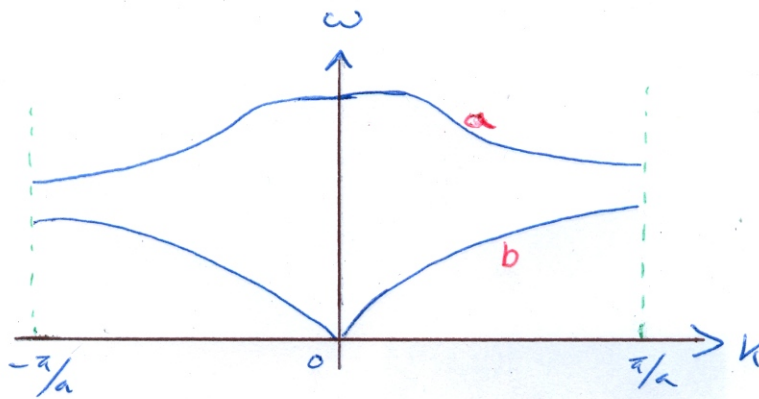Again, we only need to consider the first Brillouin zone.

Figure 22: The dispersion curve, for the diatomic case. Note: curve 'a' represents the + solution, and is the *optical branch*. Curve 'b' is the - solution, and is the *acoustic branch*. The two curves are supposed to be symmetric about $k = 0$.

Now, let us look at a couple of the limits:

- For the optical branch, at the zone centre $ka << 1$. So, we use that $\sin^2 \approx 0$, and the positive-sign in the dispersion relation. This gives:

$$\omega^2 = 2c\frac{m_1 + m_2}{m_1 m_2}$$

- Similarly, at the zone centre, for the acoustic branch:

$$\omega^2 = 2c\frac{(ka)^2}{m_1 + m_2}$$

- At the zone edge, that is $k = \pm\frac{\pi}{a}$, we have, for the optical and acoustic:

$$\omega^2_{optical} = \frac{2c}{m_2}$$
$$\omega^2_{acoustic} = \frac{2c}{m_1}$$

If we have that $m_1 > m_2$.

Now, also notice, the two branches are separated by a *band gap*, within which there are no frequencies of oscillation. That is, within the region:

$$\frac{2c}{m_1} < \omega^2 < \frac{2c}{m_2}$$

Thus, within the above range, the crystal does not vibrate. Separate branches & band gaps are typical of polyatomic lattices.

2.2.1   Acoustic & Optical Modes

To understand why we have named the modes thus, we examine behaviour as $ka \rightarrow 0$. That is, $\lambda >> a$; that is, the wavelength is a lot longer than the interatomic spacing.

Group Velocity   Consider:

$$v_g = \frac{d\omega}{dk}$$

For the optical mode, $v_g \rightarrow 0$ as $k \rightarrow 0$. So, the wave does not propogate. Which is why the dispersion curve is flat at the origin.
For the acoustic mode:

$$v_g \rightarrow \sqrt{\frac{2a^2 c}{m_1 + m_2}}$$

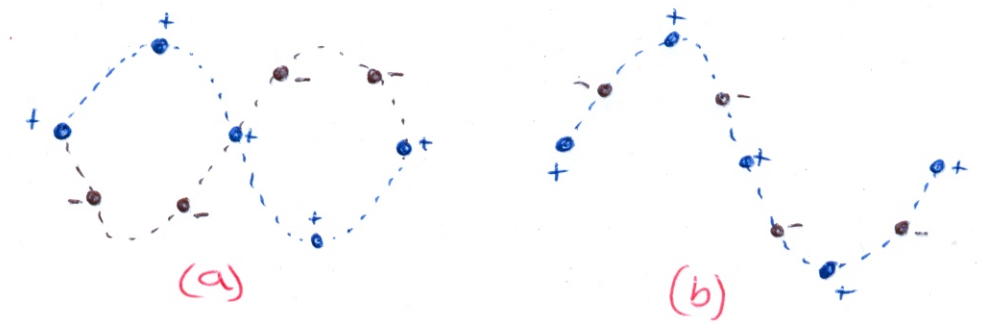Which is the speed of sound. Hence its name.

Figure 23: Vibrations for (a) optical mode, and (b) acoustic mode. Notice that the different atoms are vibrating in antiphase in optical, and inphase for acoustic.

Ratio of Amplitudes   Consider the ratio of the amplitudes of vibration for the different species. That is, $\frac{u}{v}$. At $k = 0$:

$$\frac{u}{v} = \frac{2c}{2c - \omega^2 m_1}$$

And this tends to 1 for acoustic band; and $-\frac{m_1}{m_2}$ for the optical. Thus, we see that different atoms vibrate inphase for acoustic, and anti-phase for optical modes.

For an ionic solid, the optical mode is like an oscillating dipole, and can be excited by electromagnetic radiation. Hence why it is called the optical mode. Often, the EMR is in the infra-red, rather than optical, parts of the spectrum.

Zone Edges   Consider the group velocity at the zone edges, $k = \pm\frac{\pi}{a}$. We see that $v_g \to 0$ for both modes: hence, standing waves for both modes, at the zone edges.
For the acoustic branch, we have that $\omega^2 = \frac{2c}{m_1}$. Hence, each m_1 is moving inwards, towards an enclosed m_2, which are stationary. The exact opposite is true for the optical branch.

In general, there are two transverse and one longitudinal acoustic branches. Where longitudinal is where the displacements of the atoms are parallel to $\boldsymbol{k}$, and transverse are perpendicular.

2.3   Quantisation of Phonons

Each mode of wavevector $\boldsymbol{k}$ is a simple harmonic motion of the whole crystal, with frequency $\omega(\boldsymbol{k})$. We have quantised energy levels:

$$\epsilon_n = (n + \tfrac{1}{2})\hbar\omega = n\hbar\omega + \tfrac{1}{2}\hbar\omega$$

Where n is the excitation quanta, and the other term is the zero-point energy.

Just as photons are the excitation quanta of EM waves, we have that phonons are the excitation quanta of elastic waves.

We can have an arbitrary number of such quanta in each state; which is bosonic-like. This number can change due to phonon emission/absorption.

Now, in thermal equilibrium, the average number of phonons in a particular state $\langle n(\omega) \rangle$ will be determined by the temperature. Let us compute the average energy $\bar{\epsilon}$:

$$\bar{\epsilon} = \sum_{n=0}^{\infty} p_n \epsilon_n \tag{2.3}$$

Now, let us use the Boltzmann distribution:

$$p_n = \frac{e^{-\epsilon_n/k_B T}}{\sum_{n=0}^{\infty} e^{-\epsilon_n/k_B T}} \tag{2.4}$$

Hence, we write $\bar{\epsilon}$, in terms of the energy expression we had, $\epsilon_n = (n + \frac{1}{2})\hbar\omega$. That is:

$$\begin{aligned}
\bar{\epsilon} &= \frac{\sum_n (n + \frac{1}{2})\hbar\omega e^{-(n+\frac{1}{2})\hbar\omega/k_B T}}{\sum_n e^{-(n+\frac{1}{2})\hbar\omega/k_B T}} \\
&= \frac{1}{2}\hbar\omega + \hbar\omega \frac{\sum_n n x^n}{\sum_n x^n} \qquad x \equiv e^{-\hbar\omega/k_B T}
\end{aligned}$$

Now, we identify the two sums as being something we 'know':

$$\sum_n n x^n = \frac{x}{(1-x)^2} \qquad \sum_n x^n = \frac{1}{1-x}$$

Hence, putting these in is slightly trivial:

$$\bar{\epsilon} = \frac{1}{2} + \hbar\omega \frac{x}{1-x}$$

Which is, of course, identically equal to:

$$\bar{\epsilon} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega e^{-\hbar\omega/k_B T}}{1 - e^{-\hbar\omega/k_B T}}$$

That is:

$$\bar{\epsilon} = \frac{1}{2}\hbar\omega + \hbar\omega \langle n(\omega) \rangle \tag{2.5}$$

Where we have identified the *Bose-Einstein* distribution:

$$\langle n(\omega) \rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1} \tag{2.6}$$

Thus, we have computed the average number of phonons, which have energy $\hbar\omega$ (i.e. oscillate with angular frequency ω), at a temperature T.

2.3.1   Density of States

We derive this using the *periodic boundary conditions* method, as opposed to the previously used *box conditions* method.

Let us use k-space. So, we have the following function:

$$u(x,t) = u e^{i(kx - \omega t)}$$

As well as the following periodic boundary conditions:

$$u(0,t) = u(L,t)$$

So, using the boundary conditions:

$$u e^{i(-\omega t)} = u e^{i(kL - \omega t)}$$

That is:

$$1 = e^{ikL}$$

Hence, we see that k must be quantised thus:

$$k = \frac{2\pi n}{L} \qquad n = \ldots, -1, 0, 1, \ldots \tag{2.7}$$

Now, consider a 1D section of k-space Δk_x long. We see from above that the spacing between adjacent states is just $\frac{2\pi}{L}$. Hence, the number of states in our section Δk_x is just:

$$\Delta k_x \frac{L}{2\pi}$$

In 3D, we of course have:

$$\boldsymbol{k} = (k_x, k_y, k_z) = \frac{2\pi}{L}(n_x, n_y, n_z)$$

Now, each state occupies a volume $(\frac{2\pi}{L})^3 = \frac{8\pi^3}{L}$. So, the number of states in a volume $\Delta k_x \Delta k_y \Delta k_z$ is just:

$$\left(\Delta k_x \frac{L}{2\pi}\right)\left(\Delta k_y \frac{L}{2\pi}\right)\left(\Delta k_z \frac{L}{2\pi}\right) = D(\boldsymbol{k}) d^3 k$$

That is:

$$D(\boldsymbol{k}) d^3 k = \frac{V}{8\pi^3} d^3 k \tag{2.8}$$

Now, we are often interested in the number of states within a region $k < |k| < k + dk$. We denote such a quantity $\tilde{D}(k) dk$. To find this quantity, we multiply the above $D(\boldsymbol{k})$ by the area of a shell:

$$\tilde{D}(k) dk = \frac{V}{8\pi^3} 4k^2 \pi dk$$

That is:

$$\tilde{D}(k) dk = \frac{V}{2\pi^2} k^2 dk \tag{2.9}$$

Two Dimensions   This is the case for which we have the following number of states, in an area $\Delta k_x \Delta k_y$:

$$\left(\Delta k_x \frac{L}{2\pi}\right)\left(\Delta k_y \frac{L}{2\pi}\right) = \frac{A}{4\pi^2}\Delta k_x \Delta k_y$$

That is:

$$D(\boldsymbol{k})d^2k = \frac{A}{4\pi^2}\Delta k_x \Delta k_y$$

Again, the number of states within $k < |k| < k + dk$ is:

$$\tilde{D}(k)dk = \frac{A}{4\pi^2}2\pi k dk$$

That is:

$$\tilde{D}(k)dk = \frac{A}{2\pi}k dk \tag{2.10}$$

The number of k-states in any Brillouin zone; if there are N points, is just N.

For long wavelengths, there are two transverse, and one longitudinal acoustic modes. Each has dispersion relation:

$$\omega = c_t k \qquad \omega = c_l k \qquad k \to 0 \tag{2.11}$$

Where c_t, c_l are the transverse and longitudinal sound velocities.

For each branch, we have that:

$$\tilde{D}(k)dk = \tilde{D}(\omega)d\omega \tag{2.12}$$

Hence, the number of modes lying between ω and $\omega + d\omega$ is just (for each branch):

$$\tilde{D}(\omega) = \tilde{D}(k)\frac{dk}{d\omega} = \frac{V}{2\pi^2}k^2\frac{1}{c}$$

That is, for each branch:

$$\tilde{D}(\omega) = \frac{V}{2\pi^2}\frac{\omega^2}{c^3}$$

Hence, for two transverse, and one longitudinal, the total is just:

$$\tilde{D}(\omega) = \frac{V}{2\pi^2}\left(\frac{2}{c_t^3} + \frac{1}{c_l^3}\right)\omega^2 \tag{2.13}$$

Dispersion relations from neutron scattering:

Recall, in elastic neutron scattering, energy is conserved, and we had:

$$E' = E \qquad \boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G}$$

Where a primed quantity denotes the final wavevector state, and unprimed the incident. We have that the wavevectors differ by a reciprocal lattice vector.

Now, inelastic neutron scattering provides information on the dispersion relation:

$$E' = E \pm \hbar\omega(\boldsymbol{K}) \qquad \boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{G} + \boldsymbol{K}$$

Where we have the neutrons wavevector $\boldsymbol{k}$ and phonon wavevector $\boldsymbol{K}$. Thus, a phonon may be created or absorbed.

2.4   Specific Heat of Solids

The phonon contribution to the specific heat dominates the specific heat of non-magnetic insulators.

$$c_V = \frac{\partial U}{\partial T}\bigg)_V \tag{2.14}$$

For a phonon gas, we have that the internal energy is given by:

$$U = \sum \hbar\omega \langle n(\omega)\rangle$$

Where the sum is over all states. We are actually ignoring the zero-point energy term (the $\frac{1}{2}\hbar\omega$) as it is temperature independant, and thus does not contribute to the heat capacity. Now, we also have:

$$\langle n(\omega)\rangle = \frac{1}{e^{\hbar\omega/k_B T} - 1}$$

Which is the number of phonons of frequency ω which are excited, at temperature T. Since the different ω levels are very closely spaced, we can approximate this sum by an integral:

$$U = \int \hbar\omega \langle n(\omega)\rangle \tilde{D}(\omega) d\omega$$

Where the integral is over all states of the system. We proceed by looking at the Debye model.

2.4.1   The Debye Model

Debye suggested that a good approximation to the low temperature specific heat would be to (a) ignore optical phonons [note: they have $\hbar\omega(k) >> k_B T$ even for low T; hence, their contribution to $\langle n(\omega)\rangle$ is negligible]; and (b) replace the acoustic phonon dispersion relations by their small k (i.e. small ω) forms:

$$\omega = \begin{cases} c_t k \\ c_l k \end{cases}$$

Note, there are two branches of transverse, and one longitudinal. So:

$$\tilde{D}(\omega) = \frac{V}{2\pi^2}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right)\omega^2$$

Now, we restrict ω to $\omega < \omega_D$, some *Debye frequency*, as being some cut-off. Where:

$$\int_0^{\omega_D} \tilde{D}(\omega) d\omega = 3N$$

Where N is the number of atoms. So, the point of the Debye frequency is to make sure we dont excite too many modes; modes which are not there! After a fairly trivial integration, and rearrangement, we get:

$$\frac{V}{2\pi^2}\left(\frac{1}{c_l^3} + \frac{2}{c_t^3}\right) = \frac{9N}{\omega_D^3}$$

Now, let us get back to computing the internal energy:

$$
\begin{aligned}
U &= \int_0^{\omega_D} \hbar\omega\langle n(\omega)\rangle \tilde{D}(\omega)d\omega \\
&= \int_0^{\omega_D} \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}\frac{V}{2\pi^2}\left(\frac{1}{c_l^3}+\frac{2}{c_t^3}\right)\omega^2 d\omega \\
&= \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3}{e^{\hbar\omega/k_BT}-1}d\omega
\end{aligned}
$$

Where we have used our expression we computed for ω_D. Let us continue by making a substitution:

$$
U = \frac{9N\hbar}{\omega_D^3}\left(\frac{k_BT}{\hbar}\right)^4\int_0^{\hbar\omega_D/k_BT}\frac{x}{e^x-1}dx \qquad x \equiv \frac{\hbar\omega}{k_BT}
$$

Also, let $\hbar\omega_D \equiv k_B\theta_D$. Then, the above easily becomes:

$$
U = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{e^x-1}dx
$$

Now, let us consider some limits; as the evaluation of such an integral is near-impossible, due to the non-infinte upper-limit!

High T Limit   Here, we note that $\theta_D << T$. In which case, we can do a Taylor expansion of the denominator in the integral: $e^x \rightarrow 1+x$. Thus:

$$
U = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^3}{1+x-1}dx
$$

Which is, fairly trivially:

$$
U = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3\frac{1}{3}\left(\frac{\theta_D}{T}\right)^3
$$

Which is just:

$$
U = 3Nk_BT
$$

Which gives:

$$
c_V = 3Nk_B
$$

A result we would expect from the equipartition theorem: $\frac{1}{2}k_BT$ per degree of freedom, with $6N$ degrees of freedom.

Low T Limit   Here, we have that $\theta_D >> T$. Hence, notice that the upper limit on the integral goes to infinity. That is:

$$
U = 9Nk_BT\left(\frac{T}{\theta_D}\right)^3\int_0^{\infty}\frac{x^3}{e^x-1}dx
$$

We can look up the integral:

$$
\int_0^{\infty}\frac{x^3}{e^x-1}dx = \frac{\pi^4}{15}
$$

Hence:

$$U = \frac{3}{5}\pi^4 N k_B T \left(\frac{T}{\theta_D}\right)^3$$

Hence:

$$c_V = \frac{12}{5}\pi^4 N k_B \left(\frac{T}{\theta_D}\right)^3$$

Which is known as *Debye's T^3 law*. This law is in excellent agreement with data! Typically, $\theta_D \approx 300$K.

The reason for such a success is that we assumed (in our approximations) $\omega \propto k$ for small k, and $\tilde{D}(k) \propto \omega^2$ for small ω.

So, the Debye model is good at both high and low T (high because in agreement with equipartition theorem, and low due to data). But it is only roughly ok at intermediate T. It can be improved by using experimental values for the density of states $\tilde{D}(\omega)$, which can be obtained from neutron scattering experiments.
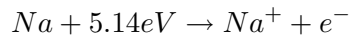
3 Electrons in Metals

3.1 Metals

Metals tend to be formed from easily ionised elements, such as Soldium Na. The electronic configuration is as follows:

$$(1s^2)(2s^2 2p^6)3s^1$$

Where parentheses indicate closed shells. Notice that the 3s^1 electron is in an unclosed shell, and is thus the *valence electron*. To ionise sodium, we must supply 5.14eV:

$$Na + 5.14eV \rightarrow Na^+ + e^-$$

In metals, the ionised state is more stable.

Consider a 'block' of metal, with ionic cores at regular intervals (forming a lattice), and an electron gas. The typical radius of ions is ≈ 0.98Å, having a separation of ≈ 3.66Å. We basically get that the electrons are spread over the whole crystal, forming a degenerate fermi gas. The Coulomb repulsion, between Na^+ ions is screened by the mobile electrons.
The ionic core & electron interaction form a weak *metallic bond* which hold the metal together. Thus, Na is a soft metal. Something like iron is a hard metal, and is so because it is held together by covalent bonds.

There are 3 different levels of treatment; we shall consider the first two, but not the third.

Free Electron Gas Here, we model the electrons as being completely free, subject only to the potential confining them to the metal. That is, we ignore any inter-electron interaction, or electron-core interaction. We have the following (quadratic) dispersion relation:

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$

Band Theory Here, we allow for the presence of the periodic array of ion core. We will see that bands are produced in the dispersion relation, because of the periodic potential. We will still ignore the inter-electron interaction though.

Many-body Theory This now allows for the Coulomb interaction between electrons, as well as the ionic cores. This 'additional' interaction is a large effect. In Na, the typical spacing of the electrons is the same as the spacing of the ion cores (as 1 electron per core). Thus, Coulomb repsulsive energy is of the order eV. The wavefunction is not a set (Slater determinant) of single electron wavefunctions. As stated above, we shall not consider this theory!

3.2 Free Electron Gas

The energy distribution of the electrons is given by:

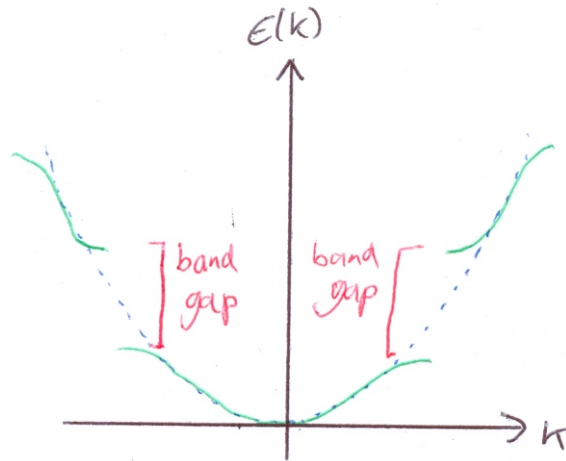$$N(\epsilon)d\epsilon = f(\epsilon)D(\epsilon)d\epsilon \tag{3.1}$$

Figure 24: The dispersion relation, in 'band theory'. Notice th deviation from the free-electron gas dispersion relation - the dotted line drawn. The dispersion relation is symmetric about the $k = 0$ axis. Notice the two band gaps.

Where $f(\epsilon)$ is the Fermi-Dirac distribution. Thus, the number of electrons with energy in the range $[\epsilon, \epsilon + d\epsilon]$ at temperature T, is given by the product of the density of states that the electron can occupy, and the probability that an electron is found in a particular state, at temperature T.

We consider the density of states, by finding the number of states in a volume $\Delta k_x \Delta k_y \Delta k_z$; giving the usual result:

$$\frac{V}{2\pi^2} k^2 dk$$

Now, the expression we want must take into account the spin-multiplicity of electrons: each 'point' in k-space can have two electrons, in ϵ-space. Hence:

$$D(\epsilon)d\epsilon = 2\frac{V}{2\pi^2}k^2 dk$$

Let us evaluate this, using the 'free electron gas dispersion relation':

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

Thus:

$$D(\epsilon) = 2\frac{V}{2\pi^2}k^2\frac{dk}{d\epsilon}$$

Plugging everything in, and doing a bit of differentiation, easily gives:

$$D(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2} \tag{3.2}$$

We have that the Fermi-Dirac distribution is:

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} \tag{3.3}$$

The chemical potential μ is fixed by the following condition:

$$\int_0^\infty f(\epsilon)D(\epsilon)d\epsilon = N$$

Where N is the total number of electrons in the system. To find this condition; we look at the case at absolute zero $T = 0$. Here, we have that $\mu = \epsilon_F$, where ϵ_F is the *Fermi-energy*. This is not a full treatment of such systems; but can be found in the Bose & Fermi Gases lecture notes. We then get:

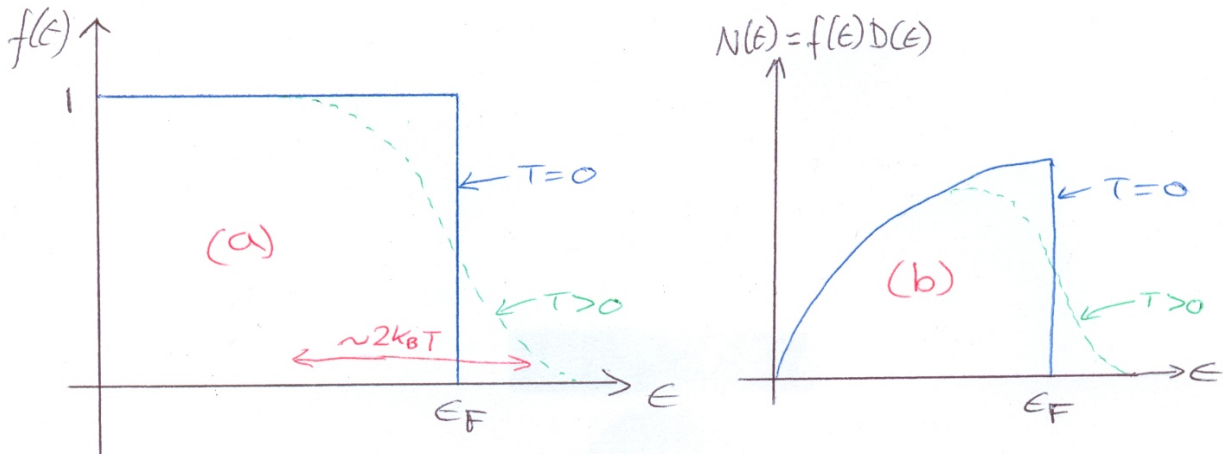$$f(\epsilon) = \begin{cases} 1 & 0 \leq \epsilon < \epsilon_F \\ 0 & \epsilon \geq \epsilon_F \end{cases}$$

Figure 25: (a) The Fermi-Dirac distribution, at $T = 0$ and $T > 0$. Notice that at $T = 0$, all states below ϵ_F are occupied, and all states above the fermi energy are empty. For temperatures above absolute zero (i.e. realistic temperatures), the idealised distribution 'crumbles'. The smearing is of the order $2k_BT$. (b) The number of electrons with a particular energy. Notice again, the distributions for temperatures at absolute zero, and slightly above.

Let us evaluate the fermi energy ϵ_F. Now, we know that the total number of electrons in the system is fixed. So, the same number of electrons at $T = 0$ as at $T \neq 0$. The number of electrons in the system, for any temperature, is given by:

$$N = \int_0^\infty f(\epsilon)D(\epsilon)d\epsilon$$

And, as we have seen, at $T = 0$, the probability distribution becomes a step function about the fermi energy. That is:

$$N = \int_0^{\epsilon_F} D(\epsilon)d\epsilon \qquad T = 0$$

So, we can easily evaluate this, using our derived density of states:

$$N = \int_0^{\epsilon_F} \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} d\epsilon$$

This easily gives:

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \tag{3.4}$$

Hence, we have computed the fermi energy, which is the energy of the most energetic electron; at absolute zero. Notice that it depends on the number density of electron $\frac{N}{V}$.

There are various associated quantities: the fermi-temperature, fermi-velcity and fermi-wavevector; all can be found via:

$$\epsilon_F = k_B T_F \qquad \epsilon_F = \tfrac{1}{2} m v_F^2 \qquad \epsilon_F = \frac{k_F^2 \hbar^2}{2m} \tag{3.5}$$

Their typical orders are:

$$\epsilon_F \approx 5eV \qquad T_F \approx 10^4 - 10^5 K \qquad k_F \approx 1\text{Å} \qquad v_F \approx 10^m s^{-1}$$

Notice that the fermi wavevector is of the order the lattice spacing.

3.2.1 Fermi Surface

The Fermi surface is the sphere in k-space corresponding to energy ϵ_F:

$$\epsilon_F = \frac{\hbar^2 k_F}{2m}$$

So, the Fermi surface is a sphere, radius k_F. In 2D, this is obviously a circle.

We have that, at $T = 0$, all states within k_F (i.e. those for which $k \leq k_F$) are occupied. And all states outside the sphere are empty (i.e. those for $k > k_F$).

3.3 Heat Capacity of Metals

For monovalent metals (i.e. those for which one electron per atom), of N atoms (and hence N electrons); one would classically expect a heat capacity:

$$C_e = \tfrac{3}{2} N k_B = \tfrac{3}{2} R$$

Per mole, and some contribution from phonons.

Experiment shows that at room temperature (note, this is well below the Fermi temperature for most metals), the heat capacity is a lot lower:

$$C_e \approx 10^{-2} - 10^{-3} R$$

Hence, we see that the contribution from phonons becomes very important at low temperatures.

The explanation for this is that electrons are fermions. For $T << T_F$, only a few electrons are near the Fermi surface, and it is only those few which can be excited into empty states.

Let us estimate for $T << T_F$ (the full calculation can be found in the Bose & Fermi lecture notes); it may be done by evaluating the following integrals properly:

$$U(T) = \int_0^\infty d\epsilon\, \epsilon f(\epsilon) D(\epsilon) \qquad N = \int_0^\infty d\epsilon\, f(\epsilon)$$

We have the following relations:

$$N(\epsilon) = D(\epsilon) f(\epsilon) \qquad D(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \epsilon^{1/2} \qquad f(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$$

Now, with reference to our previous figure, we have that the number of states being excited have a width of $\approx 2k_B T$, and height $\frac{1}{2}D(\epsilon)$. Thus, the number of excited electrons is just:

$$\frac{1}{2}D(\epsilon_F)\frac{k_B T}{2}$$

Each of these electrons has energy $\approx \frac{3}{2}k_B T$. Thus, the total energy change is just:

$$U(T) - U(0) \approx \frac{3}{8}k_B^2 T^2 D(\epsilon_F)$$

Hence, the heat capacity is:

$$C_e = \frac{\partial U}{\partial T} = \frac{3}{4}k_B^2 T D(\epsilon_F)$$

Now, it isnt too hard to derive, so we can write the following relation:

$$D(\epsilon_F) = \frac{2}{3}\frac{N}{k_B T_F}$$

Thus, giving us that:

$$C_e(T) = \frac{9}{8}\frac{Nk_B T}{T_F} \qquad T << T_F$$

Now, a proper calculation gives us:

$$C_e = \gamma T \qquad \gamma \equiv \frac{\pi^2}{2}\frac{Nk_B}{T_F} \qquad\qquad (3.6)$$

Hence, we have that the total specific heat is the sum of the electronic and phonon specific heats:

$$C = C_e + C_L$$

And, from our calculations, this is:

$$C = \gamma T + AT^3 \qquad T << \theta_D \qquad\qquad (3.7)$$

Notice, if we plot C/T against T^2, we get a straight line, with intercept γ, and gradient A. This is in very good agreement with experimental data.

Now, if we compare the γ_{expt} (i.e. obtained from experiment) with γ_{free} (calculated from the above free-electron model), we see that they are not the same. Infact, for example, Potassium:

$$\gamma_{expt} \approx 1.25\gamma_{free}$$

The explanation for this discrepancy is:

- Band theory effects play a role, which we have thus far ignored. Electrons do move in the positive potential of the ionic cores.

- We have ignored the physics of many-body interactions. So, we change m to m^* (say) in $D(\epsilon_F)$. That is:

$$\epsilon = \frac{\hbar^2 k^2}{2m^*}$$

Where m^* is the *effective mass*. It is usually close to m. However, in alloys (such as UPt_5), $m^* \approx 10^3 \times m$. These are denoted *heavy fermion metals*.

Regardless, we have the relation:

$$\frac{\gamma_{expt}}{\gamma_{free}} = \frac{m^*}{m} \tag{3.8}$$

Where all other factors will just cancel out.

3.4 Conduction & Transport Properties

We shall model electrical conduction using the *Drude model*.

The force on an electron is given by the Lorentz force law:

$$\boldsymbol{F} = -e(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B})$$

For the case where $\boldsymbol{B} = \boldsymbol{0}$, this obviously reduces to $\boldsymbol{F} = -e\boldsymbol{E}$. Hence, the equation of motion is:

$$\boldsymbol{F} = m\frac{d\boldsymbol{v}}{dt} = -e\boldsymbol{E}$$

Now, this implies that an electron would be indefinitely accelerated in the absence of any collisions, with phonons or lattice defects (impurities).

If the drift velocity $\boldsymbol{v}$ dies out in some time τ, we can incorporate the effect of collision into an effective equation of motion. This is Drude's model:

$$m\left(\frac{d}{dt} + \frac{1}{\tau}\right)\boldsymbol{v} = -e\boldsymbol{E} \tag{3.9}$$

So, we have that the motion of acceleration, by the electric field, untill collisions drop the speed. Drude's equation is for average drift velocities, which reduces the above equation to:

$$\frac{m}{\tau}\boldsymbol{v} = -e\boldsymbol{E} \tag{3.10}$$

Where $\boldsymbol{v}$ is the *steady drift velocity*. Hence:

$$\begin{aligned}
\boldsymbol{v} &= -\frac{e\tau}{m}\boldsymbol{E} \\
&\equiv -\mu\boldsymbol{E} \qquad \mu \equiv \frac{e\tau}{m}
\end{aligned}$$

Where we have defined the *mobility* μ.

Suppose that there are n electrons per unit volume, $n \equiv \frac{N}{V}$. Then, the current density is just:

$$
\begin{aligned}
\boldsymbol{j} &= -ne\boldsymbol{v} \\
&= \frac{ne^2\tau}{m}\boldsymbol{E} \\
&\equiv \sigma\boldsymbol{E} \qquad \sigma \equiv \frac{ne^2\tau}{m}
\end{aligned}
$$

Which is Ohm's law; with the *electrical conductivity* being σ. *Resistivity* is defined thus:

$$
\rho = \frac{1}{\sigma} = \frac{m}{ne^2\tau}
$$

The drift motion $\boldsymbol{v}$ is superimposed on the whole thermal motion in k-space. That is, the Fermi surface is shifted by an amount:

$$
\delta\boldsymbol{k} = \frac{m\boldsymbol{v}}{\hbar} \qquad (p = \hbar k, p = mv)
$$

Inserting our expression for $\boldsymbol{v}$:

$$
\delta\boldsymbol{k} = -\frac{e\tau}{\hbar}\boldsymbol{E}
$$

To imagine whats happening: consider a sphere, and then an electric field is applied. The application of the field shifts the sphere by a small amount, in the direction opposite to the field. States near the surface of the sphere move to new states in the shifted sphere. Now, suppose the field is switched off:

$$
\boldsymbol{v}(t) = \boldsymbol{v}_0 e^{-t/\tau}
$$

Then, when the field is switched off, the states from the original sphere which moved into states in the new sphere when the field was applied, now scatter back into the original sphere. Note, only the states near the surface of the sphere (i.e. those close to the Fermi surface) are involved in this relaxation; as it is only those which can find empty states to be scattered into. The Pauli exclusion principle prevents electrons deep within the Fermi sphere from scattering into nearby states. This scattering can take place off phonons, or impurities within the sample.

Mean free path ℓ:

$$
\ell = v_F\tau \tag{3.11}
$$

Which is the distance between the collisions of an electron, whose energy is close to the Fermi energy.

Typically, for very pure copper, ℓ at 4K is 0.3cm, and at 300K is 3×10^{-6}cm.

What are the dominant collisions?

- Phonons: these dominate at room temperatures, and are very low at low temperatures (where the number of phonons is low);

- Lattice imperfections & impurities: these dominate at low temperatures.

Note, collisions are not with the periodic potential (i.e. ionic cores) or other electrons. Electron-electron repulsion (via the Coulomb interaction) would be expected to cause scattering of electrons, but the effect is almost entirely suppressed by the Pauli principle, and the unavailability of states to be scattered into, except near the Fermi surface.

The 'relaxation time' parameter is a parallel sum of the contributions from phonons (τ_p) and impurities τ_i:

$$\frac{1}{\tau} = \frac{1}{\tau_p} + \frac{1}{\tau_i}$$

These add in parallel, as they are independent processes.
Similarly, the net resistivity is a sum of the phonon and impurity contributions:

$$\rho = \rho_p + \rho_i$$

This is known as *Matthiessen's rule*. ρ_i (the resistivity due to impurities) is roughly independent of temperature; but varies from sample to sample, for a given substance, and obviously depends upon the number of impurities. ρ_p is the same for different samples, of a given substance; and goes to zero as T goes to zero.
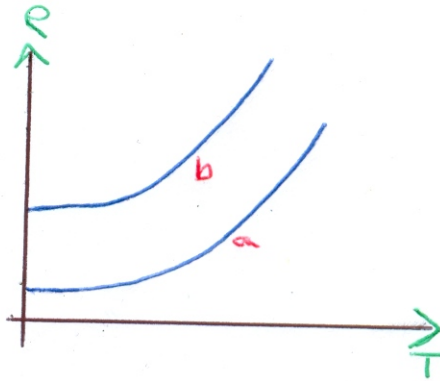

Figure 26: The dependence of resistivity on temperature. Two plots are shown, with a having less impurities than b. The intercept obviously then depends on the number of impurities.

3.5   Thermal Conductivity

At room temperature, normal electrons tend to have values of thermal conductivities 10-100 times higher than insulators. Hence, the dominant contribution to the heat current must come from electrons. Heat current is related to the temperature gradient thus:

$$j_H = -\kappa \frac{dT}{dx} \qquad \kappa = \kappa_p + \kappa_e$$

Where κ is the *thermal conductivity*; where we see that it is the sum of phonon and electron contributions; and that $\kappa_e \gg \kappa_p$. We state the following result, which comes from the kinetic

theory of gases:

$$\kappa_e = \frac{1}{3}C\bar{v}\ell$$

Where C is the specific heat, $\bar{v}$ the mean speed, and ℓ the mean free path. From before, we have that the specific heat capacity of electrons is given by:

$$C = C_e = \frac{\pi^2}{2}\frac{nk_B^2 T}{\epsilon_F}$$

Hence, if we have that the mean speed is the Fermi velocity, and that $\ell = v_F \tau$, then putting everything together results in:

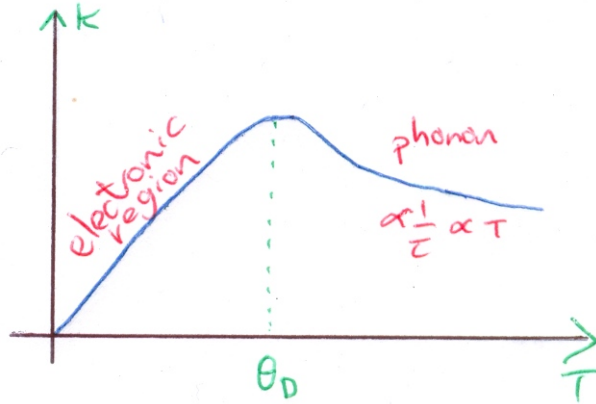$$\kappa_e = \frac{\pi^2}{3}nk_B^2 T\frac{\tau}{m}$$

Figure 27: The dependence of thermal conductivity on temperature.

At low temperatures, let us make the ratio:

$$\frac{\kappa}{\sigma T} = \frac{1}{3}\left(\frac{\pi k_B}{e}\right)^2 \equiv L$$

Where L is the *Lorenz number*, and is obiously a constant:

$$L = 2.45 \times 10^{-8}\, Watt.Ohm/deg^2$$

Notice that it is independent of electron density, mass & relaxation time. And hence should be the same for all metals.
This is roughly true, as relaxation times for electrical and thermal processes involve different matrix elements (from QM, which we havnt yet done!)
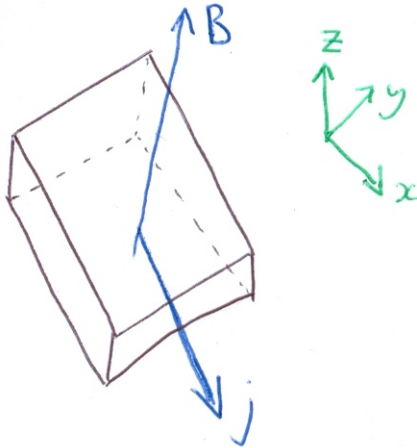
Figure 28: The setup for the Hall effect

3.6 The Hall Effect

Suppose that in addition to the electric field driving the current, there is also an applied magnetic field.

 Because of the magnetic field (in the z-direction), the electrons experience a Lorentz force $-e\boldsymbol{v} \times \boldsymbol{B}$, which causes electrons to accumulate at the edges, to setup an electric field to balance the Lorentz force. So, the Drude model equation reads:

$$m\left(\frac{d}{dt} + \frac{1}{\tau}\right)\boldsymbol{v} = -e(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B})$$

Where:

$$\boldsymbol{v} = (v, 0, 0) \qquad \boldsymbol{E} = (E_x, E_y, 0) \qquad \boldsymbol{B} = (0, 0, B)$$

Where we see that E_x is the driving field, and E_y the field setup by the accumulation of electrons. Hence:

$$\boldsymbol{v} \times \boldsymbol{B} = (0, -vB, 0)$$

In the steady state, that is:

$$\frac{d\boldsymbol{v}}{dt} = 0$$

We can decompose the Drude-model expression into its different components. Bunching them all together first:

$$\frac{m}{\tau}(v, 0, 0) = -e\left[(E_x, E_y, 0) + (0, -vB, 0)\right]$$

Hence, in the x-direction:

$$\frac{mv}{\tau} = -eE_x$$

In the y-direction:

$$0 = -e(E_y - vB) \qquad \Rightarrow \qquad E_y = vB$$

And there is no z-component.

We have that current density is drift velcity multiplied by both charge and number density: $j = -nev$. Hence, in the x-direction, this is (solving for v, trivially):

$$j_x = \frac{ne^2\tau}{m} E_x$$

Which, upon comparison with the previous definition of conductivity, is:

$$j_x = \sigma E_e \qquad \sigma \equiv \frac{ne^2\tau}{m}$$

Also, from $j_x = -nev$, we have (via the $E_y = vB$ equation):

$$E_y = -\frac{B}{ne} j_x$$

So, let us define the *Hall coefficient*:

$$R_H \equiv \frac{E_y}{Bj_x} = -\frac{1}{ne} \tag{3.12}$$

It is a measure of density and the charge of carriers.

 Note that it is independent of both electron mass and relaxation time.

 For alkali metals, there is a rough agreement with this free electron model, but for other metals, it is not so good! For some, the measured Hall coefficient is positive, indicating that the charge carriers are positive.

 This is obviously impossible to reconcile with free electron gas theory. Hence, we need band theory:

3.7   Band Theory

The free electron model was a good guide; working roughly ok for alkali metals, but not that good for anything else.

 Free electron theory does not explain why solids which all contain electrons can be conductors, semi-conductors or insulators; where:

$$\begin{aligned}
\sigma_{cond} &\approx 10^5 \rightarrow 10^{10} \\
\sigma_{semi-cond} &\approx 10^{-5} \rightarrow 10^4 \\
\sigma_{ins} &\approx 10^{-9} \rightarrow 10^{-18}
\end{aligned}$$

All having units $Ohm^{-1}m^{-1}$. This is a huge range, a variation of the order 10^{28}!

 To understand this, we need to consider the consequences of the periodic potential of the lattice. We shall treat it as a perturbation about the free electron model.

 In the free electron model, the dispersion relation was:

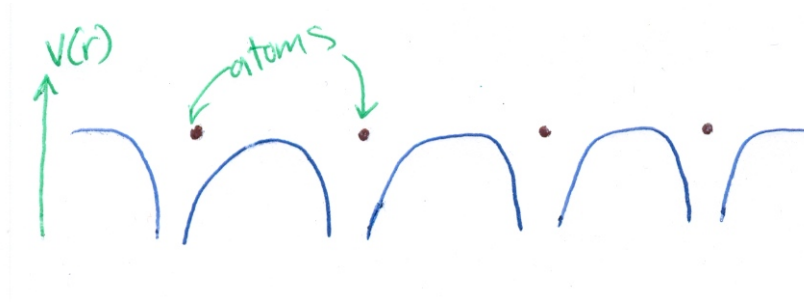$$\epsilon(k) = \frac{\hbar^2 k^2}{2m}$$

Figure 29: The periodic potential model, for a 1D lattice. The curves are the potential that a nearby electron feels.

Where the dispersion curve was a normal parabola, symmetric about $k = 0$. Its solutions to the Schrodinger equation were of the form $\psi_k(x, t) \propto e^{-i\epsilon t/\hbar + ikx}$.

Now, if the lattice is included:

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = \epsilon\psi$$

Where $V(x)$ is the periodic potential of the positive ion cores, so that:

$$V(x) = V(x + a)$$

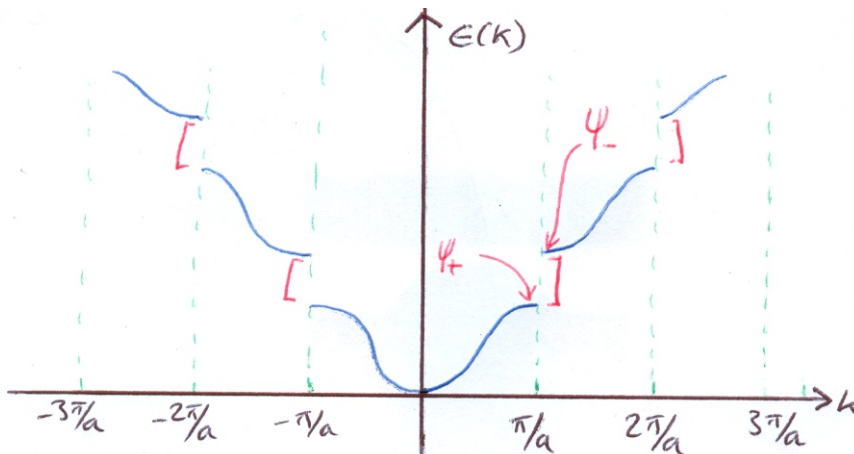Here, $\epsilon(k)$ is much more complicated!

Figure 30: The dispersion relation for band theory. Notice the band gaps forming. Notice that they form on the boundaries of the Brillouin zones. The gaps are all of different sizes, although the system is symmetric: $\epsilon(k) = \epsilon(-k)$.

To understand the gaps, note that if $k = \frac{n\pi}{a}$, then, as $\lambda = 2\pi/k$, we thus have:

$$\lambda = \frac{2a}{n} \qquad \Rightarrow \qquad 2a = n\lambda$$

Compare this last expression with the Bragg law, with $\sin\theta = 1$, and $n = 1$. So, travelling waves are reflected if $k = n\pi/a$, and cannot propagate through the crystal.

So, if we have some incoming (e^{ikx}) and reflected (e^{-ikx}) wave, then:

$$\psi_+(x) \propto e^{-ikx} + e^{-ikx} \to \sqrt{\frac{2}{L}}\cos kx$$

And:

$$\psi_-(x) \propto e^{-ikx} - e^{-ikx} \to \sqrt{\frac{2}{L}}\sin kx$$

Where we see what ψ_+, ψ_- are, from the Figure.

Let the potential due to the ionic cores be given by:
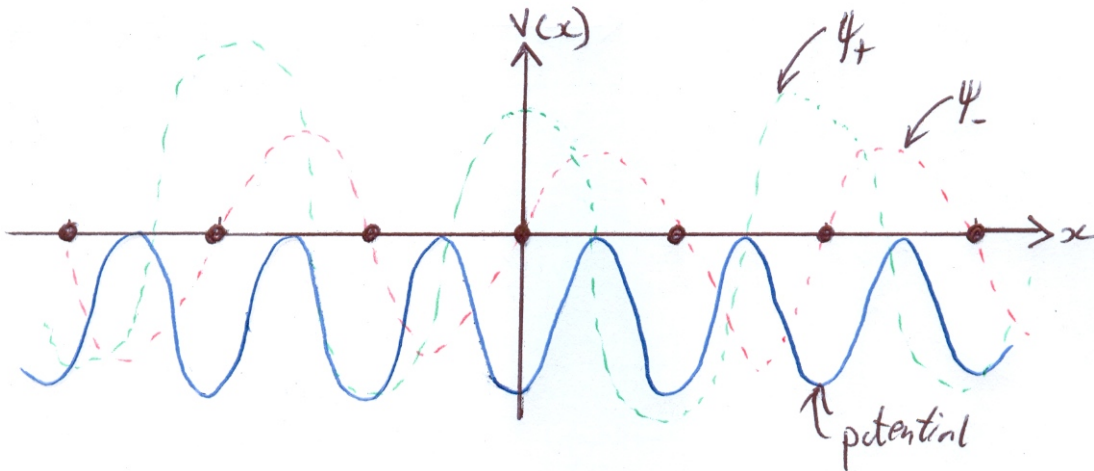
$$V(x) = u_0 - u\cos\frac{2\pi x}{a}$$

Figure 31: The potential, as given above. Notice, the solid line is the potential, the green dotted the ψ_+, and being maximum amplitude where the ionic cores (the black dots) are. The ψ_- is red dotted, and has minimum amplitude at ionic cores. The amplitude of each wave is supposed to be constant!

Note, from the figure, ψ_+ is big where ion cores are, and ψ_- is small where the ion cores are. So, at the ion cores, $|\psi_+|^2$ is max, and $|\psi_-|^2$ a min. So, we would expect $\epsilon_+ < \epsilon_-$, and the existence of band gaps.

To estimate its size, use first order perturbation theory.

$$\Delta E = \langle\psi|V(x)|\psi\rangle$$

So that the energy gap:

$$E_g = \int_0^L dx V(x)[|\psi_-|^2 - |\psi_+|^2]$$

That is:

$$E_g = -\frac{2u}{L} \int_0^L dx \cos \frac{2\pi x}{a} \left[\sin^2 \frac{\pi x}{a} - \cos^2 \frac{\pi x}{a}\right] = u$$

Hence, the amplitude of theband gap is (to first approximation) the same as the depth of the ionic potential:

$$u = \epsilon_+ - \epsilon_-$$

3.8   Zone Schemes

Recall the dispersion relation plot, with band-gaps, of energy E_g. The curves become flat at the zone boundaries, and we have that:

$$v_g = \frac{1}{\hbar} \frac{d\epsilon}{dk} = 0$$

At $k =$ Brillouin zone boundary; $k = \pm\frac{\pi}{a}, \pm\frac{2\pi}{a}, \ldots$. Thus, we get standing waves at the boundary.

The bands are a consequence of the periodic ions. The plots we have seen previously are 'extended zone schemes', with different bands in different zones.

It is often convenient to define:

$$k \mapsto k \pm \frac{2\pi n}{a}$$

So that all k lie within the first Brillouin zone (BZ).
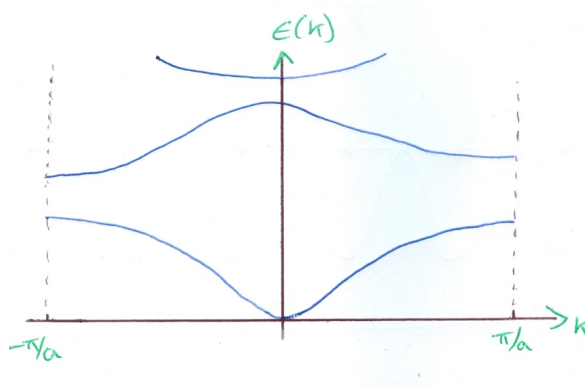

Figure 32: The extended zone scheme, where all bands are 'mapped' back into the first BZ. Shown are the full first and second bands, and the lower part of the third. Notice that they all come in flat to the first BZ boundary.

3.8.1   Block's Theorem

We had that $\psi_k(x) \propto e^{ikx}$ for the free-electron picture. We are now solving Schrodingers equation for a periodic potential:

$$V(x, y, z) = V(x + a, y, z)$$

So we modify the wavefunction thus:

$$\psi_k(x) = e^{i\boldsymbol{k}\cdot\boldsymbol{x}} u_{\boldsymbol{k}}(x, y, z)$$

Where $u_{\boldsymbol{k}}$ has the periodicity of the lattice, so that:

$$u_{\boldsymbol{k}}(x, y, z) = u_{\boldsymbol{k}}(x + a, y, z)$$

That is, the still have the same wave $e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$, but it is now modulated by something having the same periodicity of the potential.

3.8.2   Number of States in a Band

Impose the periodic boundary condition in a crystal of length L. That is:

$$\psi(x) = \psi(x + L)$$

Where $L = Na$. Hence:

$$
\begin{aligned}
\psi(x) &= e^{ikx} u_k(x) \\
&= e^{ik(x+L)} u_k(x + L) \\
&= e^{ikx} u_k(x) e^{ikL}
\end{aligned}
$$

Therefore, we see that we must have $e^{ikL} = 1$. Hence:

$$kL = 2s\pi \qquad s = 0, \pm 1, \pm 2, \ldots$$

Hence, for within the first BZ (i.e. $-\frac{\pi}{a} < k < \frac{\pi}{a}$), we then have that the possible values are:

$$k = 0, \pi\frac{2\pi}{L}, \pi\frac{4\pi}{L}, \ldots, \frac{N\pi}{L}$$

Where the upper limit is just π/a. Notice that we have taken N even, and included only the point $k = +\pi/a$; as $-\pi/a$ is the in second BZ.

So, we have N states per band; and the above obviously holds in more than one dimension. Notice, there are actually $2N$ states for an electron, as we must allow for both spin states.

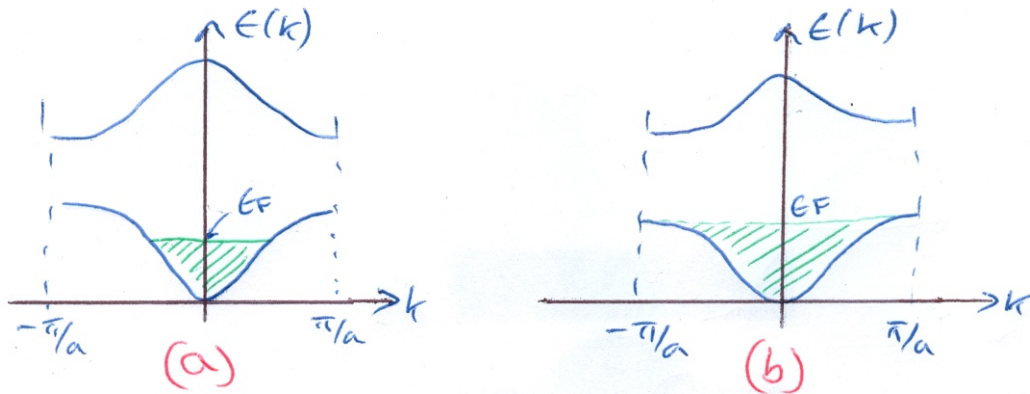### 3.9   Conductors, Semi-Conductors & Insulators

Figure 33: (a) Partially filled band, corresponding to a conductor. (b) Filled band, corresponding to an insulator

With reference to the Figure, we see that a partially filled band will behave as a conductor, since there are empty states available to the displaced electrons (due to an applied electric field), with no energy cost. Hence, we have a metal.

For filled bands, we see that on applying an electric field, there are no vacant states for electrons to move into. Only when the electric field is so strong do electrons jump up a band. This known as dielectric breakdown, and is very hard to do! Hence, such systems are insulators. A filled band carried no net current.
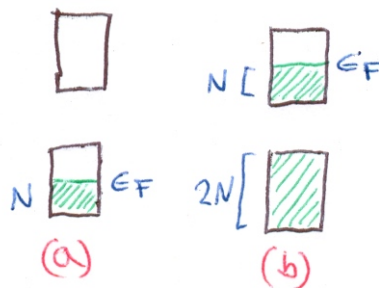

Figure 34: (a) Monovalent metal. (b) Trivalent metal. Each band has the capacity to hold $2N$ electrons.

Monovalent Metals   Example of such are Li, Na, K.

Here, we have 1 valent electron, per atom. Hence, N electrons (for N atoms) in total.

With reference to the Figure, we see that for N electrons, the first band is half-full. Hence metallic.

Trivalent Metals   Here, we will have $3N$ electrons; hence, the second band is half-full, Hence metallic

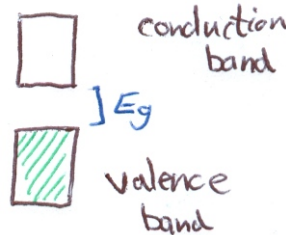### 3.9.1   Divalent Metals

Figure 35: The band scheme for divalent metals. Notice the naming of the bands. Also notice the band gap energy E_g

 Or infact, any even-valent metal. Here, we have $2N$ electrons. Hence, we would (naively) think that the first band will be filled, and will hence be an insulator. However, this is not the case. There are 3 possibilities:

Insulator   Here, consider that the first band is full. If the band gap energy E_g is large (above about 3eV), then the system is an insulator.

Semi-Conductor   If $E_g \approx 1$eV, then thermal effects can excite electrons into the conduction band. So, at $T = 0$, we will have a perfect insulator (as no thermal excitations); the valence band full, and conduction empty. But, at $T \neq 0$, the system will be able to conduct, as electrons are thermally exited from the valence band into the conduction band. Hence, a small non-zero conductivity due to these electrons, and there are 'holes' left behind.

 This is semi-conductor behaviour.

Conductor   If the energy bands overlap, then we have a conductor. We can visualise this by considering that the Fermi surface overlaps the first BZ boundaries.

 In the free electron picture, we have the dispersion relation:

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

Hence, with reference to the Figure:

$$\pi k_F^2 = \left(\frac{2\pi}{a}\right)^2$$

For free electrons, there are vacant sites for the electrons in both the first and second Bz's. See the Figure & caption for the effect of 'switching on' the periodic potential.
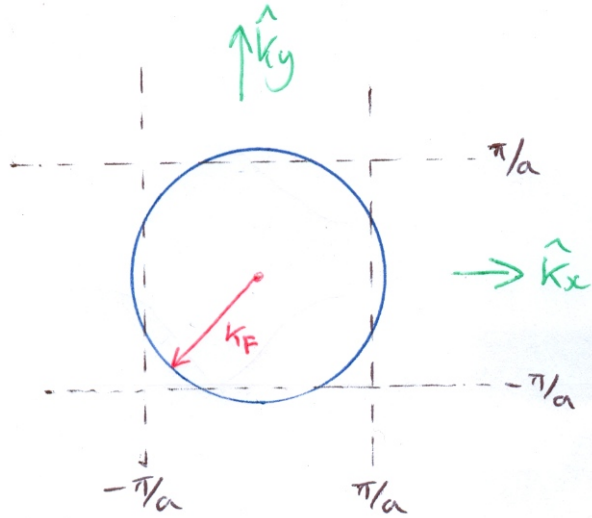
Figure 36: The 2D Fermi surface. The diagram shows that the Fermi surface overlaps the first BZ boundaries. The circle has the same area as the first BZ boundaries. Note: inside the square is the first BZ, and outside the second BZ.
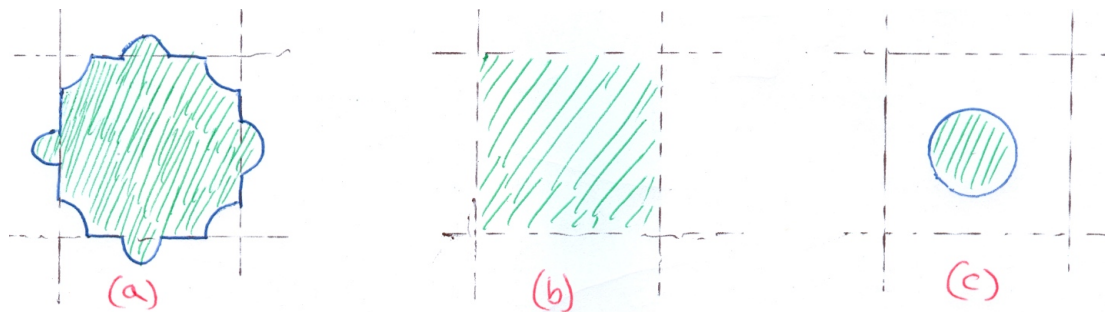
Figure 37: Effect of the periodic potential of the ionic cores in a lattice. (a) The previously circular Fermi surface is distorted into this shape, where there are empty states in both the first and second Bz's; hence metallic. It is for a weak perdiodic potential. (b) This is for a strong periodic potential. Notice that only states within the first BZ are filled, hence an insulator. (c) is for a monovalent atom, where we see that the Fermi surface is well within the first BZ; and the surface is only slightly distorted when we allow for the periodic potential.

3.10 Effective Mass

Another consequence of the periodic potential of the positive ion cores is that the electrons in the solid react to forces on it, as if it had an *effective mass* m^*. We shall state the below formula, but motivate it later:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2\epsilon(k)}{dk^2} \qquad (3.13)$$

Let us just confirm that we retain $m^* = m$ for free electrons. The dispersion relations for free electrons is:

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m}$$

And therefore, using the formula, we get:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\hbar^2}{m} = \frac{1}{m}$$

Hence we have shown that the effective mass for free electrons is the same as their 'usual' mass. However, in general, $m^* \neq m$, and the dispersion relation is not that above.

Now, let us use $\epsilon = \hbar\omega$. Hence, the group velocity:

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{d\epsilon}{dk}$$

Now, suppose we apply an electric field; let us consider how the electron will move. The change in energy, in a time δt is the force on an electron, times the distance it travels in that time. Hence:

$$\frac{d\epsilon}{dk} \delta k = -eE \cdot v_g \delta t$$

Hence, using our expression for the group velocity:

$$\frac{d\epsilon}{dk} \delta k = -eE \cdot \frac{1}{\hbar} \frac{d\epsilon}{dk} \delta t$$

That is:

$$\delta k = -eE \cdot \frac{1}{\hbar} \delta t$$

Using 'proper infinitesimals', and putting vectors on things:

$$\frac{d\boldsymbol{k}}{dt} = -\frac{e\boldsymbol{E}}{\hbar}$$

And therefore:

$$\hbar \frac{d\boldsymbol{k}}{dt} = -e\boldsymbol{E} \qquad (3.14)$$

If there are no applied magnetic fields, and if there are, then:

$$\hbar \frac{d\boldsymbol{k}}{dt} = -e(\boldsymbol{E} + \boldsymbol{v} \times \boldsymbol{B})$$

Now, the crystal momentum is just $\boldsymbol{p} = \hbar\boldsymbol{k}$, and the force is just:

$$\boldsymbol{F} = \frac{d\boldsymbol{p}}{dt}$$

To find acceleration, we need to differentiate the group velocity expression:

$$\frac{d}{dt}v_g = \frac{1}{\hbar}\frac{d}{dt}\frac{d\epsilon}{dk}$$

Which, by the chain rule (!!) gives:

$$\frac{d\boldsymbol{v}_g}{dt} = \frac{1}{\hbar}\frac{d^2\epsilon}{dk^2}\frac{d\boldsymbol{k}}{dt}$$

Where we have an expression for the last term. Hence:

$$\frac{d\boldsymbol{v}_g}{dt} = \frac{1}{\hbar}\frac{d^2\epsilon}{dk^2}\left(-\frac{e\boldsymbol{E}}{\hbar}\right)$$

Now, this is an expression for an acceleration. Hence, multiplying it by the mass (the effective mass, as we will take account of a force), and equating it to the force, we have derived:

$$m^*\frac{d\boldsymbol{v}_g}{dt} = -e\boldsymbol{E}$$

Which is what we stated to begin with.

We see that m^* is infact the curvature of the dispersion relation, and can thus be both positive and negative. If we look at the reduced zone scheme in previous Figures, $m^* > 0$ for the very centre of the bottom band, then changes to $m^* < 0$ after the point of inflection. The part of the second band next to the zone boundary has $m^* > 0$, then changes to $m^* < 0$ as the band passes its point of inflection, going towards the zone centre.

The effective mass is independent of temperature: except for lattice expansions, which is a very small effect.

Let us see how the effective mass will effect various quantities:

- Specific Heat: We have that $C = \gamma T + AT^3$, and that $\gamma \propto m$. Therefore, $\gamma \propto m^*$; where we calcuate at the Fermi energy.

- Conductivity: We had that $\sigma \propto 1/m$. Therefore, $\sigma \propto 1/m^*$. The Lorentz ratio we had before, $\kappa/\sigma T$ was actually independent of m, and therefore of m^*.

- Hall Coefficient: We had that R_H is independent of m, and therefore of m^*.

The free electron model works well for monovalent metals, but less well for other elements.
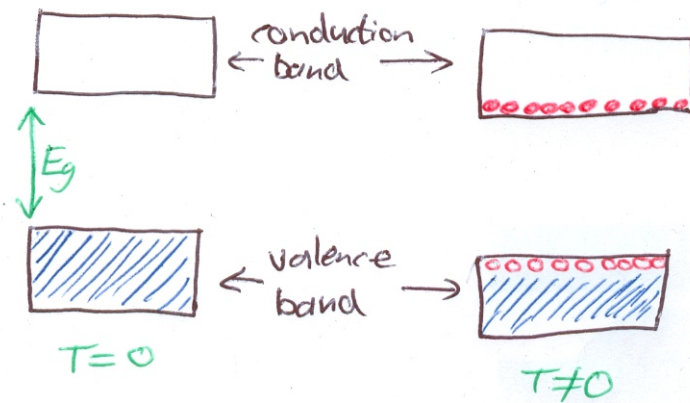
4 Semi-Conductors

Figure 38: Schematic of the bands for a semi-conductor. Notice that at $T = 0$ the valence band is completely full, and the conduction empty. For $T \neq 0$, we see that electrons have been promoted across band gap, provided E_g isn't too big,

From the Figure, we see that at temperatures above aboslute zero, electrons get promoted to the conduction band, leaving holes behind. Only a small number of electrons get promoted: hence not a very good conductor.

Both the electrons & the holes contribute to the conductivity σ, which is highly temperature dependent, as n and p are very T dependent.

- n is the number density of electrons in the conduction band;

- p is the number density of holes in the valence band.

The magnitude of the band gap E_g can be measured by absorption of light (which will knock electrons into the conduction band, hence reducing the intensity of the light, giving a spectrum).

Example are pure Si, Ge; having $E_g = 1.14, 0.74$eV, respectively. Both have diamond structure. C itself has $E_g = 5.4$eV, for diamond, and is an insulator. Alloy examples are GaAs and InSb.
These are all examples of intrinsic semi-conductors, with $n = p$. We shall also consider impurity semi-conductors. Small amounts of impurities are added to greatly increase the conductivity. If $n >> p$, then the material is called *n-type*. If $p >> n$, then *p-type*.

We shall consider semi-conductors in three parts. Firstly the properties of hole & their effects on conductivity, the Hall coefficient etc. Second, a calculation of n & p for both intrinsic & impurity semi-conductors. And finally, $p - n$ junctions.

4.1   Properties of Holes

A full band with a vacant electron state behaves just like a full band, with an additional particle: '
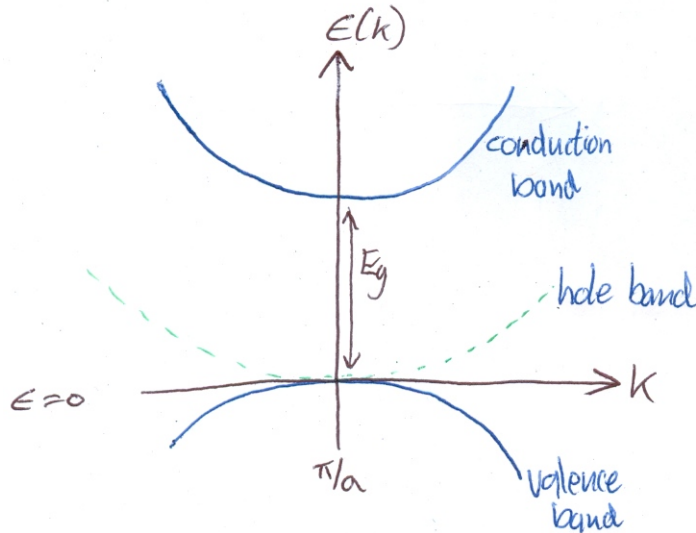*hole*, which has charge $+e$ (like a positron).

Figure 39: The zone scheme. Notice that the axis has been defined so that $\epsilon = 0$ is at the top of
the valence band.

Now, for a full band:

$$\sum_{i=1}^{N} \boldsymbol{k}_i = 0$$

Now, let $\boldsymbol{k}_e$ be the wavevector of an electron removed. Then, the wavevector of the hole is:

$$\boldsymbol{k}_h = -\boldsymbol{k}_e$$

And also:

$$\epsilon_h(\boldsymbol{k}_h) = -\epsilon_e(\boldsymbol{k}_e)$$

This then defines a hole band. The group velocity of a hole:

$$v_g^h = \frac{1}{\hbar} \frac{\partial \epsilon(\boldsymbol{k}_h)}{\partial \boldsymbol{k}_h} = v_g^e$$

Notice that this is the case as the two minus signs will cancel. The holes effective mass is:

$$\frac{1}{m_h^*} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon_h(\boldsymbol{k}_h)}{\partial k_h^2} = -\frac{1}{m_e^*}$$

Notice that $m_h^* > 0$ for the case drawn above, since the electron band has negative curvature, and thus that $m_e^* < 0$, at the top of the valence band.

We have seen that the equation of motion for electrons is:

$$\hbar \frac{d\boldsymbol{k}_e}{dt} = -e(\boldsymbol{E} + \boldsymbol{v}_e \times \boldsymbol{B})$$

The equation of motion for holes is thus:

$$\hbar \frac{d\boldsymbol{k}_h}{dt} = e(\boldsymbol{E} + \boldsymbol{v}_h \times \boldsymbol{B})$$

Note, the current carried by holes in the valence band, and electrons in the conduction band, are in the same direction.

For an electric field applied in one direction, electrons will move in the opposite direction, v_e, and produce a current in the direction of the field $j = nev_e$. Holes (positrons) will move in the same direction of the field, and produce a current in that same direction, $j_h = pev_h$.

4.1.1   Conductivity

The Drude equation:

$$m^* \left(\frac{d}{dt} + \frac{1}{\tau_e} \right) \boldsymbol{v}_e = -e\boldsymbol{E}$$

And, for the steady state:

$$\boldsymbol{v}_e = -\frac{e\tau_e}{m_e^*} \boldsymbol{E} = -\mu_e \boldsymbol{E}$$

Where we have defined the *electron mobility*:

$$\mu_e = \frac{e\tau_e}{m_e^*}$$

Also, as we have seen previously, the current density:

$$\boldsymbol{j}_e = -ne\boldsymbol{v}_e = \sigma \boldsymbol{E}$$

Where we have defined the conductivity:

$$\sigma = ne\mu_e$$

In Semi-Conductors, both electrons & holes contribute to σ:

$$\sigma = ne\mu_e + pe\mu_h$$

Where μ_h is the hole mobility:

$$\mu_h = \frac{e\tau_h}{m_h^*} = \frac{\boldsymbol{v}_h}{\boldsymbol{E}}$$

Compared to metals, semi-conductors have high mobility, but their temperature dependance is weak (a power law, rather than exponential). However, carrier concentrations, n or p, are many orders of magnitudes lower & are strongly temperature dependent:

$$n = p \approx e^{-E_g/k_B T}$$

For the intrinsic SC case.

4.1.2   The Hall Effect

We have the same setup as before; an applied electric field E_x; and perpendicular magnetic field B_z; which will setup some field E_g across the slab. As we have seen, the equation of motion for an electron is:

$$m_e^* \left(\frac{d\boldsymbol{v}_e}{dt} + \frac{\boldsymbol{v}_e}{\tau_e} \right) = -e(\boldsymbol{E} + \boldsymbol{v}_e \times \boldsymbol{B})$$

As always, we consider the steady state, where $\dot{v} = 0$. Thus:

$$\frac{m_e^* \boldsymbol{v}_e}{\tau_e} = -e(\boldsymbol{E} + \boldsymbol{v}_e \times \boldsymbol{B})$$

Using the relation $\boldsymbol{j}_e = -ne\boldsymbol{v}_e$:

$$\boldsymbol{j}_e = \frac{ne^2 \tau_e}{m_e^*}(\boldsymbol{E} + \boldsymbol{v}_e \times \boldsymbol{B})$$

Using the definition of electron mobility:

$$\boldsymbol{j}_e = n\mu_e e(\boldsymbol{E} + \boldsymbol{v}_e \times \boldsymbol{B})$$

Let us add in holes, so that the total current density is the sum:

$$\boldsymbol{j} = \boldsymbol{j}_e + \boldsymbol{j}_h$$

Hence, by analogy:

$$\boldsymbol{j} = n\mu_e e(\boldsymbol{E} + \boldsymbol{v}_e \times \boldsymbol{B}) + p\mu_h e(\boldsymbol{E} + \boldsymbol{v}_h \times \boldsymbol{B})$$

In the steady state, we will have the following:

$$\boldsymbol{B} = (0,0,B) \quad \boldsymbol{E} = (E_x, E_y, 0) \quad \boldsymbol{j} = (j,0,0) \quad \boldsymbol{v}_i = (v_i, 0, 0)$$

Where i refers to either the electron or hole drift velocities. So, expressing the equation for $\boldsymbol{j}$ is component-form:

$$(j_x, 0, 0) = n\mu_e e[(E_x, E_y, 0) + (0, -v_e B, 0)] + p\mu_h e[(E_x, E_y, 0) + (0, -v_h B, 0)]$$

Hence, looking at the first component:

$$j_x = eE_x(n\mu_e + p\mu_h)$$

The second component:

$$0 = eE_y(n\mu_e + p\mu_h) - eB(n\mu_e v_e + p\mu_h v_h)$$

Now, we also note that $v_e = -\mu_e E_x$ and $v_h = \mu_h E_x$. Hence, using these, the second equation easily becomes:

$$0 = eE_y(n\mu_e + p\mu_h) + eE_x B(n\mu_e^2 - p\mu_h^2)$$

That is:

$$E_y = \frac{E_x B(p\mu_h^2 - n\mu_e^2)}{n\mu_e + p\mu_h}$$

The Hall coefficient is defined:

$$R_H \equiv \frac{E_y}{j_x B}$$

And therefore:

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(n\mu_e + p\mu_h)^2}$$

Notice that this goes to the usual $-1/ne$ if $p = 0$; and to $1/pe$ if $n = 0$. Also notice that as $\mu_e \neq \mu_h$, the sign of R_H is not purely determined by the majority carrier. For an intrinsic SC, then the sign of R_H is entirely determined by the largest μ_i (i.e. for $n = p$).

4.2   Intrinsic Carrier Concentration

Recall the previous dispersion-relation Figure, with the $\epsilon = 0$ axis on the top of the valence band. The conduction band started at $\epsilon = E_g$, and so any conduction electrons have $\epsilon > E_g$. Also, we shall state, and show, that $\mu \approx E_g/2$; i.e. the chemical potential is half-way between the two bands.

Now, the number of electrons excited into the conduction band, with energy $\epsilon > E_g$ is:

$$N(\epsilon)d\epsilon = f(\epsilon)D(\epsilon)d\epsilon$$

Where $f(\epsilon)$ is the Fermi-Dirac distribution, the probability that the state of energy ϵ is occupied:

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

For electrons in the conduction band, $\epsilon - \mu \approx \frac{1}{2}E_g \approx 1/2\text{eV}$; but $k_B T \approx 1/40\text{eV}$. Hence, we can approximate the FD distribution:

$$f(\epsilon) \approx e^{-(\epsilon-\mu)/k_B T} \ll 1$$

Now, the density of states:

$$D(\epsilon) = D(k)\frac{dk}{d\epsilon}$$

That is:

$$D(\epsilon) = 2\frac{V}{2\pi^2}k^2\frac{dk}{d\epsilon}$$

Where the factor of '2' outfront is the spin multiplicity factor. Now, we use the following dispersion relation, for electrons in the conduction band:

$$\epsilon = E_g + \frac{\hbar^2 k^2}{2m_e^*} \qquad \Rightarrow \qquad k = \sqrt{\frac{2m_e^*(\epsilon - E_g)}{\hbar^2}}$$

Therefore, using this lot, the density of states becomes:

$$D(\epsilon) = \frac{V}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}(\epsilon - E_g)^{1/2}$$

And therefore, the number density of electrons in the conduction band is:

$$n = \frac{1}{V}\int_{E_g}^{\infty} d\epsilon f(\epsilon)D(\epsilon)$$

Which is just:

$$n \approx \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} \int_{E_g}^{\infty} d\epsilon e^{-(\epsilon-\mu)/k_B T} (\epsilon - E_g)^{1/2}$$

(using approximate symbol, as we have approximated the FD distribution; we will change to equals now, but bear that in mind). Let us change variables: $\epsilon' = \epsilon - E_g$. Then, we easily get:

$$n = \frac{1}{2\pi^2} \left(\frac{2m_e^*}{\hbar^2} \right)^{3/2} e^{(\mu-E_g)/k_B T} \int_0^{\infty} d\epsilon' e^{-\epsilon'/k_B T} \epsilon'^{1/2}$$

The integral evaluates to $\sqrt{\frac{\pi}{2}}(k_B T)^{3/2}$. Thus:

$$n = 2 \left(\frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{(\mu-E_g)/k_B T}$$

Therefore we have computed the number of electrons in the conduction band. We clean up this, by the obvious notation:

$$n = N_c e^{(\mu-E_g)/k_B T} \qquad N_c \equiv 2 \left(\frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{3/2}$$

Now, let us consider the valence band; and the hole density. Now, as $\epsilon < 0$ in the valence band, we have that $f(\epsilon) \approx 1$; which makes sense: almost all states are occupied. Hence, the probability of a hole (in the valence band):

$$f_h(\epsilon) = 1 - f(\epsilon) = e^{(\epsilon-\mu)/k_B T}$$

Now, for holes, the density of states is very similar:

$$D(\epsilon) = \frac{V}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} (-\epsilon)^{1/2}$$

The density of holes, similarly:

$$p = \frac{1}{V} \int_{-\infty}^0 d\epsilon f_h(\epsilon) D(\epsilon)$$

Which is:

$$p = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} \int_{-\infty}^0 d\epsilon e^{(\epsilon-\mu)/k_B T} (-\epsilon)^{1/2}$$

Changing variables again $\epsilon' = -\epsilon$:

$$p = \frac{1}{2\pi^2} \left(\frac{2m_h^*}{\hbar^2} \right)^{3/2} e^{-\mu/k_B T} \int_0^{\infty} d\epsilon' e^{\epsilon'} (\epsilon')^{1/2}$$

Giving the number of holes in the valence band:

$$p = 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-\mu/k_B T}$$

Again, the same obvious notation as before:

$$p = N_v e^{-\mu/k_B T} \qquad N_v \equiv 2 \left(\frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2}$$

This is the effective number of states at the top of the valence band.

Then, we make the product:
$$np = N_c N_v e^{-E_g/k_B T} \equiv A^2(T)$$

It is independent of chemical potential. It is called the "Law of Mass Action".

Now, for intrinsic semiconductors, we have that $n = p$, so this fixed μ:
$$N_c e^{(\mu - E_g)/k_B T} = N_v e^{-\mu/k_B T}$$

Giving:
$$\mu = \frac{1}{2} E_g + \frac{1}{2} k_B T \ln \frac{N_c}{N_v}$$

Which gives:
$$\mu = \frac{1}{2} E_g + \frac{3}{4} k_B T \ln \frac{m_h^*}{m_e^*}$$

Which is about $\frac{1}{2} E_g$, which is somthing we assumed to begin with.

Now:
$$n = \sqrt{np}$$

For intrinsic. This is:
$$n = \sqrt{N_c N_v} e^{-E_g/2k_B T}$$

Giving:
$$n = 2 \left(\frac{k_B T}{2\pi \hbar^2} \right)^{3/2} (m_e^* m_h^*)^{3/4} e^{-E_g/2k_B T}$$

This gives a strong T dependance, in the exponential: $n \to 0$ as $T \to 0$, very quickly.

For example, Si, with $E_g = 1.14\text{eV}$, at $T = 300\text{K}$ gives $n = p = 10^{16} m^{-3}$; and Ge, having $E_g = 0.67\text{eV}$ gives $n = p = 10^{20} m^{-3}$.

These are quite small; consider Cu, having $n \approx 10^{29} m^{-3}$.

4.3   Impurity Semi-Conductors

Si and Ge are intrinsic SC's, but the addition of impurities, "doping", the substance dramatically increases their conductivity.

For example, the addition of 1 Boron atom to 10^5 Si atoms, increases the conductivity by 10^3 at room temperature.

This arises because $n \neq p$, and the chemical potential μ is shifted.
Let ϕ be the total number of carriers. That is:
$$\phi = n + p = n + \frac{A^2(T)}{n}$$

Where we have used the above relation $np = A^2(T)$. $A^2(T)$ in infact independent of μ. This function looks like a parabola, with a minimum. The position of the minimum is easy to find:

$$\frac{d\phi}{dn} = 0$$

Notice that ϕ will have a turning point at $n = A(t)$. That is, at $n = p$. That is, the minimum number of carriers is when $n = p$. Hence, doping moves us away from the minimum.
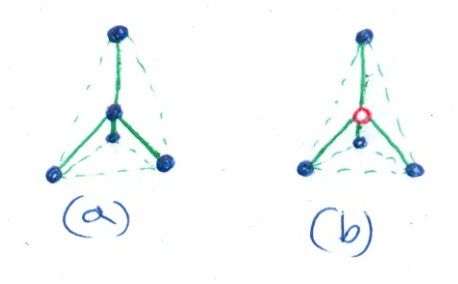
4.3.1 Donors

Figure 40: The tetrahedral structure of silicon. (a) Pure crystal. (b) The middle Si has been replaced with an impurity.

Si & Ge crystallise into a diamond tetrahedral structure, as shown in the Figure. The Si have valency 4; with 4 covalent bonds being formed between nearest neighbours.

Let us replace the central Si with a group 5 element (such as P or As). A group 5 element has 5 valent electrons. 4 of them will be involved in covalent bonding with the Si; leaving one extra. The extra electron is weakly bound, and is easily excited, thermally, into the conduction band, leaving a P^+ or As^+ behind. Let us estimate the energy needed to remove the electron.

Estimates of Ionisation Energy of P, As in Si   Let us do this by comparing with the Hydrogen atom. The ground state energy of hydrogen is given by:

$$E_0 = -\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2} = -13.6eV$$

The 'size' of a hydrogen atom is given by the Bohr radius:

$$a_0 = \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar^2}{m_e} = 0.53\text{Å}$$

To discuss group 5 elements in the Si, we must change the electron mass & use a relative permitivitty:

$$m \to m^* \qquad \varepsilon_0 \to \varepsilon\varepsilon_0$$

The binding energy & characteristic radius then changes; by allowing for these new factors:

$$E_d = -\frac{13.6}{\varepsilon^2}\frac{m^*}{m_e} \qquad a_d = a_0\varepsilon\frac{m_e}{m^*} \tag{4.1}$$

Hence, for Si, we have $m^* = 0.2m_e$ and $\varepsilon = 11.7$; giving the following:

$$E_d = -0.02eV \qquad a_d = 31\text{Å}$$

Note, at room temperature, these energies are very easily attained, via thermal excitation; with $k_B T = 1/40\text{eV}$ which is 0.025eV.

By precise calculation, for As$^+$ in Si, $E_d = 0.03\text{eV}$; and in Ge 0.009eV.

Hence, most donors will ionise, and the electrons will go into the conduction band, acting to increase the conductivity.

4.3.2   Acceptors

Here, we use impurities of group 3 elements: B or Al. Hence, they are one electron short to form the covalent bond. The covalent bond can be formed by taking an electron from the valence band, leaving a hole.

This costs energy, E_a; the binding energy of the hole. We can estimate this as for donors, by considering H-like bound state for a hole.

For B in Si, we get $E_a = 0.045\text{eV}$; and in Ge, $E_a = 0.01\text{eV}$.

Again, as these energies are very close to room-temperature, most acceptors will be ionised; lifting electrons from the valence band, to the acceptor level, leaving holes in the valence band.
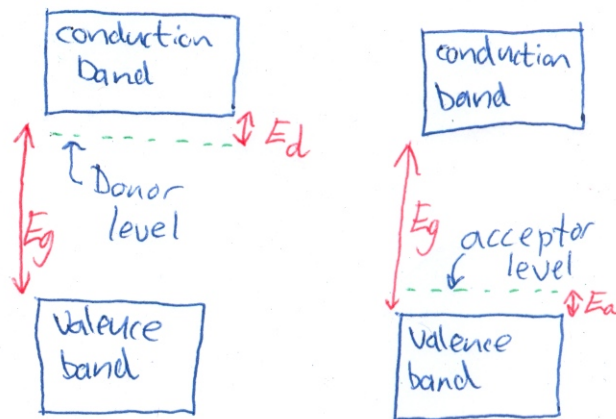

Figure 41: Schematics for both the acceptors & donors. We have that $E_g >> E_a, E_d$.

And thus, as more holes, more conductivity; as conductivity is a property arising from a band not being completely full.

In general, both acceptor & donor impurities can be present.

4.3.3   Conductivity

We have that conductivity is due to both electrons & holes:

$$\sigma = ne\mu_e + pe\mu_h$$

If it is dominated by electrons/holes then the material is a n-type/p-type semi-conductor. As a good guide, from:

$$R_H = \frac{p\mu_h^2 - n\mu_e^2}{e(p\mu_h + n\mu_e)^2}$$

If $R_H < 0$, then n-type; and if $R_H > 0$, then p-type.
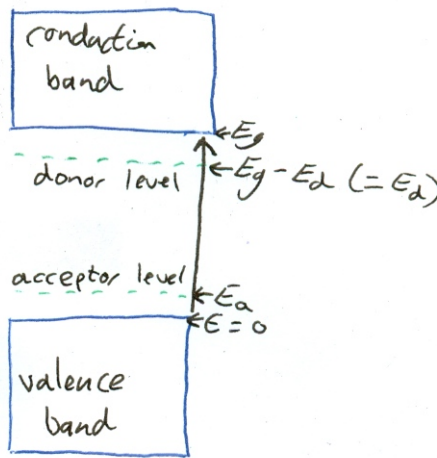
4.4   Impurity & Carrier Concentration

Figure 42: The relative energies of all the bands, together.

As a little aside, if the donor or acceptor ions are close enough to each other that their Bohr radii become comparable to their separations, then the donor & acceptor levels broaden into bands.

We have:

$$\begin{aligned}
n &= N_c e^{(\mu - E_g)/k_B T} & (4.2)\\
p &= N_v e^{-\mu/k_B T} & (4.3)
\end{aligned}$$

With:

$$N_c \equiv 2\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{3/2} \qquad N_v \equiv 2\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2} \tag{4.4}$$

We also have charge neutrality:

$$n + N_A^- = p + N_D^+ \tag{4.5}$$

Where N_A^-/N_D^+ are the concentrations of ionised acceptors/donors. And:

$$N_A^- = N_A f(E_a)$$

As the probability of an electron on the acceptor level, and:

$$N_D^+ = N_D(1 - f(E_g - E_d))$$

Where N_D, N_A are the number densities (or concentrations) of donors/acceptors. With:

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

For a given N_A, N_D, we can solve these 5 equations for n, p, N_D^+, N_A^+ & μ.

 Let us consider some cases.

4.4.1   Intrinsic Behaviour

This occurs when $n >> N_A$, and $p >> N_D$; that is, at high enough temperature, intrinsic behaviour will always occur (i.e. $n = p$).

4.4.2   Typical n-type

Have donor concentrations $N_D > N_A$; but not $N_D >> N_A$ or $N_D \approx N_A$ (i.e. not too much, or too little) THe acceptor level is filled at $T = 0$; and the donor level partially filled; because $N_D > N_A$.
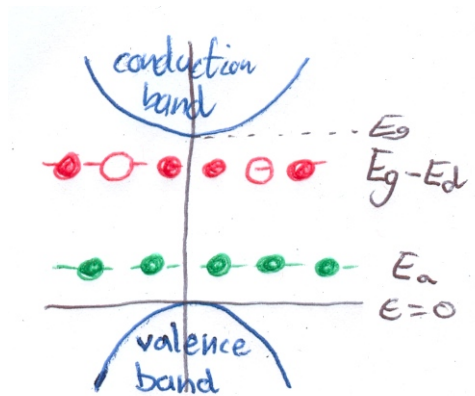

Figure 43: Schematic for the typical n-type semi-conductor. The acceptor level (bottom) is filled at $T = 0$, and the donor band only partially filled; as $N_D > N_A$.

The only level which can be partially occupied at $T = 0$ is the Fermi level:

$$\mu = \epsilon_F = E_g - E_d$$

At $T = 300$K there is only a small correction to this result.

Now, we have:

$$n = N_c e^{(\mu - E_g)/k_B T}$$

But this is just equal to:

$$n = N_c e^{-E_d/k_B T}$$

Which we wrote from the above expression for μ. Note that it is $>> N_c e^{-E_g/2k_B T}$ of the intrinsic case. We also have:

$$p = N_v e^{-\mu/k_B T} = N_v e^{-(E_g - E_d)/k_B T}$$

And this is $<< N_v e^{-E_g/2k_B T}$ of the intrinsic case.

Hence, more n.

We also have that the product np is a constant, independant of doping.

4.4.3   Typical p-type

Here, $N_A > N_D$; with the analogous conditions that the following are not true: $N_A >> N_D$, $N_A \approx N_D$.

At $T = 0$, we have $\mu = E_a$. And hence:

$$p = N_v e^{-E_a/k_B T} >> N_v e^{-E_g/2k_B T}$$

That is, a lot greater than the intrinsic case; and also that n is a lot less than the intrinsic case.

Example   Suppose in Si, there is an intrinsic carrier concentration of $2 \times 10^{16} m^{-3}$. It is doped with donors to a concentration of $10^{19} m^{-3}$. Assume all donors ionised. Now, what is the hole concentration?

We have that the product np is a constant:

$$np = (2 \times 10^{16})^2 = A^2(T)$$

From the law of mass action. And we have that $n = 10^{19}$; hence:

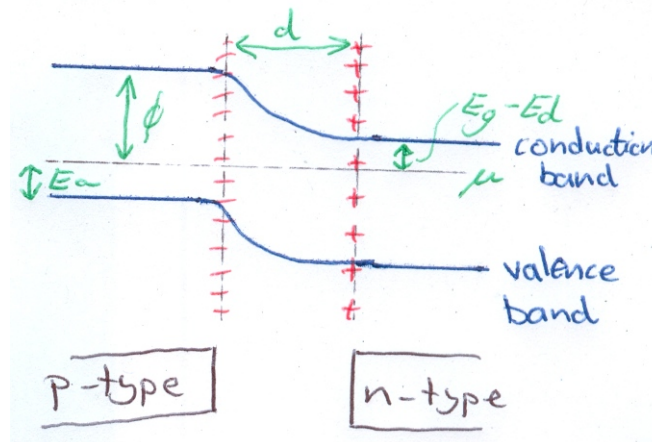$$p = \frac{(2 \times 10^{16})^2}{10^{19}} = 4 \times 10^{13} m^{-3}$$

Hence found.

Figure 44: The $p - n$ junction. The gap d is called the *depletion layer*. This will form something like a diode.

4.5 $p - n$ Junction

This is a basic semi-conductor device. For chemical equilibrium, μ is a constant, throughout. Now, since $\mu(n - type) > \mu(p - type)$ when brought into contact, there will be a flow of electrons from n- to p-type; which will annihilate with the holes, until μ is equal.

We have:

$$\phi = (E_g - E_d) - E_a$$

We will end up with positive and negative charge building up on either side of the depletion layer. No free electrons in the depletion layer.

Let us consider the thickness of the depletion layer. Now, the electric field, due to some surface charge:

$$E = \frac{\sigma}{\varepsilon_r \varepsilon_0}$$

Where $\sigma = eN_D d$; But also:

$$E = \frac{\phi}{d} = \frac{eN_D d}{\varepsilon_r \varepsilon_0}$$

Hence:

$$d = \sqrt{\frac{\phi \varepsilon_r \varepsilon_0}{eN_D}} \approx 0.2\mu m$$

After taking:

$$\phi \approx 0.5V \qquad \varepsilon_r \approx 10 \qquad N_D \approx 10^{16} cm^{-3}$$

4.5.1   Application: Solar Cells

Consider a $p - n$ junction; with a wire connecting the two ends; with light being able to fall on the connection depletion layer.
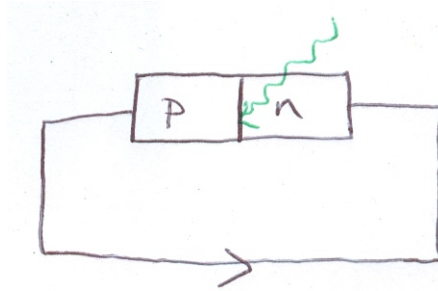
Figure 45: The solar cell. A p-n junction has light incident upon its connecting depletion layer; and current flow around a wire connecting the two ends.

 The incident photons create an electron-hole pair in the junction; the holes are driven to the p-side & the electrons to the n-side in the deplation layer.

 Therefore, a current flow from n to p; and the photon energy is converted into electrical energy.