

# Solid State Physics

Magic crystal balls.

porl

Taken from lectures given by Dr. Peter Mitchell at Manchester University 2006

Many Thanks to Louise Prideaux and Chris Carracher for giving me copies of the lectures I missed!

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We can use our knowledge of atoms, Quantum Mechanics and Statistical physics to explain what we call condensed matter physics. Condensed matter physics splits up into three branches; crystalline solids, amorphous materials and liquids. Whilst solid state physics is the study of crystalline solids and amorphous materials, this course will only be looking into the physics of crystalline solids.

So what is a crystal? What are we interested in? The easiest way to answer these questions at the moment is with an example; iron is as good as any,

[Iron is an interesting example as there are two possible crystal structures that iron can make; face centred cubic (fcc) and body centred cubic (bcc).]

Properties that we're interested in	Iron
Transition temperature – melting point	$T_M = 1808K$ (solid at room temperature)
Mechanical - strength - elasticity	Pretty strong stuff – used for buildings and ships like the titanic.
Electrical - conductivity	Resistivity $10^{-5} \Omega cm$
Magnetic - susceptibility	Ferromagnetic for $T < T_c$
Thermal - heat capacity	$C = \gamma T + \epsilon T^{\frac{3}{2}} + \beta T^3$
Optical - reflectivity -colour	Iron reflects visible light Irons coloured!

## Aim of course

We have a problem; in any simple sample of material we have about  $10^{23}$  atoms. Therefore if we try to solve a problem for this sample, we'll have a many body problem which has no exact solution. So we must develop approximation schemes and associated physical pictures (models). That is the point to this course.

We'll start with a structure of perfect infinite crystal at  $T = 0$ .

The specific heat is given by;  $C = \beta T^3$  - this is due to lattice vibrations (see the Debye model).

If the electrons are free to travel there is a second contribution;  $C = \gamma T$

If we consider spin waves (which are the magnetic equivalent of lattice vibrations) we find  $C = \epsilon T^{\frac{3}{2}}$ .

We now assume that the heat capacity is the sum of these three contributions which gives;  $C = \gamma T + \epsilon T^{\frac{3}{2}} + \beta T^3$ . This assumption is not entirely correct, there should be some small corrections which we won't worry about right now.

Contents of this course;

Section	Reference in Hook and Hall
1. Crystal Structures	1.1-1.3
2. Diffraction and Reciprocal Lattice	11.1, 11.2, 12.1 – 12.3
3. Lattice Dynamics	2.1 – 2.6, 12.4
4. Metals	Chapters 3 and 4
5. Semiconductors	Chapter 5

Texts

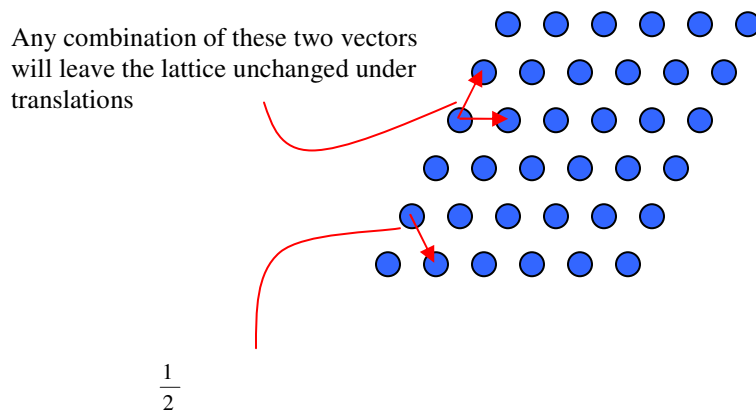
1. Hook and Hall, *Solid State Physics*, Wiley, 2<sup>nd</sup> Edition, 1991
2. Kittel, *Introduction to Solid State Physics*, Wiley, 8<sup>th</sup> Edition, 2004

# 1. Crystal Structure

## 1.1. Translation Symmetry And Bravais Lattices

At the heart of solid state (crystal) physics is the assumption of translation symmetry. A non-trivial translation will leave any structure (a 2D object) or any pattern (a 3D object) and leave it unchanged.

For example, let's consider an infinite lattice;



We need to ask which points are equivalent. The vector between any two equivalent points leaves the lattice unchanged under translations. These vectors characterise the symmetry of the pattern. Equivalent points have the same environment in the same orientation.

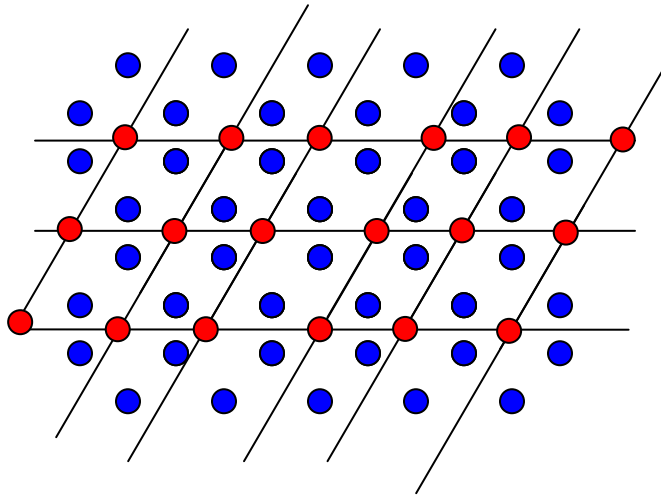
Translation symmetry: 2D can be characterised by a two dimensional lattice or net and in three dimensions by a Bravais Lattice.

### Definitions

1. A Bravais Lattice is an infinite array of points which appears exactly the same when viewed from any one of the points.
2. A Bravais Lattice consists of all points with position vector  $\bar{R}$  of the form  $\bar{R} = n_1\bar{a} + n_2\bar{b} + n_3\bar{c}$  where  $\bar{a}, \bar{b}, \bar{c}$  are any three non-coplanar vectors and  $n_1, n_2, n_3$  range through all integer values (positive, negative and zero).

## 1.2. Basis and unit cell

What is it that repeats to give the whole pattern/ structure?



There are two blue blobs in each parallelogram. The corners of each parallelogram (the red dots) are equivalent points.

“The lattice plus the basis equals the structure”.

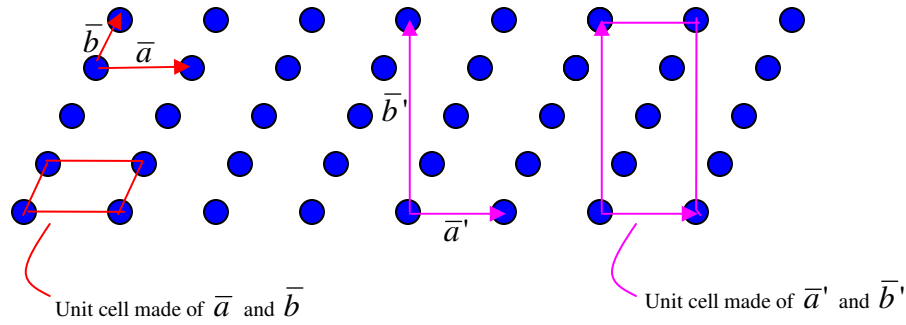
We start with a parallelogram (or a parallelepiped in three dimensions) whose edges are the lattice vectors. We associate the contents (AKA the basis) with all the lattice points. The choice is not unique, just like the choice of the lattice vectors.

Sometimes the basis is defined within a shape other than a parallelogram or a parallelepiped which tessellates the plane (or equivalent in three dimensions) i.e. it fills up all of space without overlapping or leaving gaps.

A *crystalline structure* consists of identical copies of the *basis* located at all the points of the Bravais lattice.

A *primitive unit cell* is the box which contains the basis. A unit cell may be chosen to contain more than one copy of the basis, this is known as a *non – primitive unit cell*.





The area of the unit cell made using  $\bar{a}'$  and  $\bar{b}'$  is four times greater than that of the unit cell constructed with  $\bar{a}$  and  $\bar{b}$ ;  $|\bar{a}' \times \bar{b}'| = 4|\bar{a} \times \bar{b}|$

Lattice vectors  $\bar{a}$  and  $\bar{b}$  are primitive and define a primitive unit cell. Lattice vectors  $\bar{a}'$  and  $\bar{b}'$  are non - primitive.

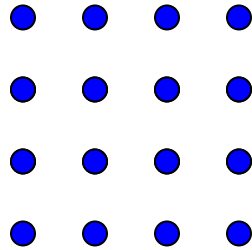
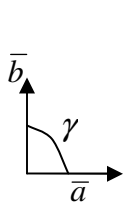
The non – primitive unit cell contains four copies of the basis.

The choice of unit cell and lattice vectors is inseparable. A non – primitive choice is usually made to reflect some symmetry in the structure which may not be apparent in the primitive unit cell.

A unit cell is a region that fills all of space, without either overlapping or leaving voids, when translated through some subset of the vectors of a Bravais lattice. A unit cell is primitive if the same is true for all the vectors of a Bravais Lattice.

A *conventional unit cell* may be chosen which is non – primitive, usually to preserve some symmetry (or Orthogonality) of the lattice vectors.

### 1.3. Classifying lattices: symmetry in 2D



Square Lattice:  $|\vec{a}| = |\vec{b}|$ ;  $\gamma = 90^\circ$

This square lattice has rotational symmetry. We say that this lattice has “four fold rotational symmetry”.

### Symmetry operations

Operations which map the pattern into itself include translation, rotation, reflection, inversion ( $\vec{r} \rightarrow -\vec{r}$ ) and various combinations of these.

A  $\frac{2\pi}{n}$  rotation is called an  $n$ -fold rotation. (For a Bravais lattice  $n = 2,3,4,6$ )

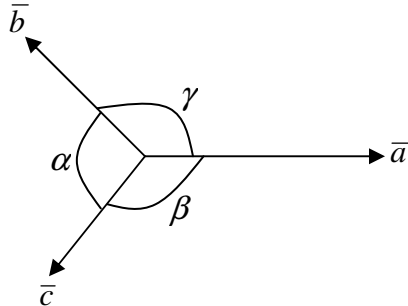
### Two Dimensional Lattice Types

All of the possible two dimensional lattices fall into one of these 5 categories;

- Square;  $|\vec{a}| = |\vec{b}|$ ;  $\gamma = 90^\circ$       4 fold - 4 mirror planes
- Hexagonal  $|\vec{a}| = |\vec{b}|$ ;  $\gamma = 120^\circ$       6 fold - 6 mirror planes
- Rectangular  $|\vec{a}| \neq |\vec{b}|$ ;  $\gamma = 90^\circ$       2 fold - 2 mirror planes
- Centred Rectangular  $|\vec{a}| \neq |\vec{b}|$ ;  $\gamma = 90^\circ$
- Oblique none of the above

## 1.4. Classifying lattices: Symmetry in 3D

There are 14 Bravais Lattices (see Kittel p. 9)



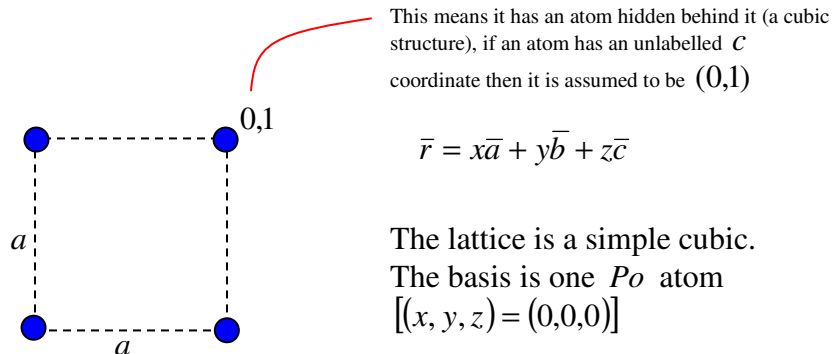
Simple Cubic	$ \bar{a}  =  \bar{b}  =  \bar{c} ; \quad \alpha = \beta = \gamma = 90^\circ$
Body – Centred Cubic	
Face – Centred Cubic	
Hexagonal	$ \bar{a}  =  \bar{b}  \neq  \bar{c} ; \quad \alpha = \beta = 90^\circ; \quad \gamma = 120^\circ$

### Projected Crystal Structures

We have a method for representing 2D unit cells: we project down the  $c$  axis and label sites with fractional  $c$  - coordinates.

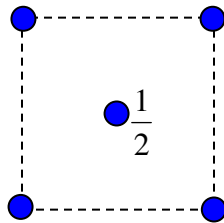
This is best explained through example;

#### Polonium, $Po$



This is a monoatomic simple cubic structure. It's not worth knowing that polonium takes this structure for temperatures upto about  $38^\circ C$  and has a half life of about 140 days.

### Chromium, *Cr*

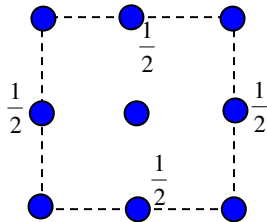


● = *Cr* atom

The lattice is a body centred cubic.  
The basis is one *Cr* atom.

This is a monoatomic body centred cubic structure.

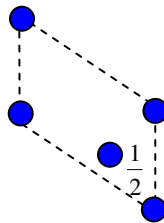
### Nickel, *Ni*



The lattice is a face centred cubic.  
The basis is one *Ni* atom.

This is a monoatomic face centred cubic structure.

### Cobalt, *Co*



The lattice is hexagonal.  
The basis is two *Co* atoms, one at  $(0,0,0)$  and one at  $\left(\frac{3}{2}, \frac{1}{3}, \frac{1}{2}\right)$

This structure is called hexagonal close packed (h.c.p) and the lattice is hexagonal.

## Note on “close packing”

The stacking of close packed layers for the hexagonal close packed (h.c.p) structure is  $[AB]_n$

$$|\bar{a}| = |\bar{b}| \quad \text{and} \quad |\bar{c}| = \sqrt{\frac{8}{3}}|\bar{a}| \approx 1.63|\bar{a}|$$

However in practise this value varies as this is not a perfect model of lattice structure;

Metal	$\frac{c}{a}$
<i>Co</i>	1.62
<i>Be</i>	1.56
<i>Zn</i>	1.86
<i>Gd</i>	1.59

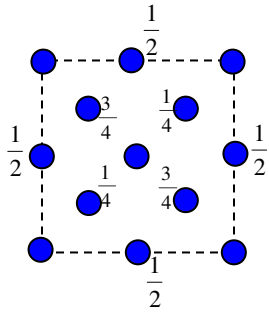
If we change the sequence to  $[ABCABCABC]_n$ , then we find that this structure is the face centred cubic structure.

There are other sequences;

Sm:  $[ABABCBCAC]_n$

## 1.5. More Crystal Structures

### Silicon

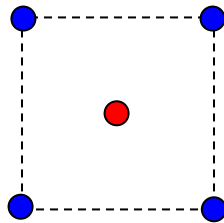


The lattice is a face centred cubic lattice and the basis is two *Si* atoms i.e. one located at  $[0,0,0]$  and one at

$$\left[ \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right]$$

This structure is called the *diamond structure* and is also present for *Ge* and *C* (in its diamondised form obviously!)

### CsCl

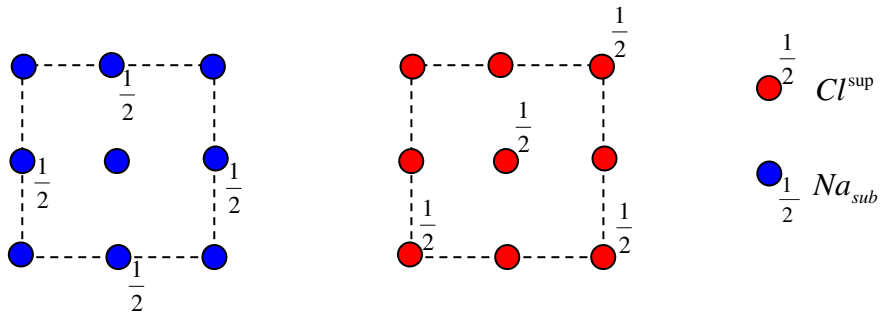


This lattice is a simple cubic lattice. The basis is one *Cs* atom located at  $(0,0,0)$  and one *Cl* atom located at  $\left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right)$

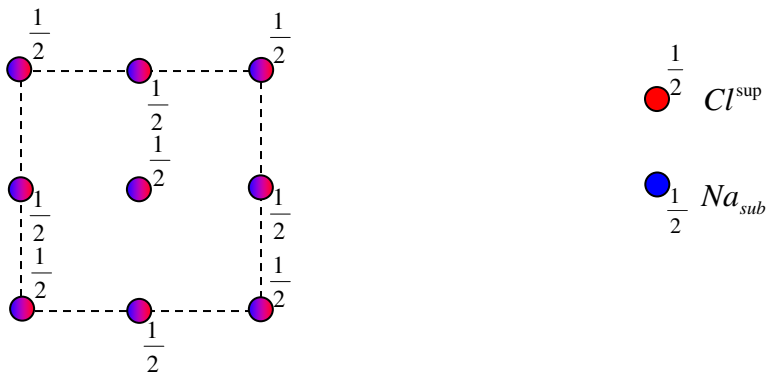
The number of nearest neighbours of the opposite sort is called the *co-ordination number* and is eight in this case.

## NaCl

This is quite a complicated structure and so it's easiest if we first break it down;

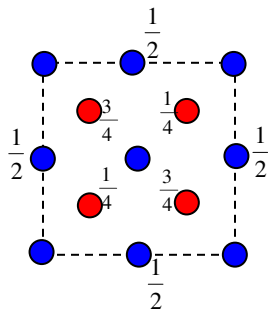


Combining these two gives the full structure;



The lattice is a face centred cubic lattice. The basis is a  $Na$  atom at  $(0,0,0)$  and a  $Cl$  atom at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . This structure is called the *rocksalt* structure and has a co-ordinate number of 6.

## Zinc Blende



● *Zn*

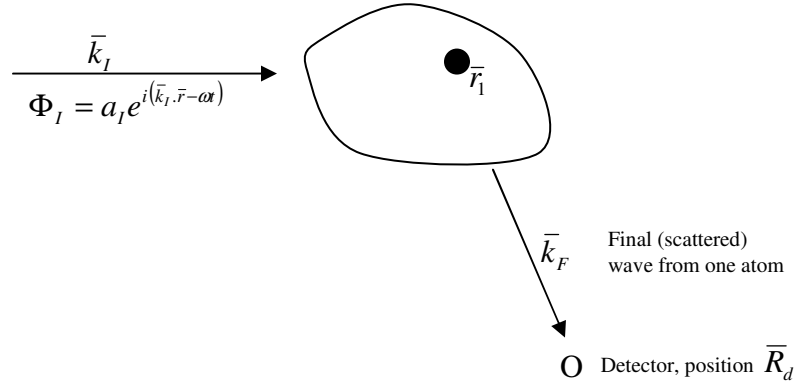
● *S*

This lattice is a face centred cubic lattice. The basis is a *Zn* atom at  $(0,0,0)$  and a *S* atom at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . The co-ordination number of this structure is 4.



## 2. Diffraction and the reciprocal lattice

### 2.1. Scattering of a plane wave by a crystal



For scattering off an individual atom, the final wavefunction is

$$\Phi_F = a_I e^{i(\bar{k}_I \cdot \bar{r} - \alpha)} \frac{b_1 e^{i\bar{k}_F \cdot (\bar{R}_d - \bar{r}_1)}}{|\bar{R}_d - \bar{r}_1|}$$

For scattering off a number of atoms,  $j$ ;

$$\Phi_F = \sum_j a_I e^{i(\bar{k}_I \cdot \bar{r} - \alpha)} \frac{b_j e^{i\bar{k}_F \cdot (\bar{R}_d - \bar{r}_j)}}{|\bar{R}_d - \bar{r}_j|}$$

For a detector which is a very long way away from the atoms (i.e. a large  $\bar{R}_d$ ) then;

$$|\bar{R}_d - \bar{r}_j| \approx |\bar{R}_d| \quad \forall j$$

$$\text{So; } \Phi_F = \frac{a_I e^{i(\bar{k}_I \cdot \bar{r} - \alpha)}}{|\bar{R}_d|} \sum_j b_j e^{i(\bar{k}_I - \bar{k}_F) \cdot \bar{r}_j}$$

This is a wave travelling in the direction of  $\bar{k}_F$  whose amplitude is determined by the sum over atoms,  $j$ .

We define the *wavevector transfer* as  $\bar{Q} = \bar{k}_I - \bar{k}_F$ .

Note that the *momentum transfer* is  $\hbar\bar{Q}$ .

For each atom,  $\bar{r}_j$  is the position of the associated lattice point,  $\bar{R}_d$ , plus the position within the basis  $\bar{r}_{bj}$ ;  $\bar{r}_j = \bar{R}_d + \bar{r}_{bj}$ .

If we split the interference term into two, one over the lattice points and the other over atoms in the basis;

$$\Phi_F = \frac{a_I e^{i(\bar{k}_I \cdot \bar{r} - \omega t)}}{|\bar{R}_d|} \sum_{\text{lattice}} e^{i\bar{Q} \cdot \bar{R}_d} \sum_{\text{basis}} b_j e^{i\bar{Q} \cdot \bar{r}_{bj}}$$

Now lattice vectors may be written as integer sums over lattice vectors  $\bar{a}, \bar{b}, \bar{c}$  so;

$$\sum_{\text{lattice}} e^{i\bar{Q} \cdot (n_1 \bar{a} + n_2 \bar{b} + n_3 \bar{c})}$$

Constructive interference occurs when all of the terms add;

$$\left. \begin{aligned} \bar{Q} \cdot \bar{a} &= 2\pi m_1 \\ \bar{Q} \cdot \bar{b} &= 2\pi m_2 \\ \bar{Q} \cdot \bar{c} &= 2\pi m_3 \end{aligned} \right\} m_1, m_2, m_3 \text{ are integers; exponential is unity.}$$

N.B.  $\bar{b} \times \bar{c}$  is orthogonal to both  $\bar{b}$  and  $\bar{c}$ .

$$\text{If we write; } \bar{Q} = \frac{2\pi \bar{b} \times \bar{c}}{\bar{a} \cdot \bar{b} \times \bar{c}} m_1 + \frac{2\pi \bar{c} \times \bar{a}}{\bar{a} \cdot \bar{b} \times \bar{c}} m_2 + \frac{2\pi \bar{a} \times \bar{b}}{\bar{a} \cdot \bar{b} \times \bar{c}} m_3$$

Then the above conditions are satisfied for all lattice points.

## 2.2. Sum over lattice points

As found in the last section, we can write  $\bar{Q} = \frac{2\pi\bar{b}\times\bar{c}}{\bar{a}\cdot\bar{b}\times\bar{c}}m_1 + \frac{2\pi\bar{c}\times\bar{a}}{\bar{a}\cdot\bar{b}\times\bar{c}}m_2 + \frac{2\pi\bar{a}\times\bar{b}}{\bar{a}\cdot\bar{b}\times\bar{c}}m_3$ .

If we write  $\bar{a}^* = \frac{2\pi\bar{b}\times\bar{c}}{\bar{a}\cdot\bar{b}\times\bar{c}}$        $\bar{b}^* = \frac{2\pi\bar{c}\times\bar{a}}{\bar{a}\cdot\bar{b}\times\bar{c}}$        $\bar{c}^* = \frac{2\pi\bar{a}\times\bar{b}}{\bar{a}\cdot\bar{b}\times\bar{c}}$

Then diffraction happens when  $\bar{Q} = m_1\bar{a}^* + m_2\bar{b}^* + m_3\bar{c}^* = \bar{G}$

$m_1, m_2, m_3$  are often labelled as  $h, k, l$ .

Since  $\bar{a}, \bar{b}$  and  $\bar{c}$  are non-coplanar vectors, so are  $\bar{a}^*, \bar{b}^*$  and  $\bar{c}^*$ , therefore these  $\bar{Q}$  values also represent a Bravais lattice (but in the space where the wavevectors exist).

We now have a Bravais lattice in wavevector space which tells us in which directions diffraction happens from a crystal. This space is called *reciprocal space* or *k-space* (or *q-space*) since the dimensions of  $k$  are  $L^{-1}$ . The lattice is called the *reciprocal lattice*.

Diffraction occurs when  $\bar{Q} = \bar{G}$ , where  $\bar{G}$  is any reciprocal lattice vector.

## 2.3. Reciprocal Lattice Vectors

Note that  $\bar{a}^*\bar{a} = 2\pi$  and that  $\bar{a}^*\bar{b} = \bar{a}^*\bar{c} = 0$

So  $\bar{a}^*$  is orthogonal to  $\bar{b}$  and  $\bar{c}$ , but this does not imply that  $\bar{a}^*$  is parallel to  $\bar{a}$ .

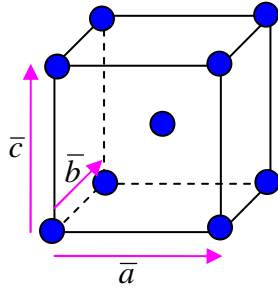
For  $\bar{R} = n_1\bar{a} + n_2\bar{b} + n_3\bar{c}$  and  $\bar{G} = m_1\bar{a}^* + m_2\bar{b}^* + m_3\bar{c}^*$ ;

$\bar{G}\cdot\bar{R} = 2\pi(n_1m_1 + n_2m_2 + n_3m_3)$       with  $n$ 's and  $m$ 's integer.

So that  $e^{i\bar{G}\cdot\bar{R}} = 1 \quad \forall \bar{R}$  of the lattice

This satisfies the constructive interference condition. If  $\bar{a}, \bar{b}$  and  $\bar{c}$  are chosen as non-primitive, then this construction for the reciprocal lattice vectors is not correct since the condition needs to be satisfied for all lattice vectors, not just the ones which can be made up using the non-primitive lattice vectors. The effect of this is to generate points which are not really reciprocal lattice vectors.

### Example: Non-primitive lattice vectors in the body centred cubic lattice



Conventional vectors are:

$$\bar{a} = a(1,0,0)$$

$$\bar{b} = a(0,1,0)$$

$$\bar{c} = a(0,0,1)$$

$$\Rightarrow \bar{a} \cdot \bar{b} \times \bar{c} = a^3$$

Thus;  $\bar{a}^* = \frac{2\pi}{a}(1,0,0)$

$$\bar{b}^* = \frac{2\pi}{a}(0,1,0)$$

$$\bar{c}^* = \frac{2\pi}{a}(0,0,1)$$

Let's choose a conventional primitive choice;

$$\bar{a}' = a\left(\frac{1}{2}, \frac{-1}{2}, \frac{1}{2}\right)$$

$$\bar{a}' \cdot \bar{b}' \times \bar{c}' = \frac{a^3}{2}$$

$$\bar{b}' = a\left(\frac{1}{2}, \frac{1}{2}, \frac{-1}{2}\right)$$

$$\bar{c}' = a\left(\frac{-1}{2}, \frac{1}{2}, \frac{1}{2}\right)$$

These vectors give;

$$\bar{b}' \times \bar{c}' = a^2\left(\frac{1}{2}, 0, \frac{1}{2}\right)$$

$$\bar{c}' \times \bar{a}' = a^2\left(\frac{1}{2}, \frac{1}{2}, 0\right)$$

$$\bar{a}' \times \bar{b}' = a^2\left(0, \frac{1}{2}, \frac{1}{2}\right)$$

And so we find that the primitive reciprocal lattice vectors are;

$$\bar{a}^{*'} = \frac{2\pi}{a}(1,0,1)$$

$$\bar{b}^{*'} = \frac{2\pi}{a}(1,1,0)$$

$$\bar{c}^{*'} = \frac{2\pi}{a}(0,1,1)$$

Any integer sum of these primitive reciprocal lattice vectors is a reciprocal lattice vector e.g;

$$2\bar{a}^* = \frac{2\pi}{a}(2,0,2) \quad m'_1 = 2, \quad m'_2 = 0, \quad m'_3 = 0$$

$$\bar{a}^* + \bar{c}^* = \frac{2\pi}{a}(1,1,2) \quad m'_1 = 1, \quad m'_2 = 0, \quad m'_3 = 1$$

However, there are vectors which can be constructed from the conventional (non-primitive) reciprocal lattice vectors which cannot be constructed from the primitive vectors e.g;

$$\bar{a}^* = \frac{2\pi}{a}(1,0,0) \quad m_1 = 1, \quad m_2 = 0, \quad m_3 = 0$$

$$\bar{a}^* + \bar{b}^* + \bar{c}^* = \frac{2\pi}{a}(1,1,1)$$

This is true for all  $m_1, m_2, m_3$  where  $m_1 + m_2 + m_3 = 2n + 1$ . These are not reciprocal lattice points and no diffraction occurs. When using conventional non-primitive lattice vectors, these are referred to as *systematic absences*. They are an artefact of the choice of a non-primitive cell.

## 2.4. Magnitude of $\bar{G}_{h,k,l}$ in cubic systems

If we consider the following vectors;

$$\bar{a} = a(1,0,0) \quad \bar{a}^* = \frac{2\pi}{a}(1,0,0)$$

$$\bar{b} = a(0,1,0) \quad \bar{b}^* = \frac{2\pi}{a}(0,1,0)$$

$$\bar{c} = a(0,0,1) \quad \bar{c}^* = \frac{2\pi}{a}(0,0,1)$$

Then we find that

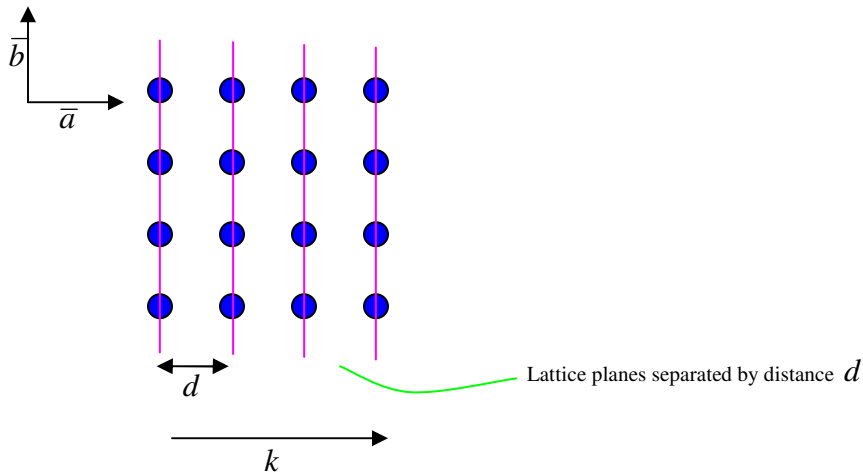
$$\begin{aligned}\bar{G}_{hkl} &= h\bar{a}^* + k\bar{b}^* + l\bar{c}^* \\ &= \frac{2\pi}{a}(h, k, l)\end{aligned}\quad [h, k, l \text{ integers}]$$

And so the magnitude is;  $|\bar{G}_{h,k,l}| = \frac{2\pi}{a}(h^2 + k^2 + l^2)^{\frac{1}{2}}$

Diffraction occurs when  $\bar{Q} = \bar{G}$  ;

$$\begin{aligned}\bar{a}' &= a\left(\frac{1}{2}, \frac{-1}{2}, \frac{1}{2}\right) & \bar{a}^* &= \frac{2\pi}{a}(1,0,1) \\ \bar{b}' &= a\left(\frac{1}{2}, \frac{1}{2}, \frac{-1}{2}\right) & \bar{b}^* &= \frac{2\pi}{a}(1,1,0) \\ \bar{c}' &= a\left(\frac{-1}{2}, \frac{1}{2}, \frac{1}{2}\right) & \bar{c}^* &= \frac{2\pi}{a}(0,1,1)\end{aligned}$$

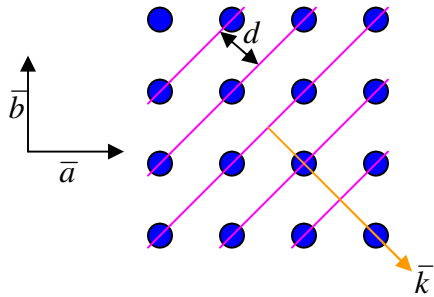
## 2.5. Lattice planes and indices



Consider lattice points as belonging to planes, separated by a distance ‘ $d$ ’. Now consider these planes as wavefronts of some wave characterised by a wavevector  $\bar{k}$  perpendicular to the wavefront.  $|\bar{k}| = \frac{2\pi}{d}$

For a simple cubic lattice;  $d = a$  ;  $\bar{k} = \frac{2\pi}{a}(1,0,0)$  or  $\bar{k} = \bar{a}^*$

Let's consider a different set of planes:

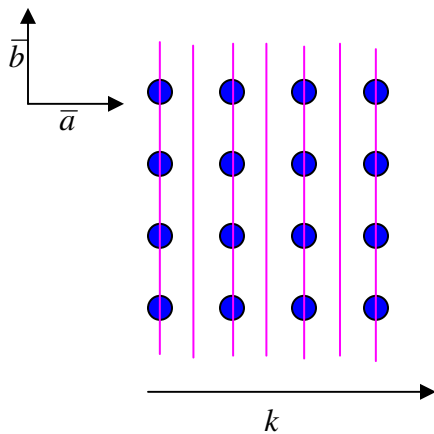


$$d = \frac{1}{\sqrt{2}}$$

$$\vec{k} = \frac{2\pi}{a}(1, -1, 0) \quad \text{or} \quad \vec{k} = \vec{a}^* - \vec{b}^*$$

The wavevectors of the waves whose wavefronts are lattice planes are the position vectors in reciprocal space of reciprocal lattice points.

But do all lattice points represent planes?



$$(2, 0, 0)?$$

Spatial harmonics. The same planes with extra wavefronts. The real space separation is  $d = \frac{a}{2}$ . Similarly  $(6, 6, 0)$  is a harmonic of  $(1, 1, 0)$  etc.

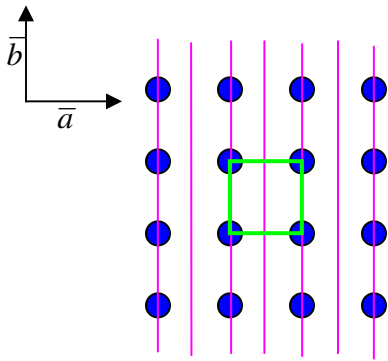
## 2.5.1.Indices: Part 1

The convention for representing lattice planes is to take the integers  $m_1, m_2, m_3$  (the coefficients of  $\bar{a}^*, \bar{b}^*, \bar{c}^*$ ) and write the negative  $u$  as  $-u = \bar{u}$

e.g.  $(1,0,0)$ ,  $(3,1,0)$ ,  $(7,15,2)$       In general  $(h,k,l)$

If the unit cell has sides  $\bar{a}, \bar{b}, \bar{c}$  then adjacent planes intersect the axes at  $(0,0,0)$  then at

$$\left( \frac{\bar{a}}{h}, \frac{\bar{b}}{k}, \frac{\bar{c}}{l} \right)$$



$(2,0,0)$  planes intersect axis at origin  
then  $\frac{a}{2}$ ,  $a$  and not at all on  $\bar{b}, \bar{c}$ .

Sets of lattice planes  $(h,k,l)$  are related by symmetry written as  $\{hkl\}$

e.g. In cubic  $\{200\} = (200), (020), (002), (\bar{2}00), (0\bar{2}0), (00\bar{2})$

## 2.5.2.Indices: Part 2

When we are interested in lattice planes only (and not harmonics), we use *Miller Indices* where  $h,k,l$  have any common factors removed.

e.g.  $(1\ 0\ 0)$   $(2\ 0\ 0)$   $(7\ 0\ 0)$  are all represented by Miller Indices  $(1\ 0\ 0)$



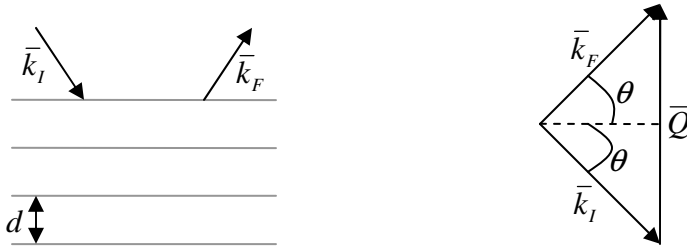
## Directions in real space

For direction:  $u\bar{a} + r\bar{b} + w\bar{c}$  we write  $[uvw]$  (with common factors removed). Sets of directions related by symmetry are written  $\langle uvw \rangle$  e.g. In a cubic crystal  $\langle 1,1,1 \rangle = [111], [1,1,\bar{1}], [1\bar{1}1], [\bar{1}\bar{1}\bar{1}], [\bar{1}\bar{1}1], [1\bar{1}\bar{1}], [1\bar{1}\bar{1}]$

## 2.6. Bragg's Law

We have diffraction when  $\bar{Q} = \bar{G}_{hkl}$ . The separation of lattice planes is  $d_{hkl} = \frac{2\pi}{|\bar{G}_{hkl}|}$ .

The Bragg angle,  $\theta$ , is half the angle between  $\bar{k}_I$  and  $\bar{k}_F$   $\left( |\bar{k}_I| = |\bar{k}_F| = \frac{2\pi}{\lambda} \right)$



$$|\bar{Q}| = 2|\bar{k}| \sin \theta = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d_{hkl}}$$

$$\text{So } \lambda = 2d_{hkl} \sin \theta$$

N.B. For a integer  $n\bar{G}_{hkl}$  has spacing  $\frac{d_{hkl}}{n}$  (i.e. harmonics)

For cubic axes:

$$|\bar{G}_{hkl}| = \frac{2\pi}{a} (h^2 + k^2 + l^2)^{\frac{1}{2}}$$

$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}$$

## 2.7. Structure Factor

As we found earlier on  $\Phi_F = \frac{a_f e^{i(\vec{k}_f \cdot \vec{R}_d - \omega t)}}{|\vec{R}_d|} \sum_{lattice} e^{i\vec{Q} \cdot \vec{R}_d} \sum_{basis} b_j e^{i\vec{Q} \cdot \vec{r}_{bj}}$

The lattice sum tells us where diffraction happens (Bragg scattering) in reciprocal space. This enables us to determine the properties of the lattice (symmetry of lattice vectors).

The sum over the basis (called the *lattice factor*) determines the relative strengths of the Bragg peaks, so it is this information which enables us to determine the basis. Note that the measured intensity is proportional to the square of the structure factor.

Since Bragg is restricted to reciprocal lattice points,  $\vec{G}_{hkl}$ , we need to calculate

$$\left| \sum_{basis} b_j e^{i\vec{G}_{hkl} \cdot \vec{r}_{bj}} \right|^2$$

### 2.7.1. Structure factor for a monoatomic structure

Where there is only one atom in the basis, we can choose its position to be at lattice points ( $\vec{r}_{bj} = \vec{0}$ ) so the structure factor for all Bragg peaks is  $b_j^2$ , such that all Bragg peaks have the same intensity.

### 2.7.2. Structure factor for a non-monoatomic structure

For a non-monoatomic structure, we evaluate the structure factor as a sum over each atom in the basis.

#### Example 1: CsCl

Simple cubic lattice:  $\vec{G}_{hkl} = \frac{2\pi}{a}(h, k, l)$

Basis is  $Cs^+$  ion at (0,0,0) and a  $Cl^-$  ion at  $\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

For X-rays, the scattering power is proportional to the number of electrons ( $Cs^+$  54,  $Cl^-$  18) so;

$$\begin{aligned}
(S.F)^2 &= \left| 54e^{\frac{2\pi i}{a}(h,k,l)(0,0,0)a} + 18e^{\frac{2\pi i}{a}(h,k,l)\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)a} \right|^2 \\
&= 18^2 \left| 3 + 18e^{\frac{2\pi i}{a}(h,k,l)\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)a} \right|^2 \\
&= 18^2 \left| 3 + 18e^{i\pi(h+k+l)} \right|^2
\end{aligned}$$

There are now two possible cases; where  $(h+k+l)$  is even or odd:

$$\frac{(S.F)^2}{18^2} = \begin{cases} 16 & h+k+l \text{ even} \\ 4 & h+k+l \text{ odd} \end{cases}$$

A measurement of the Bragg scattering from a crystal of *CoCl* gives peaks which correspond to a simple cubic reciprocal lattice, with relative intensities as given here. It is this information which enables us to say what the structure is.

## Example 2: Silicon

Take the conventional, non-primitive, lattice vectors and remember that some points are systematic absences (see example sheet). The rule for face centred cubic lattices is that  $hkl$  are either all or all even, for the reciprocal lattice points. All other cases (mixed odd/even) are systematically absent.

The basis is two silicon atoms  $\bar{r}_1 = (0,0,0)$  and  $\bar{r}_2 = a\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)$

$\bar{G}_{hkl} = \frac{2\pi}{a}(h,k,l)$  each Si atom has 14 electrons so;

$$SF^2 = \left| 14e^{2\pi i(h,k,l)(0,0,0)} + 14e^{2\pi i(h,k,l)\left(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\right)} \right|^2$$

$$\left(\frac{SF}{14}\right)^2 = \left| 1 + e^{i\pi\frac{(h+k+l)}{2}} \right|^2$$

Consider:

1.  $h, k, l$  all odd; in this case  $h+k+l$  is also odd
2.  $h+k+l = 4n$
3.  $h+k+l = 4n+2$

$$\left| \frac{SF}{14} \right|^2 = \begin{cases} 2 & \text{In case 1} \\ 4 & \text{In case 2} \\ 0 & \text{In case 3} \end{cases}$$

Not all peaks which are present have the same structure factor.

### 2.7.3. Accidental Absence

There are reciprocal lattice points where the structure factor is zero. These are called *accidental absences*.

Accidental absences arise as a result of cancellation within the basis and not as a result of the symmetry of the lattice. In silicon, the (100) is systematically absent whilst the (222) is accidentally absent.

Distortions of the electron states can result in a lack of exact cancellation of the structure factor. (We have assumed in calculating the structure factor that both atoms in the basis have the same shape, in the same orientation, which is not required by the lattice symmetry). Careful experiments reveal some diffraction at accidental absences.

## 2.8. Diffraction Experiments

Any particle beam can be used provided:

- Particles interact with the crystal, but not too strongly.
- There is an available intense beam
- There is an efficient method to detect the scattered beam
- The wavelength of the beam is less or equal to the lattice spacings.

For most simple crystal structures, lattice spacings are around  $2-5 \text{ \AA}$  ( $10^{-10} \text{ m}$ ). The ideal radiation/ particle wavelength is about  $0.5-2 \text{ \AA}$ . The most commonly used particles are X-rays (photons), electrons (at  $keV$  energies) and neutrons (Thermal).

## 2.8.1.X-Ray Diffraction

### Production of X-rays

We produce X-rays in one of two ways;

- With an X-ray tube (tricky to remember eh?)

This is a cheap easy method – we use a rotating anode tube to produce intense beams.

- Synchrotron radiation ([www.srs.ac.uk/](http://www.srs.ac.uk/) [www.esrf.fr/](http://www.esrf.fr/) [www.diamond.ac.uk](http://www.diamond.ac.uk))

This is the “bending radiation” – when highly relativistic particle (usually electrons) are accelerated in a magnetic field. e.g. Daresbury, RSRF, Diamond. This method produces intense, highly collimated, white beams, but is expensive and inconvenient.

### Detection of X-rays

We have a number of ways of detecting X-rays;

- Photographic plates
- Ionisation chambers – the movie famous clicking Geiger-Muller tube
- Scintillation detector
- Solid State detectors

### Interaction of X-rays with crystals

Incident X-rays have oscillating electric fields. As electrons are accelerated they emit radiation. The emitted X-rays have the same wavelength as the incident X-rays and so they are coherent. We find that there is stronger scattering from heavy elements.

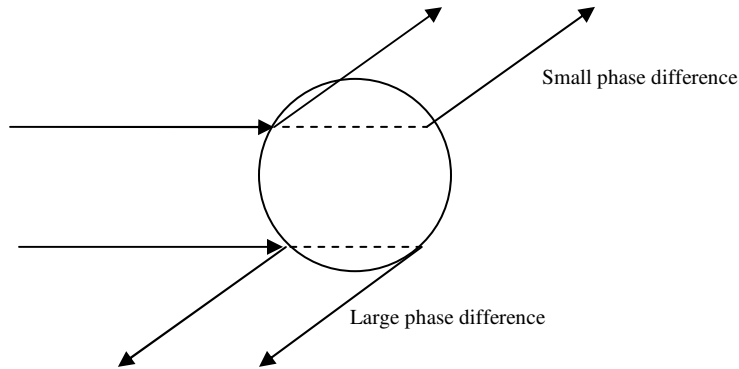
It may be difficult to distinguish atoms of similar  $Z$  and it is difficult to detect scattering from light (low  $Z$ ) elements, especially in the presence of heavier ones.

Hydrogen ( $H^+$ ) is especially difficult to ‘see’ with X-rays.

## Resonance Scattering

When the energy of the incident X-ray:  $\epsilon_i = \epsilon_m - \epsilon_n$  in an atom, we can enhance the scattering power by many orders of magnitude. This requires a tuneable source of X-rays i.e. a synchrotron.

### Form Factor



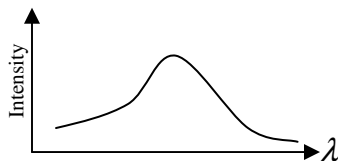
The effect of extended electron states is to provide some degree of destructive interference between scattering from electrons in the same atom. The effect increases for increasing scattering angle or increasing  $|\bar{Q}|$  and reduces scattered intensities at higher  $|\bar{Q}|$  values.

## 2.8.2. Neutron Diffraction

### Production of suitable neutrons

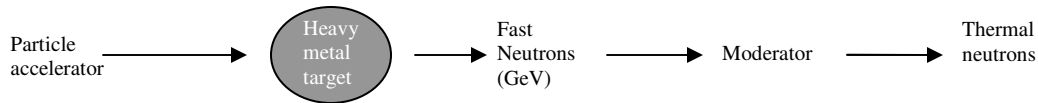
We need the wavelengths of our neutrons to be about an angstrom;  $\lambda = 1 \text{ \AA}$ . This means that the energy of our neutrons should be;  $\epsilon = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{3}{2}k_B T \rightarrow T = 480\text{k}$

1. Thermalise neutrons from fission in the core of a thermal reactor. A tube through the biological shielding gives a white beam (large spread of wavelengths), characterised by  $T \sim 300\text{k}$



e.g. Institut Lave Langerian, Grenoble, France. (UK, France, Germany collaboration)

2. Spallation: If you accelerate charged particles (usually protons) and aim the beam at a heavy metal target ( $Ta, U, Hg$ ) then neutrons get spat out. We moderate the fast neutrons which “spall” off the target.



e.g. ISIS (Rutherford lab, Oxford, UK)

## Detection of neutrons

We use an ionisation chamber containing  $^3He$  has;  $^3He + n \rightarrow ^3H + p$

There are alternative methods, but they don't work as well, one example is  $Li$  glass scintillators.

## Interaction of neutrons with crystals

1. Strong nuclear force

On the atomic scale, nuclei are effectively point potentials. Scattering length,  $b$ , may be of either sign. Typically a few  $fm$ . This is simpler than the X-ray case because there is no form factor. This method is sensitive to light atoms ( $^1H, ^2H$  contrast for example) and so is very useful in biology, polymer manufacture etc.

2. Magnetic dipole of neutron

Interacts with magnetic (unpaired) electrons. We can measure magnetic structures directly e.g. anti-ferromagnets. Scattering lengths are similar to the strong nuclear force above. This has a form factor, depending on the extent of the magnetic electrons; for example  $3d$  states are more extended than  $5f$  states etc.

[www.ncnr.nist.gov/resources/n-lengths](http://www.ncnr.nist.gov/resources/n-lengths)

### 2.8.3. Electron Diffraction

Electrons are easy to produce and detect (kV electrons have useful wavelengths). However whilst electrons look like the best horse so far, they find it difficult to penetrate solid materials because of their charge and so electron diffraction is mostly applicable to thin layers and surfaces.

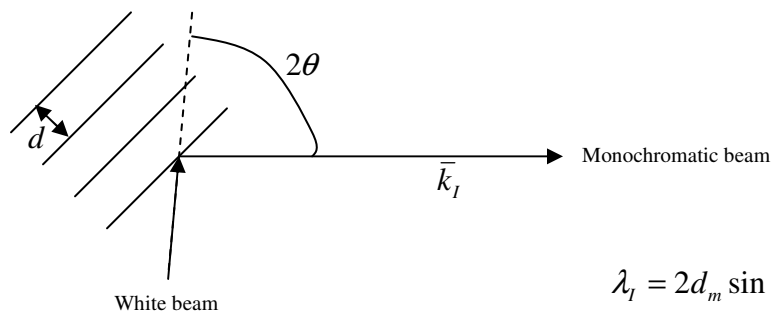
Electrons interact via the coulomb interaction (nuclei and electrons) and exchange interactions (electrons).

It is difficult to extract quantitative information than in X-ray or neutron diffraction but the symmetries seen can be useful. See Hooke and Hall Chapter 12.

### 2.8.4. Experimental Arrangements for diffraction

#### 1. Simple Crystal

We use a monochromatic incident beam, achieved by Bragg diffraction from a monochromator crystal.



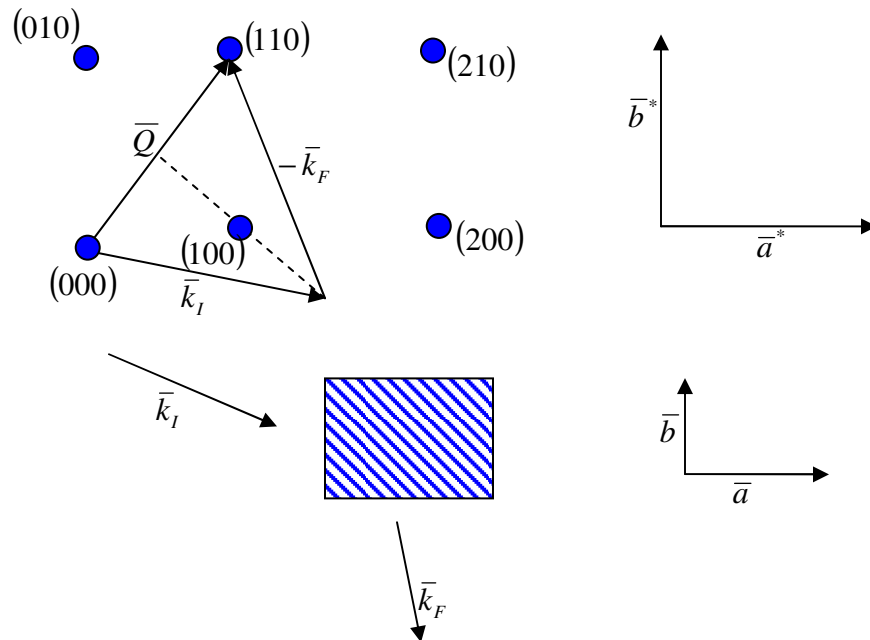
$$\lambda_l = 2d_m \sin \theta$$

$$\Rightarrow |\bar{k}_l| = \frac{\pi}{d_m \sin \theta}$$

We need to establish the diffraction condition;  $\bar{Q} = \bar{G}_{hkl}$

We consider a plane of reciprocal space including the origin, for a crystal with a simple cubic lattice.

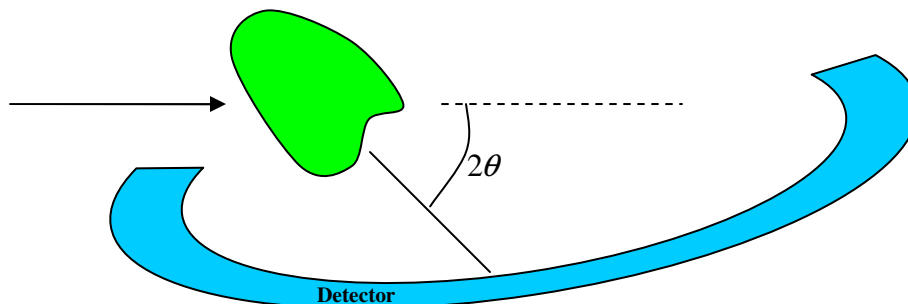


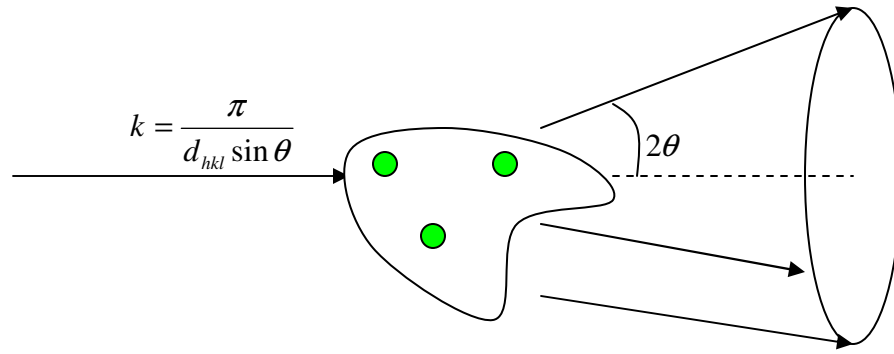


This construction tells us the, for any given wavelength  $\lambda$  (Which is equal to  $\frac{2\pi}{|\vec{k}|}$ ) what orientation we need for the incident beam,  $\vec{k}_I$ , and the final beam,  $\vec{k}_F$ , to be with respect to the crystal axes  $(\vec{a}, \vec{b}, \vec{c})$ . In general we need to calculate the relative orientations of  $\vec{a}, \vec{b}, \vec{c}$  with respect to  $\vec{a}^*, \vec{b}^*, \vec{c}^*$ .

## 2. Powder Diffraction

IT is not always possible to obtain a single crystal sample. We can use a powdered (or polycrystalline) sample and a monochromatic beam;





All orientations of crystallite present may be equally distributed, or may be *textured*.  
 Scalar form of Bragg's law is most useful. This allows us to collect lots of different data at once.

In cubic crystals; 
$$d_{hkl} = \frac{a}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}$$

We take account of the number of equivalent planes;

e.g.  $\{100\}$  is 6  
 $\{120\}$  is 24

Note; we can't distinguish peaks with the same  $d$  spacing, (333) and (511).

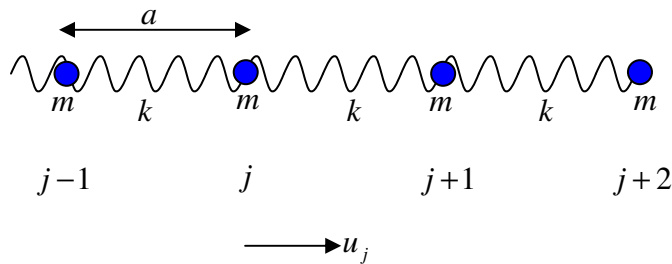
### 3. Lattice Dynamics

So far, we have assumed that the atoms are stationary. This is not true at  $T = 0k$  (zero point motion) and is even less true at non-zero temperature (thermal motion).

#### 3.1. 1D chain of identical atoms

We consider a chain of  $N$  atoms (later on we'll let  $N \rightarrow \infty$ ).

We treat interactions as springs (of spring constant  $k$ ) between the nearest neighbours. Motion is constrained to be parallel to the chain only.



Applying Newton's 2<sup>nd</sup> law to the  $j^{\text{th}}$  atom;  $m\ddot{u}_j = k(u_{j+1} - u_j) - k(u_j - u_{j-1})$

Applying periodic boundary conditions:  $u_j = u_{j+N}$

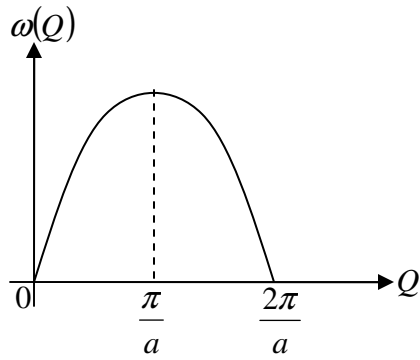
We look for wavelike solutions:  $u_j = u_0 e^{i(Qja - \omega t)}$

The boundary condition implies that  $e^{iQNa} = 1$  or  $Q = \frac{2\pi n}{Na}$   $n$  : integer

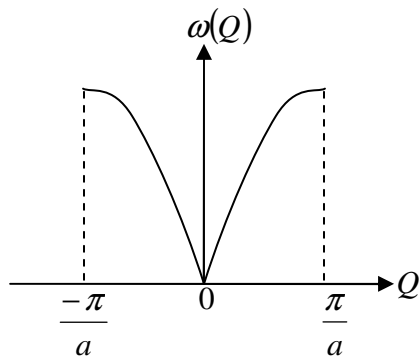
Put the trial solution into the equation of motion and divide by common factors:

$$\begin{aligned} -m\omega^2 &= k(e^{iQa} + e^{-iQa} - 2) \\ &= 2k(\cos Qa - 1) \end{aligned}$$

Taking the positive solution, with  $n$  from 1 to  $N$ :  $\omega(Q) = 2\sqrt{\frac{k}{m}} \sin\left(\frac{Qa}{2}\right)$

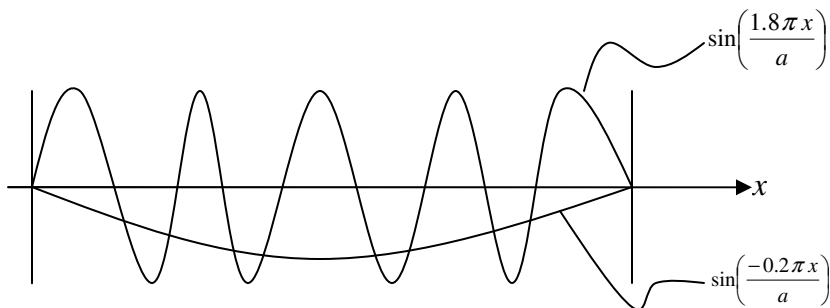


We could also take  $n$  from  $-\frac{N}{2}$  to  $\frac{N}{2}$ , this is equivalent to translating part of the curve by  $\frac{2\pi}{a}$  (reciprocal lattice vector).



Are these really the same?

If we compare for example  $\sin\left(\frac{1.8\pi x}{a}\right)$  and  $\sin\left(\frac{-0.2\pi x}{a}\right)$ ;



- Brillouin zone

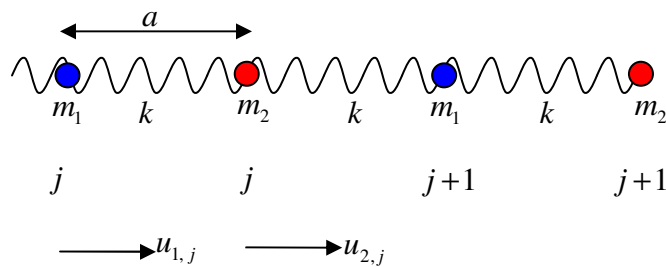
The Brillouin zone is the primitive unit cell in the reciprocal lattice chosen in such a way that all points in the zone are closer to one reciprocal lattice point than to any other. We usually represent the lattice dynamics in one Brillouin zone. The wavenumber,  $\bar{Q}$ , mapped into the Brillouin zone (reduced wavevector) is represented by  $\bar{q}$ .

- Dispersion relation

The group velocity of a wave is  $d_q \omega$ . Usually, the group velocity is zero at the zone boundary. The phase velocity is  $\frac{\omega}{q}$  and at small enough  $q$  the relation is usually linear so that the group velocity equals the phase velocity. In general this is not true.

### 3.2. Diatomic Linear Crystal

This is a 1D chain with two types of atom. We consider the same forces (spring) constants between the nearest neighbours only.



Applying Newton's 2<sup>nd</sup> law to atoms in the  $j^{\text{th}}$  cell;

$$m_1 \ddot{u}_{1,j} = k(u_{2,j} - u_{1,j}) - k(u_{1,j} - u_{2,j-1})$$

$$m_2 \ddot{u}_{2,j} = k(u_{1,j+1} - u_{2,j}) - k(u_{2,j} - u_{1,j})$$

In a similar way to previously, the periodic boundary conditions are;

$$u_{1,j} = u_{1,j+N}, \quad u_{2,j} = u_{2,j+N}$$

Again we look for wavelike solutions;

$$u_{1,j} = u_{1,0} e^{i(qja - \omega t)}$$

$$u_{2,j} = u_{2,0} e^{i(qja - \omega t)}$$

The boundary condition implies that  $q = \frac{2\pi n}{Na}$   $n$  : integer

There are now  $2N$  degrees of freedom.

Substituting in these solutions and cancelling common factors gives;

$$-m_1 \omega^2 u_{1,0} = k(u_{2,0} - u_{1,0}) - k(u_{1,0} - u_{2,0} e^{-iqa}) \quad [1]$$

$$-m_2 \omega^2 u_{2,0} = k(u_{1,0} e^{iqa} - u_{2,0}) - k(u_{2,0} - u_{1,0}) \quad [2]$$

These equations can be written in matrix form;

$$\begin{pmatrix} m_1 \omega^2 - 2k & k(1 + e^{-iqa}) \\ k(e^{iqa} + 1) & m_2 \omega^2 - 2k \end{pmatrix} \begin{pmatrix} u_{1,0} \\ u_{2,0} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

This is true for non-zero  $u_{1,0}$ ,  $u_{2,0}$  (i.e. when determinant is zero). Let's find the determinant;

$$(m_1 \omega^2 - 2k)(m_2 \omega^2 - 2k) - k^2(1 + e^{-iqa})(e^{iqa} + 1) = 0$$

$$m_1 m_2 (\omega^2)^2 - 2k(m_1 + m_2) \omega^2 - 2k^2(\cos(qa) - 1) = 0$$

$$(\omega^2)^2 - \frac{2k(m_1 + m_2)}{m_1 m_2} \omega^2 - \frac{4k^2}{m_1 m_2} \sin^2\left(\frac{qa}{2}\right) = 0$$

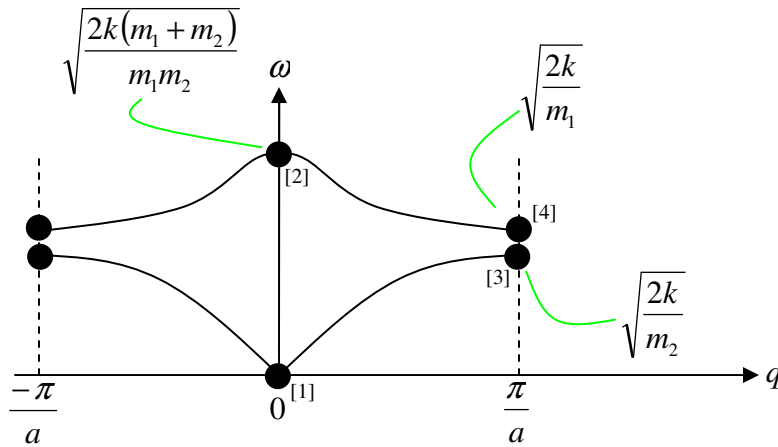
This is a quadratic expression in  $\omega^2$  :

$$\omega^2 = \frac{k(m_1 + m_2)}{m_1 m_2} \pm \frac{k}{m_1 m_2} \sqrt{(m_1 + m_2)^2 - 4m_1 m_2 \sin^2\left(\frac{qa}{2}\right)}$$

Not that for each  $q$  value there are two (positive) values of  $\omega$ . This is consistent with their being  $N$  values of  $q$  which we allowed and  $2N$  degrees of freedom. Thus there are two branches of vibrational excitation.

$$\text{If } q = 0; \omega = 0 \text{ or } \omega^2 = \frac{2k(m_1 + m_2)}{m_1 m_2}$$

$$\text{If } q = \frac{\pi}{a}; \omega^2 = \frac{2k}{m_2} \text{ or } \frac{2k}{m_1}$$



Using Equations [1] and [2]:

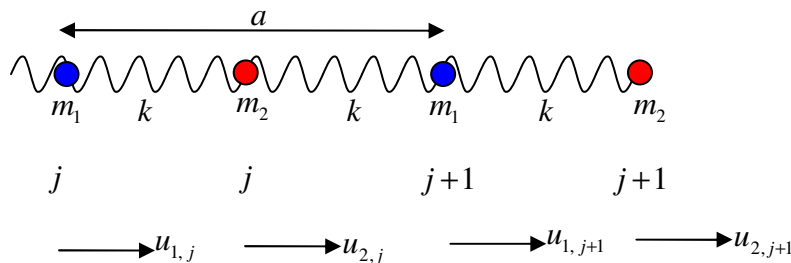
For  $q = 0, \omega = 0$ :

$$\text{[1] gives; } 0 = 2k(u_{2,0} - u_{1,0})$$

$$\text{[2] gives; } 0 = 2k(u_{1,0} - u_{2,0})$$

Therefore  $u_{1,0} = u_{2,0}$

i.e. The atoms are vibrating in phase with the same amplitude.

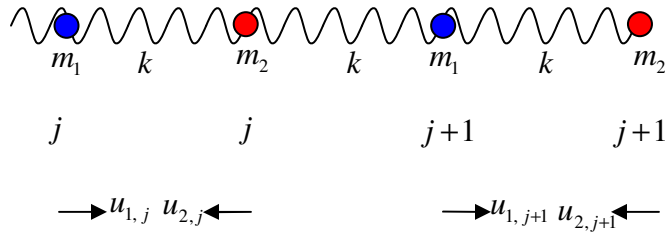


This represents a long-wavelength all-in-phase sound wave.

$$\text{For } q = 0; \omega^2 = \frac{2k(m_1 + m_2)}{m_1 m_2}$$

$$\begin{aligned} \text{In [1]: } -m_1 \frac{2k(m_1 + m_2)}{m_1 m_2} u_{1,0} &= 2k(u_{2,0} - u_{1,0}) \\ \Rightarrow -(m_1 + m_2)u_{1,0} &= m_2(u_{2,0} - u_{1,0}) \\ -m_1 u_{1,0} &= m_2 u_{2,0} \end{aligned}$$

i.e. The atoms are vibrating in antiphase with zero net momentum of the centre of mass for each pair.



For  $q = \frac{\pi}{a}$  (at the zone boundary);  $e^{iqa} = 1$

So [1] and [2] become;

$$\begin{aligned} -m_1 \omega^2 u_{1,0} &= k(u_{2,0} - u_{1,0}) - k(u_{1,0} + u_{2,0}) \\ -m_2 \omega^2 u_{2,0} &= k(-u_{1,0} - u_{2,0}) - k(u_{2,0} - u_{1,0}) \end{aligned}$$

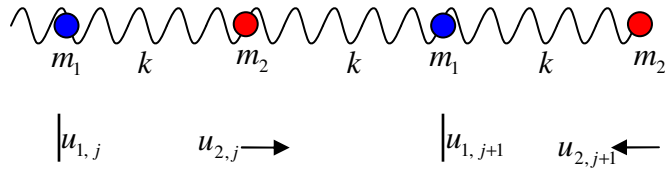
$$-m_1 \omega^2 u_{1,0} = -2k u_{1,0}$$

$$-m_2 \omega^2 u_{2,0} = -2k u_{2,0}$$

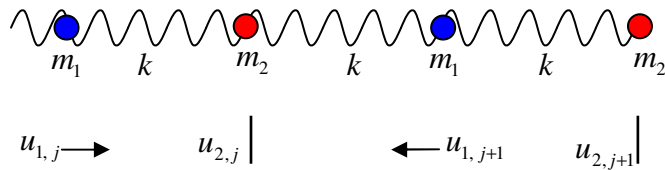
When  $\omega^2 = \frac{2k}{m_2}$  since  $m_1 \neq m_2$ ,  $u_{1,0} = 0$  so the  $m_1$  atoms are stationary.

For  $q = \frac{\pi}{a}$ , neighbouring  $m_2$  atoms vibrate in antiphase;

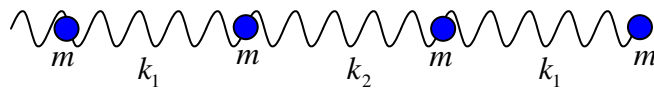




When  $\omega^2 = \frac{2k}{m_1}$ ,  $u_{2,0} = 0$ , so the  $m_2$  atoms are stationary. For  $q = \frac{\pi}{a}$ , the  $m_1$  atoms are vibrating in antiphase;



### 3.3. Linear Crystal – with one type of atom and two different springs



Solutions also give two branches as there are two atoms in the basis. This generalises in 1D

Number of branches = number of atoms in basis

One and only one mode is acoustic (frequency goes to zero as  $q$  goes to zero).

### 3.4. Vibrations in three dimensions

In general, atoms are bound in a potential which provides restoring forces in three dimensions which are not necessarily the same. Each atom has three degrees of vibrational freedom; so the number of modes is 3 times the number of atoms in the basis. Three of these modes are acoustic modes; one represents oscillations parallel to the direction of propagation (known as longitudinal) and two are transverse with oscillations perpendicular to the direction of propagation.

## Speed of sound

Velocities of longitudinal and transverse acoustic modes are, in general, all different. Where propagation is parallel to a 3 or 4 fold rotation axis, the two transverse waves are constrained to have the same frequency.

The longitudinal acoustic speeds are usually about twice the transverse speed and typical speeds are  $10^3 \text{ ms}^{-1} = 10 \text{ THz \AA}$ .

### 3.5. Quantum Effects in Lattice Dynamics

In the harmonic approximation, the Hamiltonian is the sum of  $3N$  independent oscillator Hamiltonians, all of which commute. The frequencies are the same as those of classical normal modes.

The energy in each mode is given by Bose-Einstein statistics with zero chemical potential;

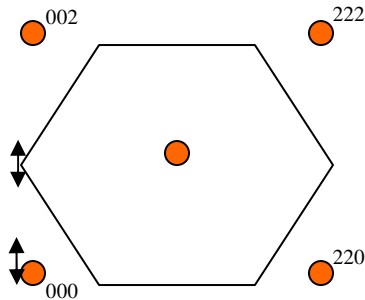
$$E(q) = \left( n + \frac{1}{2} \right) \hbar \omega(q) \quad n : \text{integer}$$

$$\langle n \rangle = \frac{1}{e^{\hbar \omega \beta} - 1} \quad \left[ \beta = \frac{1}{k_B T} \right]$$

We can treat the occupied states as Bose particles, just like photon states which are occupied electromagnetic wave states in a box. By analogy, the vibrational states in a solid are called phonons (quantised sound waves).

### 3.6. Examples of phonon-dispersion relations

Lead is a monoatomic f.c.c. (face centred cubic) lattice;



A longitudinal phonon at  $[001]$  is a transverse phonon at  $[110]$  on the zone boundary;

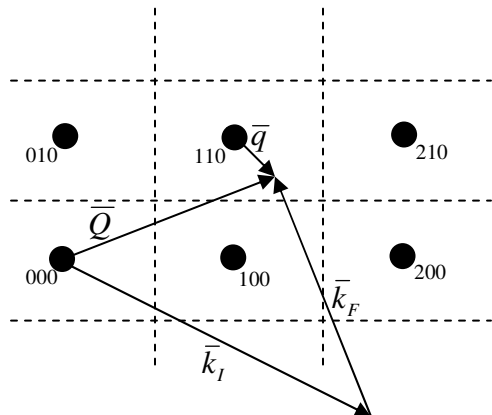
$$L[001] \equiv T[110]$$

### 3.7. Newton Inelastic Scattering

Static (average position) lattice gives Bragg scattering. Phonons can scatter neutrons (and X-rays), but the neutron energy changes on scattering. For neutrons, the energy change is a large fraction of the incident energy. For X rays, the change in energy is a very small fraction ( $10\text{meV}$  compared with  $10\text{keV}$ ). Peaks in scattering arise when the energy change ( $h\nu$ ) on scattering and the momentum change ( $\hbar\bar{Q}$ ) lie on the phonon dispersion curve.

$$h\nu = \frac{\hbar^2 |\bar{k}_I|^2}{2m} - \frac{\hbar^2 |\bar{k}_F|^2}{2m}$$

$$\hbar\bar{Q} = \hbar\bar{k}_I - \hbar\bar{k}_F$$



### 3.8. Specific Heat

$$c_v = \frac{1}{V} \partial_T \mathcal{E}$$

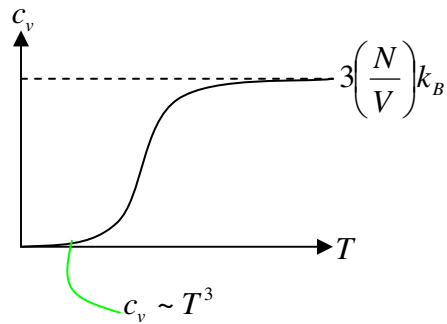
Classically, Equipartition says that the energy of each mode associated with a quadratic energy term is just  $\frac{1}{2} k_B T$ .

If we have  $N$  atoms then;  $6N \times \frac{1}{2} k_B T = 3N k_B T = \text{energy}$

It follows from this that  $c_v = 3 \left( \frac{N}{V} \right) k_B$  *Dulong-Petit law*

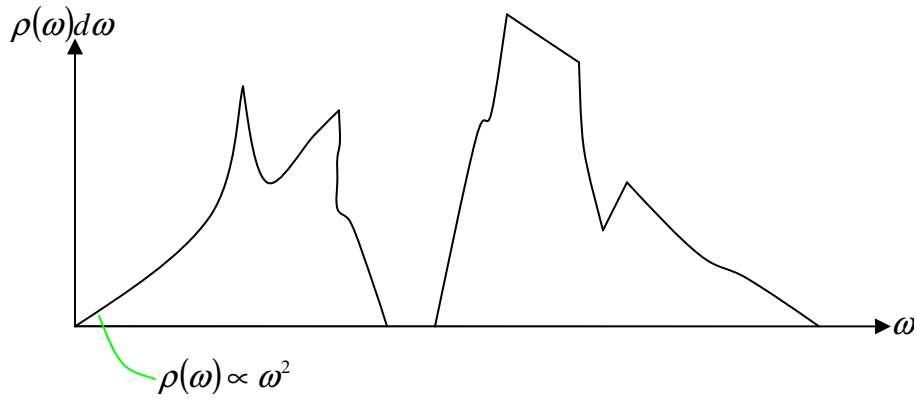
In a quantum case, the high temperature limit of the energy is  $\frac{1}{2} k_B T$ , so we expect this to hold at  $T \gg \text{highest phonon energy}$ .

#### Specific heat (insulator)



## Density of states

The energy of a phonon defined it's thermal effect. So we need the density of states;



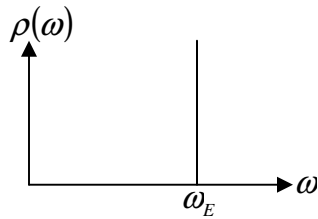
The density of states has a maximum energy, but the shape can be very complicated. The density of states is always quadratic for small energies.

$$c_V = \frac{1}{V} \partial_T \mathcal{E}$$

$$\mathcal{E} = \int_0^{\infty} \left( \frac{1}{e^{\hbar\omega\beta} - 1} + \frac{1}{2} \right) \hbar\omega \rho(\omega) d\omega$$

$$3N = \int_0^{\infty} \rho(\omega) d\omega$$

### 3.8.1. Einstein Model



$$\varepsilon = 3N \left[ \frac{1}{e^{\hbar\omega_E\beta} - 1} + \frac{1}{2} \right] \hbar\omega_E$$

$$c_V = \frac{3N}{V} k_B \frac{(\hbar\omega_E\beta)^3 e^{\hbar\omega_E\beta}}{(e^{\hbar\omega_E\beta} - 1)^2}$$

This has the correct high temperature limit (Dulong – Petit law), but let's see what happens at low temperatures;

$$c_V \approx \frac{3N}{V} k_B (\hbar\omega_E\beta)^2 e^{-\hbar\omega_E\beta}$$

This is broadly correct, but it does fall too fast as  $T \rightarrow 0$ . The problem arises from ignoring acoustic phonons (phonons where  $\omega \rightarrow 0$  as  $q \rightarrow 0$ ).

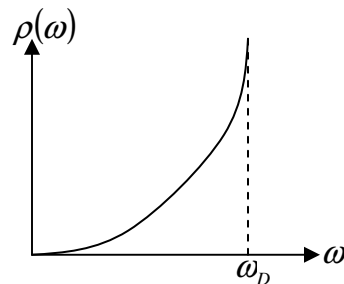
### 3.8.2. Debye Model

Use  $\omega = v|\vec{q}|$  all with same velocity,  $v$ .

$$\text{This gives; } \rho(\omega)d\omega = \frac{3V}{2\pi^2} \frac{\omega^2 d\omega}{v^3}$$

$$\text{To energy, } \omega_D, \text{ where } 3N = \int_0^{\omega_D} \frac{3V}{2\pi^2} \frac{\omega^2 d\omega}{v^3}$$

$$\text{This gives } \omega_D^3 = 6 \frac{N}{V} \pi^2 v^3$$



It may be shown that:

$$\lim_{T \rightarrow 0} c_V = \frac{2}{5} \frac{\pi^2 k_B^4}{\hbar^3 \pi^3} T^3 = \frac{12}{5} \pi^4 \left( \frac{N}{V} \right) k_B \left( \frac{k_B T}{\hbar \omega_D} \right)^3 \quad [\text{for } k_B T \ll \hbar \omega_D]$$

The low temperature form of  $c_V$  is correct for Some average speed of sound  $v$ . For the full version of  $c_V$ , we use the full density of states and do integrals numerically.

## 4. Metals

### 4.1. The Free-Electron Model

Charged particles at high densities must interact strongly with each other. But we know that metals are good conductors of electricity and heat, so let's suppose that there are free electrons and see how far we get.

#### 4.1.1. One electron states

In a volume,  $V$ , for a cube of side  $L$ , the states are  $\psi(\vec{r}) = V^{-1/2} e^{i\vec{k}\cdot\vec{r}}$

$$k_{x,y,z} = \frac{\pi}{L} n_{x,y,z} \quad n_{x,y,z} : \text{integers}$$

We allow for two spins and the density of states is  $\rho(k)dk = \frac{2V}{\pi^2} dk$

For the non-relativistic case;  $\epsilon = \frac{\hbar^2 |\vec{k}|^2}{2m}$

This gives  $\rho(\epsilon)d\epsilon = \frac{V\sqrt{2m^3}}{\pi^2\hbar^3} \epsilon^{1/2} d\epsilon$

The Fermi function is;  $f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)\beta} + 1}$

The total number of electrons,  $N$ , is found by integrating the product of the Fermi

function and the density of states;  $N = \int_0^{\infty} f(\epsilon)\rho(\epsilon)d\epsilon$

$$\text{At } T = 0; f = \begin{cases} 1 & \epsilon < \mu \\ 0 & \epsilon > \mu \end{cases}$$

This gives that  $\mu(T = 0) = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$        $n = \frac{N}{V}$



A few definitions;

- The Fermi energy;  $\epsilon_F = \mu(T = 0)$
- The Fermi wavevector  $|\bar{k}_F| = (3\pi^2 n)^{\frac{1}{3}}$
- The Fermi temperature  $k_B T_F = \epsilon_F$
- The Fermi velocity  $m v_F = \hbar k_F$

For Sodium (monoatomic b.c.c. (body centred cubic)  $a = 4.23 \text{ \AA}$ , valence 1);

- $|\bar{k}_F| = 0.92 \text{ \AA}^{-1}$
- $\epsilon_F = 3.2 eV$
- $T_F = 3.7 \times 10^4 K$
- $|\bar{v}_F| = 1.1 \times 10^6 m s^{-1}$

Note;  $T_m = 371 K$  (1% of  $T_F$ )

$|\bar{v}_F| \ll c$  (so non-relativistic  $\epsilon(k)$ )

## 4.1.2. Results of the Free Electron Model

### 1. Specific Heat

$$C_V = \frac{1}{V} \partial_T \epsilon_F$$

$$\epsilon_F = \int_0^{\infty} f(\epsilon) \rho(\epsilon) \epsilon d\epsilon$$

Since changes in  $f(\epsilon)$  are very close to  $\epsilon_F$ , we replace  $\rho(\epsilon)$  by  $\rho(\epsilon_F)$ , which gives;

$$C_V = \frac{\rho(\epsilon_F)}{V} \int_0^{\infty} \epsilon \partial_T f(\epsilon) d\epsilon$$

We can replace the lower limit with  $-\infty$  without changing the integral at all – doing so makes it easier to evaluate the integral;

$$C_V = \frac{\rho(\epsilon_F) k_B^2 T}{V} \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx \quad \text{Where } x = (\epsilon - \mu)\beta$$

This is a well evaluated integral and is just  $\frac{\pi^2}{3}$

Note; this is more general than the free electron model as in the free electron model;

$$\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{\frac{2}{3}}; \quad T_F = \frac{\epsilon_F}{k_B}$$

$$\rho(\epsilon_F) = \frac{V \sqrt{2m^2}}{\pi^2 \hbar^3} \epsilon_F^{\frac{1}{2}}$$

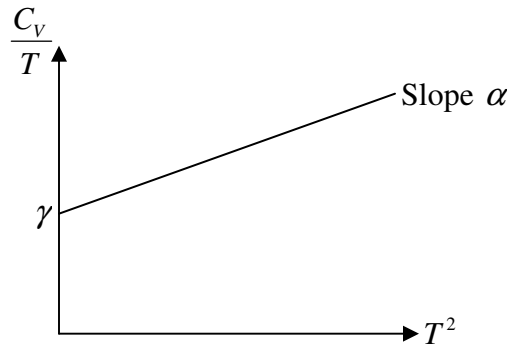
$$\Rightarrow C_V = \frac{3}{2} \frac{N}{V} k_B \left( \frac{\pi^2}{3} \frac{T}{T_F} \right)$$

This is a classical result for free particles reduced by a term of order  $\frac{T}{T_F}$ . Only electrons within  $k_B T$  of  $\epsilon_F$  contribute.

For real metals,  $C_V$ , also has a lattice term at low temperatures,  $T$ , so;

$$C_V = \gamma T + \alpha T^3$$

Let's plot  $\frac{C_V}{T}$  against  $T^2$ ;



Metal	$\gamma_{F.E.} / \text{mJmol}^{-1} \text{k}^{-2}$	$\gamma_{\text{experimental}} / \text{mJ mol}^{-1} \text{k}^{-2}$
Na	1.09	1.38
Au	0.64	0.73
Fe	0.64	5.02
Bi	1.80	0.08

There is enough agreement in the form of result (linear in  $T$ ) and in the approximate size of  $\gamma$  to say that this idea is correct.

Note: So far we've used assumptions 1,3,4 and we'll now use assumption 2.

## 2. Electrical Conductivity

Assume that after a collision, the electrons travel in a random direction. Under the influence of an electric field, the electron will acquire and acquired velocity after a time  $t$ ;

$$\bar{v}_{\text{acquired}} = \frac{-e\bar{E}}{m} t$$

So the average velocity will be;  $\bar{v}_{\text{drift}} = \frac{-e\bar{E}}{m} \tau$

The current density is therefore;  $\bar{j} = e v_{\text{drift}} n$

$$\text{So; } \bar{j} = \left( \frac{ne^2\tau}{m} \right) \bar{E}$$

Which can be written as  $\bar{j} = \sigma \bar{E}$  Where  $\sigma = \frac{ne^2\tau}{m}$

Metal	Mean collision time/ $10^{-15} s$	
Na	170	32
Au	120	30
Fe	32	2.4
Bi	0.72	0.23

### 3. Thermal Conductivity

If  $Q$  is the heat flow for a given temperature gradient in the  $z$  direction,  $d_z T$ , then the thermal conductivity,  $\kappa$ , is given by;  $Q = \kappa d_z T$ .

For any quantity,  $P$ , the flux of  $P$  in the  $z$  direction given a gradient  $d_z P$  is given by kinetic theory; flux of  $P = \frac{1}{3} \lambda \bar{v} d_z P$

Where the factor of  $\frac{1}{3}$  arises from the angular averaging,  $\lambda$  is the mean free path and  $\bar{v}$  is the mean speed.

If  $P$  is the energy density,  $\frac{\mathcal{E}}{V}$ , the flux of  $P$  is the heat flow;  $Q = \frac{1}{3} \lambda \bar{v} d_z \mathcal{E}$

Now;  $d_z \mathcal{E} = d_T \mathcal{E} d_z T$ ;

$$C_V = \frac{1}{V} d_T \mathcal{E} \quad \text{so that } Q = \frac{1}{3} \lambda \bar{v} C_V d_z T$$

$$\text{And therefore } \kappa = \frac{1}{3} \lambda \bar{v} C_V$$

$$\text{Using } \lambda = \bar{v} \tau \Rightarrow \kappa = \frac{1}{3} \bar{v}^2 \tau C_V$$

At low temperatures, all of the relevant velocities are close to  $v_F$  and therefore

$$\frac{1}{2} m \bar{v}^2 = k_B T_F$$

$$\text{But } C_V = \frac{3 N}{2 V} k_B \left( \frac{\pi^2 T}{3 T_F} \right) \quad \left[ \frac{N}{V} = n \right]$$

$$\text{Therefore } \kappa = \frac{n k_B^2 \tau}{m} \left( \frac{\pi^2 T}{3} \right)$$

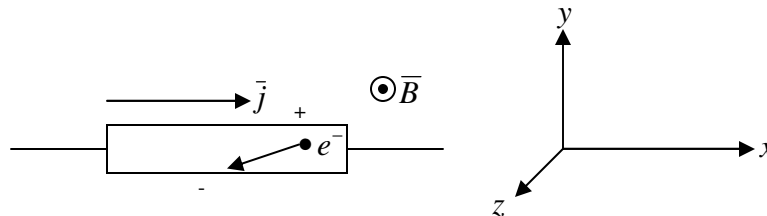
$$\text{If } \sigma = \frac{n e^2 \tau}{m}, \text{ the ratio } \frac{\kappa}{\sigma T} = \left( \frac{k_B}{e} \right)^2 \frac{\pi^2}{3} = 2.44 \times 10^{-8} N \Omega k^{-2}$$

Comparing this with the classical calculation gives the same answer multiplied by  $\left( \frac{q}{2\pi^2} \right)$ . This is called the *Wiedmann – Franz Law*.

Metal	273k		373k	
	$\kappa/W \text{ cm k}^{-1}$	$\frac{\kappa}{\sigma T} / W \Omega k^{-2}$	$\kappa/W \text{ cm k}^{-1}$	$\frac{\kappa}{\sigma T} / W \Omega k^{-2}$
Cu	3.85	$2.2 \times 10^{-8}$	3.82	2.29
Au	3.1	2.32	3.1	2.36
Fe	0.80	2.61	0.73	2.88
Bi	0.09	3.53	0.08	3.35
Na	1.38	2.12		

#### 4. Hall Effect

A current density,  $\vec{j}$ , flowing in  $\vec{B}$  generates a transverse electric field,  $\vec{E}_H$ , and the Hall coefficient,  $R_H$ ;  $H = R_H \vec{B} \times \vec{j}$



Probability of a collision in time  $dt$  is  $\frac{dt}{\tau}$ . In this time the change in momentum is;

$$d(m\bar{v}_{\text{drift}}) = \frac{-dt}{\tau} m\bar{v}_{\text{drift}}$$

$$\frac{d}{dt}(m\bar{v}) = -e(\bar{E} + \bar{v}_{\text{drift}}\bar{B}) - \frac{m\bar{v}_{\text{drift}}}{\tau} = 0$$

$$\text{In the } x \text{ direction; } 0 = -eE_x - eBv_{\text{drift},y} - \frac{mv_{\text{drift},x}}{\tau}$$

$$\text{In the } y \text{ direction; } 0 = -eE_y - eBv_{\text{drift},x} - \frac{mv_{\text{drift},y}}{\tau}$$

$$\text{Multiplying by } \frac{ne\tau}{m} \text{ and using } \sigma = \frac{ne^2\tau}{m};$$

$$\text{In the } x \text{ direction; } \sigma E_x = \frac{ne\tau}{m} Bv_{\text{drift},y} - nev_{\text{drift},x}$$

$$\text{In the } y \text{ direction; } \sigma E_y = \frac{-ne\tau}{m} Bv_{\text{drift},x} - nev_{\text{drift},y}$$

$$\text{Substituting } \bar{j} = -e\bar{v}_{\text{drift}}n$$

$$\text{In the } x \text{ direction; } \sigma E_x = \frac{e\tau}{m} B j_y + j_x$$

$$\text{In the } y \text{ direction; } \sigma E_y = \frac{-e\tau}{m} B j_x - j_y$$

Since  $j_y = 0$ , we find;

$$\text{In the } x \text{ direction; } \sigma E_x = j_x$$

$$\text{In the } y \text{ direction; } \sigma E_y = \frac{-e\tau}{m} B j_x$$

$$\text{From this we find that } \frac{E_y}{j_x B} = R_H = \frac{-1}{ne}$$

Experimentally we compare measurements to the theoretical result;  $\frac{-1}{R_H n e} = 1$

Metal	$\frac{-1}{R_H n e}$ (measured at high $B$ , low $T$ )
Na	1.2
Au	1.5
Mg	-0.4
Al	-0.3

### 4.1.3. Review of the free electron model

#### Successes

- Good quantitative agreement for Lorentz ratio at high temperatures for most metals.
- Hall effect quantitative agreement (50% or so) in some, but not all, metals.

#### Failures

- Does not explain the strong temperature dependence of conductivity.
- Specific heat is not always correct
- Wavefunction fails at intermediate temperatures
- Does not explain the positive  $R_H$  in some metals.

#### Unanswered Questions

- What causes collisions?
- Why are there no other interactions?

## 4.2. Wavefunction in a periodic potential

A periodic potential might be provided by nuclei in crystal. We assume that the effect of all the other electrons is to provide an additional potential which is also periodic.

Consider a wavefunction in a 1D periodic potential, with time dependence  $e^{-i\omega t}$ ;

$$\Psi(x,t) = \psi(x)e^{-i\omega t}$$

If the wavefunction varies by a factor  $A$  when  $x$  increases by  $a$ , the lattice parameter, then the magnitude of  $A$  must be 1 or else the wavefunction is not well defined. That is;

$$A = e^{i\theta}$$

For any  $\theta$ , we find  $k$  such that  $ka = \theta$ .

$$\Psi(la,t) = \psi_0 e^{i(kla - \omega t)}$$

Where  $l$  is an integer.

Now the wavefunction at other positions in the unit cell will be different from wavefunctions at the origin, but the same relationship applies to all points related by a lattice vector.

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

Where  $u(x)$  has the periodicity of the lattice.

The total wavefunction is a periodic function,  $u(x)$ , multiplied by a travelling wavefunction, characterised by wavenumber  $k$ .

Applying boundary conditions gives that  $k$  is an integer multiple of  $\frac{2\pi}{Na}$ .  $k$  can always be chosen in the Brillouin zone.

This can be generalised to three dimensions;  $\psi(\vec{r}) = u(\vec{r})e^{i\vec{k}\cdot\vec{r}}$



### 4.3. Free electron states in 1D k-space

[See teachweb for pics]

### 4.4. Bragg scattering of electron in 1D

If we think of a “free electron” as interacting with the crystal, it might undergo Bragg diffraction.

$$\bar{Q} = \bar{G}$$
$$\bar{Q} = \bar{k}_I - \bar{k}_F$$

In 1D, this implies a reversal of  $\bar{k}$ , so  $2|\bar{k}| = G$ .

For Bragg diffraction to occur,  $k$  must be equal to a reciprocal lattice vector, which in 1D is any integer multiple of  $\frac{\pi}{a}$ . i.e. at any zone boundary or zone centre.

These coincide with points of degeneracy; one state is incident and the other is a scattered wave. This leads to standing waves. There are two possible standing waves corresponding to  $\sin\left(\frac{\pi x}{a}\right)$  and  $\cos\left(\frac{\pi x}{a}\right)$ .

If the potential is zero on average, it is attractive near nuclei and repulsive in-between.

[Diagram from powerpoint]

The energy of the cosine state is therefore lower than that of the sin state.

#### 4.4.1. What is the meaning of $\bar{k}$ ?

For a free electron  $\hbar\bar{k} = \bar{p}$

Recall the momentum operator;  $\bar{p} = -i\hbar\nabla$ .

But the wavefunction,  $\psi(\bar{r})$ , is not an eigenstate of  $\bar{p}$ ;

$$\bar{p}\psi(\bar{r}) = \hbar k\psi(\bar{r}) - i\hbar e^{i\bar{k}\cdot\bar{r}}\nabla u(\bar{r})$$

So  $k$  is related to the momentum and reduces it when  $u(\bar{r})$  is constant (free electron limit).  $k$  is called the *crystal momentum*.

#### 4.4.2. What is the crystal velocity?

$$v = d_k \omega \quad \varepsilon = \hbar \omega$$

$$v = \frac{1}{\hbar} d_k \varepsilon$$

In three dimensions  $\bar{v} = \frac{1}{\hbar} \bar{\nabla}_k \varepsilon(\bar{k})$

The velocity of electrons affected by a periodic potential is similar to free-electron velocity for most states, but near the zone boundary (and the zone centre) the velocity is reduced to zero. This is consistent with the primitive of Bragg scattering causing standing waves.

The main conclusion is that electrons are still free to travel with non-zero velocity through the crystal in the presence of a periodic potential.

The nuclei and other electrons may affect the velocity, but they do not reduce it to zero. We say that we have “nearly-free” electrons. This is known as the *nearly free electron model*. (NFE)

#### 4.5. Effective mass

Near the zone boundary and the zone centre, the change in the group velocity from the free electron value is equivalent to changing the way the electron responds to forces, and so is also equivalent to altering the electron’s mass. This new value is called the *effective mass*. Sometimes this effective mass may be negative.

#### 4.6. What are the collisions and why does Wiedermann - Franz law fail?

**Low temperatures;** scattering dominated by defects, elastic scattering – scattering through large angles. Scattering of some electrons is restricted because final states are occupied. The effective collision time is different for electric and thermal currents, but they are of a constant ratio.

**High Temperatures;** ( $T > T_D$ ) dominated by phonon scattering with all phonon energies active and all angles possible. All collisions can degrade electrical and thermal currents, so collision times are the same.

**Intermediate Temperatures;** Dominated by acoustic phonons, which can degrade the heat current, but cannot degrade the electrical current, as only small angle scattering is allowed.

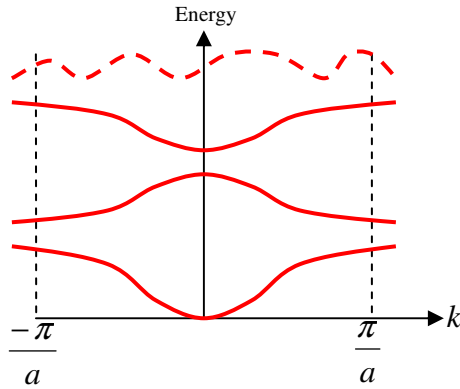
#### 4.7. Nearly-Free Electron Model

Will this solve the failures of the free electron model? Let's look at the failures of the free electron model individually;

Does not explain the temperature dependence of conductivity	Collisions with phonons whose numbers are strongly dependent upon temperature
Specific heat is not always correct	Density of states at the Fermi energy, $\epsilon_F$ , can change
Wiedmann – Franz law fails at intermediate temperatures	Complex interplay at collisions with defects and phonons.
Does not explain the positive Hall coefficients	Effective mass may be positive

## 4.8. Energy Bands

Energies with states are known as *bands* and energies without states are known as *band gaps*.



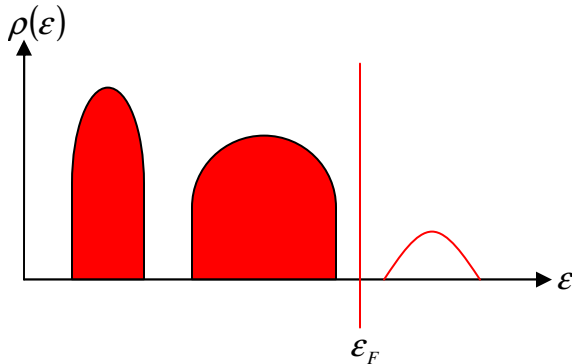
These are not quite continuous;

$$\Delta k = \frac{2\pi}{Na}$$

$$\Delta \epsilon = \frac{2\pi}{Na} \partial_k E$$

These states are eigenstates and so small perturbations (e.g. applies electric field) can change the state to a neighbouring one.

Band gaps prevent these changes.

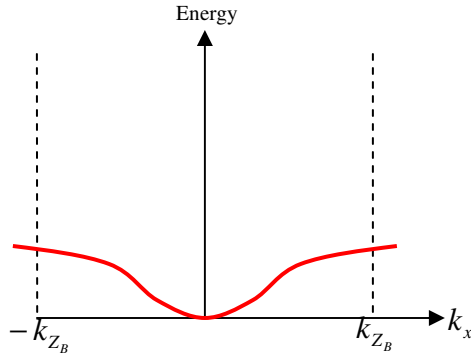


The fermi energy is defined by  $N = \int_0^{\epsilon_F} \rho(\epsilon) f(\epsilon) d\epsilon$

The Fermi level either lies within a band or between bands.

### 4.8.1. Full bands

All states in a full band are occupied at  $T = 0$ .



For any state;

$$v_x = \frac{1}{\hbar} \partial_{k_x} \varepsilon(k_x)$$

$$\begin{aligned} \bar{v}_x &= \int_{-k_{z_B}}^{k_{z_B}} \frac{1}{\hbar} \partial_{k_x} \varepsilon(k_x) dk_x \\ &= \frac{1}{\hbar} [\varepsilon(k_{z_B}) - \varepsilon(-k_{z_B})] \\ &= 0 \end{aligned}$$

Since  $k_{z_B}$  and  $-k_{z_B}$  are related by a reciprocal lattice vector, they represent the same  $k$ . Therefore, the mean velocity is always zero and this is the same in 3D.

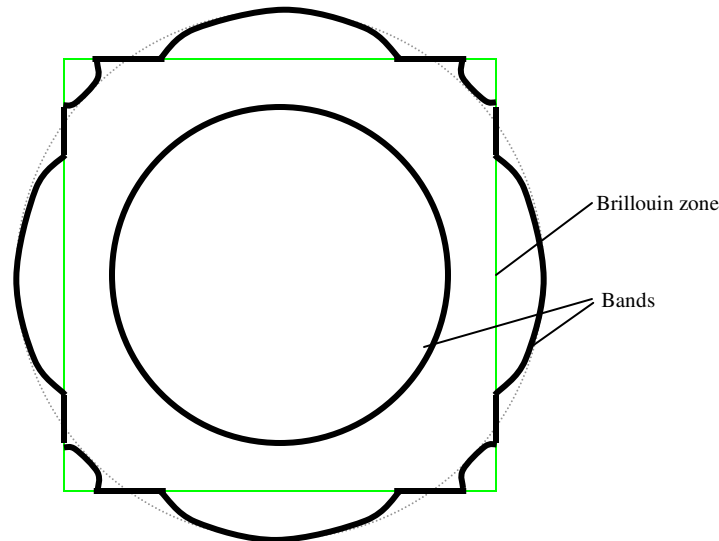
### 4.8.2. Metals, Insulators and Semiconductors

Full bands do not contribute to conduction (either heat or electricity) as the average velocity is zero. Empty bands do not contribute; this is known as an *insulator*.

If the Fermi levels lie within a band, then the small perturbations (e.g. an electric field) can cause an imbalance between the velocities and electrons may then contribute to conduction. This is known as a *metal*.

If an insulator has the Fermi energy within a small band gap (small compared with a few times  $k_B T$ ). Then at non-zero temperatures, electrons may be thermally excited from the full band to an empty band. Both bands may contribute to conduction, this is called a *semi-conductor*.

## Bands in 2D overlapping bands



[Can anyone tell me the point of the above diagram]

Ok I'm guessing here;

Deep inside the Brillouin zone, the bands would form circles (in 2D). But in the vicinity of the Brillouin zone (that's the green square) these bands are deformed.

The energies of bands may overlap and so the Fermi energy can lie in more than one band at once.

### Number of conduction electrons

Each band has a state corresponding to each  $k$  value in the Brillouin zone, of which there are  $N$ . So  $2N$  electrons may be accommodated in each band.

So for the Fermi level to lie between bands, the total number of electrons must be a multiple of  $2N$  so that all bands lower in energy are full. Each copy of the basis must contribute an even number of electrons in order for a crystal to be an insulator.

A primitive unit cell with an odd number of electrons must give rise to a metal. However, if there are overlapping bands, an even number of electrons in the basis may also give rise to a metal.

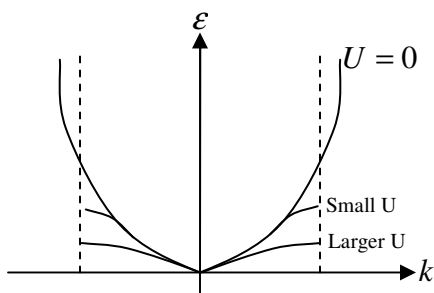
Material	Structure	Basis	Number of electrons in basis	Metal/ Insulator
Sodium	Monoatomic b.c.c	$Na$	11	Metal
Aluminium	Monoatomic f.c.c	Al	13	Metal
Vanadium	Monoatomic b.c.c	V	23	Metal
Sodium/ Chloride	Rocksalt	$Na^+Cl^-$	28	Insulator
Diamond	Diamond	2 $C$ atoms	12	Metal
Magnesium	h.c.p	2 $Mg$ atoms	24	Metal
Silicon	Diamond	2 $Si$ atoms	28	Semiconductor
Gallium Arsenide	Zinc Blend	$GaAs$	64	Semiconductor

#### 4.9. Application of NFE model to metals

The existence of electron states which extend throughout the crystal, with non-zero velocity, arises from the effect of a periodic potential. The wavefunction can be characterised by a wavevector provided that the potential is periodic.

What happens to the “core electrons”?

e.g.  $1s$  electrons in  $Na$  ;  $1s^2 2s^2 2p^6 3s^1$



The effect of the periodic potential tends to be larger than the free-electrons. States tend to be non-dispersive with no curvature.

The approximation of a weak potential breaks down and so the theory is not reliable.

But for the core states, the energies are well below the Fermi level, so they do not contribute to conduction, or specific heat, since the Fermi function is 1. So the failure of the NFE model for these states does not matter.

What about the “valence electrons”?

e.g.  $3s^1$  in sodium? Can the potential be regarded as weak?

There are two factors which conspire. Firstly the potential is strongest near the nuclei, but the Pauli Principle tends to exclude conduction electrons as there are core electrons here. Secondly, other electrons tend to ‘screen’ the potential, rather like the charges in a conductor screen electrostatic fields. The net effect is that, for s-electrons at least, the NFE theory works rather well but it is not particularly good for p and d-electrons.

## 4.10. Fermi Surfaces

Given the interplay between the periodic potential and the free electron dispersion relation, the final dispersion relations are potentially quite complicated.

The Fermi surface is the set of wavevectors  $\{\bar{k}_F\}$  which describes the states whose energy is the Fermi energy. In general this is no longer a sphere with overlapping bands, it may be multiply connected.

### Alkali Metals

With one electron per atom, the free-electron Fermi wavevector has magnitude of

$$0.62 \times \frac{2\pi}{a}.$$

The shortest zone boundary (b.c.c.) is  $\sqrt{\frac{1}{2}} \frac{2\pi}{a}$ .

The occupied states are affected very little by the potential and the Fermi surface is nearly spherical. We therefore expect alkali metals to behave like free-electron metals. For many properties, the agreement is good.

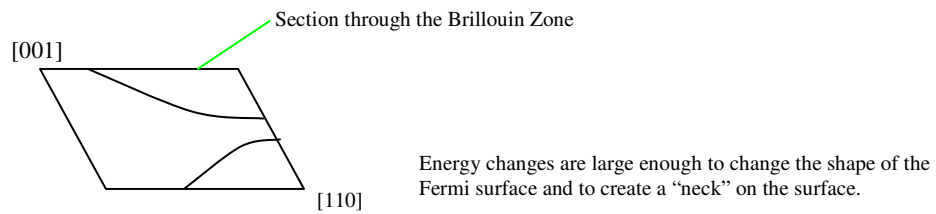


## Nobel Metals (gold, Silver, Copper)

Full d-shell and one S-electron. They adopt a monoatomic face centred cubic structure, so

nearest zone boundary is in the  $[1,1,1]$  direction with magnitude  $\frac{\sqrt{3}}{2} \cdot \frac{2\pi}{a} = 0.87 \left( \frac{2\pi}{a} \right)$

Free electron Fermi wavevector =  $0.78 \left( \frac{2\pi}{a} \right)$



For the most part, this still looks like a free Fermi Surface, but necks create new possibilities for the behaviour of electrons.

### 4.11. Effective mass; holes

For a free electron;

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

$$v(k) = \frac{1}{\hbar} \frac{\partial E}{\partial k} = \frac{\hbar k}{m}$$

$$a = \frac{\hbar}{m} \frac{dk}{dt}$$

Now, for a dispersion relation near a local maximum;  $\varepsilon(k) = \varepsilon_{\max} - \alpha(\Delta k)^2$ . We can put

$$\alpha = \frac{\hbar^2}{2m^*};$$

$$\varepsilon(k) = \varepsilon_{\max} - \frac{\hbar^2}{2m^*} \Delta k^2$$

$$v(k) = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial k} = -\frac{\hbar}{m^*} \Delta k$$

$$a = \frac{-\hbar}{m^*} \frac{d}{dt} \Delta k$$

Therefore the response is as if it were a free electron, but with a negative mass. We could treat it as a free particle with positive mass and positive charge (+e). This is known as a *hole*.

Near any turning point, we can write  $\varepsilon(k) = \varepsilon_{i.p.} + \frac{1}{2} \frac{\partial^2 E}{\partial k^2} (\Delta k)^2$ .

And the general mass in general is then  $\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2}$

Under certain circumstances, in particular when the second derivative of the dispersion relation is negative at the Fermi level, it may be advantageous to think of the charge carriers not as (negative) electrons with a negative mass, but as positive holes with a positive mass.

### Another picture for holes

The current density is the mean velocity of all the electrons times the charge. Recall that the mean velocity of all states in a band is zero.

$$\begin{aligned}
 j &= -e \int_{\text{occupied states}} v(k) \frac{dk}{4\pi^3} \\
 &= -e \left[ \int_{\text{all states}} v(k) \frac{dk}{4\pi^3} - \int_{\text{unoccupied states}} v(k) \frac{dk}{4\pi^3} \right] \\
 &= +e \int_{\text{unoccupied states}} v(k) \frac{dk}{4\pi^3}
 \end{aligned}$$

The current can be considered to be carried by positively charge particles, which are not in the states unoccupied by electrons. In general, they may have either positive or negative mass.

Under certain circumstances, particularly when the second derivative of the dispersion relation is negative at the Fermi Level, it may be advantageous to think of the charge carriers as positive holes with a positive mass, occupying the states which are in fact unoccupied by electrons.

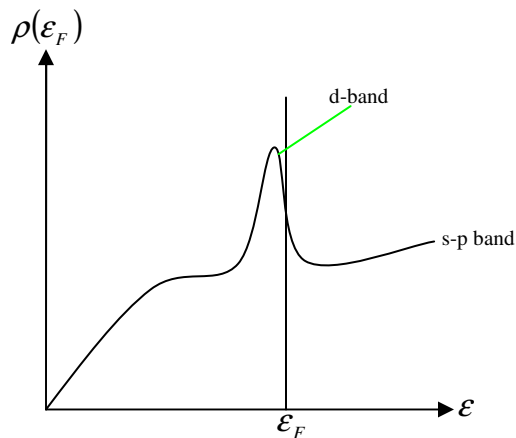
## 4.12. Metal Properties

### 4.12.1. Specific Heat

Analysis is exactly as before upto  $c_v = \frac{\pi^2 \rho(\epsilon_F) k_B^2}{3v} T$ .

We now have no simple expression for  $\rho(\epsilon_F)$ .

For example, in the d-band (transition metals) elements like iron, the d-band overlaps the s-p band (free electron like) and the d-band contribution can be large.



In iron, the coefficient of  $T$  in  $c_v(\gamma)$  is 8 times the free electron value.

In some materials (so called “heavy fermion” materials)  $\gamma$  may be upto a thousand times the Free electron value.

### 4.12.2. Electrical conductivity

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

### 4.12.3. Thermal Conductivity

$$k = \frac{nk_B^2\tau}{m^*} \left( \frac{\pi^2 T}{3} \right)$$

Note that the Lorentz ratio remains the same;  $\frac{k}{\sigma T} = \left( \frac{k_B}{e} \right)^2 \frac{\pi^2}{3} = 2.44 \times 10^{-8} \omega \Omega k^{-2}$

Deviations arise because scattering (from defects and phonons) cannot be simply characterised by one mean collision time.

### 4.12.4. Hall Effect

The electron orbit in the presence of a magnetic field may look a positive or negative charge depending on the details of the Fermi surface.

$$R_H = \begin{cases} \frac{-1}{n_e e} & \text{(electrons)} \\ \frac{+1}{n_h e} & \text{(holes)} \end{cases}$$

$$R_H = \frac{1}{n_{\text{eff}} e}$$

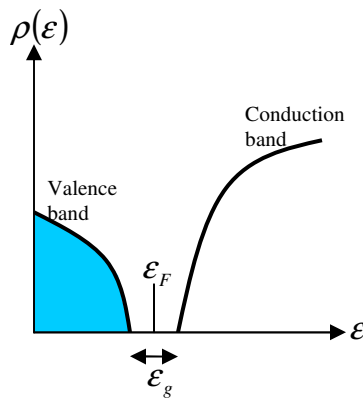
### 4.13. Summary

We can explain many properties of metals if we assume that the effect of nuclei and other electrons can be considered as a periodic potential. This effects the dispersion relation and may form complicated Fermi Surfaces which are far from the Free Electron Fermi sphere. The curvature of the bands near the Fermi level changes the effective mass. There are collisions with things which cause deviations from periodicity of the crystal structure (defects and phonons).

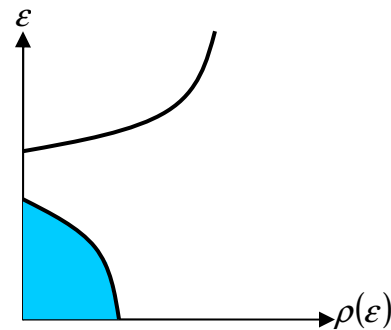
## 5. Semiconductors

The Nearly Free electron model applies equally to the case where the Fermi level lies within a small bandgap (semiconductor) as to the case of a metal.

By small, we mean there is a possibility of excitation of electrons from one band to the next below the melting point. In practice  $\epsilon_g \leq 2eV$ .



By convention, these diagrams are drawn as;



### 5.1. Semiconductor band structures

There are two cases;

- Direct gap;  $\frac{1}{2}$  conduction band
- Indirect gap;  $\frac{1}{2}$  conduction band

**Direct gap;** minimum energy of valence band is at the same wavevector as maximum energy of valence band. In this case an electron can be excited across the minimum bandgap energy by a photon. On the scale of the Brillouin Zone, the photon momentum is very small.

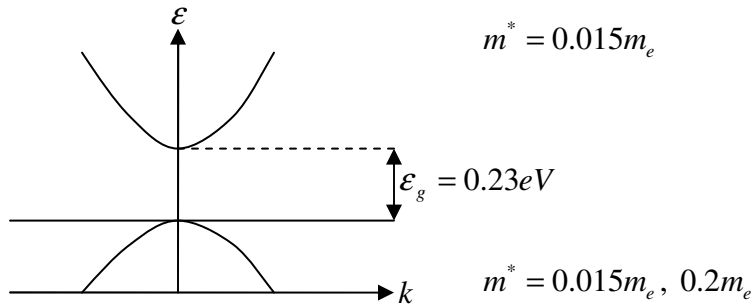
If  $\epsilon_g \sim 1eV$ , the photon momentum is about  $5 \times 10^{-4} \text{ \AA}^{-1}$ . Compared to a typical zone

boundary wavevector;  $\sim 2 \text{ \AA}^{-1}$ . This reflects the fact that the photon speed is much larger than the electron speed.

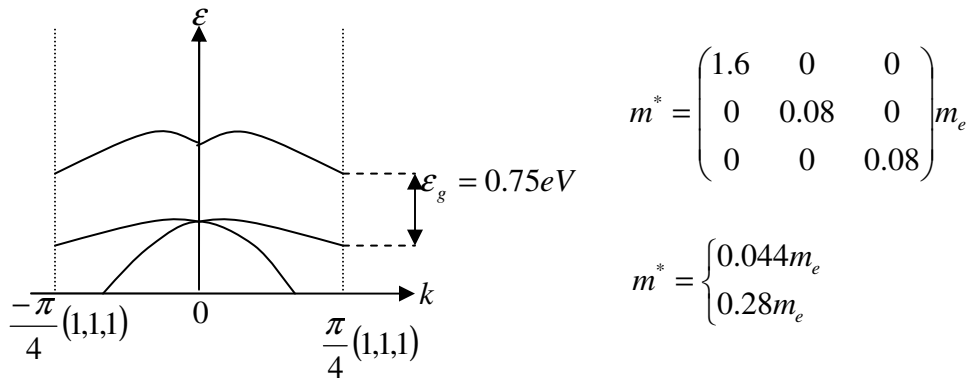
**Indirect gap:** Maximum energy of the valence band is at a different wavevector from the minimum energy of the conduction band. Excitation across the gap by a photon requires also the creation of a phonon to take up the momentum difference.

Note that, in general, the effective mass is not isotropic as it is a tensor.

Indium Antimonide – direct gap



Germanium – indirect gap



## 5.2. Intrinsic Semiconductors

Intrinsic behaviour is observed when  $\frac{1}{2}$  the conductor is sufficiently pure. We can take a single (scalar) average effective mass as far as thermal properties go. It is different, in general, for conduction ( $m_c$ ) and valence ( $m_v$ ) bands. The energy in conduction band, with respect to the minimum energy,  $\epsilon_c$  ;

$$\epsilon - \epsilon_c = \frac{\hbar^2 k^2}{2m_c}$$

The density of states is given by;  $\rho(k)dk = \frac{V}{\pi^2} k^2 dk$

Which gives;  $\rho(\epsilon)d\epsilon = \frac{V}{\pi^2 \hbar^3} \sqrt{2(\epsilon - \epsilon_c)} m_c^{\frac{3}{2}} d\epsilon$  For  $\epsilon > \epsilon_c$

Correspondingly, for the valence bands;  $\rho(\epsilon)d\epsilon = \frac{V}{\pi^2 \hbar^3} \sqrt{2(\epsilon_v - \epsilon)} m_v^{\frac{3}{2}} d\epsilon$  For  $\epsilon < \epsilon_v$

The number density of electrons in the conduction band,  $n$ , and holes in the valence band,  $p$ , are given by;

$$n = \frac{1}{V} \int_{\text{conduction band}} \rho(\epsilon) f(\epsilon) d\epsilon \quad p = \frac{1}{V} \int_{\text{Valence band}} \rho(\epsilon) (1 - f(\epsilon)) d\epsilon$$

The Fermi function is small throughout the conduction band but well away from the band edge ( $\epsilon_c$ ), so it can be ignored.

We can replace limits;

$$n = \frac{1}{V} \int_{\epsilon_c}^{\infty} \rho(\epsilon) f(\epsilon) d\epsilon \quad p = \frac{1}{V} \int_{-\infty}^{\epsilon_v} \rho(\epsilon) (1 - f(\epsilon)) d\epsilon$$

IF the chemical potential is not too close to either band;

$$(\epsilon_c - \mu) \gg k_B T ; \quad (\mu - \epsilon_v) \gg k_B T$$

Then;

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)\beta} + 1} \approx e^{-(\epsilon-\mu)\beta} \quad [\epsilon > \epsilon_C]$$

$$1 - f(\epsilon) = \frac{1}{e^{(\mu-\epsilon)\beta} + 1} \approx e^{-(\mu-\epsilon)\beta} \quad [\epsilon < \epsilon_V]$$

This gives;

$$n = \frac{1}{V} e^{-(\epsilon_V - \mu)\beta} \int_{\epsilon_C}^{\infty} \rho(\epsilon) e^{-(\epsilon - \epsilon_C)\beta} d\epsilon$$

$$n = \frac{1}{V} e^{-(\mu - \epsilon_V)\beta} \int_{-\infty}^{\epsilon_V} \rho(\epsilon) e^{-(\epsilon_V - \epsilon)\beta} d\epsilon$$

Using  $\rho(\epsilon)$ :

$$n = \frac{\sqrt{2m_C^2}}{\pi^2 \hbar^3} e^{-(\epsilon_C - \mu)\beta} \int_{\epsilon_C}^{\infty} \sqrt{\epsilon - \epsilon_C} e^{-(\epsilon - \epsilon_C)\beta} d\epsilon$$

$$n = \frac{\sqrt{2m_V^2}}{\pi^2 \hbar^3} e^{-(\mu - \epsilon_V)\beta} \int_{\epsilon_C}^{\infty} \sqrt{\epsilon_V - \epsilon} e^{-(\epsilon_V - \epsilon)\beta} d\epsilon$$

We can do this! Substitute  $x^2 = \epsilon - \epsilon_C$ :

$$\int_{\epsilon_C}^{\infty} \sqrt{\epsilon - \epsilon_C} e^{-(\epsilon - \epsilon_C)\beta} d\epsilon = 2 \int_0^{\infty} x^2 e^{-x^2\beta} dx = \frac{1}{2} \sqrt{\frac{\pi}{\beta^3}}$$

So;

$$n = \frac{1}{4} \left( \frac{2m_C}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}} e^{-(\epsilon_C - \mu)\beta}$$

$$p = \frac{1}{4} \left( \frac{2m_V}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}} e^{-(\mu - \epsilon_V)\beta}$$

$$\text{Multiplying these two gives; } np = \frac{1}{16} \left( \frac{2}{\pi \hbar^2 \beta} \right)^3 (m_C m_V)^{\frac{3}{2}} e^{-\epsilon_g \beta}$$

In a pure semiconductor;  $n_i = p_i$



$$n_i = p_i = \frac{1}{V} \left( \frac{2}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}} (m_c m_v) e^{\frac{-\epsilon_g \beta}{2}}$$

Putting this back into the expression for  $p$ , we deduce;

$$\mu = \epsilon_v + \frac{1}{2} \epsilon_g + \frac{3}{4} k_B T \ln \left( \frac{m_v}{m_c} \right)$$

So that  $\mu$  is the mid-point of the gap at  $T = 0$  and lies within a fraction of  $k_B T$  or so of the mid point at finite temperatures in intrinsic semiconductors.

### 5.3. Extrinsic Semiconductors

What happens if we introduce impurities?

Consider a simple arsenic (group 5) atom into Germanium (group 4) Each *Ge* contributes four electrons to the valence band. The *As* atom has five electrons; it donates one extra electron. The arsenic is therefore called a *donor impurity*.

We assume that the extra electron is loosely bound and that it moves in the conduction band with effective mass  $m^*$ . We treat it like a hydrogen atom.

$$\text{Force on an electron; } F = \frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} \frac{1}{\epsilon}$$

By analogy, the binding energy is;

$$\begin{aligned} E_0 &= \frac{m_e e^4}{(4\pi\epsilon_0 \hbar)^2} \left( \frac{m^*}{m_e} \right) \frac{1}{\epsilon^2} \\ &= 13.6 \text{ eV} \times 0.23 \times 0.004 \\ &= 12 \text{ MeV} \end{aligned}$$

The Bohr radius is then;

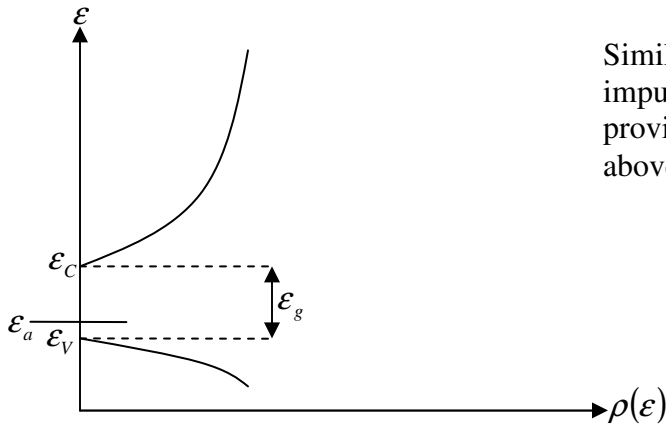
$$r_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \cdot \frac{m_e}{m^*} \cdot \mathcal{E}$$

$$= 0.53 \text{ \AA} \times 4.3 \times 15.8$$

$$= 36 \text{ \AA}$$

We conclude that the extra electron is loosely bound and that the use of the bulk dielectric constant is reasonable.

The energy to ionise the electron is only  $12\text{meV}$ , so we can represent the donor bound state as a level  $12\text{meV}$  below the conduction band.

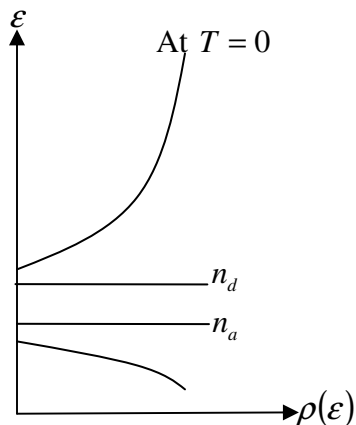


Similarly, group three impurities (e.g. Gallium) provide a hole bound state just above the valence band.

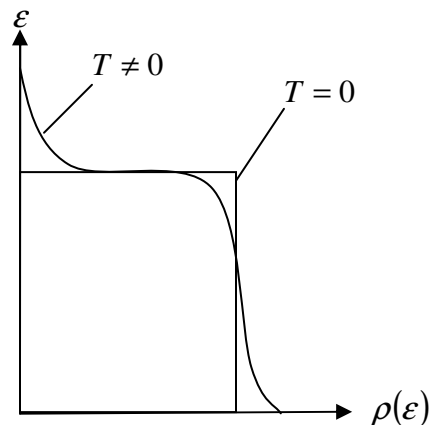
Usually, there are both donors and acceptors present. Suppose there are more donors than acceptors.

$n_d$  : number of donors

$n_a$  : number of acceptors



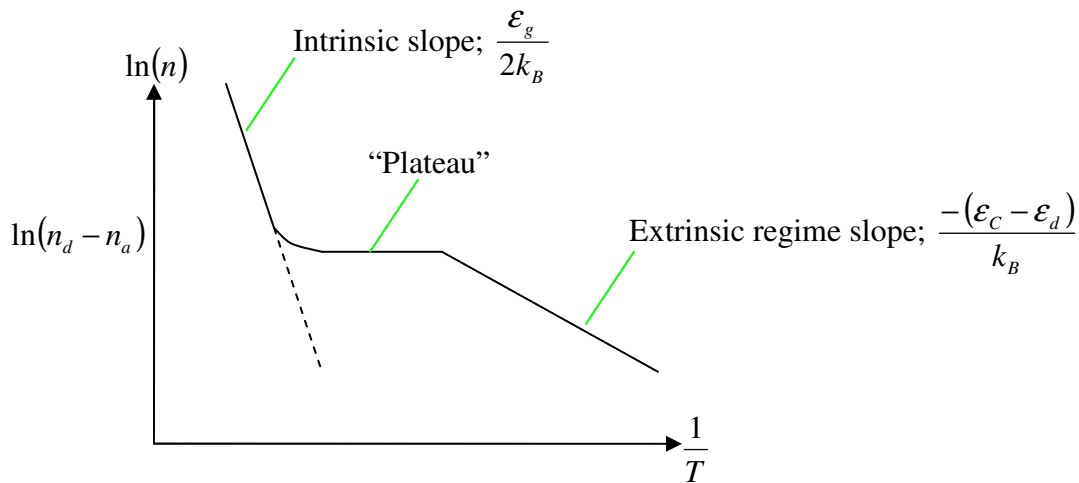
Donor level – partly full



At  $T = 0; \mu = \epsilon_d$  ;

$$n = \frac{1}{4} \left( \frac{2m_c}{\pi \hbar^2 \beta} \right)^{\frac{3}{2}} e^{-(\epsilon_c - \epsilon_d) \beta}$$

When all of the donors are ionised, the number of carriers will plateau at  $(n_d - n_a)$ . At higher temperatures, the number of intrinsic carriers becomes comparable to the number of impurities, the chemical potential ends up near the middle of the band gap and  $n$  reverts to  $n_i$ .



Note: The number of electrons in the extrinsic regime is always greater than the intrinsic value at the same temperature.

A semiconductor with more donors than acceptors is called *n-type* and one with more acceptors than donors is called *p-type*.

$$np = \frac{1}{16} \left( \frac{2}{\pi \hbar^2 \beta} \right)^3 (m_c m_v)^{\frac{3}{2}} e^{-\epsilon_g \beta}$$

This can be used to calculate the number of minority carriers at any given temperature, once the number of majority carriers is known.

## 5.4. Intrinsic versus Extrinsic

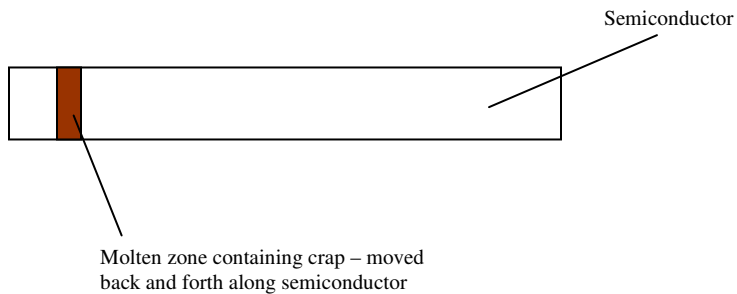
How pure do materials have to be to see intrinsic behaviour at room temperature?

For *Ge*;  $n_i(T = 300k) \sim 1.6 \times 10^{18} m^{-3}$

Comparing this with atoms;  $4.4 \times 10^{28} m^{-3}$ , so purity needs to be better than 1 in  $10^{10}$ .

## Zone Refining

This is a technique which enables purification to parts in  $10^{12}$ .



We move the molten zone back and forth; it turns out that the impurities remain in the molten zone. The result is that we have a very pure crystal with a bit of crap on the end. The pure part is then chopped up and sold on market day.

## 5.5. Semiconductor Properties

We continue to use the Nearly Free Electron model, bearing in mind that both electrons and holes may contribute. The main difference from metals is the temperature dependence of the number of carriers.

### 5.5.1. Electrical Conductivity

$$\sigma = \frac{ne^2\tau}{m_c} + \frac{pe^2\tau}{m_H}$$

It is interesting to separate mobility  $\left(\frac{\text{drift velocity}}{\text{E-field}}\right)$  which shows the temperature dependence arising from collisions, as opposed to the effects of changing the number of carriers.

$$u = \frac{|\bar{v}|}{|E|} = |e| \frac{\tau}{m^*}$$

Therefore;  $\sigma = |e|(n\mu_e + p\mu_h)$

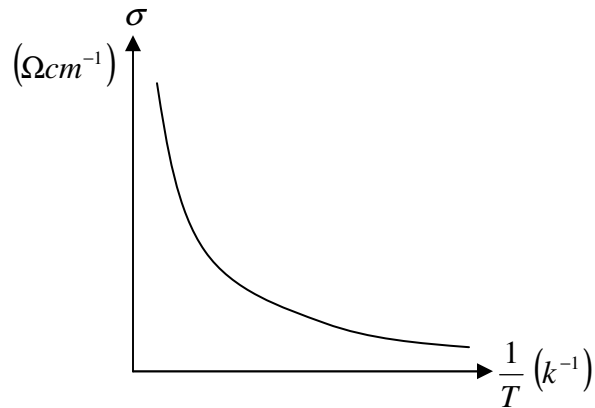
Mobility varies in a similar way to conductivity in metals. We can treat carriers as classical statistically, so;

$$\frac{1}{2} m^* \bar{v}^2 = \frac{3}{2} k_B T$$
$$\bar{\tau} = \frac{\lambda}{\sqrt{\bar{v}^2}} \propto T^{-3/2}$$

Since  $\lambda \propto \frac{1}{T}$  in the phonon regime.

So mobility;  $\mu \propto \bar{\tau} \propto T^{-3/2}$

Conductivity increases as  $T$  increases;



### 5.5.2. Hall Effect

Depending on whether conduction is dominated by electrons or holes;

$$R_H = \frac{-1}{ne} \quad \text{electrons}$$

$$R_H = \frac{+1}{pe} \quad \text{holes}$$

If there are appreciable numbers of both types, then we get more complicated expressions – see Hook and Hall p153 – 154.

Note that the Hall coefficient, together with the conductivity,  $\sigma$ , may be used to estimate the mobility,  $\mu$ ;

$$\mu = \frac{e\tau}{m^*} = \frac{-\sigma}{ne} = R_H \sigma$$