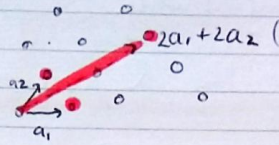
unit 1

Condensed Matter

Lecture 1

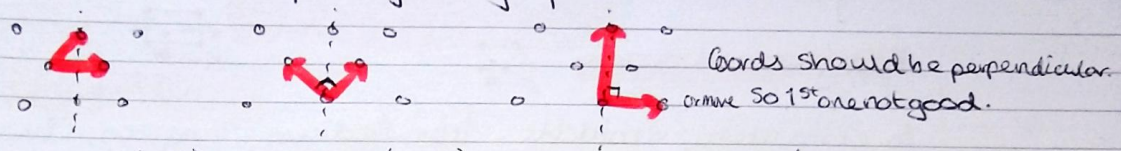
Crystal - material with translational symmetry. Glass in not one. Glass is amorphous.

Lecture 2

lattice vector 

$R_{nm} = na_1 + ma_2$

pick a_1 and a_2 to reflect symmetry of lattice best.

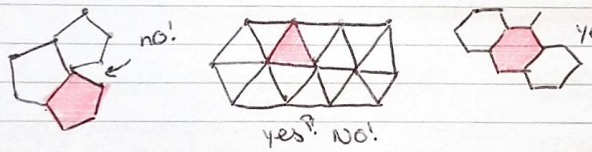


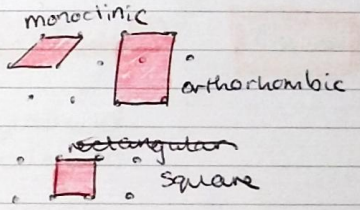
obtuse (<90°) better (>90°) more better (=90°)

a_1 and a_2 create a parallelogram that tessellates. unit cell. in 3D it's parallelpiped.

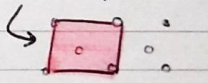
Bravais lattices

Only finite shapes a symmetry of lattice. Eg parallelograms and hexagons. No pentagons (but you can with molecules because they're singular).

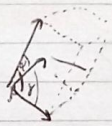




Even numbers only, no odds allowed.

no centred squares 

There are 3D lattices.

Triclinic  lowest symmetry no right angles

Plurarium: monoclinic  2 right angles

Orthorhombic  3 right angles, ~~no equal angles~~. lattice point centred on a side/ in middle.

Tetragonal  rectangle prism, 3 right angles

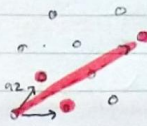
Hexagonal i'm not drawing!

Condensed Matter

Lecture 1

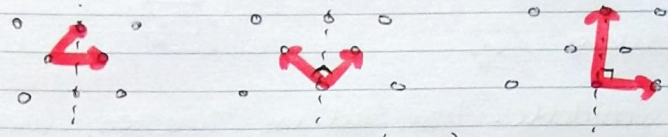
Crystal - material with translational symmetry. Glass in not one. Glass is amorphous.

Lecture 2

lattice vector  $2a_1 + 2a_2$ (not always 90°)

$R_{nm} = na_1 + ma_2$

pick a_1 and a_2 to reflect symmetry of lattice best:



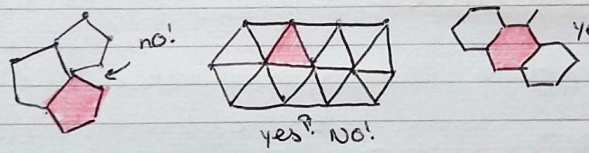
Coords should be perpendicular or more so 1st one not good.

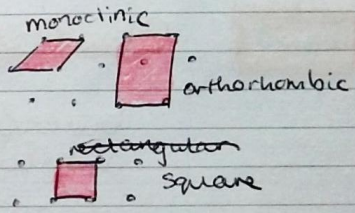
arbitrary (<90°) better (>90°) more better. (=90°)

a_1 and a_2 create a parallelogram that tesselates. unitcell. in 3D it's parallelpiped.

Bravais lattices

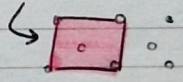
Only finite shapes a symmetry of lattice. Eg parallelograms and hexagons. No pentagons (but you can with molecules because they're singular).



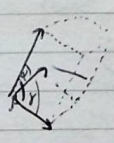


Even numbers only, no odds allowed.

no centred squares



There are 3D lattices.

Triclinic  lowest symmetry no right angles

Plutonium monoclinic  2 right angles

Orthorhombic  3 right angles, ~~no equal or parallel edges~~. lattice point centred on aside or in middle.

Tetragonal  rectangle prism, 3 right angles ⇑

Hexagonal i'm not drawing!

cubic  body centred or face centred (point in middle or faces) Faces identical

Highest symmetry.

We're only considering cubic & hexagonal.

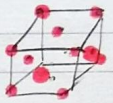
Simple cubic

Only polonium fits cubic model. lattice constant for Po = 3.35 Å

Body centred cubic  

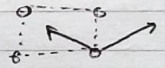
So extra atom in middle. Iron, Sodium, Tungsten, Chromium: distances to atoms not equal (corners ≠ centre).

Face centred

extra atoms on faces. Copper, Nickel. 

Hexagonal Pack

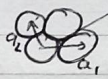
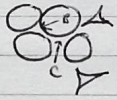
Cobalt, Magnesium.

Smallest unitcell is called primitive. 

Lecture 3

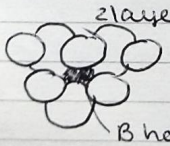
Close Packed Structure

low energy structure, highest coordination number, has 12 neighbours

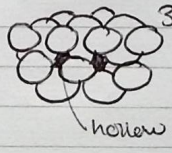
  hollow site, B and C because there are B pointing up C pointing down 

$|a_1| = |a_2|$ $\theta = 120°$

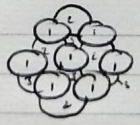
Next layer can cover B or C:

 2 layer

B has no area.

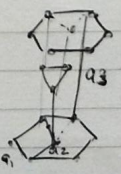
 3rd hollow.

keep putting over C

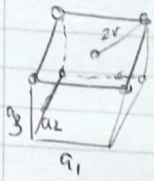
If you alternate  no hollow areas. It actually makes face-centred cubic

So if the radius is r : $|a_1| = |a_2| = 2r$

$\sqrt{\frac{2}{3}}\,2r = \sqrt{\frac{2}{3}}|a_1| = \frac{\sqrt{6}}{3}|a_1|$ so $|a_3| = 2\sqrt{\frac{2}{3}}|a_1|$



And for face centred cubic



$|a_1| = |a_2 + a_3| = 2\sqrt{2}\,r = a_0$ atomic radius r.

$$r = \frac{\sqrt{2}\,a_0}{2}$$

∴ layer spacing along diagonal, d: so corner to corner × 1/3.

$$d = \frac{\sqrt{3}}{3} a_0 = \frac{\sqrt{6}}{3} 2r$$

Lecture 4

Lattice Vectors

the vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$ are non-coplanar

$$\underline{R}_{(x,y,z)} = x\underline{a}_1 + y\underline{a}_2 + z\underline{a}_3$$

$[x, y, z]$ directions &

coordinates are written as [...]

There are a few equivalent directions that are commonly into one:

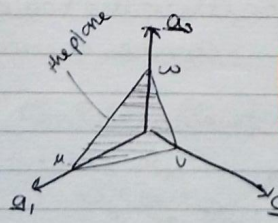
equivalent [1, 1, 1] directions: This is due to symmetry points / lines.

[1, 1, 1]
[1̄, 1, 1]
[1, 1̄, 1]
[1, 1, 1̄]
[1̄, 1̄, 1]
and more

} Shorthand <1, 1, 1>

Toby Indices

Used to denote planes in a crystal. (h, k, l) denotes a plane that intercepts the 3 cell axes at points a/h, a/k, ...

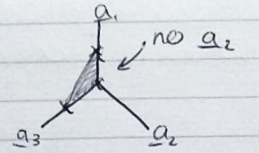


$$\left(\frac{1}{u}, \frac{1}{v}, \frac{1}{w}\right) \Rightarrow (h, k, l)$$

with this drawing it looks like

$u = 2/3$, $v = 1/3$, $w = 1/2$ so $(h, k, l) = (\frac{3}{2}, 3, 2)$

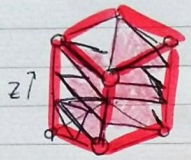
The miller indices are proportional to the inverses of the intercepts of the plane. If one of them (h, k, l) is zero, the plane doesn't intersect that axis.



sets of miller indices are written as:

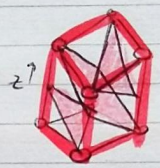
$\{h\ k\ l\}$

Miller indices look like:



(1, 1, 3)

so you fit 3 into z



(1, 1, 2)

you fit 2 into z because each one is ½ way along.

(h, k, l) is equivalent to $(\bar{h}, \bar{k}, \bar{l})$ same plane.

for Body Centred cubic, the middle atom isn't really included here. It's mainly the cube we're concerned about.

In the cubic system:

$[h, k, l]$ is 90° to (h, k, l)
not generally the case.

The layer spacing of (h, k, l) is given:

$$d_{h,k,l} = \frac{a_0}{\sqrt{h^2+k^2+l^2}}$$

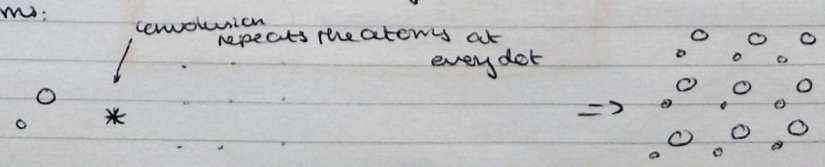
so $d_{0,0,1} = a_0$

$d_{1,1,1} = a_0/\sqrt{3}$

lecture 5

Basis

A basis is the contents of the unit cell. together the lattice & the basis make up the crystal. The basis can be one or more atoms:



Silican has a diamond type structure.

FCC lattice with 2 atom basis

lattice:	Basis
(0,0,0)	(0,0,0)
(½, ½, ½)	(¼, ¼, ¼)
(½, 0, ½)	
(0, ½, ½)	

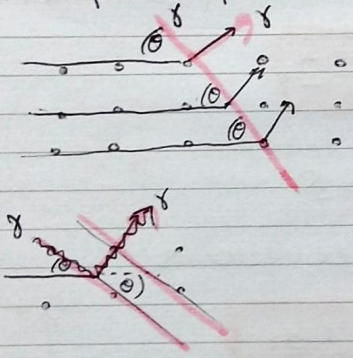
} from each lattice point, so there's 2 atoms for each lattice point.

Atoms are at:

(0,0,0) and (¼, ¼, ¼) for ¼ one.
(½, ½, 0) (¾, ¾, ¼)
... same ..... etc Just add ¼ to the lattice points.
as for
(0,0,0)

Bragg Diffraction.

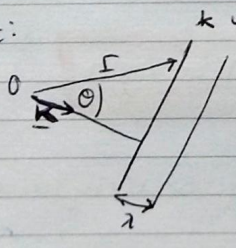
x-ray enters & leaves surface. Specular reflection from atomic planes parallel to surface.



$n\lambda = d\sin\theta$.

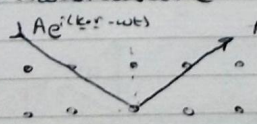
It doesn't have to be 90° however θ won't have relation to incident angle.

Solet:



forward wave $Ae^{i(\underline{k}\cdot\underline{r} - \omega t)}$

Consider a wave:



for strong constructive scattering, the waves must be in phase.

To make this so we need to make sure the planes are 90°

Let R be a lattice vector $\quad R = x\underline{a}_1 + y\underline{a}_2 + z\underline{a}_3$

$$e^{i\underline{k}\cdot\underline{R}} = e^{i\underline{k}'\cdot\underline{R}}$$

$$(\underline{k}' - \underline{k})\cdot\underline{R} = 2\pi n \qquad n \text{ is an integer}$$

$$\Delta\underline{k}(x\underline{a}_1 + y\underline{a}_2 + z\underline{a}_3) = 2\pi n$$

$$\begin{aligned} \Delta\underline{k}\cdot\underline{a}_1 &= 2\pi h \\ \Delta\underline{k}\cdot\underline{a}_2 &= 2\pi k \\ \Delta\underline{k}\cdot\underline{a}_3 &= 2\pi l \end{aligned}$$

Laue Conditions.
If this is satisfied, diffraction can occur.

reciprocal lattice vectors

$$\underline{b}_1 = \frac{2\pi\,\underline{a}_2\times\underline{a}_3}{\underline{a}_1\cdot\underline{a}_2\times\underline{a}_3}$$

$$\underline{b}_2 = \frac{2\pi\,\underline{a}_3\times\underline{a}_2}{\underline{a}_2\cdot\underline{a}_3\times\underline{a}_1}$$

$$\underline{b}_3 = \frac{2\pi\,\underline{a}_1\times\underline{a}_2}{\underline{a}_3\cdot\underline{a}_1\times\underline{a}_2}$$

So that $a_1\cdot b_1 = a_2\cdot b_2 = a_3\cdot b_3 = 2\pi$

$a_1\cdot a_2 = a_2\cdot b_3 = a_3\cdot b_1 = a_1\cdot b_3 = \dots = 0$.

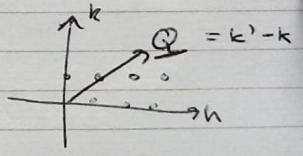
These denominators are actually the volume of the unit cell.

$$\underline{b}_1 = \frac{2\pi}{a_1}\hat{\underline{a}}_1$$

So if real space vector is $\underline{R}$

Then reciprocal space lattice vector is:

$$\underline{Q} = h\underline{b}_1 + k\underline{b}_2 + l\underline{b}_3$$

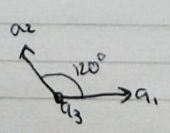


$$\underline{Q}\cdot\underline{R} = 2\pi(hx + ky + lz) = 2\pi n$$

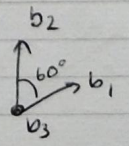
If $\Delta\underline{k} = \underline{Q}$ then the vectors satisfy laue eqns and will allow diffraction.

lecture 6

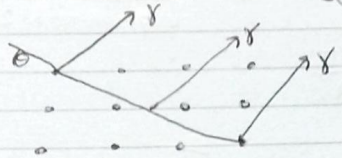
So to understand reciprocal space for hexagons



do the cross products: $\Rightarrow$



So lets look at Bragg diffraction



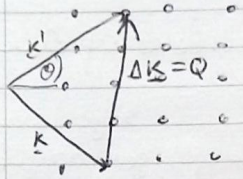
reflected rays

in Real Space

$n\lambda = 2d\sin\theta$

In reciprocal space.

$Q = n b_3 = 2k\sin\theta$.

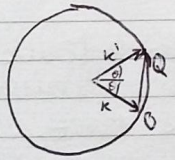


here there's 4 dots so $n=4$ in this picture.

This is useful because diffraction strongly occurs at the dots because the have conditions are met. Strong scattering / Bragg Peak.

Ewald Sphere:

you can make a sphere from the k vectors.



note that the k vectors point at origin. you can use the radius to find lattice points and get scattering

Example

X ray, $\lambda = 1.4$ Å. Scattered off silicon crystal w/ $a_0 = 5.43$ Å. at what 2θ angle is Bragg peak found for (1,1,1)?

$$\underline{Q}_{111} = 1\underline{b}_1 + 1\underline{b}_2 + 1\underline{b}_3$$

& $k = 2\pi/\lambda$

$$= \sqrt{3}\, b_1 = \sqrt{3}\, {}^{2\pi}/_{a_1}$$

$$\frac{\sqrt{3}\,2\pi}{a_1} = 2\frac{2\pi}{\lambda}\sin\theta \qquad \sin\theta = \frac{\sqrt{3}\lambda}{2a_0} = 0.2233$$

$\theta = 12.90°$

$2\theta = 25.08°$ Yay!

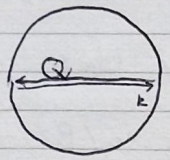
and for (5, 1, 1) $\underline{Q} = 5\underline{b}_1 + \underline{b}_2 + \underline{b}_3$ $\sqrt{25+1+1} = \sqrt{27}$

$$\underline{Q} = \sqrt{27}\,\frac{2\pi}{a_1}$$

$$\sqrt{27}\,\frac{2\pi}{a_1} = 2\,\frac{2\pi}{\lambda}\sin\theta \qquad \sin\theta = \frac{1.4}{2}\,\frac{\sqrt{27}}{5.43}$$

$2\theta = 84^\circ$ yay!

The furthest peak = largest Q = diameter of Ewald sphere.



so $Q \leq 2k = \frac{4\pi}{\lambda}$

$\sqrt{h^2+k^2+l^2}\ \lambda < 4\pi/\lambda$

So you could get maybe (10, 0, 0) but not (11, 0, 0)

You'd have to decrease λ to get higher Bragg Peaks.

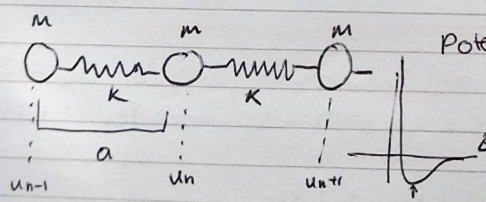
Lecture 7

Lattice Vibrations

High temperature => larger atomic motion => lattice vibrations.

The small amplitude limit is the harmonic limit.

Imagine a chain of atoms and springs:



Potential: $V(a+\Delta a) = V_a + \frac{\Delta a^2}{2}\left(\frac{d^2V}{dr^2}\right)_{r=a} + \dots$

1st derivative is zero here

The expansion looks like Hooke's law.

$$k = \left(\frac{a^2V}{dr^2}\right)_{r=a} \qquad F = k(r-a) = k\Delta a$$

$$\Delta V = \frac{1}{2}\left(\frac{d^2V}{dr^2}\right)_{r=a}(\Delta a)^2$$

Equating the total forces on the right

$$Ma = M\ddot{u}_n = k(u_{n+1} - u_n) - k(u_n - u_{n-1})$$

$$M\ddot{u}_n = k(u_{n+1} - 2u_n + u_{n-1})$$

Solve using wavelike solutions:

$$u_n = A e^{i(kx_n^0 - \omega t)} \qquad x_n^0 = na$$ undisplaced position of n^{th} atom.

Sub into equation of motion

$$-\omega^2 MA e^{i(kna-\omega t)} = kA\left[e^{ik(n+1)a-\omega t)} - 2e^{i(kna-\omega t)} + e^{ik(n-1)a-\omega t)}\right]$$

Cancelling $Ae^{ikna-\omega t}$:

$$-\omega^2 M = k[e^{ika} - 2 + e^{-ika}]$$

$$\omega^2 M = 4k \sin^2(\tfrac{1}{2}ka)$$ Dispersion relation

maximum frequency is $2\sqrt{k/M}$ cutoff frequency.

So if we plot ω:

$\sin^2$ function modulus

Because it's sinusoidal, K and $K+2\pi$ are equal, so

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

Phase & Group Velocities

$$v_p = \frac{\omega}{k} \qquad v_g = \frac{d\omega}{dk} = a\left(\frac{k}{M}\right)^{1/2} \cos\left(\frac{ka}{2}\right)$$

Funfact: X-rays get Total External Reflection because v_p is greater than the speed of light!

The long Wavelength Limit

for $\lambda >> a$; $ka << 1$ at small k.

$$v_p = a\sqrt{\frac{k}{M}}$$ velocity of sound for 1D crystal.

For Diatomic lattices:

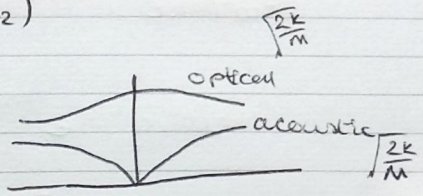
Now there's 2 kinds of atoms:

$$M\ddot{u}_n = K(u_{n+1} - 2u_n + u_{n-1})$$

$$m\ddot{u}_{n+1} = K(u_n - 2u_{n+1} + u_{n-2})$$

$$-\omega^2 M = 2K(\alpha\cos(\tfrac{ka}{2}) - 1)$$

$$-\alpha\omega^2 m = 2K(\cos(\tfrac{ka}{2}) - \alpha)$$



depending on ± part.

$$-\omega^2 = \frac{K(M+m)}{Mm} \pm K\left[\left(\frac{M+m}{Mm}\right)^2 - \frac{4}{Mm}\sin^2\left(\frac{ka}{2}\right)\right]^{1/2}$$

Phonons

Phonons are vibrations in the solid. Even at 0K the atoms vibrate w/ their Zero Point Energy.

They behave like harmonic oscillator a restricted to energy values:

$$\epsilon_n = (n + 1/2)\hbar\omega$$

The quanta of vibration mode energy is the phonon.

Phonon momentum:

crystal momentum, not kinematic. →

$$p = \hbar k$$
$$E \neq \hbar\omega$$

← exact momentum, so position can't be determined.

Electrons in a changing Potential.

Electrons obey Schrödinger's equation:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\,\psi(x) = E\psi(x)$$

if $V(x)=0$ so no potential:

$$E = \hbar^2 k^2 / 2m$$

For a periodic lattice, we expand the potential as a Fourier Series.

$$V(x) = \sum_G V_G e^{iGx}$$

$Ga = 2n\pi$. if $V(x)=V(x+a)$

So Schrödinger becomes:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{d(x)^2} + \sum_G V_G e^{iGx}\psi(x) = E\psi(x)$$

Electron density is given as: wavefunctions = Bloch functions

$$n(x) = |\psi(x)|^2$$

The kinetic energy of a G component of the wavefunction:

$$\frac{\hbar^2 |k+G|^2}{2m} = KE_G$$

Unit 2 Electrons in Crystals

Lecture 1 — Free Electron Model

remove valence electrons - free to conduct.

Energy:

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

k = wavenumber.

Dispersion relation from Drude Model

Lecture 2 — Electrons in a Periodic Potential

$$V(\underline{r}) = V_1(\underline{r}) + V_2(\underline{r})$$

$V_1(\underline{r})$: electrostatic due to array of atomic cores

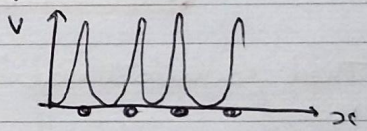
$V_2(\underline{r})$: Potential due to other outer electrons.

Schrodinger's equation in this case:

$$\psi(x) = U_k(x)\, e^{ikx}$$

$$\psi(\underline{r}) = U_k(\underline{r})\, e^{i\underline{k}\cdot\underline{r}}$$

in general



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

a = ion spacing

Hence

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

$$\psi(x+a) = J\,\psi(x)$$

with

$$J = e^{\frac{2\pi i M}{N}}$$

M is an integer

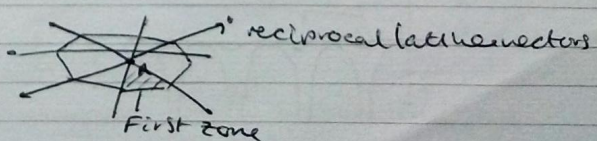
N unit cell lengths.

$$\psi(x) = U_M(x)\, e^{\frac{2\pi i M x}{Na}}$$

$$k = 2\pi M / Na$$

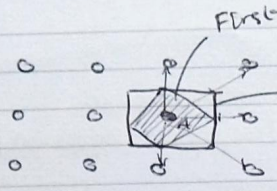
So between $\frac{-\pi}{a} \leq k \leq \frac{\pi}{a}$ is the first Brouillon zone which is also where $\frac{-N}{2} \leq M \leq \frac{N}{2}$

It's convenient to describe the first Brouillon zone as a volume in k space.



To do this make the lattice a centre & draw lines to the nearest neighbours. Then bisect all vectors & connect.

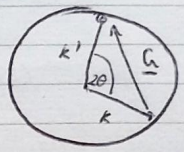
eg



First zone has use of edge $\frac{2\pi}{a}$. Its primitive.

For any location $\underline{A}'\underline{k}'$ in k space there's a corresponding location in the first Brouillon zone related by:

$$\underline{k}' = \underline{k} + \underline{G}$$



From the Ewald Sphere.

Going back to $V(x) = V(x+a)$

If $Ga = 2n\pi$

Then

$$e^{iG(x+a)} = e^{iGx} e^{iGa} = e^{iGx} e^{i2n\pi} = e^{iGx}$$

Then Schrodinger's equation becomes:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \sum_a V_a e^{iGx}\psi(x) = E\psi(x)$$

$$\psi(x) = e^{ikx}\sum_a U_a e^{iGx}$$

lecture 3

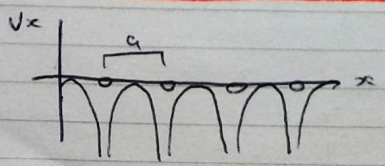
Nearly Free Electron Theory.

true ion cores. The correction to free electron theory ΔE:

$$\Delta E = \frac{\int \psi^* V'(x) \psi dx}{\int \psi^* \psi dx}$$

ψ unperturbed wavefunction
$V'(x)$ difference between true and free e^- potential.

$$V' = -\sum_{n=1}^{\infty} V_n \cos\left(\frac{2\pi n x}{a}\right)$$



From this $\psi(x) = e^{ikx}$

$|\psi|^2 = 1$

Hence $\Delta E = 0$ for all values of k.

Using perturbation theory with unperturbed states ψ_1 and ψ_2 then the wavefunctions that we use are the two orthogonal linear combinations ϕ_1 and ϕ_2 of ψ_1 ψ_2 that satisfy:

$$\int \phi_1^* V \phi_2 \, dx = 0$$

The only combinations of e^{ikx} and e^{-ikx} that satisfy this for all values of k are $\sin(kx)$ and $\cos(kx)$.

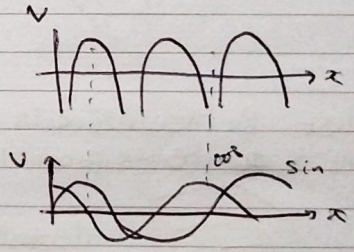
Thus...

for $\sin(kx)$ $\Delta E = \frac{1}{2} V_n$

for $\cos(kx)$ $\Delta E = -\frac{1}{2} V_n$

so $k = \pm \frac{n\pi}{a}$

for $\psi = \sin(kx)$ there are antinodes - energy raised
for $\psi = \cos(kx)$ there are attractive potential - lowered energy

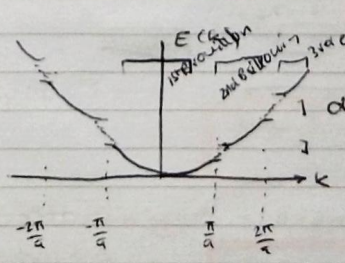


For stationary states, the group velocity = 0 hence:

$$\frac{dE}{dk} = 0$$

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

Graphing this:



1 dashed bits are forbidden!

The Bragg equation is:

$$n\lambda = 2a$$

at these values of k, the Bloch wave consists of two plane waves in opposite directions.

so. $$k = \pm \frac{n\pi}{a}$$

In this special case the two components make a standing wave:

$$\psi_+ = 2\psi_0 \cos(kx)$$
$$\psi_- = 2i\psi_0 \sin(kx)$$

Intensity $\propto$ electron density ρ

$$\rho_+ = \psi_+^2 = A^2 \cos^2(kx)$$
$$\rho_- = \psi_-^2 = A^2 \sin^2(kx)$$

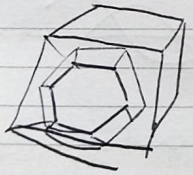
← concentrates e^- density at the ions

← concentrates them away.

Lecture 4

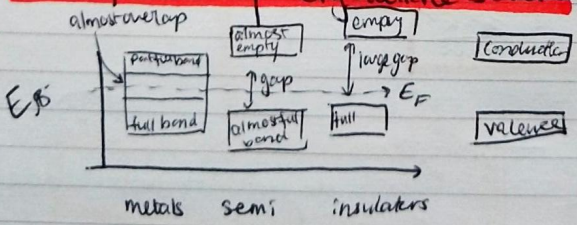
Using

The first Brillouin zone is body centered & has 14 sides. For FCC. planes are ⊥ to reciprocal lattice vectors



looks like this in 3D

Classification of Crystalline Solids



← bands diagram

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

Allowed k values in 1D crystal = those in lattice vibrations

$$k = \frac{2\pi p}{L}$$

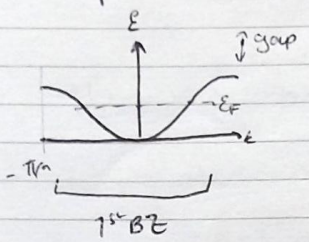
p = integer

$L = Na$ length of chain (N = No. atoms)

In first BZ there's N k-states and 2N electrons.

Monovalent Atoms

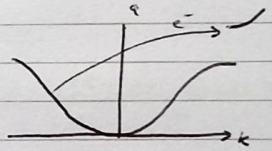
The 1st BZ is half filled by 1 e^- per ion and there's vacant states immediatly adjacent to Fermi level & hence occupied states



Divalent Atoms

Enough e^- to fill all states in band, so BZ is full.

Current carrying state can only be fitted produced using finite energy $|V_0|$ to shift e^- to 2nd BZ.



So should insulate.
However divalent metals do exist so it's Ca, Sr, Ba

Trivalent Atoms

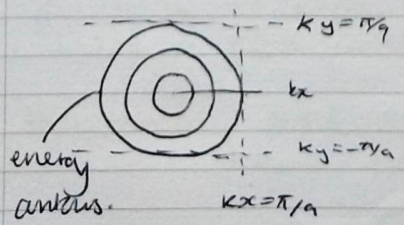
Behave like monovalent atoms. metal-like.

Lectures

Classification of Crystalline Solids

Imagine Crystal, simple $h \times h$.

Energy gaps occur at: $k_x = \pm \frac{\pi}{a}$, $k_y = \pm \frac{\pi}{a}$
These are lines as the boundaries of 1st BZ



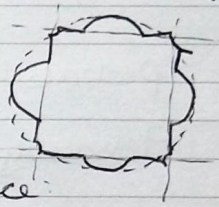
$$\epsilon = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m}$$

So these energy contours move towards the boundaries The outside bit has increased energy (look at parabola diagram) So they move in.

The contour has to meet boundary at 90°. Because group velocity becomes 0 at boundary.

$$\frac{d\omega}{dk} = \frac{dE}{\hbar\, dk} \qquad v_g \hbar = 0$$

↗ normal comp = 0



Density of running wave states in k space:

$$\rho_R(k) = \frac{L^2}{(2\pi)^2} \qquad L = Na$$

In 1st BZ

$$N_{k\,\text{states}} = \rho_R(k)\left(\frac{2\pi}{a}\right)^2 = \frac{L^2}{a^2}$$

For Divalent atoms:

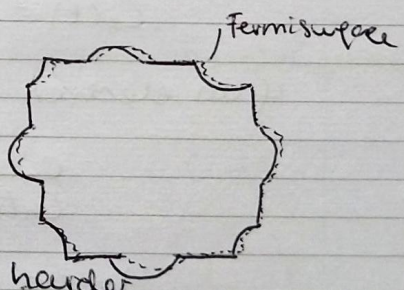
1) an area of k space equal to 1st BZ must be filled

2) all levels below E_F must be filled.

This is satisfied in picture below.

So 2nd BZ lowest ϵ < 1st BZ highest.

So there's overlapping ϵ bands.



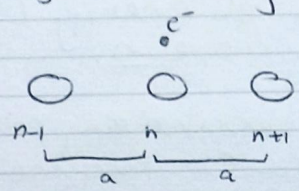
As perturbation increases, it's harder for ϵ bands to overlap. In divalent atoms first BZ is fully occupied and 2nd is empty

when electrons are removed from corners, it makes pockets of empty states. Looks like positive charge => holes => positive Hall coefficients.

In summary: odd valence => metals / metallic behaviour
even valence => insulators / metallic if band overlap

Small gap => semiconductors, large gap => insulators.

Tight Binding approach.



wavefunction — state

$$\psi = \sum_{n=1}^{N} a_n(t)\,\phi_n$$

Time dependant schrödinger

Probability amplitude = $C_n(t)$

Probability of finding an electron on an atom, n, $|C_n(t)|^2$

$$a_n \sim C_n \sim e^{(-Et/\hbar)}$$

Hence:

$$i\hbar \frac{dC_n}{dt} = BC_n - AC_{n-1} - AC_{n+1}$$

represent changes in C_n. A = Strength of coupling.

For wide separation A = 0:

$$i\hbar \frac{dC_n}{dt} = BC_n.$$

$$C_n(t) = C_n(0)\, e^{-iBt/\hbar}$$

If an electron is in state ϕ_m on atom m at t = 0:

$C_n(0) = 1$ for $n = m$

$C_n(0) = 0$ otherwise.

$$\psi = \phi_m e^{-iBt/\hbar}.$$

lecture 6

Coupled Probability Amplitudes.

If atoms aren't too close, motion is like state transfer from electron ϕ_n to neighbouring electron.

So a good linear approximation:

$$\psi = \sum_{n=1}^{N} a_n(t)\,\phi_n$$

$a_n(t)$ expansion coefficients

Some atomic states on other atoms aren't orthogonal, so $a_n(t)$ won't be equal to $C_n(t)$.

For stationary states: Probability of finding an electron on an atom, n, $|C_n(t)|^2$ is independant of time.

Hence: $$a_n \sim C_n \sim e^{-\frac{Et}{\hbar}}$$

This $$i\hbar \frac{dC_n}{dt} = BC_n - AC_n - AC_{n+1}$$

← strength of coupling

↑ ↑ changes in C_n.

In far apart atoms, $A \Rightarrow 0$:

$$i\hbar \frac{dC_n}{dt} = BC_n$$

where solutions are:

$$C_n(t) = C_n(0)\, e^{-\frac{iBt}{\hbar}}$$

If an electron is in state ϕ on atom m at $t=0$:

$C_n(0) = 1$ for $m = n$

$C_n(0) = 0$ otherwise

So that

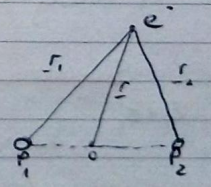
$$\psi = \phi_m e^{-iBt/\hbar}$$

In the example of H_2^+ ions. 2 protons share 1 electron.

$$i\hbar \frac{dC_n}{dt} = BC_n - AC_{n-1} - AC_{n+1}$$

$$i\hbar \frac{dC_1}{dt} = BC_1 - AC_2$$

$$i\hbar \frac{dC_2}{dt} = BC_2 - AC_1$$



We need to look for stationary state solutions to satisfy $a_n \sim C_n \sim e^{-Et/\hbar}$. use compound oscillator eqn.

$$m\ddot{x} = -\frac{mg}{l}x - S(x-y)$$

$$m\ddot{y} = -\frac{mg}{l}y + S(x-y)$$

Solutions to these are normal modes.

$$i\hbar \frac{dC_+}{dt} = (B-A)C_+ \qquad \text{and same for minus}$$

$C_+ = C_1 + C_2$ and $C_- = C_1 - C_2$.

$$C_+ \propto e^{-i(B-A)t/\hbar}$$

$$C_- \propto e^{-\frac{i(B+A)t}{\hbar}}$$

now use ψ formula with $a(t)$. Also:

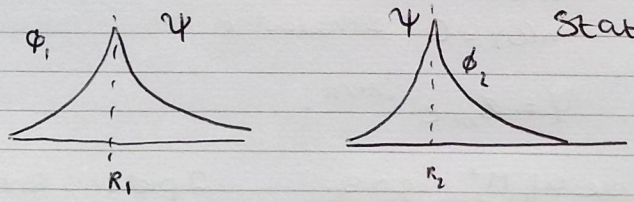
If electron is in state C_+, then $|C_-| = 0$.

$C_1 = C_2$ Thus. $a_1 = a_2$ if that the case

Hence $$\psi_+ \propto [\phi_1 + \phi_2] e^{-i(B-A)t/\hbar}$$

with an energy $E_+ = B - A$.

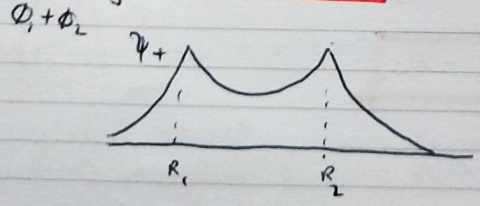
And $$\psi_- \propto [\phi_1 - \phi_2] e^{-i(B+A)t/\hbar} \qquad E_- = B + A.$$



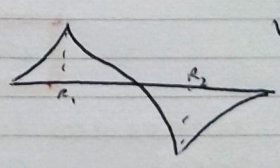
States for isolated atom

If they're together:

Symmetric state



antisymmetric $\phi_1 - \phi_2$

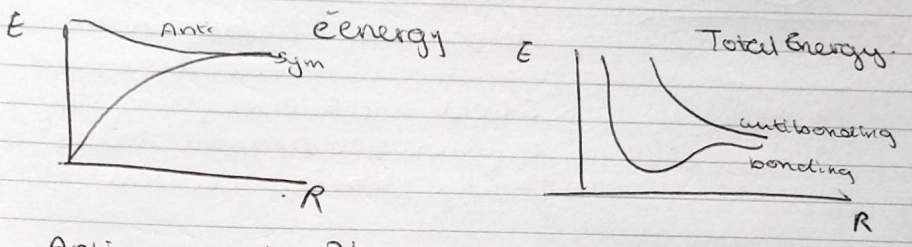


Hence we can determine which state has lower energy:

The 2 contributions to electron energy are:

1) Electrostatic potential in field of 2 protons.
2) Kinetic energy proportional to $|\nabla\psi|^2$

Comparison shows Symmetric state energy is lower. PE is lower since $|\psi|^2$ large in region where $\bar{e}$ respond most to protons's attraction.



Antisymmetric ψ = antibonding orbital

At large R values converge and Coulomes repulsion $e^2/4\pi\varepsilon_0 R$ has to be included.

A covalent bond has a linear combination of atomic orbitals.

Degeneracy ↑↑ with the approach of 2 nuclei.
The number of levels in band = No nuclei (not nucleons!).

Expected since covalent bonds are made to reduce energy. however H_2^+ is charged so it'll be different for other bonds.

Going back to electron chain, we can find solutions to the ith $\frac{dc_n}{dt}$ by combining with phonon eqn

$$M\ddot{u}_n = k(u_{n+1} + u_{n-1} - 2u_n)$$

mass of ion → M; Similar to spring constant. → k; displacement position. → u_n

Finding solutions to ith $\frac{dc_n}{dt}$ finds normal modes of chain.

lecture 7

$$C_n = C e^{i(kx_n^\circ - \omega t)}$$

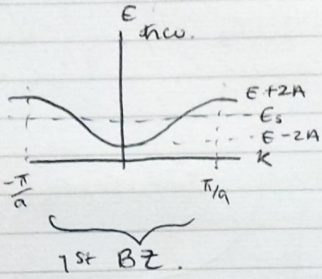
x_n° = na equilibrium position.

Subbing into ith $\frac{dc_n}{dt}$ gives:

$$\hbar\omega e^{i(kna-\omega t)} = Be^{i(kna-\omega t)} - Ae^{i(k(n-1)a-\omega t)} - Ae^{i(k(n+1)a-\omega t)}$$

$$\hbar\omega = B - Ae^{-ika} - Ae^{ika}$$

$$\hbar\omega = B - 2A\cos(ka)$$

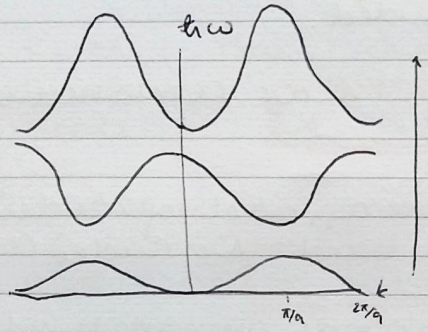


Number of allowed k values in each BZ = No Atoms in chain.

important: filled band = all states from maxima to maxima occupied
E field shifts everything down the curve by the same amount ⇒ No e^- distribution change => NO current.

Current only happens when electrons moved up a level

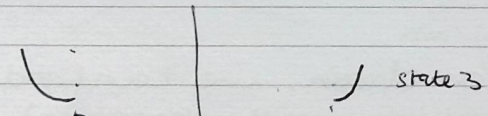
Repeated zone scheme



higher bands. minima & maxima change in each band.

A reduced zone scheme looks at only 1 BZ like 1st.

Extended BZone scheme



part of each zone ~~write~~ sketched, looks like parabola.

eg Sodium valence electrons in State 3

Unit 3: Semiconductors

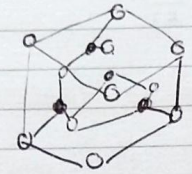
lecture 1

Semiconductor examples

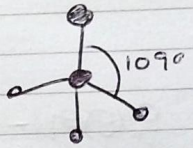
Silicon, Germanium, Gallium Arsenide, InSb, InP

Compounds are usually trivalent bonded w/ pentavalent or divalent - hexavalent (ZnS, CdS, PbTe)

Many of these have similar crystal structure as diamond. Such as Si, Ge, GaAs Face centred, basis of 2 [0,0,0] and [¼, ¼, ¼]

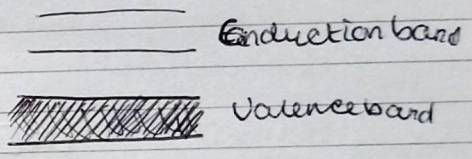


Diamond has strong 4 bonds.



This gives rise to F.C.C.

Nomenclature

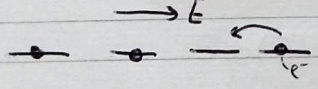


E_c - lowest E in Conduction band

E_v highest E in valence band

when electrons go up to C band, there's vacancies in valence band or "holes".

In applied fields, it acts as a positive charge +e.



force on electrons in opposite direction to E.

Both bands contribute to conduction. we need:

$n_c(T)$ electron concentration in CB

$P_v(T)$ hole concentration in VB.

To get these, use $P(E)$ and $D(E)dE$.

electrons volume

$$n_c(T) = \int_{E_c}^{\infty} P(E)\,N(E)\,dE \qquad n(E)dE = P(E)\,D(E)\,dE$$

$$P(E) = \frac{1}{1 + e^{\left(\frac{E-E_F}{kT}\right)}} \qquad E_v < E_F < E_c$$

$$D(E) = A(E-E_c)^{1/2}$$

$$A = \frac{\sqrt{2m_e^{*3}}}{\pi^2\hbar^3}$$

If we say D(E) is free electron like near band edge

m_e^* - effective mass of electron.

Derivation for $n_c(T)$ is on slides.

effective density of states.

$$n_c = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{\frac{-E_c-E_F}{kT}} = N_c e^{\frac{-E_c-E_F}{kT}}$$

Now for $P_v(T)$

$$P_e(E) + P_h(E) = 1$$

↑ finding electron in v

↑ finding hole in v

$$P_h(E) = 1 - \frac{1}{1+e^{\left(\frac{E-E_F}{kT}\right)}} = \frac{1}{1+e^{\left(\frac{E_F-E}{kT}\right)}}$$

$$D(E) = \frac{\sqrt{2m_h^{*3}}}{\pi^2\hbar^3}(E_v-E)^{1/2}$$

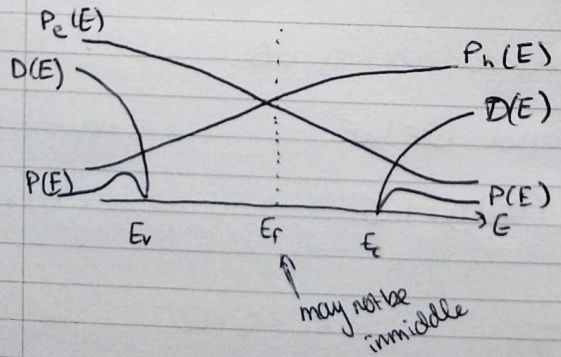
m_h^* effective hole mass

$$D(E) = B(E_v-E)^{1/2}$$

So now

$$P_v(T) = \int_{-\infty}^{E_v} P_h(E)\, D(E)\, dE$$

$$P_v = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{\frac{-E_F-E_v}{kT}}$$



Symmetrical!

Lecture 2

Hence: $n_c p_v = N_c N_v e^{-\frac{E_g}{kT}}$ E_g = gap energy

Law of mass action True for all Semiconductors

The only assumptions are $E_c - E_F >> kT$ $E_F - E_v >> kT$

$n_c p_v$ is constant at given T.

Intrinsic & Extrinsic Semi Conductors

Intrinsic

No impurities. "Pure".
An electron in Conduction band, only place they could have come from is valence band.
Due to Thermal excitation

Hence: $n_c = p_v = n_i$ ← intrinsic carrier Concentration

Where:

$n_c p_v = n_i^2$

$n_i = \sqrt{N_c N_v}\, e^{-E_g/2kT}$

$N_c = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2}$

N_v = same but swap m_e^* for m_h^*

$$n_i = 2 (m_e^* m_h^*)^{3/4} \left(\frac{kT}{2\pi\hbar^2}\right)^{3/2} e^{-E_g/2kT}$$

$\sqrt{N_c N_v}$ is effective D(E) at band edge.

eg Ge has larger intrinsic charge carrier concentration than Si.
↑ $E_g = (0.67)$ $E_g = 1.14$ ↗
So smaller gap => larger Carrier conc.

back to $n_c = p_v$

$$n_c = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2} e^{-\frac{E_c - E_F}{kT}} \qquad p_v = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2} e^{-\left(\frac{E_F - E}{kT}\right)}$$

equate them:

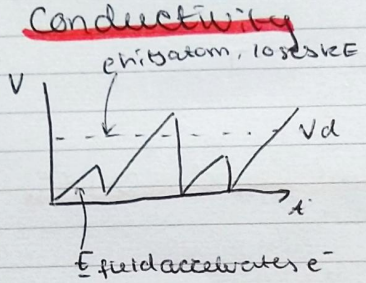
$$E_F = \frac{(E_c + E_v)}{2} + \frac{3}{4} kT \ln\left(\frac{m_h^*}{m_e^*}\right)$$

at $T = 0$ E_F in middle of gap

E_F rises as T rises because $m_h^* > m_e^*$ usually.

This is so small, it's almost negligible.

Conductivity



Gives rise to current density:

$$J = nv_d e$$

Carrier mobility:

$$\mu = \left|\frac{v_d}{E}\right|$$

$$\mu = \frac{e\tau}{m}$$ τ = mean collision time.

Hence $$\frac{e|E|\tau}{m} = v_d$$

Now introduce Ohm's law: $J = \sigma E$

$$\sigma = ne\mu \quad \text{or} \quad J = ne\mu E$$

Hence $$\sigma = n_c e \mu_e + p_v e \mu_h$$

Typical values:

	μ_e	μ_h
Ge	0.45	0.35
Si	0.15	0.05
InSb	7.7	0.075

$\mu_e > \mu_h$

↙ wow

Since $n_i = n_c = p$

$$\sigma = n_i e(\mu_e + \mu_h)$$

↓

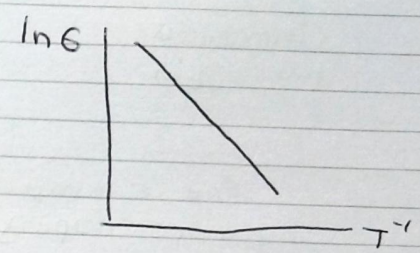
$$\sigma = 2e(\mu_e + \mu_h)(m_e^* m_h^*)^{3/4} \left(\frac{kT}{2\pi\hbar}\right)^{3/2} e^{\left(-E_g/2kT\right)}$$

mobilities depend on temperature. $\mu \propto T^{-3/2}$

So we can approximate: $\sigma \propto e^{-E_g/2kT}$

So if we plot it:

Gradient $-E_g/2k$



How to Produce Intrinsic Semiconductors

example: roomtemp Int Si. intrinsic charge carrier conc^n = ? $\{n_i$

$$n_i = 2(m_e^* m_h^*)^{3/4}\left(\frac{kT}{2\pi\hbar^2}\right)^{3/2} e^{-E_g/2kT}$$

$E_g = 1.1$ eV

$m_e^* = 0.25 m_e$

$m_h^* = 0.5 m_e$

$T = 290$K

} sub into to get $n_i = 7\times10^{14}\ m^{-3}$ yay!

To compare:

$\rho_{Si} = 2330\ kg\,m^{-3}$ $M_r = 28$

$$N_{Si} = \frac{\rho}{28\times10^{-3}} \times N_a = 5\times10^{28}\ m^{-3}$$

So actually there's few charge carriers compared to atoms.

So for pure Si, you'd need less than 1 part per 10^4 impurities.

Germanium's better ~~worse~~ at around 10^9

To do this, use zone refining.

Circular heater => melts small sample => moves impurities along with heater.

Lecture 3

Extrinsic Semiconductors.

Eccample roomtemp. conductivity for int Si?

$$\sigma = n_e e\mu_e + p_v e\mu_h$$

$E_g = 1.1$ eV
$m_e^* = 0.25 m_e$
$m_h^* = 0.5\ m_e$
$\mu_e = 0.15$
$\mu_h = 0.05$

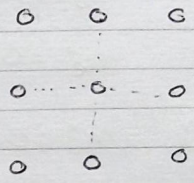
Germanium
$\sigma \sim 1\ \Omega^{-1}m^{-1}$

But σ is much higher sometimes? This is because of impurities - doping - or called n-type or p type

Group V impurities (eg P, As) w/ 5 valence electrons per atom
Group IV has 4 (silicon, Germanium)
Group III has 3 (Al, B)

How does this look?

Silicon has 4 nearest neighbours:

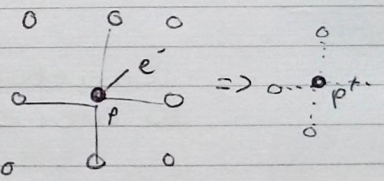


Strong covalent bonds.

Doping with Group V impurity like P:

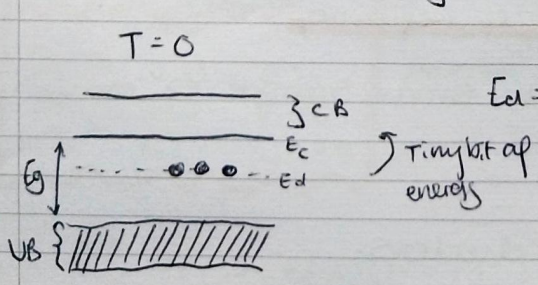
P has 5 electrons to bond with, so

4 bond but 1 is unpaired and weakly bound to P



A little bit of energy will break the electron free. Leaves ionised P and a donor electron.

Represent it on an Energy level diagram



E_d = donor e^- level

$E_c - E_d = 0.01$ to 0.1 roughly

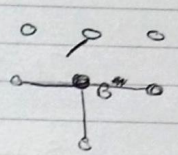
for room temp.

At room temp most donor electrons are in CB.
Typical level of doping is 1 part pm

This type of semiconductor is n-type

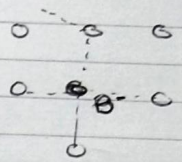
Another example: Boron (III) in Si (IV)

All 3 bonds w/ silicon, but there's one electron not paired.

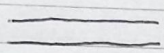


The broken bond is shared w/ all 4 Si atoms

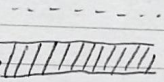
B can capture an Si-Si e^- leaves a negative B and broken Si-Si hole



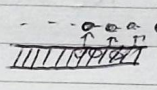
So B has donated a hole.



B introduces Ea (a = accepted)



=>

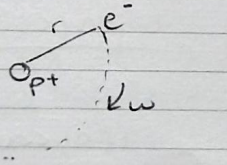


$E_a - E_v$ very small.

This type of doped crystal is p-type.

Quasi-Bohr Model for Donor Impurities.

for n-type. eg phosphorus - silicon.



$$m_e^* r \omega^2 = \frac{e^2}{4\pi\varepsilon\varepsilon_0 r^2}$$

Coulomb's law for weakly bound unpaired electron

$$m_e^* r^2 \omega = n\hbar$$

Hence:

$$r = \frac{4\pi\varepsilon\varepsilon_0 n^2\hbar^2}{e^2 m_e^*} \qquad \omega = \frac{e^4 m_e^*}{(4\pi\varepsilon\varepsilon_0)^2 n^3\hbar^3}$$

$$KE = \frac{1}{2} m_e^* (r\omega^2) = \frac{e^4 m_e^*}{2(4\pi\varepsilon\varepsilon_0)^2 n^4\hbar^2}$$

$$PE = \frac{-e^2}{4\pi\varepsilon\varepsilon_0 r} = \frac{e^4 m_e^*}{(4\pi\varepsilon\varepsilon_0)^2 n^2\hbar^2}$$