SOLID STATE PHYSICS (SSP) – PHY-550

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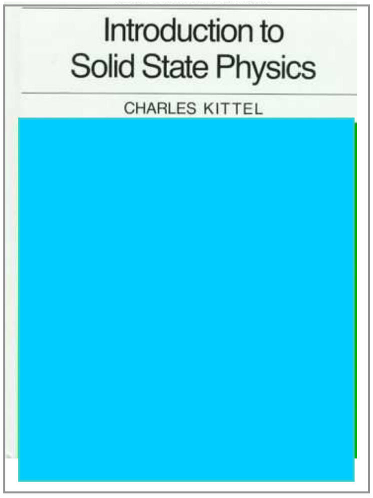
Notes will cover:

- **Crystallography**
- **Electron motion in periodic structures: free electron model**
- **Energy bands: nearly free electron model**
- **Tight binding model**
- **Electron transport in bands**
- **Semiconductors**
- **The pn junction**
- **Quantum wires**
- **Functional materials: fabrication methods**

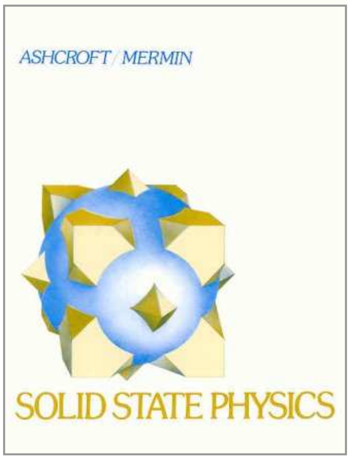
BOOKS

SSP will closely follow:



Kittel, C.
Introduction to Solid State Physics
Wiley, (8th edition, 2005)
ISBN 0-471-41526-X

This book is more advanced but still very useful for SSP:



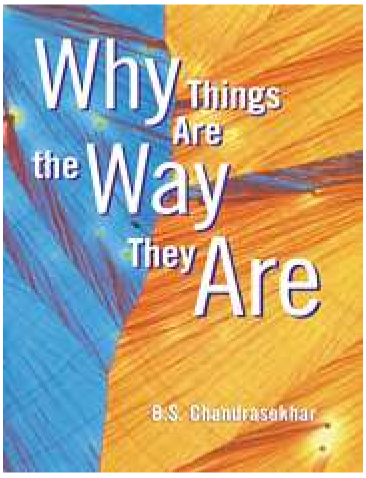
Ashcroft, N.W., Mermin, N.D.
Solid State Physics
Holt-Saunders, (international edition, 1976)
ISBN 0-03-049346-3

OTHER USEFUL BOOKS

Solymar, L., Walsh, D.
Electrical Properties of Materials
Oxford University Press, (7th edition, 2004)
ISBN-13: 978-0-19-926793-4

Singleton, J.
Band Theory and Electronic Properties of Solids
Oxford University Press, (7th edition, 2004)
ISBN 0-19-850644-9

This book is for a general readership, contains little maths!



B.S. Chandrasekar
Why Things Are The Way They Are
Cambridge University Press
ISBN-13: 978-0-52-145660-6

COURSE DETAILS

• Lectures

See timetable

• Home Page

Exercises and solutions posted on the SSP Home Page (www.ph.qmul.ac.uk →Student Handbook →Index to BSc courses→SSP→Home Page)

• Exercises

9 in total
Handed out on Thursdays
Hand in by 16:00 on the following Tuesday
Minimum of 75% hand-in rate expected
Scripts returned and solutions discussed in Tuesday 11:00-12:00 lecture
Solutions posted on SSP Home Page
20% of total mark for SSP

• Exam

2.5 hour exam
We will do exam-level worked examples together
Past exam papers available from library and some examples are available online.

Learning Aims and Objectives
Upon completion of SSP the student will be able to:

Define: Crystal lattice, lattice vector, primitive cell, unit cell

Define Bravais lattice and be familiar with common examples in 2D and 3D

Assign Miller indices to crystal planes

Use the concept of Reciprocal lattice and be familiar with the probes of crystal structure

Derive an expression for electron density using the free electron Fermi gas model

Be familiar with the Fermi-Dirac distribution, its temperature variation, and the concept of Fermi energy

Understand the concept of degeneracy

Calculate the electronic contribution to heat capacity using the free electron Fermi gas model

Be familiar with the concept of reciprocal space (or k-space) and thus be able to derive the Drude expression for electrical conductivity

Explain the origin of energy bands in crystals and explain what is meant by the Brillouin zone

Express the Bloch theorem and use the concepts for related calculations

Define: metal, semiconductor, and insulator in terms of band structure and energy gaps

Plot the temperature variation of electrical conductivity for metals, semiconductors, and insulators

Explain the significance of the dispersion relation

Derive expressions for electron velocity and effective mass in a crystal structure

Define intrinsic and extrinsic semiconductor

Explain how n- and p-type dopants work

Phenomenologically describe the operation of a pn junction

Describe molecular beam epitaxy and metal organic chemical vapour deposition

Describe the quantum well and the quantum wire

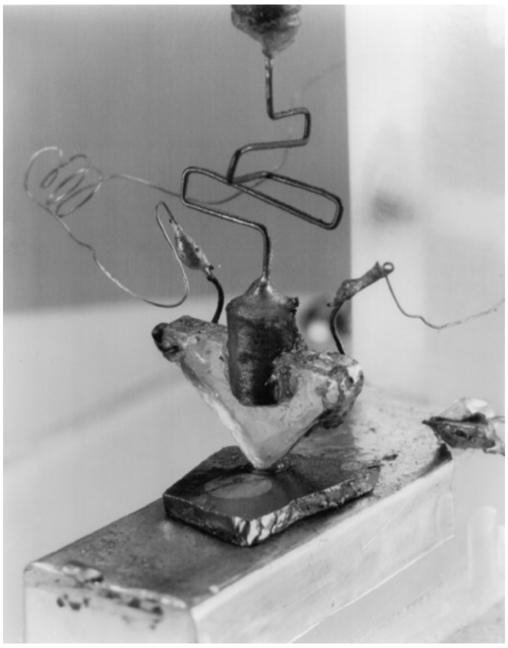
1. INTRODUCTION

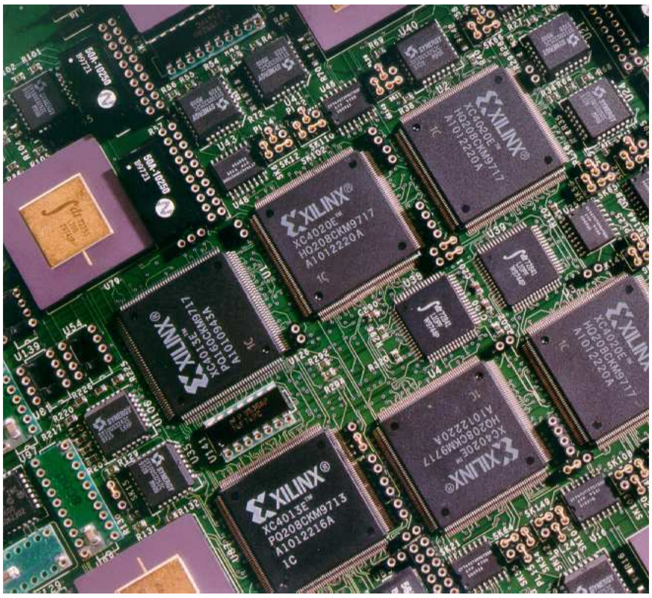
• 50% of all Physics world-wide is **SOLID STATE** ≈ **CONDENSED MATTER**

• SSP borders on:

Atomic & Molecular Physics
Chemistry
Materials Science
Mechanical Engineering
Electronic Engineering
Biology
Nanotechnology

• Microelectronics: SSP's greatest achievement in C20 physics





2006 microprocessor: 10M transistors/ cm^3

First Germanium transistor 1947

C21 will see SSP contributions to: genomics, proteomics, nanotechnology……

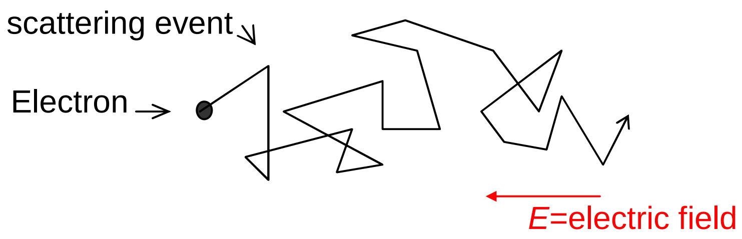
KEY CONCEPTS

- Order
- Dimensionality
- Scale

Example: electron motion in solids

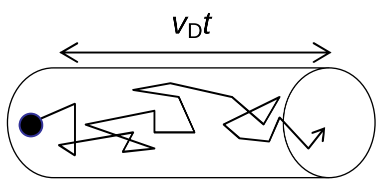
Consider the real-space motion of a free electron in an electric field inside infinate solids in 3D,2D, and 1D

3D: electron gas with net motion in opposite diection to applied electric field



There are two components of velocity: the drift velocity $v_D = \mu E$, and the thermal velocity $v_{thermal}$

μ = mobility, drift velocity per unit electric field
<l>= mean free path



Current = rate of flow of electrical charge through cross-section
$I = n$(cross-section area) $v_D e$ or
Current density, $j = n v_D e$

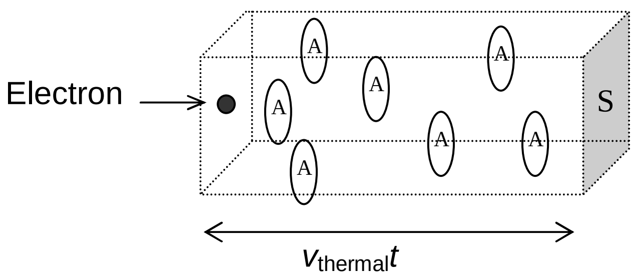
n=electron density

For Cu, $n \approx 10^{22}$ cm^{-3}and a typical current density is $j \approx 10^5$ Acm^{-2}, so $v_D \approx 1$ ms^{-1}

At room temperature, the kinetic energy of the electron, K.E.=$m v_{thermal}^2/2 \approx k_B T$ =25 meV, so

$v_{thermal} \approx 10^5$ ms^{-1}

Therefore use $v_{thermal}$ when considering scattering probability.



In time t, an electron travels in a zig-zag path of total length $v_{\text{thermal}}t$. Consider the lattice moving relative to the electron with velocity v_{thermal}. If the concentration of scatterers is N_s and the effective scattering cross section is A, the number of scatterers in an arbitrary 'box' of length $v_{\text{thermal}}t$ and cross-section S is $N_s\ v_{\text{thermal}}t\ S$, and the probability of a 'collision' between an electron and a scatterer

$$p_{\text{scatt}} = N_s v_{\text{thermal}} tS(A/S) = N_s v_{\text{thermal}} t.A$$

i.e $\quad p_{\text{scatt}} \propto v_{\text{thermal}} A$

or $\quad p_{\text{scatt}} \propto v_{\text{thermal}} r_s^2$

where $A=\pi r_s^2$, r_s is the effective radius of the scatterer.

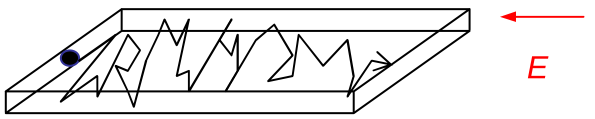
Scattering is the source of electrical resistance (transfer of momentum from the electron to the solid)

Scatterer can be:

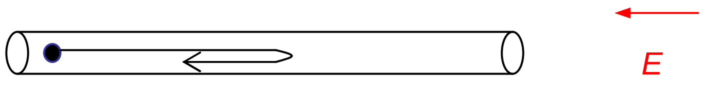
Defect
Impurity
Lattice vibration (phonon)

$\Rightarrow$ Ordering of atoms in solid is important

2D: similar to 3D except there is no vertical component of velocity, current confined to a sheet of charge (sometimes called 2DEG=2D electron gas)

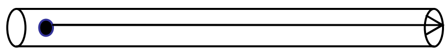


1D: very different from 2D and 3D since electron can only be scattered in the reverse direction



$\Rightarrow$ Dimensionality of solid is important

Nanoscale: 1 nm (nanometer) =10 Å (Angstrom)=10^{-9}m ≈ dimensions of about 10 atoms. Dimensions of solid < electron mean free path



No scattering!! Have ballistic conduction (or quantum wire). Completely different physics to description of macroscopic wire

⇒ Scale of solid is important

STANDARD INTEGRALS

$$\int_{-\infty}^{\infty} y^2 e^{-ay^2}\,dy = \frac{1}{2a}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

$$\int_{0}^{\infty} y^{\frac{1}{2}} e^{-y}\,dy = \frac{1}{2}\sqrt{\pi}$$

$$\int_{-\infty}^{\infty} e^{-ay^2}\,dy = \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$$

ESSENTIAL QUANTUM MECHANICS

Classical particle: described by values of physical variables, e.g. mass, position, momentum, energy, electric dipole, etc.

Quantum mechanics: use concept of a **quantum state** to describe the possible states of a particle. Laws of quantum mechanics describe which states are physically realistic and specify the ways in which a particle moves from one state to another.

Quantum state: characterised by a unique set of quantum numbers that 'index' the state. NB We can describe a quantum state even when there is nothing in it! The quantum state may have a velocity so can describe *state of motion*

Quantum numbers: sometimes quantum numbers have continuously variable values, but commonly are restricted to a set of discrete values

Quantum states and energy levels: quantum states with the same energy that belong to the same energy levels are said to be *degenerate*

The wavefunction $\psi(\mathbf{r},t)$: each quantum state has associated with it a wave function $\psi(\mathbf{r}, t)$. The wavefunction is complex, i.e. it has real ψ_{real} and imaginary parts $\psi_{\text{imaginary}}$.

The probability of finding a particle in a region of space of volume d**r** around a position **r** is given by

$$P(\mathbf{r})\mathrm{d}\mathbf{r} = |\psi(\mathbf{r})|^2 \; \mathrm{d}\mathbf{r}$$
$$= \psi^*(\mathbf{r})\psi(\mathbf{r})\mathrm{d}\mathbf{r}$$
$$= \left(\psi^2{}_{\text{real}} + \psi^2{}_{\text{imaginary}}\right)\mathrm{d}\mathbf{r}$$

$\psi^*(\mathbf{r},t)$= complex conjugate of $\psi(\mathbf{r},t)$

Since the particle must be somewhere therefore:

$$\int_{\substack{\text{All}\\\text{space}}} P(\mathbf{r})\mathrm{d}\mathbf{r} = \int_{\substack{\text{All}\\\text{space}}} |\psi(\mathbf{r})|^2 \mathrm{d}\mathbf{r} = 1$$

This is called the normalisation condition.

The Schrödinger equation:

Time-independent Schrödinger equation (TISE)**:** determines the form of the wave functions that correspond to particular allowed quantum states.

Time-dependent Schrödinger equation (TDSE): governs how a wavefunction evolves with time.

SSP will only deal with the TISE:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

The TISE in one dimension:

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

$V(\mathbf{r})$=function describing how the potential energy of a particle varies with position

m=mass of the particle under discussion

$\partial^2\psi(x)/\partial x^2$=is the second derivative of the wavefunction (colloquially know as its *curvature*)

ε=total energy of the particle under discussion

EXAMPLES

1. The free particle

For a particle in free space the potential energy is zero (V(**r**)=0) and independent of position therefore the 1D TISE becomes:

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

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

Solution: $\boxed{\psi(x) = e^{ikx}}$

In 3D: $\psi(x) = e^{ik.r}$

Where the **wavevector** k is related to the **wavelength** λ by $k=2\pi/\lambda$

Here we have used the normalisation condition:

$$\int |\psi(\mathbf{r})|^2 dr = 1$$

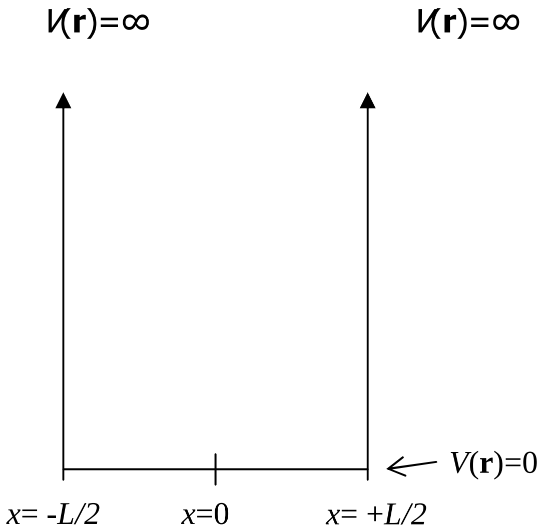
The *de Broglie* hypothesis: $\boxed{p = \frac{h}{\lambda}}$

$$\Rightarrow \quad p=mv=\hbar k$$

Also: Kinetic Energy (KE): $KE = \frac{1}{2}mv^2 = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$

In the case of a free electron all of the total energy is KE since V(**r**)=0

2. The square well



The infinite 1D potential well:

1. The wavefunctions satisfy the TISE

2. At the edges of the potential well the wavefunction is zero where the potential energy is very large

3. In the central region of the potential well, the potential energy term $V(\mathbf{r})$ is zero – this is equivalent to a small part of free space so the solution to the TISE will be similar to that for free space

4. Unlike the case of a free particle, the wavelength is restricted to just a few special values that cause the wavefunction to be zero at the edges of the potential well. The wavefunctions that satisfy this condition are known as *eigenfunctions*

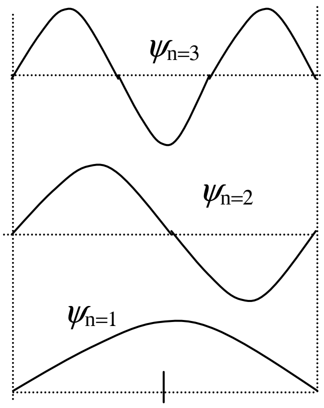
5. By virtue of the De Broglie hypothesis, the wavelength is restricted to special values. Consequently the momentum and energy of the particles trapped in the potential well are also restricted to a few special values known as *eigenvalues.*

The wavelengths are restricted to the set of values:

$$\lambda = 2L, L, \frac{2}{3}L, \frac{1}{2}L, \frac{2}{5}L ... \frac{2L}{n}$$

Where *n* is an integer (1,2,3…but not zero).

Diagrammatically:



x= -*L/2*　　　*x*=0　　　*x*= +*L/2*

In 3D: can construct a potential box of length *L* and volume $V=L^3$

The solution to the TISE with the normalisation condition applied is:

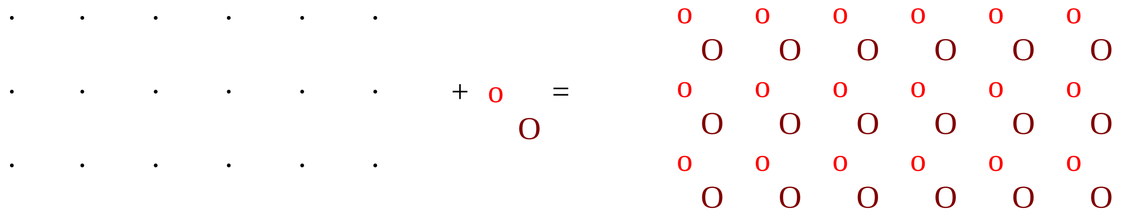
$$\psi(\boldsymbol{r}) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}.\boldsymbol{r}} \quad \text{so energy} \quad \varepsilon(\boldsymbol{k}) = \frac{\hbar^2 k^2}{2m}$$

2. CRYSTALLOGRAPHY

We will start SSP by looking at the structure of crystals

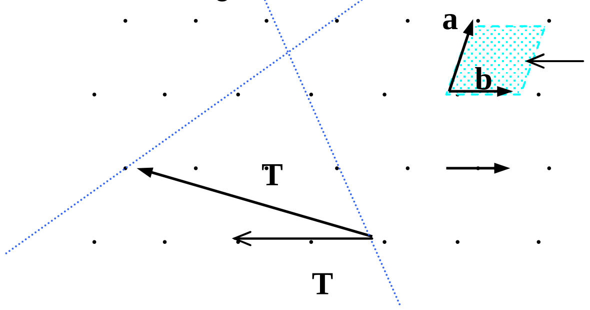
Crystal structure = lattice + basis (atom or group of atoms)

2D simple cubic lattice Basis



2D Lattice points connected by **lattice vector T**=u**a**+v**b** (**a,b** are **primitive vectors**)

2D Hexagonal lattice



2D Primitive cell

Crystal planes

Any physical property of the crystal is invariant under **T**

Lattice: arrangement of points in space such that the environment of any point is identical to that of any other point

Lattice vector: any vector joining two lattice points

Primitive vector: set of the shortest linearly independent lattice vectors

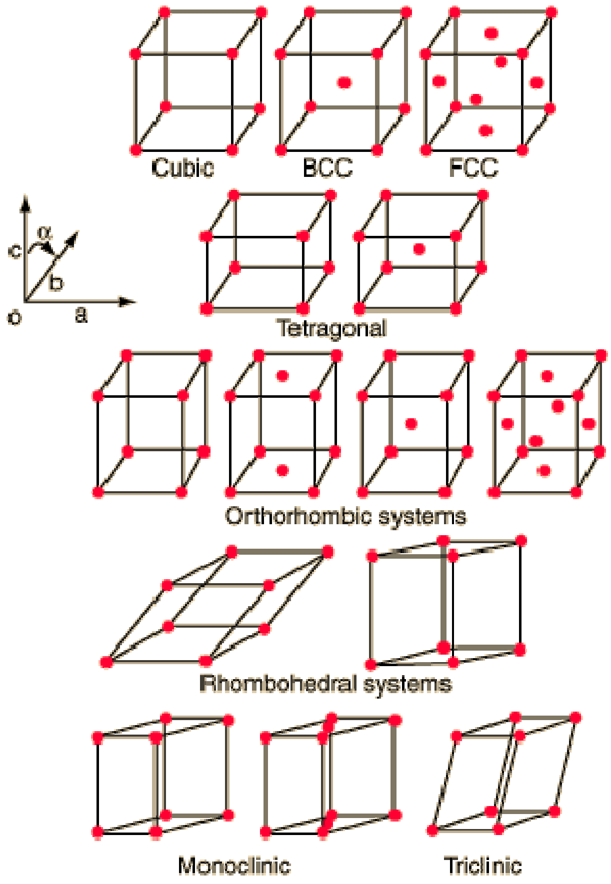
Lattice parameter: length of primitive vectors, a=|**a**|, etc.

Primitive cell: a volume (area in 2D) bounded by the primitive vectors which, when repeated by being translated by lattice vectors will fill all space (NB *translation* only, not rotation or change of shape).

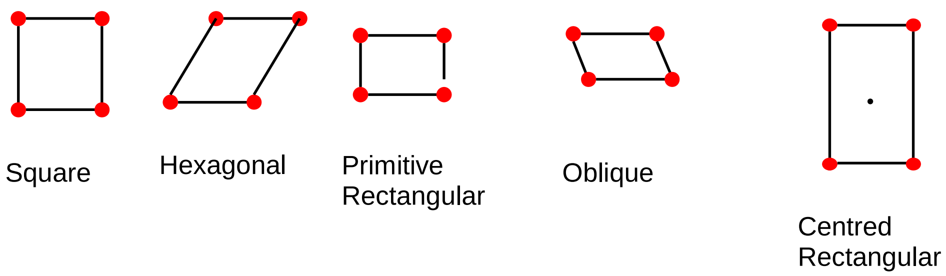
Unit cell: a volume (area in 2D) bounded by lattice vectors which, when repeated by being translated by lattice vectors will fill all space (NB could be any size)

Bravais lattice : invariant under rotation and reflection

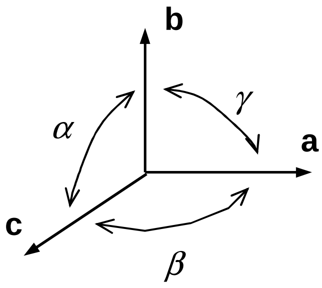
3D has 14 Bravais lattices:



2D has 5 Bravais lattices



14 Lattice types in 3D



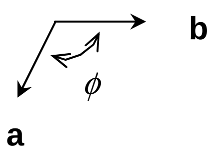
Rhombohedral

Lattice	Types	Conditions
Cubic	3	a=b=c $\alpha=\beta=\gamma=90°$
Trigonal	1	a=b=c $\alpha=\beta=\gamma<120°, \neq 90°$
Hexagonal	1	a=b≠c $\alpha=\beta=90°$ $\gamma=120°$
Triclinic	1	a≠b≠c $\alpha\neq\beta\neq\gamma$
Monoclinic	2	a≠b≠c $\alpha=\gamma=90°\neq\beta$
Orthorhombic	4	a≠b≠c $\alpha=\beta=\gamma=90°$
Tetrahedral (Tetragonal)	2	a=b≠c $\alpha=\beta=\gamma=90°$

No need to learn all of this detail except for cubic and basic ideal of hexagonal

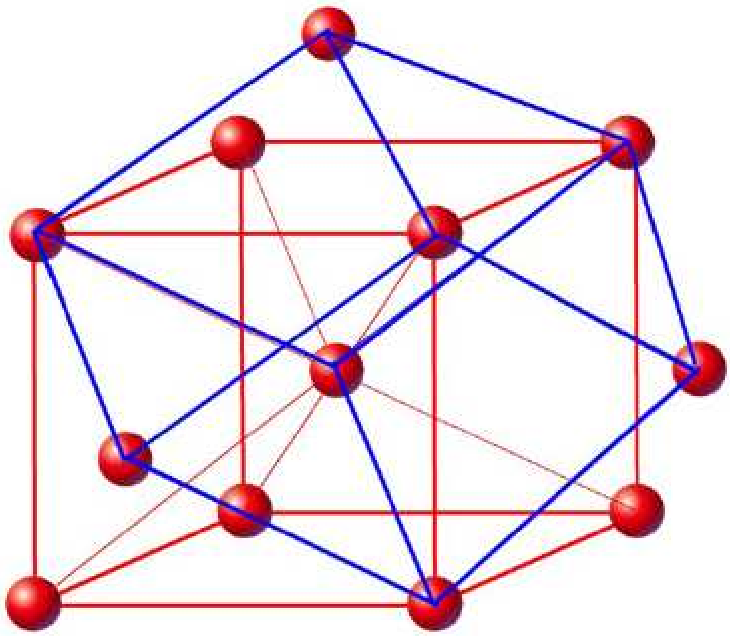
Types of cubic lattice: simple cubic (SC), body-centred cubic (BCC), face-centred cubic (FCC) e.g NaCl

5 Lattice types in 2D

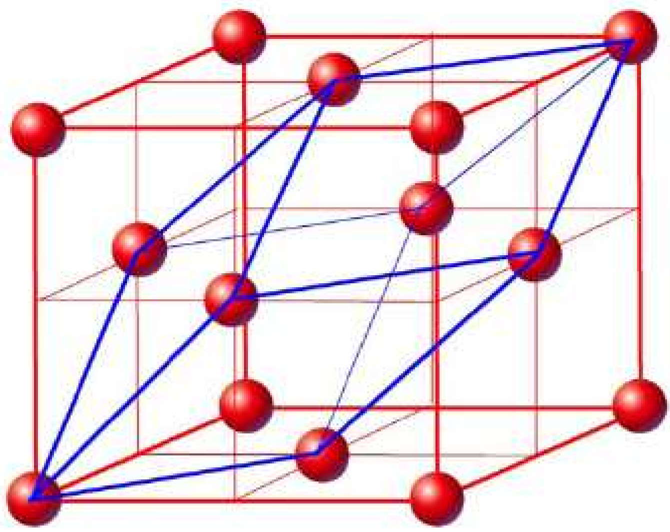


Lattice	Types	Conditions
Square	1	a=b, $\phi=90°$
Oblique	1	a≠b, $\phi\neq 90°$
Hexagonal	1	a=b $\phi=120°$
Primitive Rectangular	1	a≠b, $\phi\neq 90°$
Centred Rectangular	1	a≠b, $\phi=90°$

PRIMATIVE CELLS



Rhobohedral primitive cell of bcc system.

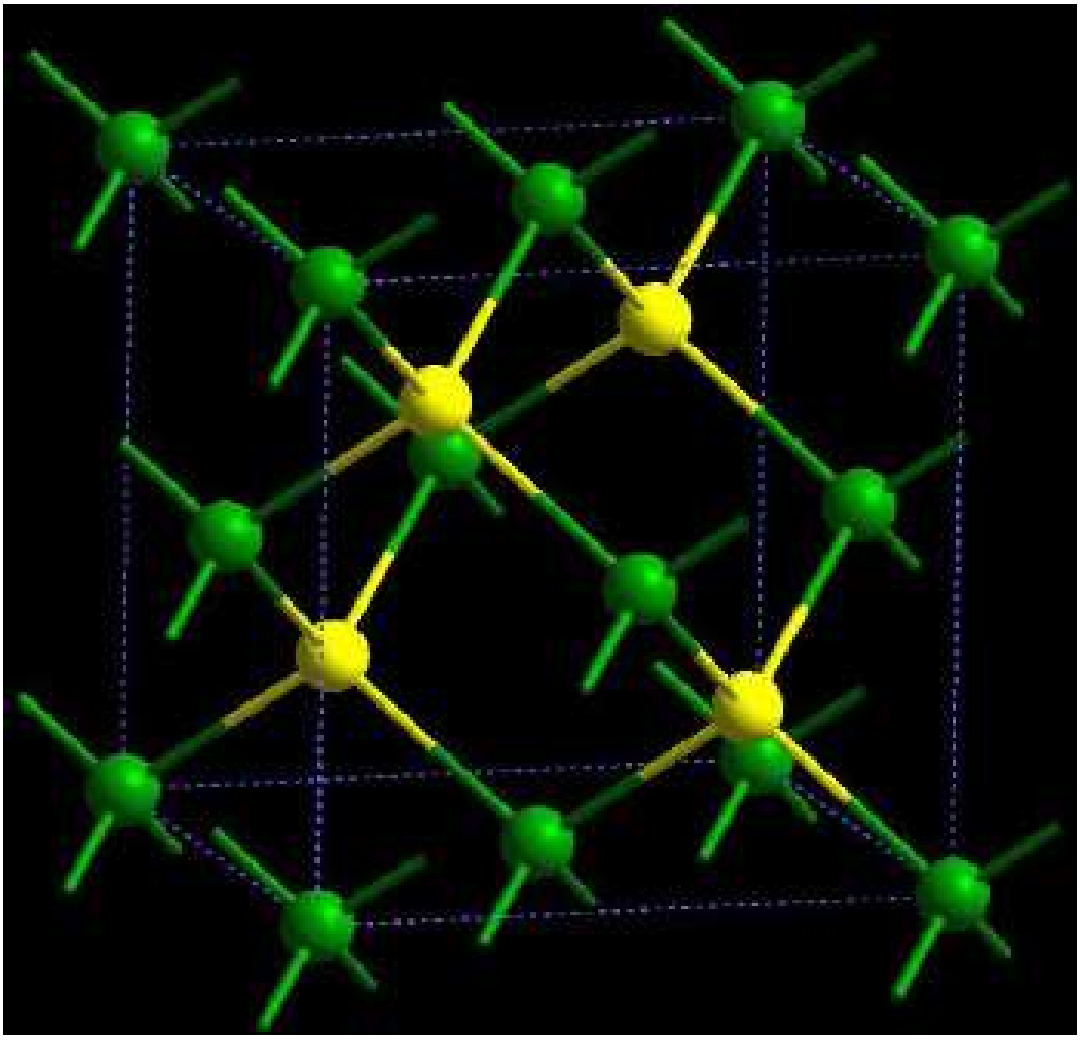


Rhobohedral primitive cell of fcc system.

In SSP we will use non-primitive, conventional unit cells.

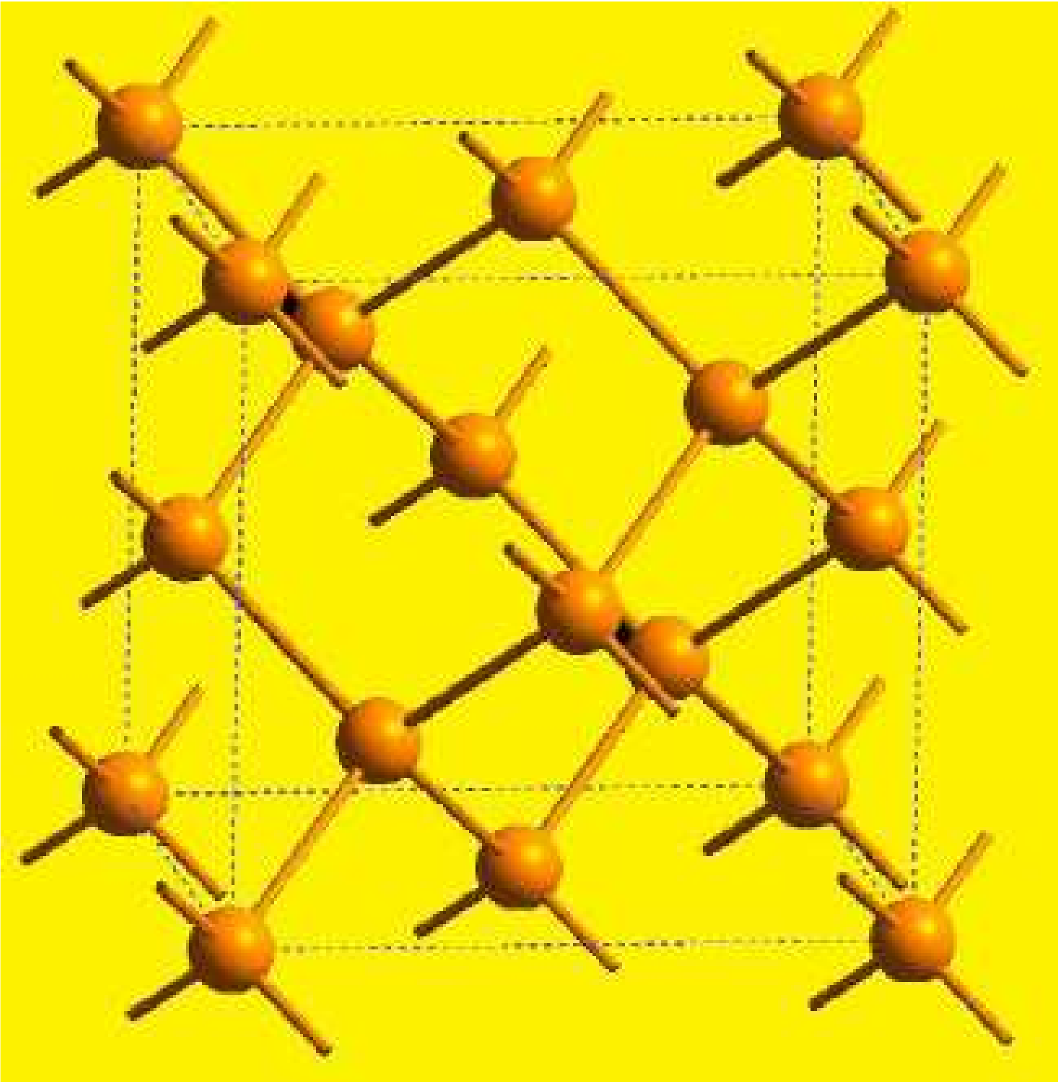
LATTICES WITH NON-MONOTONIC BASIS

GaAs



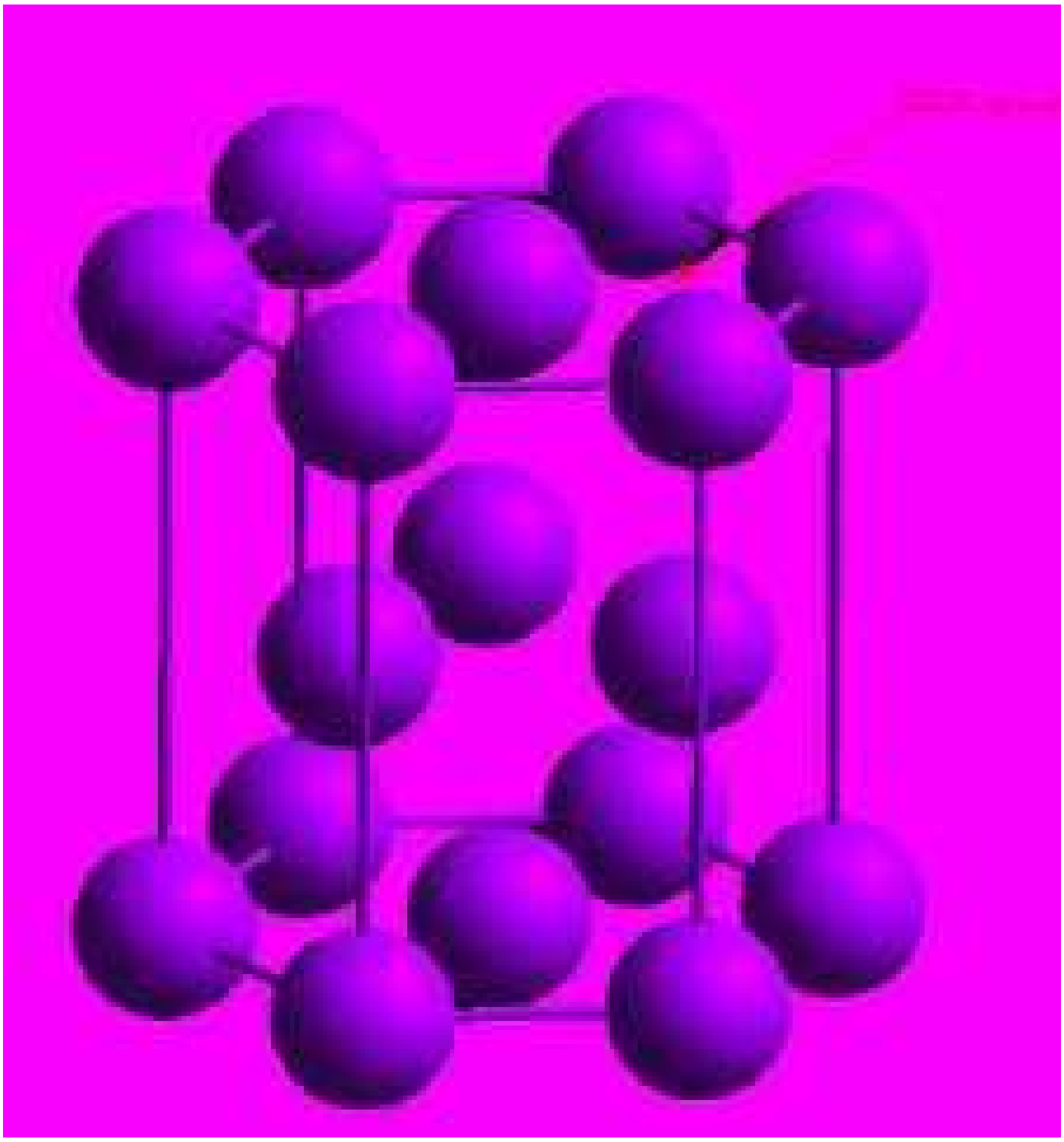
FCC with basis of Ga at (0,0,0) and As at ¼**a**+¼**b**+¼**c**

Diamond or Silicon



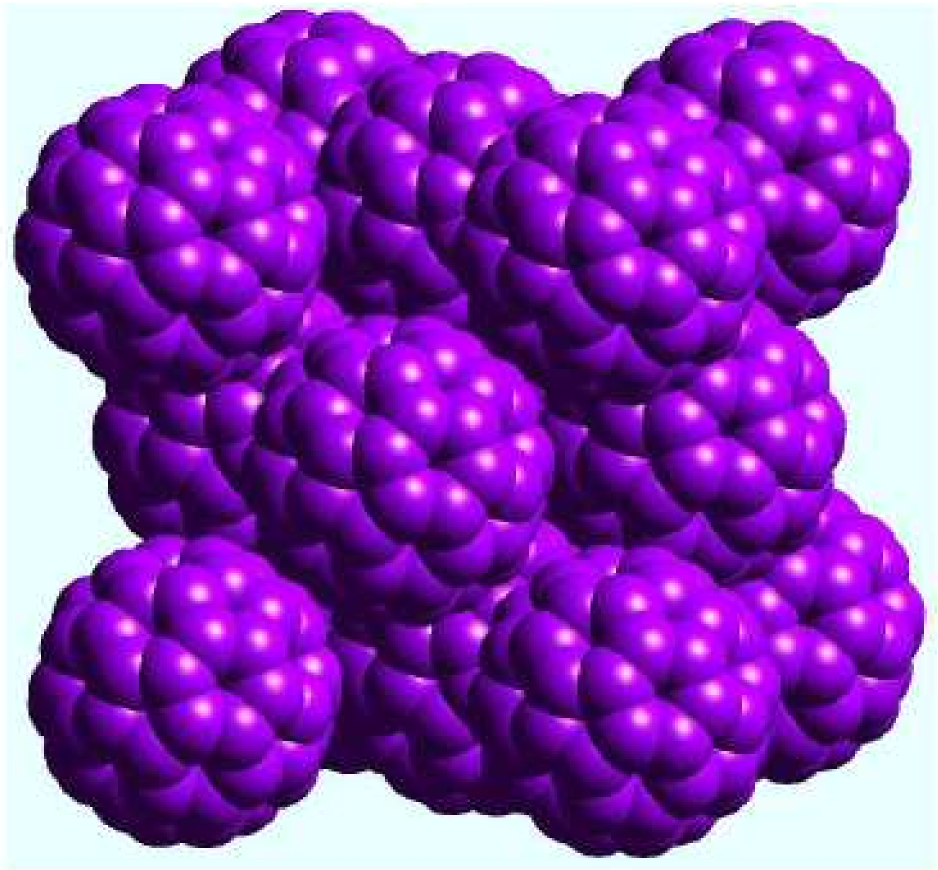
FCC with basis of Si at (0,0,0) and *inequivalent* Si at $\frac{1}{4}\mathbf{a}+\frac{1}{4}\mathbf{b}+\frac{1}{4}\mathbf{c}$

Hexagonal close packing

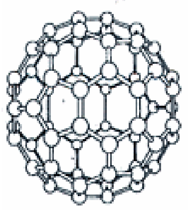


Hexagonal, basis of one atom at (0,0,0) and one at 2/3**a**+1/3**b**+1/2**c**

Buckminsterfullerene



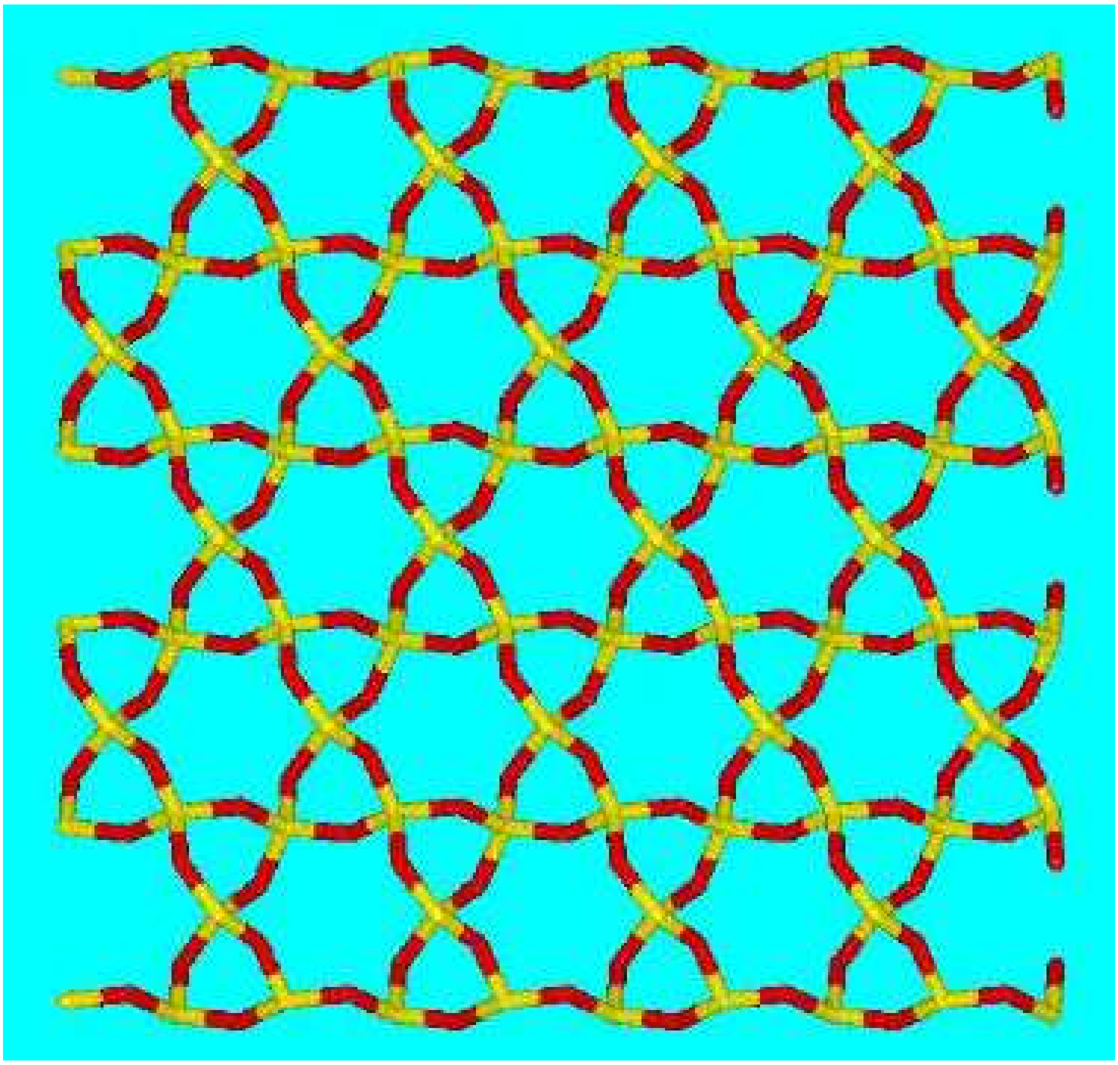
FCC with basis of one C_{60} molecule at (0,0,0). The orientation of each C_{60} molecule can be different.



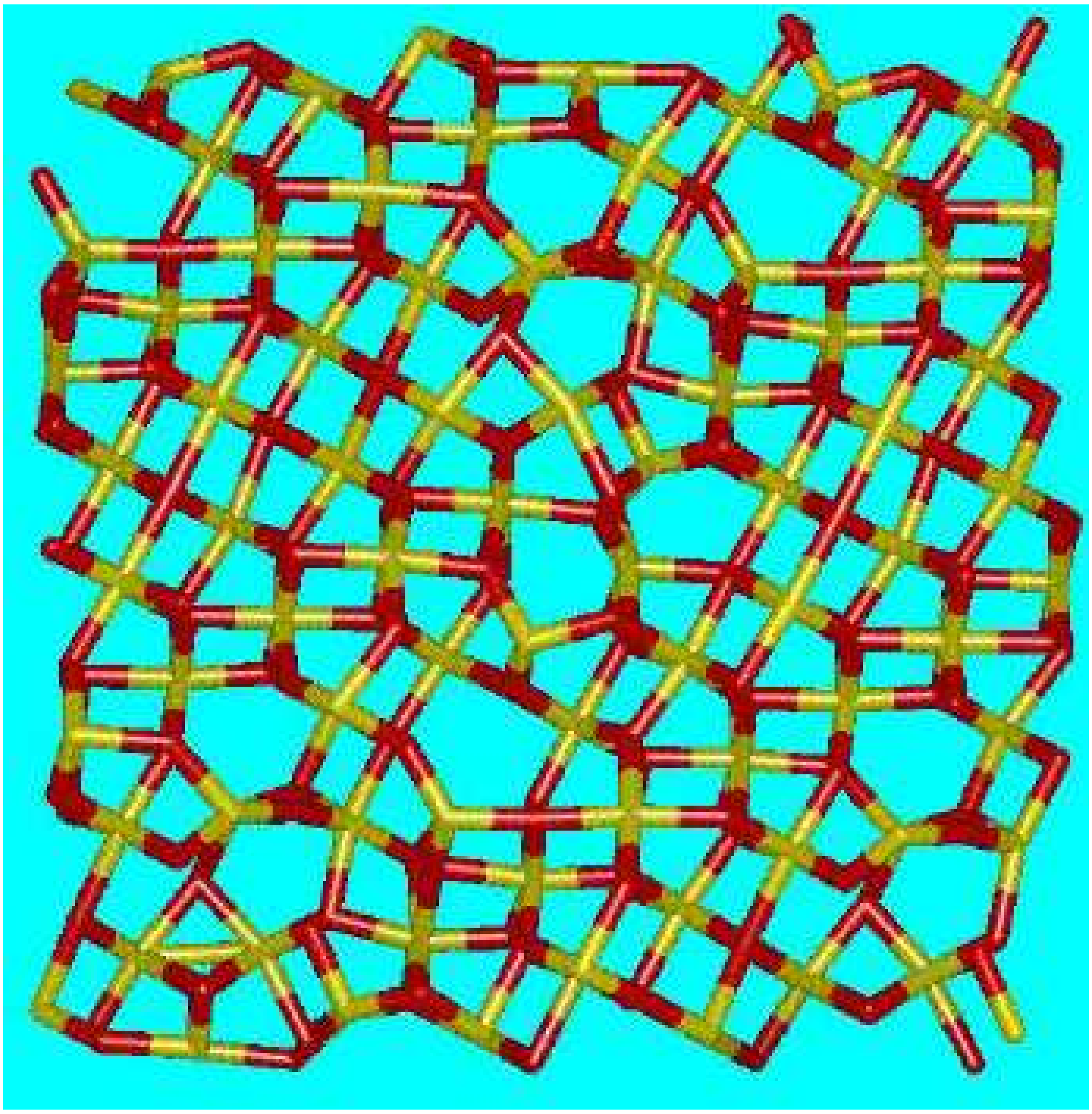
C_{60} molecule

AMORPHOUS SOLIDS

Not all solids are crystalline. If a crystalline material is represented by…



…then the equivalent amorphous structure would be:

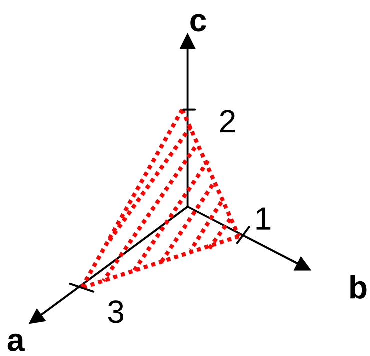


The **local** structure is similar to that of the crystal but there is no **long-range** order.

Crystal planes: defined by **Miller indices**

To index a plane,
1) find where the plane cuts the axes
2) express the intercept as u*a*, v*b*, w*c*
3) reduce the *reciprocals* to the simplest set of integers *h*,*k*,*l*
4) the plane is then the (*h*,*k*,*l*) (**note convention: round brackets**)
5) conventionally, choose *h*,*k*, and *l* with common factors removed
6) if the intercept is at infinity, corresponding index is 0
7) negative values are quoted with bar over

Example



Intercepts**:** 3**a,** 1**b,** 2**c**
Reciprocal: 1/3, 1, 1/2
Miller indices: (2,6,3)

The indices (h,k,l) refer to a single plane or a set of parallel pales.

(100) planes are a set of planes perpendicular to the *x*-axis at a distance *a* apart
(200) planes are a set of planes perpendicular to the *x*-axis at a distance *a*/2 apart

Directions: Square bracket notation [*hkl*]

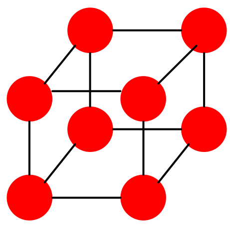
Spacing between planes in cubic lattice:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Length scale: typical interatomic distance ~ a few Ångstoms, say 0.25 nm

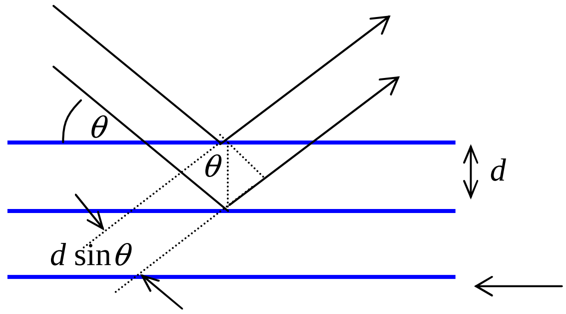
Cell volume: **|a.b**x**c|**

Lattice points per unit cell: e.g. simple cubic unit cell contains one lattice point (8 corner points shared among 8 cubes: 8 x 1/8 = 1)
Body-centred cubic: 2 points in unit cell (8 x 1/8 + 1)
Face-centred cubic: 4 points in unit cell (8 x 1/8 + 6 x 1/2)



SCATTERING OF WAVES BY A PERIODIC STRUCTURE

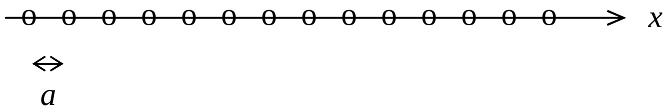
Specular, elastic scattering angle given by the Bragg law: $\boxed{2d\sin\theta = n\lambda}$



Crystal planes

Q. What about the intensity of the scattered wave?
A. Related to the <u>Fourier components</u> of electron density in the crystal planes

1D lattice,



$$n(x) = n_o + \sum [C_p \cos(2\pi px/a) + S_p \sin(2\pi px/a)] \ldots\ldots(1)$$

C_p and S_p are Fourier coefficients, $2\pi p/a$ ensures $n(x)$ is periodic in a

$$n(x+a) = n_o + \sum [C_p \cos(2\pi px/a + 2\pi p) + S_p \sin(2\pi px/a + 2\pi p)]$$

$$= n_o + \sum [C_p \cos(2\pi px/a) + S_p \sin(2\pi px/a)]$$

$$= n(x)$$

We say that $2\pi p/a$ is a reciprocal lattice point

Rewrite (1) $\quad n(x) = \sum_p n_p e^{i2\pi px/a} \quad$ p=integer including 0

I n 3D,

$n(\mathbf{r}) = \sum_G n_G e^{i\mathbf{G}.\mathbf{r}}$, where **G** is a set of reciprocal lattice vectors invariant under **T**

Many physical properties of the crystal are related to the Fourier components n_G, e.g. elastic X-ray scattering amplitude.

RECIPROCAL LATTICE VECTORS

Every crystal structure has **crystal lattice** and **reciprocal lattice**

Define:

$$\mathbf{A} = 2\pi \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}.\mathbf{b}\times\mathbf{c}} \qquad \mathbf{B} = 2\pi \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}.\mathbf{b}\times\mathbf{c}} \qquad \mathbf{C} = 2\pi \frac{\mathbf{a}\times\mathbf{b}}{\mathbf{a}.\mathbf{b}\times\mathbf{c}}$$

a,**b**,**c** = primitive vectors of **crystal lattice**
A,**B**,**C**=primitive vectors of **reciprocal lattice**

Crystal lattice vectors have dimension [length]
Reciprocal lattice vectors have dimension $[\text{length}]^{-1}$

A,**B**, and **C** are orthogonal to two primitive crystal lattice vectors:

$\mathbf{A}.\mathbf{a}=2\pi$	$\mathbf{B}.\mathbf{a}=0$	$\mathbf{C}.\mathbf{a}=0$
$\mathbf{A}.\mathbf{b}=0$	$\mathbf{B}.\mathbf{b}=2\pi$	$\mathbf{C}.\mathbf{b}=0$
$\mathbf{A}.\mathbf{c}=0$	$\mathbf{B}.\mathbf{c}=0$	$\mathbf{C}.\mathbf{c}=2\pi$

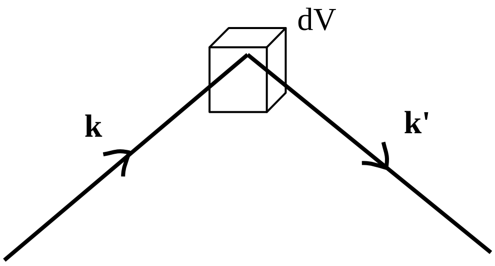
$\Rightarrow$ $\boxed{\mathbf{G}=h\mathbf{A}+k\mathbf{B}+l\mathbf{C} \quad (h,k,l) \text{ integers}}$

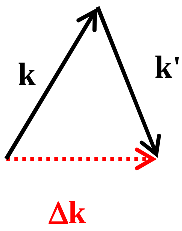
G=reciprocal lattice vector

Q. So what?
A. Reciprocal space useful for description of neutron, electron and X-ray scattering from crystal lattice

NB Kittel deals with Reciprocal lattice in much more detail but we will not go into any further detail

NEUTRON, ELECTRON, AND X-RAY SCATTERING FROM PERIODIC LATTICE





Elastic scattering of neutron, electron, X-ray from crystal volume dV

(Elastic means energy, $\cong\omega$, is conserved, $\Rightarrow$ ω=ck $\Rightarrow$ k=k')

Integrate $n(\mathbf{r})$ over all the crystal volume, find (see Kittel for proof)

$$\boxed{\Delta\mathbf{k}=\mathbf{G}}$$ **(Another statement of the Bragg condition)**

i.e. scattering amplitude is negligible when Δk differs from any reciprocal lattice vector

Neutrons: magnetic moment $\Rightarrow$ interacts with magnetic materials or nuclei of non-magnetic materials

$$\varepsilon=\frac{h^2}{2m_n\lambda^2},\quad m_n=1.67\times10^{-24}\text{ g}\quad\Rightarrow\quad\lambda=\frac{0.28}{E(\text{eV})^{1/2}}\ (\text{in Å})$$

Electrons: charged $\Rightarrow$ interact strongly with matter $\Rightarrow$ penetrate short distance

$$\varepsilon=\frac{h^2}{2m_e\lambda^2},\quad m_e=0.91\times10^{-27}\text{ g}\quad\Rightarrow\quad\lambda=\frac{12}{E(\text{eV})^{1/2}}\ (\text{in Å})$$

X-rays: nuclei do not scatter X-rays effectively $\Rightarrow$ X-ray photons ‘see’ only electrons

$$\varepsilon=hc/\lambda,\quad\Rightarrow\ \lambda=\frac{12.4}{E(\text{keV})}\ (\text{in Å})$$

3. ELECTRON MOTION IN PERIODIC STRUCTURES: FREE ELECTRON FERMI GAS

Free electron Fermi gas= gas of non-interacting electrons subject to Pauli principle

- **Weakly bound electrons move freely through metal**
- **Assume valence electrons →conduction electrons**
- **Neglect electron –ion core interaction**

Valence electron= immobile electron involved in the bonding
Conduction electron= mobile electron able to move within the solid

Good model for **metals**; can explain:

σ	Electrical conductivity
$\sigma(\omega)$	Optical properties
K	Thermal conductivity
C_v	Specific heat capacity

3D Schrödinger equation for free electron,

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_{\boldsymbol{k}}(\boldsymbol{r})=\varepsilon_{\boldsymbol{k}}\psi_{\boldsymbol{k}}(\boldsymbol{r})$$

Consider metal cube of side $L=V^{1/3}$

Periodic boundary conditions for box dimensions L

$$\psi(x,y,z+L)=\psi(x,y,z)$$
$$\psi(x,y+L,z)=\psi(x,y,z)$$
$$\psi(x+L,y,z)=\psi(x,y,z)$$

Solution: $\boxed{\psi_{\boldsymbol{k}}(\boldsymbol{r})=\frac{1}{\sqrt{V}}e^{i\boldsymbol{k}.\boldsymbol{r}}}$ with energy $\boxed{\varepsilon(\boldsymbol{k})=\frac{\hbar^2 k^2}{2m}}$

(we have used the normalisation condition $\int dr\left|\psi(\mathbf{r})\right|^2=1$)

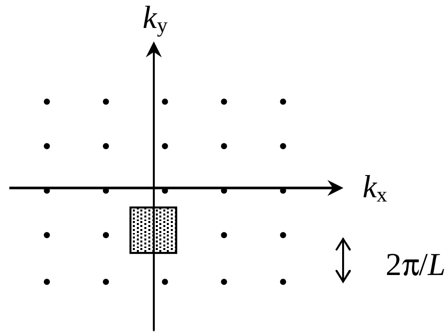
Boundary conditions permit only discrete values of *k* since:

$$e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1$$

$$\Rightarrow \quad k_x = \frac{2\pi n_x}{L} \;,\; k_y = \frac{2\pi n_y}{L} \;,\; k_z = \frac{2\pi n_z}{L}, \qquad n_x, n_y, n_z \quad \text{integers}$$

$\Rightarrow$ In '*k*-space' (2D representation)

In d dimensions, the volume per point is $(2\pi/L)^d$

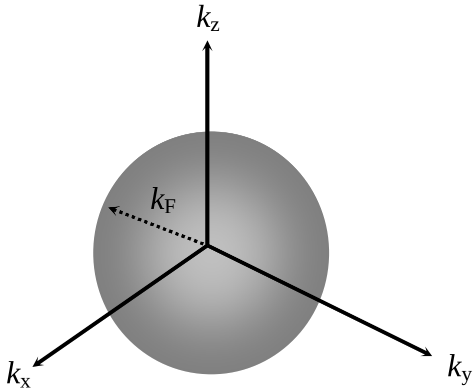


$\Rightarrow$ *k*-space volume Ω will contain $\dfrac{\Omega}{(2\pi/L)^3} = \dfrac{\Omega V}{8\pi^3}$ allowed values of *k*

In practice: *L* is very large $\Rightarrow$ allowed *k*-space points form continuum

The **ground state** of *N* free electrons described by *k*-space sphere of radius k_F (Fermi wavevector), energy at the surface (Fermi energy):

$$\boxed{\varepsilon_F = \frac{\hbar^2 k_F{}^2}{2m}}$$



Total number of allowed *k* values within sphere is $\left(\dfrac{4\pi k_F^3}{3}\right)\left(\dfrac{V}{8\pi^3}\right) = \dfrac{k_F^3}{6\pi^2}V$

Each *k*-value leads to two one-electron levels (one for each spin value – Pauli exclusion principle) $\Rightarrow \quad N = 2.\ \dfrac{k_F^3}{6\pi^2}V$

$$\boxed{\text{Electronic density, } n = \frac{k_F^3}{3\pi^2}}$$

Pauli exclusion principle: no two electrons can have all quantum numbers identical

Density of states (in energy);

Number of states $< \varepsilon$, $$N = \frac{V}{3\pi^2}\left(\frac{2m\varepsilon}{\hbar^2}\right)^{\frac{3}{2}}$$

Need number of states per unit energy, per unit volume, often called the **density of states**

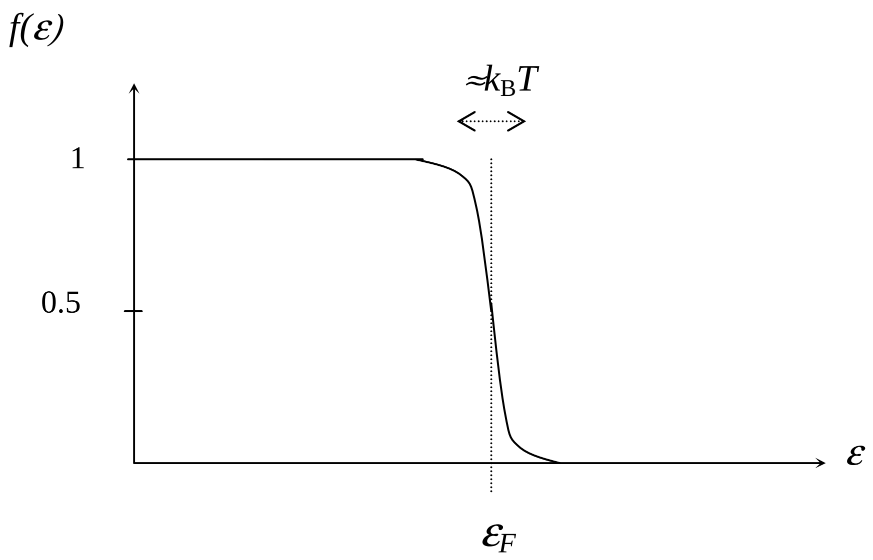
$$\boxed{D(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\varepsilon^{\frac{1}{2}}}$$

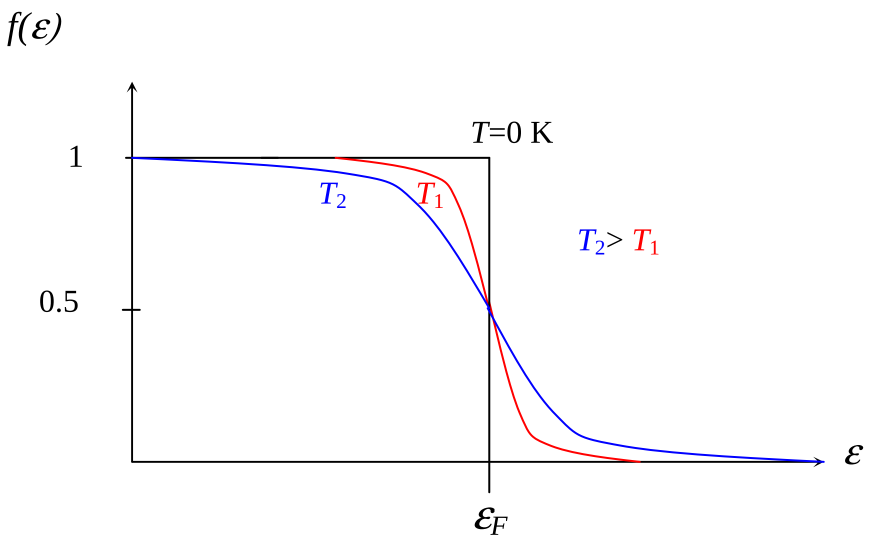
THERMAL PROPERTIES OF THE FREE ELECTRON FERMI GAS: THE FERMI-DIRAC DISTRIBUTION

N weakly interacting Fermions in thermal equilibrium at temperature *T* have occupancy probability $f(\varepsilon)$ given by the **Fermi-Dirac distribution**

$$\boxed{f(\varepsilon) = \frac{1}{e^{(\varepsilon-\varepsilon_F)/k_BT} + 1}}$$

Where: ε_F is the **Fermi energy** and k_B is the **Boltzman constant**

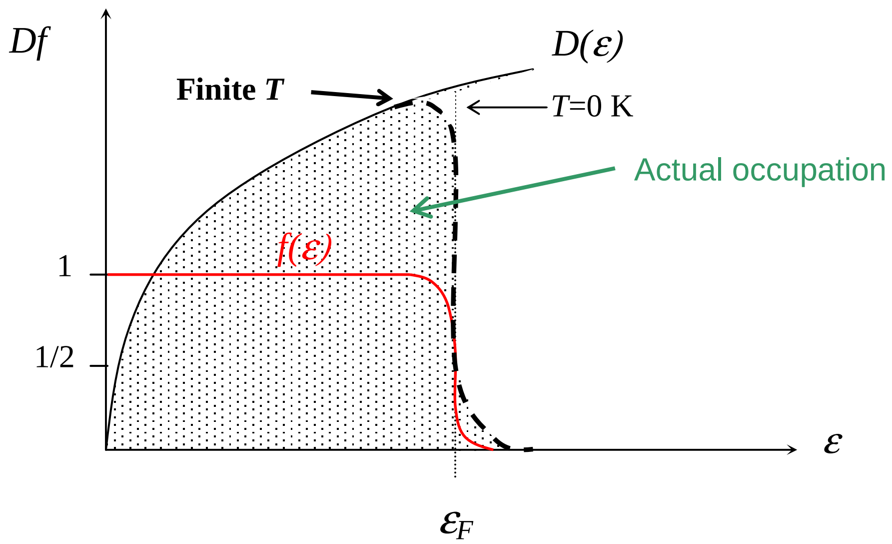




⇒ **Fermi energy, ε_F , is the energy of the topmost filled state at absolute zero**

- At all temperatures $f(\varepsilon) = 1/2$ when $\varepsilon = \varepsilon_F$

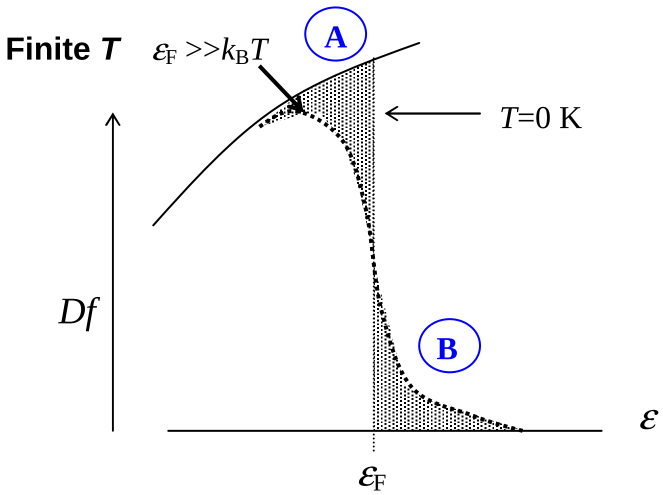
Some textbooks will use the chemical potential μ instead of ε_F in the Fermi Dirac equation. This strictly correct but we will use ε_F because $\varepsilon_F = \mu$ to good approximation for most purposes



$$N = \int_0^\infty D(\varepsilon) f(\varepsilon) d\varepsilon$$ = shaded area

For real metals, $\frac{N}{V}$ is very high so that $\varepsilon_F \gg k_B T$ (typically $\varepsilon_F \sim 5$ eV, NB $k_B T$ $= 1/40$ eV @ RT

HEAT CAPACITY OF A FREE ELECTRON GAS



As T increases from 0 K, points in shaded area **A** become unoccupied and points in **B** become occupied ⇒ increase in energy U

U~(number of electrons that have increased energy) x (energy increase for each one)

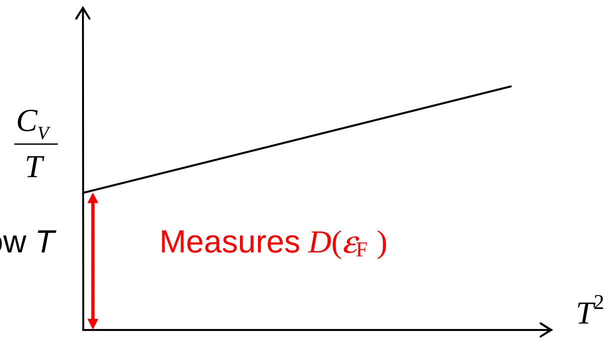
$\sim (D(\varepsilon_F)k_BT)\text{x } k_BT$

$\sim D(\varepsilon_F)k_B^2T^2$

⇒ Electronic heat capacity, $$\boxed{C_{el} = \frac{\partial U}{\partial T} \approx 2.D(\varepsilon_F).k_B^2T}$$

In real metals, $C_v = AT^3 + 2D(\varepsilon_F)k_B^2T$

Heat capacity of lattice



Electronic contribution dominates at low T

ELECTRICAL CONDUCTIVITY OF FREE ELECTRON GAS

Remember that for free electron, $\boxed{\varepsilon(\mathbf{k}) = \dfrac{\hbar^2 k^2}{2m} = \dfrac{p^2}{2m}}$

Momentum related to wavevector by: $m\mathbf{v} = \hbar\mathbf{k}$

In electric field **E** and magnetic field **B** the force on electron,

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

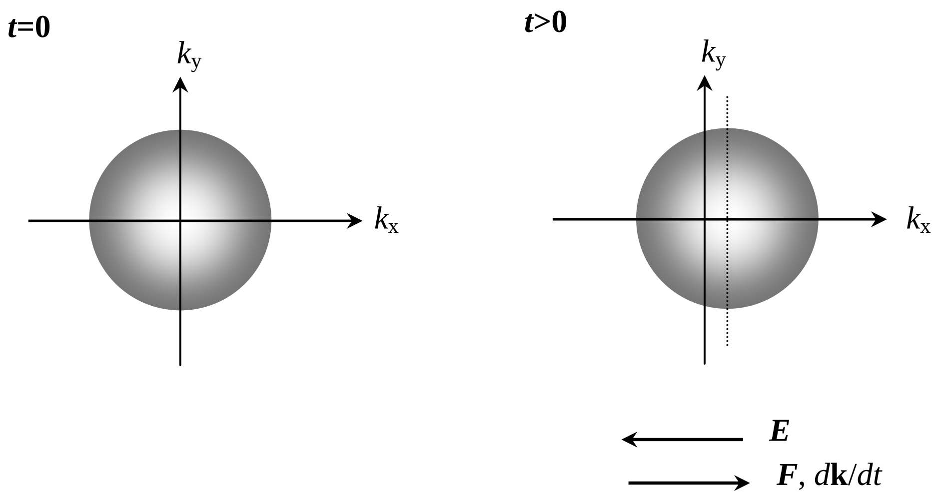
When **B**=0,

$\mathbf{F} = -e\mathbf{E}$

Equation of motion, $F = m\dfrac{d\mathbf{v}}{dt} = \hbar\dfrac{d\mathbf{k}}{dt}$

Fermi sphere is displaced at constant rate as the k value of the state occupied by each electron changes uniformly and equally,

$\mathbf{k}(t) - \mathbf{k}(0) = -\dfrac{e\mathbf{E}t}{\hbar}$



Sphere reaches steady state due to scattering:

τ = relaxation time
= scattering time
= time to change state by collision with impurities/ lattice imperfection/lattice vibrations

$$F = m\frac{dv}{dt} = \hbar\frac{dk}{dt} \qquad \Rightarrow \qquad \delta k = -\frac{eE\tau}{\hbar}$$ for each electron

If *n* electrons per unit volume and $\mathbf{v}_{\mathrm{inc}}$=<u>incremental</u> (drift) velocity increase:

$$\mathbf{j} = n(-e)\mathbf{v}_{inc} = n(-e)\left(-\frac{e\mathbf{E}\tau}{\hbar}\right)\left(\frac{\hbar}{m}\right) = \left(\frac{ne^2\tau}{m}\right)\mathbf{E} = \sigma\mathbf{E}$$

NB Kittel uses **v** for actual velocity and also for <u>incremental</u> velocity

Electrical conductivity σ defined as $\mathbf{j} = \sigma\mathbf{E}$,

$$\Rightarrow \qquad \boxed{\sigma = \frac{ne^2\tau}{m}}$$ Drude equation

Resistivity is defined as $1/\sigma$ so $\boxed{\rho = \frac{m}{ne^2\tau}}$

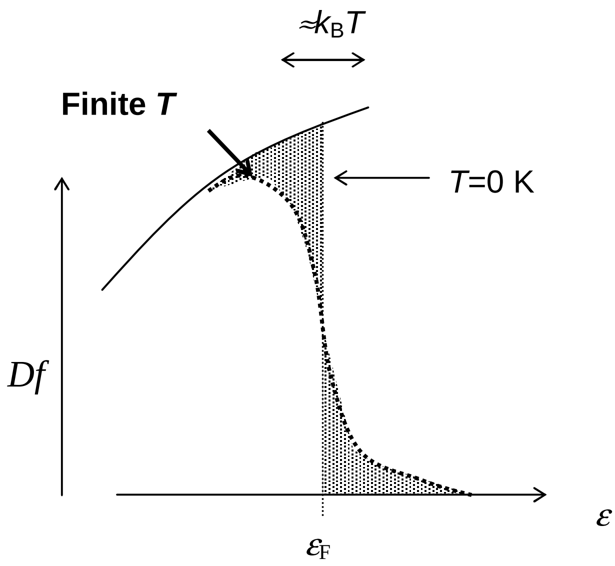
At RT, τ~10^{-14} s

l=**mean free path** between collisions=$v\tau$

For electrons at the Fermi surface, *l*= $v_F\tau$

At RT, l~0.1 μm, i.e. > lattice spacing

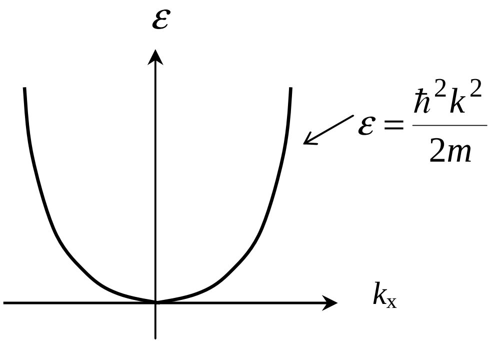
DEGENERACY



System is said to be **degenerate** when $\varepsilon_F \gg k_B T$

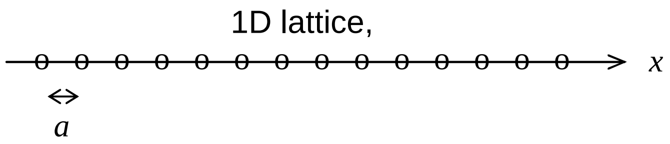
4. ENERGY BANDS: NEARLY FREE ELECTRON MODEL

So far we have *completely* ignored the details of the potential seen by the electrons, V=0



Now let's have a *periodic* potential $\Rightarrow$ two consequences:
• restricts the form of the wavefunction;
• suggests Fourier analysis might be useful.

Consider 1D lattice



Schrödinger equation is then

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi(r) = E\psi(r)$$

Where $V(r) = V(r+T)$, where T is lattice vector. Also, the probability density for the electrons must be a periodic function, so that it is the same in every unit cell, so

$$|\psi(r)|^2 = |\psi(r+T)|^2$$

and thus it follows that ψ only varies by a phase factor from cell to cell:

$$\psi(r+T) = e^{i\phi}\psi(r)$$

and for our 1D lattice above we would have

$$\psi(x+a) = e^{i\phi}\psi(x)$$

$$\psi(x+Na) = e^{iN\phi}\psi(x)$$

But from periodic boundary conditions for a system with N cells:

$$\psi(x+Na) = e^{iN\phi}\psi(x) = \psi(x)$$

so now

$$\phi = \frac{2\pi n}{N}$$

where *n* is an integer. This corresponds to:

$\phi = ka$, where $k = \frac{2\pi n}{Na}$ is one of the allowed wavevectors in the system of length *Na*.

Now let's write the wavefunction in the form:

$$\psi_k(x) = u_k(x)e^{ikx}$$

which must satisfy

$$\psi_k(x+a) = \psi_k(x)e^{i\phi}$$

if *u(x+a)=u(x)*

This is *Bloch's theorem*: the wavefunction for an electron in a periodic potential can be written as a phase factor e^{ikx} times a function with the same periodicity as the potential.

In one dimension, consider the two free electron wavefunctions

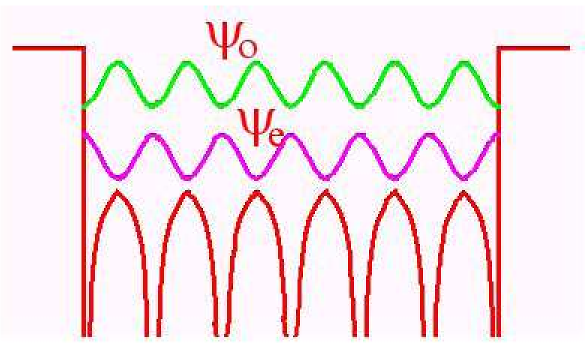
$\psi_+(x) = \frac{1}{\sqrt{L}} e^{i\pi x/a}$ and $\psi_-(x) = \frac{1}{\sqrt{L}} e^{-i\pi x/a}$

where the $L^{-1/2}$ normalizes over the length of the crystal, *L*: these both give constant electron densities *1/L*. But consider the combinations:

$$\psi_e(x) = \frac{1}{\sqrt{2}}(\psi_+(x) + \psi_-(x)) = \sqrt{\frac{2}{L}}\cos(\pi x/a)$$

$$\psi_o(x) = \frac{1}{\sqrt{2}}(\psi_+(x) - \psi_-(x)) = \sqrt{\frac{2}{L}}\sin(\pi x/a)$$

The new states are standing waves, not travelling waves.



It is clear that the even function has more charge density near the nuclei than the odd function, so we expect it to have lower energy. The crystal potential has split the degeneracy of the states with k = −π/a and k = π/a – there is an *energy gap* between them. As (π/a) − (−π/a) = 2π/a = G, a reciprocal lattice vector, we can imagine a wave with k = π/a being Bragg reflected by interacting with the potential to give a wave with k = −π/a.

Region in **k** space between $-\pi/a$ and π/a is the first **Brillouin zone** of the lattice

Q. Why?

A. Consider reflections of waves by periodic arrays of scatterers

(We will consider 1D only) Rem. $\omega = \frac{\hbar}{k}, \quad \varepsilon = \frac{\hbar^2 k^2}{2m}$

$\psi_k \propto e^{i(k_x x - \omega t)}$ is the Schrödinger wave to the right ....(1)

$\psi_k \propto e^{i(-k_x x - \omega t)}$ is the Schrödinger wave to the left

wave (1) when at site *n* is $\psi_k \propto e^{i(k_x na - \omega t)}$

Suppose that it reflects by an amount *r*, reflected wave at *n* is:

$\psi_k \propto r e^{i(k_x na - \omega t)}$

Reflected wave at *x* is $\psi_k \propto r e^{i(-k_x x + 2k_x na - \omega t)}$ ....(2)

because (2) is travelling to the left and has correct form at *x*=*na*. Reflected wave is.

$$\psi_k \propto \left(\sum_n e^{2ik_x na} \right) . r e^{i(-k_x x - \omega t)} \text{ ....(3)}$$ for all sites.

Consider $$\delta = \sum_{n=-\infty}^{\infty} e^{2ik_x na}$$

When $2k_x na = 2\pi n$, then $\delta \to \infty$ otherwise $\delta \sim 1$

So **coherent scattering** when $k_x a = \pi$ or $\boxed{k_x = \frac{\pi}{a}}$

also when $k_x = \frac{2\pi}{a}$, $k_x = \frac{3\pi}{a}$, $k_x = \frac{4\pi}{a}$, ...

So waves with $k_x = \pm\frac{\pi}{a}$ scatter into each other.

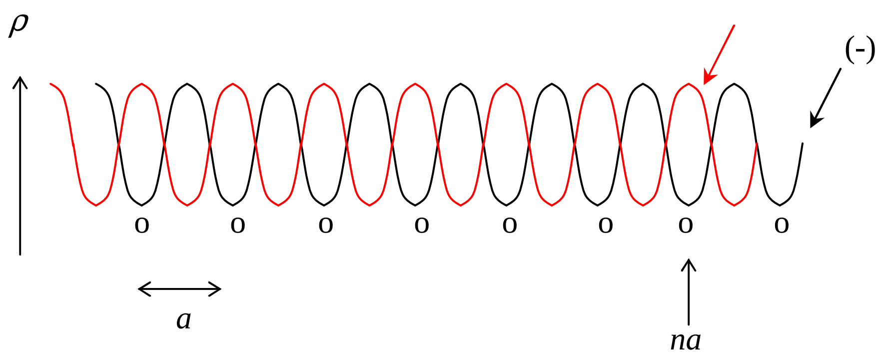
Waves $\psi_k \propto e^{i(\pm k_x x - \omega t)}$ can add to give standing waves

$$\varphi(\pm) = e^{i(k_x x - \omega t)} \pm e^{-i(k_x x - \omega t)},$$ where $k=\pi/a$

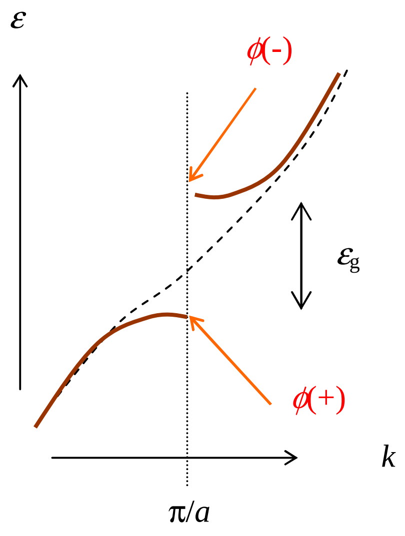
$$\varphi(+) = (e^{i\pi x/a} + e^{-i\pi x/a}).e^{\omega t} = 2\cos(kx).e^{-i\omega t}$$
$$\varphi(-) = (e^{i\pi x/a} - e^{-i\pi x/a}).e^{i\omega t} = 2i\sin(kx).e^{-i\omega t}$$

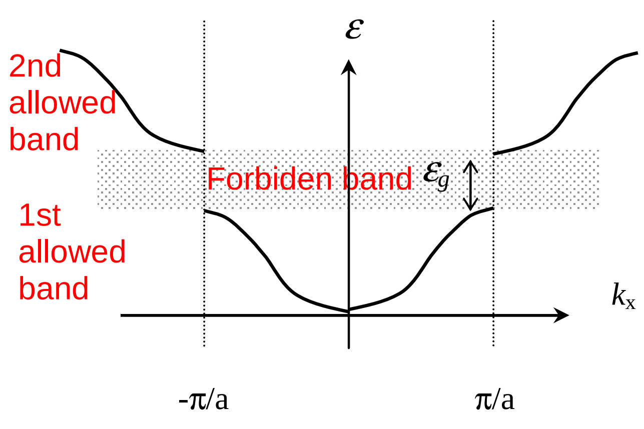
$\Rightarrow$ Electron density $\rho(+) = |\varphi(+)|^2 \propto \cos^2\left(\frac{\pi x}{a}\right)$

similarly, $\rho(-) \propto \sin^2\left(\frac{\pi x}{a}\right)$

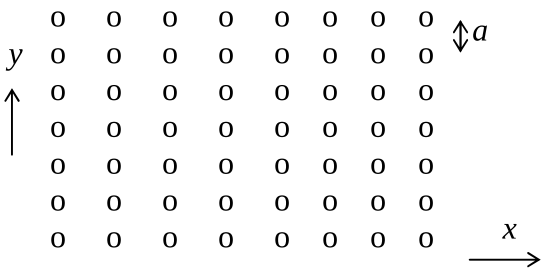


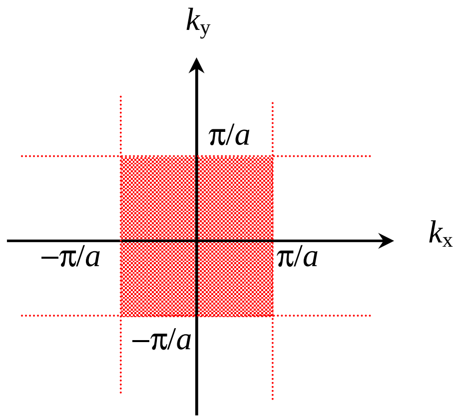
$\rho(+)$ density greatest at +ve core sites
$\rho(-)$ density greatest between +ve core sites





In 2D (simple cubic)





In 3D energy gaps occur across <u>planes</u> in **k** space
Planes are determined by 3D **direct lattice**

NB Kittel goes into the origin of energy gaps and Brillouin zones in much greater depth than we will. The derivations in chapter 7 are beyond what we will consider in SSP

BLOCH'S THEOREM

$$\boxed{\psi_k(\mathbf{r}+\mathbf{T}) = e^{i\mathbf{k}.\mathbf{T}}.\psi_k(\mathbf{r})} \quad \text{.............................(4)}$$

← **GENERAL RESULT FROM QM**:
For any ψ that satisfies the SE there exists a vector $\mathbf{k}$ such that translation by a lattice vector $\mathbf{T}$ is equivalent to multiplying by the phase factor exp[$i\mathbf{k}.\mathbf{T}$]

THIS IS BLOCH'S THEOREM

Alternative form

$$\boxed{\psi_k(\mathbf{r}) = U_{\mathbf{k}}(\mathbf{r}).e^{i\mathbf{k}.\mathbf{r}}} \quad \text{.................. .... (5)}$$

where $U_{\mathbf{k}}(\mathbf{r})= U_{\mathbf{k}}(\mathbf{r}+\mathbf{T})$, i.e. has same periodicity as the **Bravais lattice**
Eq.(5) implies (4) since $U_{\mathbf{k}}(\mathbf{r})=\exp(-i\mathbf{k}.\mathbf{r})\,\psi(\mathbf{r})$ has the periodicity of the **Bravais lattice**

Q. What about the free electron model?
A. Equivalent to Bloch theorem with V(r)→0

$$\psi_k(\mathbf{r}) = U_{\mathbf{k}}(\mathbf{r}).e^{i\mathbf{k}.\mathbf{r}}$$

where $U_{\mathbf{k}}(\mathbf{r}+\mathbf{T})=U_{\mathbf{k}}(\mathbf{r})$, satisfies Bloch's theorem, because

$$\psi_k(\mathbf{r}+\mathbf{T}) = U_{\mathbf{k}}(\mathbf{r}+\mathbf{T}).e^{i\mathbf{k}.(\mathbf{r}+\mathbf{T})} = U_{\mathbf{k}}.e^{i\mathbf{k}.\mathbf{r}}.e^{i\mathbf{k}.\mathbf{T}} = e^{i\mathbf{k}.\mathbf{T}}.\psi_k(\mathbf{r})$$

As $U_{\mathbf{k}}(\mathrm{r})\rightarrow 1$, $\mathrm{V}(\mathrm{r})\rightarrow 0$, $\psi(\mathbf{r})\rightarrow$free electron

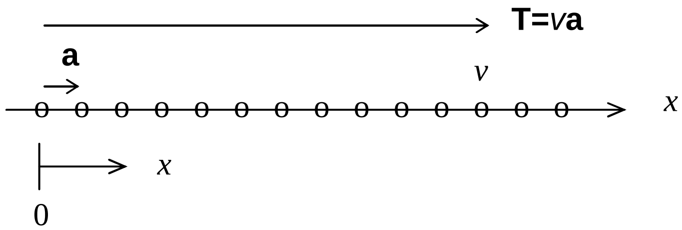
Bloch theorem also basis of the nearly free electron model

PERIODICITY IN K-SPACE

NB Kittel gives 3D case for general lattice. We will use 1D concepts only

Bands

1D lattice,



Consider 1D Bloch theorem, $\psi_k(\mathbf{r} + v\mathbf{a}) = e^{i\mathbf{k}.v\mathbf{a}}.\psi_{\mathbf{k}}(\mathbf{r})$

If ,

$\mathbf{k} \rightarrow \mathbf{k}+(2\pi/\mathbf{a})n$, *n* any integer

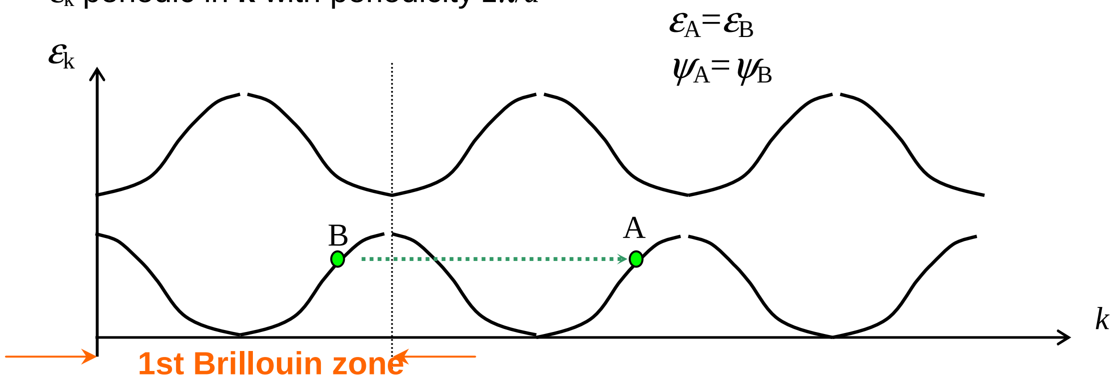
$k \rightarrow k+(2\pi/a)n$, drop vector notation

$$\Rightarrow \quad e^{ikva} \rightarrow e^{i(k+\frac{2\pi}{a}n)va} = e^{ikva}.e^{i2\pi vn} = e^{ikva}$$ i.e, unchanged

So,
$$\psi_{k+\frac{2\pi n}{a}}(x) \equiv \psi_k(x)$$

So,
$$\varepsilon_{k+\frac{2\pi}{a}} \equiv \varepsilon_k$$

ε_k periodic in **k** with periodicity $2\pi/a$



Various way of presenting this information:

Periodic zone
Reduced zone
Extended zone

<u>IMPORTANT CONCEPT: Electron velocity in solid</u>

$\psi_{\mathbf{k}}$, $\varepsilon_{\mathbf{k}}$ Bloch state

The group velocity of a wave packet (remember $\varepsilon = \hbar\omega$) is given by:

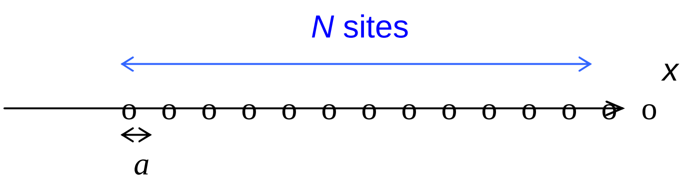
$$v_{\mathbf{k}} = \nabla_{\mathbf{k}}\omega = \frac{1}{\hbar}\frac{\partial \varepsilon_{\mathbf{k}}}{\partial \mathbf{k}} = \frac{1}{\hbar}\nabla_{\mathbf{k}}\varepsilon_{\mathbf{k}}$$

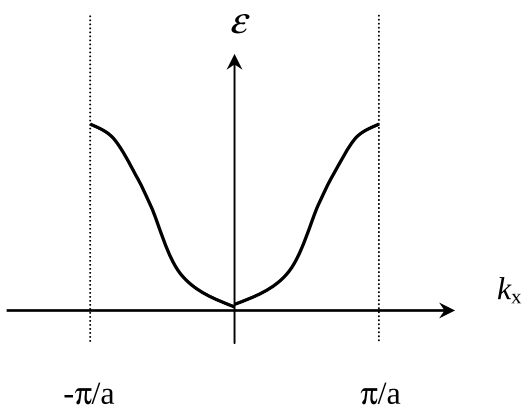
In 1D, $$v_{\mathbf{k}} = \frac{1}{\hbar}\frac{\partial \varepsilon_{\mathbf{k}}}{\partial \mathbf{k}}$$

$\Rightarrow$ $$\boxed{v_k = \frac{1}{\hbar}\text{ (slope of } \varepsilon_k \text{ vs. k curve)}}$$

NUMBER OF STATES IN A BAND

1D lattice





There are $1/2\pi$ states per unit length of real space per unit length of k-space

So in above band there are the following number of states:

$$\left(\frac{1}{2\pi}\right).Na\ .\left(\frac{2\pi}{a}\right) = N$$, also include a factor of 2 for ↑↓ spin states

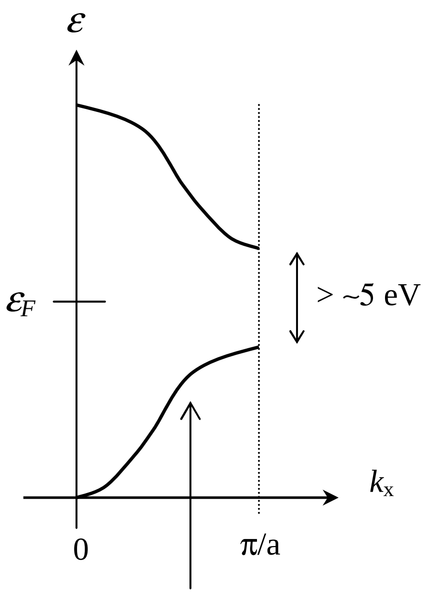
⇒ There are 2*N* states in a band

Conclude: for *N* sites, there are 2*N* states in one band

Same conclusion in 3D

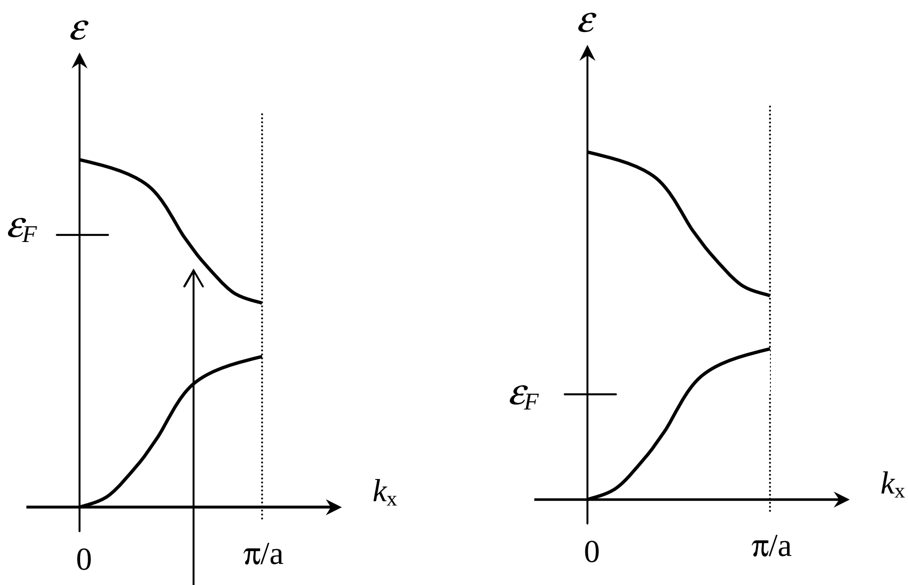
IMPORTANT DEFINITIONS

Insulator (1D)



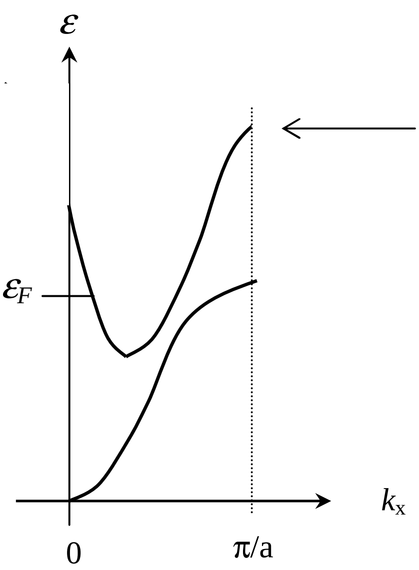
Completely full band

Metal (1D)



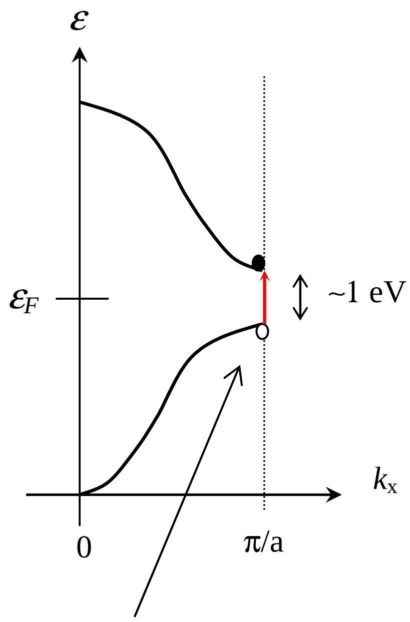
Partly filled band

Metal (2D)



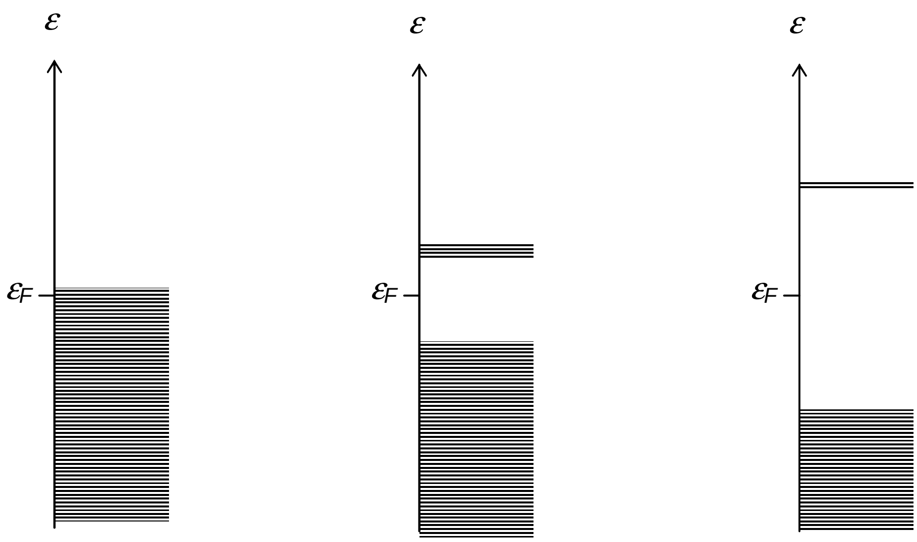
Brillouin zone in k_y direction

Semiconductor (1D, intrinsic)



Electrons thermally excited across the band gap

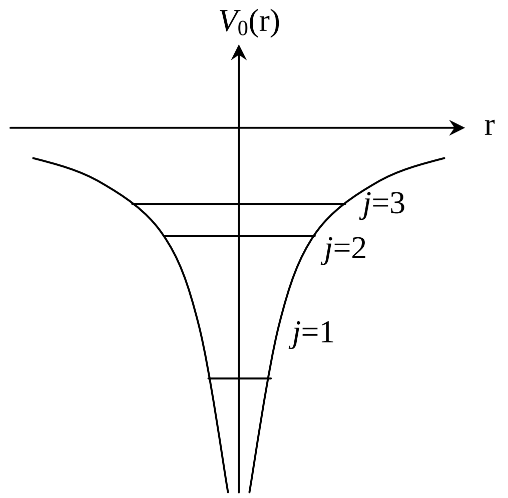
NB Text books will often use these diagrams to represent metals, insulators, and semiconductors:



Metal **Semiconductor** **Insulator**

5. TIGHT BINDING MODEL

For materials that are formed from closed-shell atoms or ions, the free electron model seems inappropriate. In the tight-binding model, we look at how the wavefunctions of atoms or ions interact as they are brought together to form a solid.



The atomic wavefunctions $\varphi_j(\mathbf{r})$ are defined by the S.E.:

$$\left[-\frac{\hbar^2}{2m}\nabla_{\mathbf{r}}^2 + V_0(\mathbf{r})\right]\varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})$$

or written as the Hamiltonian, $H_{\text{Atomic}}\varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})$

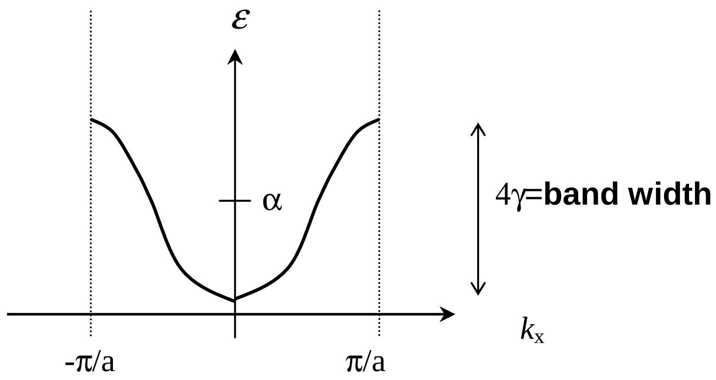
Assume:

- ***V*(r) is so large electrons are mostly bound to ionic cores (opposite to nearly-free-electron model)**
- **close to lattice point $H_{\text{Crystal}}=H_{\text{Atomic}}$**
- **bound levels of H_{Atomic} are localised**

Bloch functions $\psi_{j,\mathbf{k}}$ made from linear combination of atomic wavefunctions $\varphi_j(\mathbf{r})$ (LCAO method, O=orbital)

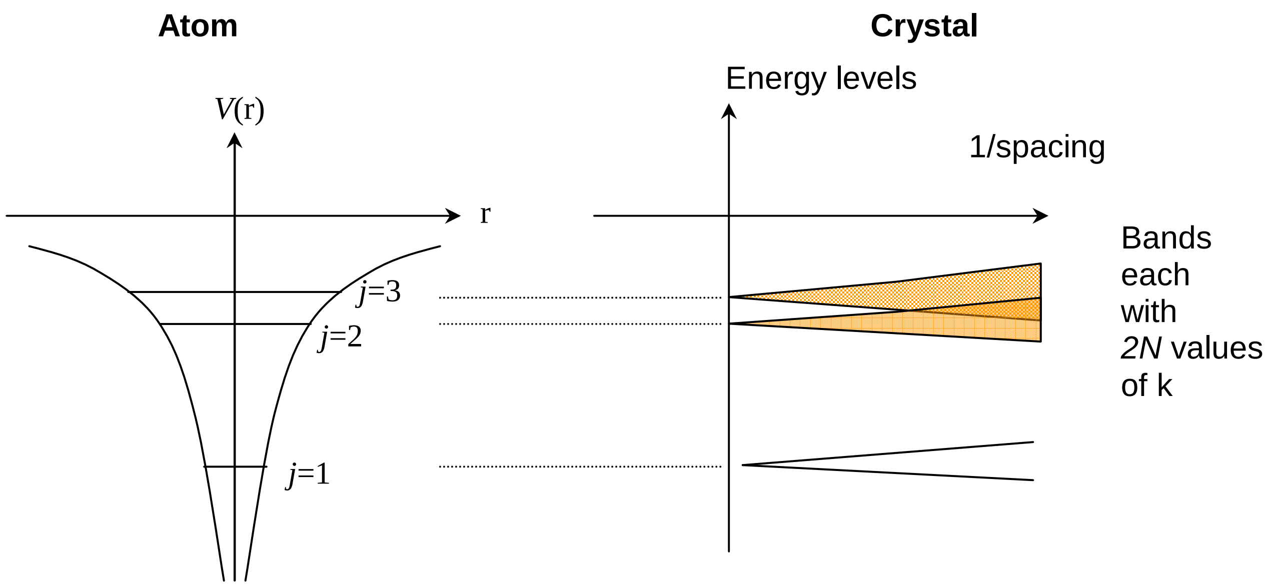
In 1D:

$$\varepsilon(\mathbf{k}) = \varepsilon_{\varphi} - \alpha - 2\gamma\cos(k_x a)$$



ε_{φ} =atomic energy level
α=measure of wavefunction localisation on one lattice site
γ=transfer integral=measure of how easy it is to transfer an electron from one atom to another, 4$\gamma$is the energy band-width centred on energy α.

Representation of tight-binding band formation as the spacing between atoms is reduced:



Exercise: the tight-binding model gives us an analytical form for the dispersion relation, ε vs. k, can you calculate the electron velocity and effective mass for this form of band?

From the tight-binding model we can make the following points about real band structure:

• *N* single atoms with *j* atomic levels (with two electrons per level) have become j bands with 2*N* values of *k*

• The transfer integrals give a direct measure of the bandwidth: small transfer integrals give a narrow bandwidth and heavy effective masses (see above exercise)

• The ‘shape’ of the bands in *k*-space will be determined in part by the real-space crystal structure; if the atoms in a certain direction are far apart. Then the bandwidth will be narrow for motion in that direction

• Bands reflect the character of the atomic levels

6. **ELECTRON TRANSPORT IN BANDS**

Remember:

- Equation of motion, $F = m\dfrac{d\mathbf{v}}{dt} = \hbar\dfrac{d\mathbf{k}}{dt}$

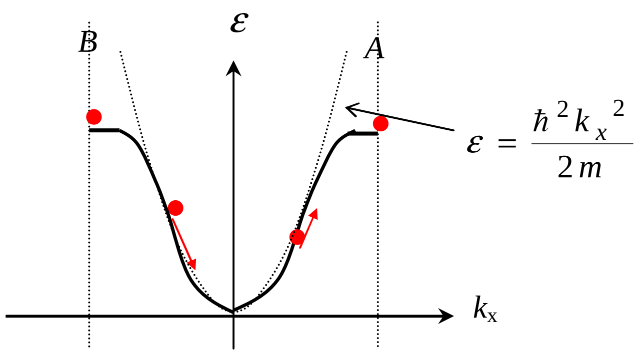
- **Scattering** processes: defects, **phonons** (quantised lattice vibrations), boundaries of conductor, other electrons

- τ = relaxation time
  = scattering time
  = time to change state due to scattering process

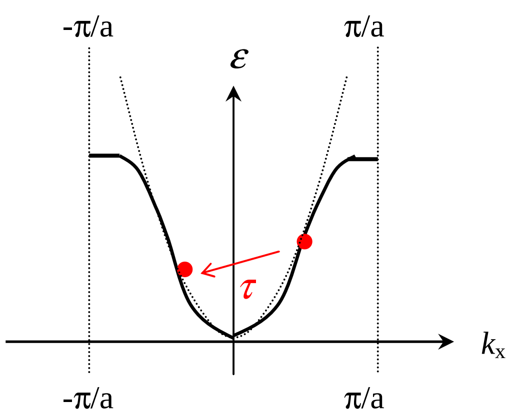
- $1/\tau$ = scattering probability per unit time

Bloch oscillator

A and B are equivalent state: real and k-space path of electron is a 1D oscillator.



Scattering event

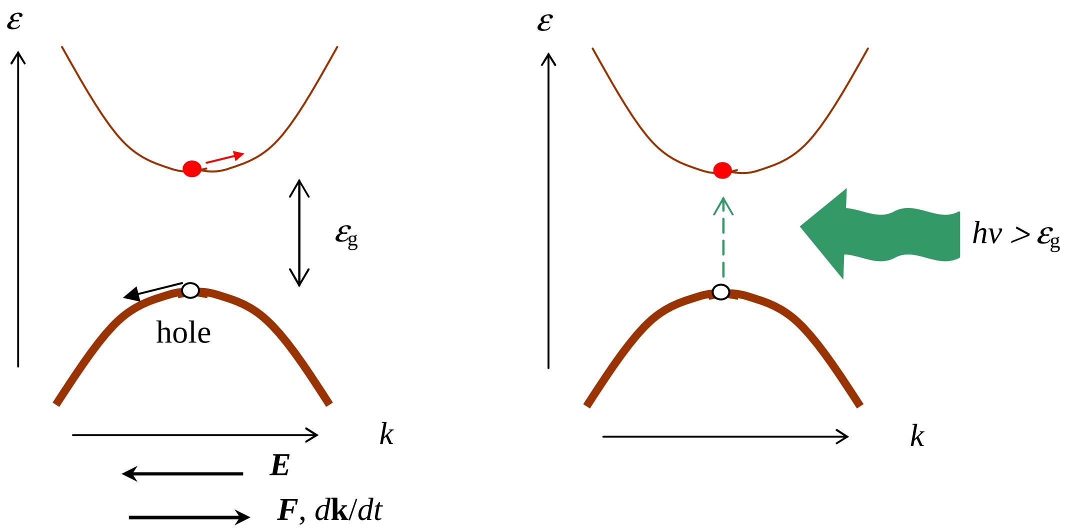


Δk=shift in mean k

$$\Delta k = \frac{F}{\hbar}\tau = \frac{eE}{\hbar}\tau$$

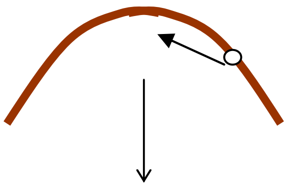
HOLES

Vacant state in otherwise filled band=hole
Hole behaves as +*e* charge for: spatial position and acceleration



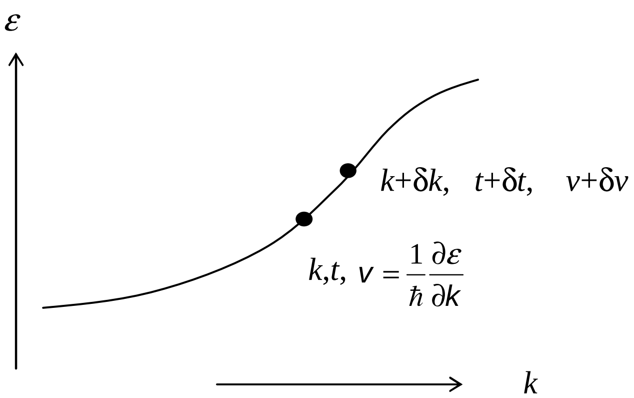
Photon of energy $h\nu > \varepsilon_g$ creates electron-hole pair

Holes ‘float’ to loose energy



Increasing hole kinetic energy

IMPORTANT CONCEPT: Effective mass (1D)
Defined by analogy to Newton’s second law



$$\delta v = \frac{1}{\hbar}\frac{\partial^2 \varepsilon}{\partial k^2}\delta k$$

$$a = \frac{\delta v}{\delta t} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k^2} F = \frac{F}{m^*}$$

where m* is the **effective mass**

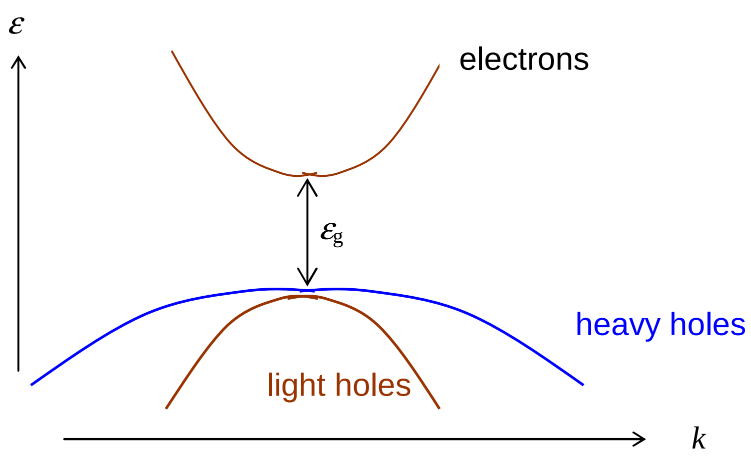
$$\boxed{\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon}{\partial k^2}}$$, effective mass at *k*

In semiconductors *m** can be 0.1 $\rightarrow$ 0.01 of rest mass m_e
m* **can be negative near zone boundary**

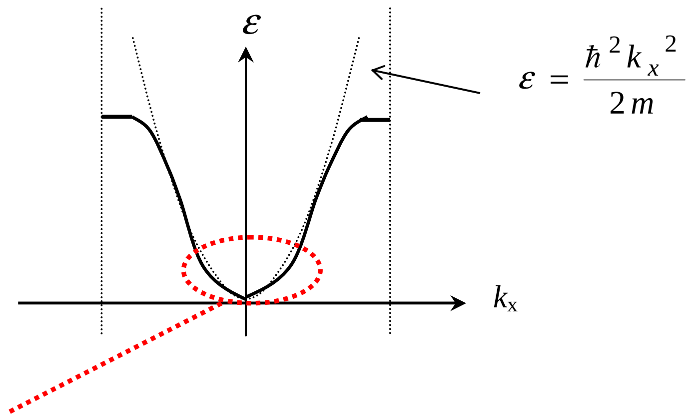
Q. How can *m be negative?**

A. In going from k to $k+\delta k$, more momentum is transferred to the lattice from the electron than is gained by the electron due to the applied force

Q. What about the hole effective mass, is it the same as that of the electron?
A. Not necessarily. E.g. GaAs has heavy and light holes



PARABOLIC BANDS



Parabolic band at low ε, simplest band approximation (use Taylor expansion of ε)

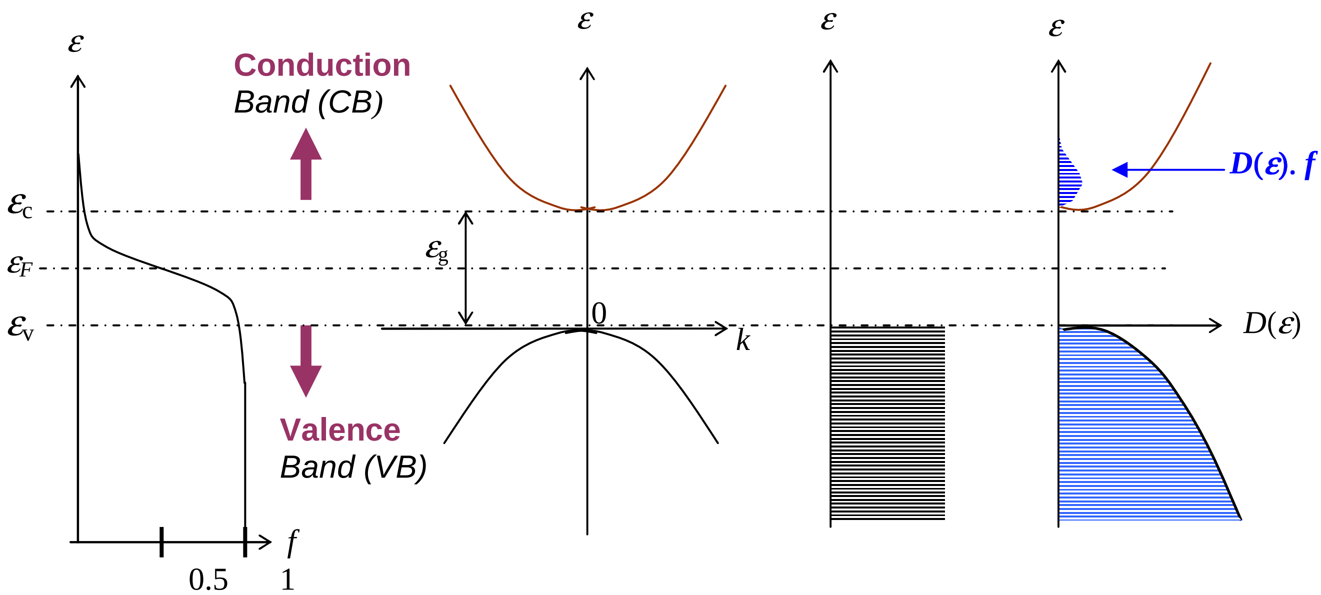
Good for electrons in **conduction band** of semiconductor

7. SEMICONDUCTORS

INTRINSIC SEMICONDUCTORS

Intrinsic= no ‘doping’(impurities)

Several ways of representing the band structure:



Where: ε_F=**Fermi energy**, f=**Fermi-Dirac** distribution, $D(\varepsilon)$=**density of states,**
ε_c=**conduction band energy** ε_v=**valance band energy**

Here we have assumed parabolic bands, i.e. we can use concepts from free electron model

Remember, $f(\varepsilon) = \dfrac{1}{e^{(\varepsilon-\varepsilon_F)/k_BT}+1}$

Assume CB occupancy <<1, $f(\varepsilon) \approx \dfrac{1}{e^{(\varepsilon-\varepsilon_F)/k_BT}} = e^{-\left(\frac{\varepsilon-\varepsilon_F}{k_BT}\right)}$

Probability of hole in VB, 1- $f(\varepsilon) \approx 1 - \dfrac{1}{e^{(\varepsilon-\varepsilon_F)/k_BT}} = e^{-\left(\frac{\varepsilon_F-\varepsilon}{k_BT}\right)}$

Remember, $D_c(\varepsilon) = Cm*_c^{\frac{3}{2}}(\varepsilon - \varepsilon_c)^{\frac{1}{2}}$, $D_v(\varepsilon) = Cm*_v^{\frac{3}{2}}(\varepsilon_v - \varepsilon)^{\frac{1}{2}}$

Where, m_c*=conduction band effective mass, m_v*=valence band effective mass, and *C*= constant (see free electron Fermi gas section)

Number of electrons in CB,

$$n = \int_{\varepsilon_c}^{\infty} f.D_c d\varepsilon \approx Cm*_c^{\frac{3}{2}} \int_{\varepsilon_c}^{\infty} (\varepsilon - \varepsilon_c)^{\frac{1}{2}}.e^{-\frac{(\varepsilon - \varepsilon_F)}{k_B T}} d\varepsilon$$

substitute y=$(\varepsilon - \varepsilon_c)/k_B T$

$$n \approx C(m*_c k_B T)^{\frac{3}{2}}.e^{-\frac{(\varepsilon_c - \varepsilon_F)}{k_B T}} \int_0^{\infty} y^{\frac{1}{2}}.e^{-y} dy$$

which gives,

$$\boxed{n = 2\frac{(2\pi m*_c k_B T)^{\frac{3}{2}}}{h^3}.e^{-\frac{(\varepsilon_c - \varepsilon_F)}{k_B T}} = N_c.e^{-\frac{(\varepsilon_c - \varepsilon_F)}{k_B T}}}$$

where N_c is the effective number density of *accessible* states at ε_c

Similarly the hole density, *p* is given by

$$\boxed{p = 2\frac{(2\pi m*_v k_B T)^{\frac{3}{2}}}{h^3}.e^{-\frac{(\varepsilon_F - \varepsilon_v)}{k_B T}} = N_v.e^{-\frac{(\varepsilon_F - \varepsilon_v)}{k_B T}}}$$

$\Rightarrow$ $$\boxed{np \approx N_c.N_v.e^{-\frac{\varepsilon_g}{k_B T}} = W.T^3.e^{-\frac{\varepsilon_g}{k_B T}}}$$

where *W* is a constant that depends on the extreme features of the CB and VB

This is known as the law of mass action

In an **intrinsic** semiconductor the only source of electrons in the CB is thermal excitation from the VB

$$\Rightarrow \quad \boxed{n_{\mathrm{i}} = n = p = W^{\frac{1}{2}} T^{\frac{3}{2}} . e^{-\frac{\varepsilon_{\mathrm{g}}}{2 k_{\mathrm{B}} T}}}$$

n_{i}=**intrinsic carrier density**

NB $\varepsilon_{\mathrm{g}}/2$ rather than ε_{g} appears in the above equation because creation of an electron in the CB *automatically* generates a hole in the VB

How does the **Fermi energy** change with *T*?

From calculation of n_{i} and $D(\varepsilon)$, $\quad \dfrac{N_{\mathrm{c}}}{N_{\mathrm{v}}} = \left(\dfrac{m^*_{\mathrm{c}}}{m^*_{\mathrm{v}}}\right)^{\frac{3}{2}} = e^{\left(\frac{2\varepsilon_F - \varepsilon_{\mathrm{c}} - \varepsilon_{\mathrm{v}}}{k_{\mathrm{B}} T}\right)}$

$$\Rightarrow \quad \varepsilon_F = \frac{1}{2}(\varepsilon_{\mathrm{c}} - \varepsilon_{\mathrm{v}}) + \frac{3}{4} k_{\mathrm{B}} T \ln\left(\frac{m^*_{\mathrm{c}}}{m^*_{\mathrm{v}}}\right)$$

$\Rightarrow$ **When *T*=0 K or $m_{\mathrm{c}}^* = m_{\mathrm{v}}^*$, ε_{F} lies in the middle of the band gap**

ENERGY GAP OF SELECTED SEMICONDUCTORS

MATERIAL	E_g (T = 300 K)	E_g (T = 0 K)	E_0 (LINEAR EXTRAPOLATION TO T = 0)	LINEAR DOWN TO
Si	1.12 eV	1.17	1.2	200 K
Ge	0.67	0.75	0.78	150
PbS	0.37	0.29	0.25	
PbSe	0.26	0.17	0.14	20
PbTe	0.29	0.19	0.17	
InSb	0.16	0.23	0.25	100
GaSb	0.69	0.79	0.80	75
AlSb	1.5	1.6	1.7	80
InAs	0.35	0.43	0.44	80
InP	1.3		1.4	80
GaAs	1.4		1.5	
GaP	2.2		2.4	
Grey Sn	0.1			
Grey Se	1.8			
Te	0.35			
B	1.5			
C (diamond)	5.5			

EXTRINSIC SEMICONDUCTORS

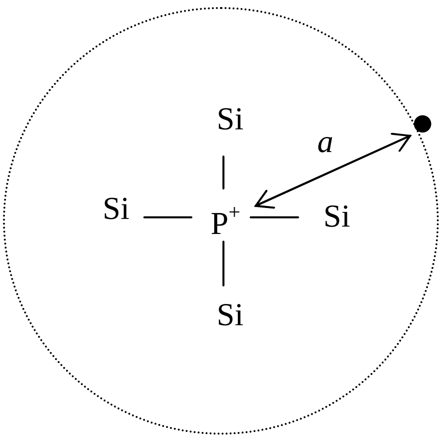
For practically all applications, the conductivity of semiconductors such as GaAs, Ge, and Si is dominated by **extrinsic carriers** provided by **doping** the semiconductor with **low concentrations** of impurities

Two types of impurity (or **dopant**):

DONORS

Impurity of valence ν+1 in semiconductor of valence ν, e.g. P or As in Si or Ge

3A	4A	5A
B	C	N
Al	Si	P
Ga	Ge	As



Extra electron

P^+ ion **donates** one electron to the semiconductor, *n* increases relative to *p*, material is said to be **n-type and** the electron the **majority carrier**

N_D=donor density

Orbiting electron analogous to hydrogen atom with,
(i) free electron mass m_e replaced by m^*_c
(ii) electron moves through medium of relative permativity ε_r

$$\Rightarrow \text{ Energy levels of a donor, } \varepsilon_D(n) = \frac{e^4 m^*_c}{2(4\pi\varepsilon_r\varepsilon_0\hbar n)^2} = -\frac{m^*_c}{m_e}\cdot\frac{1}{\varepsilon_r^{\,2}}\cdot\frac{13.6}{n^2}\ \text{eV, with}$$

n=integer

Also, for n=1, $a = \dfrac{(4\pi\varepsilon_r\varepsilon_0\hbar^2)}{e^2 m^*_c} \approx 10\ \text{nm}$

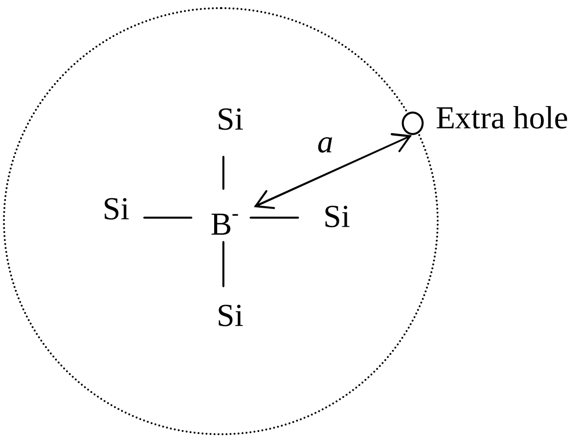
Typical values:
ε_r~10-15 for many semiconductors
$m^*_c \approx 0.07\ m_e$ in GaAs

$\Rightarrow \varepsilon_D(1) \approx 5$ meV   i.e. very low binding energy

ACCEPTORS

Impurity of valence ν-1 in semiconductor of valence ν, e.g. B or Al in Si or Ge

3A	4A	5A
B	C	N
Al	Si	P
Ga	Ge	As



B$^-$ ion **accepts** one electron from the semiconductor, *p* increases relative to *n*, material is said to be **p-type and** the hole the **majority carrier**

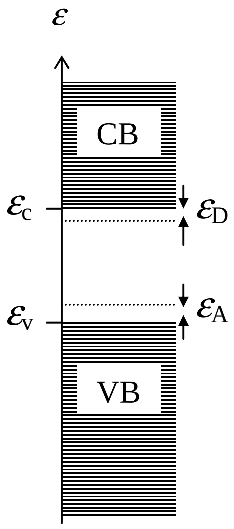
N_A=acceptor density

By similar arguments,

$$\varepsilon_A(n) = -\frac{m^*_v}{m_e}\cdot\frac{1}{\varepsilon_r^{\,2}}\cdot\frac{13.6}{n^2} \approx 5\ \text{meV}$$

Low binding energies mean donors and acceptors will be fully ionised at RT

BAND PICTURE



EXTRINSIC CARRIER DENSITY

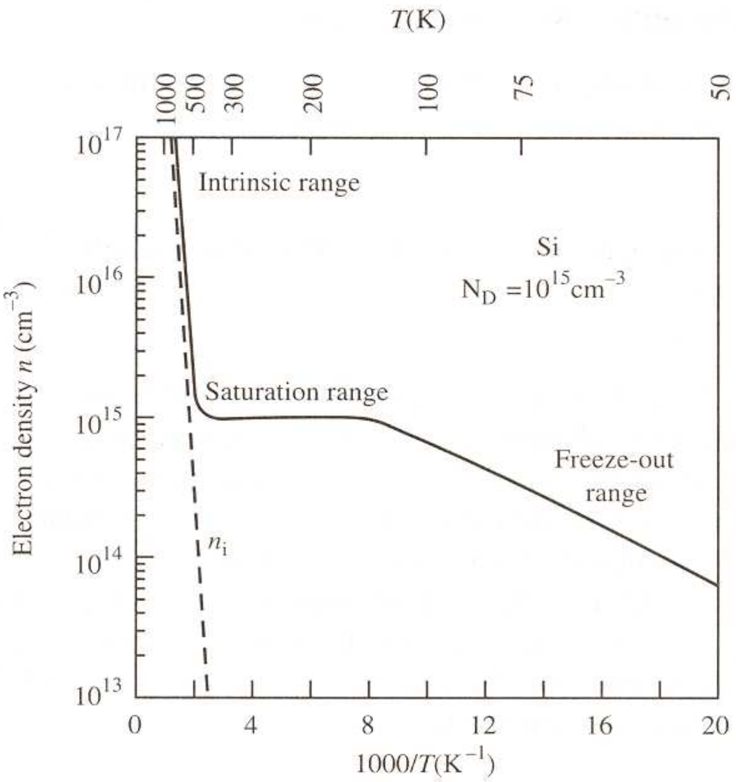
Law of mass action still applies

$$np \approx W.T^3.e^{-\frac{\varepsilon_g}{k_B T}}$$

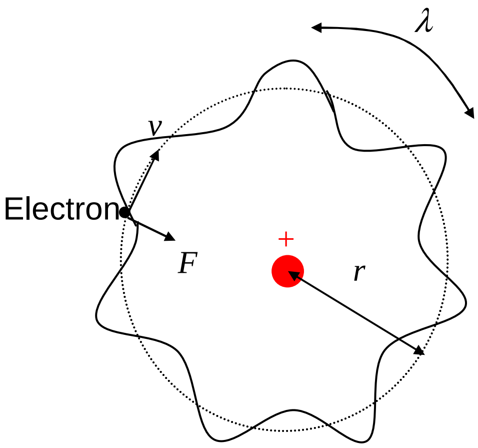
Charge neutrality condition:

$$\boxed{n - p = N_D - N_A}$$

Exercise: can you explain this diagram for the temperature variation of n-type Si?



ADDITIONAL NOTES: ENERGY LEVELS OF HYDROGEN (SEMICLASSICAL DERIVATION)



$$F = \frac{e^2}{4\pi\varepsilon_0 r^2}$$ Coulomb force

Electron describes a circular orbit $\Rightarrow$ momentum, p, is constant $\Rightarrow$ $\lambda = h/p$

For the orbit to be a stationary state $2\pi r = n\lambda$, (n=integer)

$rp = nh/2\pi = n\nabla$

Since ,$p = m_e v$, $m_e vr = n\nabla$

Equation of motion, $F = m_e v^2/r$

$$\Rightarrow \quad \frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \quad \text{or} \quad m_e v^2 = \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\boxed{\Rightarrow \quad r = \frac{4\pi\hbar^2\varepsilon_0 n^2}{m_e e^2}}$$

For n=1, $r_1 = \dfrac{4\pi\hbar^2\varepsilon_0}{m_e e^2} = 5.3 \text{ x } 10^{-11}$ m (or 0.53 Å), called **Bohr radius**

Energy of electron-nucleus system = kinetic + potential

$$\Rightarrow \quad \varepsilon = \varepsilon_k + \varepsilon_p = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0 (2r)}$$

$$\boxed{\varepsilon = -\frac{m_e e^4}{2(4\pi\varepsilon_0 \hbar n)^2} = -\frac{13.6}{n^2} \text{ eV}}$$

EXTRINSIC CARRIER DENSITY (CONTD.)

NB
N_D refers to +ve charge (i.e. ionised donors) ,
N_A refers to –ve charge(i.e. ionised acceptors)

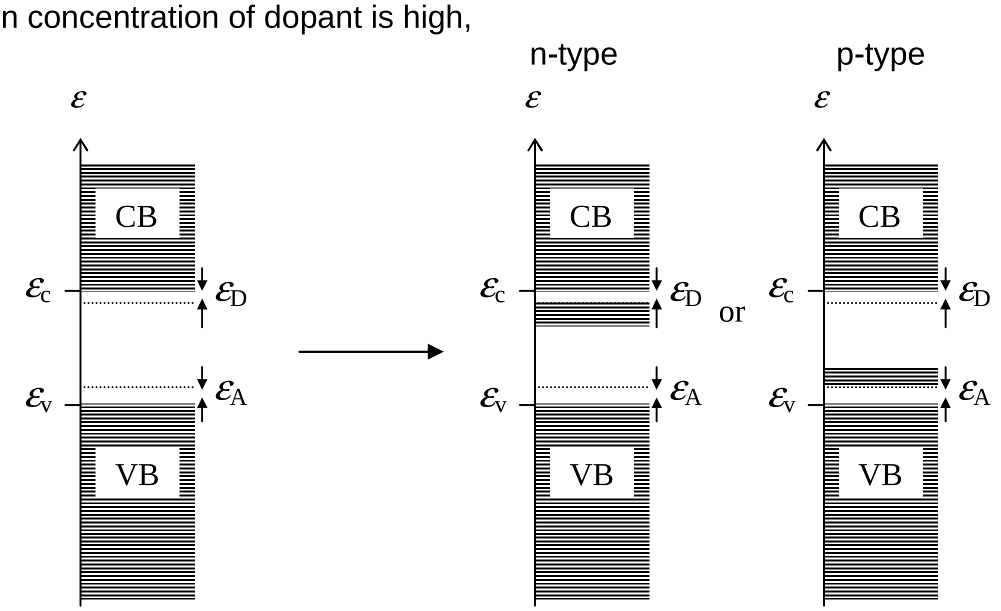
The diagram tells us that for Si, n_i is very low at RT so only if N_D is less than 10^{12}-10^{15} cm^{-3} will Si behave like an intrinsic semiconductor – in reality this is impossible!

⇒ At RT the electronic properties of most semiconductors are controlled by the impurities (donors/acceptors)

BUT if $N_D = N_A$, the semiconductor is said to be **compensated** and behave like an intrinsic semiconductor

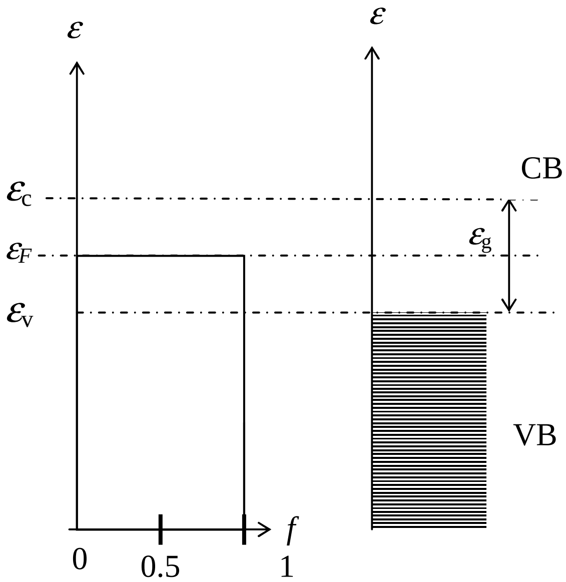
IMPURITY BANDS

When concentration of dopant is high,

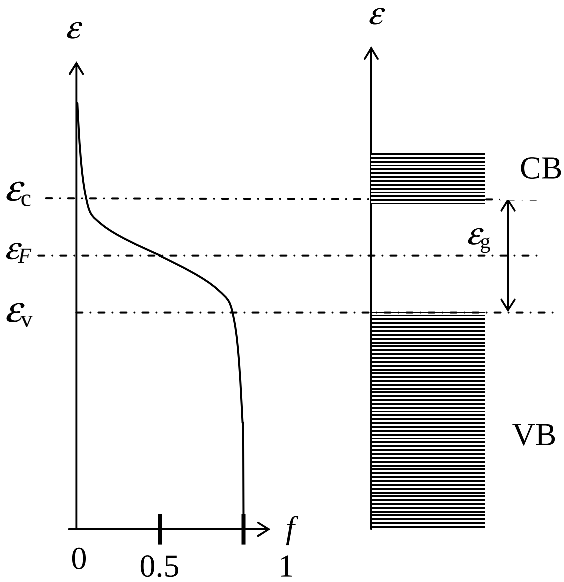


LOCATING THE FERMI ENERGY

Intrinsic semiconductor



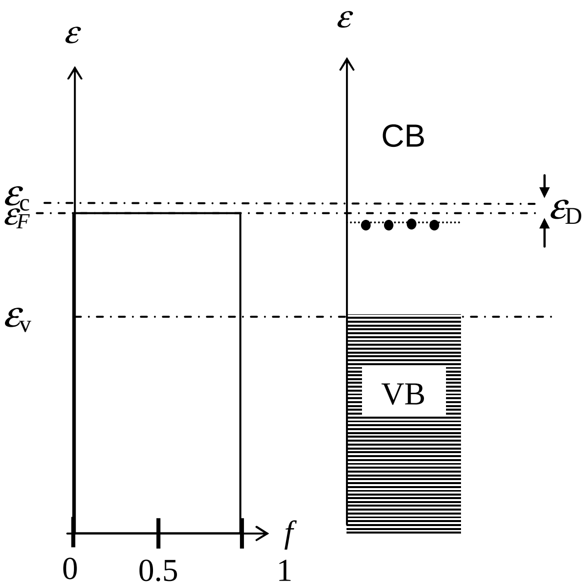
T=0K



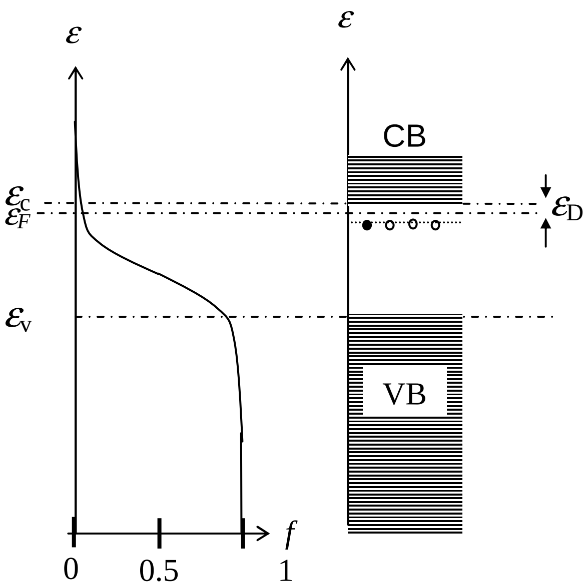
T>0K

n-type doping

At 0K the highest occupied levels will be the donor levels, the lowest empty levels will be at the bottom of the conduction band, so the Fermi energy will lie between the donor levels and the bottom of the CB. Fermi energy said to be ‘pinned’ by doner concentration.

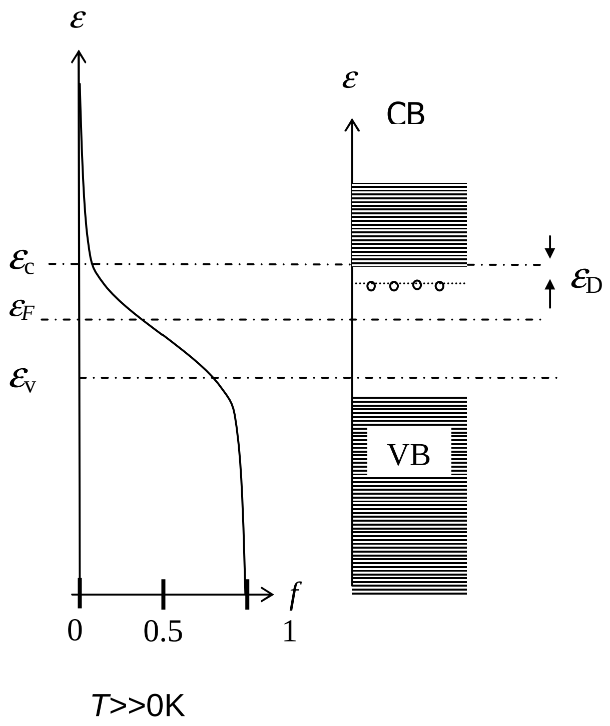


T=0K



T>0K

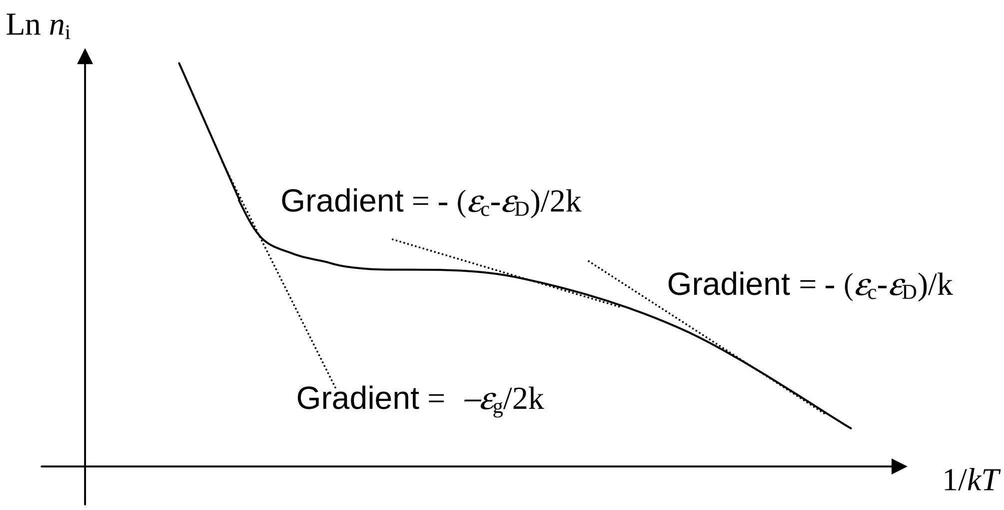
If the temperature is raised, electrons are excited from the donor levels into the CB (above left).



At very high temperature all donors are ionised and further electrons must come from the valence band, we are then back to the in the intrinsic regime so the Fermi energy is located at the mid-point of the band gap.

CARRIER CONCENTRATIONS

Detailed calculations show that electron density for an n-type material varies as below.



Law of mass action applies irrespective of doping:

$$np \approx N_c . N_v . e^{-\frac{\varepsilon_g}{k_B T}}$$

At RT $np=10^{38}$ m^{-6} for Ge and 10^{33} m^{-6} for Si. So if there is no doping $n=p=3\ 10^{16}$ m^{-3} for Si. So to observe intrinsic behaviour at room temperature, need fewer carriers than this from impurities, i.e. a concentration of less than one part in 10^{12} – unachievable.

Detailed result: at low temperature in an n-type material, the number of ionised donors is given by

$$n_D^+ = N_D \left[\frac{1}{\exp((\varepsilon_D - \varepsilon_F)/kT) + 1} \right]$$

MODILITY AND CONDUCTIVITY

It both electrons and holes are present, both contribute to the electrical conductivity

$$\boxed{\sigma = ne\mu_e + pe\mu_h}$$

where μ is the **mobility**.

Remember that the free electron model is a good approximation for electrons in the CB or holes in the VB of a semiconductor, therefore the expression for electrical conductivity is used

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

or resistivity**,** $1/\sigma$

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

where *n* is electron charge density, τ is the scattering time, and *m* is the electron rest mass

Mobilty, the drift velocity per unit electric field, $\mu = |v_D|/E$, for electrons is defined as

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

and for holes

$$\boxed{\mu_h = \frac{e\tau_h}{m_h^*}}$$

τ_e and τ_h are not necessarily the same.

LATTICE VIBRATIONS (PHONONS)

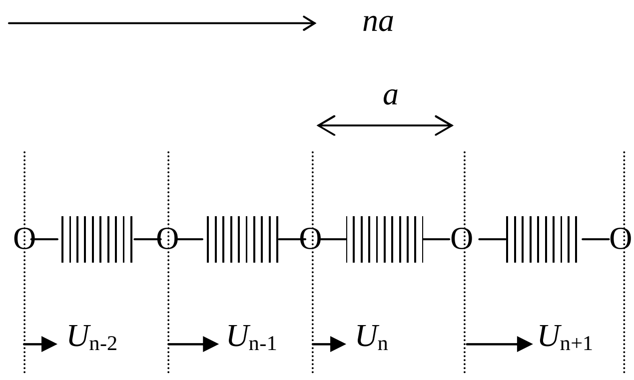
● Even in the ground state atoms have some kinetic energy (zero-point motion)

● Vibrational energy can move through the structure as sound waves or heat transport

● Atoms away from regular sites alter the way electrons move through solids to produce electrical resistance

Assume every atom's interaction with its neighbours may be represented by a spring, so that the force on each 'spring' is proportional to the change in length of the spring (called the harmonic approximation). Also assume only forces between nearest neighbours are significant.

Longitudinal vibrational waves in a 1D lattice



Atom n should be at *n*a but is displaced by an amount U_n. The 'unstretched spring' corresponds to an interatomic spacing *a*.

The force on atom *n* is

$$F_n = \alpha(u_{n+1} - u_n) - \alpha(u_n - u_{n-1}),$$

where α is the spring constant. Thus the equation of motion is

$$m\ddot{u}_n = \alpha(u_{n+1} - u_{n-1} - 2u_n),$$

for atoms of mass *m*. Now look for wave-like solutions

$$u_n(t) = A\exp(ikna - i\omega t)$$

substitute and find

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

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

This gives the angular frequency

$$\omega = \omega_0 \left|\sin\left(\frac{ka}{2}\right)\right|,$$

with a maximum cut-off frequency $\boxed{\omega_0 = \sqrt{\frac{4a}{m}}}$

Group velocity, $v_g = \nabla\omega = \frac{\omega_0 a}{2}\cos\left(\frac{ka}{2}\right)$

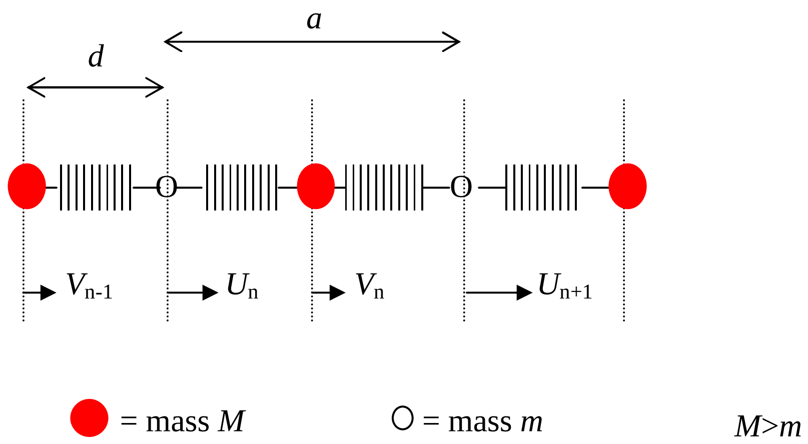
In the limit of long wavelength, i.e. $k \to 0$, then $\omega \to \omega_0 ka/2$, and so in this limit $v_g = \omega_0 a/2$. **This is the velocity of sound in the lattice.**

Knowing $v_{sound} \approx 10^3$ ms^{-1} and $a \approx 10^{-10}$ m, we find

$$\omega_0 \approx 10^{13}\,\text{rad.s}^{-1}$$

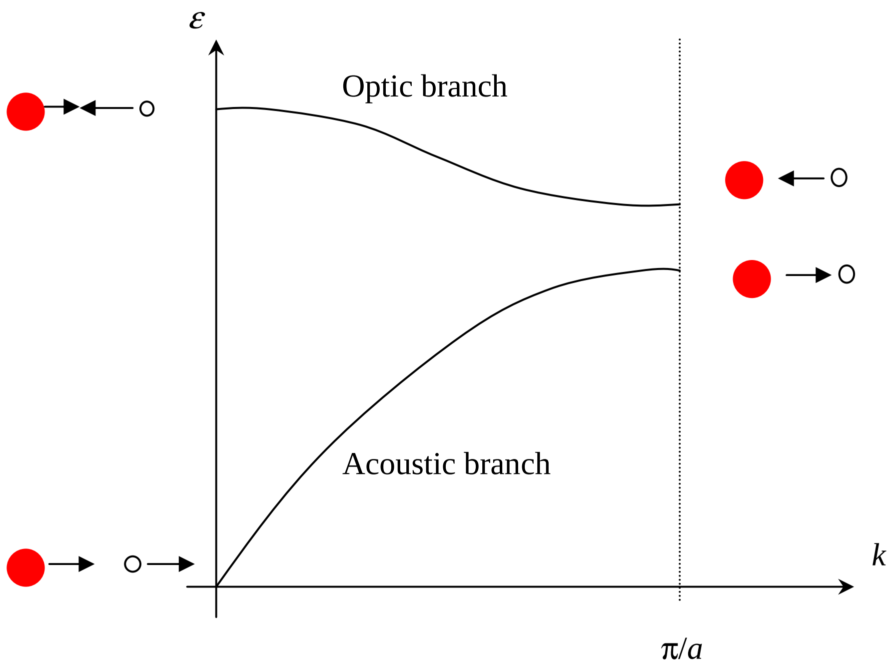
so that the maximum frequencies of lattice vibrations are THz (10^{12} Hz).

For more than one atom per unit cell the picture is much more complicated:



If atomic spacing $d=a/2$

$$\omega^2 = \alpha\left(\frac{1}{m}+\frac{1}{M}\right) \pm \alpha\sqrt{\left(\frac{1}{m}+\frac{1}{M}\right)^2 - \frac{4\sin(ka/2)}{mM}}$$



Acoustical branch has ω=0 at k=0
Optic branch has $\omega\neq0$ at k=0

At k=0:

- On the acoustic branch, atoms move in phase

● On optic branch, atoms move in antiphase, keeping the centre of mass of the unit cell static

● If atoms have different charges, optic mode gives oscillation dipole moment to the unit cell. This dipole moment can couple to an electromagnetic field – hence this branch is called the optic branch

At $k=\pi/a$:

● Only one atomic species moves in each mode

SCATTERING BY CHARGED IMPURITIES

Assume that a carrier is scattered when its potential energy in the field of the scatterer is similar to its kinetic energy. The Coulombic potential at distance *r*

$$V \propto \frac{1}{r}$$

The kinetic energy is thermal so $\varepsilon \propto T$

Therefore we can define the effective radius of the scatterer as

$$r_s \propto \frac{1}{T}$$

Hence we get a scattering cross-section

$$\pi r_s^2 \propto T^{-2}$$

The rate at which the carrier encounters scatterers is proportional to the carrier thermal velocity

$$v_{\text{thermal}} \propto \sqrt{T}$$

so overall $\boxed{p_{\text{scatt}} \propto T^{-3/2}}$

SCATTERING BY LATTICE VIBRATIONS (PHONONS)

Probability of interacting with a phonon is proportional to the number of phonons, which is proportional to *T* at room temperature (see previous section on phonons). Again the rate at which carriers pass though the crystal is determined by the thermal velocity

$v_{\text{thermal}} \propto \sqrt{T}$ so $\boxed{p_{\text{scatt}} \propto T^{3/2}}$

OVERALL EFFECT

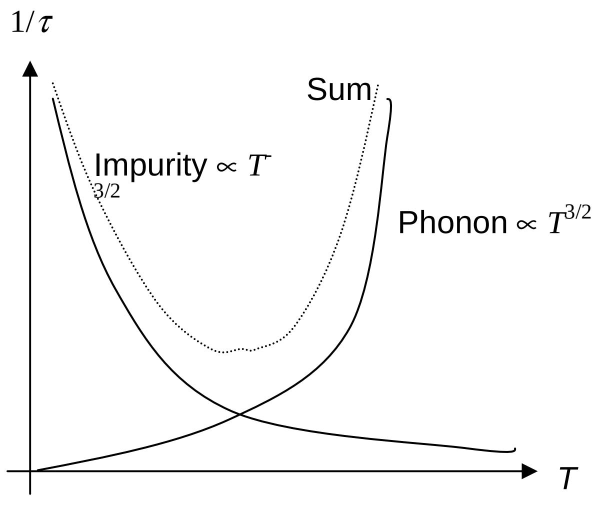
Two scattering mechanism with scattering times τ_1 and τ_2 can be represented by a single scattering time τ calculated by

$$\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}$$

So considering charged impurity scattering and phonon scattering

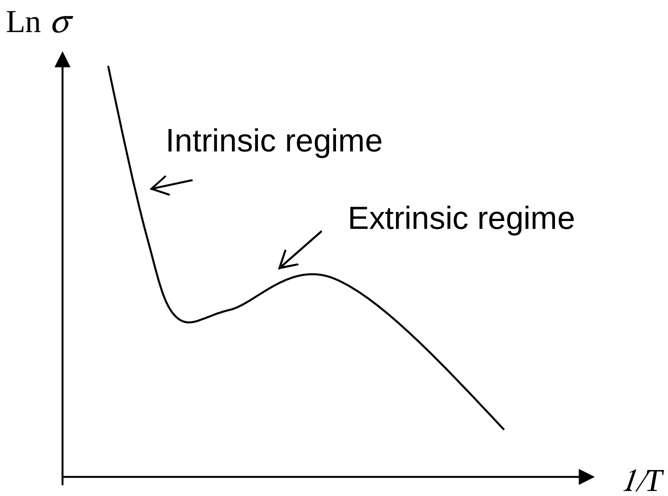
$$\frac{1}{\tau} = \frac{1}{\tau_{\text{Im}\,p}} + \frac{1}{\tau_{Phonon}}$$

(Remember that the probability of scattering is equal to $1/\tau$)



Mobility peaks at intermediate temperatures – typically 100-200 K

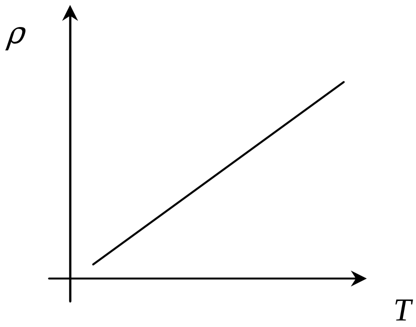
To find the conductivity we need to multiply by the number of carriers giving the result in the following graph



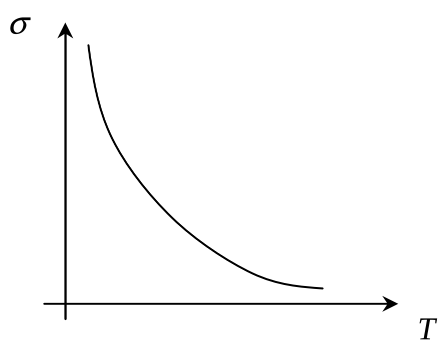
ELECTRICAL CONDUCTIVITY IN METALS

Not easy to treat theoretically. Phonon scattering dominates scattering in metals because the high electron concentration screens charged impurities. Scattering time depends on the details of the electron-phonon interaction.

Empirically find that resistivity is proportional to temperature for *T* in the range 100-300 K

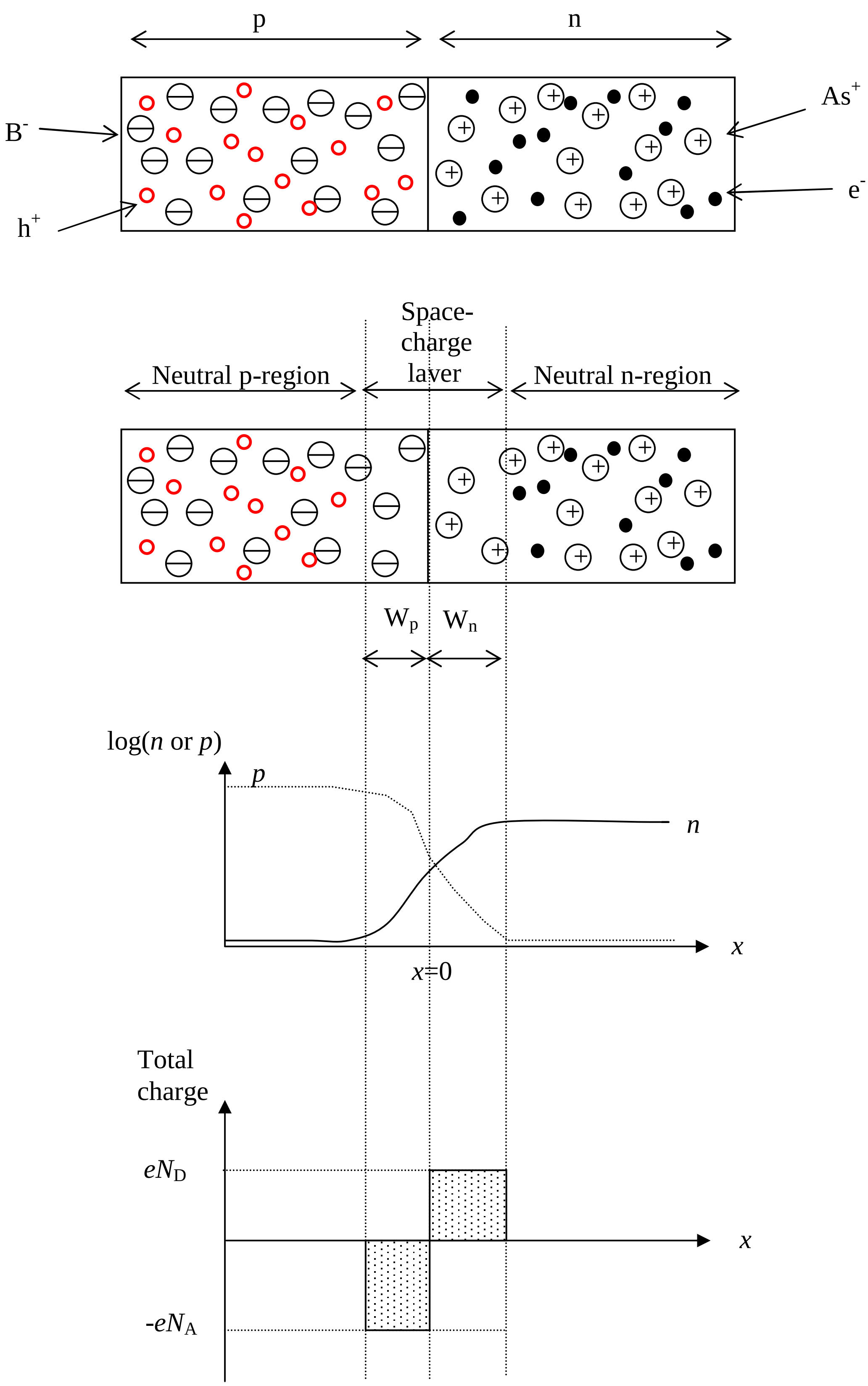


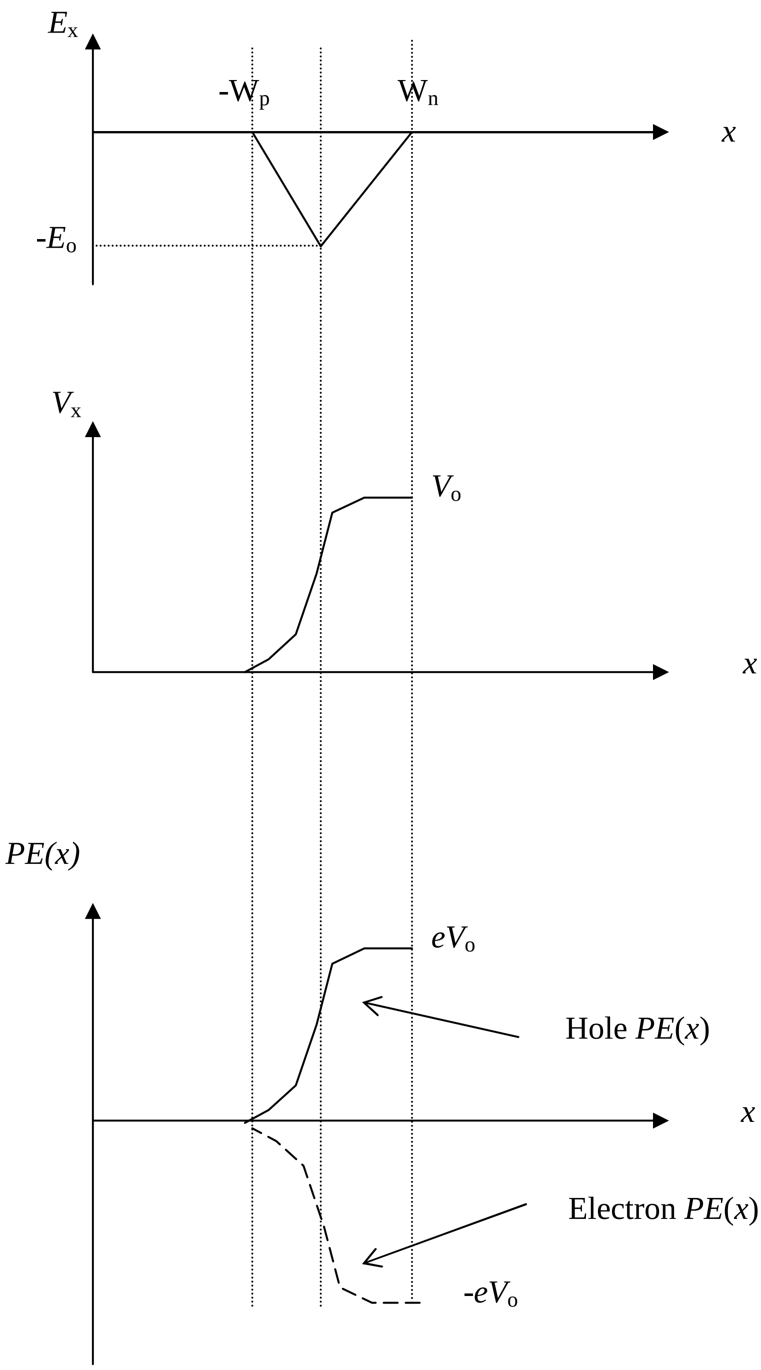
or



8. THE PN JUNCTION

IDEAL pn JUNCTION

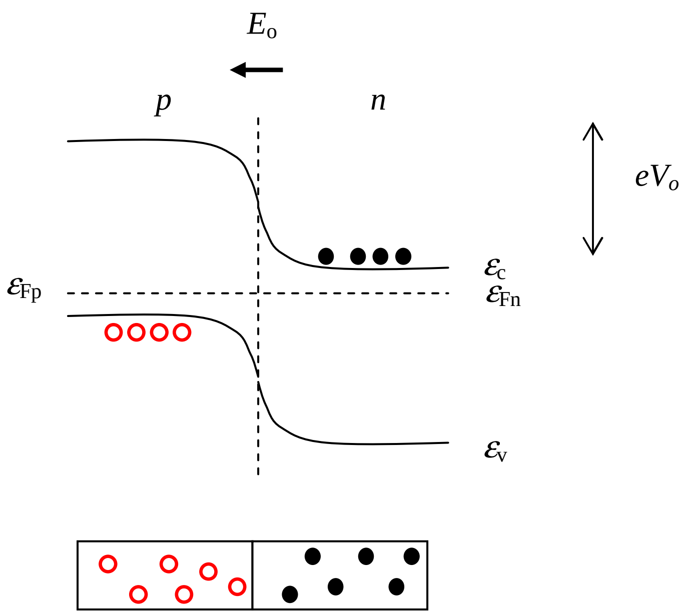




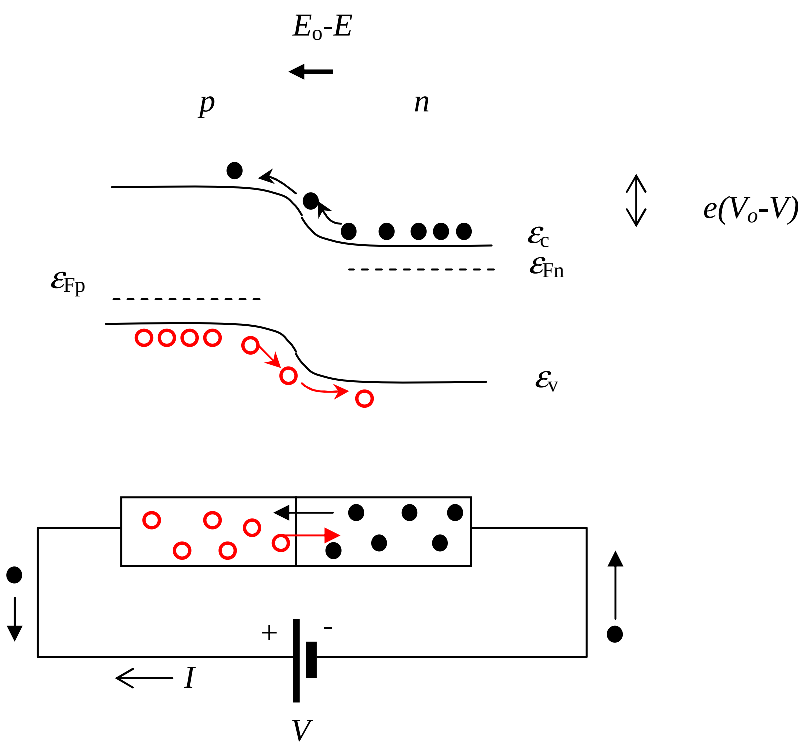
E_x
$-W_p$
W_n
x
$-E_o$
V_x
V_o
x
$PE(x)$
eV_o
Hole $PE(x)$
x
Electron $PE(x)$
$-eV_o$

IDEAL pn JUNCTION: BAND PICTURE

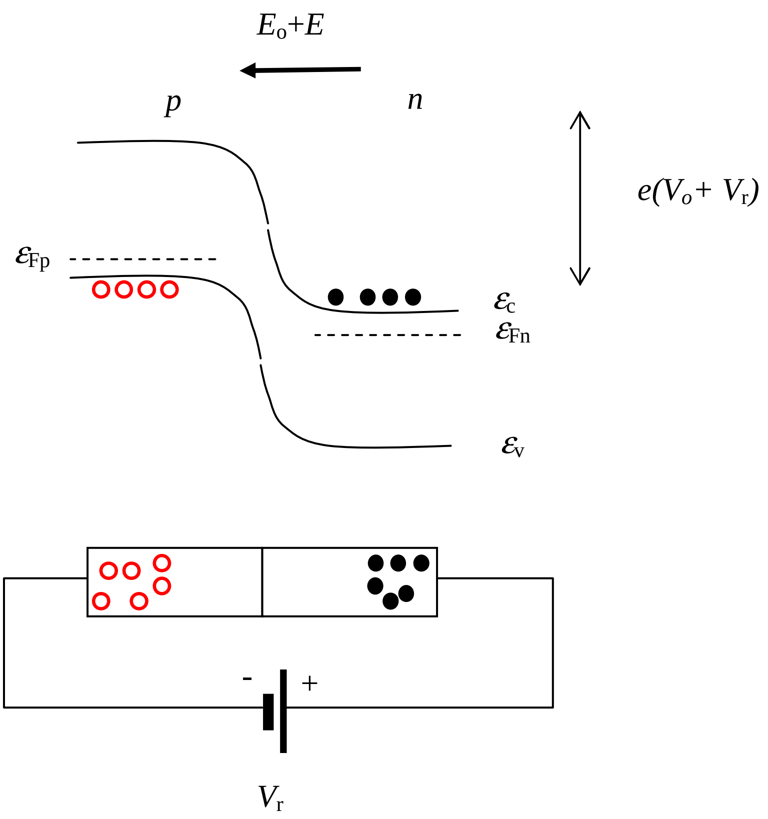
Open circuit



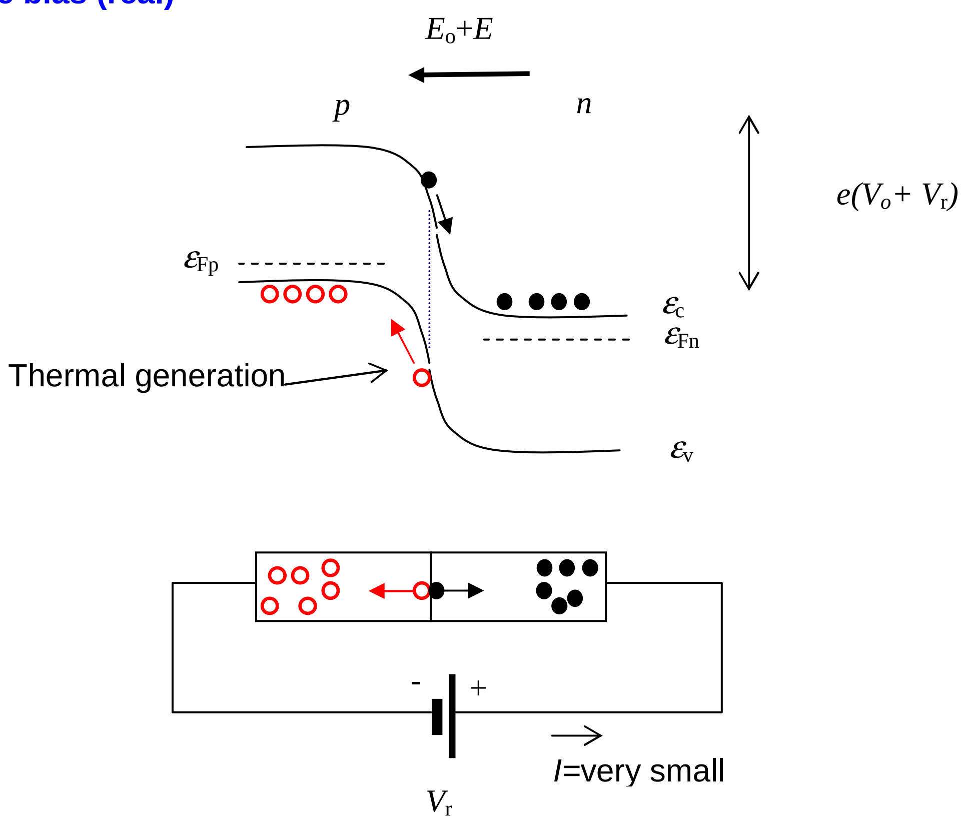
Forward bias



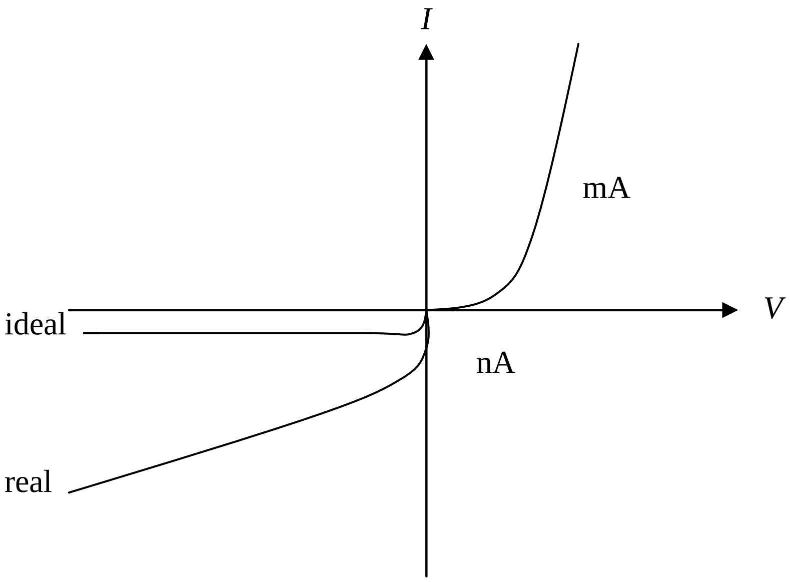
Reverse bias (ideal)



Reverse bias (real)



pn JUNCTION: *I-V* CHARACTERISTIC

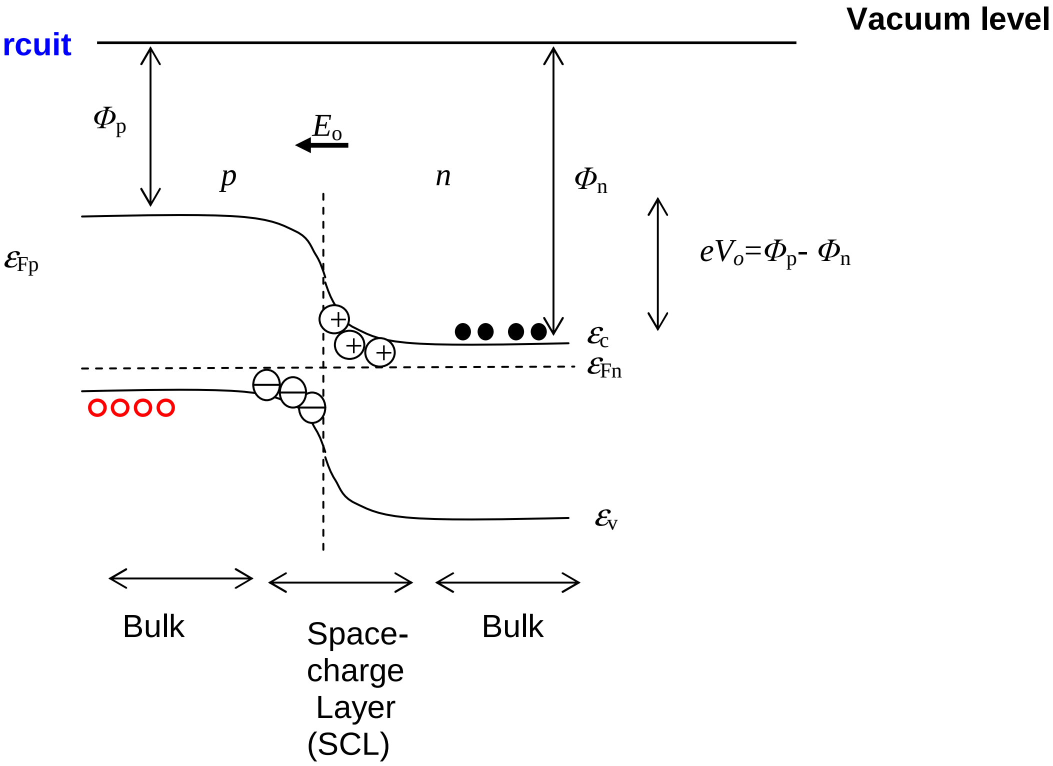


NB note the difference in scales

pn junction basis of: diode, bipolar transistor, photodetector, solar cell…

pn JUNCTION: CURRENT FLOWS

Open circuit



Work Function, Φ: external work done to remove electron from solid (measured in J or eV relative to the **vacuum level**)

For semiconductor Φ_n: external energy required to remove electron from ε_c to vacuum

Therefore, the built in potential is related to work function in the n- and p-regions by:

$$eV_o=\Phi_p- \Phi_n$$

Far away from the junction $\varepsilon_c - \varepsilon_{Fn}$ and $\varepsilon_v - \varepsilon_{Fp}$ are the same as before the junction was made.

When the junction is made, electrons and hole diffuse toward each other and recombine close to the n-p interface: this gives rise to the SCL (fixed, immobile charge).

The electrostatic potential energy decreases from 0 inside the p-region to -eV_o inside the n-region. The total energy of an electron must decrease going from the p- to the n-region by eV_o, i.e. an electron on the n-region at ε_c must overcome and energy barrier eV_o to go over to ε_c in the p-region.

In the SCL region, ε_F is much less close to ε_c or ε_v than in the n- or p-regions, therefore the carrier density is much lower in the SCL.

There are TWO sources of current density for each charge carrier:

J_{diff}=diffusion of electons (holes) from n-(p-) to p-(n-)region (driven by the concentration gradient)

J_{drift}=electrons(holes) drifting in the built in electric field from p- (n-) region to the n-(p-)region (NB opposite direction to J_{diff})

In open circuit conditions $J_{diff}(0) + J_{drift}(0) = 0$

The probability of overcoming the built-in potential is proportional to exp($-eV_o/kT$) : c.f. equation for n in an intrinsic semiconductor.

$J_{diff}(0)=A \exp(-eV_o/kT)$, where A=constant

Forward bias

When the *pn* junction is forward biased the majority of the applied voltage drops across the SCL with the applied voltage in opposition to the built-in voltage V_o. The potential energy barrier is now reduced from eV_o to $e(V_o - V)$, where V is the applied bias voltage so the diffusion current density is given by:

$$J_{\text{diff}}(V) = A\exp\left[-\frac{e(V_0 - V)}{kT}\right]$$

There is still a drift current density $J_{\text{drift}}(V)$ due to electron drift in the new electric field in the SCL, E_o-E so the total current is given by:

$J = J_{\text{diff}}(V) + J_{\text{drift}}(V)$.

$J_{\text{drift}}(V)$ is very difficult to calculate so use approximation

$J_{\text{drift}}(V) = J_{\text{drift}}(0)$

$J = J_{\text{diff}}(V) + J_{\text{drift}}(0)$, hence

$$J \approx J_{diff}(V) + J_{drift}(0) = J_{diff}(V) - J_{diff}(0) = A\exp\left[-\frac{e(V_0 - V)}{kT}\right] - A\exp\left[\frac{-eV_0}{kT}\right]$$

$$J \approx A\exp\left(-\frac{eV_0}{kT}\right)\left[\exp\left(\frac{eV}{kT}\right) - 1\right]$$

Add the hole contribution to get the **diode** equation:

$$\boxed{J = J_0\left[\exp\left(\frac{eV}{kT}\right) - 1\right]}$$

where J_0 is a temperature-dependant constant.

Reverse bias

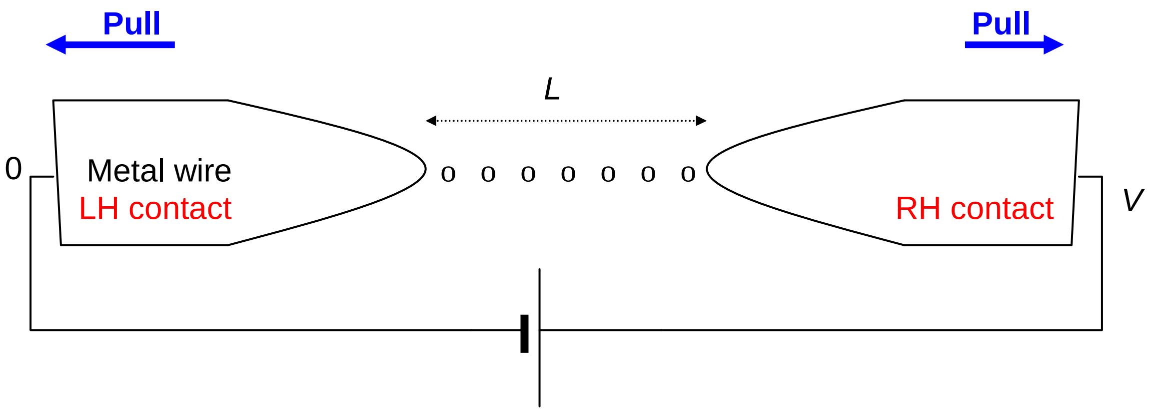
The reverse bias V=-V_r adds to the built-in potential V_o. The potential energy barrier becomes e(V_0 +V_r) hence there is negligible diffusion current density. There is a small drift current density due to thermal generation of electron-hole pairs in the SCL. The ideal reverse current is therefore small, independent of applied voltage, and proportional to the carrier thermal generation rate in the SCL. In real pn junctions we get more current due to avalanche and Zener breakdown.

9. QUANTUM WIRES

QUANTUM WIRES (SEMICLASSICAL DERIVATION)

Q. So far we have dealt with infinite 1D arrays of atoms, what happens when the array consists of just a few atoms?

Break junction experiment

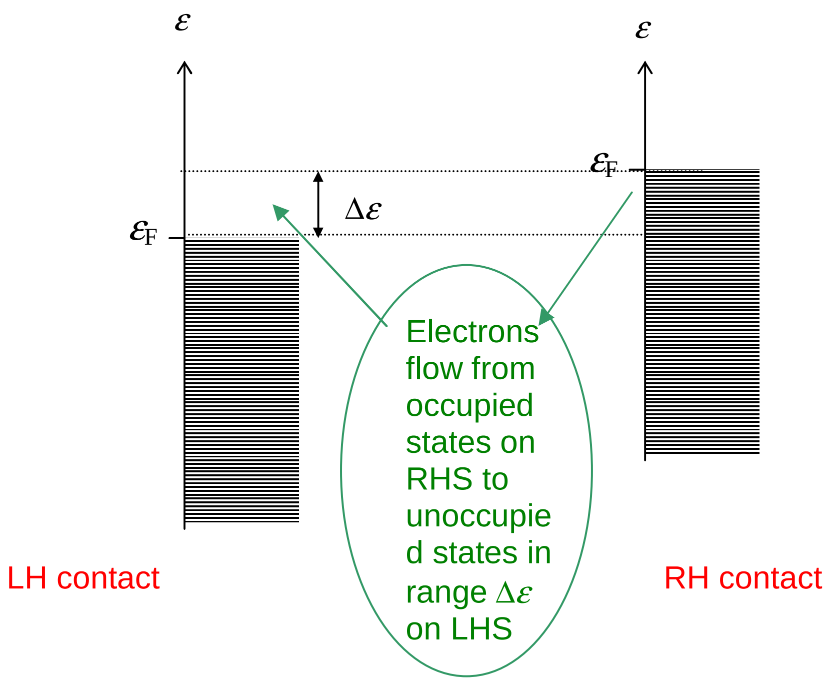


Current, $I=veN/L$, where N = total number of electrons in 1D wire length L

Conductance, $G = I/V = veN/LV$

Drop in potential energy of electron going from one end to the other, $\Delta\varepsilon = eV$

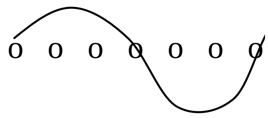
$$\Rightarrow \quad G = \frac{ve^2 N}{L\Delta\varepsilon}$$



N = 2 x number of quantum states in range $\Delta\varepsilon$

From Pauli principle

In 1D wire, only discrete values of electron wavelength λ are possible



$$\lambda_n = \frac{L}{n} \qquad n=1,2,3\ldots\ldots$$

Remember momentum is related to wavevector by $m\mathbf{v} = \hbar\mathbf{k} \;\Rightarrow\; mv = h/\lambda$

Electron velocity, $v = \dfrac{h}{\lambda m} \quad \Rightarrow \quad v_n = \dfrac{nh}{Lm}$

$\Rightarrow$ Number of electrons in velocity range Δv, $N = 2\dfrac{Lm\Delta v}{h}$

Also, kinetic energy of electron, $\varepsilon = \dfrac{mv^2}{2}, \;\Rightarrow\; \Delta\varepsilon = mv\Delta v \;\Rightarrow\; N = 2\dfrac{L\Delta\varepsilon}{vh}$

$$\Rightarrow \boxed{G = \frac{2e^2}{h} \quad \text{Ohms}^{-1}}$$

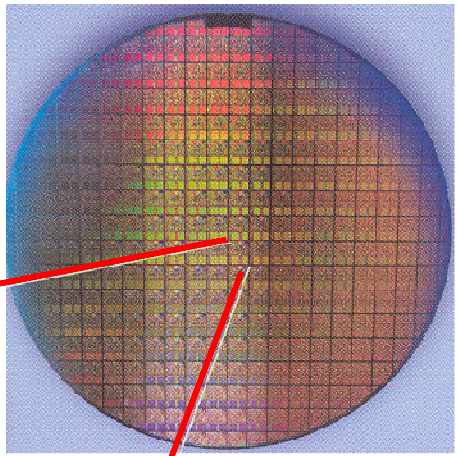
Remarkable result!!! Answer is *completely* independent of system parameters, i.e. temperature, sample material, sample dimensions, etc.

Called the 'conductance quantum' = 7.73 x 10 $^{-5}$ Ohms^{-1}

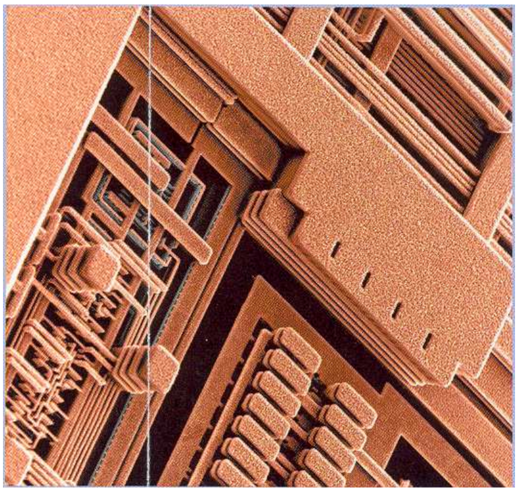
$\Rightarrow$ **Quantum of resistance = 1/*G* = 12.9 kΩ**

10. FUNCTIONAL MATERIALS: FABRICATION METHODS

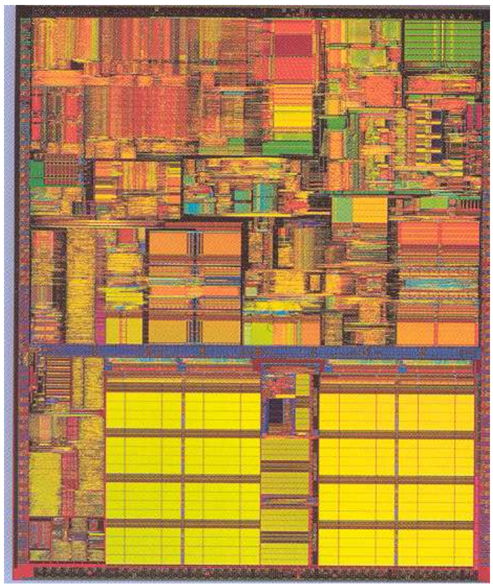
SILCON WAFER



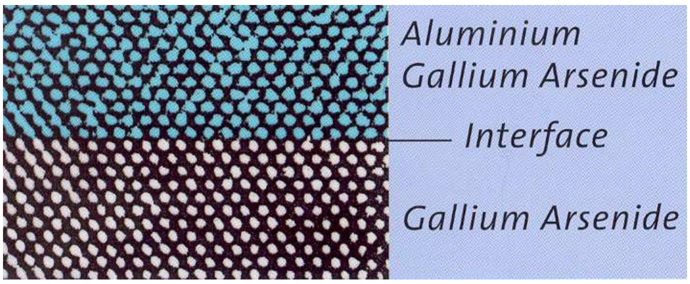
Detail

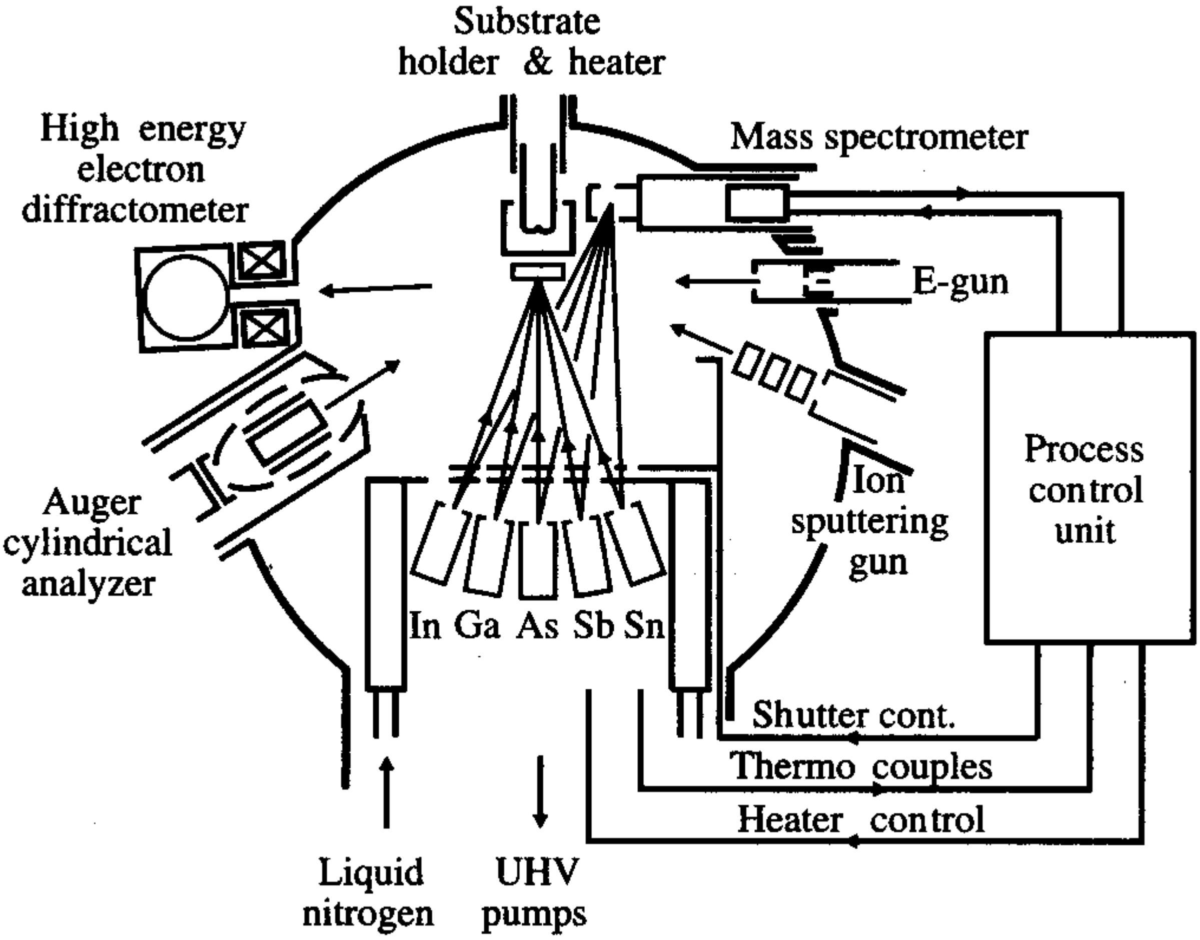


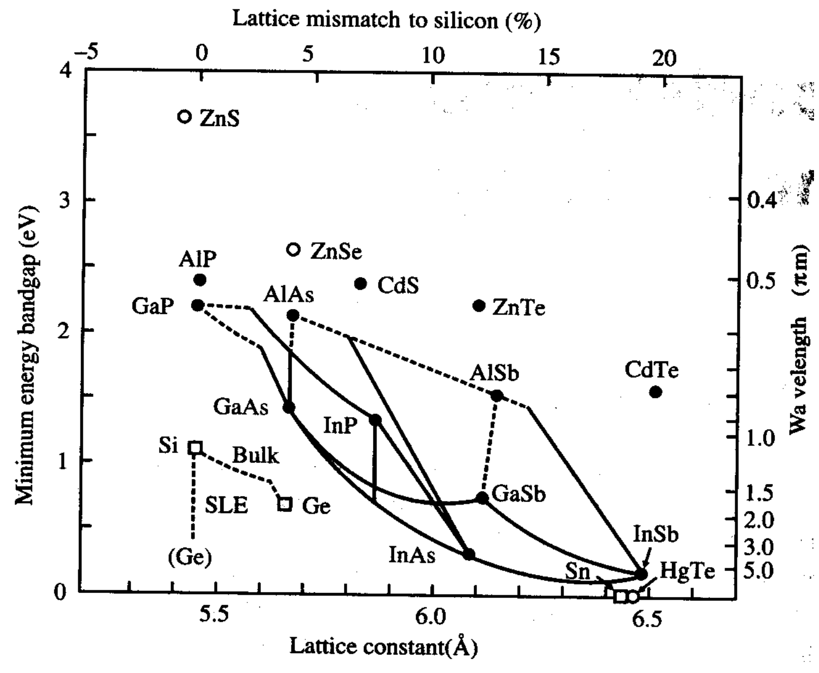
Circuit



MOLECULAR BEAM EPITAXY (MBE)




Substrate
holder & heater
High energy
electron
diffractometer
Mass spectrometer
E-gun
Process
control
unit
Ion
sputtering
gun
Auger
cylindrical
analyzer
In Ga As Sb Sn
Shutter cont.
Thermo couples
Heater control
Liquid
nitrogen
UHV
pumps


Lattice mismatch to silicon (%)
–5
0
5
10
15
20
Minimum energy bandgap (eV)
4
3
2
1
0
Wa velength (πm)
0.4
0.5
1.0
1.5
2.0
3.0
5.0
ZnS
ZnSe
AlP
GaP
AlAs
CdS
ZnTe
AlSb
CdTe
GaAs
InP
Si
Bulk
SLE
Ge
GaSb
(Ge)
InAs
InSb
Sn
HgTe
5.5
6.0
6.5
Lattice constant(Å)

METAL ORGANIC CHEMICAL VAPOUR DEPOSITION (MOCVD)