# Quantum Condensed Matter Physics
## Lecture 5



## David Ritchie

# Quantum Condensed Matter Physics

1. Classical and Semi-classical  models for electrons in solids (3L)

2. Electrons and phonons in periodic solids (6L)

Types of bonding; Van der Waals, ionic, covalent. Crystal structures. Reciprocal space, *x-ray diffraction and Brillouin zones. Lattice dynamics and phonons; 1D monoatomic and diatomic chains, 3D crystals*. Heat capacity due to lattice vibrations; Einstein and Debye models. Thermal conductivity of insulators. Electrons in a periodic potential; Bloch's theorem. Nearly free electron approximation; plane waves and bandgaps. Tight binding approximation; linear combination of atomic orbitals, linear chain and three dimensions, two bands. Pseudopotentials.. ……….

3. Experimental probes of band structure (4L)

4. Semiconductors and semiconductor devices (5L)

5. Electronic instabilities (2L)

6. Fermi Liquids (2L)

# The reciprocal lattice and diffraction

- Reciprocal lattice concept arises from scattering of waves by crystals.
- Builds on Fraunhofer diffraction from a grating generalised to scattering from a 3D periodic lattice.
- Consider scattering of a plane wave off a single atom or more generally the basis forming the unit cell

- Incoming wave of wavevector $\mathbf{k}_0$ is incident on potential centred at $\mathbf{R}_i$
- At large distances scattered wave is circular
- Total field taken as a scalar

$$\psi \propto e^{i\mathbf{k}_0 \cdot (\mathbf{r}-\mathbf{R}_i)} + f \frac{e^{ik_0|\mathbf{r}-\mathbf{R}_i|}}{|\mathbf{r}-\mathbf{R}_i|}$$

- Details of scattering buried in Form Factor $f$
- This is a function of scattering angle, type and arrangement of atoms etc.
- Total scattered intensity assumed small
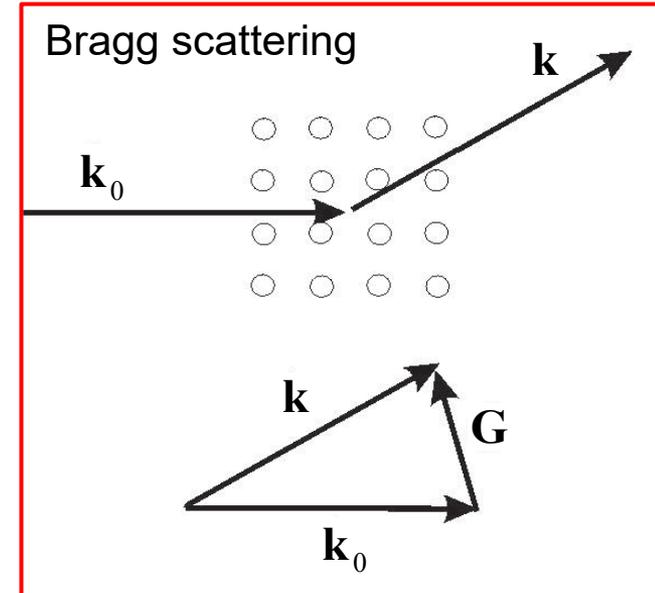
# The reciprocal lattice and diffraction

- At large distance from the scattering centre $k_0 \mid \mathbf{r} - \mathbf{R}_i \mid \approx k_0 r - k_0 \left( \frac{\mathbf{r} \cdot \mathbf{R}_i}{r} \right)$

- Defining scattered wavevector $\mathbf{k} = k_0 \left( \frac{\mathbf{r}}{r} \right)$ momentum transfer $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$

- The waveform is given by: $\psi \propto e^{-i\mathbf{k}_0 \cdot \mathbf{R}_i} \left[ e^{i\mathbf{k}_0 \cdot \mathbf{r}} + c e^{ik_0 r} f \dfrac{e^{-i\mathbf{q} \cdot \mathbf{R}_i}}{r} \right]$

- Effective scattering amplitude $f(\theta) = f \exp[-i\mathbf{q} \cdot \mathbf{R}_i]$

- Summing over identical lattice sites the scattered intensity is proportional to the differential scattering cross-section:

$$\frac{d\sigma}{d\Omega} = \left| f(\theta) \right|^2 = \left| f \sum_{\mathbf{R}_i} \exp[-i\mathbf{q} \cdot \mathbf{R}_i] \right|^2$$

- We add terms with different phases $\mathbf{q} \cdot \mathbf{R}_i$ leading to cancellation unless Bragg condition $\mathbf{q} \cdot \mathbf{R} = 2\pi m$ is satisfied for all $\mathbf{R}$ with $m$ an integer

- If two vectors satisfy the Bragg condition then so will their sum hence the special values of $\mathbf{q} \equiv \mathbf{G}$ satisfying this lie on a *reciprocal lattice*

- Primitive vectors of the reciprocal lattice in terms of real space lattice primitive vectors:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3} \quad \text{and cyclic permutations}$$

# Diffraction conditions

- For elastic scattering conservation of energy requires $\left|\mathbf{k}\right| = \left|\mathbf{k}_0\right|$ and Bragg condition requires $\mathbf{k} - \mathbf{k_o} = \mathbf{G}$ where $\mathbf{G}$ is a reciprocal lattice vector

- Combining these two conditions $\mathbf{k} \cdot \mathbf{G} / 2 = \left(\mathbf{G} / 2\right)^2$

- This defines a plane perpendicular to $\mathbf{G}$ which intersects $\mathbf{G}$ at its midpoint

- The set of all such planes defines the incident wavevectors that satisfy the conditions for diffraction

- Ewald construction – in reciprocal space
- Reciprocal lattice points shown
- $\mathbf{k}_0$ incident wavevector with origin chosen (point $a$) so it ends on a reciprocal lattice point
- Sphere radius $\left|\mathbf{k}_0\right|$ drawn about origin of $\left|\mathbf{k}_0\right|$
- Diffracted beam forms if sphere intersects any other reciprocal lattice point

- Origin of $\mathbf{k}_0$ is on perpendicular bisector of $\mathbf{G}$
- Angle $\theta$ is the Bragg angle and we obtain

$$2\left|\mathbf{k}\right|\sin\theta = \left|\mathbf{G}\right|$$
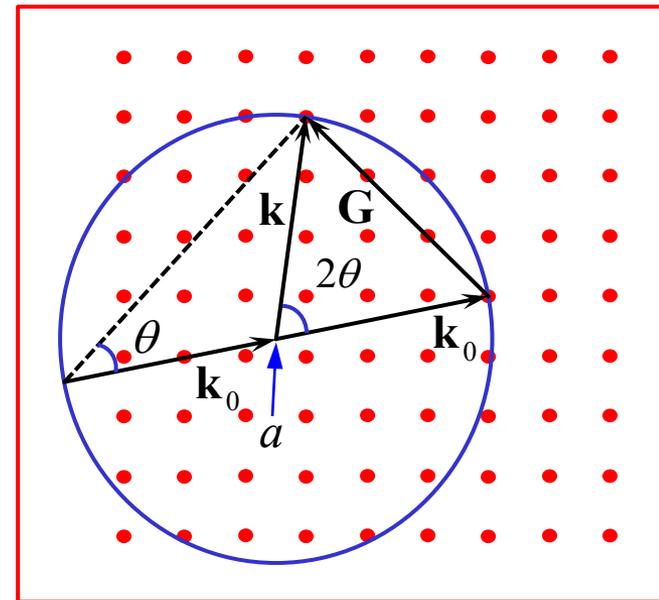
# Diffraction conditions

- From last slide $2|\mathbf{k}|\sin\theta = |\mathbf{G}|$

- The spacing between parallel lattice planes perpendicular to $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is given by $d(hkl) = 2\pi / |\mathbf{G}|$

- Given that $|\mathbf{k}| = 2\pi / \lambda$ we can write

$$2(2\pi / \lambda)\sin\theta = 2\pi / d(hkl) \Rightarrow 2d(hkl)\sin\theta = \lambda$$

- Where $\theta$ is the angle between the incident beam and the crystal planes and equals half the angle of deflection

- The indices defining an actual crystal plane may contain a common factor $n$ and we can generalize this equation to give the conventional form of Bragg's law:

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

# High resolution x-ray diffraction

- Find thickness and composition of SiGe thin films on Si substrates

- From Bragg's law thickness

$$t = \lambda \left( 2 \cos \omega \Delta \omega \right)^{-1}$$

- Vertical lattice constants $c_L, c_S$ found from

$$\frac{c_L}{c_S} = \frac{\sin \omega_S}{\sin \omega_L}$$

- Hence concentration of Ge found
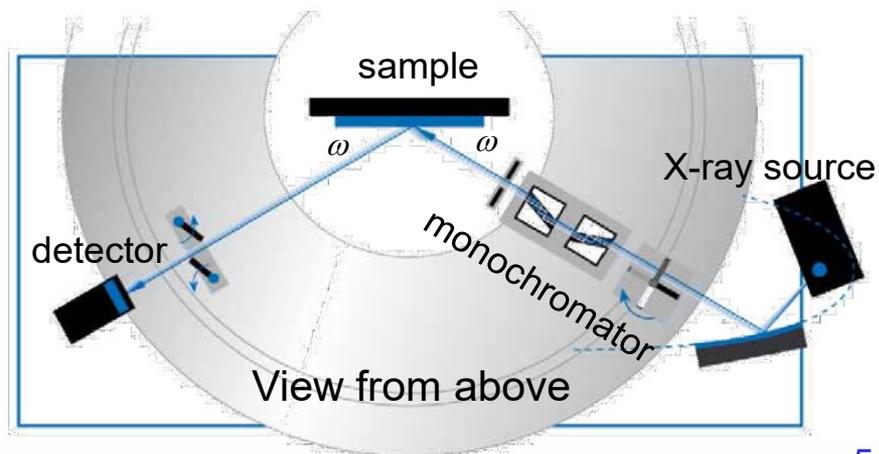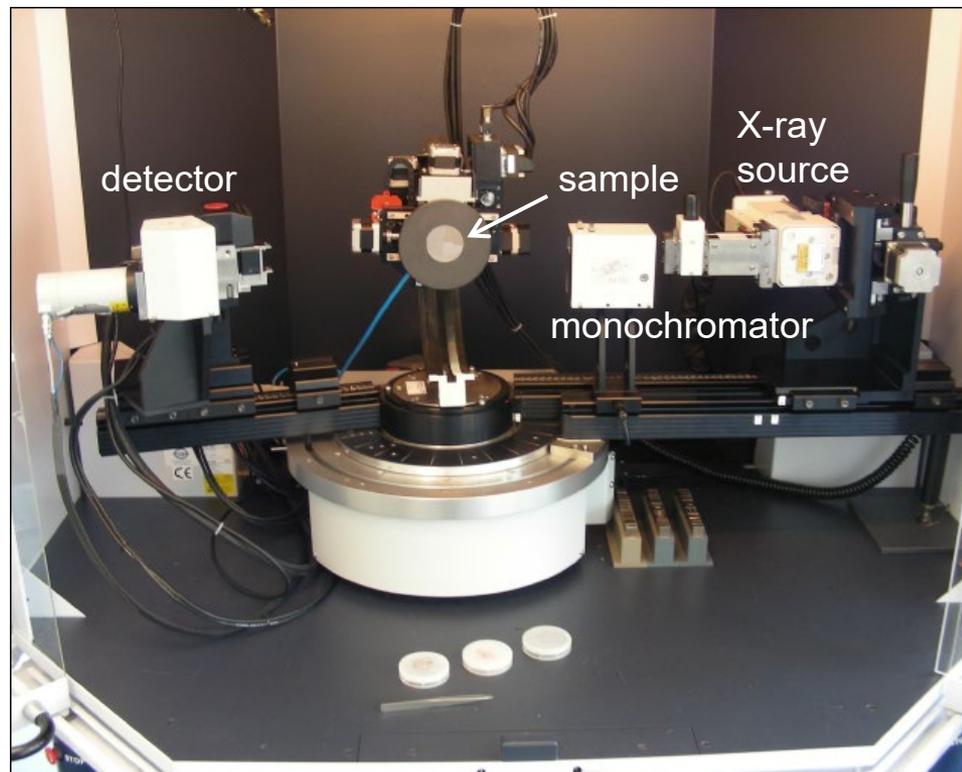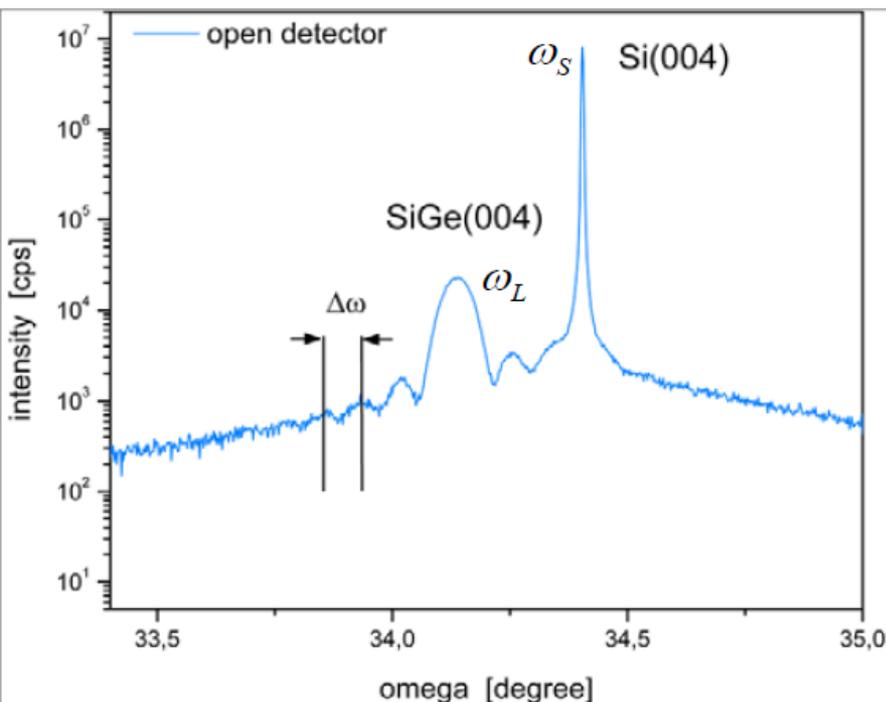
# X-ray analysis of superlattice structure

100nm GaAs

3nm $In_{0.15}Ga_{0.85}As$

$d_{SL}$

15 x

26nm GaAs

substrate GaAs
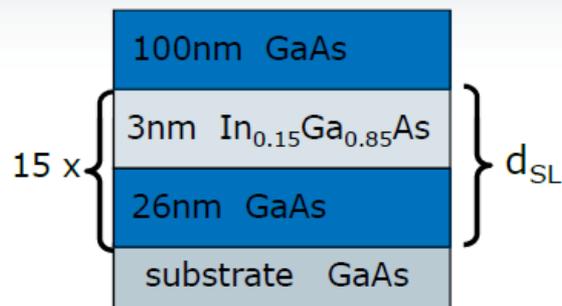
- Position of zero-th order SL peak: $<\Delta c / c>$

- Distance between SL-peaks: $d_{SL} \approx \dfrac{\lambda}{2 \cos\theta \, \Delta\theta}$

measurement

GaAs(004)

SL 0

$\Delta\theta$

SL -1

SL +1

SL -2

SL +2

Intensity [counts]

$2\theta$ [degrees]
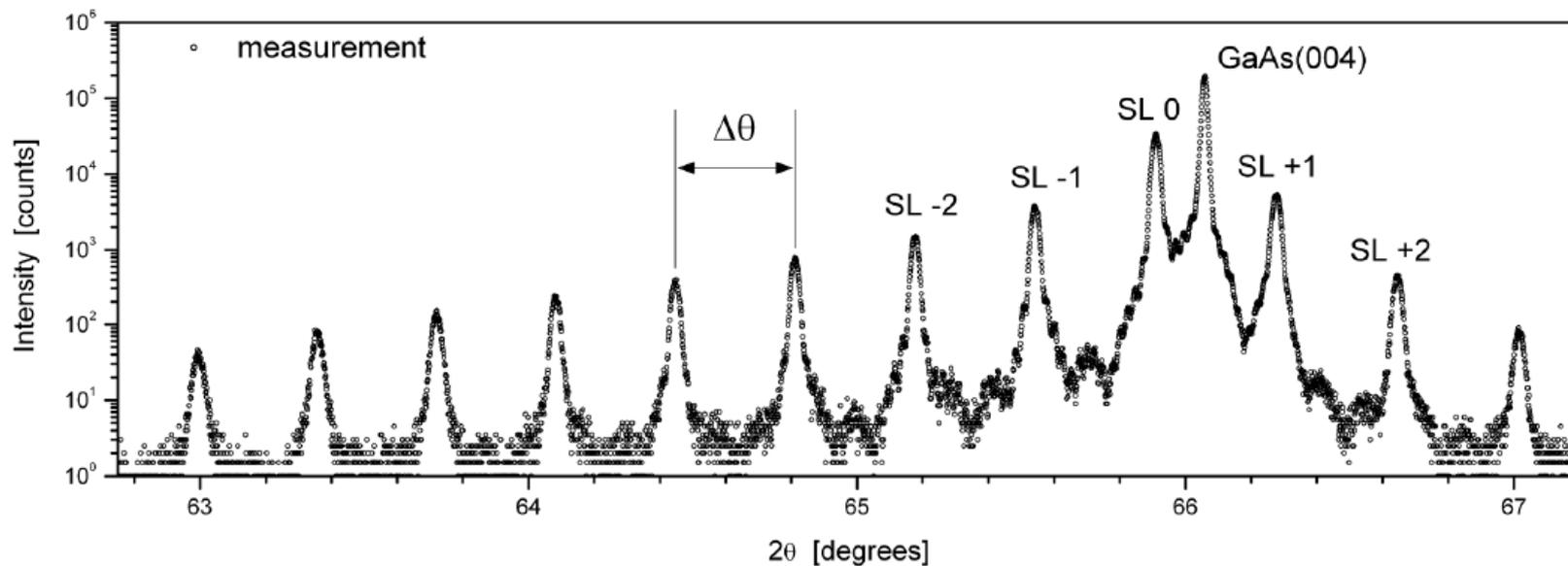
# Diffraction conditions and Brillouin zones

- The set of reciprocal space planes satisfying the Bragg condition is constructed by finding those planes which are perpendicular bisectors of every reciprocal lattice vector $\mathbf{G}$.

- The planes so constructed divide reciprocal space up into cells. The cell closest to the origin is called the first Brillouin zone. The $n^{th}$ Brillouin zone consists of all the fragments exterior to the $(n-1)^{th}$ plane but interior to the $n^{th}$ plane.

- The first Brillouin zone is the Wigner-Seitz cell of the reciprocal lattice which has an important role in discussion of electronic states in a periodic potential.



Legend:
- ● Reciprocal lattice point
- ← Reciprocal lattice vector
- ⋯⋯ vector perpendicular bisector
- ▮ (yellow) 1st Brillouin zone
- ▮ (cyan) 2nd Brillouin zone

- The volume of each Brillouin zone (adding up the fragments) is equal to the volume of the primitive unit cell of the reciprocal lattice, which is $(2\pi)^3/\Omega_{cell}$ where $\Omega_{cell}$ is the volume of the primitive unit cell of the crystal.
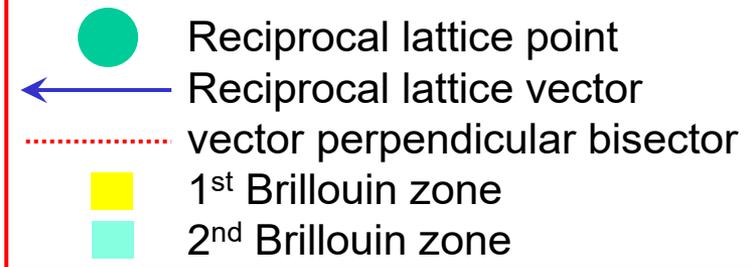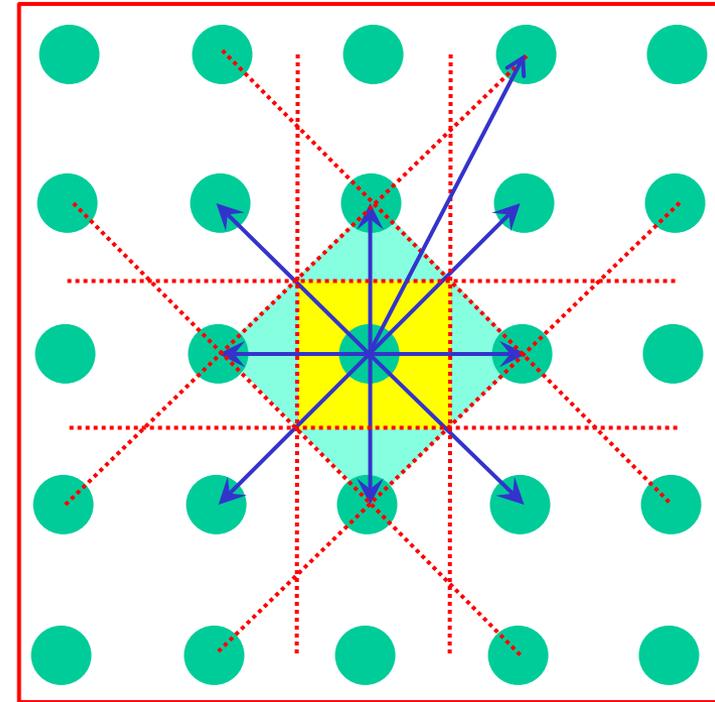
# Brillouin zone in 3D

- Using $\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \wedge \mathbf{a}_3}{\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3}$ etc we can calculate primitive vectors in reciprocal space for a number of lattices

- Reciprocal lattice of simple cubic lattice is also simple cubic

- Reciprocal lattice of face centred cubic is body centred cubic

- Reciprocal lattice of body centred cubic is face centred cubic

- Example: face centered cubic lattice
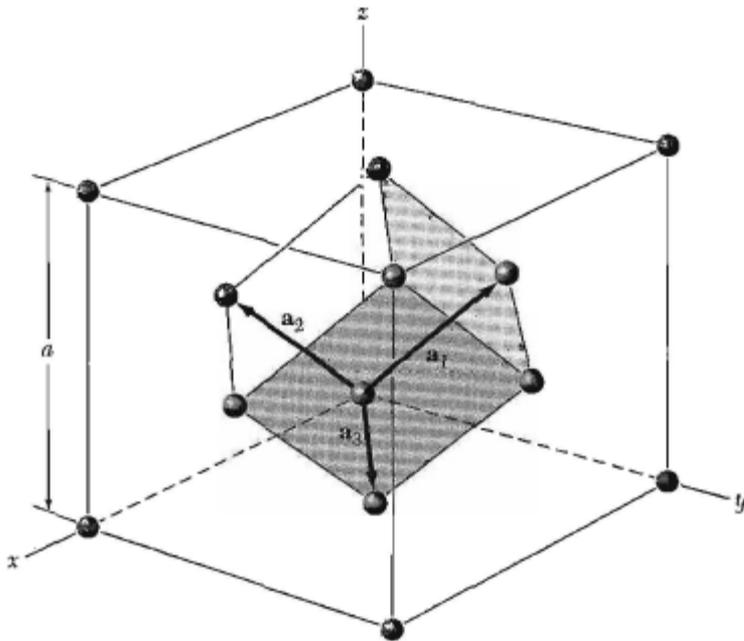
Primitive vectors of FCC lattice
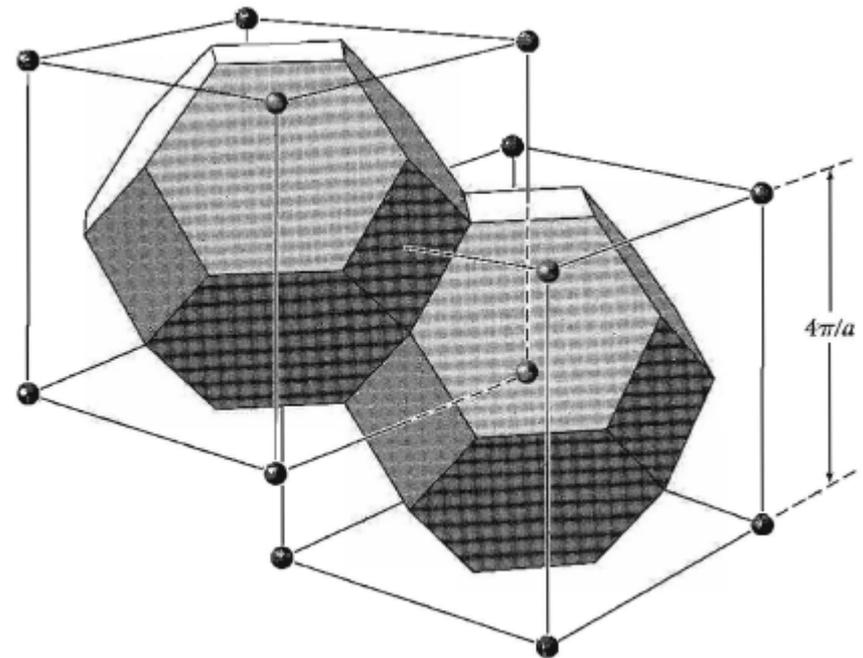
Reciprocal lattice of FCC is BCC
Brillouin zones shown

(Taken from Kittel)

# Lattice dynamics and phonons – 1D monatomic chain

- Consider a row of identical atoms distance $a$ apart connected by springs of constant $K$ and free to move horizontally
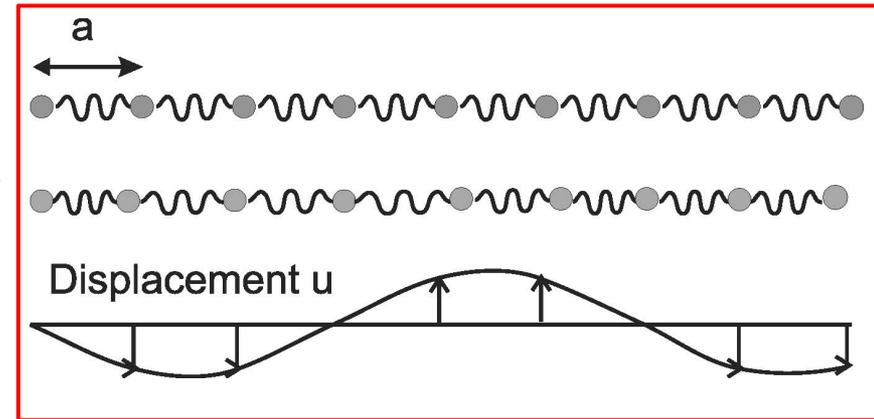
- Displacement of $n^{th}$ atom at point $r_n = na$ is given by $u_n$, equation of motion:

$$m \frac{\partial^2 u_n}{\partial t^2} = K(u_{n+1} - u_n) + K(u_{n-1} - u_n)$$

- We guess wave solution: $u_n(t) = u_o \cos(q r_n - \omega(q) t)$
  wavelength $\lambda = 2\pi / q$ and period $T = 2\pi / \omega(q)$

- Substituting into equation of motion we obtain

$$m\omega^2(q) = 2K(1 - \cos(qa)) = 4K \sin^2(qa / 2)$$

- Hence *dispersion relation* between frequency and wavevector

$$\omega(q) = 2(K / m)^{1/2} \sin(qa / 2)$$

# Lattice dynamics and phonons – 1D monatomic chain

- From last slide $\omega(q) = 2(K/m)^{1/2} \sin(qa/2)$

- Periodic in $q$ with period $2\pi/a$

- Long wavelength modes $(qa \to 0)$
  linear dispersion $\omega(q) = qa\sqrt{K/m}$

- Same as for a wire with tension $Ka$
  and density $m/a$

- compressive waves with velocity
  $$v = a(K/m)^{1/2}$$

- These waves behave like sound
  waves - *acoustic* mode
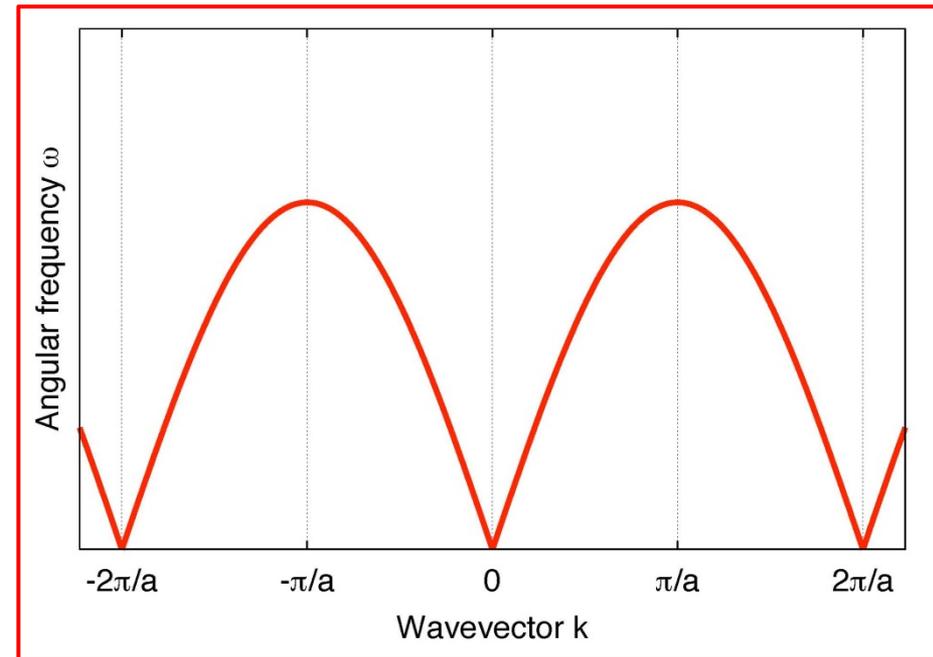


- For larger $q$ dispersion is periodic, phase shift between neighbouring atoms given by $e^{iqa}$

- So for $qa = 2\pi$ neighbouring atoms move in phase, for $qa = \pi$ they move in anti-phase

- We simplify things by only considering a range of $\frac{\pi}{a} \le q \le \frac{\pi}{a}$

- This corresponds to the first Brillouin zone

# Lattice dynamics and phonons – 1D diatomic chain

- The monoatomic chain contains only acoustic modes. The spectrum becomes more complicated with more atoms per unit cell.

- Assume two different atoms with different masses and spring constants
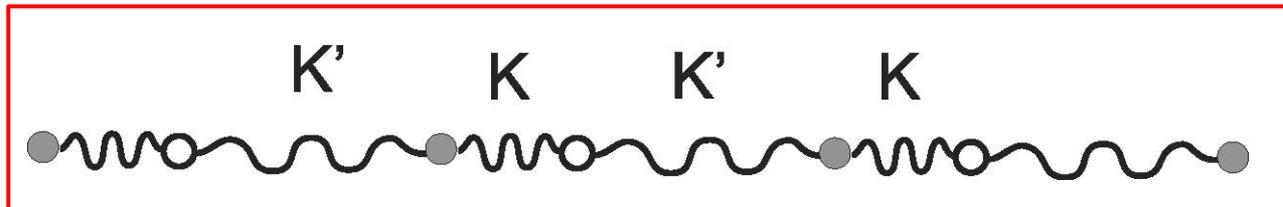


- There are two equations of motion

$$m_A \frac{\partial^2 u_{nA}}{\partial t^2} = K(u_{nB} - u_{nA}) + K'(u_{n-1,B} - u_{nA})$$

$$m_B \frac{\partial^2 u_{nB}}{\partial t^2} = K'(u_{n+1A} - u_{nB}) + K(u_{n,A} - u_{nB})$$

- The solution is quite complicated – so look at a limit

- Suppose the atoms are the same mass so $m_A = m_B$ and are quite strongly bonded in molecular pairs so $K \gg K'$

- Every 'molecule' will have a mode where the atoms oscillate out of phase at a frequency $\omega_o^2 = 2K/m$

# 1D diatomic chain – different spring constants

- The coordinate undergoing oscillation is $u_{opt}(q = 0) = u_A - u_B$
- We have assumed this is at $q = 0$ where each molecule undergoes the oscillation in phase with the next
- Since $K \gg K'$ the restoring force and frequency is largely independent of $q$

- There are two branches to the dispersion curve
- The acoustic branch the (low) frequency vanishes linearly with wavevector.
- The optical branch has finite (high) frequency as $q \to 0$ and is referred to as optical because of interaction with light
- Atomic displacements for two modes quite different



Note that $a_2$ is the distance between two 'molecules'
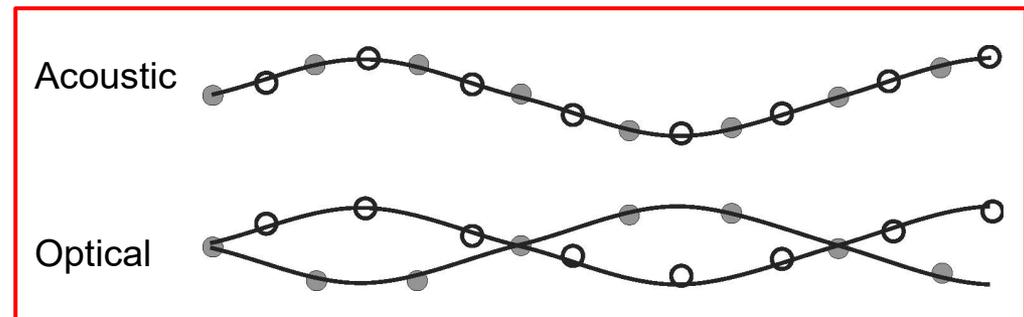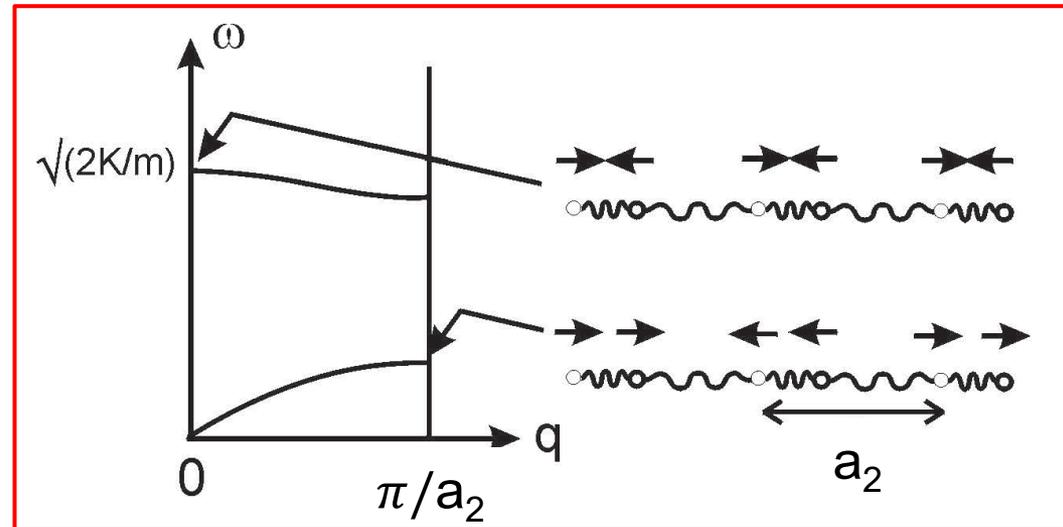
# 1D diatomic chain – different masses

- Using the equations of motion assuming $K' = K$ but $m_A \neq m_B$

$$m_A \frac{\partial^2 u_{nA}}{\partial t^2} = K(u_{nB} + u_{n-1,B} - 2u_{nA}), \quad m_B \frac{\partial^2 u_{nB}}{\partial t^2} = K(u_{n+1A} + u_{n,A} - 2u_{nB})$$

- With lattice constant $a$, substituting in travelling wave solutions with amplitudes $\alpha, \beta$ on alternate planes:

$$u_{nA} = \alpha \exp(inka) \exp(-i\omega t), \quad u_{nB} = \beta \exp(inka) \exp(-i\omega t)$$

and solving the simultaneous equations leads to

$$m_A m_B \omega^4 - 2K(m_A + m_B)\omega^2 + 2K^2(1 - \cos ka) = 0$$

- May be solved for $\omega^2$ - see diagram
- Assuming $k = \pm\pi/a$ or $ka \ll 1 \Rightarrow \cos ka = 1 - k^2 a^2 / 2$ we obtain the limiting results shown
- Notice there are no solutions for $\omega$ between $\sqrt{2K/m_A}$ and $\sqrt{2K/m_B}$
- If we look there for real $\omega$ solutions we find $k$ is complex – so wave is damped
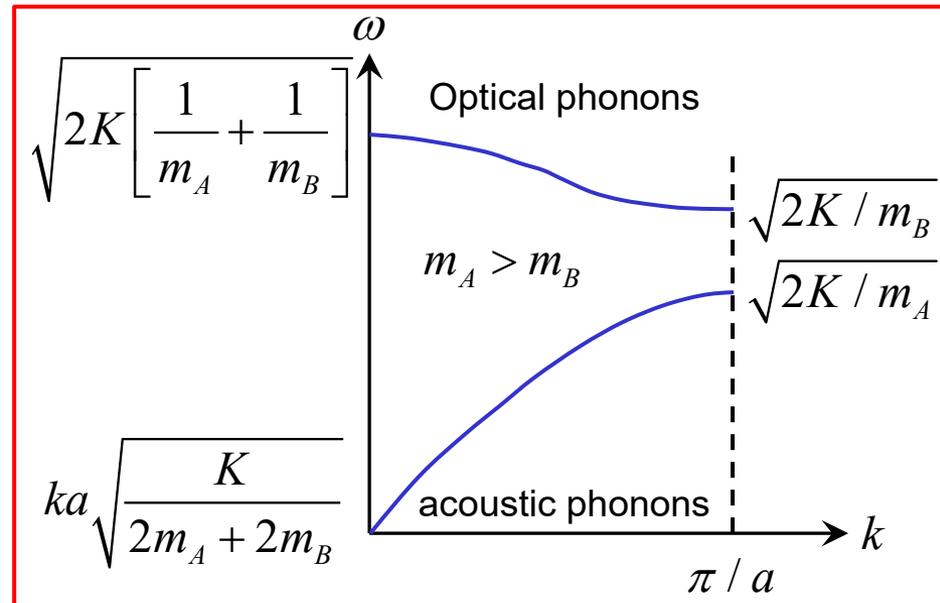
# Lattice dynamics and phonons – 3D crystal

- Extending to 3D requires a dispersion relation $\omega(\mathbf{k})$ describing waves propagating in different directions

- As well as compressional waves there are transverse waves resulting in three branches of phonons, two transverse and one longitudinal.

- There are always $3$ acoustic modes and for a solid with $m$ atoms per unit cell there will be $3(m-1)$ optical modes – again split into two transverse and one longitudinal.

- Phonon dispersion in Ge - each panel a different direction

- Diamond structure

- 2 atoms per unit cell

- Measured by inelastic neutron scattering
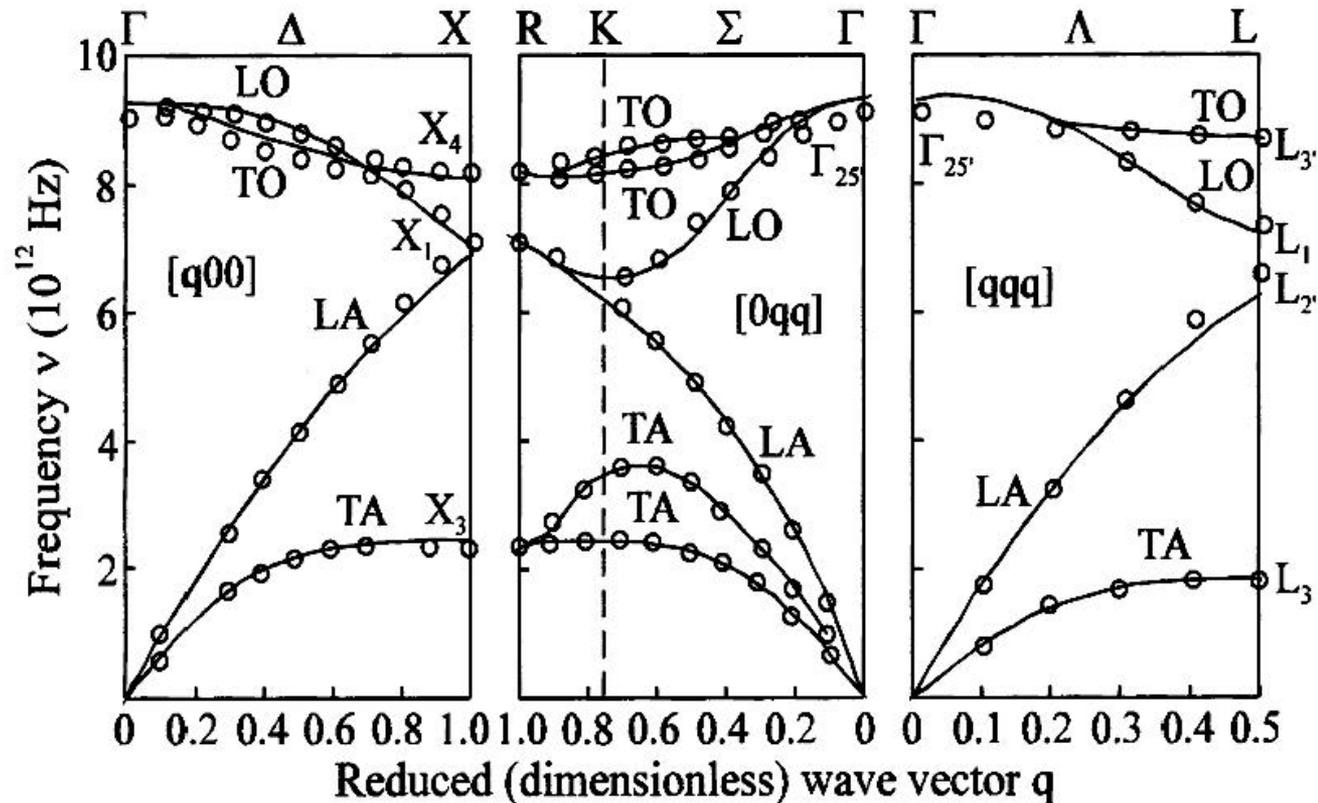
# Inelastic neutron scattering

- Incident neutron transfers some of its (well controlled) energy $\varepsilon$ and momentum $\hbar\mathbf{k}$ to phonon

- Measurement made of outgoing neutron energy and momentum $\varepsilon(\mathbf{k}'), \mathbf{k}'$

- Most common method for measuring phonon dispersion curves $E(\mathbf{Q})$

- Can also measure phonon lifetimes

- Quantitative technique, can measure throughout Brillouin zone

- Neutrons produced by nuclear reactor – so large facilities required.

Phys Rev Lett **110**, 157401 (2013)

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

$$\mathbf{Q} = \mathbf{k} - \mathbf{k}' + \mathbf{G}$$

$$E(\mathbf{Q}) = \varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}')$$

$\mathbf{k}', \varepsilon(\mathbf{k}')$ Scattered n

$\mathbf{k}, \varepsilon(\mathbf{k})$ Incident n

phonon

$\mathbf{Q}, E(\mathbf{Q})$
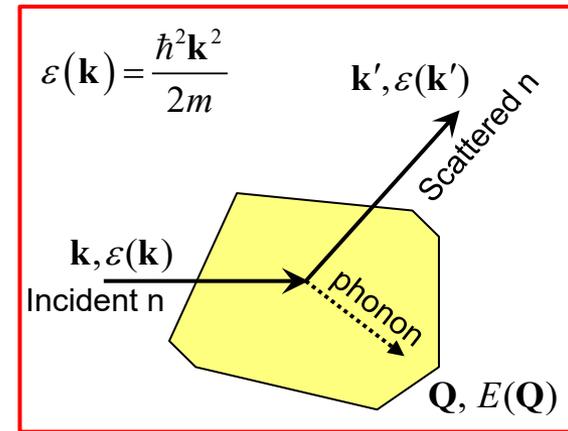


Multi axis crystal spectrometer at the National Institute for Standards and Technology Centre for Neutron Research in Gaithersburg, Maryland, USA –said to be the most intense neutron beam in the world.

# Summary of Lecture 5

- Reciprocal lattice and diffraction

- Diffraction conditions

- High resolution x-ray diffraction

- Diffraction conditions and Brillouin zones

- Brillouin zones in 3D

- Lattice dynamics and phonons – 1D monatomic chain

- 1D diatomic chains – different spring constants

- 1D diatomic chains – different masses

- Inelastic neutron scattering for determination of phonon dispersion

# Quantum Condensed Matter Physics
## Lecture 5
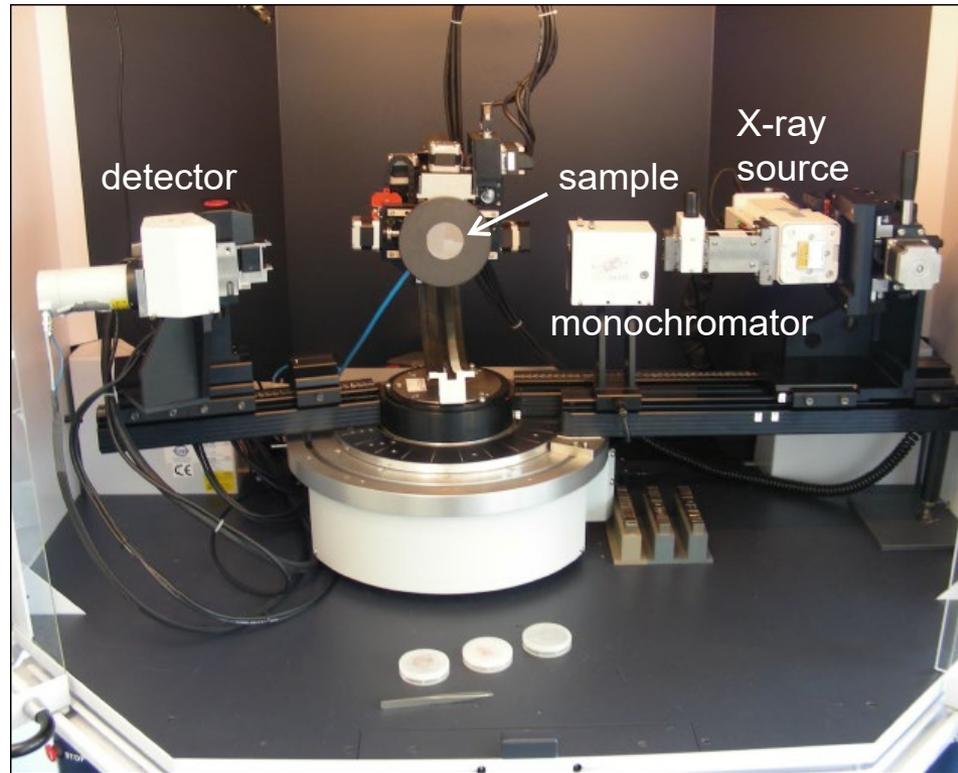


**The end**

# Quantum Condensed Matter Physics
## Lecture 6



## David Ritchie

# Quantum Condensed Matter Physics

1. Classical and Semi-classical models for electrons in solids (3L)

2. Electrons and phonons in periodic solids (6L)

Types of bonding; Van der Waals, ionic, covalent. Crystal structures. Reciprocal space, x-ray diffraction and Brillouin zones. Lattice dynamics and phonons; 1D monoatomic and diatomic chains, 3D crystals. *Heat capacity due to lattice vibrations; Einstein and Debye models. Thermal conductivity of insulators. Electrons in a periodic potential; Bloch's theorem.* Nearly free electron approximation; plane waves and bandgaps. Tight binding approximation; linear combination of atomic orbitals, linear chain and three dimensions, two bands. Pseudopotentials.. ……….

3. Experimental probes of band structure (4L)

4. Semiconductors and semiconductor devices (5L)

5. Electronic instabilities (2L)

6. Fermi Liquids (2L)

# Lattice dynamics and phonons – density of states

- We need to calculate density of states for phonons
- In 1D monoatomic chain of N atoms (N large), there are N degrees of freedom and hence N modes.
- So the allowed points in k-space are

$$k_n = \frac{2\pi}{L} n \ ; \ n = \left[ -\frac{N}{2}, -\frac{N}{2} + 1, ..., \frac{N}{2} \right]$$

- Here $-\pi / a < k < \pi / a$ and the lattice constant $a = L / N$
- Same spacing of k-states as for electrons, but discrete nature of atoms leads to maximum momentum – from counting degrees of freedom on Brillouin zone boundary
- In 3D each branch of phonon spectrum has N states but $N = L^3 / \Omega_{cell}$ where $\Omega_{cell}$ is the volume of the unit cell and $L^3 = V$ the volume of the crystal
- Volume associated with each allowed k-point is $\Delta k = (2\pi)^3 / L^3$
- There are $3$ acoustic branches and $3(m-1)$ optical branches ($m$ atoms per unit cell)

# Lattice dynamics and phonons – Density of states

- We start with the optical branches and use the Einstein Model which assumes a flat dispersion: $\omega(\mathbf{k}) = \omega_0$ In this case the density of states is simply $D_E(\omega) = N\delta(\omega - \omega_0)$

- For the acoustic modes, which disperse linearly as $\omega \to 0$ we have $\omega = vk$ where $v$ is the speed of the mode and following similar arguments as for electrons we obtain the Debye model result

$$D_D(\omega) = \frac{4\pi k^2}{(2\pi / L)^3} \frac{dk}{d\omega} = \frac{V\omega^2}{2\pi^2 v^3}$$
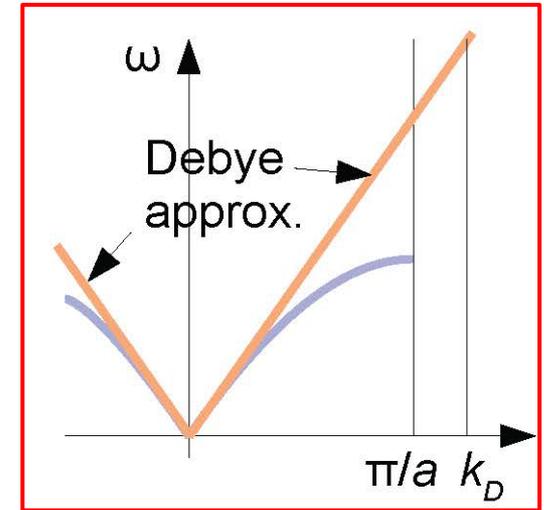
- This cannot apply as the dispersion approaches the zone boundary, in the Debye model the spectrum is cut off at a frequency $\omega_D$ and wavevector $k_D$

- This frequency is determined by counting the total number of states and setting this equal to $N$,

hence: $\int_0^{\omega_D} D_D(\omega)d\omega = N$ Which gives $\omega_D^3 = \frac{6\pi^2 v^3 N}{V}$ .

- This corresponds to replacing the correct cutoff (determined by intersecting Brillouin zone planes) by a sphere of radius $k_D = \omega_D / v$

# Heat capacity due to lattice vibrations- Einstein model

- Phonons obey Bose-Einstein statistics, their number is not conserved so the chemical potential is zero and we use the Planck distribution

$$n(\omega) = \frac{1}{\exp(\hbar\omega / k_B T) - 1}$$

- Note that $n \to 0$ for $k_B T < \hbar\omega$ and $n \to k_B T / \hbar\omega$ for $k_B T > \hbar\omega$

- The internal energy is given by: $U = \int D(\omega) n(\omega) \hbar\omega \, d\omega$

- For the Einstein model given that

$$D_E(\omega) = N\delta(\omega - \omega_0)$$

- We obtain $U_E = \dfrac{N\hbar\omega_0}{e^{\hbar\omega_o / k_B T} - 1}$ and for the specific heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = N k_B \left(\frac{\hbar\omega_0}{k_B T}\right)^2 \frac{e^{\hbar\omega_0 / k_B T}}{(e^{\hbar\omega_0 / k_B T} - 1)^2}$$

- At low temperatures this varies as $\exp(-\hbar\omega_0 / k_B T)$ and is very small, but it saturates at a value of $N k_B$ (the Dulong and Petit law) above the characteristic temperature $\theta_E = \hbar\omega_0 / k_B$

# Heat capacity due to lattice vibrations – Debye model

- At low temperatures the contribution of optical modes is small and the Debye spectrum is appropriate giving for each mode:

$$U_D = \int D(\omega)n(\omega)\hbar\omega \, \mathrm{d}\omega = \int_0^{\omega_D} \frac{V\omega^2}{2\pi^2 v^3} \frac{\hbar\omega}{e^{\hbar\omega/k_B T}-1} \, \mathrm{d}\omega$$

- Defining the Debye temperature $\theta_D = \hbar\omega_D / k_B$ and using $\omega_D^3 = 6\pi^2 v^3 N / V$ from above, we obtain $\quad \theta_D = (6\pi^2 N / V)^{1/3} \hbar v / k_B$

- By writing $x = \hbar\omega / k_B T$ and including a factor of 3 for different modes we obtain for the internal energy

$$U_D = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\hbar\omega/k_B T}-1} \, \mathrm{d}\omega = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} \, \mathrm{d}x$$

- and by differentiating with respect to temperature, the heat capacity – plotted right

$$C_V = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, \mathrm{d}x$$

For $T \gg \theta_D, x \to 0 \Rightarrow C_V \approx 3Nk_B$
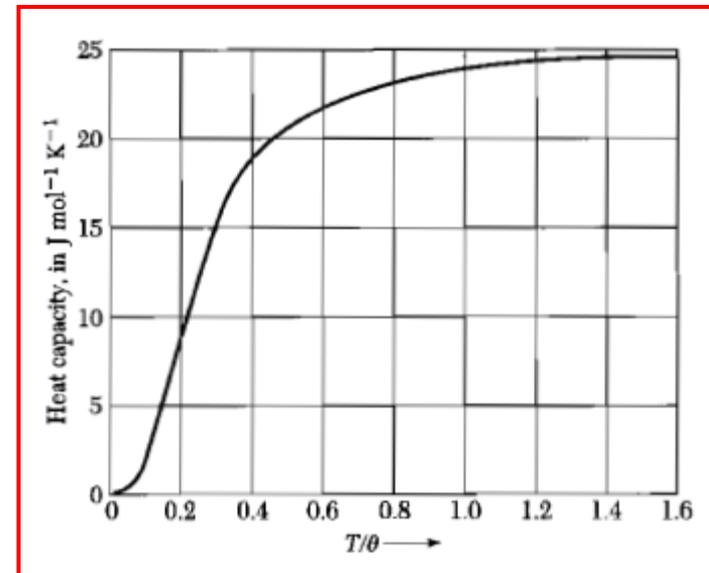
# Heat capacity due to lattice vibrations - Debye model

- From last slide $U_D = 9Nk_BT\left(\dfrac{T}{\theta_D}\right)^3 \displaystyle\int_0^{\theta_D/T} \dfrac{x^3}{e^x - 1}dx$

- We approximate for very low temperatures by allowing $\theta_D / T \to \infty$ and using the standard integral $\displaystyle\int_0^\infty \dfrac{x^3}{e^x - 1}dx = \dfrac{\pi^4}{15}$

- Hence $U_D = 3\pi^4 Nk_BT^4 / 5\theta_D^3$ .

- Differentiating with respect to temperature

$$C_V = \frac{12\pi^4}{5}Nk_B\left(\frac{T}{\theta_D}\right)^3$$



$\theta_D = 92\text{K}$

- $T^3$ temperature dependence
- Experimental results for solid Argon
- Clearly a good approximation

# Heat capacity due to lattice vibrations and electrons

- In metals we have both electrons and lattice vibrations giving rise to a low temperature heat capacity of the form

$$C_v = \alpha T + \beta T^3 \Rightarrow C_v / T = \alpha + \beta T^2$$

- If we plot $C_v / T$ $vs$ $T^2$ we obtain a straight line.

- $\alpha$ the $T = 0$ intercept is determined by the electron specific heat

- $\beta$ the gradient is determined by lattice specific heat



FIG. 5. Atomic heat of copper.
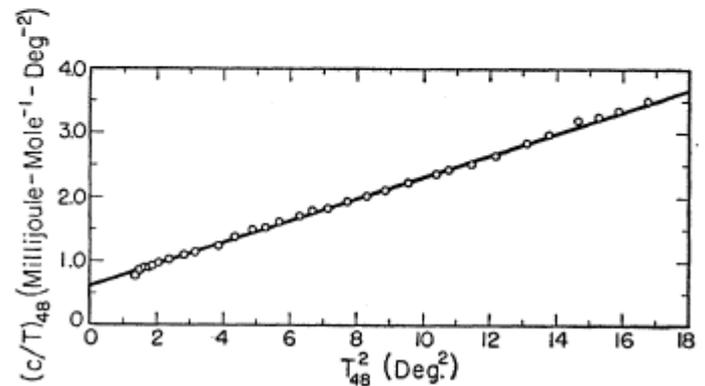


FIG. 6. Atomic heat of silver.

W S Corak et al Phys Rev **98**, 1699, (1955)



$C/T = 2.08 + 2.57\, T^2$

Potassium

**Figure 9** Experimental heat capacity values for potassium, plotted as C/T versus $T^2$. (After W. H. Lien and N. E. Phillips.)

W H Lien and N E Phillips Phys Rev **133**, A1370 (1964)

# Einstein and Debye models

- Comparison of Einstein and Debye models of specific Heat

- At low temperatures difficult to thermally excite optical modes hence Einstein is below Debye

- Comparison of (a) Debye density of States with (b) density of states of a real material

- Complex shape due to adding different branches of phonon spectrum and *van Hove* singularities
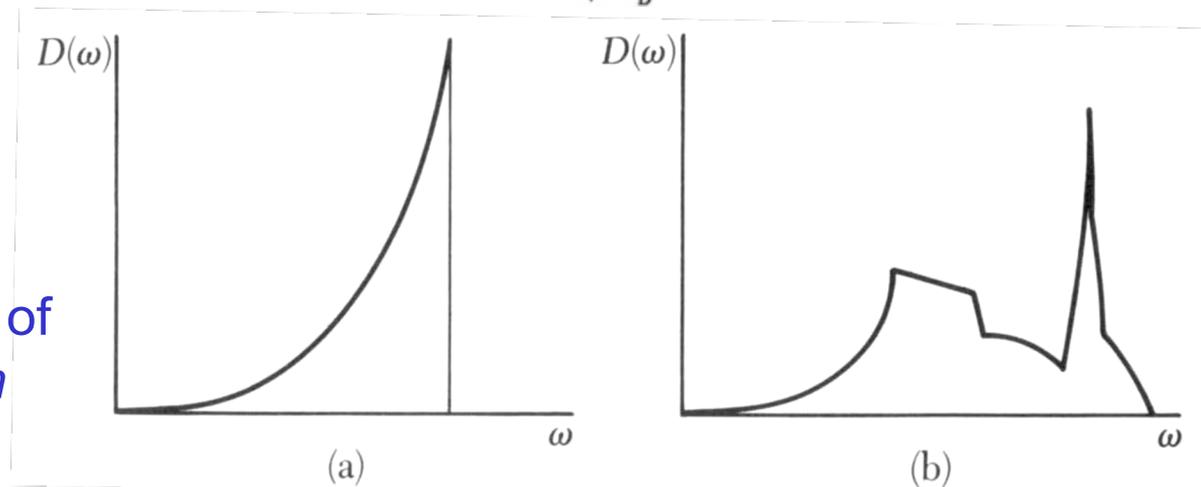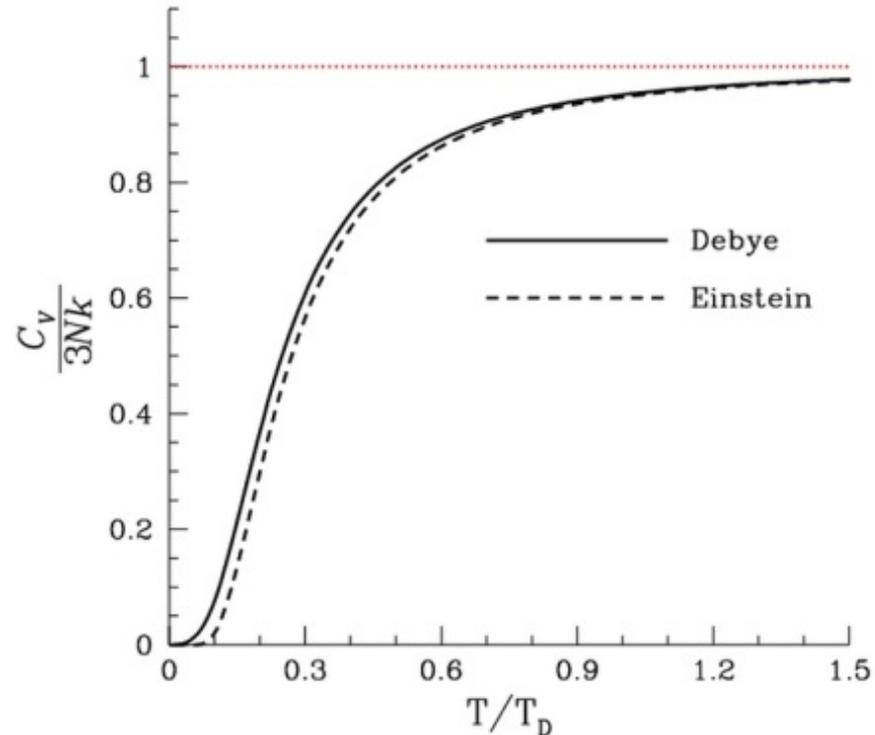
# Thermal conductivity of insulators

- The thermal conductivity, $\kappa$ is defined by $\mathbf{J}_q = -\kappa \nabla T$ where $\mathbf{J}_q$ is the flux of heat (energy per unit area per unit time)

- Kinetic theory gives $\kappa = \frac{1}{3} C_v l v = \frac{1}{3} C_v v^2 \tau$ , $C_v$ the phonon specific heat per unit volume, $v$ phonon velocity, $l = v\tau$ mean free path and $\tau$ scattering time

- Debye theory: $C_v \propto T^3$ at low $T$ and constant at high $T$. $v$ is velocity of sound and almost constant, $\tau$ depends on several scattering mechanisms

- Phonons can be scattered by (i) other phonons – in "normal" and "umklapp" processes (ii) point defects (iii) sample boundaries (iv) crystal dislocations.

- The overall scattering time given by: $\tau^{-1} = \tau_{ph}^{-1} + \tau_{def}^{-1} + \tau_{boun}^{-1} + \tau_{dis}^{-1}$



First Brillouin zone

Normal: $\mathbf{k_3} = \mathbf{k_1} + \mathbf{k_2}$    Umklapp: $\mathbf{k_3} + \mathbf{G} = \mathbf{k_1} + \mathbf{k_2}$

- At low $T$, $l$ is large and $\tau$ is often determined by sample boundaries – constant with $T$ so $\kappa \propto T^3$

- In middle range of $T$, $\kappa$ often peaks and impurity scattering is important.

- As $T$ increases up to and beyond, $T_{Debye}$, phonon numbers and scattering increases (umklapp particularly important) $\kappa$ decreases rapidly
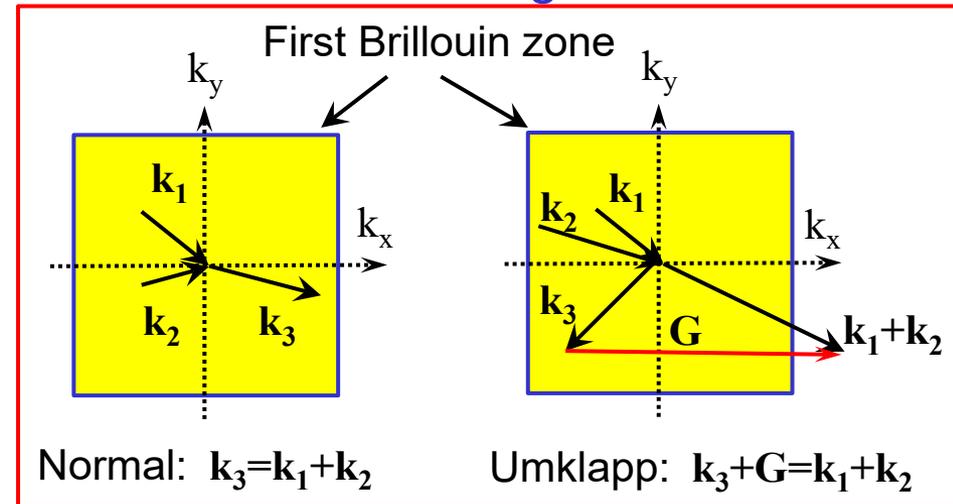
# Thermal conductivity of insulators

- Rapid increase with $\kappa \propto T^3$ at low temperatures – boundary scattering can dominate so size of sample important

- $\kappa$ peaks in middle range of $T$ and impurities determine peak value

- $\kappa$ rapidly decreases at higher $T$ as more phonons are excited with umklapp particularly important due to with large changes in wavevector

- Diamond has a very high thermal conductivity at room $T$ - 5 times copper

Thermal conductivity of LiF
Effect of boundary scattering

(A) 7.3mm
(B) 4mm
(C) 2.1mm
(D)1.1mm

Curves correspond to different widths of specimen Phys Rev **156**, 975 (1967)
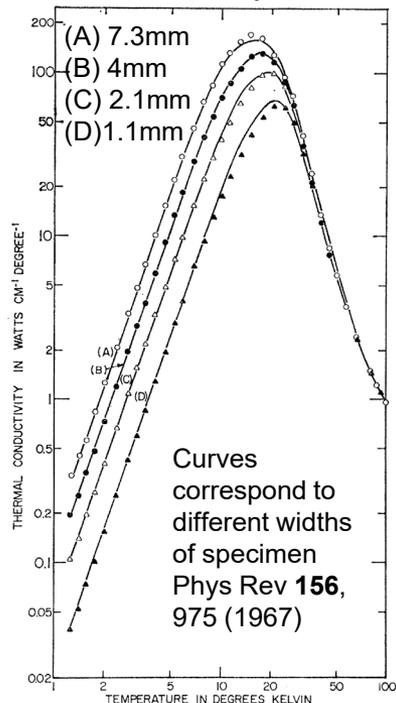
Thermal conductivity of LiF
Effect of impurities (isotopes)

0.02% $^6$Li
0.01% $^6$Li
4.6% $^6$Li
90.4% $^6$Li
25% $^6$Li
50.1% $^6$Li

Curves correspond to different isotopic purity of specimens Proc. R. Soc. Lond. A 1965 **289** 66-80
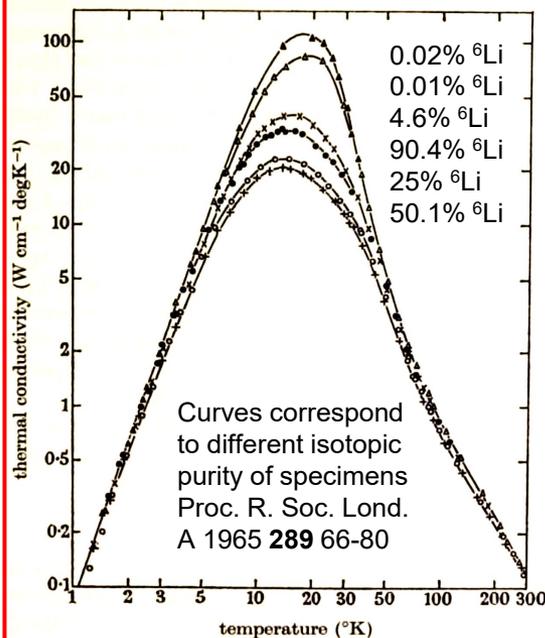
Thermal conductivity of diamond

0.1% $^{13}$C

1% $^{13}$C

0.001% $^{13}$C
0.1% $^{13}$C
1% $^{13}$C

Wei et al PRL **70**, 3674 (1993)
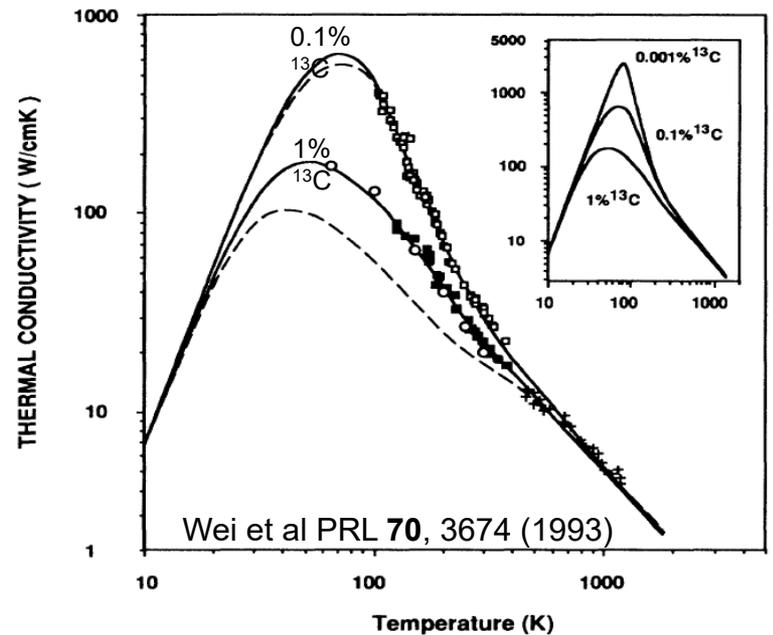
# Electrons in a periodic potential

- So far we have ignored the electrostatic potential due to the positively charged ions.

- We are looking to find the set of plane waves which satisfy the periodic boundary conditions

- Hamiltonian $\hat{H}|\psi\rangle = (-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}))|\psi\rangle = E|\psi\rangle$ where $V(\mathbf{r})$ is periodic

- Because $V(\mathbf{r})$ has the same periodicity as the lattice it can be Fourier expanded as $V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$

- We define its Fourier components at reciprocal lattice vectors $\mathbf{G}$ as

$$V_{\mathbf{G}} = \frac{1}{\text{Vol.}}\int e^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) d^3\mathbf{r} = \frac{1}{\text{Vol. per cell}}\int_{\text{unit cell}} e^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) d^3\mathbf{r}$$

- Since the potential is real $V_{\mathbf{G}}^* = V_{-\mathbf{G}}$

- For $\mathbf{G} = 0$ the Fourier component $V_{\mathbf{G}} = V_0$ is the average of the potential which we set to zero

- Construct eigenstate $|\psi\rangle$ from plane wave states $|\mathbf{k}\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}$ (which form a complete set of basis vectors obeying periodic boundary conditions) giving

$$|\psi\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

# Electrons in a periodic potential

- Apply the Hamiltonian $\hat{H} = -\dfrac{\hbar^2}{2m}\nabla^2 + \sum_{\mathbf{G}} V_{\mathbf{G}} \mathbf{e}^{i\mathbf{G}\cdot\mathbf{r}}$ to $\left|\psi\right\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$ obtaining

$$\sum_{\mathbf{k}} E_{\mathbf{k}}^{0} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \left[\sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}\right]\left[\sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\right] = E\sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

- where $E_{\mathbf{k}}^{0} = \hbar^2 k^2 / 2m$. The potential energy term can be re-written as

$$V(r)\psi = \sum_{\mathbf{G},\mathbf{k}} V_{\mathbf{G}} c_{\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}} = \sum_{\mathbf{G},\mathbf{k}} V_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

since the summation is over all possible values of $\mathbf{G}, \mathbf{k}$. We can now write

$$\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} \left\{ (E_{\mathbf{k}}^{0} - E)c_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \right\} = 0$$

- Since $\left|\mathbf{k}\right\rangle = e^{i\mathbf{k}\cdot\mathbf{r}}$ form an orthogonal set of functions the coefficient of each term in the sum must vanish and we get the eigenvalue equation:

$$(E_{\mathbf{k}}^{0} - E)c_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0$$

# Electrons in a periodic potential

- From the last slide $(E_{\mathbf{k}}^0 - E)c_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0$

- In this equation $\mathbf{k}$ can be anywhere in reciprocal space

- The first Brillouin zone contains all of the useful information about k-space

- We write $\mathbf{q} = \mathbf{k} + \mathbf{G}'$ relating the general wavevector $\mathbf{k}$ to $\mathbf{q}$ which lies in the first Brillouin zone, $\mathbf{G}'$ is a reciprocal lattice vector

- Hence we can write $E_{\mathbf{k}}^0 = \hbar^2 k^2 / 2m = \hbar^2 (\mathbf{q} - \mathbf{G}')^2 / 2m$

- And thus

$$\left[ \frac{\hbar^2}{2m} (\mathbf{q} - \mathbf{G}')^2 - E \right] c_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}} V_{\mathbf{G}} c_{\mathbf{q}-\mathbf{G}'-\mathbf{G}} = 0$$

- Finally writing $\mathbf{G}'' = \mathbf{G} + \mathbf{G}'$ we obtain

$$\left[ \frac{\hbar^2}{2m} (\mathbf{q} - \mathbf{G}')^2 - E \right] c_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}'} c_{\mathbf{q}-\mathbf{G}''} = 0$$

- This equation can be used to specify the coefficients $c_{\mathbf{k}}$ which are used to construct the wavefunctions

$$|\psi\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} |\mathbf{k}\rangle = \sum_{\mathbf{k}} c_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

# Electrons in a periodic potential - Bloch's Theorem

- From the last slide
$$\left[\frac{\hbar^2}{2m}(\mathbf{q}-\mathbf{G}')^2 - E\right]c_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}''}V_{\mathbf{G}''-\mathbf{G}'}c_{\mathbf{q}-\mathbf{G}''} = 0$$

- This equation only involves coefficients $c_{\mathbf{k}}$ in which $\mathbf{k} = \mathbf{q} - \mathbf{G}$ with $\mathbf{G}$ being general reciprocal lattice vectors

- If we choose a value of $\mathbf{q}$ then the only $c_{\mathbf{k}}$ that feature in the equation above are those of the form $c_{\mathbf{q}-\mathbf{G}}$ and these specify the wavefunction

- Hence for each distinct value of $\mathbf{q}$ there is a wavefunction
$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}}c_{\mathbf{q}-\mathbf{G}}e^{i(\mathbf{q}-\mathbf{G})\cdot\mathbf{r}}$$

- Which can be written
$$\psi_{\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}}\sum_{\mathbf{G}}c_{\mathbf{q}-\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{q}\cdot\mathbf{r}}u_{j,\mathbf{q}}(\mathbf{r})$$

- Where $u_{j,\mathbf{q}}(\mathbf{r})$ is built from the periodic function $e^{-i\mathbf{G}\cdot\mathbf{r}}$ and must have the same periodicity as the lattice

- Bloch's theorem: *"Eigenstates of the 1D Hamiltonian can be chosen as a plane wave multiplied by a function with the periodicity of the Bravais lattice"*

# Bloch's theorem

- We now join this all up and apply it to electrons subject to a periodic potential

- The energy eigenstates of electrons in a lattice:

$$\hat{H}\psi(\mathbf{r}) = \left[\frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

  where $V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r})$ for all $\mathbf{R}$ in a Bravais lattice.

- The $\psi_{\mathbf{k}}^{(n)}$ can be chosen so that

$$\psi_{\mathbf{k}}^{(n)}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}^{(n)}(\mathbf{r}) \qquad \text{where} \qquad u_{\mathbf{k}}^{(n)}(\mathbf{r} + \mathbf{R}) = u_{\mathbf{k}}^{(n)}(\mathbf{r})$$

- Note that potential is periodic and $\psi$ = plane wave x periodic function

- $n$ is the *band index* – necessary because there may be several distinct eigenstates of $\hat{H}$ with the same symmetry label $\mathbf{k}$

- Or, alternatively if we apply a translation $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{R}$ then we obtain

$$\psi_{\mathbf{k}}^{(n)}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}}^{(n)}(\mathbf{r})$$

# Bloch's Theorem

- Bloch states (plane wave $\times$ periodic function) are similar to eigenstates of free electrons (just plane waves), but the choice of periodic function gives additional freedom in labelling states.

- Remember that $e^{i\mathbf{g}\cdot\mathbf{r}}$ is periodic with same periodicity as the Bravais lattice (follows from definition of reciprocal lattice vectors $\mathbf{g}$ ).

- We can use this to relabel a Bloch state $\mathbf{k}$ with a different wavevector $\mathbf{k}-\mathbf{g}$ by introducing a different periodic function $u^{(n)} = e^{i\mathbf{g}\cdot\mathbf{r}}u^{(m)}$ :

$$\psi_{\mathbf{k}}^{(m)}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}^{(m)}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\mathbf{g}\cdot\mathbf{r}}\left[ e^{i\mathbf{g}\cdot\mathbf{r}}u_{\mathbf{k}(\mathbf{r})}^{(m)} \right] = e^{i(\mathbf{k}-\mathbf{g})\cdot\mathbf{r}}u_{\mathbf{k}-\mathbf{g}}^{(n)}(\mathbf{r}) = \psi_{\mathbf{k}-\mathbf{g}}^{(n)}(\mathbf{r})$$

- The $(m),(n)$ labels are called band indices. In this case, there are two different states $\left|\psi_{\mathbf{k}}^{(m)}\right\rangle, \left|\psi_{\mathbf{k}}^{(n)}\right\rangle$ labelled with the same $\mathbf{k}$ vector, but belonging to different bands $m, n$ $\left(\psi_{\mathbf{k}}^{(m)}(\mathbf{r}) = e^{-i\mathbf{g}\cdot\mathbf{r}}\psi_{\mathbf{k}}^{(n)}(\mathbf{r})\right)$

- For every state labelled with a $\mathbf{k}$ vector outside the first Brillouin zone, there is an identical state which can be labelled with a vector $\mathbf{q} = \mathbf{k}-\mathbf{g}$ inside the first Brillouin zone.

- Corollary: any quantity that depends on the wavefunction, in particular *energy,* is periodic in wavevector space.

# Summary of Lecture 6

- Lattice dynamics and phonons – density of states,

- Einstein and Debye models of lattice specific heat capacity

- Comparison with experimental results

- Electrons in a periodic potential,

- Bloch's theorem

# Quantum Condensed Matter Physics
## Lecture 6
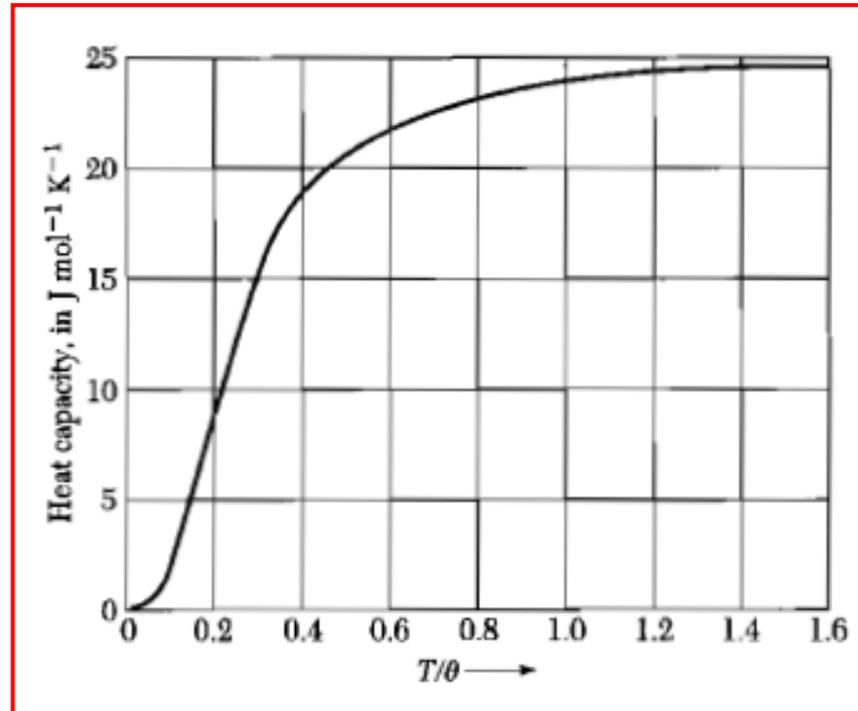


**The end**

# Quantum Condensed Matter Physics
## Lecture 7



**David Ritchie**

# Quantum Condensed Matter Physics

1. Classical and Semi-classical  models for electrons in solids (3L)

2. Electrons and phonons in periodic solids (6L)

Types of bonding; Van der Waals, ionic, covalent. Crystal structures. Reciprocal space, x-ray diffraction and Brillouin zones. Lattice dynamics and phonons; 1D monoatomic and diatomic chains, 3D crystals. Heat capacity due to lattice vibrations; Einstein and Debye models. Thermal conductivity of insulators. Electrons in a periodic potential; Bloch's theorem. *Nearly free electron approximation; plane waves and bandgaps. Tight binding approximation; linear combination of atomic orbitals, linear chain and three dimensions,* two bands. Pseudopotentials.. ……….

3. Experimental probes of band structure (4L)

4. Semiconductors and semiconductor devices (5L)

5. Electronic instabilities (2L)

6. Fermi Liquids (2L)

# Nearly Free Electron Approximation

- To find approximate single electron states in a periodic potential by hybridising nearly degenerate plane wave states

- Recall that the single-electron state was obtained from plane wave expansion $\left|\psi_{\mathbf{k}}\right\rangle = \sum_{\mathbf{G}} \mathbf{c}_{\mathbf{k-G}} \left|\mathbf{k} - \mathbf{G}\right\rangle$

- If the lattice potential is weak compared to kinetic energy the eigenstates are constructed from $\left|\mathbf{k}\right\rangle$ plus a small number of lattice harmonics states $\left|\mathbf{k} - \mathbf{G}\right\rangle$

- we use second order perturbation theory to calculate the degree of admixture of the harmonic states. The energy shift due to admixing $\left|\mathbf{k} - \mathbf{G}\right\rangle$ is given by

$$\Delta E_{\mathbf{k}} = \left|V_{\mathbf{G}}\right|^2 / (E_{\mathbf{k}}^0 - E_{\mathbf{k-G}}^0)$$

- $V_{\mathbf{G}}$ is the Fourier component of the lattice potential at reciprocal lattice vector $\mathbf{G}$ given by $\quad V = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$

- This energy shift and the associated admixture of lattice harmonics is largest when the states are nearly degenerate so $\quad E_{\mathbf{k}}^0 \simeq E_{\mathbf{k-G}}^0$

- To work out the perturbed energy levels we use the equation from above

$$\left(E_{\mathbf{k}}^0 - E_{\mathbf{k-G}}^0\right)c_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} c_{\mathbf{k-G}} = 0$$

- restricting $\mathbf{G}$ vectors to those linking nearly degenerate states with $E_{\mathbf{k}}^0 \approx E_{\mathbf{k-G}}^0$

# Nearly Free Electron approximation

- One-dimensional chain
- States $|\mathbf{k}\rangle$ and $|\mathbf{k}-\mathbf{G}\rangle = |\mathbf{k}-2\pi/a\rangle$ are nearly degenerate
- Potential $V_G$ admixes $|\mathbf{k}-\mathbf{G}\rangle$ with $|\mathbf{k}\rangle$
- $|\psi\rangle = c_{\mathbf{k}}|\mathbf{k}\rangle + c_{\mathbf{k}-\mathbf{G}}|\mathbf{k}-\mathbf{G}\rangle$
- $V_G$ admixes other states, but further away in energy so less important
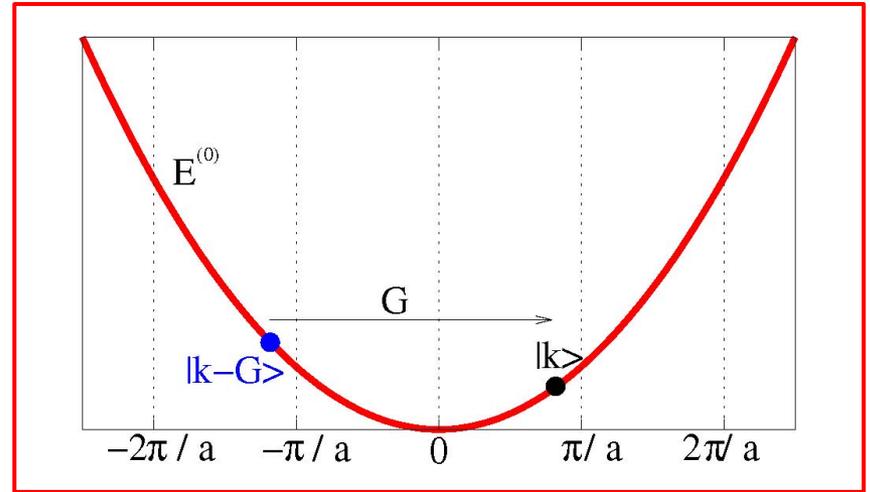


- Apply Hamiltonian using $E_{\mathbf{k}}^0 = \frac{\hbar^2|\mathbf{k}|^2}{2m}$, $E_{\mathbf{k}-\mathbf{G}}^0 = \frac{\hbar^2|\mathbf{k}-\mathbf{G}|^2}{2m}$, $V = \sum_{\mathbf{G}} V_{\mathbf{G}} e^{i\mathbf{G}\cdot\mathbf{r}}$

$$\hat{H}|\psi\rangle = \left(\hat{\mathbf{p}}^2/2m + V\right)\left(c_{\mathbf{k}}|\mathbf{k}\rangle + c_{\mathbf{k}-\mathbf{G}}|\mathbf{k}-\mathbf{G}\rangle\right) = E\left(c_{\mathbf{k}}|\mathbf{k}\rangle + c_{\mathbf{k}-\mathbf{G}}|\mathbf{k}-\mathbf{G}\rangle\right)$$

$$= c_{\mathbf{k}} E_{\mathbf{k}}^0 |\mathbf{k}\rangle + c_{\mathbf{k}} V|\mathbf{k}\rangle + c_{\mathbf{k}-\mathbf{G}} E_{\mathbf{k}-\mathbf{G}}^0 |\mathbf{k}-\mathbf{G}\rangle + c_{\mathbf{k}-\mathbf{G}} V|\mathbf{k}-\mathbf{G}\rangle$$

- Left multiplying by $|\mathbf{k}\rangle$ and $|\mathbf{k}-\mathbf{G}\rangle$ with $\langle\mathbf{k}|V|\mathbf{k}\rangle = V_0$, $\langle\mathbf{k}|V|\mathbf{k}-\mathbf{G}\rangle = V_{\mathbf{G}}$
  and $\langle\mathbf{k}-\mathbf{G}|V|\mathbf{k}\rangle = V_{\mathbf{G}}^* = V_{-\mathbf{G}}$ for a real potential we obtain

$$c_{\mathbf{k}} E = c_{\mathbf{k}} E_{\mathbf{k}}^0 + c_{\mathbf{k}} V_0 + c_{\mathbf{k}-\mathbf{G}} V_{\mathbf{G}}, \quad c_{\mathbf{k}-\mathbf{G}} E = c_{\mathbf{k}} V_{-\mathbf{G}} + c_{\mathbf{k}-\mathbf{G}} V_0 + c_{\mathbf{k}-\mathbf{G}} E_{\mathbf{k}-\mathbf{G}}^0$$

- A special case of equation from above: $\left(E_{\mathbf{k}}^0 - E\right) c_{\mathbf{k}} + \sum_{\mathbf{G}} V_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} = 0$

# Nearly Free Electron approximation

- From the last slide if we set $V_0 = 0$ and rearrange

$$c_{\mathbf{k}}\left(E - E_{\mathbf{k}}^0\right) = c_{\mathbf{k-G}}V_{\mathbf{G}}, \quad c_{\mathbf{k-G}}\left(E - E_{\mathbf{k-G}}^0\right) = c_{\mathbf{k}}V_{\mathbf{-G}}$$

$$\Rightarrow \begin{pmatrix} E - E_{\mathbf{k}}^0 & -V_{\mathbf{G}} \\ -V_{\mathbf{-G}} & E - E_{\mathbf{k-G}}^0 \end{pmatrix}\begin{pmatrix} c_{\mathbf{k}} \\ c_{\mathbf{k-G}} \end{pmatrix} = 0$$

$$\Rightarrow \left(E - E_{\mathbf{k}}^0\right)\left(E - E_{\mathbf{k-G}}^0\right) - |V_{\mathbf{G}}|^2 = E^2 - E\left(E_{\mathbf{k}}^0 + E_{\mathbf{k-G}}^0\right) + E_{\mathbf{k}}^0 E_{\mathbf{k-G}}^0 - |V_{\mathbf{G}}|^2 = 0$$

$$E = \tfrac{1}{2}\left\{\left(E_{\mathbf{k}}^0 + E_{\mathbf{k-G}}^0\right) \pm \sqrt{\left(E_{\mathbf{k}}^0 - E_{\mathbf{k-G}}^0\right)^2 + 4|V_{\mathbf{G}}|^2}\right\} \approx \tfrac{1}{2}\left(E_{\mathbf{k}}^0 + E_{\mathbf{k-G}}^0\right) \pm |V_{\mathbf{G}}|$$

- Which gives a symmetrical splitting of levels about the free electron value where $E_{\mathbf{k}}^0$, $E_{\mathbf{k-G}}^0$ cross close to the Brillouin zone boundary at $k = \pm\pi/a$

- At the zone boundary the Bloch states are formed from either the sum of or difference between the two unperturbed states $|\mathbf{k}\rangle$, $|\mathbf{k-G}\rangle$

- Both sum and difference wavefunctions are standing waves, in one case nodes are located near atomic cores in the other between them.
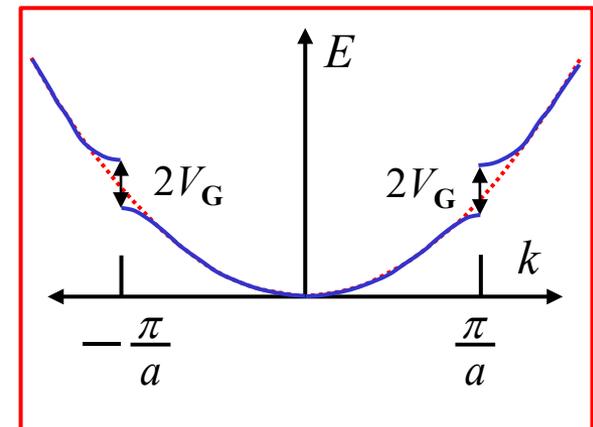
# Nearly Free Electron approximation

- Another approach - start from an equation with reciprocal space periodicity built in:

$$\left[ \left( \frac{\hbar^2}{2m} (\mathbf{q} - \mathbf{G}')^2 - E \right) c_{\mathbf{q}-\mathbf{G}'} + \sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}'} c_{\mathbf{q}-\mathbf{G}''} \right] = 0$$

- $\mathbf{q}$ is in the first Brillouin zone and is obtained from $\mathbf{k}$ by subtracting $\mathbf{G}'$ if necessary

- If the potential is zero then $E = \frac{\hbar^2}{2m} (\mathbf{q} - \mathbf{G}')^2$ and we obtain a set of parabolic bands with energies given by

$$E_0^n(k) = \frac{\hbar^2}{2m} (k - 2\pi n / a)^2 , \qquad n = ..., -2, -1, 0, 1, 2, ...$$

- Introduce a small periodic perturbation $V(x) = 2V_{2\pi/a} \cos\left(2\pi x / a\right)$

- Perturbation only important for momenta where we have degenerate states, for example $n = 0, 1$ at $k = \pi / a$ and from the equation above

$$\begin{pmatrix} \dfrac{\hbar^2}{2m} k^2 - E & V_{2\pi/a} \\ V_{2\pi/a}^* & \dfrac{\hbar^2}{2m} (k - \dfrac{2\pi}{a})^2 - E \end{pmatrix} \begin{pmatrix} c_k \\ c_{k-2\pi/a} \end{pmatrix} = 0$$

# Nearly Free Electron approximation

- The solution of this equation is

$$E^{\pm}(k) = \frac{\hbar^2}{2m}\frac{1}{2}\left(k^2 + \left(k - \frac{2\pi}{a}\right)^2\right) \pm \frac{1}{2}\sqrt{\left(\frac{\hbar^2}{2m}k^2 - \frac{\hbar^2}{2m}\left(k - \frac{2\pi}{a}\right)^2\right)^2 + 4V_{2\pi/a}^2}$$

- And at $k = \pi/a$ the energy levels are $E^{\pm}(\pi/a) = E^0_{\pi/a} \pm |V_{2\pi/a}|$

- By differentiating $E^{\pm}(k)$ with respect to $k$ and evaluating at $k = \pi/a$ we find that $\partial E/\partial k = 0$ so the constant energy surfaces are perpendicular to the Bragg plane.

- Assuming an attractive potential so $V_{2\pi/a} < 0$ then we find ( $\alpha, \beta$ constants)

$$\left|\psi^+(x)\right|^2 = \alpha^2 \sin^2(\pi x/a), \quad E(\pi/a) = E^0_{\pi/a} + |V_{2\pi/a}|$$

$$\left|\psi^-(x)\right|^2 = \beta^2 \cos^2(\pi x/a), \quad E(\pi/a) = E^0_{\pi/a} - |V_{2\pi/a}|$$

- Which implies that for the lower energy state the electron density is highest at $x = \ldots -2a, -a, 0, a, 2a, 3a\ldots$ corresponding to the ionic core "s-type"

- The upper energy state has the highest electron density between ionic cores at values of $x = \ldots -\frac{3}{2}a, -\frac{1}{2}a, \frac{1}{2}a, \frac{3}{2}a\ldots$ "p-type"

# Nearly Free Electron approximation – real space

Periodic potential $V(x)$

$$V(x) = 2V_{2\pi/a}\cos(2\pi x / a)$$

$$V_{2\pi/a} < 0$$

Ion cores
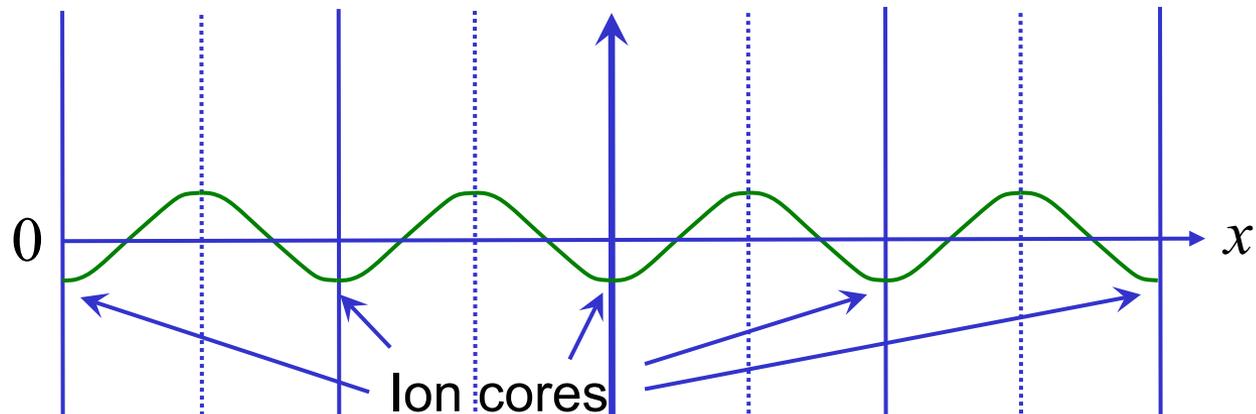
Square of wavefunctions

$$\left|\psi^-(x)\right|^2 = \beta^2 \cos^2(\pi x / a)$$

$$E(\pi / a) = E^0_{\pi/a} - |V_{2\pi/a}|$$

low energy "s-type"
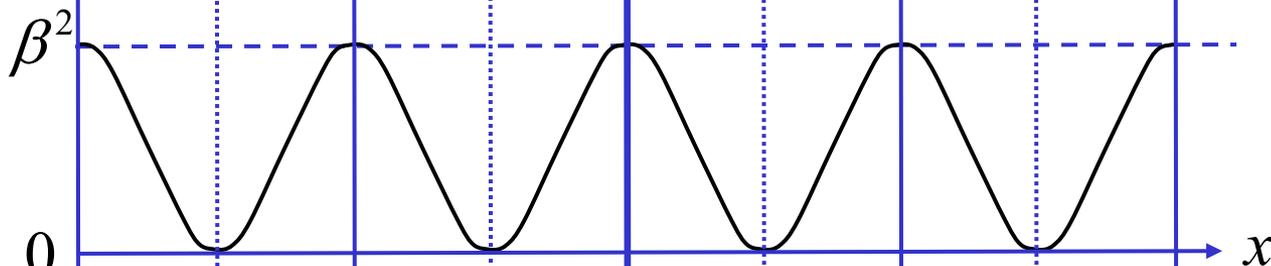
$$\left|\psi^+(x)\right|^2 = \alpha^2 \sin^2(\pi x / a)$$

$$E(\pi / a) = E^0_{\pi/a} + |V_{2\pi/a}|$$

high energy "p-type"

$\beta^2$

$\alpha^2$

$-2a$    $-a$    $0$    $a$    $2a$
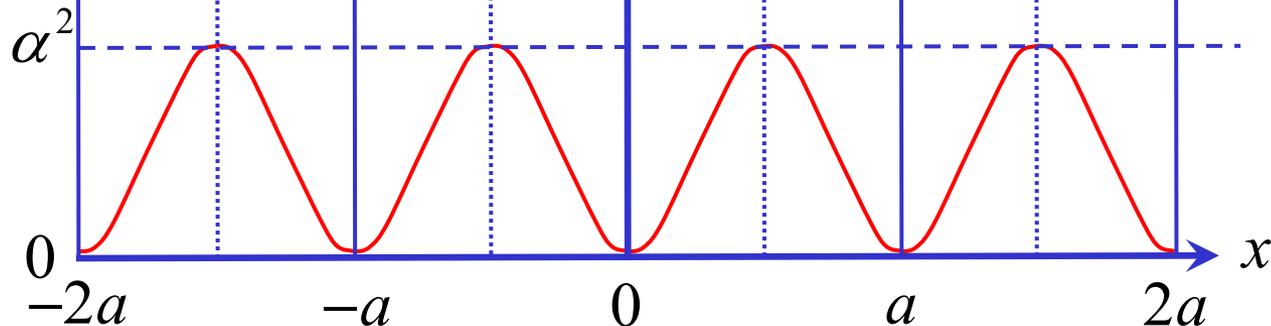
# Nearly Free Electron approximation - reciprocal space

- (a) and (b) show free electron parabolas

- (c) introduces distortion due to a Bragg plane splitting the degeneracy

- (d) the parts of (c) corresponding to the original free electron parabola

- (e)  the effect of the additional Bragg planes on the free electron parabola – extended zone scheme

- (f) as (e) but reduced zone scheme

- (g) as (f) repeated zone scheme



From Singleton
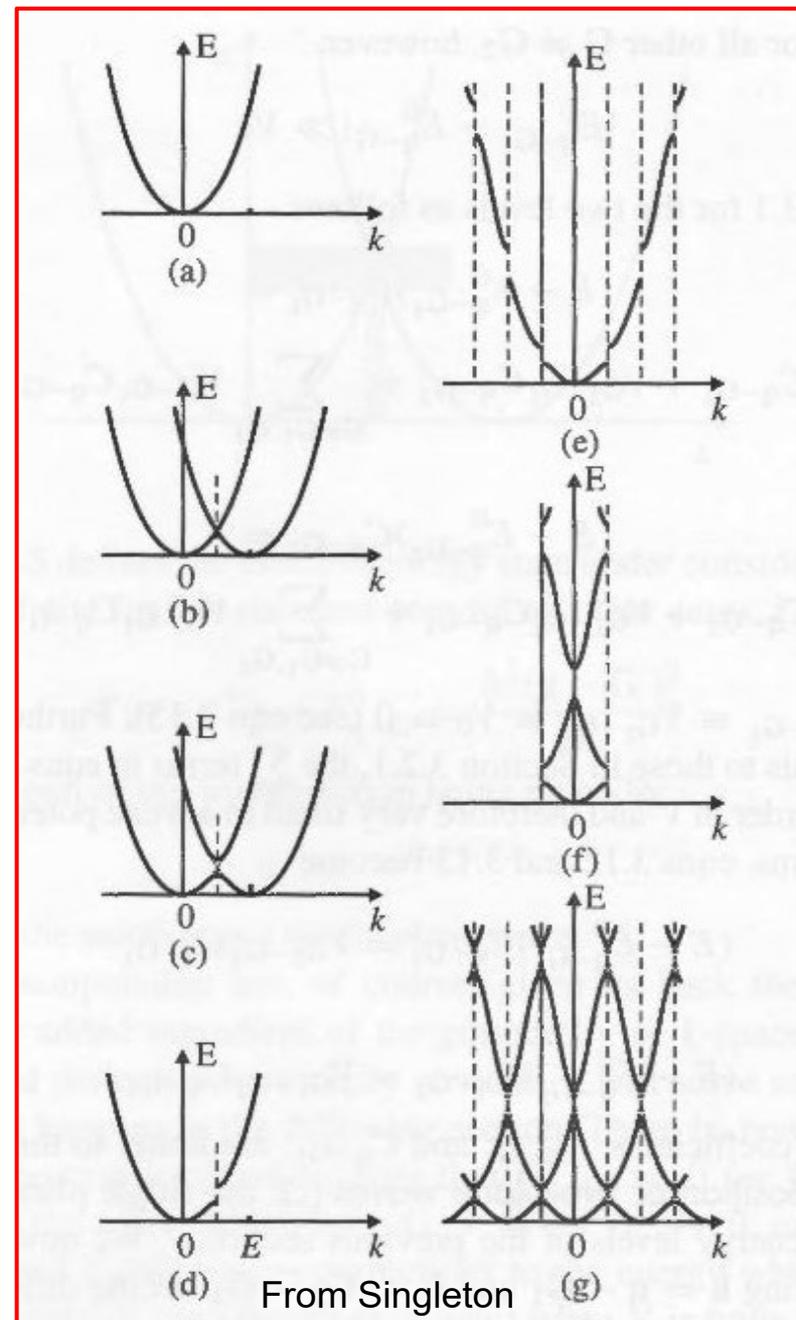
# NFE approximation: calculations for 3D metals

- Top figure energy vs $k_x, k_y$ for $k_z = 0$ within first Brillouin zone

- Energy contours circular near bottom of band but distort as band approaches Brillouin zone boundary (BZB)

- Near top of band they enclose corners of Brillouin zone

- Bottom figure equal energy surface in 3D reciprocal space

- Shape of surface shows energy is periodic in reciprocal space

- Bloch's theorem: for every $\left| \psi_{\mathbf{k+G}}^n \right\rangle$ there is an identical state $\left| \psi_{\mathbf{k}}^m \right\rangle$ so $E_{\mathbf{k}}$ is periodic in reciprocal space

- Equal energy surface intersects BZB at right angles – hybridisation and band distortion strongest
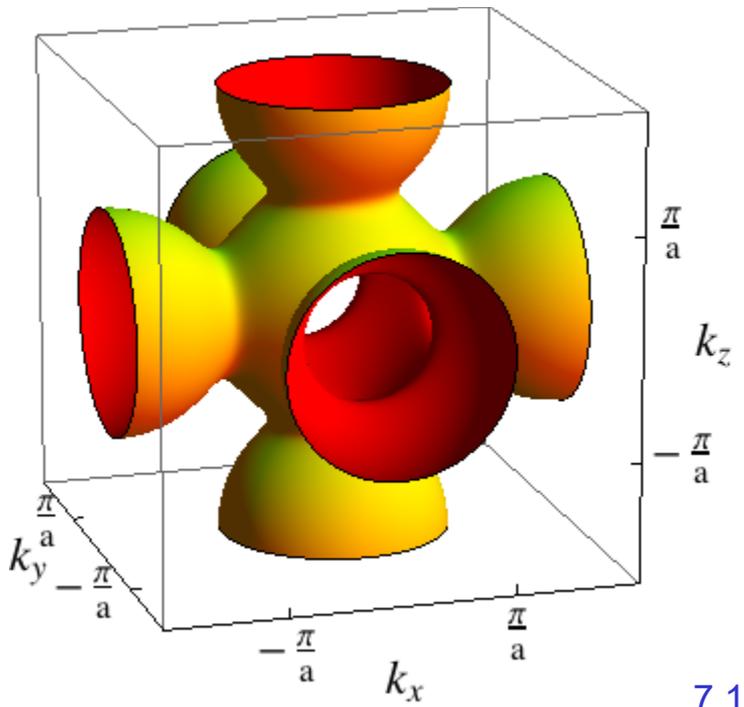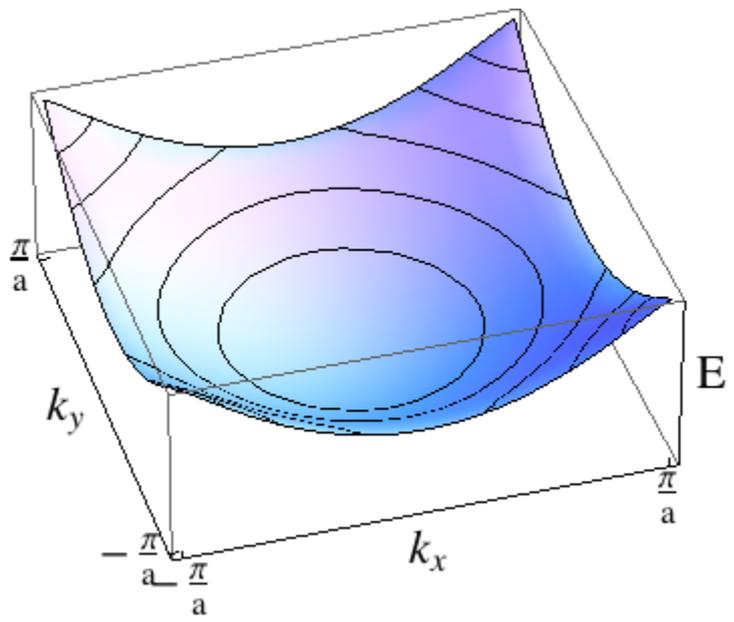
# Tight Binding – Linear combination of atomic orbitals

- Builds up wavefunctions in the solid from wavefunctions of individual atoms
- Diatomic molecule – for identical atoms $\hat{H} = T + V_a + V_b$ where $T$ is the kinetic energy and $V_a, V_b$ are the (identical) potentials on the two atoms
- Basis set is two states $|a\rangle, |b\rangle$ that satisfy

$$\left(T + V_a\right)|a\rangle = E_0|a\rangle, \qquad \left(T + V_b\right)|b\rangle = E_0|b\rangle$$

- With $E_0$ as the eigenenergy of the atomic state
- We look for solutions $|\psi\rangle = \alpha|a\rangle + \beta|b\rangle$ , substitute into $\hat{H}|\psi\rangle = E|\psi\rangle$ and premultiply by $|a\rangle, |b\rangle$
- Define $\tilde{E}_0 = \hat{H}_{aa} = \langle a|T + V_a + V_b|a\rangle = E_a + \langle a|V_b|a\rangle$ - shift of the atomic energy of atom $a$ by the crystal potential of the other atoms
- Define $t = \hat{H}_{ab} = \langle a|T + V_a + V_b|b\rangle$ the hopping matrix element coupling the two atomic states together – the sign depends on the orbital symmetry e.g for two s-states with an attractive potential $V_i < 0$ then $t < 0$ but for two p$_x$-states with atoms aligned along x then $t > 0$

- We obtain simultaneous equations:
$$\begin{pmatrix} \tilde{E}_0 - E & t \\ t^* & \tilde{E}_0 - E \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = 0$$

# Tight Binding – Linear combination of atomic orbitals

- For $t < 0$ the eigenstates are: $\quad \left|\psi\right\rangle = \dfrac{1}{\sqrt{2}}\left[\left|a\right\rangle \mp \left|b\right\rangle\right], \quad E = \tilde{E}_0 \pm |t|$

- For the lower energy (bonding state) the electron density has a maximum between the atoms. For the higher energy (antibonding state) the electron density has a node between the atoms

- We next consider what happens when we bring together more atoms in a linear chain

- The 1s band of a ring of 20 hydrogen atoms
- The one electron energies are calculated in the tight-binding approximation using nearest neighbour overlap integrals

(From Kittel)
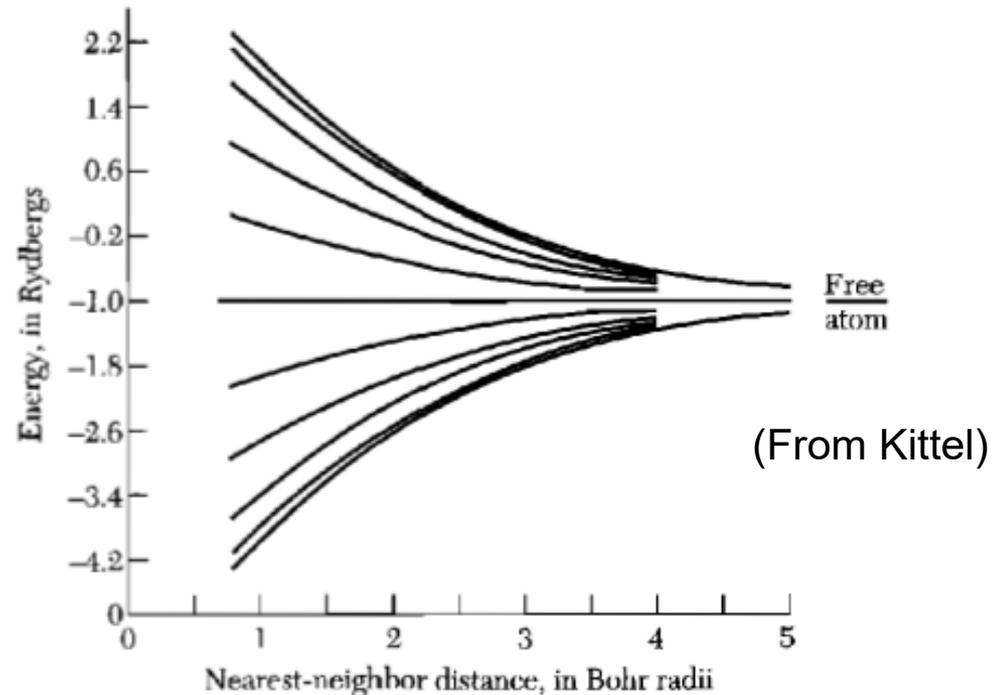
# Tight binding – Linear chain

- Generalising this approach to a linear chain of atoms subject to periodic boundary conditions

- Bloch's theorem dictates that a wavefunction using one orbital per unit cell must be of the form $|\psi\rangle = \sum_n e^{i\mathbf{k}\cdot\mathbf{R_n}} |n\rangle$

- $\mathbf{R}_n$, $|n\rangle = \phi(\mathbf{r} - \mathbf{R}_n)$ are the position and orbital of atom $n$

- We check $|\psi\rangle$ obeys Bloch's Theorem using $\hat{T}_\mathbf{a}\psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{a})$ which will map $|n\rangle = \phi(\mathbf{r} - \mathbf{R}_n)$ onto $|m\rangle = \phi(\mathbf{r} - \mathbf{R}_m)$ where $\mathbf{R}_n - \mathbf{a} = \mathbf{R}_m$

$$\hat{T}_\mathbf{a}\phi(\mathbf{r} - \mathbf{R_n}) = \phi(\mathbf{r} - \mathbf{R_n} + \mathbf{a}) = \phi(\mathbf{r} - (\mathbf{R_n} - \mathbf{a})) = \phi(\mathbf{r} - \mathbf{R_m})$$

- Applying the translation operator to $|\psi\rangle$

$$\hat{\mathbf{T}}_\mathbf{a}|\psi\rangle = \hat{\mathbf{T}}_\mathbf{a}\sum_\mathbf{n} e^{i\mathbf{k}\cdot\mathbf{R_n}}|n\rangle = \sum_\mathbf{m} e^{i\mathbf{k}\cdot\mathbf{R_n}}|m\rangle = e^{i\mathbf{k}\cdot\mathbf{a}}\sum_\mathbf{m} e^{i\mathbf{k}\cdot\mathbf{R_m}}|m\rangle = e^{i\mathbf{k}\cdot\mathbf{a}}|\psi\rangle$$

- So $|\psi\rangle$ obeys Bloch's Theorem

- We apply the Hamiltonian $\hat{H}$ to $|\psi\rangle$ and left multiply by $\langle 0|$ to find an equation for the dispersion $E(k)$

$$E(k) = \langle 0|\hat{H}|\psi\rangle = \sum_n e^{i\mathbf{k}\cdot\mathbf{R_n}}\langle 0|\hat{H}|n\rangle$$

# Tight binding – Linear chain

- From last slide $E(k) = \langle 0|\hat{H}|\psi\rangle = \sum_n e^{i\mathbf{k}\cdot\mathbf{R_n}}\langle 0|\hat{H}|n\rangle$

- Neglect matrix elements between orbitals *not* next to each other

- Define 'transfer integrals' $t^* = t = \langle n|\hat{H}|n+1\rangle$ and $\tilde{E}_0 = \langle n|\hat{H}|n\rangle$

- Hence $\mathbf{R}_n = 0, \pm\mathbf{a}$ and we obtain for the energy dispersion relation

$$E_k = \tilde{E}_0 + 2t\cos(ka)$$

- Diagram shows eigenvalues confined to a band of energy centred on $\tilde{E}_0$ where we assume $t < 0$ - applies to s-orbitals

- The weaker the wavefunction overlap the narrower the band

- Because we apply periodic boundary conditions the allowed values of $k$ are discrete but close together spaced by $\Delta k = 2\pi/L$ where $L = Na$

- If $N$ is very large the energies form a continuous band

Note – some textbooks will define:

$$t = -\langle n|\hat{H}|n+1\rangle$$
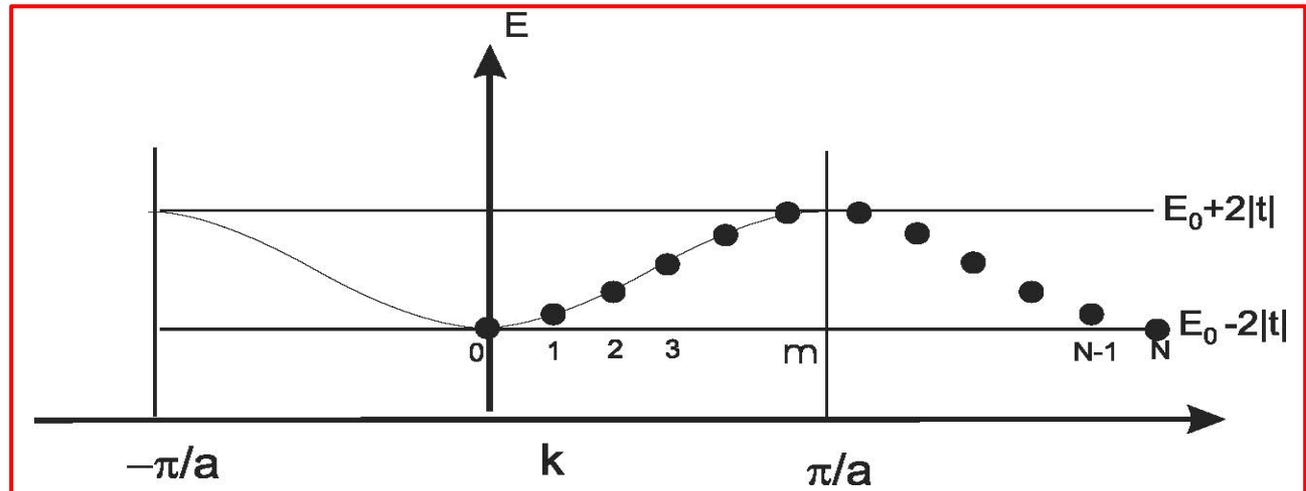
# Tight binding – three dimensions

- To extend to three dimensions again use $\left|\psi\right\rangle = \sum_n e^{i\mathbf{k}\cdot\mathbf{R_n}}\left|n\right\rangle$ but extend the sum over all atoms in the 3D solid

- The dispersion $E(\mathbf{k}) = \sum_n e^{i\mathbf{k}\cdot\mathbf{R_n}}\left\langle 0\right|\hat{H}\left|n\right\rangle$ now contains contributions from nearest neighbour interactions in all three directions

- Assume that $\left\langle 0\right|\hat{H}\left|n\right\rangle = 0$ if atom n is not a nearest neighbour to atom $0$.

- If atom $n$ is a nearest neighbour to atom $0$ then $\left\langle 0\right|\hat{H}\left|n\right\rangle = t$

- For simple cubic crystal then $\mathbf{R}_n = (\pm a, 0, 0); \ (0, \pm a, 0); \ (0, 0, \pm a)$

- Hence summing over all values of $\mathbf{R}_n$

$$E_k = \tilde{E}_0 + 2t\left[\cos\left(k_x a\right) + \cos\left(k_y a\right) + \cos\left(k_z a\right)\right]$$

- Energies are confined to a band of width $12t$

- Figures assume $k_z = 0, \ a = 1$
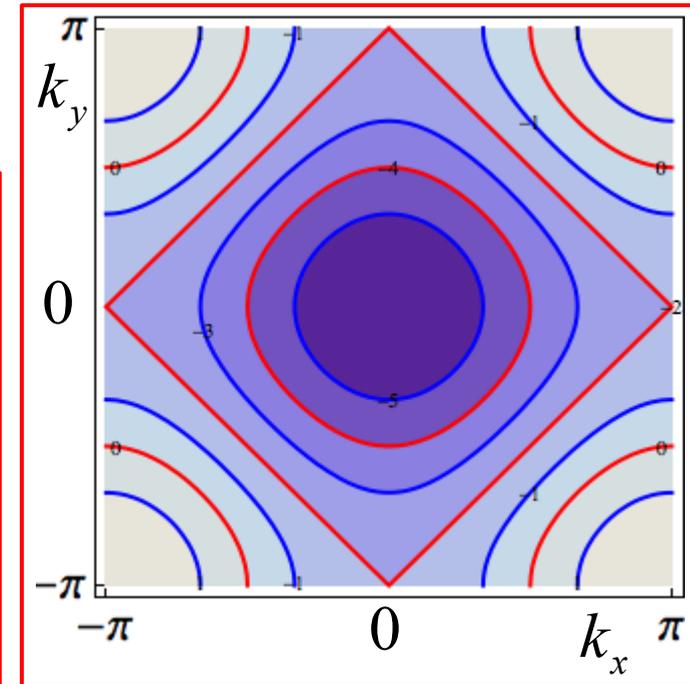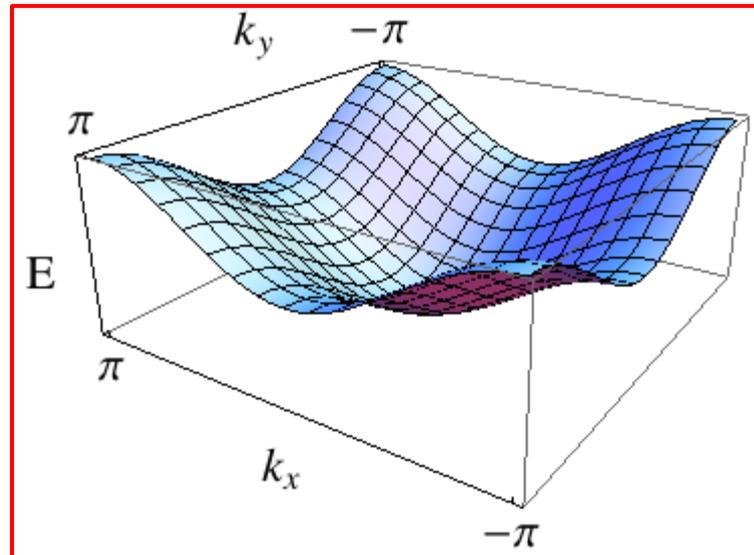
# Tight binding - 3D simple cubic crystal
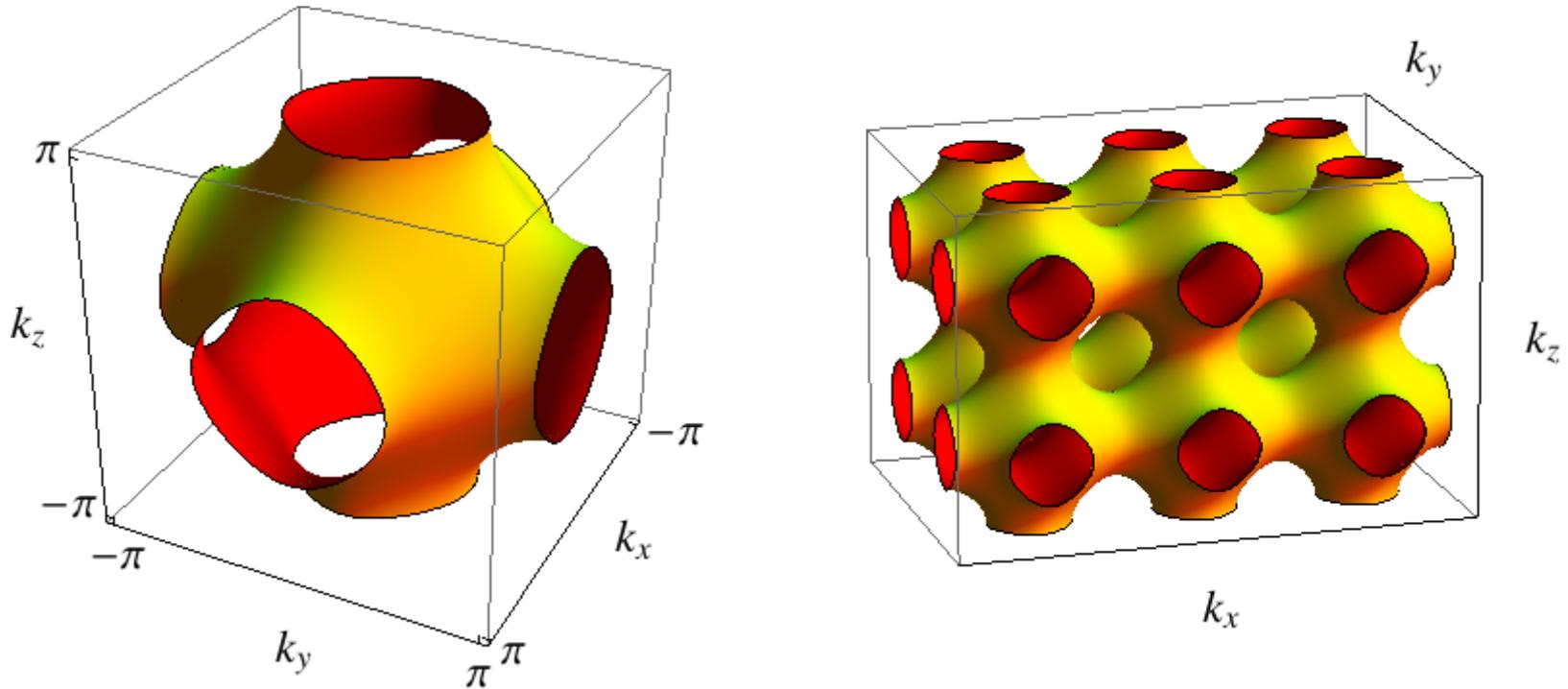


- Three dimensional constant energy surface in reciprocal space
- Calculated using tight binding for a single orbital per atom in a simple cubic lattice

$$E_k = \tilde{E}_0 + 2t\left[\cos\left(k_x a\right) + \cos\left(k_y a\right) + \cos\left(k_z a\right)\right]$$

- For FCC and BCC lattice bands calculated by tight binding see problem 2.4

# Summary of Lecture 7

- Nearly free electron approximation,

- Splitting of energy levels due to periodic potential

- Real space potential and wavefunctions,

- Reciprocal space band structure,

- Calculations for 3D metals

- Tight binding approximation – Linear combination of atomic orbitals

- Linear chain

- Three dimensional cubic crystal

# Quantum Condensed Matter Physics
## Lecture 7
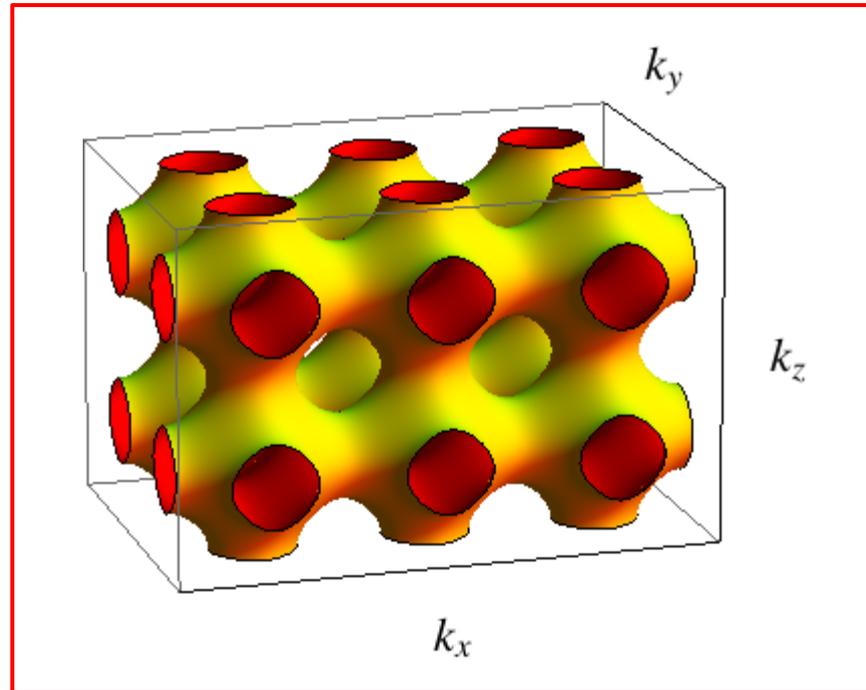


**The end**

# Quantum Condensed Matter Physics
## Lecture 8
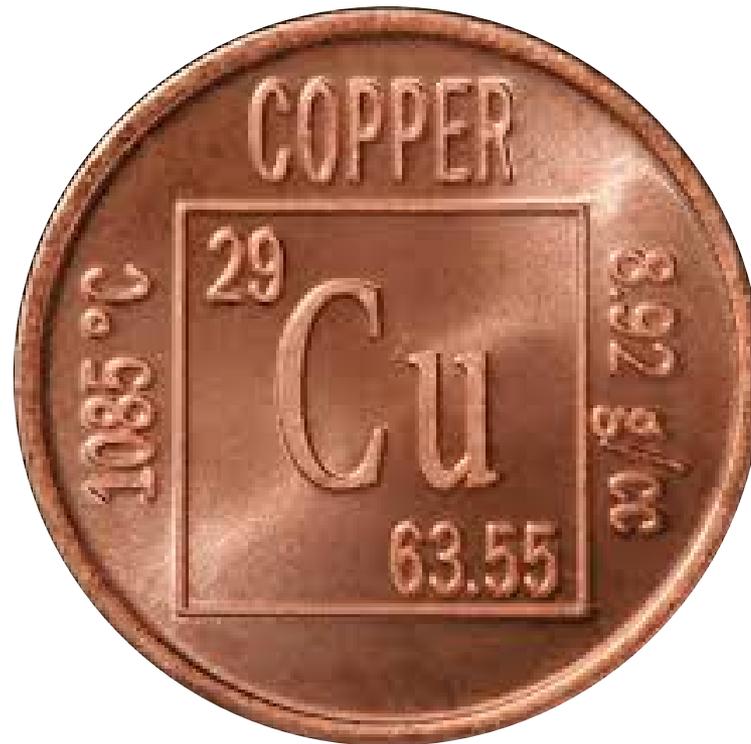


**David Ritchie**

# Quantum Condensed Matter Physics

1. Classical and Semi-classical  models for electrons in solids (3L)

2. Electrons and phonons in periodic solids (6L)

………. Nearly free electron approximation; plane waves and bandgaps. Tight binding approximation; linear combination of atomic orbitals, linear chain and three dimensions, *two bands. Pseudopotentials. Band structure of real materials; properties of metals (aluminium and copper) and semiconductors.*

Semi-classical model of electron dynamics in bands; Bloch oscillations, effective mass, density of states, electrons and holes in semiconductors

3. Experimental probes of band structure (4L)

4. Semiconductors and semiconductor devices (5L)

5. Electronic instabilities (2L)

6. Fermi Liquids (2L)

# Tight binding – number of orbitals per atom

- To now we have calculated Bloch states with a single orbital for each atom – this only gives a single energy band

- The number of orbitals in the band that correspond to a non-degenerate atomic level is $2N$ for $N$ atoms - explained below

- Values of $\mathbf{k}$ within the first Brillouin zone define independent wavefunctions

- The simple cubic Brillouin zone has $-\pi/a < k_x < \pi/a$ etc and the volume in k-space is $8\pi^3/a^3$

- The number of orbitals (counting both spin orientations) per unit volume of k-space is $V/4\pi^3$ where $V$ is the volume of the crystal

- Hence the number of orbitals is $\left(8\pi^3/a^3\right) \times \left(V/4\pi^3\right) = 2V/a^3$

- Since $V$ is the volume of the crystal and $1/a^3$ the number of atoms per unit volume the number of atoms $N = V/a^3$

- Hence the number of orbitals is twice the number of atoms

# Tight binding – two bands

- To understand many materials we must extend this method so it produces several bands – we need to build Bloch states from several orbitals per site.

- We combine two orbitals $\left|a_n\right\rangle, \left|b_n\right\rangle$ to form a hybridised local orbital and combine these to form a Bloch state - coefficients $\alpha_{\mathbf{k}}, \beta_{\mathbf{k}}$ can depend on $\mathbf{k}$

$$\left|\psi\right\rangle = \sum_n e^{i\mathbf{k}\cdot\mathbf{R_n}}\left(\alpha_{\mathbf{k}}\left|a_n\right\rangle + \beta_{\mathbf{k}}\left|b_n\right\rangle\right)$$

- Inserting $\left|\psi\right\rangle$ into Schrodinger equation $\hat{H}\left|\psi\right\rangle = E\left|\psi\right\rangle$ left multiplying by basis states $\left\langle a_0\right|, \left\langle b_0\right|$ and turning into eigenvector problem we obtain

$$\begin{pmatrix} E_a(\mathbf{k}) - E & V_{\mathbf{k}} \\ V_{\mathbf{k}}^* & E_b(\mathbf{k}) - E \end{pmatrix}\begin{pmatrix} \alpha_{\mathbf{k}} \\ \beta_{\mathbf{k}} \end{pmatrix} = 0$$

- $E_a = \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n}\left\langle a_0\left|\hat{H}\right|a_n\right\rangle$ is the dispersion of a band formed exclusively from atomic orbitals $\left|a_n\right\rangle$

- $E_b = \sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n}\left\langle b_0\left|\hat{H}\right|b_n\right\rangle$ is dispersion of a band formed from $\left|b_n\right\rangle$ orbitals

- The off-diagonal matrix elements: $V_{\mathbf{k}} = \sum_{\mathbf{R_n}} e^{i\mathbf{k}\cdot\mathbf{R_n}}\left\langle a_0\left|\hat{H}\right|b_{\mathrm{n}}\right\rangle$ and with some relabelling

$$V_{\mathbf{k}}^* = \sum_{\mathbf{R_n}} e^{i\mathbf{k}\cdot\mathbf{R_n}}\left\langle b_0\left|\hat{H}\right|a_{\mathrm{n}}\right\rangle$$

# Tight binding – two bands

- The eigenvalue problem gives rise to two possible energies at each wavevector – forming two bands from two orbitals

- The effect of the off-diagonal elements is to hybridise the two bands (formed from each set of atomic orbitals) where they become nearly degenerate.

- We could have approached this problem by forming two Bloch states, one from each set of atomic orbitals

$$\left|\psi_a\right\rangle = \sum_n e^{i\mathbf{k}.\mathbf{R_n}}\left|a_n\right\rangle, \qquad \left|\psi_b\right\rangle = \sum_n e^{i\mathbf{k}.\mathbf{R_n}}\left|b_n\right\rangle$$

- Then combining the Bloch states using $\left|\psi\right\rangle = \alpha_{\mathbf{k}}\left|\psi_a\right\rangle + \beta_{\mathbf{k}}\left|\psi_b\right\rangle$ we obtain the same form as above for $\left|\psi\right\rangle$

- So the two routes are the same – (1) bandstructure arising from hopping between hybridised molecular orbitals or (2) hybridisation between bands arising from atomic orbitals

- To extend to multiple orbitals per unit cell we generalise the summation:

$$\left|\psi\right\rangle = \sum_{n,\nu} e^{i\mathbf{k}\cdot\mathbf{R_n}} c_{\mathbf{k}}^{\nu}\left|n^{\nu}\right\rangle$$

- Where $\nu$ labels the different orbitals $\left|n^{\nu}\right\rangle$ which exist in the $n^{th}$ unit cell and $c_{\mathbf{k}}^{\nu}$ is the associated coefficient determining the level of mixing of the orbital

- The number of bands is equal to the number of local orbitals per unit cell

# Tight Binding versus Nearly Free Electron approximation

- Tight Binding (TB) and nearly free electron (NFE) approx. do similar things:

- Both construct a Bloch state from a reduced set of basis functions

- Coefficients found by solving eigenvector/eigenvalue equation

- NFE basis set is selected from plane wave states $|\mathbf{k} - \mathbf{G}\rangle$ for which matrix elements $V_{\mathbf{G}}$ are large and which are nearly degenerate with $|\mathbf{k}\rangle$

- For smooth potential we disregard high $\mathbf{G}$ Fourier components - set of basis functions is small. Computers can use large plane wave basis sets.

- In the NFE approximation kinetic energy appears on diagonal of energy matrix and potential on off-diagonal terms – very efficient if potential is weak.

- TB allows reasonable answers with relatively little computation

- Atomic orbital states associated with different unit cells of crystal form a complete basis set in which Bloch states can be expanded

- Number of bands equals the number of atomic orbitals used per unit cell

- If the hopping matrix elements are less than separation between bands then bands do not cross – strength of the potential is larger than kinetic energy

- In TB potential energy appears on diagonal. Hopping elements – equivalent of kinetic energy, form off-diagonal terms

# Pseudopotentials

- The NFE and TB methods are not accurate predictors of band structure

- Commonly used to form simple models with parameters determined by experiment or more complex calculations

- Band gaps in semiconductors often small – only a few Fourier components of potential required because effective scattering potential for valence electrons is much smaller than full atomic potential

- Effective potential called pseudopotential which reproduces valence states as lowest eigenstates of problem – we can forget about core states.

- The true potential $V(r)$ has a wavefunction for valence electrons $\Phi(r)$ that oscillates near the core

- Pseudopotential $V_s(r)$ has a wavefunction $\Phi_s(r)$ that is smooth near the core

- Pseudo potential wavefunction approximates wavefunction far from core

- Very successful empirical pseudopotential method - band structure calculated using a few $V_{\mathbf{G}}$ obtained from fits to measurement of optical reflectance and absorption
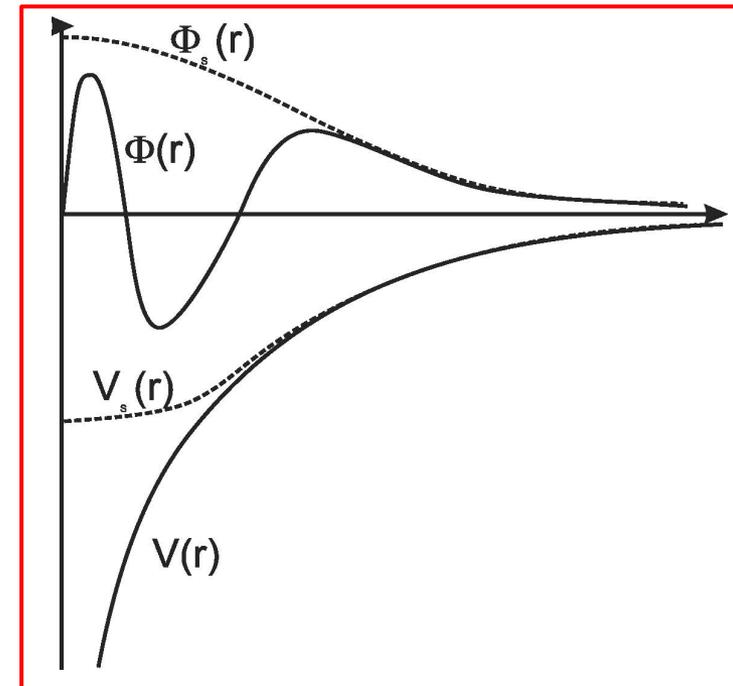
# Band structures of real materials

- Band gaps arise because of interference between forward and backward going degenerate plane waves mixing to form standing waves

- Band gap in 3D arises from splitting of degeneracy due to scattering from Fourier component of lattice potential so we require $E_0(\mathbf{k}) = E_0(\mathbf{k} - \mathbf{G})$ for a given $\mathbf{G}$ we find the $\mathbf{k}$ so

$$| \mathbf{k} |^2 = | \mathbf{k} - \mathbf{G} |^2 \Rightarrow \mathbf{k} \cdot \mathbf{G} / 2 = \left| \mathbf{G} / 2 \right|^2$$

- Satisfied by any $\mathbf{k}$ lying in a plane perpendicular to and bisecting $\mathbf{G}$

- This is the boundary of a Brillouin zone and the Bragg scattering condition

- Energy eigenstates form discrete bands $E_n(\mathbf{k})$ which are continuous functions of momentum $\mathbf{k}$ and labelled by a band index $n$

- Bandstructure is periodic in reciprocal lattice $E_n(\mathbf{k}) = E_n(\mathbf{k} - \mathbf{G})$

- Eigenstates are in form given by Bloch's theorem $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r})$ which continues to hold if $\mathbf{k} \to \mathbf{k} + \mathbf{G}$ so $\mathbf{k}$ can always be chosen in the first Brillouin zone

- $\hbar\mathbf{k}$ is '*crystal momentum',* enters conservation laws for scattering processes e.g., if an electron absorbs the momentum of a phonon of wavevector $\mathbf{q}$, the final state will have a Bloch wavevector $\mathbf{k}' = \mathbf{k} + \mathbf{q} + \mathbf{G}$ where $\mathbf{G}$ is the reciprocal lattice vector necessary to keep $\mathbf{k}'$ inside the first Brillouin zone

# Band structures of real materials

- The spacing between **k**-points in 1D is $2\pi/L$ where $L$ is the linear dimension of the crystal. Generalising to 3D, the volume associated with each **k**-value is: $(\Delta \mathbf{k})^3 = (2\pi)^3/V$ with $V$ the volume of the crystal.

- Within each Brillouin zone the number of **k**-states allowed by periodic boundary conditions equals the number of unit cells in the crystal.

- This is so large bands are continuous and we use the density of states

- Electrons are fermions so each **k**-point is occupied by two $(\uparrow, \downarrow)$ electrons

- In a system with one electron per unit cell (e.g. lattice of sodium atoms) half the states will be filled in the first Brillouin zone – hence a metal

- With a system with two electrons per unit cell the first Brillouin zone will be filled meaning that it may be an insulator if the band gap is large enough, but if the Fermi energy lies within a band the material will be a metal.

- If bands overlap so there are 2 or more partially filled bands we have a metal

- When the energy between electrons due to Coulomb repulsion is larger than the bandwidth then materials can be 'Mott insulators'. They can undergo a metal to insulator transition if electron density or temperature changes.

# Band structures of real materials - notation

- The bandstructure $E_n(\mathbf{k})$ defines a 3D function which is difficult to visualise

- By convention, cuts through this function are plotted along particular directions in k-space

- A shorthand is used to label points in k-space

- Diagram shows 1st Brillouin zone for several crystal lattices with labelled points

- The zone centre $\Gamma = (0,0,0)$

- Example: for FCC the X point $\frac{2\pi}{a}(1,0,0)$ etc is at the zone edge in 6 $(100)$ directions

- L is on the zone boundary at $\frac{\pi}{a}(1,1,1)$ in 8 $(111)$ directions

- K is at zone edge in $(110)$ direction

- W is at square/hexagon intersection



Face centred cubic

Body centred cubic

$K$

Simple cubic

Hexagonal
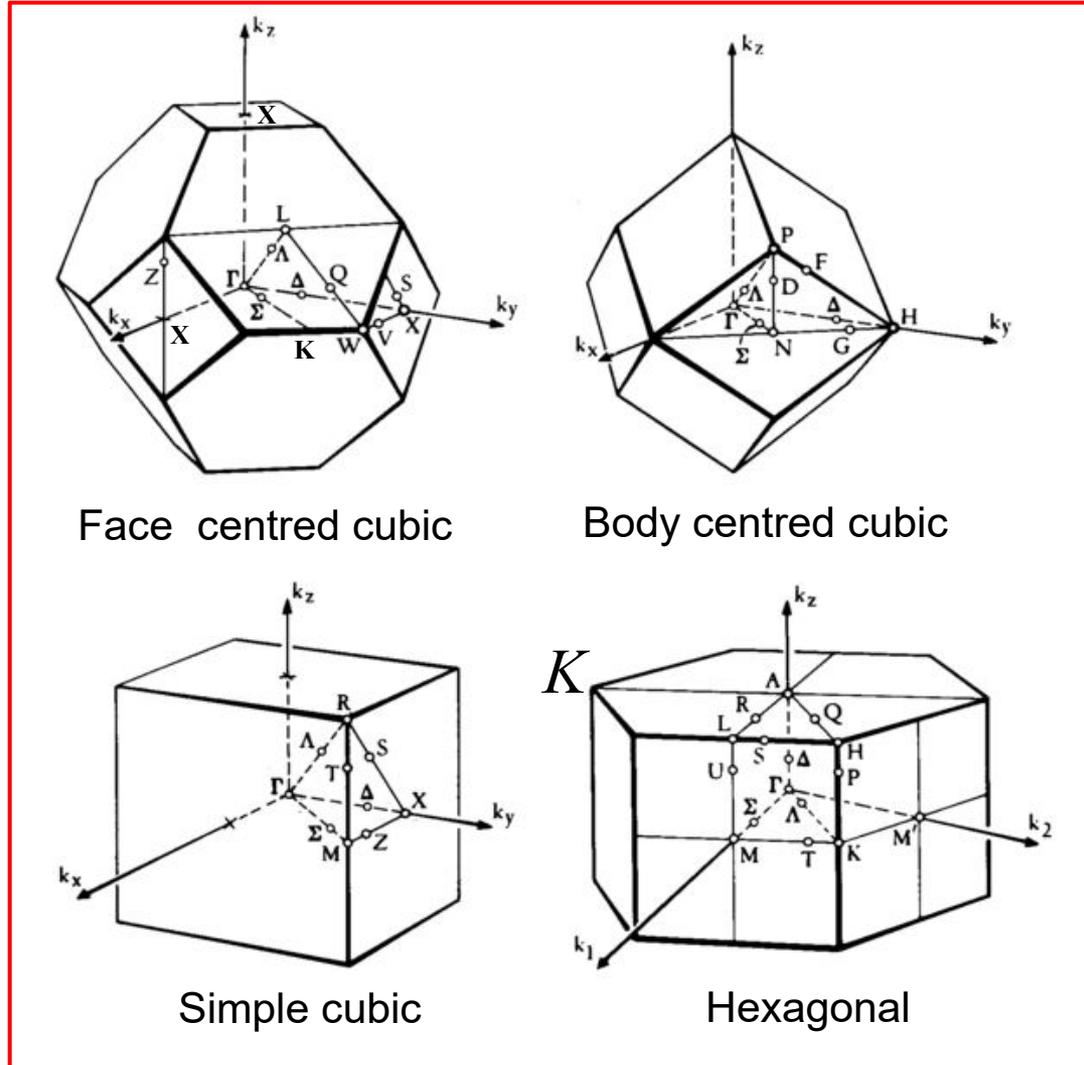
# Examples of band structures - Metals

- With an odd number of electrons per primitive unit cell, chemical potential must lie within a band, hence no energy gap. Because low-energy electronic excitations are possible, the system is a metal.

- In a simple metal such as $Na$ ($3s^1$ with 1 valence electron) or $Al$ ($3s^2 3p^1$ with 3 valence electrons) Fermi surface is close to a free-electron sphere

- In other cases (e.g. $Cu$ $3d^{10} 4s^1$) the sphere extends in some directions to meet the Brillouin zone boundary surface. There can be situations where several bands are cut by the Fermi energy, and the topology of Fermi surfaces is sometimes complicated – studied by de Hass - Van Alphen effect.

Fermi surface of copper

- Even with the right number of electrons to fill bands and make a semiconductor, the bands may still overlap. Consequently, the fermi surface will intersect more than one band, making a pocket of electrons in one band and removing a pocket of electrons from the band below (making *holes*). This accounts for the metallicity of Ca and Mg and (which have two electrons per unit cell), and also As, Sb, Bi,. These are known as semimetals
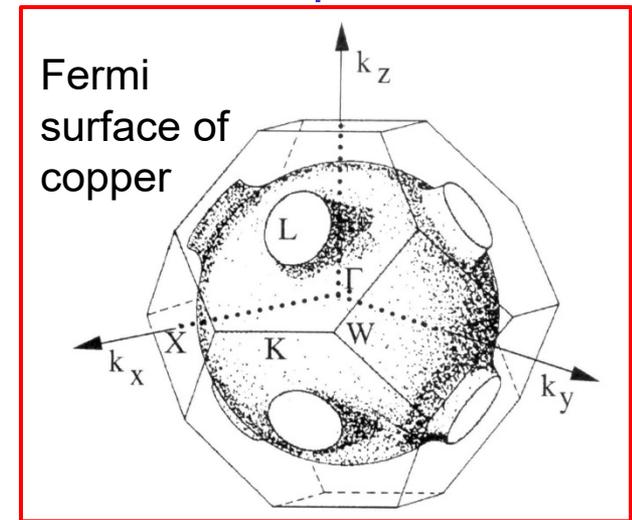
# Aluminium band structure

- Has three valence electrons in configuration $3s^2 3p^1$
- FCC crystal structure hence BCC reciprocal lattice – shown below
- First Brillouin zone full, valence electrons spread into 2nd, 3rd and 4th
- Band structure close to free electron parabola except when near Brillouin zone boundaries, bands fill up to Fermi level
- No clear band gap in all the directions - hence a metal
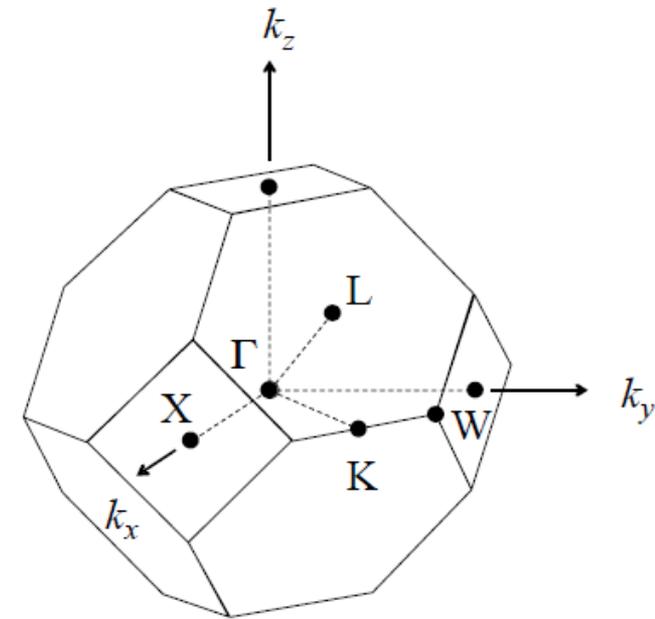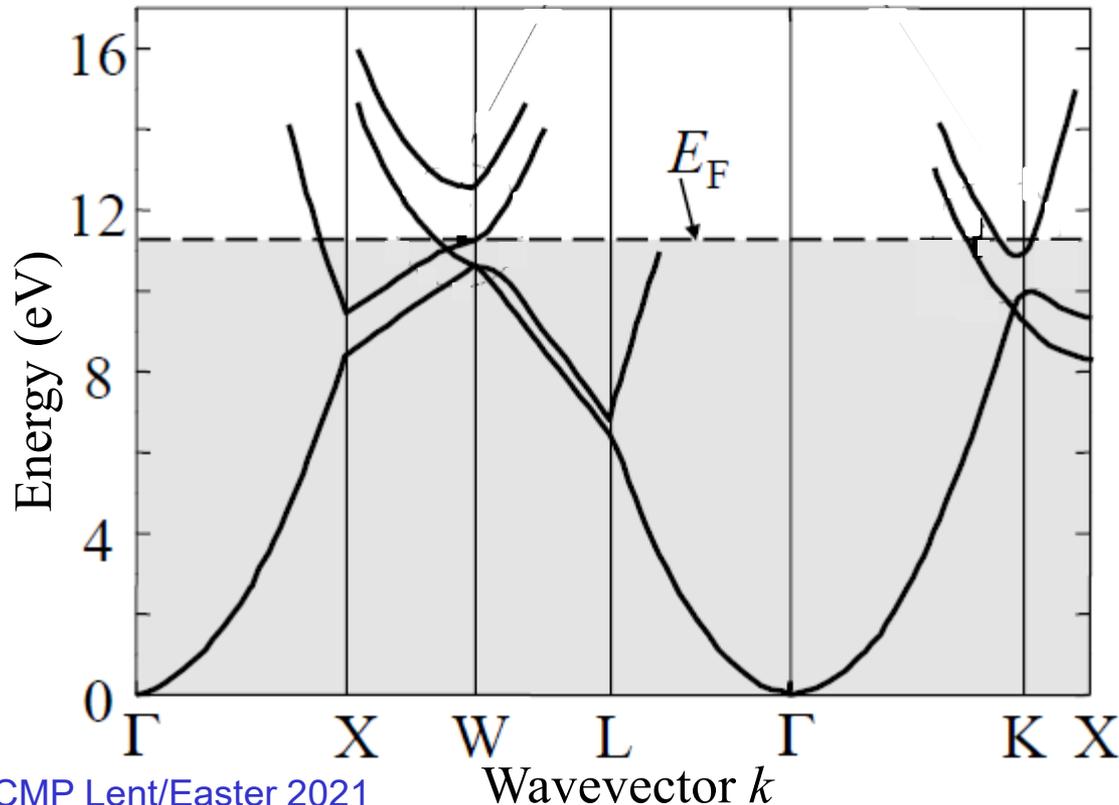


Brillouin zone of FCC lattice

# Aluminium band structure

- Transitions from filled states below $E_F$ to empty states above $E_F$

- Fermi's golden rule states density of states determines transition rates - depends on both initial and final density of states

- High density of states for parallel bands - Hence reflectivity dip at $1.5eV$

- Band structure suggests transitions possible over range of energies $> 1.5eV$ not parallel bands so less significant but does reduce reflectivity

Transition energy ~ 1.5eV



From Lecture 1

Reflectivity of Aluminium

Theory

$\hbar\omega_p = 15.8eV$

Experimental data

Data from Ehrenreich et al (1963)

B Segall Phys Rev **124**, 1797 (1961)
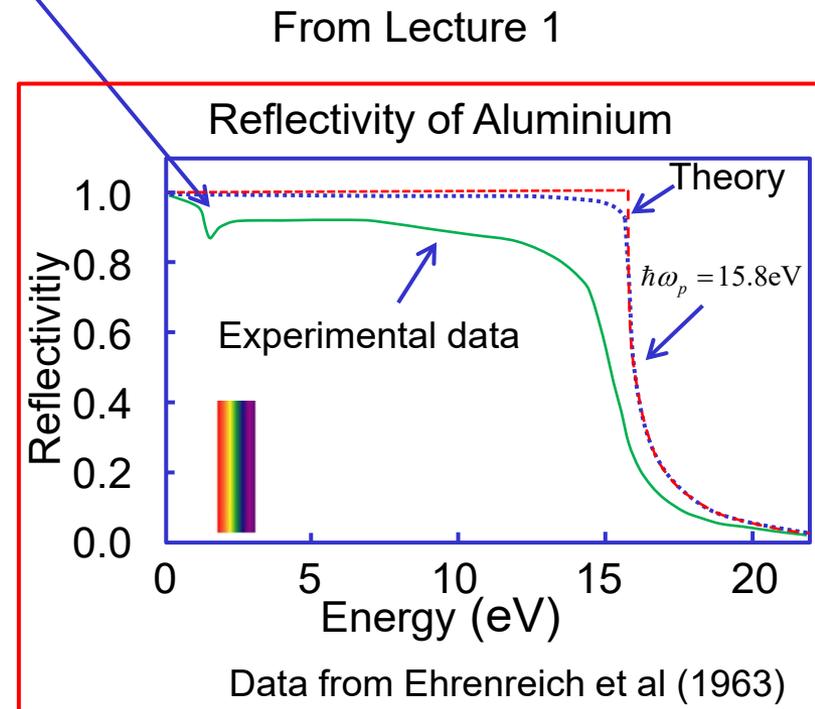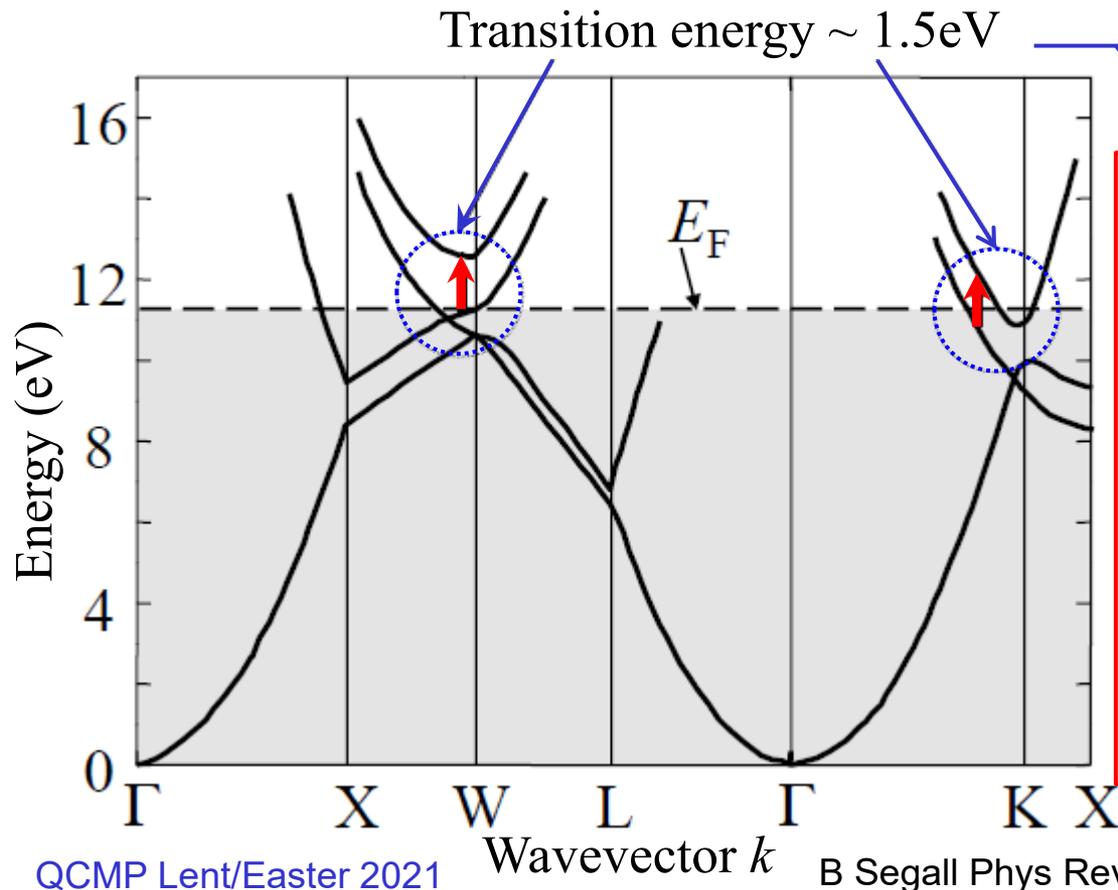
# Copper band structure

Electron configuration $[Ar]3d^{10}4s^1$
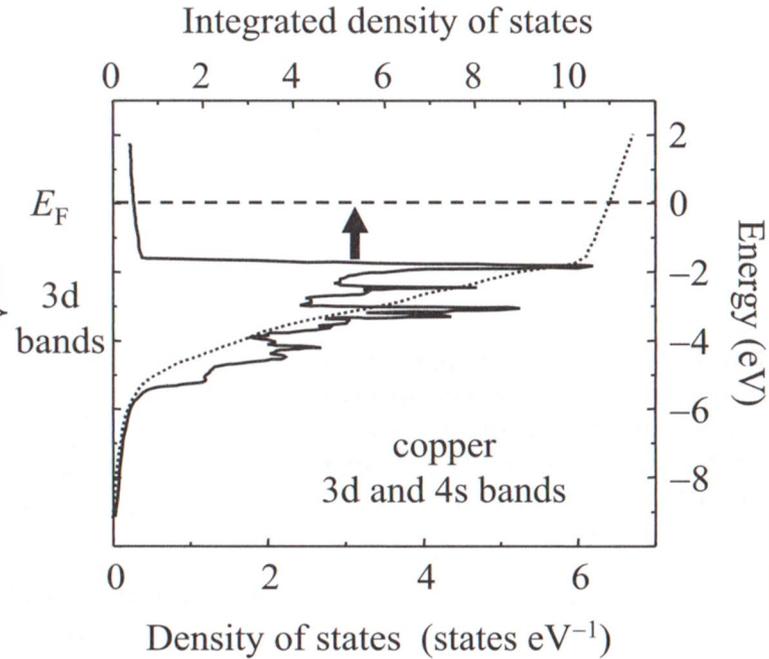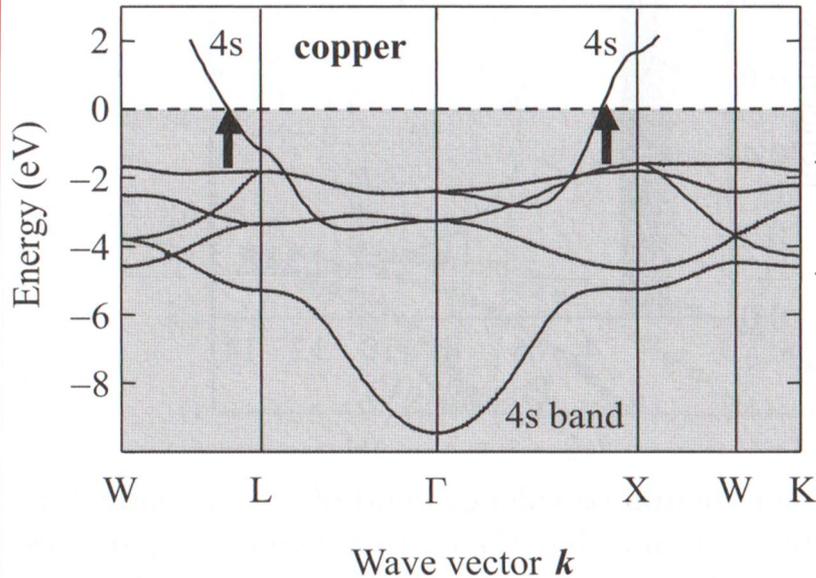


- 3d tightly bound, narrow band, high DoS, full – 10 electrons
- 4s free electron like, lower DoS, broader band - 1 electron
- Fermi surface in the 4s band and above 3d band
- Transitions possible - filled 3d to 4s states above $E_F$
- Well defined threshold for transitions about 2eV
- Reflectivity above 2eV reduced due to interband absorption well below plasma frequency at 10.8eV
- Reflectivity falls in visible part of spectrum – hence colour

From *Optical properties of solids*   Mark Fox
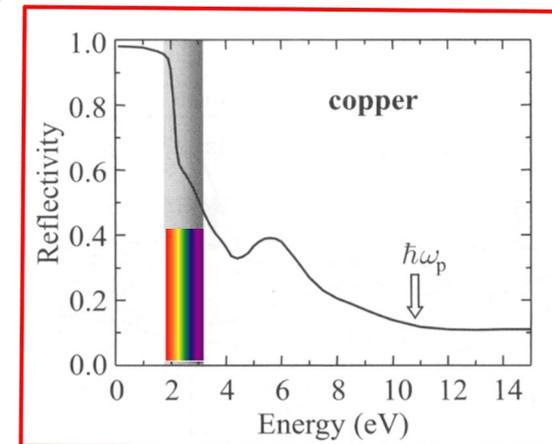
# Semiconductors

- If there is an even number of electrons per unit cell, it is possible (with no band overlap) for all of the occupied states to fill bands, with an energy gap to the empty states.

- The system will be a semiconductor or insulator – the case for the group IV elements, C, Si, Ge as well as III-V compounds such as GaAs, InP.

- These semiconductors have 2 atoms per unit cell (diamond or zincblende structure) and 8 valence electrons per unit cell — 4 filled bands.

- Maximum in valance band for both Si and GaAs is at $\Gamma$.

- Minimum in conduction band is also at $\Gamma$ for GaAs (direct bandgap) but is at $X$ for Si (indirect bandgap). Bandgap shown in blue
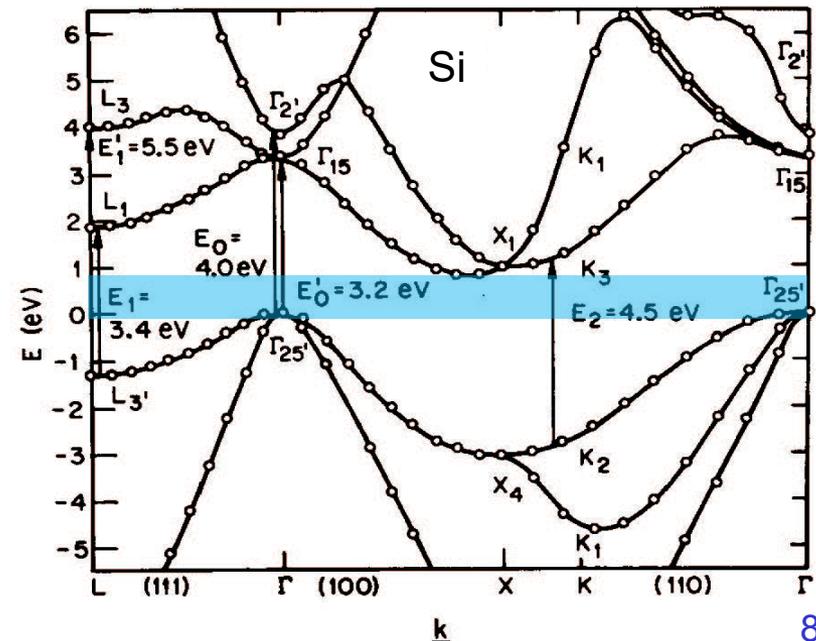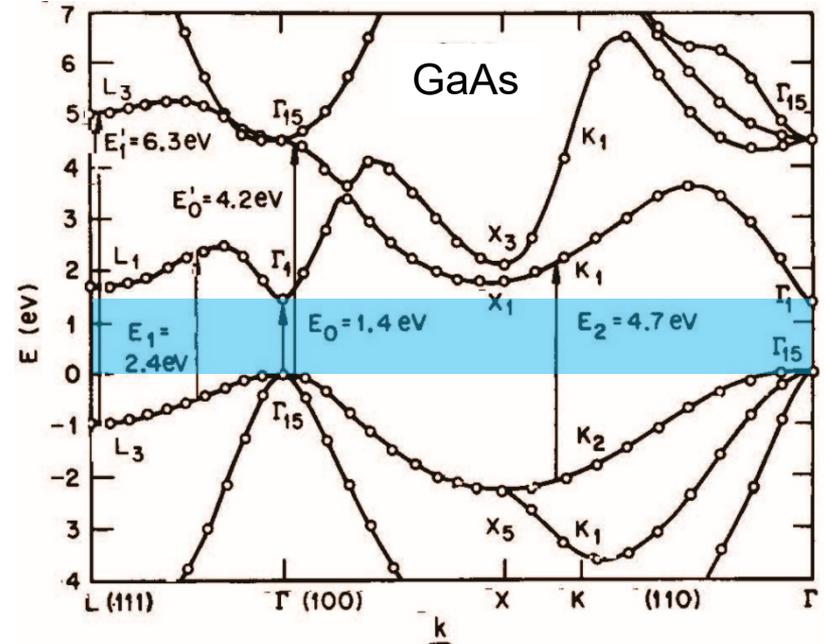
# Summary of Lecture 8

- Tight binding - number of orbitals,

- Tight binding - two bands,

- Tight binding versus nearly free electron approximations

- Pseudopotentials

- Bandstructure of real materials

- Metals, semi-metals

- Example - Aluminium

- Example - Copper

- Example – Si and GaAs Semiconductors

# Quantum Condensed Matter Physics
## Lecture 8



**The end**