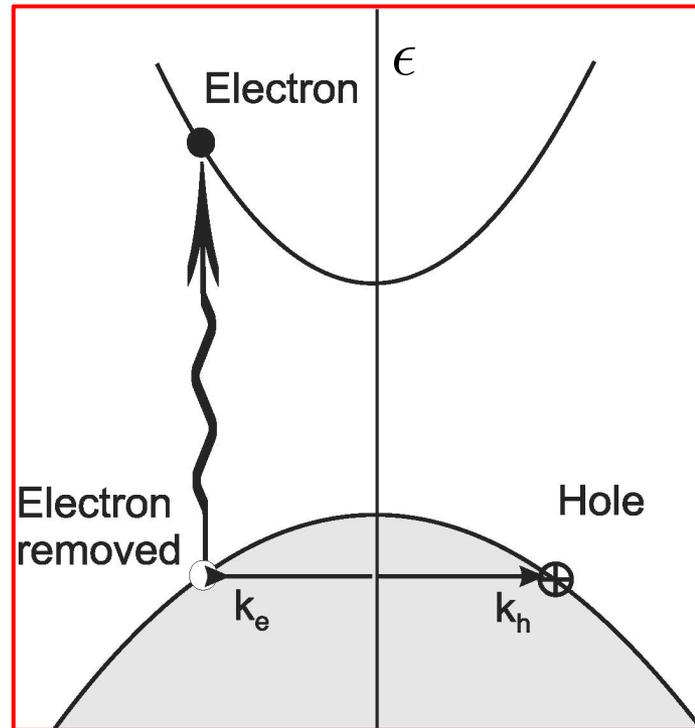


Quantum Condensed Matter Physics

Lecture 9



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

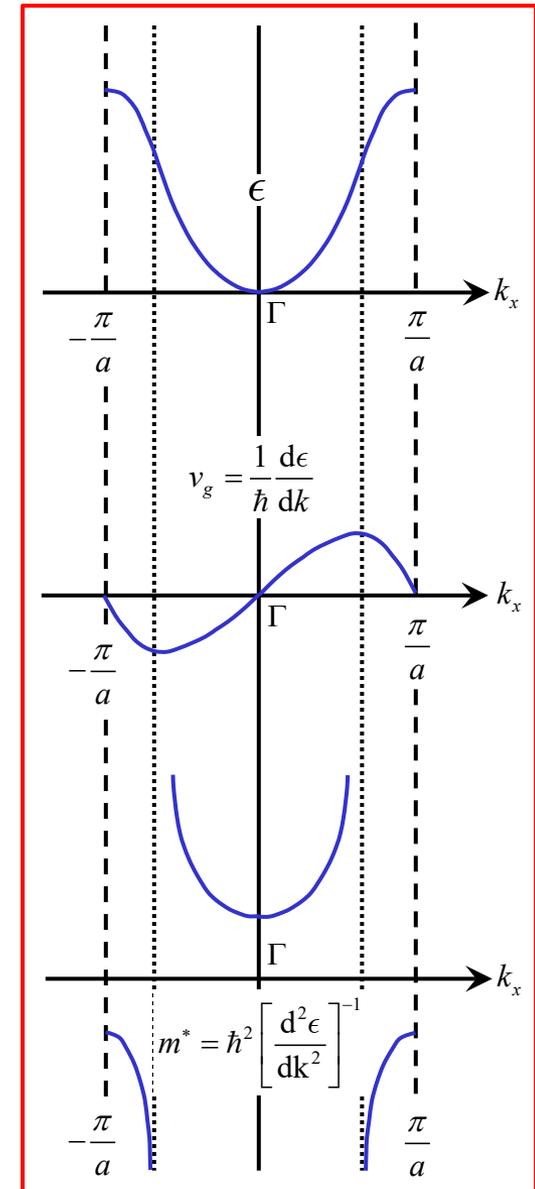
3. Experimental probes of band structure (4L)
4. Semiconductors and semiconductor devices (5L)
5. Electronic instabilities (2L)
6. Fermi Liquids (2L)

Semiclassical model of electron dynamics

- We now discuss the dynamics of electrons in energy bands
- The bandstructure is dispersive so we should treat particles as wave-packets, a superposition of different $|\mathbf{k}\rangle$
- The band energy $\epsilon(\mathbf{k})$ is the frequency associated with the phase rotation of the wavefunction $\psi_{\mathbf{k}} \propto e^{-i\epsilon(\mathbf{k})t/\hbar}$
- For the motion of a wave in a dispersive band we should use the group velocity $v_g = d\omega / dk$ which as a vector is $\mathbf{v}_g = \dot{\mathbf{r}} = \hbar^{-1} \nabla_{\mathbf{k}} \epsilon(\mathbf{k})$
- Note that the effects of the lattice potential are contained in $\epsilon(\mathbf{k})$
- If a force is applied to a particle, the rate of doing work on that particle is given by
$$\frac{d\epsilon_{\mathbf{k}}}{dt} = \frac{d\mathbf{k}}{dt} \cdot \nabla_{\mathbf{k}} \epsilon(\mathbf{k}) = \mathbf{F} \cdot \mathbf{v} \Rightarrow \mathbf{F} = \hbar \frac{d\mathbf{k}}{dt}$$
- And introducing electric and magnetic fields
$$\mathbf{F} = \hbar d\mathbf{k} / dt = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) = -e(\mathbf{E} + \hbar^{-1} \nabla_{\mathbf{k}} \epsilon(\mathbf{k}) \times \mathbf{B})$$
- An electric field shifts the crystal momentum $\hbar\mathbf{k}$ in the direction of the field
- A magnetic field causes an electron to move in k-space in a plane perpendicular to the field on a path of constant energy
- This is the basis of techniques to measure the Fermi surface of metals

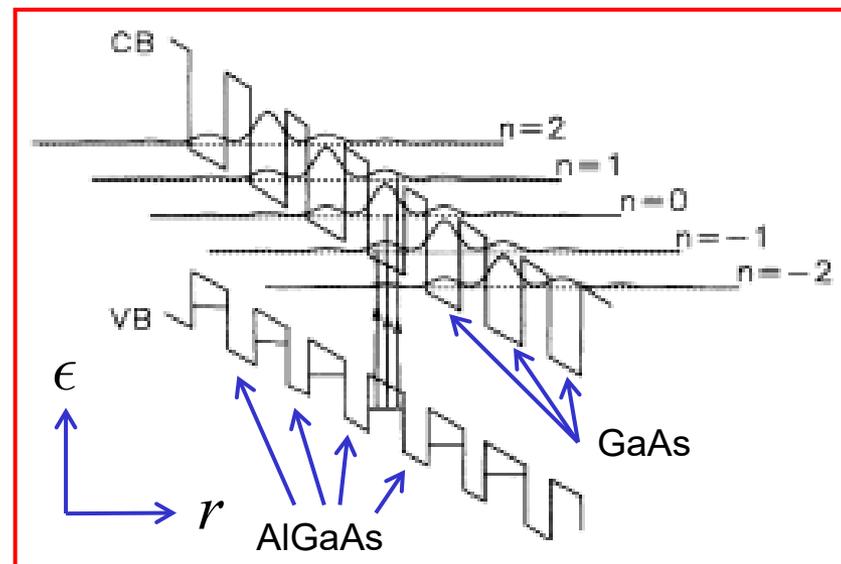
Semiclassical model of electron dynamics

- The diagram shows the energy, ϵ group velocity $\hbar^{-1}d\epsilon/dk$ and effective mass $m^* = \hbar^2 / (d^2\epsilon/dk^2)$ of an electron for a 1D band
- Applying an electric field $k(t) = k(0) - eEt/\hbar$ k increases steadily with time throughout, initially its velocity increases as for a free electron.
- As the electron moves up the band $d^2\epsilon/dk^2$ decreases and the effective mass increases until the acceleration stops and the velocity is constant.
- As $d^2\epsilon/dk^2$ changes sign the effective mass becomes negative and the velocity starts to fall until it reaches zero at the zone boundary, becoming negative as it passes to the next zone
- As k increases further moving up and down the band structure, the velocity oscillates with time and the electron's position oscillates with time
- So applying a DC voltage results in an AC current
- No net current flows and we have an insulator!



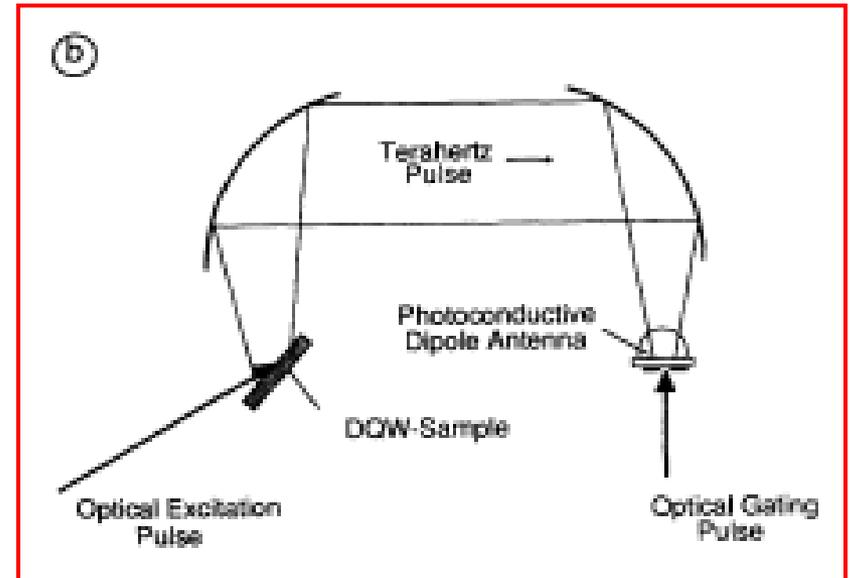
Bloch oscillations

- So far all attempts to observe *Bloch oscillations* in a crystal have failed.
- This is due to scattering off impurities and phonons in the solid as the momentum approaches π / a , however it is possible with artificial structures
- Using alternating thin layers of GaAs (9.7nm) and $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ (1.7nm) repeated 35 times, an artificial periodic potential is created with a periodicity 40 times longer than the atomic spacing, known as a *superlattice*.
- The momentum at the zone boundary for this superlattice is 40 times lower than in a crystal and the wavepacket does not need such large velocities.
- The diagram shows energy versus position of the conduction and valence bands of the superlattice
- The tilting is produced by the applied electric field. The levels shown form a *Wannier-Stark* ladder for electron wavepackets made by excitation from the valence band in one quantum well, either vertically ($n = 0$) or to neighbouring ($n = \pm 1$) or next-neighbouring ($n = \pm 2$) wells of the electron lattice.



Bloch Oscillation measurements

- Experiment used terahertz time domain spectroscopy
- A technique only sensitive to coherent emission processes
- Experimental setup to observe the dipole radiation from oscillating charge is shown in the figure
- An unfocused optical femtosecond beam from a Ti-sapphire laser with a pulse duration of 100 fs , strikes the sample at an angle of 45°
- The sample is held in a cryostat at 10 K.
- Terahertz radiation, emitted collinearly with the reflected optical excitation beam leaves cryostat and is collected with a pair of off-axis paraboloid mirrors and detected by a photoconductive dipole antenna
- This photoconductive dipole antenna is gated by a second, time-delayed portion of the femtosecond laser beam to measure electric field emitted from sample as a function of time on ps timescale.

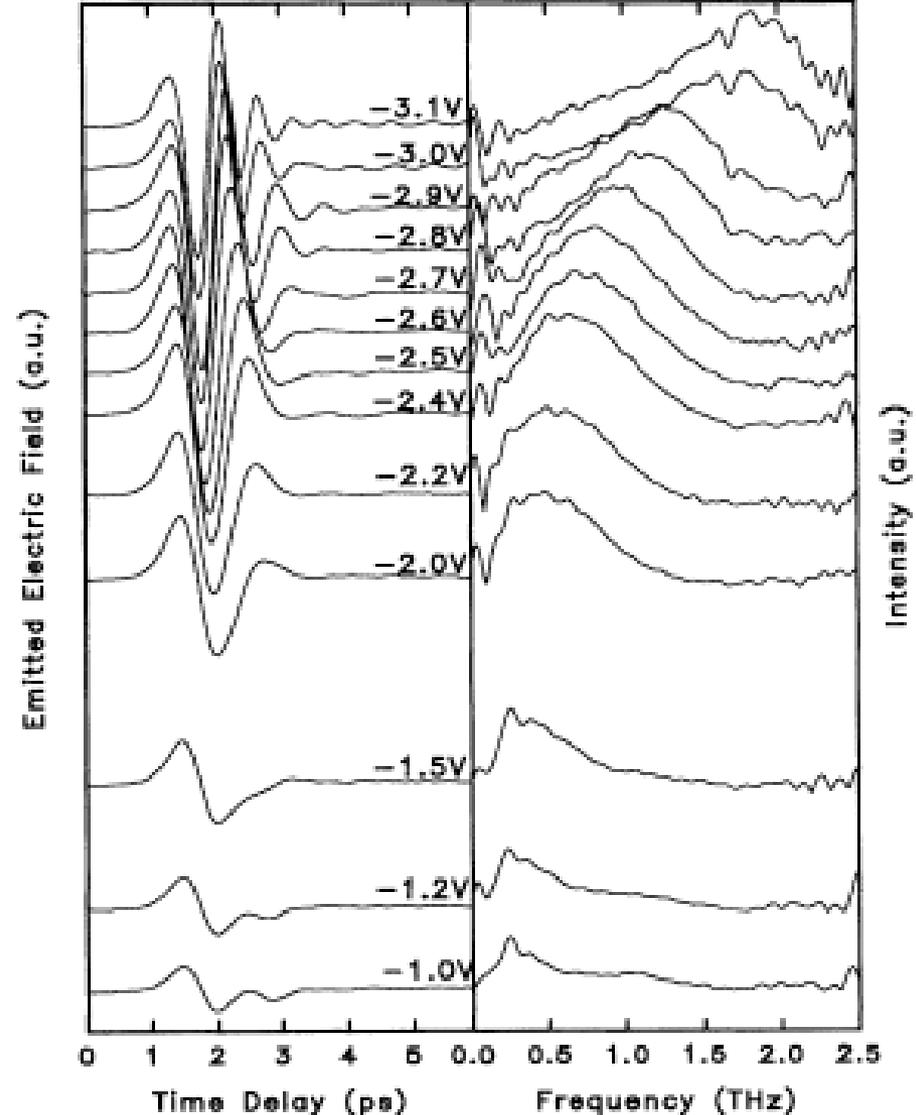


H G Roskos et al Phys Rev Lett **68**, 2216 (1992)

C Waschke et al Phys Rev Lett **70**, 3319 (1993)

Bloch Oscillation measurements

- In the experiment, electron and hole pairs are excited optically by a 100 fs pulsed laser with energy just above the band gap of GaAs
- The coherent terahertz radiation is measured as a function of time (left panel) for different DC electrical biases, more oscillations are seen as the bias becomes more negative
- The spectral content is determined by taking a Fourier transform of the results (right panel)
- The frequency of the Bloch oscillation peak increases as the bias becomes more negative than -2.4 V



Density of states – energy bands

- Earlier in the course we discussed the density of states of a free electron gas.
- The maxima E_{max} and minima E_{min} of all bands have a locally quadratic dispersion with respect to momentum measured from the maxima or minima
- We can define the effective masses with α referring to Cartesian coordinates

$$m_{\alpha}^* = \hbar^2 \left[\partial^2 E(\mathbf{k}) / \partial k_{\alpha}^2 \Big|_{\mathbf{k}_{min}} \right]^{-1}$$

- The 3D density of states near the minimum is given by

$$g(E \geq E_{min}) = \frac{V}{2\pi^2} \left(\frac{m^*}{\hbar^2} \right)^{3/2} \sqrt{E - E_{min}}$$

- The bare mass has been replaced by an effective mass $m^* = (m_x^* m_y^* m_z^*)^{1/3}$ which averages the curvature of the bands in 3D
- A similar form applies near the band maxima with $g(E) \propto \sqrt{E_{max} - E}$
- The flatter the band the higher the effective mass and the larger the density of states

Density of states

- For any form of $E(\mathbf{k})$ the density of states is given by

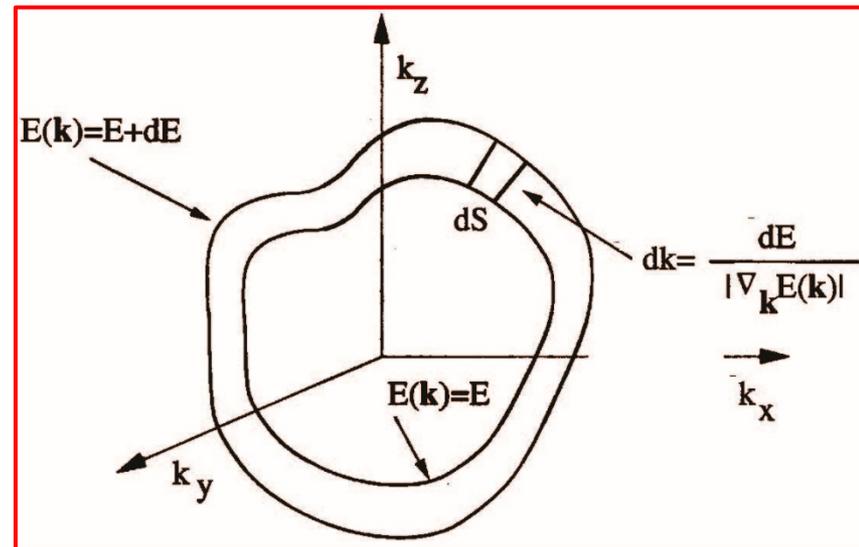
$$g(E) = \sum_n g_n(E) = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \delta(E - E_n(\mathbf{k}))$$

- Because of the δ function the momentum integral is over a surface in k-space S_n which depends on the energy E , e.g. $S_n(E_F)$ is the Fermi surface
- We can separate the integral into a 2D surface integral along a contour of constant energy and an integral perpendicular to this surface dk_{\perp} , hence

$$g_n(E) = \int_{S_n(E)} \frac{dS}{4\pi^3} \int \delta(E - E_n(\mathbf{k})) dk_{\perp}$$

$$= \int_{S_n(E)} \frac{dS}{4\pi^3} \frac{1}{|\nabla_{\perp} E_n(\mathbf{k})|}$$

given $\delta(f(x) - f(x_0)) = \delta(x - x_0) / |f'(x_0)|$



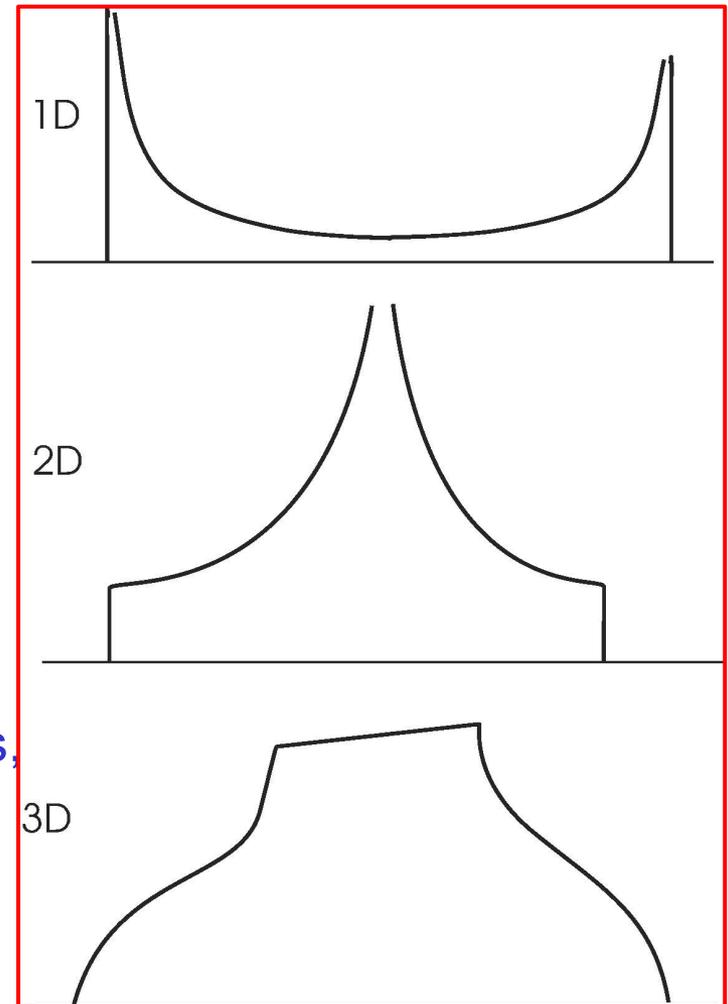
- $\nabla_{\perp} E_n(\mathbf{k})$ is the derivative of the energy in the normal direction which becomes zero at the edges of the bands and the saddle points which can exist in 2D and 3D bands, hence the cusps in the DoS

Density of states

- Maxima, minima, and saddle points are all generically described by dispersion (measured relative to the stationary point) of

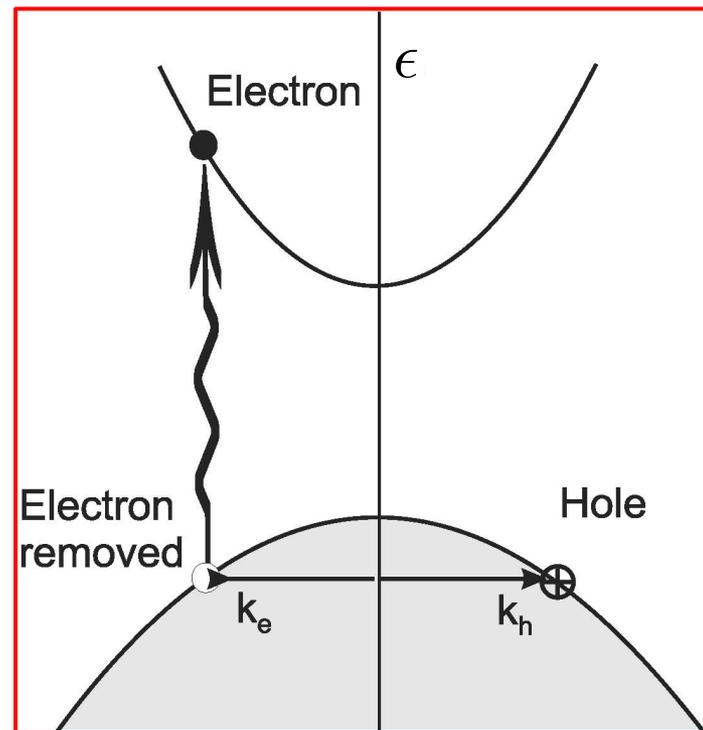
$$E(\mathbf{k}) = E_0 \pm \frac{\hbar^2}{2m_x} k_x^2 \pm \frac{\hbar^2}{2m_y} k_y^2 \pm \frac{\hbar^2}{2m_z} k_z^2$$

- If all the signs are positive, this is a band minimum; if all negative, a band maximum; when the signs are mixed there is a saddle point.
- In the vicinity of each of these critical points, (van Hove singularities) the density of states or its derivative is singular. In two dimensions, a saddle point gives rise to a logarithmically singular density of states, whereas in three dimensions there is a discontinuity in the derivative.
- Examples of the generic behaviour of the density of states in 1D, 2D and 3D are shown in the figure



Electrons and holes in semiconductors

- Filled bands are inert, if all the states in a Brillouin zone are occupied, total current is obtained by integrating the group velocity over the whole zone
- The group velocity is $v_g = \hbar^{-1} d\epsilon / dk$ and $\epsilon(k)$ is a periodic function so the integral yields zero and there is no net current
- All insulators have even valence or a lattice containing an even number of atoms in the basis hence filled bands
- Consider what happens if we move an electron from the valence band to the conduction band by absorption of a photon
- This creates an electron hole-pair
- For typical values of energy the photon momentum is very small compared to the electron momentum and it adds negligible momentum to the system
- Hence the *hole momentum* is the negative of the momentum of the empty electron state so $\mathbf{k}_h = -\mathbf{k}_e$



Electrons and holes in semiconductors

- *Hole energy.* If the zero of energy is at the top of the band. The lower in the band the missing electron lies the higher the energy of the system. The energy of the hole is opposite in sign to the energy of the missing electron because it takes more work to remove an electron from a low orbital than a high orbital.

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

- *Hole velocity.* if we combine these two rules together then since there are two sign changes $\mathbf{v}_h = \hbar^{-1} \nabla_{\mathbf{k}_h} \epsilon_h(\mathbf{k}_h) = \hbar^{-1} \nabla_{\mathbf{k}_e} \epsilon_e(\mathbf{k}_e) = \mathbf{v}_e$ and the velocity of the hole equals the velocity of the electron

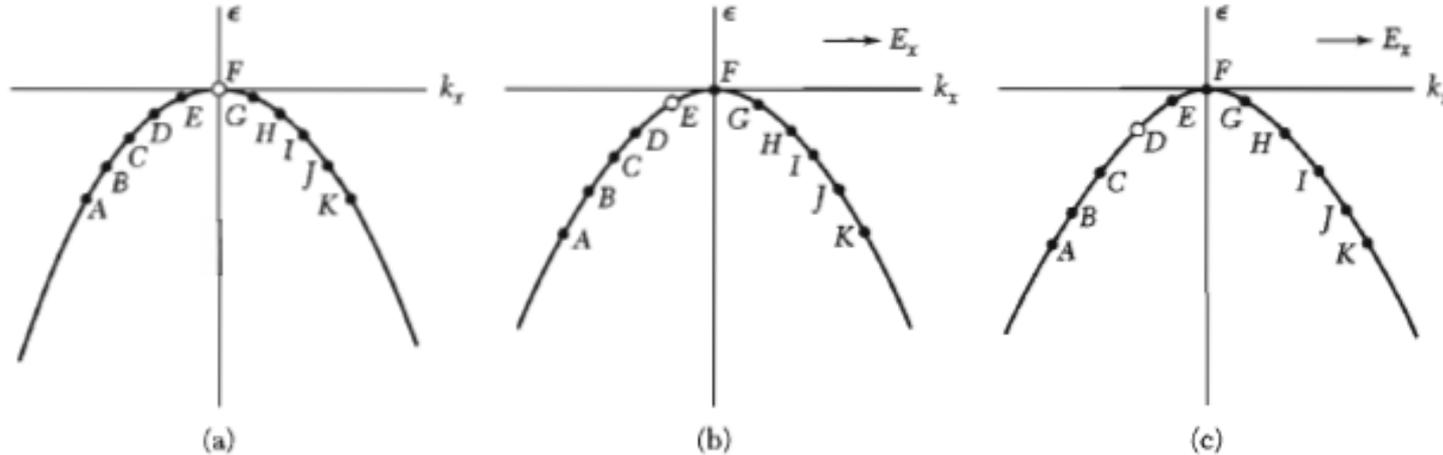
- *Effective mass.* The effective mass $m^* = \hbar^2 / (\partial^2 \epsilon / \partial k^2)$ and substituting in the equations for ϵ, \mathbf{k} means that $m_h^* = -m_e^*$ so the electron mass is negative and the hole mass is positive at the top of the valence band

- *Hole charge.* We take the equation of motion for the electron

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

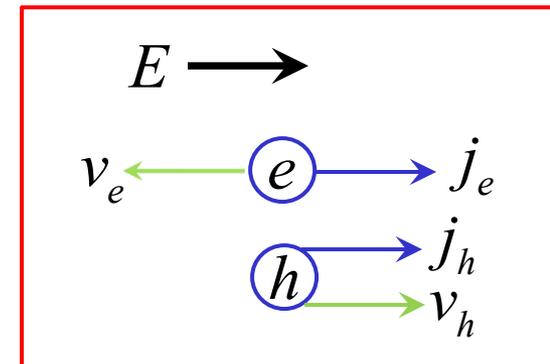
- Make the replacements $k_e \rightarrow -k_h, v_e \rightarrow v_h$ hence $\hbar \frac{d\mathbf{k}_h}{dt} = e(\mathbf{E} + \mathbf{v}_h \times \mathbf{B})$ and the effective charge of a hole is positive,

Electrons and holes in semiconductors



From Kittel

- (a) At $t=0$ all states are filled except F at the top of the band the velocity v_e is zero at F because $v_e = \hbar^{-1} d\omega / dk = 0$
- (b) An electric field E_x is applied in the $+x$ direction, force on the electrons is in the $-k_x$ direction and all electrons make transitions together in the $-k_x$ direction moving the hole to state E . A current flows
- (c) After more time the electrons move again in k -space, the hole is now at D
- Motion of electrons in the conduction band and holes in the valence band in an electric field E
- The drift velocities are in opposite directions but currents are in the direction of E

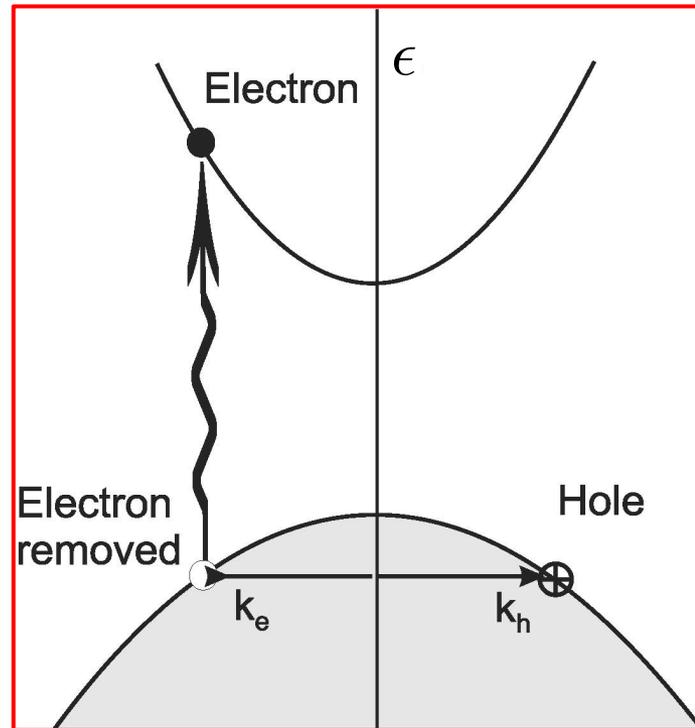


Summary of Lecture 9

- Semi-classical model of electron dynamics
- Bloch oscillations – experiment using semiconductor superlattice
- Density of states in energy bands
- Comparison of electrons and holes in semiconductors: wavevector, energy, velocity, mass, charge

Quantum Condensed Matter Physics

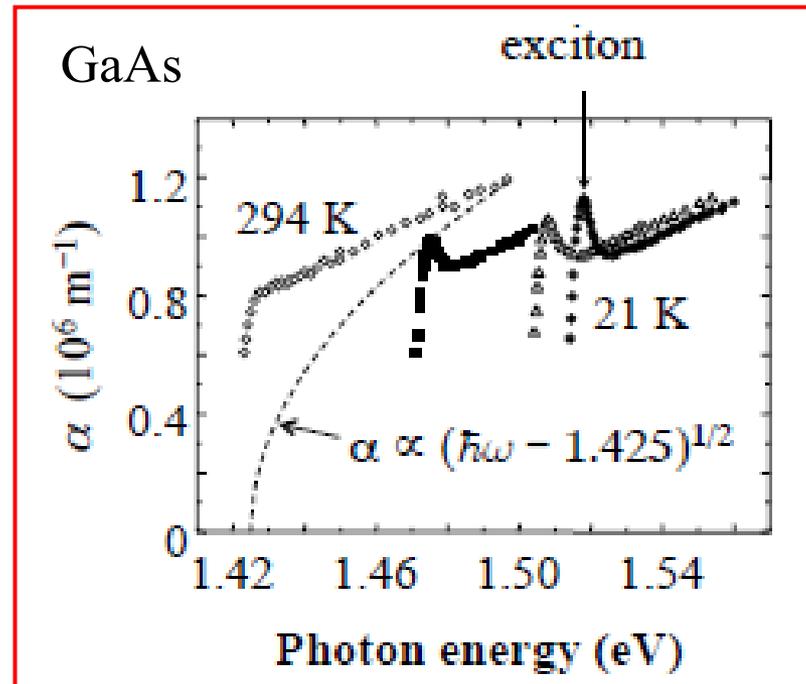
Lecture 9



The end

Quantum Condensed Matter Physics

Lecture 10



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)
3. Experimental probes of band structure (4L)

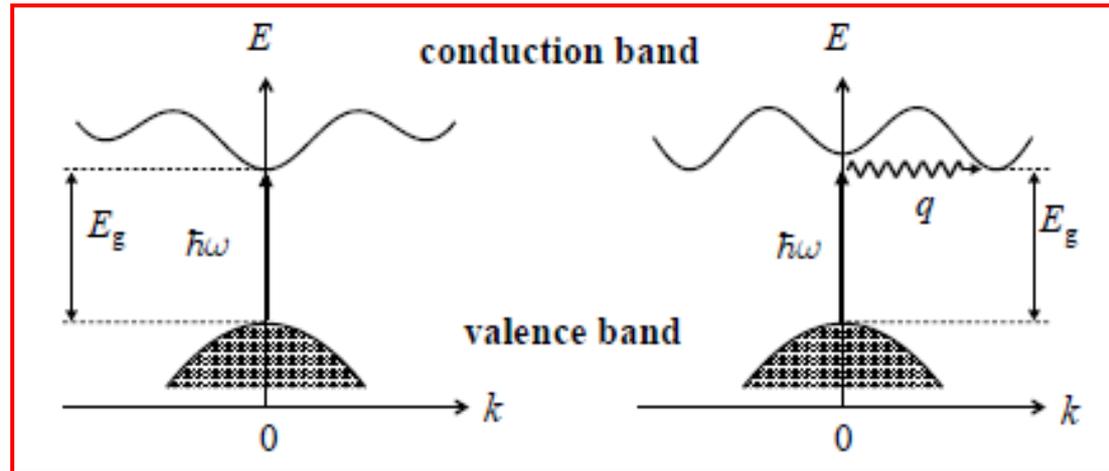
Photon absorption; transition rates, experimental arrangement for absorption spectroscopy, direct and indirect semiconductors, excitons.

Quantum oscillations; de Haas-Van Alphen effect in copper and strontium ruthenate. Photoemission; angle resolved photoemission spectroscopy (ARPES) in GaAs and strontium ruthenate. Tunnelling; scanning tunnelling microscopy. Cyclotron resonance. Scattering in metals; Wiedemann-Franz law, theory of electrical and thermal transport, Matthiessen's rule, emission and absorption of phonons. Experiments demonstrating electron-phonon and electron-electron scattering at low temperatures.

4. Semiconductors and semiconductor devices (5L)
5. Electronic instabilities (2L)
6. Fermi Liquids (2L)

Experimental probes of the band structure

- One way to investigate the band structure is the excitation of an electron by a photon from an occupied state to an empty state in the conduction band leaving behind a hole in the valence band and creating an electron-hole pair
- Photons cause nearly vertical transitions - the wavevector of a photon with energy close to the band gap is much smaller than is possible for an electron
- In a direct band gap semiconductor (GaAs) the lowest energy available states for electron and hole are at the same wavevector, the optical threshold is at the vertical transition
- For indirect semiconductors (Si, Ge) the valence band maximum is at a different wavevector to the conduction band minimum
- For excitation at the minimum energy a phonon must be excited as the photon is absorbed, 2nd order process, much less likely than a direct transition



For phonons and photons $v = \omega / k = E / 2\pi k$ the factor of around 10^5 between the two velocities is the difference between vertical & horizontal transitions

Transition rates for photon absorption

- The initial and final electron states are related by $\epsilon_f = \epsilon_i + \hbar\omega$
- optical absorption will have a threshold where $\epsilon_f - \epsilon_i = E_g$ above which there is a continuous range of possible transitions determined by the upper and lower limits of the bands
- The optical absorption coefficient is determined by the quantum mechanical transition rate $W_{i \rightarrow f}$ for exciting an electron in an initial quantum state ψ_i to a final state ψ_f by absorption of a photon of frequency ω
- Transition rate is given by Fermi's golden rule $W_{i \rightarrow f} = \frac{2\pi}{\hbar} |M|^2 g(\hbar\omega)$ which depends on the dipole matrix element M and the density of states $g(\hbar\omega)$
- The matrix element is calculated using the initial and final states and the perturbation due to the interaction of the electric field of the photon $\mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}}$ and the electric dipole moment $\mathbf{p}_e = -e\mathbf{r}$

$$M = \langle \psi_f | \hat{H}' | \psi_i \rangle, \quad \hat{H}' = -\mathbf{p}_e \cdot \mathbf{E}_0 e^{i\mathbf{k}\cdot\mathbf{r}}$$

- The electron states are described by Bloch functions which are a plane wave with wavevectors $\mathbf{k}_i, \mathbf{k}_f$ multiplied by functions u_i, u_f with the periodicity of the lattice

$$\psi_i(\mathbf{r}) = \frac{1}{\sqrt{V}} u_i e^{i\mathbf{k}_i \cdot \mathbf{r}}, \quad \psi_f(\mathbf{r}) = \frac{1}{\sqrt{V}} u_f e^{i\mathbf{k}_f \cdot \mathbf{r}}$$

Transition rates for photon absorption

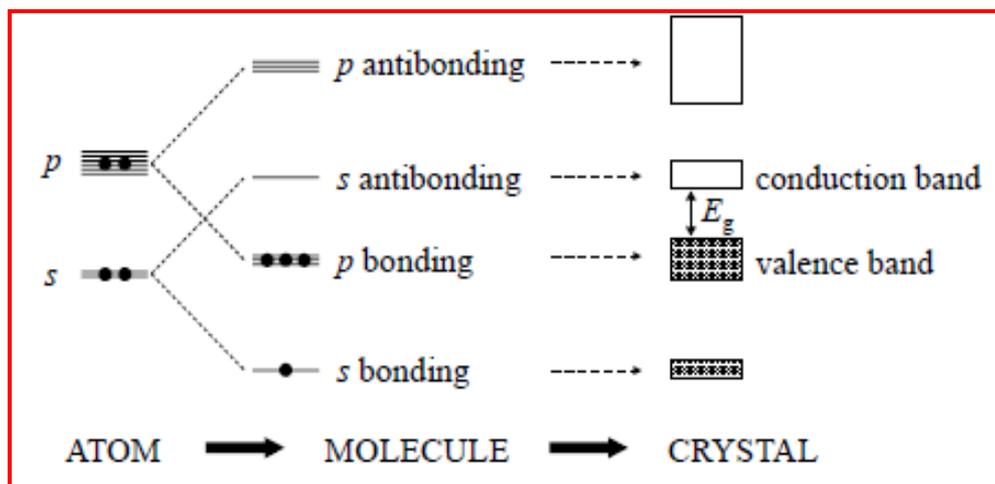
- We calculate the matrix element by integrating over the whole crystal

$$M = \frac{e}{V} \int u_f^*(\mathbf{r}) e^{-i\mathbf{k}_f \cdot \mathbf{r}} (\mathbf{E}_0 \cdot \mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}}) u_i(\mathbf{r}) e^{i\mathbf{k}_i \cdot \mathbf{r}} d^3 \mathbf{r}$$

- This can be simplified using conservation of momentum $\hbar \mathbf{k}_f - \hbar \mathbf{k}_i = \hbar \mathbf{k}$ so the phase factor is zero – if this is not so, the integral will sum to zero
- u_i, u_f are functions with the periodicity of the lattice so we can separate the integral over the whole crystal into a sum over identical unit cells – which are in phase
- Hence $|M| \propto \int_{\text{unit cell}} u_i^*(\mathbf{r}) x u_f(\mathbf{r}) d^3 \mathbf{r}$ where we assume the light is polarised along the x-axis
- To evaluate this matrix element we need to know the form of u_i, u_f which are derived from the atomic orbitals of the constituent atoms, so vary from one material to another.
- The wavevector of the photon is $k = 2\pi / \lambda \approx 10^7 \text{ m}^{-1}$ but the wavevector of the electrons are much larger – less than $\pi / a \approx 10^{10} \text{ m}^{-1}$ so we can neglect the photon momentum and $\mathbf{k}_f = \mathbf{k}_i$ hence photon absorption is vertical on the $E - k$ diagram

Transition rates for photon absorption

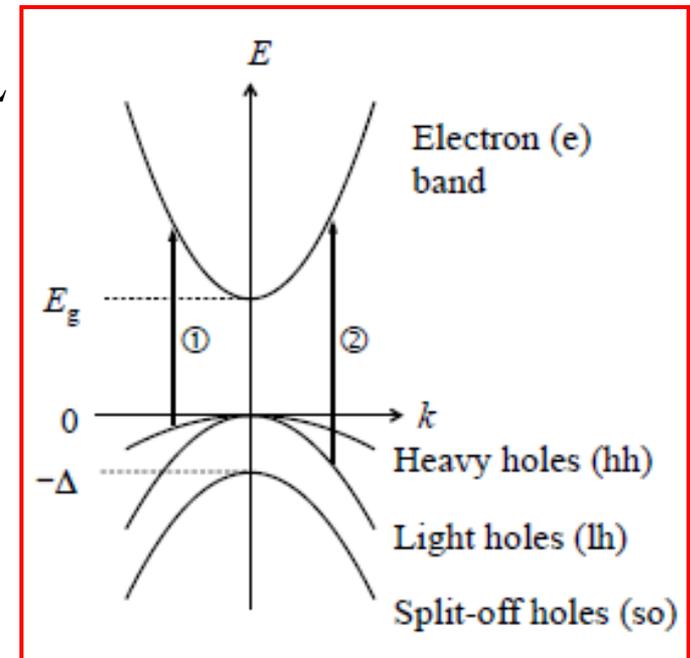
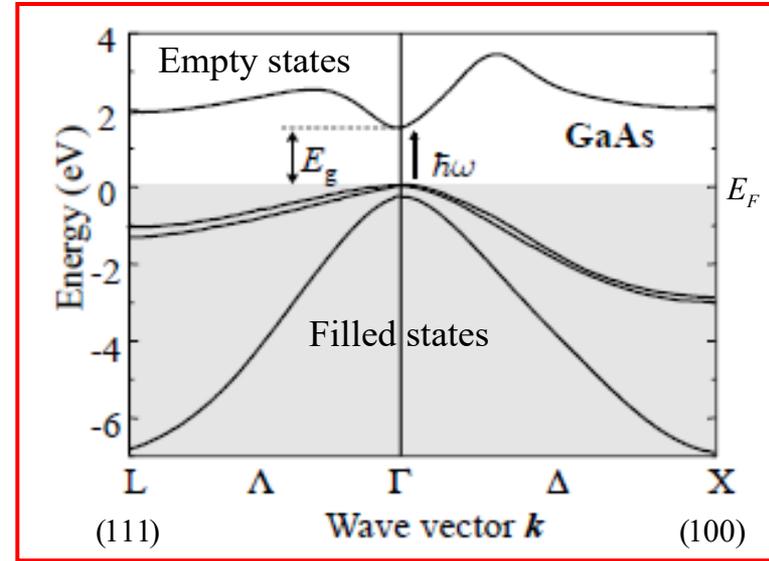
- We need to consider the atomic states involved in the transition and how they affect the dipole matrix element
- The semiconductors we consider all have 4 valence electrons
- Obvious for Si, Ge (group VI), for GaAs 3 electrons from Ga (Group III) and 5 electrons from As (group V) are shared forming zincblende crystal
- The valence electron configuration of the 4 electron atom (Ge) is $4s^24p^2$
- Diagram shows evolution of s- and p- atomic states to s- and p-bonding and antibonding molecular states to the valence and conduction bands of the crystal. The level ordering is correct for GaAs and Ge but different for Si
- Diagram suggests that the top of the valence band is derived from p-bonding orbitals while the bottom of the conduction band is from s-antibonding orbitals
- Hence optical transitions between the valence band and the conduction band are electric-dipole allowed



M Fox Optical properties of solids

GaAs band structure

- GaAs band structure shown in diagram for 2 directions in reciprocal space (100), (111)
- GaAs is a direct bandgap semiconductor
- 3 valence bands - occupied states corresponding to 3 p-bonding orbitals
- Single empty conduction band corresponds to s anti-bonding state
- Strictly valid only at zone centre Γ
- Atomic character only well defined at high symmetry points - changes away from Γ, X, L
- Lower diagram shows simplified structure for small k with parabolic dispersion
- One electron band, three hole bands
- Bandgap given by E_g , split-off hole band lower in energy by Δ
- Heavy hole and light hole transitions to conduction band shown



Transition rates for photon absorption

- The factor of $g(\omega)$ that appears in Fermi's golden rule is the joint density of states due to the fact that both initial and final states lie in continuous bands
- E - k relations for conduction, heavy-hole, light-hole, split-off hole bands

$$\epsilon_c(k) = E_g + \frac{\hbar^2 k^2}{2m_e^*}, \quad \epsilon_{hh}(k) = -\frac{\hbar^2 k^2}{2m_{hh}^*}, \quad \epsilon_{lh}(k) = -\frac{\hbar^2 k^2}{2m_{lh}^*}, \quad \epsilon_{so}(k) = -\Delta - \frac{\hbar^2 k^2}{2m_{so}^*}$$

- Conservation of energy during a heavy-hole or light hole transition requires

$$\hbar\omega = E_g + \frac{\hbar^2 k^2}{2m_e^*} + \frac{\hbar^2 k^2}{2m_h^*} \quad \text{where } m_h^* \text{ is the heavy hole or light hole mass}$$

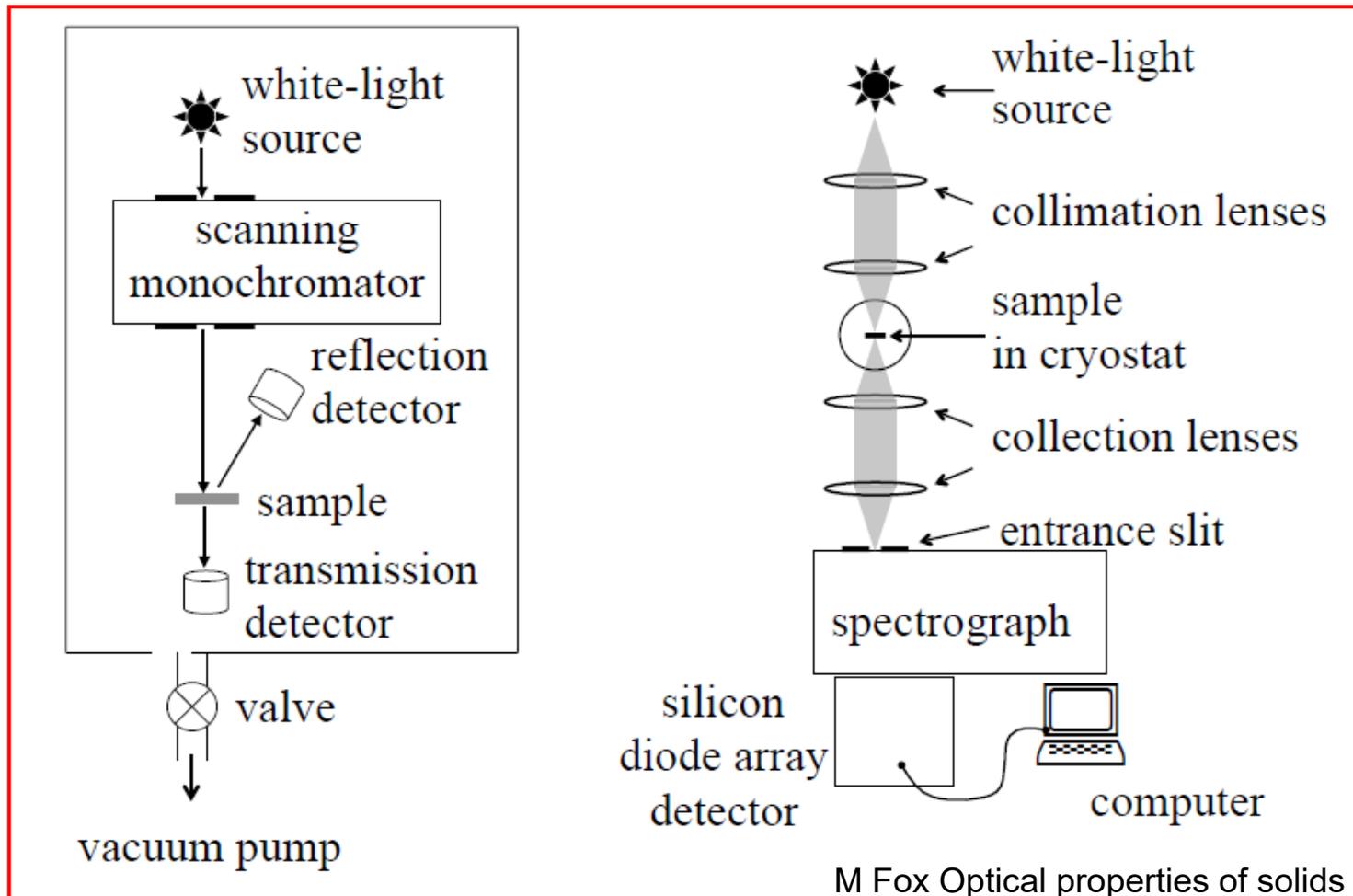
- We define reduced electron-hole mass by $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ hence we can write $\hbar\omega = E_g + \hbar^2 k^2 / 2\mu$
- Using formula for density of states per unit volume we find

$$\hbar\omega < E_g, \quad g(\hbar\omega) = 0$$

$$\hbar\omega > E_g, \quad g(\hbar\omega) = \left(\frac{1}{2\pi^2}\right) \left(\frac{2\mu}{\hbar^2}\right)^{3/2} \sqrt{\hbar\omega - E_g}$$

- So the density of states factor rises as $\sqrt{\hbar\omega - E_g}$ for energies greater than the bandgap

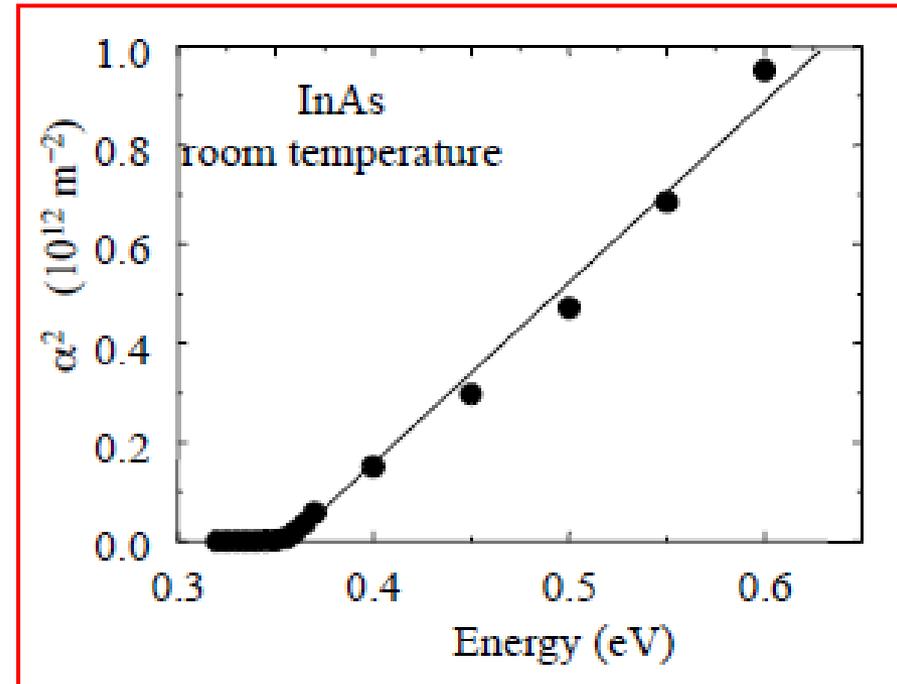
Experimental arrangements for optical absorption spectroscopy



- Beer's law: $\delta I = -\alpha \delta z \times I(z) \Rightarrow I(z) = I_0 \exp(-\alpha z)$
- α defined as fraction of intensity I (power per unit area) absorbed per unit length

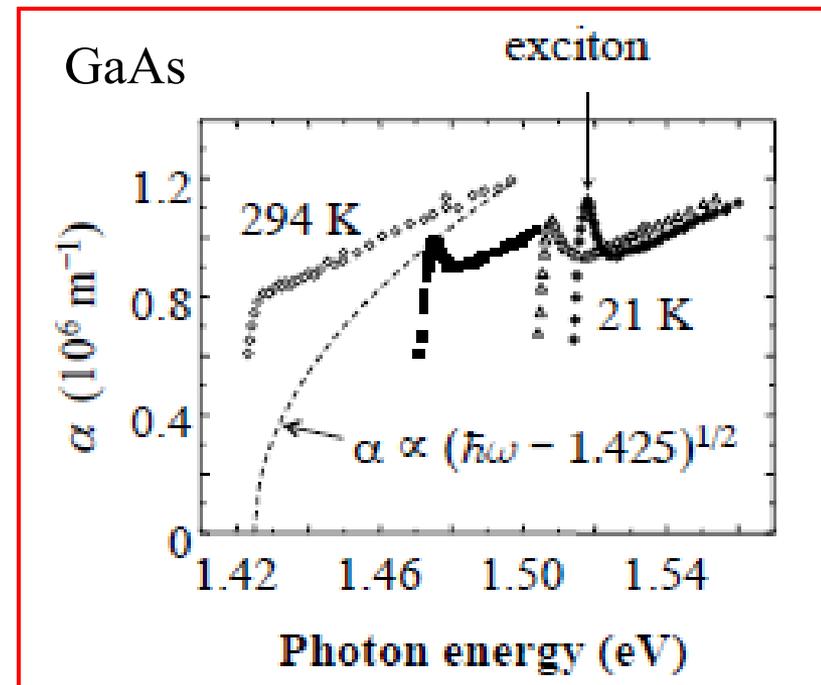
Photon absorption – direct semiconductors

- Having discussed the matrix element and DoS contributions to Fermi's golden rule, $W_{i-f} = \frac{2\pi}{\hbar} |M|^2 g(\hbar\omega)$, we can deduce frequency dependence of the absorption coefficient α (fraction of power absorbed per unit length)
- We expect that for $\hbar\omega < E_g$ there will be no absorption and $\alpha = 0$
- For $\hbar\omega > E_g$ we expect that $\alpha \propto \sqrt{\hbar\omega - E_g}$ with the absorption increasing above the bandgap
- Also since $g(\hbar\omega) \propto \mu^{3/2}$ we expect transitions with larger reduced masses give rise to stronger absorption
- These results can be compared to experimental data
- The diagram shows the square of the absorption coefficient plotted versus photon energy for III-V direct band-gap semiconductor InAs
- The linear dependence confirms $\alpha^2 \propto \hbar\omega - E_g$, it gives a bandgap of 0.35eV in good agreement with electrical measurements



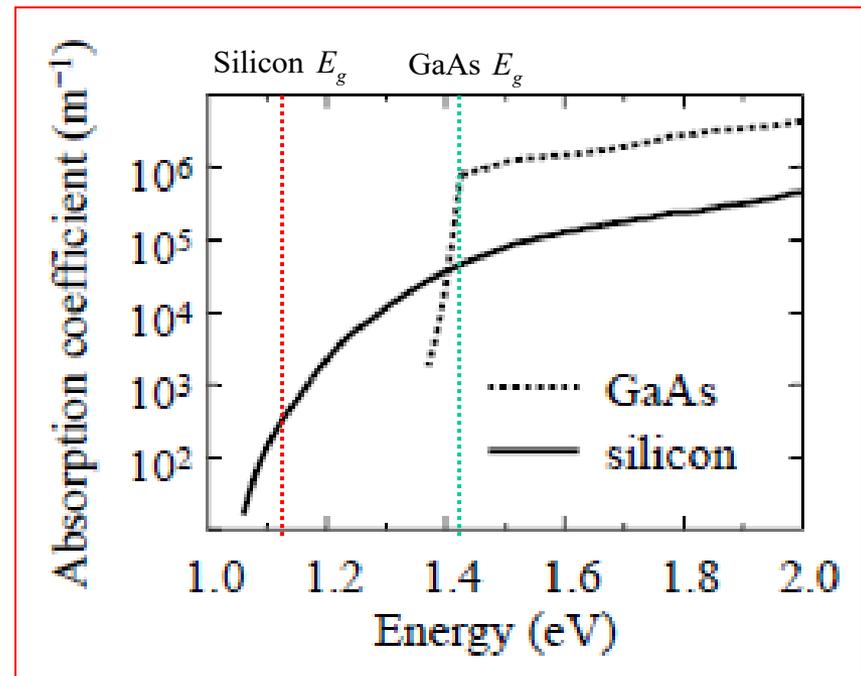
Photon absorption

- In many III-V semiconductors including GaAs the frequency dependence of absorption $\alpha \propto \sqrt{\hbar\omega - E_g}$ is only approximately obeyed for a number of reasons
- We neglect Coulomb attraction between the electrons and holes which can enhance absorption and lead to formation of a bound pair – an *exciton*
- These effects get larger as bandgap increases and temperature is lowered – hence previous example is InAs narrow BG semiconductor (0.35eV) at 298K
- The semiconductor crystal may include impurities and defects with energies within the bandgap – hence additional absorption below the bandgap energy
- The parabolic band approximation is only valid near $k = 0$ - as the photon energy increases above the bandgap the joint DoS is no longer $\propto \sqrt{\hbar\omega - E_g}$
- In this case we need to use the full band structure to evaluate the DoS



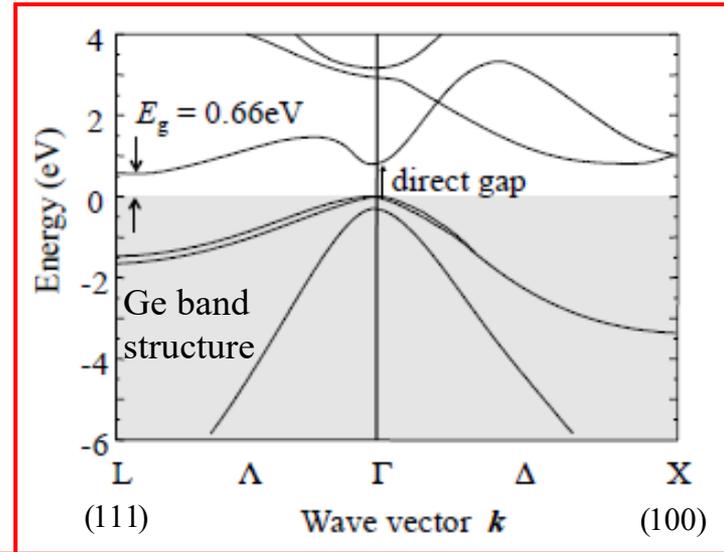
Photon absorption – indirect semiconductors

- Important semiconductors e.g. Si and Ge have their conduction band minimum away from Brillouin zone centre and the valence band maximum
- A transition between band edges needs a big change in electron wavevector
- Transition must involve a phonon to conserve momentum
- Consider an indirect transition exciting a valence band electron (ϵ_i, k_1) to a state (ϵ_f, k_2) in the conduction band. Photon energy $\hbar\omega$, phonon energy $\hbar\Omega$
- Conservation of energy $\epsilon_f = \epsilon_i + \hbar\omega \pm \hbar\Omega$ and momentum $\hbar\mathbf{k}_f = \hbar\mathbf{k}_i \pm \hbar\mathbf{q}$
- The \pm allows for the possibility of phonon absorption (+) or emission(-)
- Have neglected photon's momentum which is small on these scales
- Indirect transitions which involve both photons and phonons are second order process which are much less likely than the absorption of a photon be a direct and semiconductor
- Hence absorption rate for indirect semiconductors much smaller above band edge –for Si/GaAs one tenth



Photon absorption – indirect semiconductors

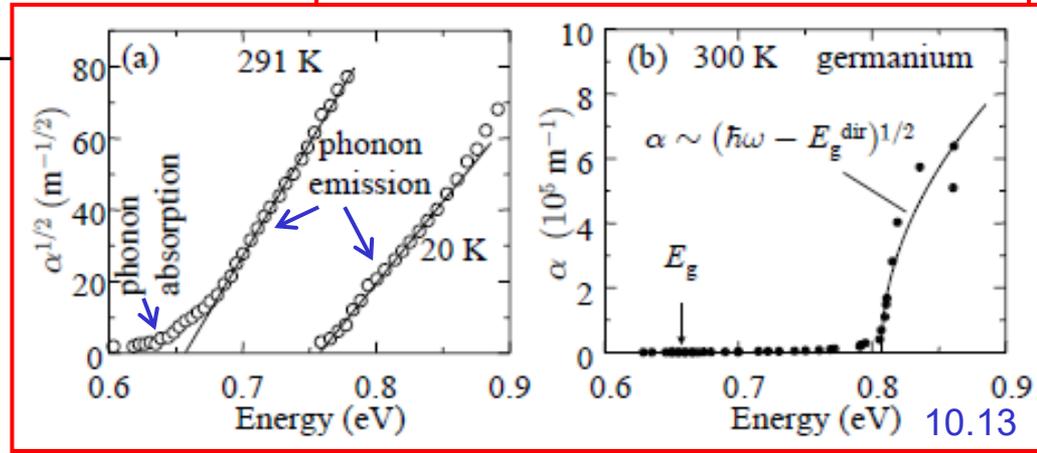
- Derivation of QM transition rate for indirect band gap semiconductor gives for absorption coefficient $\alpha(\hbar\omega) \propto (\hbar\omega - E_g \mp \hbar\Omega)^2$ - see Yu and Cardona
- Frequency dependence different to that for direct bandgap semiconductors – can be used to determine if bandgap is direct or not .
- Threshold close to bandgap, depends if the phonon is absorbed or emitted
- Band structure for Ge similar to GaAs but indirect with band gap of 0.66eV - less than 0.8eV direct gap at 298K
- Figure (a) shows indirect absorption in Ge near bandgap with $\sqrt{\alpha} \propto \hbar\omega$
- Expect contributions from phonon emission and absorption – latter only possible at high temperatures where phonons are excited



- (b) shows band edge absorption above 0.8eV with $\alpha \propto \sqrt{\hbar\omega - E_g}$
- Direct absorption much larger than indirect absorption

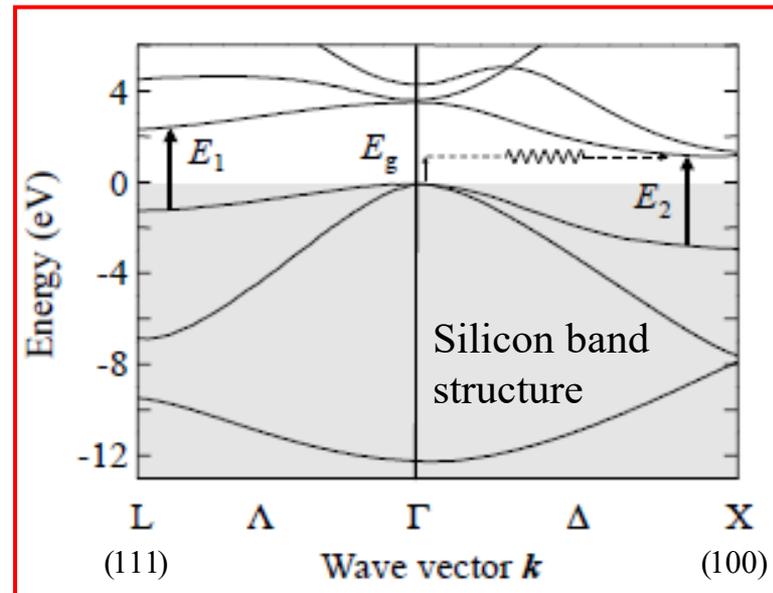
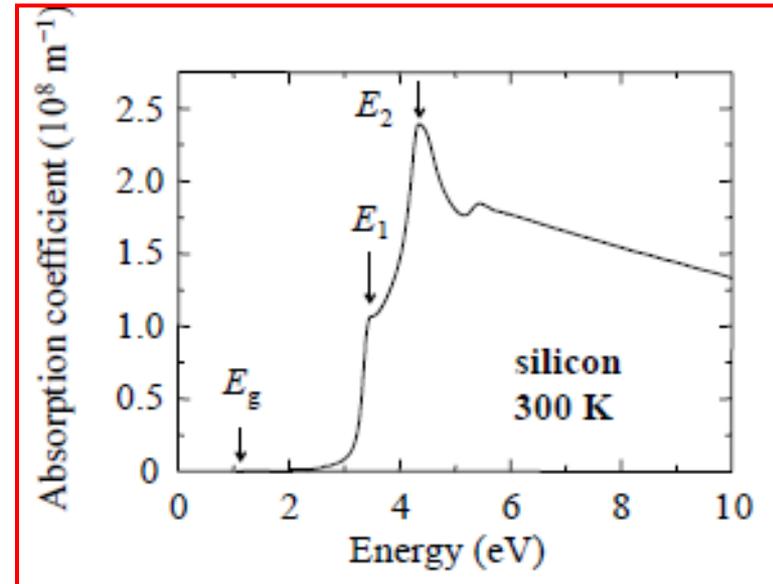
(a) GG McFarlane and V Roberts Phys Rev **97**, 1714-6 (1955)

(b) WC Dash and R Newman Phys Rev **99**, 1151 (1955)



Photon absorption – indirect semiconductors

- Figure shows interband absorption of Si to relatively high energy - $E = \hbar\omega \approx 10\text{eV}$
- Very large absorption $\alpha \approx 10^8 \text{ m}^{-1}$ above 3eV with two peaks E_1, E_2
- Compares to indirect region just above bandgap with $\alpha \approx 10^2 - 10^6 \text{ m}^{-1}$
- Band structure of silicon shown, indirect bandgap value - $E_g \approx 1.1\text{eV}$
- Minimum direct separation between conduction and valence bands near L point 3.5eV (E_1)
- Second absorption near X 4.2eV (E_2)
- In both regions conduction and valence bands parallel and dE / dk very small
- Hence very high joint density of states and very high direct transition rate and absorption



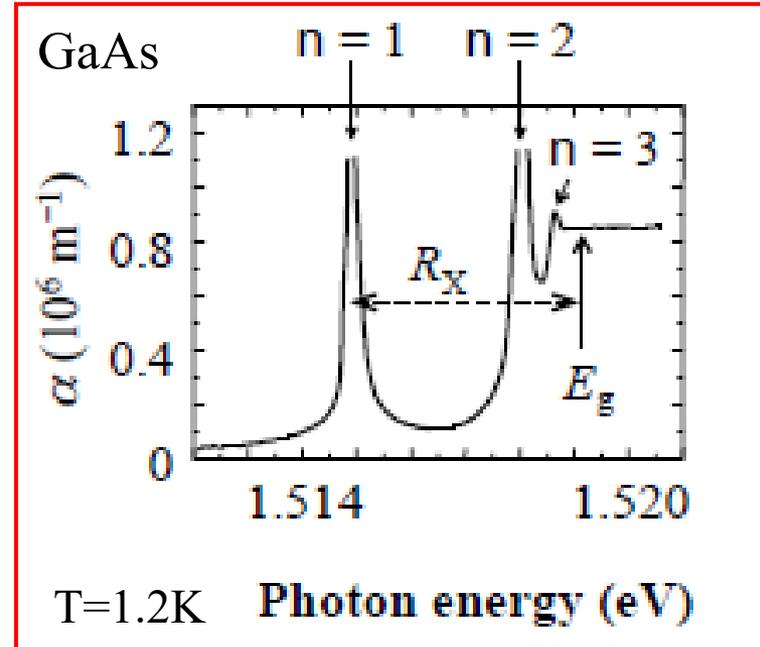
Excitons

- Peak in GaAs absorption spectrum at low temperatures signifies presence of excitons
- An exciton is a bound electron-hole pair analogous to the hydrogen atom
- In an exciton electron and heavy hole masses are combined in a reduced effective mass $1/\mu^* = 1/m_e^* + 1/m_{hh}^*$
- GaAs has permittivity $\epsilon_r = 12.8$
- We can use modified equation for the energy levels of a hydrogen atom to calculate energy levels of excitons

$$E_n = -\frac{\mu^*}{m_e \epsilon_r^2} \cdot \frac{13.6\text{eV}}{n^2} = -\frac{R_x}{n^2}$$

- n is the energy level quantum number
- Energy of exciton is equal to energy required to create an electron-hole pair minus the binding energy or

$$\epsilon_n = E_g - R_x / n^2$$



GW Fehrenbach et al J Lumin. 30, 154-61 (1985)

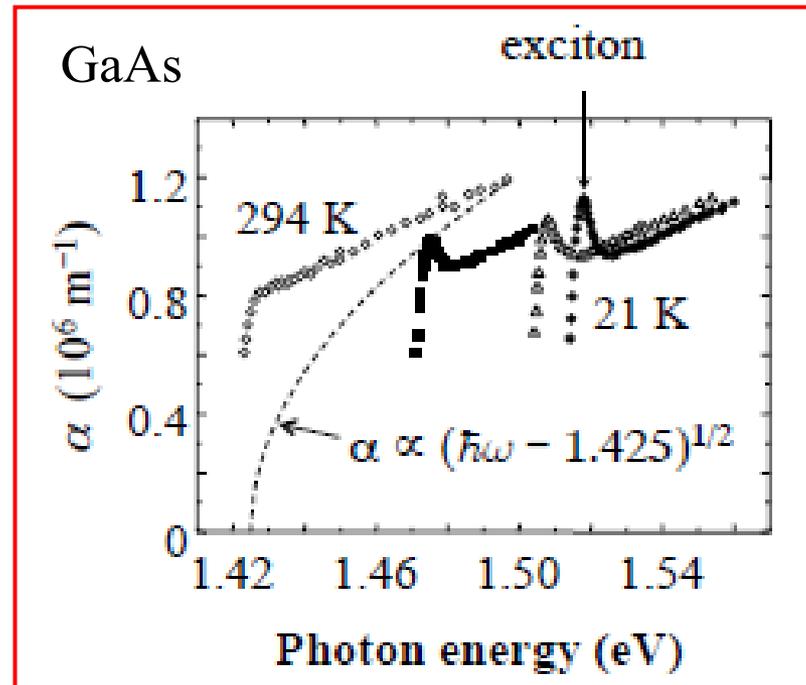
- Figure shows absorption by three exciton energy levels below the conduction band in pure GaAs
- Using $\mu^* = 0.05m_e$ we obtain $R_x = 4.2\text{meV}$ in good agreement with the results
- Quantum confined structures greatly enhance exciton effects

Summary of Lecture 10

- Transition rates for photon absorption, Fermi's golden rule, matrix elements, density of states
- GaAs band structure
- Photon absorption in direct semiconductors, InAs, GaAs
- Photon absorption in indirect semiconductors, contribution of phonons in Ge, above bandgap absorption in Si.
- Excitons

Quantum Condensed Matter Physics

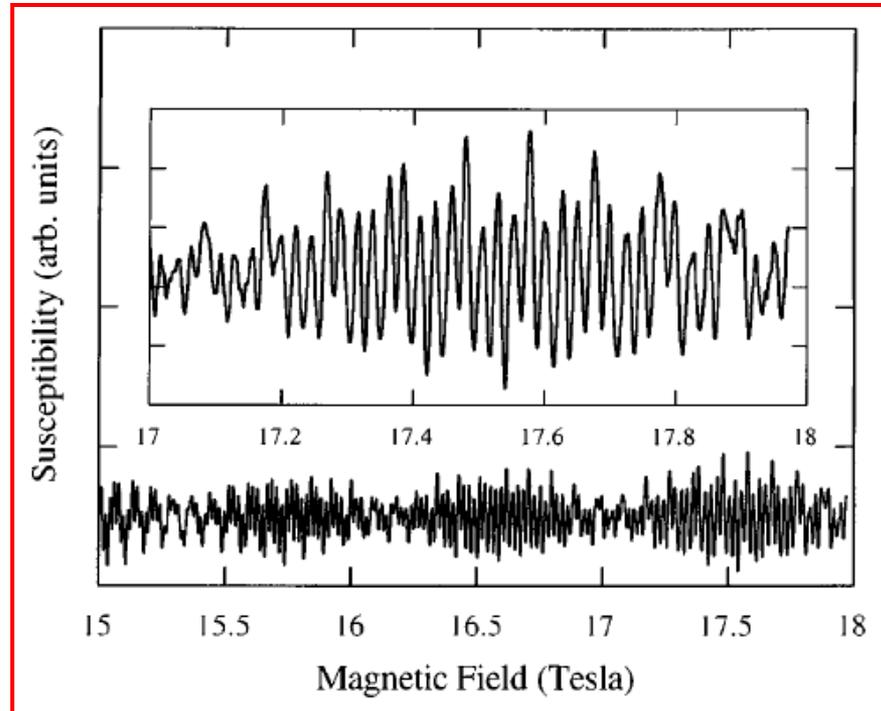
Lecture 10



David Ritchie

Quantum Condensed Matter Physics

Lecture 11



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)
3. Experimental probes of band structure (4L)

Photon absorption; transition rates, experimental arrangement for absorption spectroscopy, direct and indirect semiconductors, excitons. *Quantum oscillations; de Haas-Van Alphen effect in copper and strontium ruthenate.* Photoemission; angle resolved photoemission spectroscopy (ARPES) in GaAs and strontium ruthenate. Tunnelling; scanning tunnelling microscopy. Cyclotron resonance. Scattering in metals; Wiedemann-Franz law, theory of electrical and thermal transport, Matthiessen's rule, emission and absorption of phonons. Experiments demonstrating electron-phonon and electron-electron scattering at low temperatures.

4. Semiconductors and semiconductor devices (5L)
5. Electronic instabilities (2L)
6. Fermi Liquids (2L)

Quantum oscillations

- For pure samples, many material properties have been found to oscillate as a function of applied magnetic field
- The form of these quantum oscillations can be used to infer the shape of the Fermi surface and other key electronic properties
- A full quantum mechanical treatment of the motion of electrons in a strong magnetic field is problematic
- When the lattice potential can be neglected - for free electrons the Schrodinger equation can be solved directly
- For real materials the lattice potential is essential to the band structure and cannot be neglected
- We use a semi-classical treatment using the Bohr-Sommerfeld quantisation condition

Quantum oscillations

- The canonical momentum for a particle in a magnetic field, \mathbf{p} , (conjugate to the position \mathbf{r}) is the sum of the kinetic momentum $m\mathbf{v} = \hbar\mathbf{k}$ and the field momentum $q\mathbf{A}$ so $\mathbf{p} = \hbar\mathbf{k} + q\mathbf{A}$
- We assume that orbits in a magnetic field are quantized according to the Bohr-Sommerfeld relation $\oint \mathbf{p} \cdot d\mathbf{r} = (n + \frac{1}{2})2\pi\hbar$ where n is an integer
- Particles with charge q moving in a strong magnetic field orbit along a path determined by the Lorentz force $m\dot{\mathbf{v}} = q\dot{\mathbf{r}} \times \mathbf{B}$.
- This relation connects the components of velocity and acceleration of the particle at \mathbf{r} in the plane perpendicular to \mathbf{B} and can be integrated to give $m\mathbf{v}_\perp = q\mathbf{r} \times \mathbf{B}$ where \mathbf{r} is measured from the centre of the orbit
- Hence $\mathbf{p} = m\mathbf{v} + q\mathbf{A} = q(\mathbf{r} \times \mathbf{B} + \mathbf{A}) \Rightarrow \oint \mathbf{p} \cdot d\mathbf{r} = q\oint \mathbf{r} \times \mathbf{B} \cdot d\mathbf{r} + q\oint \mathbf{A} \cdot d\mathbf{r}$ integrating around a loop
- Now $\oint \mathbf{A} \cdot d\mathbf{r} = \int_S \nabla \times \mathbf{A} \cdot d\mathbf{S} = \int_S \mathbf{B} \cdot d\mathbf{S} = \Phi$ by Stokes' theorem, and $\oint \mathbf{r} \times \mathbf{B} \cdot d\mathbf{r} = -\mathbf{B} \cdot \oint \mathbf{r} \times d\mathbf{r} = -2\mathbf{B}A_r = -2\Phi$ since $\oint \mathbf{r} \times d\mathbf{r}$ equals twice the area A_r enclosed by the loop
- Putting this together: $\oint \mathbf{p} \cdot d\mathbf{r} = -2q\Phi + q\Phi = -q\Phi = (n + \frac{1}{2})2\pi\hbar$

Quantum oscillations

- From the last slide $\oint \mathbf{p} \cdot d\mathbf{r} = -q\Phi = (n + \frac{1}{2})2\pi\hbar$
- We arrive at the conclusion that the flux threading the real space orbit for an electron is quantised $\Phi_n = A_r^n B = (n + \frac{1}{2})2\pi\hbar / e$
- Can we relate motion of the electron in real space to motion in k-space?
- From earlier $m\mathbf{v}_\perp = \hbar\mathbf{k}_\perp = q\mathbf{r} \times \mathbf{B}$ so with constant \mathbf{B} , \mathbf{k} is perpendicular to \mathbf{r} and its magnitude is a factor Bq / \hbar different from \mathbf{r} .
- So the k-space orbit has the same shape as the real space orbit, but is turned by 90 degrees and stretched by Bq / \hbar

- This means that the area enclosed by the k-space orbit A_k is

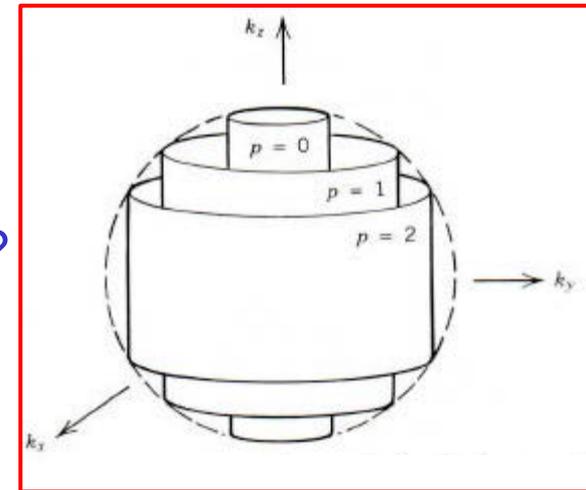
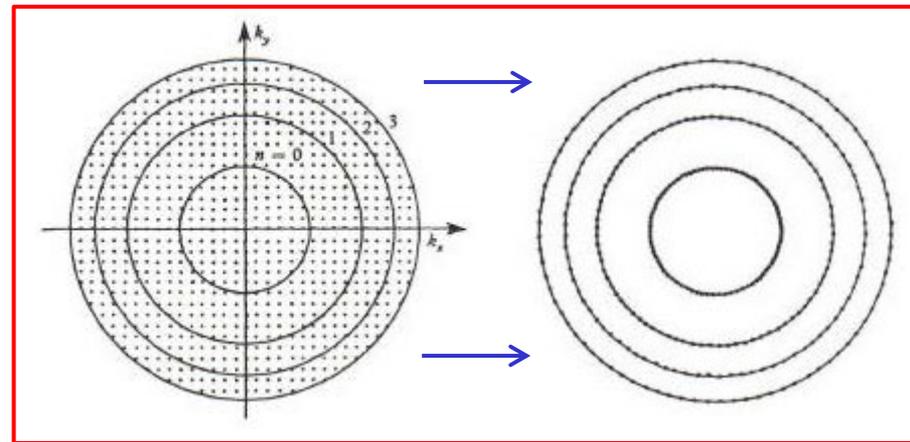
$$A_k = (e / \hbar)^2 B^2 A_r$$

- Where q has been replaced by the electron charge e
- Combining this result with $A_r^n = (n + \frac{1}{2})2\pi\hbar / Be$ from above
- We obtain

$$A_k = \frac{2\pi e}{\hbar} B (n + \frac{1}{2})$$

- Which is an expression for the area of an orbit in k-space as a function of integer n and suggests that the area is quantised

Density of states oscillations

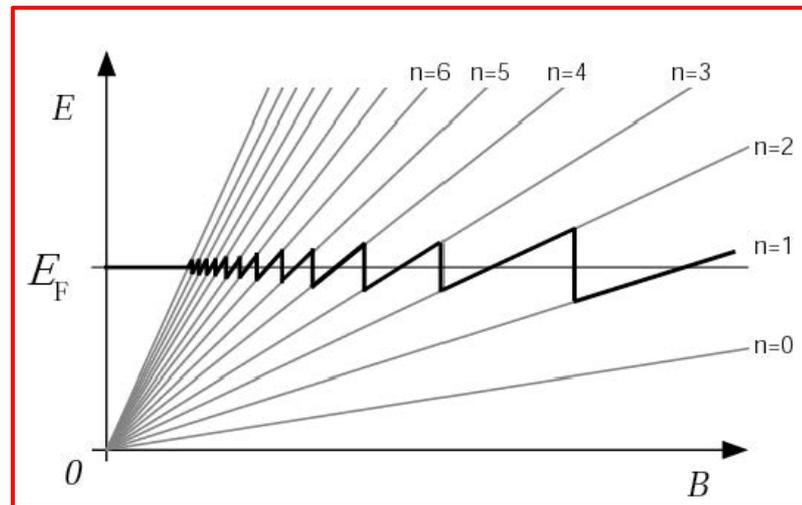
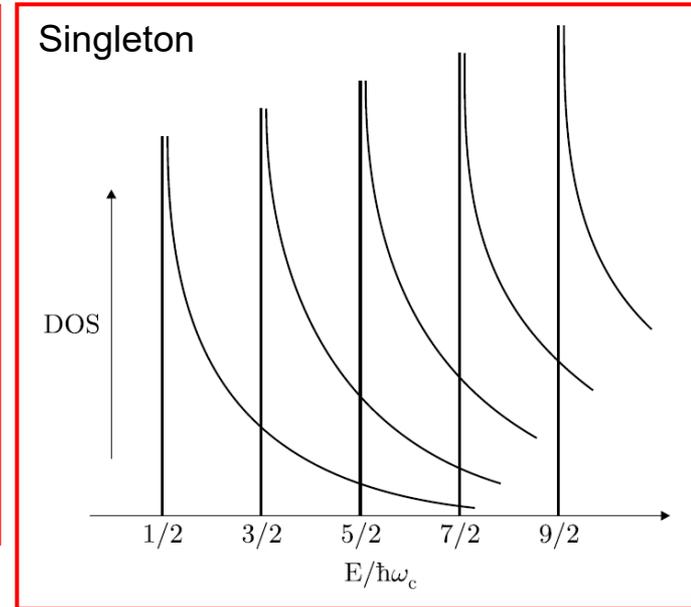
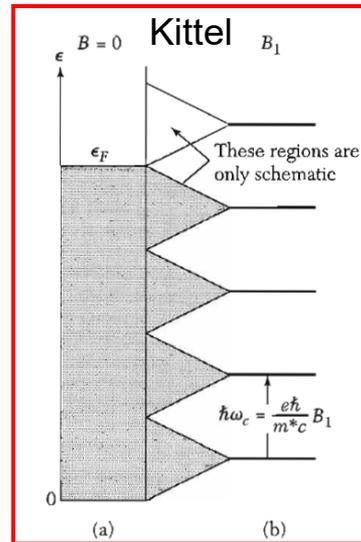


- In a magnetic field, the allowed k-states no longer form a regular lattice as k is not a good quantum number
- All the k-states in the vicinity of a k-orbit superimpose to form the orbital motion of the electrons
- Electrons now live in a set of cylinders “Landau tubes” with area $A_k = \frac{2\pi e}{\hbar} B \left(n + \frac{1}{2} \right)$ which cut through the zero field Fermi surface
- What is the \mathbf{B} field dependence of the DoS $g(E_F)$?
- Consider a slice $\perp \mathbf{B}$ through Fermi surface area
- This will only contribute to $g(E_F)$ if its area coincides with the area of a Landau tube A_k
- As \mathbf{B} increases one tube after another will satisfy this condition at field values of $B_n^{-1} = \frac{2\pi e}{\hbar A_k} \left(n + \frac{1}{2} \right)$
- Consequently the contribution of this slice to $g(E_F)$ oscillates with a period given by the *Onsager relation*:

$$\Delta \left(\frac{1}{B} \right) = \frac{1}{B_{n+1}} - \frac{1}{B_n} = \frac{2\pi e}{\hbar} \frac{1}{A_k}$$

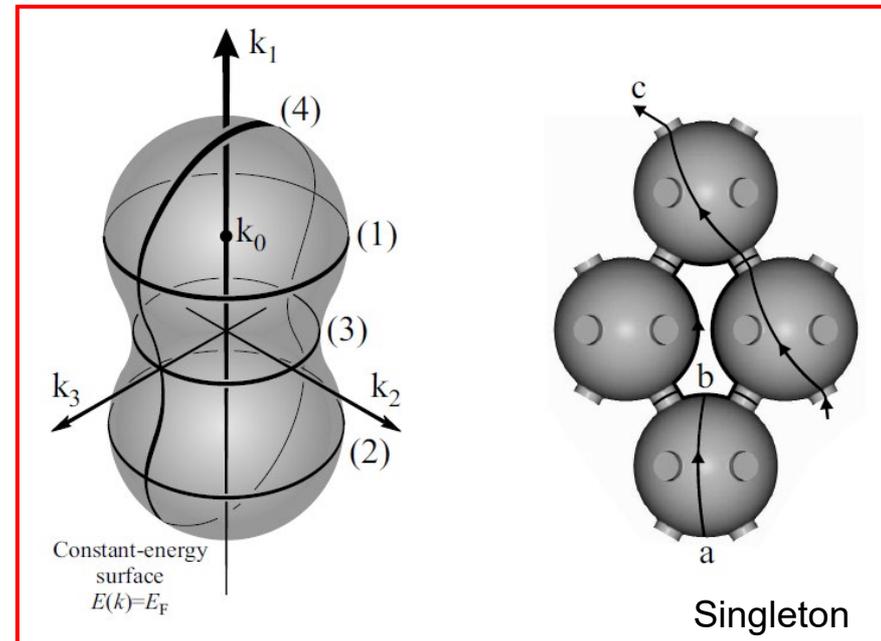
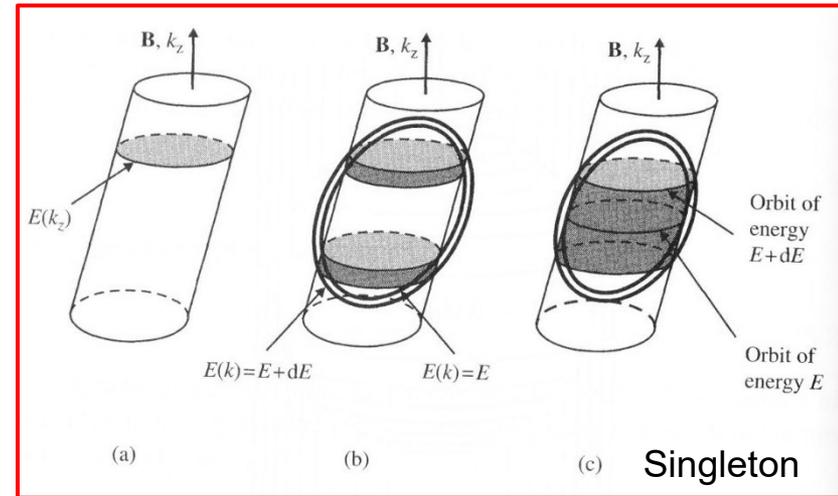
Density of states oscillations

- Energy of the band electrons is completely quantised into ladder of Landau levels in the plane perpendicular to B
- Motion parallel to B is unconstrained
- The DoS is an infinite ladder of Landau levels each with a 1D density of states function superimposed
- As each of the sharp peaks in the DoS moves through the chemical potential there is a modulation of the density of states and chemical potential
- This affects a number of different properties of the material



Fermi surface orbits

- We can only measure quantum oscillations associated with extremal orbits – a Landau tube touches rather than cuts through the Fermi surface
- In these regions are many close lying orbits with nearly identical cross-section causing DoS to add coherently
- For the rest of the Fermi surface the oscillations attributed to each orbit have different periods and add incoherently wiping out the effect
- Several different frequencies may be superimposed corresponding to different possible extremal orbits – e.g. neck and belly orbits in Cu and Au
- Measurement of observed frequencies as a function of B allows Fermi surface to be mapped
- Open orbits do not give rise to quantum oscillations



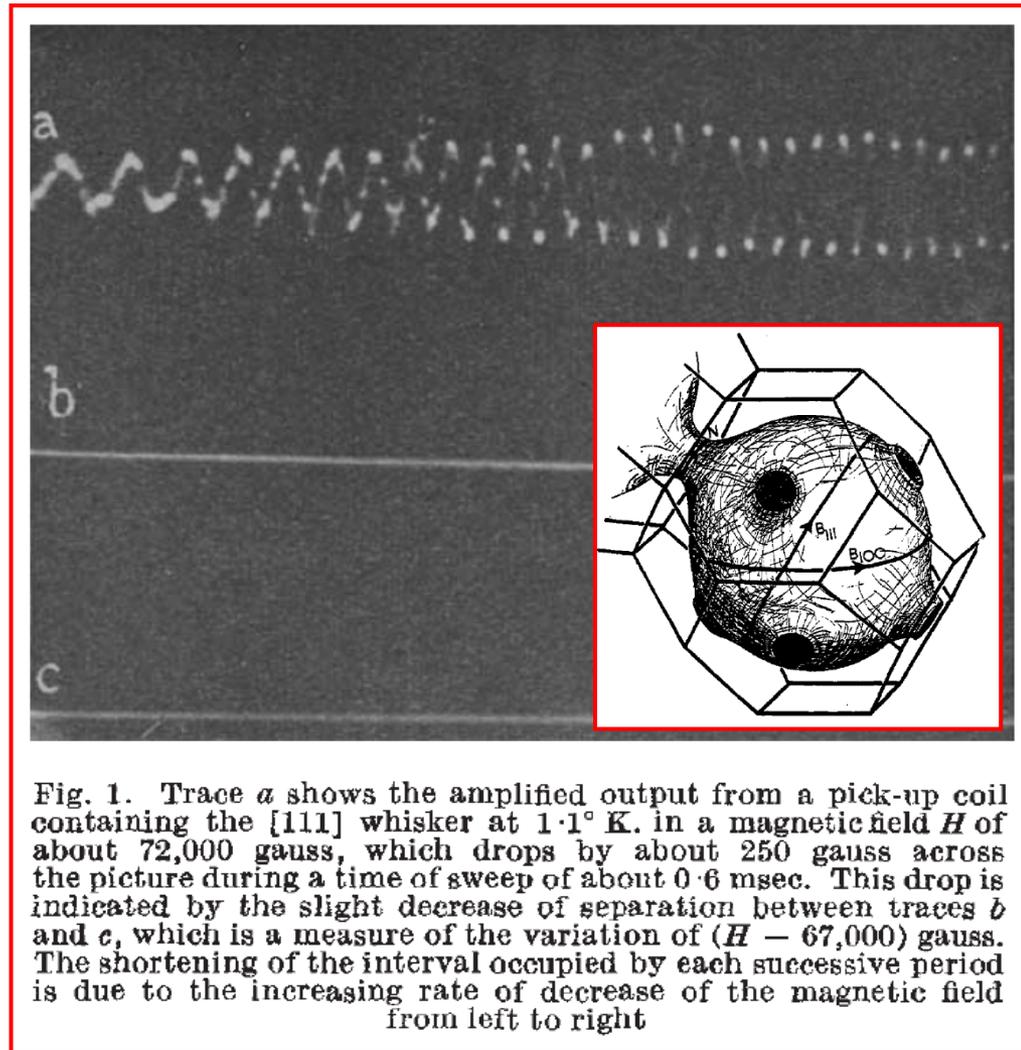
de Haas-Van Alphen effect

- Many observable properties depend on the DoS at the Fermi level
- Magnetic susceptibility $\chi(B)$ is proportional to $g(E_F)$, measurements at low temperatures exhibit oscillations, when plotted against $1/B$ allow the determination of extremal Fermi surface cross-section – the *de Haas-Van Alphen effect*
- Experiments require high purity samples – electronic mean free path must be long enough to allow the electrons to complete one orbit before scattering
- High magnetic field: which makes the cyclotron orbits tighter and helps to fulfil the mean free path condition
- Low temperature: the DoS oscillations are smeared out when the Fermi surface is smeared by thermal broadening, typically $T < 1\text{K}$ for transition metal compounds and $< 100\text{mK}$ for heavy fermion compounds
- Measurement system consists of sample coil and compensating coil in series opposition - without a sample the voltages induced cancel
- Voltage induced $V = \alpha(dM / dB)(dB / dt)$ where α is a constant
- If we know dB / dt we can find dM / dB in which dHvA oscillations occur
- Use either large static field up to 20 T plus small modulation field of a few mT or pulsed fields up to 60T rising to that value in a few mS

De Haas Van Alphen effect in Copper

- First observed at the Cavendish by David Shoenberg in 1959
- Impulsive field – discharged 4000 μ F capacitor at 2500V through liquid air cooled magnet rising to 2×10^5 gauss in 10mS
- Magnetic moment oscillations measured by coil around sample
- Whisker of Cu oriented along (111) axis, oscillation period of 1.7×10^{-9} gauss $^{-1}$ effective mass of 1.3 times electron mass
- Other whiskers along (100) and (110) directions did not show the effect – not clear why

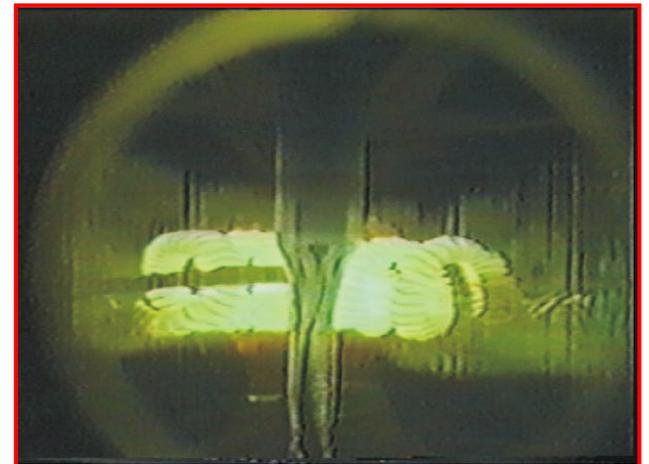
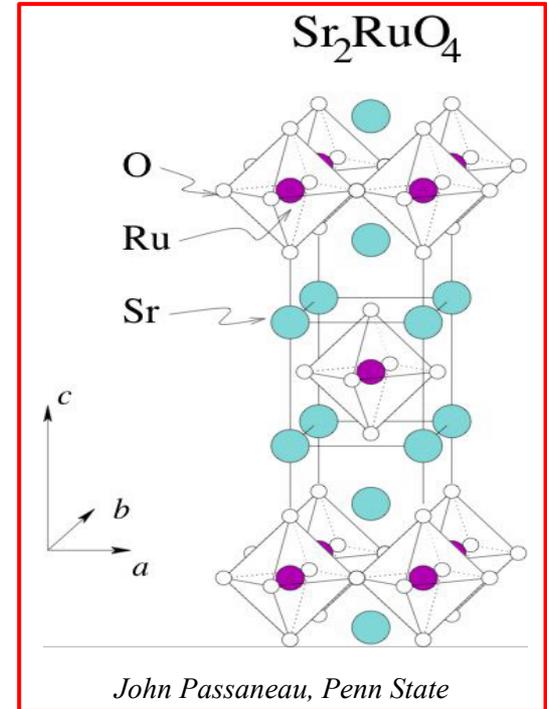
$$\left[1\text{T} = 10^4 \text{Gauss} \right]$$



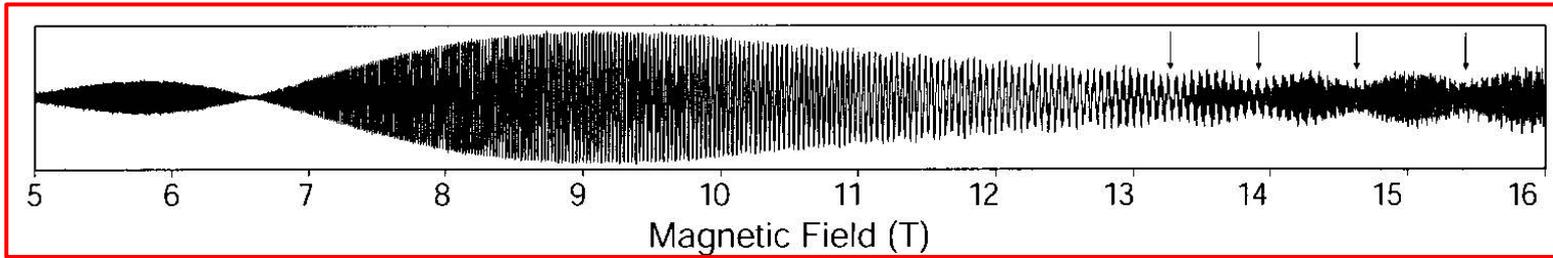
D Shoenberg Nature **183**, 171 (1959), Proc Roy Soc
79, 1 (1962)

De Haas Van Alphen effect in Sr_2RuO_4

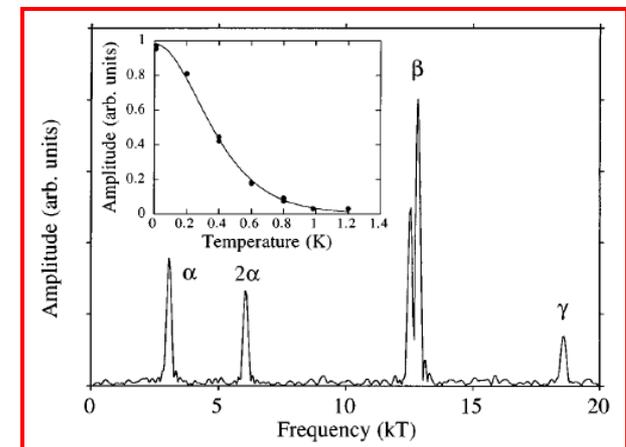
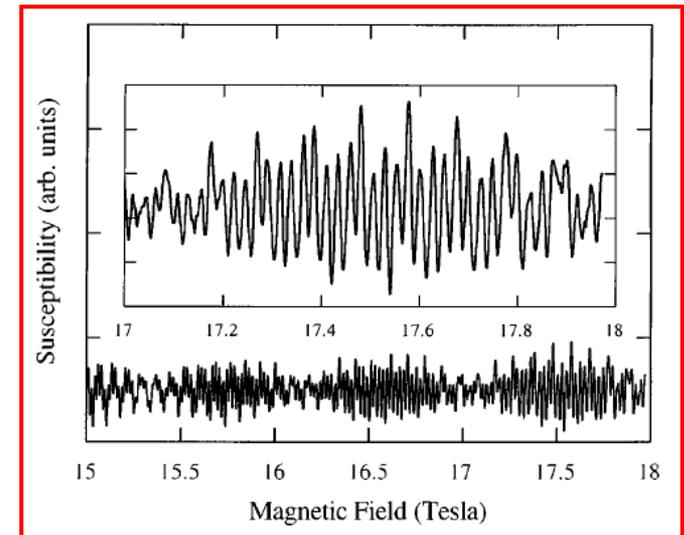
- 2D layered perovskite structure
- Metallic properties – superconducting at temperatures $<1\text{K}$ and well described by Fermi liquid theory – similar to ^3He
- High purity crystals prepared by floating zone method – moving vertical polycrystalline rod down through focussed IR radiation from halogen lamps
- Only small region is molten ($\sim 2100^\circ\text{C}$) at any one time, at liquid/solid boundary impurities diffuse into liquid region
- As liquid region moves through crystal, impurities move with it leaving pure single crystal behind
- Material not in contact with container – often main source of contamination
- Impurities collect at one end of crystal which can be cut off



De Haas Van Alphen effect in Sr_2RuO_4



- Field modulation technique used to measure susceptibility at temperatures between 20mK and 1.2K in static fields up to 18T
- Beating in oscillations clearly visible
- Fourier transform of data plotted as a function of $1/B$ reveals three main peaks α, β, γ plus harmonic at 2α
- Splitting in β causes beats in long field sweeps
- Amplitude of oscillations rises dramatically below 1K following predictions of Fermi liquid theory



A P Mackenzie et al Phys Rev Lett
76, 3768 (1996)

De Haas Van Alphen effect in Sr_2RuO_4

- Observed frequencies are proportional to k-space area
- Consistent with a Fermi surface with two electron cylinders (β, γ) centered on ΓZ line and one hole cylinder (α) running along corners of Brillouin zone
- Results compared with calculated Fermi surface parameters

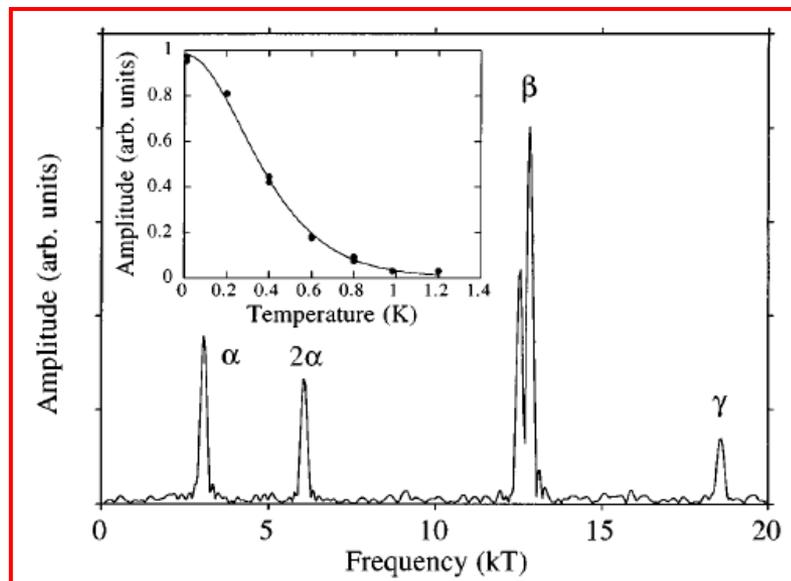
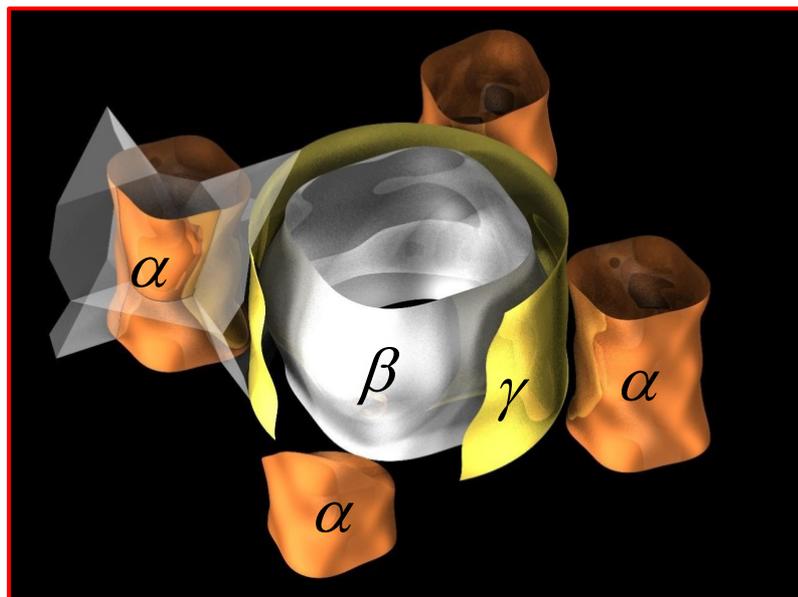


TABLE I. Measured and calculated Fermi surface parameters for Sr_2RuO_4 . The uncertainties in the measured frequencies and cyclotron masses are 1% and 5%, respectively.

	α	β	γ
Frequency F (kT)	3.05	12.7	18.5
Average k_F (\AA^{-1})	0.302	0.621	0.750
$\Delta k_F/k_F$ (%)	0.21	1.3	<0.9
Cyclotron mass (m_e)	3.4	6.6	12.0
Band calc. F (kT)	3.4	13.4	17.6
Band calc. $\Delta k_F/k_F$ (%)	1.3	1.1	0.34
Band mass (m_e)	1.1	2.0	2.9

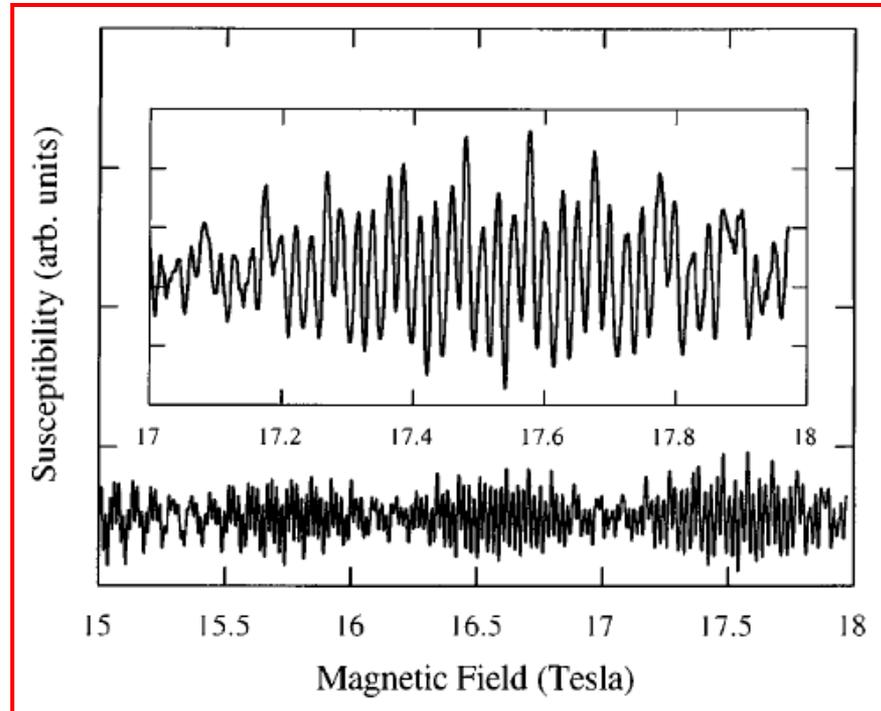


Summary of Lecture 11

- Quantum oscillations
- Density of states oscillations
- de Haas-van Alphen effect (dHvA)
- Fermi surface orbits
- dHvA in copper
- dHvA in strontium ruthenate

Quantum Condensed Matter Physics

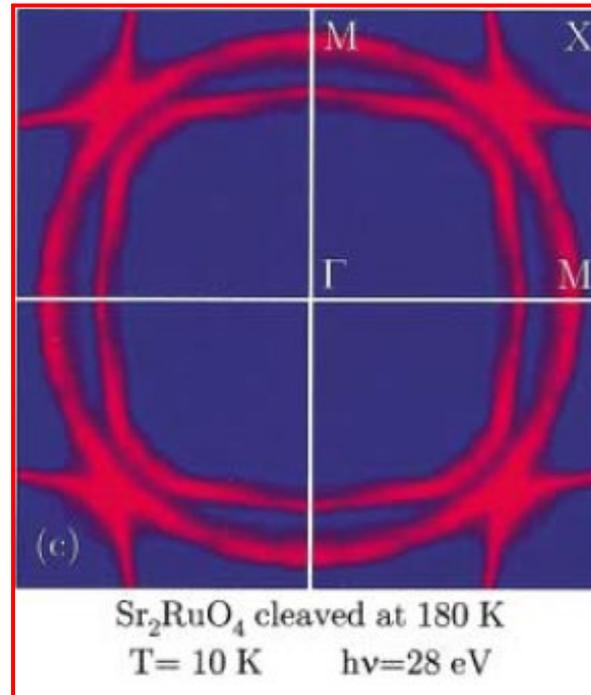
Lecture 11



The end

Quantum Condensed Matter Physics

Lecture 12



David Ritchie

Quantum Condensed Matter Physics

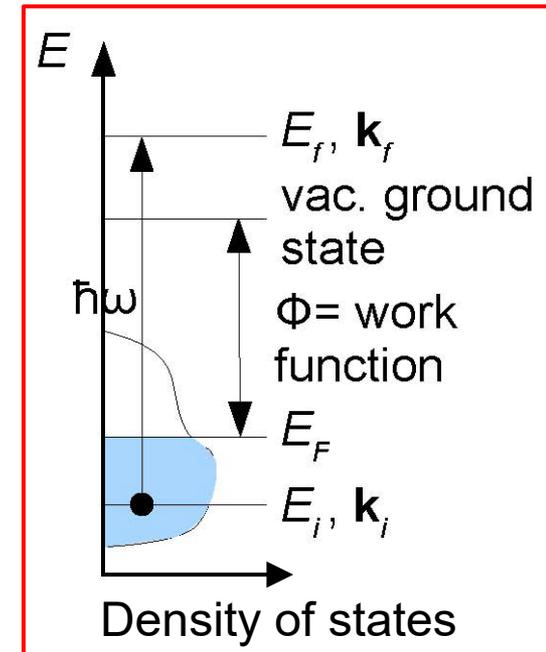
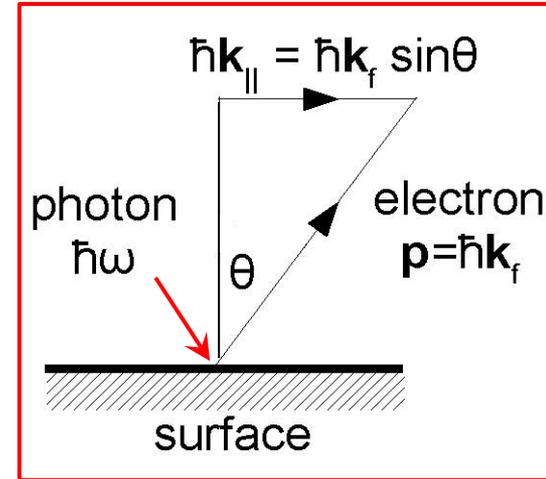
1. Classical and Semi-classical models for electrons in solids (3L)
2. Electrons and phonons in periodic solids (6L)
3. Experimental probes of band structure (4L)

Photon absorption; transition rates, experimental arrangement for absorption spectroscopy, direct and indirect semiconductors, excitons. Quantum oscillations; de Haas-Van Alphen effect in copper and strontium ruthenate. *Photoemission; angle resolved photoemission spectroscopy (ARPES) in GaAs and strontium ruthenate. Tunnelling; scanning tunnelling microscopy. Cyclotron resonance.* Scattering in metals; Wiedemann-Franz law, theory of electrical and thermal transport, Matthiessen's rule, emission and absorption of phonons. Experiments demonstrating electron-phonon and electron-electron scattering at low temperatures.

4. Semiconductors and semiconductor devices (5L)
5. Electronic instabilities (2L)
6. Fermi Liquids (2L)

Photoemission

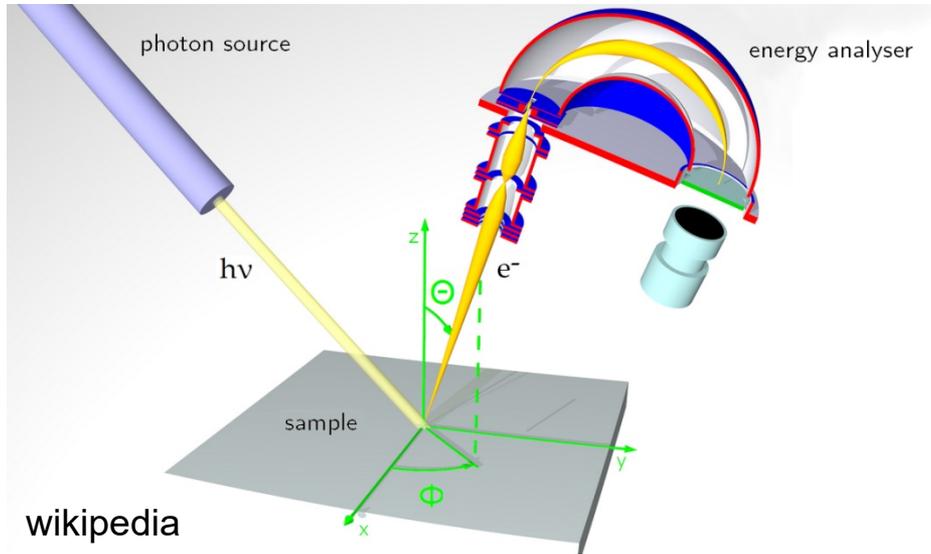
- The most direct way to measure the electron spectral function is by photoemission
- In a photoemission experiment photons are incident on a solid sample. Electrons are excited from occupied states in the band structure to states above the vacuum energy
- The excited electron leaves the crystal and is collected in a detector that analyses both its energy and momentum
- The incident photon carries very little momentum compared to the crystal momentum, so the momentum of the emitted electron parallel to the surface is close to that of its original state in the band structure of the solid
- The perpendicular component of the momentum is not conserved – changes as electrons escape through surface



Photoemission

- We relate the energy of the outgoing electrons, E_f , to the energy of the incoming photons $\hbar\omega$, the work function ϕ and the initial energy of the electron in the solid E_i
$$E_f = \frac{\hbar^2 k_f^2}{2m} = E_i + \hbar\omega - \phi, \quad k_{f\parallel} = k_{i\parallel}$$
- In this equation E_i is referenced to the Fermi energy E_F , but E_f is referenced to the vacuum ground state energy
- We use the detector angle θ to find k_{\parallel} with $\hbar k_{\parallel} = \hbar k_f \sin \theta$
- Problems occur if sample surface is rough as momentum parallel to the surface is changed
- Photoemission data is easiest to interpret when there is little dispersion of electron bands perpendicular to the surface – as in anisotropic layered materials
- Analysing both the energy and momentum of the outgoing electron allows the determination of the band structure directly. Integrating over all angles gives a spectrum proportional to the total density of states.
- Photoemission gives information only about the occupied states – inverse photoemission involves injecting an electron into a sample and measuring the ejected photon, allowing the mapping of unoccupied bands

Angle Resolved Photoemission Spectroscopy (ARPES) equipment

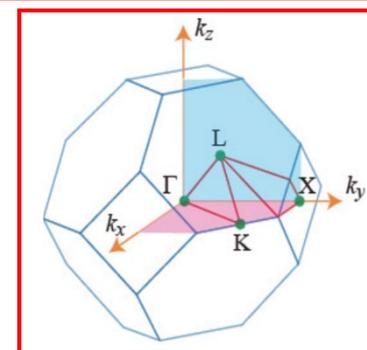
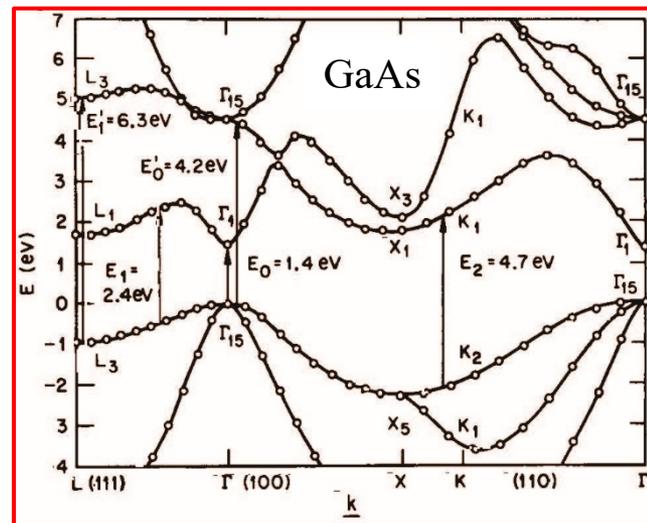


Scientaomicron DA30 ARPES system

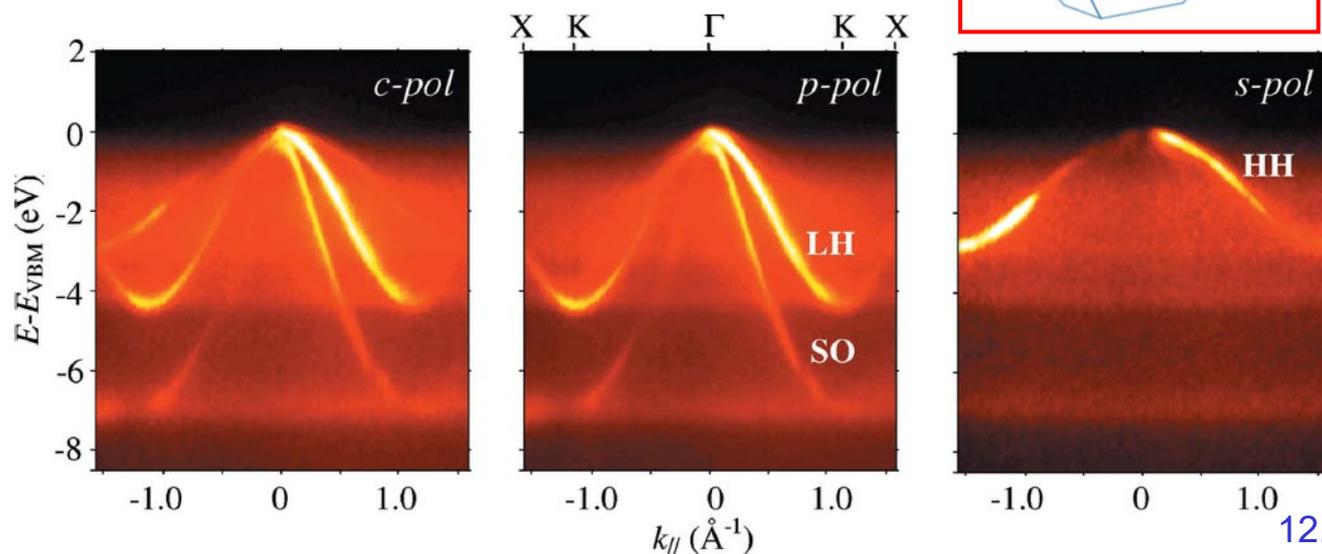
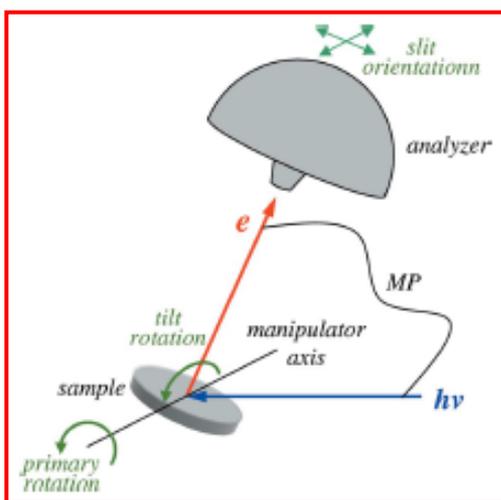
- ARPES Systems use ultrahigh vacuum techniques $P \leq 10^{-9}$ mbar so electrons travel to detector without encountering a gas atom
- 3-axis sample rotation
- Cryogenic temperatures for samples
- Detectors available for electron spin direction measurements

Angle resolved photoemission - GaAs

- Sample is GaAs 50nm thin film doped with Be protected by 1nm thick As cap layer
- Soft x-rays of different polarizations (893eV) give photo-electrons enough energy to escape.
- ADRESS beamline at Swiss Light Source used
- UHV conditions – 5×10^{-11} mbar, $T=11$ K
- Thermal broadening 50-150meV
- Results show Band dispersion $E(k)$ including light hole, heavy hole and split-off hole bands

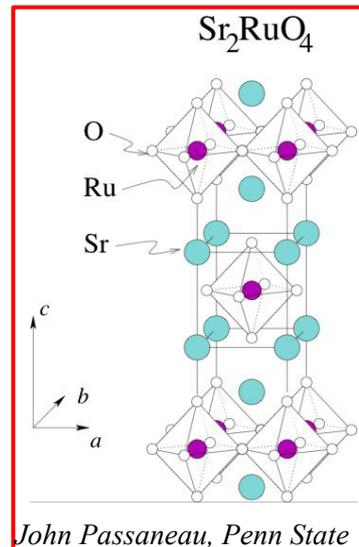
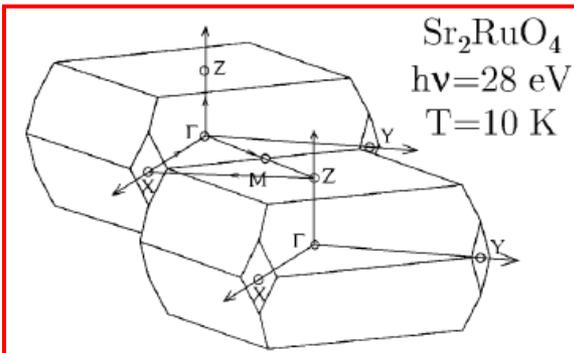
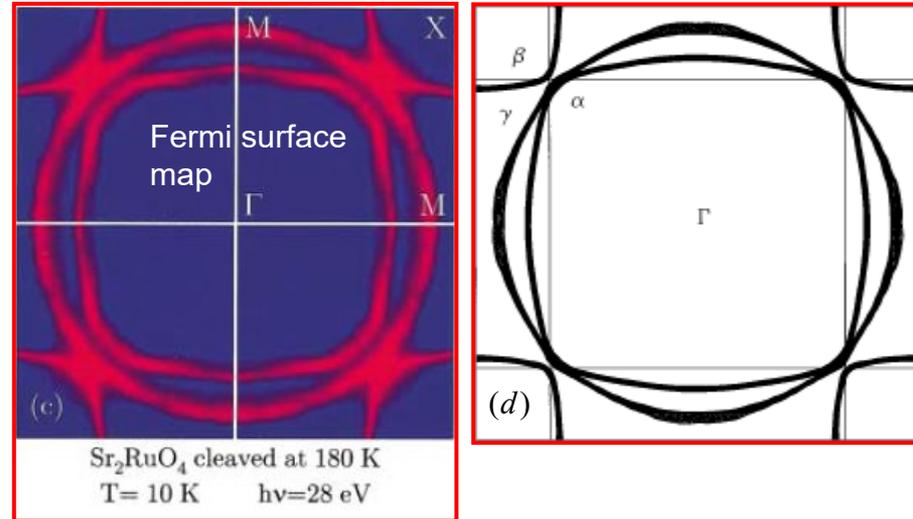
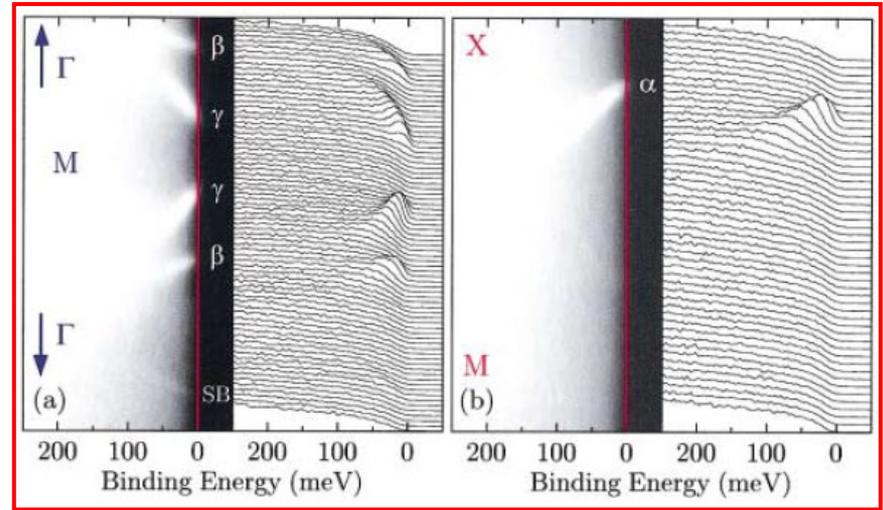


M Kobayashi et al Appl Phys Lett **101**, 242103 (2012)
 V N Strocov et al J Synch. Rad. **21**, 32 (2014)



Angle resolved Photoemission - layered metal Sr_2RuO_4

- 28eV photons, electron energy resolution $< 21\text{meV}$
- Bands nearly 2D in character
- (a) energy scans from Γ to centre of zone face M (b) from X to corner M
- Several bands sharpen as they approach and cross E_F
- (c) shows positions of peaks as a function of momentum at E_F
- (c) should be compared to band structure calculation of Fermi surfaces in (d)

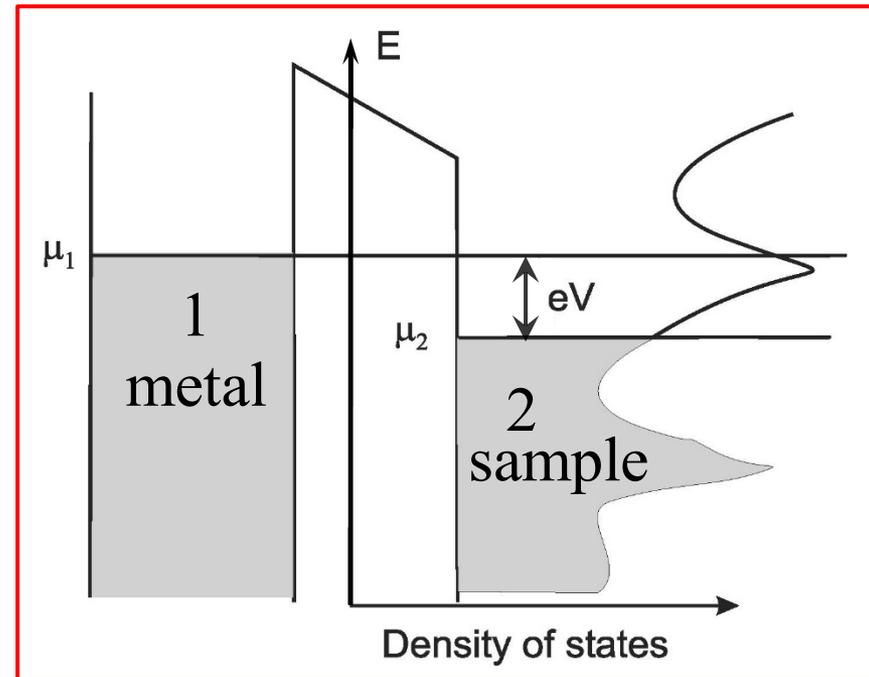


Experiment: A Damascelli et al Phys Rev Lett **85**, 5194 (2000)

Theory: I I Mazin and D J Singh Phys Rev Lett **79**, 733 (1997)

Tunnelling

- Tunnelling spectroscopies, which inject or remove electrons through a barrier have now evolved to be very important probes of materials
- A potential barrier allows a probe (usually a simple metal) to be maintained at an electrical bias different from the chemical potential of the material
- The current passed through the barrier comes from non-equilibrium injection – tunnelling
- Model for tunnelling from a metal into more complex material shown in figure
- Current is given by integrated area between two chemical potentials – provided the matrix element for tunnelling is taken into account
- If DoS for metal (or probe) – labelled 1 is slowly varying, the differential conductance dI/dV is proportional to DoS of material itself at the bias eV above the chemical potential μ_2



Tunnelling

- With the metal/probe (1) and sample (2) maintained at different electrical potentials separated by a bias voltage, the current through the junction can be predicted to be of the form

$$I \propto \int_{\mu+eV}^{\mu} g_1(\omega)g_2(\omega)T(\omega)d\omega$$

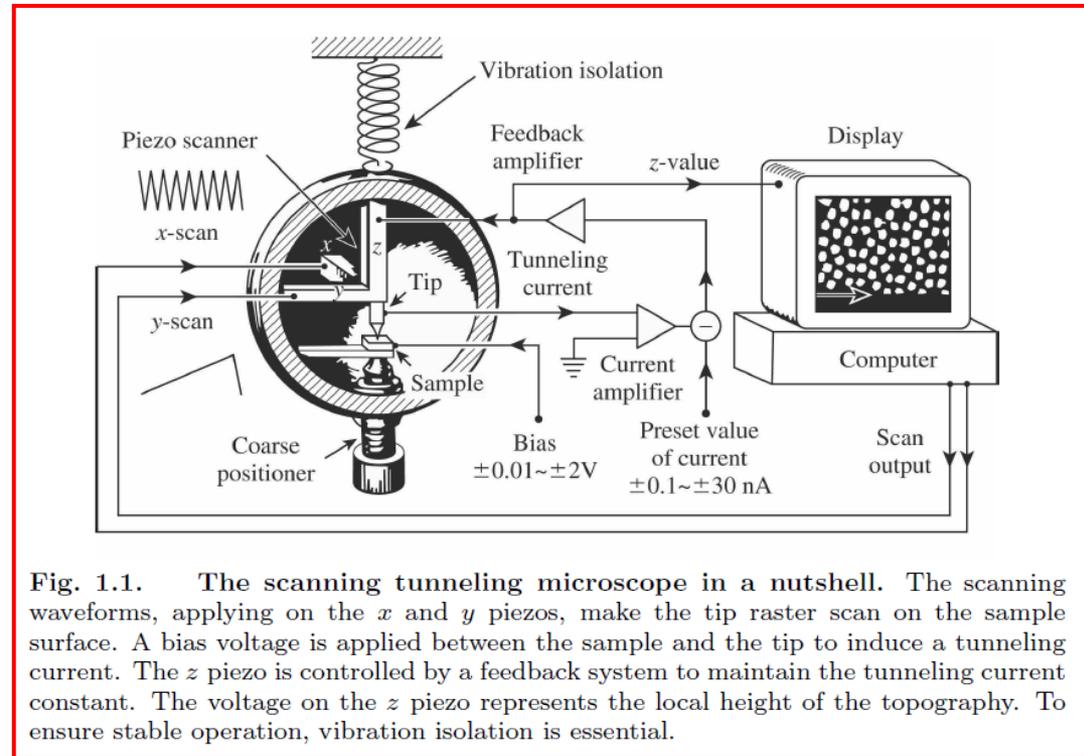
- Where $T(\omega)$ is the transmission through the barrier for an electron of energy $\hbar\omega$ and g_1, g_2 are the densities of states
- If the barrier is very high so $T(\omega)$ is not a strong function of energy and if the density of states in the contact/probe, g_1 , is approximately constant the energy dependence comes from the density of states, g_2 inside the sample being investigated
- Hence the differential conductivity is proportional to the density of states in the sample

$$\frac{dI}{dV} \propto g_2(\mu + eV)$$

- It is difficult to maintain large biases so most experiments are limited to probing electronic structure within a volt or so of the Fermi energy

Scanning tunnelling microscopy

- A scanning tunnelling microscope (STM) uses a sharp metal tip positioned by 3 piezoelectric transducers with vacuum as the tunnel barrier.
- The tunnelling probability is an exponential function of the barrier thickness
- High spatial resolution possible - 0.1nm lateral and 0.01nm depth, individual atoms can be imaged and manipulated despite nm or larger tip
- Tip close to surface - electron wavefunctions overlap
- On applying bias to sample a tunnel current is measured
- Current converted to a voltage and fed back to the z-piezo controller to keep the current constant
- Z piezo voltage gives surface topography when scanned
- Invented by Binnig and Rohrer at IBM labs in Zurich - won Nobel prize in 1986



Introduction to scanning tunnelling microscopy C J Chen
G Binnig et al Appl Phys Lett **40**, 178 (1982)
G Binnig et al Phys Rev Lett **49**, 57 (1982)

Scanning tunnelling microscopy catalysts

- Scanning tunnelling microscopy used to study processes on single crystal surfaces
- E.g. design of new catalysts - in this case to produce hydrogen from hydrocarbons and water
- STM image shows the surface of a Ni single crystal
- Some of the Ni atoms are substituted by Au atoms. The Au atoms are darker and the Ni atoms around a Au atom are brighter
- This is not because the Au atoms are depressed but they have a lower local DoS and the Ni atoms adjacent to a Au atom have enhanced DoS due to perturbation by Au atom
- Because DoS is closely related to catalytic reactivity the perturbed Ni atoms are more highly reactive and act as a better catalyst

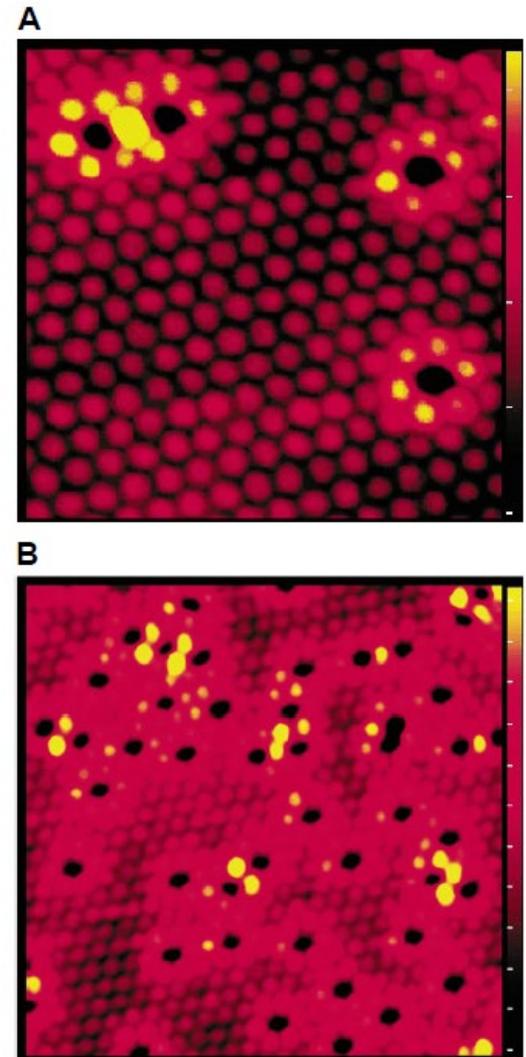
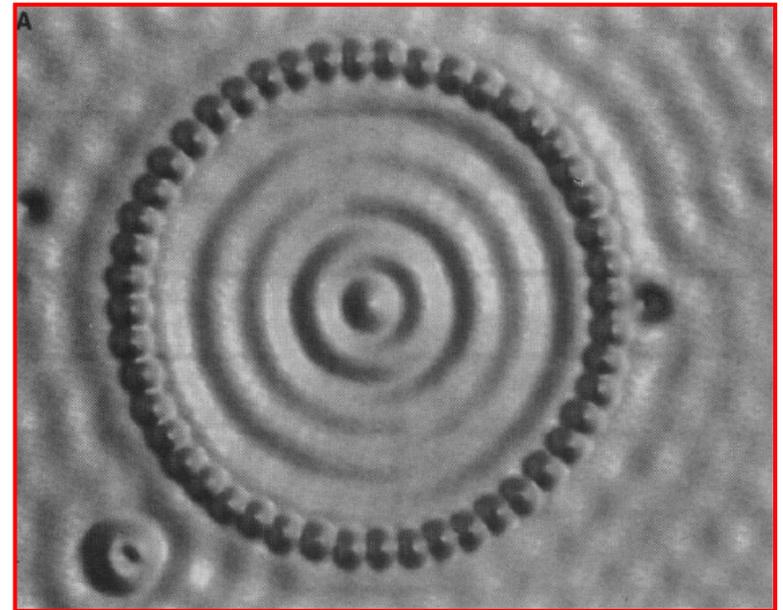
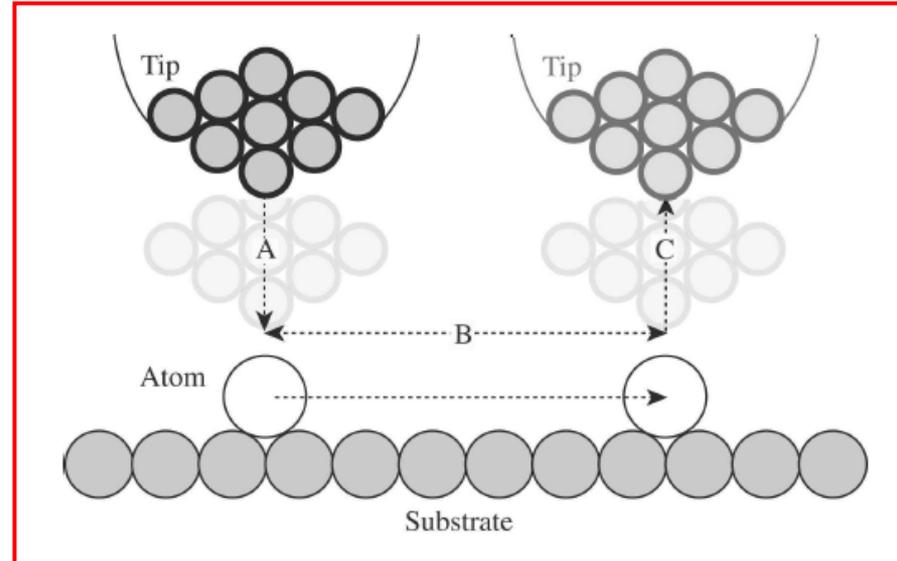


Fig. 1. Two STM images of a Ni(111) surface with 2% (A) and 7% (B) of a monolayer of Au. The Au atoms appear black in the images. The Ni atoms next to the Au atoms appear brighter because of a change in geometry and electronic structure, indicating that the chemical activity of the Ni atoms may be modified by nearest-neighbor Au atoms.

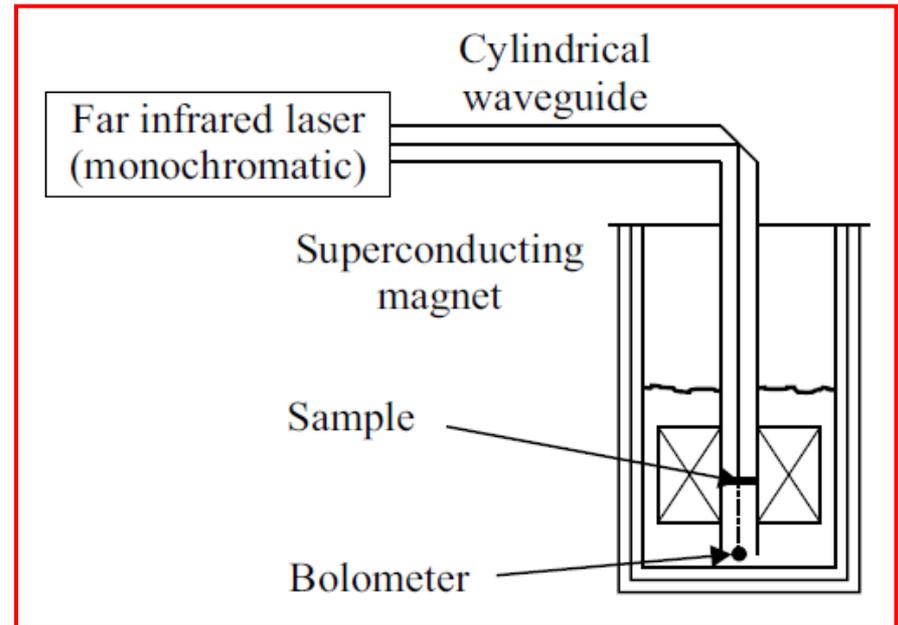
Scanning tunnelling microscopy – positioning single atoms

- The tip is positioned above the adatom to be moved
- The tunnelling current is increased lowering the tip until the tip/adatom interaction energy reaches diffusion activation – where adatom can move across ridge between stable positions
- Pull atom to desired location, reduce current to move tip away
- In UHV at 4K Fe atoms can be moved on Cu(111) surface to form a 48 atom ring with a diameter of 7.13nm
- Atom ring acts to confine Cu surface state electrons
- Tunnelling spectroscopy shows discrete resonances in local density of states indicating size quantisation



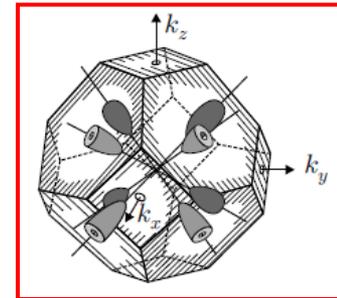
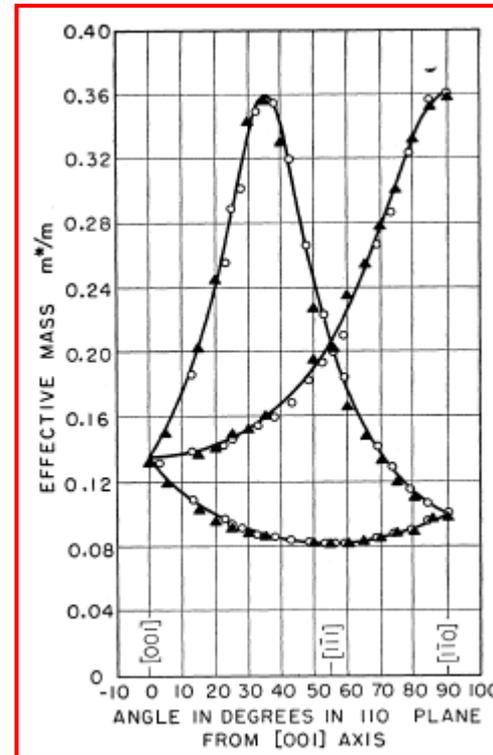
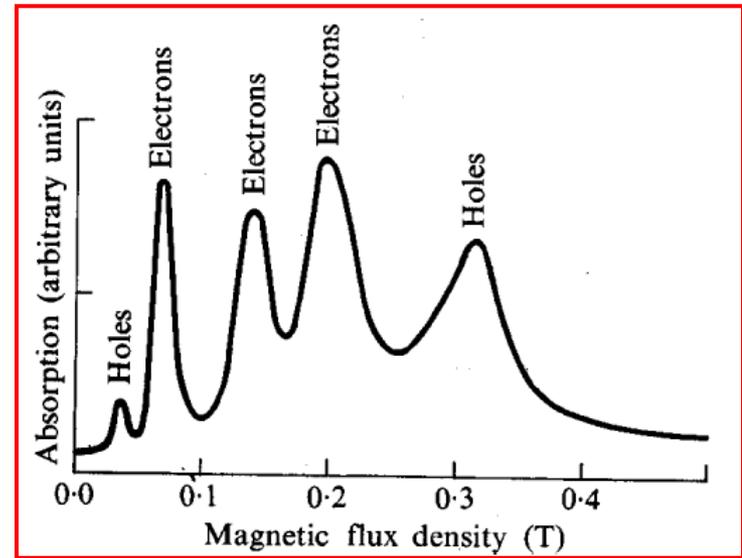
Cyclotron resonance

- It is possible to make a direct measurement of the cyclotron resonance frequency $\omega_c = eB / m^*$ and hence effective mass using millimetre waves or far infrared radiation to excite transitions between Landau levels
- This experiment is known as cyclotron resonance
- For semiconductor samples which have much lower carrier density than metals, the radiation can easily penetrate samples
- Measurements are usually made in transmission, either by fixing the magnetic field and varying the energy of the radiation or using a fixed frequency source such as a far infrared laser (shown here) and sweeping the magnetic field detecting the radiation with a bolometer.
- The linewidth of the resonance gives information about the scattering rate
- In lightly doped samples carriers must be excited into bands by raising the temperature or illuminating the samples with above bandgap radiation



Cyclotron resonance in Ge

- Figure shows absorption by cyclotron resonance in a single crystal of Ge at 4K
- Electrons and holes present because of above bandgap illumination
- Microwave frequency 24GHz and magnetic field applied in (110) plane at 60 degrees to [100] axis
- Resonance due to light and heavy holes visible as are three electron resonances
- The three electron resonances occur because the anisotropic band minima lie along [111] axes and the static magnetic field makes three different angles with these 4 axes
- Experimental and calculated effective masses are shown in the figure

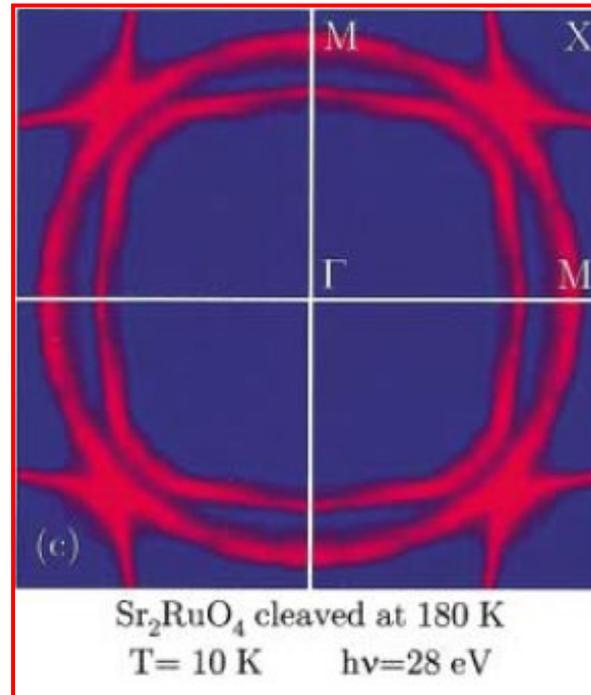


Summary of Lecture 12

- Photoemission
- Angle resolved photoemission spectroscopy (ARPES)
- ARPES equipment
- ARPES applied to GaAs and strontium ruthenate
- Tunnelling, scanning tunnelling microscope (STM)
- STM applied to catalysts and positioning atoms
- Cyclotron resonance - example germanium

Quantum Condensed Matter Physics

Lecture 12



The End