The Solid State

WS 2013/14

Lectures (Tuesday & Friday)

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Last time:

Thermal properties cont'd

Metals (free electron model)

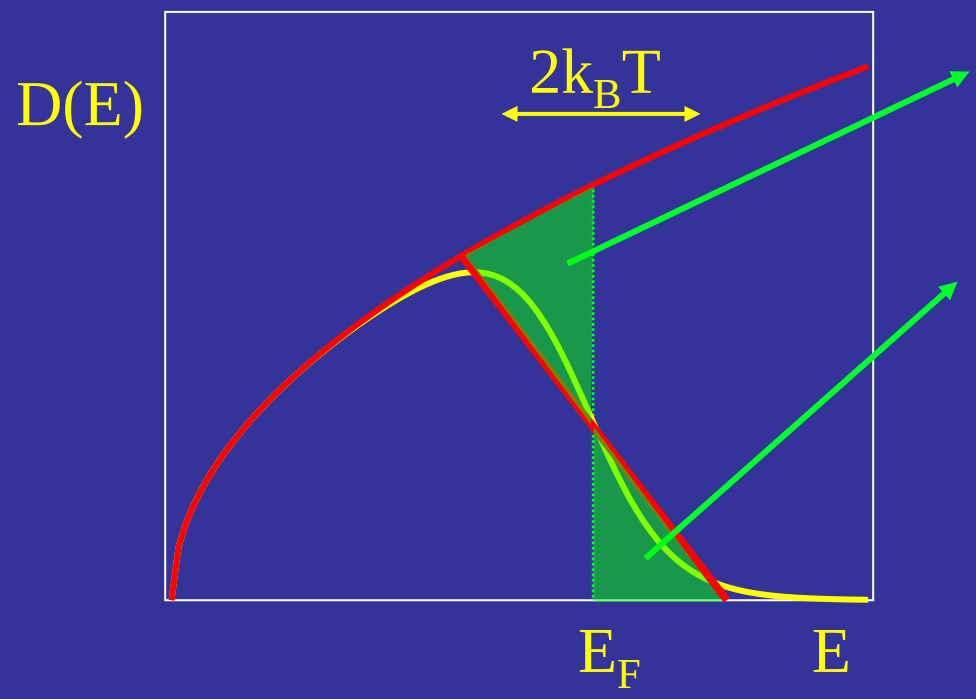
Today:

Metals (free electron model) cont'd

band structure

Heat capacity of the electron gas

$$C_{el} = \frac{dU_{el}}{dT} = \frac{d}{dT}\int_0^\infty E \cdot D(E) \cdot f_{FD}(E,T)\, dE$$



$$-\frac{1}{2}k_B T \times \frac{1}{2}D(E_F)\cdot(E_F - \frac{k_B T}{2})$$

$$+\frac{1}{2}k_B T \times \frac{1}{2}D(E_F)\cdot(E_F + \frac{k_B T}{2})$$

$$\Delta U = \frac{k_B{}^2 T^2}{2} D(E_F)$$

$$C_{el} = k_B{}^2 D(E_F)\cdot T$$

$$\Rightarrow C_{el} \propto T$$

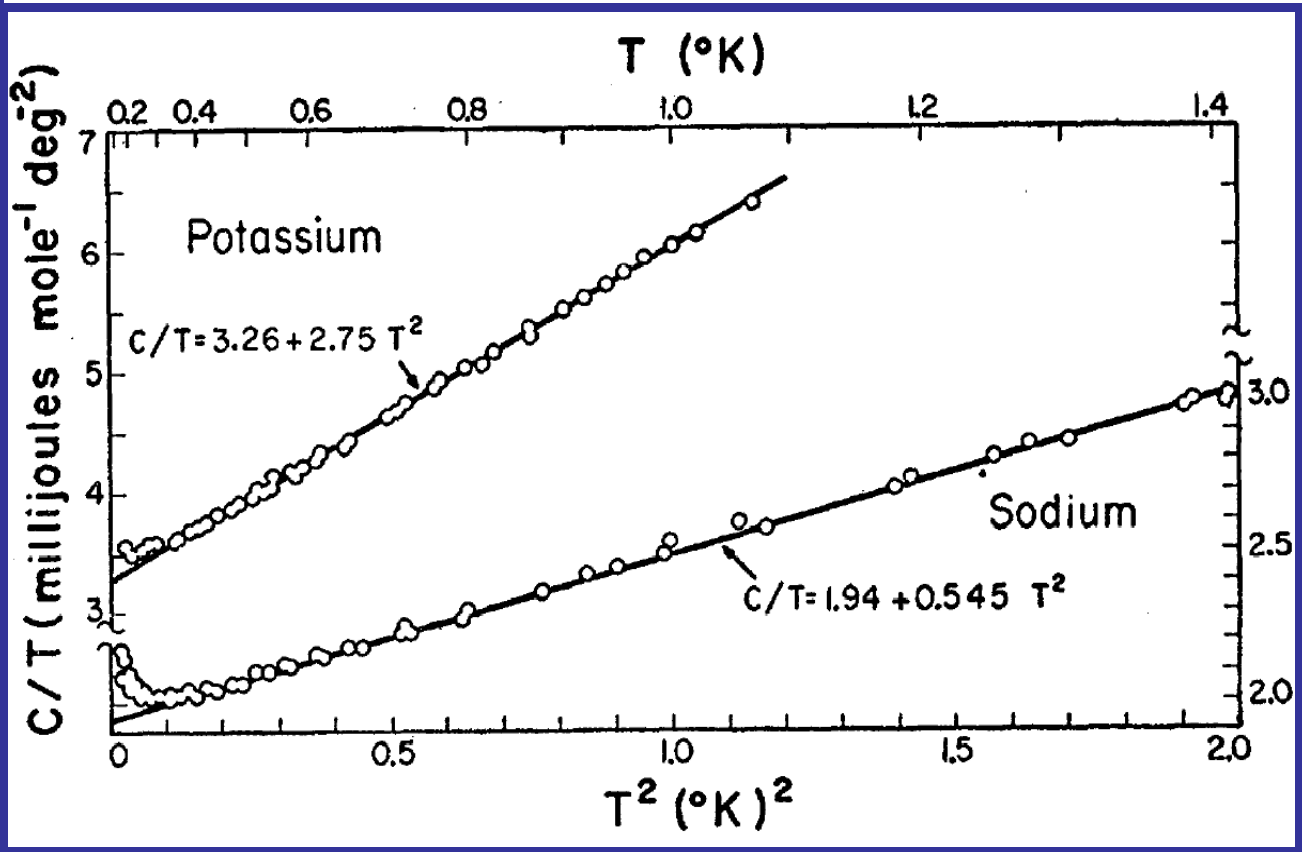
Electronic heat capacity

PHYSICAL REVIEW VOLUME 118, NUMBER 4 MAY 15, 1960

Heat Capacity of Sodium and Potassium at Temperatures below 1°K

WILLIAM H. LIEN AND NORMAN E. PHILLIPS
Department of Chemistry and Lawrence Radiation Laboratory, University of California, Berkeley, California

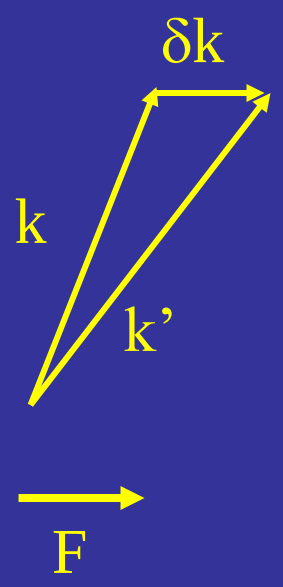
(Received December 17, 1959)



$$C = \gamma T + AT^3$$

Phonons

Electrical conductivity



2nd Newton: $m\frac{dv}{dt} = F$ or $\delta k = \frac{1}{\hbar}\int F dt$

Relaxation time τ: $\delta k \to 0$

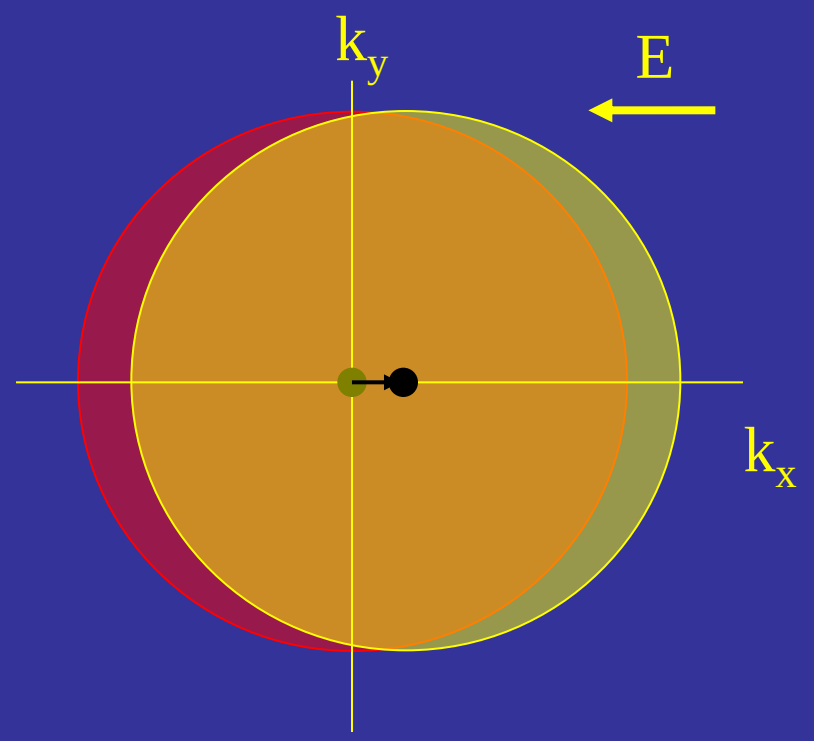
e-p, e-e scattering, Impurity scattering

$$\delta k = \frac{1}{\hbar} F \tau$$

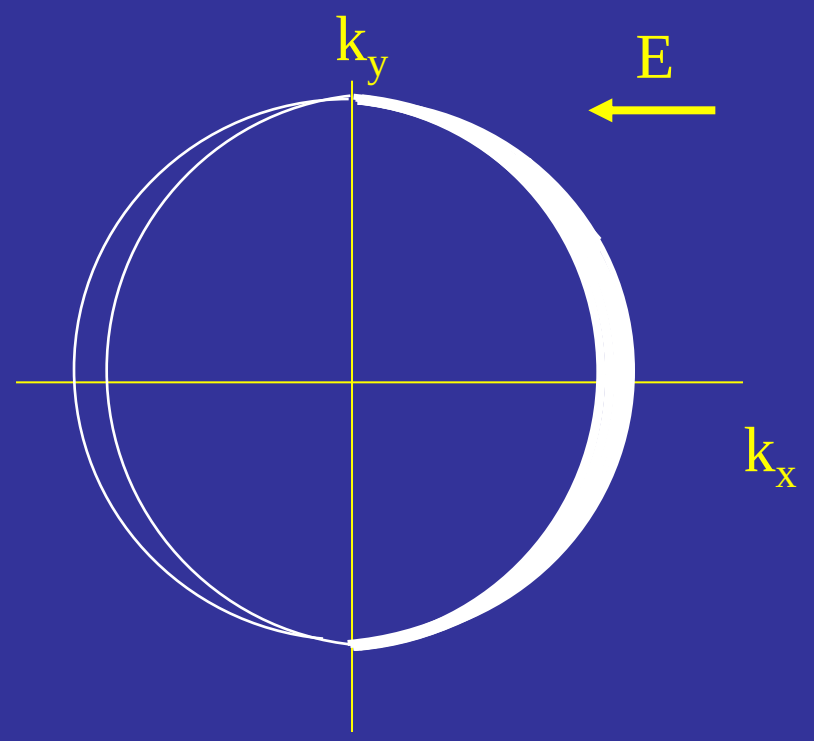
Equation of motion:

$$\hbar\left(\frac{d}{dt} + \frac{1}{\tau}\right)k = F$$

Displacement fermi sphere



$$\delta k = \frac{1}{\hbar} F \tau$$



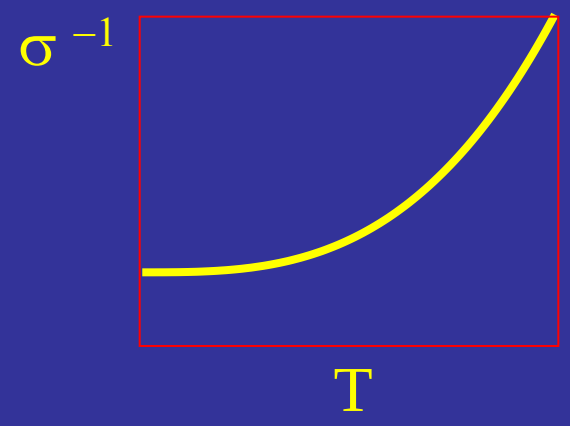
$$\delta k = \frac{1}{\hbar} F \tau$$

Ohm's law

$$\delta k = \frac{1}{\hbar} F\tau$$

$$\delta k = \frac{qE\tau}{\hbar}; \qquad v_{drift} = \delta v = \frac{qE\tau}{m}$$

$$F = qE$$



Current density $\quad j = nq\delta v = \dfrac{ne^2\tau E}{m}$

Ohm's law $\quad \sigma = \dfrac{j}{E} = \dfrac{ne^2\tau}{m}$

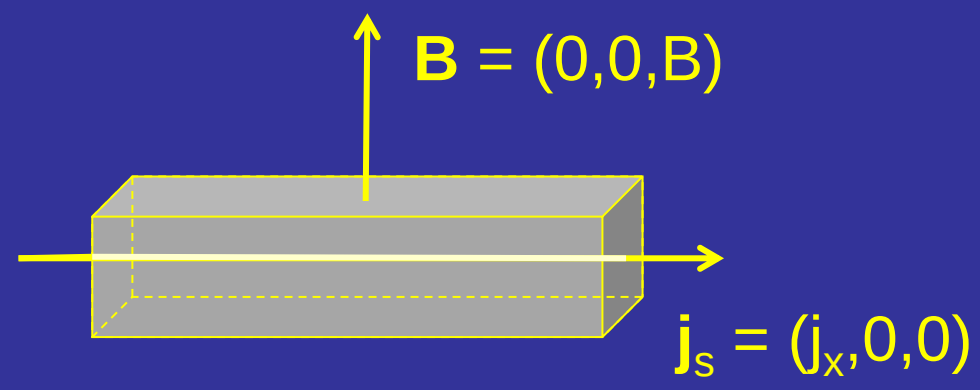
$$\left.\begin{array}{l} \sigma \sim 10^7\ \Omega^{-1}m^{-1} \\ n \sim 10^{28}\ m^{-3} \end{array}\right\} \quad \tau \sim 10\,fs \quad \Rightarrow \quad \ell = v_F\tau \sim 10\,nm$$

Very pure metals, low T: $\quad \ell > 1\,cm$!!

Hall effect

$$\hbar\left(\frac{d}{dt}+\frac{1}{\tau}\right)k = F$$

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



stationary case: $j_y = 0 \Rightarrow E_y = -(e\tau/m)E_xB = R_Hj_xB$

Hall coefficient $R_H = -(ne)^{-1}$

experimentally determine

- sign of charge carriers (electrons/holes)
- density of carriers

typical values for *good* metals $|R_H| \sim 10^{-10}m^3/C$

Thermal conductivity

$$J = -K \cdot \nabla T$$

Electronic heat conductivity: $K = \frac{1}{3} C_{el} \cdot v \cdot \ell = \frac{\pi^2 k_B{}^2 n \tau}{3m} T$

Wiedemann-Franz law: $\frac{K}{\sigma} = L \cdot T$

L: Lorenz number $\pi^2/3(k_B/e)^2 = 2.45\ 10^{-8}\ W\Omega/K^2$

Table 10-2 Lorentz number $L = K/\sigma T$ in units of 10^{-8} W·Ω/K², for several metals at 0°C and 100°C

Metal	0°C	100°C	Metal	0°C	100°C
Ag	2.31	2.37	Pb	2.47	2.56
Au	2.35	2.40	Pt	2.51	2.60
Cd	2.42	2.43	Sn	2.52	2.49
Cu	2.23	2.33	W	3.04	3.20
Mo	2.61	2.79	Zn	2.31	2.33

Free electron gas parameters

$$N = \int_0^\infty D(E) \cdot f_{FD}(E)\, dE$$

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

$$E_F = \frac{\hbar^2 k_F^{\,2}}{2m}$$

$$k_F = \left(3\pi^2 n\right)^{1/3}$$

$$E_F = \frac{1}{2} m v_F^{\,2}$$

$$v_F = \frac{\hbar k_F}{m}$$

$$T_F = E_F / k_B$$

$$T_F = \frac{\hbar^2}{2mk_B}\left(3\pi^2 n\right)^{2/3}$$

$$D(E_F) = \frac{Vm}{\pi^2 \hbar^3}\sqrt{2mE_F}$$

$$D(E_F) = \frac{V}{\pi \hbar^2} \cdot \left(\frac{3}{\pi} n\right)^{1/3} m$$

Sodium

Na $1s^2 2s^2 2p^6 3s$ = [Ne]3s BCC lattice, 4.29 Å

$$n = 2.65 \cdot 10^{22}\ \mathrm{cm}^{-3}$$

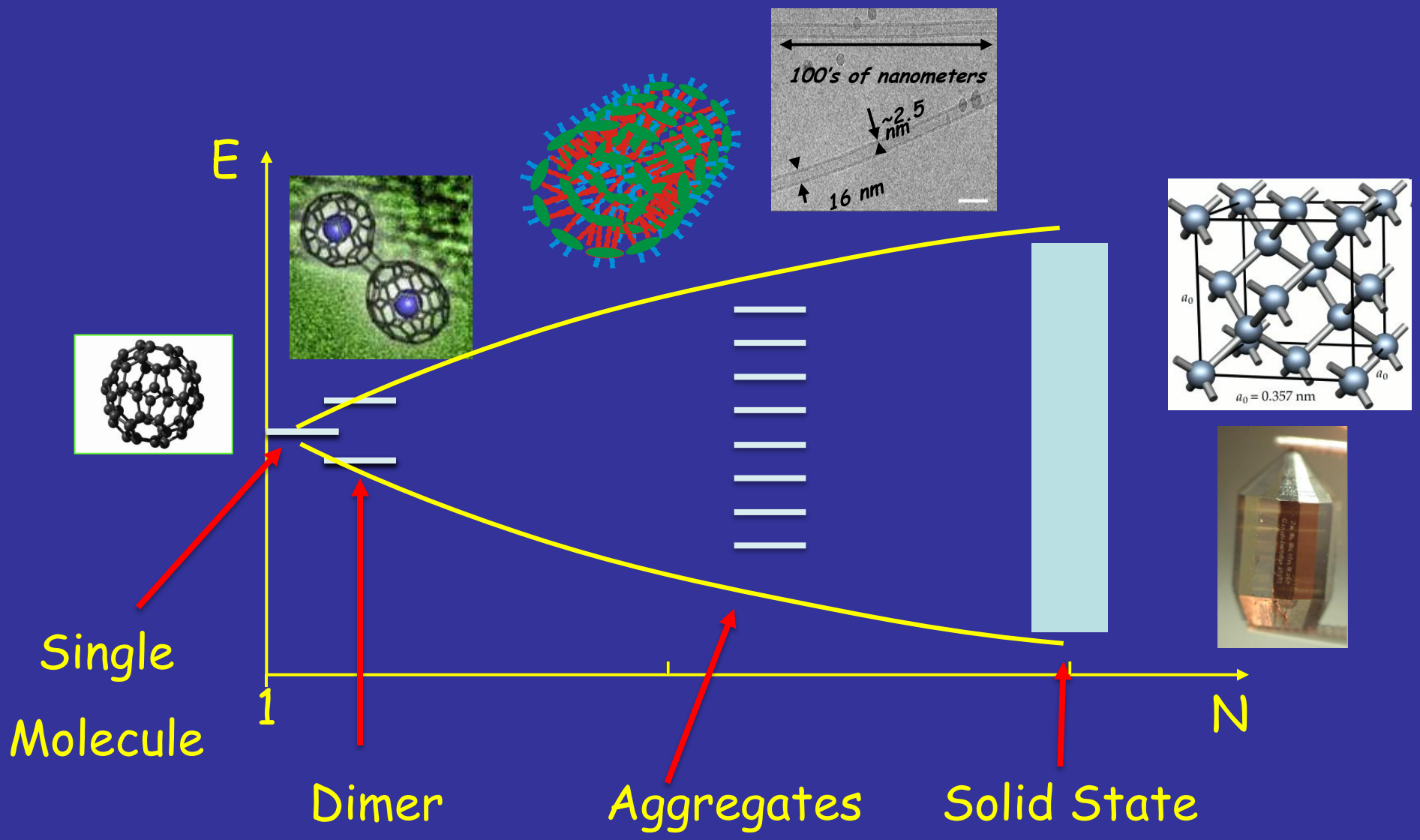
$$E_F = 3.23\ \mathrm{eV}$$

$$k_F = 2.65 \cdot 10^{22}\ \mathrm{cm}^{-1}$$

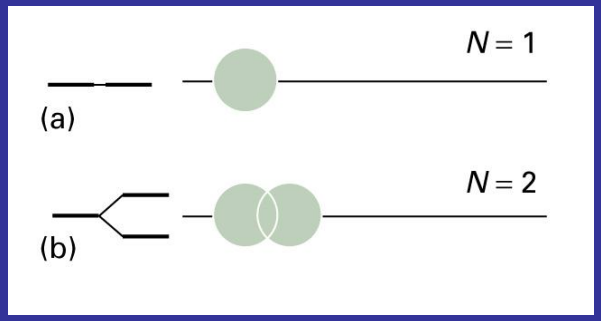
$$v_F = 1.07 \cdot 10^{8}\ \mathrm{cm/s}$$ → Non relativistic

$$T_F = 3.75 \cdot 10^{4}\ \mathrm{K}$$ → Degenerate quantum gas
E_F hardly depends on T

Formation of bands and band-gaps



Binding between atoms (simplified)



Hamilton operator $\hat{H} = \hat{H}_A + \hat{H}_B + \hat{\beta}$

with $H_A|\Psi_A\rangle = E_0|\Psi_A\rangle \qquad \hat{H}_B|\Psi_B\rangle = E_0|\Psi_B\rangle$

and $\hat{\beta}|\Psi_A\rangle = \beta|\Psi_B\rangle \qquad \hat{\beta}|\Psi_B\rangle = \beta|\Psi_A\rangle$

Compact notation for schrödinger equation

$$\begin{pmatrix} E_0 & \beta \\ \beta & E_0 \end{pmatrix}\begin{pmatrix} c_A|\Psi_A\rangle \\ c_B|\Psi_B\rangle \end{pmatrix} = E\begin{pmatrix} c_A|\Psi_A\rangle \\ c_B|\Psi_B\rangle \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} E_0 - E & \beta \\ \beta & E_0 - E \end{pmatrix}\begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

Solutions

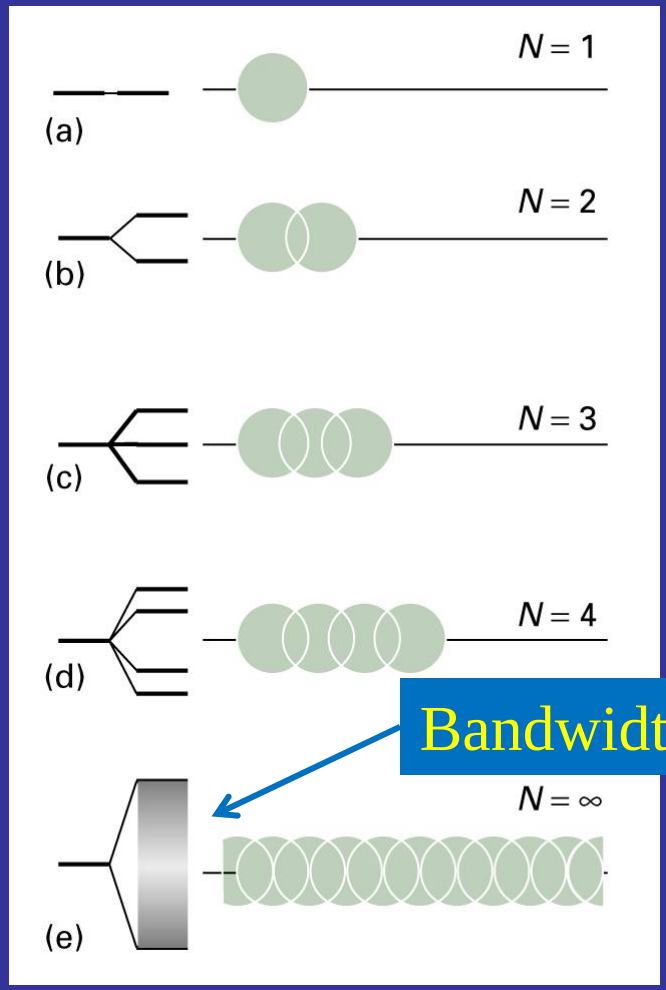
$E = E_0 - b;\ \ c_A = -c_B$ (bonding orbital)

$E = E_0 + b;\ \ c_A = c_B$ (anti-bonding orbital)

Generalize to N atoms with only nearest neighbor interaction

Same principle: $\hat{\beta}$ operator can only move electrons between orbitals of neighboring atoms:

$$\begin{pmatrix} E_0 & \beta & 0 & 0 & 0 & 0 & 0 \\ \beta & E_0 & \beta & 0 & 0 & 0 & 0 \\ 0 & \beta & E_0 & \beta & 0 & 0 & 0 \\ 0 & 0 & \beta & E_0 & \beta & 0 & 0 \\ 0 & 0 & 0 & \beta & E_0 & \beta & 0 \\ 0 & 0 & 0 & 0 & \beta & E_0 & \beta \\ 0 & 0 & 0 & 0 & 0 & \beta & E_0 \end{pmatrix}$$



Eigenvalues are:

$$E_k = E_0 + 2\beta\cos\left(\frac{k\pi}{N+1}\right) \text{ with } k = 1\ldots N \text{ and } \lim_{N\to\infty} E_N - E_1 = -4\beta$$

(proof: http://digilander.libero.it/foxes/matrix/eigen_tridiad_uniform.pdf)

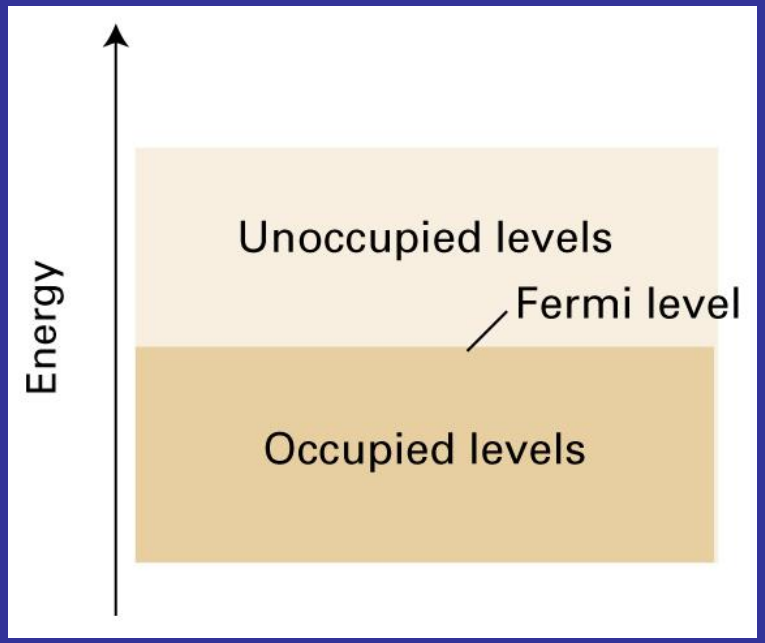
Band filling

Need not all be filled: Fermi level

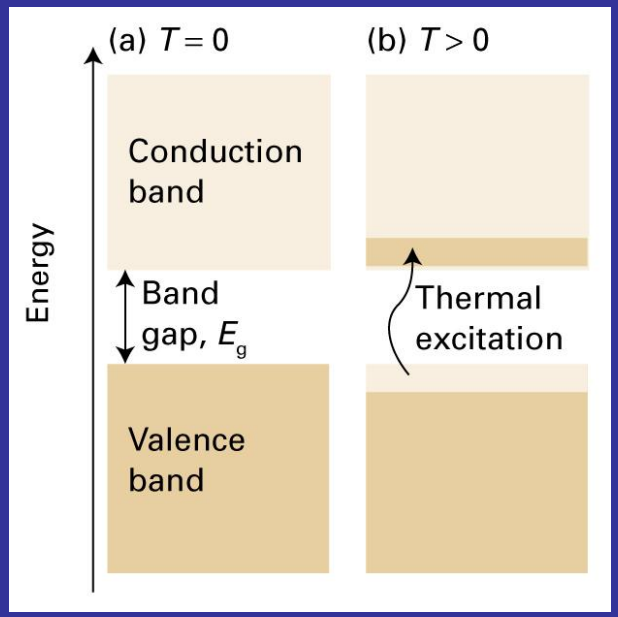
N atoms with one s electron: N levels, filling N/2 → metal

N atoms with two s electrons: N levels, filling N → insulator (at T=0)

Metal

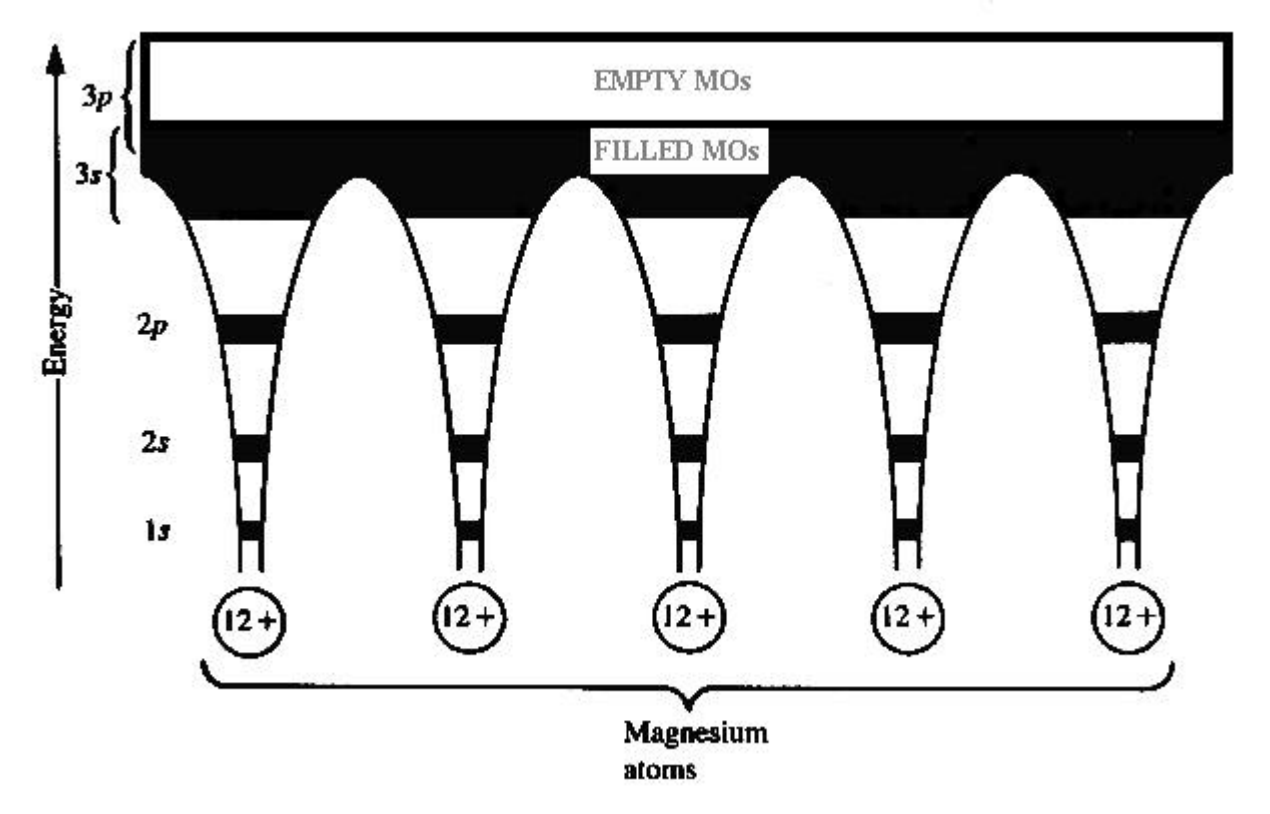


Insulator

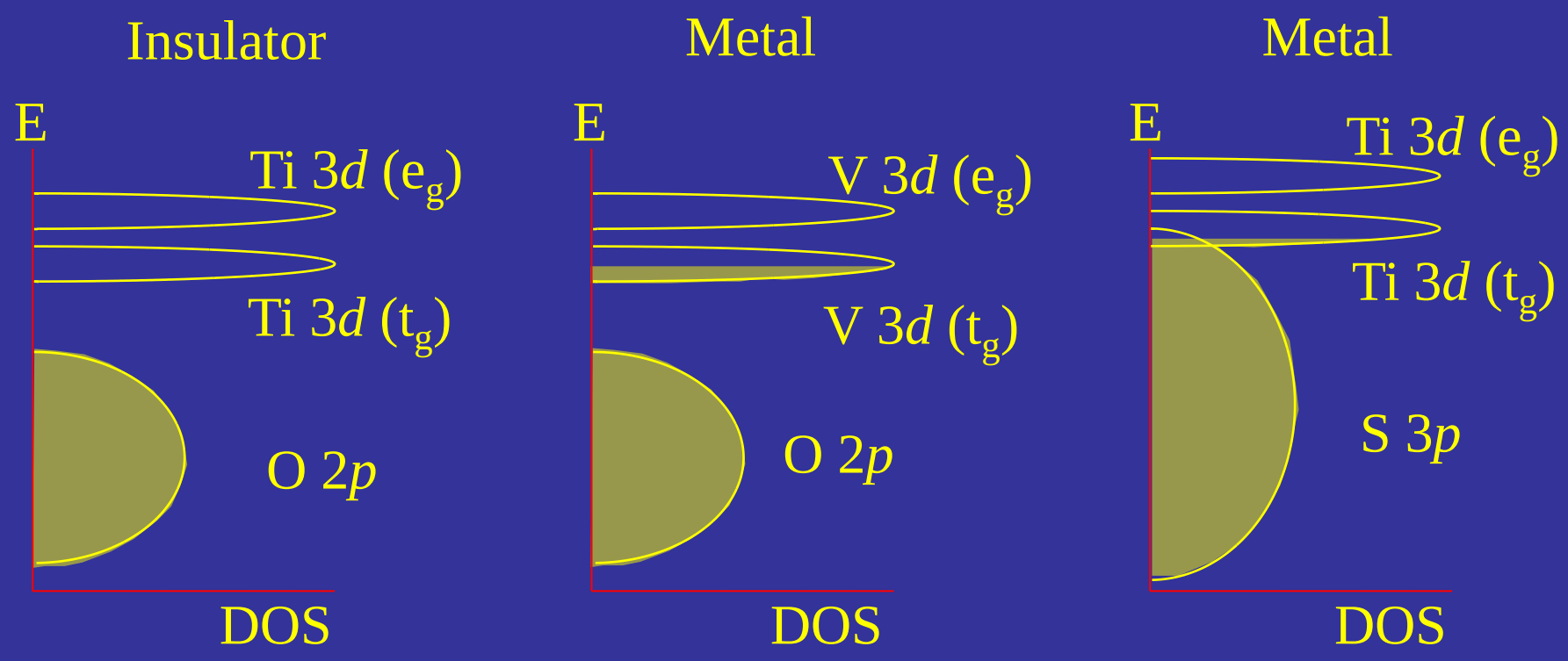


Why is magnesium a metal

Magnesium has electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2$
We need partially filled bands for metals
Should Mg not be an insulator?



Overlapping bands



TiO_2
Empty *d*-bands

VO_2
Partially filled *d*-bands

TiS_2
Overlapping bands

Ti: [Ar]$3d^2 4s^2$
V: [Ar]$3d^3 4s^2$

Back to free electrons

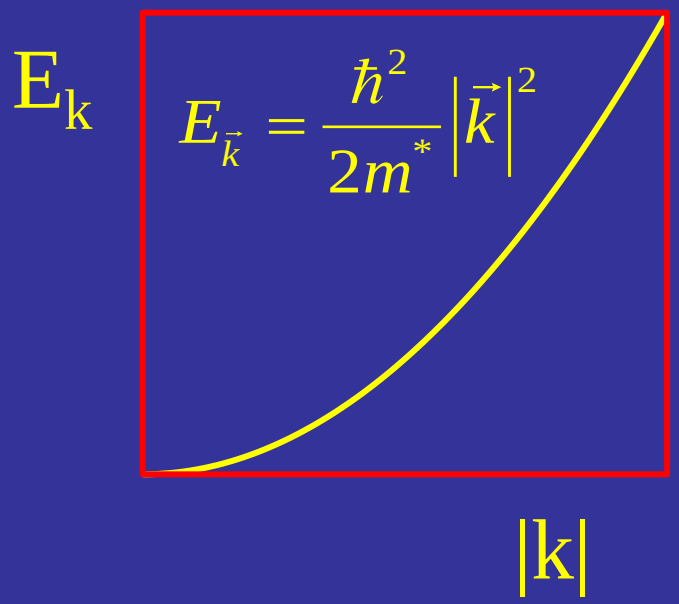
Crystal potential

$$\left(\frac{-\hbar^2}{2m}\nabla^2 + \cancel{U}\right)\psi = i\hbar\frac{d\psi}{dt}$$

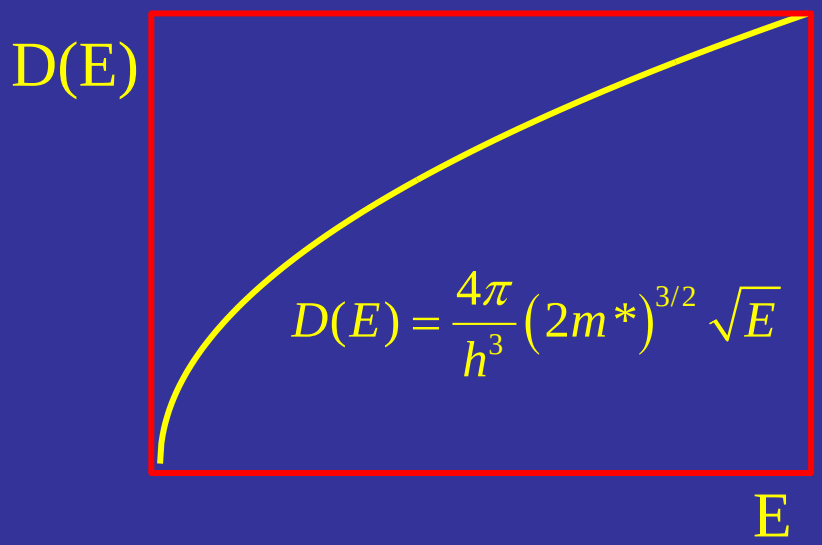
Plane wave solutions:

$$\psi_{\vec{k}}(r,t) = \psi_0 e^{i(\omega t - \vec{k}\cdot\vec{r})}$$

Dispersion relation



Density of states



Incorporating the periodic potential

Crystal potential is periodic: $V(\vec{r}) = V(\vec{r} + \vec{R}_{\vec{n}})$ $\quad \vec{R}_{\vec{n}} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

Schrödinger equation: $\left(\frac{-\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\Psi_\lambda = E_\lambda \Psi_\lambda$

Introduce translation operator: $T_{\vec{n}}\psi(\vec{r}) \equiv \psi(\vec{r} + \vec{R}_{\vec{n}})$

For the translational invariant Hamiltonian: $[H, T_{\vec{n}}] = 0$

$$T_{\vec{n}} \cdot H\Psi_\lambda = H \cdot T_{\vec{n}}\Psi_\lambda = E_\lambda\, T_{\vec{n}}\Psi_\lambda$$

So if Ψ_λ is an eigenstate with energy E_λ then also $T_{\vec{n}}\Psi_\lambda$

Bloch theorem

Translation operator for free electrons

$$T_{\vec{n}} e^{-i\vec{k}\cdot\vec{r}} = e^{-i\vec{k}\cdot\vec{n}} e^{-i\vec{k}\cdot\vec{r}}$$

Bloch theorem I: for any wave function that satisfies the s-eq. of a periodic system there is a wavevector k such that

$$\Psi(\vec{r}+\vec{n}) = e^{i\vec{k}\cdot\vec{n}} \cdot \Psi(\vec{r})$$

Bloch theorem II: the wavefunction for a periodic system can be written as $\Psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \cdot u_{\vec{k}}(\vec{r})$

with $u_k(r) = u_k(r+n)$ periodic

Bloch theorem

The eigenstates of a periodic one-electron Hamiltonian can be chosen to have the form of a plane wave times a function with the periodicity of the Hamiltonian

The wavevector k

Periodic boundary conditions (Born-von Karman)

For a crystal of $N_1 \times N_2 \times N_3$ primitive cells demand that

$$\Psi(\vec{r} + N_1\vec{a}_1) = \Psi(\vec{r})$$
$$\Psi(\vec{r} + N_2\vec{a}_2) = \Psi(\vec{r})$$
$$\Psi(\vec{r} + N_3\vec{a}_3) = \Psi(\vec{r})$$

which gives $e^{i\vec{k}\cdot(N_1\vec{a}_1)} = e^{i\vec{k}\cdot(N_2\vec{a}_2)} = e^{i\vec{k}\cdot(N_3\vec{a}_3)} = 1$

an thus $\vec{k} = \frac{n_1}{N_1}\vec{b}_1 + \frac{n_2}{N_2}\vec{b}_2 + \frac{n_3}{N_3}\vec{b}_3$

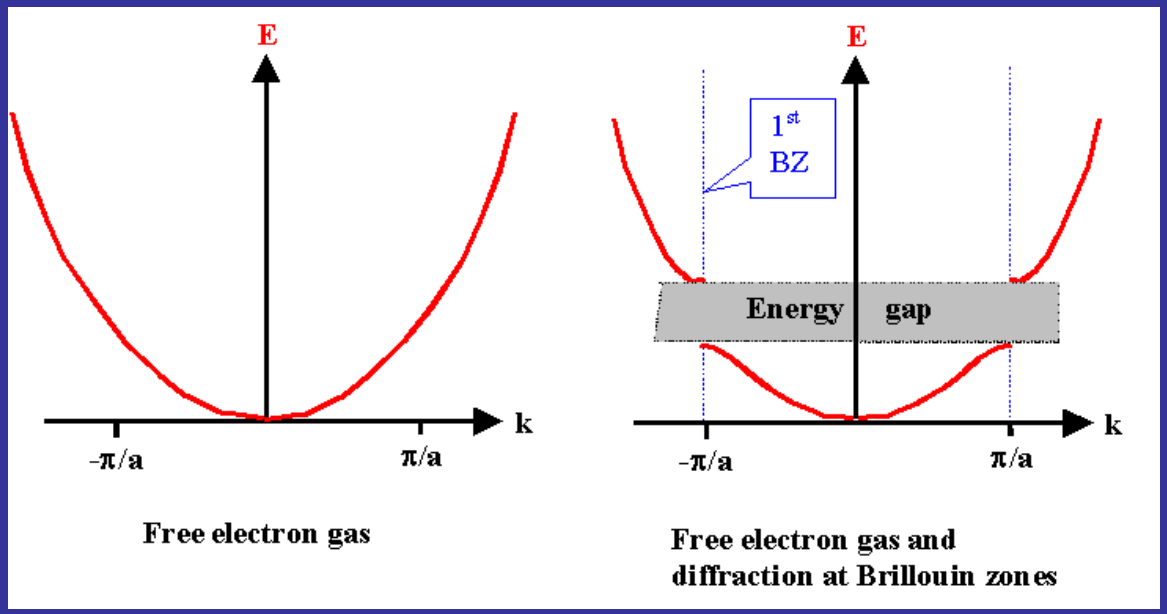
with $\vec{b}_i$ the unit vectors of the reciprocal lattice

Bragg scattering of electrons

Bragg law: $\Delta\vec{k} = \vec{G}$

Electrons with wavevectors differing by a reciprocal lattice vector G can Bragg scatter into each other: mixing of states with e^{ikr} and $e^{i(k-G)r}$ with $|k| = |k + G|$

This leads to energy gaps in the dispersion



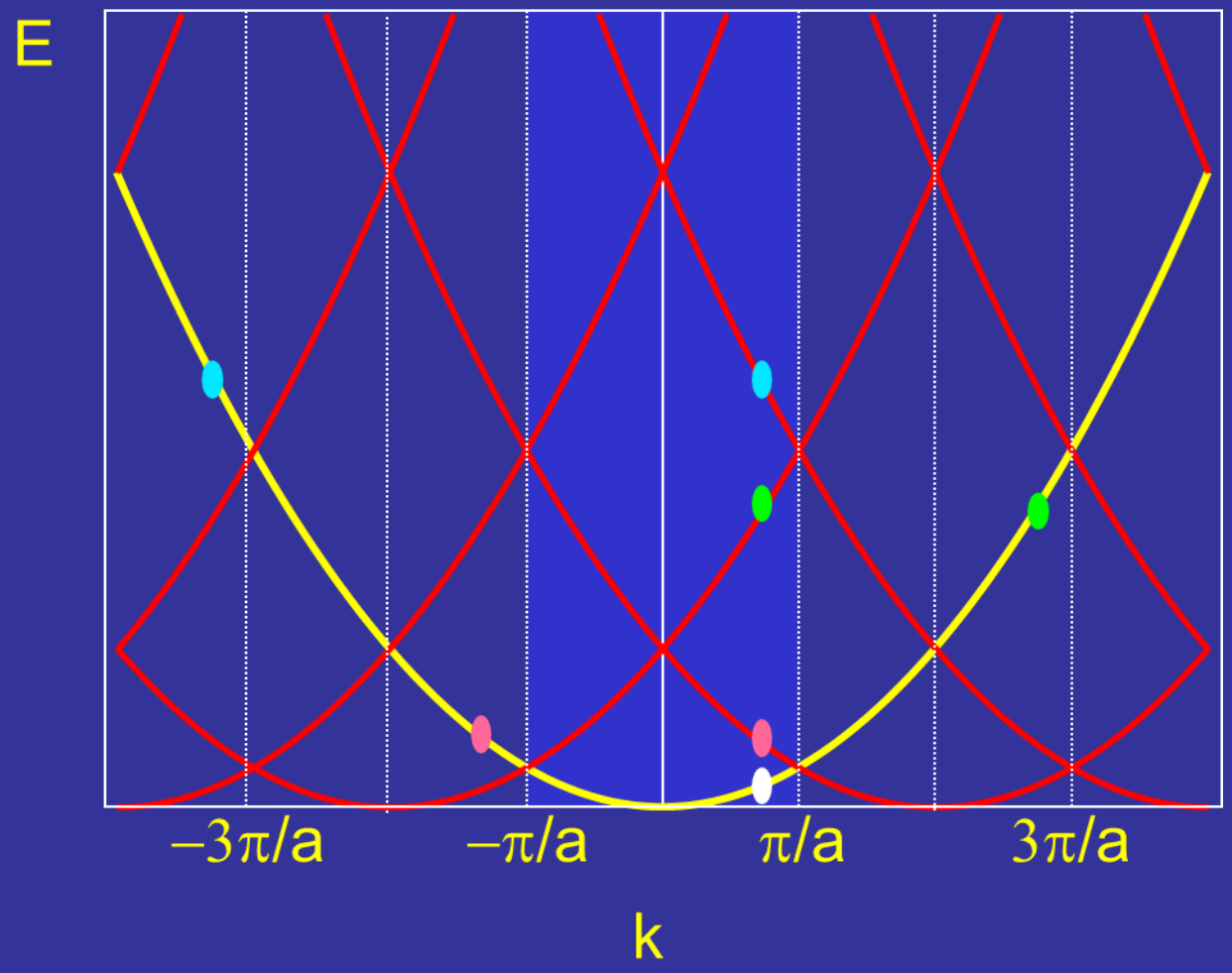
Extended and reduced zone schemes

Wavefunctions with $k > G$ can be mapped onto $k < G$:

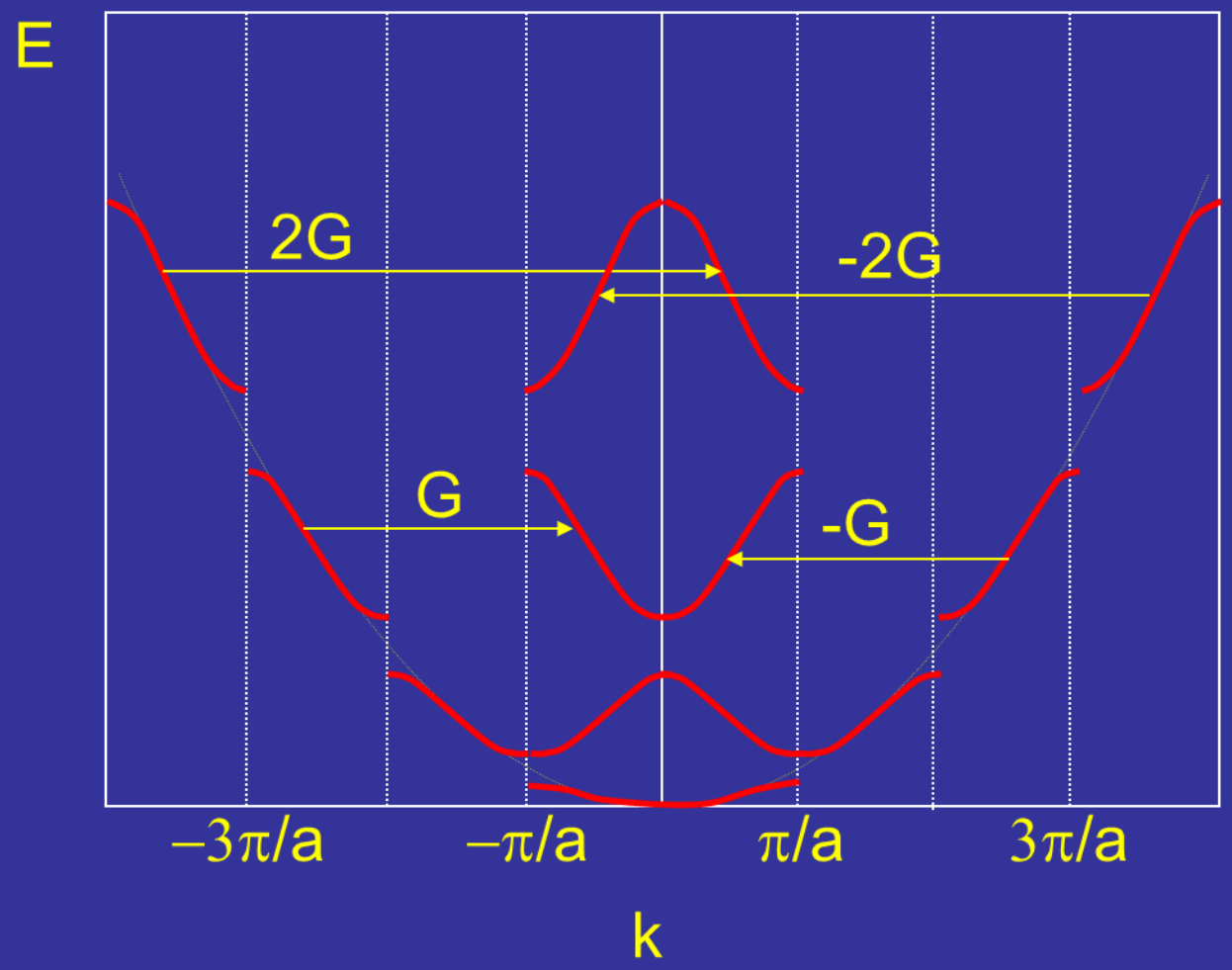
$$\Psi_{\vec{k}'}(\vec{r}) = e^{i\vec{k}'\cdot\vec{r}} \cdot u_{\vec{k}'}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} \cdot \left(e^{-i\vec{G}\cdot\vec{r}} u_{\vec{k}'}(\vec{r})\right) = e^{i\vec{k}\cdot\vec{r}} \cdot u_{\vec{k}}(\vec{r})$$

with $u_{\vec{k}}(\vec{r}) = e^{-i\vec{G}\cdot\vec{r}} u_{\vec{k}'}(\vec{r})$ also a periodic function (Bloch function)

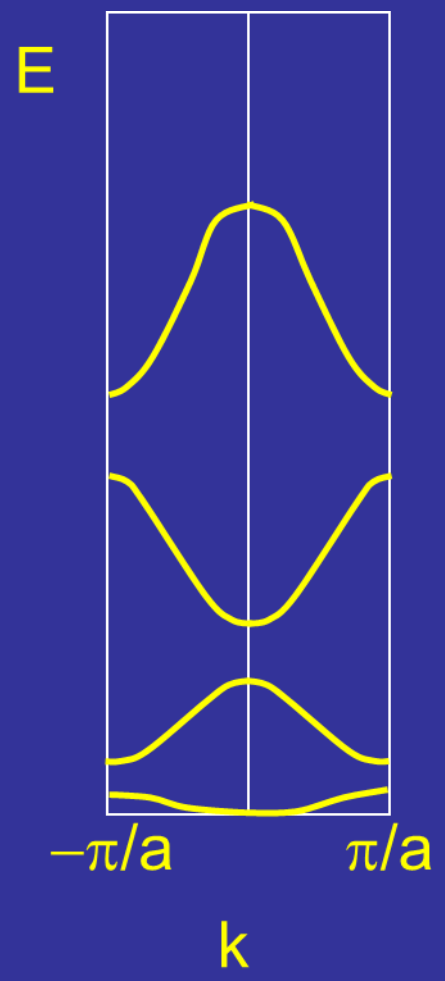
Mapping to the first Brillouin zone



Extended zone scheme



Reduced zone scheme



Diamond band structure

VOLUME 16, NUMBER 9 PHYSICAL REVIEW LETTERS 28 FEBRUARY 1966

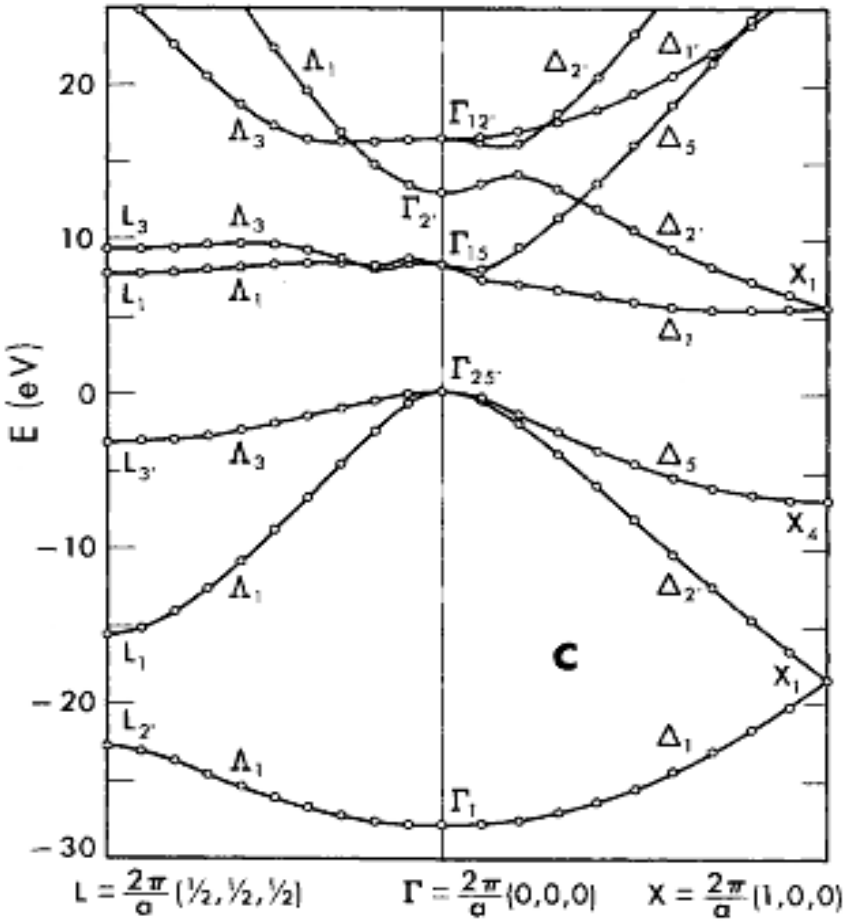
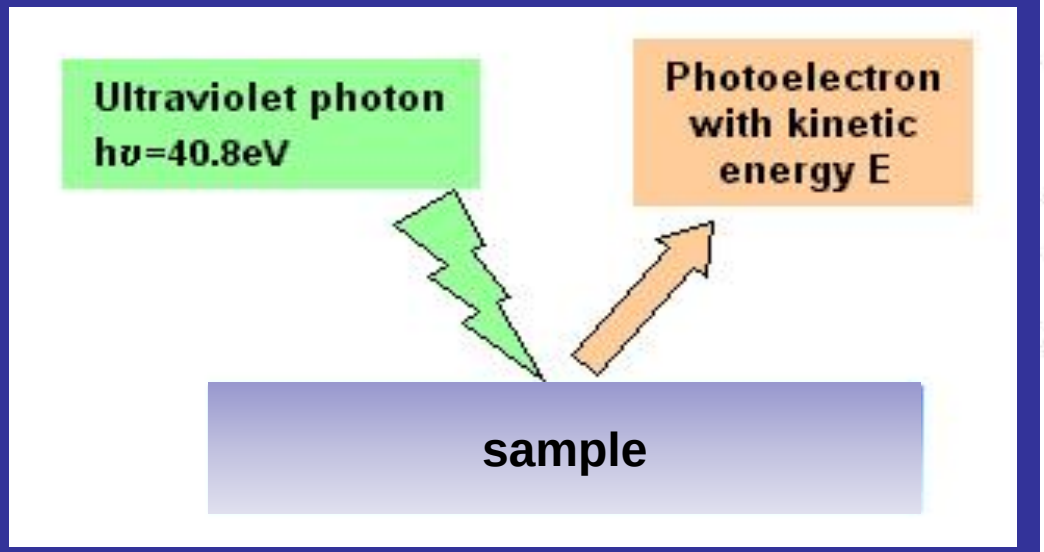


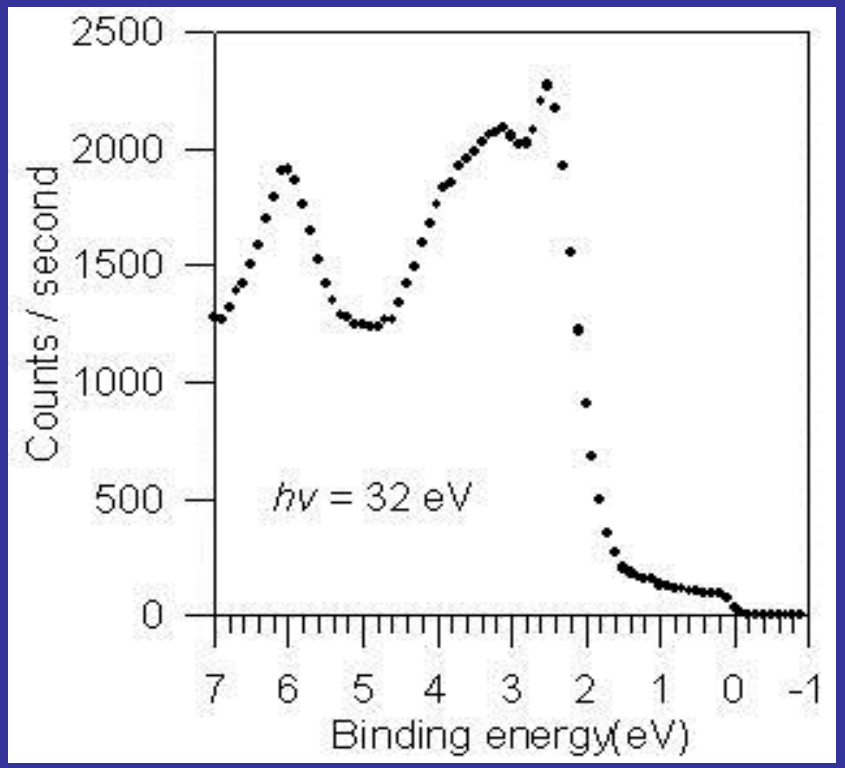
FIG. 1. The electronic band structure of diamond.

BAND STRUCTURE AND OPTICAL PROPERTIES OF DIAMOND*

W. Saslow,† T. K. Bergstresser, and Marvin L. Cohen‡
Department of Physics, University of California, Berkeley, California
(Received 27 January 1966)

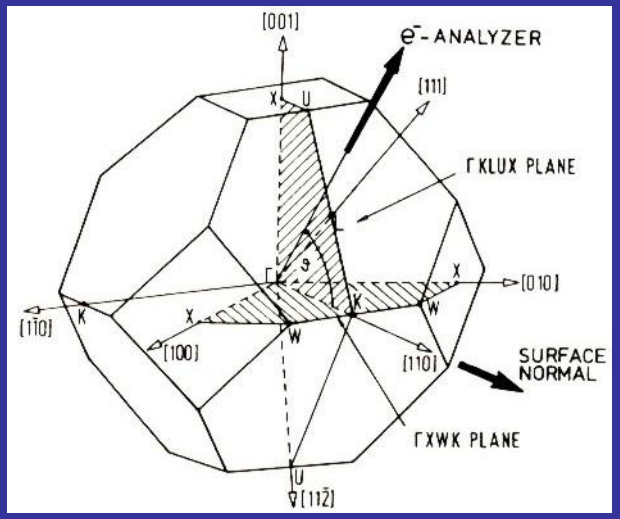
Photoelectron Spectroscopy - PES

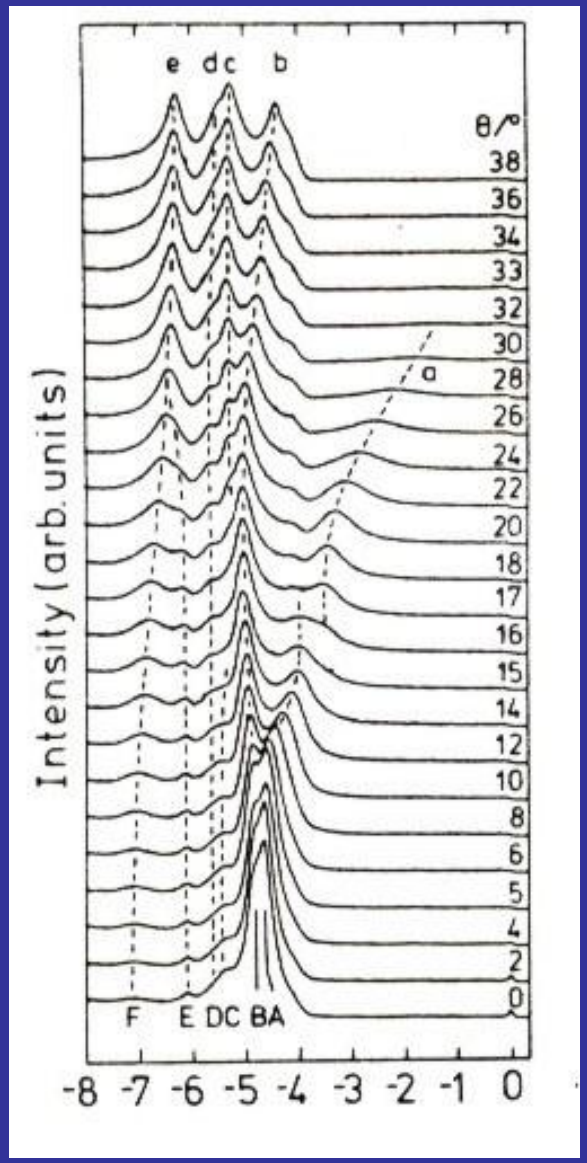


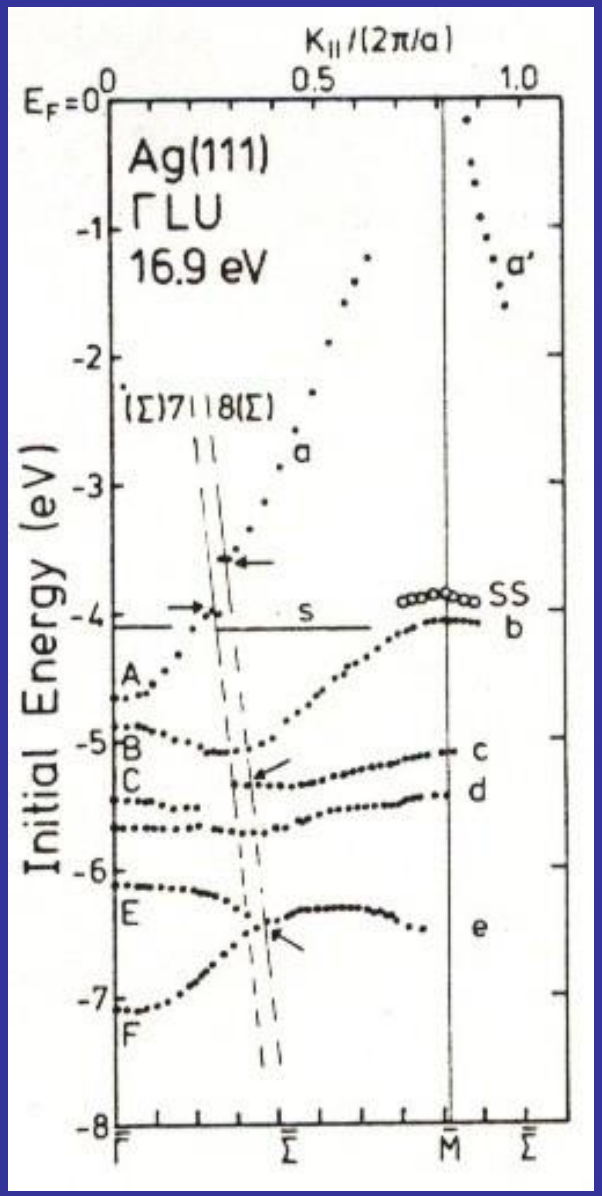
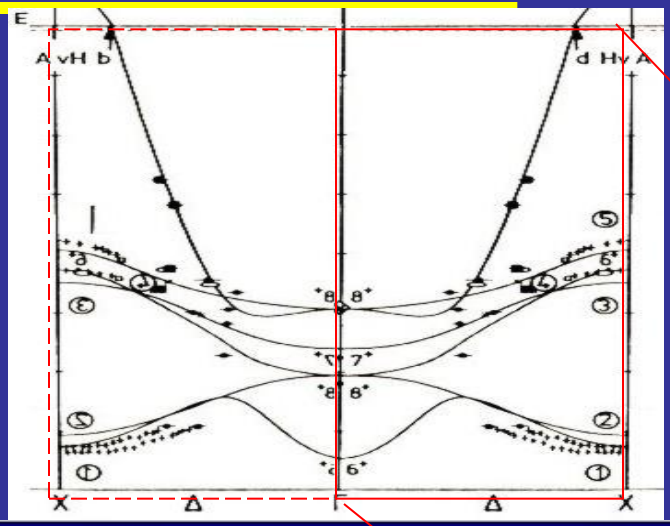
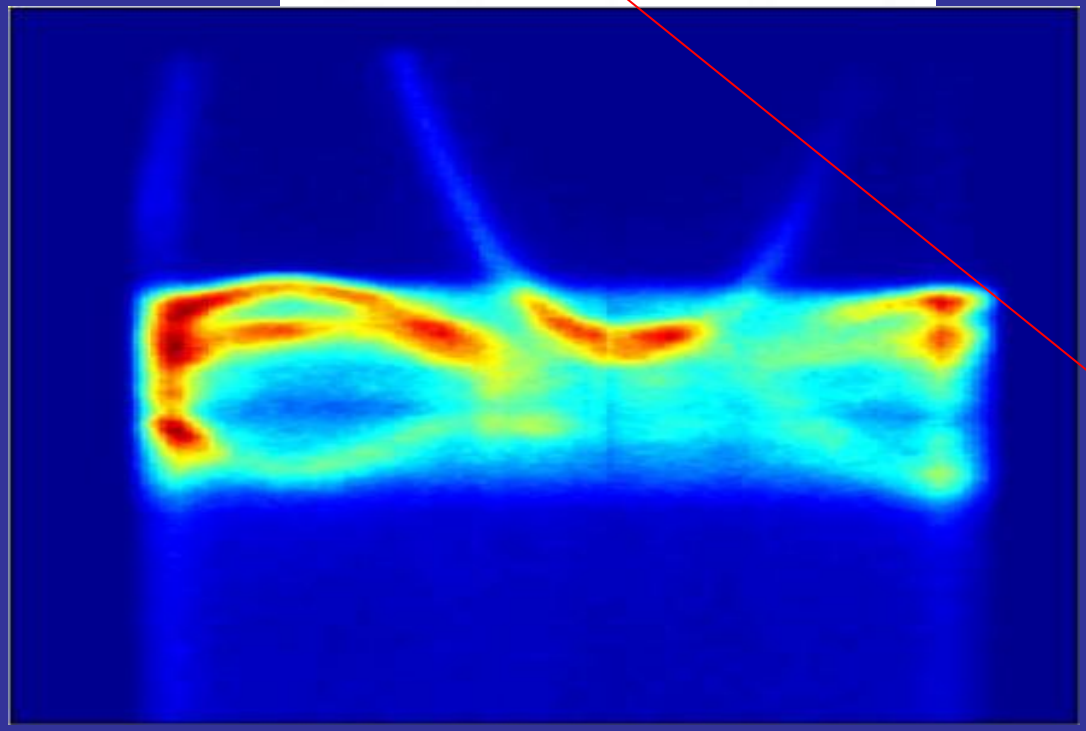
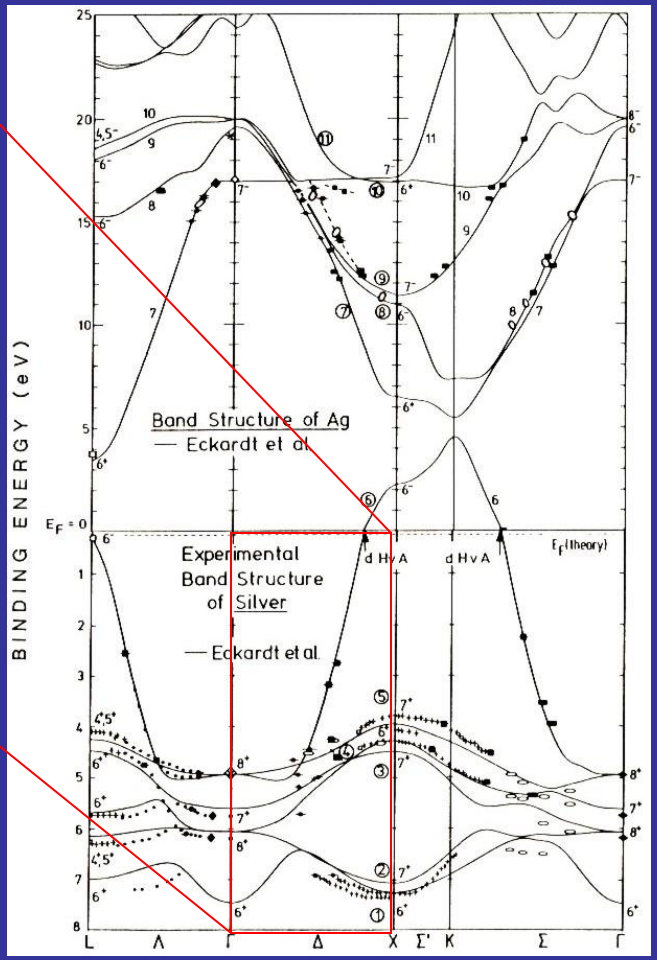


Gold, U. Johansson, R. Nyholm

Angle resolved (AR-) PES







ARPES: band dispersion of silver