

# Advanced solid state physics

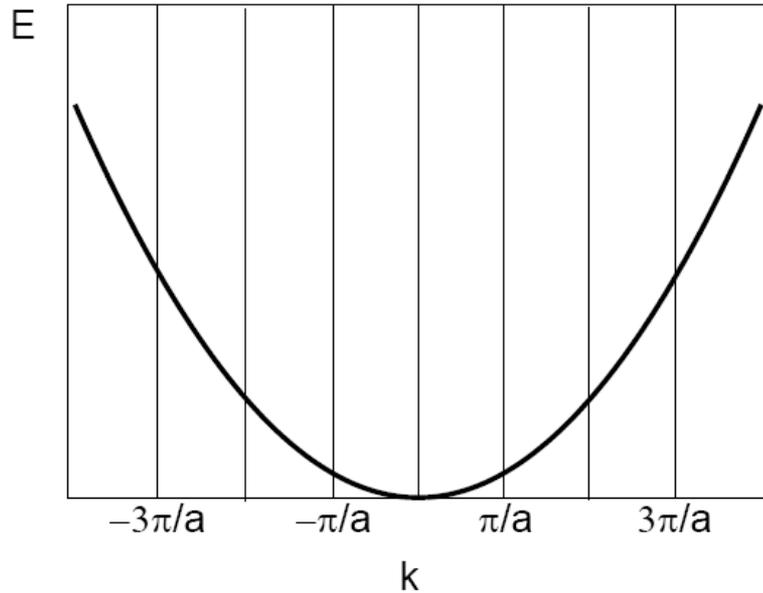
## Energy bands in solids

Some pictures are taken from Ashcroft and Mermin from Kittel from Mizutani and from several sources on the web.

we are starting to remind...

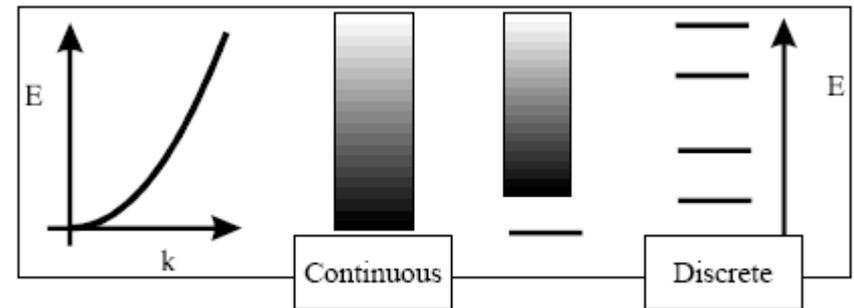
### Free Electron Dispersion Relation

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



$$p = mv = \hbar \cdot k$$

$$E = \frac{1}{2}mv^2 = \frac{\hbar^2 k^2}{2m}$$



Some pictures are taken from Ashcroft and Mermin from Kittel from Mizutani and from several sources on the web.

Goal: Calculate electrical properties (eg. resistance) for solids

Approach:

- Macroscopic theory:  $V, I, R$        $V = IR$
- Microscopic theory:  $J, E, \sigma$        $\mathbf{J} = \sigma \mathbf{E}$        $\frac{l}{\sigma A} = R$
- Phenomenological model of transport:  $n, \tau, m$        $\sigma = \frac{ne^2\tau}{m}$
- Relate parameters in phenomenological theory to electronic energy levels and wavefunction

You will be able to relate a bandstructure to macroscopic parameters for the solid

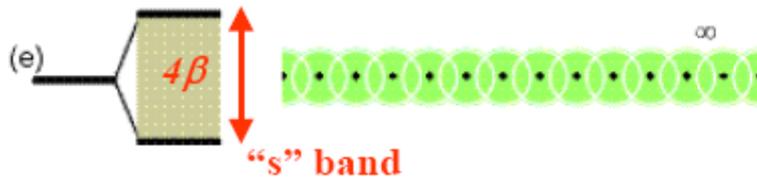
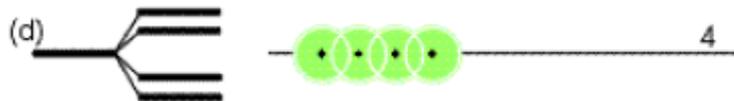
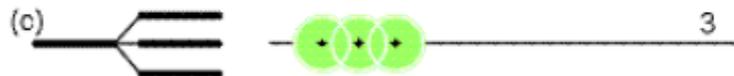
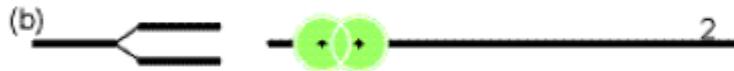
$$\sigma = e^2 v_F^2 \tau g(E_F)$$

$$C_V = \left. \frac{\partial ((E/V))}{\partial T} \right|_{V,N} = \frac{\pi^2}{3} k_B^2 T g(E_{F0}) = \gamma T$$

Density of States is the Central Character in this Story

# Band Formation in 1-D Solid

♦ Simple model for a solid: the one-dimensional solid, which consists of a single, infinitely long line of atoms, each one having one s orbital available for forming molecular orbitals (MOs).

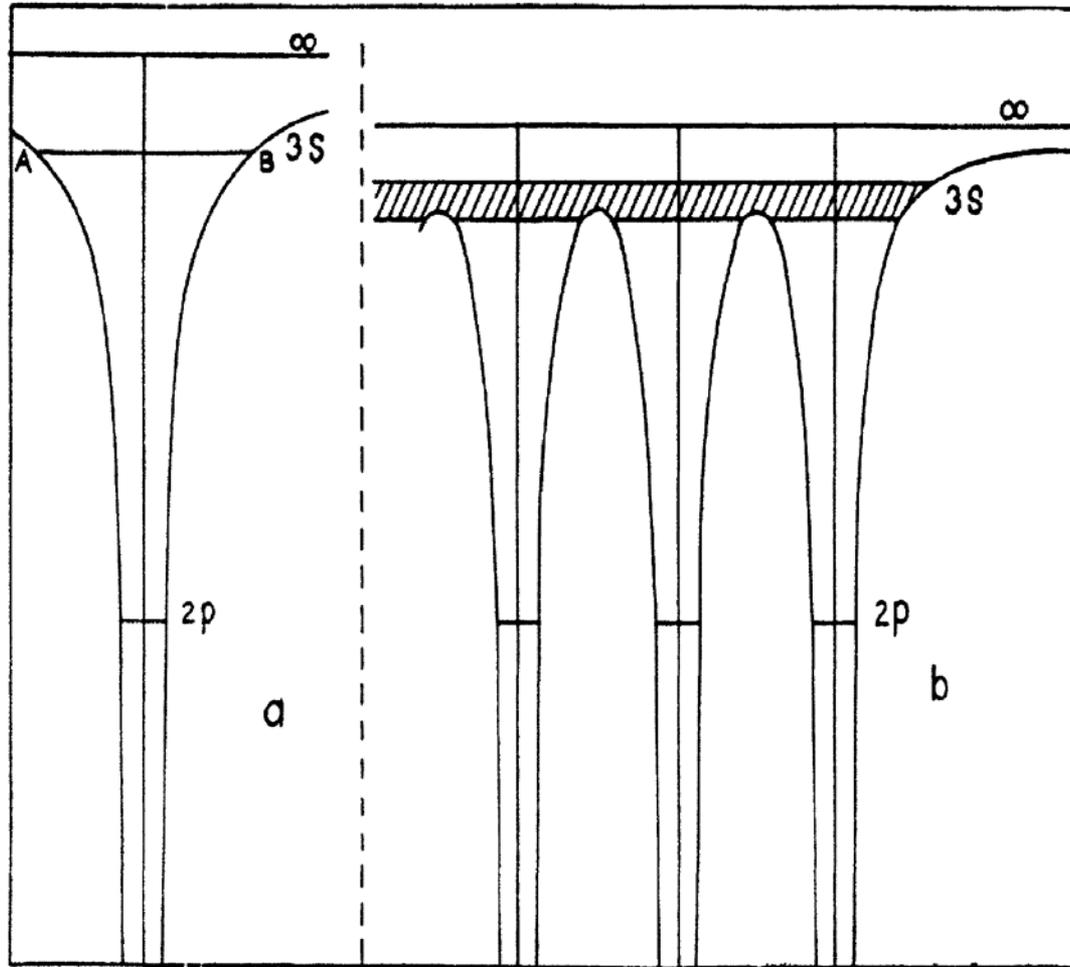


*When the chain is extended:*

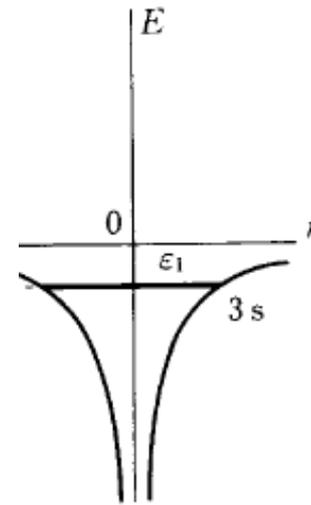
→ The *range of energies* covered by the MOs is *spread*

→ This range of energies is filled in with *more and more orbitals*

→ The *width of the* range of energies of the MOs is *finite*, while the number of molecular orbitals is *infinite*: This is called a *band*.



- The letters s, p, d, f, . . . , are often used to signify the states with ,  $\ell = 0, 1, 2, 3, \dots$ , each preceded by the principal
- $n=1, \ell = 0, m = 0, s = 1/2 \rightarrow (1s)^2$
- $n=2, \ell = 0, m = 0, s = 1/2 \rightarrow (2s)^2$
- $n=2, \ell = 1, m = 0, 1, s = 1/2 \rightarrow (2p)^6$
- $n=3, \ell = 0, m = 0, s = 1/2 \rightarrow (3s)^2$
- etc.
- Na 11 electrons with four different orbital energy levels 1s, 2s, 2p and 3s.
- $(1s)^2(2s)^2(2p)^6(3s)^1$



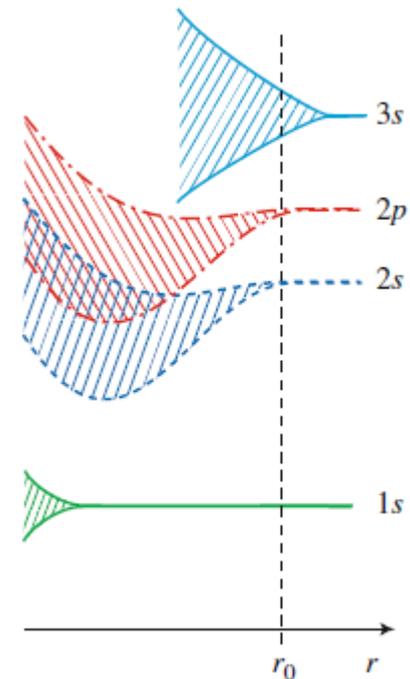
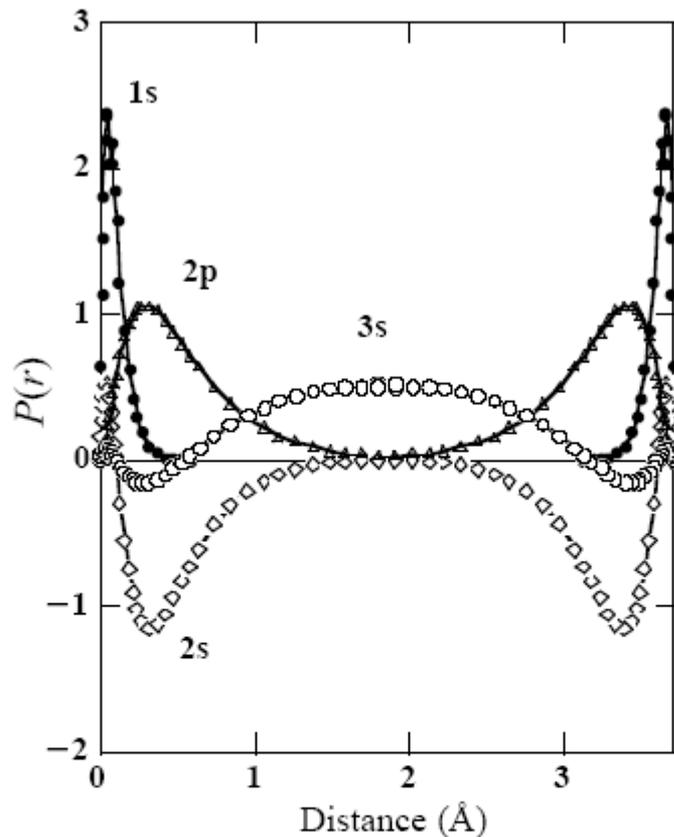


Figure 2.1. 1s, 2s, 2p and 3s wave functions for a free Na atom. Identical wave functions are shown in duplicate both at the origin and  $3.7 \text{ \AA}$  (or  $0.37 \text{ nm}$ ) corresponding to the interatomic distance in Na metal.  $P(r)$  represents  $r$  times the radial wave function  $R(r)$ .  $P(r) = rR(r)$  is used as a measure of the probability density, since the probability of finding electrons in the spherical shell between  $r$  and  $r + dr$  is defined as  $4\pi r^2 |R(r)|^2 dr$ . The wave functions are reproduced from D. R. Hartree and W. Hartree, *Proc. Roy. Soc. (London)* **193** (1947) 299.

from Alloul, Mizutani

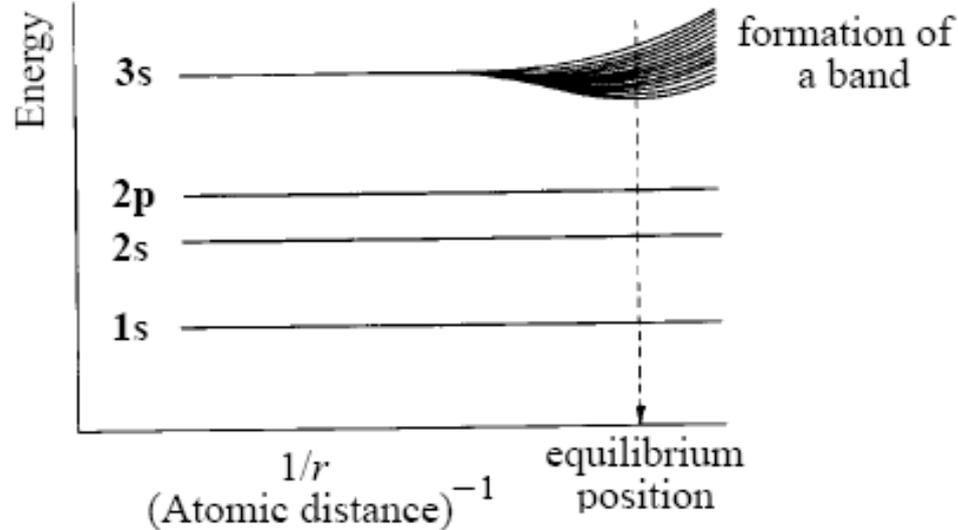


Figure 2.2. Schematic illustration for the formation of an energy band. The energy levels for a huge number of Na free atoms are degenerate when their interatomic distances are very large. The outermost 3s electrons form an energy band when the interatomic distance becomes comparable to the lattice constant of sodium metal.

- the energy levels for the  $10^{23}$  3s electrons are split into quasi-continuously spaced energies when the interatomic distance is reduced to a few-tenths nm.
- The quasi-continuously spaced energy levels thus formed are called an **energy band**.

- Apart from metallic bonding, there are three other bonding styles: **ionic** bonding, **covalent** bonding and **van der Waals** bonding (inert gases).
- Typical examples of ionic bonding are the crystals NaCl and KCl. They are made up of positive and negative ions, which are alternately arranged at the lattice points of two interpenetrating simple cubic lattices.
- The electron configurations for both  $K^+$  and  $Cl^-$  ions in a KCl crystal are equally given as  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$ .

**See Mizutani for other examples!**

# Free electron under the periodic boundary condition

## Brillouin zones (refreshing)

$\vec{R} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$  direct lattice vector of a Bravais lattice

↳ reciprocal lattice is defined by the set of all wave vectors  $\vec{q}$  such that

$$e^{i\vec{q}\cdot\vec{R}} = 1$$

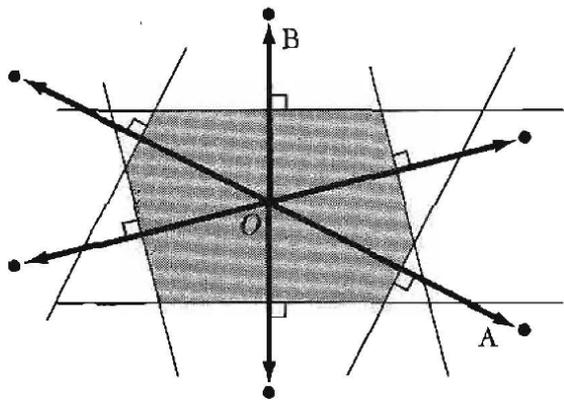
↳  $\vec{q} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3$

where

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \text{and cyclic}$$

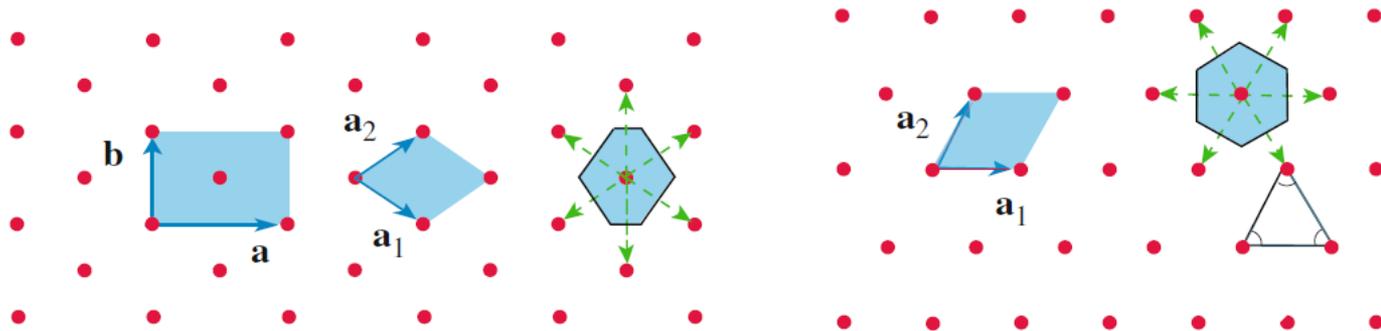
Brillouin zone: region of  $q$ -space that is closer to a given lattice point

wigner-Seitz cell in the reciprocal space



**Figure 10** Construction of the first Brillouin zone for an oblique lattice in two dimensions. We first draw a number of vectors from  $O$  to nearby points in the reciprocal lattice. Next we construct lines perpendicular to these vectors at their midpoints. The smallest enclosed area is the first Brillouin zone.

from Kittel



**Fig. 2.17** First Brillouin zones of the centered rectangular and hexagonal 2D lattices: construction displayed *on the right* for each reciprocal lattice

from Alloul

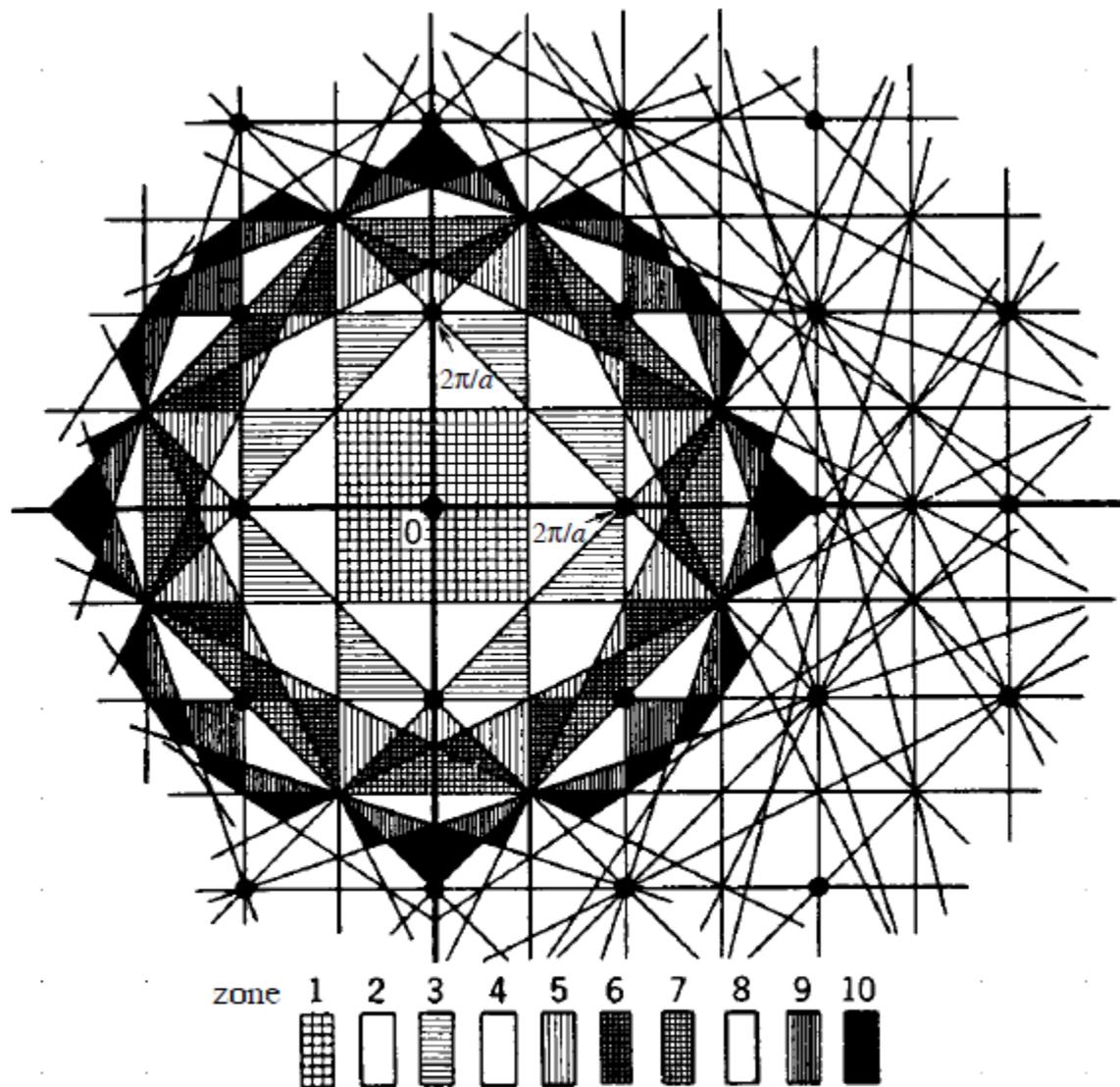
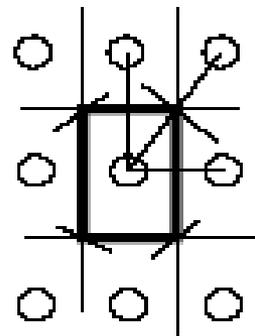


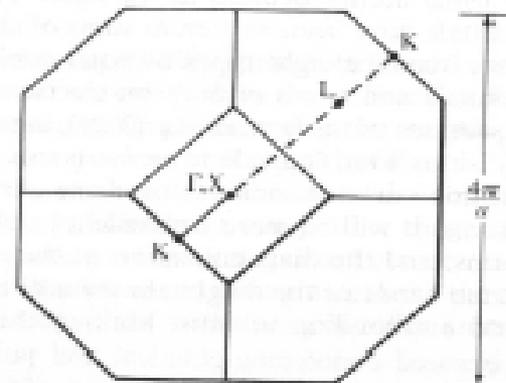
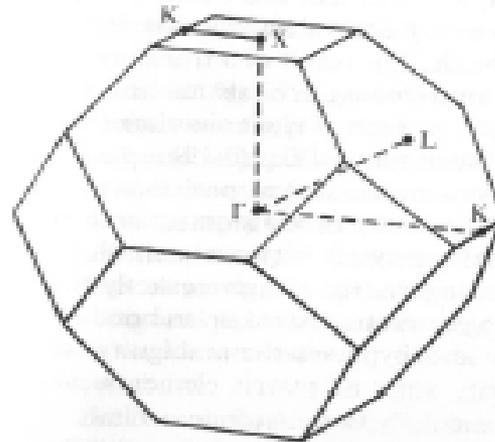
Figure 5.11. Brillouin zones of a two-dimensional square lattice. [L.Brillouin, *Wave Propagation in Periodic Structures*, (Dover Publications, 1953)]

# Brillouin zones

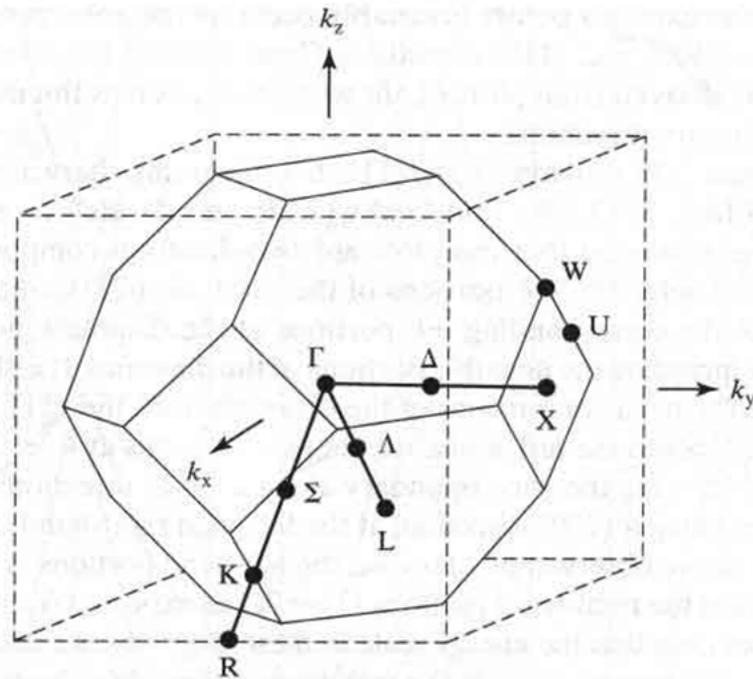


2d rectangular lattice

3d fcc lattice  
has a bcc  
reciprocal  
lattice

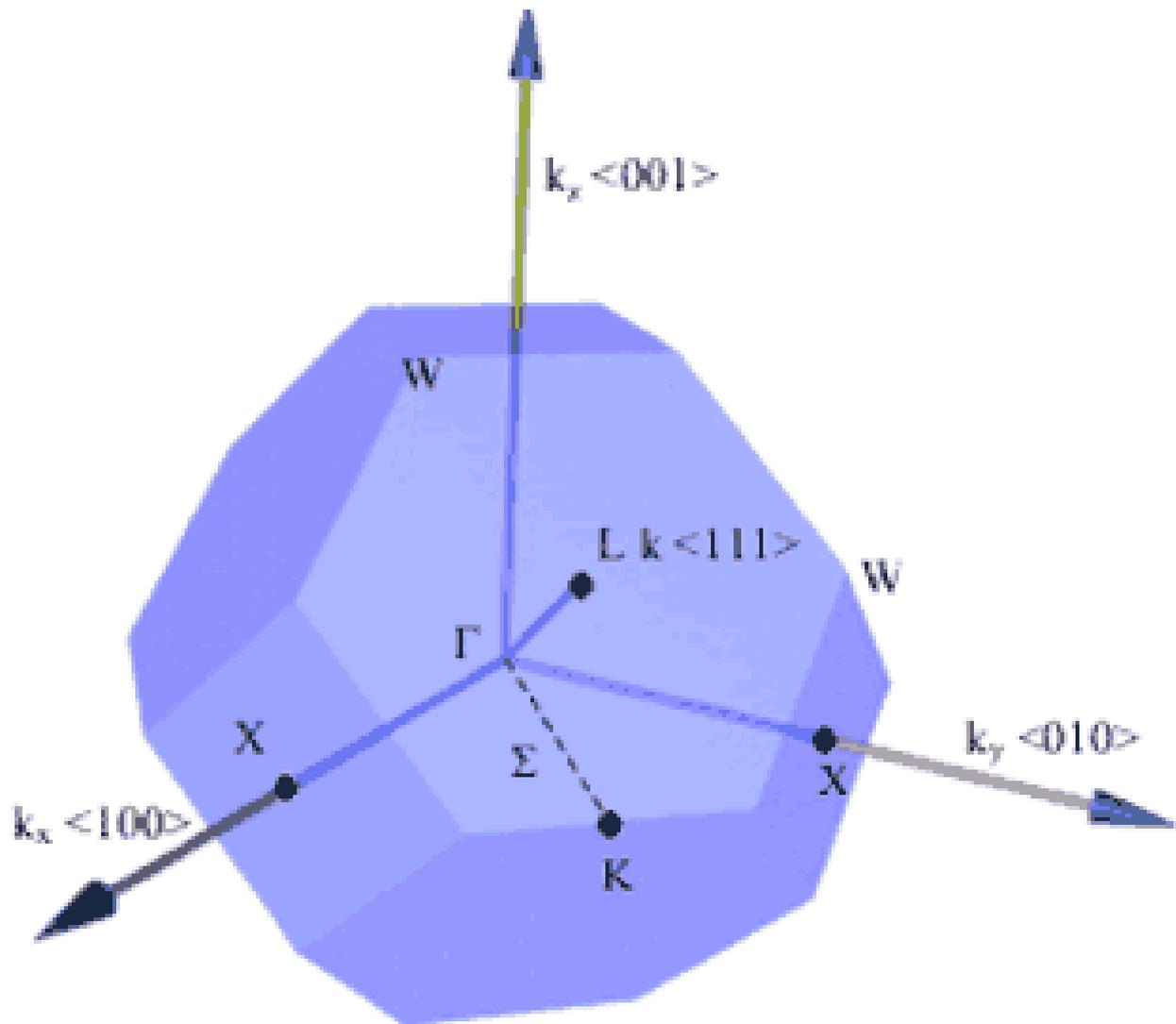


The Brillouin Zone and symmetry points for the zincblende (diamond, or face-centered cubic) lattice. The view at the right is along a  $[110]$  axis; that at the left has been tilted.



**3.12** First Brillouin zone for materials crystallizing in the diamond and silicon structures. (After Blakemore.<sup>[1]</sup> Reprinted with permission.)

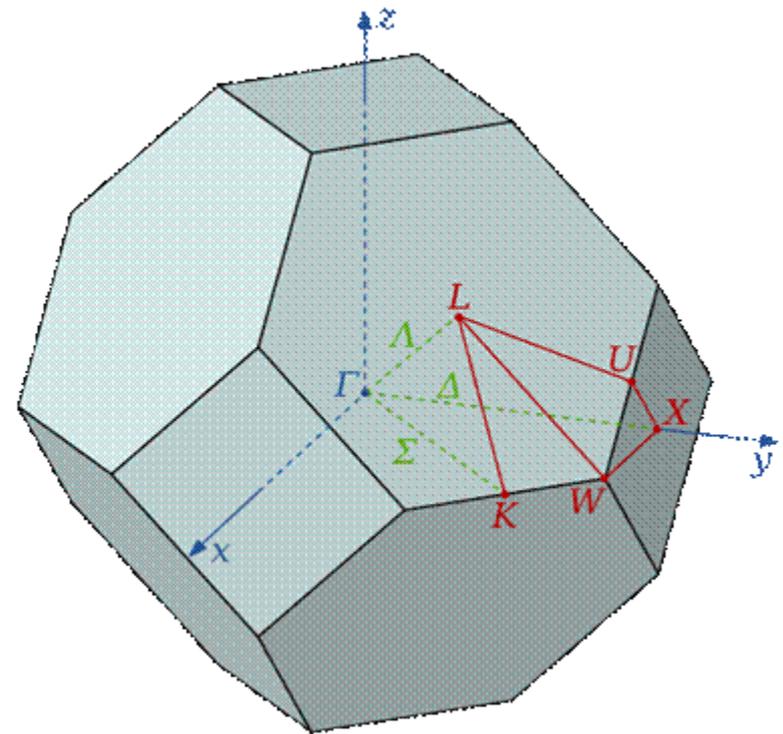
$\Gamma$ ... identifies the zone center ( $k = 0$ )  
 $X$ ... denotes the zone end along a  $\langle 100 \rangle$  direction, and  
 $L$ ... denotes the zone end along a  $\langle 111 \rangle$  direction.



Several points of high symmetry are of special interest – these are called critical points.

Symbol	Description
$\Gamma$	Center of the Brillouin zone
<b>Simple cube</b>	
M	Center of an edge
R	Corner point
X	Center of a face
<b>Face-centered cubic</b>	
K	Middle of an edge joining two hexagonal faces
L	Center of a hexagonal face
U	Middle of an edge joining a hexagonal and a square face
W	Corner point
X	Center of a square face
<b>Body-centered cubic</b>	
H	Corner point joining four edges
N	Center of a face
P	Corner point joining three edges
<b>Hexagonal</b>	
A	Center of a hexagonal face
H	Corner point
K	Middle of an edge joining two rectangular faces
L	Middle of an edge joining a hexagonal and a rectangular face
M	Center of a rectangular face

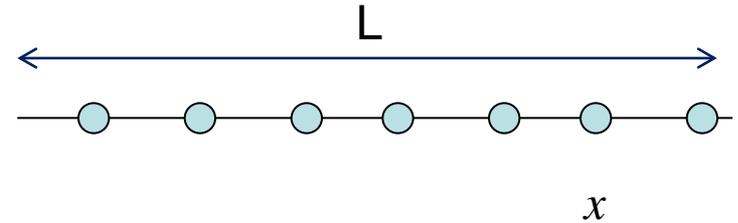
Label	Cartesian Coordinates
$\Gamma$	$(0, 0, 0)$
$\Delta$	$(0, 2\pi x/a, 0)$
$X$	$(0, 2\pi/a, 0)$
$Z$	$(\frac{1}{2}x\pi/a, 2\pi/a, 0)$
$W$	$(\pi/a, 2\pi/a, 0)$
$Q$	$(\pi/a, (2-x)\pi/a, x\pi/a)$
$L$	$(\pi/a, \pi/a, \pi/a)$
$\Lambda$	$(x\pi/a, x\pi/a, x\pi/a)$
$\Sigma$	$(2\pi x/a, 2\pi x/a, 0)$
$K = U$	$(\frac{3}{2}\pi/a, \frac{3}{2}\pi/a, 0)$
$S$	$(2\pi x/a, 2\pi x/a, 0)$
$X'$	$(2\pi/a, 2\pi/a, 0)$



- Points (and lines) inside the Brillouin zone are denoted with *Greek* letters.
- Points on the surface of the Brillouin zone with *Roman* letters.
- The center of the Wigner-Seitz cell is always denoted by a  $\Gamma$

- 1D

$$\psi(x + L) = \psi(x).$$



$$k_x = \frac{2\pi}{L}n_x \quad (n_x = 0, \pm 1, \pm 2, \pm 3, \dots).$$

$$\psi(x, y, z) = \sqrt{\frac{1}{V}} \exp(i\mathbf{k} \cdot \mathbf{r})$$

### 3D

$$\mathbf{k} = \left(\frac{2\pi}{L}\right)(n_x \mathbf{i} + n_y \mathbf{j} + n_z \mathbf{k}),$$

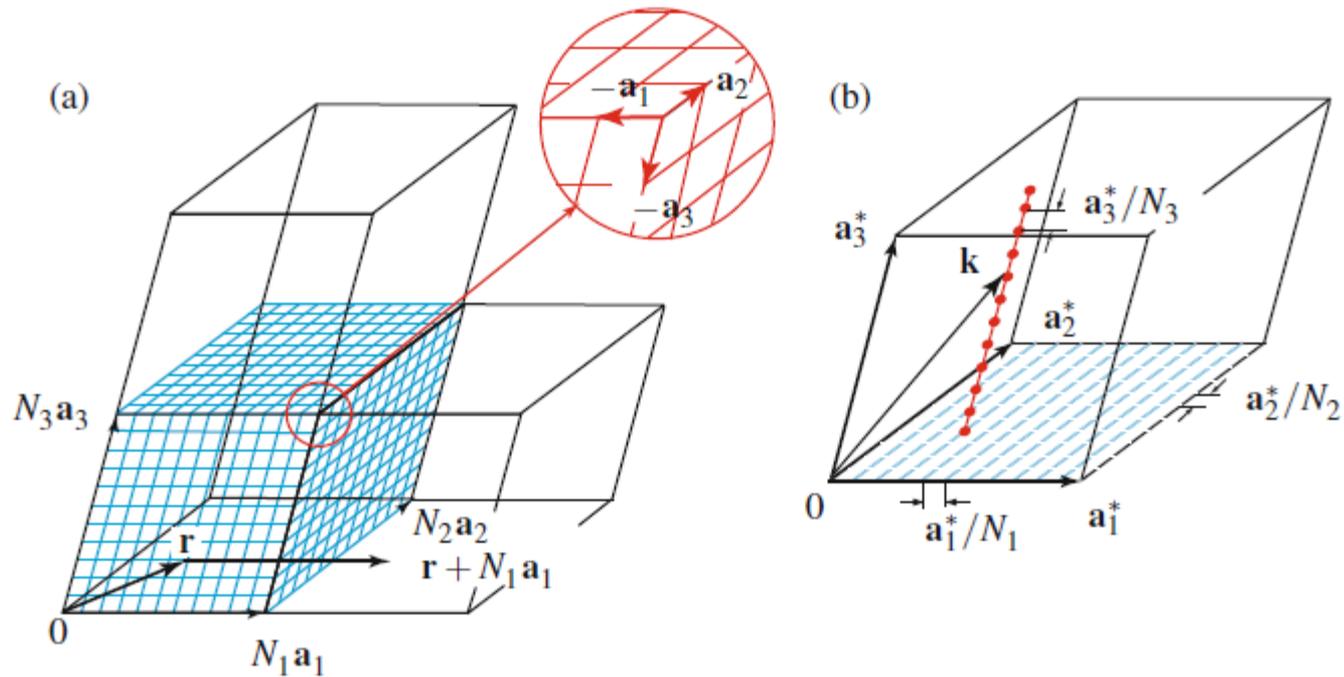
- Free electron in a box

$$\psi(x, y, z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{\pi n_x x}{L}\right) \sin\left(\frac{\pi n_y y}{L}\right) \sin\left(\frac{\pi n_z z}{L}\right).$$

$$k_x = \frac{\pi}{L} n_x \quad (n_x = 1, 2, 3, \dots).$$

$$E = \frac{\int \psi^* \left(\frac{-\hbar^2}{2m}\right) \nabla^2 \psi dV}{\int \psi^* \psi dV} = \left(\frac{\hbar^2}{2m}\right) \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2).$$

from Alloul



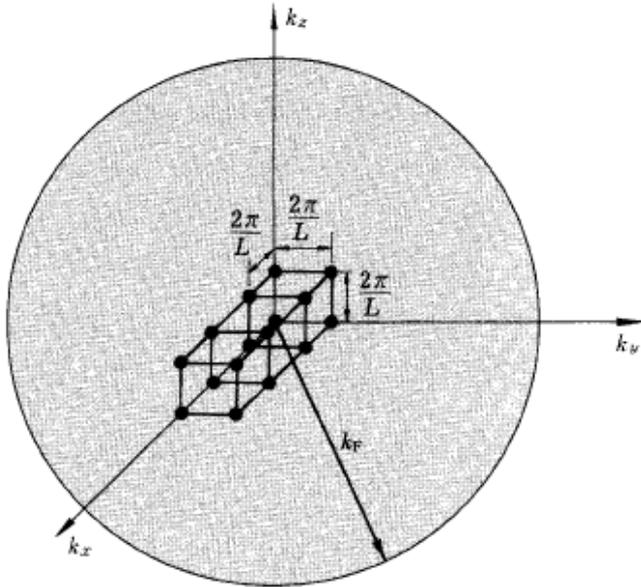
**Fig. 3.1** (a) Periodic boundary conditions applied to a solid containing  $N_1N_2N_3$  unit cells. (b) Quantised values of  $\mathbf{k}$  in the primitive unit cell ( $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$ ) of the reciprocal lattice

# Construction of the Fermi sphere

Pauli exclusion principle

Fermi level  $\rightarrow$  the last occupied level = chemical potential

Mizutani



$$n = 0, \pm 1, \pm 2, \dots$$

$$k_x = \left(\frac{2\pi}{L}\right)n_x$$

$$k_y = \left(\frac{2\pi}{L}\right)n_y$$

$$k_z = \left(\frac{2\pi}{L}\right)n_z$$

$$\frac{N_0}{2} = \frac{4\pi}{3} k_F^3 \left(\frac{2\pi}{L}\right)^3$$

$$k_F = \left[ 3\pi^2 \left(\frac{N_0}{V}\right) \right]^{1/3},$$

Figure 2.7. Construction of the Fermi sphere. The reciprocal space is quantized in units of  $2\pi/L$  in the  $k_x$ ,  $k_y$ , and  $k_z$ -directions and is made up of cubes with edge length  $2\pi/L$  as indicated in the figure. Electrons of up and down spins occupy the corner of each cube or integer set  $(n_x, n_y, n_z)$  in accordance with the Pauli exclusion principle while making  $n_x^2 + n_y^2 + n_z^2$  as low as possible. The sphere with radius  $k_F$  represents the Fermi sphere.

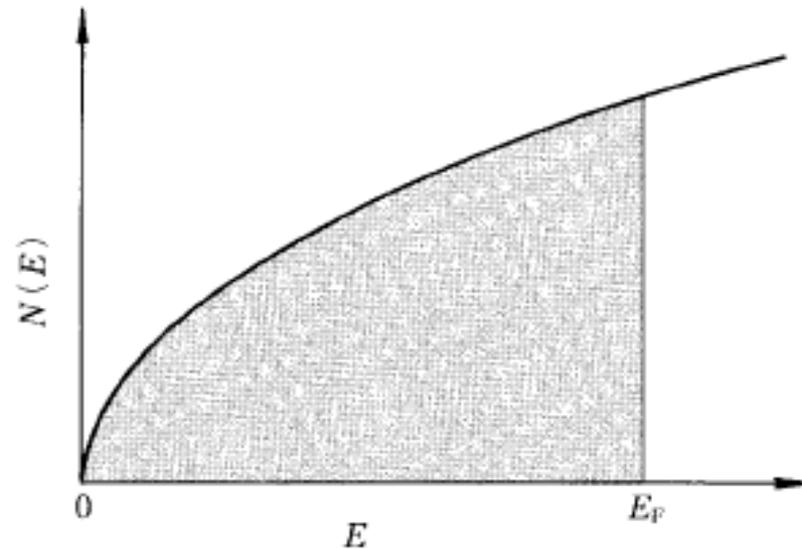
The value of the Fermi level at absolute zero ( $-273.15 \text{ }^\circ\text{C}$ ) is called the **Fermi energy** and is a constant for each solid.

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{\hbar^2}{2m}\right) \left[ 3\pi^2 \left(\frac{N_0}{V}\right) \right]^{2/3},$$

density of states  $dn = N(E)dE$

$$N = \int_0^{E_F} N(E)dE.$$

$$N(E) = \frac{dN}{dE} = \left(\frac{V}{2\pi^2}\right)\left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E},$$



The parabolic density of states for free electrons. The states are filled with electrons up to the Fermi energy  $E_F$ . The filled area is shaded.

- a mole of sodium metal weighs 22.98 g with
- its density 0.97 g/cm<sup>3</sup>. Since it is a monovalent metal,  $N_0$  (# electrons) is equal to the Avogadro number  $N_A$ .
- $N_A=6.02310^{23}$  and  $V=23.69310^{21}$  nm<sup>3</sup> results in a Fermi radius  $k_F=9.1$  nm<sup>-1</sup> for sodium metal.

$$\hbar = 1.05 \times 10^{-27} \text{ erg s and } m = 9.1 \times 10^{-28} \text{ g}$$

$$E_F = 36.46 \times 10^{-2} \left( \frac{N}{V} \right)^{2/3} \text{ eV,}$$

N= number of valence electrons per atom (e/a)

bcc structure,  $a= 0.422$  nm, the volume per atom  $\Omega = (0.422)^3/2 = 0.0376$  nm<sup>3</sup>

Na  $\rightarrow$  monovalent: 1 electron/atom-  $\rightarrow E_F= 3.2$  eV

Fermi temperature:  $E_F= K_B T_F$  if  $E_F= 5\text{eV}$   $\rightarrow T_F= 60000$  K

Table 2.2. *Fermi energies in representative metals*

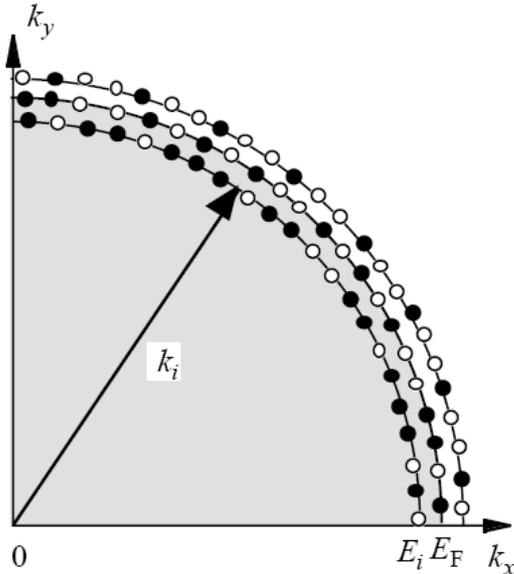
element	$ela$	$\Omega(\text{\AA})^3$	$E_F^{\text{free}}$ (eV)	$E_F^{\text{band}}$ (eV)	$E_F^{\text{free}}/E_F^{\text{band}}$
Cu	1.0	11.81	7.03	9.09	0.77
Ag	1.0	17.06	5.50	7.5	0.73
Au	1.0	16.96	5.52	9.4	0.58
Zn	2.0	15.24	9.42	10.8	0.87
Cd	2.0	21.58	7.59	8.85	0.86
Be	2.0	8.13	14.31	11.9	1.20
Mg	2.0	23.23	7.09	7.1	1.0
Al	3.0	16.60	11.65	11.3	1.0
K	1.0	71.32	2.12	2.24	0.94
Na	1.0	37.71	3.24	3.30	0.98
$\beta\text{-Cu}_{50}\text{Zn}_{50}$	1.50	12.76	8.75	9.93	0.88

*Source:*

T. B. Massalski and U. Mizutani, *Prog. Mat. Sci.* **22** (1978) 151

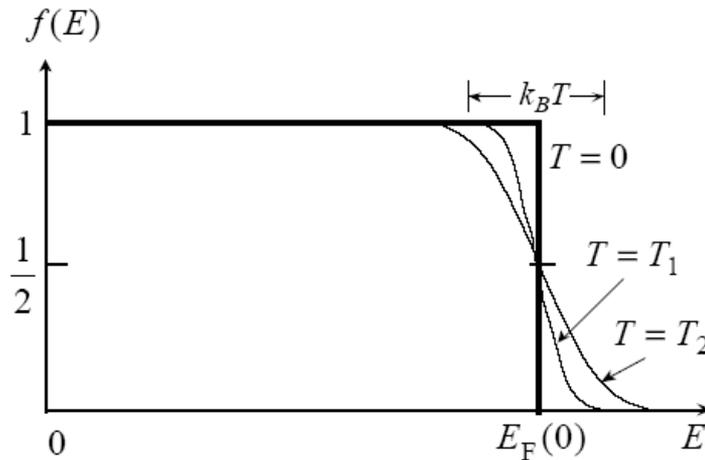
# Electrons in a metal at finite temperatures

Mizutani



$$f(E, T) = \frac{N}{Z} = \frac{1}{1 + \exp\left(\frac{E - E_F(T)}{k_B T}\right)}$$

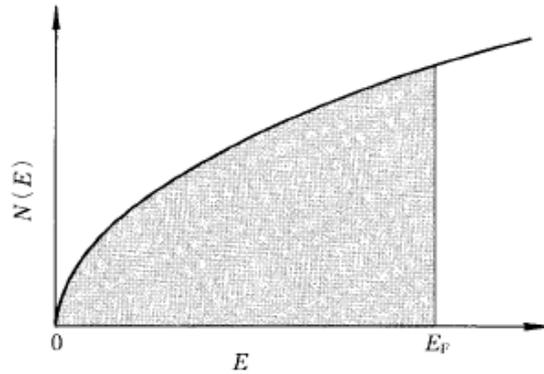
Figure 3.1 A quarter of the cross-section of the Fermi sphere at a finite temperature



$$f(E_F) = \frac{1}{2}$$

Figure 3.2. Fermi-Dirac distribution function. The smeared region  $0 \leq f(E) \leq 1$  extends over  $k_B T$  about the Fermi energy  $E_F$  at finite temperatures. It increases with increasing temperature ( $T_2 > T_1$ ). A change in the Fermi energy is ignored here.

# Mizutani



The parabolic density of states for free electrons. The states are filled with electrons up to the Fermi energy  $E_F$ . The filled area is shaded.

$$E_F(T) = E_F(0) \left[ 1 - \left( \frac{\pi^2}{12} \right) \left( \frac{k_B T}{E_F(0)} \right)^2 \right]$$

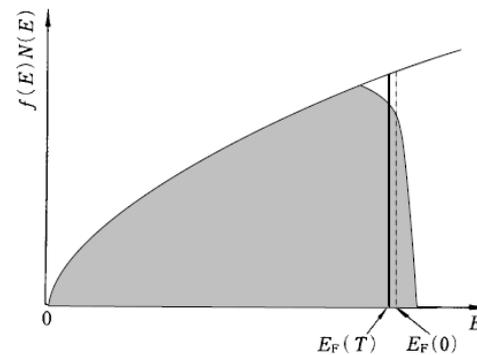
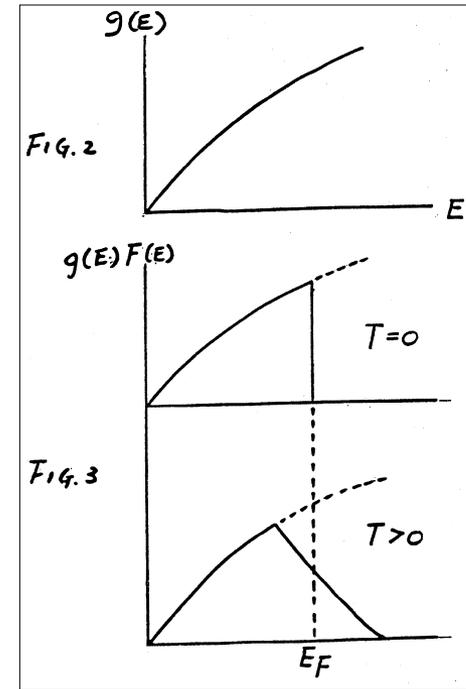


Figure 3.3. Free-electron-like density of states curve  $N(E)$  multiplied by the Fermi-Dirac distribution function  $f(E)$ . The shaded area represents the density of states occupied by electrons at a finite temperature. The Fermi energy at a finite temperature changes by an amount given by equation (3.19) relative to that at 0 K.

# 1D free electrons

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

$$L = na$$

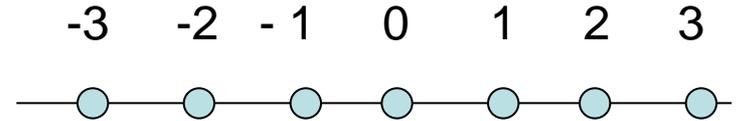
$$E(k) = E(k + G_i)$$

$$G_l = \frac{2\pi}{a} \ell$$

$$\psi(x) \propto e^{ika}$$

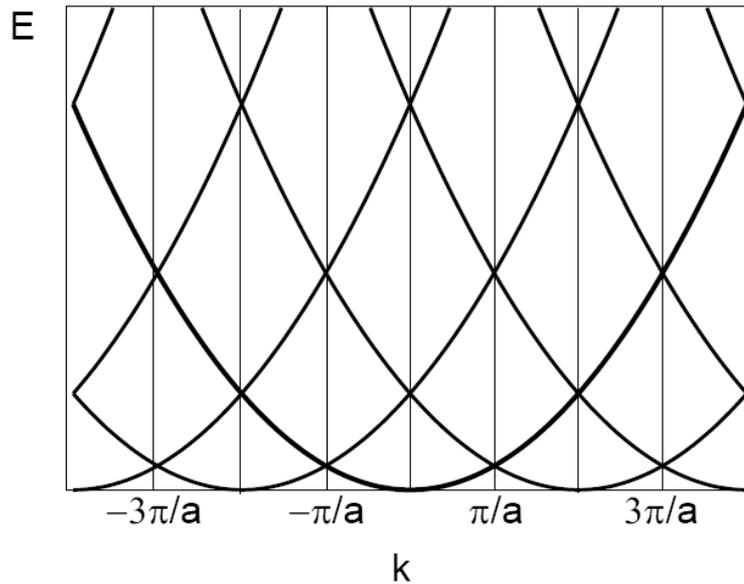
$$n = \dots \pm 2, \pm 1, 0$$

$$\ell = \dots \pm 2, \pm 1, 0$$

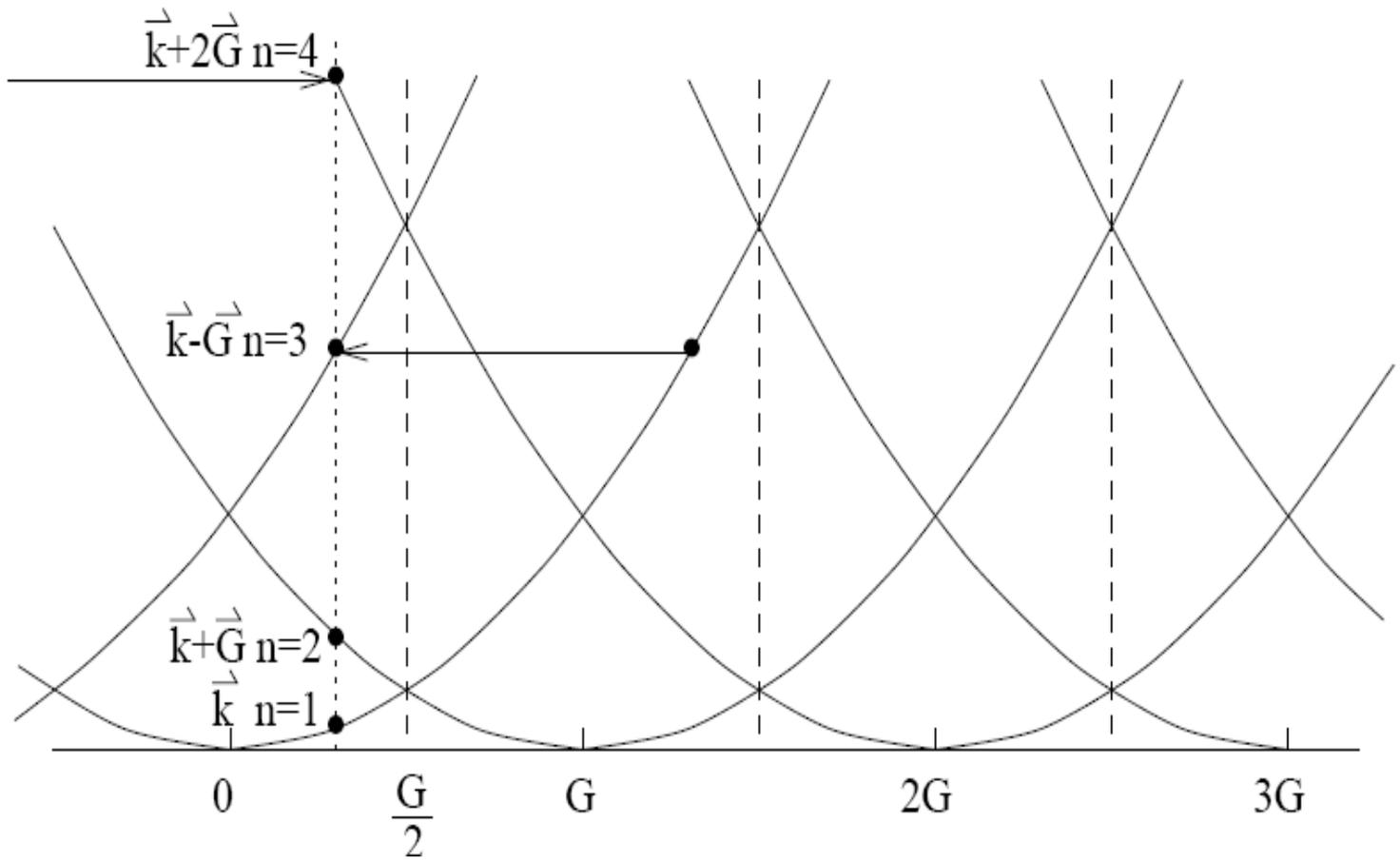


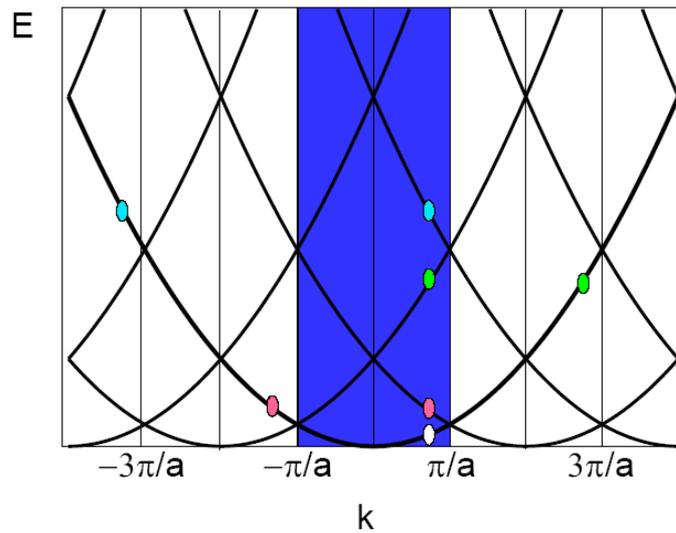
$$E(k) = \frac{\hbar^2}{2m} \left( k + \frac{2\pi}{a} \ell \right)^2$$

empty lattice  
model

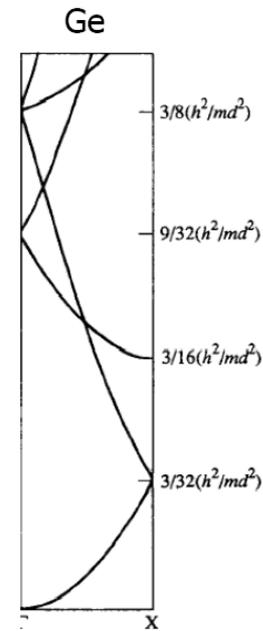
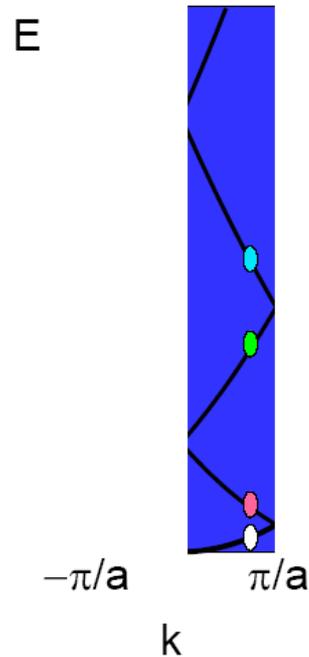
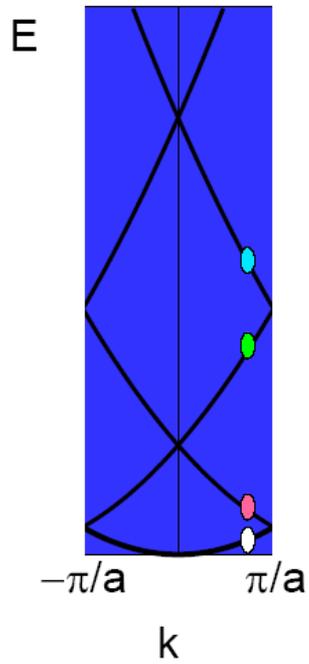


$\ell :$                       1                      0                      -1

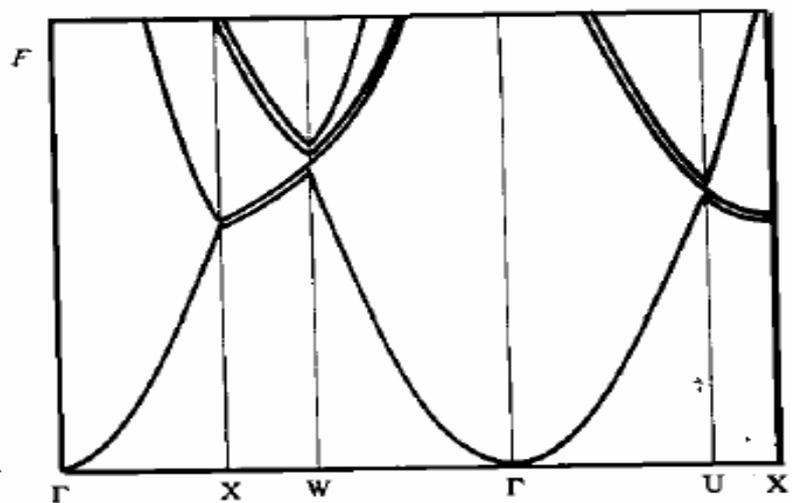




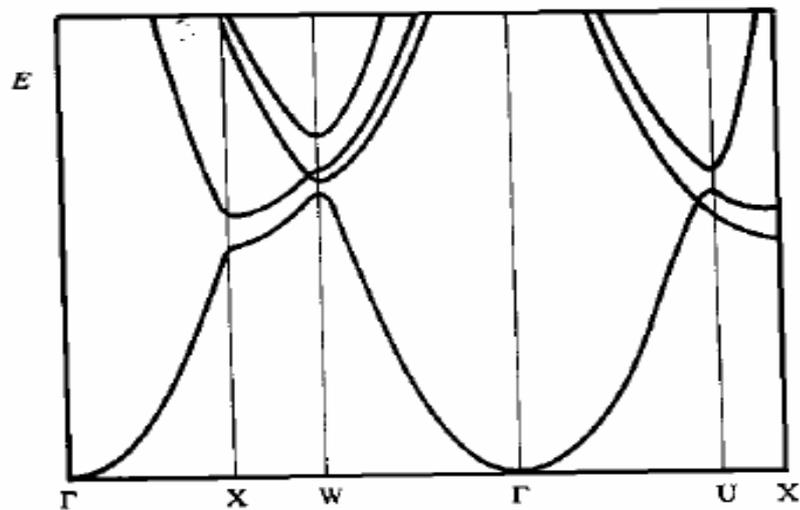
Expect all solutions to be represented within the Brillouin Zone (reduced zone)



Band structures from this approximation are able to give a qualitative picture of the band structure of real simple metals, for example Al. In the picture below (after Myers) the empty lattice approximation is compared to a detailed band structure calculation. Bands drawn adjacent to one another in the upper figure are in reality degenerate. The main differences in the lower figure are the occurrence of band gaps in the real structure and that degenerate bands are split up.



Empty lattice - fcc

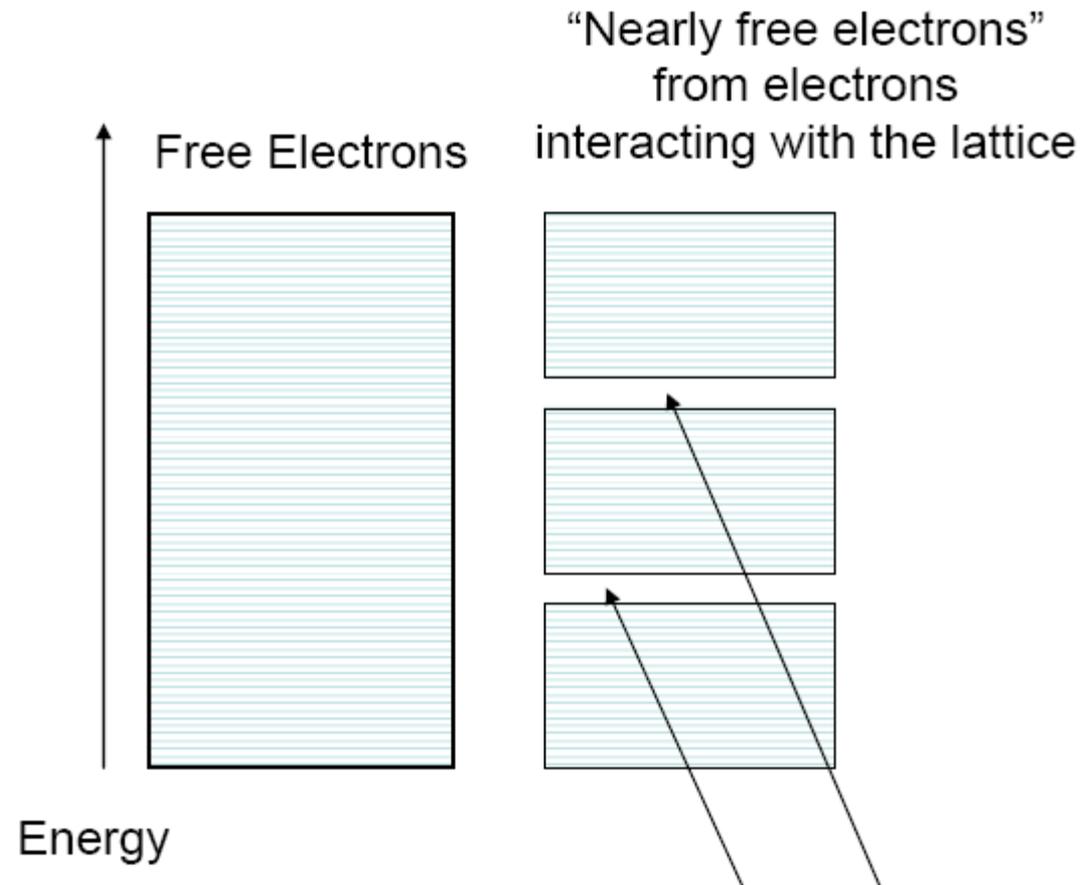


Calculation - Al

# Nearly-free Electron Model

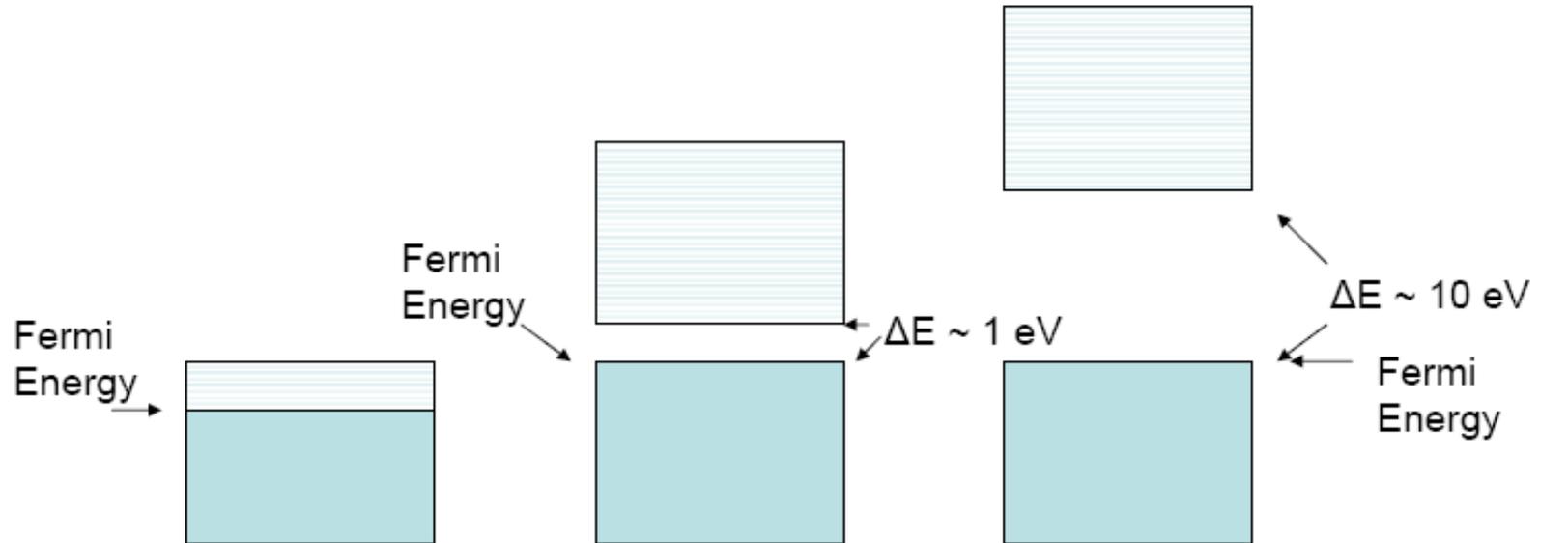
(NEF model)

The interactions of the electrons with the lattice result in energy gaps in the possible electron levels



Energy gaps where electrons cannot have these energy levels

# Conductors, Insulators, Semiconductors



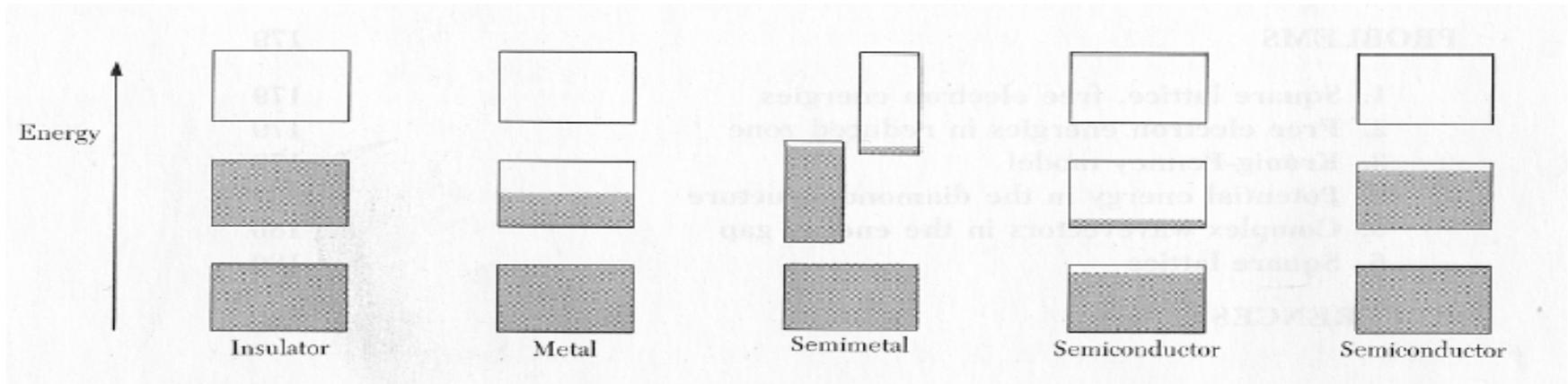
Conductor:  
Fermi energy lies within a band of accessible states

Semiconductor:  
Fermi energy lies in the gap, gap is relatively small in size ( $\sim 1 \text{ eV}$ ) so that some  $e^-$ 's can be excited

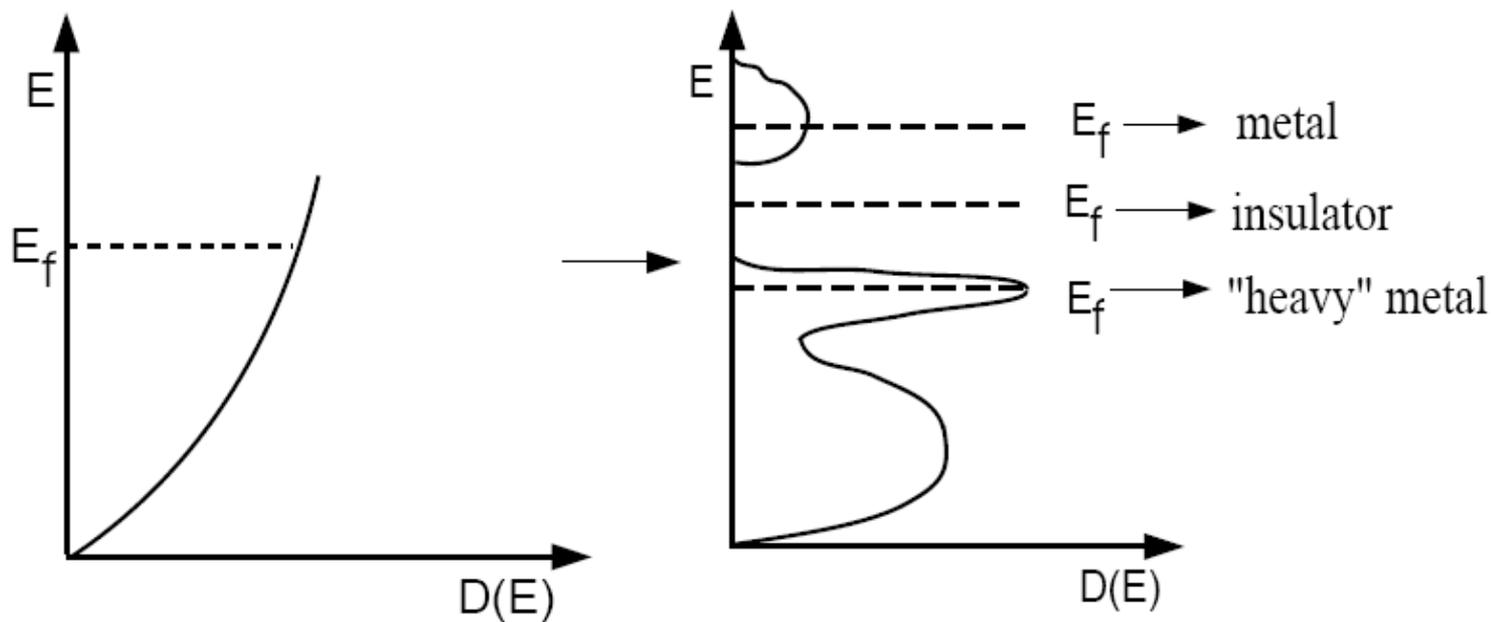
Insulator: Fermi energy lies in the gap, gap is relatively large in size ( $\sim 10 \text{ eV}$  – electrons cannot be excited to higher states)

# More complicated materials

- Even more complicated energy “band” structures exist:



$T \neq 0 K$



*The additional effects of the lattice potential can have a profound effect on the electronic density of states (RIGHT) compared to the free-electron result (LEFT).*

## Bloch's Theorem

*'When I started to think about it, I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal....*

*By straight Fourier analysis I found to my delight that the wave differed from the plane wave of free electrons only by a periodic modulation'*

*F. BLOCH*

For wavefunctions that are eigenenergy states in a periodic potential...

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\tilde{\mathbf{u}}_{\mathbf{k}}(\mathbf{r})$$

or

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

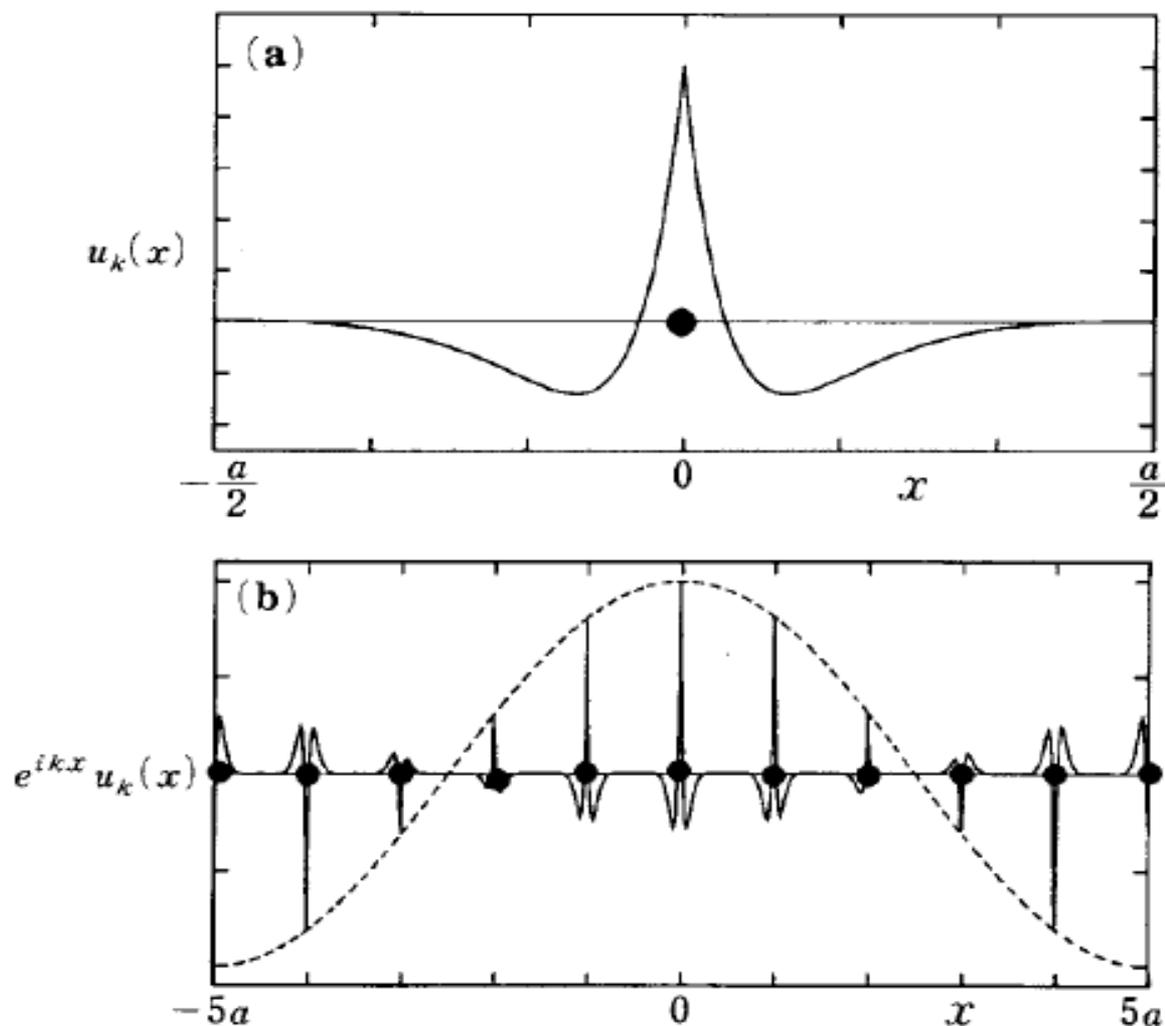
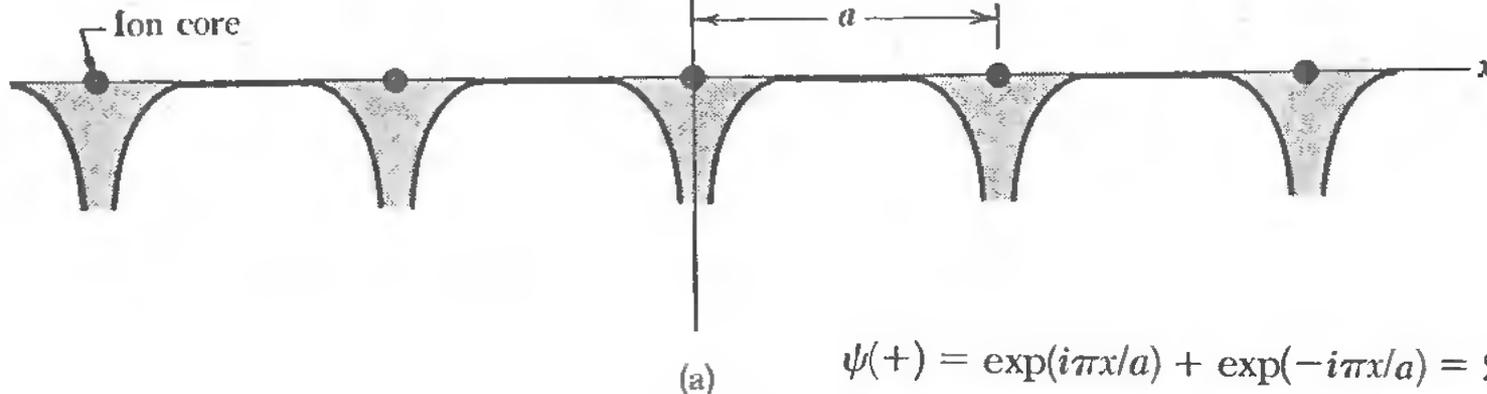


Figure 5.2. (a) The periodic function  $u_k(x)$  centered at the origin of the unit cell in the range  $-a/2 < x \leq a/2$ . (b) The Bloch wave constructed by using the function shown in (a). Only the real part is shown. The function  $u_k(x)$  is placed at every origin of the unit cell and modulated by the plane wave  $\exp(ikx)$ . A solid circle represents the ion at the center of each unit cell.

NFE approximation

$U$ , potential energy

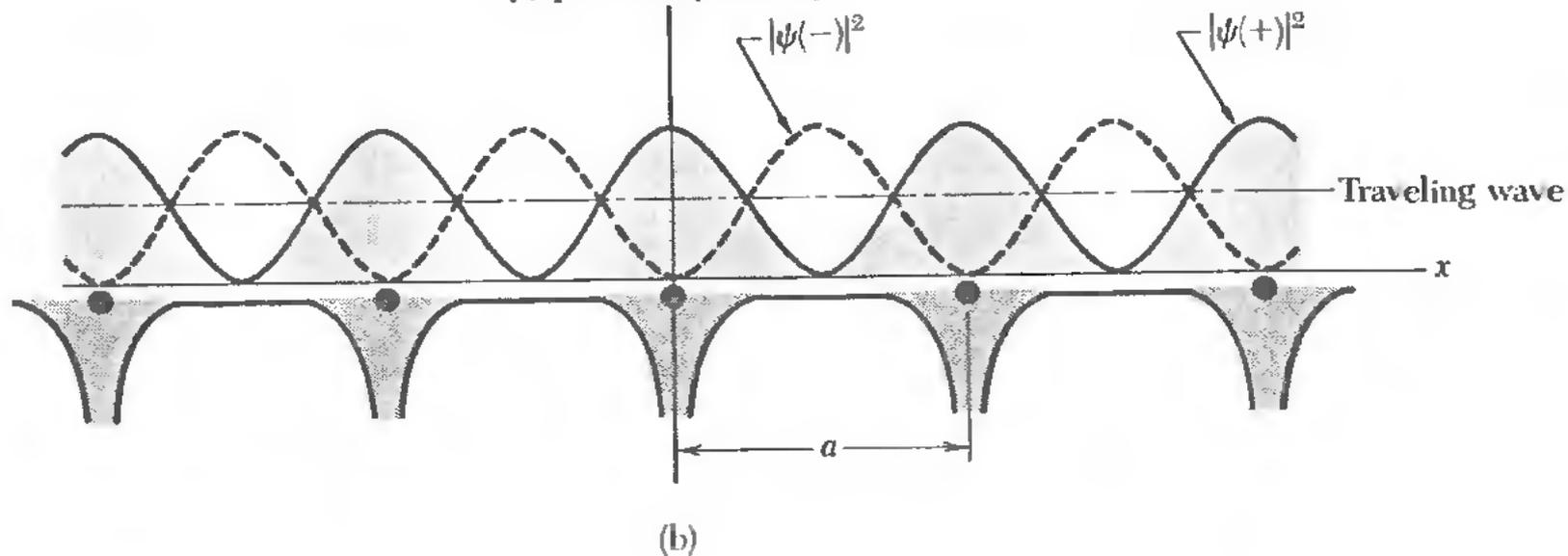
Kittel



$$\psi(+)=\exp(i\pi x/a)+\exp(-i\pi x/a)=2\cos(\pi x/a);$$

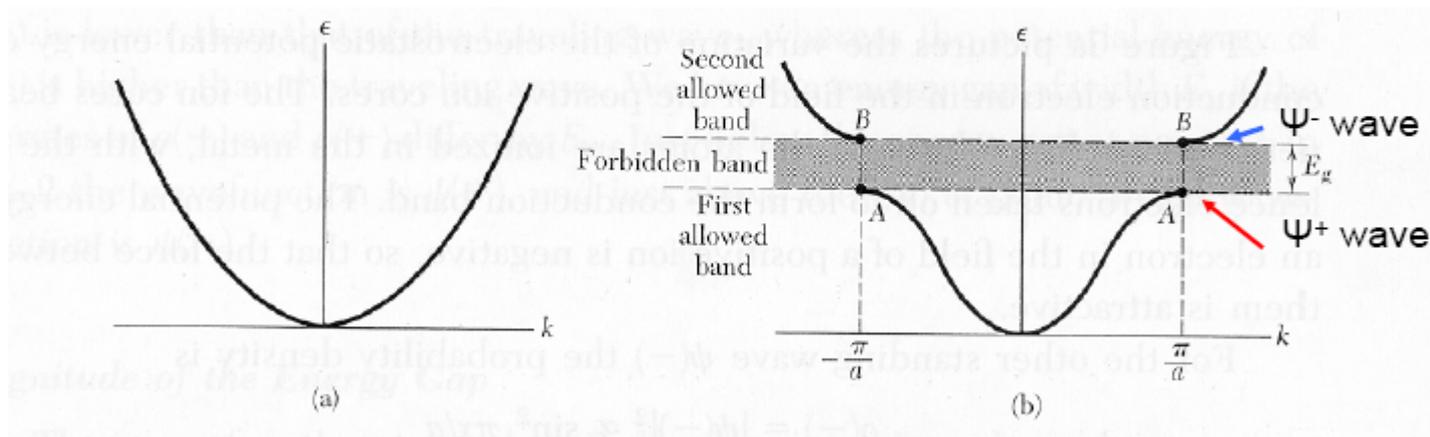
$$\psi(-)=\exp(i\pi x/a)-\exp(-i\pi x/a)=2i\sin(\pi x/a).$$

$\rho$ , probability density



# The Energy Gap

- So, there are 2 solutions for the energies at this K-value
- This is what gives rise to the energy gap

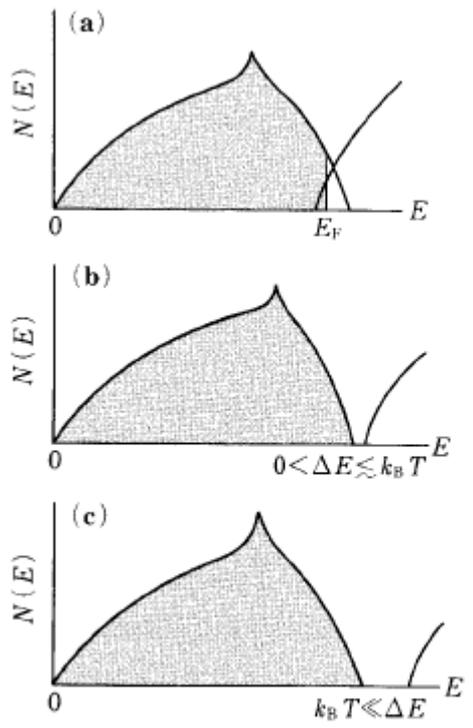
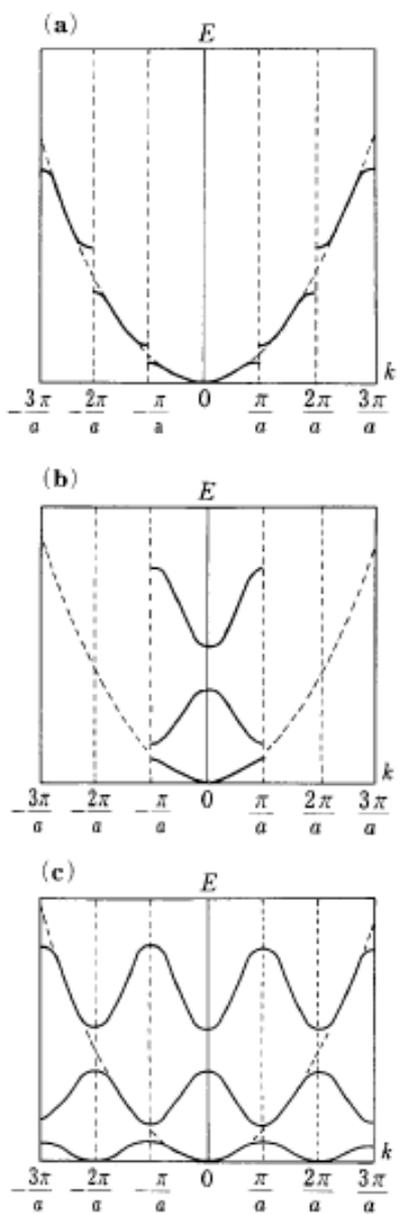


$$E_g = \int U(x) [|\psi^+|^2 - |\psi^-|^2] dx$$

(difference between the expectation values of these 2 energy levels)

(perturbation theory)

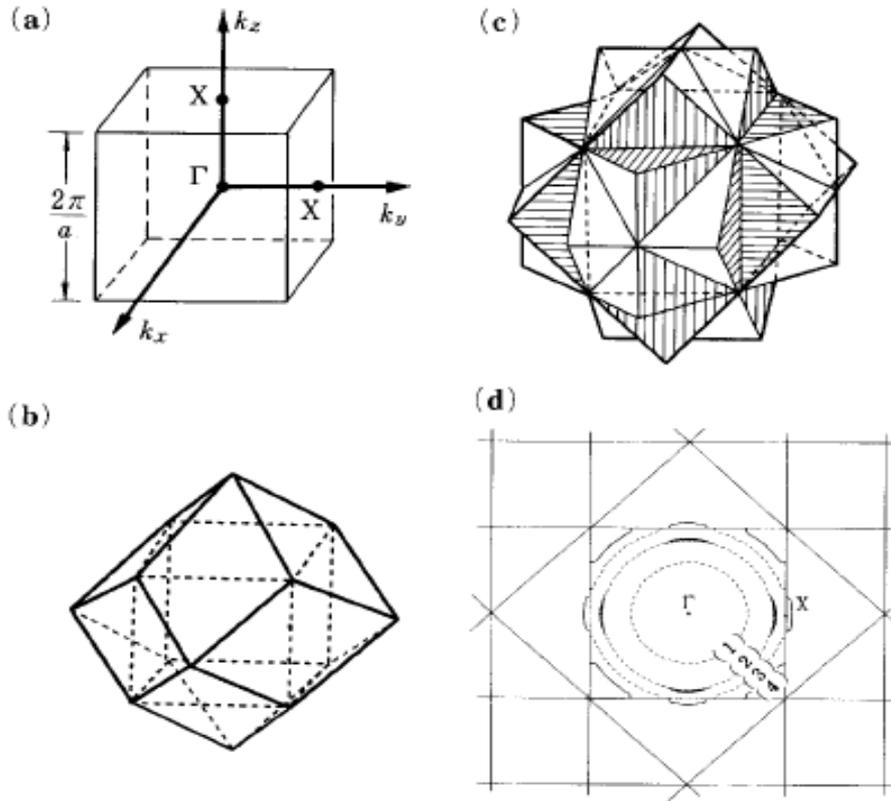
# Mizutani



Schematic density of states curves. (a) Metals, (b) semiconductors, and (c) insulators.

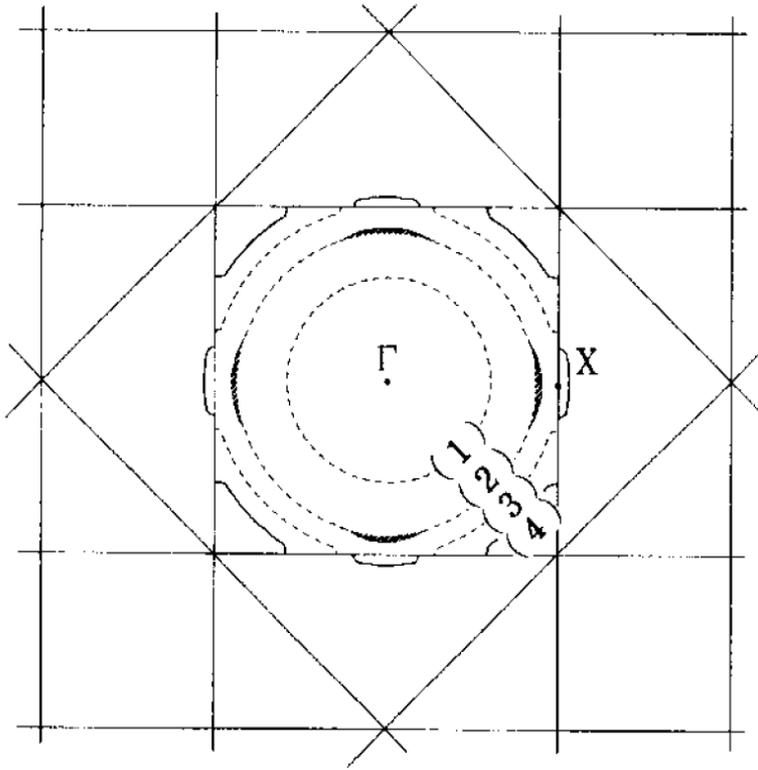
$E$ - $k$  relations in (a) the extended zone scheme, (b) the reduced zone scheme, and (c) the periodic (or repeated) zone scheme.

# Fermi surface-Brillouin zone interaction

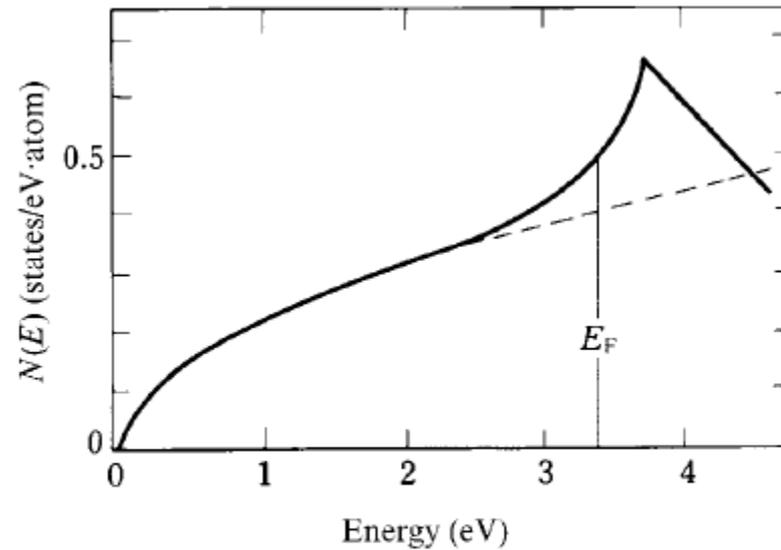


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Figure 5.18. Brillouin zones of the simple cubic lattice with lattice constant  $a$ . (a) The first zone, (b) the second zone (the first zone is seen as dashed lines), (c) the third zone, and (d) the cross-section of the Fermi surface and the Brillouin zones obtained by cutting through the  $\Gamma$  point parallel to the  $k_x k_y$ -plane. In (d), the Fermi surface contours with various electron concentrations  $el/a$  are shown by dashed curves: (1) spherical surface with  $el/a \approx 0.5$ , (2) distortion is seen along  $\Gamma X$  directions (distorted area is shown by hatches), (3) the Fermi surface partly touches the first zone, and (4) a part of the Fermi surface appears in the second zone (the Fermi surface with  $el/a = 2.0$  is shown by a solid curve).



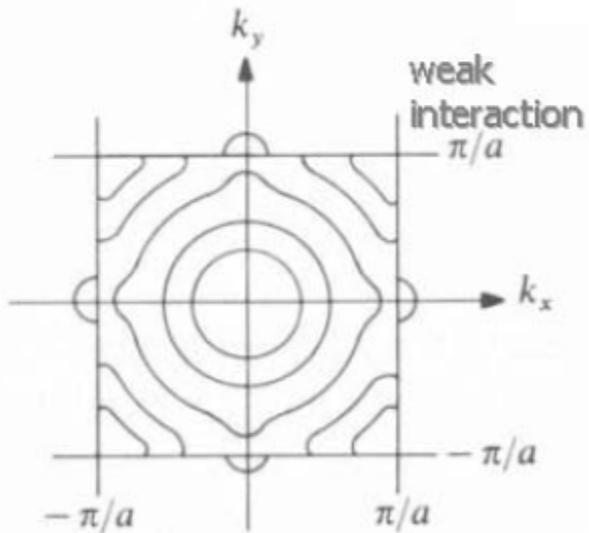
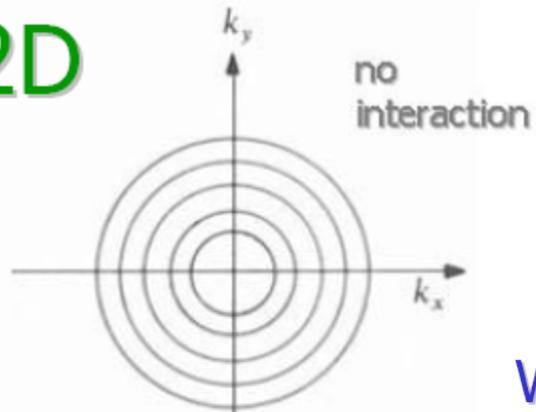
The Fermi surface begins to be distorted from a sphere before making contacts with the Brillouin zone planes.



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Figure 6.4. Density of states curve of bcc Li metal. A cusp is caused by the interaction with the  $\{110\}$  zone planes of the first Brillouin zone. [F. S. Ham, *Phys. Rev.* **128** (1962) 2524]

2D



When  $k$  near to BZ boundary:  
→ E contours become distorted

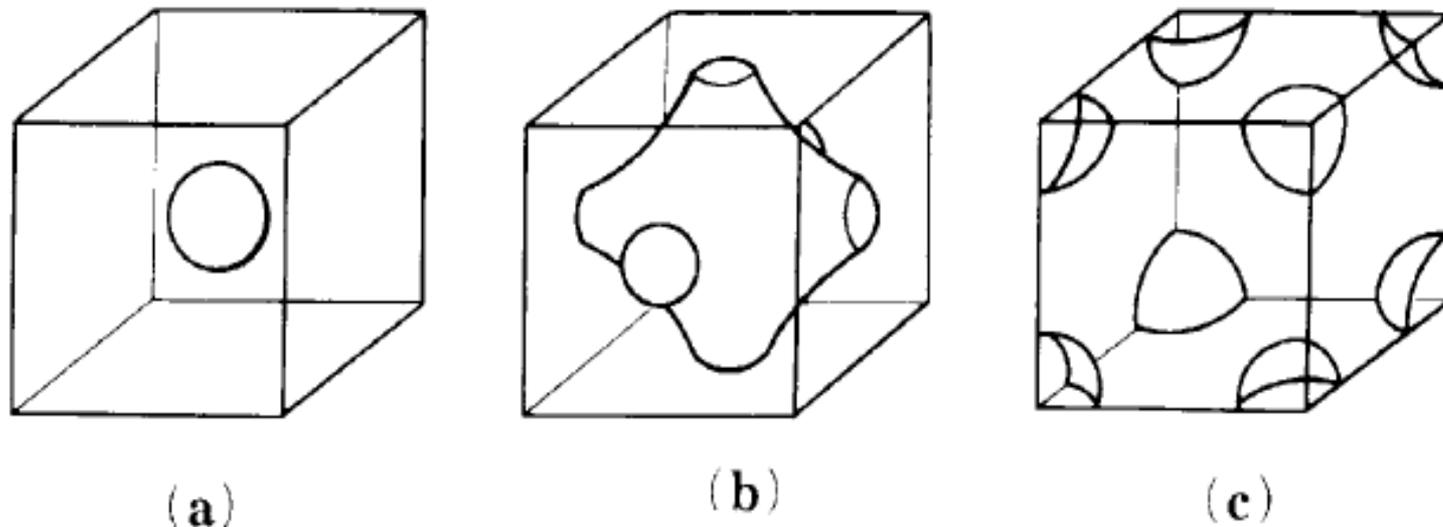


Figure 8.2. The equi-energy surface in the first Brillouin zone of the simple cubic lattice calculated in the tight-binding method: (a) spherical surface near the bottom of the band, (b) the band is half-filled and the Fermi surface makes partial contact with the face of the Brillouin zone, and (c) the Fermi surface when the first zone is almost filled. [From ref. 2.]

# Approaches to Calculating Electronic Bandstructure

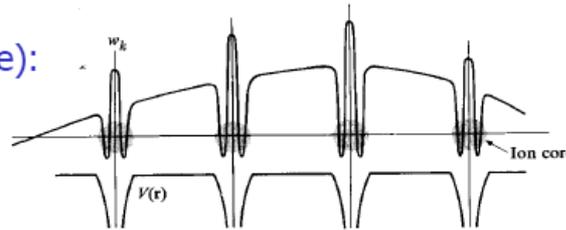
## Nearly Free Electron Approximation:

- Superposition of a few plane waves

$$\psi(r) = \sum_{\mathbf{R}} c_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}$$

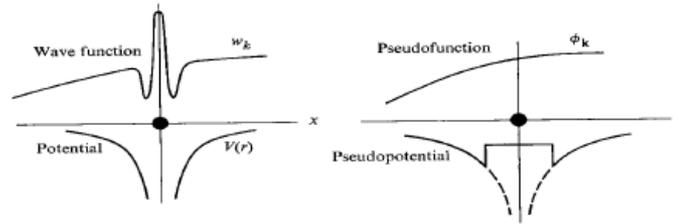
## Cellular Methods (Augmented Plane Wave):

- Plane wave between outside  $r_s$
- Atomic orbital inside  $r_s$  (core)



## Pseudopotential Approximation:

- Superposition of plane waves coupled by pseudopotential



## k.p:

- Superposition of bandedge ( $k=0$ ) wavefunctions

## Tight-binding Approximation (LCAO):

- Superposition of atomic orbitals

$$\psi_i(r) = \sum_{\alpha} \sum_{\mathbf{R}_n} c_{i,\alpha[\mathbf{R}_n]} \phi_{\alpha}(r - \mathbf{R}_n)$$

see Mizutani for details

One-electron approximation  
 Local density functional method  
 Band theories in a perfect crystal  
 Tight-binding method  
 Orthogonalized plane wave method  
 Pseudopotential method  
 Augmented plane wave method  
 Korringa-Kohn-Rostoker method  
 LMTO

# Effective mass

## Semiclassical Equations of Motion

$$\langle \mathbf{v}_n(\mathbf{k}) \rangle = \frac{\langle \mathbf{p} \rangle}{m} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E_n(\mathbf{k})$$

$$\mathbf{F}_{\text{ext}} = \hbar \frac{d\mathbf{k}}{dt}$$

$$E = \frac{\hbar^2 k^2}{2m}$$
$$\frac{dE}{dk} = \frac{\hbar^2 k}{m} \Rightarrow \frac{\hbar \langle p \rangle}{m} = \nabla_{\mathbf{k}} E$$

Lets try to put these equations together...

$$a(t) = \frac{dv}{dt} = \frac{1}{\hbar} \frac{\partial}{\partial t} \frac{\partial E_N(k)}{\partial k} = \frac{1}{\hbar} \frac{\partial^2 E_N(k)}{\partial k^2} \frac{dk}{dt}$$
$$= \left[ \frac{1}{\hbar^2} \frac{\partial^2 E_N(k)}{\partial k^2} \right] F_{\text{ext}}$$

$$F = m^* \cdot a$$

Looks like Newton's Law if we define the mass as follows...

$$m^*(k) = \hbar^2 \left( \frac{\partial^2 E_N(k)}{\partial k^2} \right)^{-1}$$

dynamical effective mass



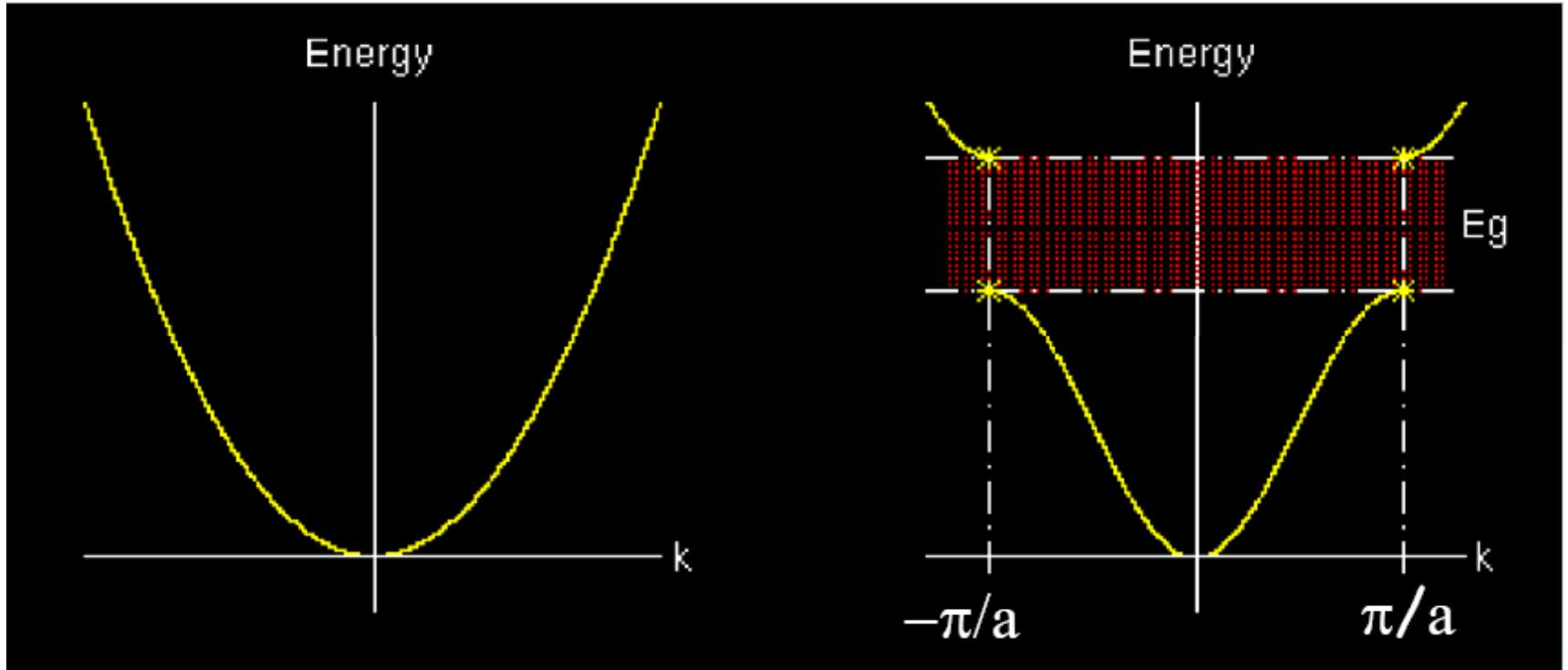
mass changes with k...so it changes with time according to k

Extension to 3-D requires some care,

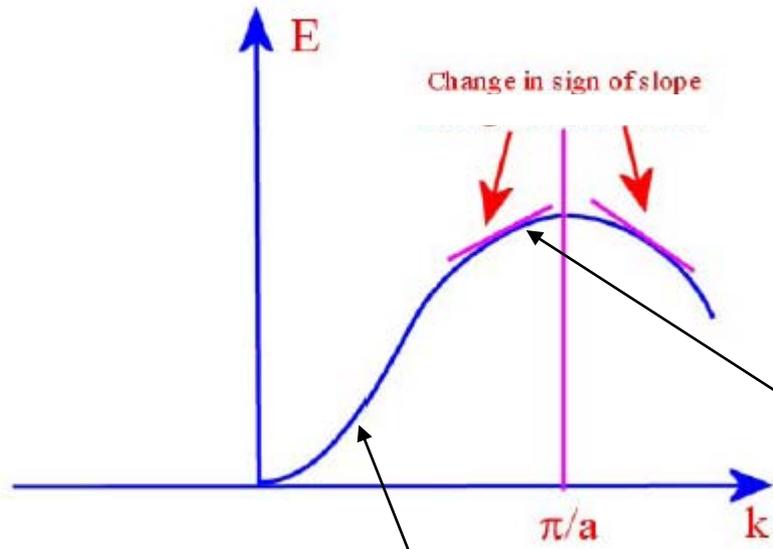
F and a don't necessarily point in the same direction

$$\mathbf{a} = \overline{\overline{\mathbf{M}}}^{-1} \mathbf{F}_{\text{ext}} \quad \text{where} \quad \overline{\overline{\mathbf{M}}}_{i;j}^{-1} = \frac{1}{\hbar^2} \frac{\partial^2 E_N}{\partial k_i \partial k_j}$$

$$\begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix} = \frac{d}{dt} \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} = \begin{pmatrix} \frac{1}{m_{xx}} & \frac{1}{m_{xy}} & \frac{1}{m_{xz}} \\ \frac{1}{m_{yx}} & \frac{1}{m_{yy}} & \frac{1}{m_{yz}} \\ \frac{1}{m_{zx}} & \frac{1}{m_{zy}} & \frac{1}{m_{zz}} \end{pmatrix} \begin{pmatrix} F_x \\ F_y \\ F_z \end{pmatrix}$$



[http://people.seas.harvard.edu/~jones/ap216/lectures/ls\\_2/ls2\\_u7/sse\\_tut\\_1/solid1.html](http://people.seas.harvard.edu/~jones/ap216/lectures/ls_2/ls2_u7/sse_tut_1/solid1.html)

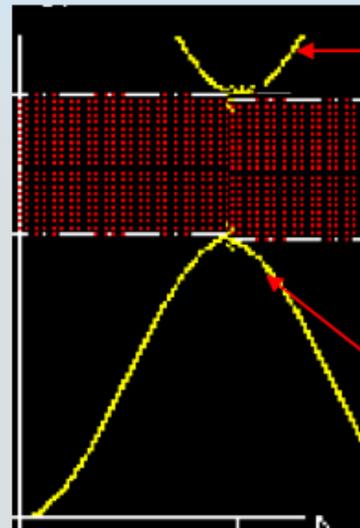
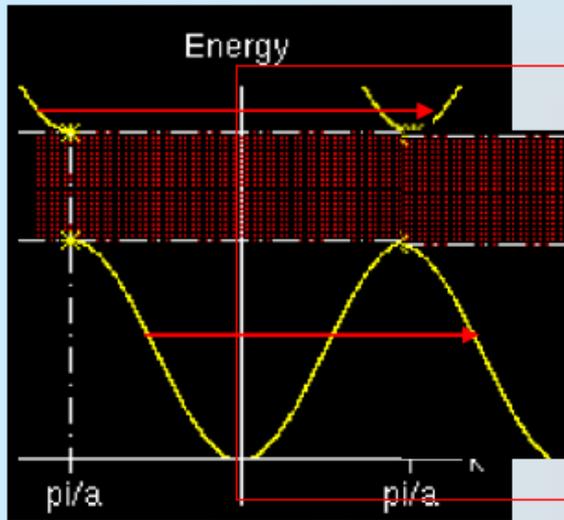


Change in sign of slope

$\pi/a$   $k$

$$\frac{\partial^2 E}{\partial k^2} < 0 \rightarrow m^* < 0$$

$$\frac{\partial^2 E}{\partial k^2} > 0 \rightarrow m^* > 0$$

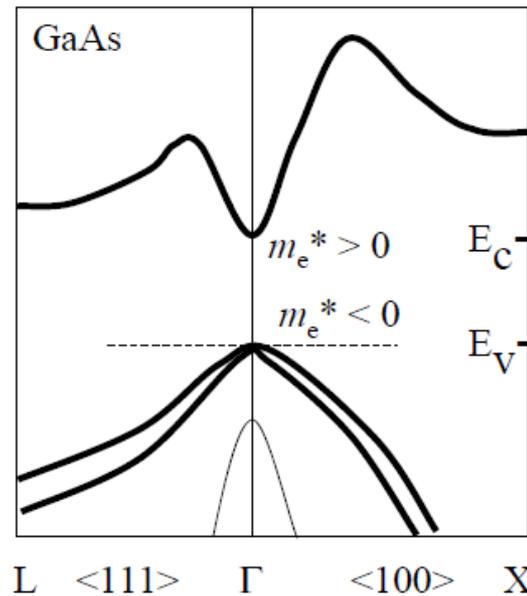


Quadratic spectrum

$$p^2/2m^*$$

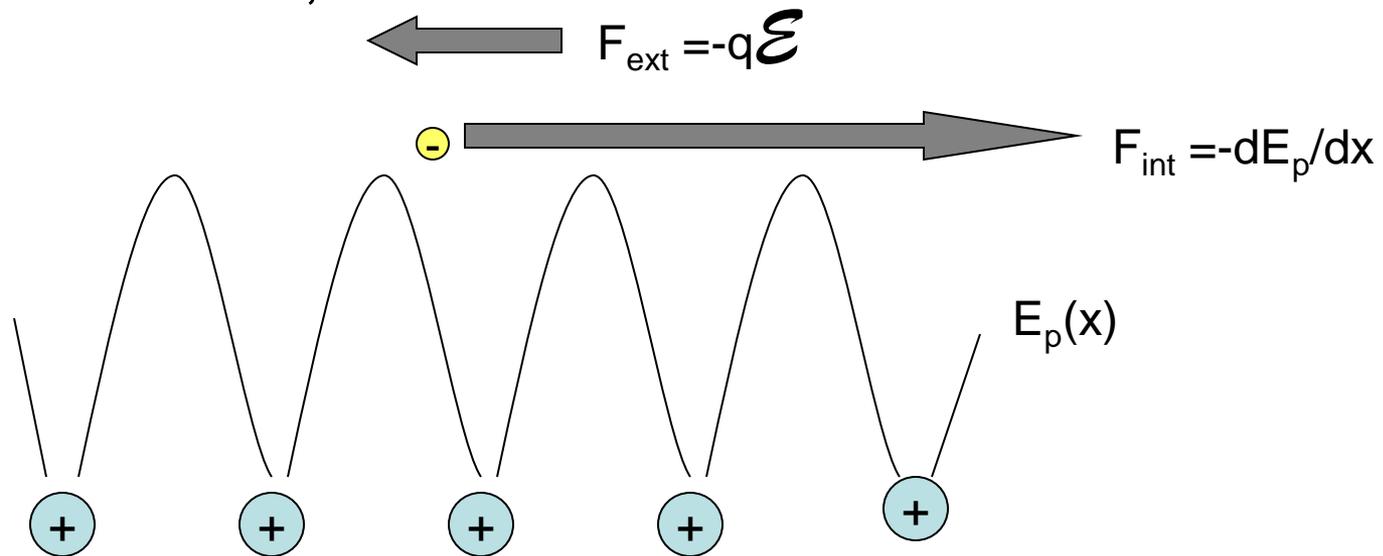
Effective mass

Negative effective mass - holes



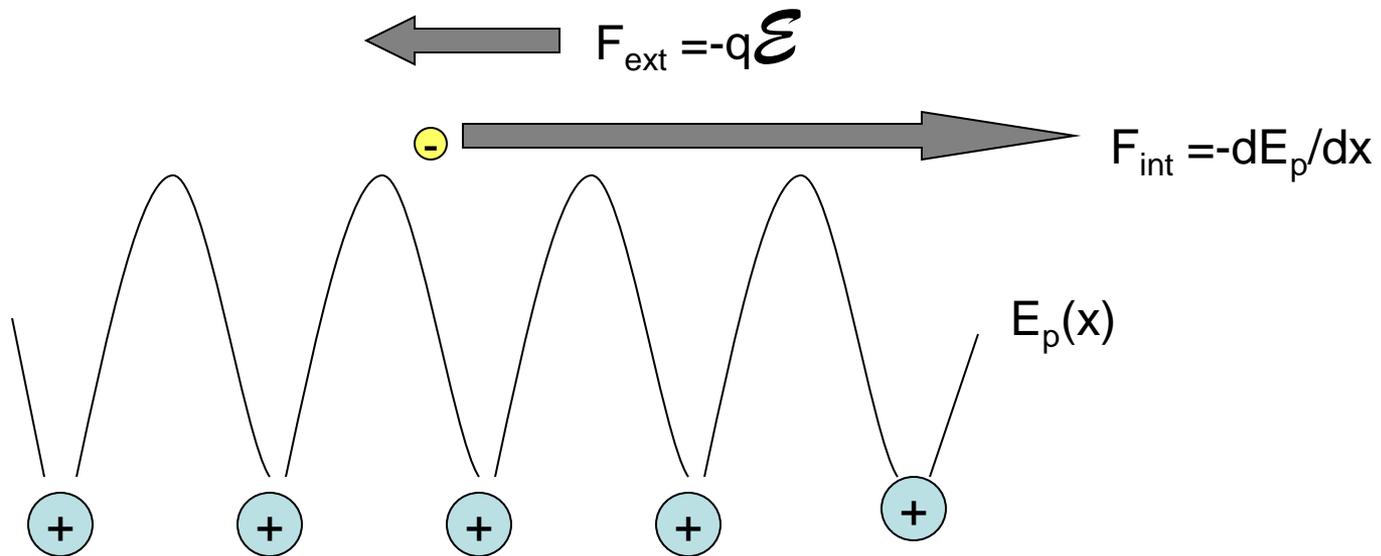
# Interpretation

- The electron is subject to internal forces from the lattice (ions and core electrons) AND external forces such as electric fields
- In a crystal lattice, the net force may be opposite the external force, however:



# Interpretation

- electron acceleration is not equal to  $F_{\text{ext}}/m_e$ , but rather...
- $a = (F_{\text{ext}} + F_{\text{int}})/m_e = F_{\text{ext}}/m^*$
- The dispersion relation  $E(K)$  compensates for the internal forces due to the crystal and allows us to use *classical* concepts for the electron as long as its mass is taken as  $m^*$



# Examples of Energy Bands in Solids

What we can find out:

1. Is the material a metal, a semiconductor (direct or indirect gap), semimetal or insulator?
2. To which atomic (molecular) levels do the bands on the band diagram correspond? Which bands are important in determining the electronic structure? What are the bandwidths, bandgaps?

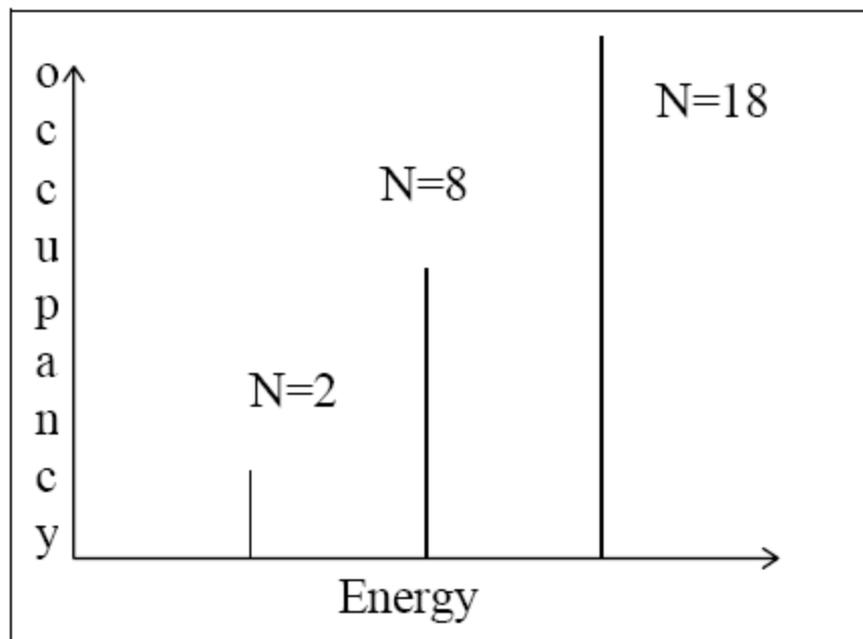
What information does  $E(\vec{k})$  diagram provide concerning the following questions:

- (a) Where are the carriers in the Brillouin zone?
- (b) Are the carriers electrons or holes?
- (c) Are there many or few carriers?
- (d) How many carrier pockets of each type are there in the Brillouin zone?
- (e) What is the shape of the Fermi surface?
- (f) Are the carrier velocities high or low?
- (g) Are the carrier mobilities for each carrier pocket high or low?

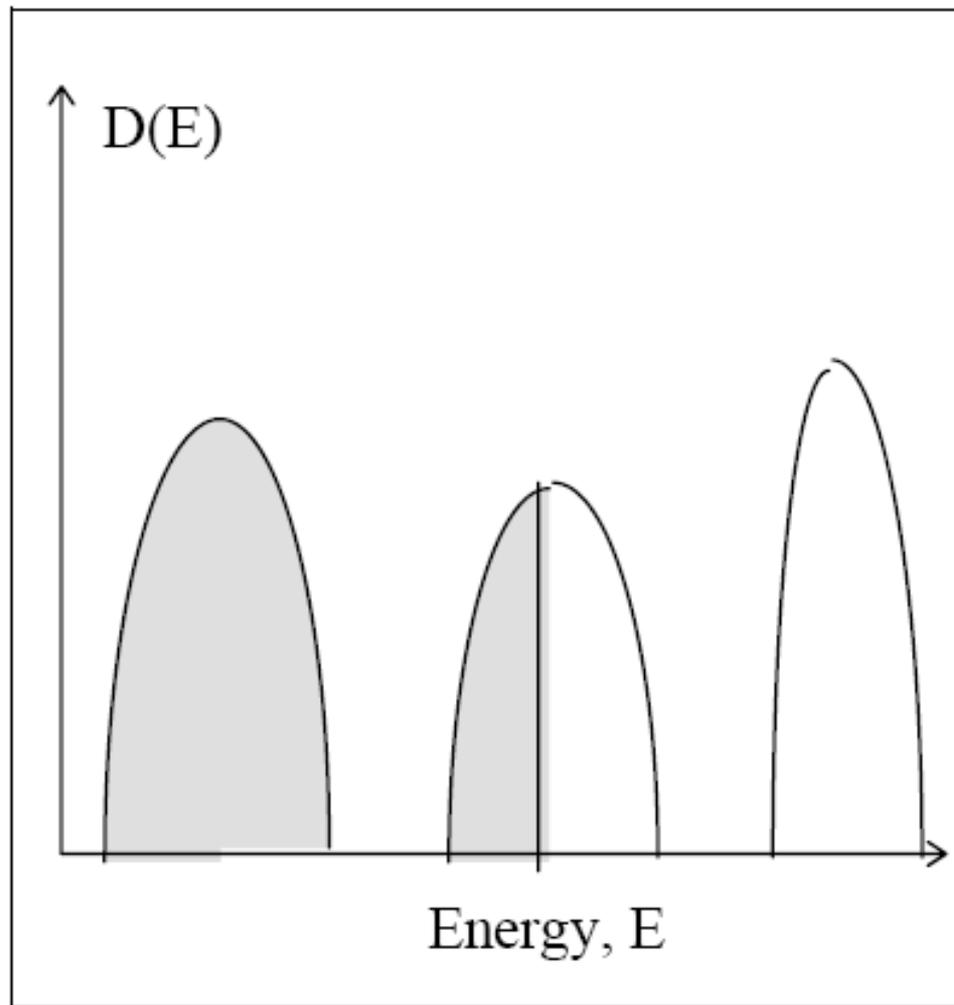
A. R. Mackintosh

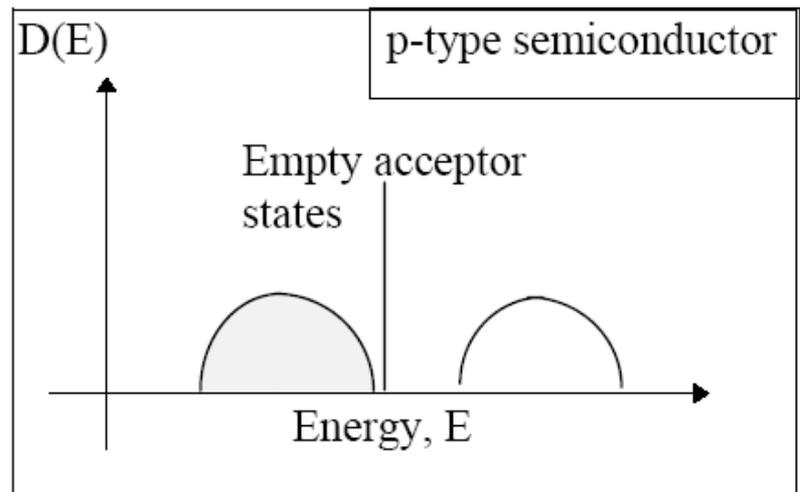
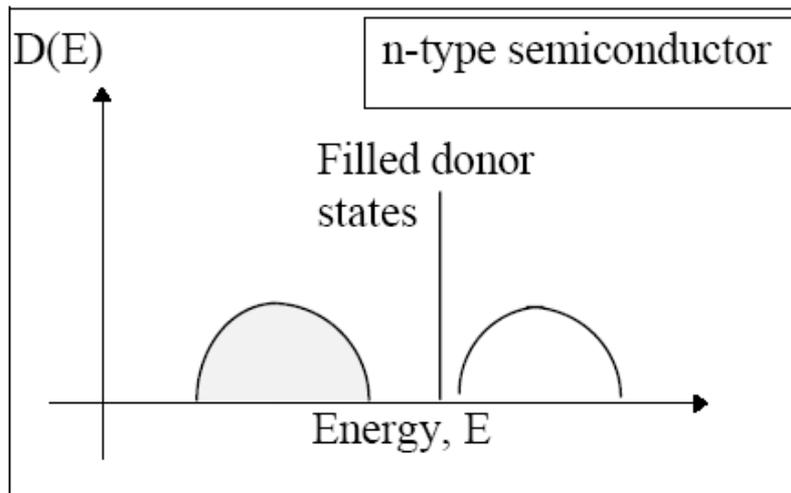
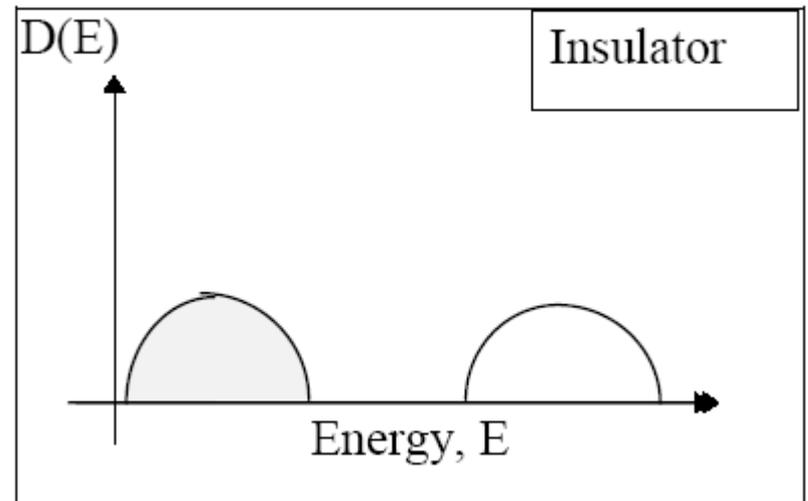
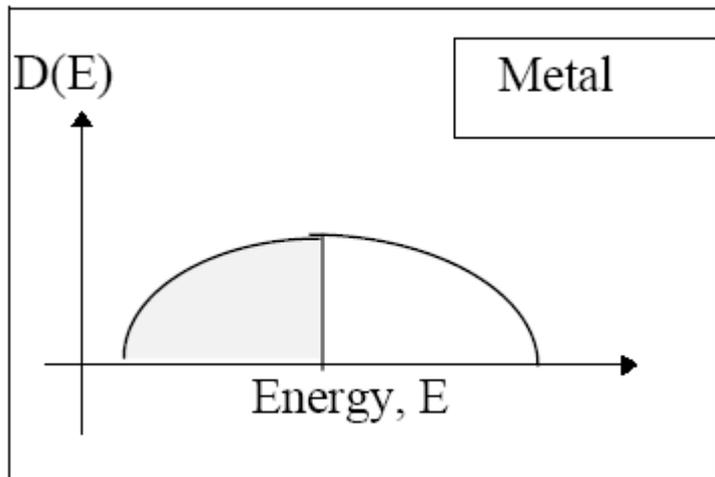
*Few people would define a metal as “a solid with a Fermi surface.” This may nevertheless be the most meaningful definition of a metal one can give today; it represents a profound advance in the understanding of why metals behave as they do. The concept of the Fermi surface, as developed by quantum physics, provides a precise explanation of the main physical properties of metals.*

**Metal is a solid with a Fermi surface!**

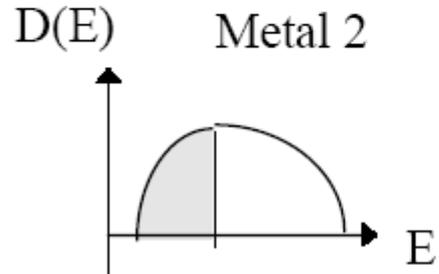
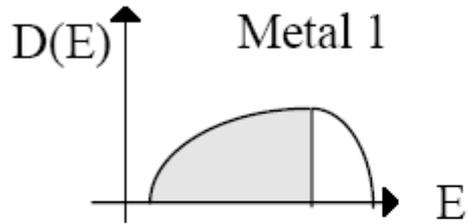


*In atoms*, electrons occupy discrete quantum states described by the quantum numbers  $n, l, m, m_s$ . These *electronic* states can be *degenerate*; states with up and down spin have the same energy in the absence of a magnetic field; in some cases angular momentum states have the same energy as well. The diagram on the left shows the occupancy of the states for a typical atom.

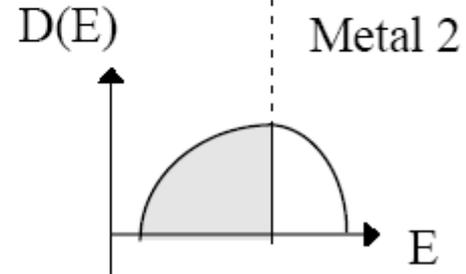
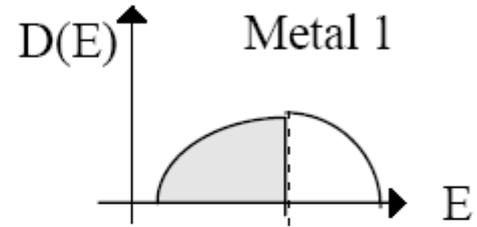




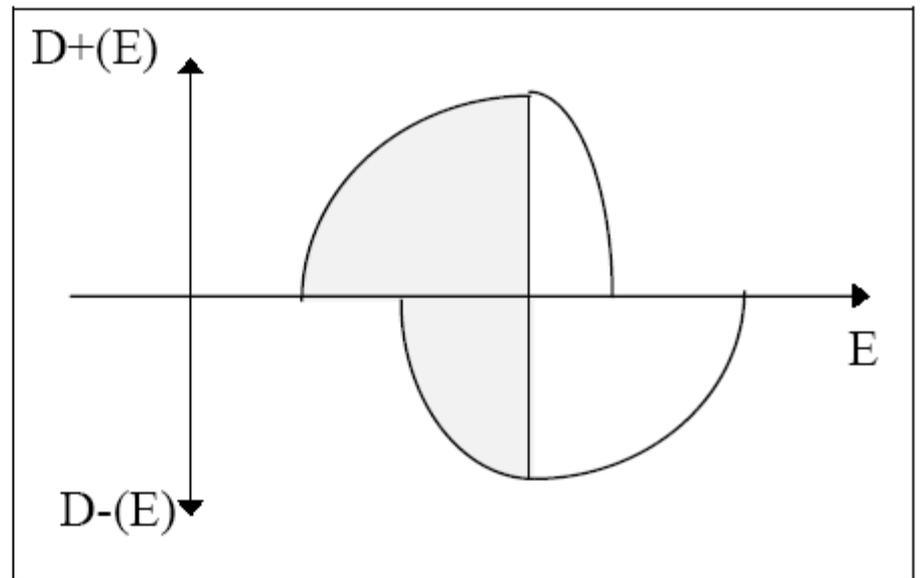
Before joining

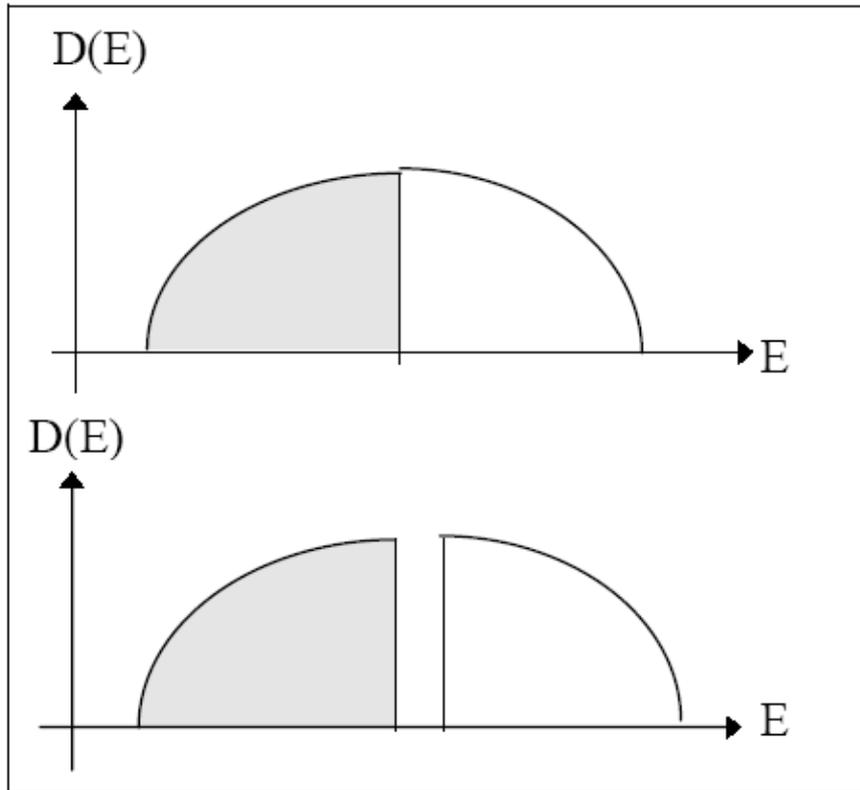


After joining



*Ferromagnetism* If the bands of the spin up and spin down electrons do not have the same energies, then one spin band is preferentially occupied. This gives macroscopic regions of net spin leading to magnetisation. We shall discuss the phenomenon of magnetism in solids in much more detail later on.





*Superconductivity.* A gap, caused by electron-lattice interactions, appears at the Fermi level. States below the gap are highly correlated (Cooper pairs) and the existence of the gap means that they cannot be scattered. The energy gap is of the order of  $kT_c$  where  $T_c$  is the *critical temperature*. Below this temperature, the material is a superconductor; above it the material is (usually) a normal metal. We give a brief introduction to superconductivity at the end of the course.

# Alkali metals: Li $1s^2s^1$ , Na $[\text{Ne}]3s^1$ , K $[\text{Ar}]4s^1$ , Rb $[\text{Kr}]5s^1$ , Cs $[\text{Xe}]6s^1$

from the UvA-VU Master Course: Advanced Solid State Physics by Anne de Visser (University of Amsterdam),

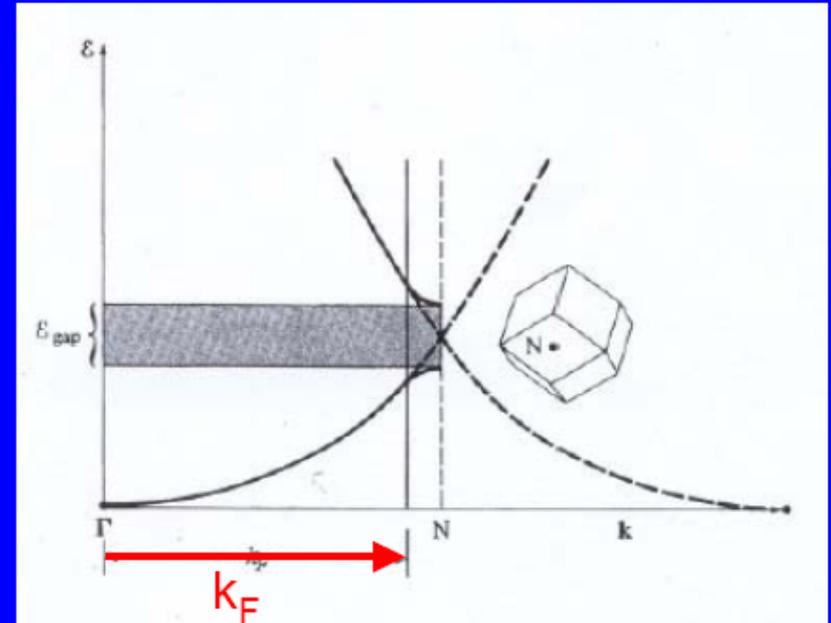
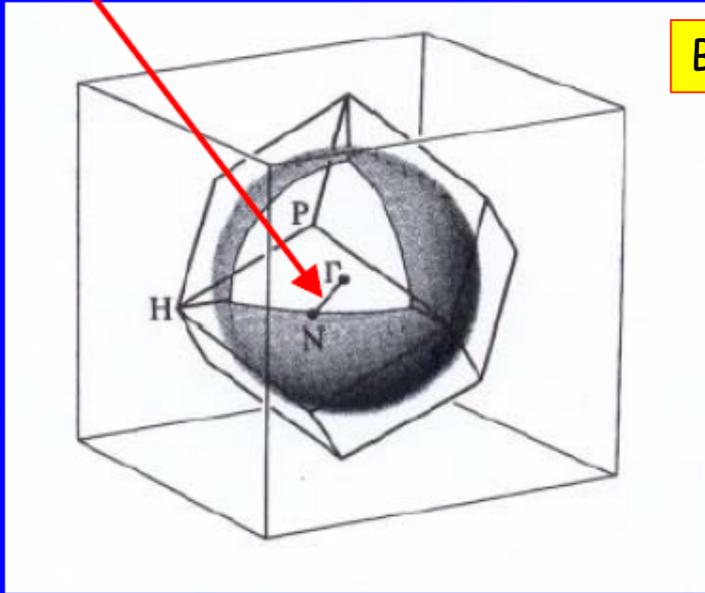
bcc lattice: density  $n = 2/a^3 = k_F^3/(3\pi^2) \rightarrow k_F = 0.62 (2\pi/a)$

$$\Gamma N = \frac{2\pi}{a} \sqrt{\left(\frac{1}{2}\right)^2 + \left(\frac{1}{2}\right)^2 + 0^2} = 0.707 \frac{2\pi}{a}$$

number of states  $\frac{4\pi k_F^3}{3} \frac{V}{8\pi^3} = \frac{k_F^3}{6\pi^2} V$

density of electrons  $n = \frac{N}{V} = 2 \times \frac{k_F^3}{6\pi^2} = \frac{k_F^3}{3\pi^2}$

BZ is half-filled



Fermi sphere contained in first BZ

$2(L/2\pi)^3$  #electrons in the reciprocal unit cell

$$V_B = 2 \left( \frac{2\pi}{a} \right)^3$$

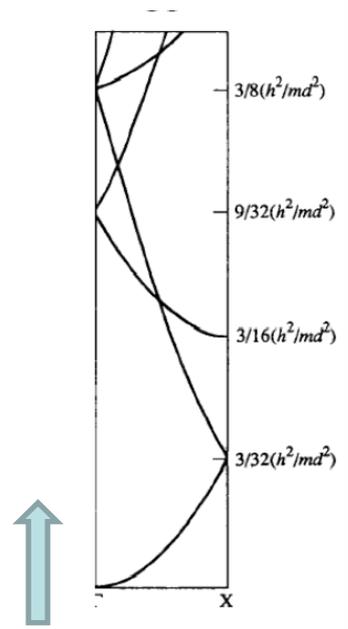
$$[2V/(2\pi)]^3 \times 2(2\pi/a)^3 = 4V/a^3 \text{ electrons}$$

“The first Brillouin zone of the bcc lattice can accommodate 2 electrons per atom.”

$2V/a^3$  atoms (2 atoms/u.c.)

For the case of sodium, the 3s conduction band is very nearly free electron-like and the  $E(\vec{k})$  relations are closely isotropic. Thus the  $E(\vec{k})$  relations along the  $\Delta(100)$ ,  $\Sigma(110)$  and  $\Lambda(111)$  directions are essentially coincident and can be so plotted, as shown on the figure. For these metals, the Fermi level is determined so that the 3s band is exactly half-occupied, since the Brillouin zone is large enough to accommodate 2 electrons per unit cell.

Na metal is known to be almost a free-electron-like metal.



empty  
lattice  
calculation

Mizutani

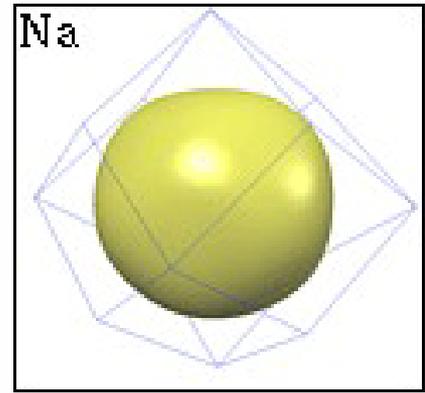
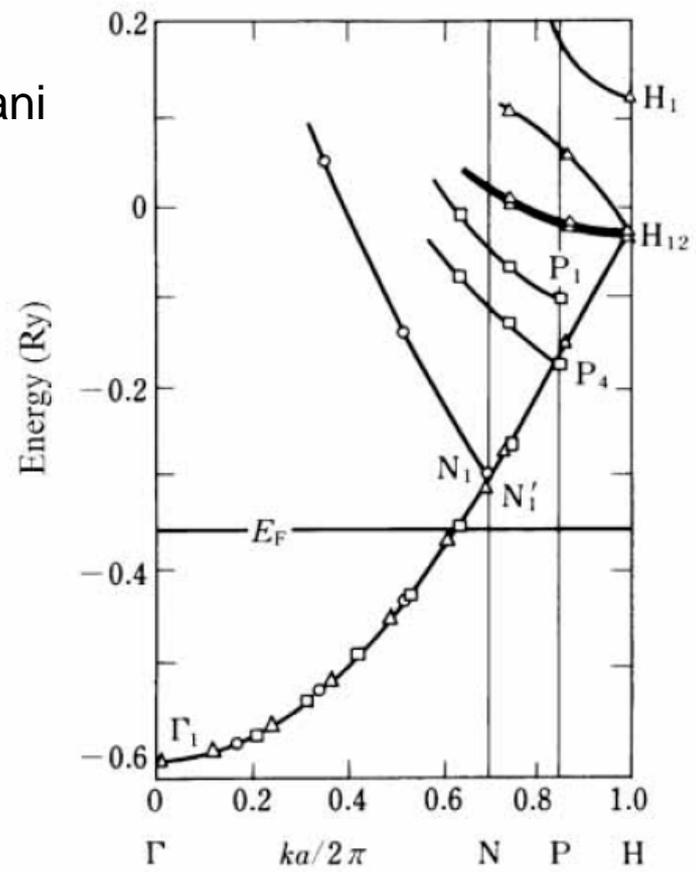


Figure 6.1.  $E-k$  relations along  $\Gamma N$ ,  $\Gamma P$  and  $\Gamma H$  directions of pure Na metal. Note that the dimensionless wave number  $ka/2\pi$  is employed. [F. S. Ham, *Phys. Rev.* **128** (1962) 821]

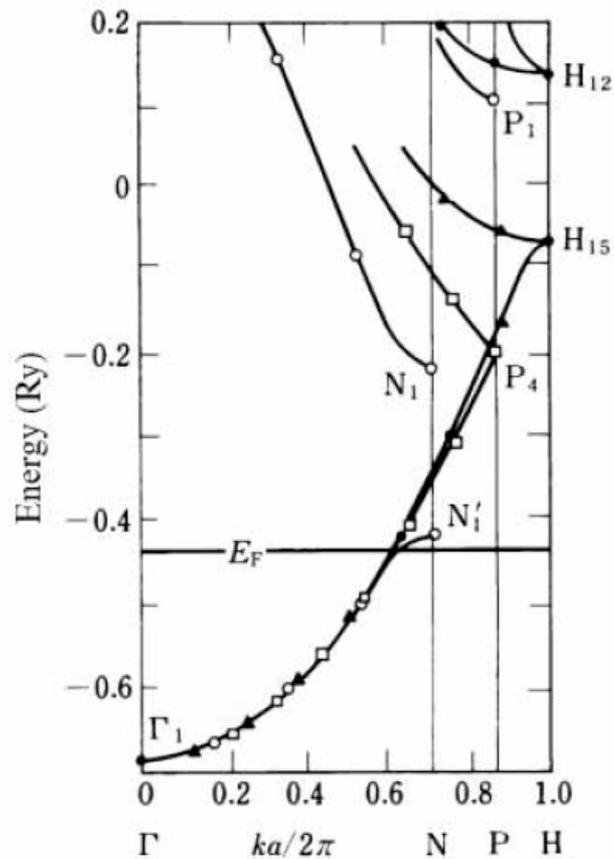


Figure 6.3.  $E$ - $k$  relations of pure Li metal along  $\Gamma$ N,  $\Gamma$ P and  $\Gamma$ H directions. Note that the dimensionless wave number  $ka/2\pi$  is employed. [F. S. Ham, *Phys. Rev.* **128** (1962) 82]

A substantial deviation from the free-electron model in Li metal arises because the Li atom has a very small ion core consisting of only  $(1s)^2$  electrons so that the valence electron is much closer to the nucleus than in other alkali metals. Indeed, the lattice constant of Li metal is 0.351 nm at room temperature, which is shorter than that (0.429 nm) of Na metal.

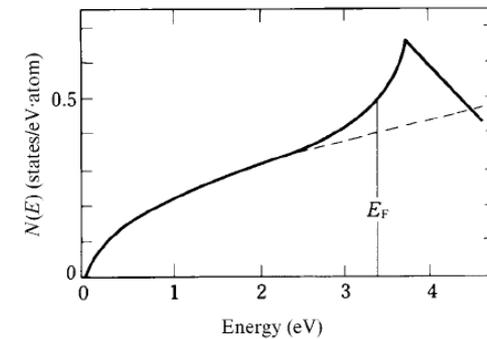
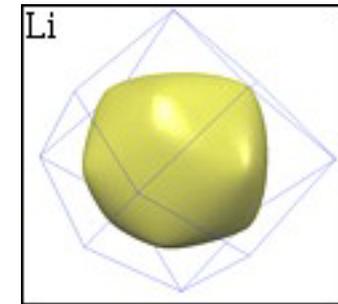
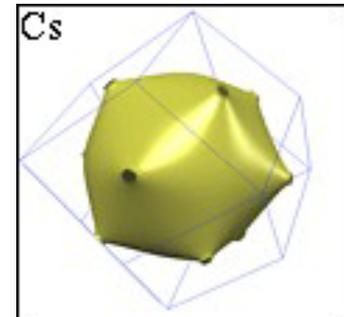
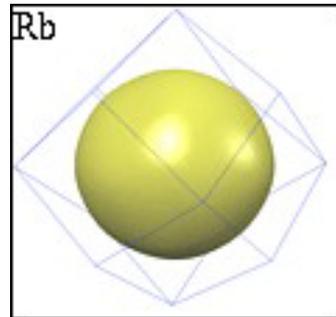
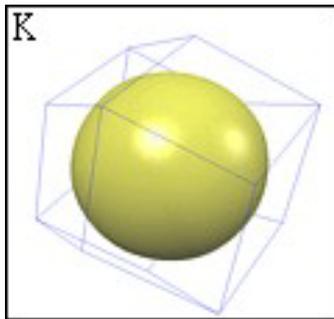


Figure 6.4. Density of states curve of bcc Li metal. A cusp is caused by the interaction with the  $\{110\}$  zone planes of the first Brillouin zone. [F. S. Ham, *Phys. Rev.* **128** (1962) 2524]

Van Hove  
anomaly



<http://www.phys.ufl.edu/fermisurface>

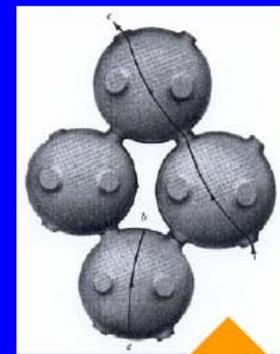
# Monovalent metals

Noble metals: Cu [Ar]3d<sup>10</sup>4s<sup>1</sup>

Ag [Kr]4d<sup>10</sup>4s<sup>1</sup>

Au [Xe]4f<sup>14</sup>3d<sup>10</sup>4s<sup>1</sup>

Bandstructure of copper (fcc lattice): 6 bands



free electron-like FS

d band

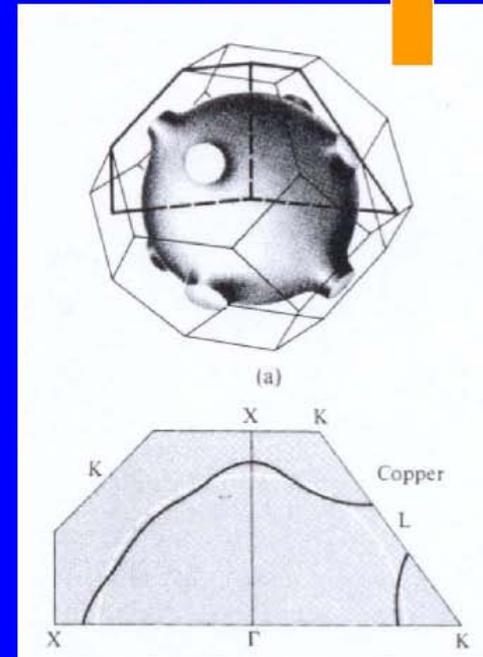
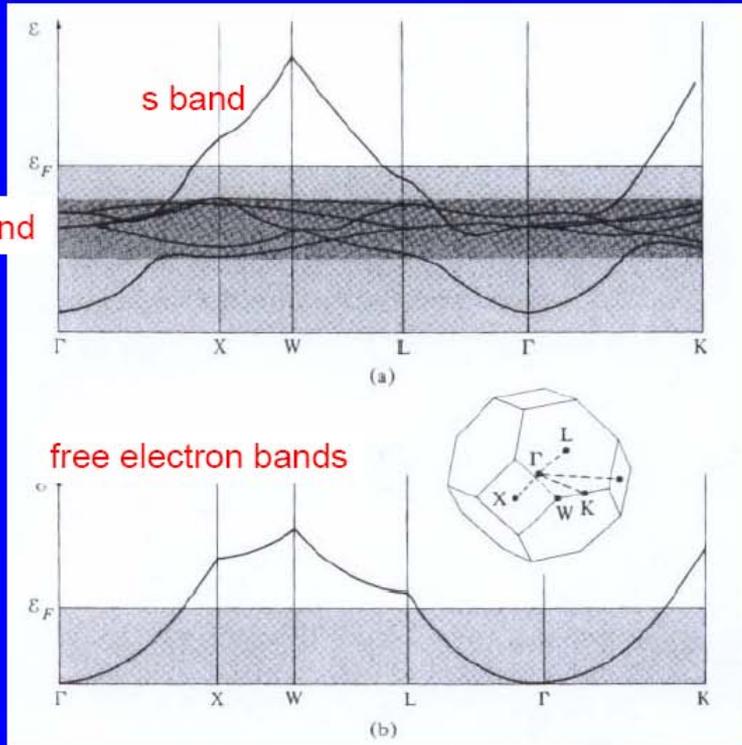


Figure 6.22: DFT-LDA band structure for Cu in the fcc structure (upper panel). The *s* bands are located in the region shaded in light grey and show a dispersion highly reminiscent of free electrons (the band structure of which is shown in the lower panel for comparison). In contrast, the bands deriving from the *d* orbitals (lying in the dark shaded region) are rather flat and have no correspondence in the free electron band structure [from Ashcroft and Mermin].

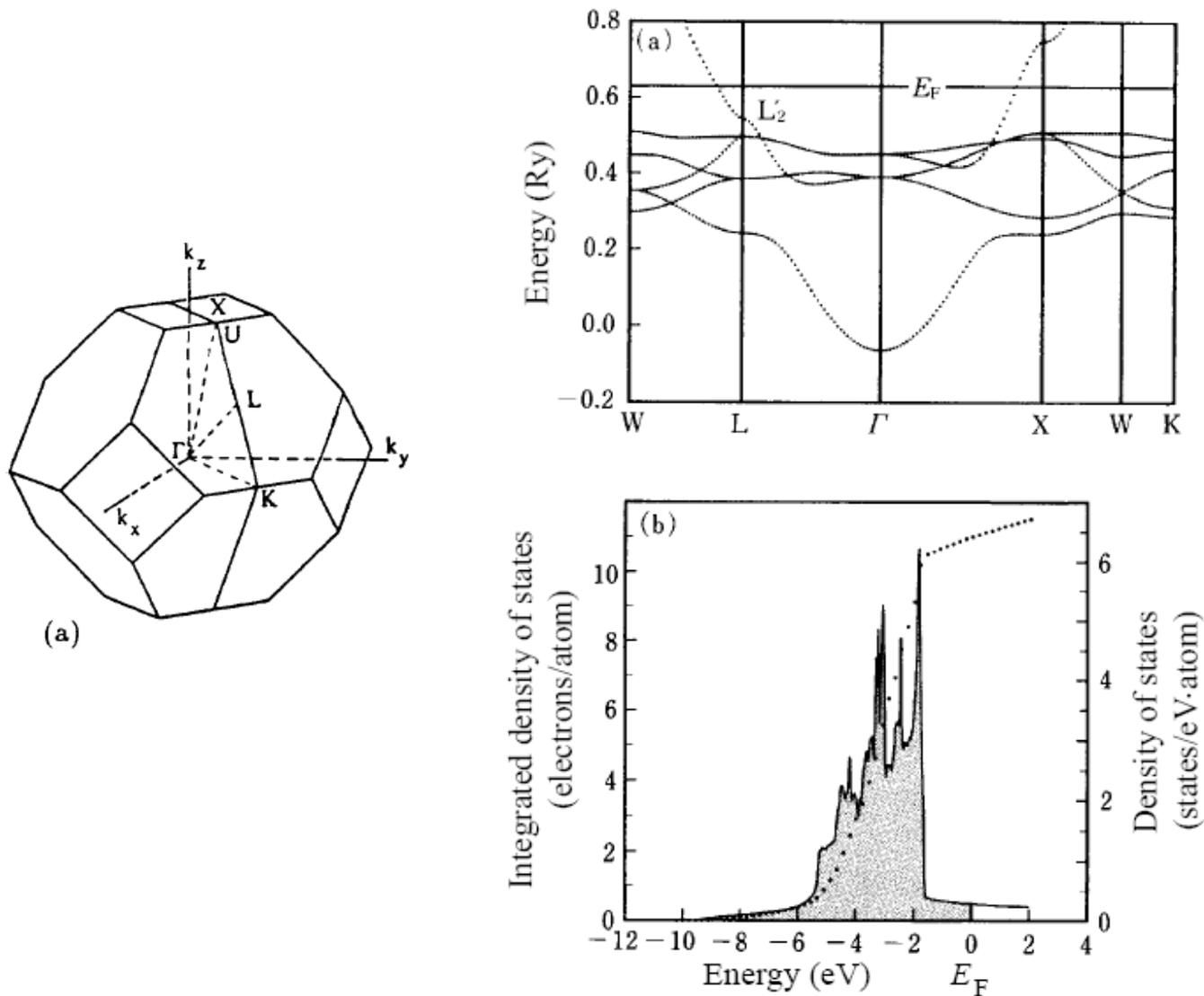


Figure 6.6. (a) *E-k* relations and (b) the corresponding density of states curve of pure Cu metal. Dotted data points in (b) represent the integrated density of states, i.e., the total number of 3d, 4s and 4p electrons per atom integrated up to the energy  $E$ . [V. L. Moruzzi, J. F. Janak and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon Press, 1978)]

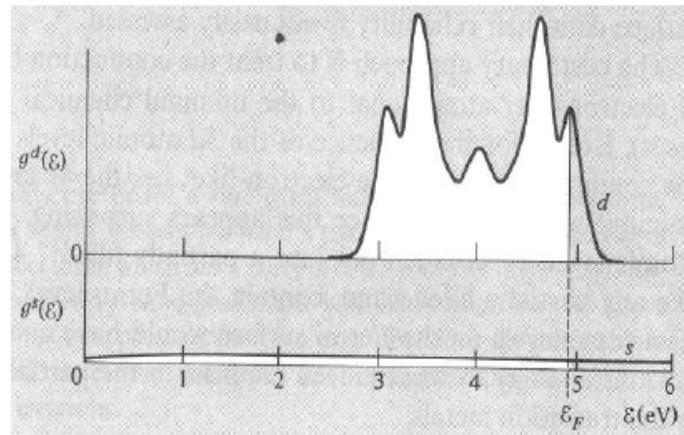
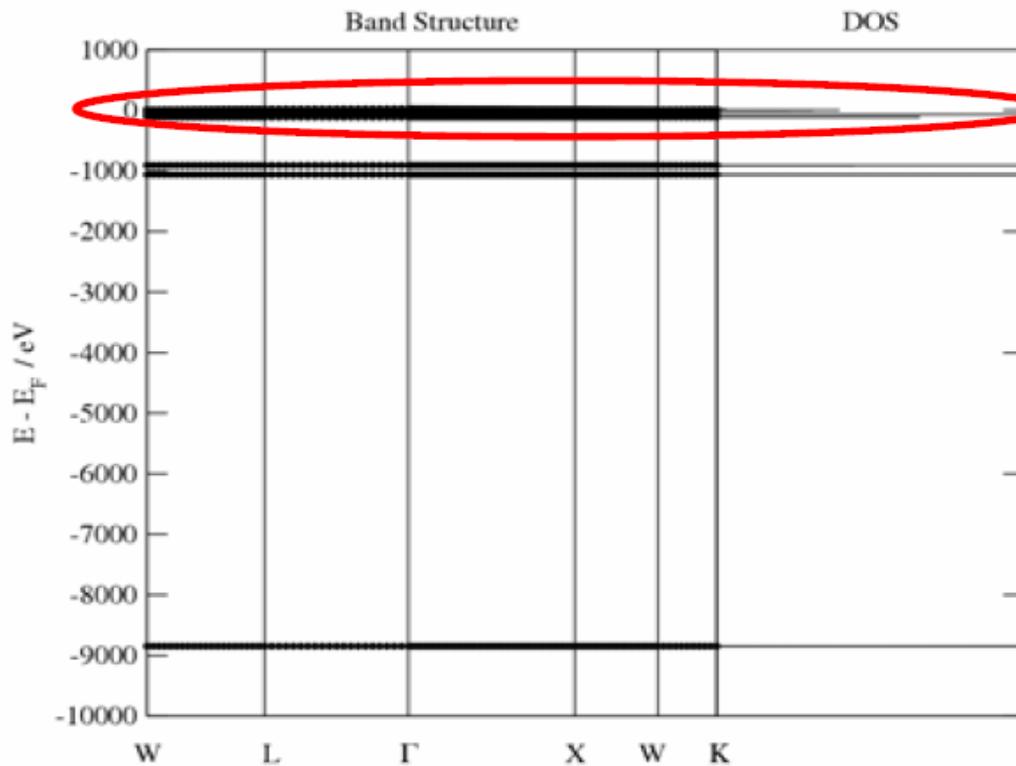


Figure 6.23: Qualitative picture of the two contributions to a TM (fcc) density of states (DOS): a wide featureless and free-electron like  $s$  band and a narrow, structured  $d$  band. Due to the larger number of  $d$  states, the  $d$  band contribution to the DOS dominates, and the varying properties over a TM series can be understood as arising from a differing degree of filling of the  $d$  band (different Fermi level position) [from Ashcroft and Mermin].

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# Examples: Copper

**Electronic configuration:  $1s^2 2s^2 2p^6$      $3s^2 3p^6$      $3d^{10} 4s^1$**   
**core                    semicore                    valence**

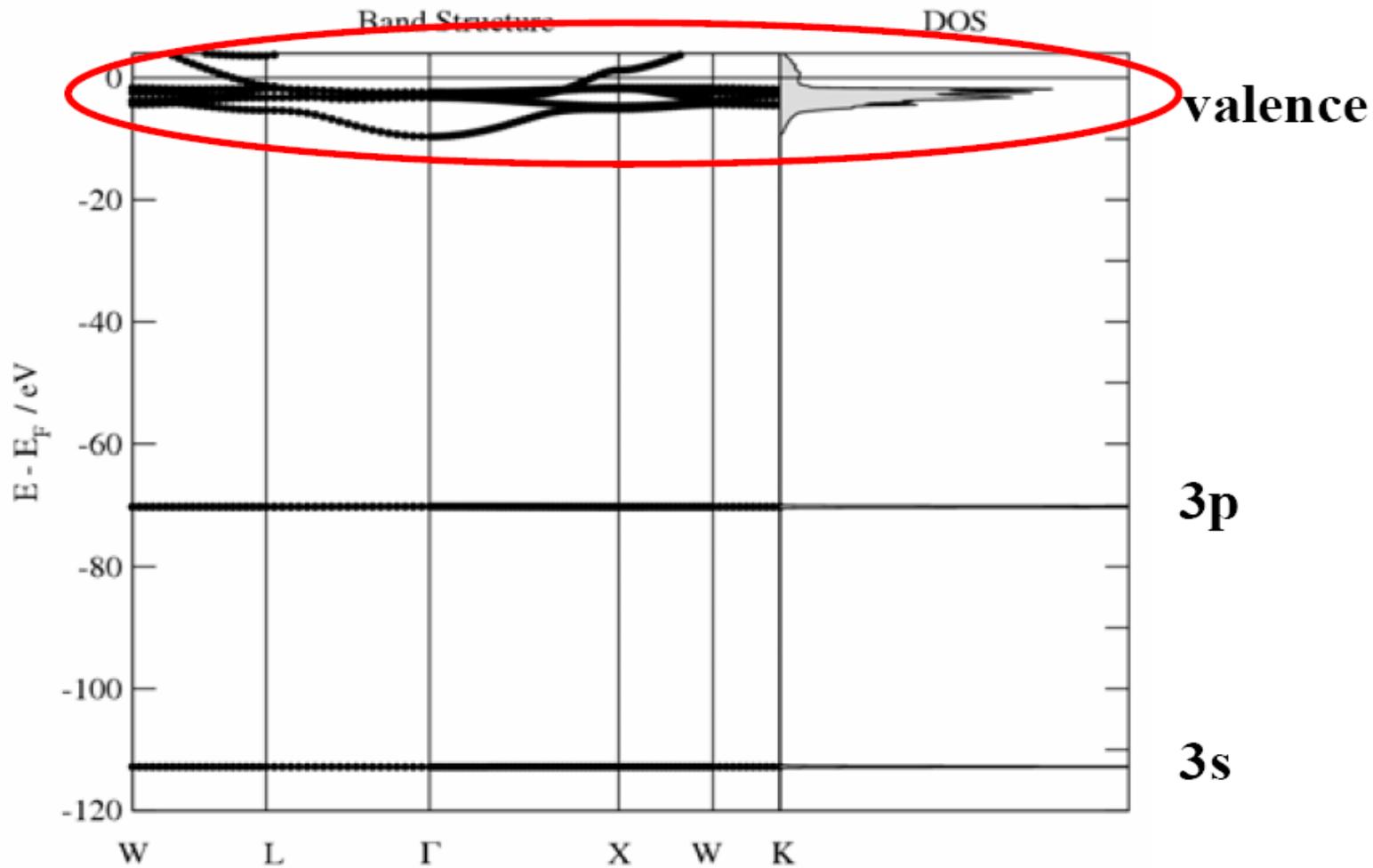


**semicore and valence**  
**2s 2p**

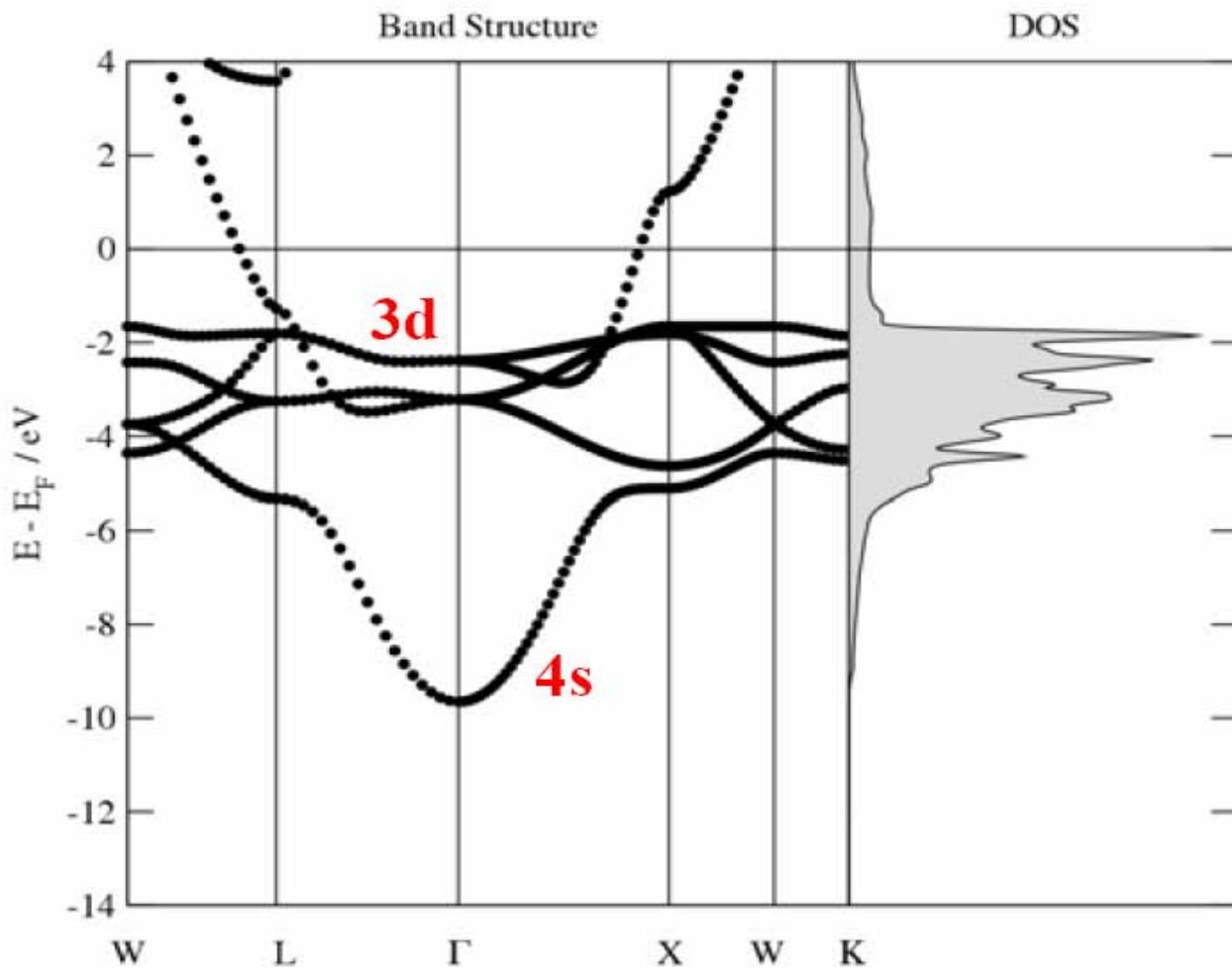
**core states show  
no dispersion  
=> very localized**

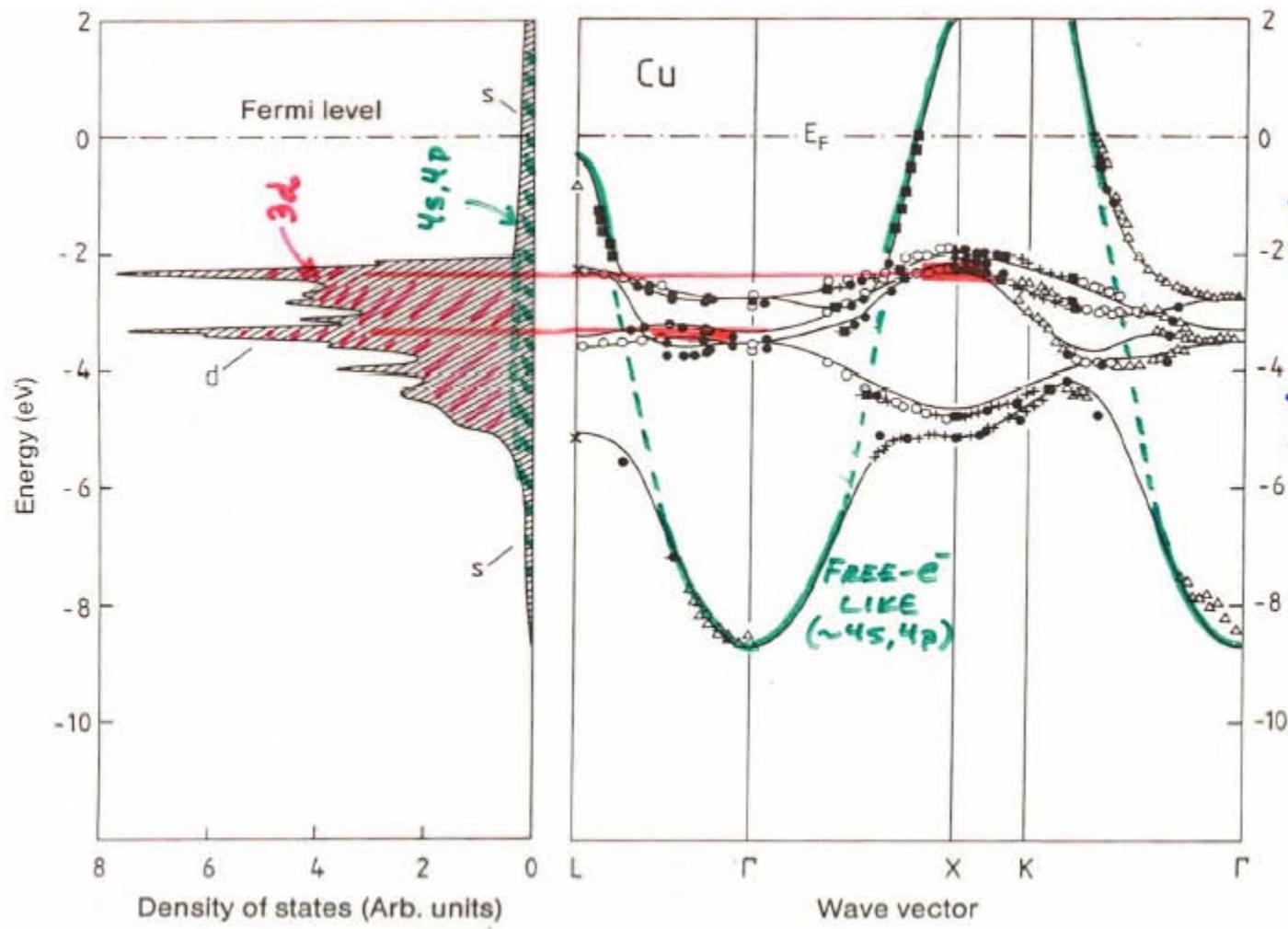
**1s**

# Copper: Semicore and Valence States



# Copper: Valence States

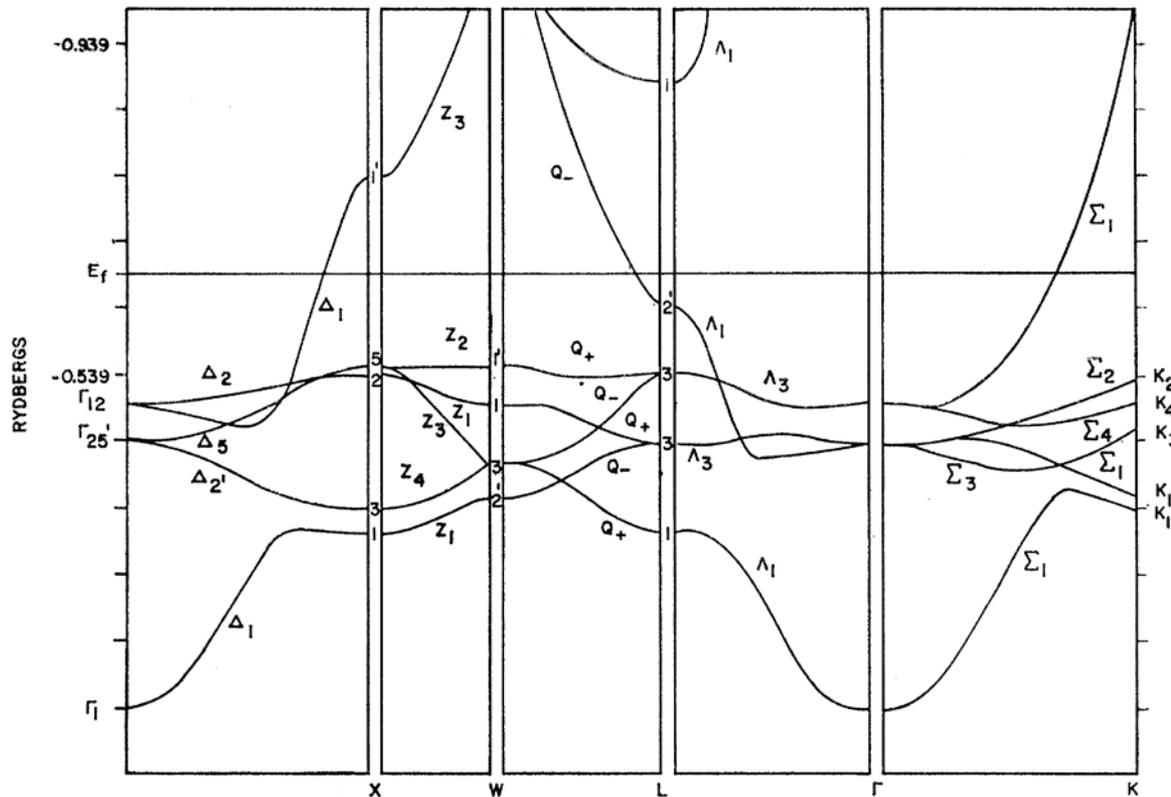




Cu  $1s^2 \dots 3d^{10} 4s^1$   
ELECTRONIC BANDS  
+ DENSITY OF STATE

MIXING  
 3d LIKE  
 MIXING

In the case of copper, the bands near the Fermi level are derived from the 4s and 3d atomic levels. The so-called 4s and 3d bands accommodate a total of 12 electrons, while the number of available electrons is 11. Therefore the Fermi level must cross these bands. Consequently copper is metallic.



As another unique feature of the electronic structure of noble metals, the parabolic  $E-k$  relation is intervened by the less dispersive  $E-k$  curves due to 3d electrons centered at about a few eV below the Fermi level.

This means that the 4s and 4p free-electron-like states are hybridized with the 3d states to form a composite band. In spite of strong hybridization, ten 3d electrons per atom are distributed in a rather narrow energy range.

The Fermi surface of a noble metal should occupy only 50% by volume of the first Brillouin zone of the fcc lattice.

## Polyvalent Metals

see Mizutani

Ca free atom are composed of  $(1s)^2, (2s)^2, (2p)^6, (3s)^2, (3p)^6, (4s)^2$  electrons

The two outermost 4s electrons per atom contribute to the formation of the valence band of Ca metal.

• Since the number of electrons per atom,  $e/a$ , is equal to 2.0, it is just high enough to fill the first Brillouin zone.

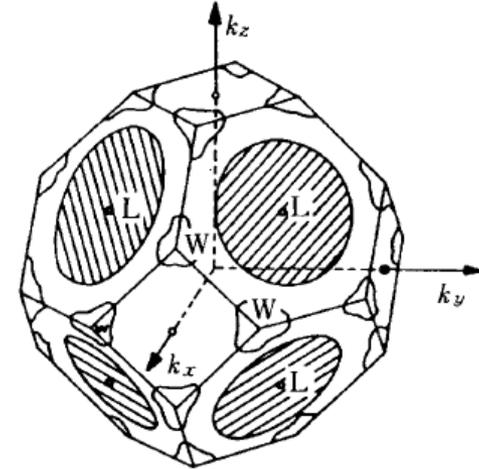
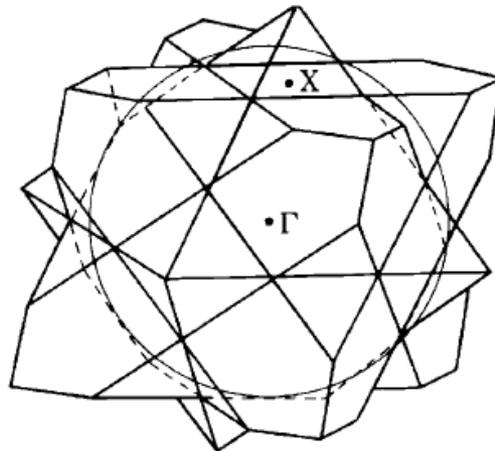


Figure 6.7. The Fermi surface and the first Brillouin zone of pure Ca. The hatched regions represent electrons overlapped into the second zone across the points L. Holes can be seen in the first zone around the points W. [A. P. Cracknell, *The Fermi Surface of Metals* (Taylor & Francis Ltd, 1971)]

However, a Fermi surface does exist, as is depicted in Fig. 6.7 in the extended zone scheme. The Fermi surface marked by hatches indicates electrons overlapped into the second Brillouin zone across the points L. Naturally, the same amount of holes must be left behind in the first zone. This is found at the corners W in the first zone. This is why Ca becomes a metal in spite of  $e/a = 2.0$ . A metal is said to be compensated, when there exist an equal number of holes and electrons in the two successive zones.

- The simplest example of a polyvalent **metal** is aluminum with 3 electrons/atom and having a  **$3s^23p$**  electronic configuration for the valence electrons.
  - Because of the partial filling of the  $3s^23p^6$  bands, aluminum is a **metal**. Aluminum crystallizes in the FCC structure
- The energy bands for aluminum are very **free electron-like**.

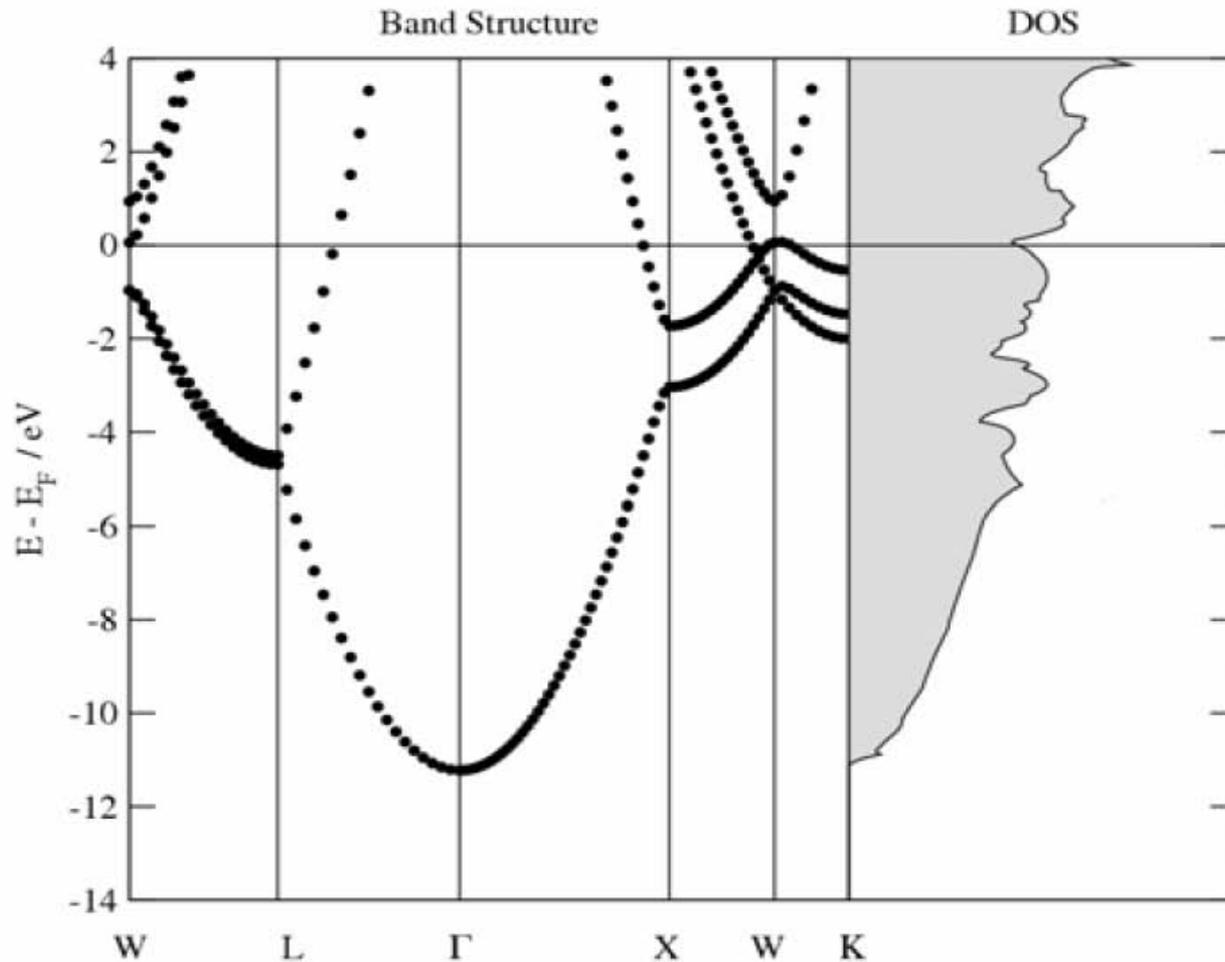


from Mizutani

Figure 6.11. The free-electron Fermi surface and the first and second Brillouin zones of fcc Al in the extended zone scheme. Electrons overlap into the third and fourth zones.

# Aluminium: Valence States

Electronic configuration:  $1s^2 2s^2 2p^6 3s^2 3p^1$



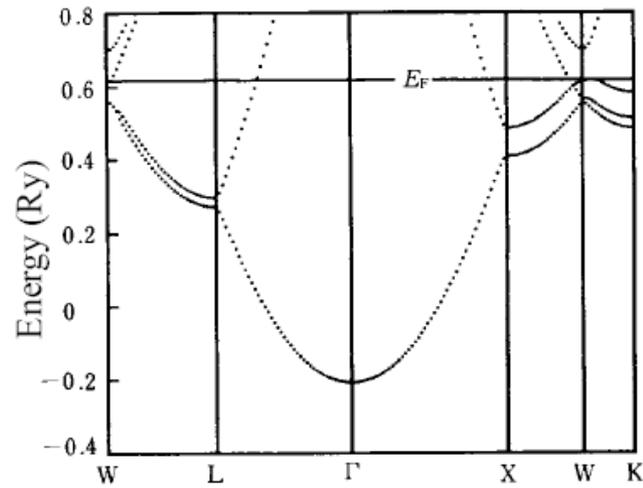


Figure 6.12.  $E$ - $k$  relations in pure Al. [V. L. Moruzzi, J. F. Janak and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon Press, 1978)]

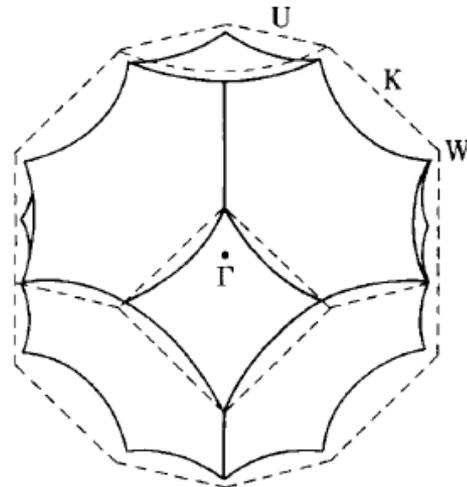


Figure 6.13. The Fermi surface of holes in the second Brillouin zone of pure Al in the reduced zone scheme. [W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, New York, 1966)]

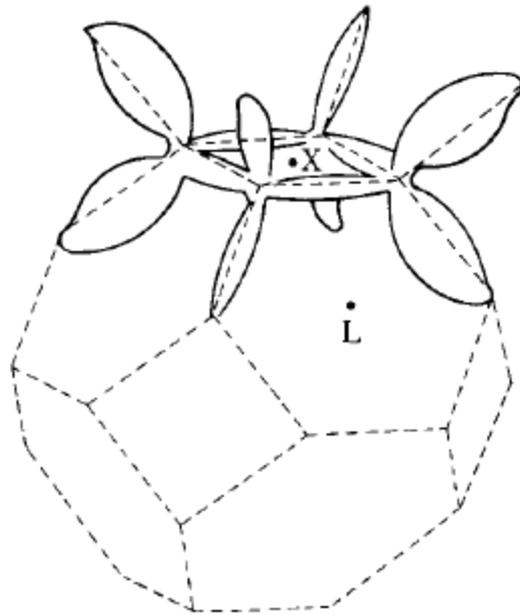


Figure 6.14. The Fermi surface of electrons in the third Brillouin zone of pure Al in the reduced zone scheme. [A. P. Cracknell, *The Fermi Surface of Metals* (Taylor & Francis Ltd, 1971)]

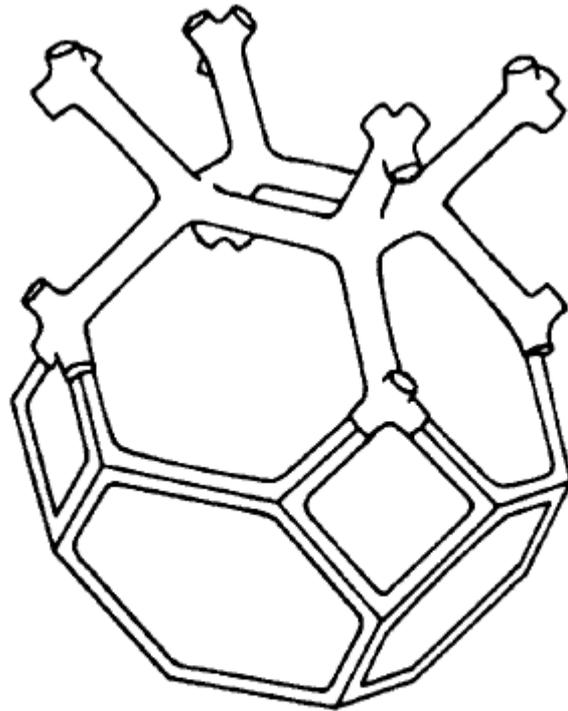


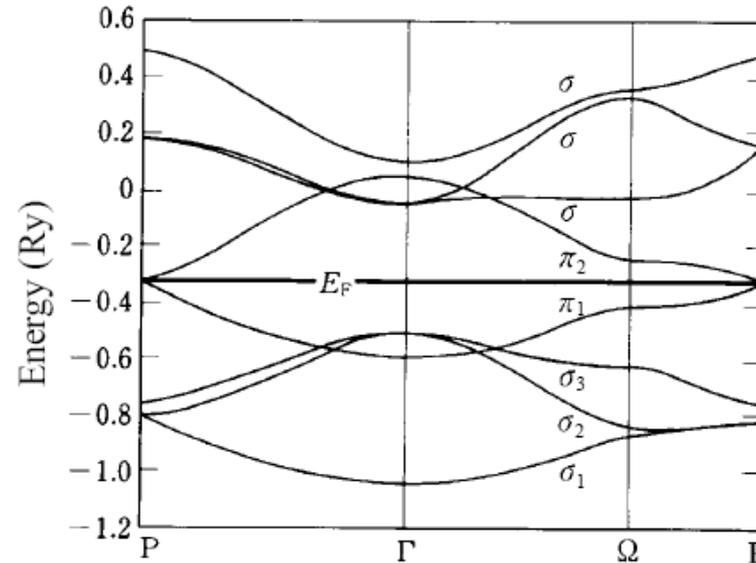
Figure 6.15. The Fermi surface of electrons in the third Brillouin zone of pure Pb. The Fermi surface is called the “jungle gym”. [A. P. Cracknell, *The Fermi Surface of Metals* (Taylor & Francis Ltd, 1971)]

# semimetal

- electronic band structure intermediate between metals and semiconductors

- small Fermi surfaces of both electrons and holes

- a very small overlap between the bottom of the conduction band and the top of the valence band



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18.  $E-k$  relations of graphite obtained from the two-dimensional lattice model. [G. S. Painter and D. E. Ellis, *Phys. Rev.* **B1** (1970) 4747]

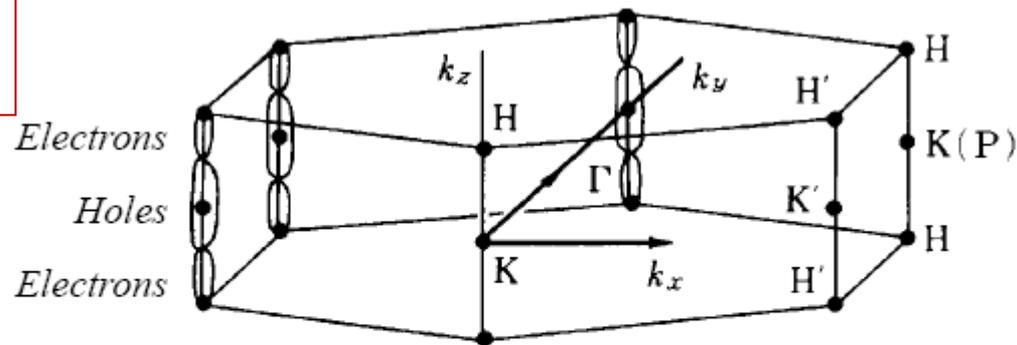


Figure 6.19. The Fermi surface of electrons and holes of pure graphite in the reduced zone scheme. The point K corresponds to the point P in Fig. 6.17. [A. P. Cracknell, *The Fermi Surface of Metals* (Taylor and Francis, Ltd, 1971)]

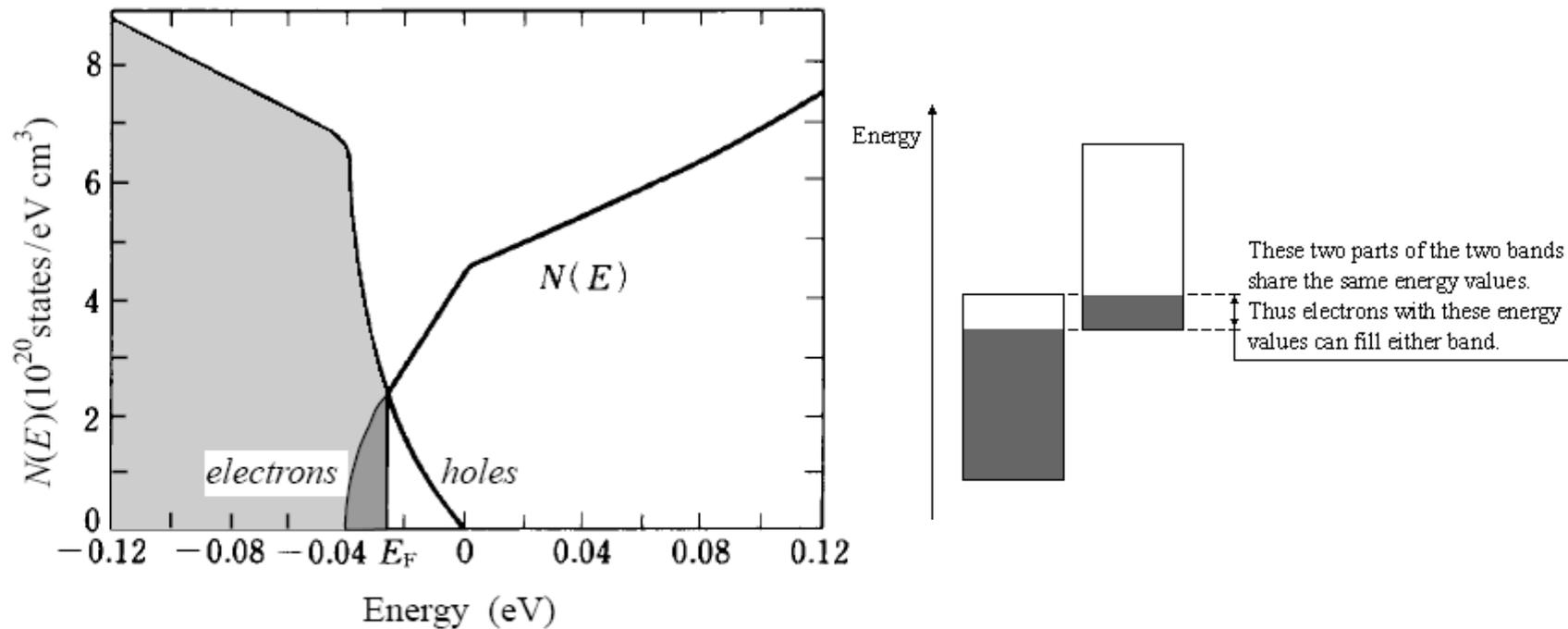


Figure 6.20. Density of states curve near the Fermi level in pure graphite. The Fermi level is located at about  $-0.02$  eV, since the origin of the energy is taken at the point H in the  $E_3$  band. [M. S. Dresselhaus *et al.*, *Phys. Rev.* **15B** (1977) 3180]

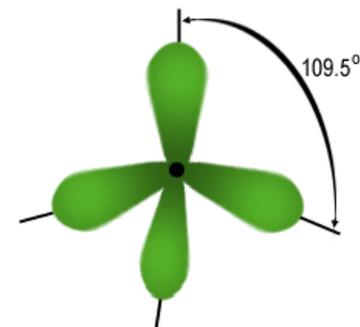
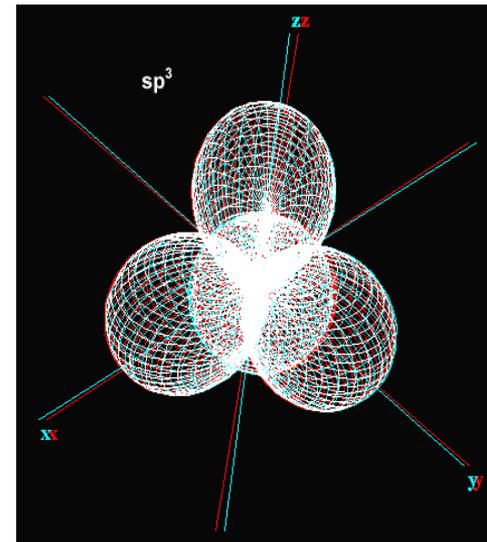
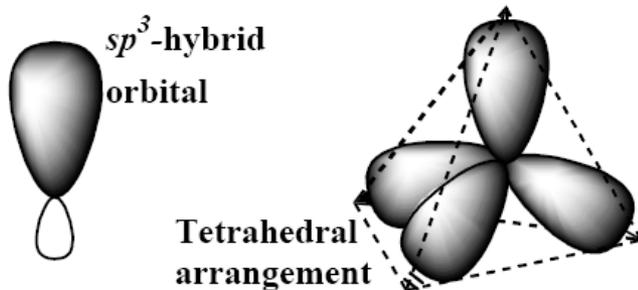
It can be seen that the two bands slightly overlap each other so that electrons and holes coexist at the Fermi level.

# Semiconducting elements without and with dopants

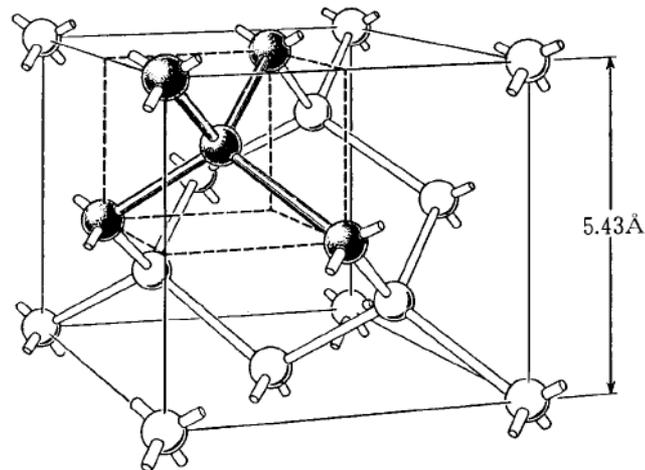
The elements C (diamond), Si, Ge and Sn(  $\alpha$  ) belong to the group IVB elements in the periodic table and all of them are covalently bonded.

•  **$sp^3$  Hybridization** – a combination of **one s** and **three p** orbitals

– The resulting four  **$sp^3$  hybrid** orbitals are identical and point toward the corners of a tetrahedron (used to describe the **tetrahedral e-group arrangement**, bond angles  $109.5^\circ$ )



- Two interpenetrating fcc lattices and, hence, the structure is fcc but with two atoms in each unit cell.
- In Si, two 3s and two 3p electrons per atom are hybridized to form directionally-bonded states and the Brillouin zone is completely filled with eight electrons per unit cell. Hence, **no Fermi surface exists**.

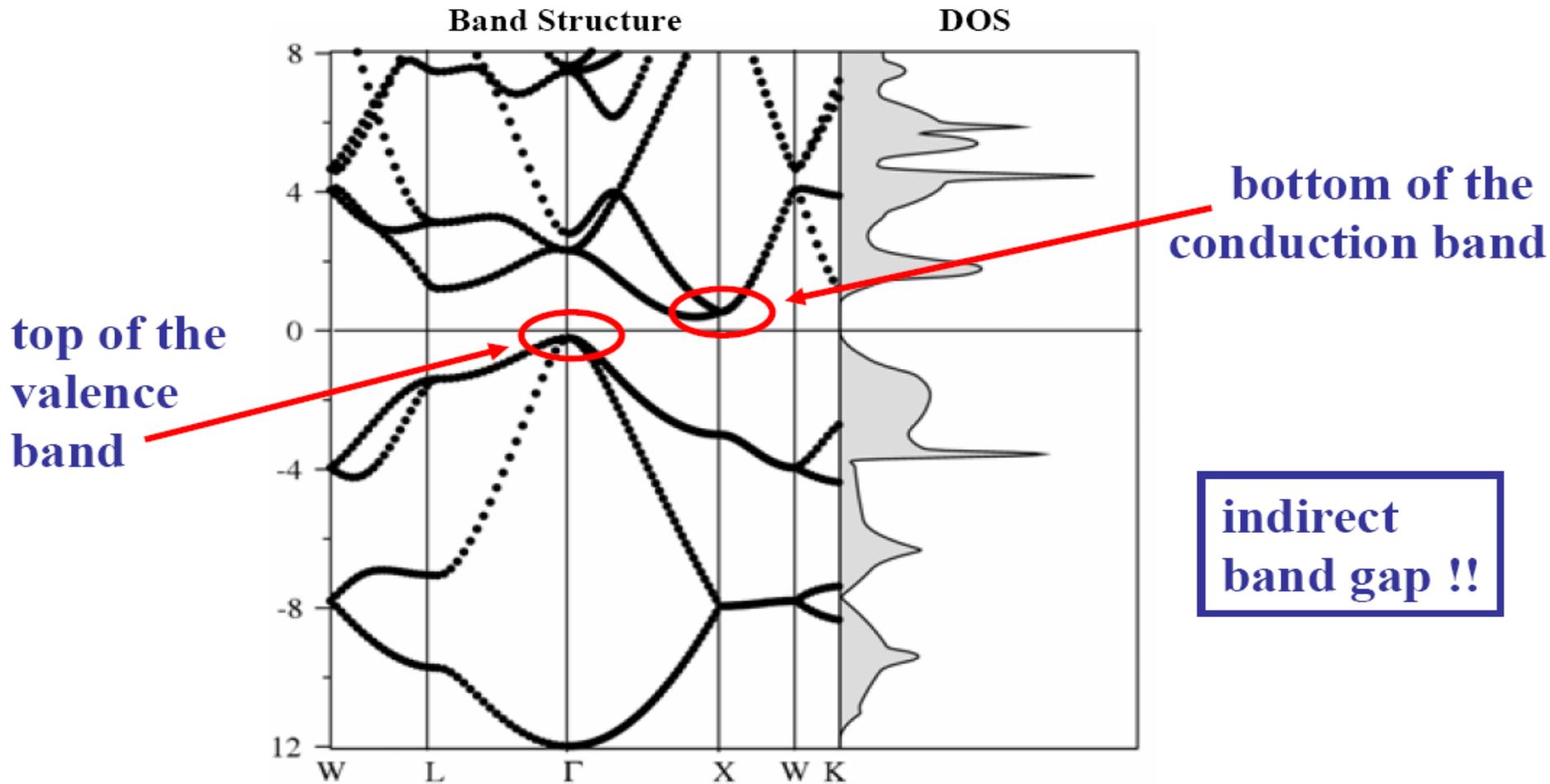


Kittel

Figure 6.23. Crystal structure of Si in the diamond structure. There are eight atoms in the unit cell. [W. Shockley, *Electrons and Holes in Semiconductors* (van Nostrand Co., 1950)]

# Silicium: Valence States

Electronic configuration:  $1s^2 2s^2 2p^6 3s^2 3p^2$



Energy gaps of typical semiconductors are as follows:

5.3 eV for C (diamond), 1.1 eV for Si, 0.7 eV for Ge,

2.8 eV for SiC, 4.6 eV for BN and 1.4 eV for GaAs.

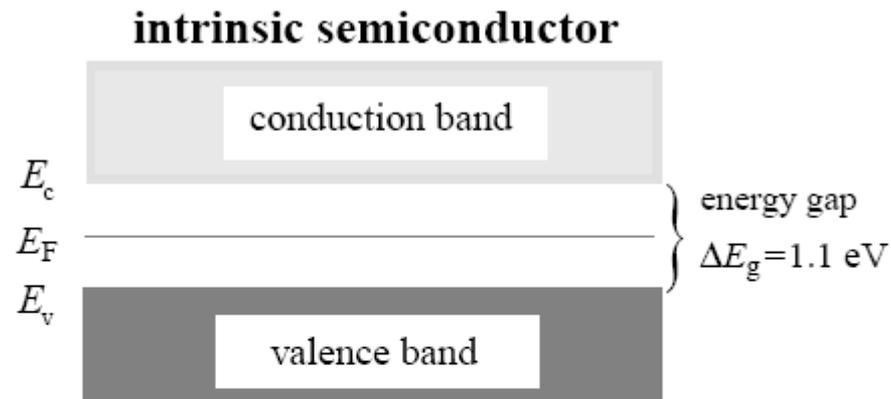
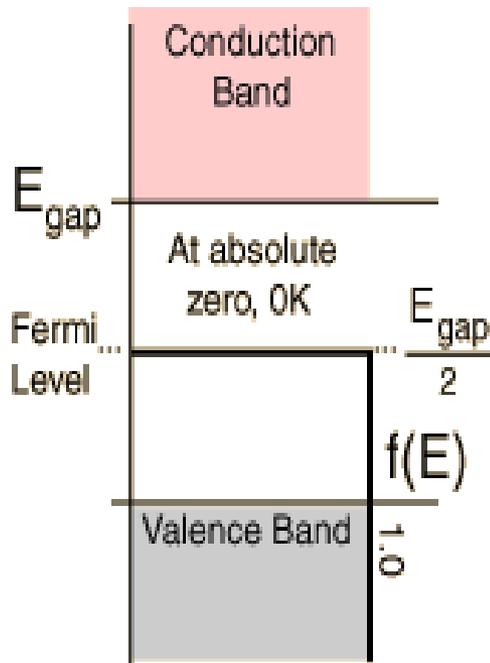


Figure 6.26. Schematic illustration of the band structure of an intrinsic semiconductor. The binding energy is measured in a vertical direction. The valence band and conduction band are separated by the energy gap  $\Delta E_g$ . It is 1.1 eV for Si. Energies at the top of the valence band and the bottom of the conduction band are denoted as  $E_v$  and  $E_c$ , respectively.

# Is there a Fermi energy of intrinsic Semiconductors?



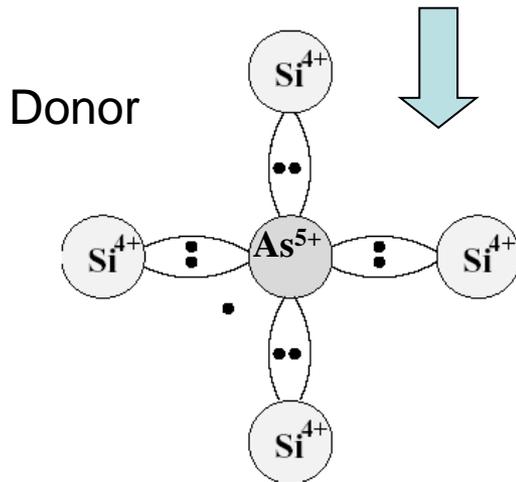
Context of Fermi level for a semiconductor

- If  $\mathcal{E}_F$  is defined as the energy separating the highest occupied from the lowest unoccupied level, then **it is not uniquely specified in a solid with an energy gap**, since any energy in the gap meets this test.
- People nevertheless speak of “*the Fermi energy*” on an **intrinsic semiconductor**. What they mean is the **chemical potential**, which is well defined at any non-zero temperature. As  $T \rightarrow 0$ , the chemical potential of a solid with an energy gap approaches the energy of the middle of the gap and one sometimes finds it asserted that this is the “*Fermi energy*”. With either the correct or colloquial definition,  $\mathcal{E}_n(\mathbf{k}) = \mathcal{E}_F$  does not have a solution in a solid with a gap, which therefore has no Fermi surface!

## extrinsic semiconductors

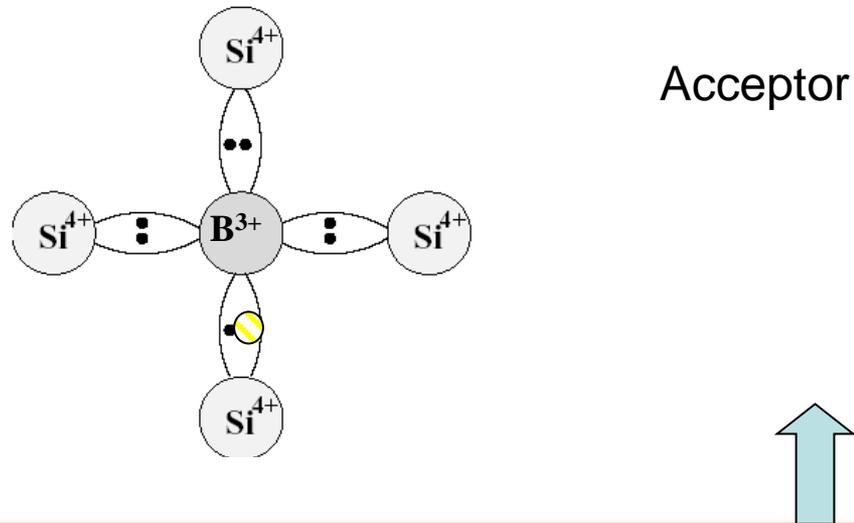
Si semiconducting properties depend significantly on whether **pentavalent** or **trivalent** impurities are added.

Pentavalent atoms like **P**, **As** and **Sb** from group **VB** of the periodic table will have one more valence electron than is required for the covalent bonding.



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extra electron bound to the impurity atom may be easily excited into the conduction band, provided that the temperature is high enough to promote it there from a level in the gap. This leaves a positive ion behind and four remaining valence electrons which form a covalent bond in the same manner as in the host Si atoms.



• trivalent atoms like **B, Al, Ga and In** from **group III B** in the periodic table possess **one electron less** than the number required for covalent bonding.

Hence, an electron from one of the adjacent Si atoms will enter the orbit about the trivalent impurity atom. This causes the trivalent atom to be negatively charged and the host Si atoms to lose an electron in this process.

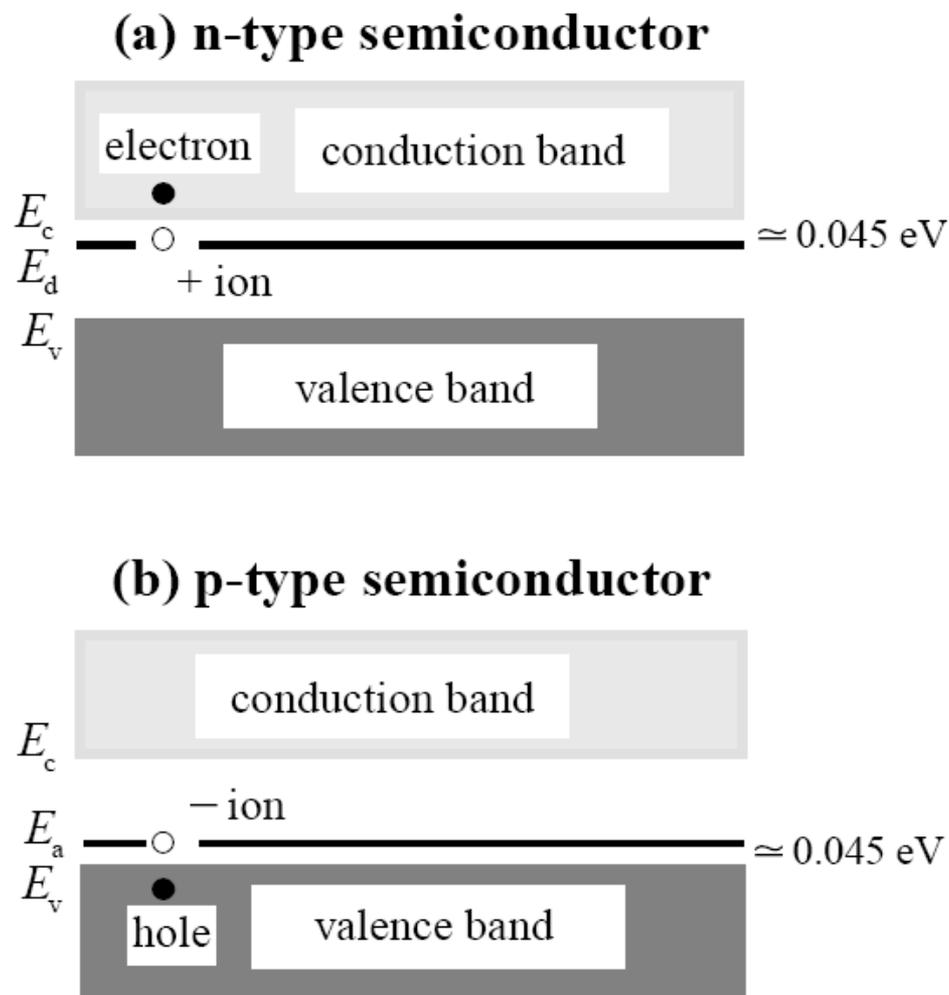
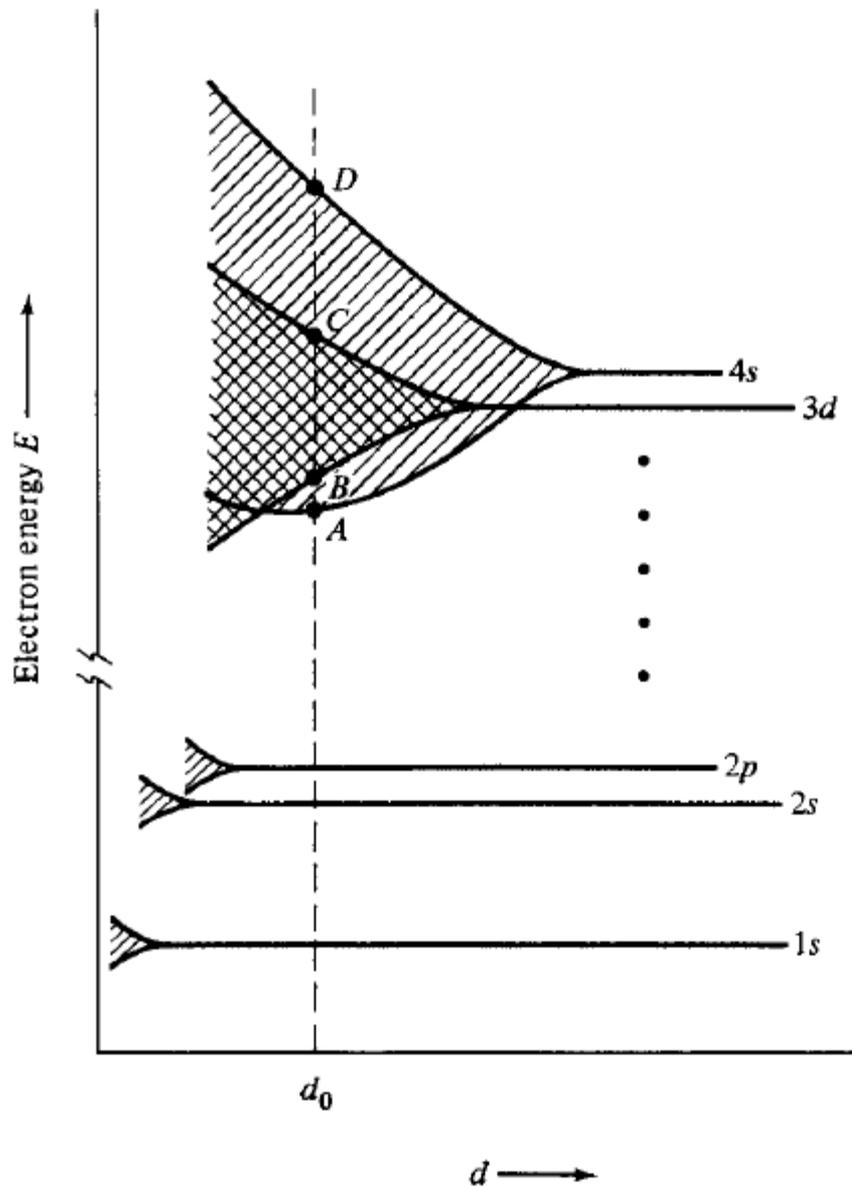


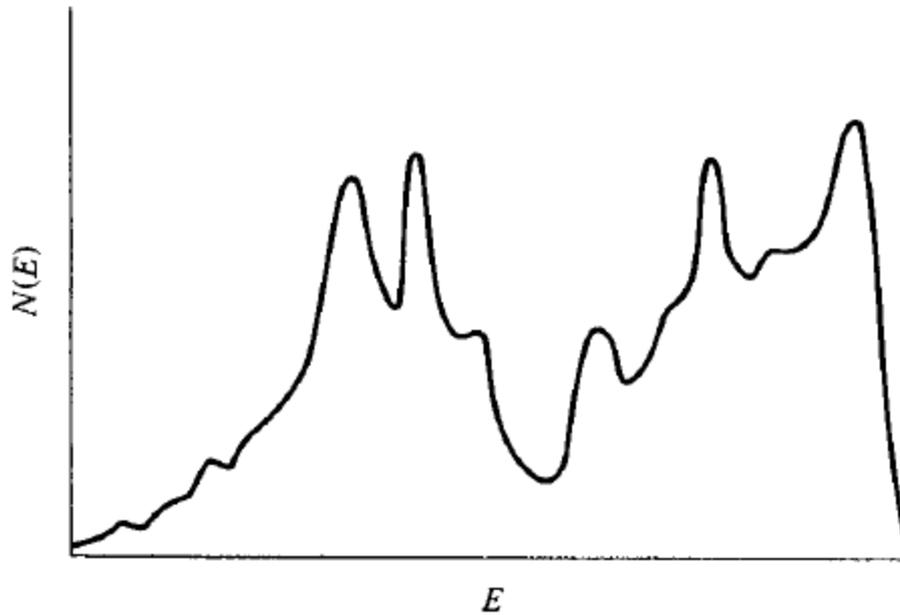
Figure 6.27. Schematic illustration of the band structure of a doped semiconductor. (a) n-type semiconductor. The energy of the donor level is marked  $E_d$ . The energy difference  $E_c - E_d$  is about 0.045 eV for P in Si. (b) p-type semiconductor. The energy of the acceptor level is marked  $E_a$ . The energy difference  $E_a - E_v$  is about 0.045 eV for B in Si.

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Splitting of electron energy levels as the interatomic distance decreases.

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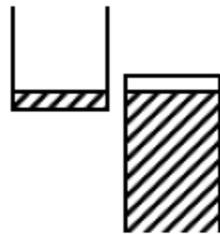
One calculation of the density of levels as a function of energy in the  $3d$  band of nickel.



**Semiconductor**   **Semimetal**

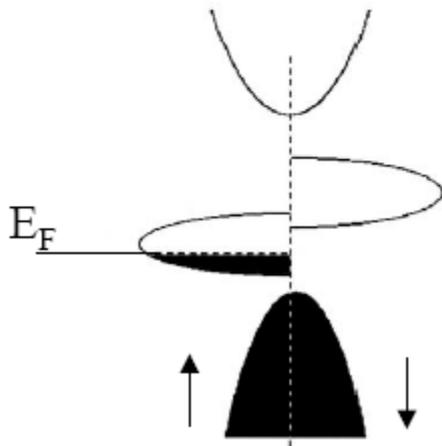
Ge, Si, ...

Bi, Sb, ...



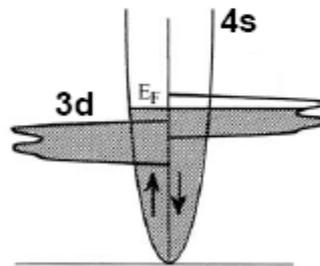
**Half-metal**

$\text{CrO}_2$ ,  $\text{Mn}_2\text{VAI}$



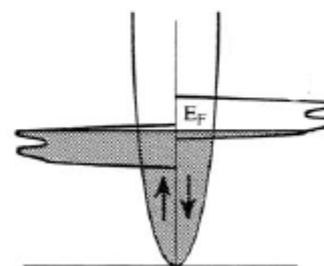
**strong ferromagnet**

Co, Ni, ...



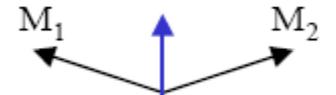
**weak ferromagnet**

Fe, ...



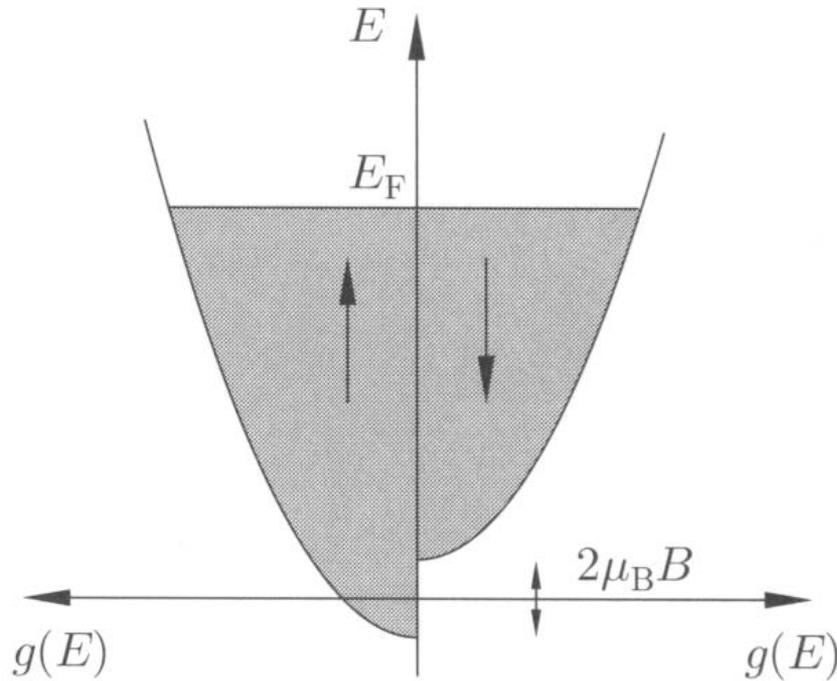
**weak ferromagnetism**

$\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{La}_2\text{CuO}_4$



- localized electron spin canting in AFM
- by DM interaction

# Pauli Paramagnetism



Density of states showing splitting of energy bands in a field  $B$ . The splitting is shown greatly exaggerated.

*The small size of the paramagnetic susceptibility of most metals was a puzzle until Pauli pointed out that it was a consequence of the fact that electrons obey Fermi Dirac rather than classical statistics.*



W. Pauli  
Nobel Prize 1945

Spin - Magnetization  
for small fields  $B$  ( $T=0$ )

$$E_B = -\vec{\mu}_B \cdot \vec{B}$$

$$n = g(E_F) \cdot \Delta E$$

$$\Delta E = 2\mu_B \cdot B$$

$$M = \mu_B (n_{\uparrow} - n_{\downarrow}) = g(E_F) \mu_B^2 B$$

Pauli paramagnetism is a weak effect compared to paramagnetism in insulators (in insulators one electron at each ion contributes, in metals only the electrons at the Fermi level contribute).

### Magnetic Spin - Susceptibility

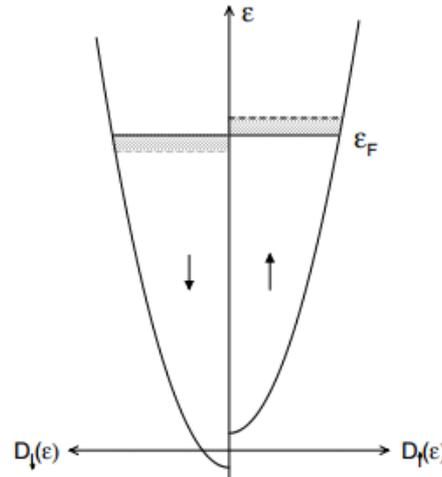
$$\chi_P = \frac{M}{H} = \frac{\mu_0 M}{B} = \mu_0 \mu_B^2 g(E_F)$$

$$g(E_F) = \frac{3N}{2E_F} = \frac{3N}{2k_B T_F}$$

$$\chi_P = \frac{M}{H} = \frac{\mu_0 M}{B} = \frac{3\mu_0 \mu_B^2 N}{2E_F}$$

(Pauli Paramagnetism)

Culity, Graham  
Introduction to  
magnetic materials  
Wiley 2009.



The Hamiltonian for the band electrons are changed, when applying a field along the  $z$  axis,  $\mathbf{H} = (0, 0, H)$ :

$$\Delta\mathcal{H} = \sum_i 2\mu_B \mathbf{H} \cdot \mathbf{s}_i = \sum_i \mu_B H \sigma_z(i) \quad (1)$$

implying that the spin-up and spin-down bands are shifted rigidly up and down by an equal amount:

$$\epsilon_{\uparrow}(\mathbf{q}) = \epsilon(\mathbf{q}) + \Delta, \quad \epsilon_{\downarrow}(\mathbf{q}) = \epsilon(\mathbf{q}) - \Delta, \quad \Delta = \mu_B H \quad (2)$$

The Fermi energy is common for the spin-up and spin-down electrons, and the spin-up electrons in the cross-hatched area on the figure are removed and appear instead as spin-down electrons in the corresponding cross-hatched spin-down area. To a first approximation the small changes of the total density of states between  $\epsilon_F$  and  $\epsilon_F \pm \Delta$  may be neglected (at least in the limit of  $H \rightarrow 0$ ), and the two spin-components of the density of states:

$$D_{\uparrow}(\epsilon) = \frac{1}{2}D(\epsilon - \Delta), \quad D_{\downarrow}(\epsilon) = \frac{1}{2}D(\epsilon + \Delta) \quad (3)$$

may both be approximated with  $\frac{1}{2}D(\epsilon_F)$  at  $\epsilon = \epsilon_F$ . This means that, at zero temperature, the field-induced magnetization of the band electrons is

$$M = \mu_B(n_{\downarrow} - n_{\uparrow}) \simeq \mu_B \left( D_{\downarrow}(\epsilon_F)\Delta + D_{\uparrow}(\epsilon_F)\Delta \right) \simeq \mu_B D(\epsilon_F)\Delta = \mu_B^2 D(\epsilon_F) H \quad (4)$$

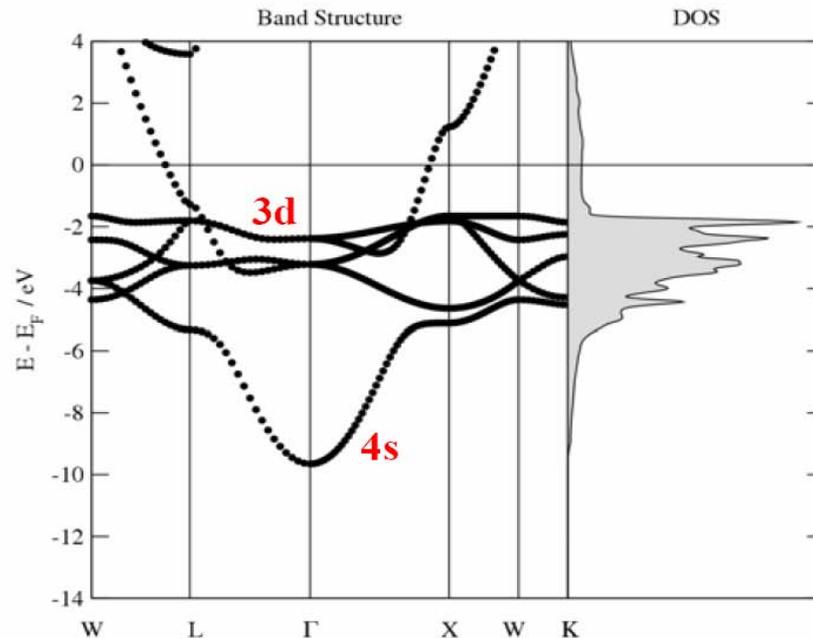
or that the zero-temperature susceptibility is

$$\chi = \frac{M}{H} = \mu_B^2 D(\epsilon_F) \quad (5)$$

- Copper is diamagnetic, since (a) its Fermi energy is close to the band edge [i.e.  $g(E_F)$  is small] and thus  $\chi_p$  is relatively small, and (b) copper has ten  $d$ -electrons (i.e.  $Z \approx 10$ ) orbiting on a fairly large radius, which results in a large  $\chi_{dia}$ .
- Also in bivalent metals (e.g. Be)  $g(E_F)$  is small  $\rightarrow$  they are diamagnetic
- In semiconductors, the valence bands are filled, i.e.  $g(E_F) = 0$   
 $\rightarrow$  semiconductors have no paramagnetic susceptibility and are diamagnetic

## Copper: Valence States

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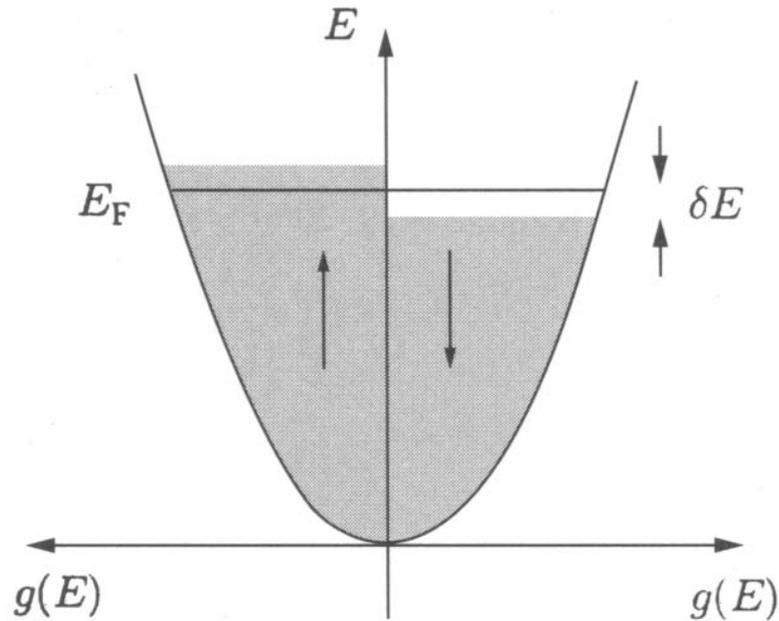
# Direct Exchange between delocalized Electrons

## Itinerant ferromagnetism

Spontaneously Split bands: e.g. Fe  $M = 2.2\mu_B/\text{f.u.}$  is non integer  
.... this is strong evidence for band ferromagnetism

**Mean field Model:** all spins feel the same exchange field  $\lambda M$  produced by all their neighbors, this exchange field can magnetize the electron gas spontaneously via the Pauli Paramagnetism, if  $\lambda$  and  $\chi_P$  are large enough.

Quantitative estimation: what is the condition that the system as a whole can save energy by becoming ferromagnetic ?



$$M = \mu_B (n_{\uparrow} - n_{\downarrow})$$

*moving  $D_e(E_F)\delta E/2$  electrons from spin down to spin up band*

kinetic energy change:  $\Delta E_{K.E.} = \frac{1}{2} D_e(E_F)(\delta E)^2$

exchange energy change:

$$\Delta E_{P.E.} = -\int_0^M \mu_0 (\lambda M') dM' = -\frac{1}{2} \mu_0 \lambda M^2 = -\frac{1}{2} \mu_0 \lambda \mu_B^2 (n_{\uparrow} - n_{\downarrow})^2$$

see Mizutani

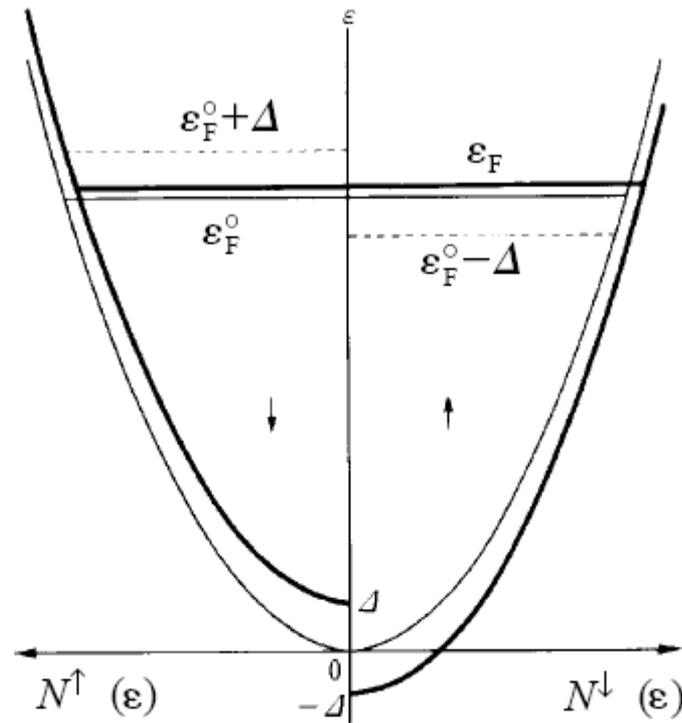


Figure 13.5. Splitting of spin-up and spin-down sub-bands due to the exchange energy. The Fermi level  $\epsilon_F^0$  without the exchange energy is shown by the thin line. The Fermi level is displaced to  $\epsilon_F^0 + \Delta$  and  $\epsilon_F^0 - \Delta$  in the respective bands due to the exchange energy. A new Fermi energy  $\epsilon_F$  is formed after charge transfer.

total energy change:

$$U \equiv \mu_0 \mu_B^2 \lambda$$

$$n_{\uparrow} - n_{\downarrow} = D_e(E_F) \delta E$$

$$\Rightarrow \Delta E = \Delta E_{K.E.} + \Delta E_{P.E.} = \frac{1}{2} D_e(E_F) (\delta E)^2 (1 - U D_e(E_F))$$

there is an energy gain by spontaneous magnetization, if

$$U D_e(E_F) \geq 1$$

... **Coulomb Effects** must be strong and **density of states** at the Fermi energy must be large in order to get spontaneous **ferromagnetism** in metals.

### Stoner Criterion



Edmund C.  
Stoner  
(1899-1968)

*The interaction energy (electronic correlations) dominates the kinetic energy, which leads to a magnetic ordering in metals*

from Mizutani

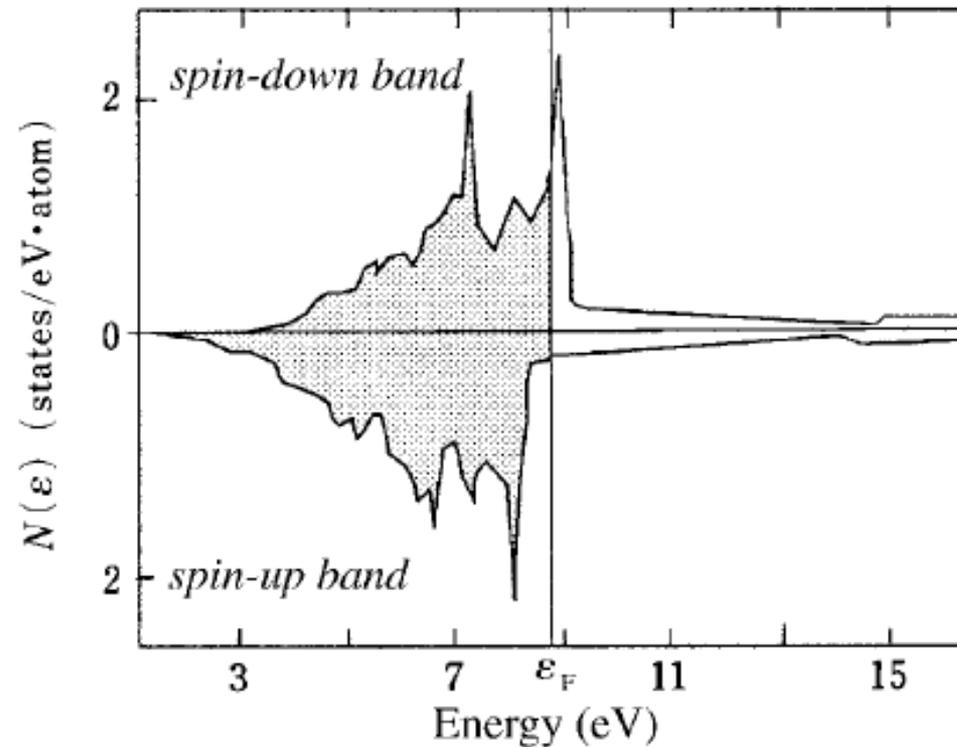
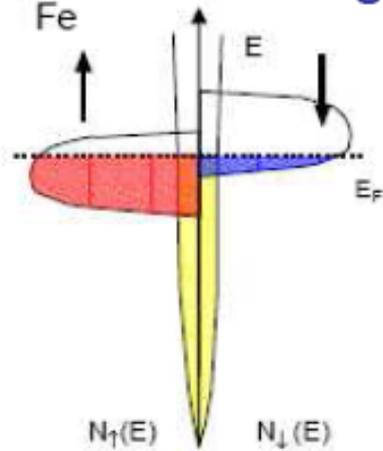
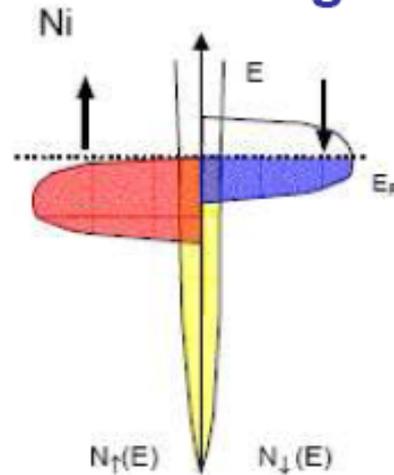


Figure 13.6. Valence band in the ferromagnetic state of pure Ni. The spin-up band is shifted to lower binding energies relative to the spin-down band due to the exchange energy. [D.A. Papaconstantopoulos, *Handbook of the Band Structure of Elemental Solids* (Plenum Press, 1986)]

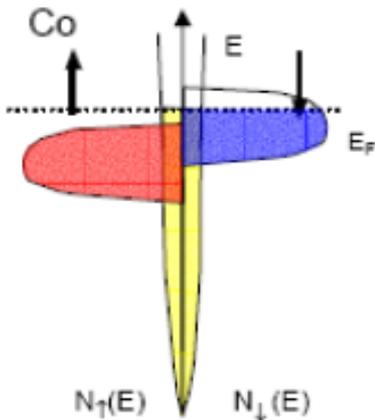
### Fe – weak ferromagnetic



### Ni – strong ferromagnetic



### Co – strong ferromagnetic



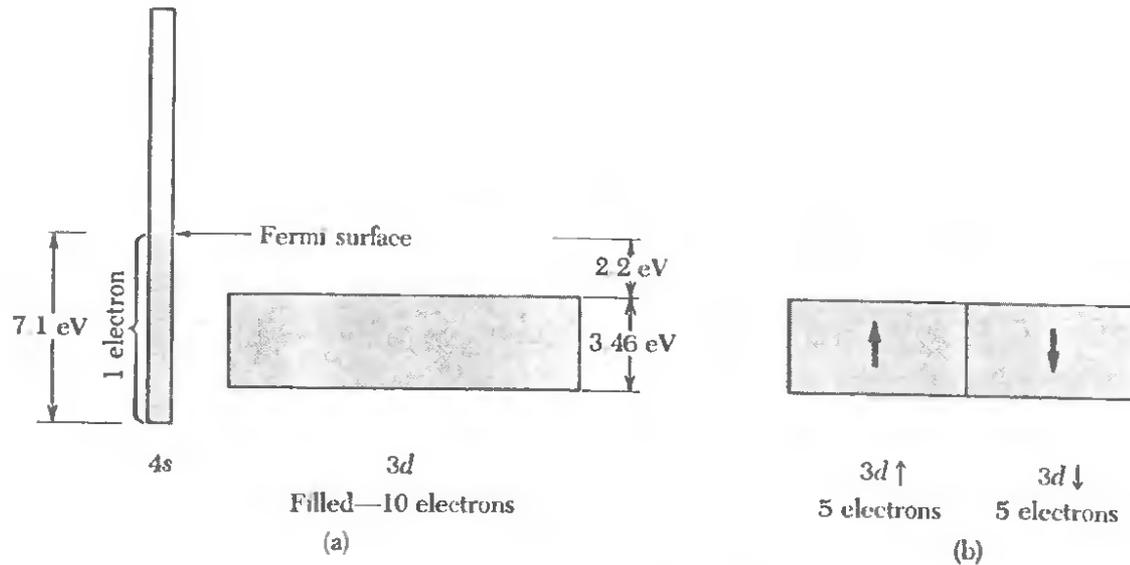
#### Magnetisation/atom

Fe:  $2.2 \mu_B$   
 Co:  $1.6 \mu_B$   
 Ni:  $0.6 \mu_B$

#### polarization

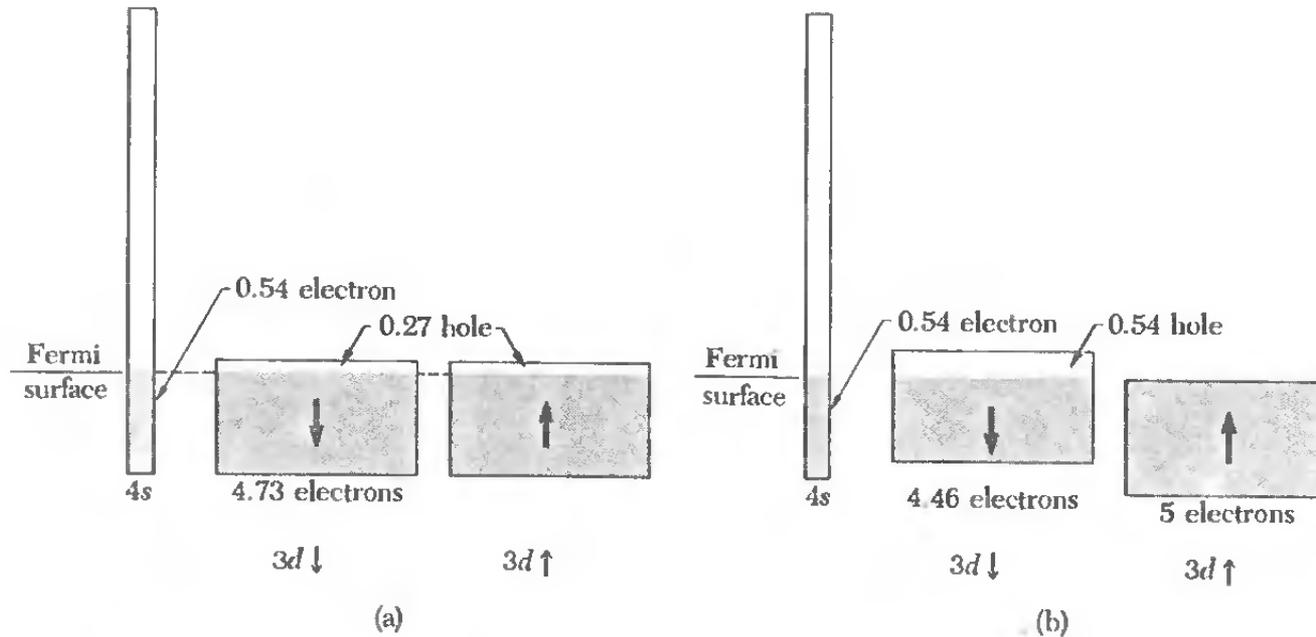
$P_{Fe}$ : 0.44  
 $P_{Co}$ : 0.45  
 $P_{Ni}$ : 0.33  
 ↑

$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}}$$



**Figure 6a** Schematic relationship of 4s and 3d bands in metallic copper. The 3d band holds 10 electrons per atom and is filled in copper. The 4s band can hold two electrons per atom; it is shown half-filled, as copper has one valence electron outside the filled 3d shell.

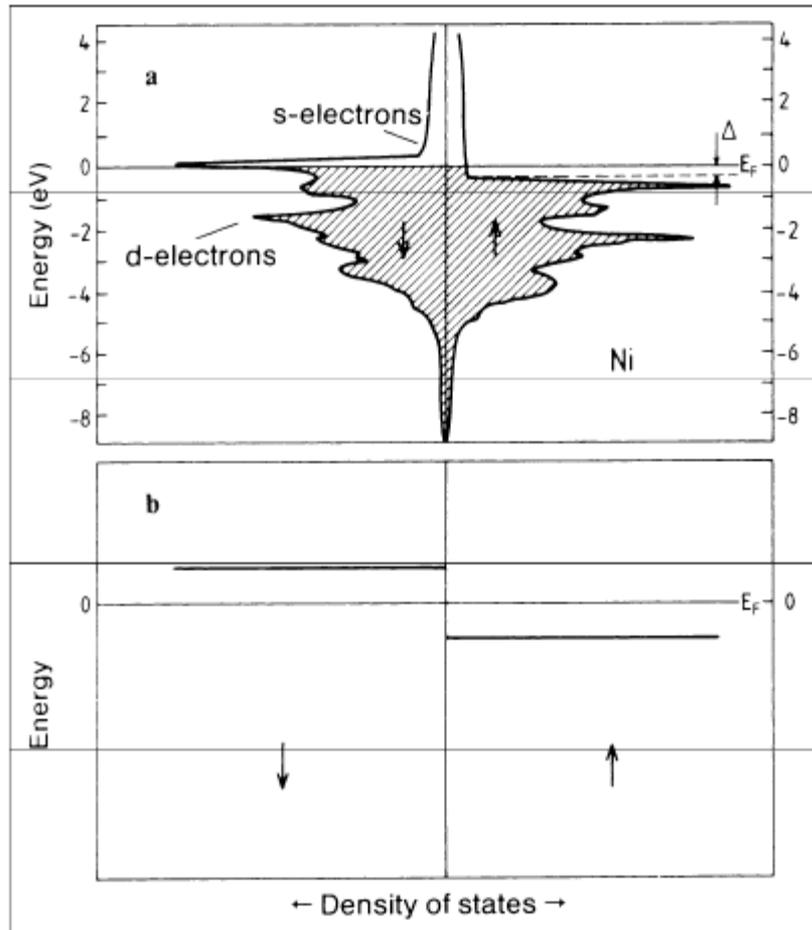
**Figure 6b** The filled 3d band of copper shown as two separate sub-bands of opposite electron spin orientation, each band holding five electrons. With both sub-bands filled as shown, the net spin (and hence the net magnetization) of the d band is zero.



**Figure 7a** Band relationships in nickel above the Curie temperature. The net magnetic moment is zero, as there are equal numbers of holes in both  $3d \downarrow$  and  $3d \uparrow$  bands.

**Figure 7b** Schematic relationship of bands in nickel at absolute zero. The energies of the  $3d \uparrow$  and  $3d \downarrow$  sub-bands are separated by an exchange interaction. The  $3d \uparrow$  band is filled; the  $3d \downarrow$  band contains 4.46 electrons and 0.54 hole. The 4s band is usually thought to contain approximately equal numbers of electrons in both spin directions, and so we have not troubled to divide it into sub-bands. The net magnetic moment of 0.54  $\mu_B$  per atom arises from the excess population of the  $3d \uparrow$  band over the  $3d \downarrow$  band. It is often convenient to speak of the magnetization as arising from the 0.54 hole in the  $3d \downarrow$  band.

kittel



$$\left| I \frac{D(E_F)}{2n} = I \tilde{D}(E_F) \right| > 1$$

Figure shows the calculated valence band structure for the spin-up and spin-down electrons in ferromagnetic Ni metal. It can be seen that the spin-up band is shifted to higher binding energies relative to the spin-down band because of the exchange energy. The Fermi level is determined by fitting a total of 10 electrons per atom into the hybridized 3d and 4s bands. It is clear that the 3d spin-up band is fully filled by electrons while the Fermi level falls in the middle of the 3d spin-down band, leaving holes in this sub-band. The number of holes per atom is calculated to be  $\sim 0.6$ . This is obviously proportional to the magnetization of pure Ni metal and is consistent with the observed non-integer value

$\text{Ni}_{1-x}\text{Cu}_x$   
average electron concentration

(Cu: [Ar] 3d<sup>10</sup> 4s<sup>1</sup>)

$$11x + 10(1 - x) = 10 + x$$

M=0, for x = 0.6

the Ni 3d spin-down band possessing 0.6 holes per atom will be filled when x=0.6

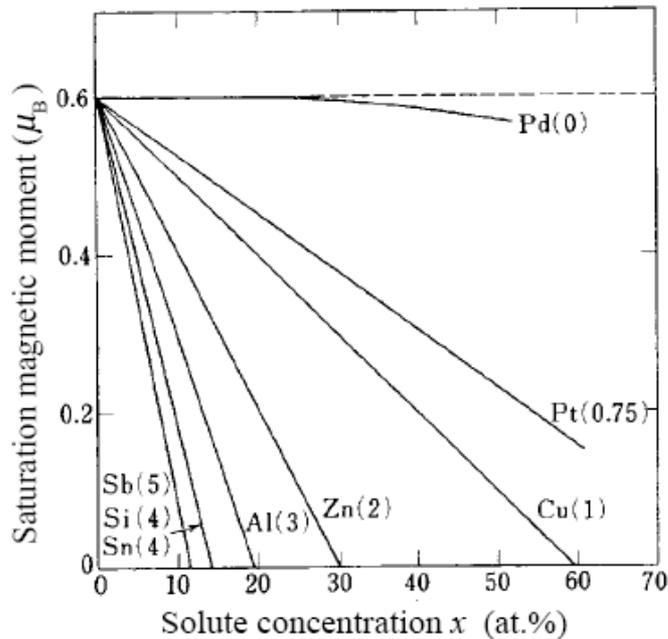
$\text{Ni}_{1-x}\text{Zn}_x$

(Zn: [Ar] 3d<sup>10</sup> 4s<sup>2</sup>)

$$12x + 10(1 - x) = 10 + 2x$$

X= 0.3

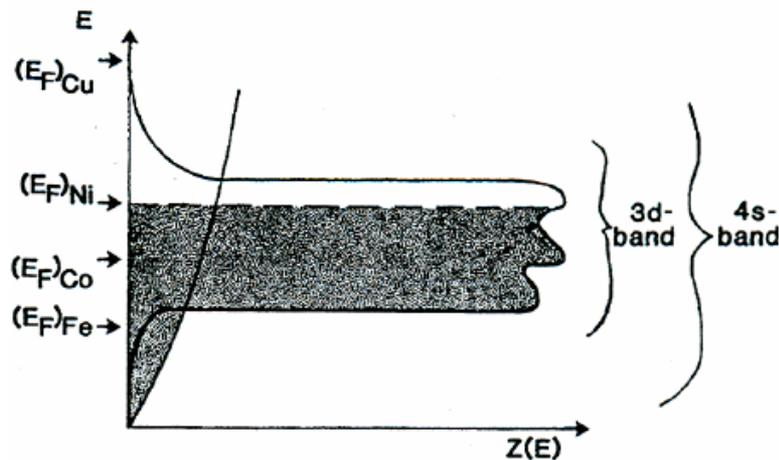
Hence, the Ni 3d spin-down band will be filled at x=0.3



Mizutani

Figure 13.7. Solute concentration dependence of saturation magnetic moment in  $\text{Ni}_{100-x}\text{M}_x$  alloys. The number in parentheses indicates the number of valence electrons per atom. [A. H. Morrish, *The Physical Principles of Magnetism* John Wiley & Sons, Inc., 1965]

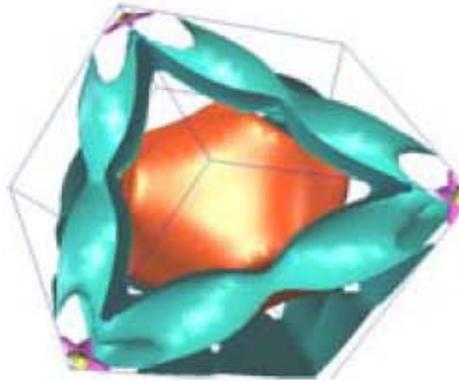
The ferromagnetic materials iron, cobalt, and nickel are characterized by unfilled  $d$ -bands which overlap with the next higher  $s$ -band.



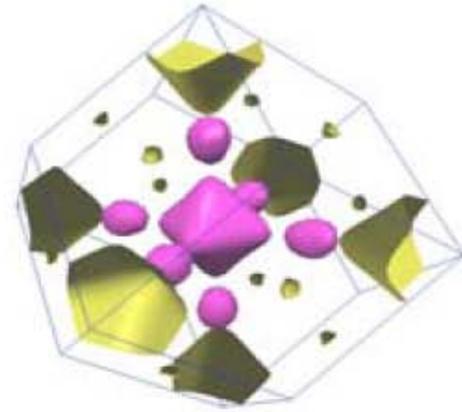
Density of states at  $E_F$  are relatively large for Fe, Co, and Ni  $\rightarrow$  only small amount of energy is needed to transfer considerable amount of electrons from spin-down to spin-up; in ferromagnets, this transfer occurs spontaneously in zero-field (in paramagnets, an external field is needed)

# Fermi Surface: Magnetic Metals

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**Fe up**



**Fe down**

**web page: <http://www.phys.ufl.edu/fermisurface/>**

from  
Mizutani

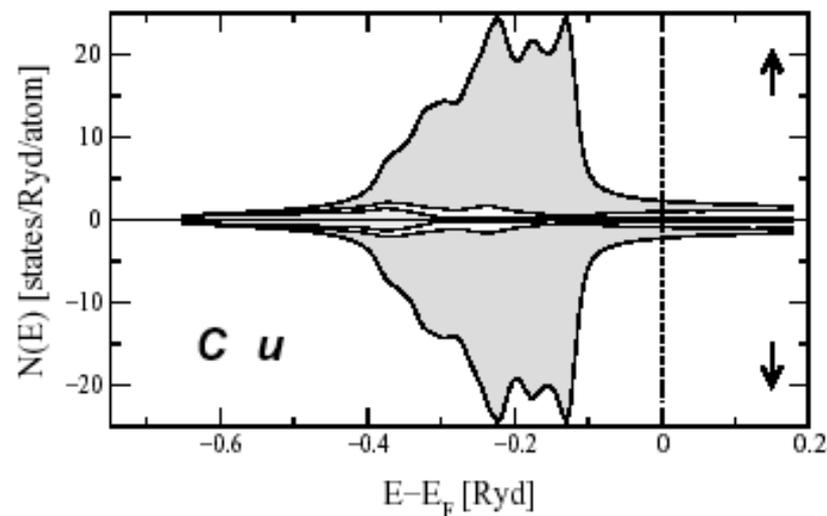
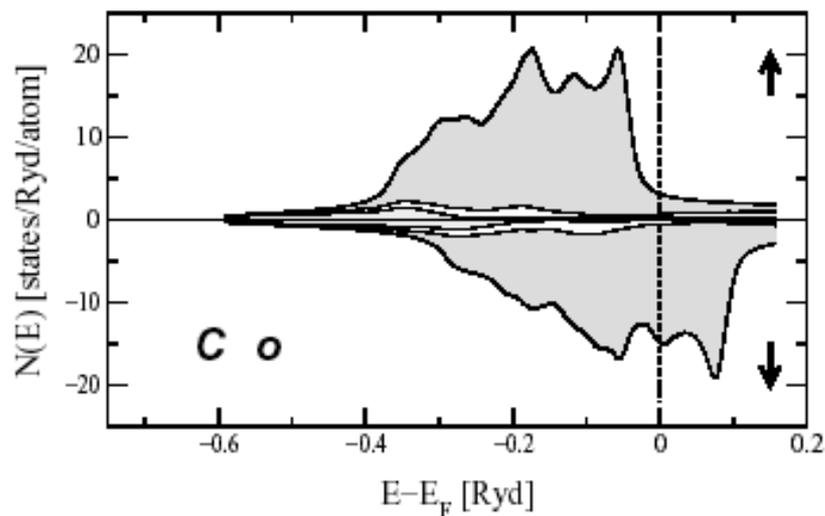


Figure 2.6: Spin-projected densities of states for Co and Cu; the differently shaded grey areas indicate the amount of  $s$ ,  $p$  and  $d$  states.

Estimate of magnetic moments for ferromagnetic metals:

Mn:  $3d^5 4s^1$  → antiferromagnetic

Fe:  $3d^6 4s^2$ ;  $3d$ -band filled with 7.78 electrons →  $\mu_m = 2.22 \mu_B$

Co:  $3d^7 4s^2$ ;  $3d$ -band filled with ca. 8.28 electrons →  $\mu_m = 1.72 \mu_B$

Ni:  $3d^8 4s^2$ ; overlap of  $s$ - and  $d$ -bands →  $3d$ -band filled with 9.4 electrons →  $\mu_m = 0.6 \mu_B$

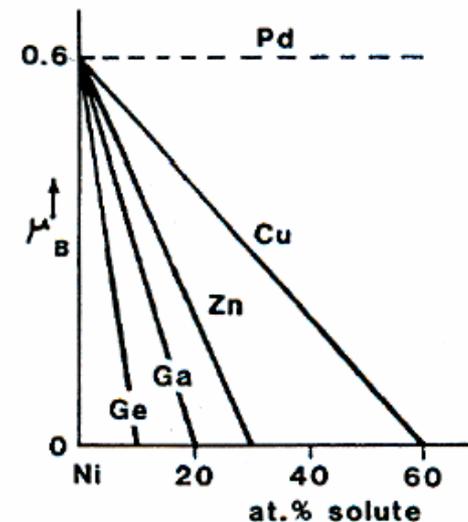
Cu:  $3d^{10} 4s^1$  → diamagnetic

Magnetic behavior of Ni-based alloys:

Ni–Cu: extra electron of Cu fills the  $d$ -band of Ni →  $\mu_B$  is reduced (at 60% Cu,  $\mu_B = 0$ )

Ni–Zn: two extra electrons →  $\mu_B$  is reduced (at 30% Zn,  $\mu_B = 0$ )

Ni–Pd: Pd ( $4d^{10}$ ) has same number of valence electrons → no immediate change of  $\mu_B$



# Experimental techniques and principles of electronic structure-related phenomena

de Haas–van Alphen effect

Positron annihilation

Compton scattering effect

Photoemission spectroscopy

Inverse photoemission spectroscopy

Angular-resolved photoemission spectroscopy (ARPES)

Soft x-ray spectroscopy

Electron-energy-loss spectroscopy (EELS)

Optical reflection and absorption spectra

see Mizutani

INTRODUCTION TO THE ELECTRON  
THEORY OF METALS

UICHIRO MIZUTANI

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