

9. ENERGY BAND THEORY.

Aim: To understand the effects of the periodic potential in crystalline materials on the electronic states and electron dynamics. We also treat the physical basis of the difference between insulators, semiconductors and metals.

In the previous Lecture we treated the outer electrons as freely moving in a box potential. In reality, however, the periodicity of the crystal leads to a **periodic potential**. The potential is lower close to the positive ions on the lattice (and in some cases basis) positions. The electrons experience a potential with the same periodicity as the lattice. This leads to some important consequences:

1. The reciprocal space can be divided into Brillouin zones. Physical properties related to the periodic potential can conveniently be described in **the first Brillouin zone**.
2. The continuous $\varepsilon(\mathbf{k})$ curve is split up into several energy bands separated by energy gaps.

We give first a general treatment of the Schrödinger equation in a periodic potential and then we consider a few solvable approximate models.

1. Wave equation in a periodic potential (K p. 169-174).

The Schrödinger equation is:

$$[-(\hbar^2/4\pi^2 2m) \nabla^2 + U(\mathbf{r})] \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

We use the independent electron approximation: The equation describes the motion of one electron in the potential $U(\mathbf{r})$.

We expand the periodic potential in a Fourier series over the reciprocal lattice vectors \mathbf{G} .

The wave function can be written as a superposition of plane waves with all wave vectors \mathbf{k} , that are allowed by the periodic boundary conditions. These allowed \mathbf{k} -values are the same as in the case of the free electron model.

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} c_{\mathbf{k}} \exp(i\mathbf{k}\mathbf{r}).$$

Substitution of these two series in the Schrödinger equation, transforms it to an infinite set of algebraic equations, Kittel eq. 27, p. 172. It is called **the central equation**. (Note that in the derivation in Kittel, \mathbf{k} and \mathbf{G} can be replaced with the corresponding vectors and $\mathbf{x} \rightarrow \mathbf{r}$.) We have one set of equations for each allowed value of \mathbf{k} . For each \mathbf{k} -state, the wave function is determined only by the coefficients $c_{\mathbf{k}-\mathbf{G}}$. We write

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} \exp(i(\mathbf{k}-\mathbf{G})\mathbf{r}),$$

and take \mathbf{k} to be within the first Brillouin zone by convention. To specify the state all the c 's have to be determined in principle, but in practise a small number of $c_{\mathbf{k}-\mathbf{G}}$ will often be sufficient.

The energy eigenvalues are obtained from the determinant of the matrix of the coefficients multiplying the c 's. For a given \mathbf{k} , each root lies in a different **energy band**.

Some important properties of the wave function follows from this representation:

1. **Bloch's theorem:** The wave function can be written as a plane wave multiplied with a function with the periodicity of the lattice. (K. p. 173)
2. The wave function is periodic in reciprocal space: From the series expansion for $\psi_{\mathbf{k}}(\mathbf{r})$, it can be easily shown that $\psi_{\mathbf{k}-\mathbf{G}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r})$. This means that we only need the solution in the first Brillouin zone, higher zones will give equivalent information (but motion in higher zones is not unphysical as for phonons). Especially $\varepsilon(\mathbf{k}\pm\mathbf{G}) = \varepsilon(\mathbf{k})$.
3. In real space, under a lattice translation, the wave vector is multiplied with the phase factor $\exp(i\mathbf{k}\mathbf{T})$.
4. The quantity $(\hbar/2\pi)\mathbf{k}$ is called the crystal momentum of the electron. It enters into conservation laws for collision processes, analogously to the case of phonons.

The periodicity of the energy and wavefunction in reciprocal space implies that they can be represented in different ways (**K p. 223-226**). Using the first zone only to depict the energy bands (the reduced zone scheme) is perhaps most common. In the extended zone scheme one energy band is assigned to each Brillouin zone. In the periodic zone scheme all bands are drawn in every zone.

2. The empty lattice (K p. 176-177).

This is the simplest approximation that still gives a discernible band structure. We assume that the periodic potential $U \rightarrow 0$, but retain the periodicity of the lattice and reciprocal space. In this limit the free electron model gives the relation $\varepsilon(\mathbf{k}) \sim k^2$. However, because of the periodicity, now only k -values in the first Brillouin zone should be used. Hence the part of the "free electron parabola" $\varepsilon(\mathbf{k})$, that is outside the first zone should be translated by an appropriate reciprocal lattice vector into the first zone. We obtain an infinite set of $\varepsilon(\mathbf{k})$ -contours in the first zone. In the case of a nonzero U , they will give rise to the different energy bands in the solid.

The procedure is given by Kittel, p. 176. $\varepsilon(\mathbf{k})$ is determined first for $\mathbf{G}=0$ and then using all the reciprocal lattice vectors pertaining to the structure under study. Each \mathbf{G} will give rise to a different energy band, however some may be degenerate (have the same energy). The energy bands can be drawn in different directions in \mathbf{k} -space. The direction is specified by $\mathbf{k} = 2\pi/a(x, y, z)$, where the numbers within parenthesis are the x -, y - and z -coordinates of the wave vector (We assume a cubic symmetry of the coordinate system). The reciprocal lattice vector can be written in terms of the Miller indices (Note that, as used previously for the cubic structures, they refer to the cubic unit cell.) as:

$$\mathbf{G} = 2\pi/a (h, k, l).$$

Then the energy is immediately obtained as:

$$\varepsilon(\mathbf{k}) = (\hbar^2/2ma^2) [(x+h)^2 + (y+k)^2 + (z+l)^2].$$

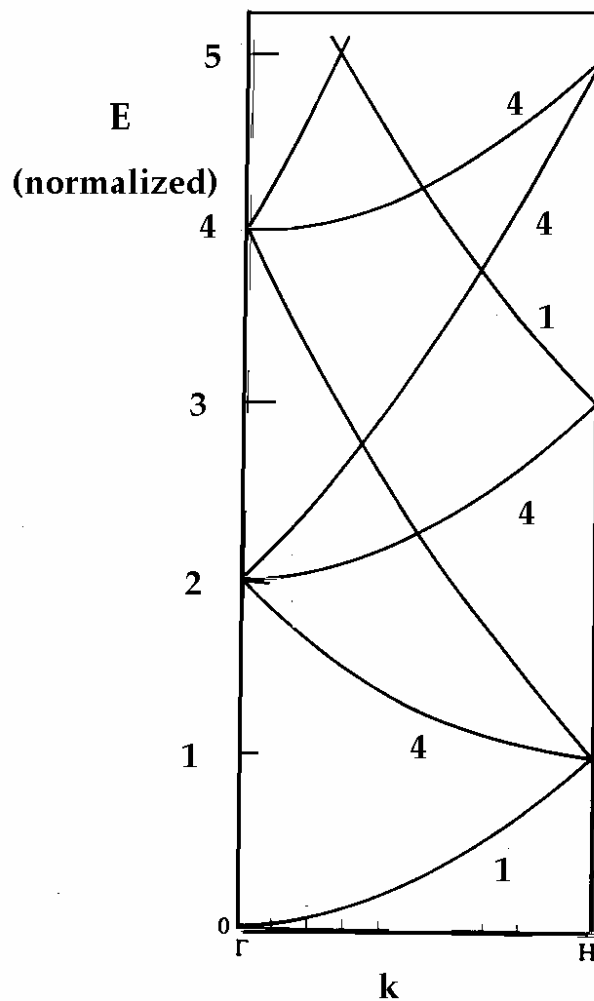
In many cases we normalize the energy by dividing with the factor $(\hbar^2/2ma^2)$.

Ex: Consider the bcc lattice in the $[100]$ -direction. Hence $\mathbf{k} = 2\pi/a (1,0,0)$. To obtain the energy bands take $\mathbf{G}=0$ and $\mathbf{G} = 2\pi/a (h,k,l)$, with (h,k,l) equal to $\{110\}$, $\{200\}$and so on. Use ALL \mathbf{G} 's of all the types, e.g. those of type 110 include (110) , (011) , (101) and all combinations with one or two negative indices. There are thus 12 different \mathbf{G} 's of type 110! Do the calculation and check the figure below! Remember to include also the negative indices!

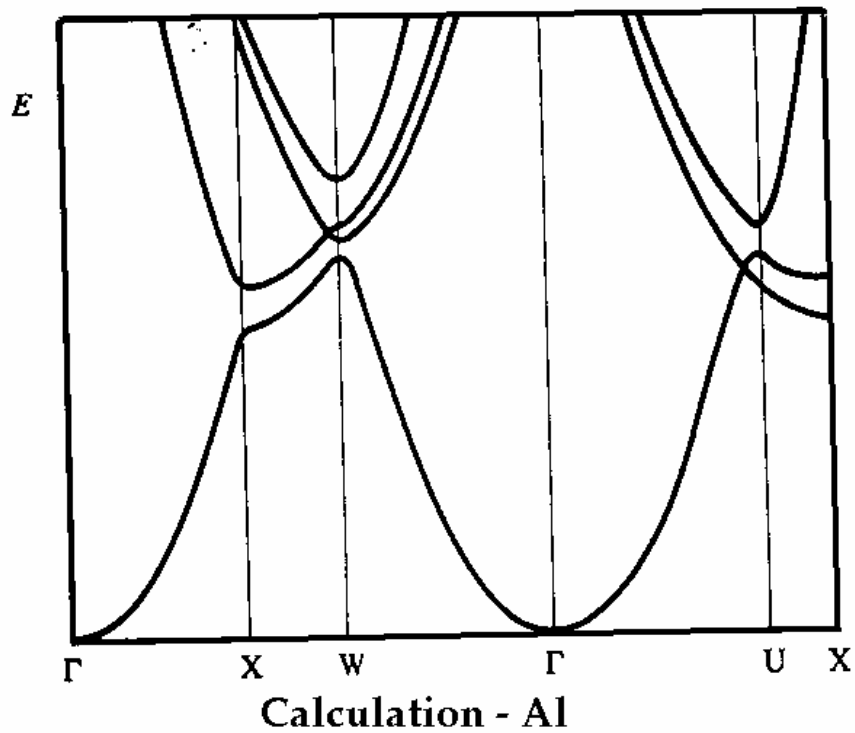
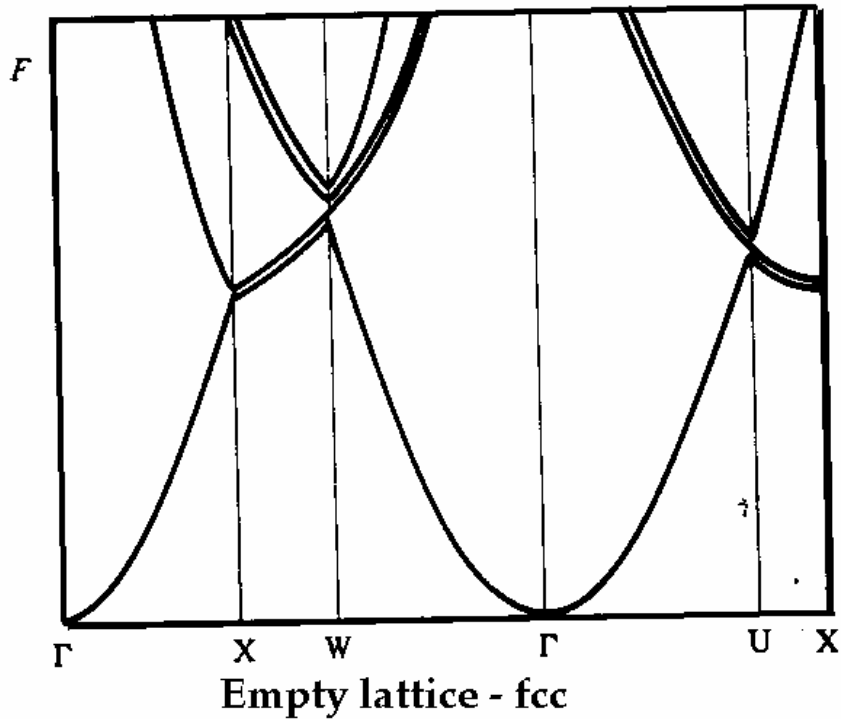
The Empty lattice

bcc structure - $[100]$ direction

degeneracy



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.



3. Nearly free electron model (K p. 164-167, 177-180).

This is the case of a weak periodic potential. The model is good for the simple metals. However, it is also instructive to see how the periodic potential affects the bandstructure, as compared to the empty lattice. First we consider some simple one-dimensional arguments. We write the periodic potential as

$$U = -U_0 + U_1 \cos(2\pi x/a), \text{ and consider the limiting cases.}$$

1. For small k , the wavelength is much larger than $2a$, The wave will not sense the periodicity in the potential, but only the average value. The free electron model is a good approximation here.

2. We now consider large values of k close to the boundary of the Brillouin zone. Here $k = \pm\pi/a = \pm G/2$ and Bragg reflection takes place. The wave function is the sum of waves of equal amplitude, moving to positive and negative x , i.e. a **standing wave**. This can also be seen by keeping only the terms including k and $k-G$ in the series expansion for $\psi_k(x)$. There are two possible linear combinations leading to standing waves and hence two solutions at the zone boundary. For the "+" solution, the electron density is largest at the ion position; the "-" solution has the largest electron density between the ions. Hence the former solution will have a lower energy than the latter. An **energy gap**, equal to U_1 , appears at all zone boundaries in the solid.

We now make a more formal treatment of the energy bands close to the zone boundary. We start with the central equation connecting all Fourier coefficients $c(\mathbf{k}-\mathbf{G})$. The equation system has to be truncated in order to make it solvable. We make the approximations:

1. Only one reciprocal lattice vector, \mathbf{g} , is considered. The potential is described by the Fourier coefficients $U_{\mathbf{g}} = U_{-\mathbf{g}} = U$. A block of the determinant giving the energy eigenvalues is shown in K, p. 174.

2. At the zone boundary we neglect all Fourier coefficients of the wave function except $c(G/2)$ and $c(-G/2)$. This gives us an easily solvable system of two equations. The energies are given by K eq. (47), p. 178.

3. Close to the zone boundary we also keep only two coefficients in the expansion of the wavefunction (pertaining to k and $k-G$). The solution is also here readily carried out and the energy bands are given by K. eq. (50). The energy bands and coefficients can be computed, see for example K p.179-180.

4. Electrons in bonds: The tight binding model (K p. 232-235).

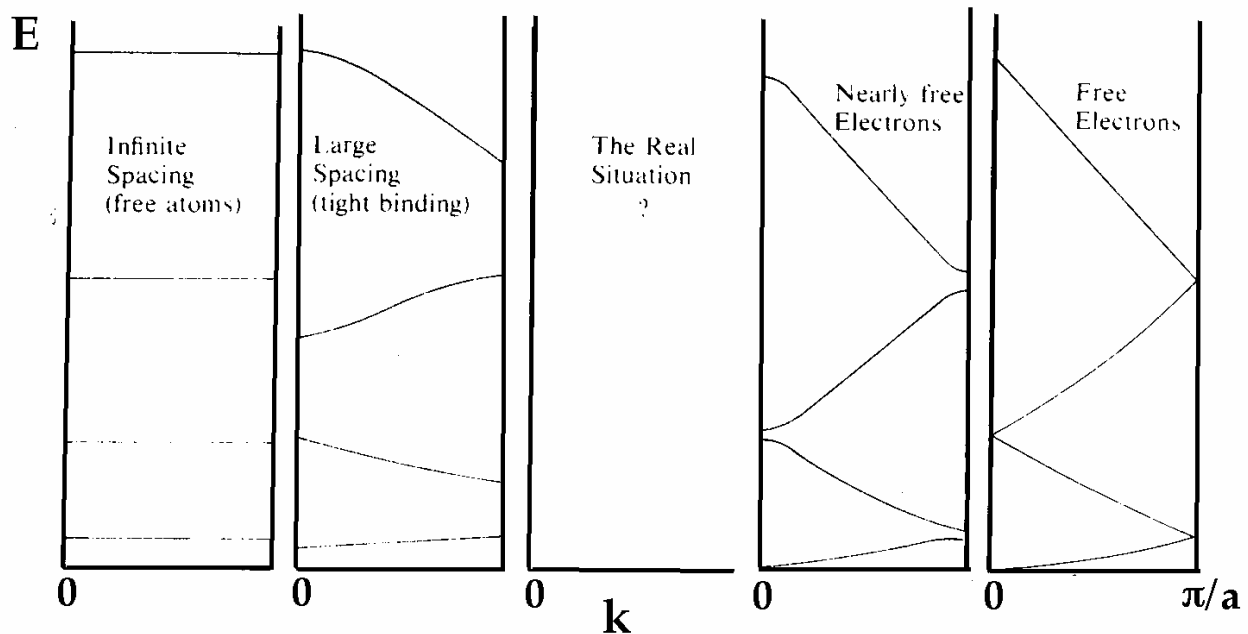
The electrons in insulators and semiconductors participate in chemical bonds. The situation is far from nearly free electrons and a different model is needed. The tight binding model starts from the energy levels of single atoms and considers how these are broadened by the overlap of the atomic electron distributions in solids. Besides being applicable to materials with covalent bonds, the model is also useful for the d-electrons in transition metals and f-electrons in the rare earths. The tight binding bands are generally narrower and flatter than the free electron-like ones.

In the case of two atoms, the atomic energy level is split into bonding and antibonding linear combinations. For a large number, N , atoms we obtain N closely spaced orbitals, giving rise to an energy band.

We treat a simple model valid for s-electrons to illustrate the physics involved. The wave function $\psi_{\mathbf{k}}(\mathbf{r})$ is written as a linear combination of atomic orbitals. The coefficients are chosen in order to give the Bloch form. The energy is obtained from the matrix elements of the Hamiltonian, by usual quantum mechanical procedures. There are two contributions: The interatomic one and the overlap energy arising from the overlap of electron distributions on neighbouring atoms. The energy as a function of \mathbf{k} is given explicitly for the cubic structures (K p.235).

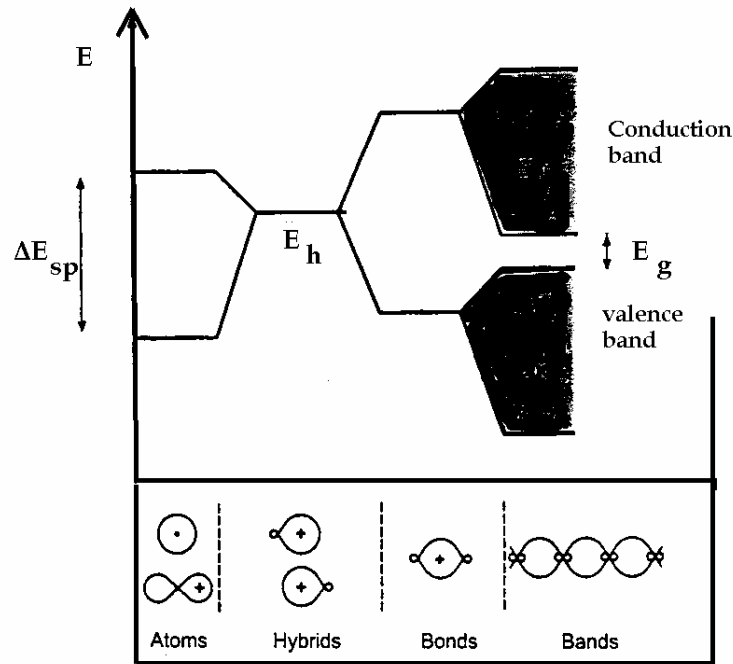
The various models and types of energy bands from the case of free atoms to the case of free electrons in metals are illustrated in the scheme below:

Schematic energy bands within different models and approximations



Hybridisation: In solids it may be energetically favorable that the states in a single atom are mixed or hybridized before giving rise to energy bands (after Elliott).

1. Hybrid orbitals are constructed as linear combinations of atomic states belonging to the same atom. For example as combinations of s- and p-orbitals.
2. The overlap between orbitals on neighboring atoms lead to "bonding" and "antibonding" bands.



The most famous example concerns the elements with four valence electrons (one s and three p), i.e. C (diamond), Si, Ge. In these materials the atomic orbitals are hybridized and form sp^3 hybrids. The overlap of orbitals lead to bonding and antibonding combinations which become bands when the number of atoms becomes large. If the overlap is not large enough, a band gap exists between the "antibonding" and "bonding" bands. In the group IV elements, the lower band is completely filled with four electrons per atom and the upper one is empty. Hence this is the origin of the semiconducting nature of these elements.

5. Metals and Insulators (K p. 180-182).

From the periodic boundary conditions we obtain the allowed values of k . In one dimension $k = n \frac{2\pi}{L}$, where n is an integer $\leq N/2$ and $> -N/2$. In three dimensions we have the same condition on the x-, y- and z- components of \mathbf{k} . If $L = Na$, then the number of primitive cells is N^3 i.e. equal to the number of k -states in the first Brillouin zone. Taking into account the electron spin the number of electrons is twice the number of k -states. Hence, two electrons per primitive cell go into each energy band.

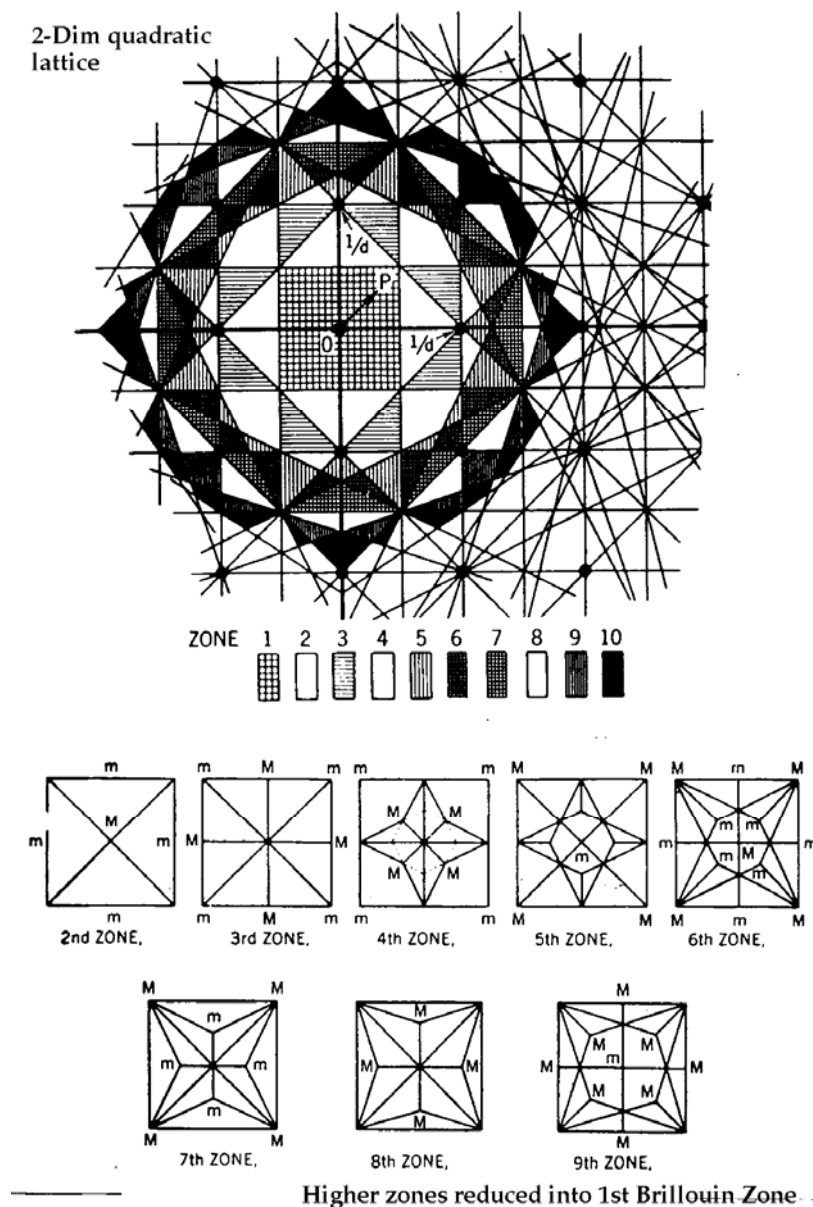
Metals have a partially filled upper band. This is called the **conduction band**. Insulators and semiconductors have a completely filled **valence band** and an empty conduction band.

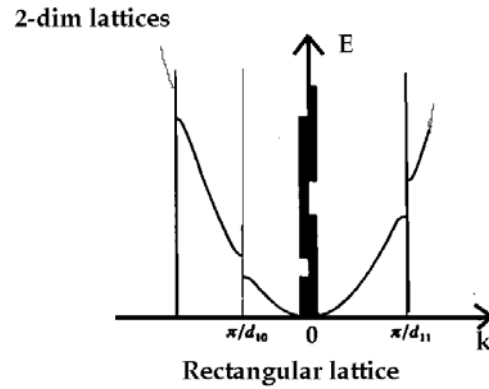
In one dimension compounds with odd number of outer electrons are metals, and those with even number are insulators. This is not so in higher dimensions since: a) Bands in different directions in the Brillouin zone may overlap in energy and b) hence more than one band may be partly filled (see Kittel p. 181).

Example: Two-dimensional quadratic lattice. The reciprocal lattice is also quadratic with lattice constant $2\pi/a$. The first Brillouin zone is easily found but the higher zones form a complex pattern in k-space, as seen in the first figure below.

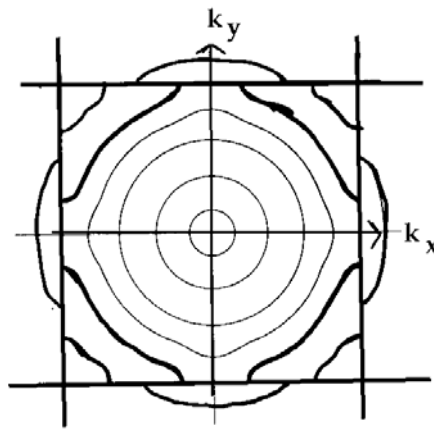
The second figure (after Myers) shows that bands in different directions overlap. The energy bands in the edge and diagonal directions in the first Brillouin zone are shown.

When depicting constant energy contours in k-space, we often use the extended zone scheme, with one band of electron states in each zone. Hence the second band occurs in the second Brillouin zone and so on. In this representation, there are two electrons per primitive cell in each zone. In the free electron model these contours are circular. This is so also here for small values of k. However, the band gaps at the zone boundaries will distort the contours close to them. This is illustrated close to the boundary between the first and second zone in the lower part of the second figure.





Constant energy contours in reciprocal space



The band gaps distort the Fermi sphere at the zone boundaries

In **three dimensions** these features are qualitatively the same. We take Ω to be the volume of the primitive cell. Then the volume of the Brillouin zone is $8\pi^3/\Omega$, and the density of k-states becomes

$$N(\mathbf{k}) = V / 4\pi^3,$$

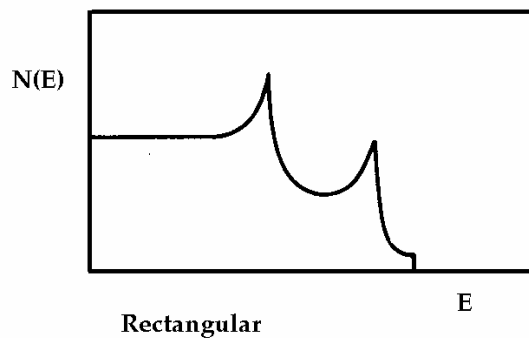
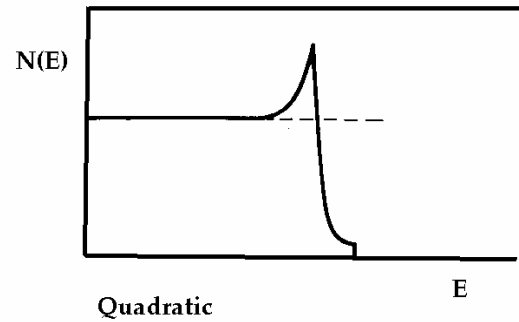
Where we have included a factor of two due to the electron spin.

The density of states can be obtained by an equation analogous to that derived for the phonon case:

$$D(\varepsilon) = (V / 4\pi^3) \int dS_\varepsilon / |\nabla_{\mathbf{k}} \varepsilon|.$$

When the denominator in the integral is zero, peaks due to van Hove singularities occur just as for the phonons. Flat bands give rise to a high density of states. It is thus higher close to the zone boundaries as illustrated for two dimensional lattices below (after Myers).

Density of states of two-dimensional lattices



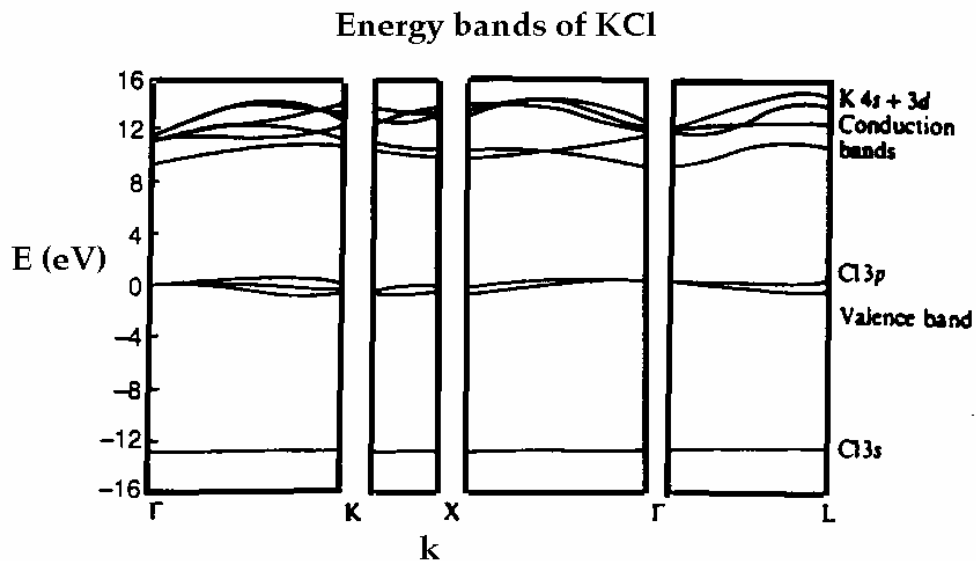
Link to applet on 2-dimensional lattice:

<http://buckminster.physics.sunysb.edu/intlearn/electrons/electrons.html>

6. Examples of real band structures.

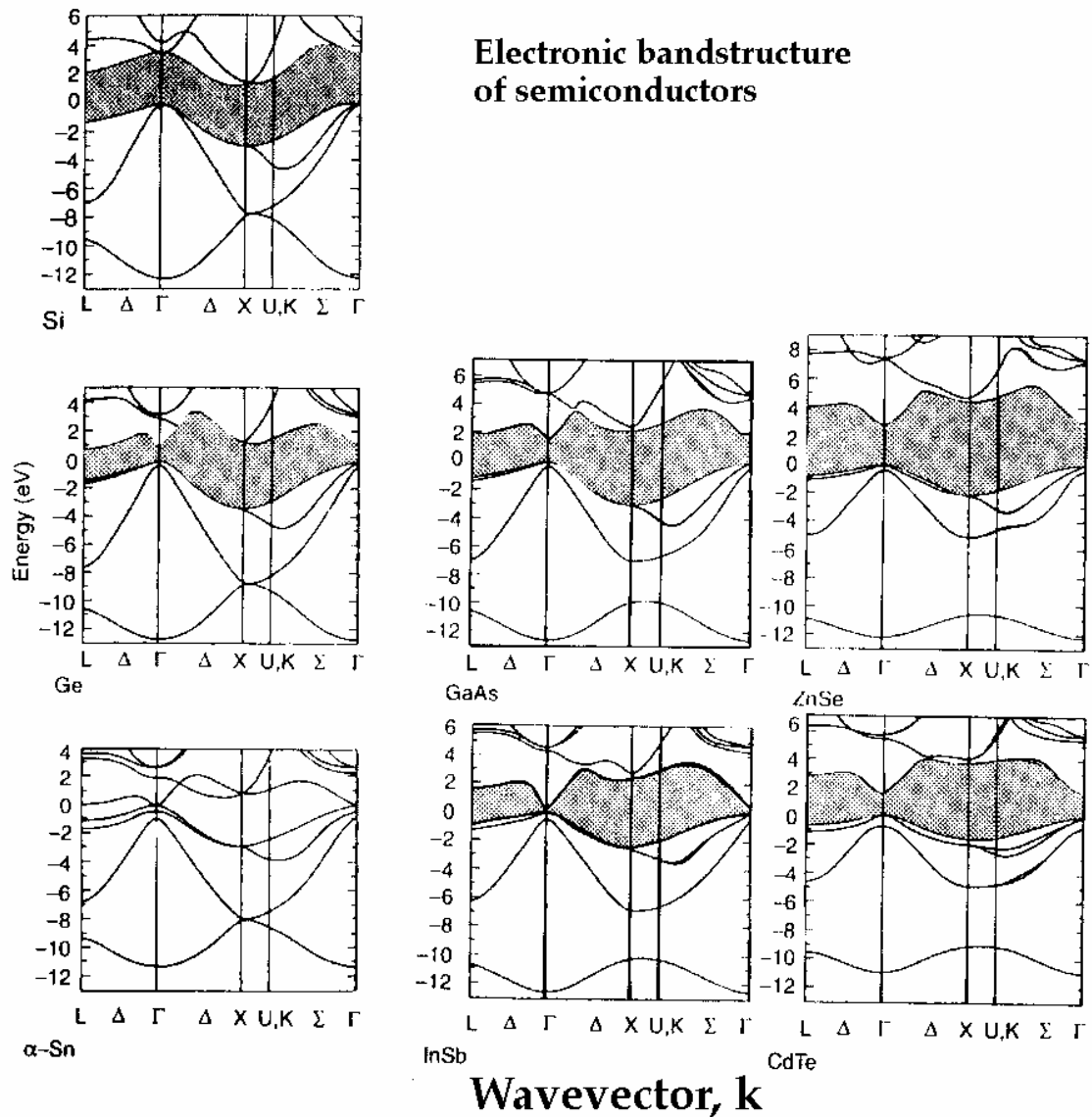
A. Insulators

We first depict the band structure of an ionic crystal, KCl (after Elliott). The bands are very narrow, almost like atomic ones. The band gap is large around 9 eV. For alkali halides they are generally in the range 7-14 eV.



B. Semiconductors

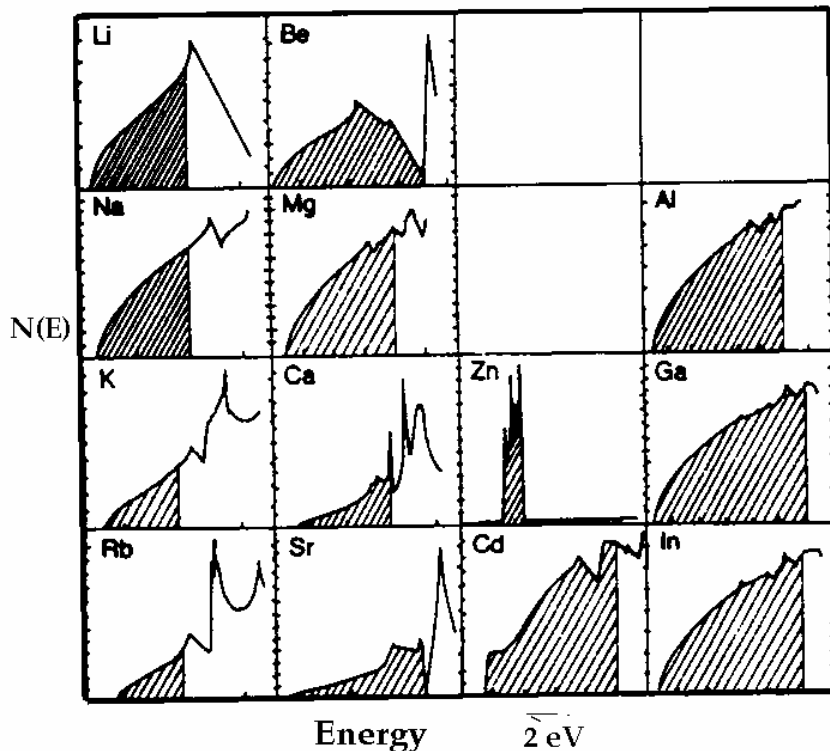
As an example of covalent crystals we treat semiconductors, where hybridisation occurs (we have tetrahedral sp^3 bonds), as mentioned above. The bands are quite wide. We compare the bands of the elemental semiconductors (pure covalent bonds) with those of the III-V and II-VI compounds with the same number of valence electrons. In the latter compounds there is an increasing amount of ionic binding. It is seen that the bandgap increases and the bandwidth becomes smaller as we move to the right in the figure (after Elliott). The materials become more like ionic compounds.



C. Metals

We review the bandstructure of metals, as well as the Fermi surface and the density of states. The most free-electron like metals are the alkali metals Na, K ... The density of states of some metals are plotted in the Figure below (after Elliott). Also Mg and the group III elements Al, Ga and In show a very free-electron like behaviour. Some departures occur in the third and fourth row of group I, IIA and IIB. These are due to the presence of d-electrons in the core. They are seen as

sharp peaks in the case of Zn. Deviations from free electron behavior are also seen for Li and Be. These are connected to the p states but we do not go into this further.



a) Monovalent metals.

These are the alkali metals with bcc structure. Due to the very free electron-like bandstructure of the occupied states, the Fermi surface is almost spherical. It lies completely within the first Brillouin zone. In Na the conduction band contains 3s-electrons.

b) Divalent metals.

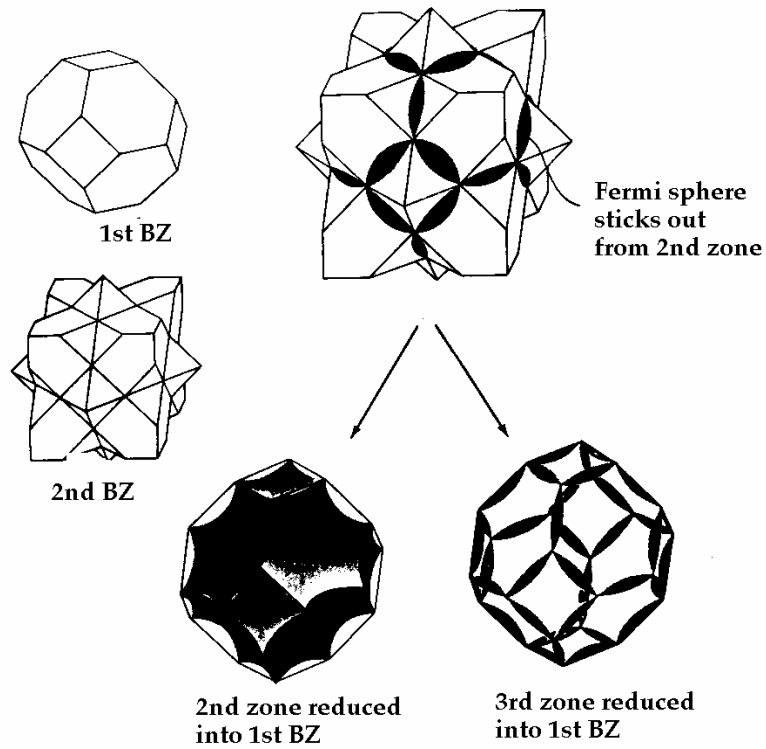
Here Mg is the most free electron like one. It has hcp structure, but fcc is exhibited by Ca and Sr. The Fermi surface is in both the first and second Brillouin zone. The volume enclosed by it is equal to the volume of a Brillouin zone.

c) Trivalent metals.

Al which has a fcc structure is the most common one. We have already seen the band structure of aluminium. Here the bands are very free electron-like (remember we compared with the empty lattice) and the conduction bands are partly filled. The Fermi surface is very complex and occurs in the second, third and fourth Brillouin zones. Remember that the reciprocal lattice of fcc is bcc.

The Fermi surface in the higher zones is conveniently pictured in the first zone after translation by suitable reciprocal lattice vectors. This is to say, we are going from the extended to the reduced zone scheme. The figures below illustrate this representation.

fcc lattice



Finally we show a figure of the Fermi surface in zones 1-4 for the di- and trivalent metals. Here we also use the representation in the first zone.

fcc

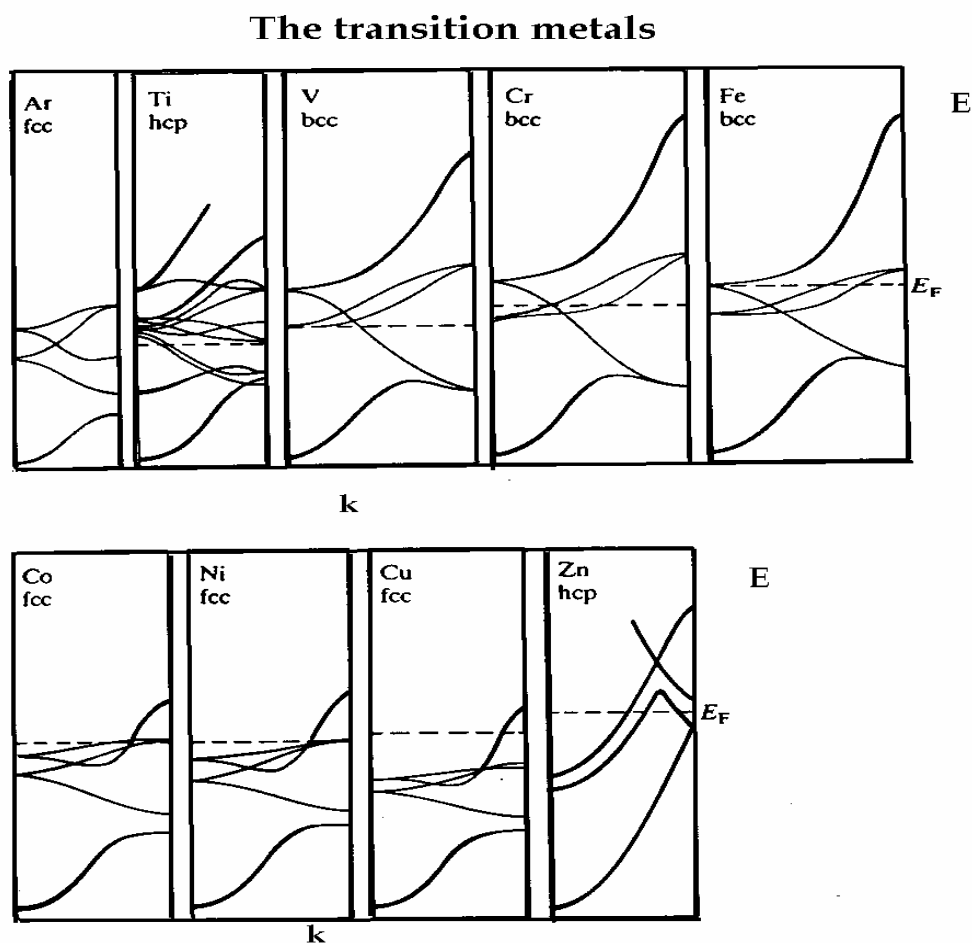
	First zone	Second zone	Third zone	Fourth zone
Valence 2			None	None
Valence 3	None			

d) Transition metals.

We concentrate on the first row of transition metals from Ti to Zn. The band-structure is schematically illustrated in the figure below (after Myers).

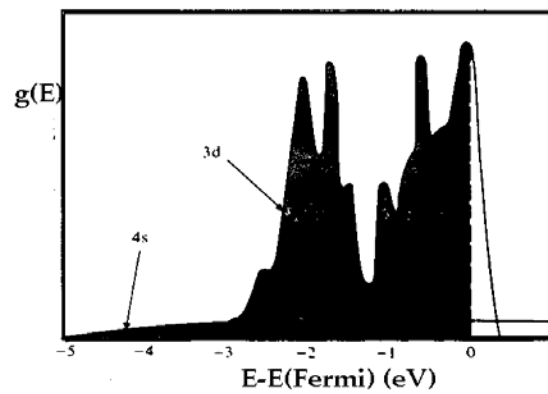
The outer electrons of these elements are 3d and 4s ones. Hence we have both 3d and 4s bands in the region around the Fermi level. The d-bands are the more narrow ones and have consequently a higher density of states. They can qualitatively be described by tight binding calculations. It is seen that the d-bands fall in energy as we proceed from Ti onwards in the figure. In the noble metals, the d-bands are completely filled and are situated a few eV below the Fermi level. Hence Cu, Ag and Au are very free electron like up to energies of 2-4 eV.

As for an example of the density of states, we depict it for Ni. Here the d- band is not completely filled. The d- band peaks are seen superimposed on a background from the 4s-states.



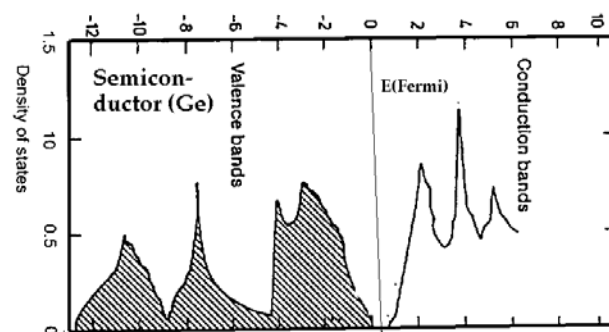
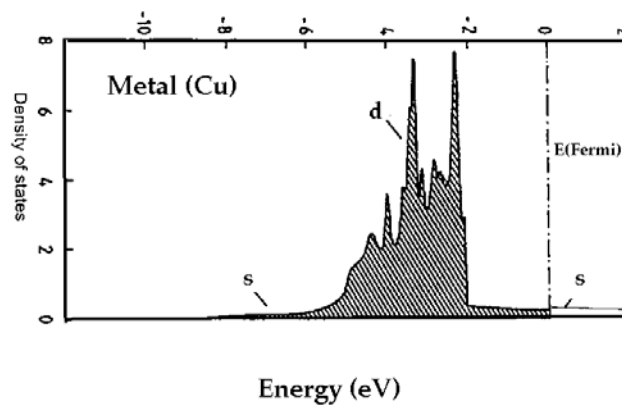
We finish with examples of the density of states (after Elliott). The last figure shows the DOS for the cases of a metal, Cu, and a semiconductor Ge. Copper has a free electron-like s-band, upon which d-bands are superimposed. The peaks are due to the d-bands. For Ge the valence and conduction bands are clearly seen.

Tight binding calculation for Ni



The electron density is high at the Fermi level because the 3d band is intersected by $E(\text{Fermi})$

Higher heat capacity than expected from 4s-electrons alone



Link to applet showing Fermi surfaces of metals:

<http://www.phy.tu-dresden.de/%7Efermisur/>