BAND STRUCTURE OF CRYSTALLINE SOLIDS
Metals, Insulators, Semiconductors

1) BASIC EQUATIONS

- Bloch Theorem and energy bands
- Case of the chain of atoms (1D)
- Tight binding (LCAO)

2) BAND STRUCTURES: 2D and 3D

- General Bloch theorem: Brillouin zones
- LCAO versus nearly free electrons

3) METALS, INSULATORS and SEMICONDUCTORS

- Filling of the energy bands
- Metals: partly filled band(s)
- Insulators: energy gaps
- Semiconductors: small energy gap

4) EXPERIMENTAL OBSERVATIONS OF THE BAND STRUCTURES

- Metals: Scanning tunelling microscopy (STM) and density of states
- Angular Resolved Photoemission Spectroscopy (ARPES)

H. Alloul, EPFL 23/04/09
1) Approximations are required

2) First assumption

The nuclei are fixed in space

3) Second assumption

Only an average of the coulomb interaction between electrons is taken into account in $V_{at}$

4) Approximate solutions obtained assuming tight binding of the electrons

A simple case: the linear chain

Periodic Hamiltonian: Bloch theorem
GENERAL HAMILTONIAN FOR A SOLID

\[ N_n \text{ nuclei charge } Z \text{, mass } M \]
\[ \text{located in } \mathbf{R}_i \text{ (momentum } \mathbf{P}_i) \]
\[ N_e \text{ electrons mass } m_0 \]
\[ \text{located in } \mathbf{r}_j \text{ (momentum } \mathbf{p}_j) \]

\[ H = \frac{1}{2M} \sum_{i=1}^{N_n} \mathbf{P}_i^2 + \frac{1}{2m_0} \sum_{j=1}^{N_e} \mathbf{p}_j^2 \]
\[ + \frac{Z^2}{2} \sum_{i,j=1, i \neq j}^{N_n} V_c(\mathbf{R}_i - \mathbf{R}_j) - Z \sum_{i=1}^{N_n} \sum_{j=1}^{N_e} V_c(\mathbf{R}_i - \mathbf{r}_j) \]
\[ + \frac{1}{2} \sum_{i,j=1, i \neq j}^{N_e} V_c(\mathbf{r}_i - \mathbf{r}_j) \]

Kinetic energies

nuclei-nuclei
nuclei-electrons

coulomb interactions

electrons-electrons

\[ V_c(r) = \frac{e^2}{4\pi\varepsilon_0 |r|} \]

\[ N_n \approx 10^{23}; N_e \approx Z \times 10^{23} \]

Impossible to resolve

Approximations are required!!

Analytic: Hydrogen atom only
Computer: about ten interacting particles

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GENERAL HAMILTONIAN FOR A SOLID

First approximation (Born-Oppenheimer)

The nuclei are fixed in space

\( R_i \) and \( P_j \) are parameters in the hamiltonian

The only quantum operators are \( r_i \) et \( p_j \)

Purely electronic hamiltonian

\[
H_e = \frac{1}{2m_0} \sum_{j=1}^{N_e} p_j^2 \quad \text{kinetic energies}
\]

\[
- Z \sum_{i=1}^{N_n} \sum_{j=1}^{N_e} V_c \left( R_i - r_j \right) \quad \text{nuclei-electrons}
\]

\[
+ \frac{1}{2} \sum_{i,j=1, i \neq j}^{N_e} V_c \left( r_i - r_j \right) \quad \text{electrons-electrons}
\]

In a crystalline solids the \( R_j \) are periodically ordered

still \( N_e \approx Z \times 10^{23} \) Impossible to solve

Other approximations !!

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The potential seen by an electron depends on the positions of the other electrons!!

**Second approximation:**

The electronic coulomb interactions are replaced by a potential which only depends on the mean value of the electronic density

\[
H_e = \frac{1}{2m_0} \sum_{j=1}^{N_e} p_j^2 + \sum_{i=1}^{N_n} \sum_{j=1}^{N_e} V_{at} (R_i - r_j)
\]

(Here \(V_{at}\) takes into account the coulomb interactions with the electronic density and the nuclear charge)

\[
H_e = \sum_{j=1}^{N_e} \left[ \frac{p_j^2}{2m_0} + \sum_{i=1}^{N_n} V_{at} (R_i - r_j) \right] = \sum_{j=1}^{N_e} H_1
\]

Within this approximation the hamiltonian separates

\[
H_1 = \frac{p^2}{2m_0} + \sum_{l=1}^{N_n} V_{at} (r - R_l)
\]

The problem of \(N_e\) interacting electrons becomes a set of \(N_e\) independent one electron problems
For an isolated atom

\[ V_{at}(r) = \frac{e^2}{4\pi\varepsilon_0} \left( -\frac{Z}{r} + \int \frac{d^3r'}{|r - r'|} \right) \]

eigenfunctions of the hamiltonian, 

electron-electrons

Mean value of the electronic density

\[ \rho(r) = \sum_{l=1}^{N_e} |\psi_l(r)|^2 \]

\( \psi_l(r) \): eigenfunctions of the hamiltonian, 

\( V_{at} \) is then determined by an iteration process

For a solid 

\( V_{at} \) takes all electrons into account, even those bound to the near neighbors

LDA

\( V_{at} \) decreases faster at large distance

than a coulomb potential

(charge neutrality of the material)

\( V_{at} \) has bound states
ONE ELECTRON HAMILTONIAN FOR A SOLID

\[ H_1 = \frac{p^2}{2m_0} + \sum_{l=1}^{N_n} V_{at}(r - R_l) \]

ATOMICAL ORBITALS

\[ \left[ \frac{p^2}{2m_0} + V_{at}(r) \right] \chi_n(r) = E_n \chi_n(r) \]

Valence electron of the « atom »

\[ \chi_0(r), E_0 \]

For the atom at site \( R_l \)

\[ \left[ \frac{p^2}{2m_0} + V_{at}(r - R_l) \right] \chi_0(r - R_l) = E_0 \chi_0(r - R_l) \]

bra - ket formalism \( \langle r | R_l \rangle \equiv \chi_0(r - R_l) \)

\[ \left[ \frac{p^2}{2m_0} + V_{at}(r - R_l) \right] |R_l\rangle = E_0 |R_l\rangle \]

We shall consider the specific case where the valence electron remains practically bound to an atomic state.

The energy states generated by the valence states of the atom do not differ much from \( E_0 \) and are far from \( E_1, \ldots, E_n \)

TIGHT BINDING APPROXIMATION

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We seek a solution which is a
Linear combination of atomic orbitals (LCAO)

\[ \psi_k(r) = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} a_{k,l} \chi_0(r - R_l) \]

\[ |\psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} a_{k,l} |R_l\rangle \]

A new write up of Schrödinger equation

\[ \sum_{l=1}^{N_n} a_{k,l} H_1 |R_l\rangle = \sum_{l=1}^{N_n} a_{k,l} E_k |R_l\rangle \]

or

\[ H_1 |R_l\rangle = E_0 |R_l\rangle + V_l(r) |R_l\rangle \quad \text{avec} \quad V_l(r) = \sum_{m=1, m \neq l}^{N_n} V_{at}(r - R_m) \]

With

\[ -t_{n,l} = \langle R_n | V_l(r) | R_l \rangle \]

Mathematical simplification

\[ \langle R_n | R_l \rangle = \delta_{n,l} \]

\[ - \sum_{l=1}^{N_n} t_{n,l} a_{k,l} = (E_k - E_0) a_{k,n} \]

Solving Schrödinger equation becomes

the determination of the eigenvalues of the \( t_{nl} \) matrix

\[ N_n \text{ values for } n \]

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REPRESENTATION OF $V_l$ and $t_{n,l}$

$$
\sum_{l=1}^{N_n} V_{at}(r - R_l)
$$

$$
V_l(r) = \sum_{m=1, m \neq l}^{N_n} V_{at}(r - R_m)
$$

$$
-t_{nl} = \langle R_n | V_l | R_l \rangle
$$

$$
= \int \chi_0^*(r - R_n) V_l(r) \chi_0(r - R_l) d^3r
$$

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**LINEAR CHAIN OF ATOMS**

![Diagram of a linear chain of atoms]

**Periodic Hamiltonian** (except for chain ends)

Can be transformed in a strictly periodic problem

**Ring of atoms**

**Periodic limits condition**

**Periodic Potential** \( V(x + a) = V(x) \)

**Bloch theorem**

**Eigenstates**

**Bloch Functions**

\[
\psi_k(x) = e^{ikx} u_k(x)
\]

**Notice**

If \( V \) is constant \( u_k(x) \equiv 1 \) and \( \psi_k(x) = e^{ikx} \)

\( \hbar k \) is a momentum?

**Plane Waves**

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LINEAR CHAIN OF ATOMS

\[ LCAO = \text{Bloch function} \]

\[ \psi_k(x) = e^{ikx} u_k(x) \quad u_k(x + a) = u_k(x) \]

\[ |\psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} a_{k,l} |R_l\rangle \quad \iff \quad \psi_k(x) = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} a_{k,l} \chi_0(x - R_l) \]

\[ u_k(x) = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} a_{k,l} e^{-ikx} \chi_0(x - R_l) \]

\[ u_k(x + a) = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} a_{k,l} e^{-ik(x+a)} \chi_0(x + a - R_l) \]

\[ = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} a_{k,l} e^{-ikx} e^{-ika} \chi_0(x - R_{l-1}) = u_k(x) \]

\[ a_{k,l-1} = a_{k,l} e^{-ika} \quad \iff \quad a_{k,l} = a_{k,0} e^{ikla} \]

Normalization of \[ |\psi_k\rangle \quad \Rightarrow \quad a_{k,0} = 1 \]

\[ a_{k,l} = e^{ikla} \]

\[ |\psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} e^{ikla} |R_l\rangle \]

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\[-t_{nl} = \langle R_n | V_l | R_l \rangle = \int \chi_0(r-R_n) V_l(r) \chi_0(r-R_l) d^3r = -t_{|n-l|}\]

\[t_{nl} \leq 0 \text{ if } n, l \text{ are not near neighbors, so } |n - l| \leq 1\]

**Transfer Integrals**

\(l, n \text{ near neighbors } l - n = 1\)

\[-t_1 = \langle R_n | V_{n+1} | R_{n+1} \rangle \approx \int \chi_0^*(r-R_n) V_{at}(r-R_n) \chi_0(r-R_{n+1}) d^3r\]

\[t_1 \geq 0 \text{ transfer integral}\]

\(l = n\)

\[-t_0 = \langle R_n | V_n | R_n \rangle \approx 2 \int \chi_0^*(r-R_n) V_{at}(r-R_{n+1}) \chi_0(r-R_n) d^3r\]

\[t_0 \geq 0 \text{ drift integral}\]
LINEAR CHAIN OF ATOMS

EIGENSTATES

\[ a_{k,n} = e^{ikna} \]

\[ |\psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} e^{ikl} |R_l\rangle \]

\[ -\sum_{l=1}^{N_n} t_{n,l} a_{k,l} = (E_k - E_0) a_{k,n} \]

(restricted to near neighbor \( t_{n,l} \))

\[ -t_1(a_{k,n+1} + a_{k,n-1}) = (E_k - E_0 + t_0) a_{k,n} \]

\[ E_k = E_0 - t_0 - 2t_1 \cos ka \]

BAND OF ENERGY LEVELS

Mean displacement \( t_0 \) drift integral

\[ t_0 = -2 \langle R_n | V_{n+1} | R_n \rangle \geq 0 \]

Width \( 4t_1 \) \( t_1 \) transfer integral

\[ t_1 = -\langle R_n | V_n | R_{n+1} \rangle \geq 0 \]

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LINEAR CHAIN OF ATOMS

Eigenvalues: energy bands

$E_0 - t_0 + 2t_1$

$E_0$

$E_0 - t_0$

$E_0 - t_0 - 2t_1$

$E$

$k$

$4t_1$

$-\pi/a$

$\pi/a$

Eigenfunctions

$k = 0$

Bonding orbitals

$k = \pi/a$

Antibonding orbitals

$\text{Re}(\psi_k)$

$\pi/k$

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**LINEAR CHAIN OF ATOMS**

**Periodic limits: Quantization**

\[
\psi_k(x) = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} e^{i k l a} \chi_0(x - l a)
\]

\[
|\psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} e^{i k l a} |R_l\rangle
\]

\[
\psi_k(x + N_n a) \equiv \psi_k(x)
\]

\[
= \frac{1}{\sqrt{N_n}} \sum_{l=1}^{N_n} e^{i k l a} \chi_0[x - (l - N_n) a]
\]

\[
e^{i k l a} = e^{i k (l - N_n) a}
\]

\[
e^{-i k N_n a} = 1 \quad \iff \quad k = \frac{2\pi m}{N_n a} \quad \text{avec} \quad 0 < m < N_n - 1
\]

**First Brillouin Zone**

\[
-\frac{\pi}{a} < k \leq \frac{\pi}{a}
\]

**One generally uses**

**N_n values for k** (modulo \(2\pi/a\))

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LINEAR CHAIN OF ATOMS

Eigenstates: energy band

- $E(k)$
- $E_0 - t_0 + 2t_1$
- $E_0 - t_0$
- $E_0 - t_0 - 2t_1$

Number of k values = number of atoms $N_n$

Density of states

$D(E)$

$E_0 - t_0 - 2t_1$  $E_0 - t_0$  $E_0 - t_0 + 2t_1$  $E$

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Nearly free electrons weak $V_{at}$

The periodic potential lifts the degeneracy of the repeated free electron band and creates gaps between energy bands.

The width of the energy gaps depends of the magnitude of the periodic potential potentiel ($V_l$ are Fourier components of the periodic potential)
Molecular orbitals

Molecular orbitals

SCANNING TUNNELING MICROSCOPY

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Case of the chain of atoms (1D)
Tight binding (LCAO)

2) BAND STRUCTURES : 2D and 3D

General Bloch theorem : Brillouin zones
LCAO versus nearly free electrons

3) METALS, INSULATORS and SEMICONDUCTORS

Filling of the energy bands
Metals: partly filled band(s)
Insulators: energy gaps
Semiconductors: small energy gap

4) EXPERIMENTAL OBSERVATIONS OF THE BAND STRUCTURES

Metals: Scanning tunelling microscopy (STM) and density of states
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BLOCH THEOREM IN 3D

\[
\left[ \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) \right] \psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r})
\]

(periodic potential
\[ V(\mathbf{r} + \mathbf{R}_l) \equiv V(\mathbf{r}) \]
\[ \forall \mathbf{R}_l \in \text{lattice}. \]

Eigenstates: Bloch functions with energies eigenvalues \( E_{n,k} \)

\[
\psi_{n,k}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} u_{n,k}(\mathbf{r})
\]

\[
u_{n,k}(\mathbf{r} + \mathbf{R}_l) = u_{n,k}(\mathbf{r})
\]

\( \psi_{n,k} \) is not an eigenfunction of \( \hat{p} \)

\[
\hat{p} \psi_{n,k}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} (\mathbf{\hbar k} - i \mathbf{\hbar \nabla}) u_{n,k}(\mathbf{r})
\]

\[
\hat{p}^2 \psi_{n,k}(\mathbf{r}) = e^{i \mathbf{k} \cdot \mathbf{r}} (\mathbf{\hbar k} - i \mathbf{\hbar \nabla})^2 u_{n,k}(\mathbf{r})
\]

\( \mathbf{\hbar k} \): quasi momentum or crystal momentum

For a given \( \mathbf{k} \) \( u_{n,k} \) is solution of

\[
\frac{1}{2m} (\mathbf{\hbar k} - i \mathbf{\hbar \nabla})^2 u_{n,k}(\mathbf{r}) + V(\mathbf{r}) u_{n,k}(\mathbf{r}) = E_{n,k} u_{n,k}(\mathbf{r})
\]

(solution in a unit cell)

\( n \) is a band index
PERIODIC LIMITS

(Born - Von Karman)

Polyedron

$(N_1 a_1, N_2 a_2, N_3 a_3)$

Number of unit cells:

$N_1 N_2 N_3 = N_m$

Periodicity

$\psi_{n,k} \left( \mathbf{r} + N_i \mathbf{a}_i \right) \equiv \psi_{n,k} (\mathbf{r}) \text{ for } (i = 1,2,3)$

with $k = \sum_{i=1,2,3} x_i \mathbf{a}_i^*$

$k$ is quantized

$N_1 N_2 N_3 = N_m$

In the unit cell of the reciprocal lattice

elementary cell volume

$\frac{1}{N_m} \left( \frac{2\pi}{v} \right)^3$

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BLOCH STATES
IN THE RECIPROCAL LATTICE

Any $k$ can be translated in the unit cell around $k=0$

$$k = k_0 + K \text{ where } K \in \mathbb{R} \mathbb{R}.$$  

$$\psi_{n,k}(\mathbf{r}) \equiv \psi_{n,k_0}(\mathbf{r})$$

$$E_{n,k_0+K} \equiv E_{n,k_0}$$

In the reciprocal space representation the Bloch states are periodic.

A single unit cell of the reciprocal lattice
Is needed to define all the Bloch states

Particular choices : Brillouin Zones

$n^{th}$ Brillouin zone :
Spatial volume which requires to cross $n-1$ Bragg planes to reach the origin of the reciprocal lattice

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Linear chain of atoms (Nearly free electrons)

Extended zone scheme

\[ E(k) \]

-4\(\pi\) -2\(\pi\) -\(\pi\) 0 \(\pi\) 2\(\pi\) \(ka\)

Reduced zone scheme

\[ E(k) \]

\(\pi\) 0 \(\pi\)

\[ K = \frac{2\pi}{a} \]

\[ -\frac{\pi}{a} < k \leq \frac{\pi}{a} \]

Wigner et Seitz unit cell of the reciprocal lattice.

First Brillouin zone
BRILLOUIN ZONES

Repeated zone scheme

1st Zone
2nd Zone
3rd Zone
4th Zone

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2D SQUARE LATTICE (TIGHT BINDING)

\[ R_l = a(l_x, l_y) \]

CLOA

\[ |\psi_k\rangle = \frac{1}{\sqrt{N_n}} \sum_l a_{k,l} |R_l\rangle \]

\[ a_{k,n} = e^{ik.R_n} \]

\[ -t_1 \sum_d a_{k,n+d} = (E_k - E_0 + t_0) a_{k,n} \]

First neighbours \[ d = \pm ax, \pm ay \]

\[ E_k = E_0 - t_0 - 2t_1 \left( \cos k_x a + \cos k_y a \right) \]
nth Brillouin zone:
Spatial volume which requires to cross n-1 Bragg planes
to reach the origin of the reciprocal lattice

$r.r.$ square unit cell $a \rightarrow R.R.$ square unit cell $2\pi/a$
$E_k = E_0 - t_0 - 2t_1 \left( \cos k_x a + \cos k_y a \right)$

1st Brillouin zone

- $\pi/a < k_x < \pi/a$
- $-\pi/a < k_y < \pi/a$

Contours with constant $E_k$ levels

Bandwidth $8t_1 = 2\pi t_1$
3D LCAO (cubic lattice)

\[ E_k = E_0 - t_0 - 2t_1 \left( \cos k_x a + \cos k_y a + \cos k_z a \right) \]

(Bandwidth \( 2t_1 = 2z \))

\[ E = E_0 - t_0 - 2t_1 \]

\[ \cos k_x a + \cos k_y a + \cos k_z a = 1 \]

\[ E = E_0 - t_0 \]

\[ \cos k_x a + \cos k_y a + \cos k_z a = 0 \]
**ATOMIC ORBITALS**

**Neon:**
Ne (1s$^2$ 2s$^2$ 2p$^6$)

**Na** (Sodium):
Na (1s$^2$ 2s$^2$ 2p$^6$ 3s)

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Ne BAND STRUCTURE

\[ r\psi(r) \]

Count of states (orbital * spin)

- \(2p^6\)
- \(3N_n \times 2\)
- \(2s^2\)
- \(N_n \times 2\)
- \(1s^2\)
- \(N_n \times 2\)

Interatomic distance

Last band is filled

INSULATOR

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SODIUM BAND STRUCTURE

Interatomic distance $r_0$

Count of states
(orbital * spin)

- $3s^1$ \(N_n \times 2\)
- $2p^6$ \(3N_n \times 2\)
- $2s^2$ \(N_n \times 2\)
- $1s^2$ \(N_n \times 2\)

Last band is half filled
METAL

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NEARLY FREE ELECTRONS (2D or 3D)

\[
\left[ \frac{\mathbf{p}^2}{2m} + 2\nu_1 (\cos \frac{2\pi x}{a} + \cos \frac{2\pi y}{a}) \right] \psi_n (\mathbf{r}) = E_n \psi_n (\mathbf{r})
\]

Weak potential \( \nu_1 \)

No energy gap

Strong potential \( \nu_1 \)

Energy gap

In 2D or 3D the bands may overlap for weak enough potentials

An even number of electrons per atom can correspond to unfilled bands: METAL

(ex: Alkaline earth metals)

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Number of valence electrons

Even

Odd

$E_{F_2}$

$E_{F_1}$

TIGHT BINDING

NEARLY FREE

METALS

ATOMES ISOLES

$V$

$E$

TIGHT BINDING

Even electron number: METAL or INSULATOR in 2D or 3D

Odd electron number: METAL

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Cubic centered lattice
f.c.c. reciprocal lattice

First Brillouin zone

Quasi-spherical Fermi surface

Volume = \( \frac{1}{2} V \) (1st BZ)

Na
< 0.1%

K
< 0.2%

Rb
< 1%

Cs
< 4%

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Noble metal fcc lattice

reciprocal lattice: centered cubic

First Brillouin Zone

Angular Resolved Photoemission (ARPES)

UV source

Energy analyser

sample
detector

Fermi level

$3d^{10}$

$4s$

$\Delta E/\alpha$

$E(k)$ (eV)

$E_F$

$\hbar \nu$

$I$

$E$

$E$ and $k$ conserved

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NOBLE METALS

lattice. Face centered cubic

R.R. centered cubic

First Brillouin zone

Quasi-spherical FERMI SURFACE

\[ E = E_F \]

Volume = \( \frac{1}{2} V (1ZB) \)

Cu

Ag

Au

Silver

Gold

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Germanium Semiconductor

Band gap

Conduction bands

$D_c(E)$

Valence bands

$D_v(E)$

Valence bands filled à $T=0$

Insulator

$E(k)$ (eV)

$D(E)$

$D_c(E)$

$D_v(E)$

$\Gamma \Gamma \Gamma \Gamma$ $X$

$\Gamma \Gamma \Gamma \Gamma$

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ALUMINIUM: A TRIVALENT METAL

face centered cubic lattice

Free electrons

Nearly free electrons

First Brillouin zone

2\textsuperscript{nd} B.Z.

3\textsuperscript{rd} B.Z.

All the states of the 1\textsuperscript{st} Brillouin zone are filled

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ALUMINIUM: A TRIVALENT METAL

1st B. Z

Fermi sphere
FREE ELECTRONS
Volume = 1.5 V (1st BZ)

2nd B. Z.

3rd B. Z.
(3rd band)
Occupied states folded in the 1st B. Z.

2nd B. Z.
(2nd band)
non occupied states folded in the 1st B. Z.

ACTUAL FERMI SURFACE

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SOME FERMI SURFACES

K

Cu
1 el/ atom

Be

Mg
2 el/ atom

Al

Pb
3 el/ atom

4 el/ atom

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BAND STRUCTURE IN CRYSTALS DES (LCAO, NEARLY FREE)
Number of states per energy band
= number $N_m$ of cells in the crystal

- Filled bands - Insulator
  - Optical properties (gaps)
  - Semiconductors (small energy gap)

- Partly filled bands - Metal
  - Low energy excited states

Even electron number → Metal
Insulators → Non magnetic