

Fundamentals of Solid State Physics

Metals and Insulators

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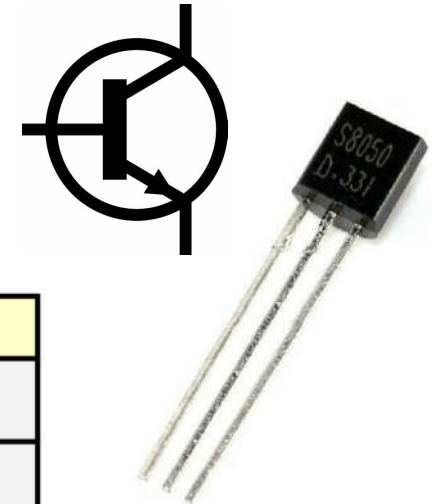
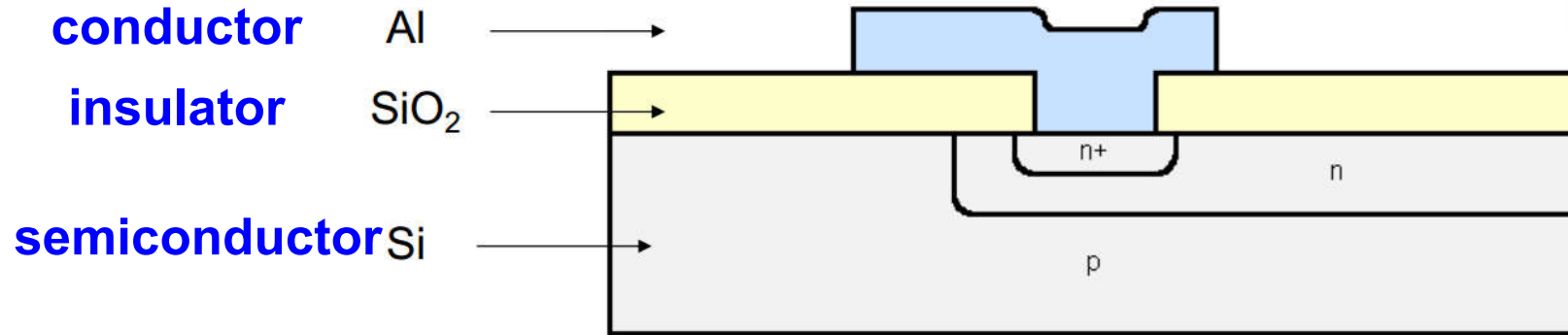
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Electronic Properties of Materials

CMOS transistor

- Complementary **Metal-Oxide-Semiconductor**



Metal

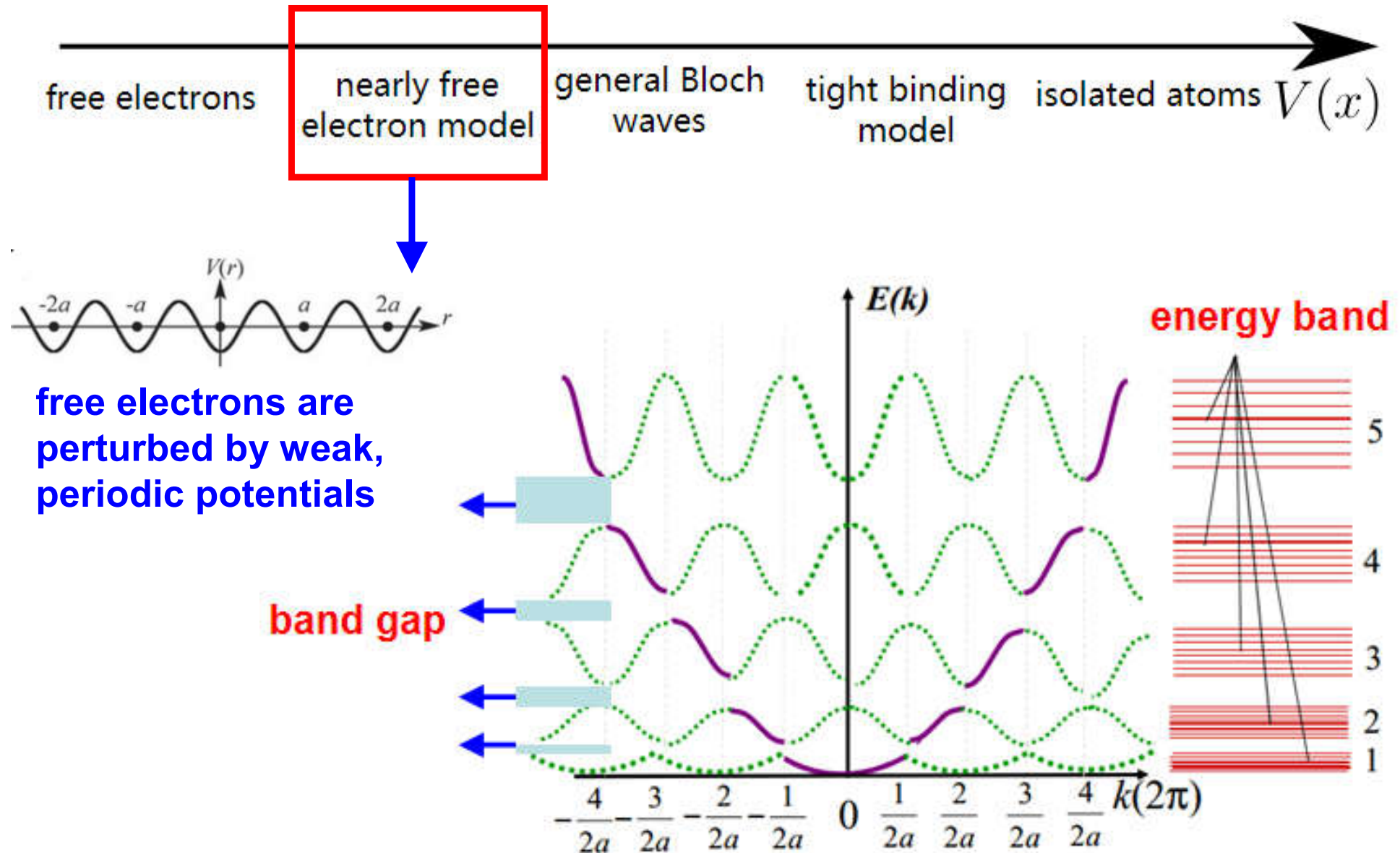


SiO_2

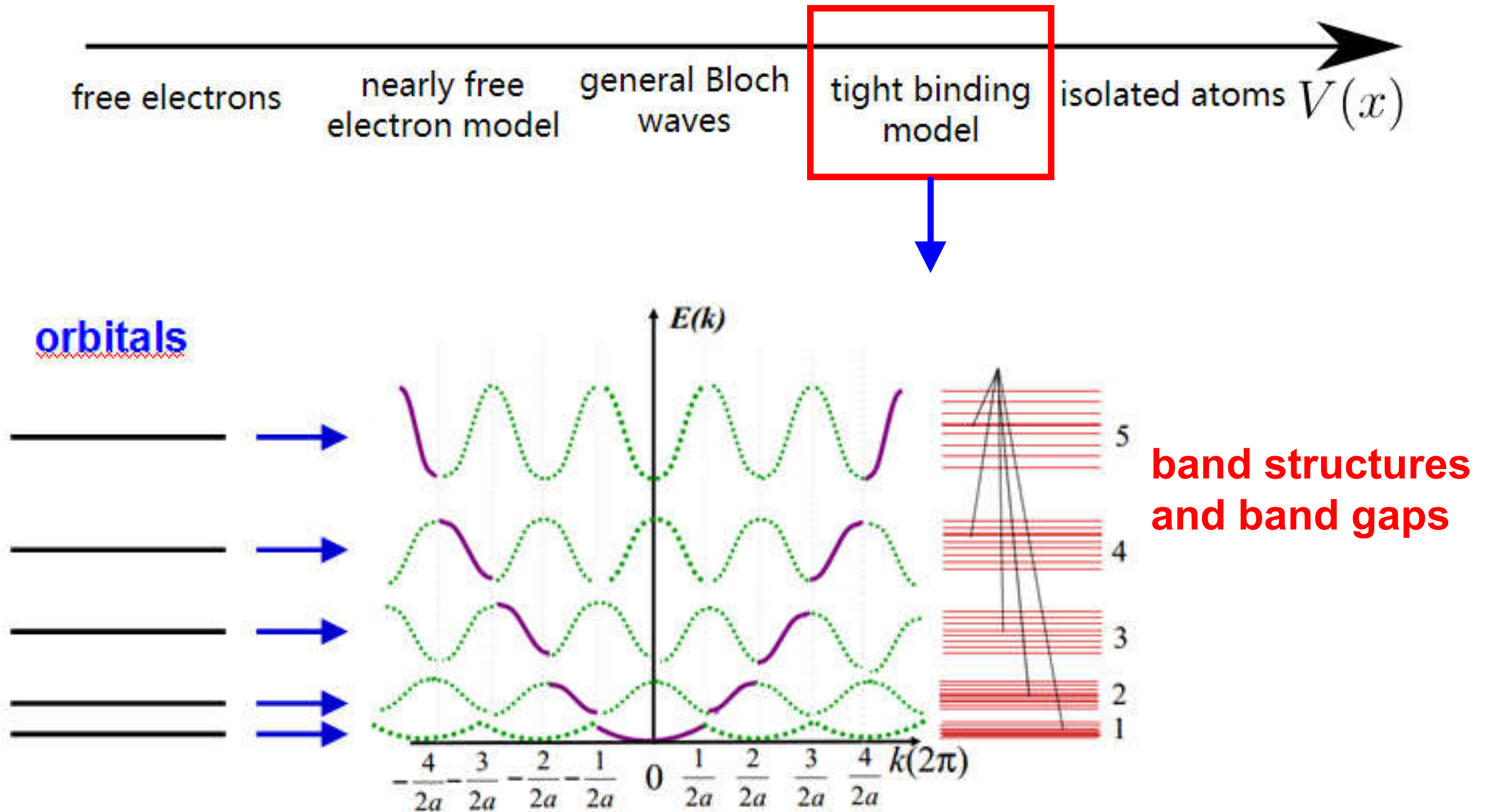


Silicon

Formation of Band Gaps

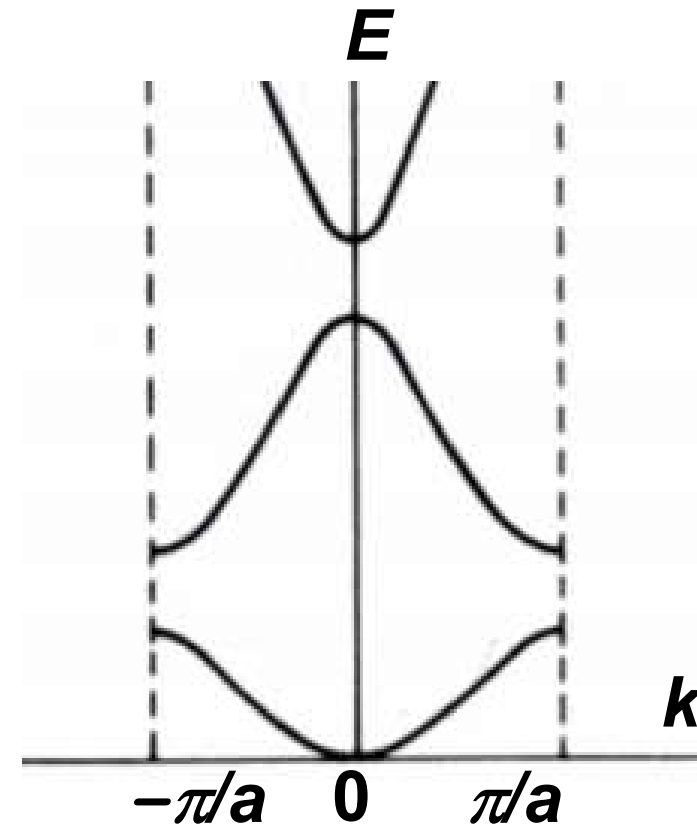
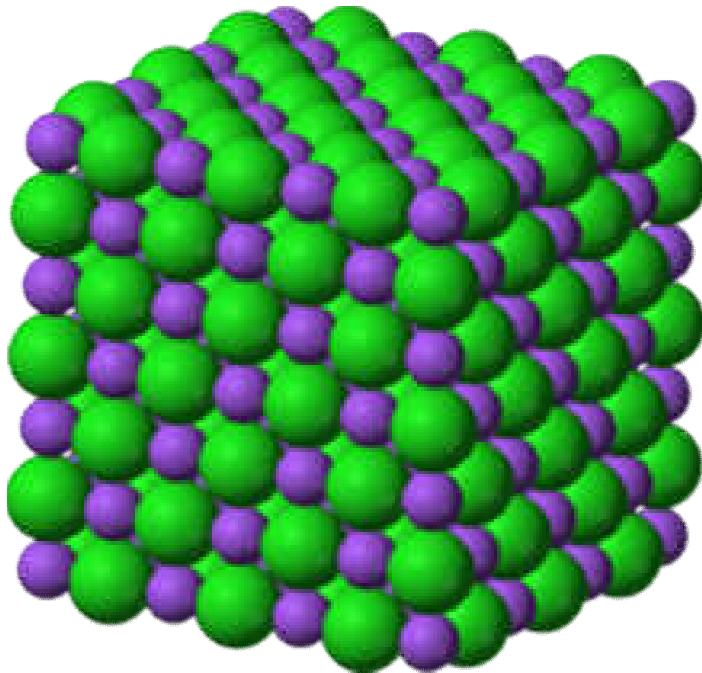


Formation of Band Gaps



discrete orbitals are combined to form quasi-continuous bands

Formation of Band Gaps



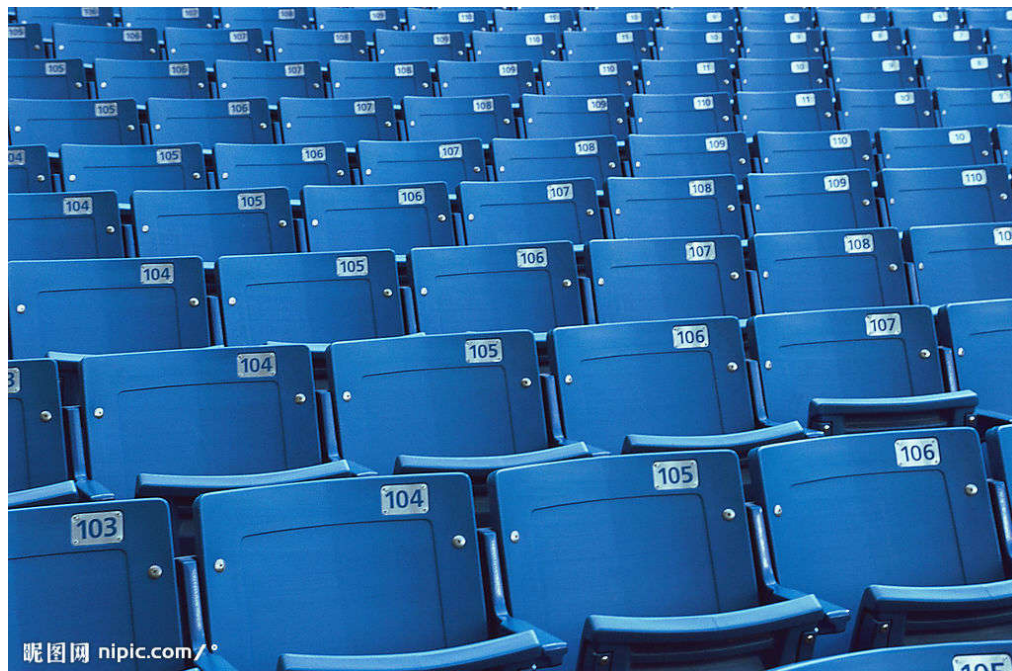
Fill electrons into these bands

Q: Is it a metal or insulator?

State vs. Electron

energy state / level / orbital
能态 / 能级 / 轨道

electron / phonon / ...
电子 / 声子 / ...



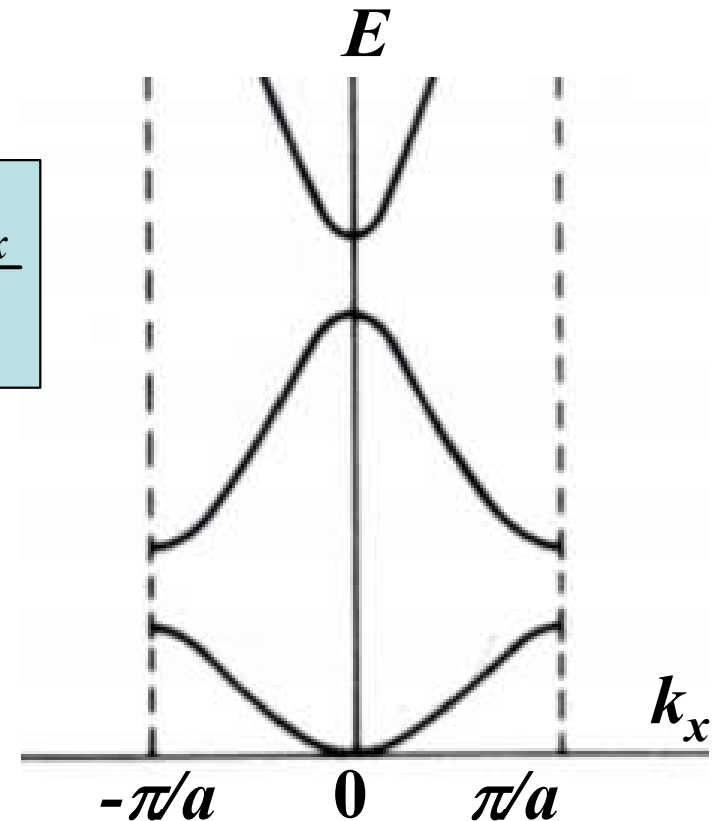
**Number of states are infinite.
Number of electrons are finite.**

Energy States

How many energy states in each band?

$$\begin{aligned}
 N &= 2 \cdot \frac{\text{size of FBZ}}{\text{density of } k \text{ points}} \\
 &= 2 \cdot \frac{2\pi / a}{2\pi / L_x} \\
 &= 2 \frac{L_x}{a} \\
 &= 2n
 \end{aligned}$$

$$k_x = \frac{2\pi n_x}{L_x}$$



FBZ - First Brillouin Zone

N - total number of states

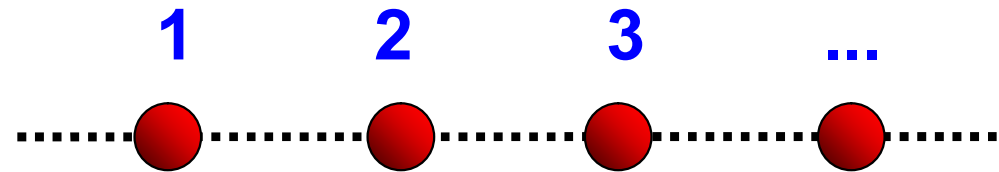
$n = L/a$ - number of primitive cells

2 - spin up and down

Q: How about 2D and 3D cases?

1D Chain of *Monovalent* Atoms

Each atom has *one* valence electron (Na, K, ...)



$$N = 2n$$

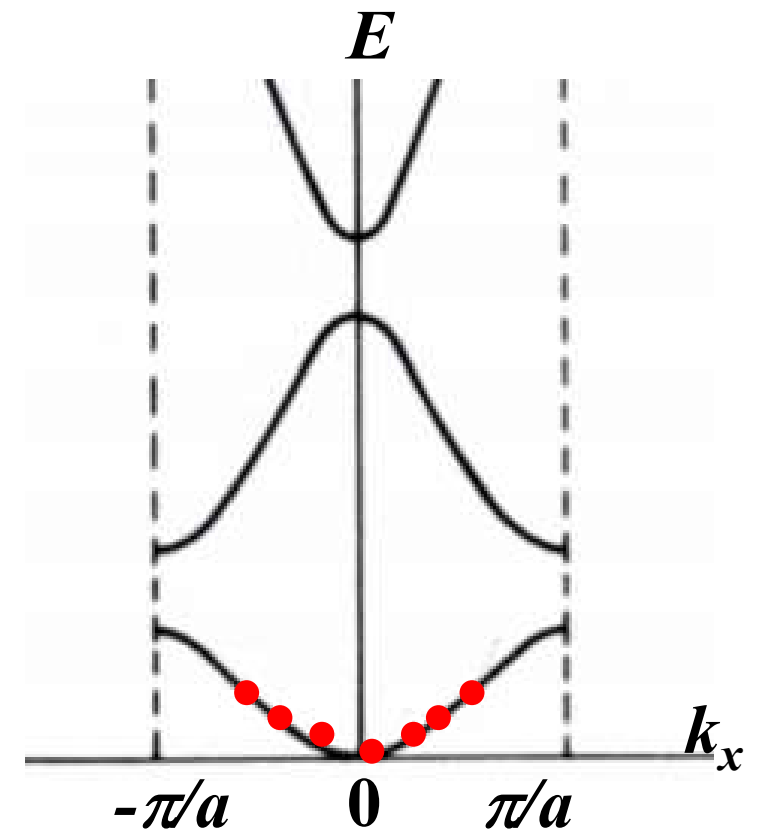
= total number of states

$$n = L/a$$

= number of primitive cells

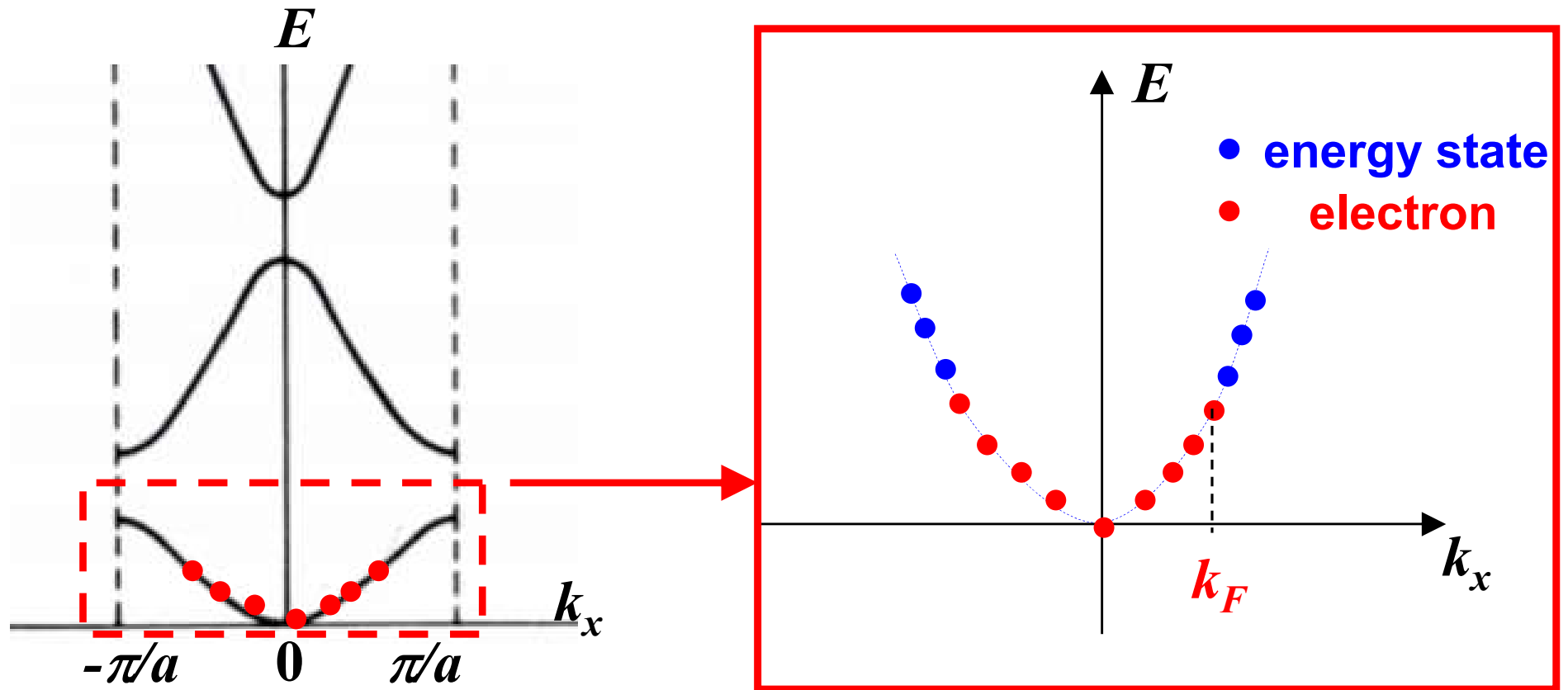
= number of valence electrons

Electrons only fill half of the first band



• electron

1D Chain of *Monovalent* Atoms



*Electrons only fill half
of the first band*

parabolic function

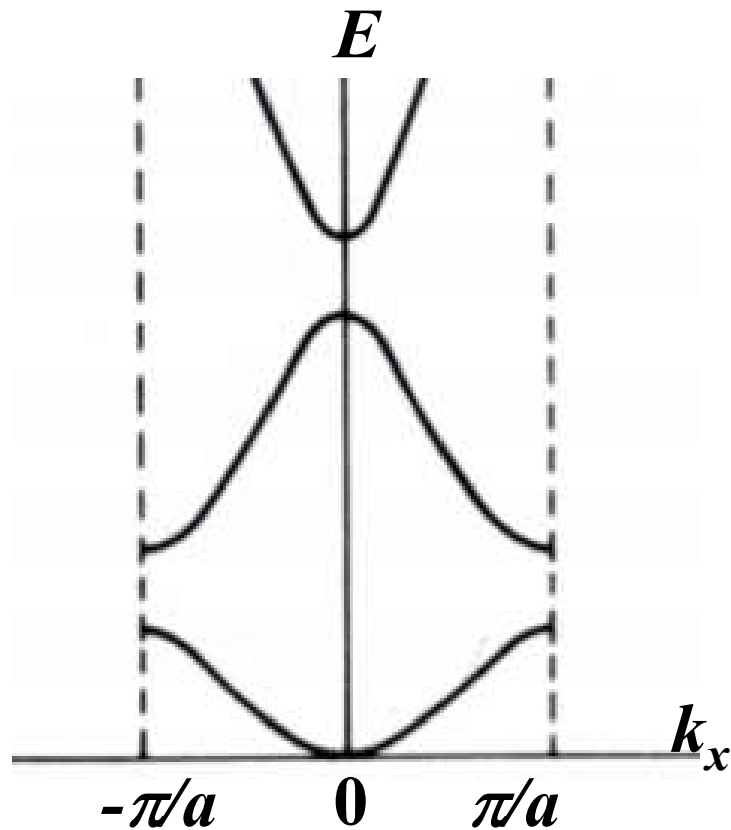


Free Electrons

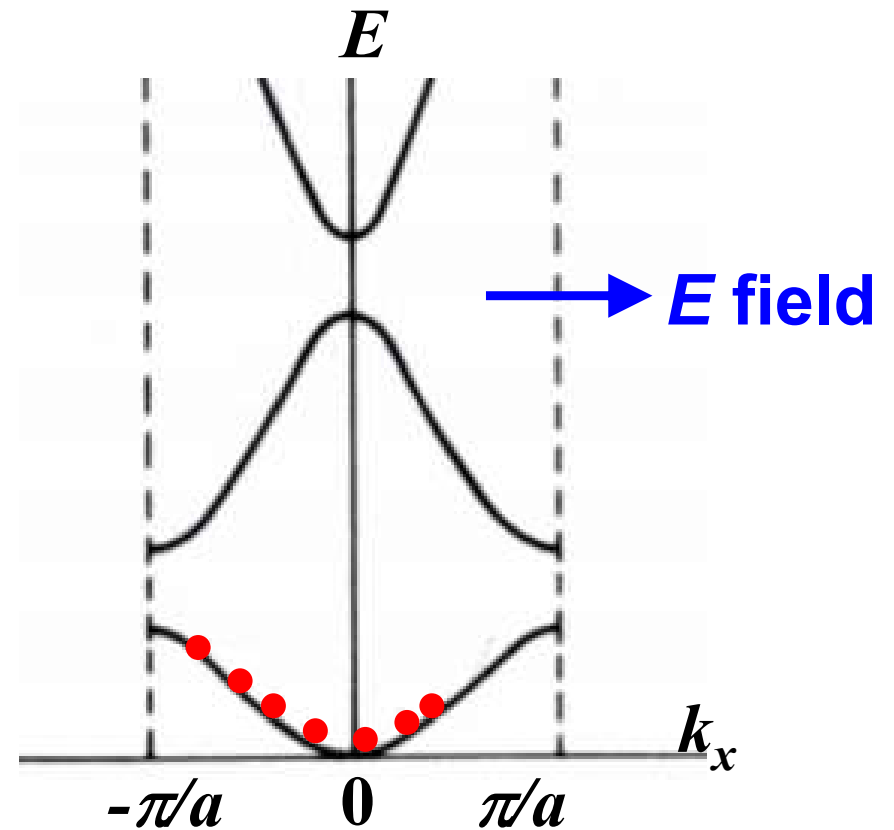


Conductor

1D Chain of *Monovalent* Atoms



when $E = 0$, $v = 0$
no current



when $E \neq 0$, $v > 0$
electric current

$$\mathbf{j} = \sigma \mathbf{E}$$

1D Chain of *Monovalent* Atoms

Question:

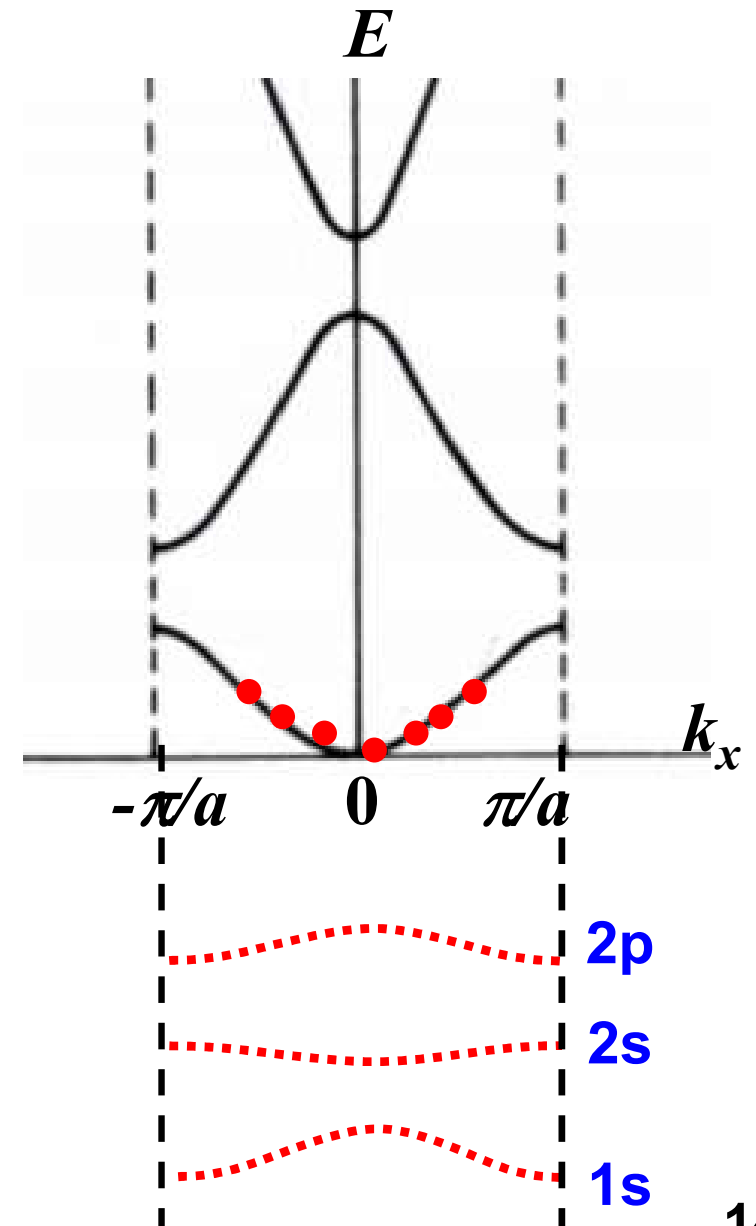
A Na atom has 11 electrons.

$[1s^2 2s^2 2p^6] 3s^1$

Where are the rest 10 electrons?

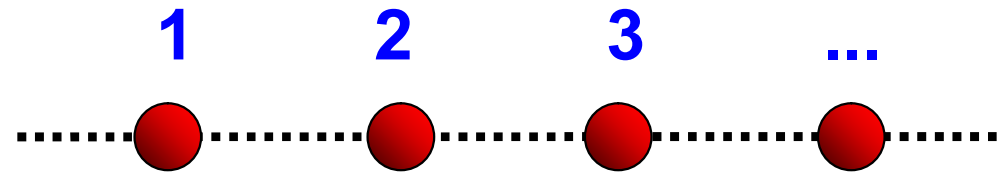
Answer:

Localized electrons have lower energies. All the lower bands are completely full. So they have no contribution to conductivity.



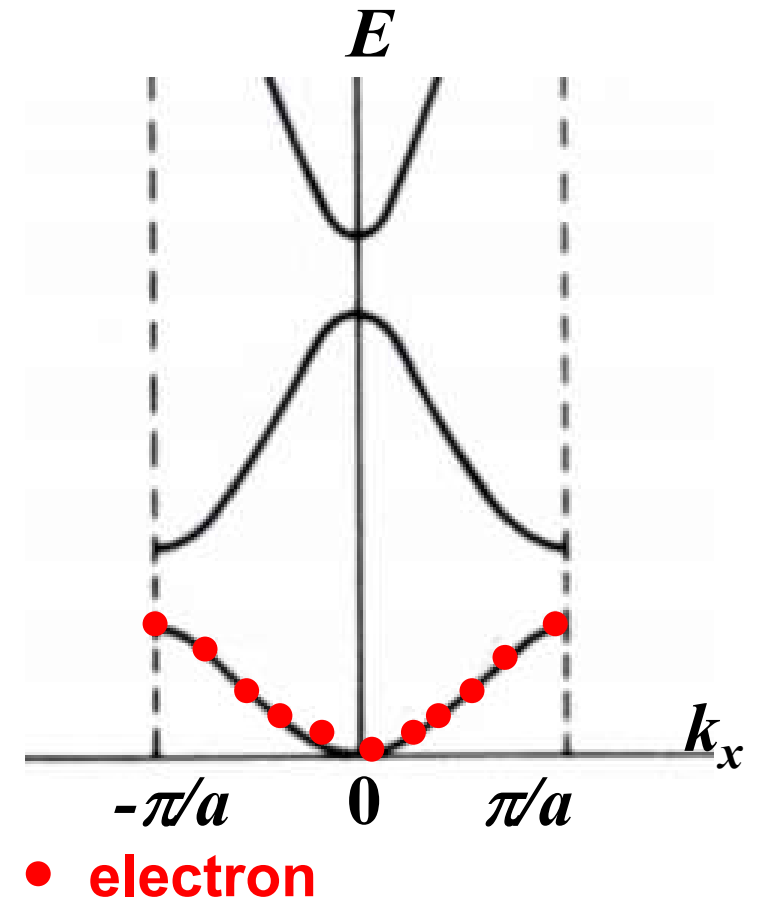
1D Chain of *Divalent* Atoms

Each atom has *two* valence electrons (Mg, Ca, ...)



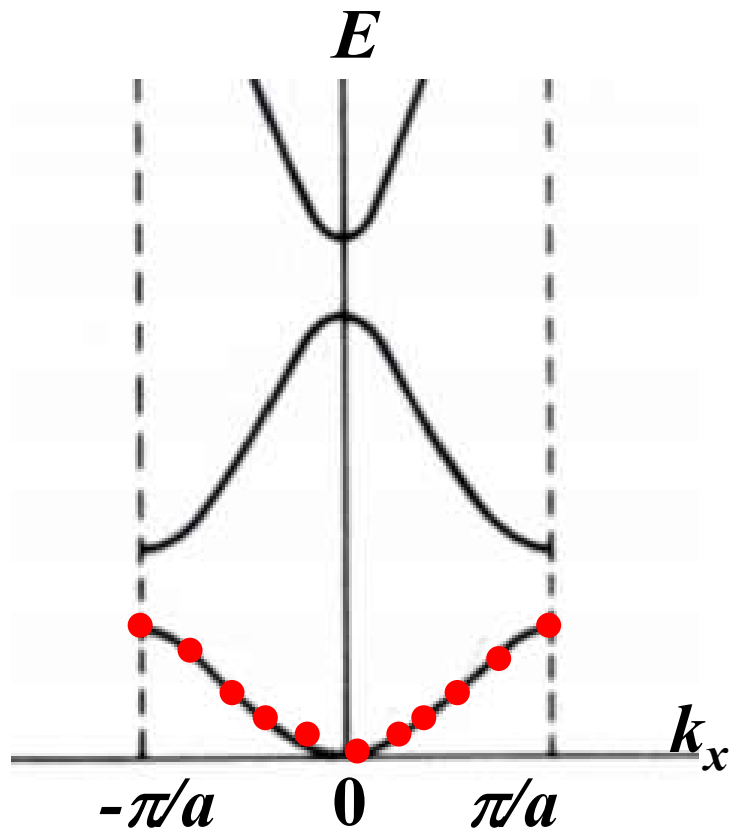
$N = 2n$
= total number of states

number of valence electrons
= $2L/a = 2n$



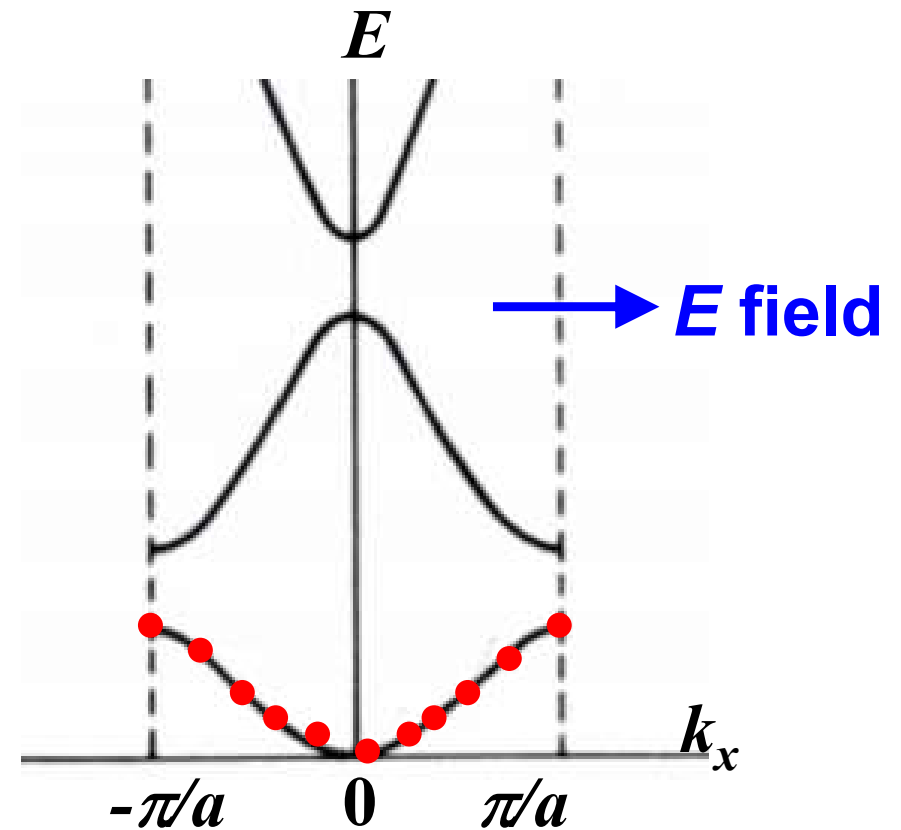
Electrons fill the entire band

1D Chain of *Divalent* Atoms



when $E = 0$, $v = 0$
no current

Electrons fill the entire band →

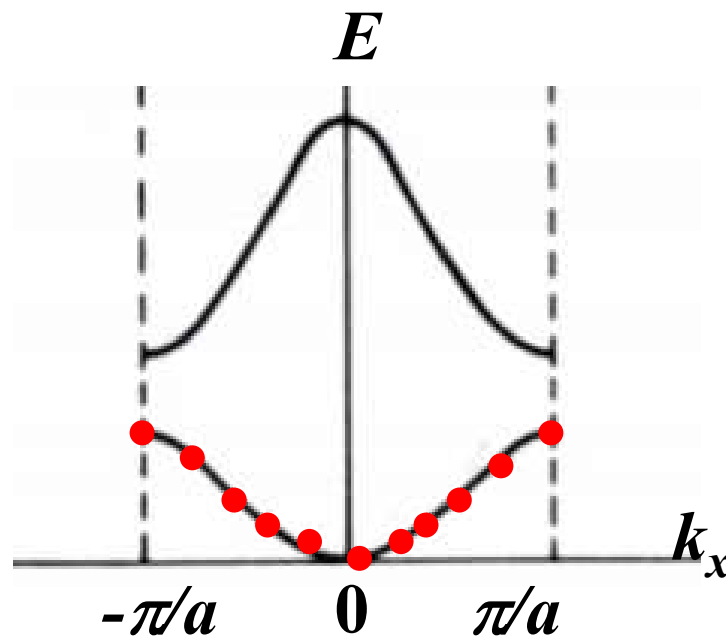


when $E \neq 0$, $v = 0$
no current

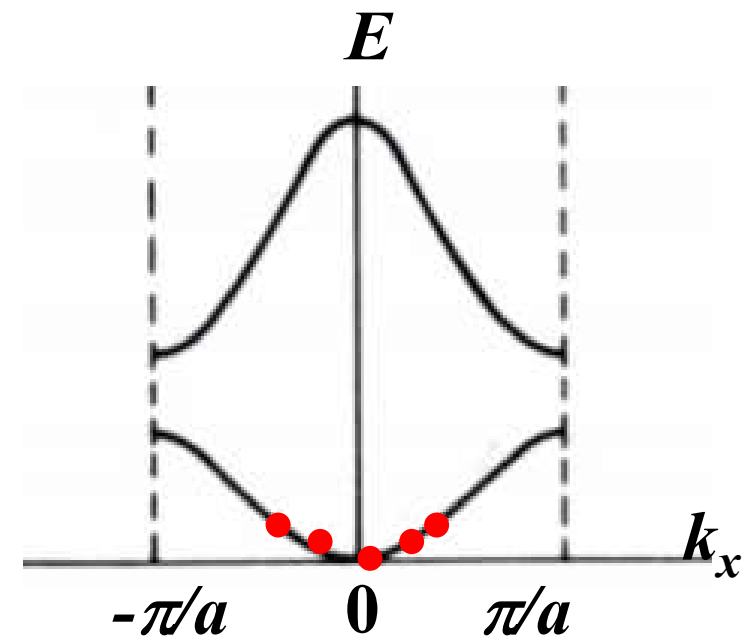
Insulator
(at $T = 0$ K)

Metal vs. Insulator

- Metals and Insulators are fundamentally different
 - Insulators are not just “bad” metals
 - An insulator has all bands completely filled or empty
 - A metal has partially filled bands



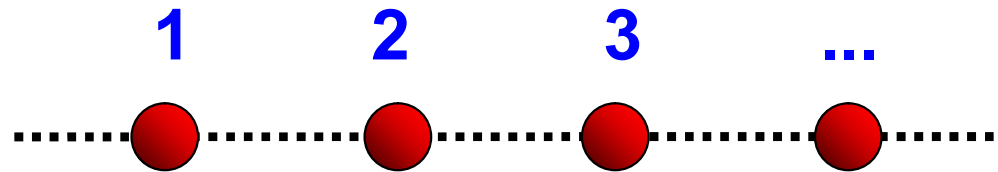
Insulator



Metal

1D Chain of *Trivalent* Atoms

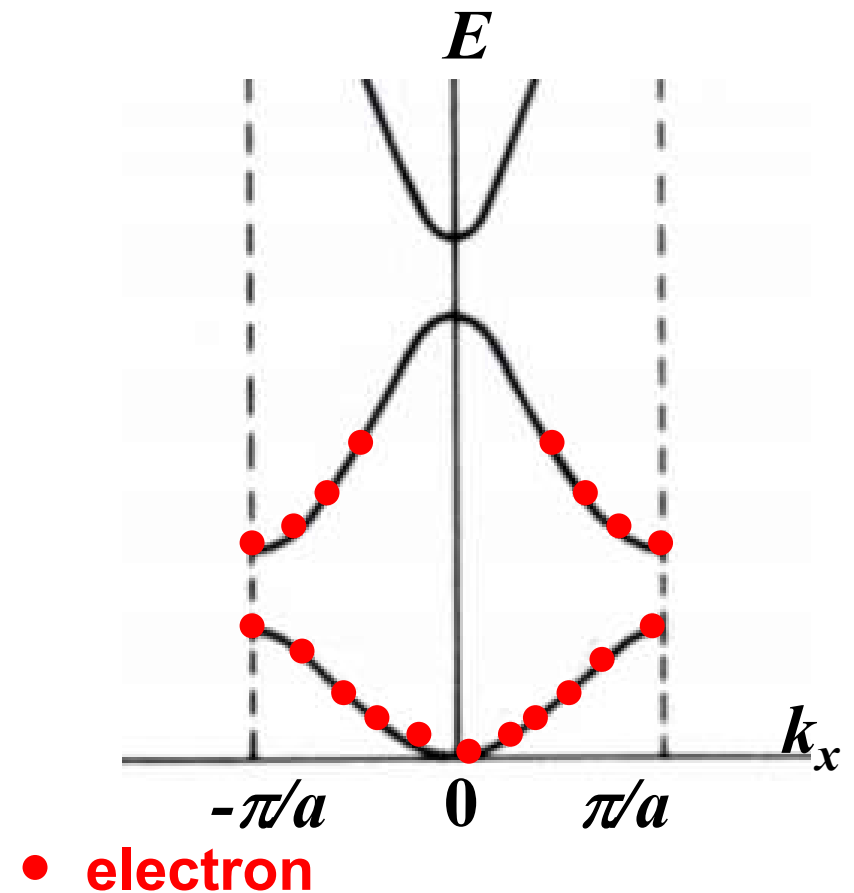
Each atom has *three* valence electrons (Al, Ga, ...)



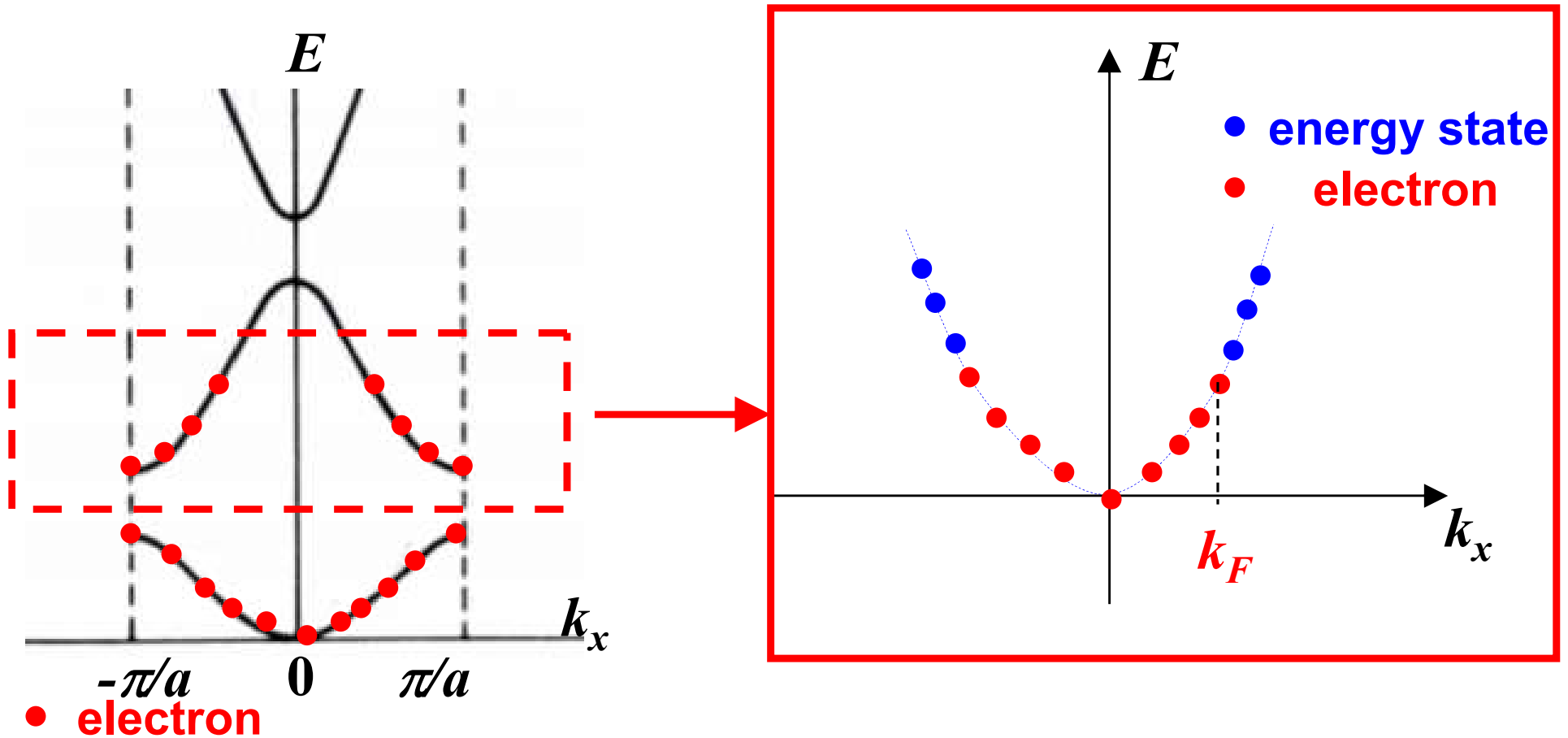
$N = 2n$
= total number of states

number of valence electrons
= $3L/a = 3n$

*Electrons start to fill the
second band*



1D Chain of *Trivalent* Atoms

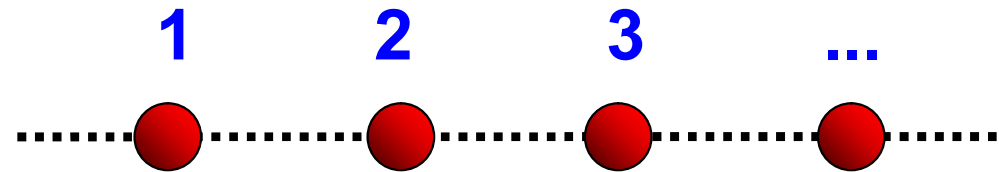


Free Electrons

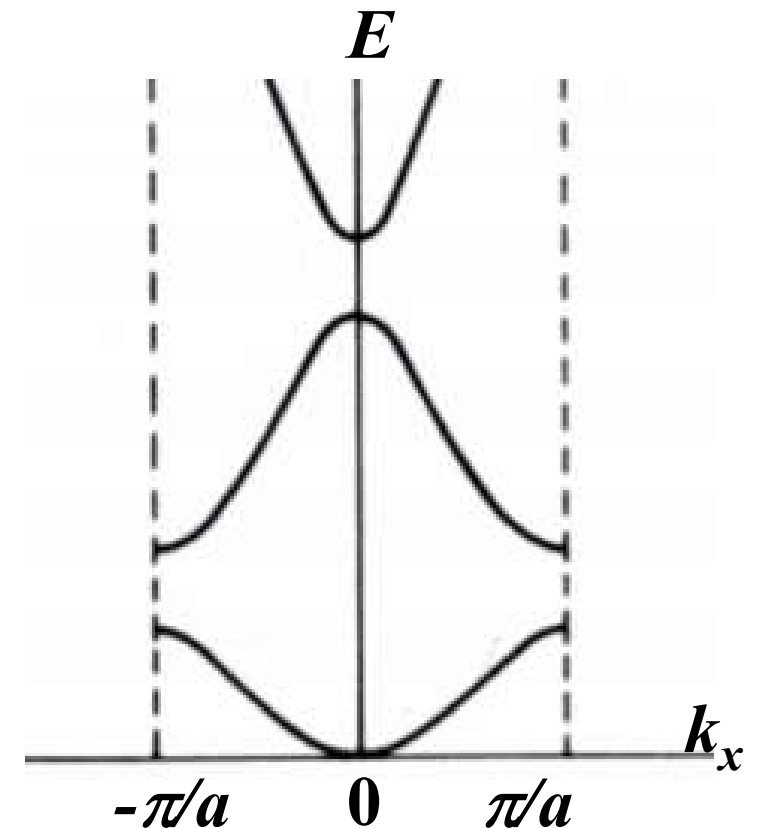
Conductor

1D Chain of *Quadrivalent* Atoms

Each atom has *four* valence electrons (C, Si, ...)



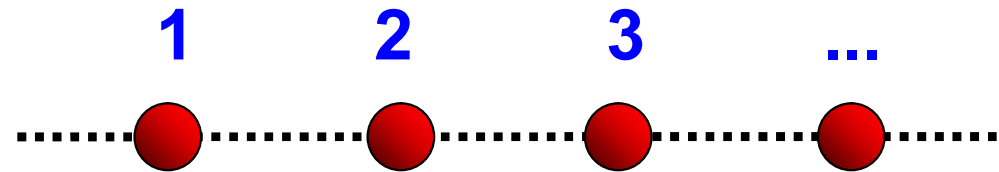
**Q: How do electrons fill the bands?
Is it a conductor, or an insulator?**



• electron

1D Chain of *Divalent* Atoms

Each atom has *two* valence electrons (Mg, Ca, ...)

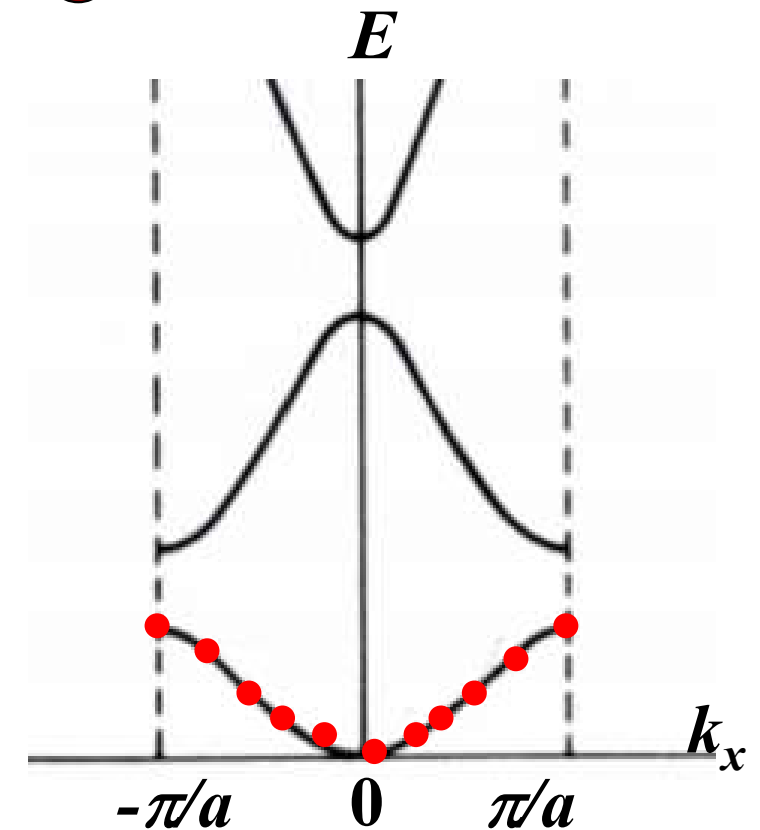


Electrons fill the entire band

--->

insulator

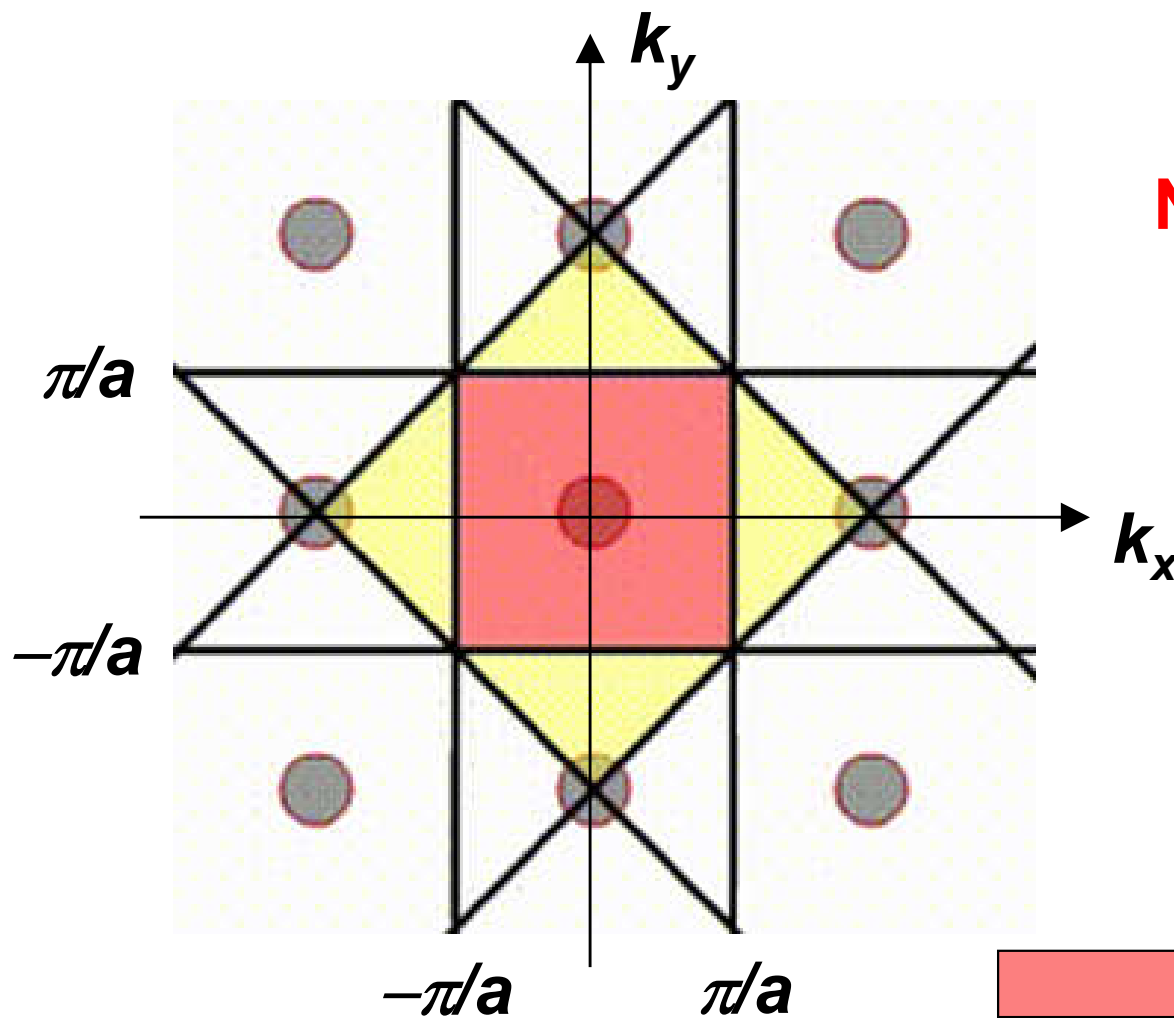
Q: But we know divalent metals like Mg and Ca are conductors, why?



• electron

2D case

Assume a square lattice in the reciprocal space



Number of states in each
Brillouin zone

$$N = 2n$$

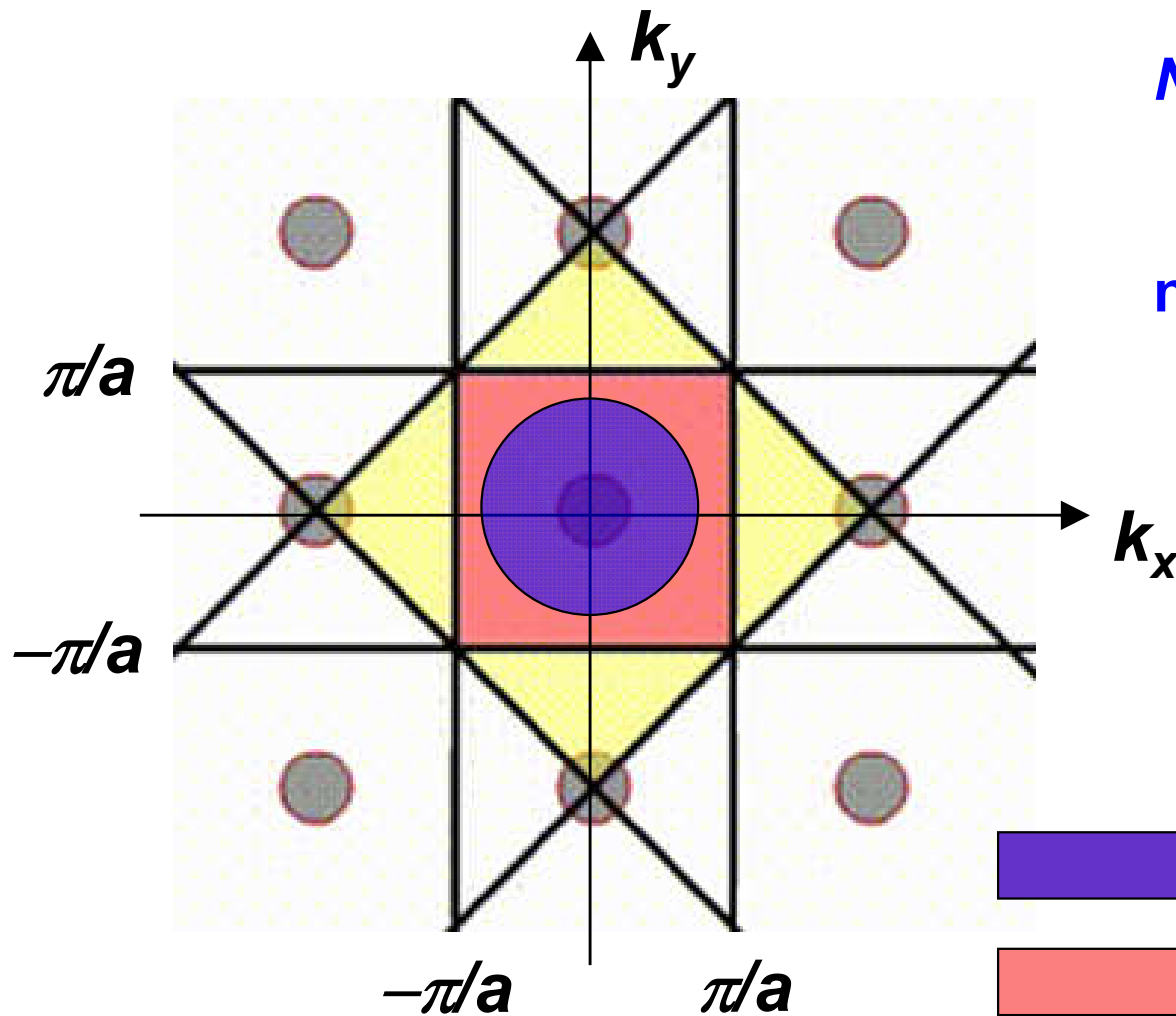
= total number of states

First BZ

Second BZ

2D case of *Monovalent* Atoms

Each atom has *one* valence electrons (Na, K, ...)



$$N = 2n$$

= total number of states

number of valence electrons

$$= A/a/a = n$$

FBZ is not full



Conductor

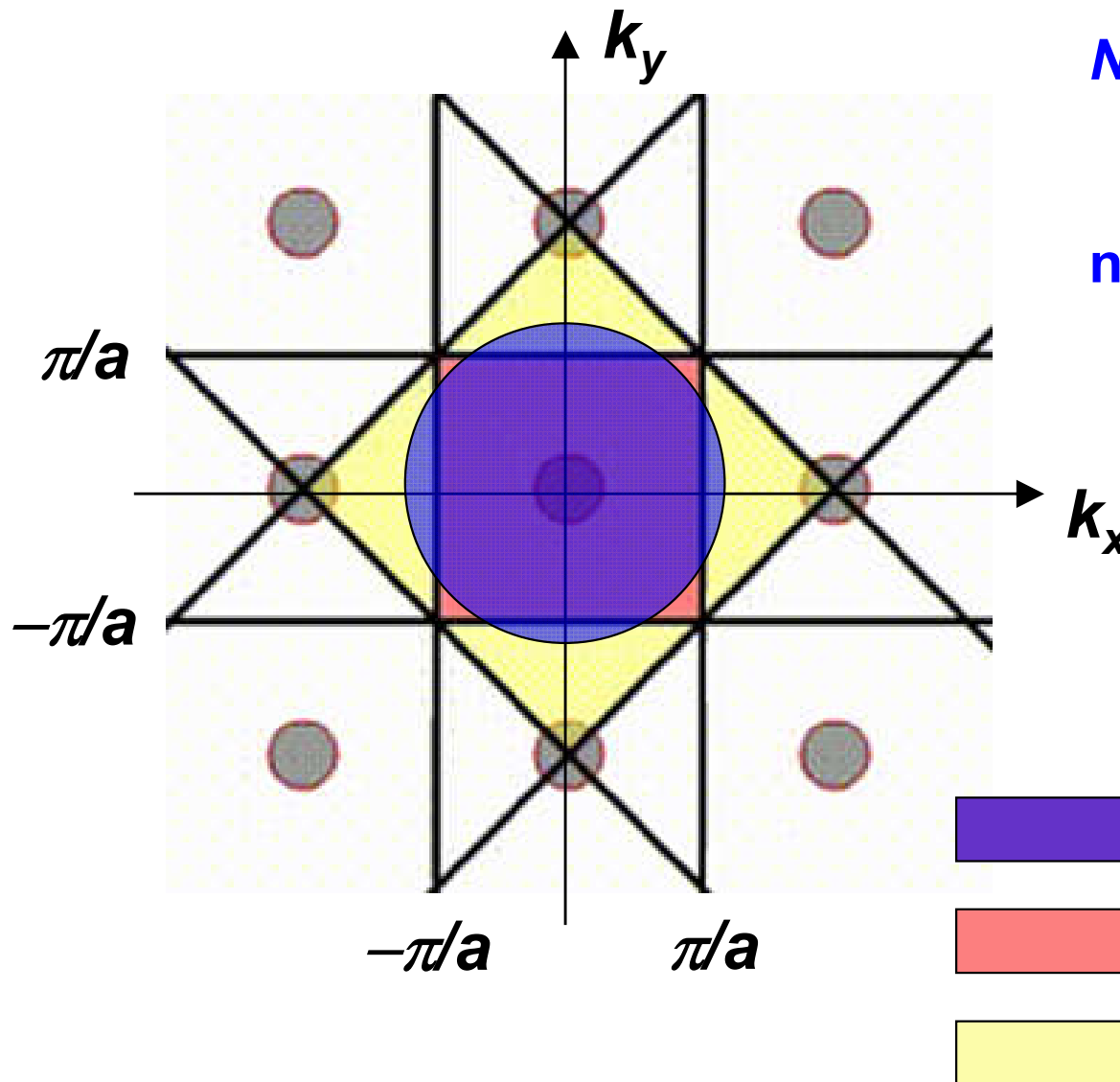
 **electrons**

 **First BZ**

 **Second BZ**

2D case of *Divalent* Atoms

Each atom has *two* valence electrons (Mg, Ca, ...)



$$N = 2n$$

= total number of states

number of valence electrons

$$= 2A/a/a = 2n$$

*start to fill SBZ, but
FBZ is still not full*

Conductor (semimetal)

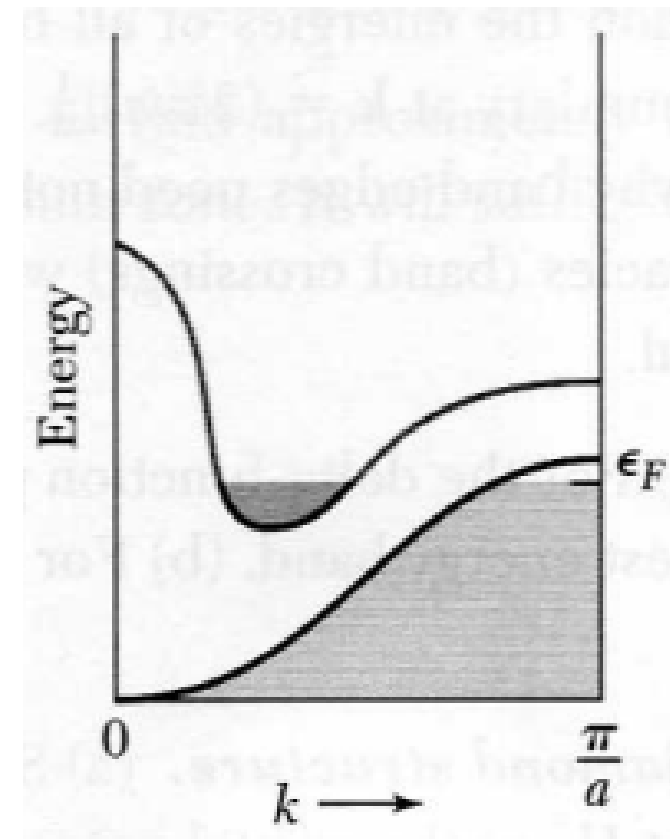
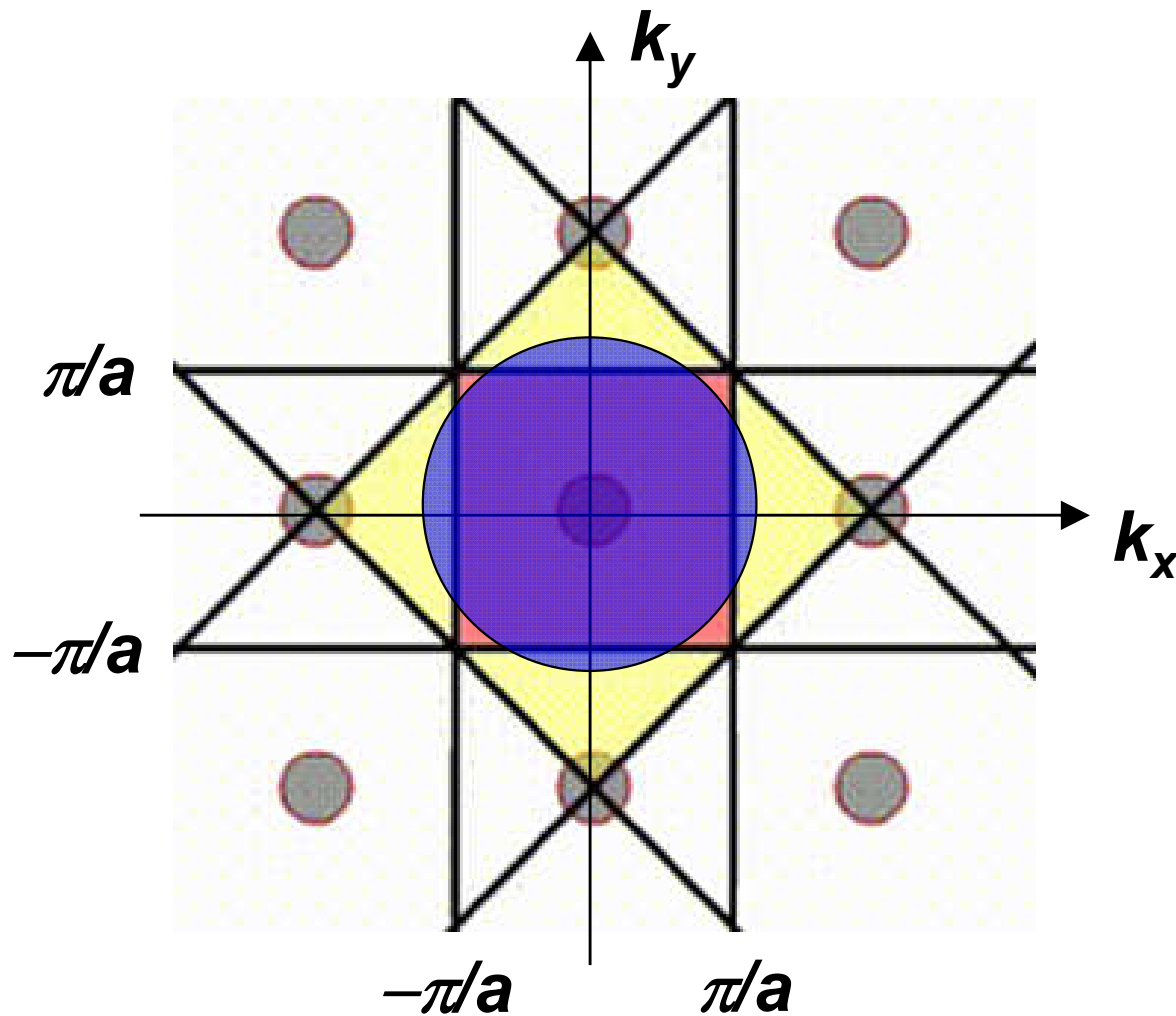
electrons

First BZ

Second BZ

2D case of *Divalent* Atoms

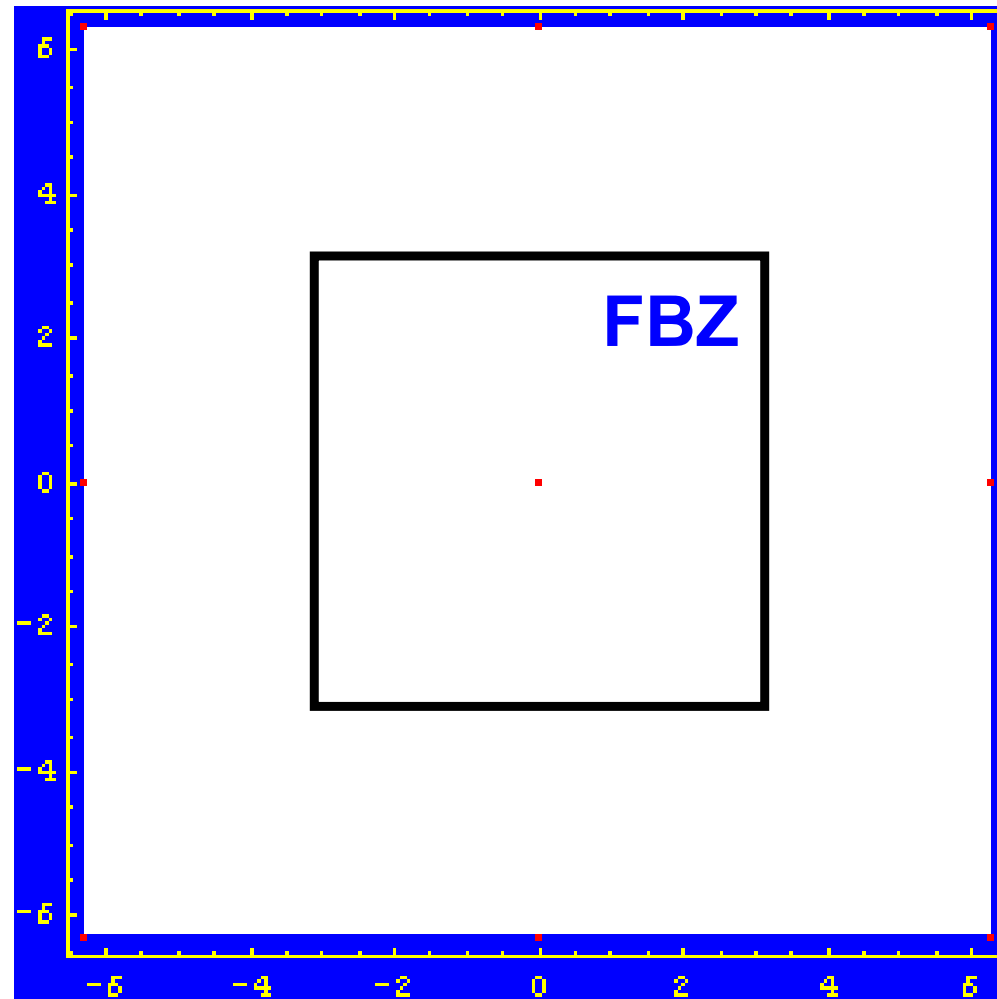
Each atom has *two* valence electrons (Mg, Ca, ...)



semimetal 半金属

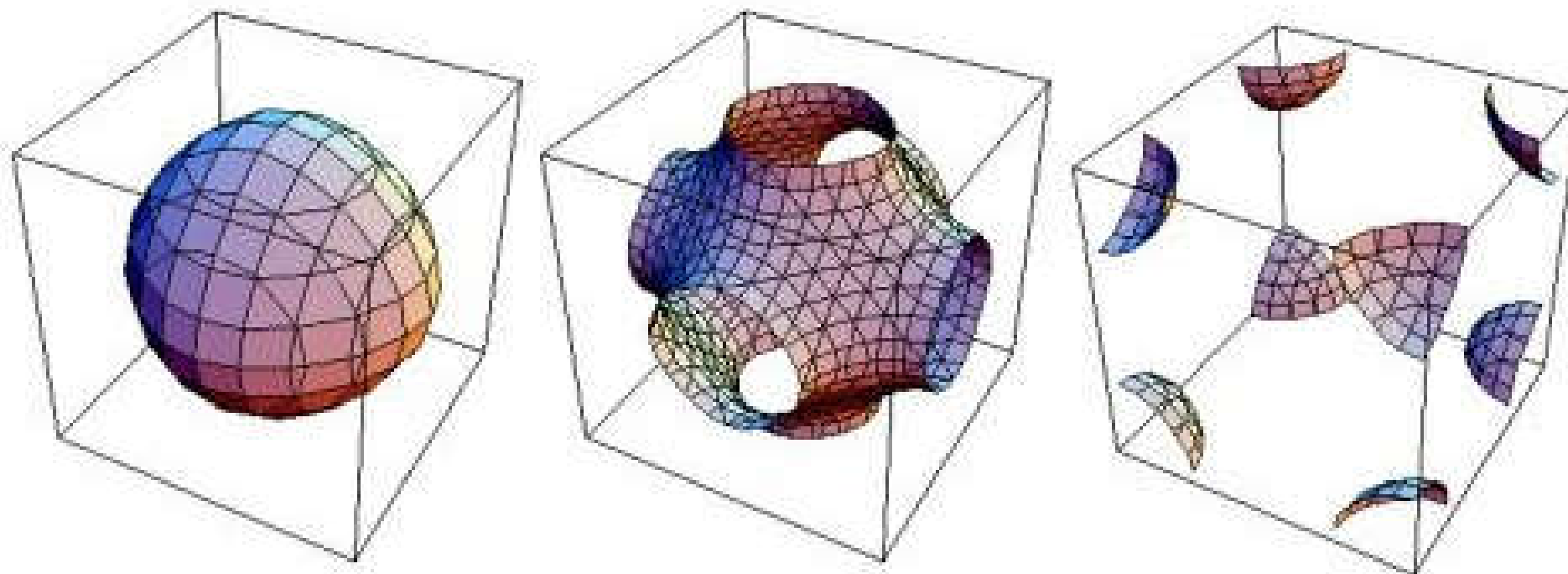
2D Fermi Surface

simple square



3D Fermi Surface

simple cubic



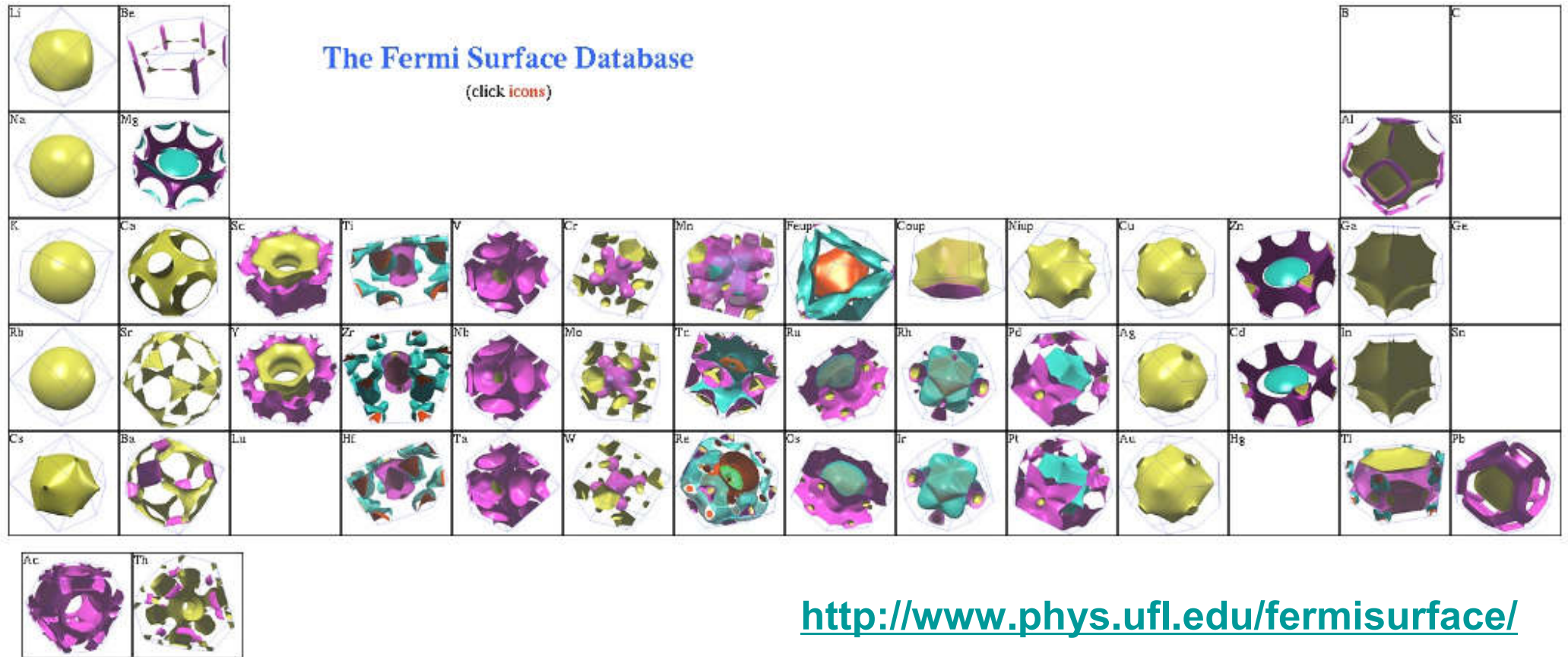
Increasing Fermi Energy



generated with a tight binding model:

<http://home.cc.umanitoba.ca/~loly/fermisurf2.html>

3D Fermi Surface – More Examples



Fermi surface is the surface in reciprocal space which separates occupied from unoccupied electron states at $T = 0$ K.

Metals in the Periodic Table

Metals, Nonmetals, and Metalloids

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|--|----|----|----|----|----|----|----|----|----|----|-----|----|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---|----|----|----|----|----|----|----|----|----|----|----|
| H | | | | | | | | | | | | | | | | | He | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | Ds | Rg | Uub | — | Uuq | — | — | — | — | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <table border="1" style="width: 100%; text-align: center;"> <tbody> <tr> <td>Ce</td><td>Pr</td><td>Nd</td><td>Pm</td><td>Sm</td><td>Eu</td><td>Gd</td><td>Tb</td><td>Dy</td><td>Ho</td><td>Er</td><td>Tm</td><td>Yb</td><td>Lu</td> </tr> <tr> <td>Th</td><td>Pa</td><td>U</td><td>Np</td><td>Pu</td><td>Am</td><td>Cm</td><td>Bk</td><td>Cf</td><td>Es</td><td>Fm</td><td>Md</td><td>No</td><td>Lr</td> </tr> </tbody> </table> | | | | | | | | | | | | | | | | | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr |
| Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

金属

metals

类金属

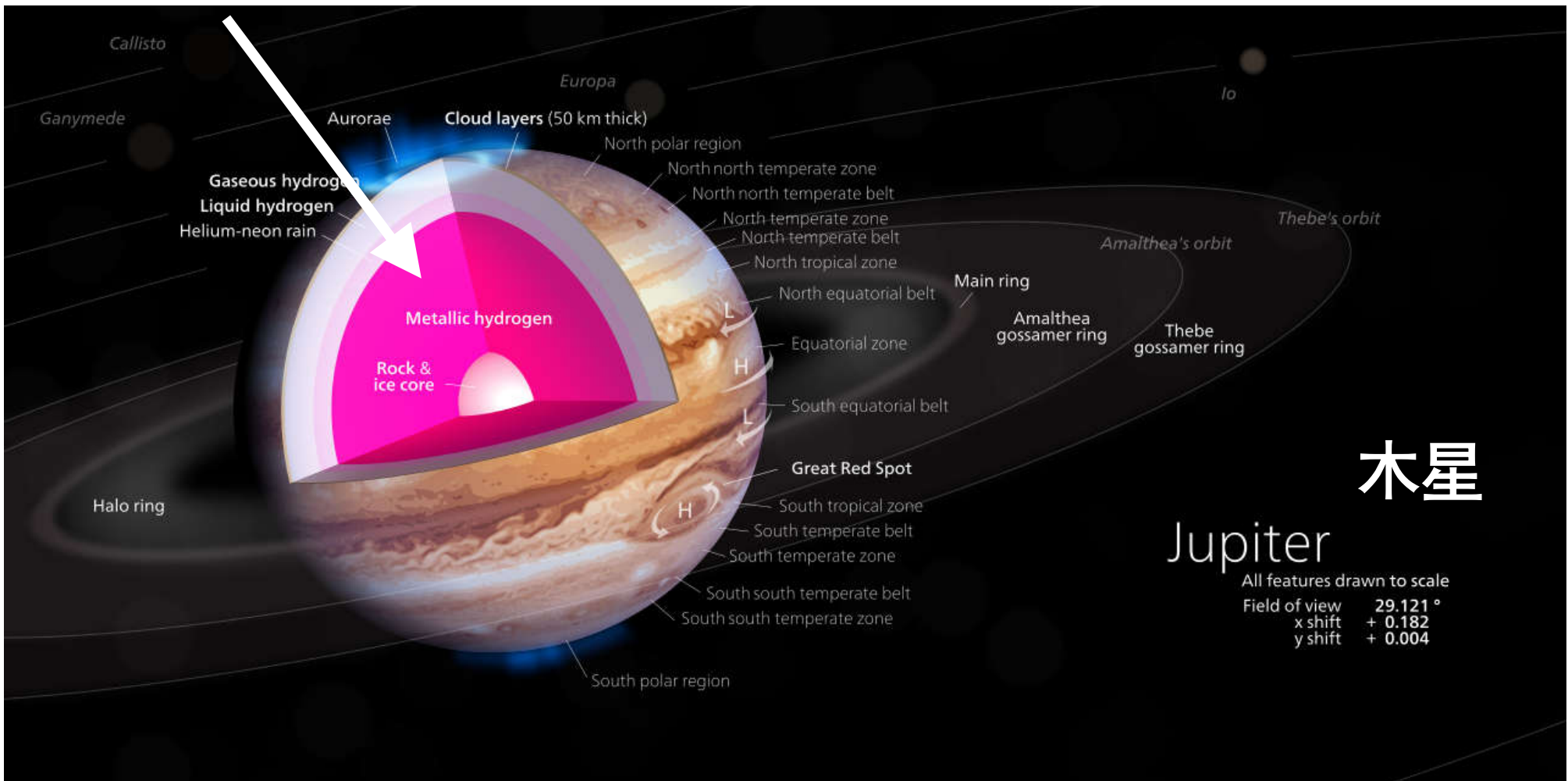
metalloids

非金属

nonmetals

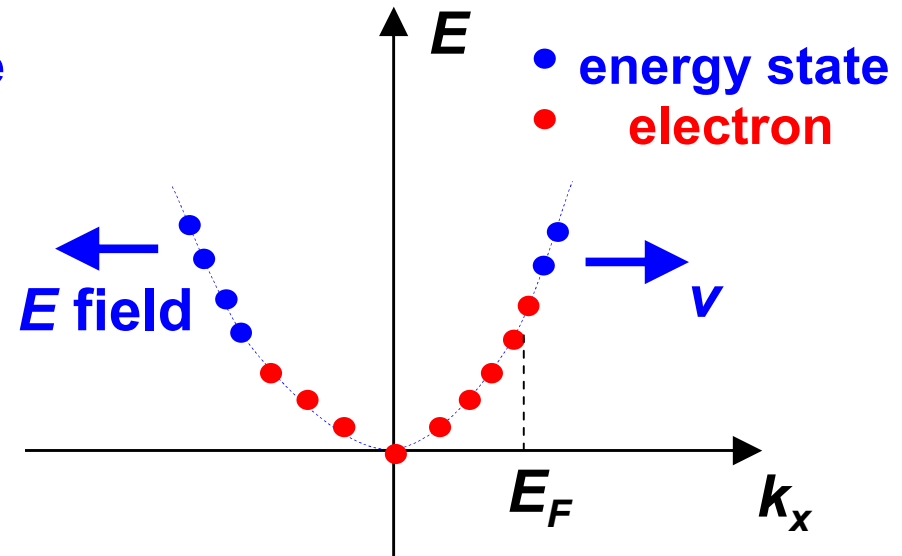
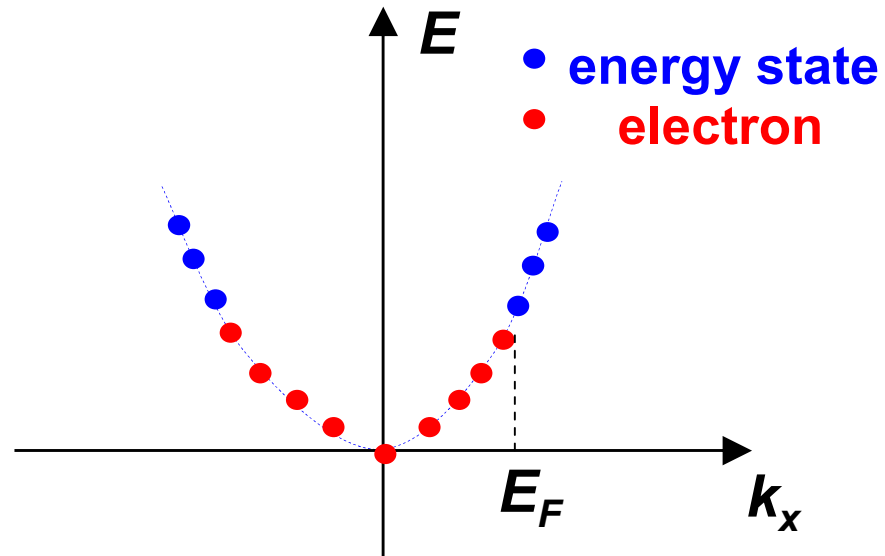
Solid Hydrogen is also Metallic

Metallic hydrogen only exists under very high pressure



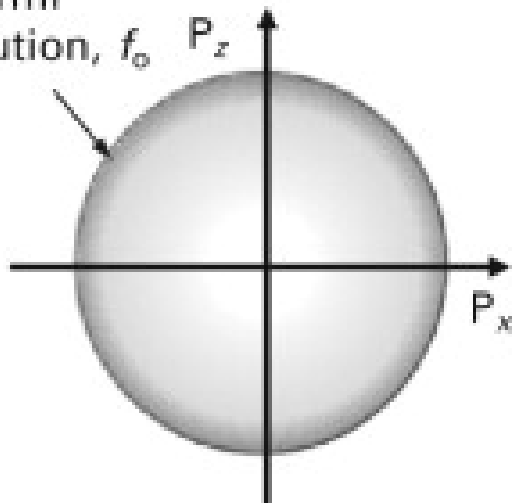
Electrical Conductivity - Revisit

1D



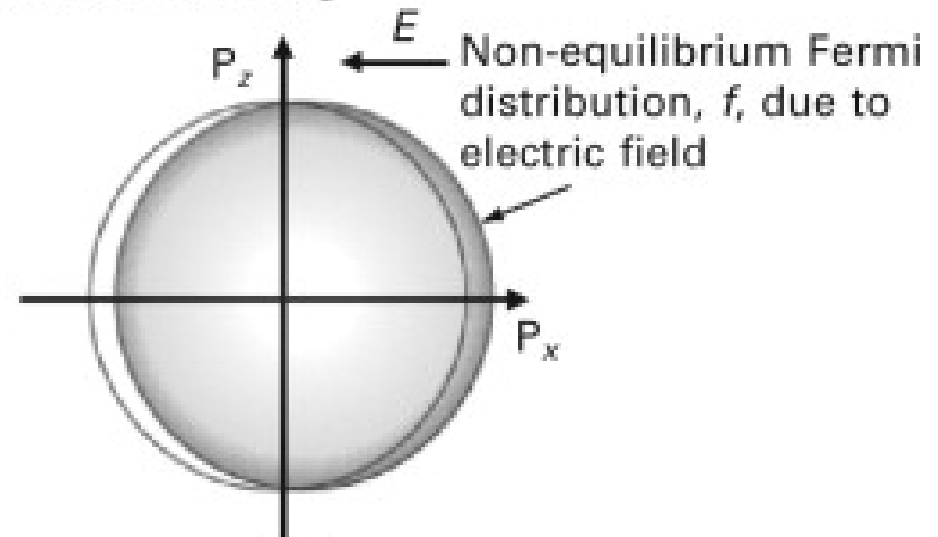
2D

Equilibrium
Fermi
distribution, f_0



3D

Diffuse scattering

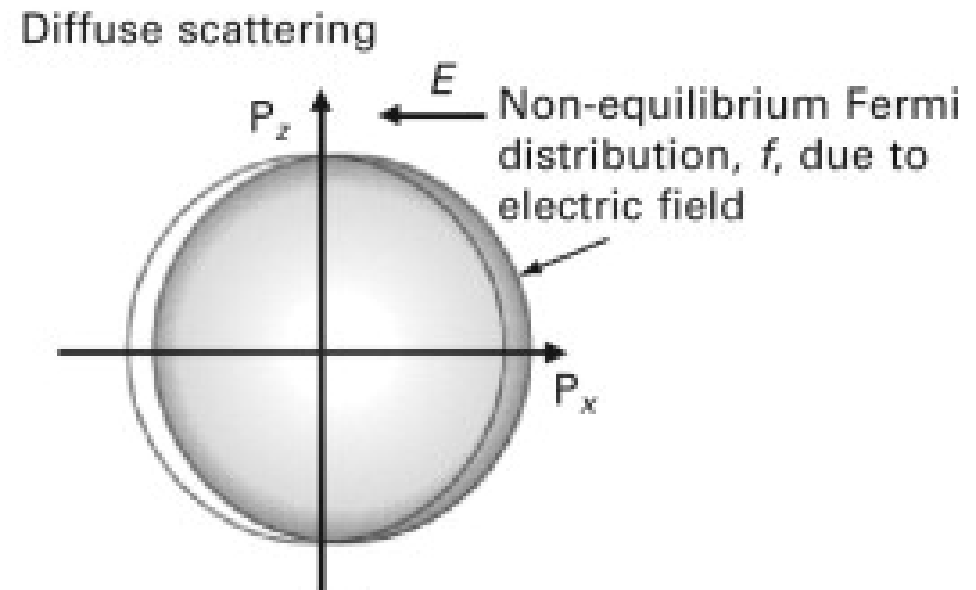
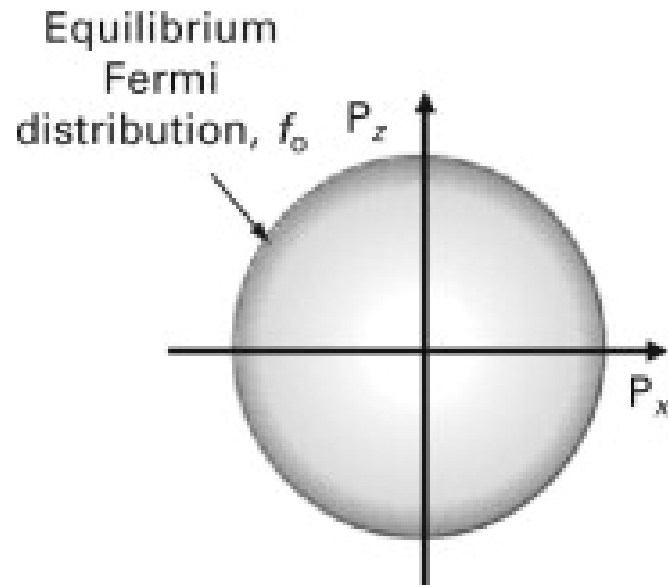


Electrical Conductivity - Revisit

- Only electrons **near the Fermi surface** contribute to electrical (and thermal) conductivity in metals

$$\sigma = e^2 \cdot \tau(E_F) \cdot \int_{\text{occupied levels}} \frac{2d\mathbf{k}}{(2\pi)^3} \cdot \frac{1}{M^*(\mathbf{k})}$$

Ashcroft & Mermin, Chap.13

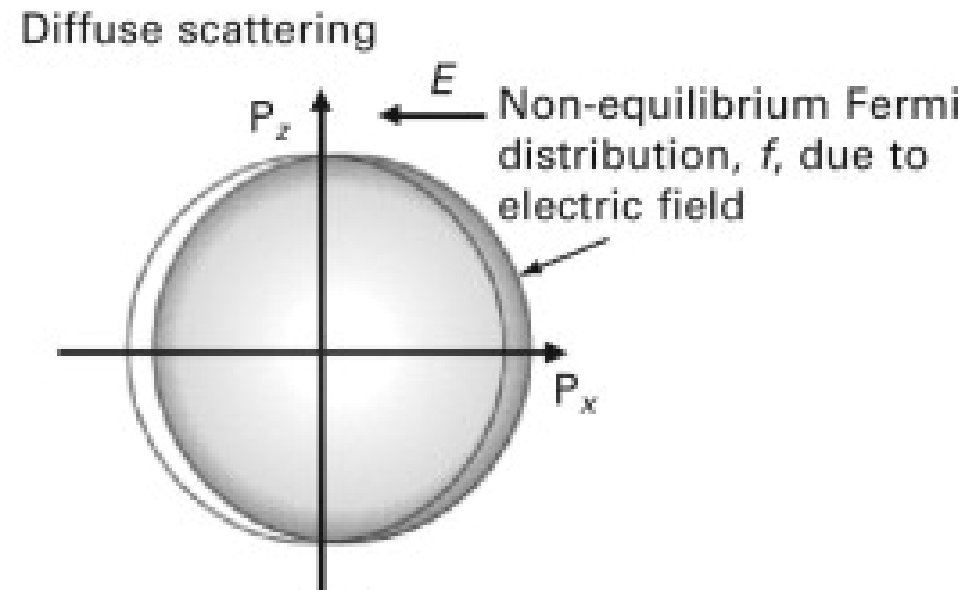
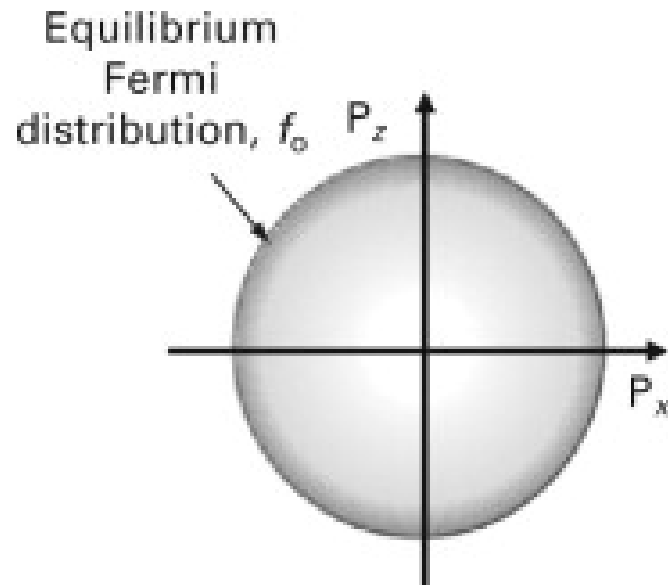


Electrical Conductivity - Revisit

- Only electrons **near the Fermi surface** contribute to electrical (and thermal) conductivity in metals

compare

$$\sigma = ne \frac{v}{E} = ne\mu = \frac{ne^2\tau}{m^*}$$



Electrical Conductivity - Revisit

- Only electrons **near the Fermi surface** contribute to electrical (and thermal) conductivity in metals



Electrical Conductivity - Revisit

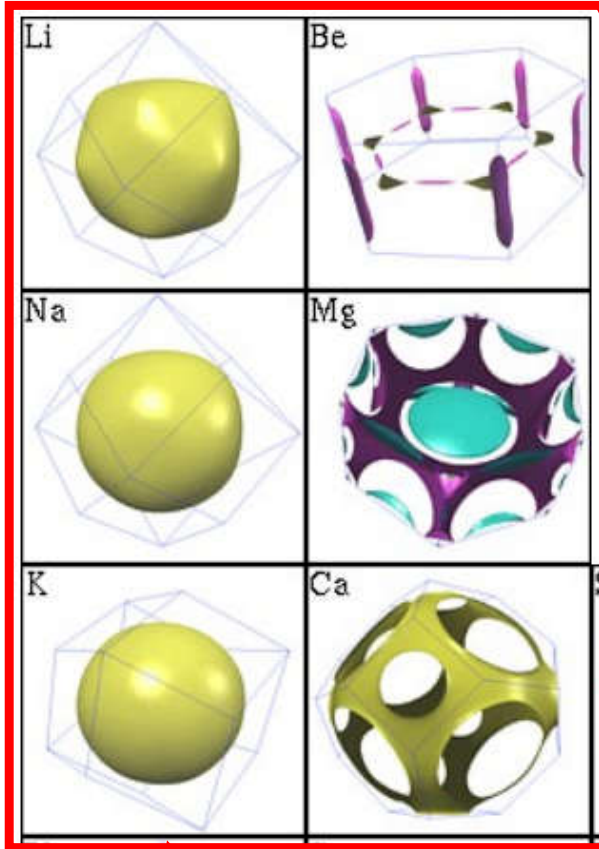
$$\sigma = ne \frac{v}{E} = ne\mu = \frac{ne^2\tau}{m^*}$$

| | | Classical | Quantum |
|------------------|--------|---------------------------------|--|
| electron density | n | all valence electrons | electrons near Fermi surface (depend on E field) |
| μ | τ | | |
| velocity | v | average (depend on temperature) | Fermi velocity v_F |
| mass | m | free electron m_0 | effective mass m^* |

3D Fermi Surface

IA

IIA



Metals in Group IA and IIA have very different properties

Periodic Table of the Elements

| 1 IA | 2 IIA | 3 IIIB | 4 IVB | 5 VB | 6 VIB | 7 VIIB | 8 VIIIB | 9 | 10 | 11 IB | 12 IIB | 13 IIIA | 14 IVA | 15 VA | 16 VIA | 17 VIIA | 18 VIIIA |
|-----------------------------|------------------------------|--------------------------------|----------------------------------|----------------------------------|-------------------------------|----------------------------------|-------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------------------------------|---------------------------------|--------------------------------|-----------------------------------|---------------------------------|-----------------------------------|----------------------------------|
| 1 H Hydrogen 1.008 | 2 He Helium 4.003 | | | | | | | | | | | 5 B Boron 10.811 | 6 C Carbon 12.011 | 7 N Nitrogen 14.007 | 8 O Oxygen 15.999 | 9 F Fluorine 18.998 | 10 Ne Neon 20.180 |
| 3 Li Lithium 6.941 | 4 Be Beryllium 9.012 | | | | | | | | | | | 13 Al Aluminum 26.982 | 14 Si Silicon 28.086 | 15 P Phosphorus 30.974 | 16 S Sulfur 32.065 | 17 Cl Chlorine 35.453 | 18 Ar Argon 39.948 |
| 11 Na Sodium 22.990 | 12 Mg Magnesium 24.305 | 21 Sc Scandium 44.956 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.942 | 24 Cr Chromium 51.996 | 25 Mn Manganese 54.938 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933 | 28 Ni Nickel 58.693 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.38 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.631 | 33 As Arsenic 74.922 | 34 Se Selenium 78.971 | 35 Br Bromine 79.904 | 36 Kr Krypton 84.798 |
| 19 K Potassium 39.098 | 20 Ca Calcium 40.078 | 39 Y Yttrium 88.906 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.906 | 42 Mo Molybdenum 95.95 | 43 Tc Technetium 98.907 | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.906 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.868 | 48 Cd Cadmium 112.411 | 49 In Indium 114.818 | 50 Sn Tin 118.710 | 51 Sb Antimony 121.760 | 52 Te Tellurium 127.6 | 53 I Iodine 126.904 | 54 Xe Xenon 131.294 |
| 55 Rb Rubidium 84.468 | 56 Sr Strontium 87.62 | 57-71 | 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.948 | 74 W Tungsten 183.84 | 75 Re Rhenium 186.207 | 76 Os Osmium 190.23 | 77 Ir Iridium 192.227 | 78 Pt Platinum 195.085 | 79 Au Gold 196.967 | 80 Hg Mercury 200.592 | 81 Tl Thallium 204.383 | 82 Pb Lead 207.2 | 83 Bi Bismuth 208.980 | 84 Po Polonium [209] | 85 At Astatine [209] | 86 Rn Radon 222.018 |
| 87 Cs Cesium 132.905 | 88 Ba Barium 137.328 | 89-103 | 104 Rf Rutherfordium [261] | 105 Db Dubnium [262] | 106 Sg Seaborgium [266] | 107 Bh Bohrium [264] | 108 Hs Hassium [269] | 109 Mt Meitnerium [268] | 110 Ds Darmstadtium [269] | 111 Rg Roentgenium [272] | 112 Cn Copernicium [277] | 113 Uut Ununtrium unknown | 114 Fl Flerovium [289] | 115 Uup Ununpentium unknown | 116 Lv Livermorium [293] | 117 Uus Ununseptium unknown | 118 Uuo Ununoctium unknown |
| Lanthanide Series | | 57 La Lanthanum 138.905 | 58 Ce Cerium 140.116 | 59 Pr Praseodymium 140.908 | 60 Nd Neodymium 144.243 | 61 Pm Promethium [144.913] | 62 Sm Samarium 150.36 | 63 Eu Europium 151.964 | 64 Gd Gadolinium 157.25 | 65 Tb Terbium 158.925 | 66 Dy Dysprosium 162.500 | 67 Ho Holmium 164.930 | 68 Er Erbium 167.259 | 69 Tm Thulium 168.934 | 70 Yb Ytterbium 173.055 | 71 Lu Lutetium 174.967 | |
| Actinide Series | | 89 Ac Actinium [227.028] | 90 Th Thorium 232.038 | 91 Pa Protactinium 231.036 | 92 U Uranium 238.029 | 93 Np Neptunium [237.048] | 94 Pu Plutonium 244.064 | 95 Am Americium [243.061] | 96 Cm Curium [247.070] | 97 Bk Berkelium [247.070] | 98 Cf Californium [251.080] | 99 Es Einsteinium [254] | 100 Fm Fermium [257.095] | 101 Md Mendelevium [258.1] | 102 No Nobelium [259.101] | 103 Lr Lawrencium [262] | |

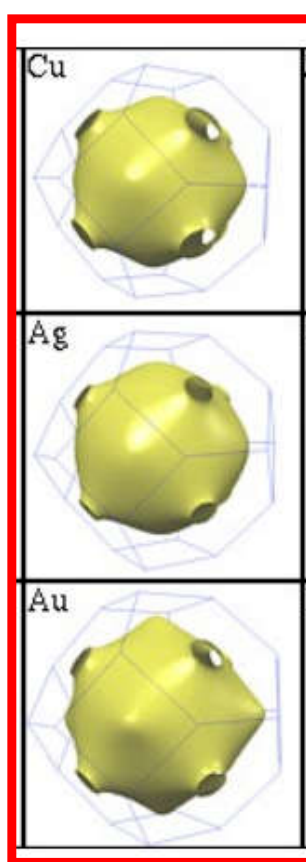
Alkali Metal Alkaline Earth Transition Metal Basic Metal Semimetal Nonmetal Halogen Noble Gas Lanthanide Actinide

spherical shape
close to free electrons

3D Fermi Surface

IB

Metals in Group IB are very good conductors



Periodic Table of the Elements

| Atomic Number | Symbol | Atomic Mass |
|---------------|-------------------|-------------|
| 1 | H | 1.008 |
| 2 | He | 4.003 |
| 3 | Li | 6.941 |
| 4 | Be | 9.012 |
| 5 | B | 10.811 |
| 6 | C | 12.011 |
| 7 | N | 14.007 |
| 8 | O | 15.999 |
| 9 | F | 18.998 |
| 10 | Ne | 20.180 |
| 11 | Na | 22.990 |
| 12 | Mg | 24.305 |
| 13 | Al | 26.982 |
| 14 | Si | 28.086 |
| 15 | P | 30.974 |
| 16 | S | 32.065 |
| 17 | Cl | 35.453 |
| 18 | Ar | 39.948 |
| 19 | K | 39.098 |
| 20 | Ca | 40.078 |
| 21 | Sc | 44.956 |
| 22 | Ti | 47.867 |
| 23 | V | 50.942 |
| 24 | Cr | 51.996 |
| 25 | Mn | 54.938 |
| 26 | Fe | 55.845 |
| 27 | Co | 58.933 |
| 28 | Ni | 58.693 |
| 29 | Cu | 63.546 |
| 30 | Zn | 65.38 |
| 31 | Ga | 69.723 |
| 32 | Ge | 72.631 |
| 33 | As | 74.922 |
| 34 | Se | 78.971 |
| 35 | Br | 79.904 |
| 36 | Kr | 84.798 |
| 37 | Rb | 84.468 |
| 38 | Sr | 87.62 |
| 39 | Y | 88.906 |
| 40 | Zr | 91.224 |
| 41 | Nb | 92.906 |
| 42 | Mo | 95.95 |
| 43 | Tc | 98.907 |
| 44 | Ru | 101.07 |
| 45 | Rh | 102.906 |
| 46 | Pd | 106.42 |
| 47 | Ag | 107.868 |
| 48 | Cd | 112.411 |
| 49 | In | 114.818 |
| 50 | Sn | 118.711 |
| 51 | Sb | 121.760 |
| 52 | Te | 127.6 |
| 53 | I | 126.904 |
| 54 | Xe | 131.294 |
| 55 | Cs | 132.905 |
| 56 | Ba | 137.328 |
| 57-71 | Lanthanide Series | |
| 72 | Hf | 178.49 |
| 73 | Ta | 180.948 |
| 74 | W | 183.84 |
| 75 | Re | 186.207 |
| 76 | Os | 190.23 |
| 77 | Ir | 192.217 |
| 78 | Pt | 195.085 |
| 79 | Au | 196.967 |
| 80 | Hg | 200.592 |
| 81 | Tl | 204.383 |
| 82 | Pb | 207.2 |
| 83 | Bi | 208.980 |
| 84 | Po | [209] |
| 85 | At | unknown |
| 86 | Rn | 222.018 |
| 87 | Fr | 223.020 |
| 88 | Ra | 226.025 |
| 89-103 | Actinide Series | |
| 104 | Rf | [261] |
| 105 | Db | [262] |
| 106 | Sg | [266] |
| 107 | Bh | [264] |
| 108 | Hs | [269] |
| 109 | Mt | [268] |
| 110 | Ds | [271] |
| 111 | Rg | [272] |
| 112 | Cn | [285] |
| 113 | Uut | unknown |
| 114 | Ff | [289] |
| 115 | Uup | unknown |
| 116 | Lv | [293] |
| 117 | Uus | unknown |
| 118 | Uuo | unknown |
| 57 | La | 138.905 |
| 58 | Ce | 140.116 |
| 59 | Pr | 140.908 |
| 60 | Nd | 144.243 |
| 61 | Pm | 144.913 |
| 62 | Sm | 150.36 |
| 63 | Eu | 151.964 |
| 64 | Gd | 157.25 |
| 65 | Tb | 158.925 |
| 66 | Dy | 162.500 |
| 67 | Ho | 164.930 |
| 68 | Er | 167.259 |
| 69 | Tm | 168.934 |
| 70 | Yb | 173.055 |
| 71 | Lu | 174.967 |
| 89 | Ac | 227.028 |
| 90 | Th | 232.038 |
| 91 | Pa | 231.036 |
| 92 | U | 238.029 |
| 93 | Np | 237.048 |
| 94 | Pu | 244.064 |
| 95 | Am | 243.061 |
| 96 | Cm | 247.070 |
| 97 | Bk | 247.070 |
| 98 | Cf | 251.080 |
| 99 | Es | [254] |
| 100 | Fm | 257.095 |
| 101 | Md | 258.1 |
| 102 | No | 259.101 |
| 103 | Lr | [262] |

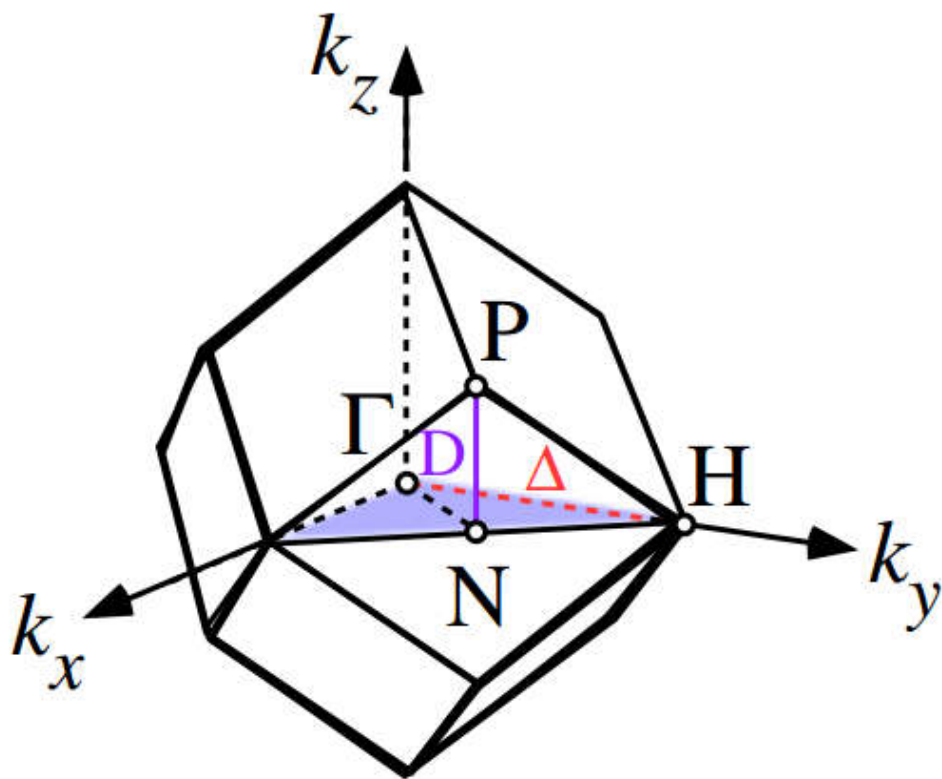
Legend:

- Alkali Metal
- Alkaline Earth
- Transition Metal
- Basic Metal
- Semimetal
- Nonmetal
- Halogen
- Noble Gas
- Lanthanide
- Actinide

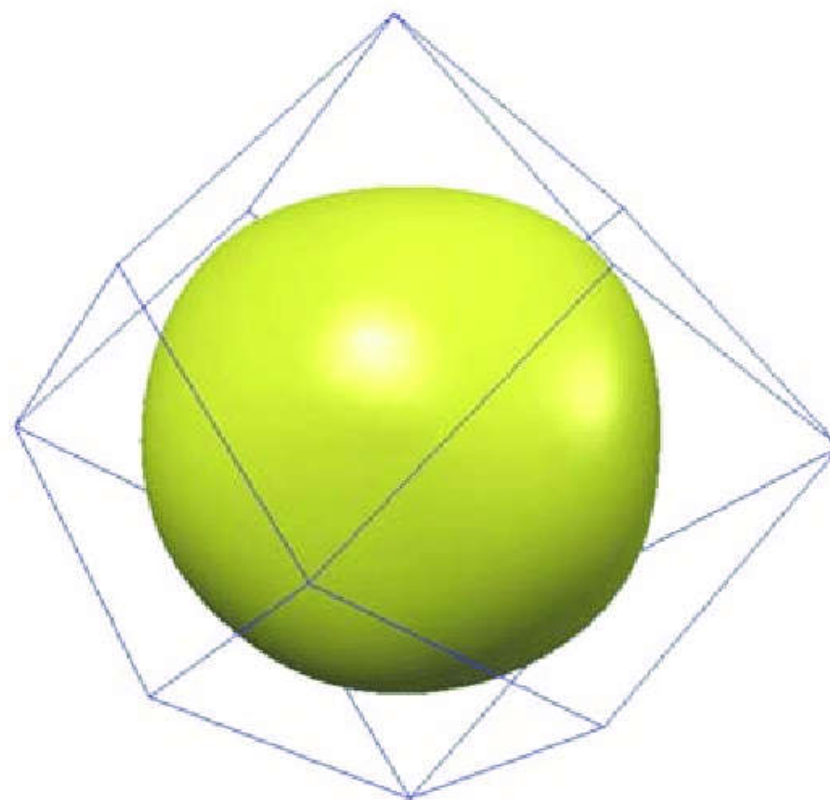
spherical shape
close to free electrons

3D case

sodium (BCC)



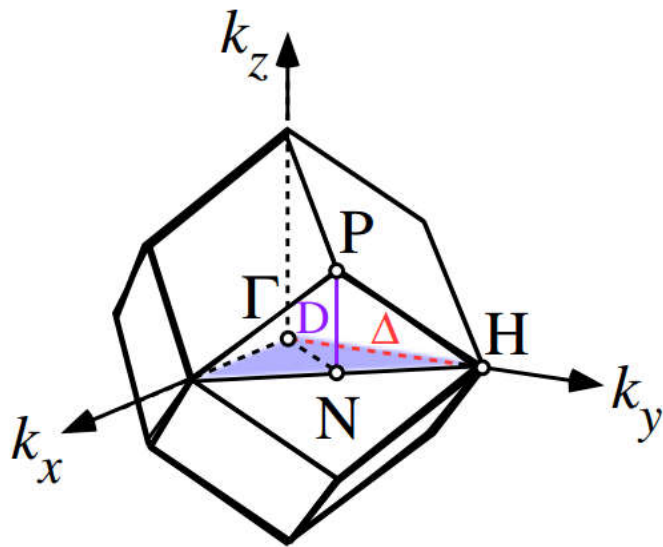
First BZ



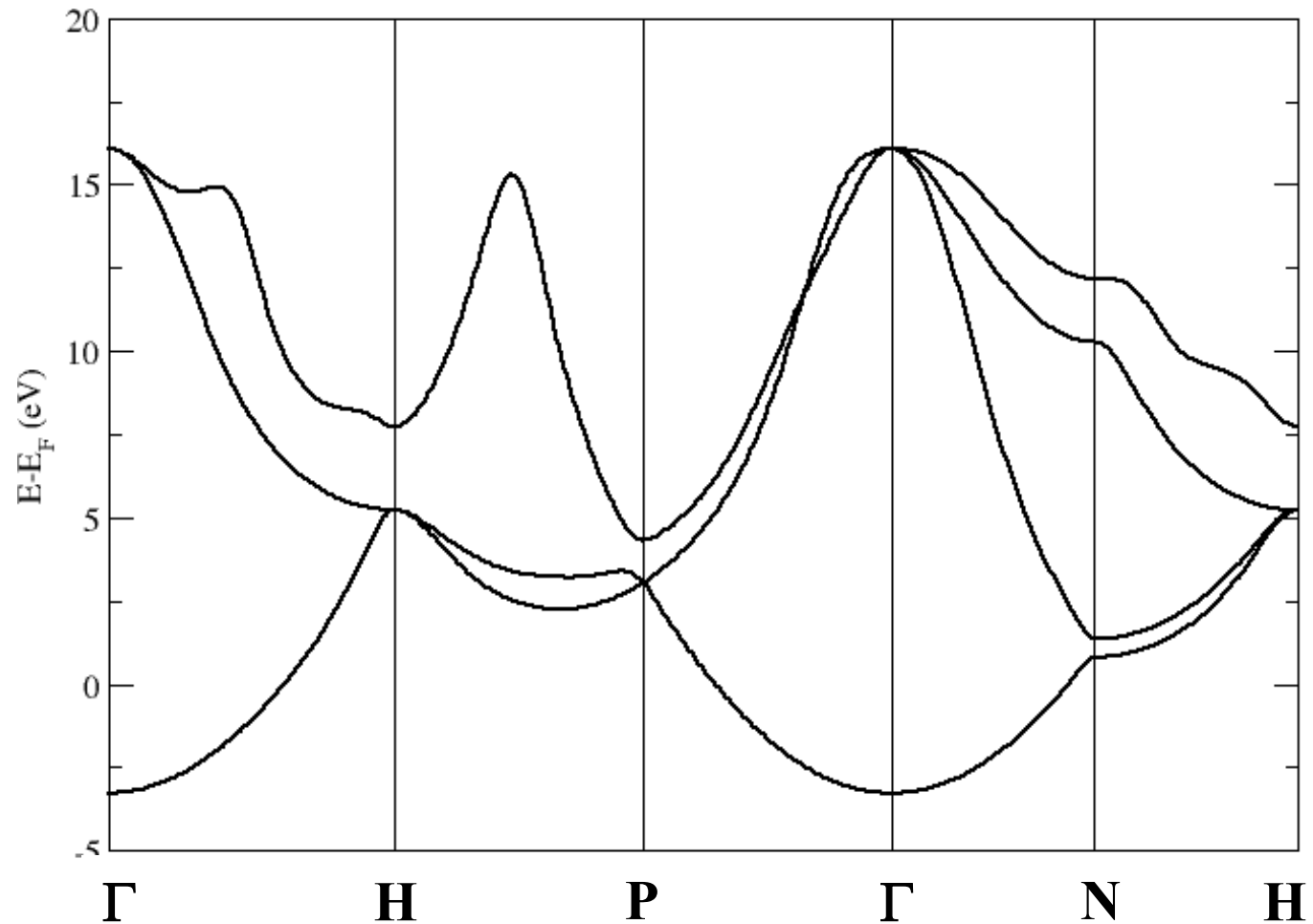
Fermi Surface

3D case

sodium (BCC): band structure

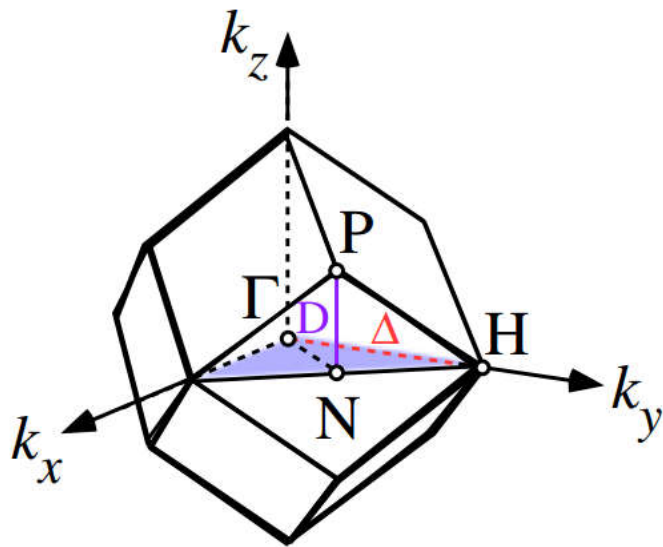


First BZ

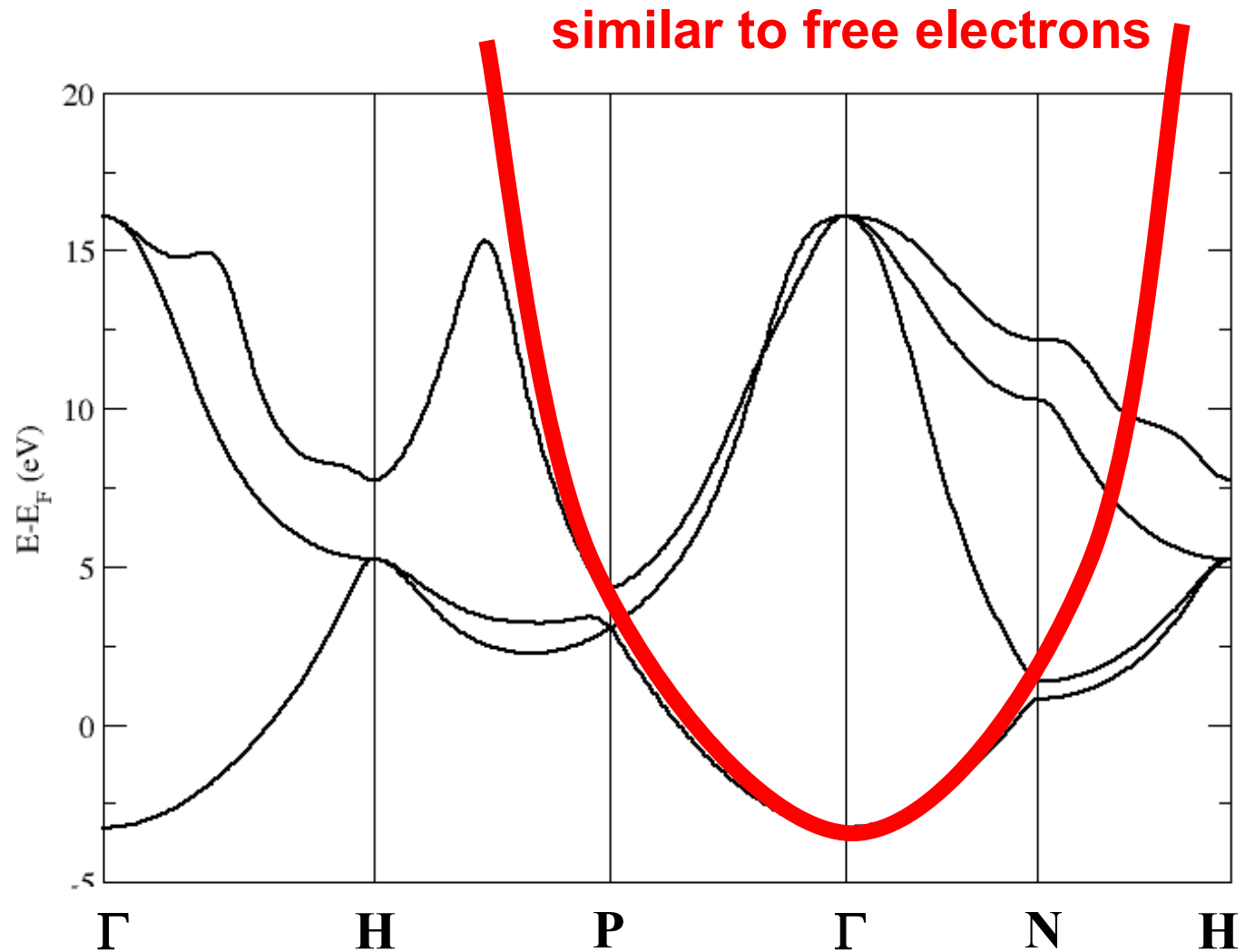


3D case

sodium (BCC): band structure

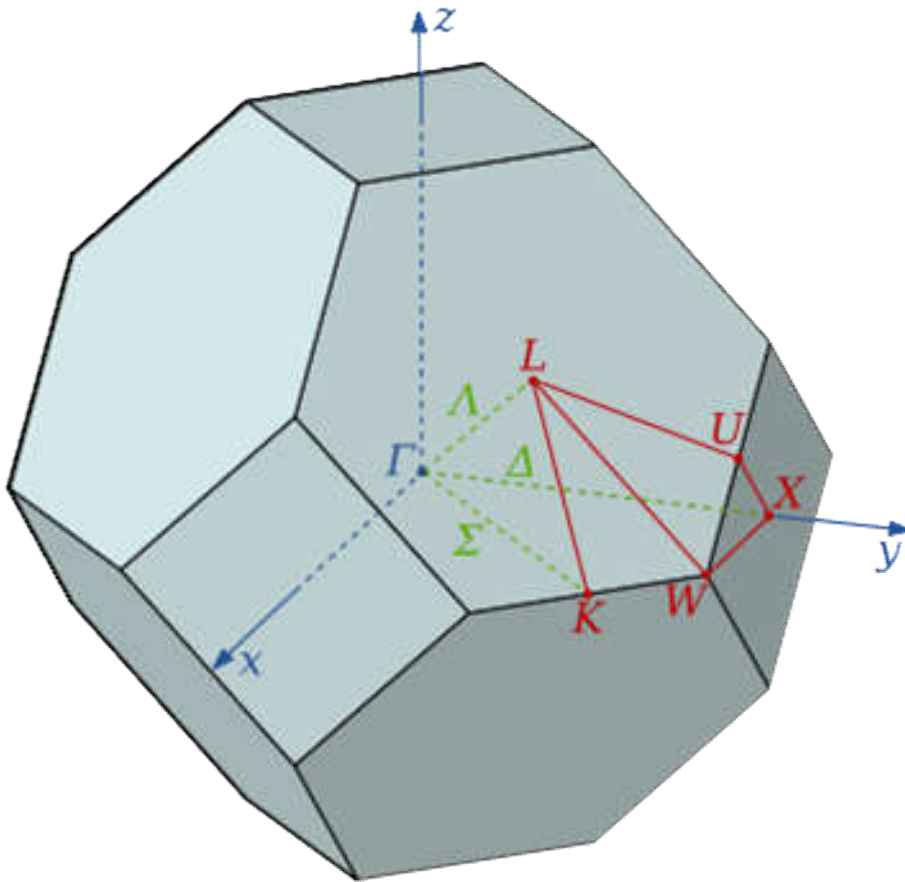


First BZ

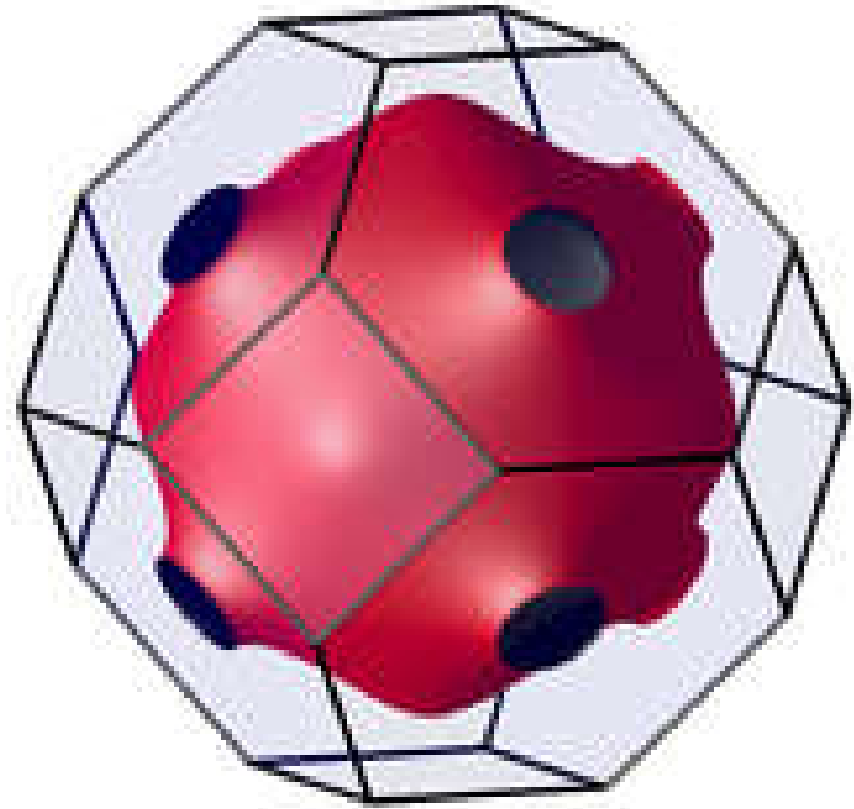


3D case

copper (FCC)



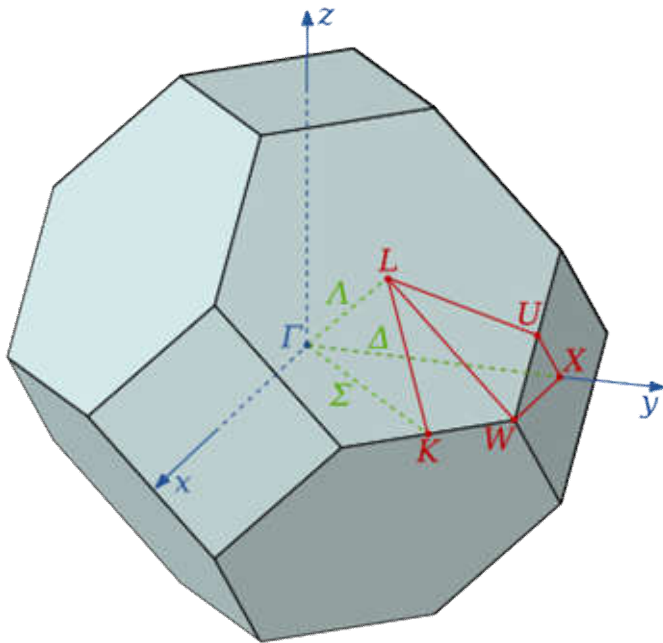
First BZ



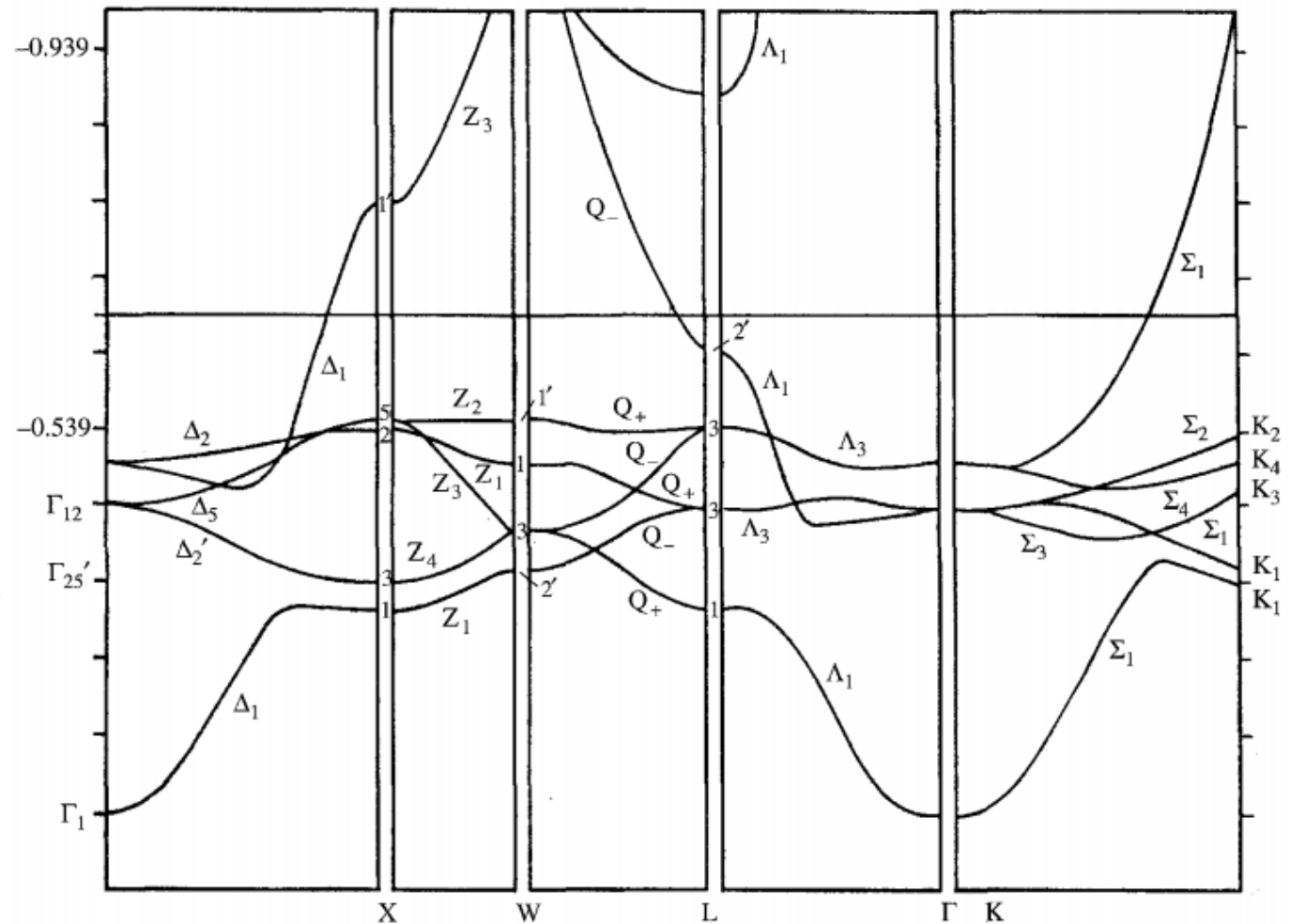
Fermi Surface

3D case

copper (FCC): band structure



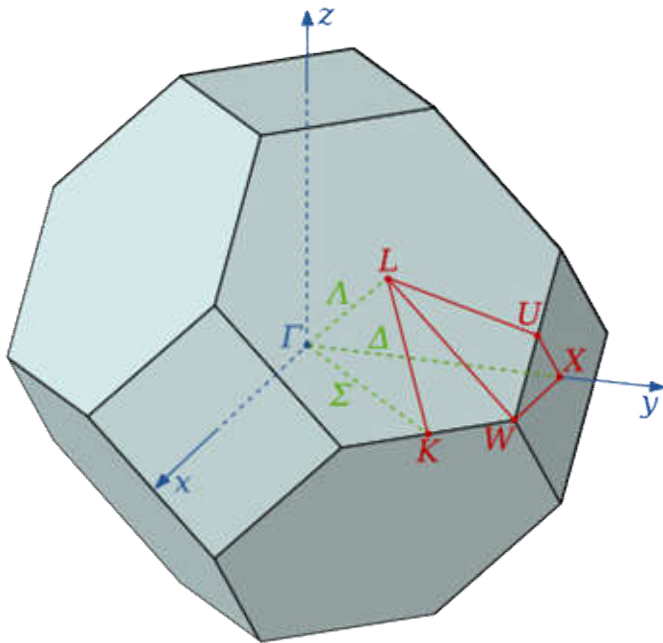
First BZ



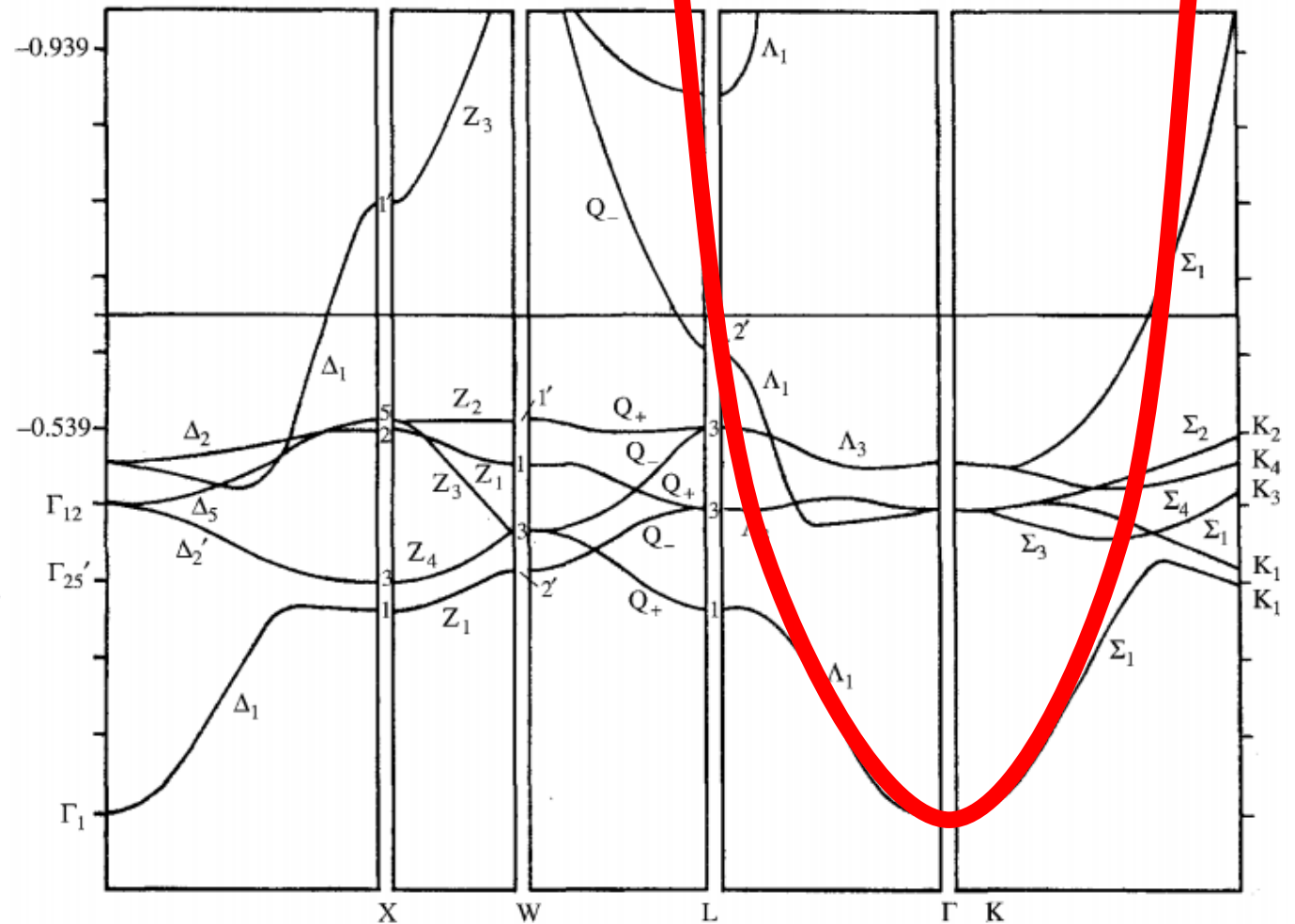
3D case

copper (FCC): band structure

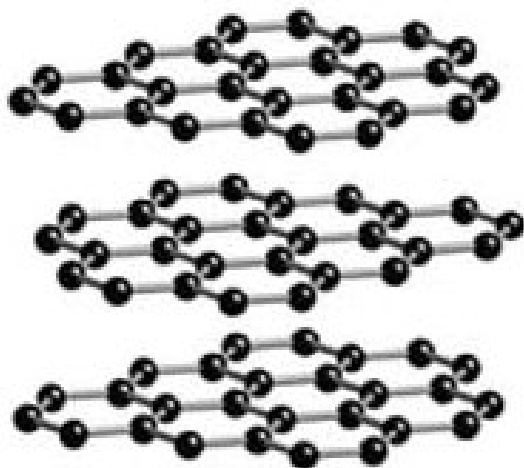
similar to free electrons



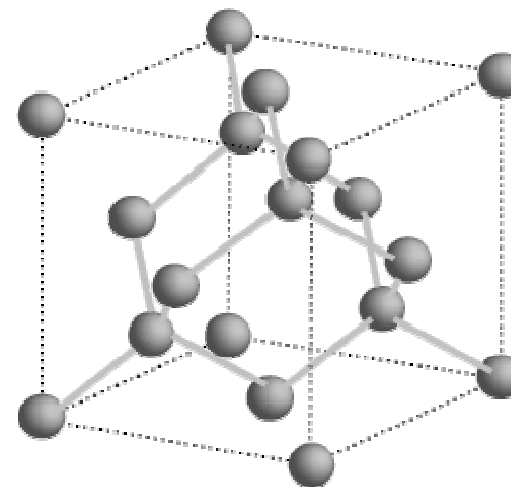
First BZ



Example - Carbon

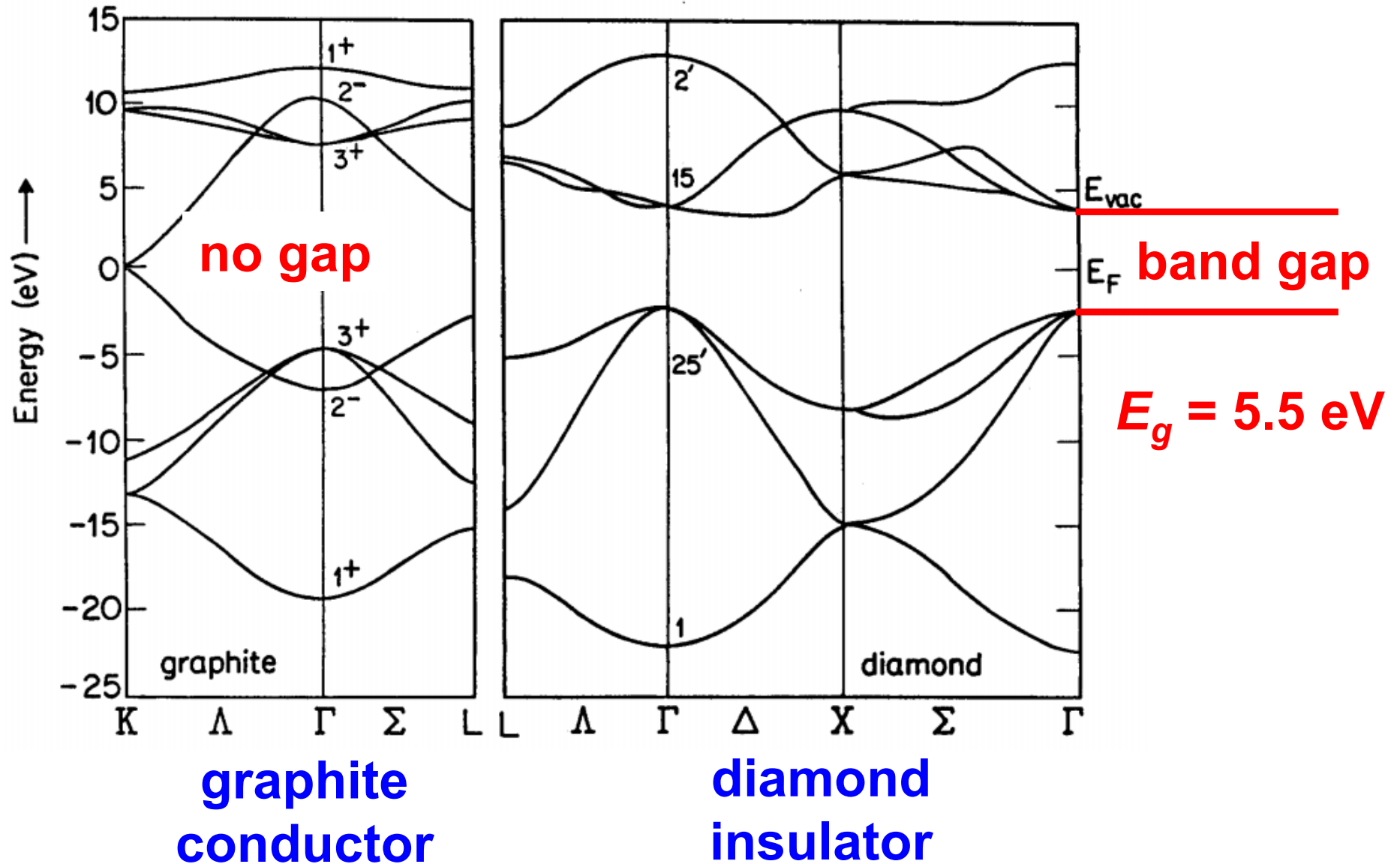


graphite
 $\sigma \sim 10^5 \text{ S/m}$



diamond
 $\sigma \sim 10^{-13} \text{ S/m}$

Example - Carbon



Temperature Dependence of σ

- For metals

- n and m^* have weak dependence on T
- τ has a strong dependence on T
- higher T \rightarrow shorter l and $\tau \rightarrow$ smaller $\mu \rightarrow$ smaller σ

$$\frac{1}{\rho} = \sigma = ne\mu = \frac{ne^2\tau}{m^*}$$

$$\tau = \frac{l}{v}$$

τ - relaxation time (s)
 l - mean free path (m)

- At $T = 0$ K, perfect metals should have no collision, infinite l and $\tau \rightarrow$ infinite σ

Temperature Dependence of σ

- Resistivity originates from the collision with imperfect crystals

Matthiessen's rule

$$\rho = \rho_i + \rho_p$$

impurity

phonon
(thermal vibration)

$$\rho_i \sim \frac{1}{l_i} \sim n_i = \text{constant}$$

$$\rho_p \sim \frac{1}{l_p} \sim n_p \sim k_B T$$

(at high T)

$$\rho(T) = \rho_0 [1 + \alpha \Delta T]$$

Temperature Dependence of σ

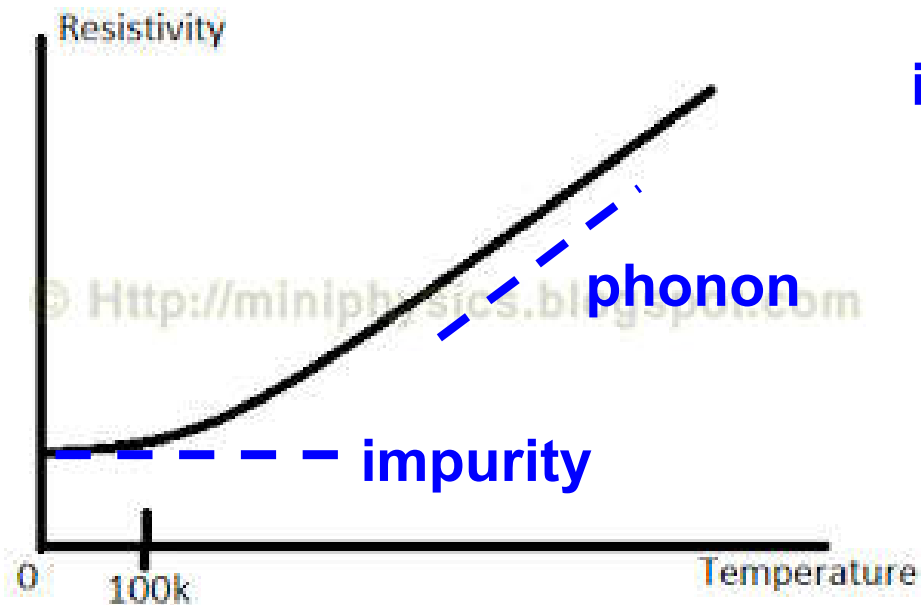
- Resistivity originates from the collision with imperfect crystals

Matthiessen's rule

$$\rho = \rho_i + \rho_p$$

impurity

phonon
(thermal vibration)

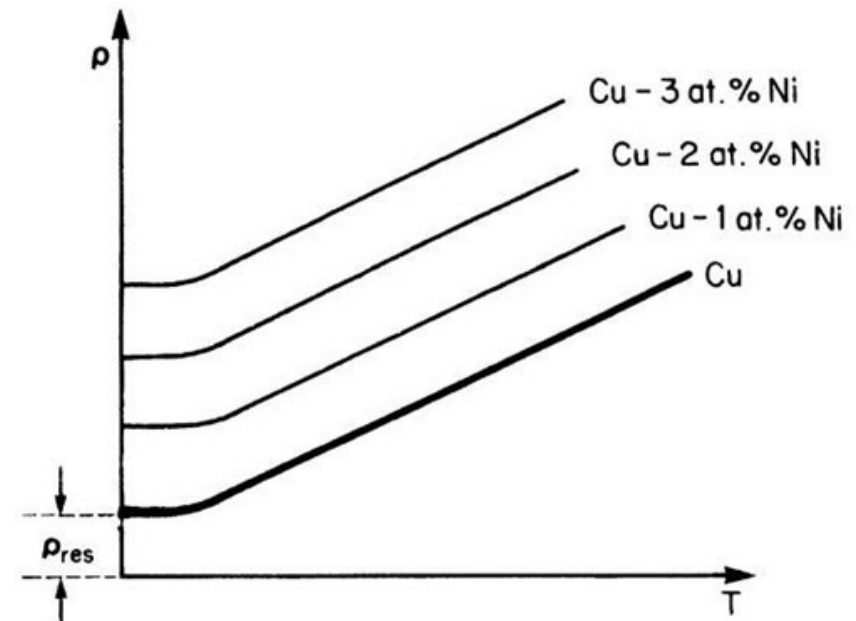
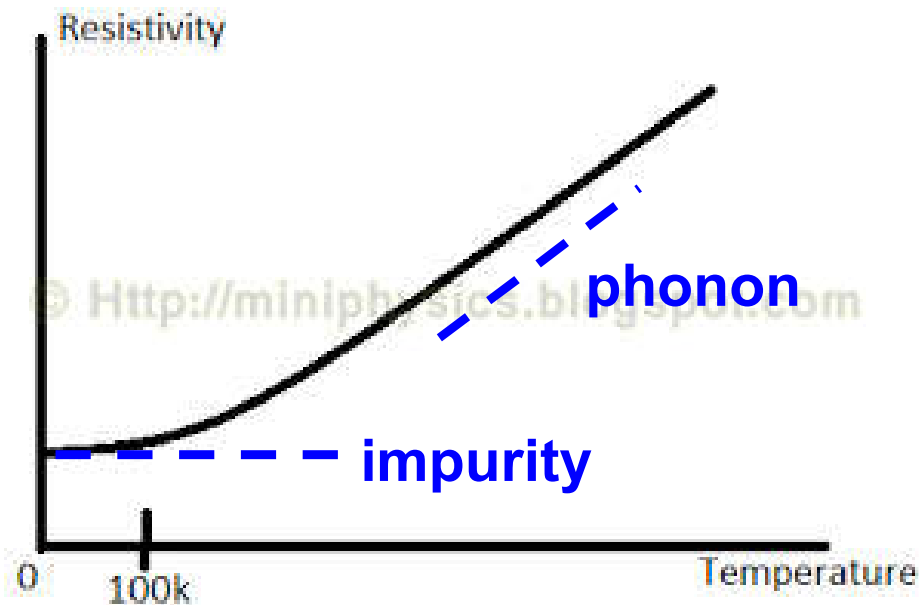


$$\rho(T) = \rho_0 [1 + \alpha \Delta T]$$

Temperature Dependence of σ

- Resistivity originates from the collision with imperfect crystals

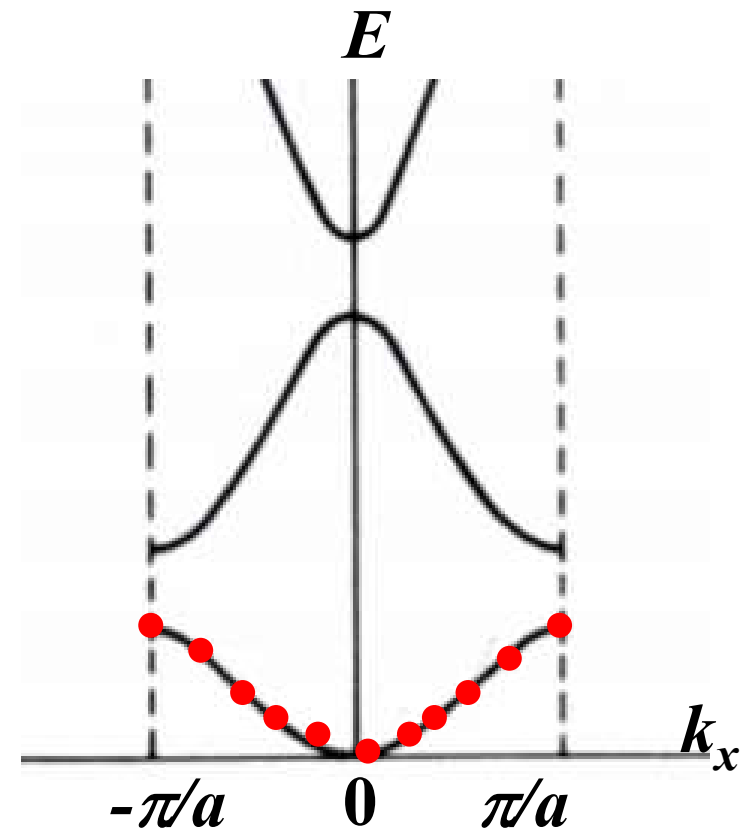
$$\rho(T) = \rho_0 [1 + \alpha \Delta T]$$



<http://what-when-how.com/electronic-properties-of-materials/electrical-conduction-in-metals-and-alloys-electrical-properties-of-materials-part-2/>

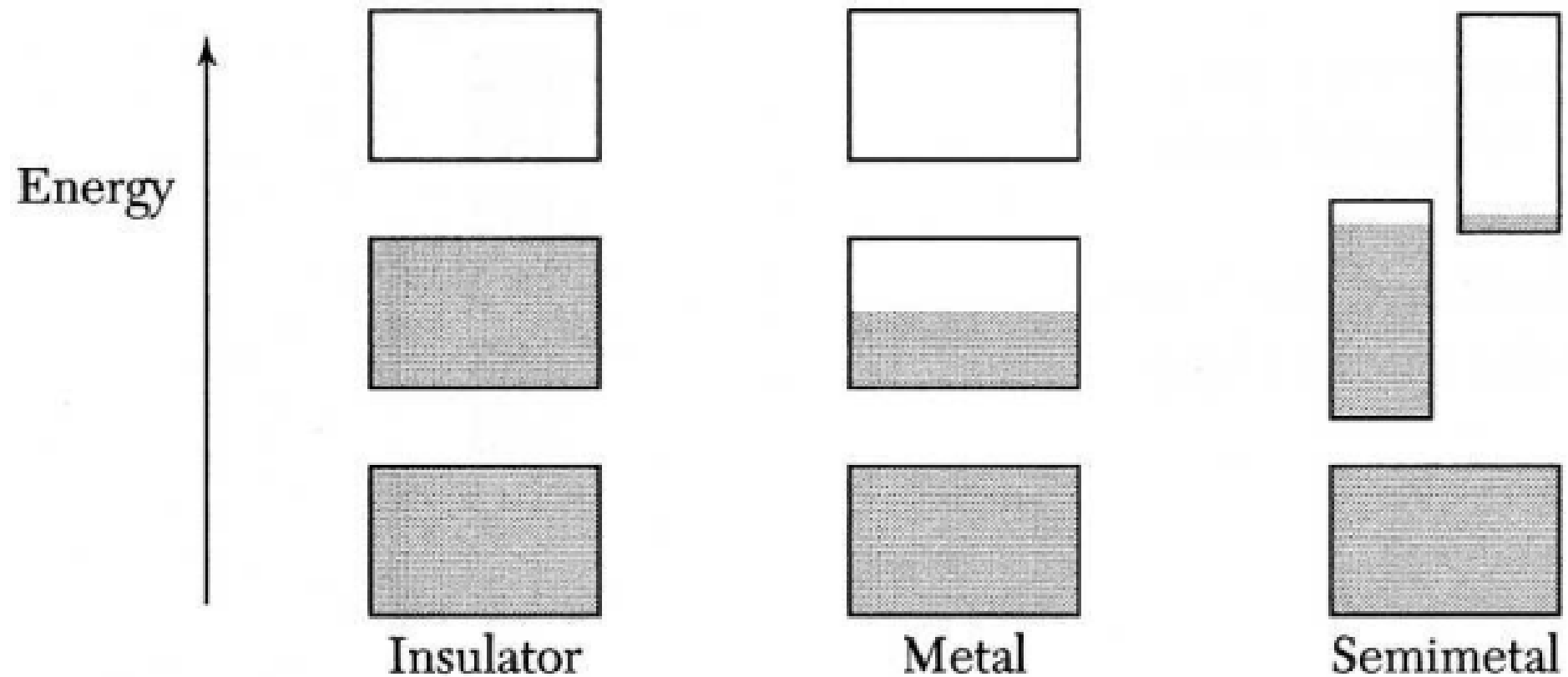
Summary

- **Electronic properties of solids depend on**
 - **band structure**
 - **electron density**
- **also depend on**
 - **defects**
 - **temperature**
 - **electric field**
 - **...**



● **electron**

Summary



Thank you for your attention