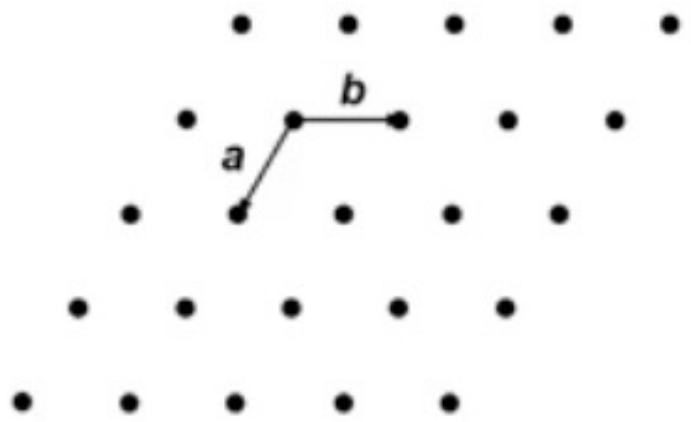
Learning Objectives

Electronic Band Structure of Graphene

By the end of this lecture, you will be able to:

- Construct reciprocal lattice vectors for non-orthogonal hexagonal systems and identify the hexagonal first Brillouin zone
- Locate special k-points (Gamma, M, K, K') in hexagonal Brillouin zones and convert between reciprocal lattice and Cartesian coordinates
- Distinguish sigma and pi band contributions in graphene and apply orbital orthogonality at high-symmetry points
- Predict bonding character of pi orbitals at Gamma, M, and K points using phase relationship analysis
- Explain semi-metallic behavior, Dirac points, and linear dispersion as unique features of graphene's electronic structure

Reciprocal Space 2D Hexagonal Lattice



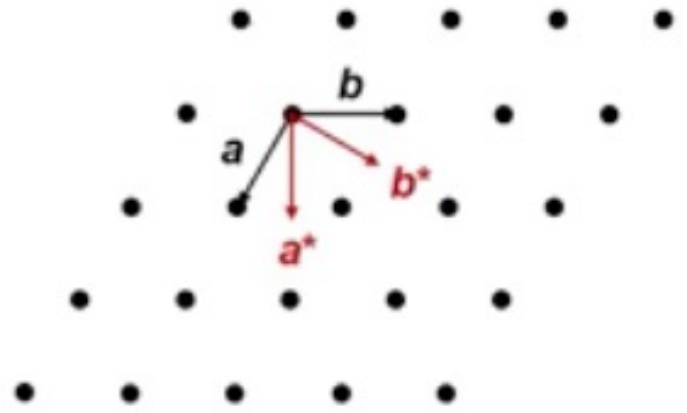
real-space lattice

$$\boldsymbol{T} = u\boldsymbol{a} + v\boldsymbol{b}$$

$a = b$, $\gamma = 120^{\circ}$

u, v = integers

Reciprocal Space 2D Hexagonal Lattice



real-space lattice

$$\boldsymbol{T} = u\boldsymbol{a} + v\boldsymbol{b}$$

$a = b$, $\gamma = 120^\circ$

u, v = integers

Reciprocal space lattice vectors

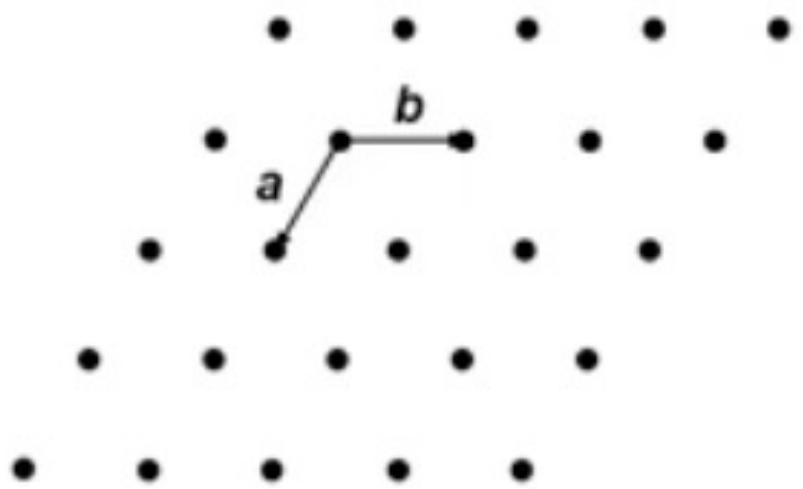
$\boldsymbol{a}^*$ perpendicular to $\boldsymbol{b}$

$\boldsymbol{a}^* \cdot \boldsymbol{a} = 2\pi$

$\boldsymbol{b}^*$ perpendicular to $\boldsymbol{a}$

$\boldsymbol{b}^* \cdot \boldsymbol{b} = 2\pi$

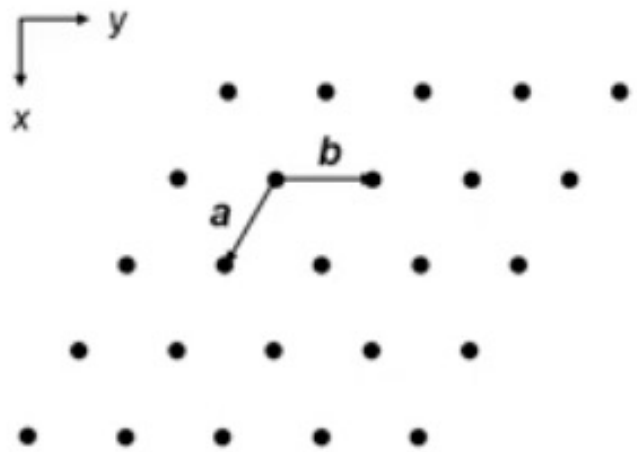
Reciprocal Space 2D Hexagonal Lattice



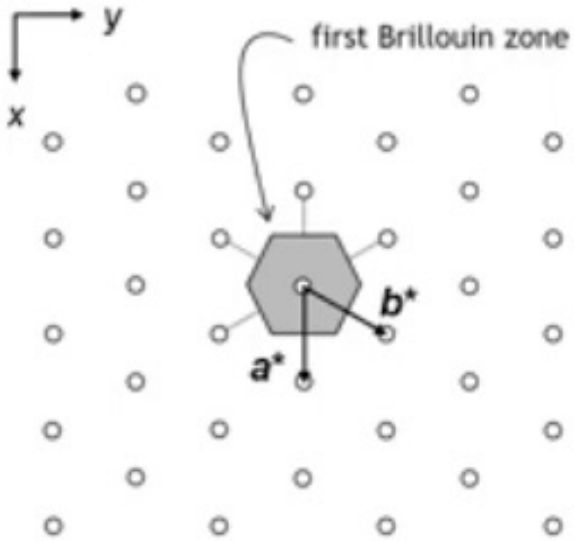
real-space lattice

reciprocal-space lattice

Reciprocal Space 2D Hexagonal Lattice



real-space lattice



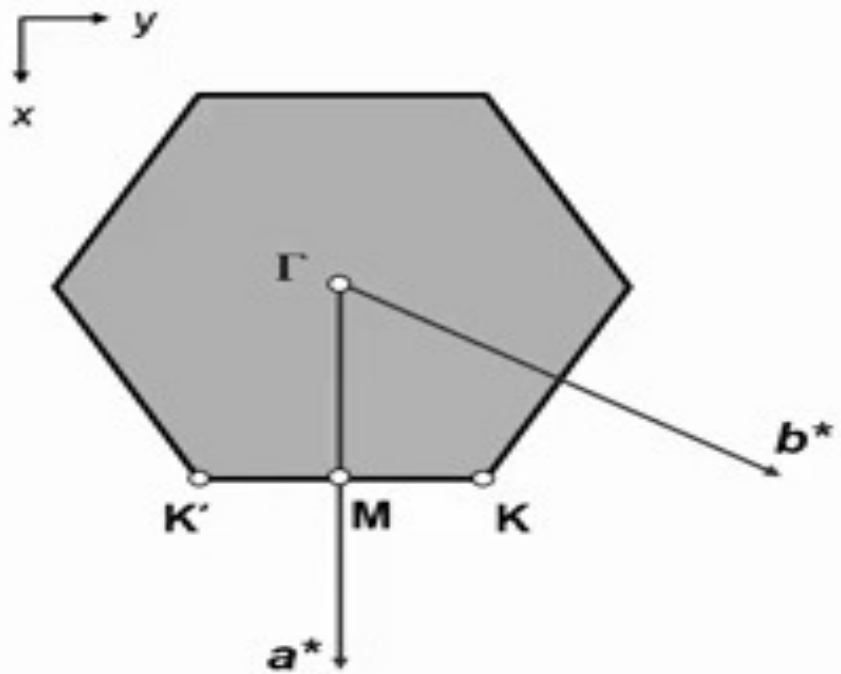
reciprocal-space lattice

$$\boldsymbol{a} = \frac{\sqrt{3}a}{2}\hat{x} - \frac{a}{2}\hat{y} \qquad \boldsymbol{b} = a\hat{y}$$

$$\boldsymbol{a}^* = \frac{4\pi}{\sqrt{3}a}\hat{x} \qquad \boldsymbol{b}^* = \frac{2\pi}{\sqrt{3}a}\hat{x} + \frac{2\pi}{a}\hat{y}$$

a = length of real-space unit cell vector

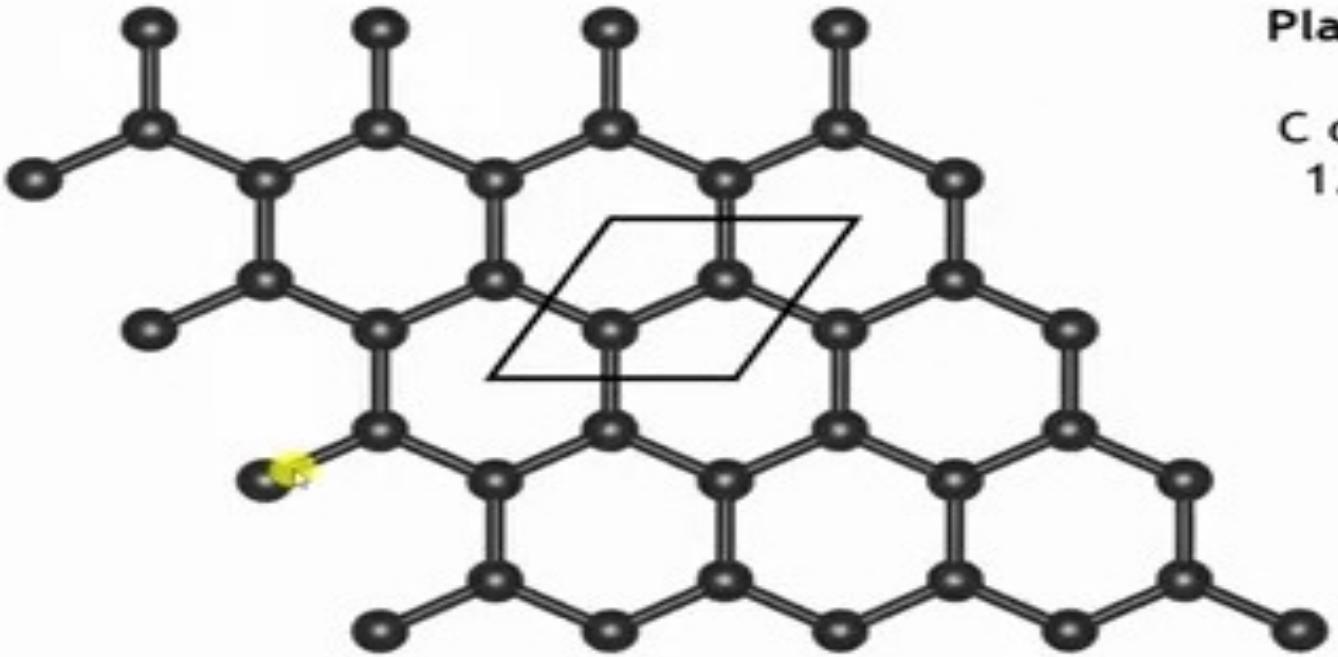
Special Points in a 2D Hexagonal Lattice



label	coordinates
Γ	$0\,\boldsymbol{a}^* + 0\,\boldsymbol{b}^*$
M	$(1/2)\,\boldsymbol{a}^* + 0\,\boldsymbol{b}^*$
K	$(1/3)\,\boldsymbol{a}^* + (1/3)\,\boldsymbol{b}^*$
K'	$(2/3)\,\boldsymbol{a}^* - (1/3)\,\boldsymbol{b}^*$

label	wave vector (Cartesian)
Γ	$0\,\boldsymbol{k}_x + 0\,\boldsymbol{k}_y$
M	$(2\pi/\sqrt{3}a)\,\boldsymbol{k}_x + 0\,\boldsymbol{k}_y$
K	$(2\pi/\sqrt{3}a)\,\boldsymbol{k}_x + (2\pi/3a)\,\boldsymbol{k}_y$
K'	$(2\pi/\sqrt{3}a)\,\boldsymbol{k}_x - (2\pi/3a)\,\boldsymbol{k}_y$

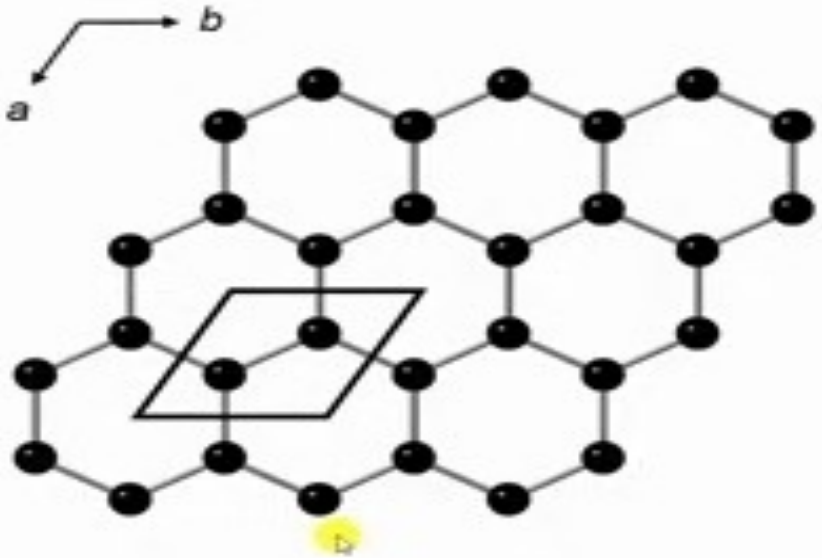
Graphene

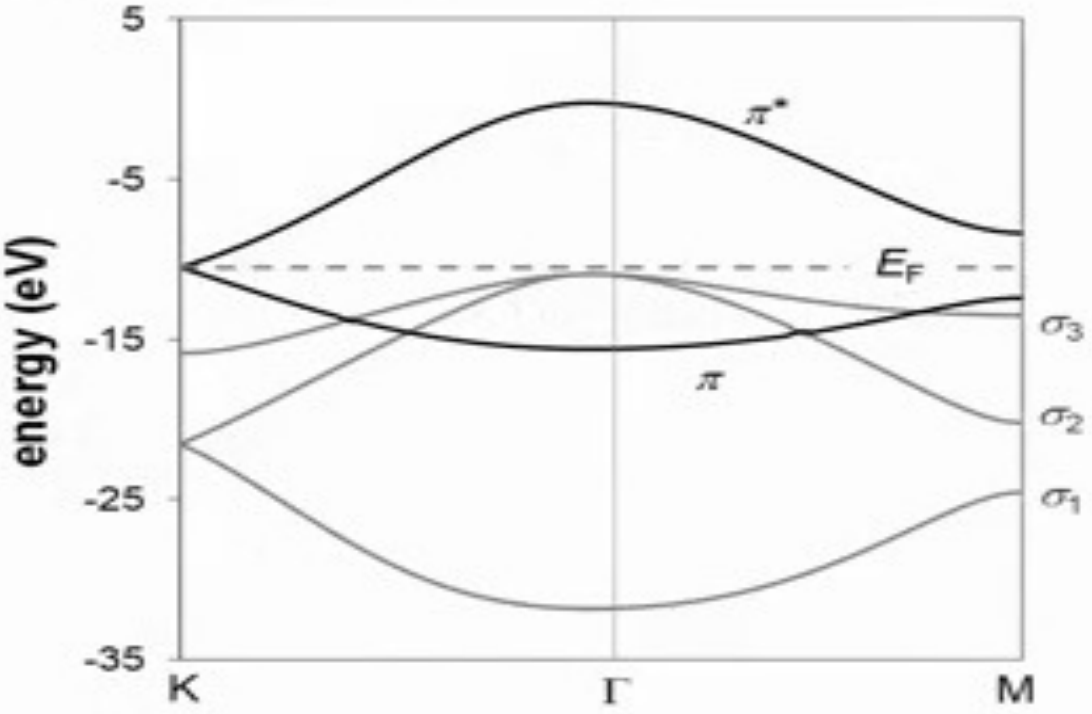


Plane group = p6mm

C on Wyckoff site 2b
1/3, 2/3; 2/3,1/3

Graphene – Band Structure





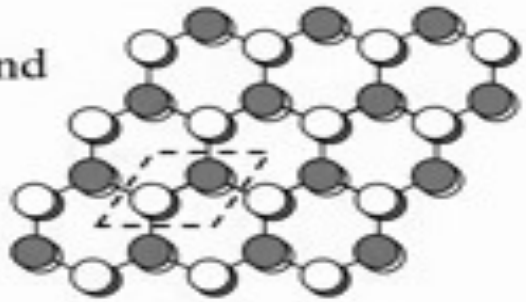
The $2p_z$ orbitals are orthogonal to the other orbitals at all points in the Brillouin zone. This gives 2 pi bands and 6 sigma bands in the band structure.

At Γ the C 2*s* does not mix by symmetry with C $2p_x$ and $2p_y$. σ_1 is purely C 2s bonding at Γ, while σ_2 and σ_3 are antibonding 2*p* at Γ.

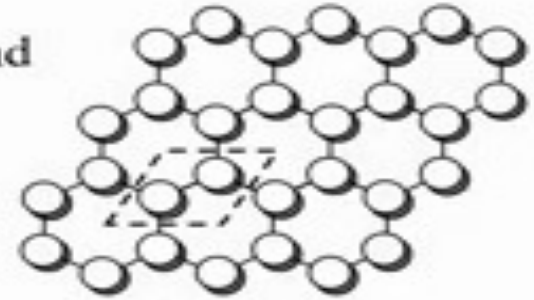
Graphene - Band Structure

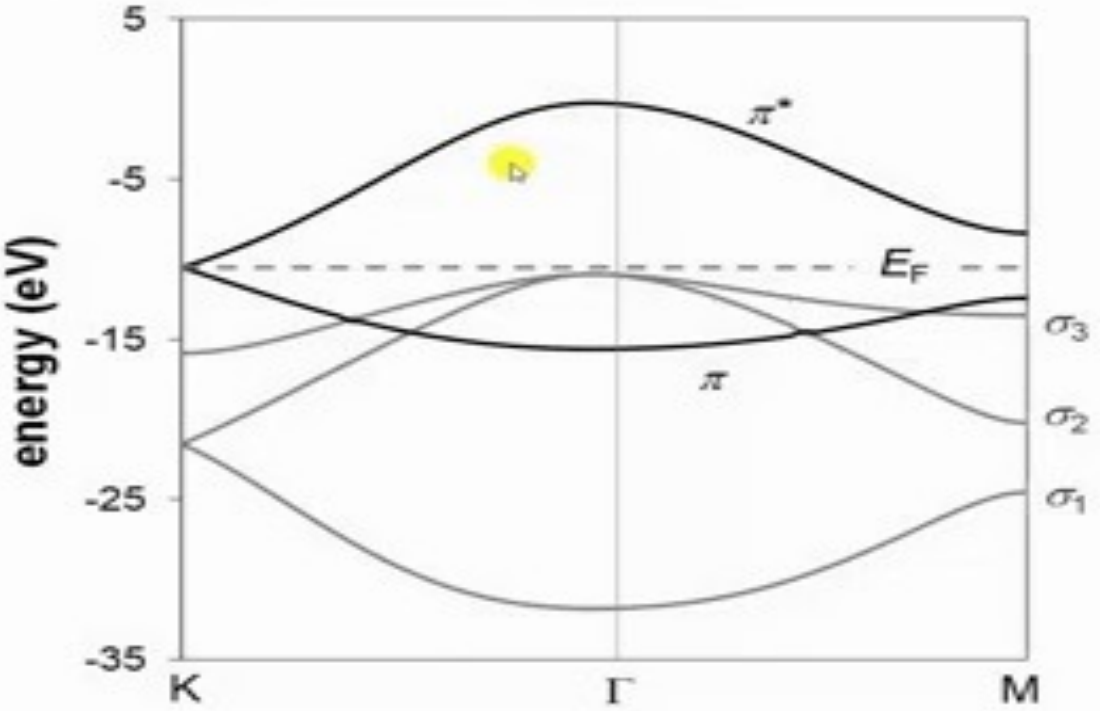
$\Gamma = 0\ \boldsymbol{a}^* + 0\ \boldsymbol{b}^*$

π^* band



π band



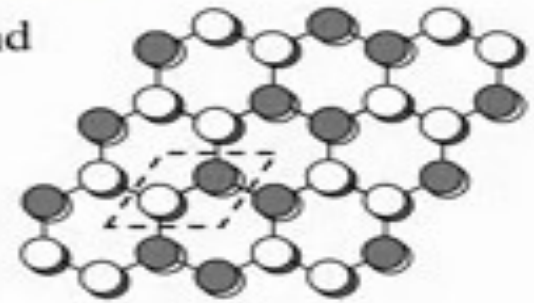


At Γ the π band is purely bonding and the π* band is antibonding (maximum separation between the two).

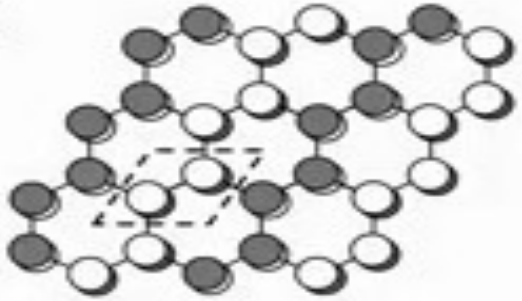
Graphene - Band Structure

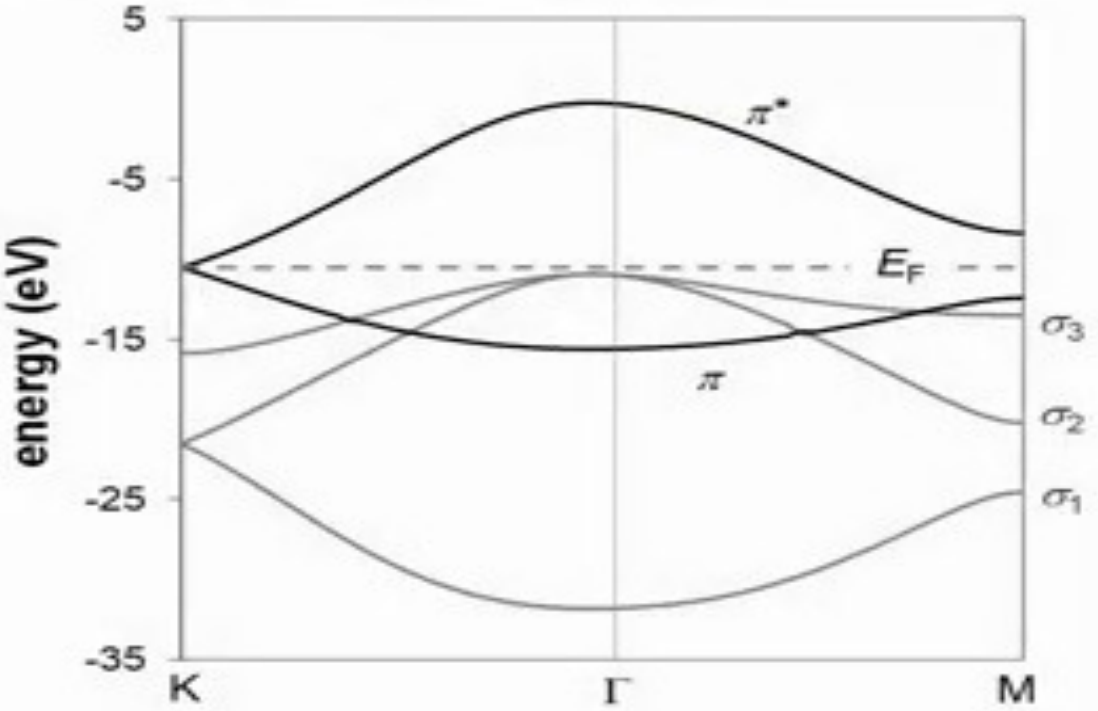
$$M = (1/2)\,\boldsymbol{a}^* + 0\,\boldsymbol{b}^*$$

π^* band



π band



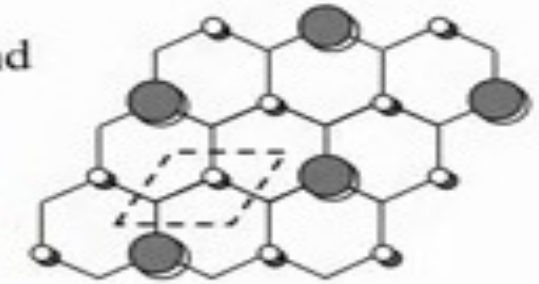


At M the π band is weakly bonding and the π* band is weakly antibonding.

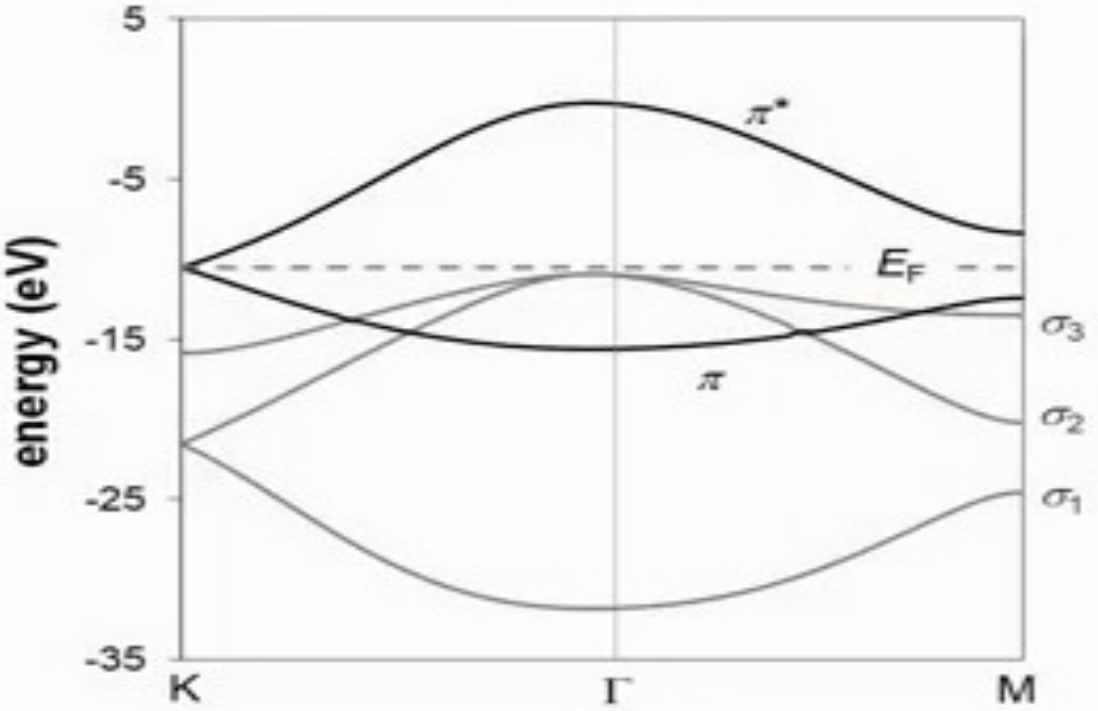
Graphene - Band Structure

$$K = (1/3)\,\boldsymbol{a}^* + (1/3)\,\boldsymbol{b}^*$$

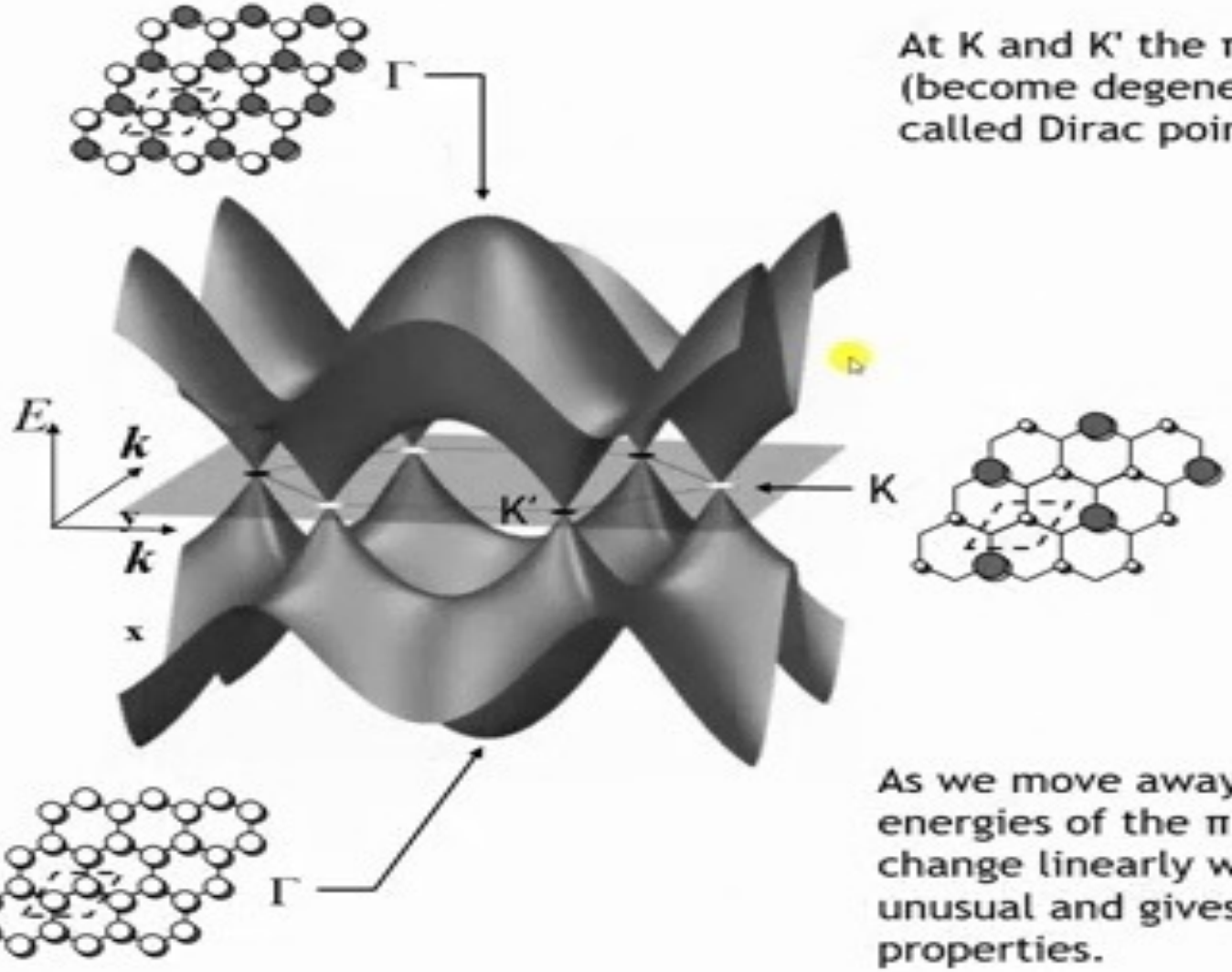
π* band



π band



At K the π and π* bands are both nonbonding and become degenerate, thus the bands just touch and graphene is a semimetal. (Here only the real part of the wavefuction is shown)



At K and K' the π and π* touch (become degenerate) these are called Dirac points

As we move away from K and K' the energies of the π and π* bands change linearly with ***k***. This is unusual and gives graphene special properties.

3. In the graphene band structure, which atomic orbitals are primarily responsible for forming the π (pi) and π* (pi-star) bands near the Fermi level?

A. 2px and 2py orbitals

B. All 2s and 2p orbitals combined

C. 2pz orbitals

D. 2s orbitals

C. 2pz orbitals

✓ **That's right!**

The 2pz orbitals are perpendicular to the graphene plane and form the π-system, which dictates the electronic properties near the Fermi level.

4. How many carbon atoms are in the conventional unit cell of graphene?

A. 1

B. 2

C. 4

D. 6

B. 2

✓ That's right!

The unit cell contains two carbon atoms from the two different sublattices of the honeycomb structure.

5. At which high-symmetry point in the first Brillouin zone do the π and π* bands of graphene become degenerate (i.e., they touch)?

A. The K (and K') points

B. The Γ (Gamma) point

C. The M point

D. They do not touch at any point.

A. The K (and K') points

✓ **That's right!**

At the K point (a corner of the hexagon), the crystal orbitals become non-bonding, causing the valence (π) and conduction (π*) bands to touch precisely.

6. What is the crystal orbital character of the lowest energy π (pi) band at the Γ (Gamma) point?

A. Non-bonding

B. Fully bonding

C. Fully anti-bonding

D. Weakly bonding (2 bonding, 1 anti-bonding)

B. Fully bonding

✓ That's right!

At Γ (k=0), all unit cells are in phase. This leads to pi-bonding interactions between all adjacent carbon atoms, resulting in the lowest energy state.

Learning Objectives

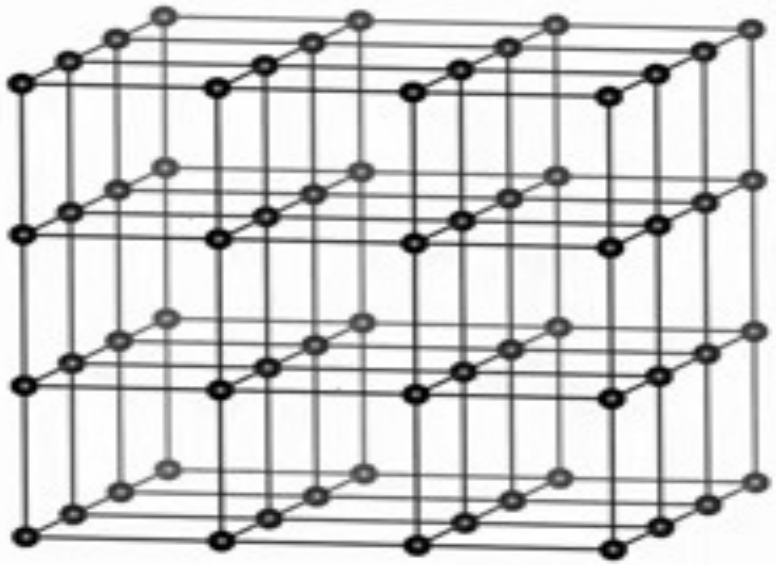
3D Band Structures: Primitive Cubic Systems

By the end of this lecture, you will be able to:

- Construct 3D reciprocal lattice vectors using cross products and identify special k-points (Gamma, X, M, R) in primitive cubic Brillouin zones
- Predict band dispersion for s and p orbitals by analyzing nearest-neighbor bonding patterns at high-symmetry points
- Explain how p-orbital directionality causes band splitting and determines which bands remain degenerate at specific k-points
- Apply sigma and pi overlap analysis to rationalize subtle energy variations between k-points
- Predict Peierls distortions in half-filled p-band systems and calculate Fermi level positions from valence electron count

Reciprocal Space Vectors in 3D

Real space lattice



$$r = xa + yb + zc$$

Reciprocal space lattice

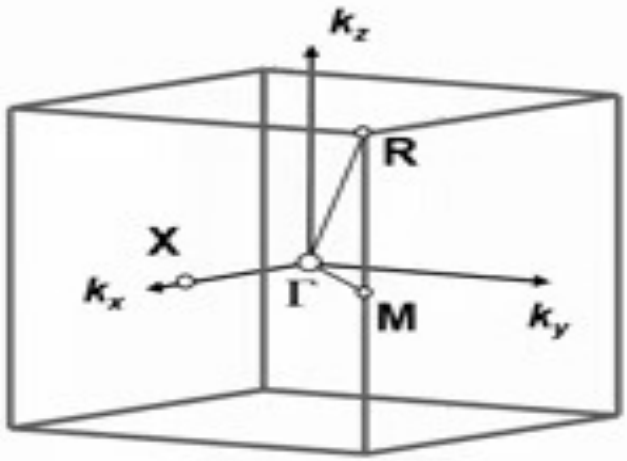
$$k = ma^* + nb^* + oc^*$$

$$a^* = \frac{2\pi}{V}(b \times c)$$

$$b^* = \frac{2\pi}{V}(c \times a)$$

$$c^* = \frac{2\pi}{V}(a \times b)$$

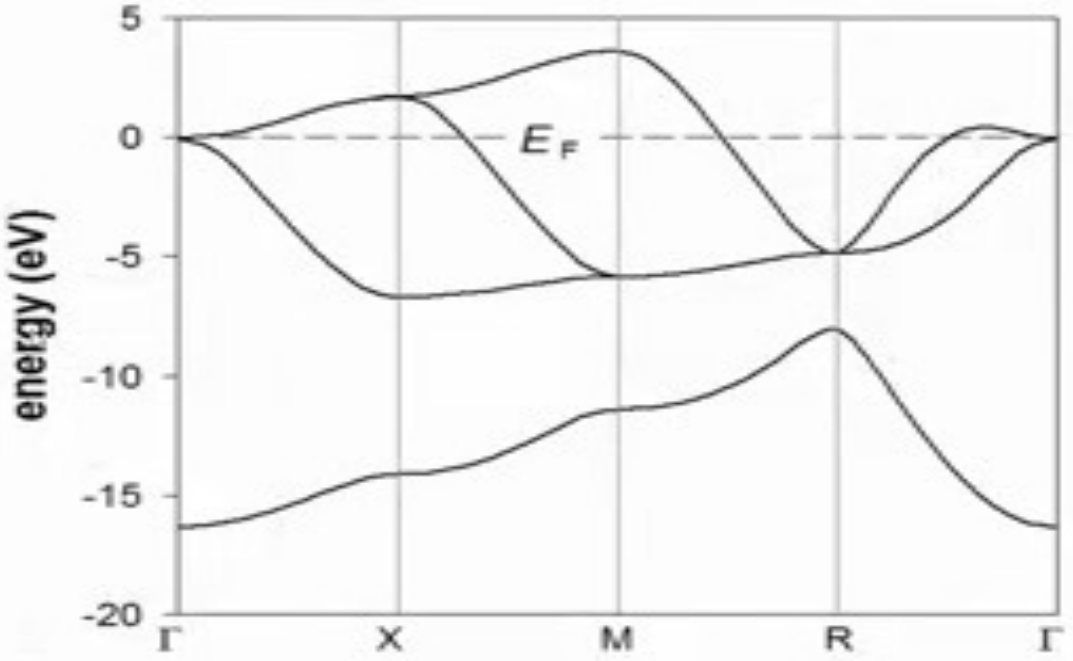
First Brillouin Zone - Primitive Cubic



label	coordinates
Γ	$0\,\boldsymbol{a}^* + 0\,\boldsymbol{b}^* + 0\,\boldsymbol{c}^*$
X	$(1/2)\,\boldsymbol{a}^* + 0\,\boldsymbol{b}^* + 0\,\boldsymbol{c}^*$
M	$(1/2)\,\boldsymbol{a}^* + (1/2)\,\boldsymbol{b}^* + 0\,\boldsymbol{c}^*$
R	$(1/2)\,\boldsymbol{a}^* + (1/2)\,\boldsymbol{b}^* + (1/2)\,\boldsymbol{c}^*$

label	wave vector (Cartesian)
Γ	$0\,\boldsymbol{k}_x + 0\,\boldsymbol{k}_y + 0\,\boldsymbol{k}_z$
X	$(\pi/a)\,\boldsymbol{k}_x + 0\,\boldsymbol{k}_y + 0\,\boldsymbol{k}_z$
M	$(\pi/a)\,\boldsymbol{k}_x + (\pi/a)\,\boldsymbol{k}_y + 0\,\boldsymbol{k}_z$
R	$(\pi/a)\,\boldsymbol{k}_x + (\pi/a)\,\boldsymbol{k}_y + (\pi/a)\,\boldsymbol{k}_z$

Band Structure Primitive Cubic Metal (α-Po)



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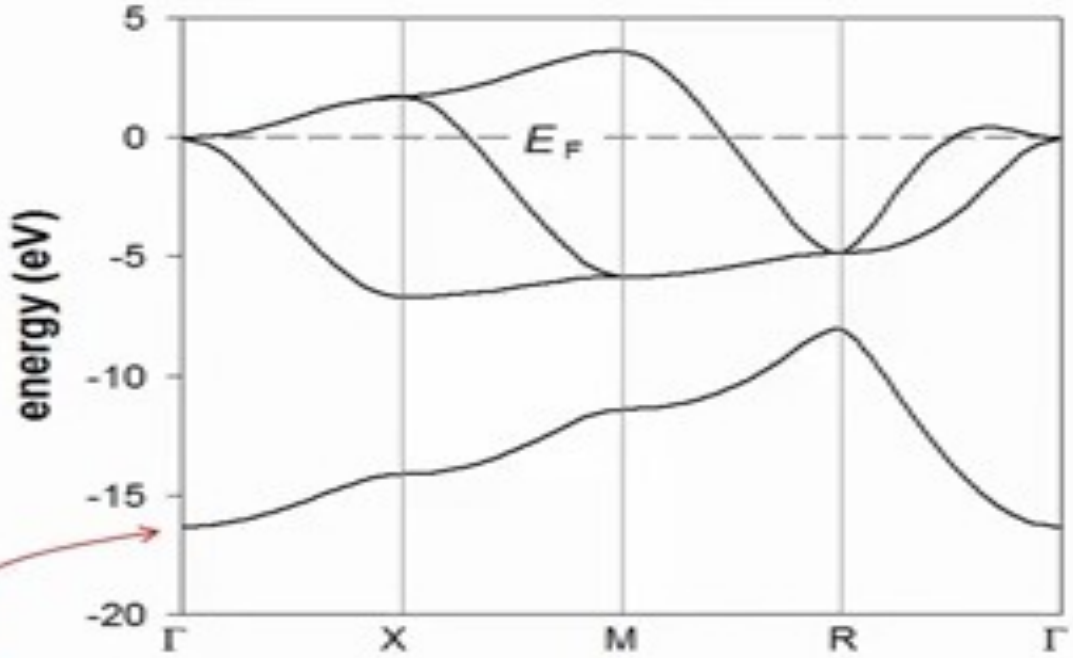
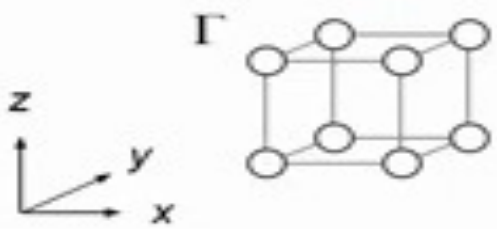


6s



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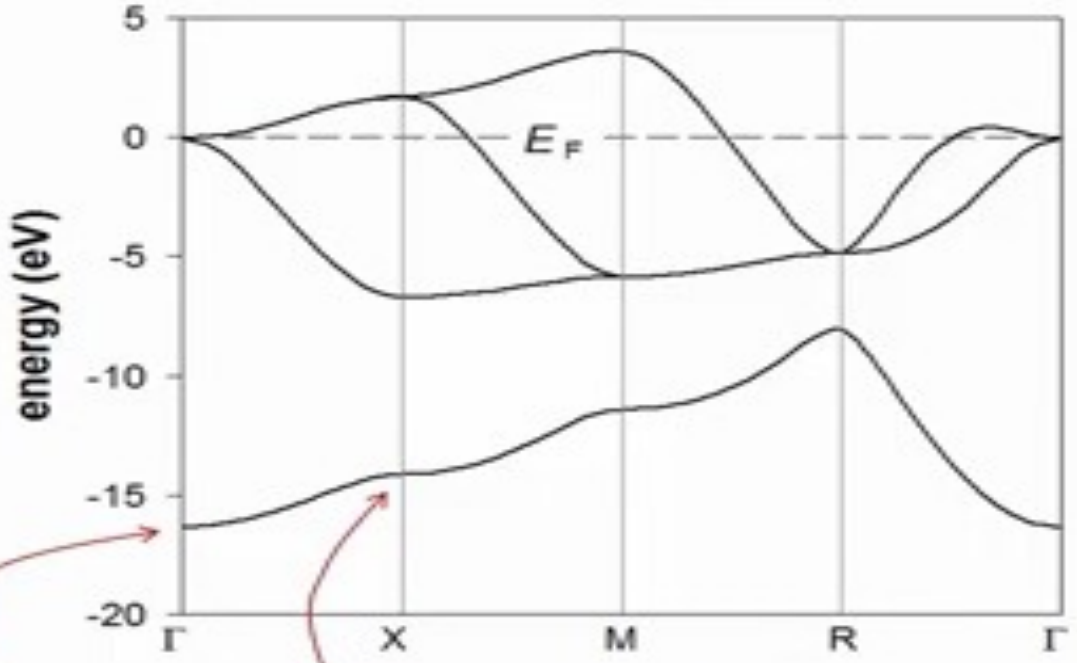

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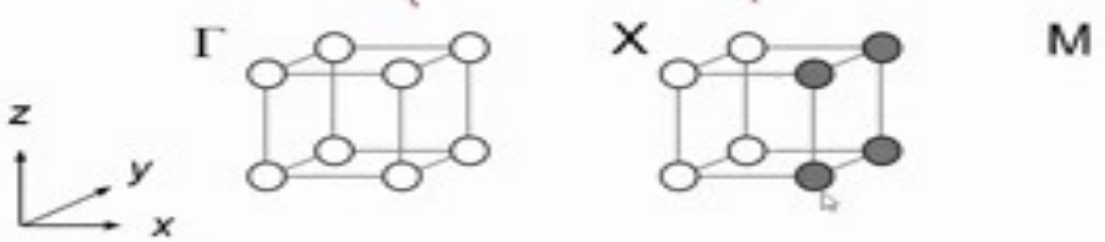

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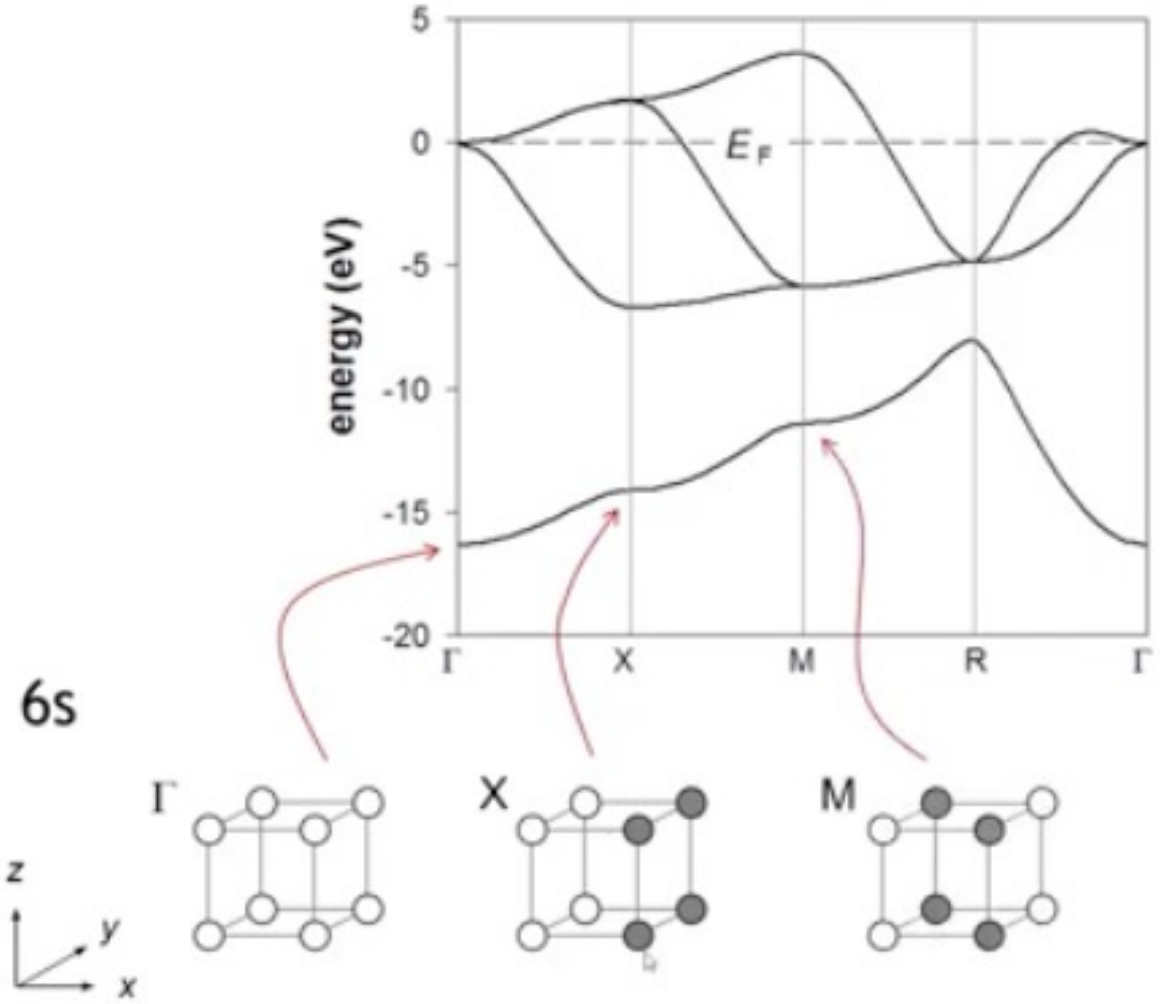

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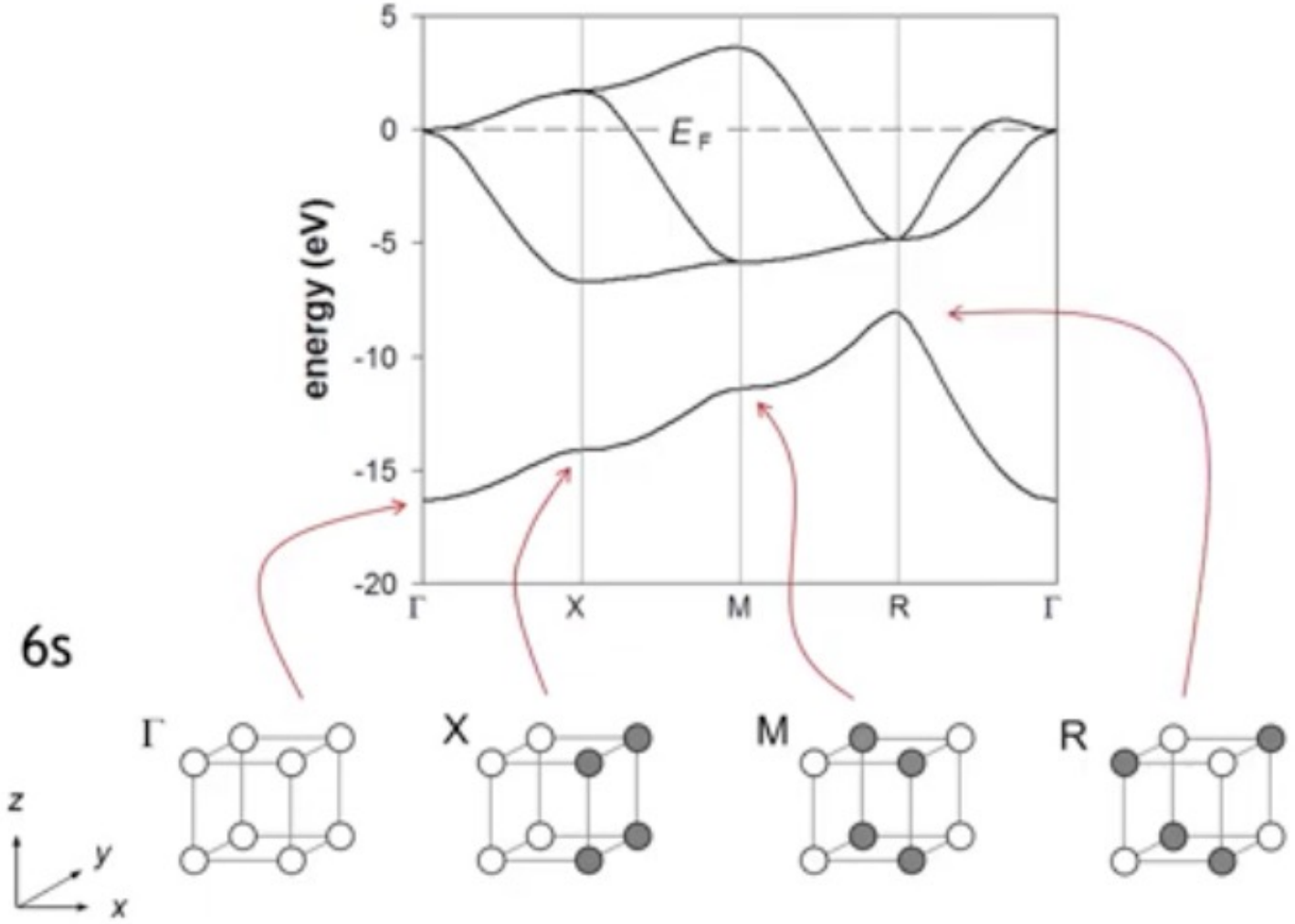

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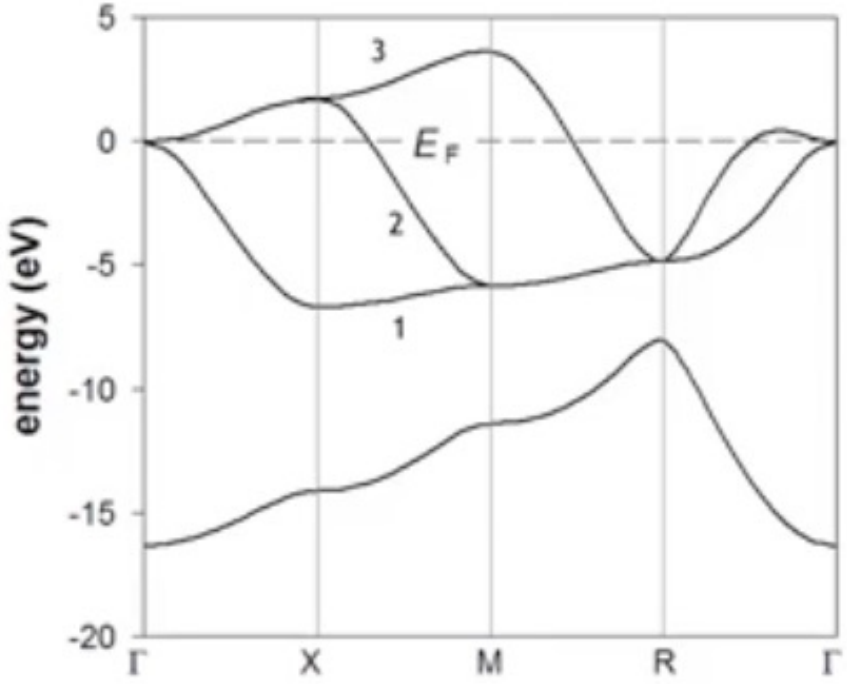
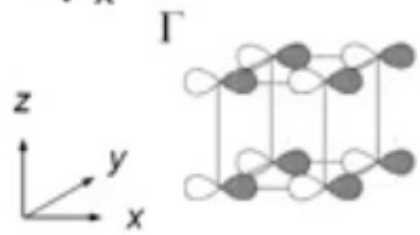


$6p_x$



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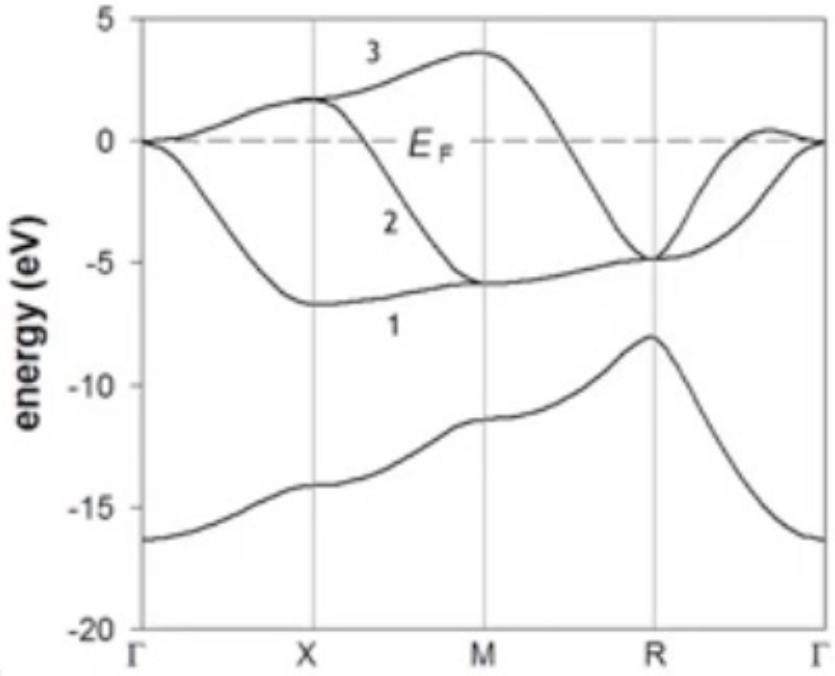

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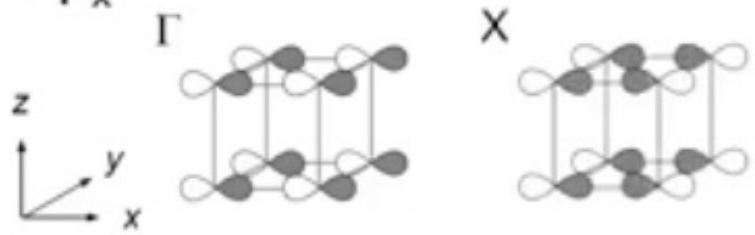

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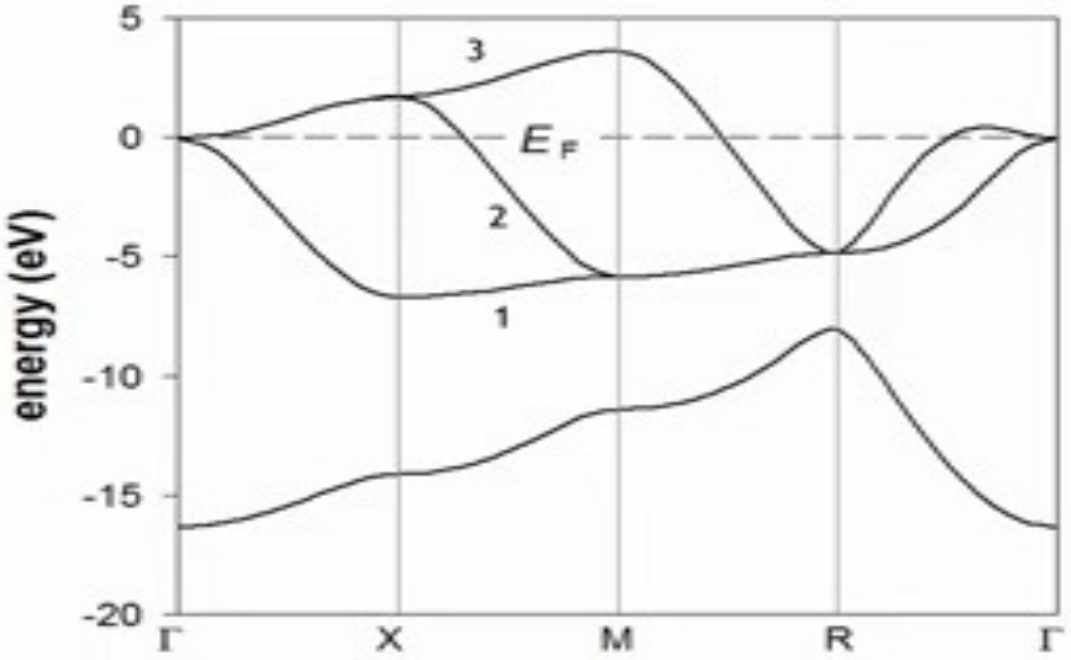

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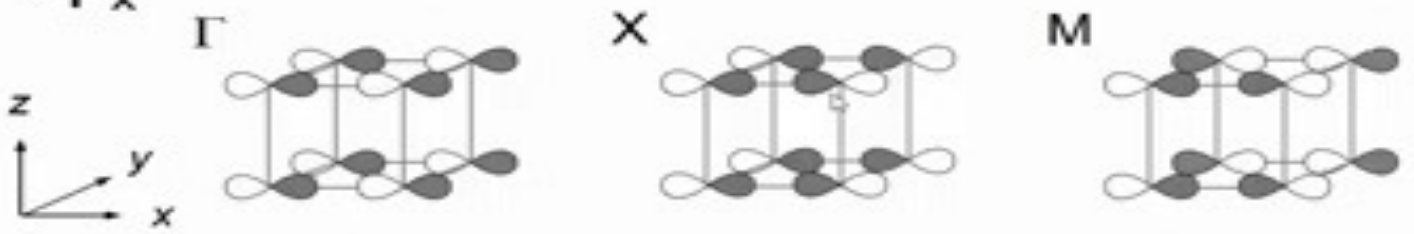

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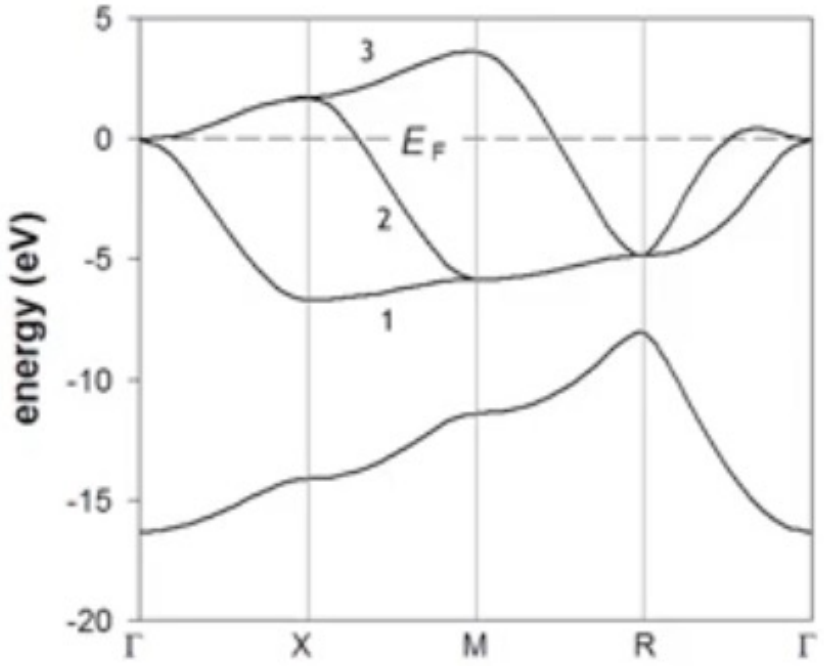

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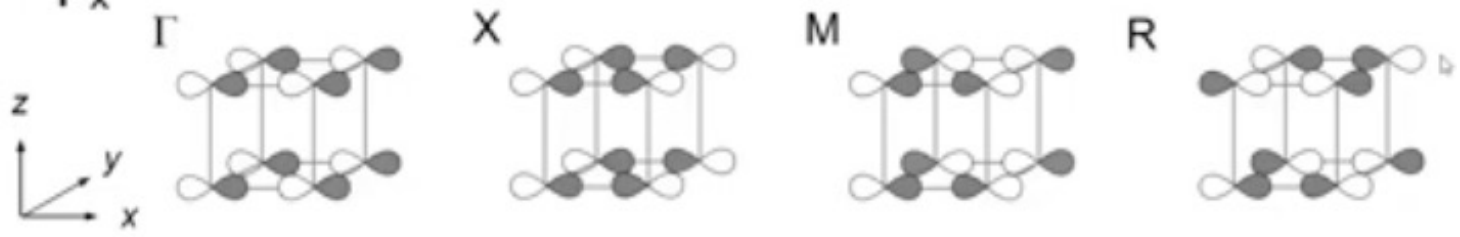

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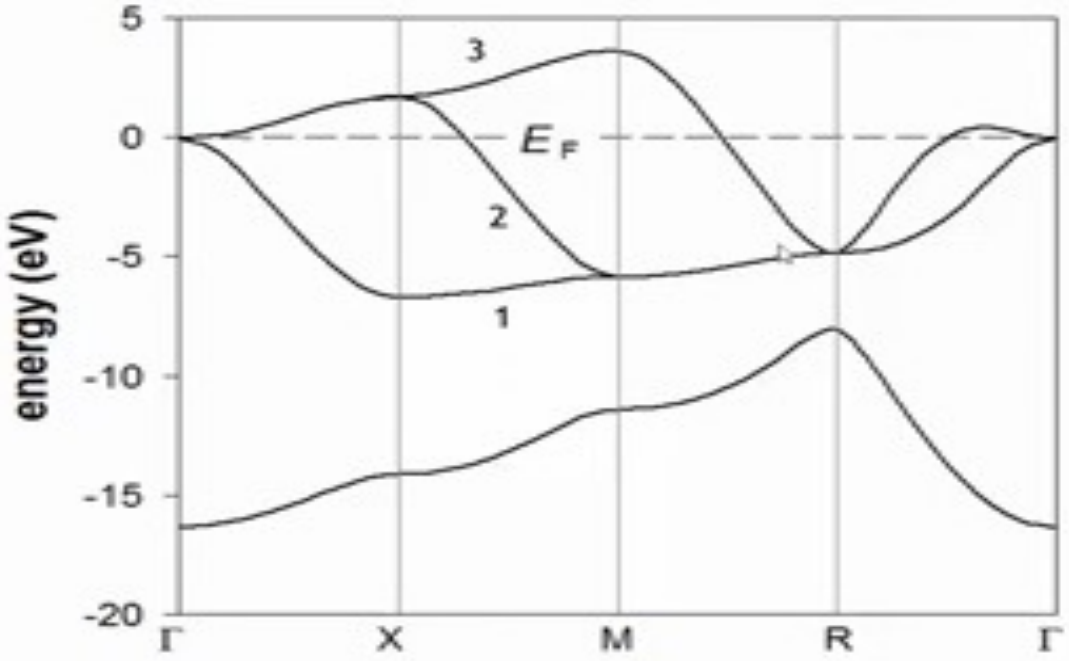
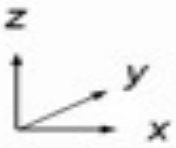


$6p_z$



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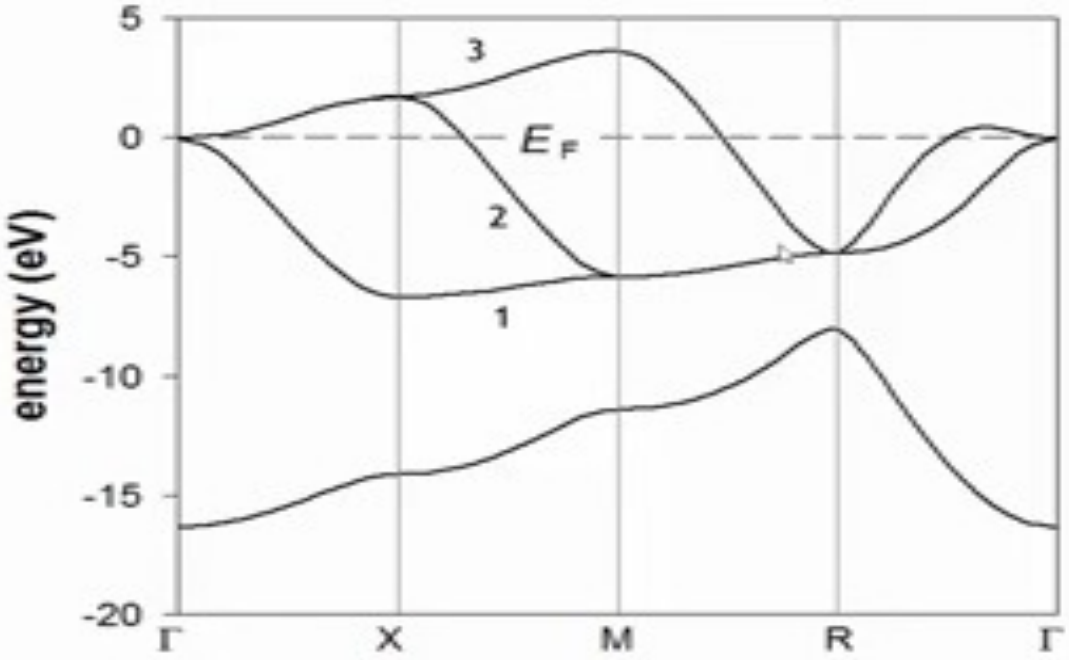

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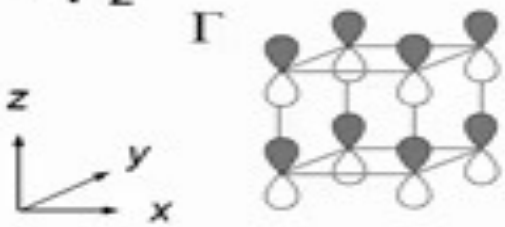

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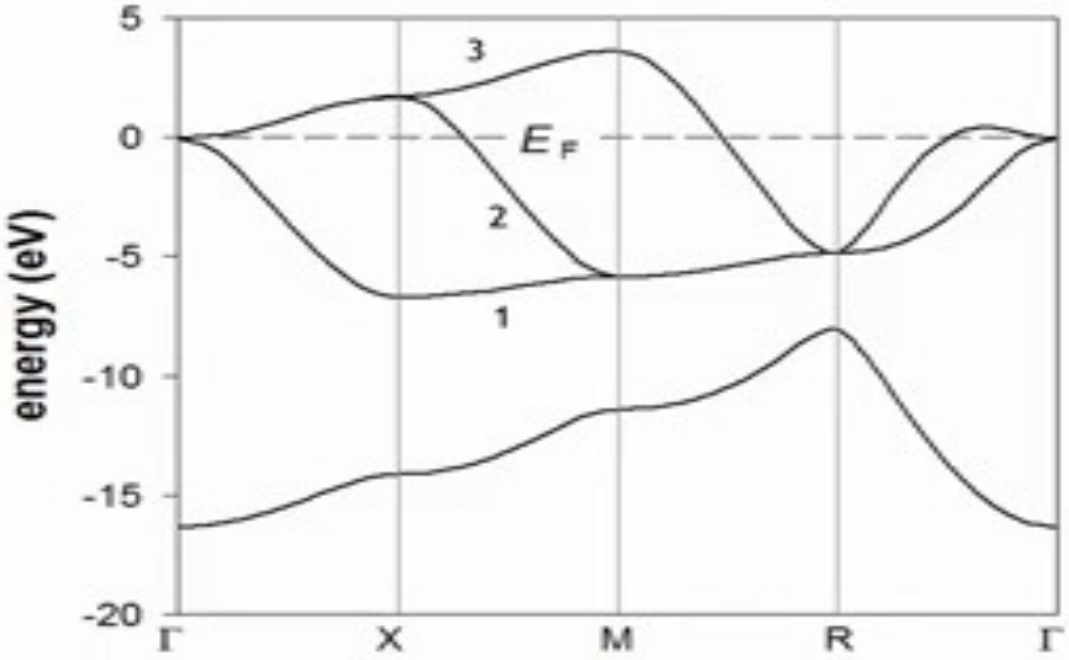

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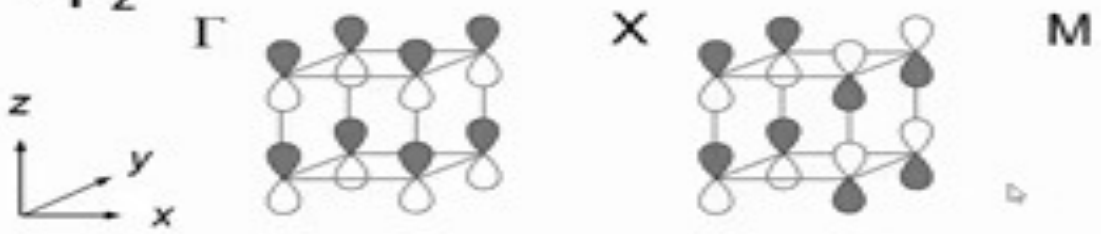

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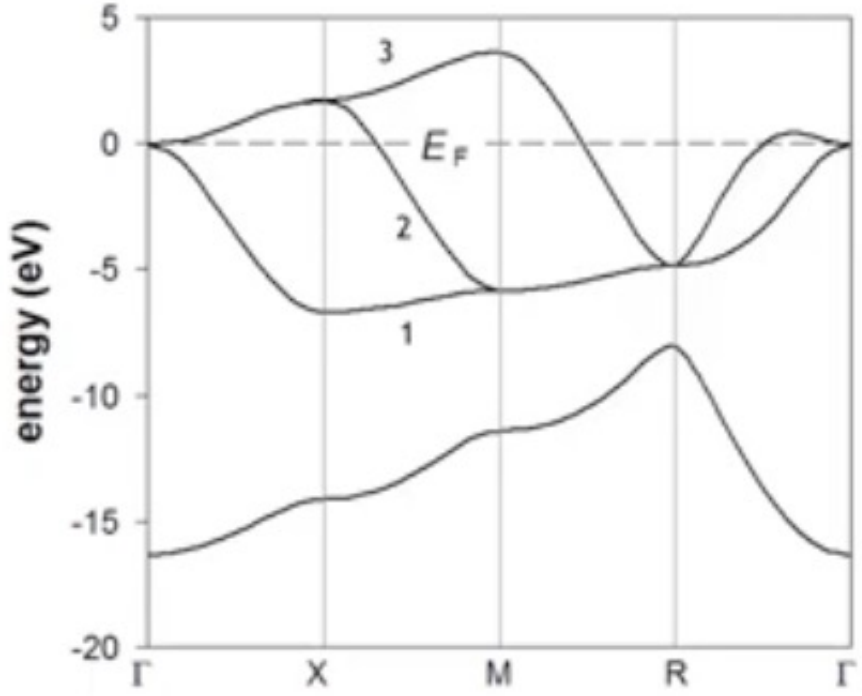

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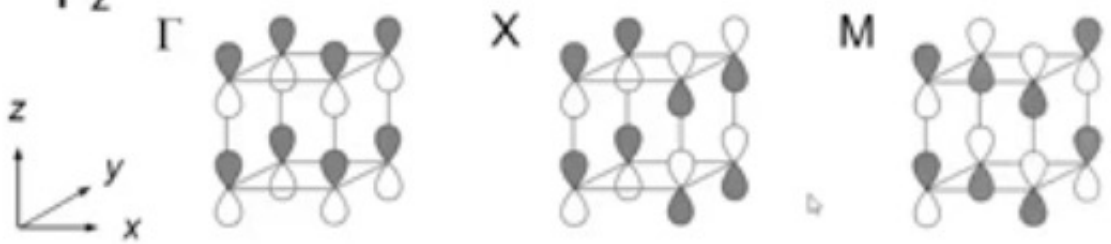
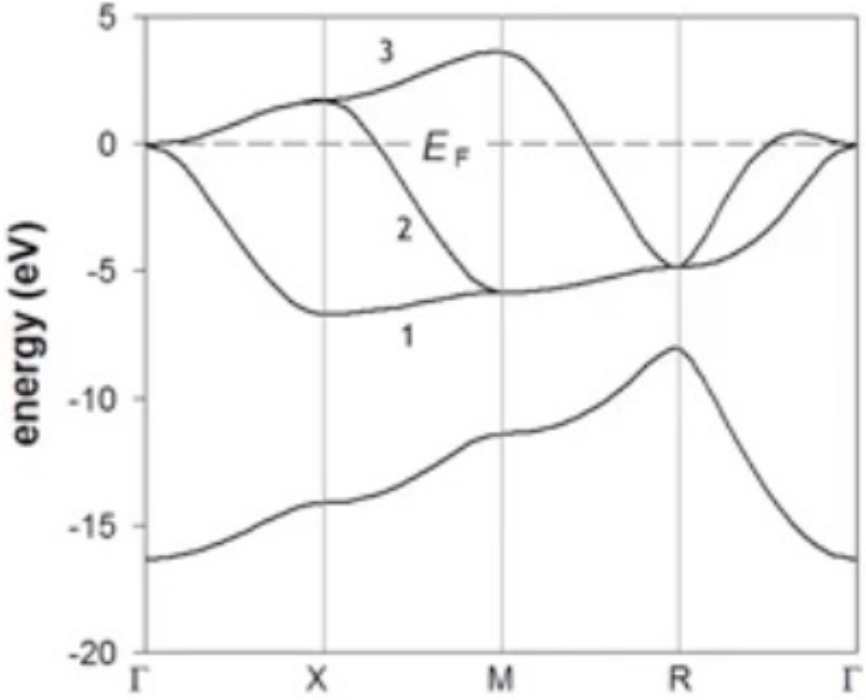
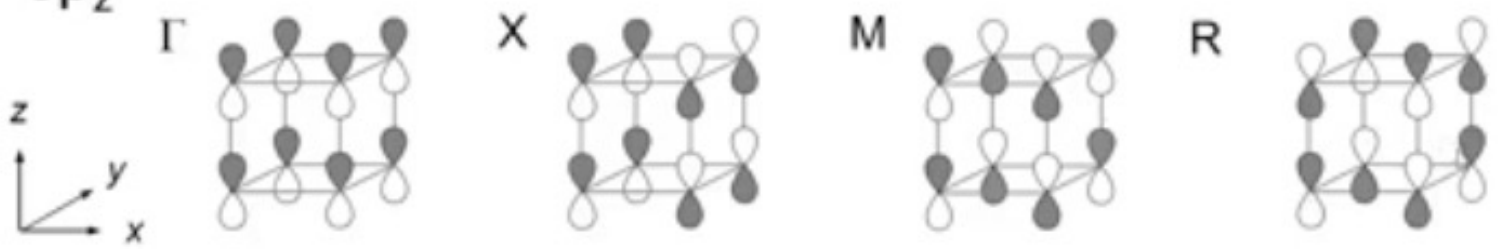


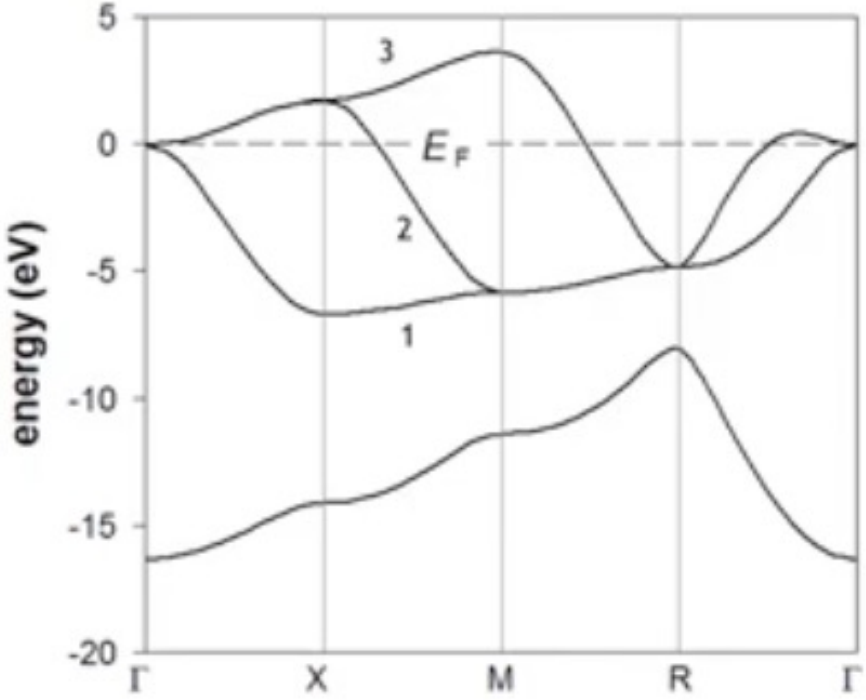
Band Structure Primitive Cubic Metal (α-Po)



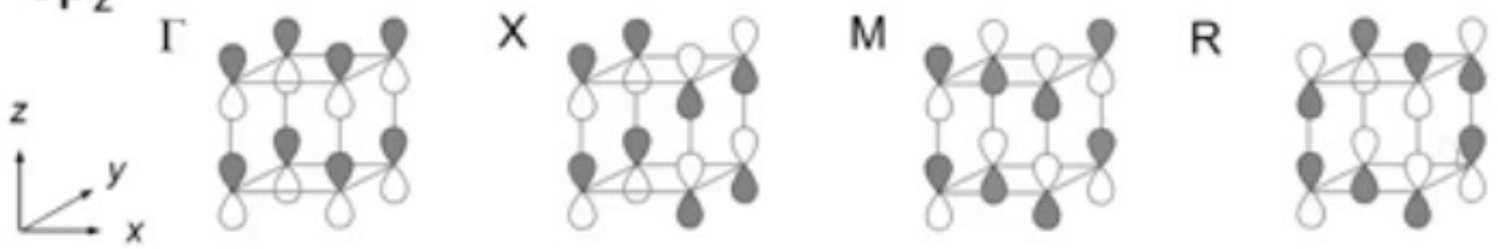
$6p_z$



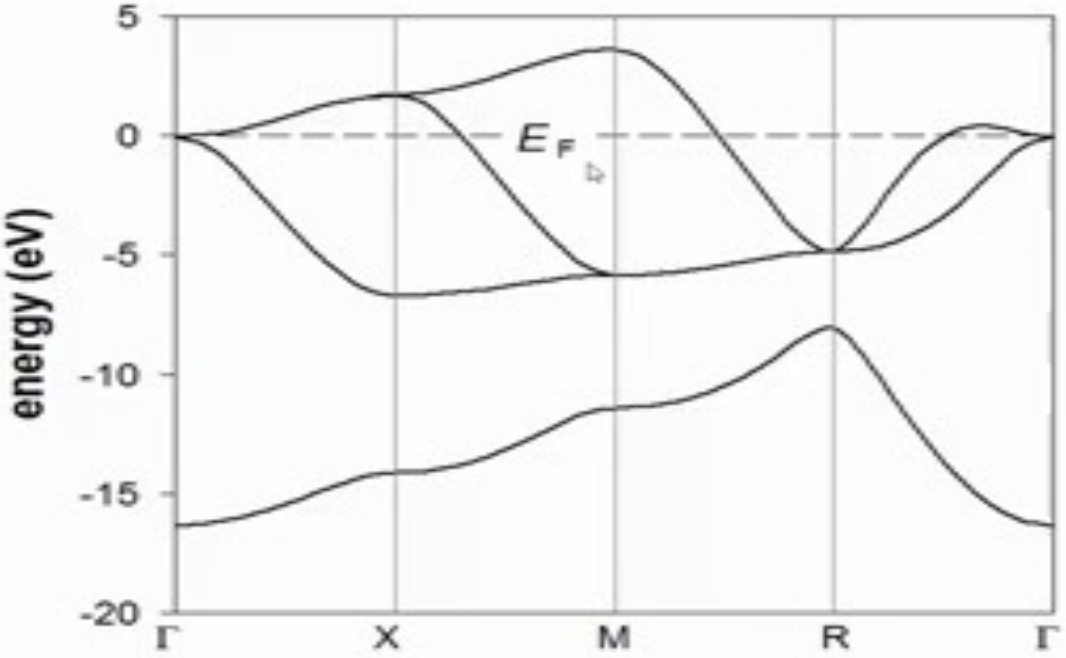
Band Structure Primitive Cubic Metal (α-Po)

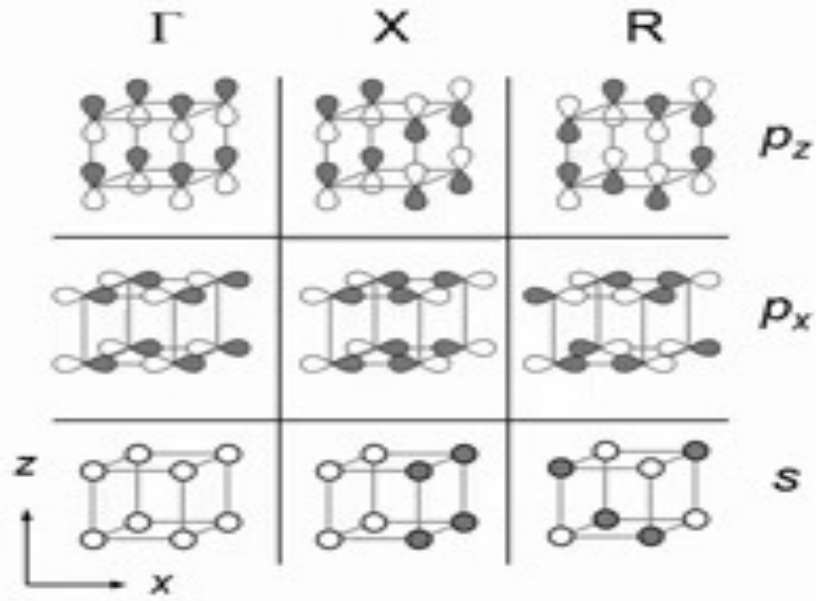


$6p_z$

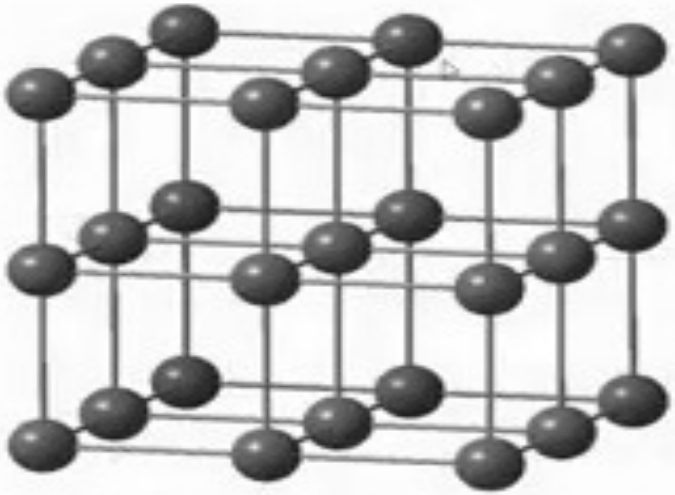


Band Structure Primitive Cubic Metal (α-Po)



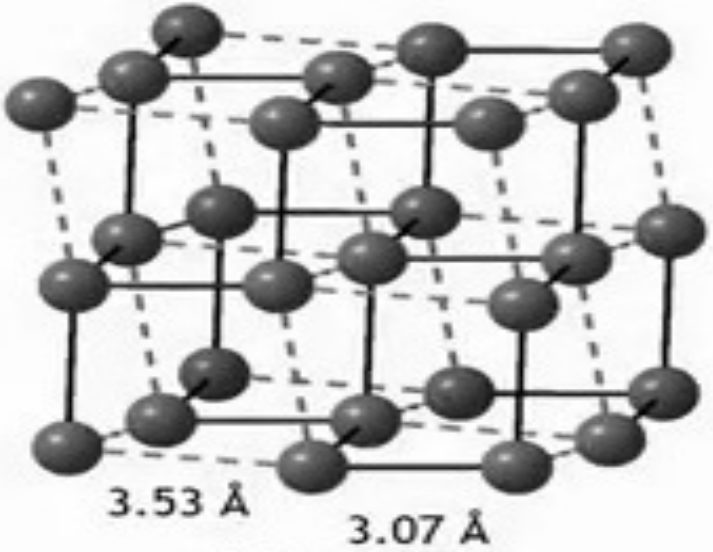


Peierls Distortion in 3D



α-polonium
(cubic)

6*p* bands 2/3 filled



bismuth
(rhombohedral)

6*p* bands 1/2 filled

Band Structure of Bismuth: Pseudopotential Approach*

STUART GOLIN

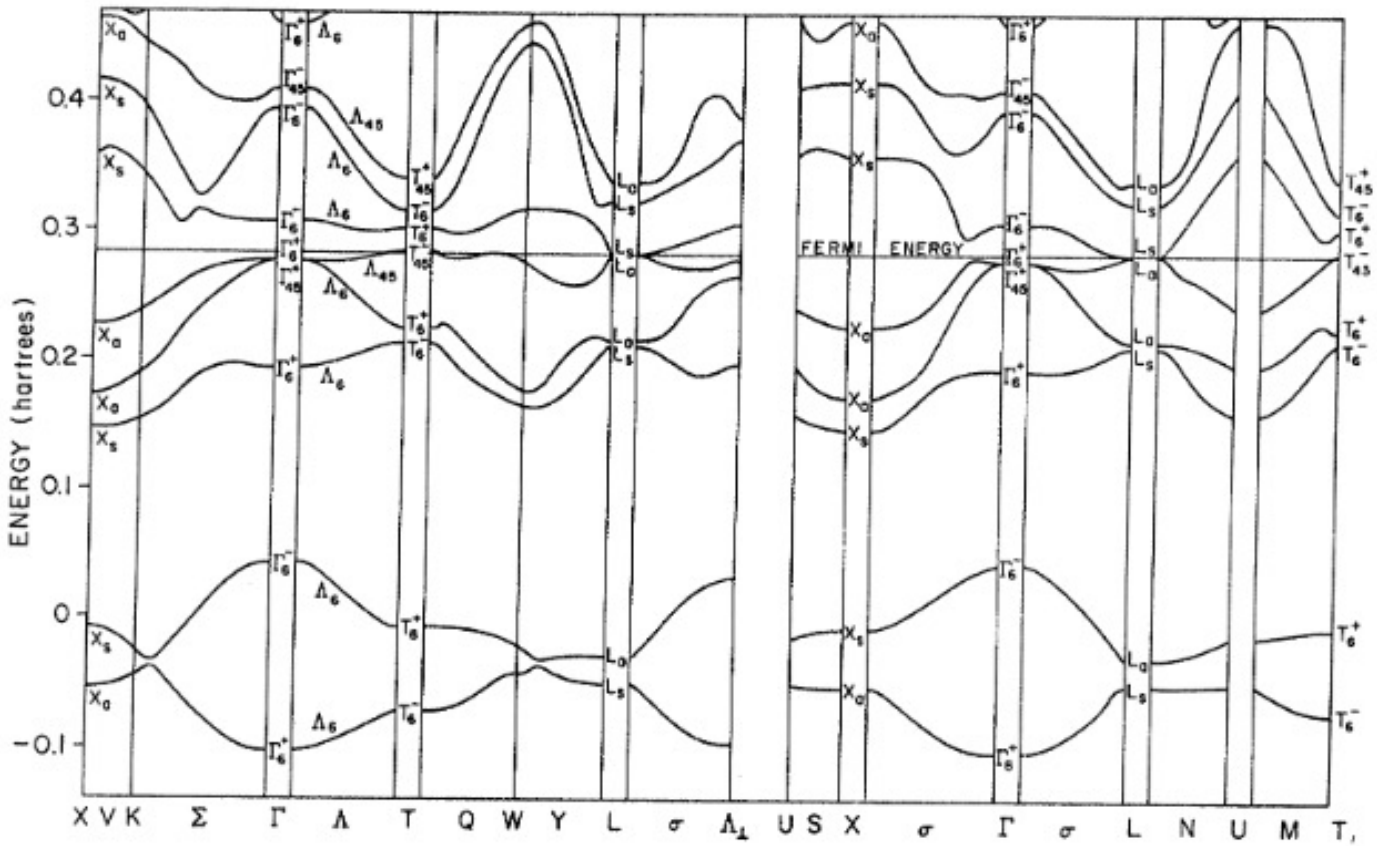


FIG. 2. The band structure of bismuth along various lines and planes. [The direction L-$\Lambda_\perp$ is perpendicular to the trigonal axis ($\Lambda_\perp$ is on that axis) and is of interest in interpreting tunneling measurements. See C. B. Duke (private communication); see also D. J. Ben-Daniel and C. B. Duke, Phys. Rev. Letters 14, 902 (1965).]

2. For the 6s band of alpha-Polonium (PC structure), what is the correct ordering of energy levels for the high-symmetry k-points, from lowest to highest?

A. $\Gamma < X < M < R$

B. $M < X < \Gamma < R$

C. $\Gamma = R < X = M$

D. $R < M < X < \Gamma$

A. $\Gamma < X < M < R$

✓ **That's right!**

This reflects the increasing number of anti-bonding nearest-neighbor interactions: Γ (0 anti-bonding), X (2), M (4), and R (6).

3. In the band structure of alpha-Polonium, the 6px, 6py, and 6pz orbitals are degenerate at Γ. How can the 6px band be uniquely identified along the $\Gamma \to X$ path, where $X = (\frac{1}{2}, 0, 0)$?

A. The 6px band rises significantly in energy, while the 6py and 6pz bands drop.

B. All three p-bands remain degenerate along the $\Gamma \to X$ path.

C. The 6px band drops significantly in energy, while the 6py and 6pz bands do not.

D. The 6px band hybridizes with the 6s band at X, while the others do not.

C. The 6px band drops significantly in energy, while the 6py and 6pz bands do not.

✓ **That's right!**

The k-vector at X introduces a phase change along the x-direction, which turns the 6px σ-anti-bonding interaction (at Γ) into a σ-bonding one (at X).

Homework

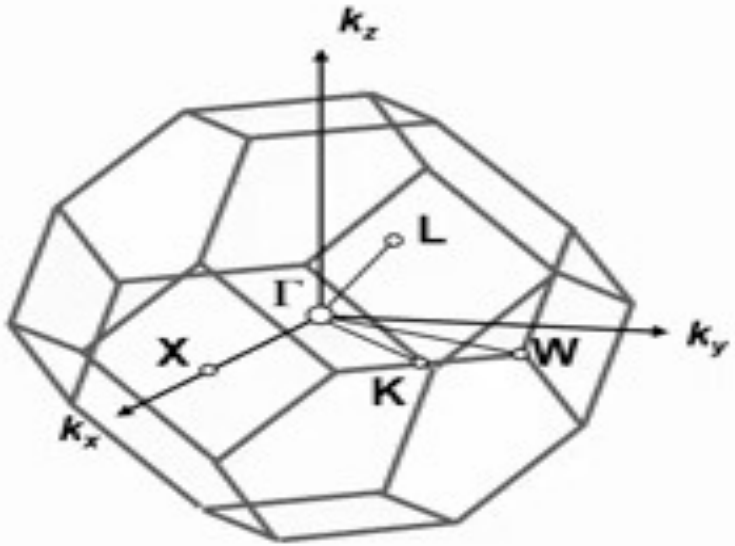
6.12

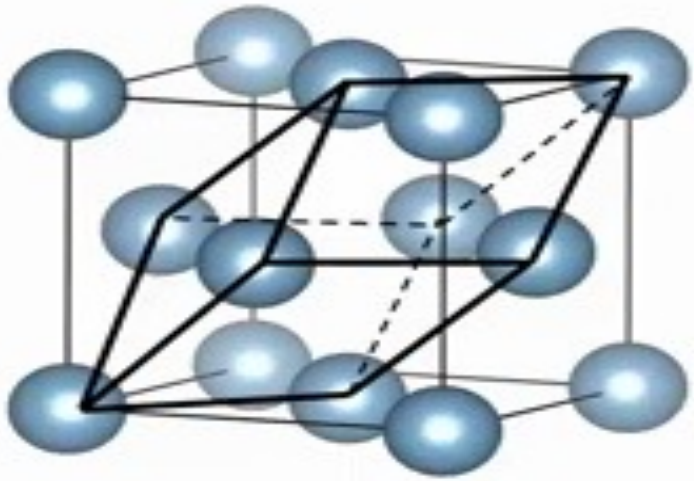
Learning Objectives

Band Structures of Face-Centered Cubic Crystals

- Understand the first Brillouin zone structure for face-centered cubic lattices
- Analyze the electronic band structure of FCC metals using aluminum as a representative example
- Examine band structures of diamond structure materials (carbon, silicon, germanium)
- Distinguish between valence bands, conduction bands, and band gaps in semiconductors
- Explain the progression from insulator to semiconductor to metal down Group 14 elements
- Understand how orbital overlap influences bonding/anti-bonding states and metallic vs semiconducting behavior

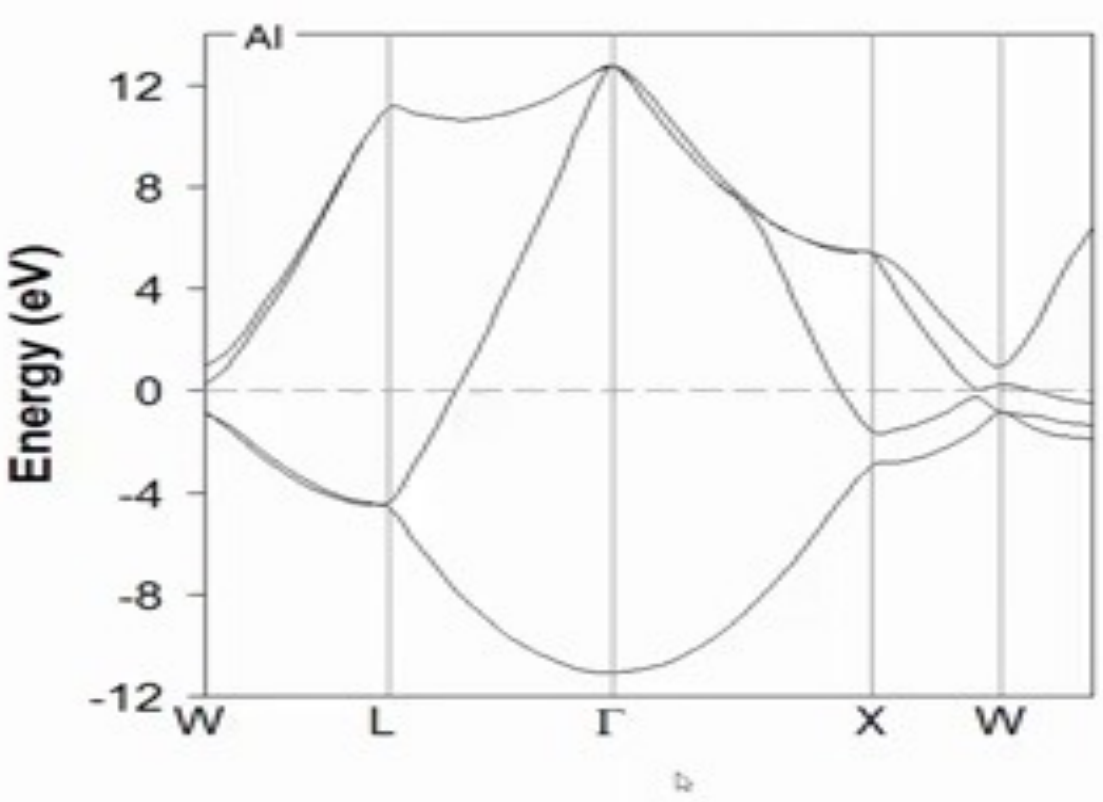
First Brillouin Zone - Face Centered Cubic

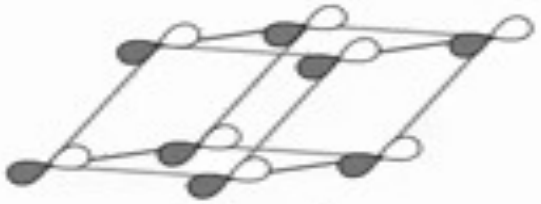




label	coordinates
Γ	$0\,\boldsymbol{a}^* + 0\,\boldsymbol{b}^* + 0\,\boldsymbol{c}^*$
X	$0\,\boldsymbol{a}^* + (1/2)\,\boldsymbol{b}^* + (1/2)\,\boldsymbol{c}^*$
W	$(1/4)\,\boldsymbol{a}^* + (3/4)\,\boldsymbol{b}^* + (1/2)\,\boldsymbol{c}^*$
L	$(1/2)\,\boldsymbol{a}^* + (1/2)\,\boldsymbol{b}^* + (1/2)\,\boldsymbol{c}^*$

Aluminum



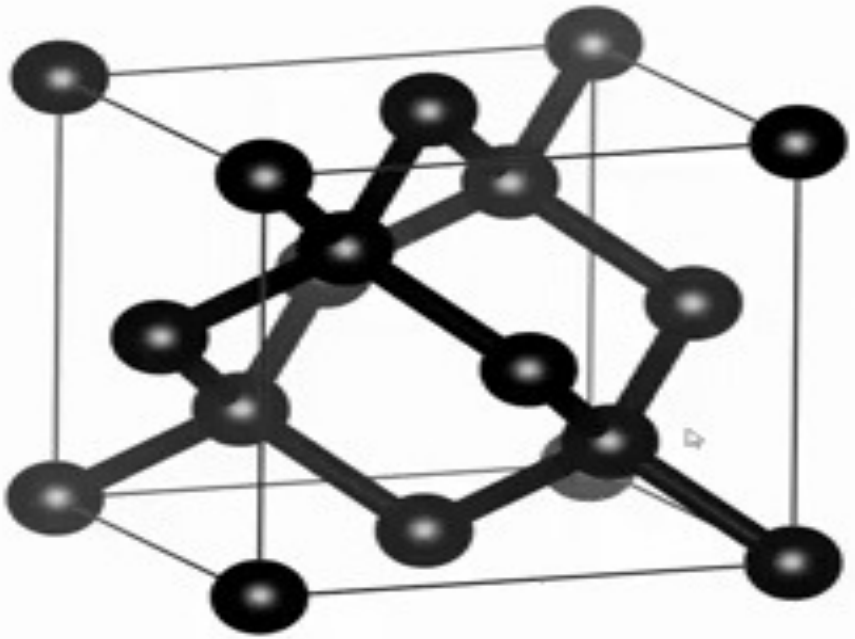


p-p antibonding

s-s bonding

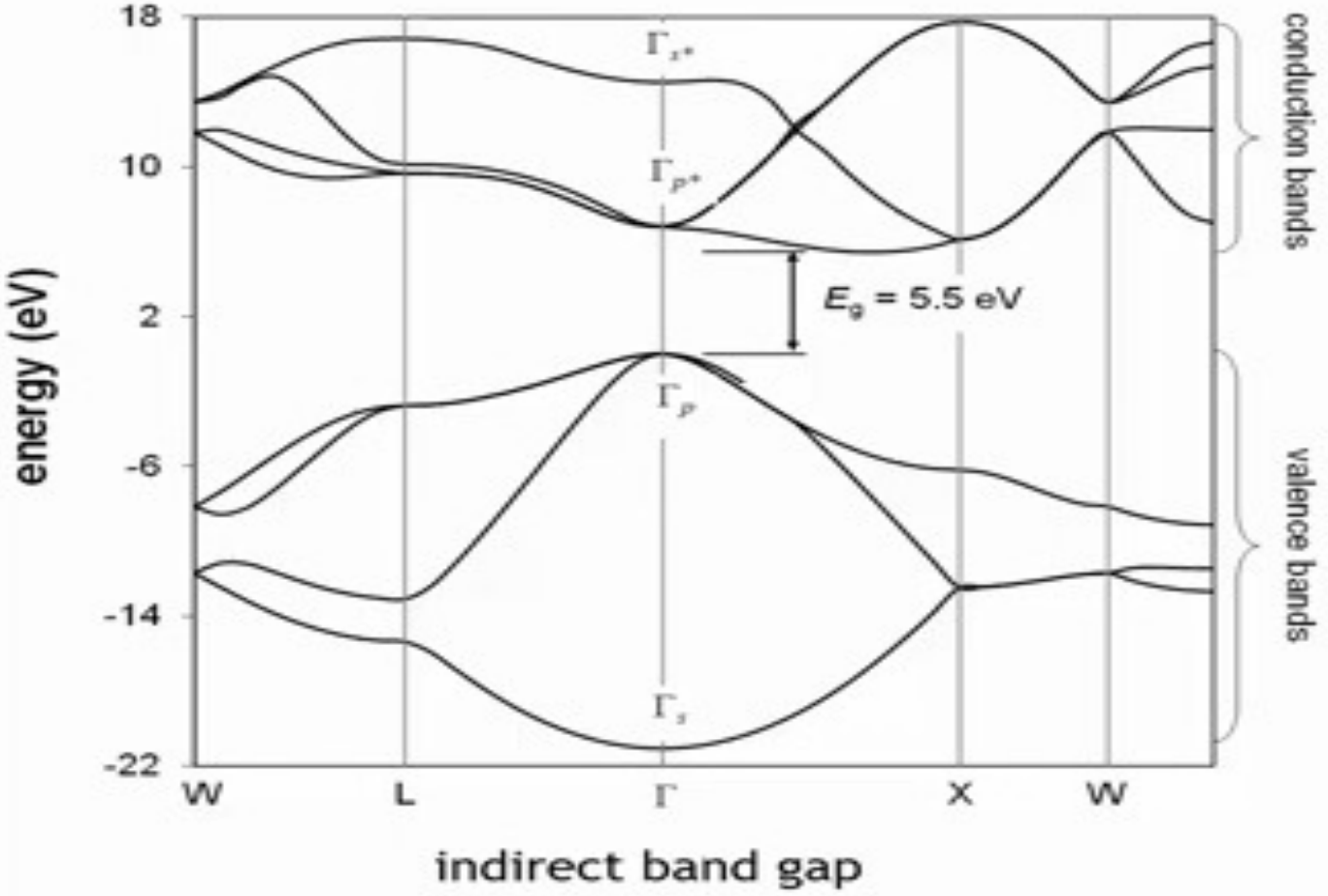
Γ

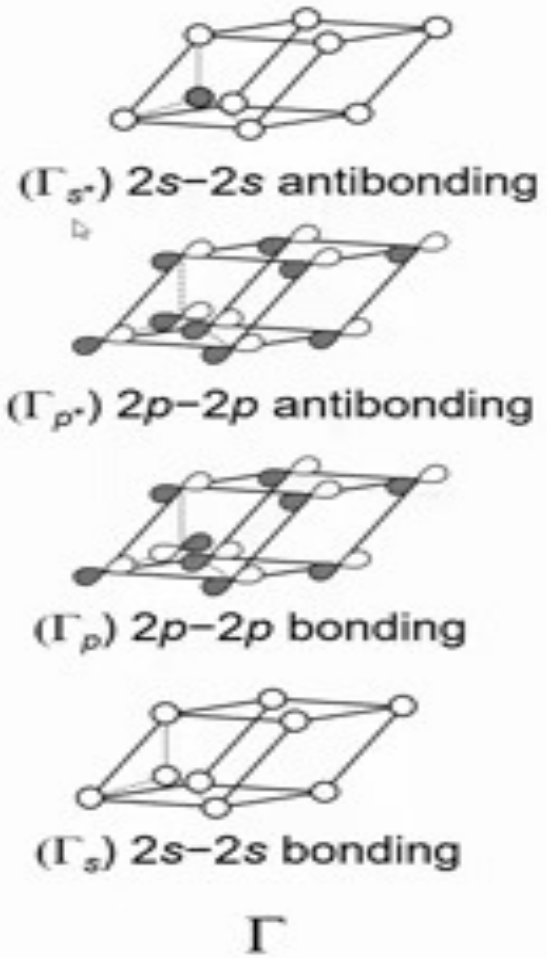
Diamond



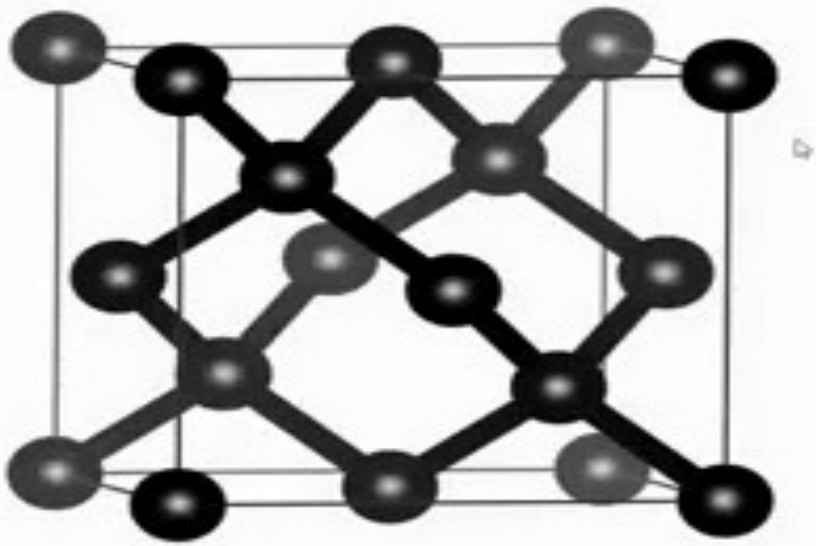
Space Group = $Fd\bar{3}m$
a = 3.57 Å
8 atoms/unit cell
C–C distance = 1.54 Å

Diamond

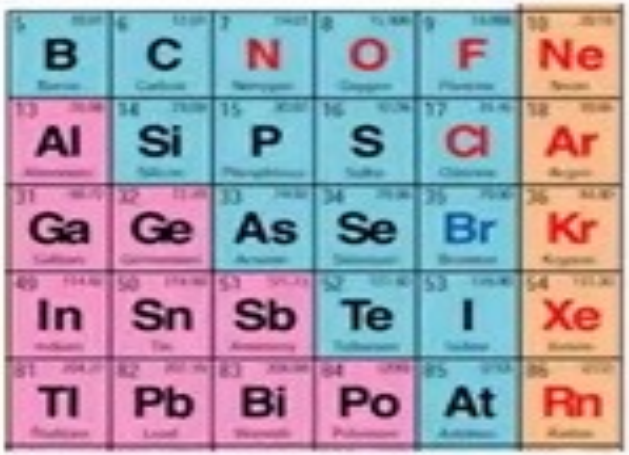

18
10
2
-6
-14
-22
energy (eV)
W
L
Γ
X
W
Γ_{s^*}
Γ_{p^*}
E_g = 5.5 eV
Γ_p
Γ_s
conduction bands
valence bands
indirect band gap


(Γ_{s^*}) 2s–2s antibonding
(Γ_{p^*}) 2p–2p antibonding
(Γ_p) 2p–2p bonding
(Γ_s) 2s–2s bonding
Γ

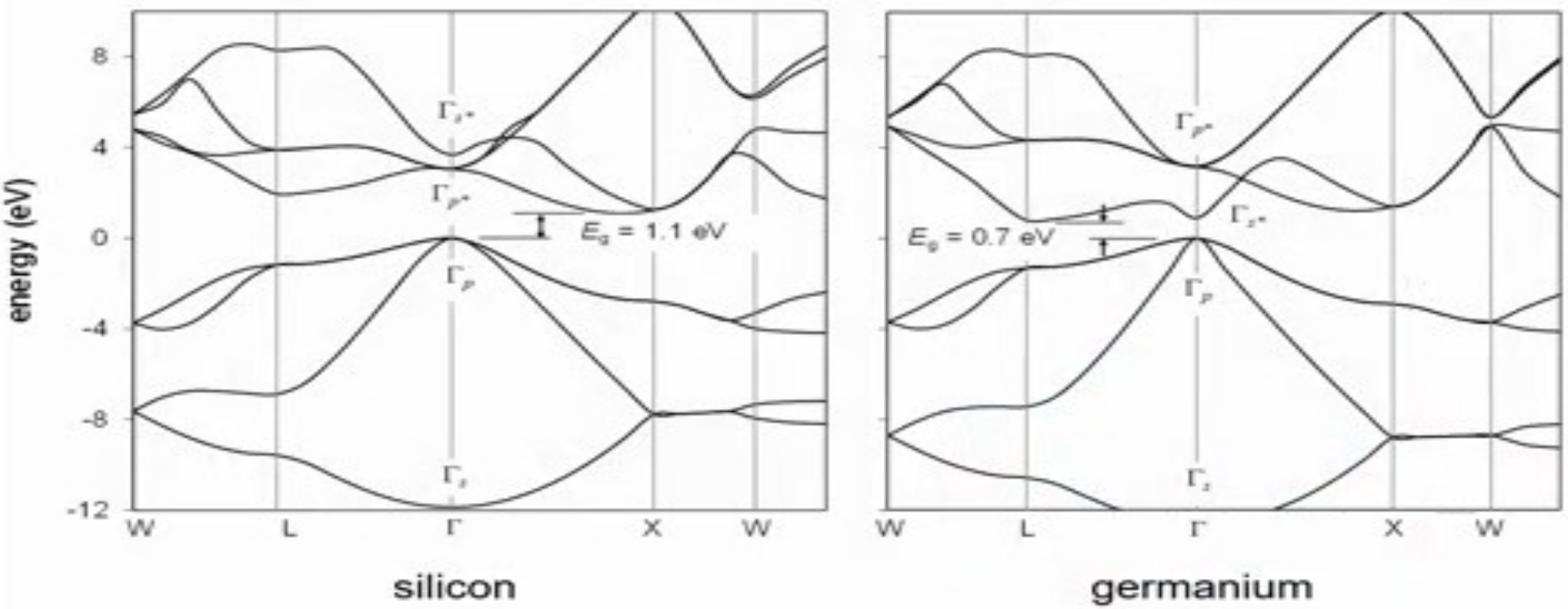
Diamond-like Group 14 Elements



Element	Bond distance (Å)	Band gap (eV)
C	1.54	5.5
Si	2.35	1.1
Ge	2.45	0.7
Sn	2.81	0.1



Silicon and Germanium



silicon

germanium

indirect band gaps

4. Why is aluminum (Al) considered a metal, based on its band structure?

A. Its Fermi level cuts through wide, partially filled bands.

B. It has a large band gap of 5.5 eV.

C. Its 3s and 3p bands are completely full.

D. There is no S-P mixing at the Gamma point.

A. Its Fermi level cuts through wide, partially filled bands.

✓ That's right!

Aluminum has 3 valence electrons to fill 4 bands (which hold 8 electrons total), so the bands are only 3/8 full, allowing for conductivity.

10. What is the primary physical reason for the trend from insulator (C) to semiconductor (Si, Ge) to metal (Pb) down Group 14?

A. Bond distances increase, decreasing orbital overlap and making anti-bonding states less anti-bonding.

B. The number of valence electrons increases down the group.

C. Relativistic effects become dominant for carbon and silicon.

D. The elements become more electronegative down the group.

A. Bond distances increase, decreasing orbital overlap and making anti-bonding states less anti-bonding.

✓ **That's right!**

This decrease in overlap causes the anti-bonding S* band to drop in energy, shrinking and eventually closing the band gap.