令和６年度　ナノ社会人教育プログラム

コース１
ナノマテリアル・ナノデバイスデザイン学

Electron Theory in Solids

Band Theory

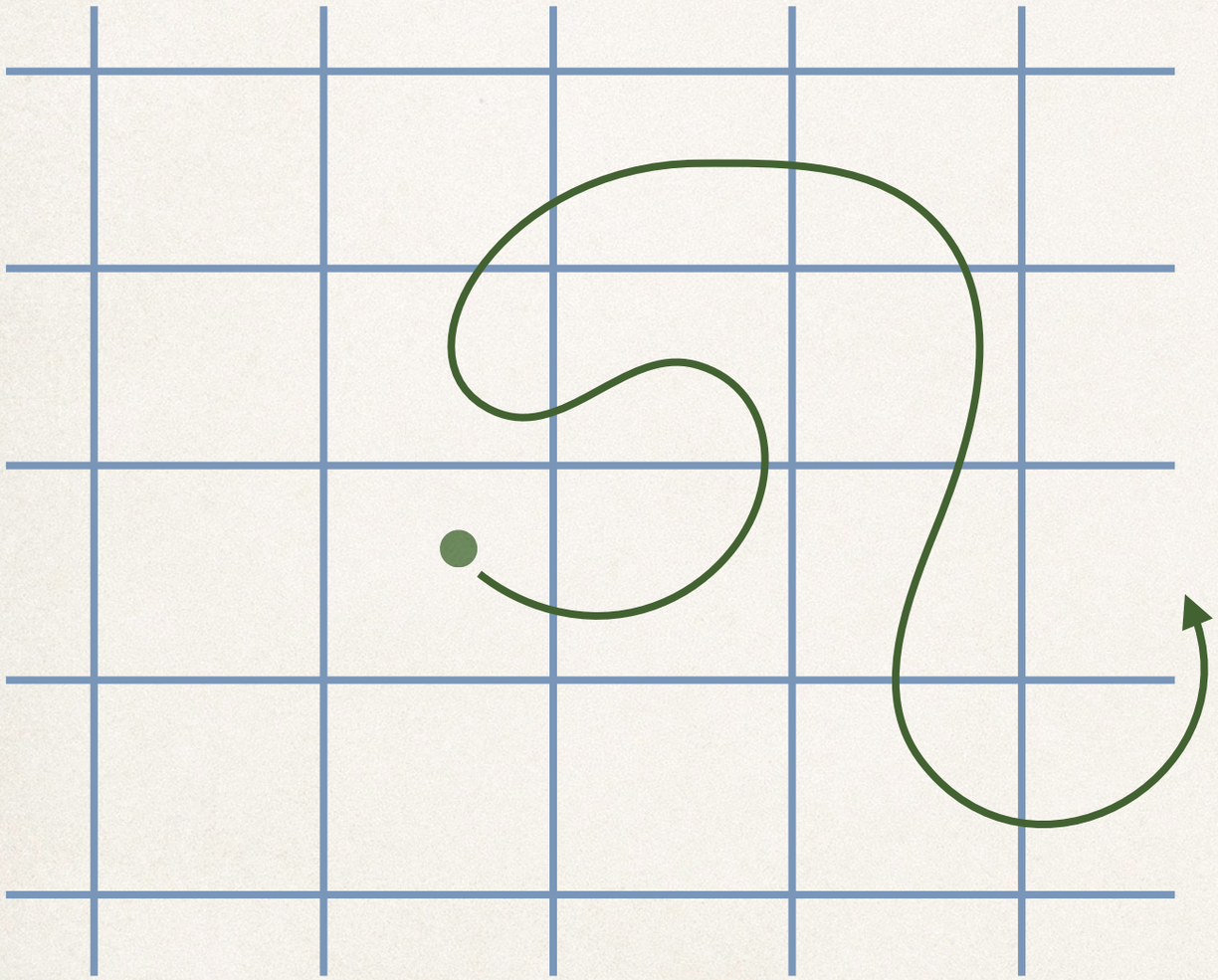
固体中の電子

Koun SHIRAI

Sanken Osaka University and Vietnam Japan University

One-electron picture

One electron



One-electron
Schrödinger equation

$$\left(-\frac{\nabla^2}{2m} + \underline{\underline{V(\mathbf{r})}}\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

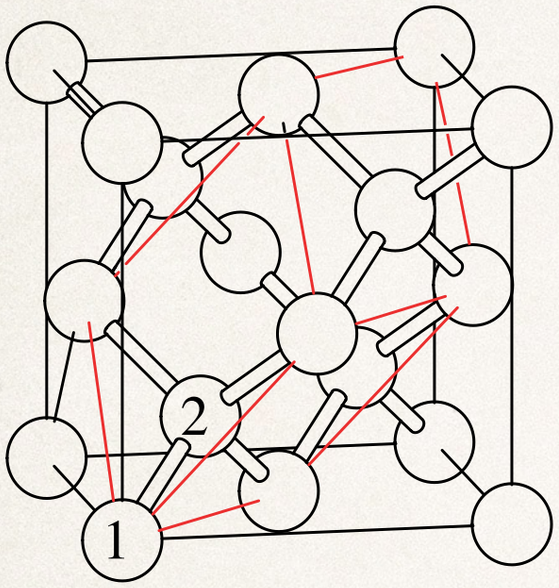
External potential

Forget the fact that the potential $V(\mathbf{r})$ is created by electrons including the electron under consideration.

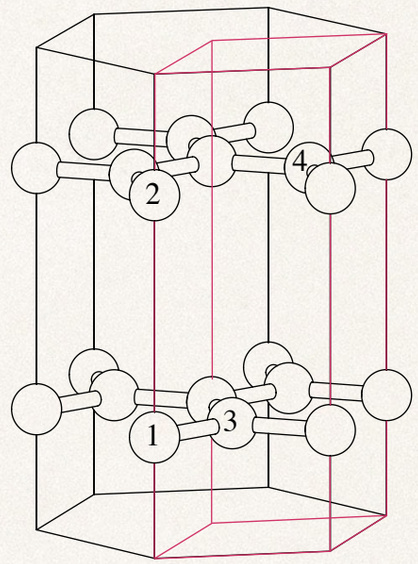
3.0 Preliminary

Microscopic structures of solids

Crystal structures



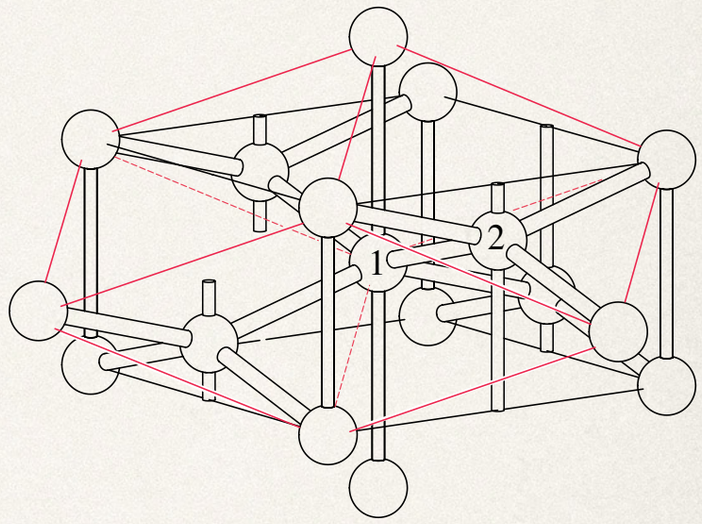
Diamond O_h^7 $Fd3m$



Graphite D_{6h}^4

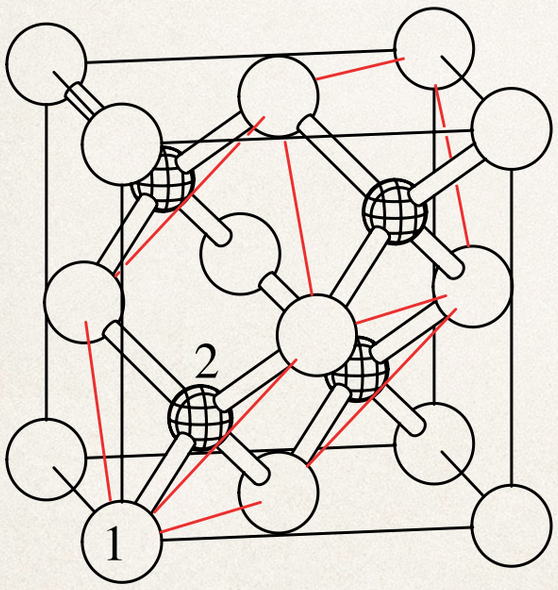
$P6_3/mmc$

When c/a=√(2), this is equivalent to diamond structure

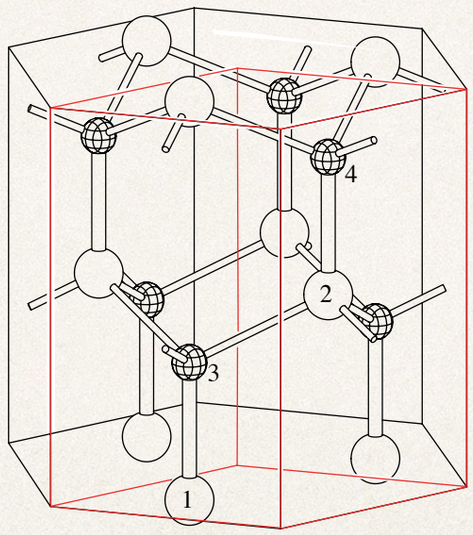


β-Tin D_{4h}^{19}

$I4_1/amd$



Zincblende T_d^2 $T\bar{4}3m$



Wurtzite C_{6v}^4

$P6_3mc$

6_3: a six-fold screw along the c-axis
m: a mirror plane with normal (100)
c: glide plane in the c-axis with normal (120)

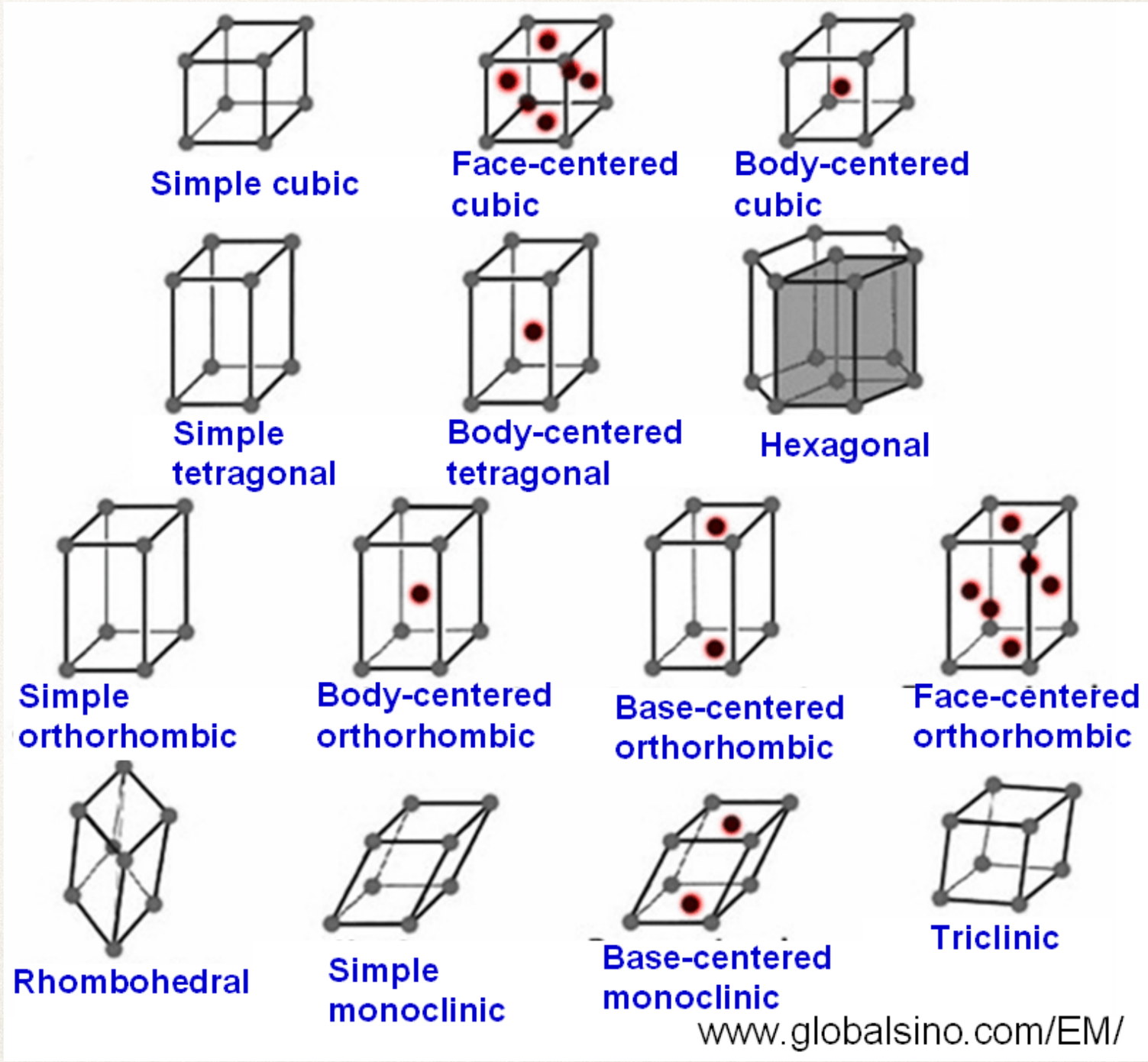
Bravais Lattice

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

$$\{\mathbf{a}_i\} \quad i = 1,2,3$$

Primitive lattice vectors

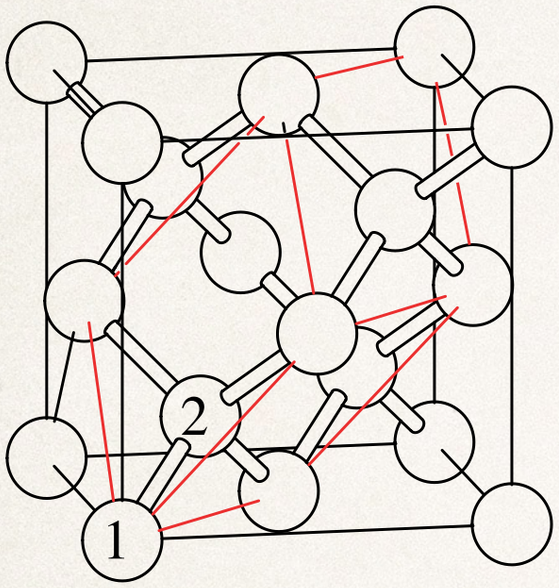
14 types of Bravais lattices



3.1 Bloch Theorem

Effects of lattice periodicity

Crystal structures



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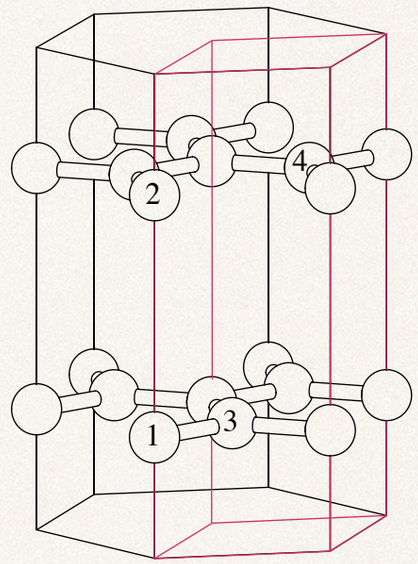

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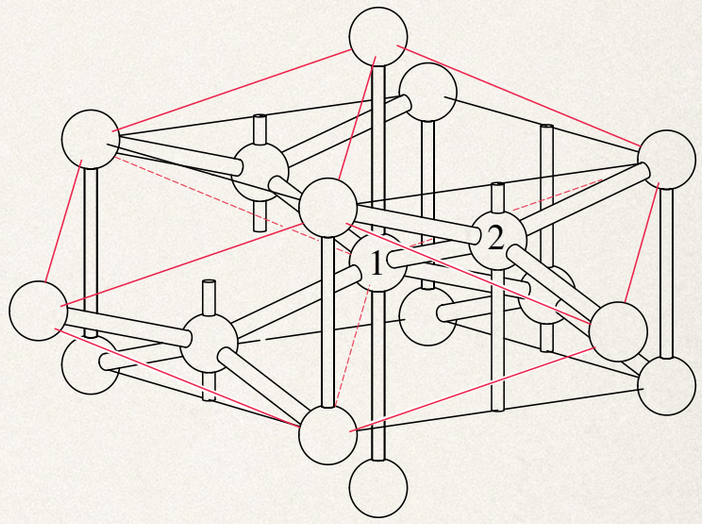

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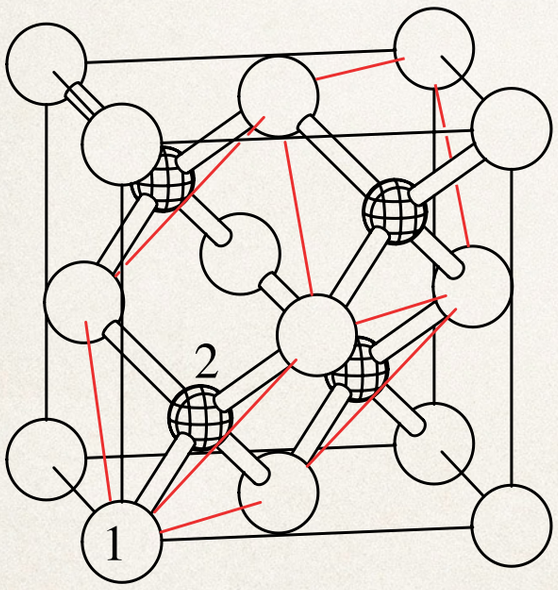

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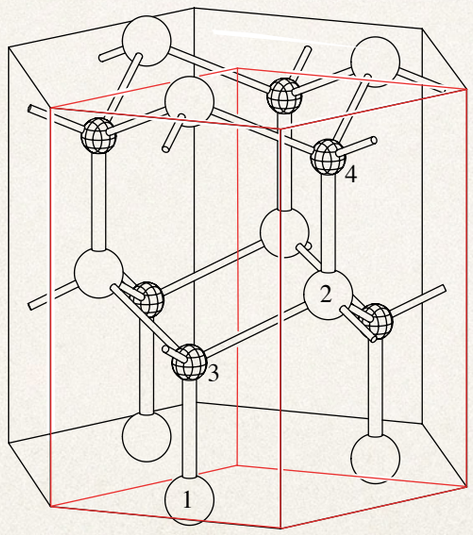

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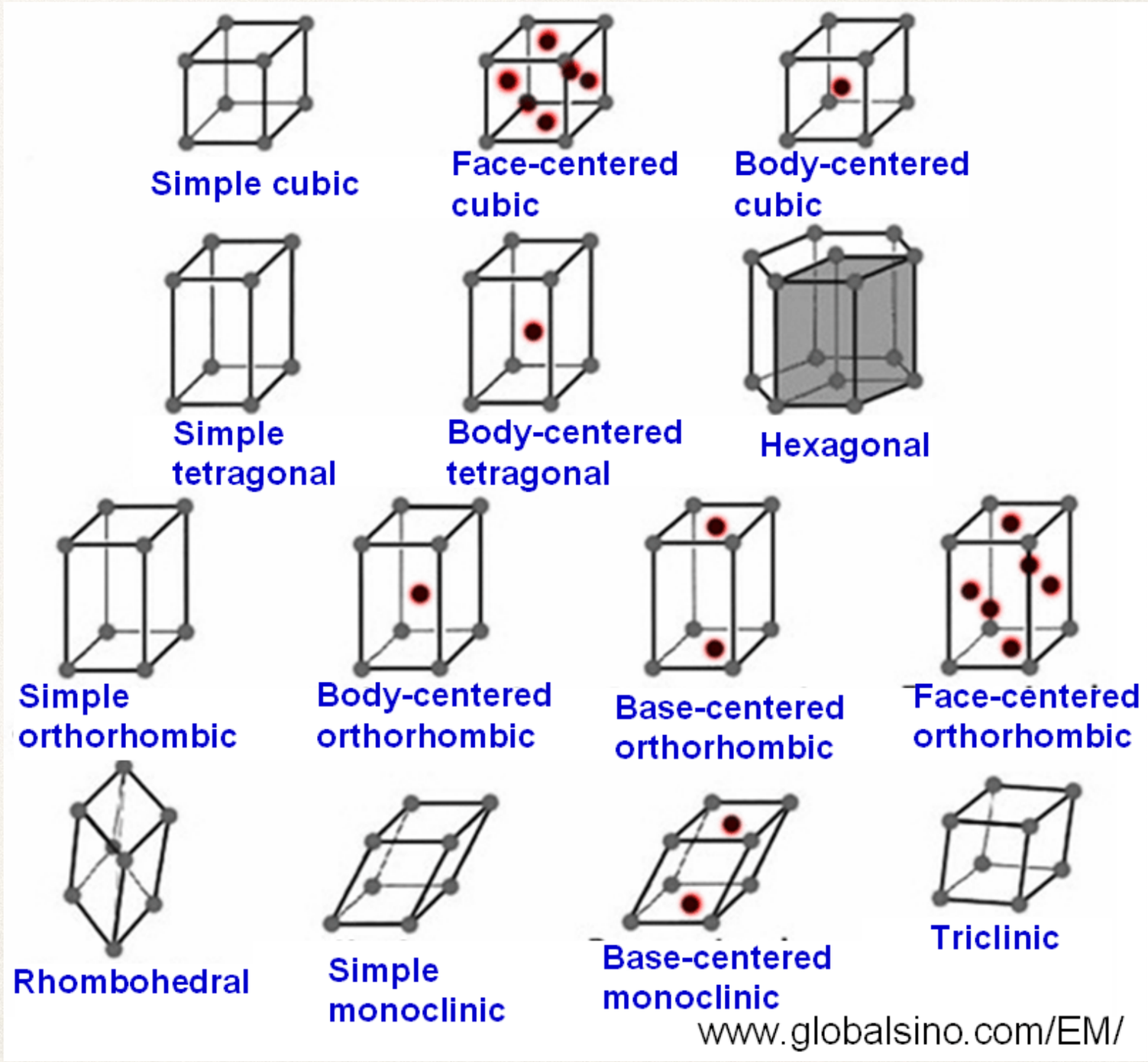
Primitive lattice vectors

14 types of Bravais lattices



Periodic structure

Real lattice vector

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

$\{\mathbf{a}_i\}$ $i = 1,2,3$

Primitive lattice vectors

Reciprocal vector

$$\mathbf{K} = m_1\mathbf{b_1} + m_2\mathbf{b_2} + m_3\mathbf{b_3}$$

$\{\mathbf{b}_i\}$ Primitive reciprocal vectors

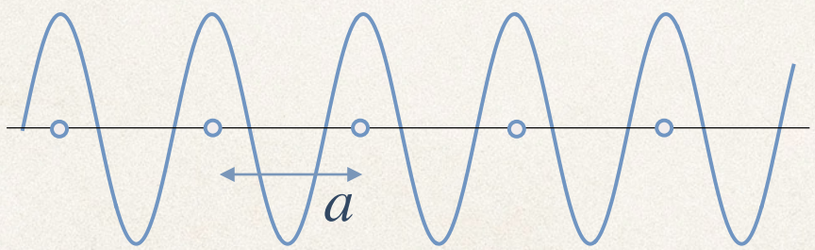
$$\mathbf{b_i} \cdot \mathbf{a_j} = 2\pi\delta_{i,j}$$

$$\mathbf{b_i} = 2\pi\frac{\mathbf{a_j} \times \mathbf{a_k}}{\mathbf{a_i} \times (\mathbf{a_j} \cdot \mathbf{a_k})} = 2\pi\frac{\mathbf{a_j} \times \mathbf{a_k}}{\Omega}$$

Ω: Volume of the unit cell

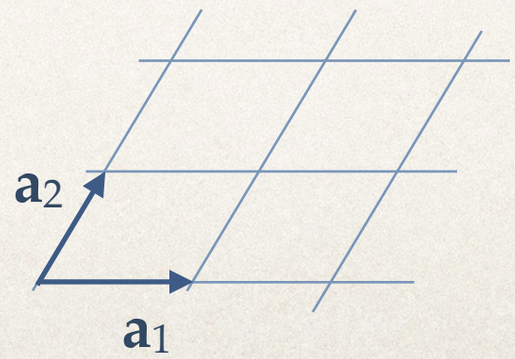
Potential

$$V(\mathbf{r}) = \sum_{\mathbf{K}} V(\mathbf{K})\exp(i\mathbf{K} \cdot \mathbf{r})$$

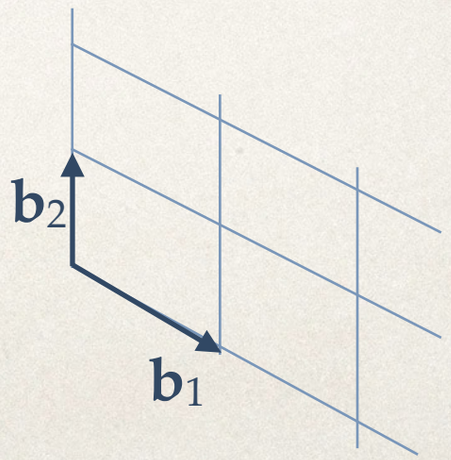


$$K = \frac{2\pi}{a}$$

Real space



Reciprocal space



Wavefunctions

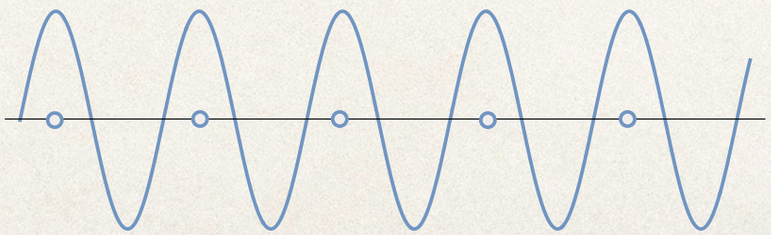
$$\psi(\mathbf{r}) = \sum_{\mathbf{K}} \psi(\mathbf{K}) \exp(i\mathbf{K} \cdot \mathbf{r}) \quad ?$$

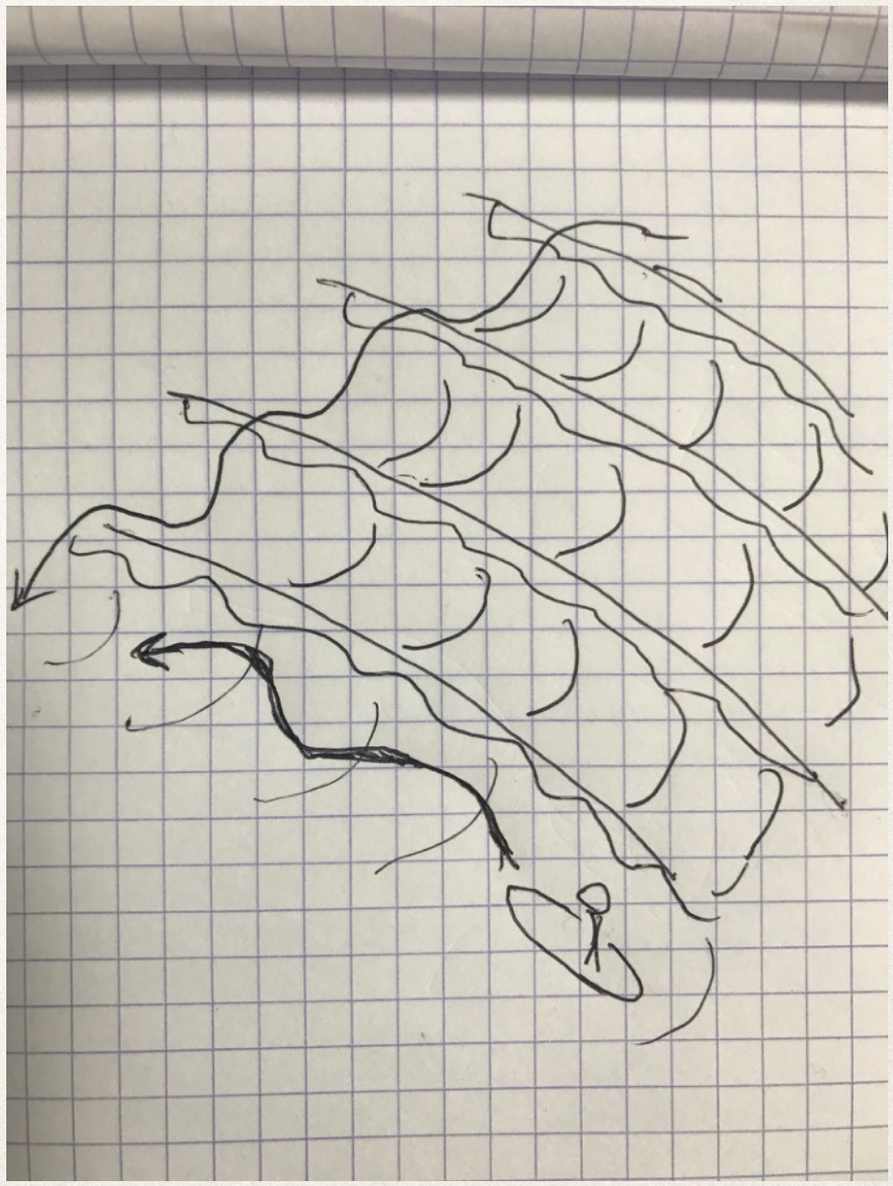
⟶ No!

However,

the charge density must have the lattice periodicity.

$$\rho(\mathbf{r}) = \psi(\mathbf{r})^* \psi(\mathbf{r})$$





Bloch Theorem

Wavefunctions in a crystal

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$$

$u_{\mathbf{k}}(\mathbf{r})$: periodic function of the lattice vector $\mathbf{R}_j$

$$T(\mathbf{R})\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{R})\psi_{\mathbf{k}}(\mathbf{r})$$

$T(\mathbf{R})$: Translational operator $\quad T(\mathbf{R})f(\mathbf{r}) = f(\mathbf{r}+\mathbf{R})$

$$\begin{aligned} T(\mathbf{R})\psi_{\mathbf{k}}(\mathbf{r}) &= T(\mathbf{R})\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \\ &= \exp(i\mathbf{k}\cdot(\mathbf{r}+\mathbf{R}))u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) \\ &= \exp(i\mathbf{k}\cdot\mathbf{R})\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) \end{aligned}$$

$$\begin{aligned} &= \exp(i\mathbf{k}\cdot\mathbf{R})\psi_{\mathbf{k}}(\mathbf{r}) \\ &= \exp(i\mathbf{k}\cdot\mathbf{R})\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \end{aligned}$$

$$u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{\mathbf{k}}(\mathbf{r})$$

Born-von Karman boundary conditions

$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

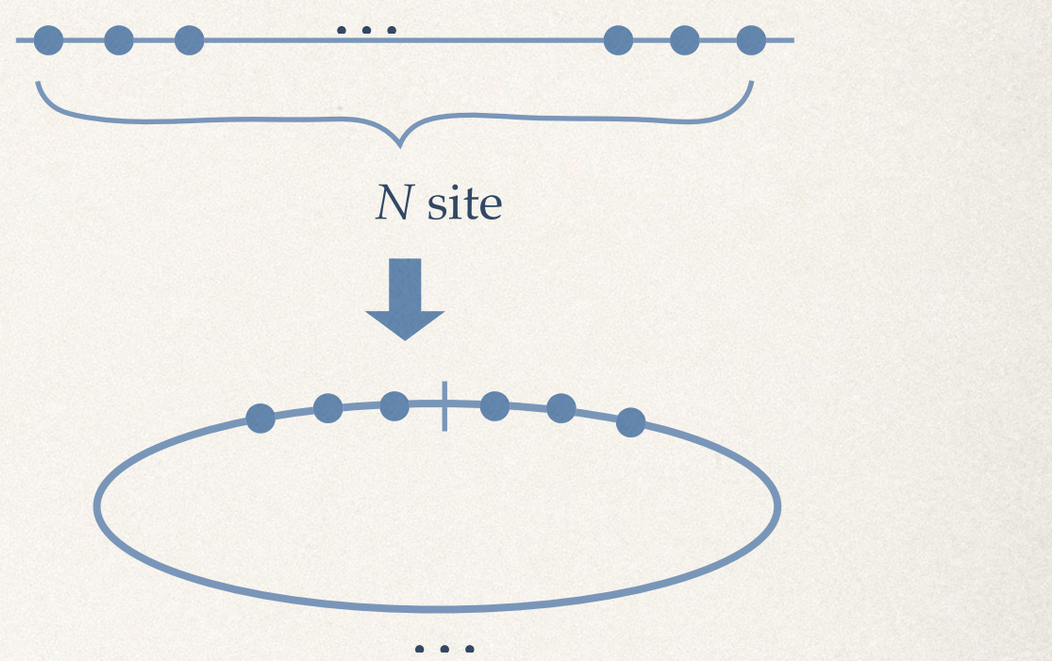
$\{\mathbf{a}_i\}$ $i = 1,2,3$

Primitive lattice vectors

$$\psi_{\mathbf{k}}(\mathbf{r} + N_i\mathbf{a_i}) = \exp(iN_i\mathbf{k}\cdot\mathbf{a}_i)\psi_{\mathbf{k}}(\mathbf{r})$$

$$\exp(iNka) = 1 \longrightarrow k = \frac{m}{N}\frac{2\pi}{a}$$

b



In 3D,

$$\mathbf{k} = \sum_{i=1}^{3}\frac{m_i}{N_i}\mathbf{b_i}$$ Reciprocal vectors

$$\mathbf{K} = m_1\mathbf{b_1} + m_2\mathbf{b_2} + m_3\mathbf{b_3}$$

$\{\mathbf{b}_i\}$ Primitive reciprocal vectors

$$\mathbf{b_i}\cdot\mathbf{a_j} = 2\pi\delta_{i,j}$$

$$\mathbf{b_i} = 2\pi\frac{\mathbf{a_j}\times\mathbf{a_k}}{\mathbf{a_i}\times(\mathbf{a_j}\cdot\mathbf{a_k})} = 2\pi\frac{\mathbf{a_j}\times\mathbf{a_k}}{\Omega}$$

Ω: Volume of the unit cell

Features of Bloch functions

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$$

- $\mathbf{k}$ is a good quantum number.

  Eigenfunctions must have Bloch functions.

  However, Bloch functions are not necessarily the eigenfunctions.

- Eigenfunctions are expressed by a linear combination of Bloch functions with the same $\mathbf{k}$. $\left\{ u_{\mathbf{k}}^{j}(\mathbf{r}) \right\}$
- Two eigenfunctions belonging to different $\mathbf{k}$'s are orthogonal each other.

$\varepsilon(\mathbf{k})$ has lattice periodicity

$\varepsilon(\mathbf{k})$: eigenvalue of H

$$\psi_{\mathbf{k}n}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}n}(\mathbf{r}) \xrightarrow{\text{eigenvalue}} \varepsilon_n(\mathbf{k})$$

n: extra index of eigenfunctions

$$\psi_{\mathbf{k}+\mathbf{K}n}(\mathbf{r}) = \exp(i\mathbf{k}+\mathbf{K}\cdot\mathbf{r})u_{\mathbf{k}+\mathbf{K}n}(\mathbf{r}) \qquad \varepsilon_n(\mathbf{k}+\mathbf{K})$$

$$= \exp(i\mathbf{k}\cdot\mathbf{r})\exp(i\mathbf{K}\cdot\mathbf{r})u_{\mathbf{k}+\mathbf{K}n}(\mathbf{r})$$

$$u_{\mathbf{k}n'}(\mathbf{r}) \longrightarrow \varepsilon_{n'}(\mathbf{k})$$

Band structure

Plane-wave expansion

$$\psi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r})$$
$$= \sum_{\mathbf{K}} c_{\mathbf{k}+\mathbf{K}} e^{i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}}$$

Periodic functions

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{k}+\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}$$

additional index ↓ n: band index

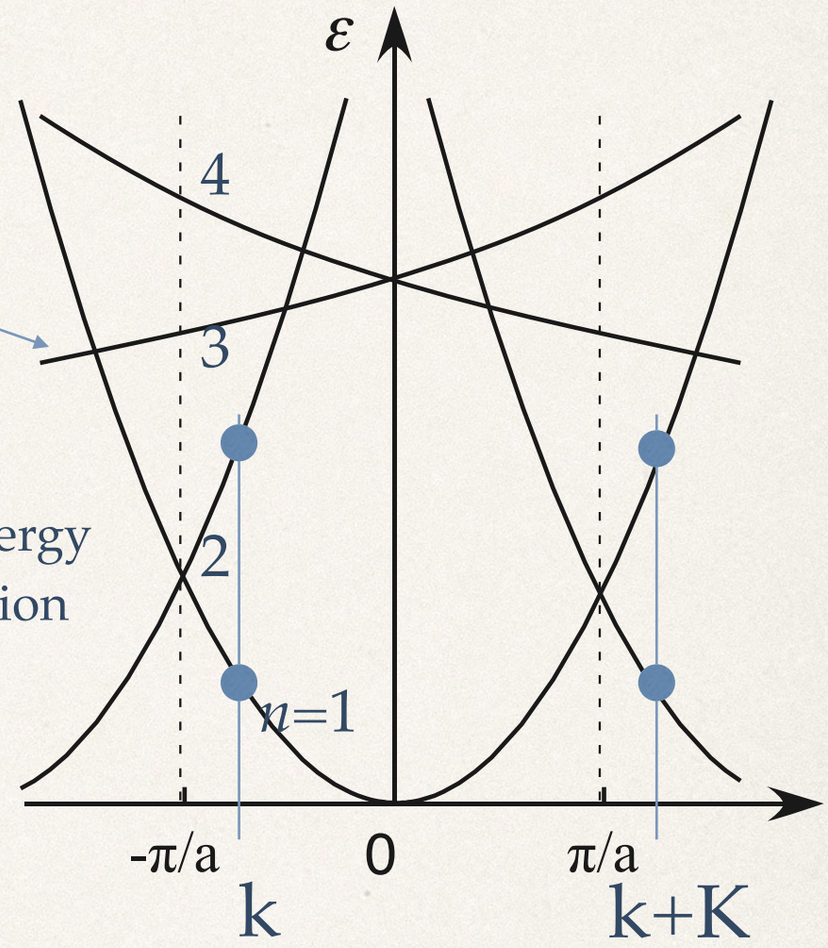
$$u_{\mathbf{k}n}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}n} e^{i\mathbf{K}\cdot\mathbf{r}}$$

$$\psi_{\mathbf{k}n}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}n}(\mathbf{r})$$

band

$\varepsilon_n(\mathbf{k})$

k-dependent energy
= band dispersion



$$\mathbf{k} \to \mathbf{k} + \mathbf{K}$$

$$\psi_{\mathbf{k}+\mathbf{K}}(\mathbf{r}) = \exp(i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r})u_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$$
$$= \exp(i\mathbf{k}\cdot\mathbf{r})\exp(i\mathbf{K}\cdot\mathbf{r})u_{\mathbf{k}+\mathbf{K}}(\mathbf{r})$$

periodic in $\mathbf{R}$

Even when k is restricted in the range $-\pi/2 < k < \pi/2$, additional band index n covers all the possible states.

Free electrons

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right\} \psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

When $V = 0$ → free electrons

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$\varepsilon^0 = \frac{\hbar^2}{2m}\mathbf{k}^2$$

However,

Bloch theorem → $\varepsilon^0 = \frac{\hbar^2}{2m}(\mathbf{k} - \mathbf{K})^2$

Why does the band structure emerge even from free electrons?

Example)

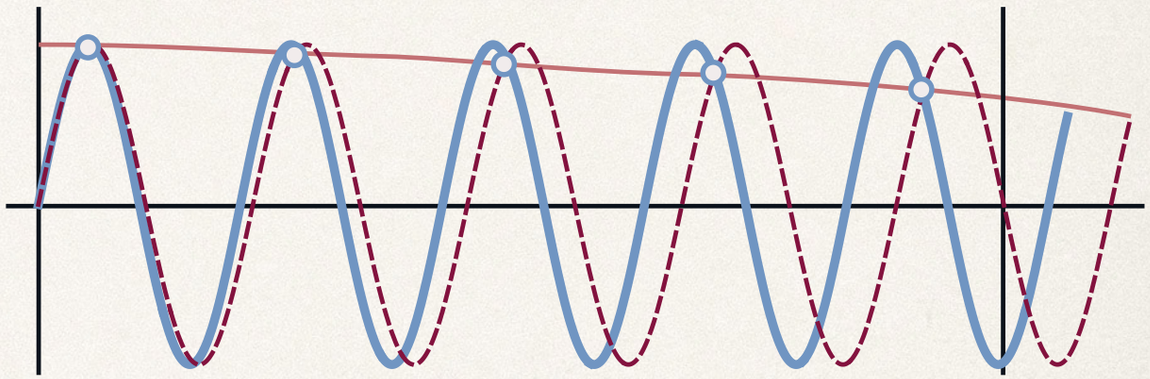
$$e^{5.2xi} = \underbrace{e^{0.2xi}}_{e^{ikx}} \underbrace{e^{5xi}}_{\text{periodic function}}$$

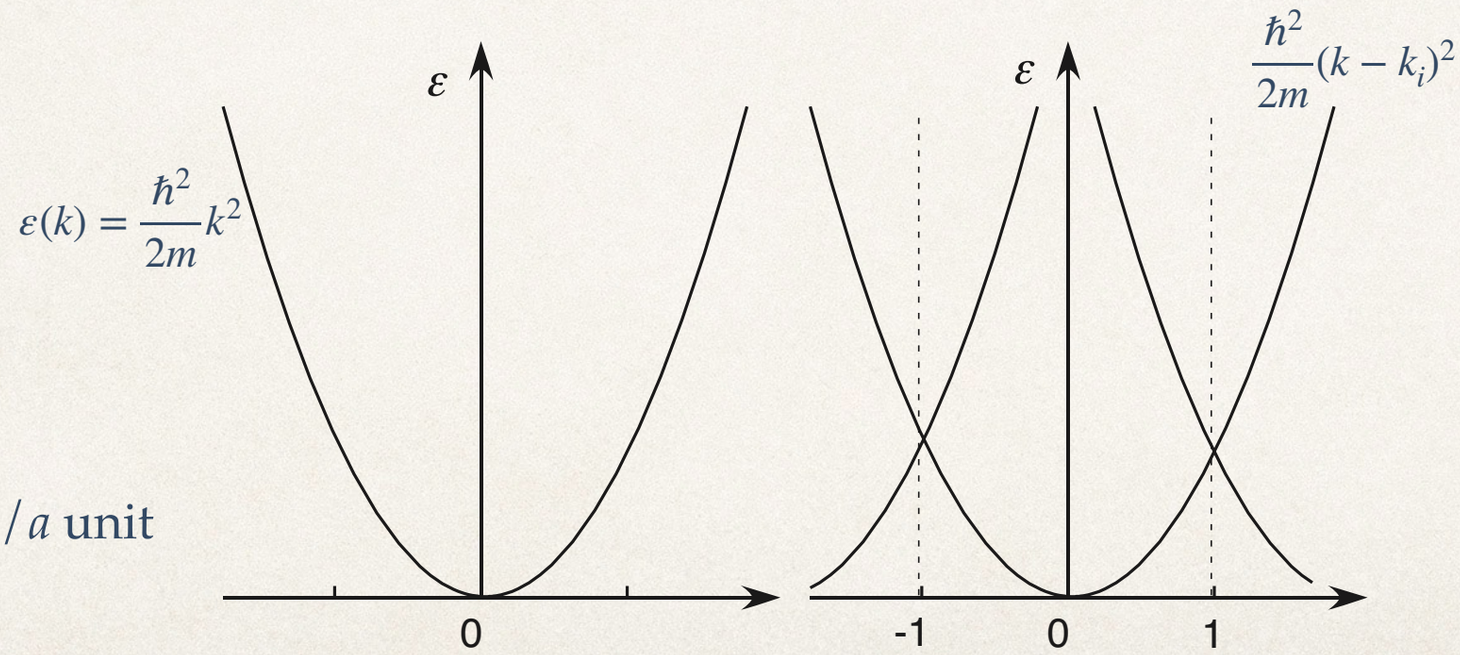
$0<k<1$

periodic function

$u(x+n) = u(x)$

(envelope) + (periodic function)



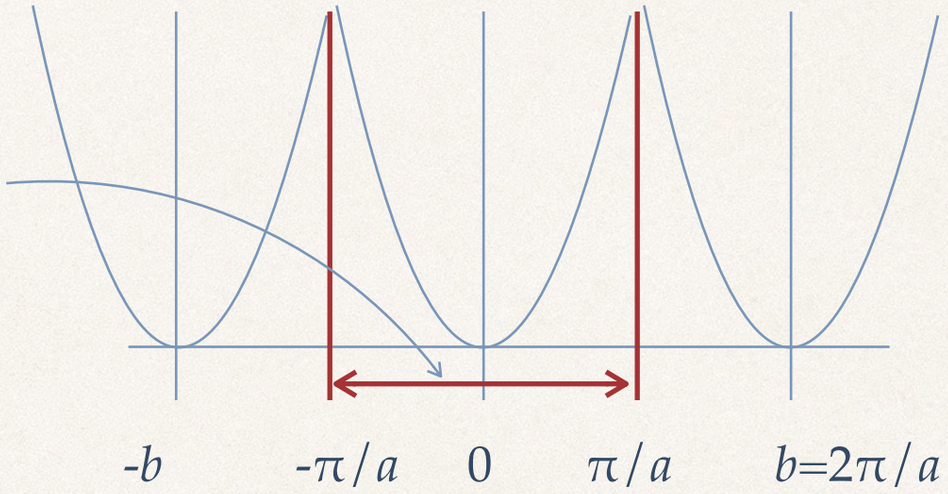


Brillouin zone (BZ)

The minimum region in the **k** space needed to indicate the periodicity.

Construction of a Brillouin zone (BZ)

First Brillouin zone



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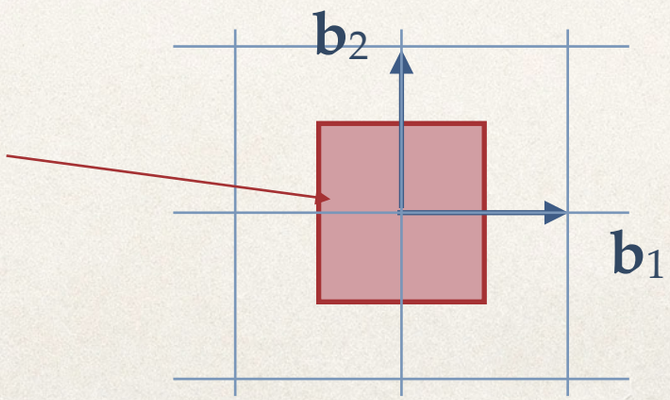

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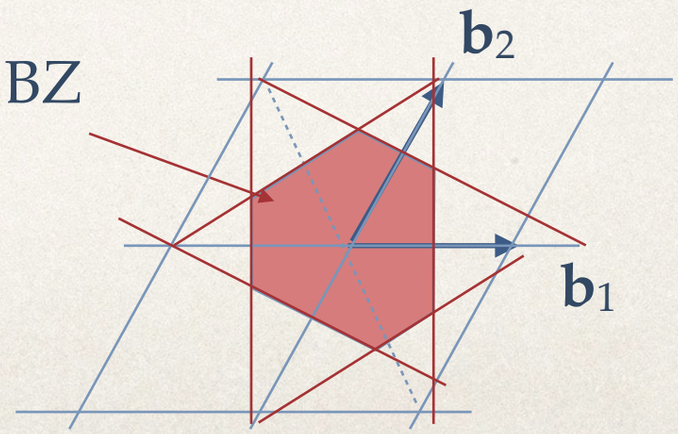
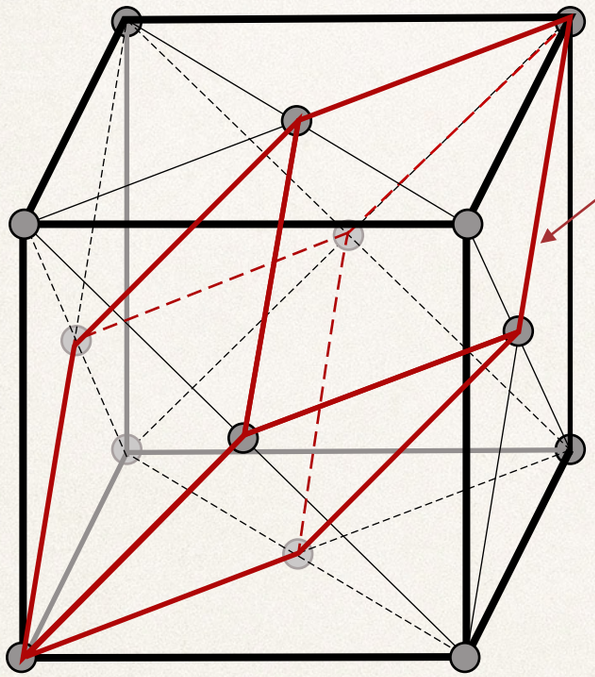
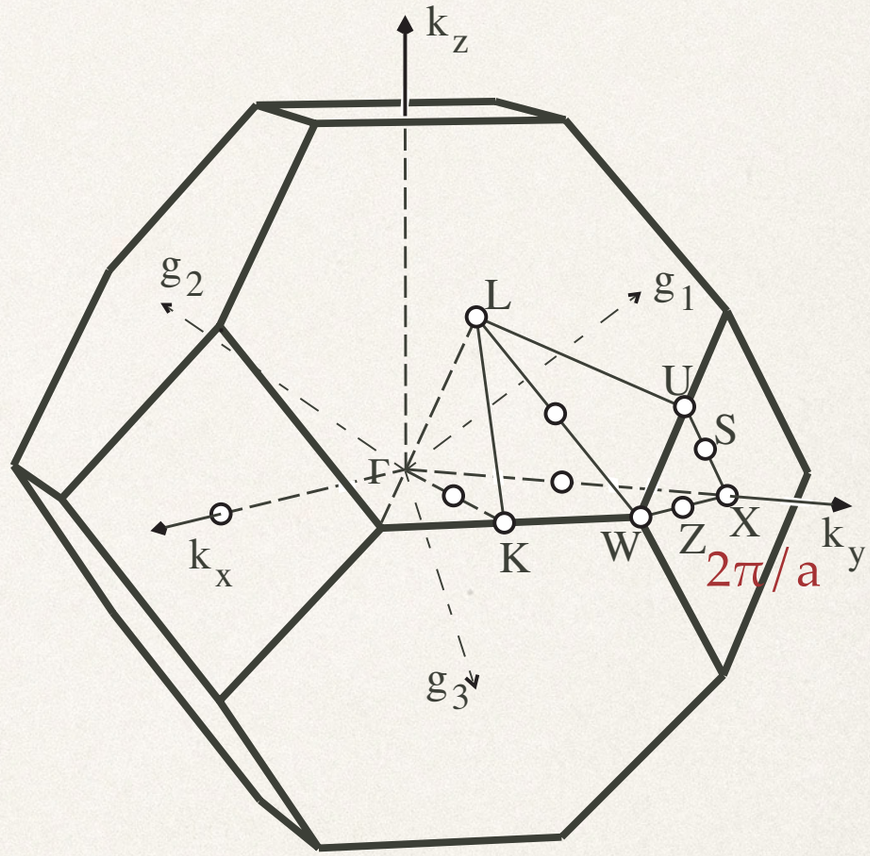


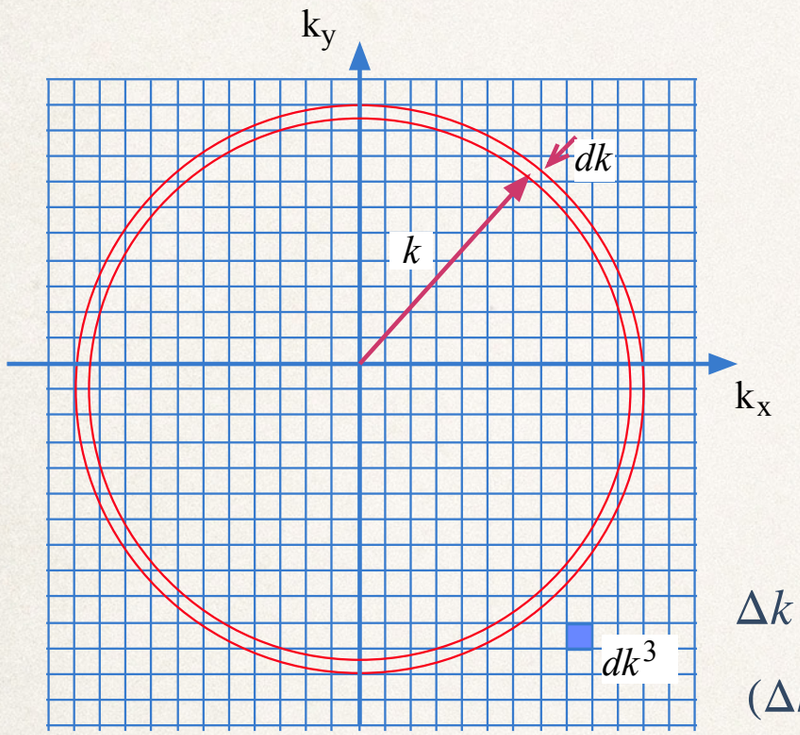
Face-Centered-Cubic lattice





Density-of-States (DOS)

Density of states in the energy space



spin states

$$\mathcal{N} = \frac{2}{N}\frac{1}{(\Delta k)^3}\frac{4\pi}{3}k^3 \qquad N = N_1 \bullet N_1 \bullet N_3$$

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

$$\frac{d\varepsilon}{dk} = \frac{\hbar^2}{2m}k$$

$$D(k) = \frac{d\mathcal{N}}{dk} = \frac{V}{N}\frac{1}{(2\pi)^3}8\pi k^2$$

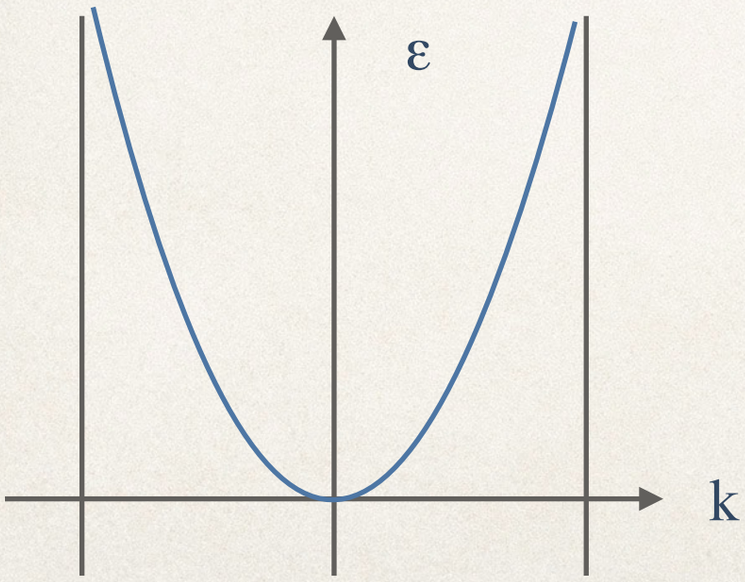
$$D(\varepsilon) = \frac{d\mathcal{N}}{dk}\frac{dk}{d\varepsilon} = \frac{V_c}{(2\pi)^3}8\pi k^2\frac{2m}{\hbar^2 k}$$

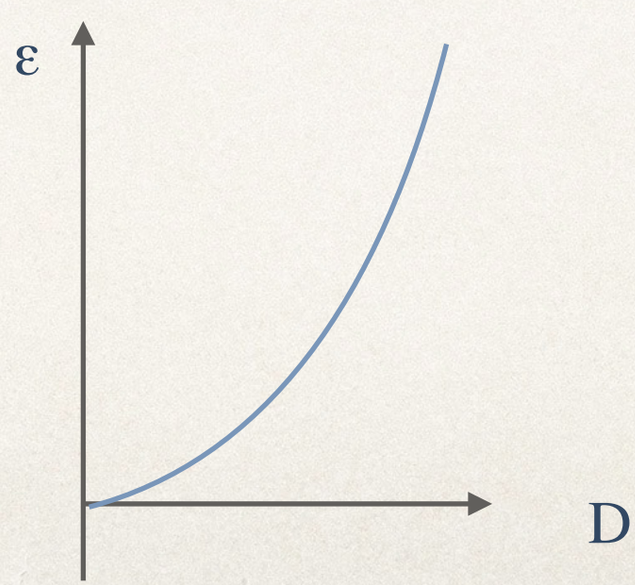
$$= V_c\frac{2\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\sqrt{\varepsilon}$$

V_c: volume of unit cell

$$\Delta k = 2\pi\frac{1}{L}$$

$$(\Delta k)^3 = \frac{(2\pi)^3}{V}$$

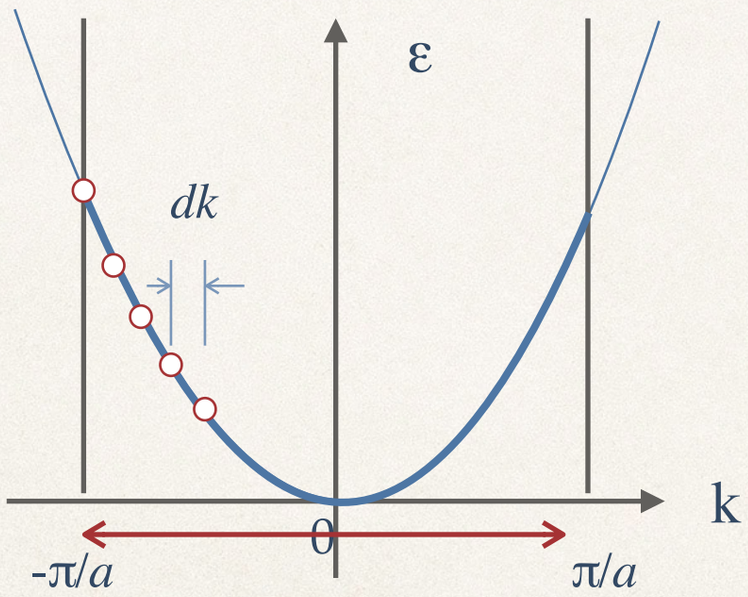




	$D(\varepsilon)$
1d	$1/\sqrt{\epsilon}$
2d	const
3d	$\sqrt{\epsilon}$

Electron occupation

One band in a Brillouin zone contains exactly two electrons in a primitive unit cell.



First Brillouin zone

$$\int_{BZ} D(k)dk = 2$$

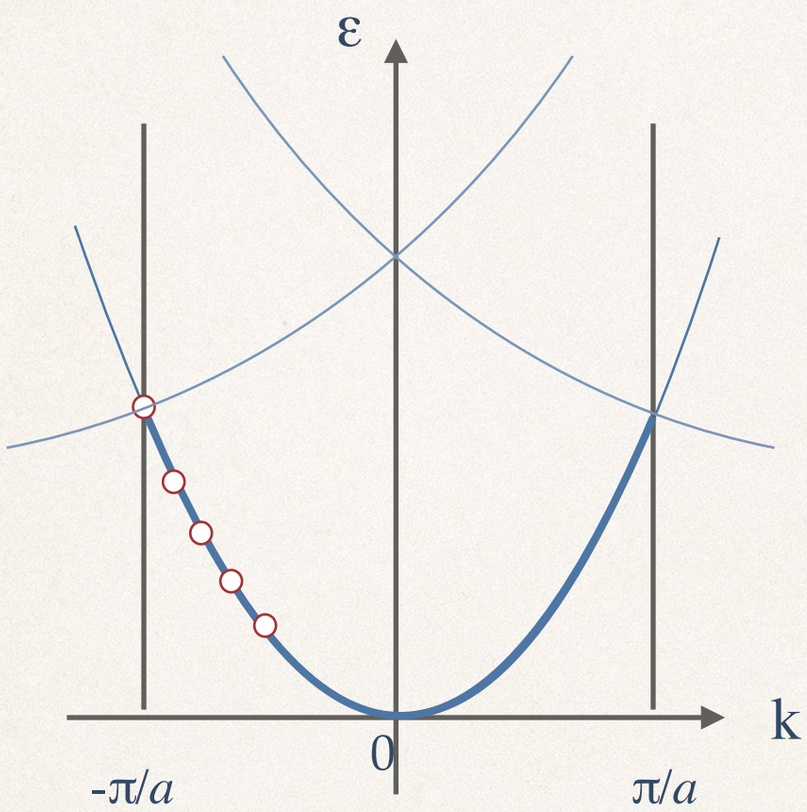
the volume of BZ

One BZ

One unit cell

two electrons in a cell

Fermi energy



E_F: Fermi energy (level)

$$\int_0^{E_F} D(\epsilon)d\epsilon = N_{el}$$

Fermi surface

3.2 Band theory - 1

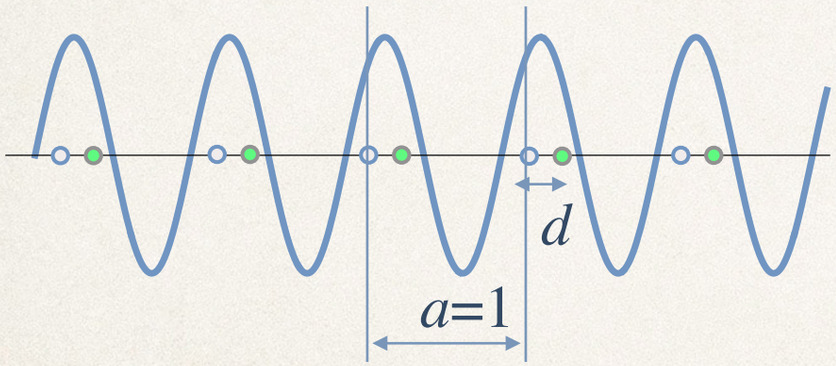
Nearly free electron approximation

Nearly-free-electron approximation

Potential

$$V(\mathbf{r}) = \sum_{\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}} V(\mathbf{K})$$

$$V(\mathbf{K}) = \frac{1}{\Omega_c}\int d\mathbf{r} e^{-i\mathbf{K}\cdot\mathbf{r}} V(\mathbf{r})$$



$b=2\pi/a$

$$\frac{1}{N}\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}} = \delta_{\mathbf{k},\mathbf{K}}$$

$$\sum_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} = \underset{1}{e^{-i\mathbf{K}\cdot(\mathbf{0},\mathbf{0},\mathbf{0})}} + \underset{1}{e^{-i\mathbf{K}\cdot(\mathbf{1},\mathbf{0},\mathbf{0})}} + \underset{1}{e^{-i\mathbf{K}\cdot(\mathbf{2},\mathbf{0},\mathbf{0})}} \ldots = N$$

2π 4π

atom potential

$$V(\mathbf{r}) = \sum_{\mathbf{R}\kappa j} U_\kappa(\mathbf{r} - \mathbf{R} - \mathbf{d}_{\kappa j})$$

Atom potential of
j-th atom of the same chemical species κ

$$= \sum_{\mathbf{R}\kappa j} \frac{1}{\Omega}\int d\mathbf{r} e^{-i\mathbf{K}\cdot\mathbf{r}} U_\kappa(\mathbf{r} - \mathbf{R} - \mathbf{d}_{\kappa j})$$

$$= \sum_{\mathbf{R}\kappa j} \frac{1}{\Omega}\int d\mathbf{r}' e^{-i\mathbf{K}\cdot(\mathbf{r}'+\mathbf{R}+\mathbf{d}_{\kappa j})} U_\kappa(\mathbf{r}')$$

$$= \frac{1}{\Omega}\sum_{\kappa}\sum_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} \sum_{j} e^{-i\mathbf{K}\cdot\mathbf{d}_{\kappa j}} \int d\mathbf{r} e^{-i\mathbf{K}\cdot\mathbf{r}} U_\kappa(\mathbf{r})$$

$$= \sum_{\kappa} \underbrace{\left(\sum_{j} e^{-i\mathbf{K}\cdot\mathbf{d}_{\kappa j}} \sum_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} \right)}_{S_\kappa(\mathbf{K})} \underbrace{U_\kappa(\mathbf{K})}_{\text{form factor}}$$

structural factor

Schrödinger equation

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} c_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \longleftarrow e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{K}} c_{\mathbf{k}+\mathbf{K}} e^{i\mathbf{K}\cdot\mathbf{r}}$$

$$\mathbf{q} = \mathbf{k} - \mathbf{K}$$

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right\} \psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

$$\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \left\{ \left(\frac{\hbar^2}{2m} q^2 - \varepsilon \right) c_{\mathbf{q}} + \sum_{\mathbf{K}'} V(\mathbf{K}') c_{\mathbf{q}-\mathbf{K}'} \right\} = 0$$

matrix form

unit: $\frac{\hbar^2}{2m} = 1$

$$\begin{vmatrix} \mathbf{k}^2 - \varepsilon & V(\mathbf{K}_1) & V(\mathbf{K}_2) & \cdots \\ V(\mathbf{K}_1) & (\mathbf{k}-\mathbf{K}_1)^2 - \varepsilon & V(\mathbf{K}_2 - \mathbf{K}_1) & \cdots \\ V(\mathbf{K}_2) & V(\mathbf{K}_2 - \mathbf{K}_1) & (\mathbf{k}-\mathbf{K}_2)^2 - \varepsilon & \cdots \\ \cdots & & & \\ \cdots & & & \end{vmatrix} = 0$$

$$\left(\frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2 - \varepsilon \right) c_{\mathbf{k}-\mathbf{K}} + \sum_{\mathbf{K}'} V(\mathbf{K}' - \mathbf{K}) c_{\mathbf{k}-\mathbf{K}'} = 0$$

When $V = 0$

$$\varepsilon^0 = \frac{\hbar^2}{2m} (\mathbf{k} - \mathbf{K})^2$$

free electrons

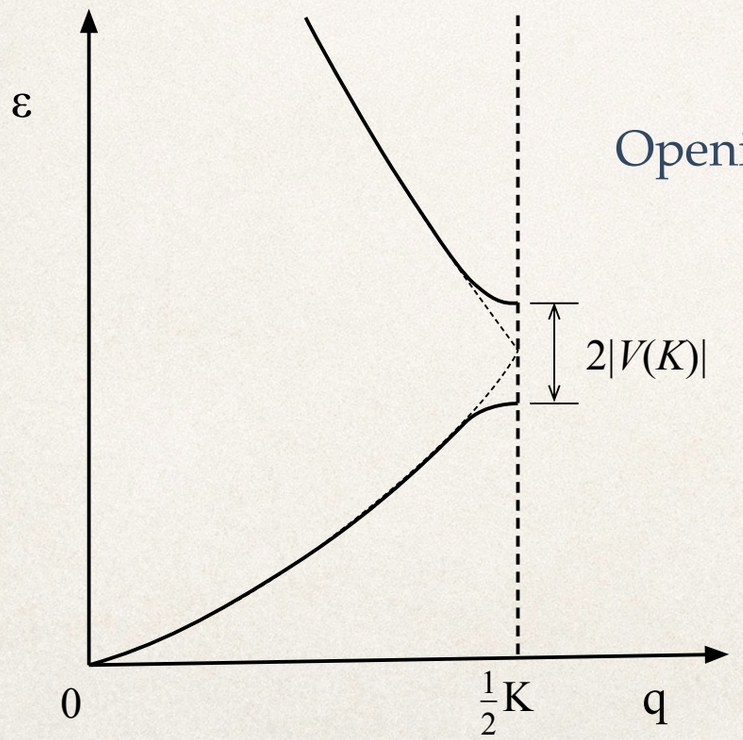
Role of crystal potentials

At a zone boundary $\mathbf{k} = \frac{1}{2}\mathbf{K}$

$$\begin{vmatrix} (\mathbf{K}/2)^2 - \varepsilon & V(\mathbf{K}) \\ V(\mathbf{K}) & (\mathbf{K}/2)^2 - \varepsilon \end{vmatrix} = 0$$

Degenerate case

$$\varepsilon = \varepsilon^0_{\mathbf{K}/2} \pm |V(\mathbf{K})|$$

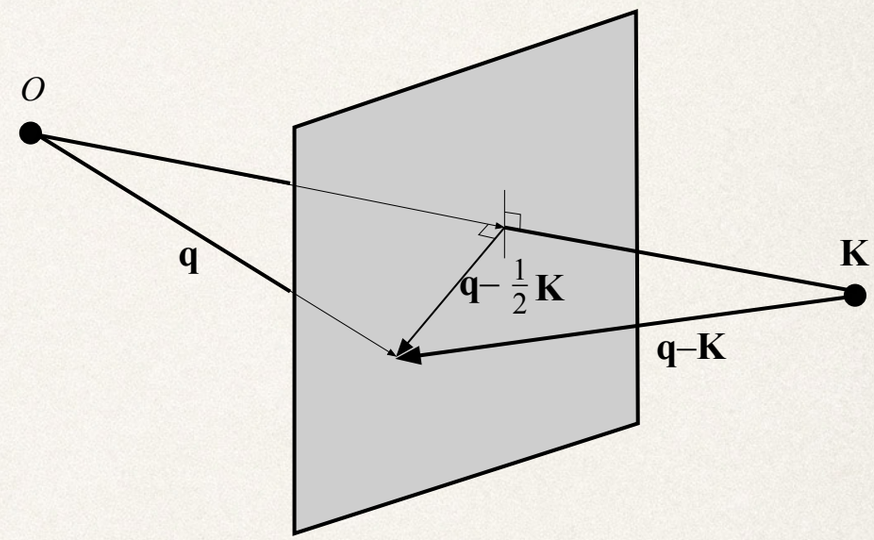


Opening a gap

$$\mathbf{q} = \mathbf{k} - \mathbf{K}$$

Bragg reflection

$$|\mathbf{q}| = |\mathbf{q} - \mathbf{K}|$$



When Bragg reflection occurs, an energy gap is opened at that point **q**.

Bragg reflection

われる．ここでは弾性散乱を考えていて，X線の波長は反射のときに変化しな
散乱（弾性波の励起を伴う散乱）については章末において述べる．

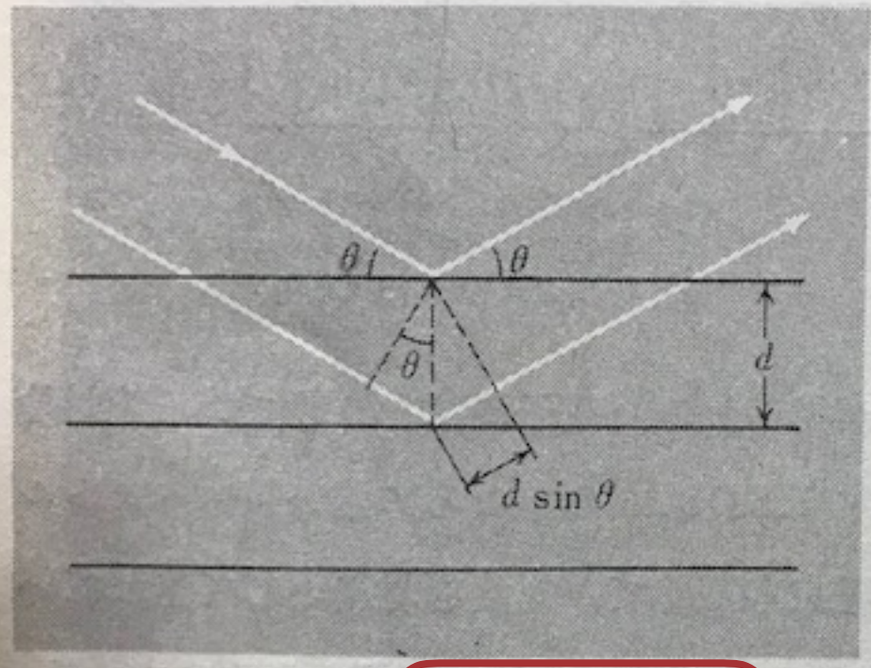


図 2・3　ブラッグの式 $2d\sin\theta=n\lambda$ の導出．ここにdは平行な原子面の面間隔．$2n\pi$は，つぎつぎの面からの反射波間の位相差である．反射面は試料の外形上の表面とは関係がない．

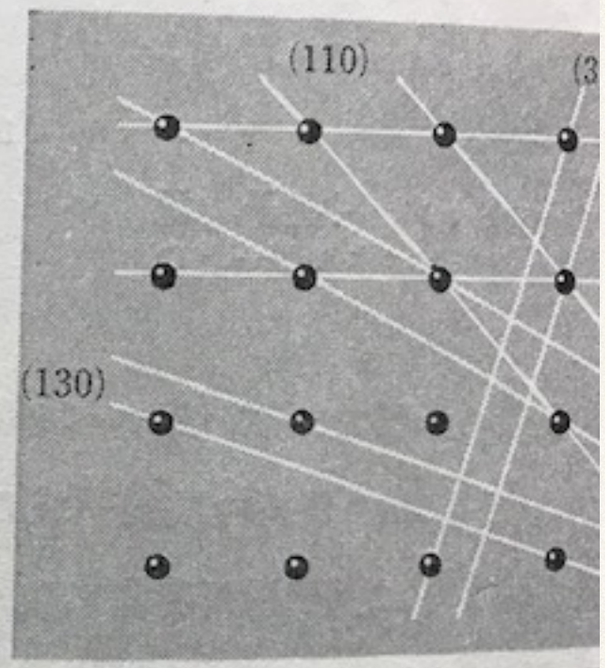


図 2・4　単純立方結晶格子での反面には指数を付けて区別している．1組の平行な2面を示す．平行な面離は指数が増すと減少する．それゆ数の反射を起こすには短い波長の波る．

$$|\mathbf{q}| = |\mathbf{q} - \mathbf{K}|$$

$$|\mathbf{q}|^2 = |\mathbf{q} - \mathbf{K}|^2$$

$$K^2 = 2Kq\cos\theta$$

$$K = 2q\cos\theta$$

$$\frac{\lambda}{d} = 2\cos\theta$$

Correspondence to *X*-ray diffraction

Structural factor

$$S(hkl)=\sum_j f_j \exp\left[-2\pi i\left(x_j h+y_j k+z_j l\right)\right]$$

$$=\sum_\kappa f_\kappa \underbrace{\sum_j \exp\left[-2\pi i\left(x_j h+y_j k+z_j l\right)\right]}_{S_\kappa(hkl)}$$

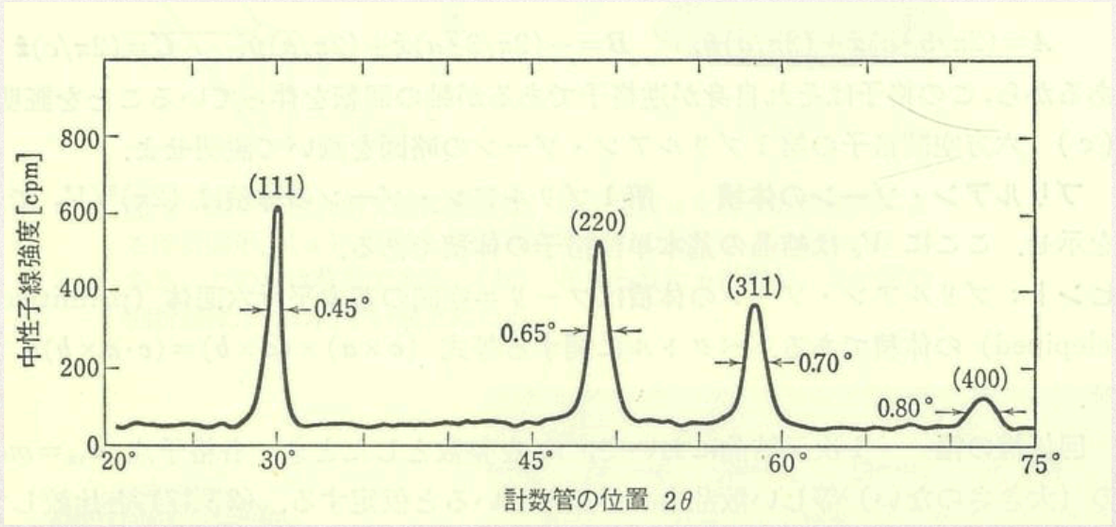
(hkl) Muller index

κ: chemical species of symmetry equivalent

$S_\kappa(hkl)$ FCC $1+\exp\left[i\pi(h+k)\right]+\exp\left[i\pi(k+l)\right]+\exp\left[i\pi(l+h)\right]$

→ vanishes when both even and odd numbers are present

Diamond $\left(1+\exp\left[i\pi(h+k)\right]+\exp\left[i\pi(k+l)\right]+\exp\left[i\pi(l+h)\right]\right)\left(1+\exp\left[i\frac{\pi}{2}\underbrace{(k+l)}_{h+k+l}\right]\right)$



→ Extinction rule for FCC

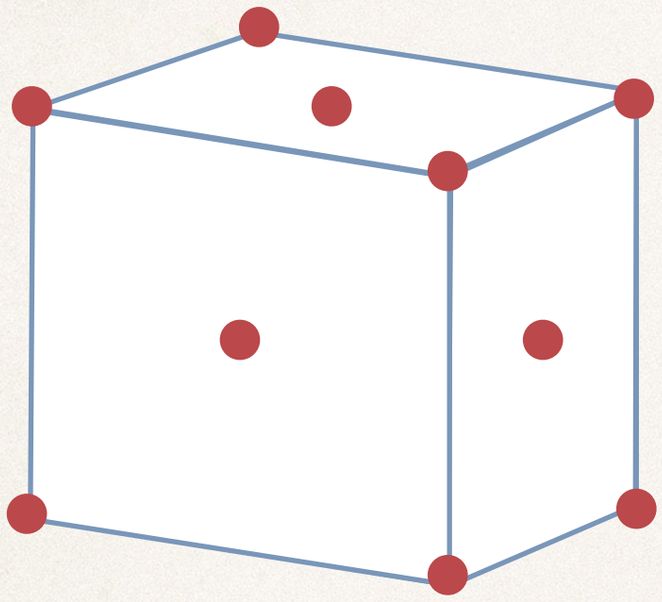
+

hkl: even for all and

$h+k+l \neq 4n$

C. Kittle, *Introduction of Solid State Physics*, (1976), p.66

FCC



$$(0,\ 0,\ 0)$$

$$\left(\frac{1}{2},\ \frac{1}{2},\ 0\right)$$

$$\left(\frac{1}{2},\ 0,\ \frac{1}{2}\right)$$

$$\left(0,\ \frac{1}{2},\ \frac{1}{2}\right)$$

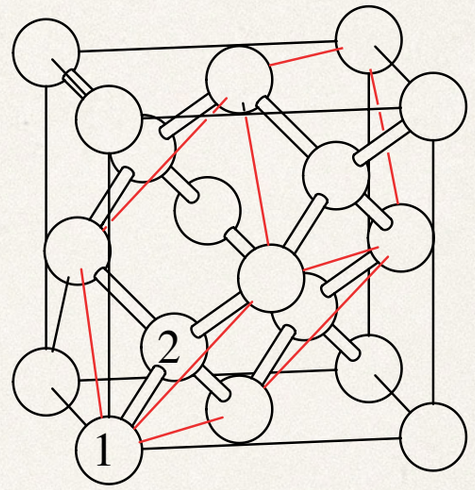
$$\begin{aligned} S(\mathbf{K}) &= \sum_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} \\ &= \sum_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} \left(1 + e^{-i\frac{1}{2}\mathbf{K}\cdot(110)} + e^{-i\frac{1}{2}\mathbf{K}\cdot(101)} + e^{-i\frac{1}{2}\mathbf{K}\cdot(011)}\right) \\ &= \sum_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} \left(1 + e^{-i\frac{1}{2}(h+k)} + e^{-i\frac{1}{2}(h+l)} + e^{-i\frac{1}{2}(k+l)}\right) \end{aligned}$$

Examples of free-electron bands

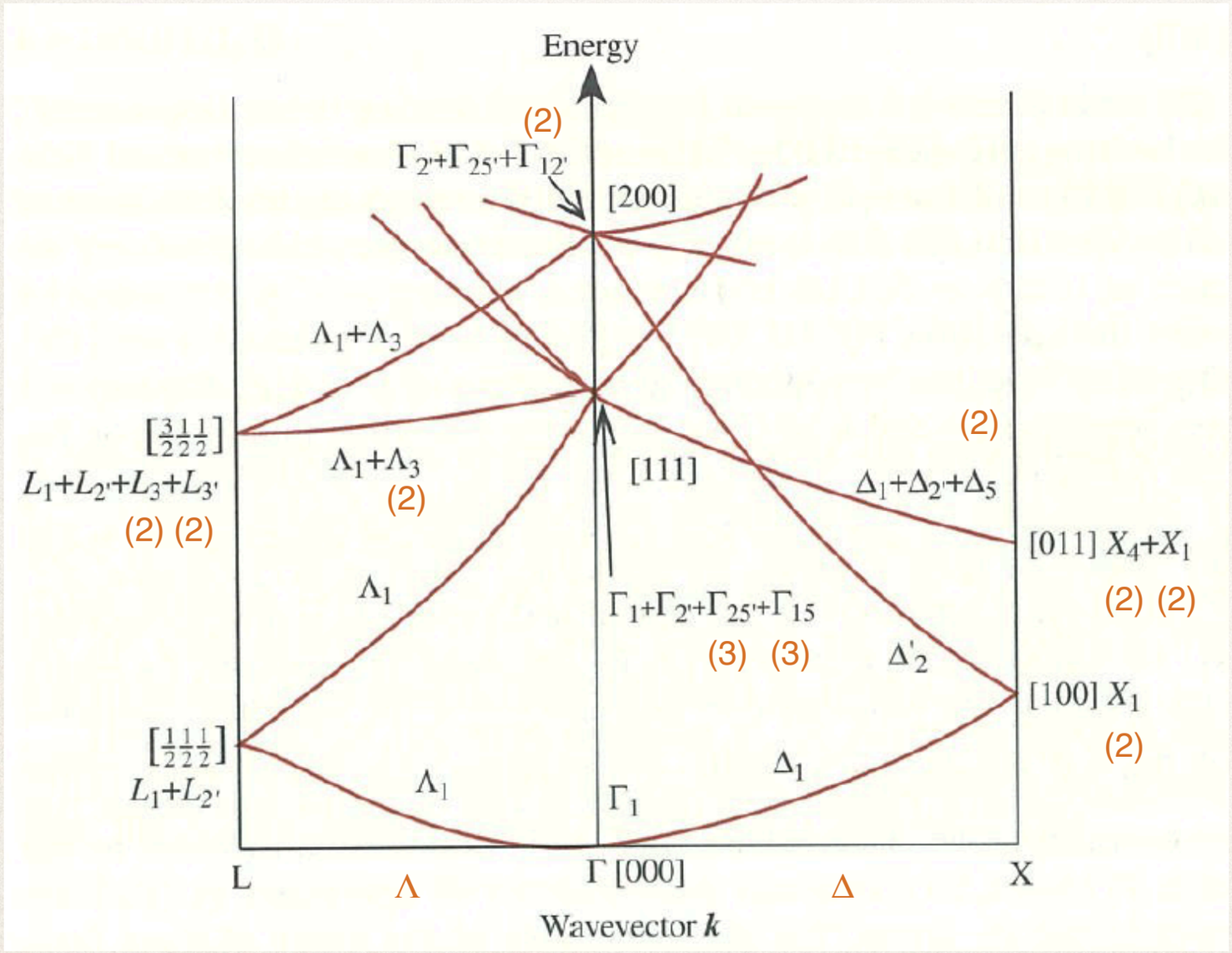
Diamond structure

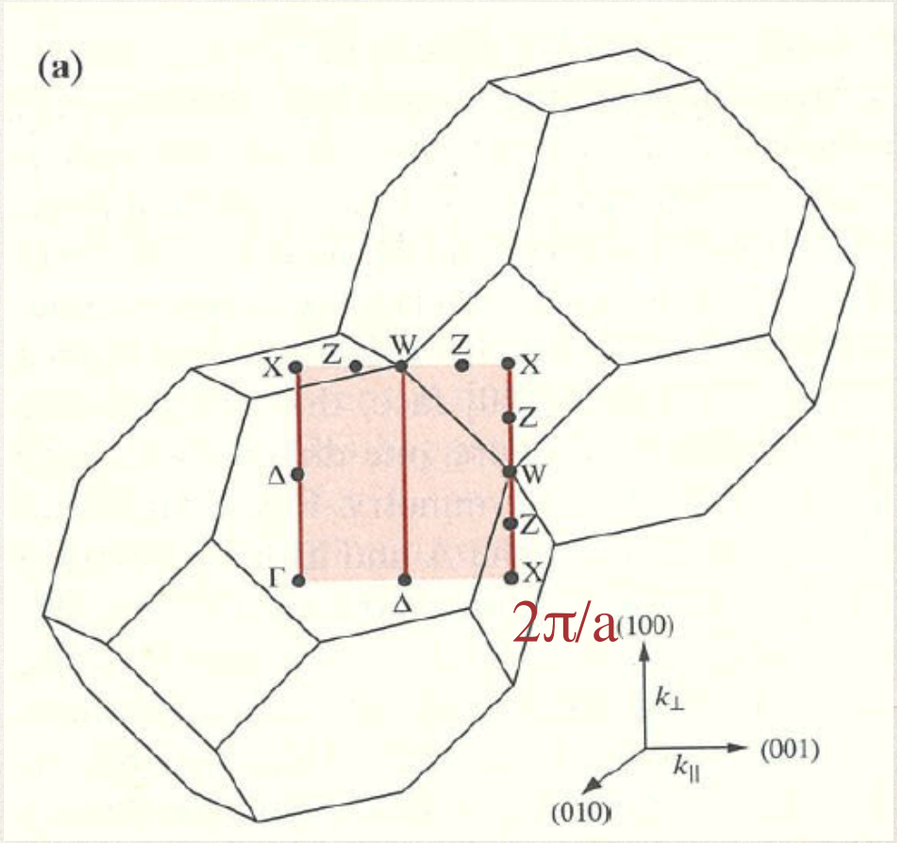
2 at/cell

8 el/cell



Si





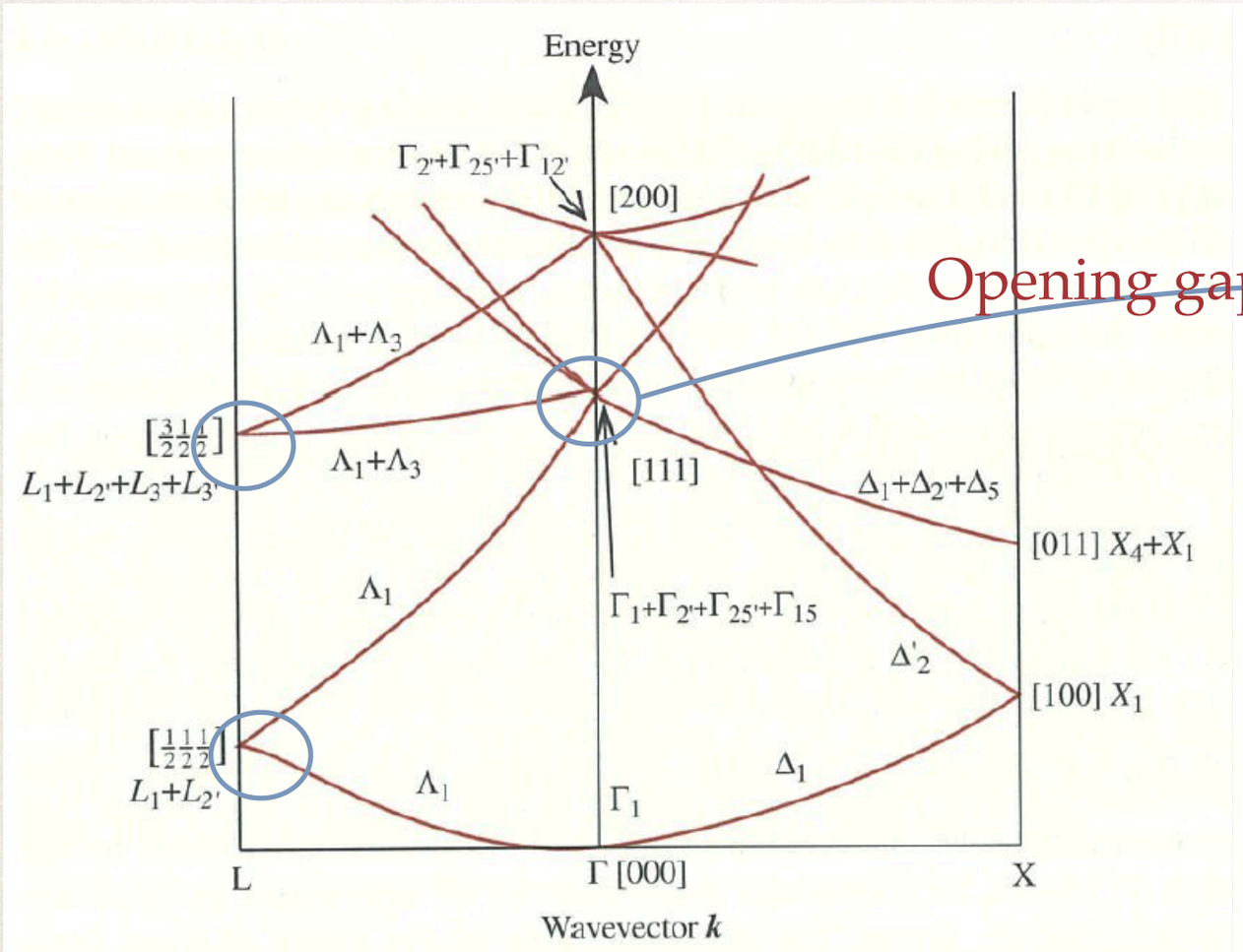
Yu & Cardona, Fundamentals of Semiconductor Physics (*FS*), p. 53

Comparison of free-electron band with the real band

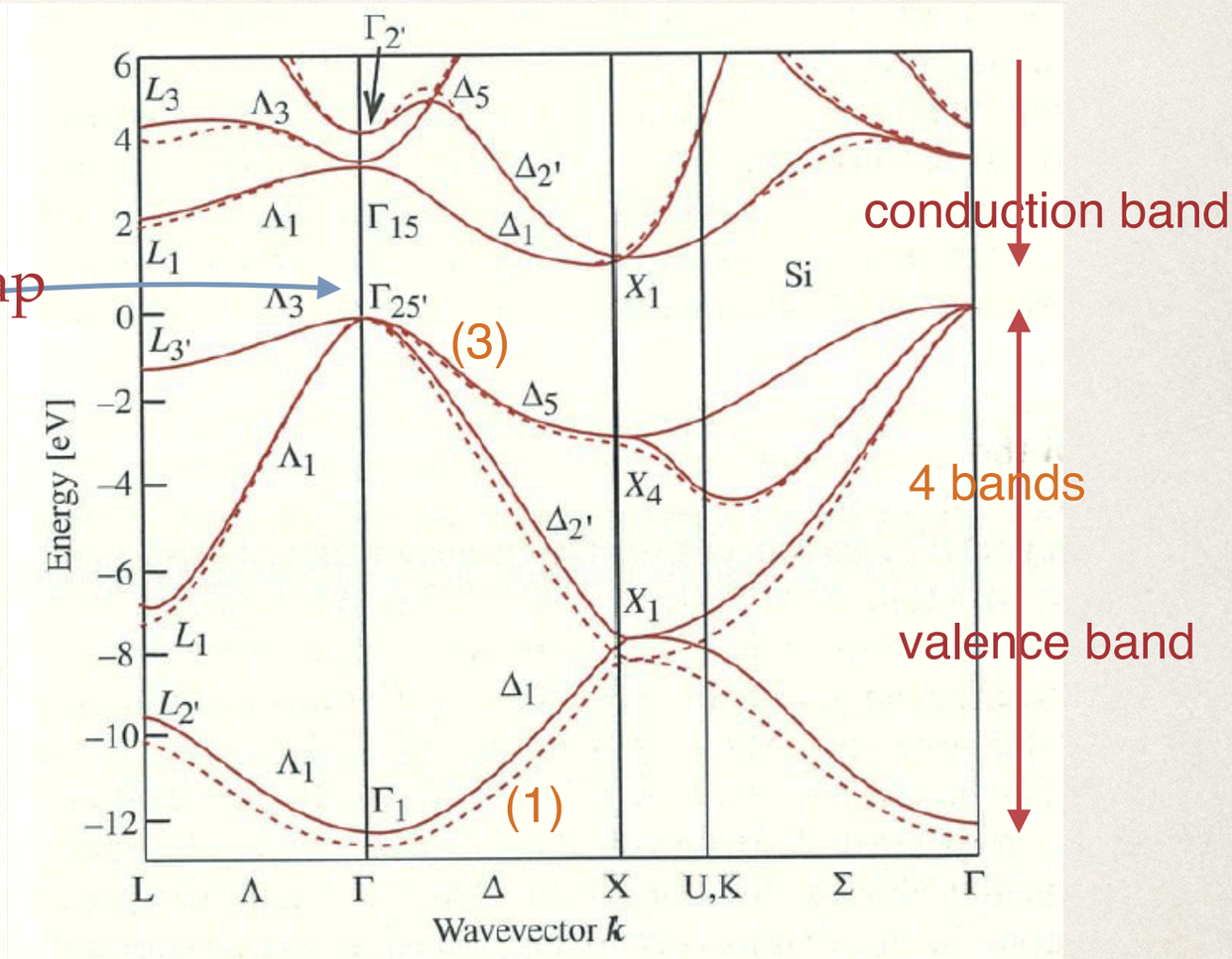
Bragg reflection and band gap

Si crystal

$N_{el} = 8$



Opening gap



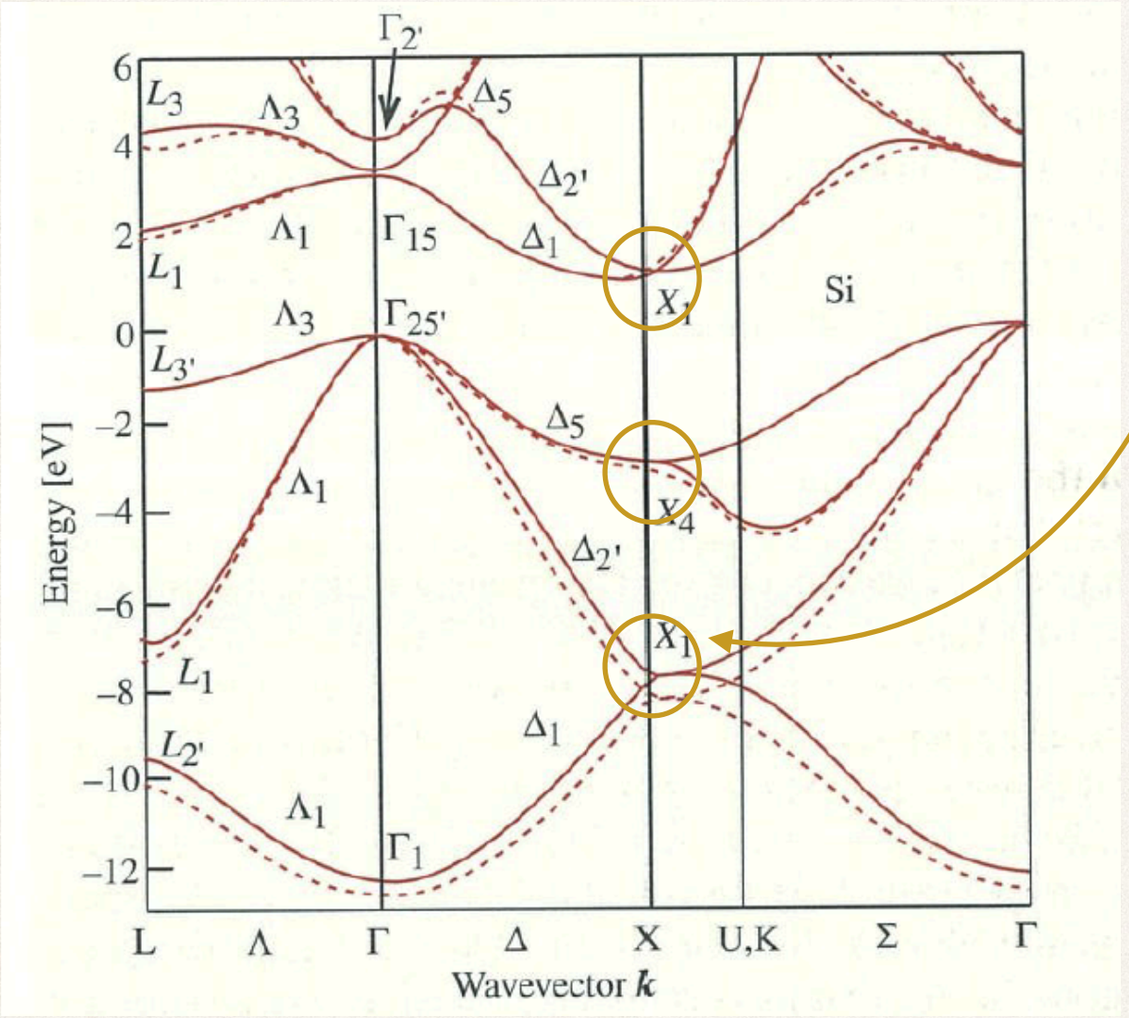
conduction band

4 bands

valence band

Yu & Cardona, *FS*, p.53

Symmetry consequence



Yu & Cardona, *FS*, p.53

Why not splitting?

at $\mathbf{k} = X$ $\quad \frac{2\pi}{a}(1,0,0)$

Bragg reflection would be expected by

$$\mathbf{K} = (2,0,0)$$

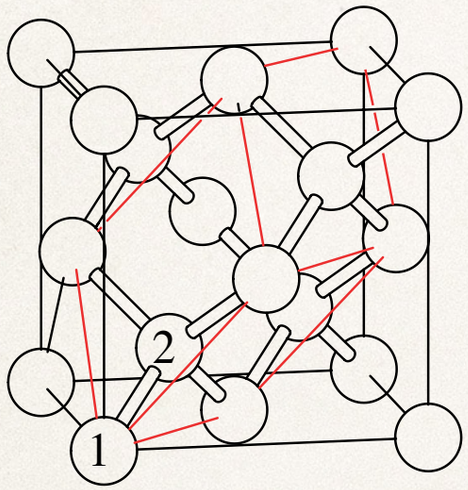
But for the diamond structure

$$V(2,0,0) = 0$$

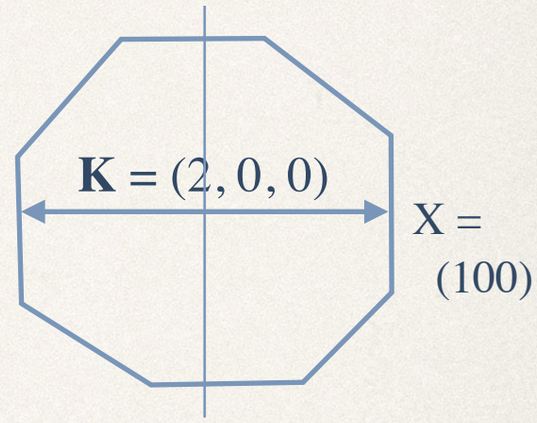
No reflection!

Exercise 1

For the diamond structure, show the crystal potential $V(K) = 0$ at K=(2, 0, 0).



Hint: show $S(K) = 0$



2 atom/primitive unit cell

1: $(0, 0, 0)$

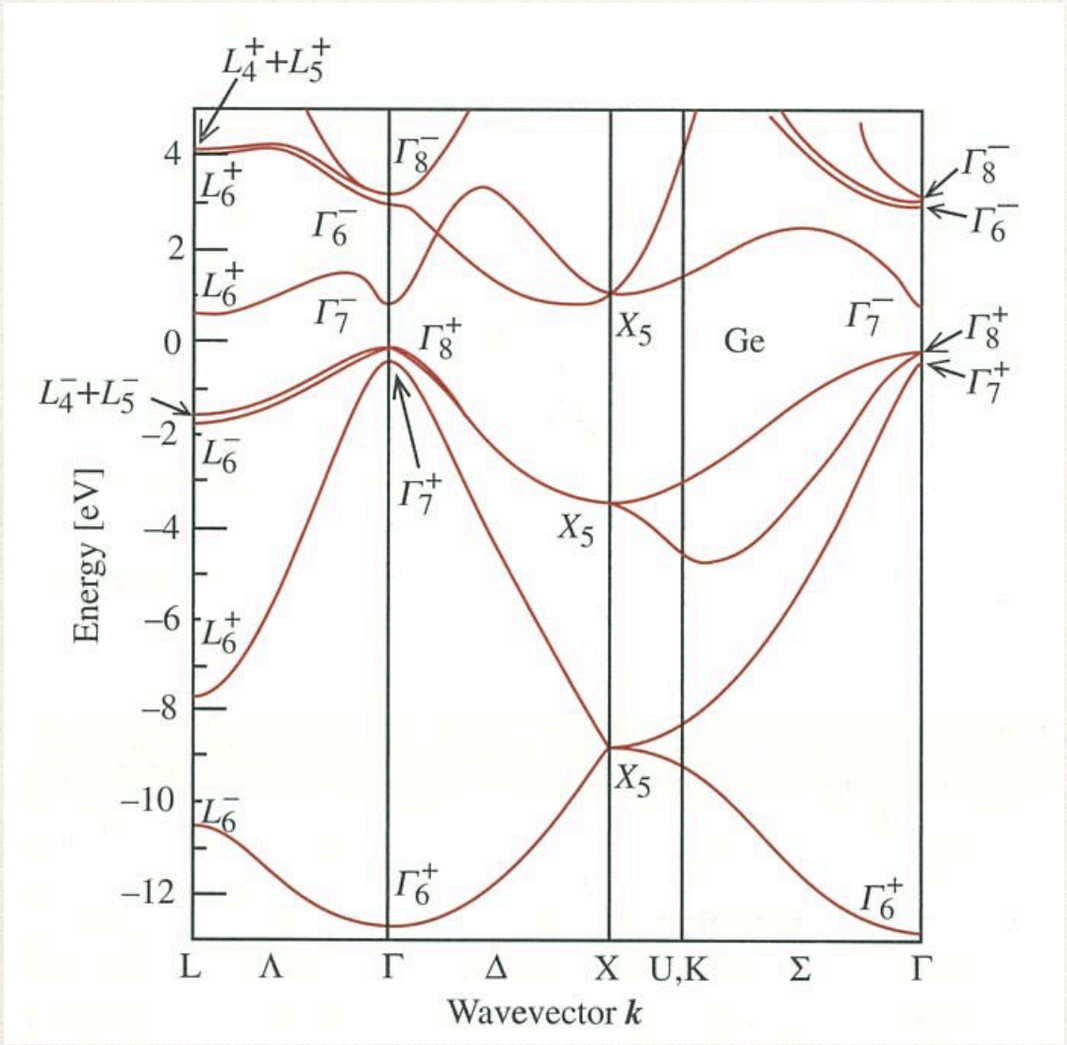
2: $\frac{1}{4}(1, 1, 1)$

$$S(\mathbf{K}) = \sum_{\mathbf{R}} e^{-i\mathbf{K}\cdot\mathbf{R}} = \sum_{\mathbf{R}} \sum_{j} e^{-i\mathbf{K}\cdot\mathbf{d}_j}$$

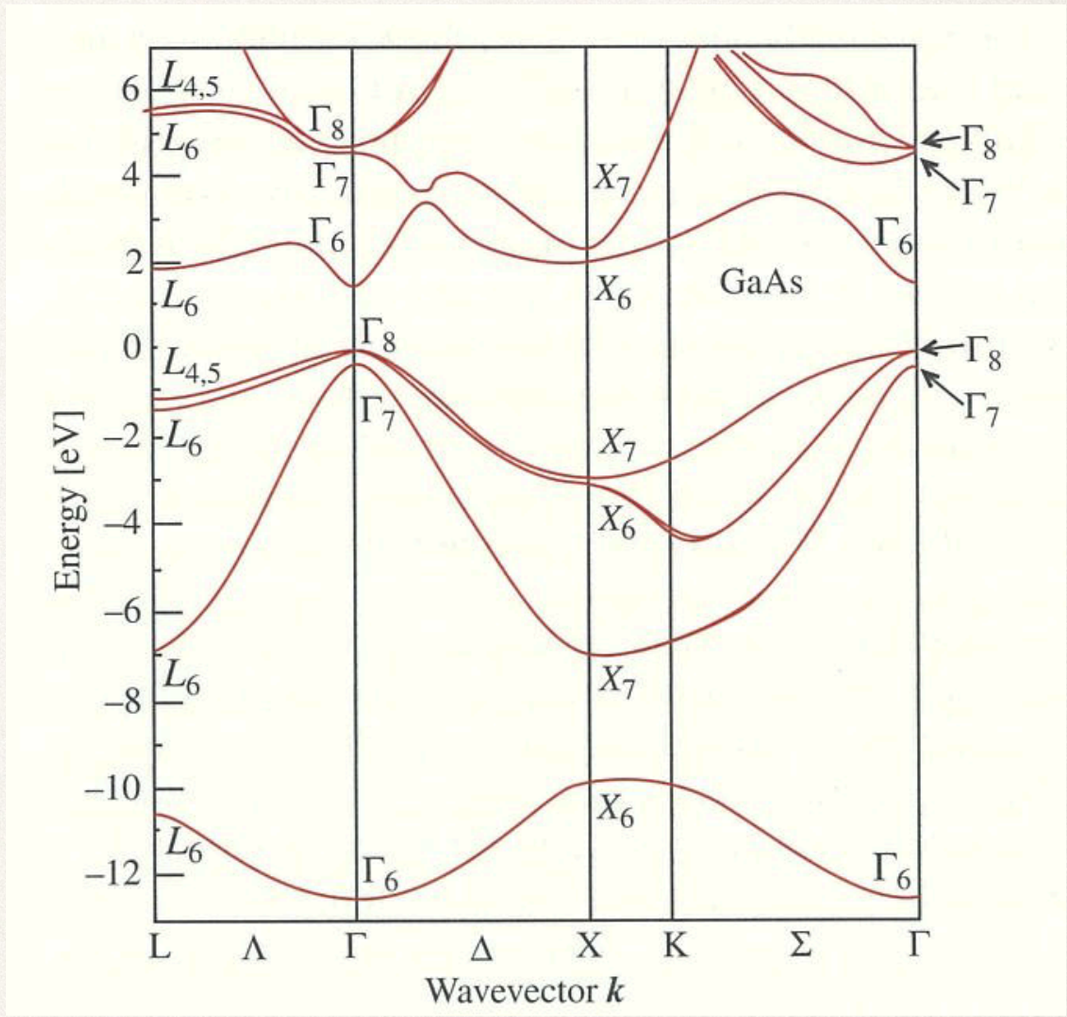
j	1	2	
$\mathbf{K}\cdot\mathbf{d}_j$	0	π	$S(\mathbf{K})$
$e^{-i\mathbf{K}\cdot\mathbf{d}_j}$	1	-1	0

Energy band with spin freedom

Ge



GaAs



Yu & Cardona, *FS*, p.64

3.3 Band theory - 2

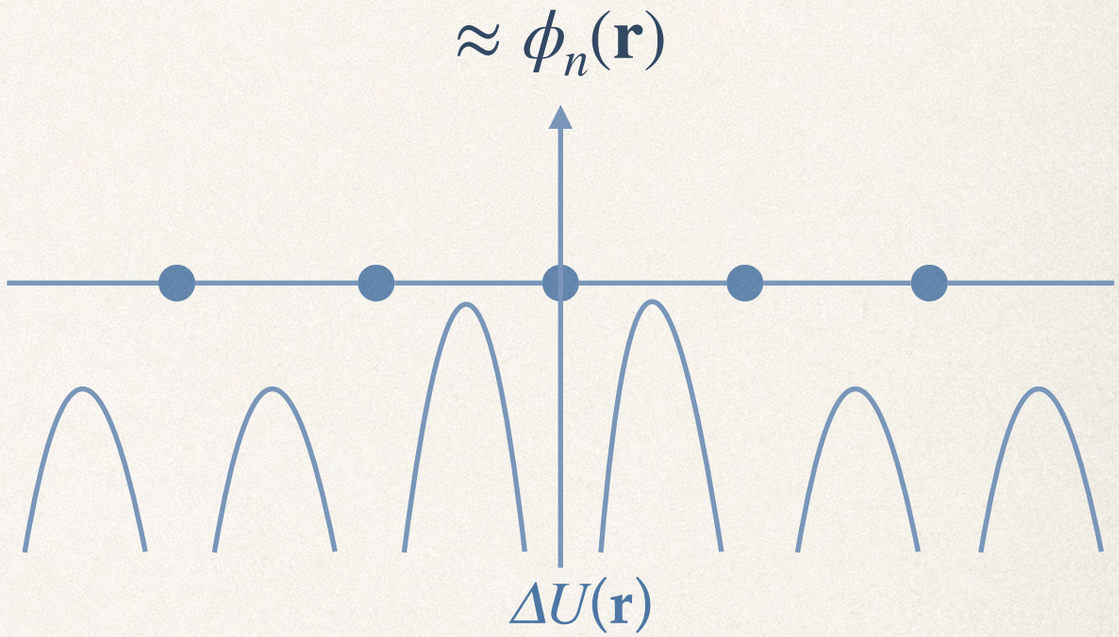
Tight-binding approximation

Atomic Orbitals

Atomic orbitals

$$H_{\text{at}}\phi_n(\mathbf{r}) = E_n\phi_n(\mathbf{r})$$

$$H_{\text{at}} = -\frac{\hbar^2}{2m}\nabla^2 + U_{\text{at}}(\mathbf{r})$$



Crystal potential

$$V(\mathbf{r}) = U_{\text{at}}(\mathbf{r}) + \Delta U(\mathbf{r})$$

$$H = H_{\text{at}} + \Delta U(\mathbf{r})$$

Linear-Combination-Atomic-Orbitals

(LCAO)

$$\varphi_n(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r}-\mathbf{R})$$

atomic orbitals

Bloch condition $\quad T(\mathbf{R}')\varphi_n(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi_n(\mathbf{r}-(\mathbf{R}-\mathbf{R}'))$ $\qquad \mathbf{R}-\mathbf{R}'=\mathbf{R}''$

$$= \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot(\mathbf{R}''+\mathbf{R}')} \phi_n(\mathbf{r}-\mathbf{R}'')$$

$$= e^{i\mathbf{k}\cdot\mathbf{R}'} \sum_{\mathbf{R}''} e^{i\mathbf{k}\cdot\mathbf{R}''} \phi_n(\mathbf{r}-\mathbf{R}'') = e^{i\mathbf{k}\cdot\mathbf{R}'} \varphi_n(\mathbf{r})$$

$$\psi(\mathbf{r}) = \sum_n b_n \varphi_n(\mathbf{r})$$

$$H\psi(\mathbf{r}) = (H_{\text{at}} + \Delta U(\mathbf{r}))\psi(\mathbf{r}) = \varepsilon(\mathbf{k})\psi(\mathbf{r})$$

$$\int \phi_m^*(\mathbf{r}) H_{\text{at}} \psi(\mathbf{r}) d\mathbf{r} =$$

$$\int (H_{\text{at}}\phi_m(\mathbf{r}))^* \psi(\mathbf{r}) d\mathbf{r} = E_m \int \phi_m^*(\mathbf{r})\psi(\mathbf{r}) d\mathbf{r}$$

$$\int d\mathbf{r}\phi_m^*(\mathbf{r}) \times$$

$$(\varepsilon(\mathbf{k}) - E_m) \int \phi_m^*(\mathbf{r})\psi(\mathbf{r}) d\mathbf{r} - \int \phi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = 0$$

$$\int \phi_m^*(\mathbf{r})\phi_n(\mathbf{r})d\mathbf{r} = \delta_{mn}$$ Ortho-normal conditions

$$(\varepsilon(\mathbf{k}) - E_m)b_m + (\varepsilon(\mathbf{k}) - E_m)\sum_n \left(\sum_{\mathbf{R}\neq 0} \int \phi_m^*(\mathbf{r})\phi_n(\mathbf{r}-\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}d\mathbf{r} \right) b_n =$$

$$+\sum_n \left(\int \phi_m^*(\mathbf{r})\Delta U(\mathbf{r})\phi_n(\mathbf{r})d\mathbf{r} \right) b_n \quad + \sum_n \left(\sum_{\mathbf{R}\neq 0} \int \phi_m^*(\mathbf{r})\Delta U(\mathbf{r})\phi_n(\mathbf{r}-\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}d\mathbf{r} \right) b_n$$

Matrix representation $\mathbf{b} = \{b_n\}$

(m, n) component

$$(\varepsilon(\mathbf{k}) - E_m)S_{m,n} \qquad H'_{m,n}(\mathbf{k}) = \sum_{\mathbf{R}} \int \phi_m^*(\mathbf{r})\Delta U(\mathbf{r})\phi_n(\mathbf{r}-\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}d\mathbf{r}$$

Overlap integral $S_{m,n}(\mathbf{k},\mathbf{R}) = \int \phi_m^*(\mathbf{r})\phi_n(\mathbf{r}-\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}d\mathbf{r}$

$$S_{m,n}(\mathbf{k}) = \sum_{\mathbf{R}} S_{m,n}(\mathbf{k},\mathbf{R})$$

$$\varepsilon(\mathbf{k})\mathbf{S}\cdot\mathbf{b} = \mathbf{H}\cdot\mathbf{b}$$

$$H_{m,n} = E_m S_{m,n} + H'_{m,n}$$

$$\left|\varepsilon(\mathbf{k})\mathbf{S} - \mathbf{H}\right| = 0$$

Generalized secular equation ⟶ Numerically undesirable

Improvement

Orthogonalize atomic orbitals at different sites

$$\int \phi_m^*(\mathbf{r})\phi_n(\mathbf{r}-\mathbf{R})d\mathbf{r} = \delta_{mn}$$

Löwdin functions

Wannier functions

$$H'_{m,n}(\mathbf{R}) = \int \phi_m^*(\mathbf{r})\Delta U(\mathbf{r})\phi_n(\mathbf{r}-\mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}d\mathbf{r}$$

Treat as fitting parameters ⟶ Slater-Koster matrix elements

Standard secular equation

$$\left|(\varepsilon(\mathbf{k}) - E_m)\mathbf{1} - \mathbf{H}\right| = 0$$

Exercise 2: Calculated the TB band of a SC lattice in one dimension,

using only *s*-orbitals and nearest-neighbor interactions.

Ignore overlap integral.

Plot the result along the k_x line.

Interpret the band dispersion.

$$\varphi_s(\mathbf{r}) = \sum_R e^{ikR}\phi_s(\mathbf{r}-\mathbf{R})$$

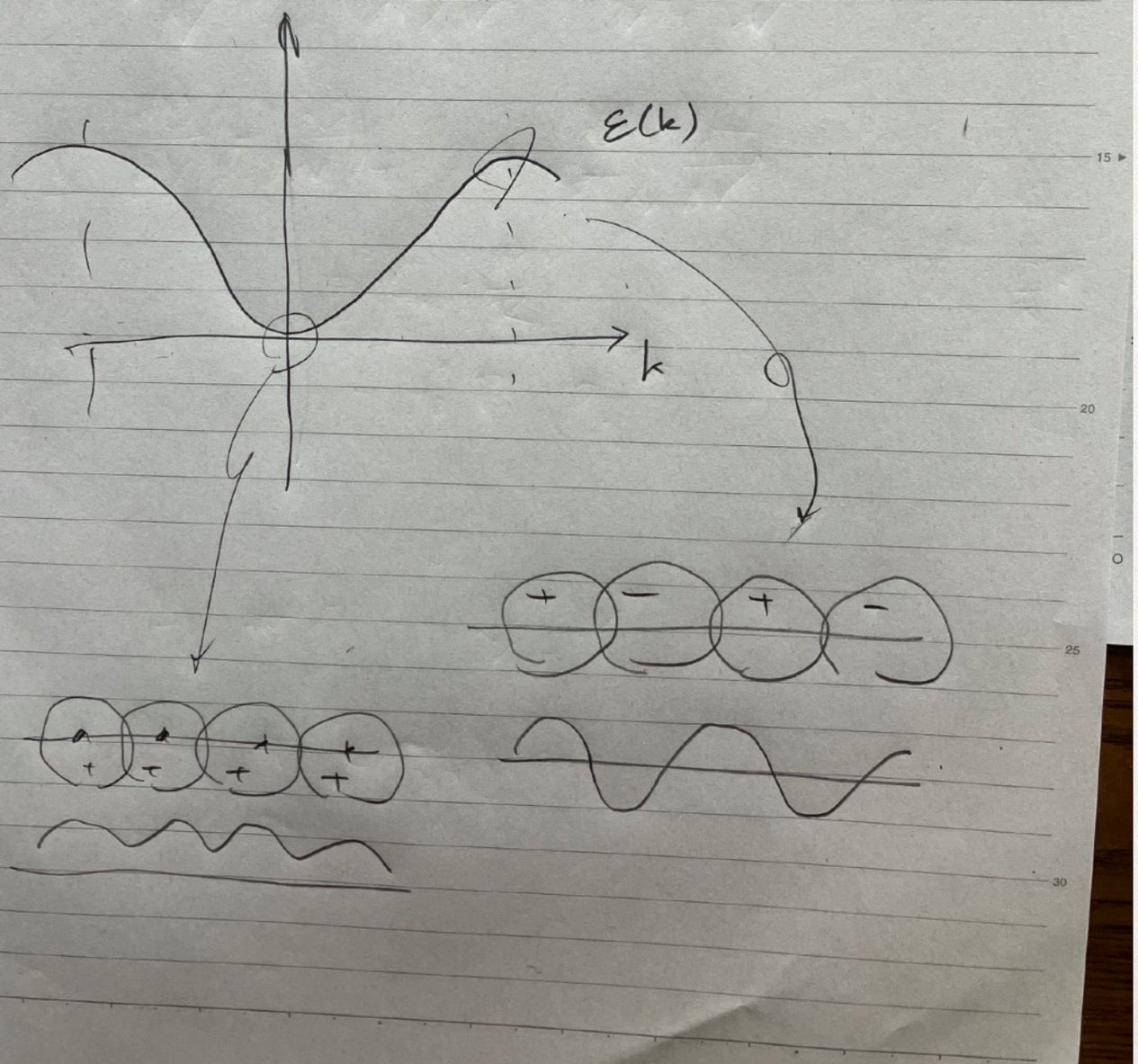
$$(\varepsilon(\mathbf{k}) - E_m)b_s = \underbrace{b_s\left(\int \phi_m^*(\mathbf{r})\Delta U(\mathbf{r})\phi_n(\mathbf{r})d\mathbf{r}\right)}_{\alpha} + \underbrace{b_n\left((e^{ika}+e^{-ika})\right.}_{2\cos(ka)}\underbrace{\left.\int \phi_m^*(\mathbf{r})\Delta U(\mathbf{r})\phi_n(\mathbf{r}-\mathbf{R})d\mathbf{r}\right)}_{\gamma}$$

$$\varepsilon(\mathbf{k}) = E_m + \alpha + 2\gamma\cos(ka)$$

$$\varepsilon(k) = \underbrace{E_s + \alpha}_{\text{const}} + 2\gamma \cos(ka)$$

$$\gamma = \int \phi^*(r)\, \Delta U(r)\, \phi(r-a)\, dr$$

< 0 attractive potential.



KOKUYO

Chemical interpretation

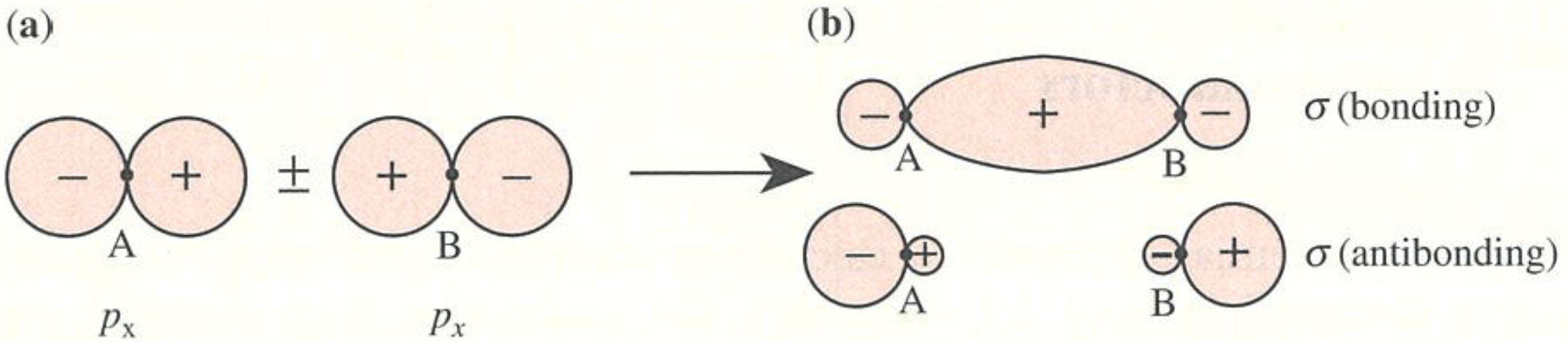


Fig. 2.18a,b. Overlap of two p_x orbitals along the x axis to form bonding and antibonding σ orbitals

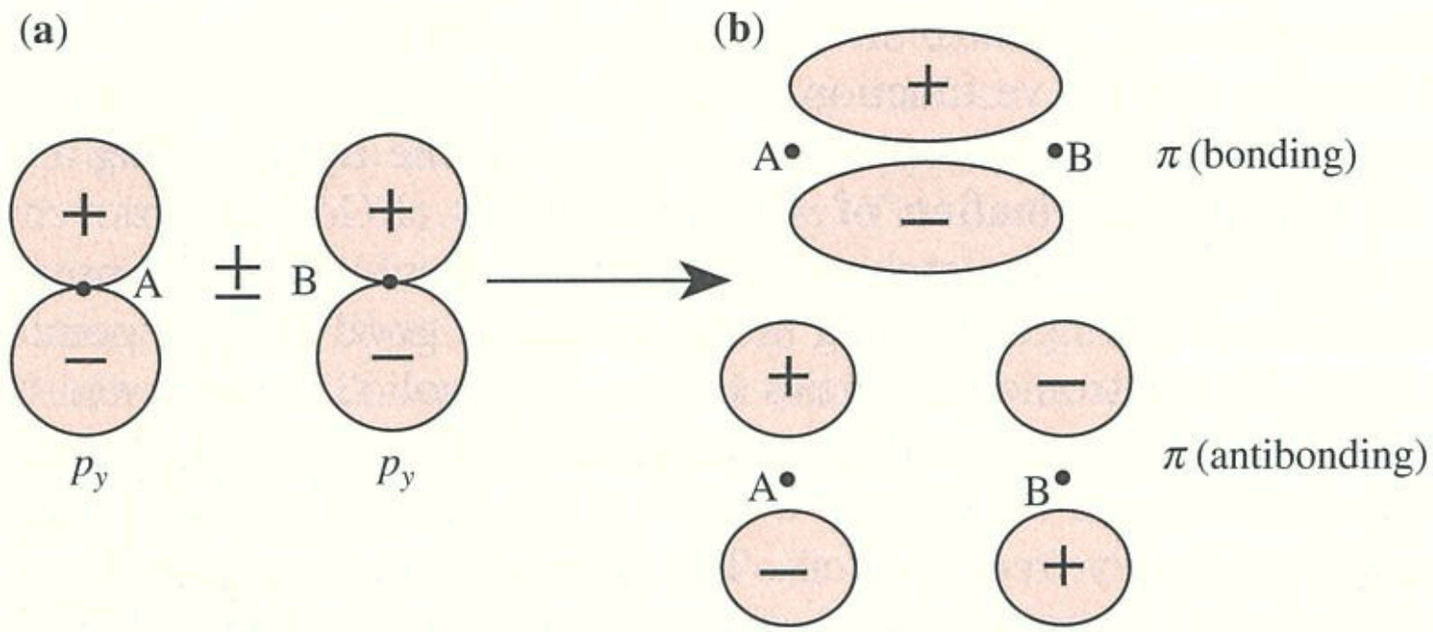
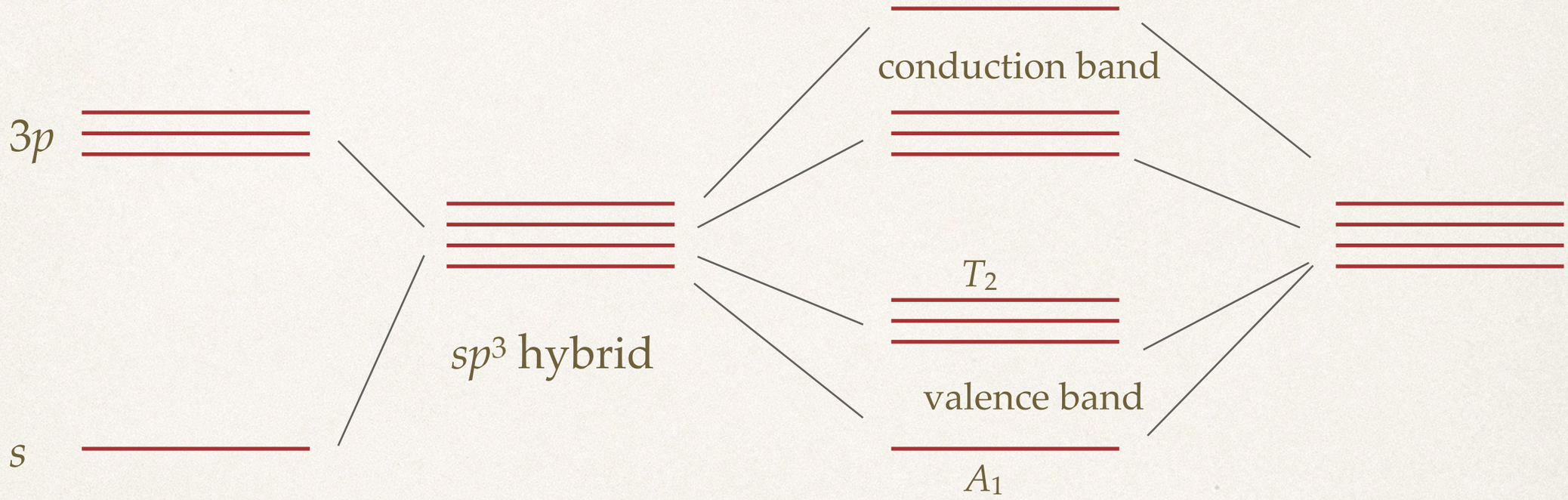


Fig. 2.19a,b. Overlap of two p_y orbitals to form bonding and antibonding π orbitals

Chemical bond scheme



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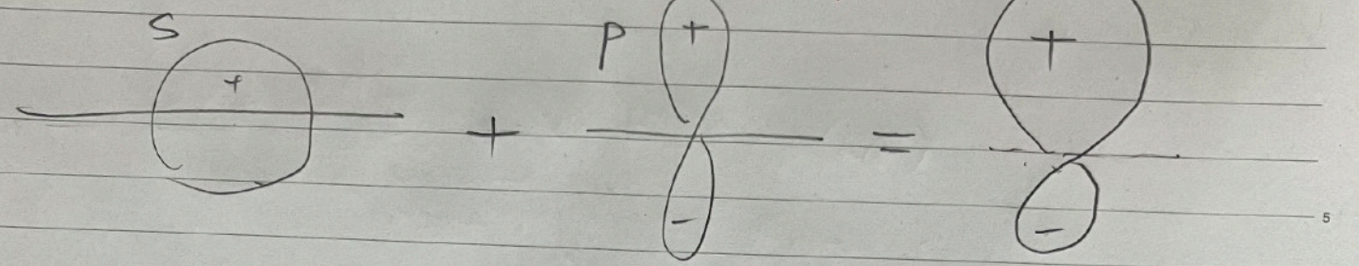
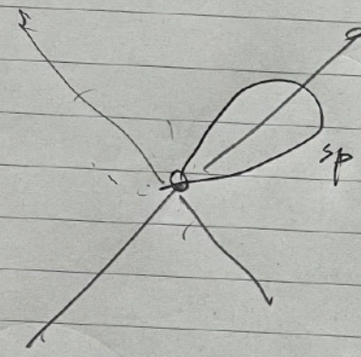
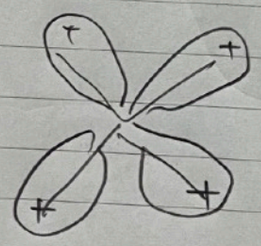


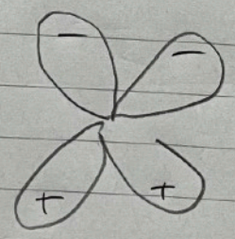
sp orbital.



four-coordinated bond.



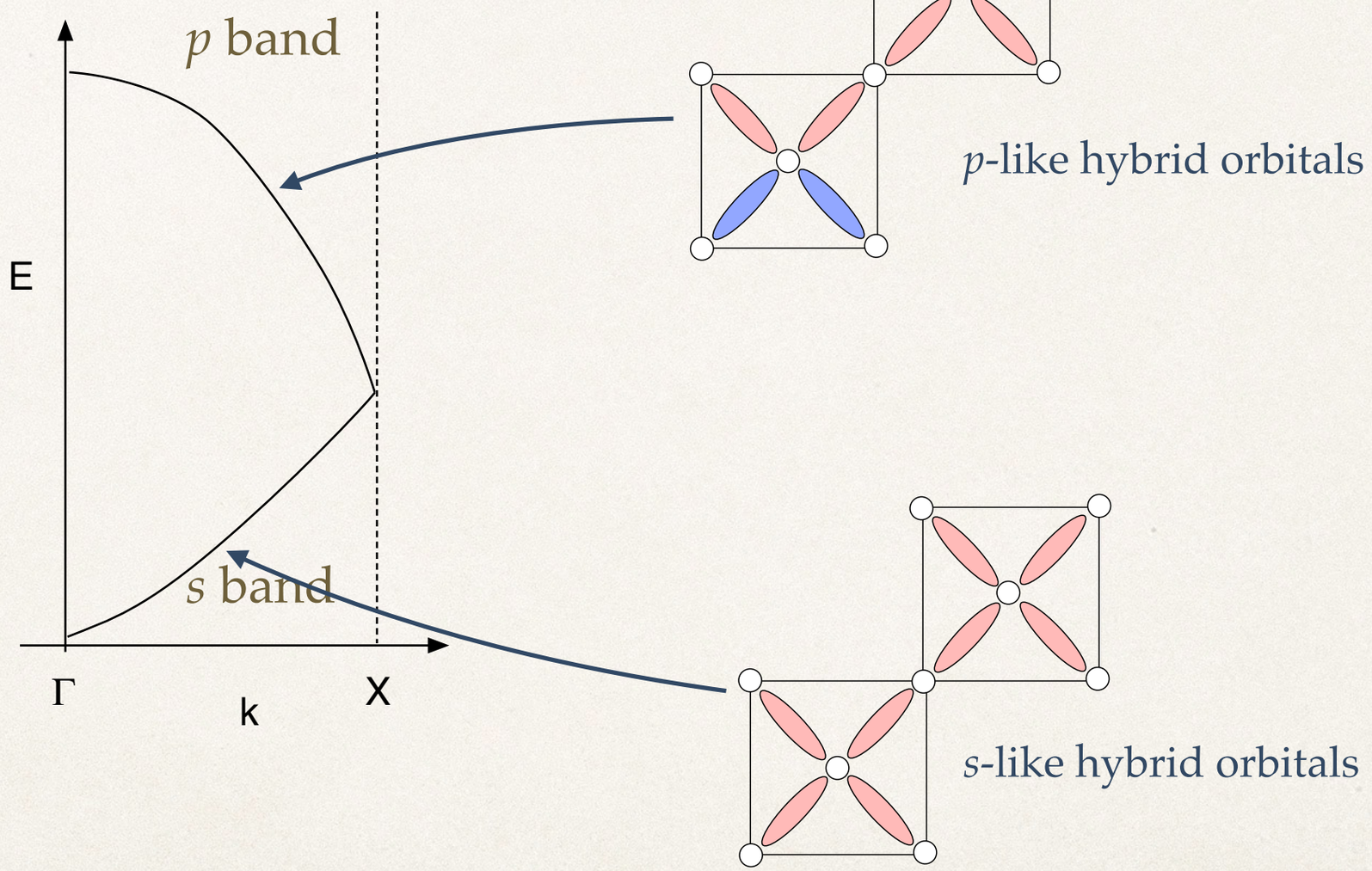
s band



p band

Correspondence to the band structure

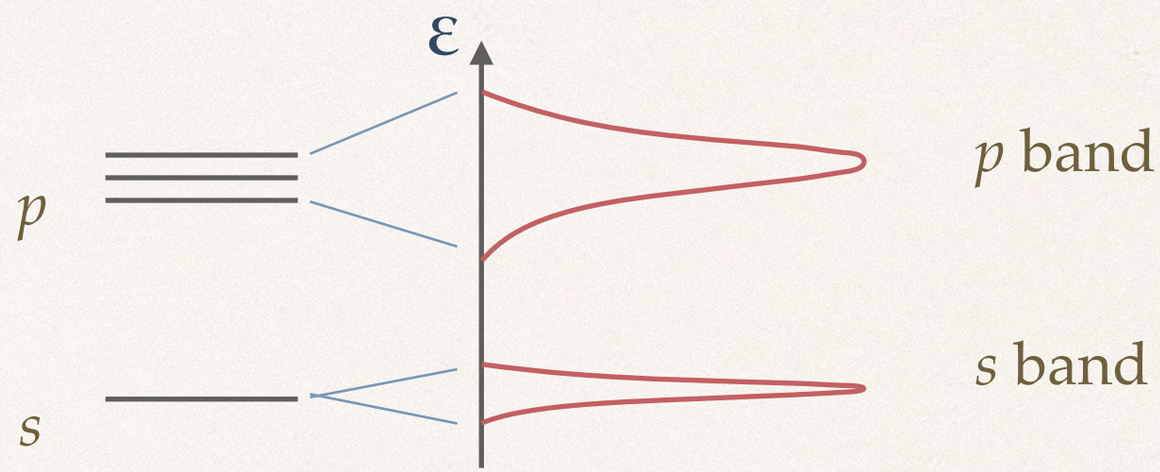
sp^3 hybrid orbitals



Blocks of bands

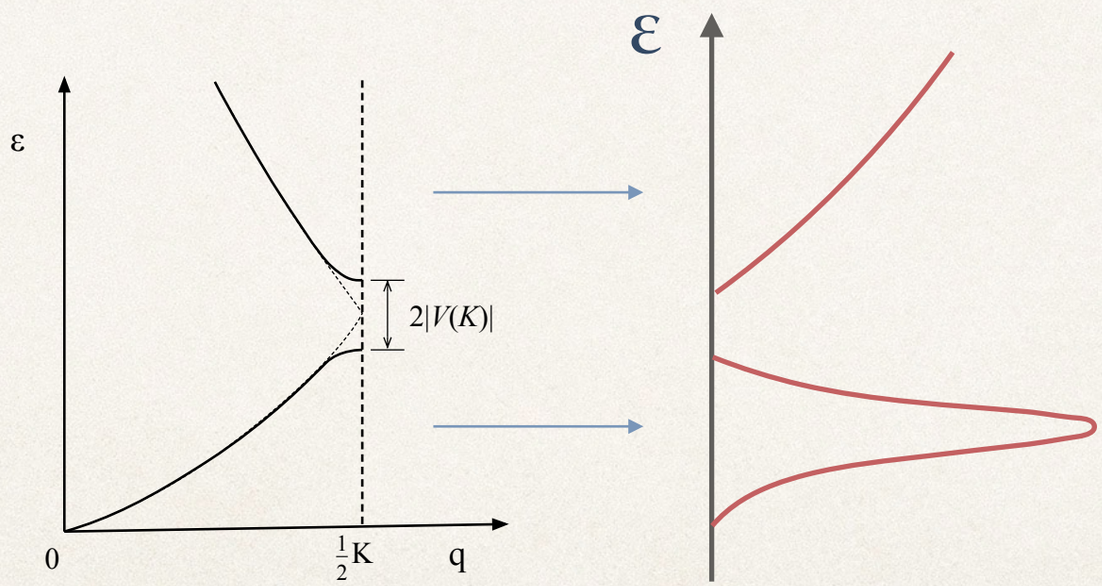
Tight-binding model

DOS (Density Of States)



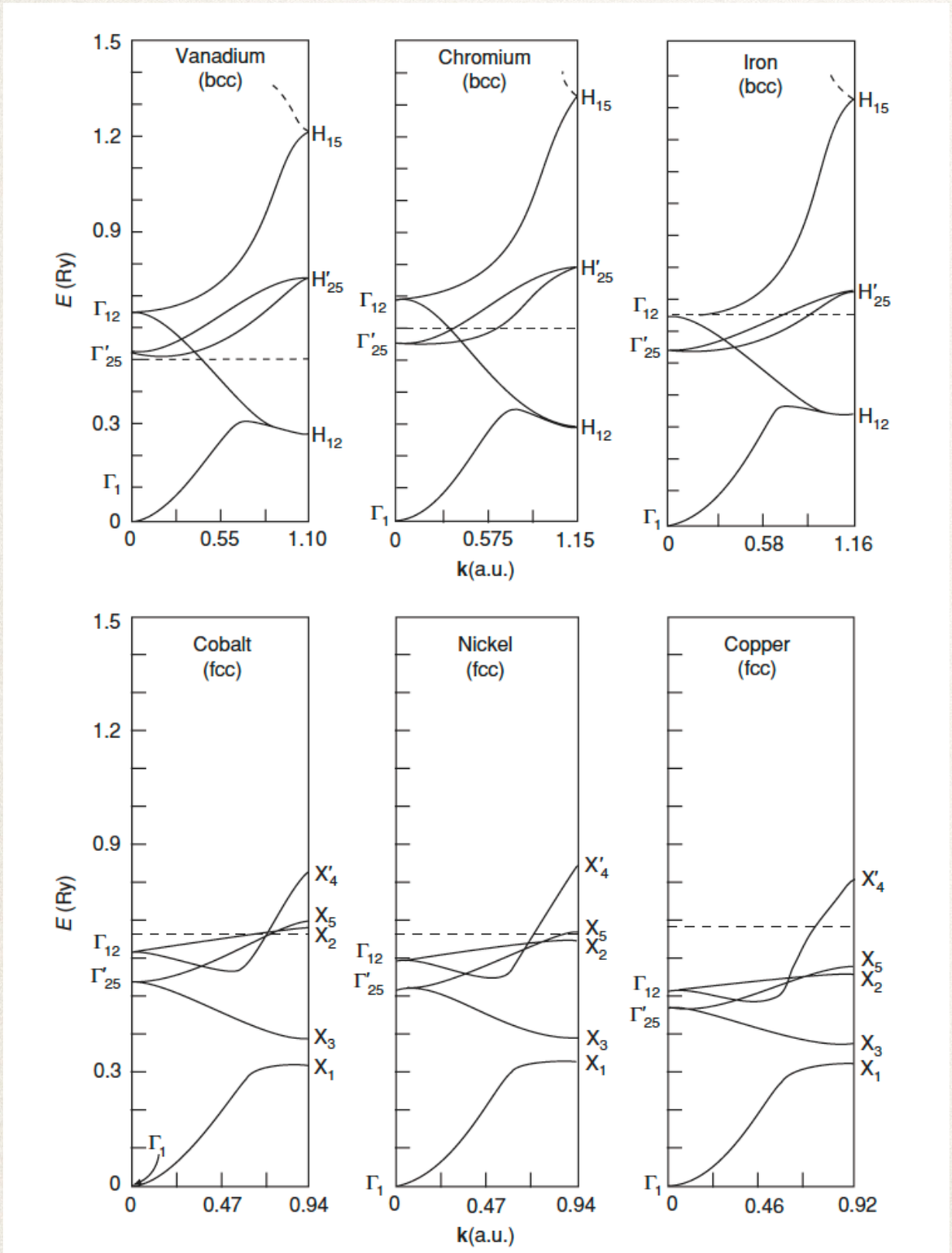
Atomic orbital characters

Free-electron model



Opening gap creates distinct bands

d bands of transition metals



$s + 5d$ bands

R. M. Martin, *Electronic Structure: Basic theory and practical methods*, Cambridge (2004), p. 321.

3.4 Electron dynamics

Semiclassial model

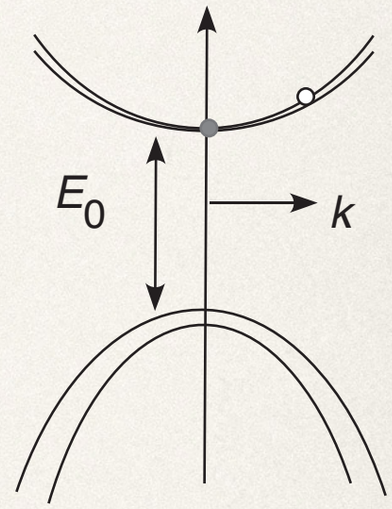
Effective mass

The k•p method for nondegenerate bands

$$\left[\frac{p^2}{2m}+\frac{\hbar\mathbf{k}\cdot\mathbf{p}}{m}+\frac{\hbar^2k^2}{2m}+U(r)\right]u_{n\mathbf{k}}(\mathbf{r})=E_{n\mathbf{k}}u_{n\mathbf{k}}(\mathbf{r})$$

$$\varphi_{n\mathbf{k}}(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})u_{n\mathbf{k}}(\mathbf{r})$$

Bloch function



Second-order perturbation

$$E_{n\mathbf{k}}=E_{n0}+\frac{\hbar^2k^2}{2m}+\frac{\hbar^2}{m}\sum_{n'\neq n}\frac{\left|\langle u_{n0}|\mathbf{k}\cdot\mathbf{p}|u_{n'0}\rangle\right|^2}{E_{n0}-E_{n'0}}$$

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

$$\frac{1}{m_c^*}=\frac{1}{m}+\frac{2}{m^2k^2}\sum_{n'\neq n}\frac{\left|\langle u_{n0}|\mathbf{k}\cdot\mathbf{p}|u_{n'0}\rangle\right|^2}{E_{n0}-E_{n'0}}=\frac{1}{m}+\frac{2\left|\langle\Gamma_{1c}|\mathbf{k}\cdot\mathbf{p}|\Gamma_{4v}\rangle\right|^2}{m^2E_0k^2}$$

nonzero matrix elements $\langle\Gamma_{4v}|\mathbf{k}\cdot\mathbf{p}|\Gamma_{1c}\rangle$ →

$$\langle X|p_x|\Gamma_1\rangle=\langle Y|p_y|\Gamma_1\rangle=\langle Z|p_z|\Gamma_1\rangle=iP$$

$$P=\frac{2\pi\hbar}{a_0}$$

$$\frac{P^2}{m}\approx 10\ \text{eV}$$

$$\frac{m}{m_c^*}\approx 1+\frac{2P^2}{mE_0}$$

Equation of motion

Equation of motion

$$\mathbf{v}_n = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$$

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

$$\frac{\partial \varepsilon}{\partial k} = \frac{\hbar^2}{m}k = \hbar v$$

$$\hbar\dot{\mathbf{k}} = -e\left(\mathbf{E} + \frac{1}{c}\mathbf{v}\times\mathbf{B}\right)$$

Almost classical equation!

except replacing the electron mass by effective mass.

The effective mass has sign.

is the curvature of $\varepsilon(\mathbf{k})$

Effective mass (band mass)

$$\left[\mathbf{M}_n^*\right]^{-1}_{ij} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon_n(\mathbf{k})}{\partial k_i \partial k_j}$$

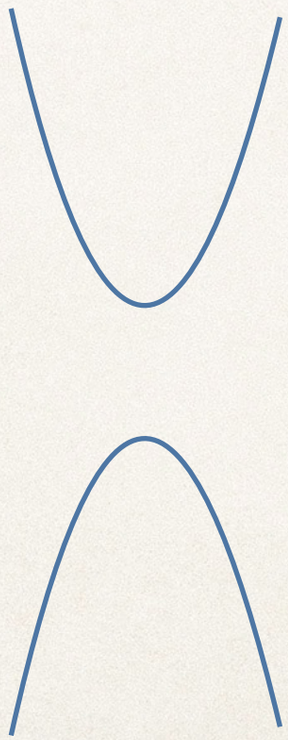
isotropic case →

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon(k)}{\partial k^2}$$

Electrons and holes

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{\partial^2 \varepsilon(k)}{\partial k^2}$$ ← Curvature of band dispersion $\varepsilon_n(\mathbf{k})$

mobility $\mu = \frac{e}{m^*}\tau$ ← scattering time



$m^* > 0$ electron

$m^* < 0$ hole

$$\frac{m}{m_c^*} \approx 1 + \frac{2P^2}{mE_0}$$

matrix element

$$\langle \Gamma_{4v} | \mathbf{k} \cdot \mathbf{p} | \Gamma_{1c} \rangle$$

direct gap

Smaller the band gap is, more faster the electron is.

	Ge	GaN	GaAs	GaSb	InP	InAs	ZnS	ZnSe	ZnTe	CdTe
E_0 [eV]	0.89	3.44	1.55	0.81	1.34	0.45	3.80	2.82	2.39	1.59
m_c^*/m (exp)	0.041	0.17	0.067	0.047	0.073	0.026	0.20	0.134	0.124	0.093
m_c^*/m ((2.44))	0.04	0.17	0.078	0.04	0.067	0.023	0.16	0.14	0.12	0.08

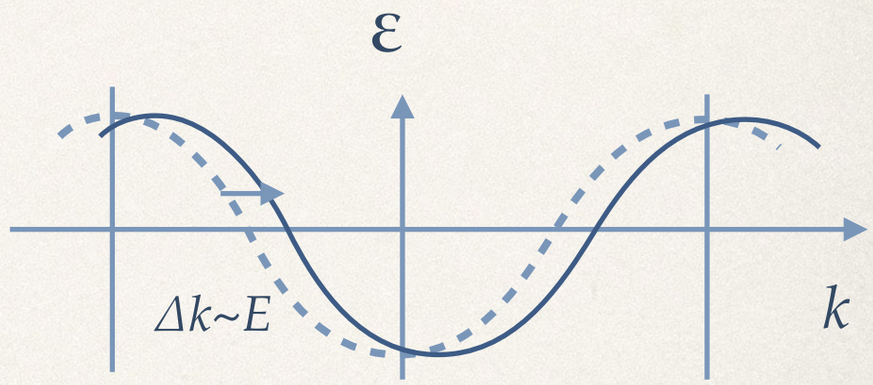
Yu & Cardona, *FS*

Electrical Conductivity

Electron current $\mathbf{j}_e = -e\int_{\text{occupied}} \frac{d\mathbf{k}}{4\pi^3}\mathbf{v}(\mathbf{k})$ $\mathbf{v}_n = \frac{1}{\hbar}\frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}$

in periodic structure

$$\int_{\text{zone}} \frac{d\mathbf{k}}{4\pi^3}\mathbf{v}(\mathbf{k}) = 0$$

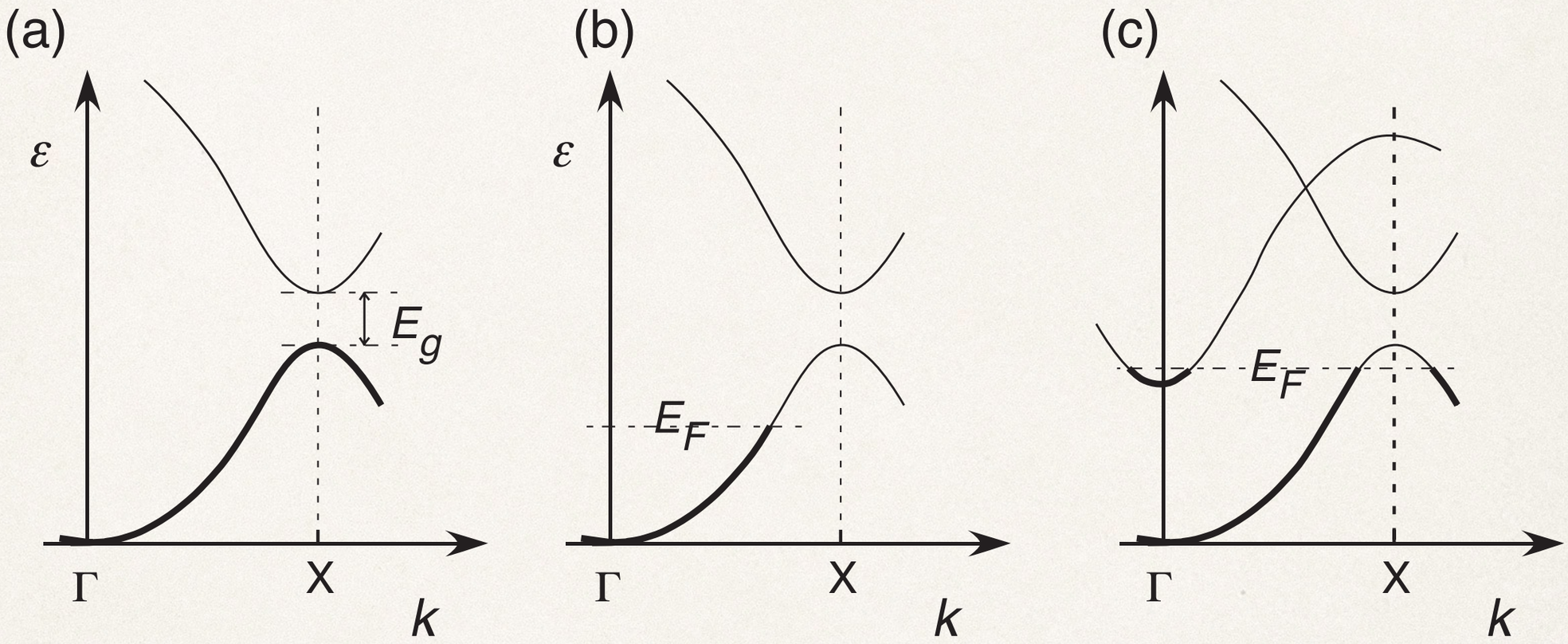


Fully-occupied band does not carry electronic current. → Insulator

Electron vs. hole

$$\int_{\text{zone}} f = \int_{\text{occupied}} f + \int_{\text{unoccupied}} f = 0 \longrightarrow \mathbf{j}_h = +e\int_{\text{unoccupied}} \frac{d\mathbf{k}}{4\pi^3}\mathbf{v}(\mathbf{k})$$

Classification of crystals



Number of electrons	even	odd	even
	Insulator	Metal	

3.5 Success of band theory

Classification of crystals

Metal and insulator

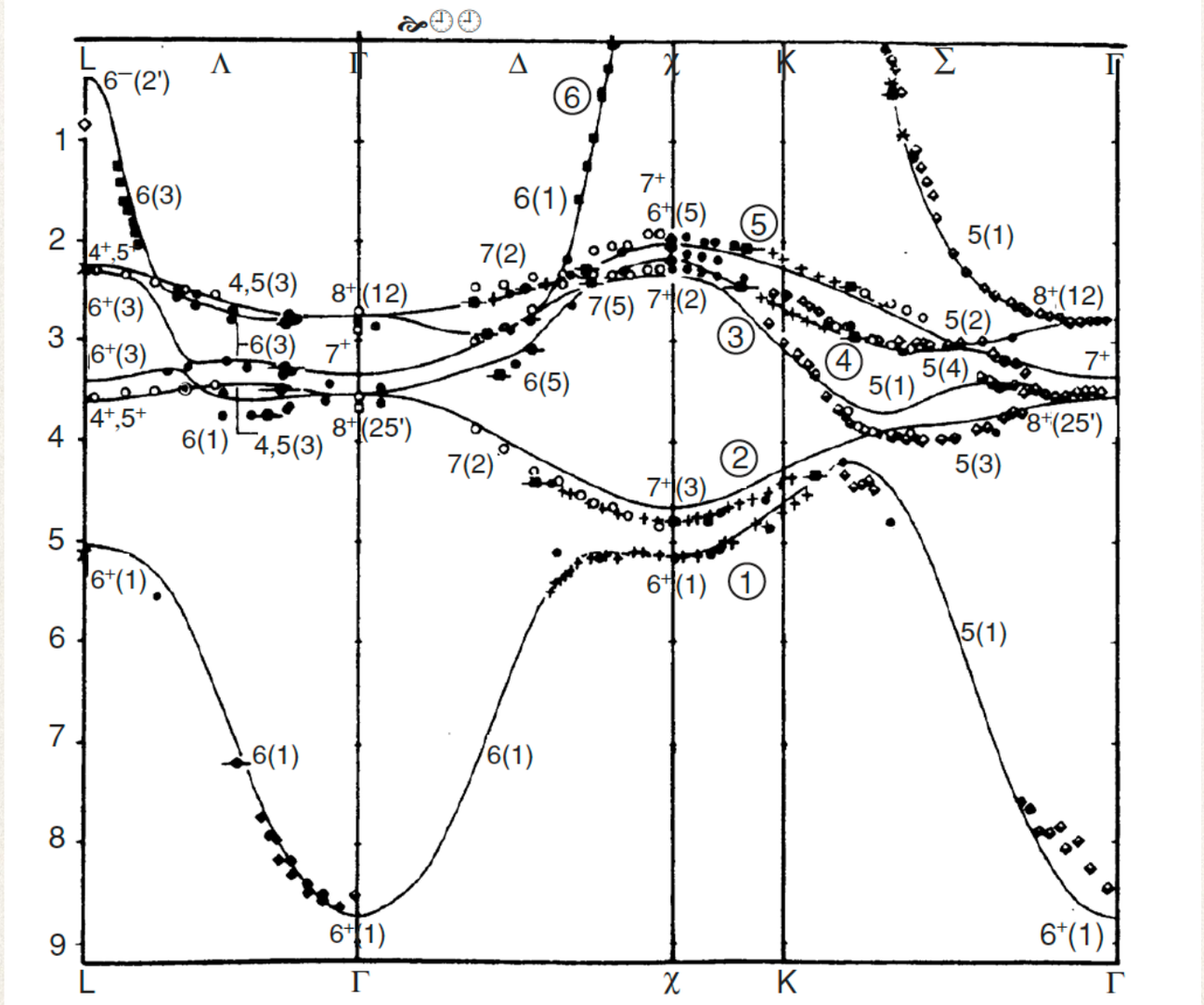
Optical properties

Conduction characteristics

Electron and hole bands

Mobility

The band structure of Cu



Calc.

The classic APW calculations using the Chodorow potential

G. A. Burdick, Phys. Rev. **128**, 138 (1963)

Exp.

angle-resolved photoemission (points)

P. Thiry, *et al.*, Phys. Rev. Lett. **43**, 82 (1979)