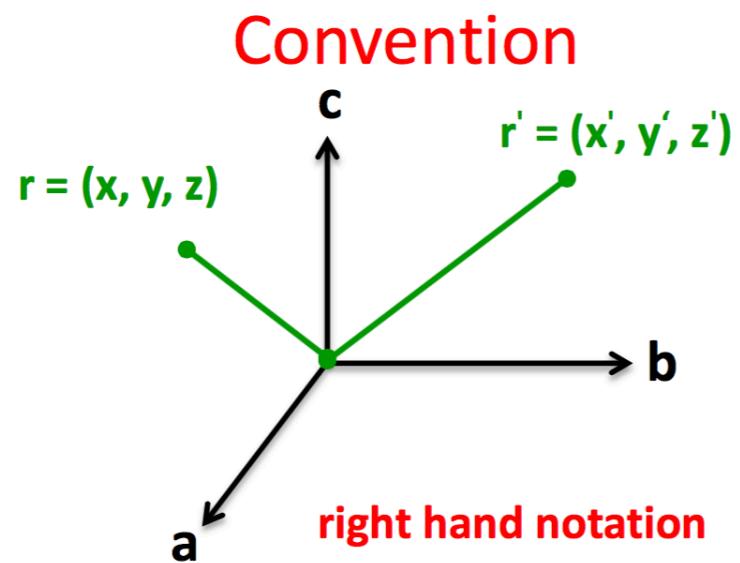


Symmetry operations: Point symmetry operations

Point symmetry operation: It is a symmetry operation specified w.r.t. to point in space which does not move during the operations.

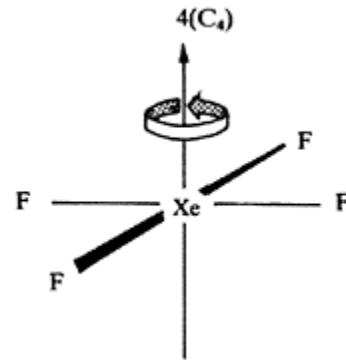
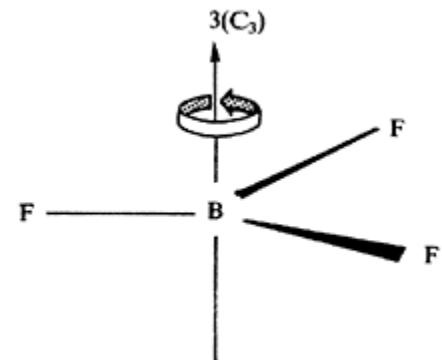
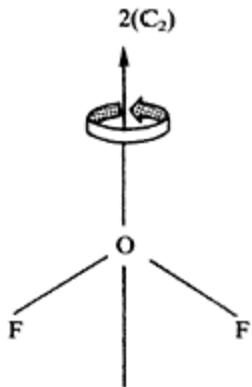
$$\mathbf{r}' = \mathbf{R} \times \mathbf{r}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$



Point symmetry operation (R)

2. Rotations (n)

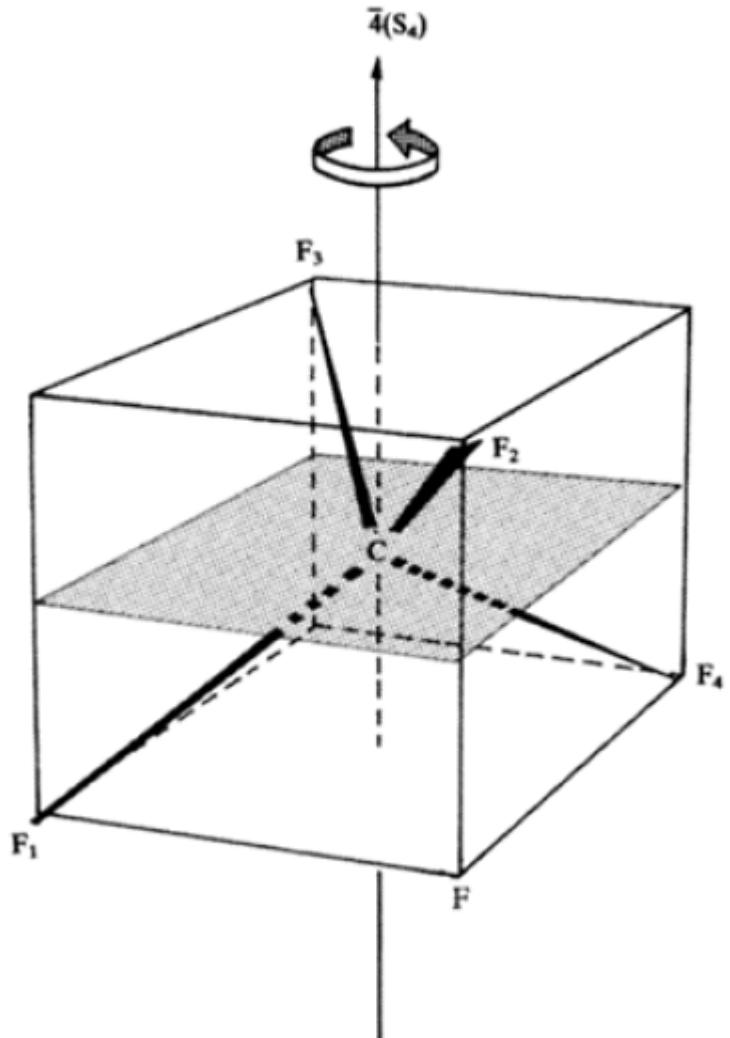


Point symmetry operation (R)

4. Rotation inversion (\bar{n})

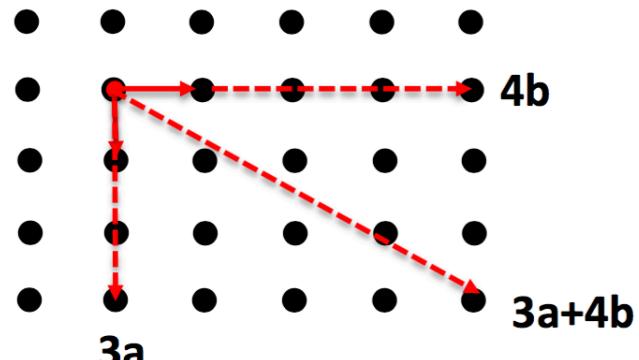
$90^\circ \quad \bar{1}$
 $F_1 \longrightarrow F \longrightarrow F_3$

Improper axis of symmetry (S_n)



Crystal symmetry symmetry operation (R)

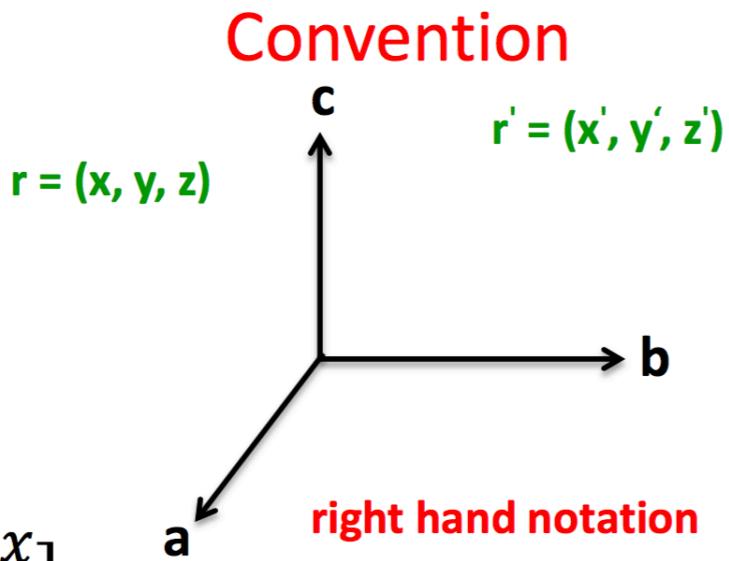
- Relationship of different point symmetries generates space symmetry
- Combing the point symmetry operations with translational symmetry



$$T_n = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

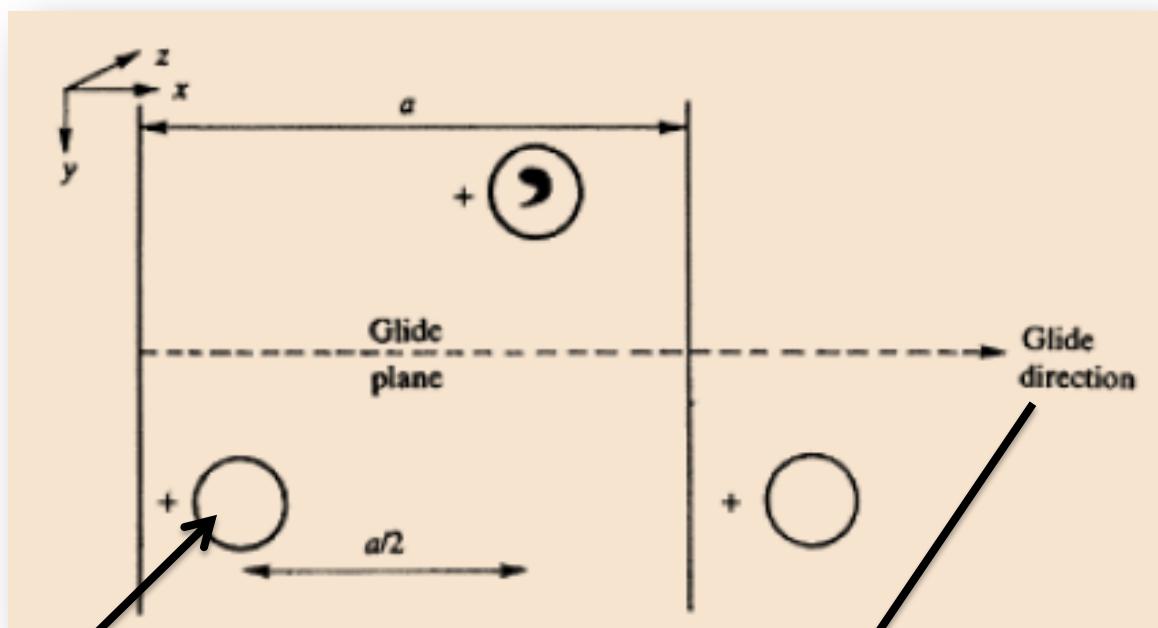
$$\mathbf{r}' = \mathbf{R} \times \mathbf{r}$$



“Permitted rotations”
 $n = 1, 2, 3, 4,$ and 6

Translational symmetry elements:

Glide plane: Translation with reflection



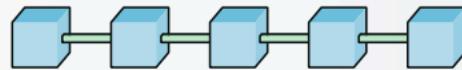
(+) molecule lies above the plane in the z-direction

The plane of symmetry is in the xz plane perpendicular to the paper

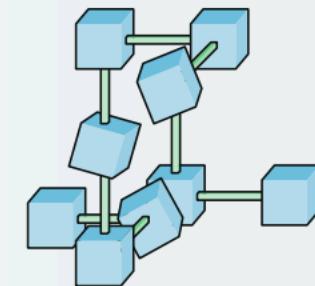
The translation takes place in the x direction ($a/2$).

Crystalline

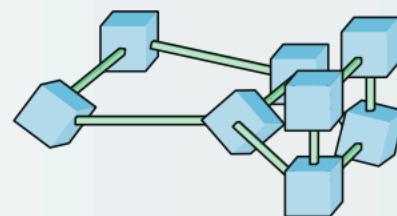
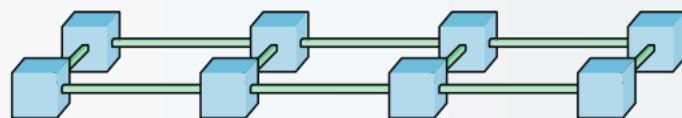
1D



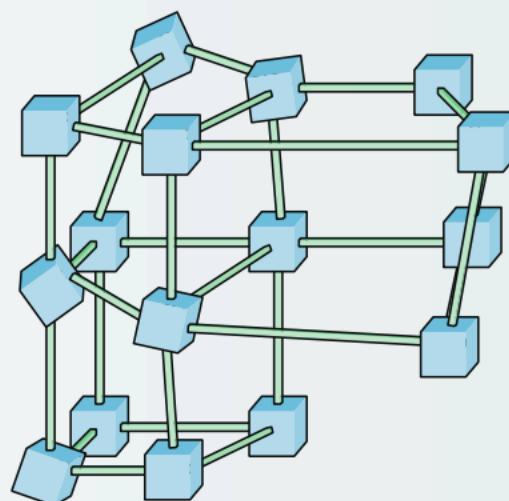
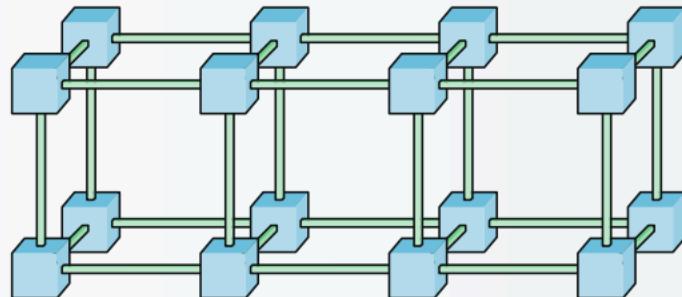
Amorphous



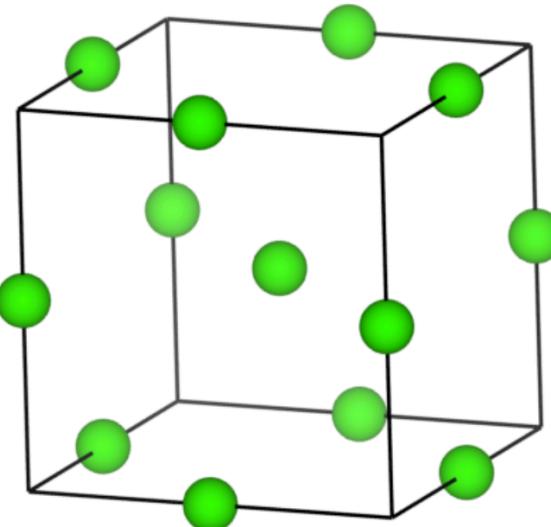
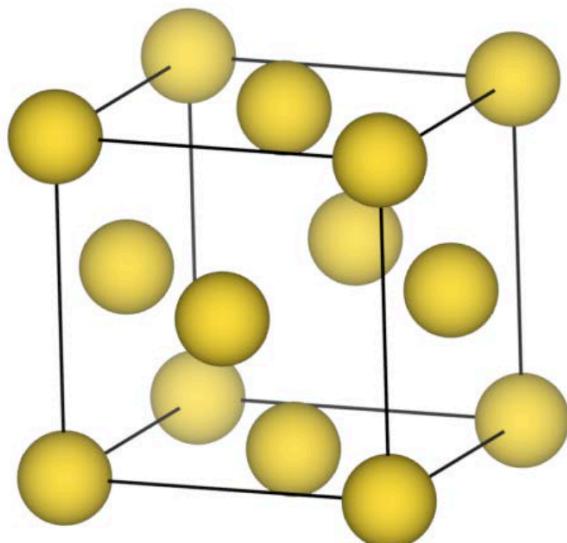
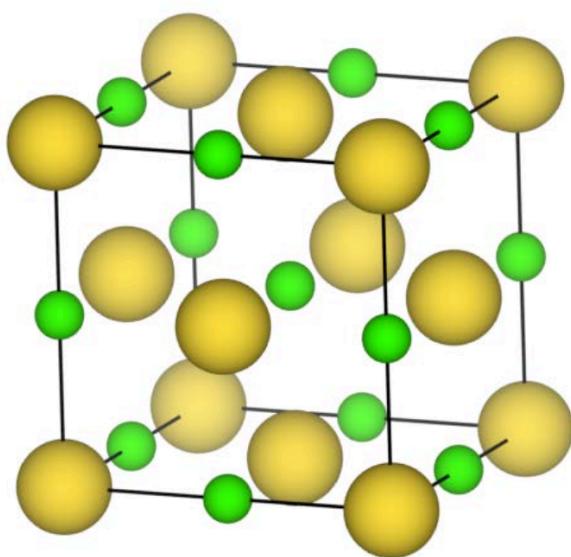
2D

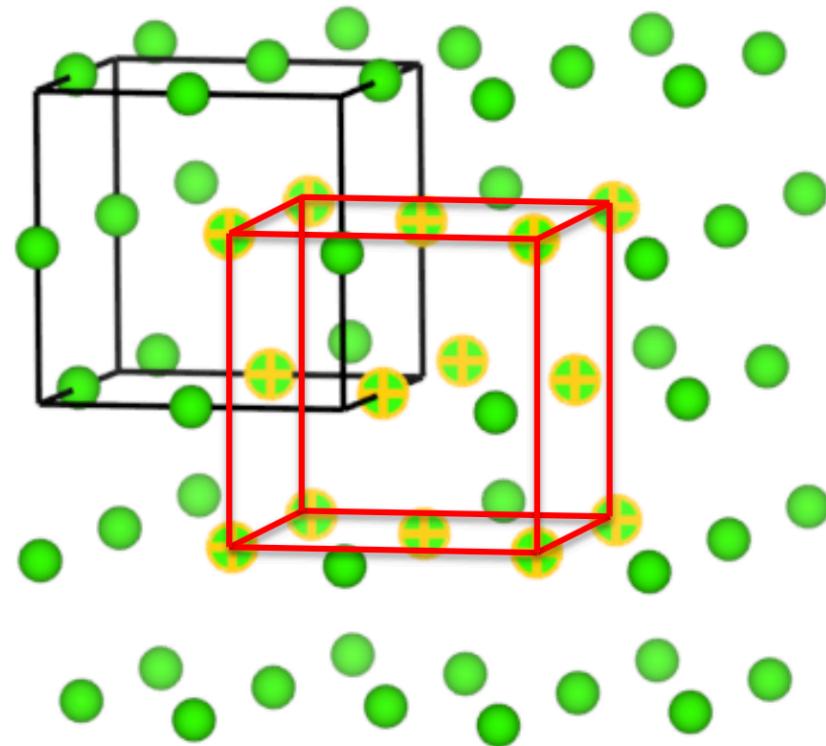
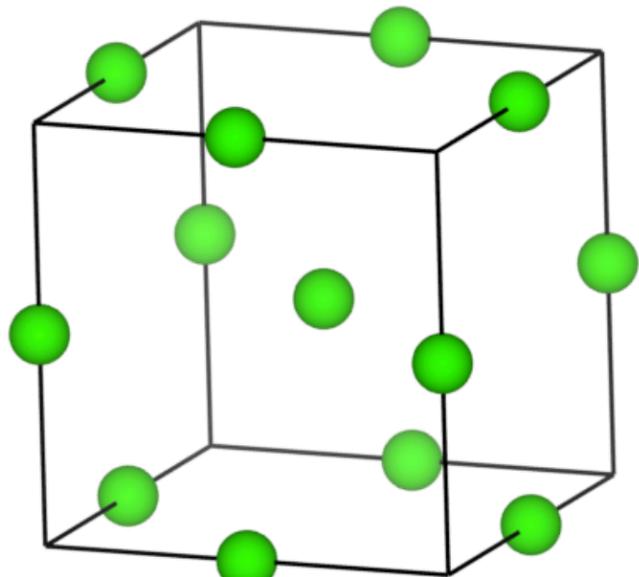


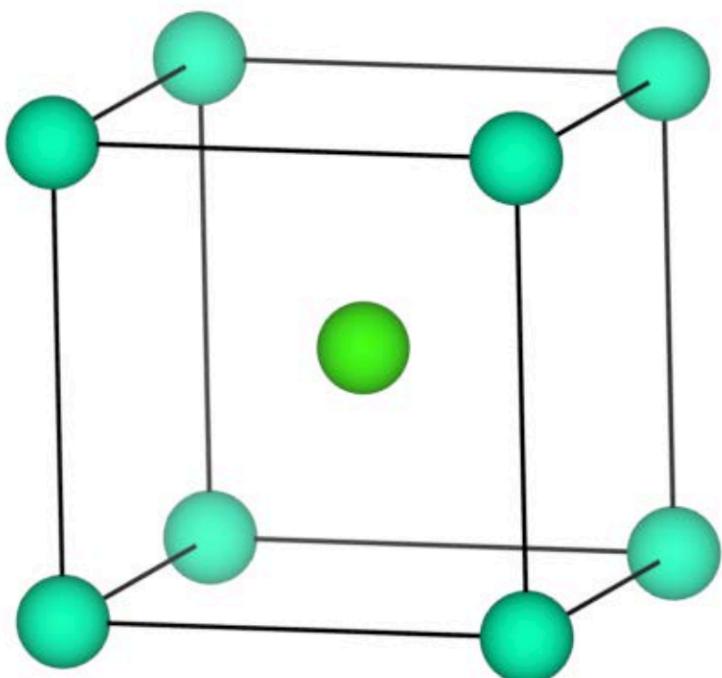
3D



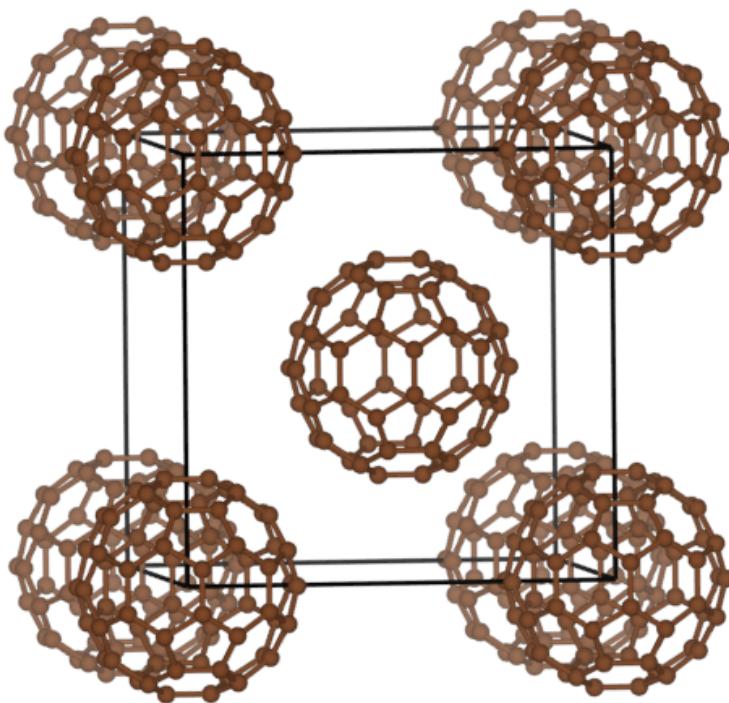
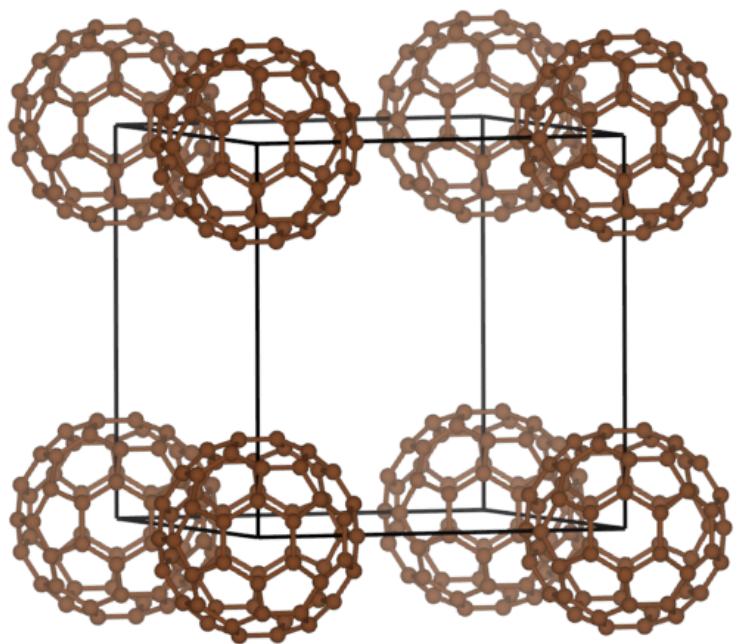
NaCl





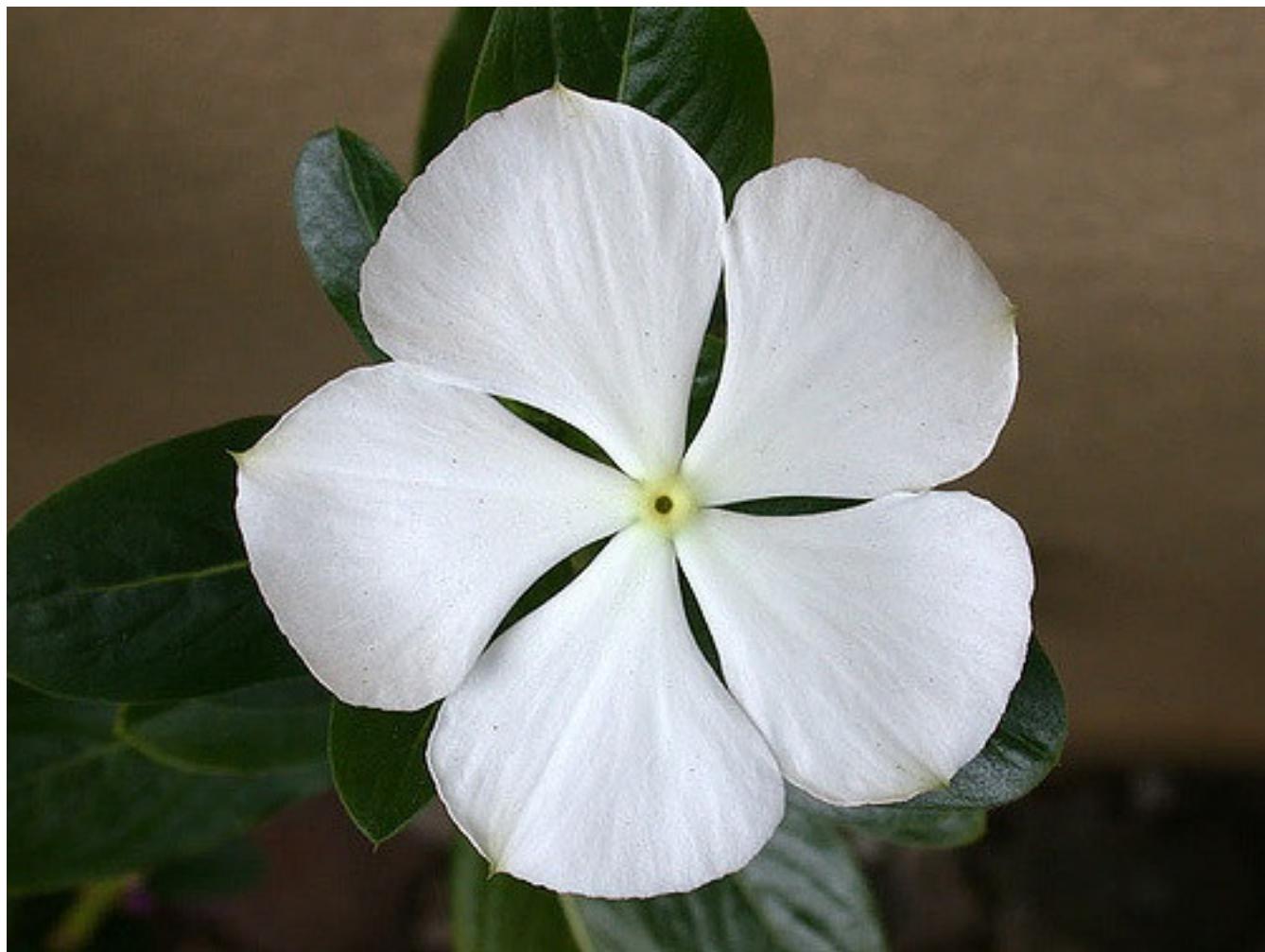


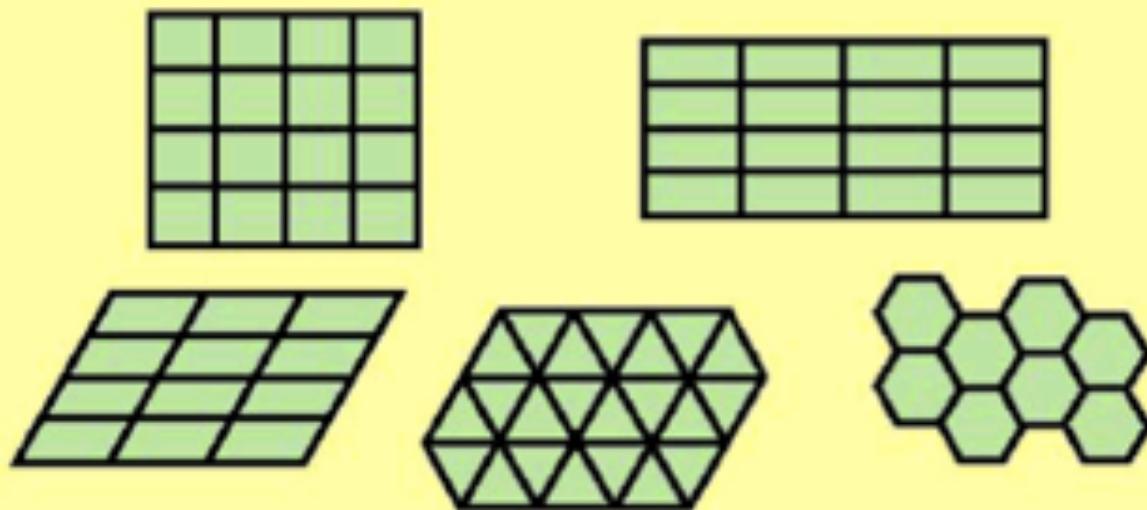
C_{60} [Fullerene ; Fm-3m]



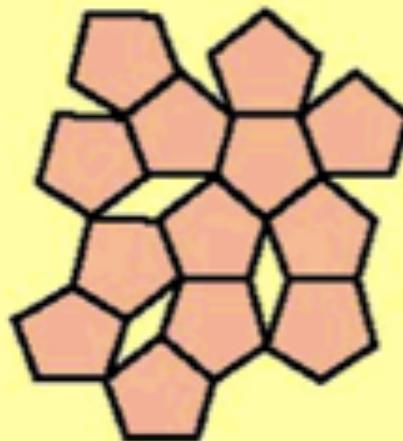
Packing Spheres and Tiling



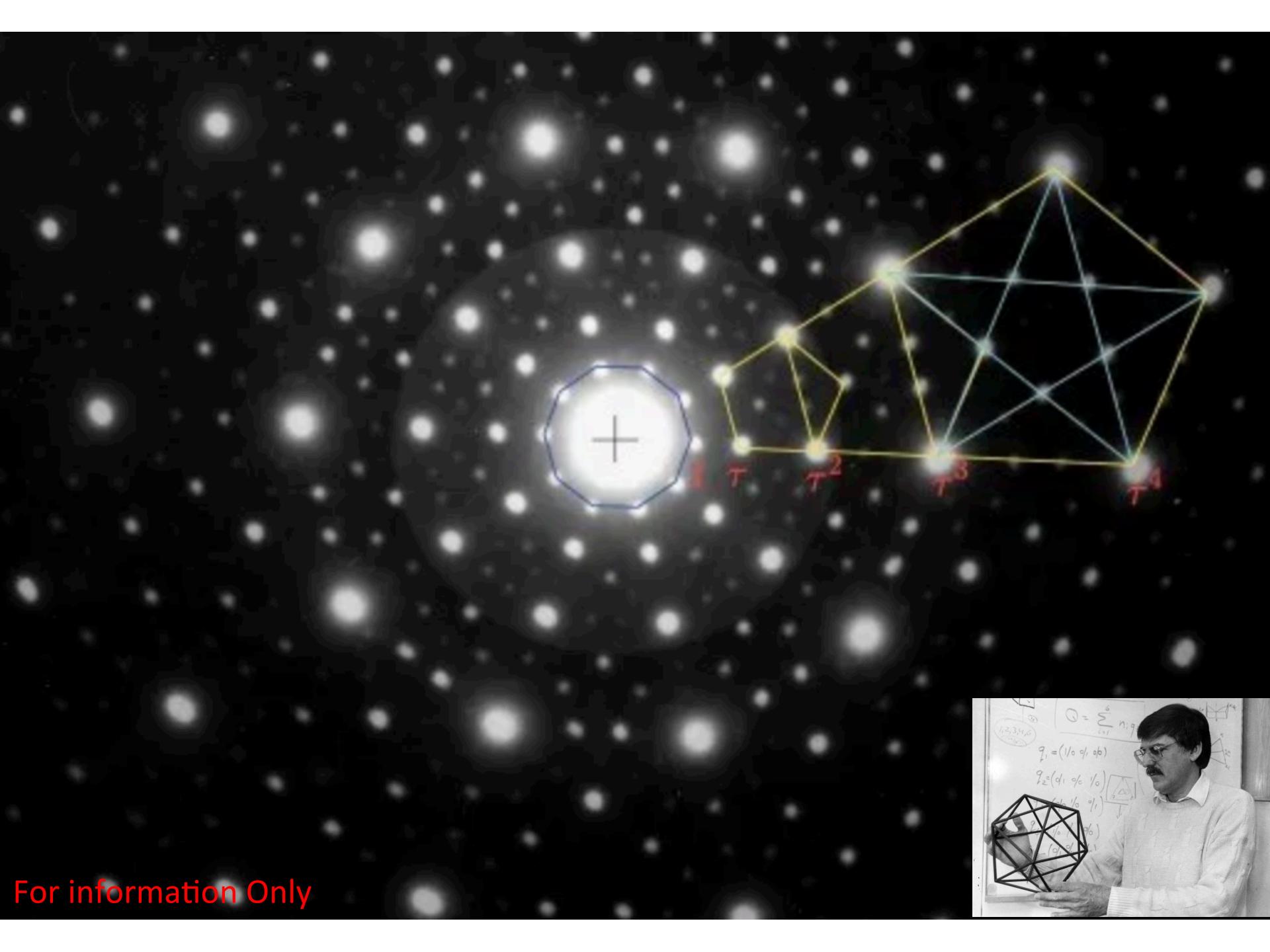




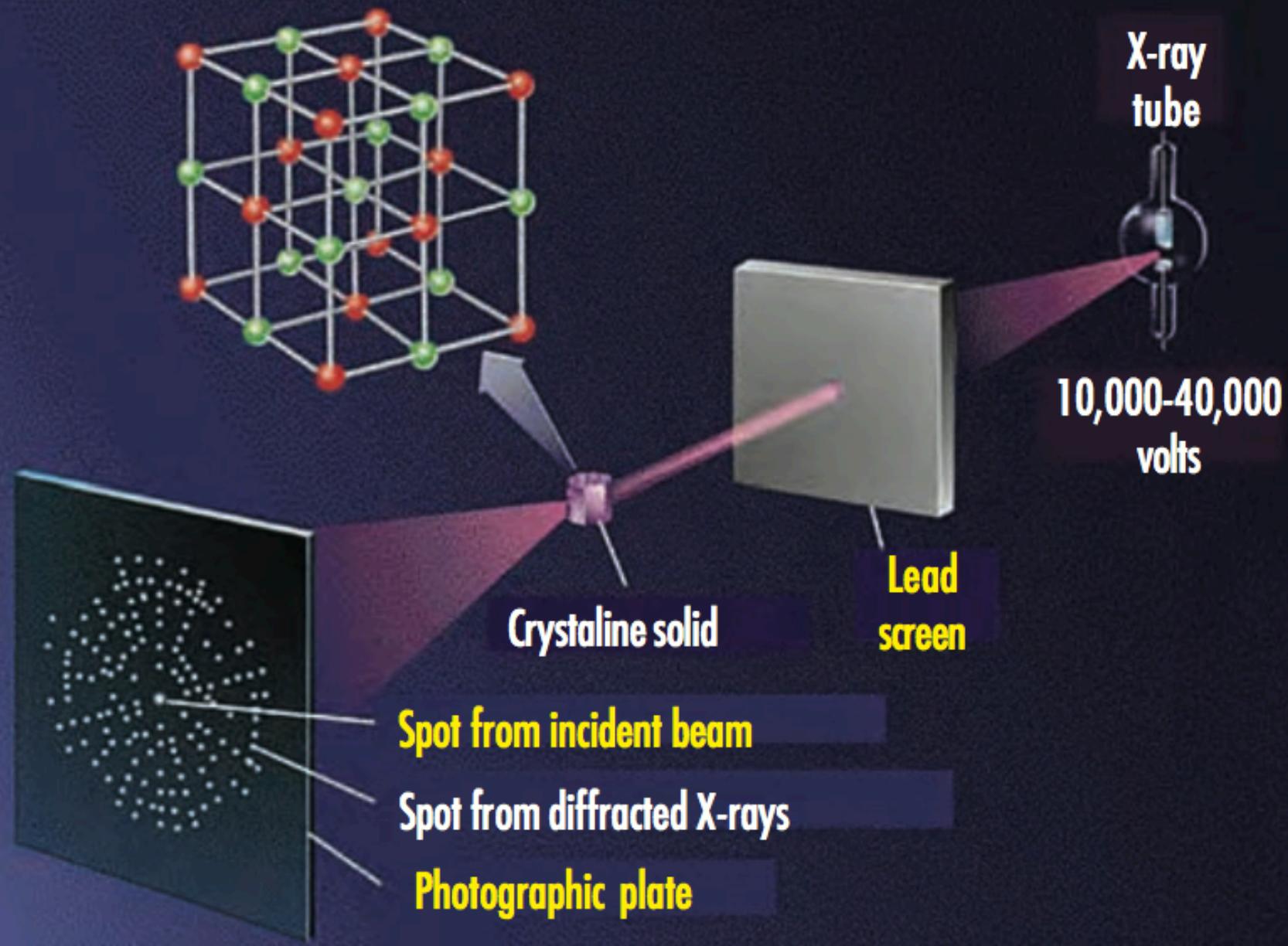
Symmetry Axes
Compatible
w / Periodicity



5-fold
Symmetry is
FORBIDDEN

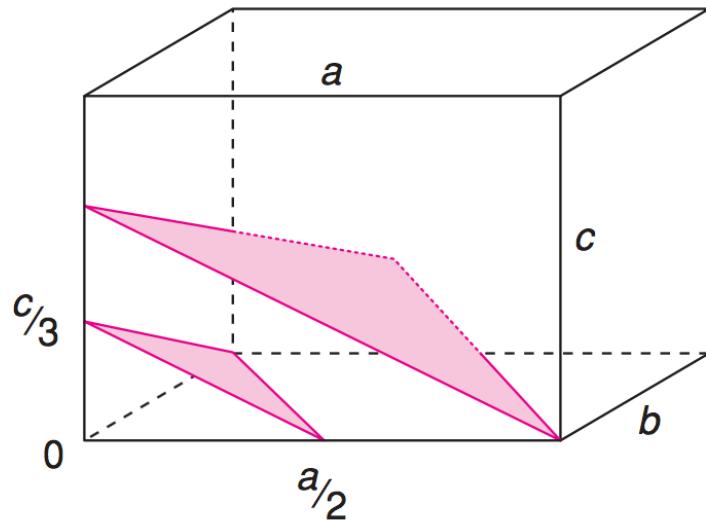
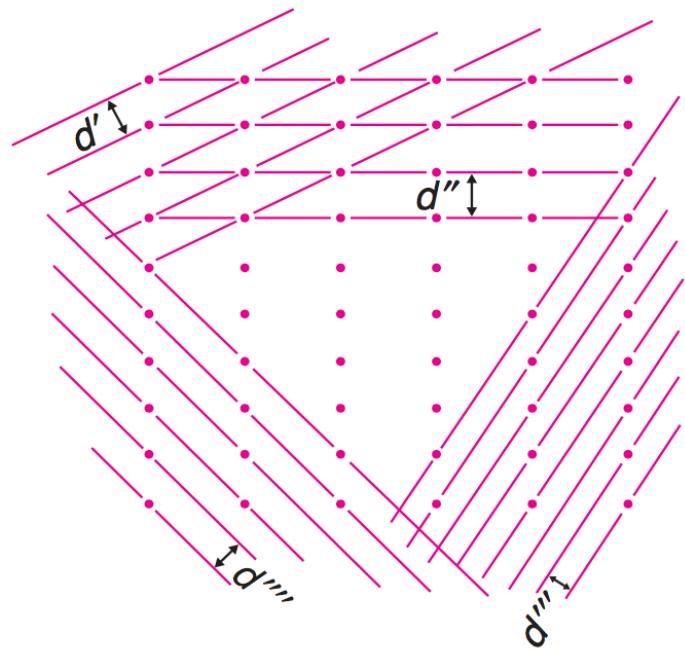


For information Only



Lattice planes are labelled by assigning three numbers known as Miller indices to each set.

Note: Follow Bragg's Law
 $2d \sin\theta = n\lambda$



Miller indices based on cubic crystal lattice can be easily described with cartesian coordinates.

The Miller index of a plane, specified as a sequence (hkl) of three numbers enclosed in parentheses, identifies the plane with axis intercepts of

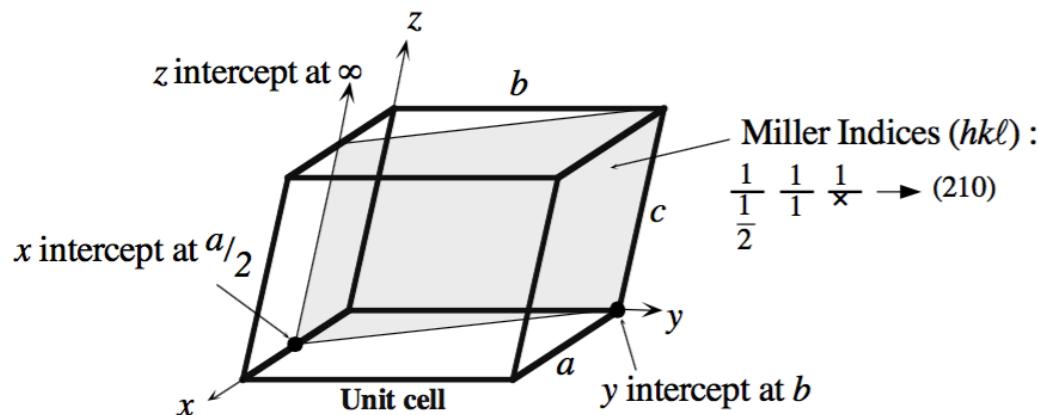
$$x = \frac{1}{h}$$

$$y = \frac{1}{k}$$

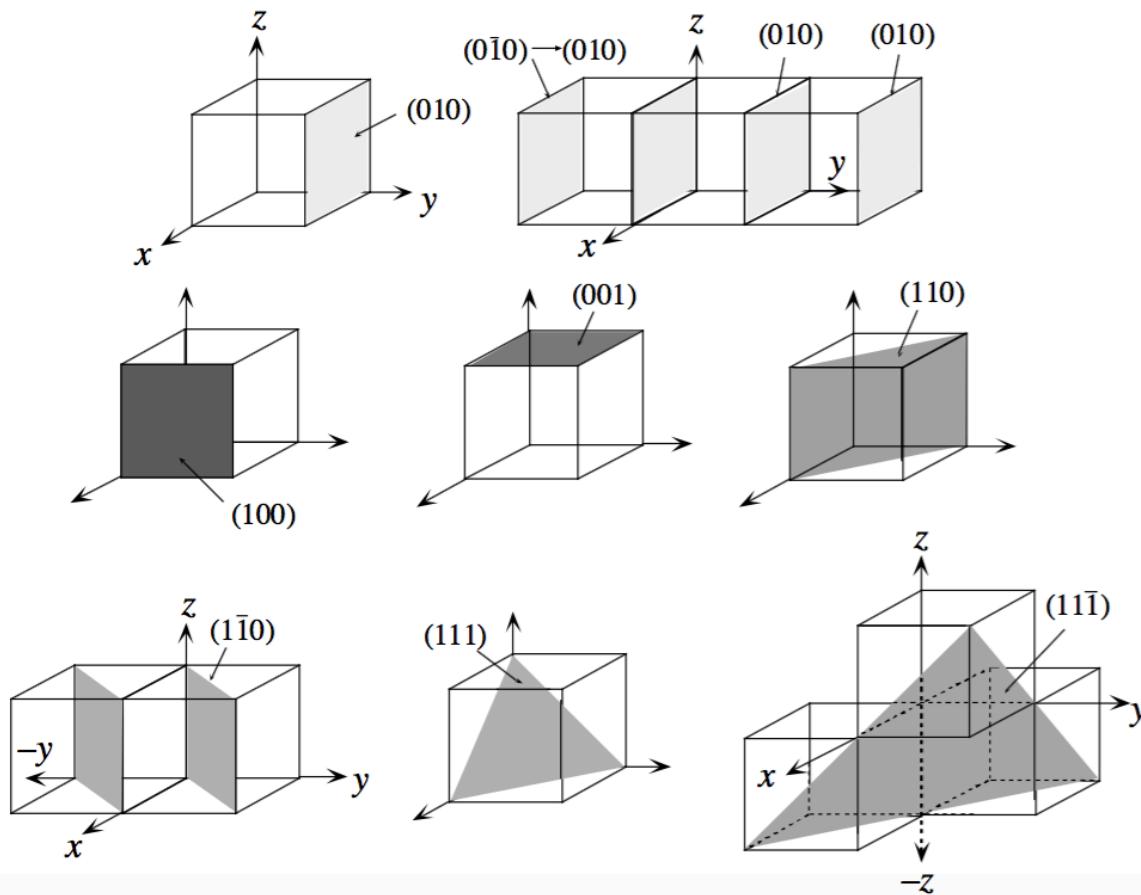
$$z = \frac{1}{l}$$

where h, k, and l are integers.

Examples:



(a) Identification of a plane in a crystal



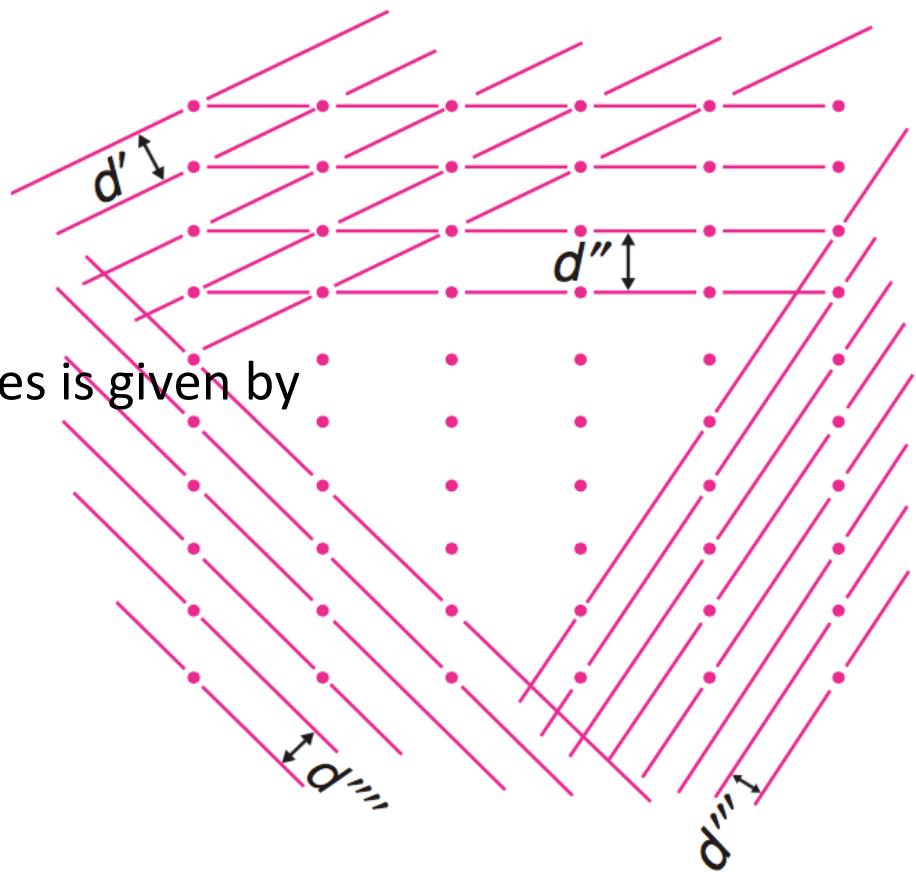
d-Sapcing

For cubic crystals,
the d-spacing for any set of planes is given by

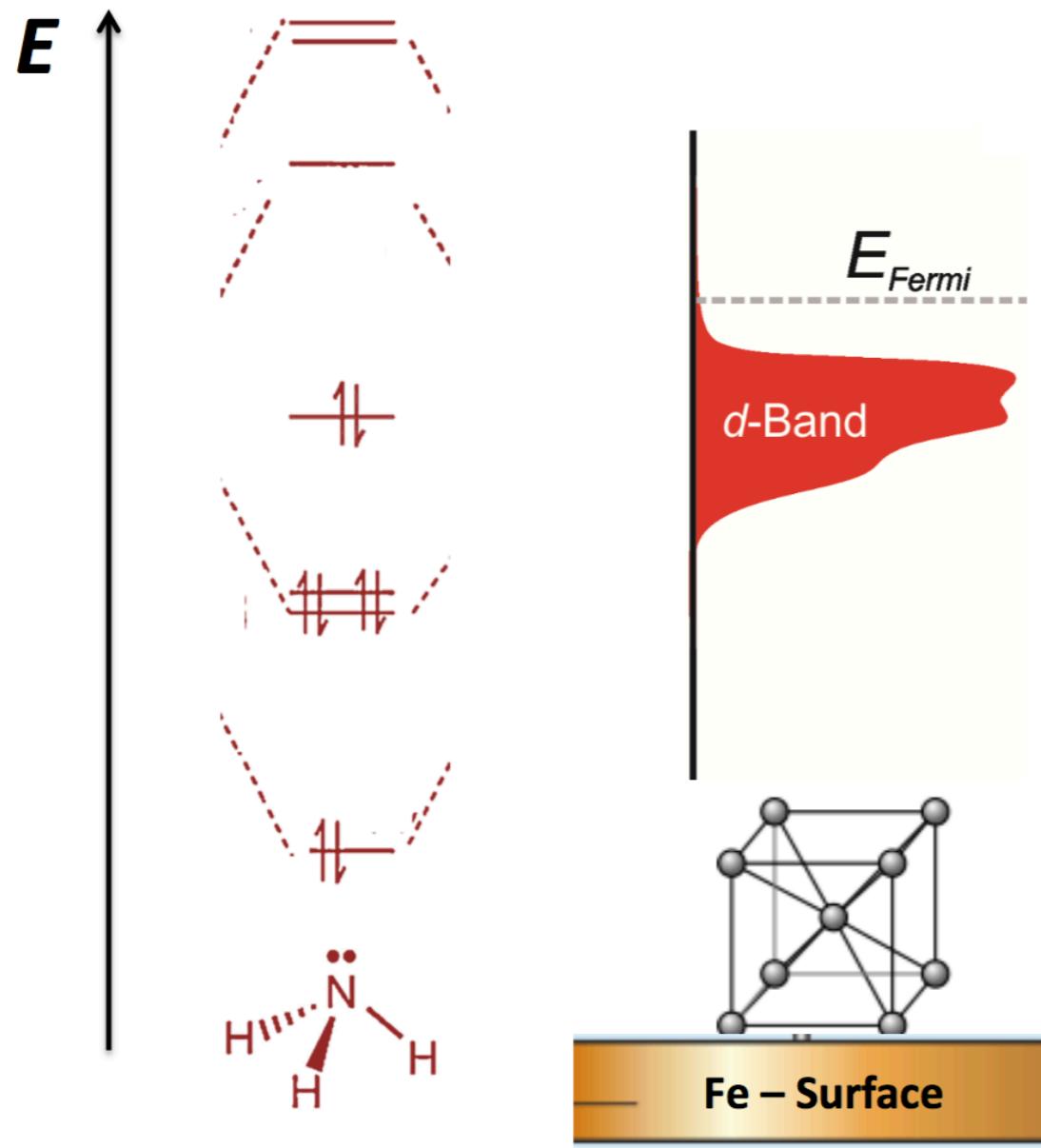
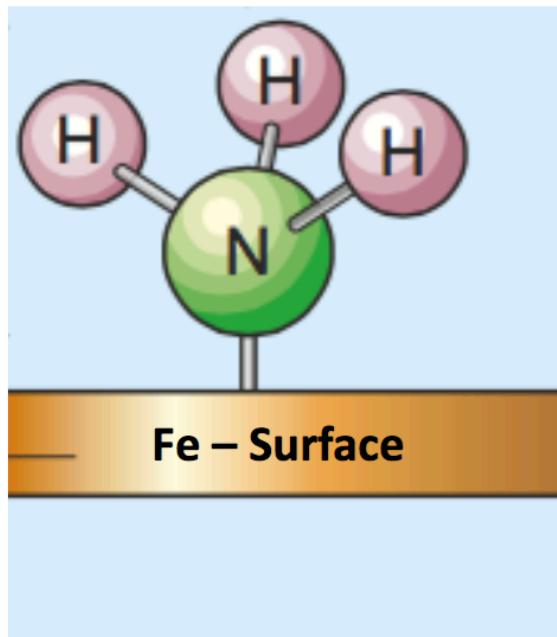
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

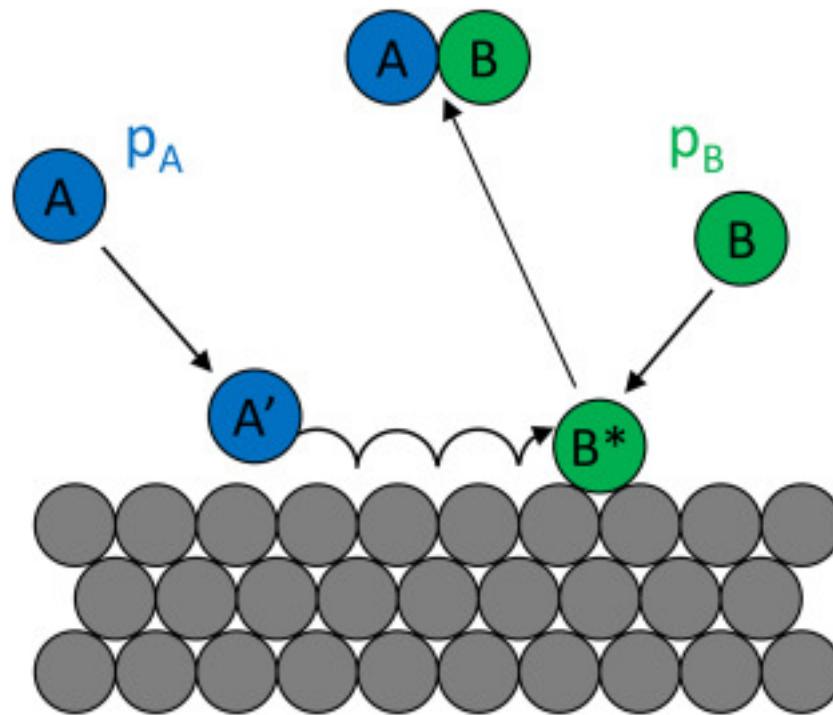
For tetragonal crystals,
the d-spacing for any set of planes is given by

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$



Chemical processes on solid surfaces

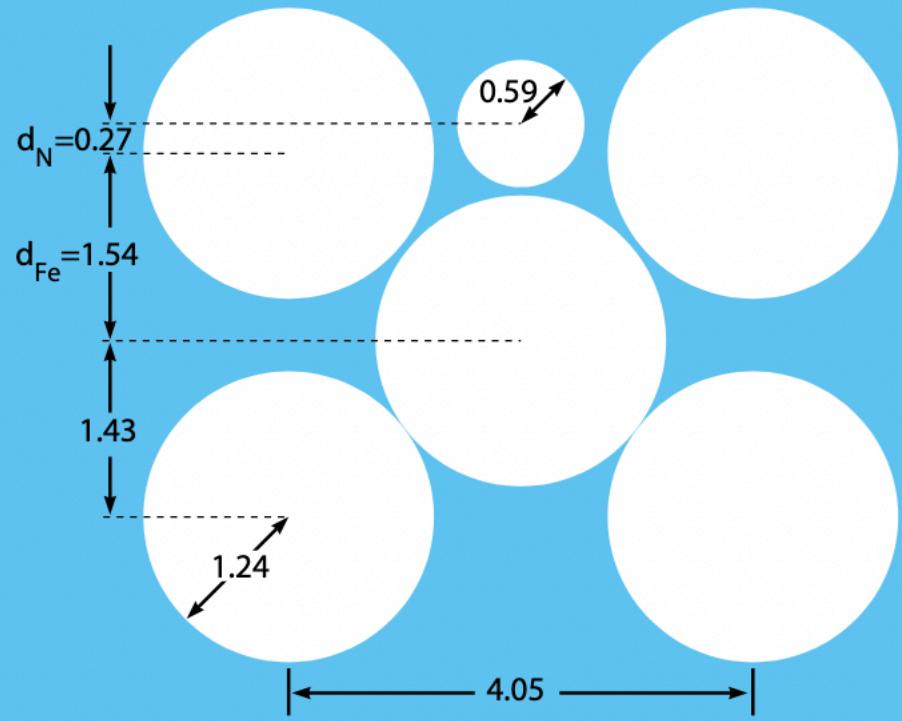
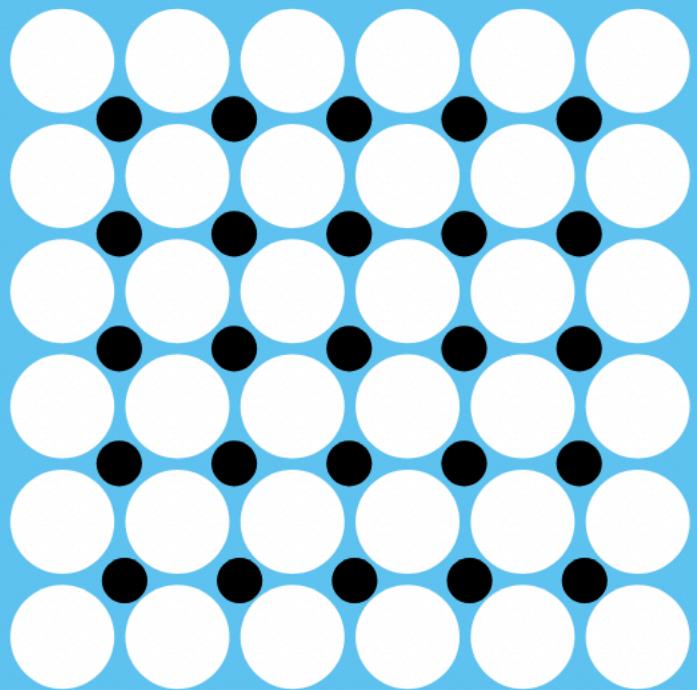




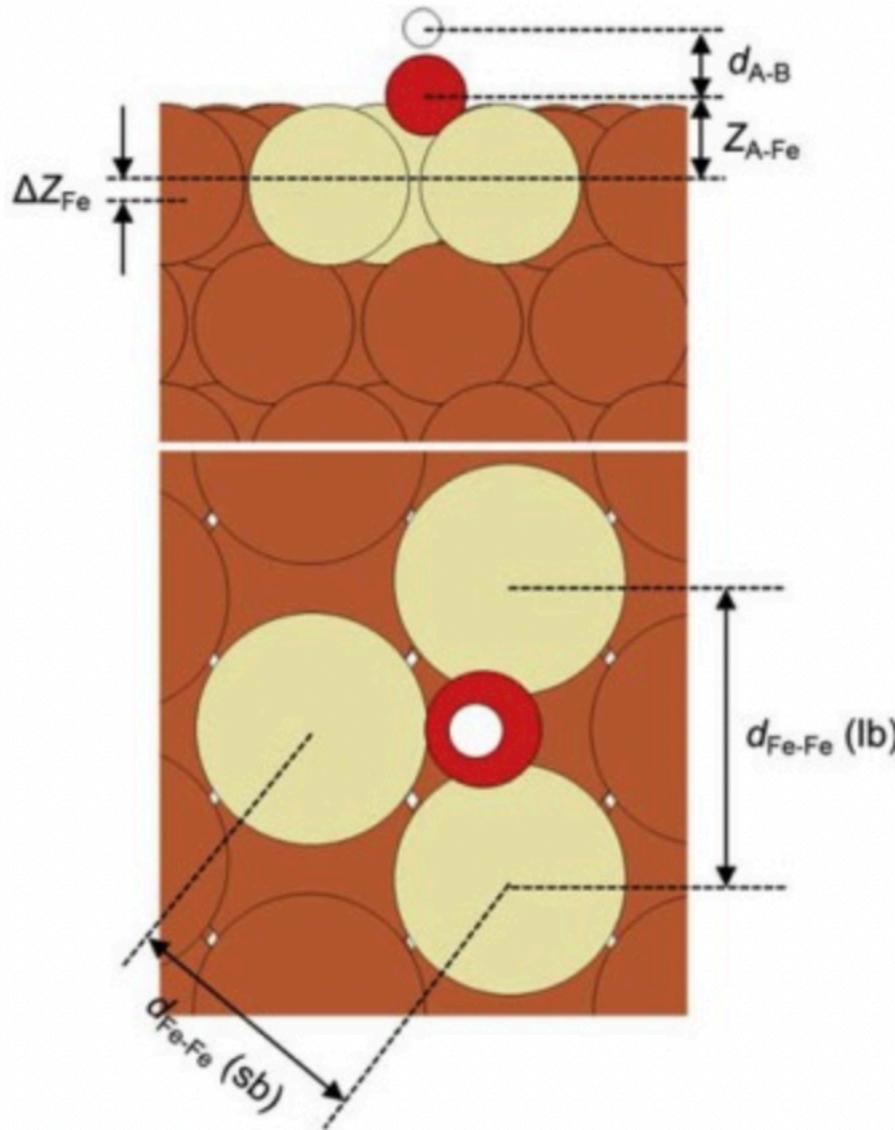
Scientific Background on the Nobel Prize in Chemistry 2007

Chemical Processes on Solid Surfaces

It was, moreover, possible to characterize in detail the kinetics of the nitrogen adsorption (Ertl et al. 1982). The formation of atomic nitrogen occurs initially with a low activation energy but with a very small prefactor making the process slow. Ertl also found that the activation energy was different for different crystal planes, but in such a way that the reaction could anyway proceed on all three major crystal planes (111), (110) and (100). Furthermore with increasing surface coverage the barrier increases in such a way that the kinetic difference between the crystal planes decreases.



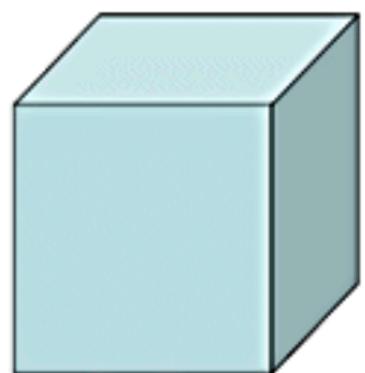
Structure of an overlayer of nitrogen atoms (small filled circles) on a (100) surface of iron (large open circles). Left: top view; right: side view. (Adapted from Imbihl et al. 1982)



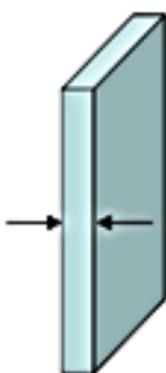
Fe(110) surface, the most stable facet of this body-centered cubic (bcc) metal.

ΔZ_{Fe} denotes the average difference in vertical distances between the plane of the highlighted Fe atoms and that of a clean, relaxed Fe(110) surface.

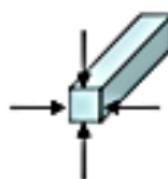
$d_{Fe-Fe} (lb)$ denotes the average distance between adjacent Fe atoms in contact with the adsorbate.



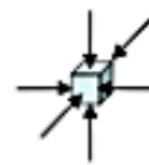
Bulk
3D



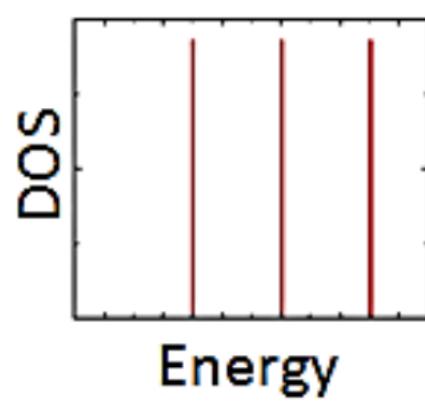
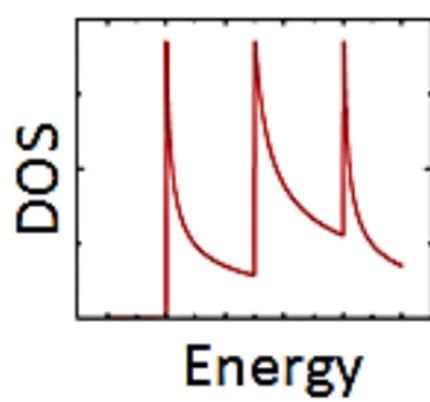
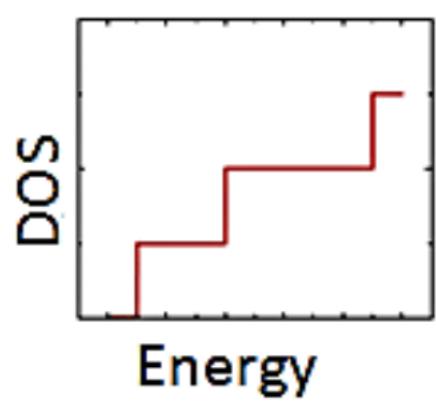
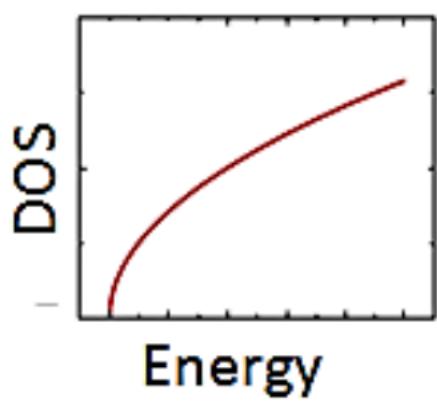
Quantum well
2D



Quantum wire
1D

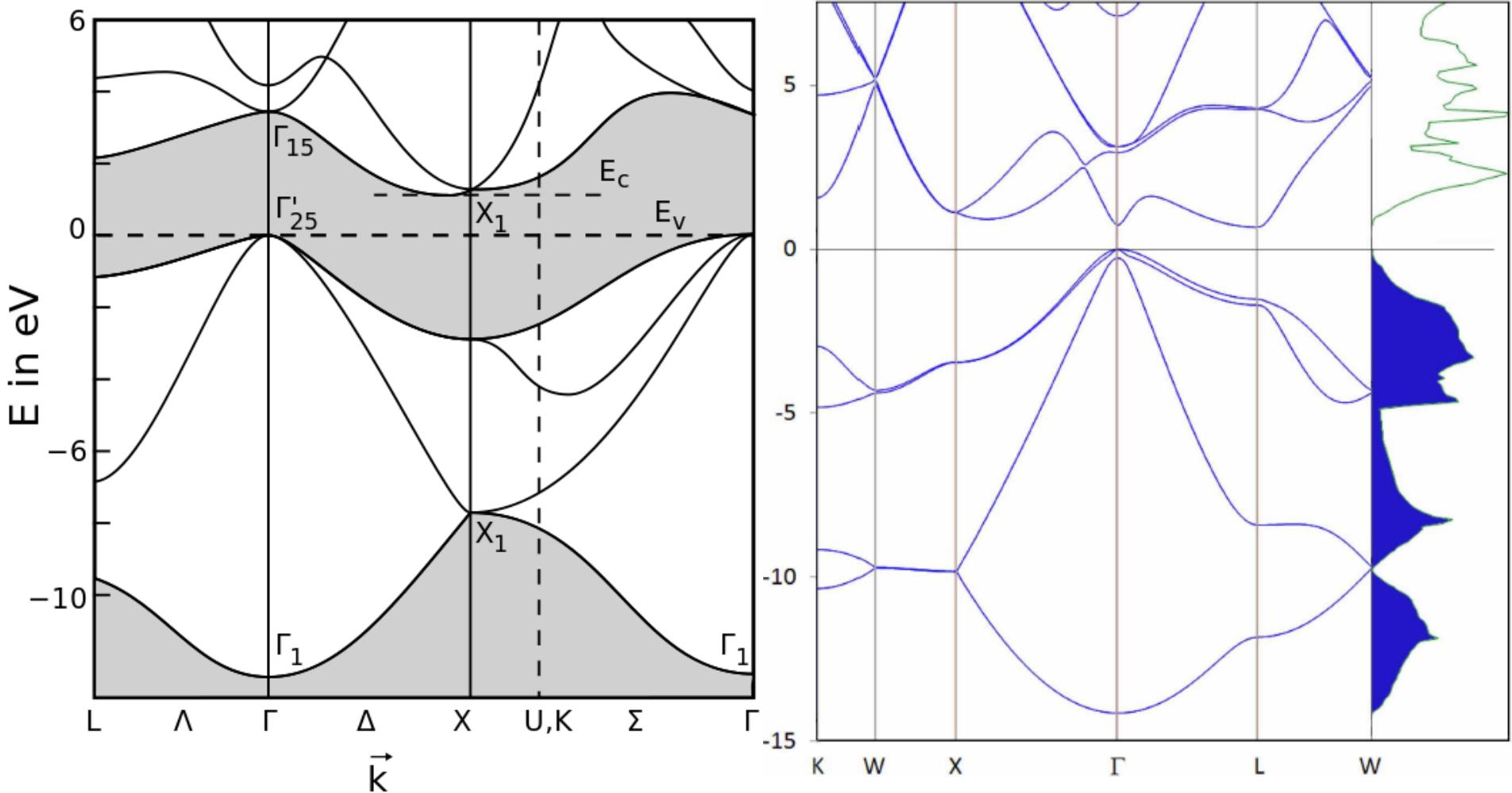


Quantum dot
0D



Evolution of the density of states (DOS) with dimensionality of the system

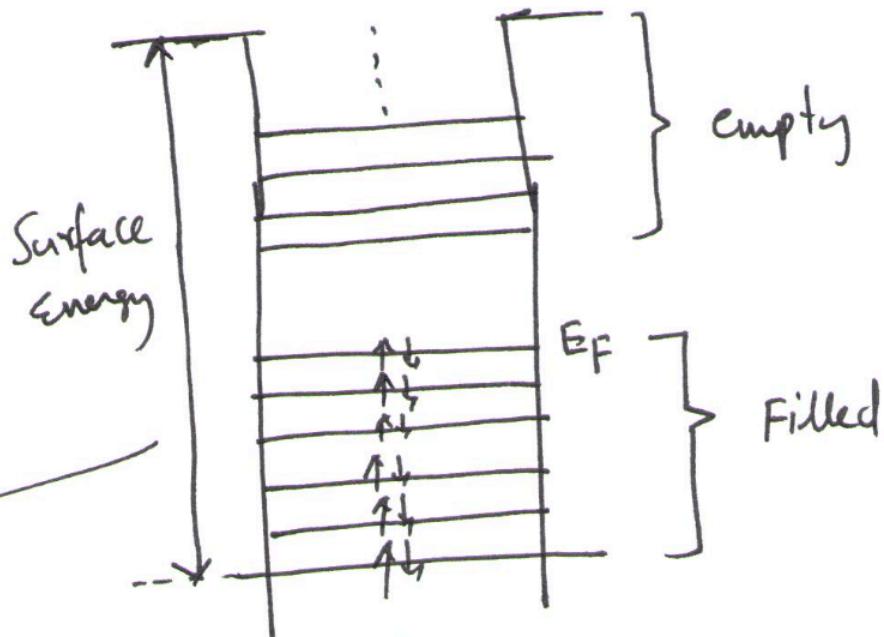
Typical Band Structure and DOS



Fermi Energy

$$E_F \approx \frac{\hbar^2 k_F^2}{2m}$$

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$



effect of temperature
on the occupancy of the energy levels.

The probability that a particular state of energy E is occupied at a temp T is given by Fermi function

$$f(E) = \left[e^{\left[\frac{E - E_F}{k_B T} \right]} + 1 \right]^{-1}$$

$$f(E) = \left[\exp \left[\frac{E - E_F}{k_B T} \right] + 1 \right]^{-1}$$

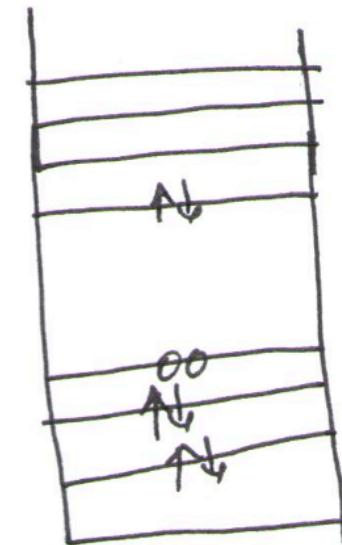
at $T=0 \Rightarrow f(E) = 1$ for $E < E_F$

$f(E) = 0$ for $E > E_F$

$$T > 0$$

There may be a case $E = E_F$

$$f(E_F) = \frac{1}{2}$$



Density of states

Number of electronic states present in a unit energy range

Finite States

$$D(E) = \frac{dn}{dE}$$

dn = number of states

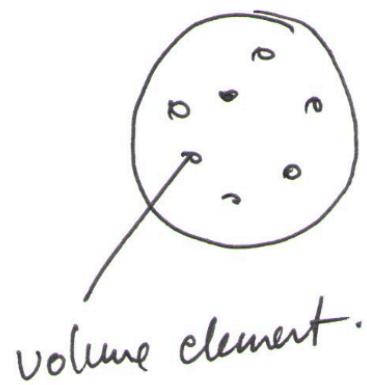
between E and $E+dE$

$$D(E) = 2 \frac{dn}{dE} \quad (2 \text{ is for } \uparrow \downarrow)$$

The volume of the Fermi sphere is $\frac{4}{3} \pi k_F^3$
 The volume element that represent a ~~volume element~~ ^{the occupied state} $\left(\frac{2\pi}{L}\right)^3$

The total number of electronic states

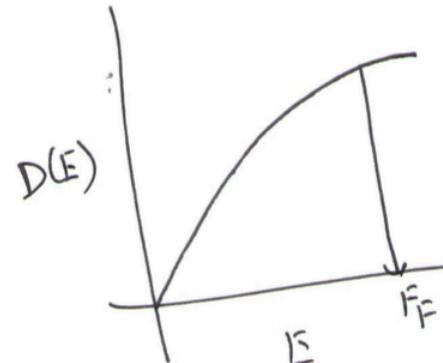
$$= \frac{\frac{4}{3} \pi k_F^3}{\left(\frac{2\pi}{L}\right)^3}$$



$$= \frac{\frac{4}{3} \pi k_F^3 L^3}{2 \cancel{\pi^8}} = \frac{L^3}{6 \pi^2} k_F^3$$

Number of electrons = $N = \frac{L^3}{6\pi^2} k_F^3$

$$\therefore N = \frac{L^3 k_F^3}{3\pi^2}$$



$$k_F^3 = \frac{3\pi^2 N}{L^3}$$

$$k_F = \left[\frac{3\pi^2 N}{V} \right]^{1/3}$$

$$E_F = \frac{\hbar^2}{2m} \left[\frac{3\pi^2 N}{V} \right]^{2/3}$$

$$N = \frac{V}{3\pi^2} \left[\frac{2m E_F}{\hbar^2} \right]^{3/2}$$

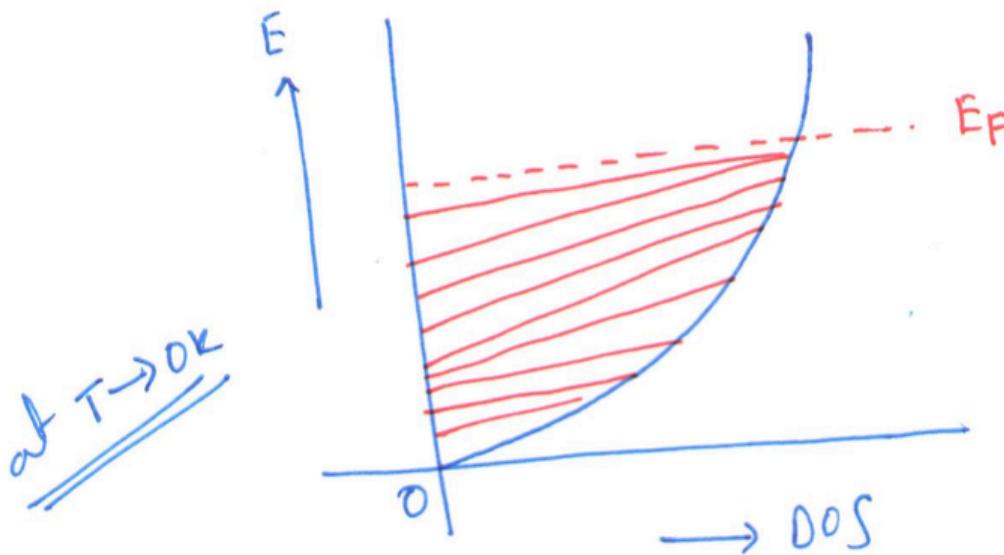
$$E_F \int_0^{\infty} D(E) dE = N$$

in E and $E+dE$.

$$\Rightarrow D(E) = \int \frac{V}{3\pi^2} \left[\frac{2m E_F}{\hbar^2} \right]^{3/2} dE$$

$$D(E) = \frac{V}{2\pi^2} \left[\frac{2m}{\hbar^2} \right]^{3/2} \sqrt{E}$$

$D(E)$ has a \sqrt{E} dependency.



DOS $T > 0$? populate to higher energy levels.

The population (or) the probability that a particular state E is occupied at a temperature T is given by Fermi function $f(E)$

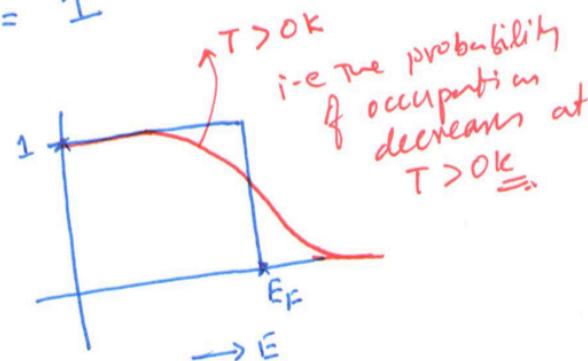
$$f(E) = \left[\exp \left[\frac{E - E_F}{k_B T} \right] + 1 \right]^{-1}$$

at
 $T=0K$
 $E < E_F$

at $T=0K$
 $E > E_F$

$$f(E) = [e^{-\infty} + 1]^{-1} = [0 + 1]^{-1} = 1$$

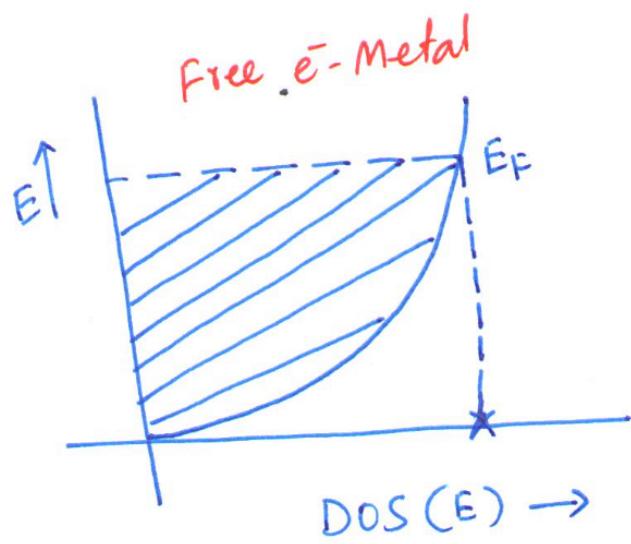
$$f(E) = 0$$



At $E = E_F$

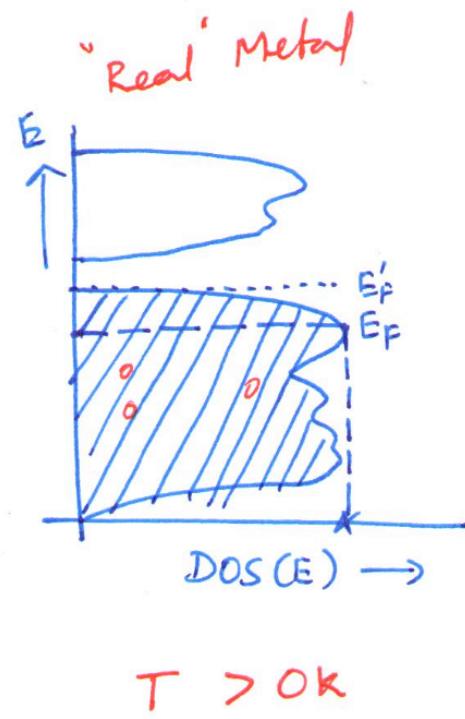
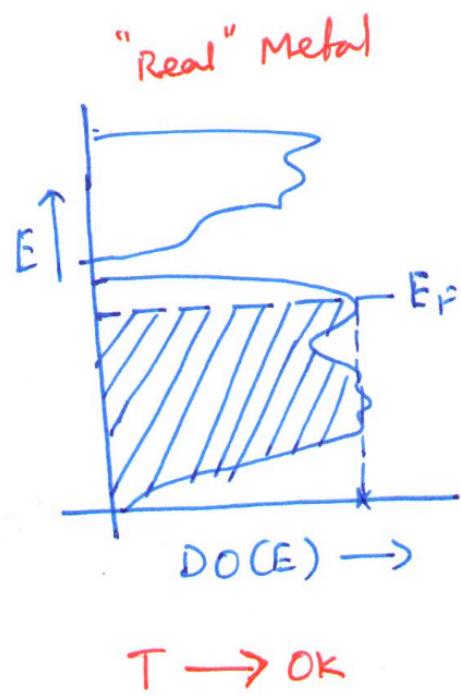
$$f(E) = [1 + 1]^{-1} = \left(\frac{1}{2} \right) \rightarrow \begin{array}{l} \text{At } T > 0K \\ \text{the probability of} \\ \text{occupation is } \frac{1}{2} \end{array}$$

Metals, DOS(E_F) and Bands:



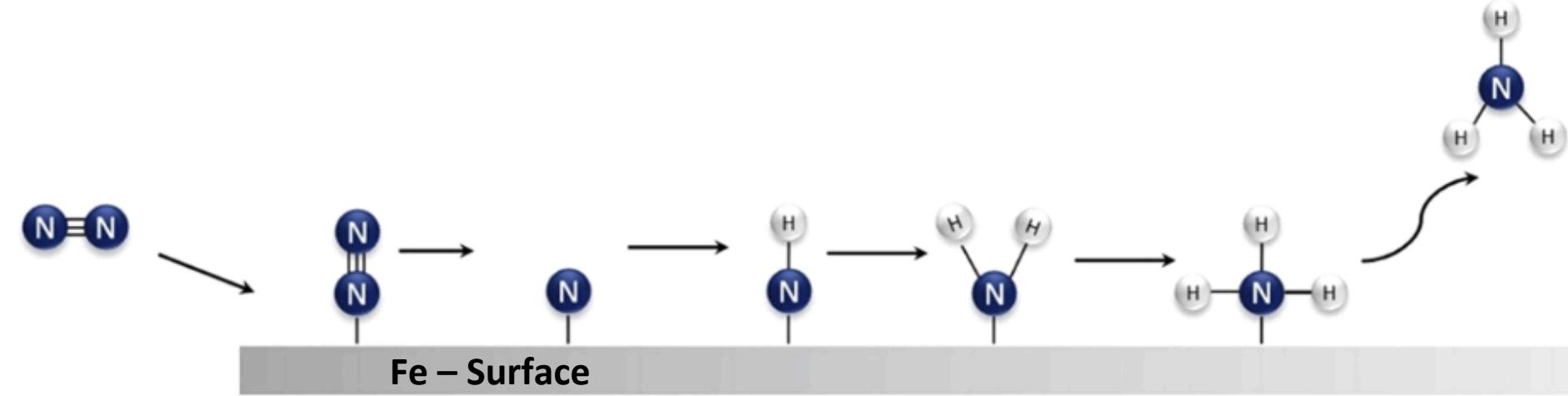
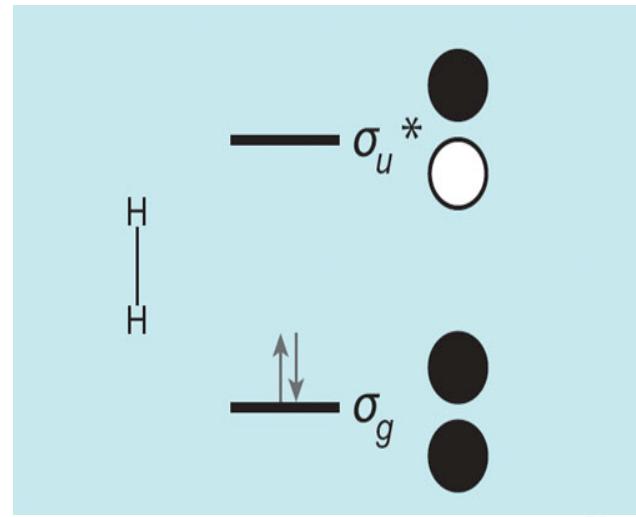
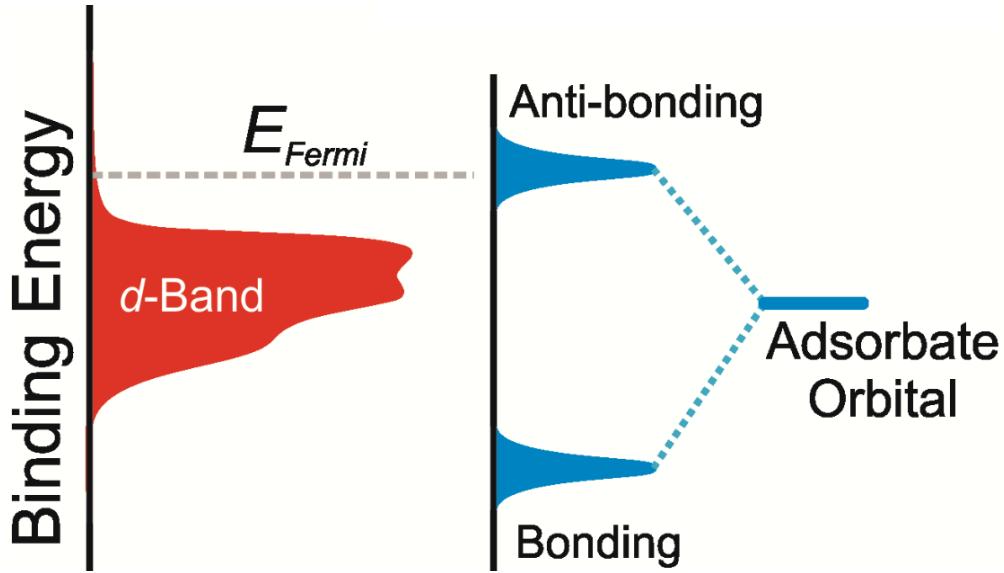
$$T \rightarrow 0K$$

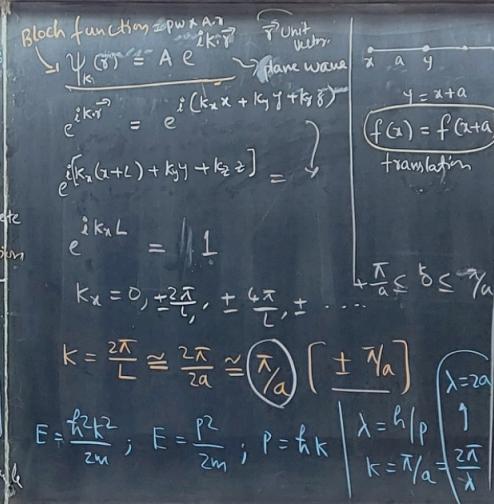
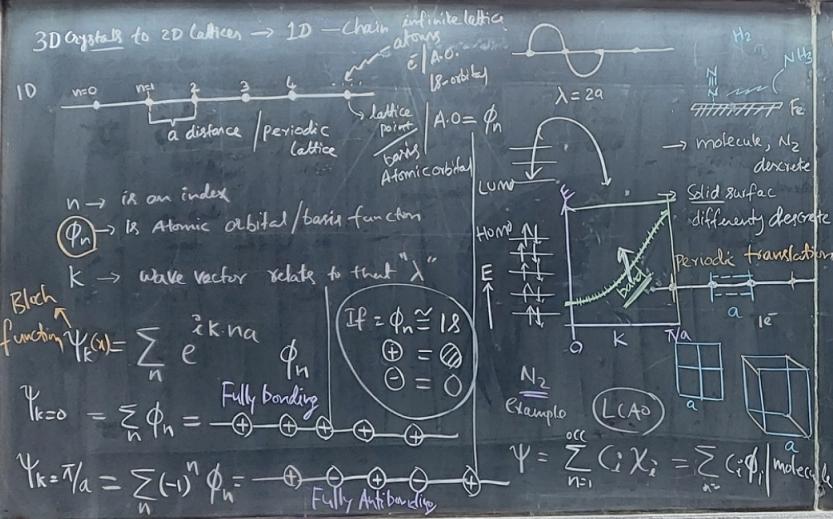
$$\int_0^{E_F} D(E) dE = N$$



Some holes will
be left-over
in valence band

Chemical Processes.....





$$\boxed{\begin{aligned} \hat{H}\Psi(x) &= E\Psi(x) \\ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \Psi(x) + V(x) &= E\Psi(x) \end{aligned}} \quad \text{---} \quad \begin{array}{c} \text{---} \\ a \\ \rightarrow x \end{array}$$

$\frac{d^2}{dx^2} \Psi(x) + \frac{2mE}{\hbar^2} \Psi(x) = 0$

$K^2 = \frac{2mE}{\hbar^2}$

$E = \frac{\hbar^2 K^2}{2m}$

$\Psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$

↓ A Normalization

BANDS: Let's see how the bands can be generated!
through Bloch function

Bloch Function:

$$\psi_{\mathbf{k}} = \sum_n e^{i\mathbf{k}n\mathbf{a}} x_n$$

↑
plane wave

atomic orbital
sitting in the lattice,
so periodicity ...

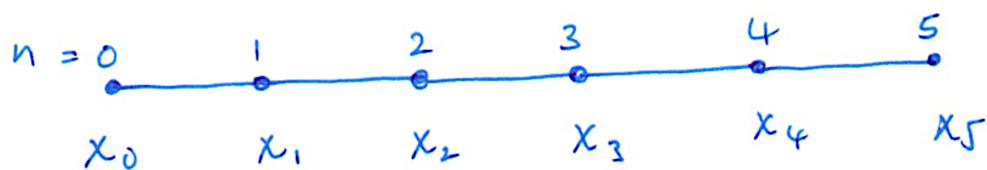
$a \rightarrow$ lattice spacing

$\mathbf{k} \rightarrow$ is a wave vector (remember the previous free e^- model)

$x_n \rightarrow$ atomic orbital (basis function)

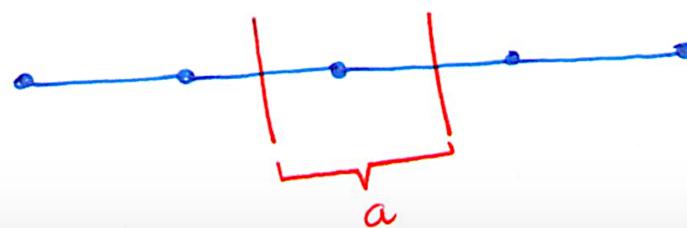
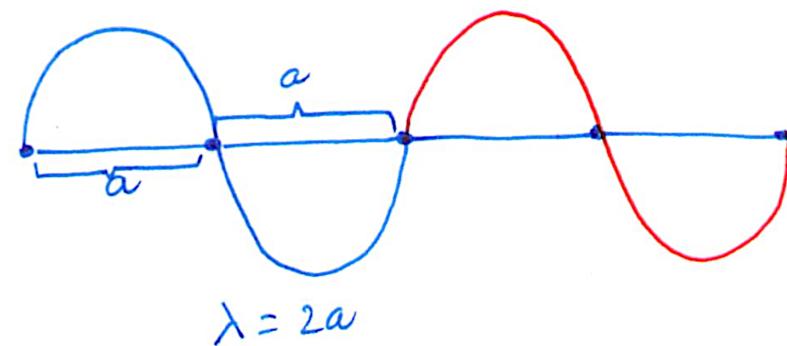
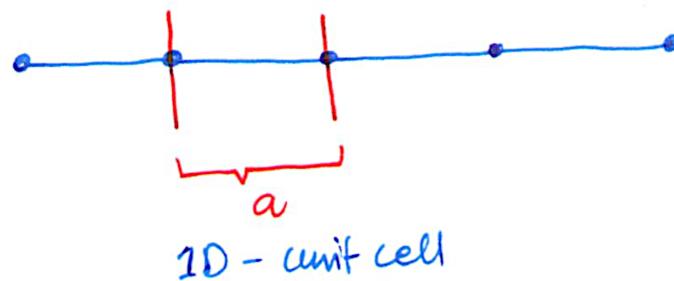
$n \rightarrow$ lattice number (index)

Let's consider a one dimensional periodic lattice



- \rightarrow may be H-atom, simply one e^- .

the unit cell can be constructed in various ways



As is above, a one dimensional periodic lattice, may be assumed, or considered as a chain of equally spaced hydrogen atoms.

Let's also work for "k" to see it as wavevector.

$$K = \frac{2\pi}{\lambda} \Rightarrow K = \frac{2\pi}{2a} \Rightarrow k = \frac{\pi}{a}$$


also quantum
number k

$$\text{i.e. } -\frac{\pi}{a} \leq k \leq \frac{\pi}{a} \quad \text{which is First}$$

Brillouin Zone

"free e derivation
of metal"
 $k = \pm \frac{2\pi n}{L}$

The values of k defines the boundaries of
Brillouin zone

for $k = 0$

$$\psi_k = \sum_n e^{ikna} x_n$$

$$\psi_{k=0} = \sum_n e^0 x_n$$

$$\therefore \boxed{\psi_{k=0} = \sum_n x_n}$$

for $k = \frac{\pi}{a}$

$$\psi_{k=\frac{\pi}{a}} = \sum_n e^{i\pi n} x_n$$

$$\therefore \psi_{k=\frac{\pi}{a}} = \sum_n (-1)^n x_n$$

in other words

$$\psi_{k=0} = x_0 + x_1 + x_2 + \dots + x_n$$

for \bullet
 $H \rightarrow s\text{-orbital}$

$$\psi_{k=0} = \bullet + \bullet + \bullet + \bullet + \dots + \bullet \quad \hookrightarrow \text{bonding state}$$

$$\psi_{k=\frac{\pi}{a}} = x_0 - x_1 + x_2 - x_3 + x_4 - \dots + x_n$$

for
hydrogen s-orbital

$$\psi_{k=\pi/a} = \bullet + 0 + \bullet + 0 + \bullet + \dots + 0 \quad \hookrightarrow \text{anti-bonding state}$$

As you see k -counts the nodes as well, apart from it generic wave-vector nature

$$k = \frac{2\pi}{\lambda} \quad \text{and} \quad k = \frac{2n\pi}{L} = \frac{2n\pi}{2a} = \frac{n\pi}{a}$$

$$\therefore k = \frac{n\pi}{a}$$

$$\Rightarrow \frac{2\pi}{\lambda} = \frac{n\pi}{a} \Rightarrow n\lambda = 2a$$

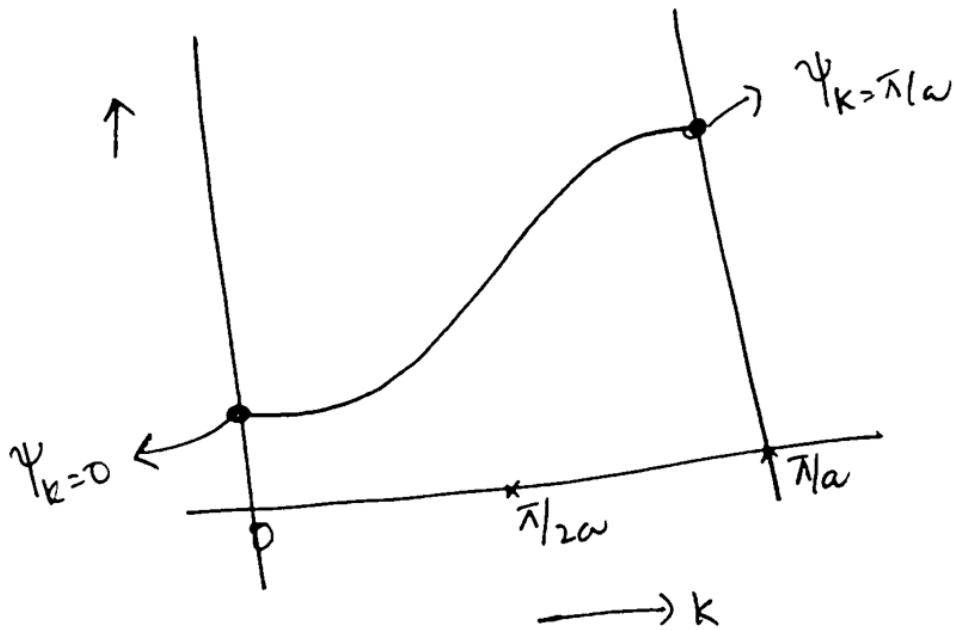
$\approx \boxed{n\lambda = 2d \sin\theta}$

Bragg's law

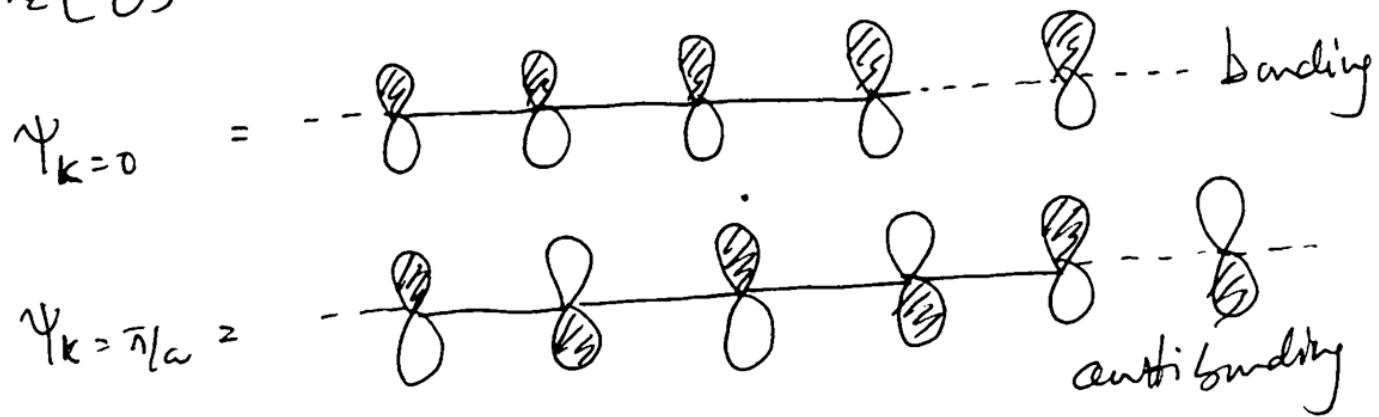
Now let's come back to the Ψ_k

We have seen Ψ_k for two k -values. We can also choose other values of k . Note: $E(k) = E(-k)$

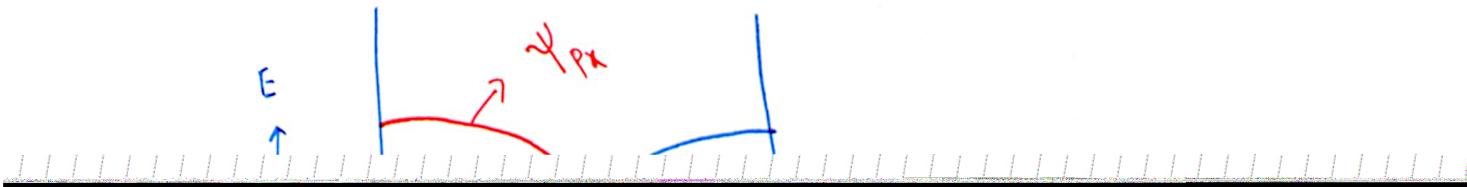
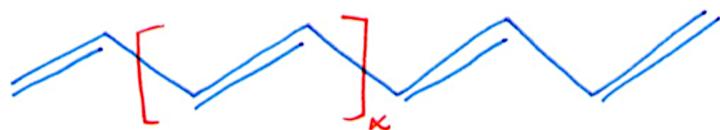
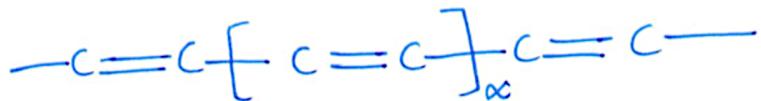
The graph of $E(k)$ vs k is called band structure.



We can also consider a p-orbital centring on each lattice-point for example P_z [8]. Therefore



The P- π orbital can be a good model to study the one dimensional polyenes and therefore conducting polymers.



Note if we consider the P_x of P-orbitals the band level takes the opposite of P_z band. As shown below.

$$\psi_{k=0} = \text{anti bonding}$$

$$\Psi_{k=\pi/a} = \infty \quad \infty \quad \infty \quad \infty \quad \text{bonding}$$

