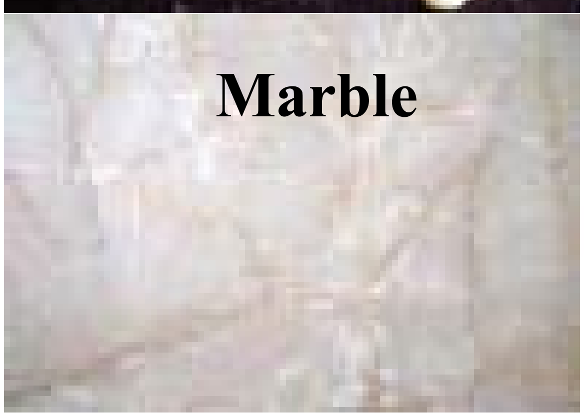
INORGANIC SOLIDS



Cement

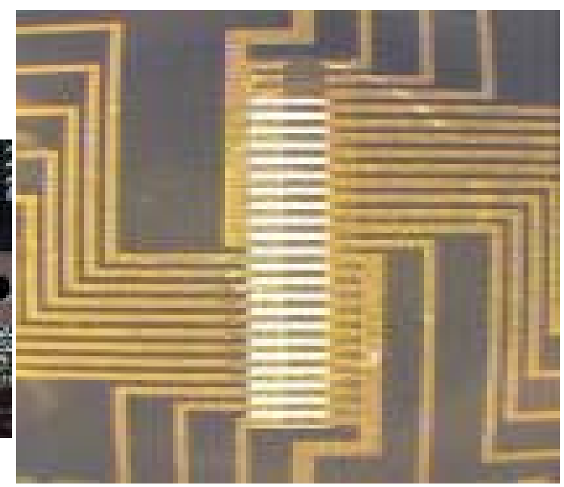
Pigment

Visible rays : 300 – 600 nm

Human Eyes
Resolution = 0.07 mm

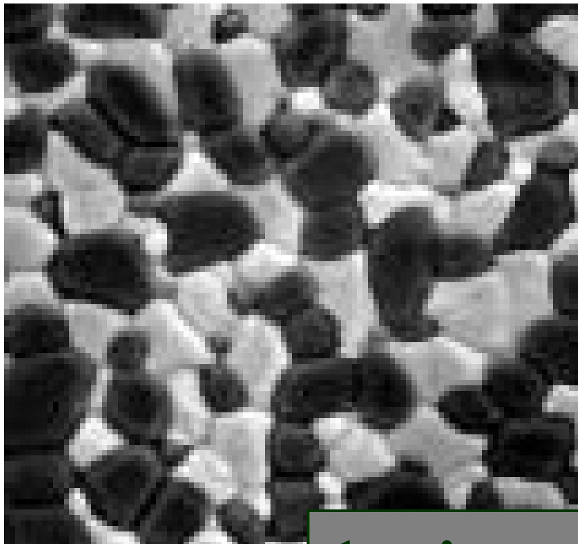
CD

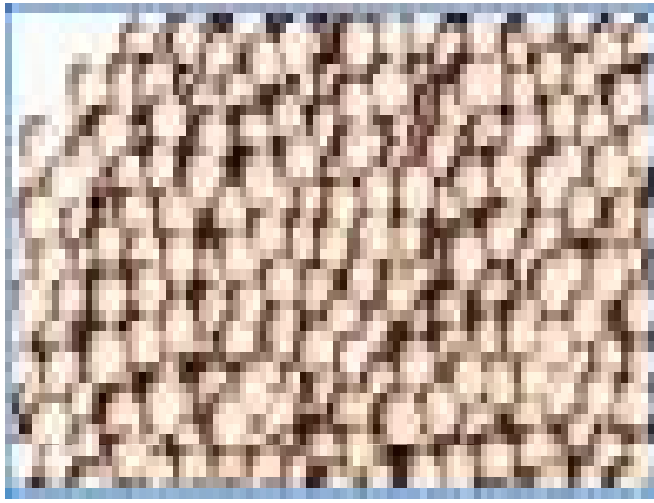
IC

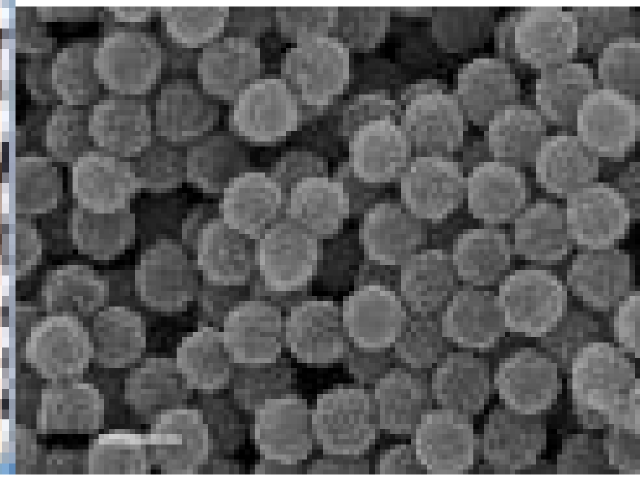


Inside a solid : how the grains look

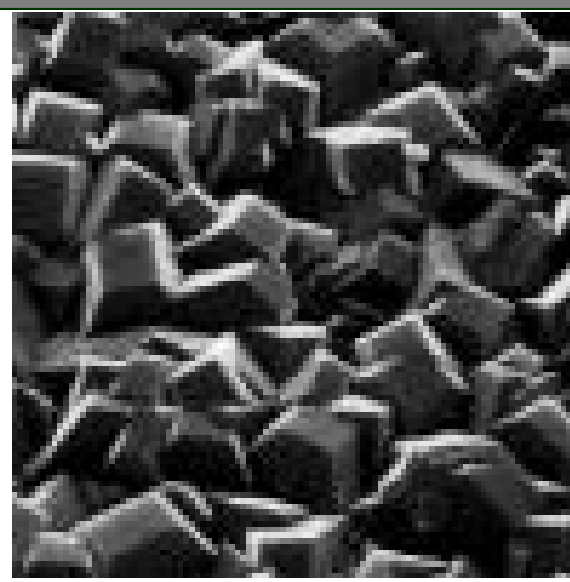
SEM 100nm

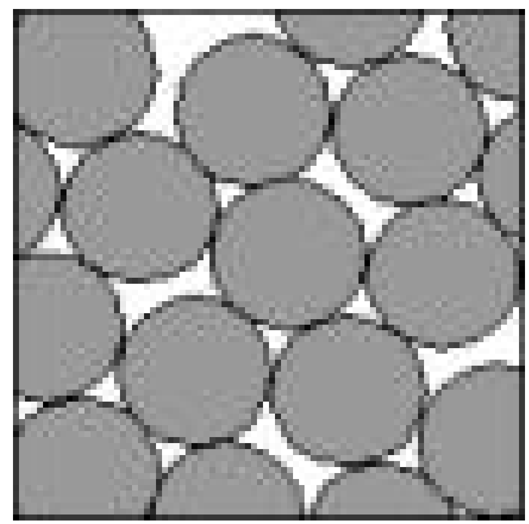




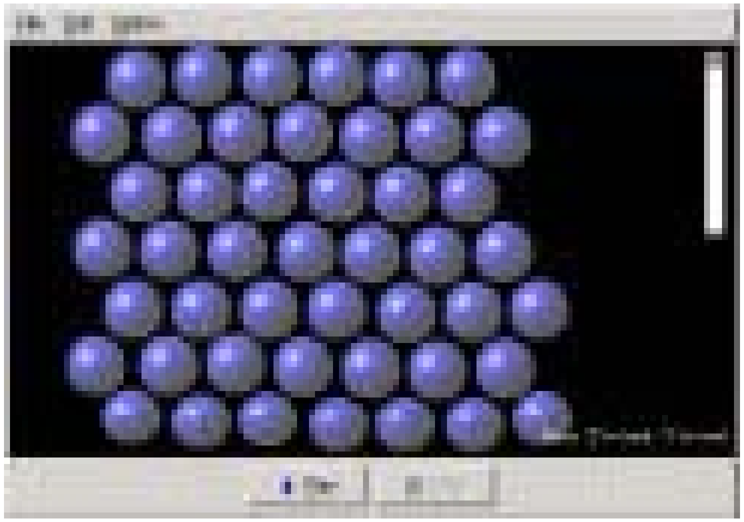


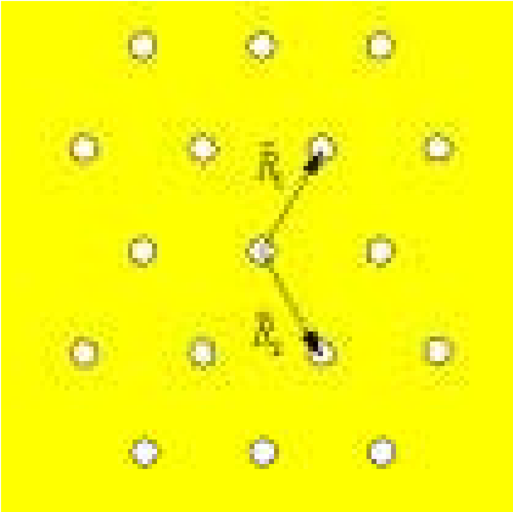
1 micron to 10 microns : Normal grains in solids
1 micron = 1/1000 mm

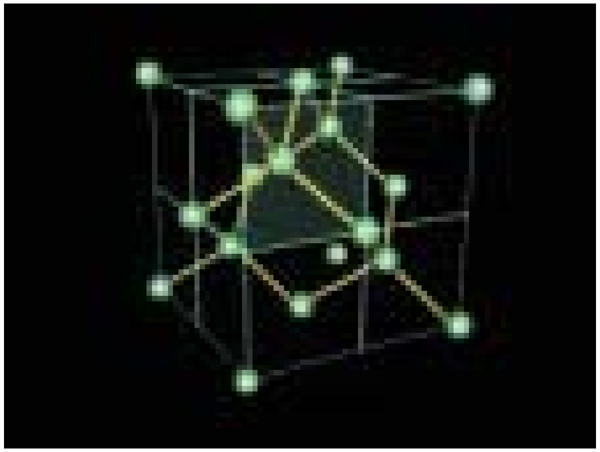




Ordered arrangement of atoms : crystalline solids

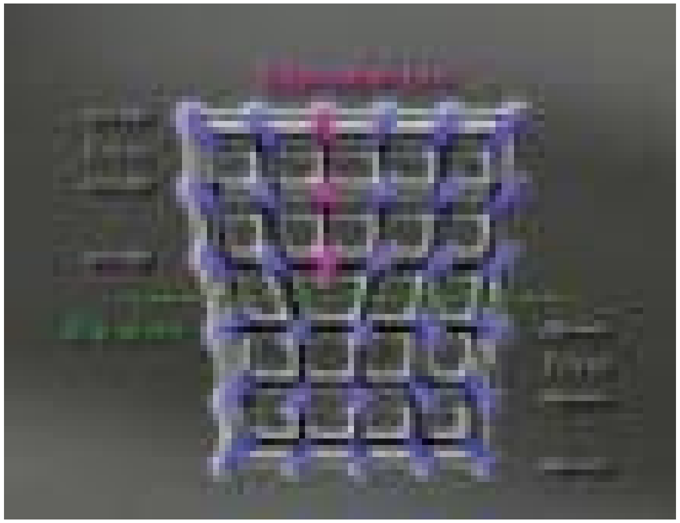






Diamond

ATOMIC LIMIT



1 atom(dia) : 0.1 – 0.2 nm
1 small crystal : ~10^{21} atoms

3-Dimensional

X-rays : 0.1 - 0.2 nm

Dislocation

Solids

AKG - 132

CRYSTALLINE

(Long range order)

NaCl, Diamond

Periodic arrangement of atoms/ions

over a large distance

~1000Å – 10,000Å or more

AMORPHOUS

(Short – range order)

Glass, polymers

(~10 - 40Å)

Entropy → Zero

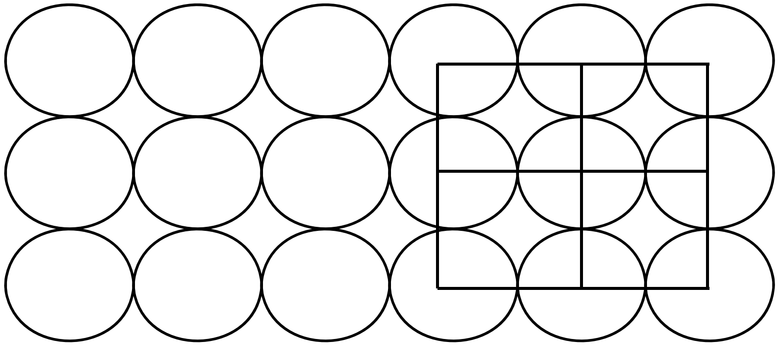
(Perfect order ---- Crystal)

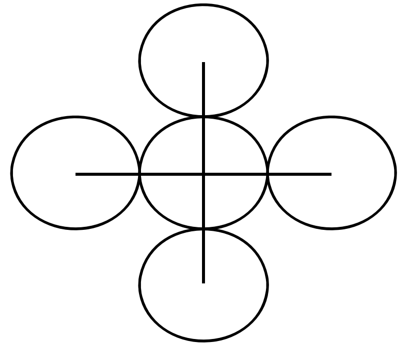
ΔH should be –ve

ΔG = -ve

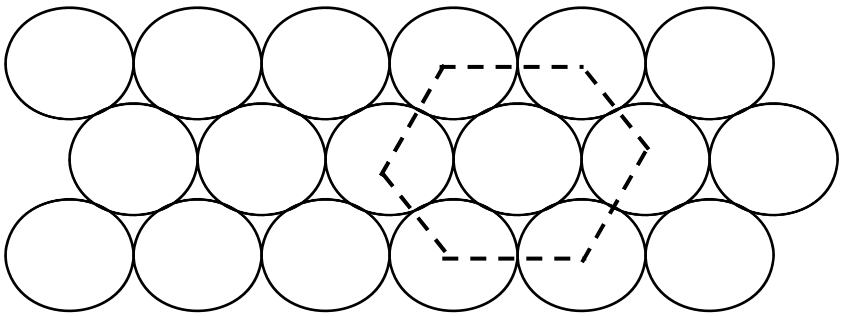
Packing of atoms / ions

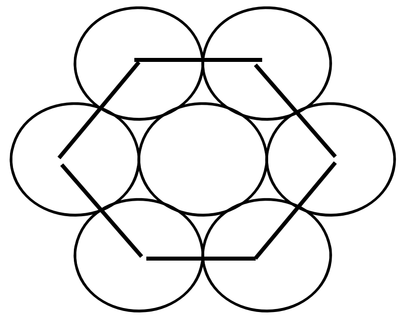
HCP CCP



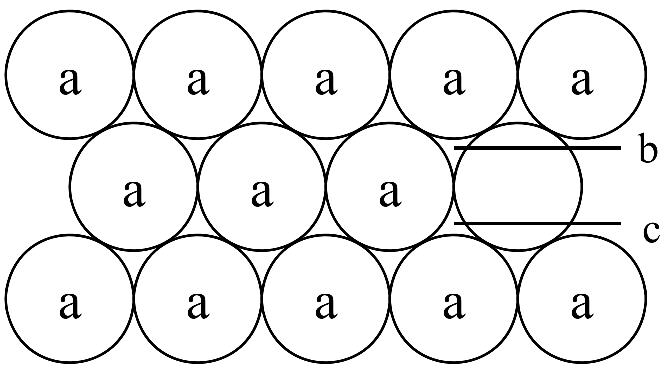


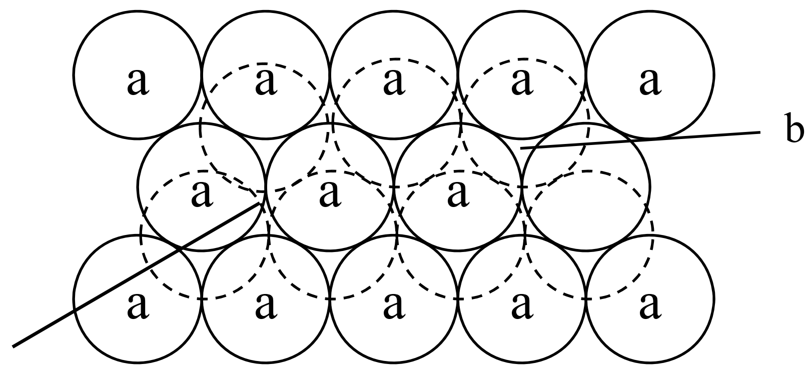
Square close packing (Layer)





Hexagonal close packing (Layer)





Tetrahedral holes

(octahedral hole)

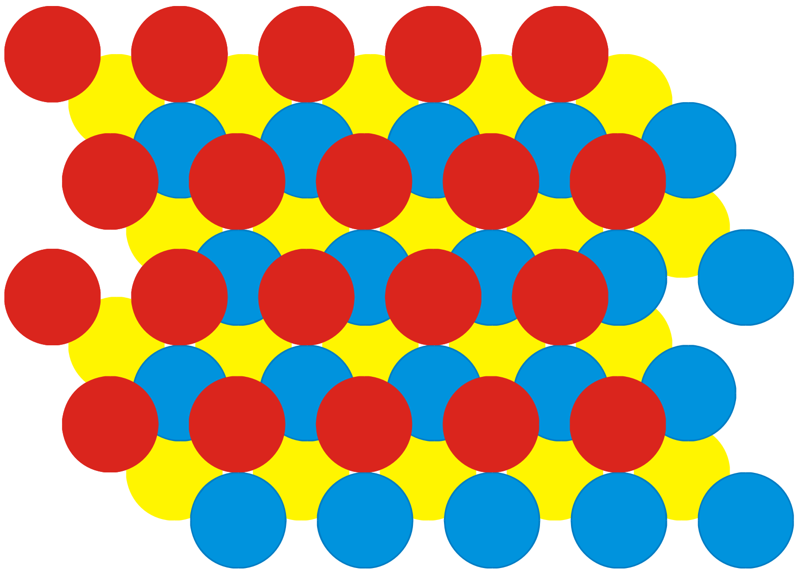
HCP

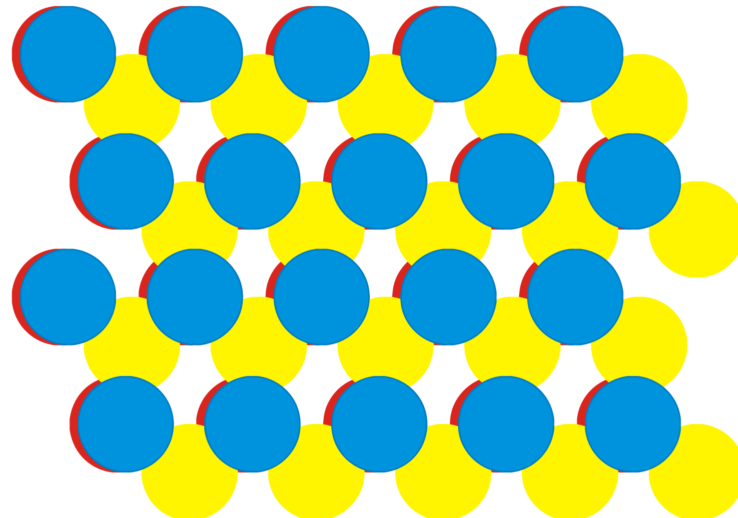
ABABABAB………

Close – packed structures: fcc and hcp type

ABCABC… arrangement

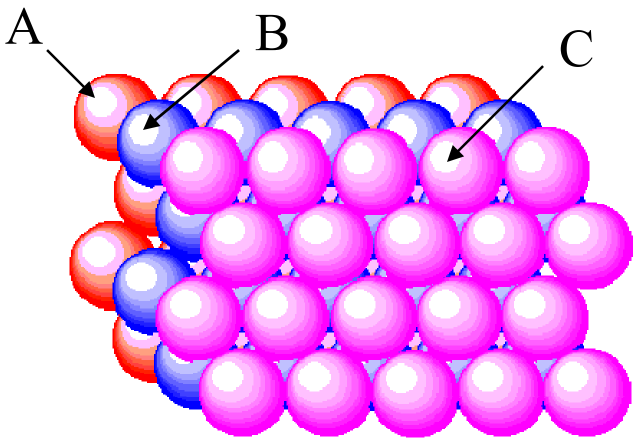
fcc





ABAB… arrangement

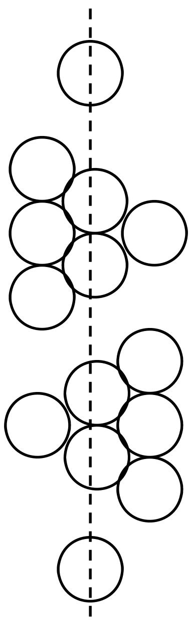
hcp



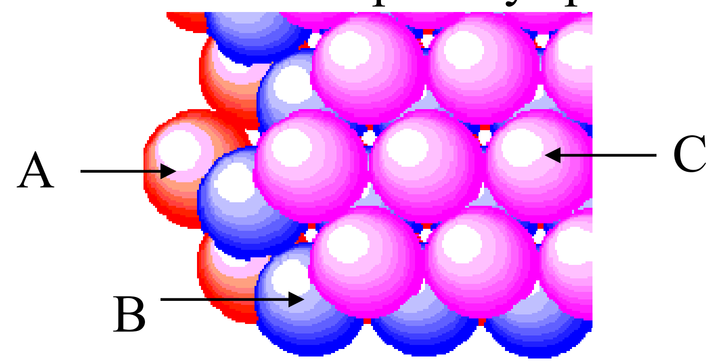
ABC ABC ………
Cubic Close packing (ccp)

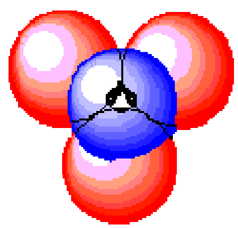
Close packed layers are parallel
------ diagonal across one face

74% of the total volume occupied by spheres

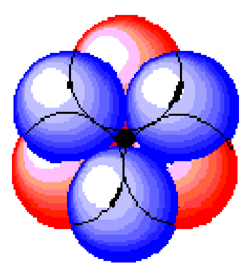


Layers of spheres
in CCP





Tetrahedral



Octahedral

CCP -- 2 tetra
1 oct
per sphere

Interstices

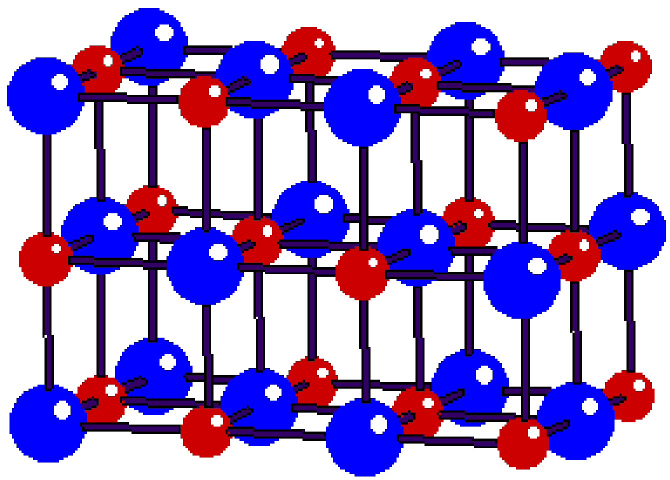
Ionic structures

AKG - 135

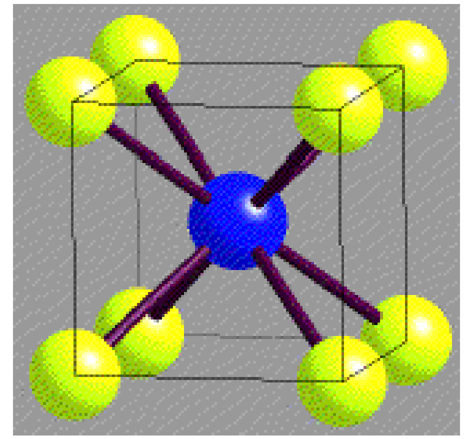
NaCl, CsCl

(Radius ratio rules)

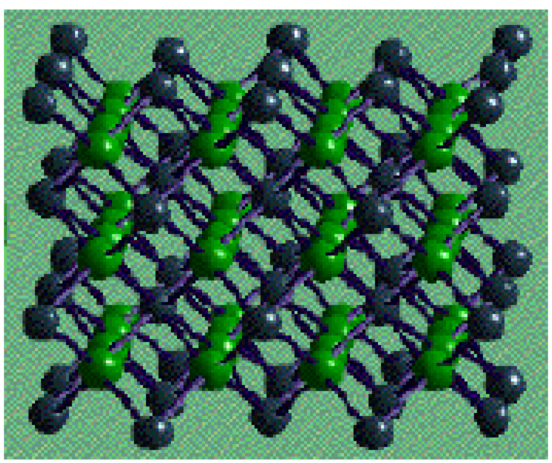
CsCl 8:8



NaCl (Rock Salt)

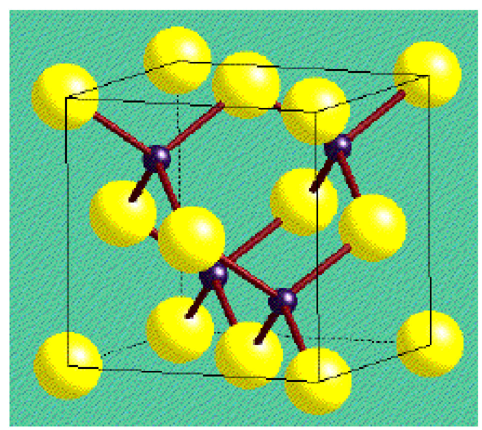


unit cell

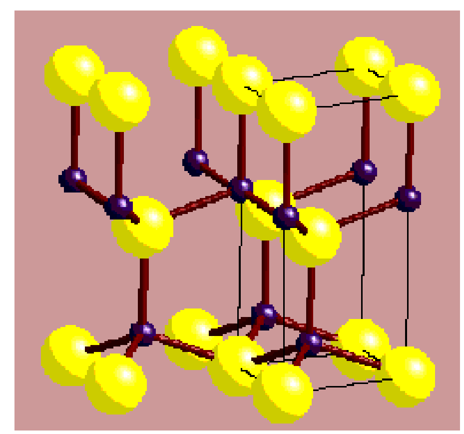


CaF_2 (Fluorite)

Zinc sulphide structures



Sphalerite

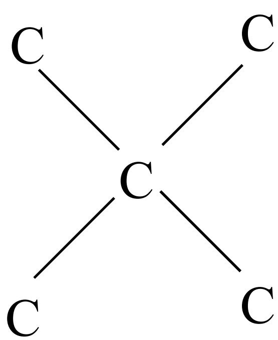


Wurtzite

COVALENT SOLIDS

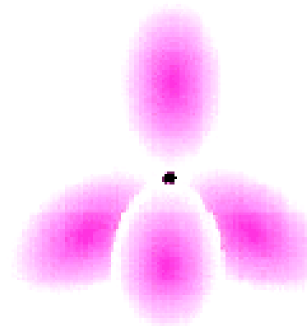
Diamond

As Sphalerite ZnS



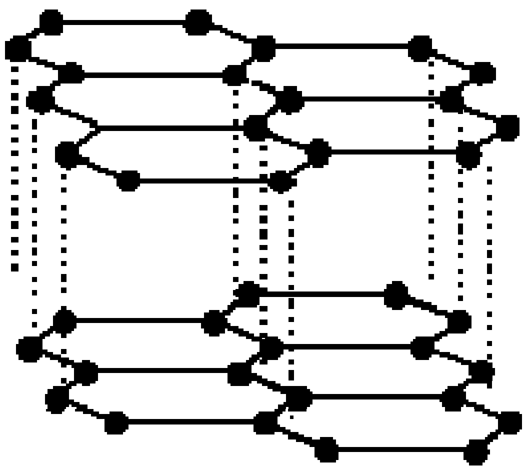
C.C.P. of ‘C’
All tetrahedral sites are occupied by ‘C’

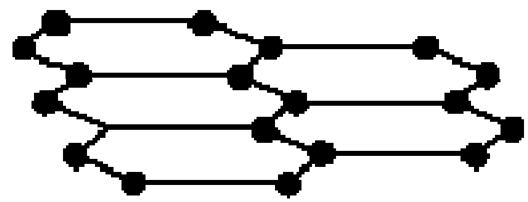
C – Sp^3 hybridized



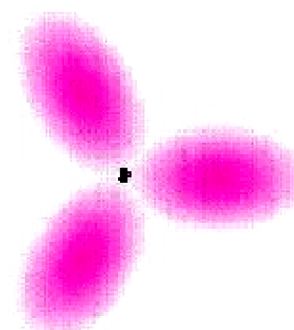
sp^3 hybrid orbitals
tetrahedral

Graphite Layered Solid





C – Sp^3 hybridized



sp^2 hybrid orbitals
triangular planar

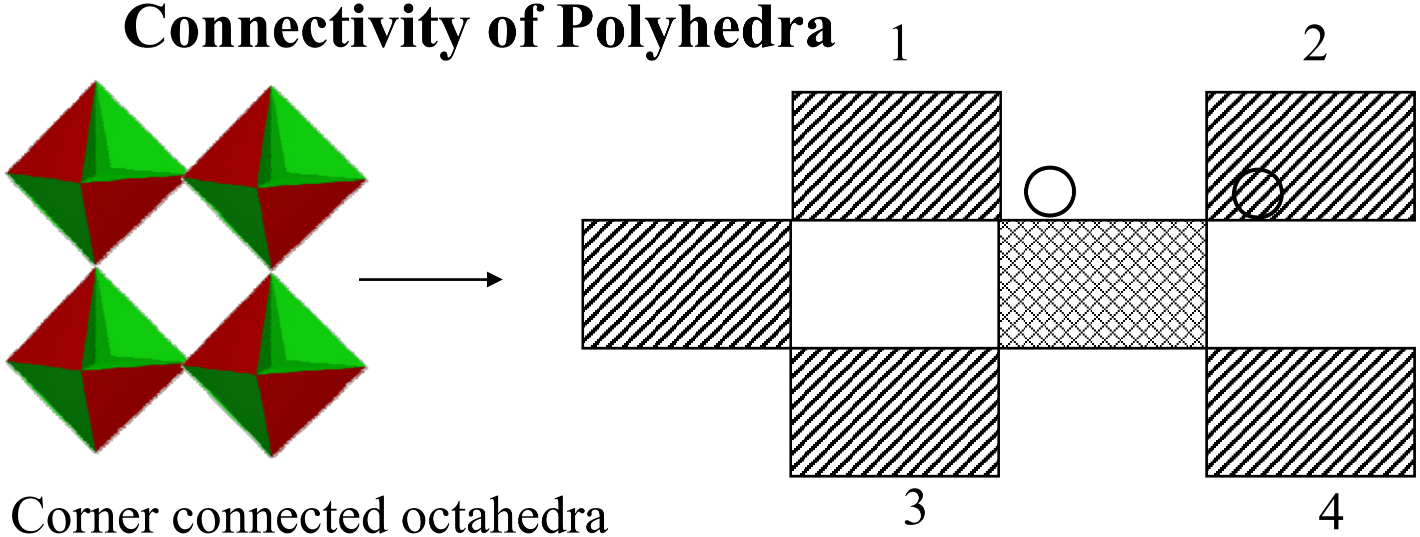
⟷ Weak interaction

(Vander Waals)

Molecular Solids
Benzene (L.T.)

Connectivity of Polyhedra

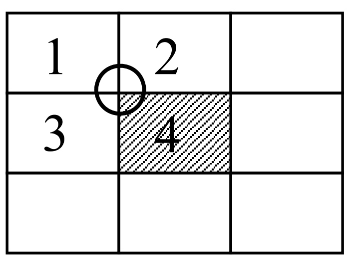
AKG - 137



Corner connected octahedra
Each octahedra ---- 6 other octahedra

Each atoms (X) shared by 2 octahedras

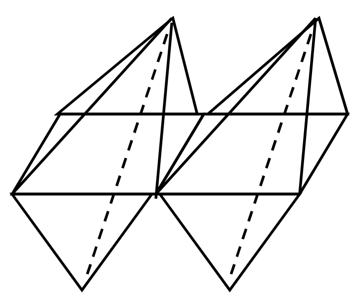
6 X (in one octahedra) $\rightarrow$ X_3



Each atom sharing -- 6 octahedra
6 atoms (in one octahedra) ---- X : Not possible

Edge- shared octahedra

Layers of edge-shared octahedra



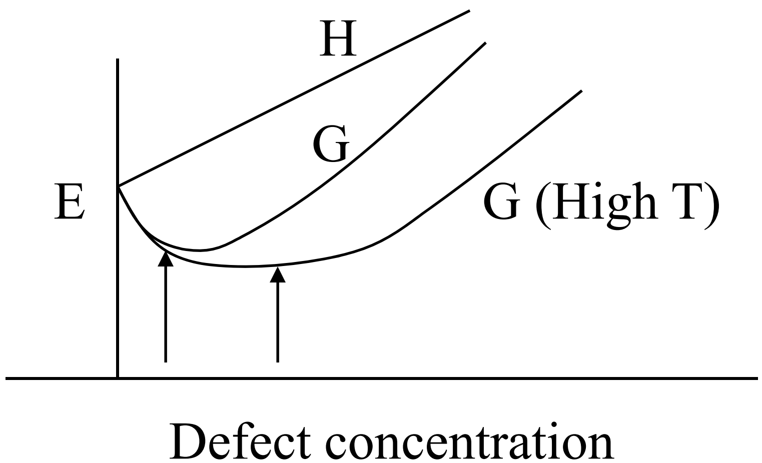
4 atoms share 4 octahedra ---Plane
2 atoms unshared (2X)
$\rightarrow$ X_3

Defects in Solids

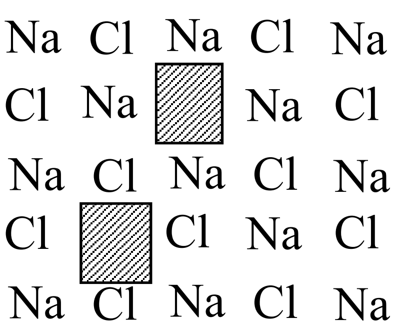
AKG - 138

INTRINSIC | EXTRINSIC (impurities)

Point defects | **Extended defects** (ordered defects)

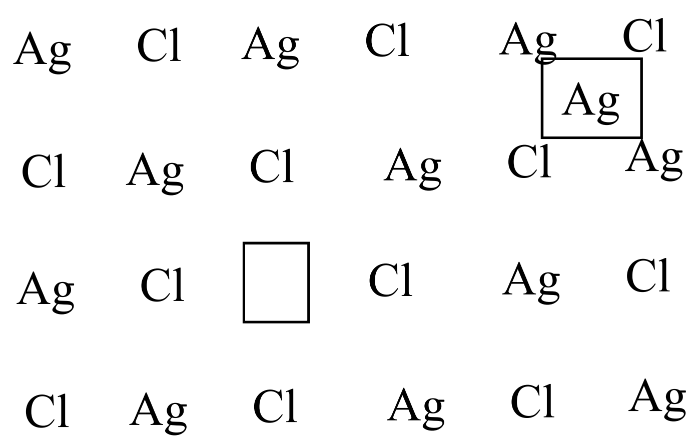


$G = H – TS$
Entropy increases (with defects)
Minimum shifts to higher defect
Concentration (increase in T)



Schottky defect
(Point defect)

Overall stoichiometry unaffected – equal Nos. of + & - defects

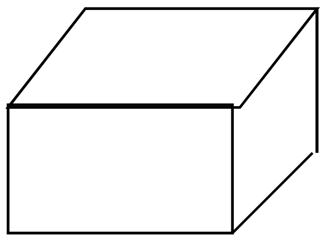


FRENKEL Defect
(Interstitial & occupied)

~ 1 defect/10^{14} formula unit in NaCl (130^{o}C)

Estimation of defects

--- Density measurements



TiO   Ti : O   1 : 1

ρ = 4.92 g/cc (experimental density)

a = 4.18Å   Mass = 63.88

Z = 4   Mass per unit cell = 63.88 x 4

$\rho = M/V = 5.81\ g/cm^{-3}$ Which is greater than measured ρ

Vacancies present

— Conductivity measurements

Extrinsic Point defects

As in Si

↓

Increase in e^-
(n-type semiconductor)

Ca in ZrO_2
Y in ZrO_2

| Ca^{2+}
| Y^{3+}
| Zr^{4+}

↓

O^{2-} ion vacancies

Ca-stabilised ZrO_2
Y-stabilised ZrO_2

(Solid electrolyte Oxygen ion)

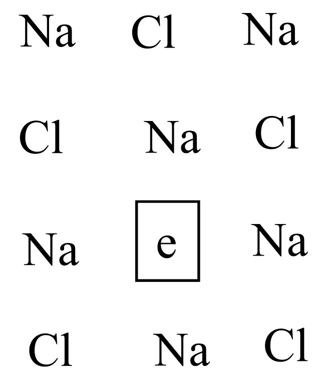
Colour Centre (F-center)

AKG - 140

(Extrinsic point defect)

Farbenzenter

Alkali halide —Heated in vapor of alkali metal→

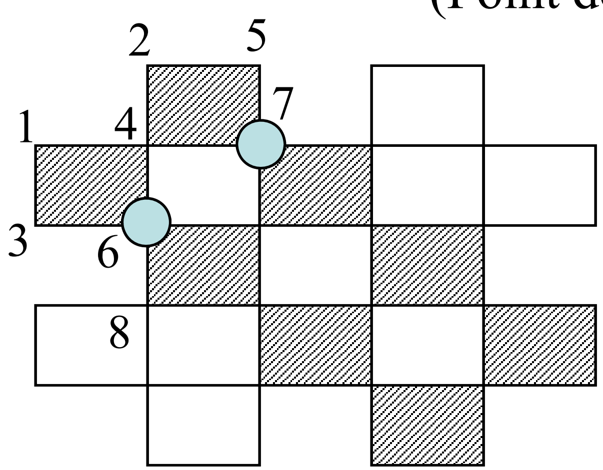


A e^- in halide ion vacancy

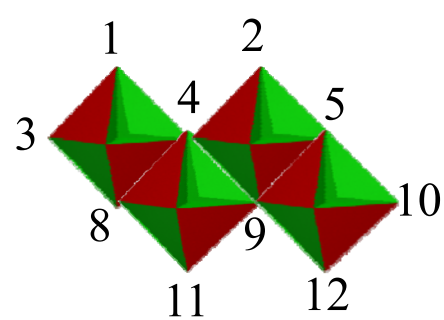
Excitation of e- → e- in a box → quantized energy levels → Colour

Extended defects

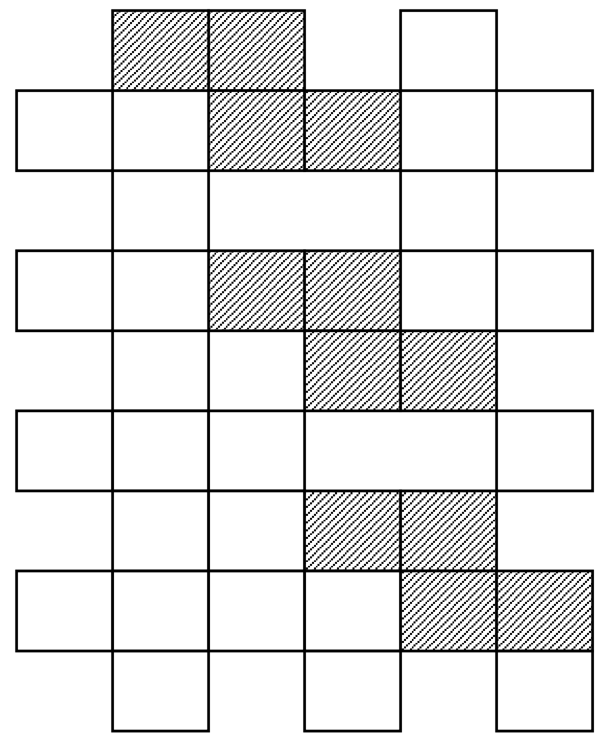
Clustering of defects → Line defect
(Point defect)



Corner-shared octahedra



Edge-shared octahedra



Crystallographic shear plane

Non-stoichiometry

AKG - 141

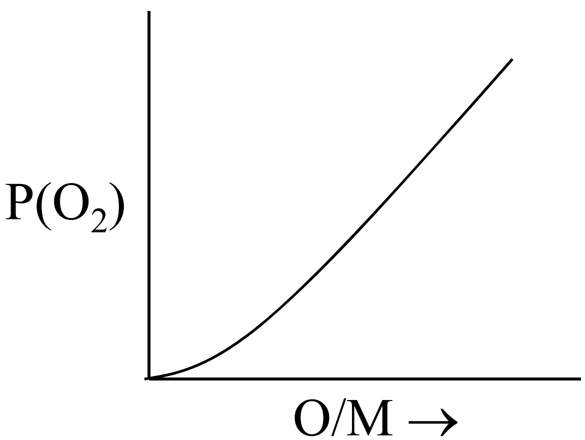
--- Variable composition

Wuestite — FeO (nominal composition)

$Fe_{0.89}O \rightarrow Fe_{0.96}O$

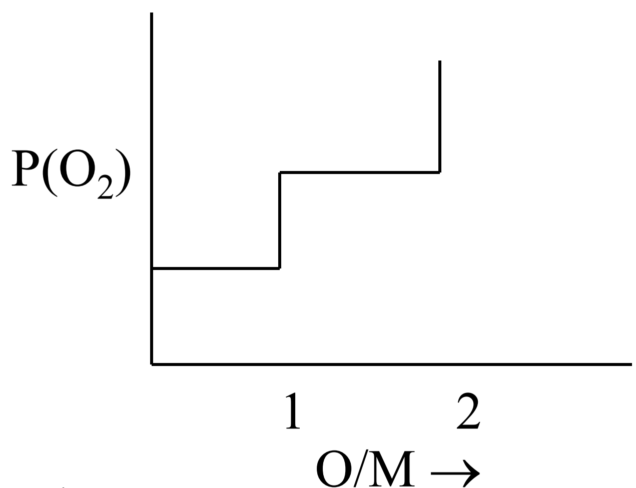
Rock-salt (NaCl structure)

TiHx	$(1 \leq x \leq 2)$
ZrHx	$(1.5 < x \leq 1.6)$
TiOx	$(0.7 \leq x < 1.25)$
VOx	$(0.9 \leq x \leq 1.2)$



Non-stoichiometric compound

$F = C-P+1$
$= 2-2+1 = 1$

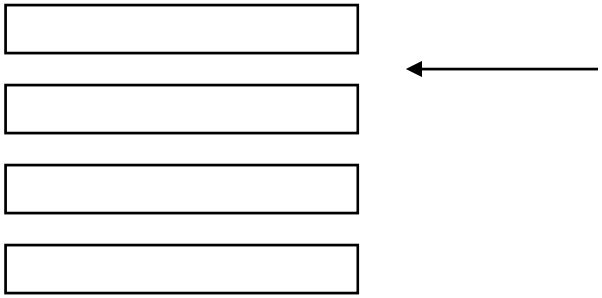


F (No. of degrees of freedom)

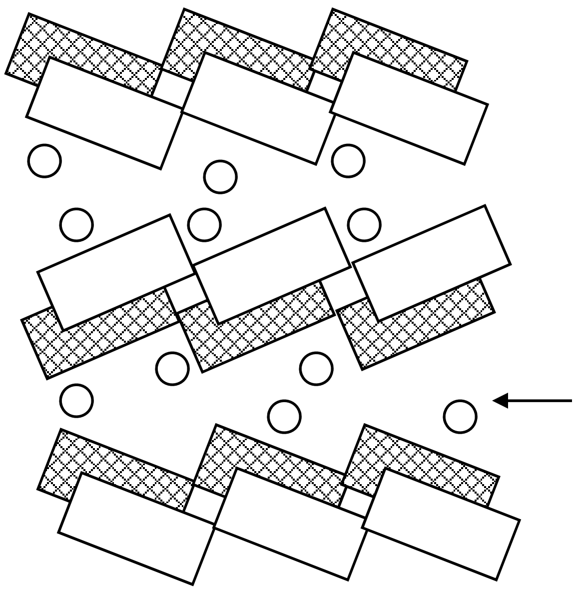
MO and MO_2

$F = C-P+1$
$= 2-3+1$
$= 0$

LAYERED SOLIDS



Strongly bonded layers
(weak interaction between layers)



Li ions

$LiTiNbO_5$

(TiO_6 & NbO_6 octahedra forming layers)

Graphite, FeOCl, TaS_2	Uncharged layers
$LaCoO_2$ Clays: montmorillonite $LiNbTiO_5$	Negatively charged layers -- cations
Hydrotalcites	Positively charged layers -- anions

Ion-Exchange Intercalation

INTERCALATION REACTIONS

—Reactions of Solids — General molecule or ion — inserted into a Solid lattice

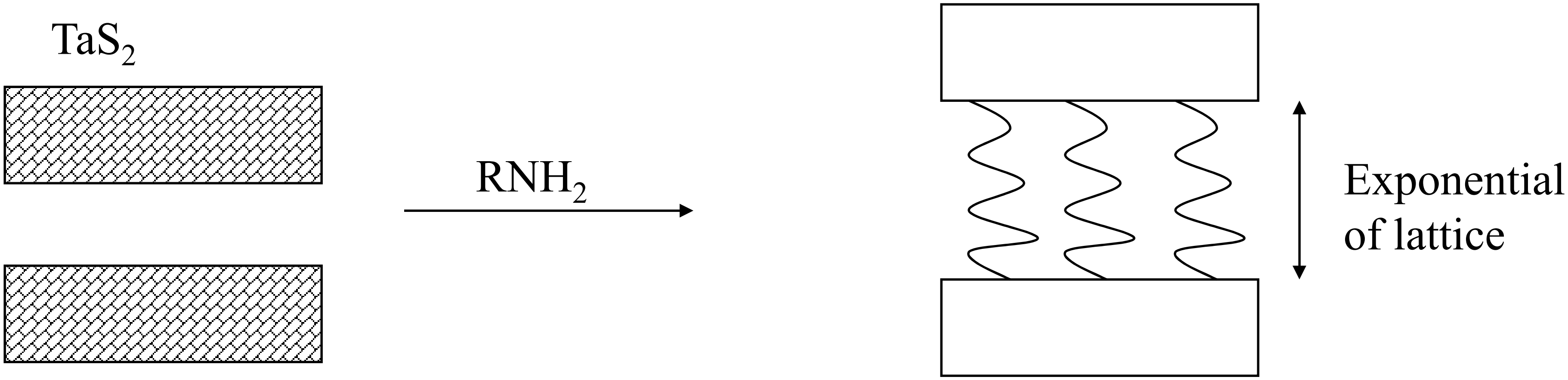
(No major change in structure of solid)

1. Strong Covalent network of atoms
   — remains unchanged
2. Vacant sites — interconnected
   → Diffusion of Guest species

Layered structures:

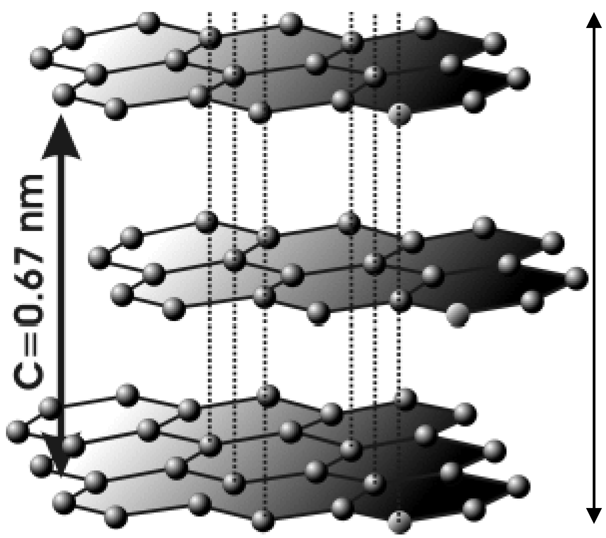
Natural — Van der Waals interaction between layers — interlayer space
— empty lattice sites

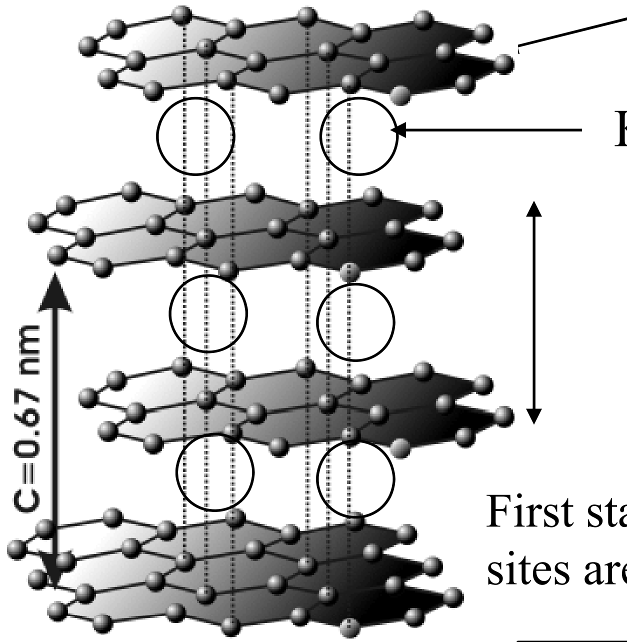
Charged compounds — weak electrostatic force — interlayer sites — partially or completely filled with



INTERCALATION of ‘K’ in Graphite

Staging of Graphite

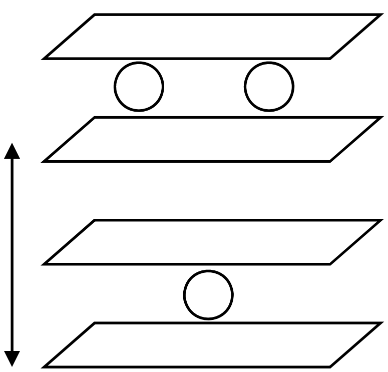




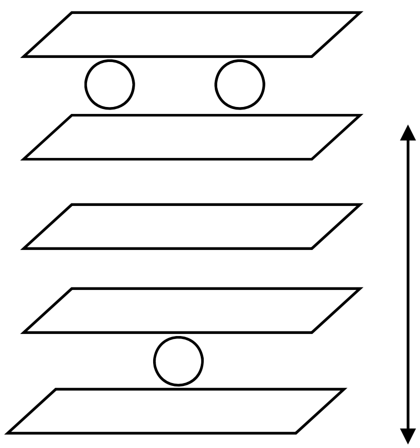
C (graphite) + K (vapour) (64^oC)

First stage (all inter layer sites are filled)

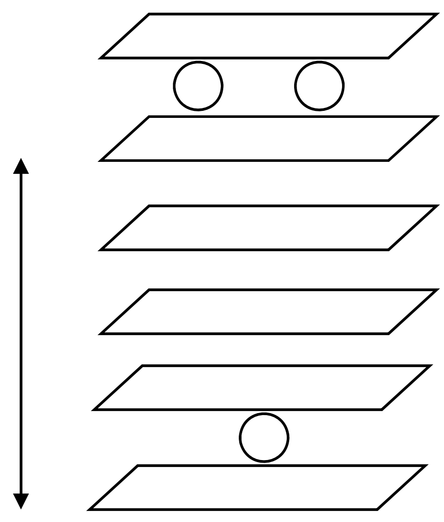
C_8 k



2nd C_{24} k



3rd C_{36} k



4th C_{48} k

C_8 Br

Layers are +vely charged

ZEOLITES

ZEO to boil

Lith Stone

Natural Zeolite

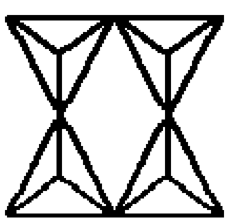
↓ **evolve water (heated)**

$[M^{n+}]_{x/n}[AlO_2]_x[SiO_2]_{1-x}$

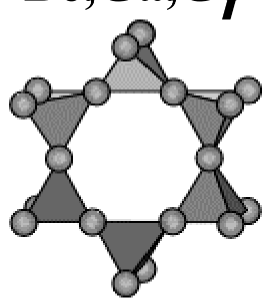
Framework Structures (mainly Aluminosilicates) — **Cavities Channels**

for charge balance

Tetrahedra (MO$_4$) of Al,Si,B,P Be,Ga,Ge

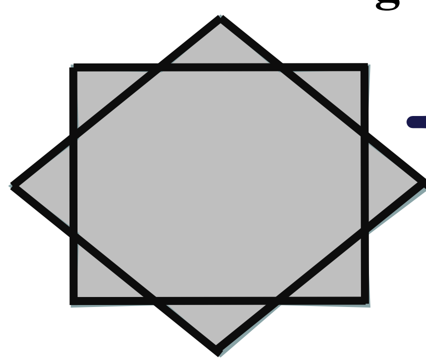


4 -



6 -

Linked together

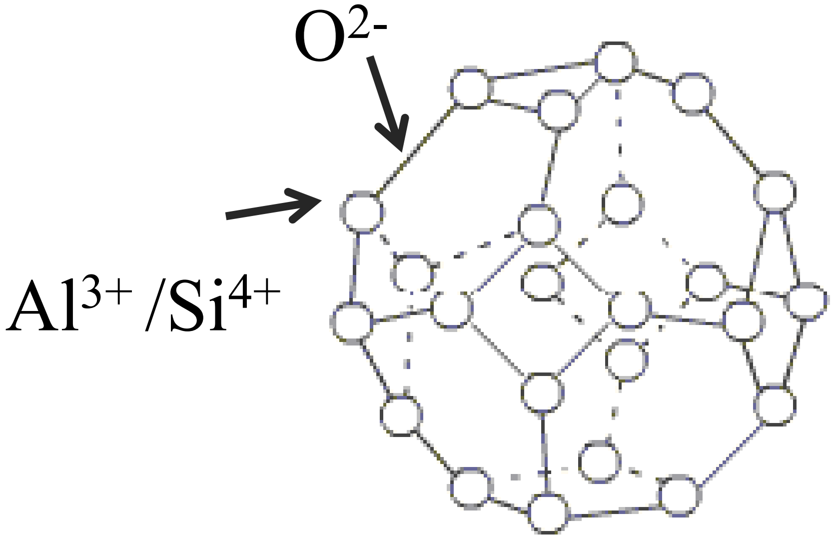


8 – membered ring (tetrahedra)

Lowenstein's Rule

Al — O — Si ✓

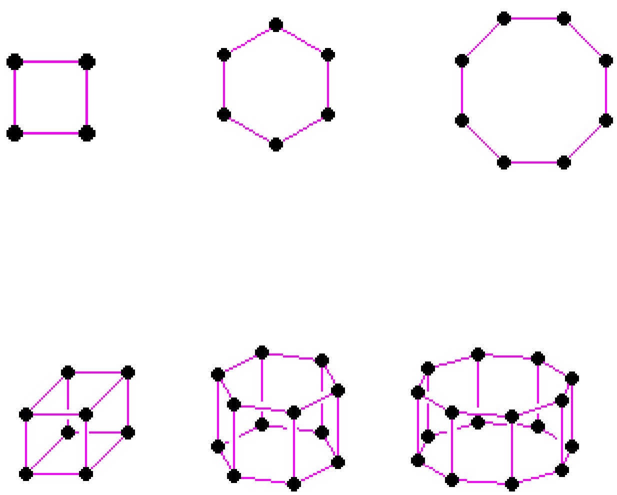
Al — O — Al ✗



Sodalite cage (β – cage)

6 - & 4 – membered rings

Building Blocks for other Zeolites



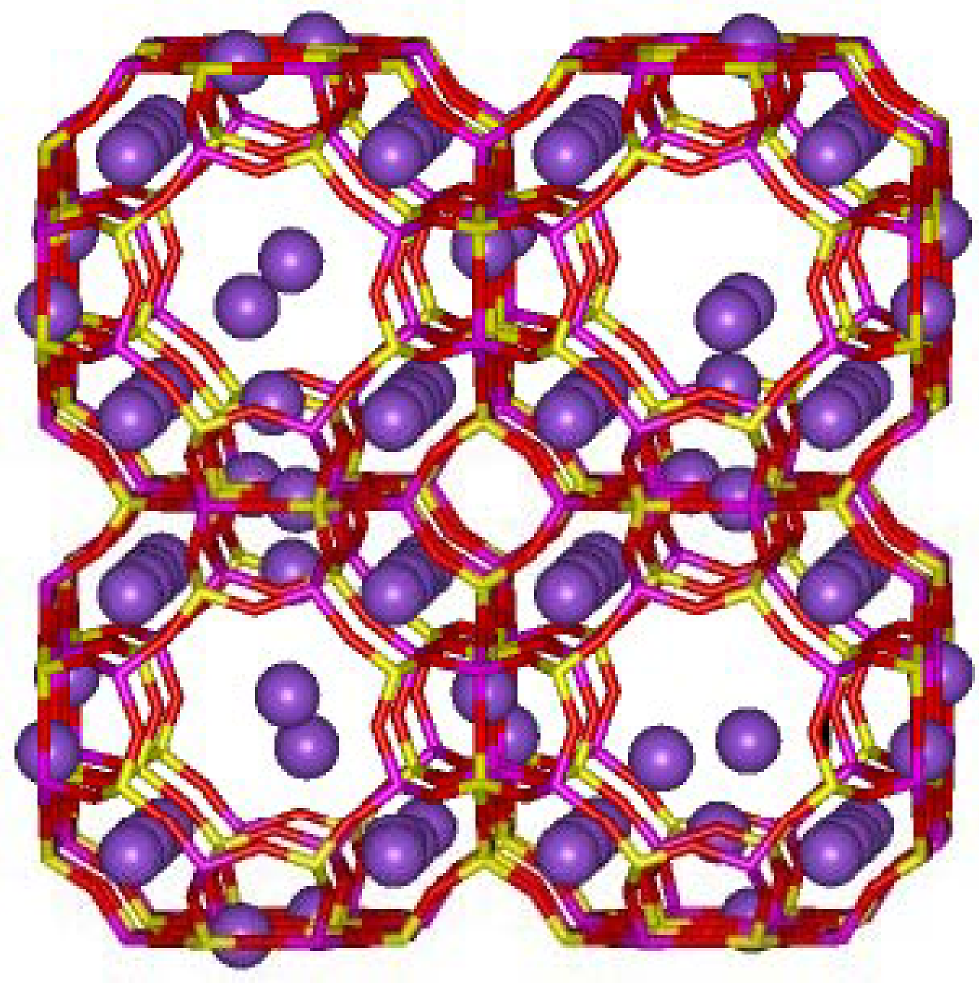
Joining 4, 6 or 8 - membered rings to other rings

Zeolite A

Sodalite cages

Linked by 4 – membered rings

Faujasite – Six membered linker



Properties of Zeolites :

1. Absorption of small molecules (size and shape selective) .

Zeolite A – water/ **not** ethanol.

More Al^{+3} / Si^{+4} ratio → More cation

Zeolite A (1:1) - Better absorption of hydrophiles

Hydrophobic Zeolite (high Si^{+4} content) –

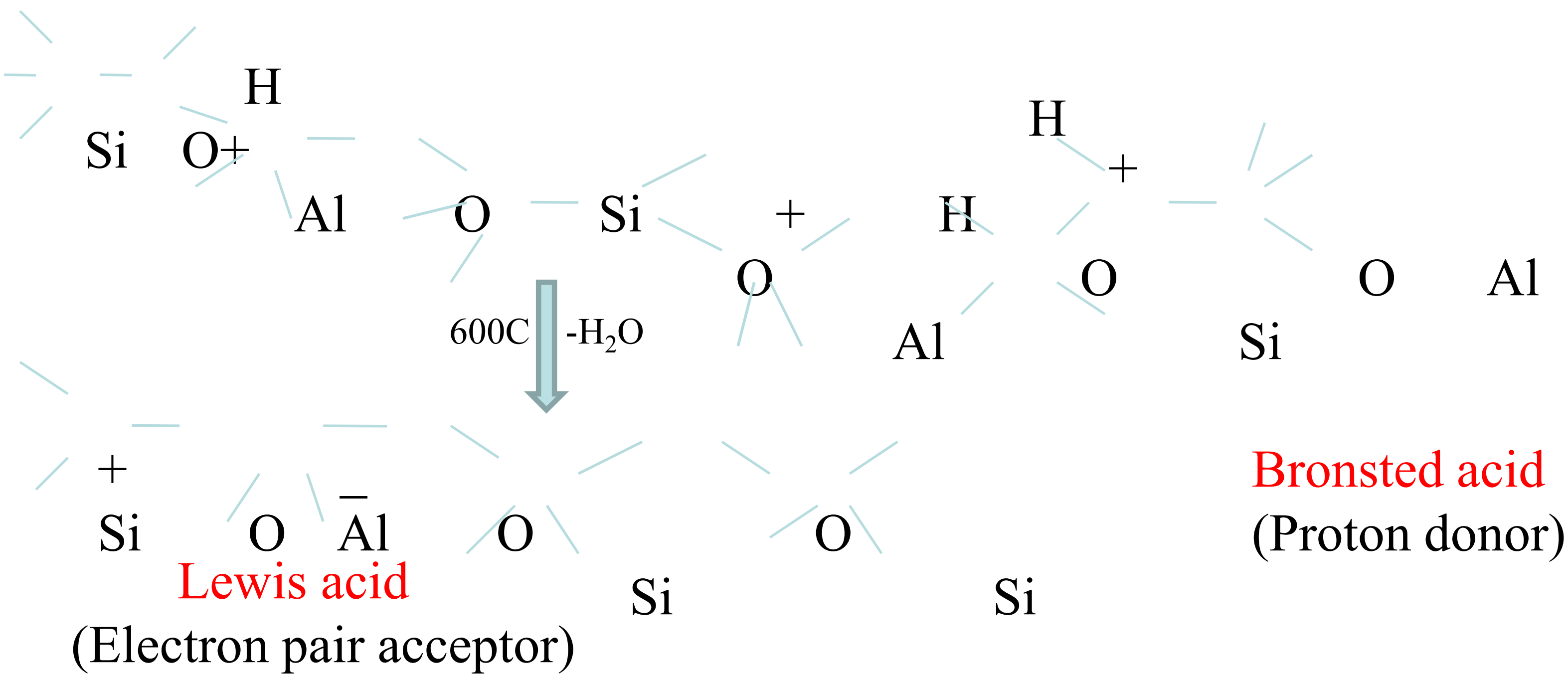
Absorbs non-polar, benzene etc.

2. Ion – Exchange (Wide application)

$$Na - \text{Zeolite A} + \tfrac{1}{2}\, Ca^{+2} \rightarrow Ca_{0.5}\ \text{Zeolite A} + Na^{+}$$

(Removes hardness of water
Water softening
Radioactive Sr^{+2} / Cs^{+} removal)

3. Catalysis : H – Zeolites (Acidic derivatives)



- Rearrangements / Dehydration (Isomerization)

- Shape selective catalysis
  Example . CH_3-C_6H_5-CH_3

The zeolite, ZSM -5 has the molecular formula, $Na_3Al_3Si_{93}O_{192}$.

ZSM -5 $Na_3Al_3Si_{93}O_{192} \equiv Na_3(AlO_2)_3(SiO_2)_{93}$, Al :Si = 1: 31 ratio

synthesis is carried out in the presence of $[(n\text{-Propyl})_4N]OH$ as template

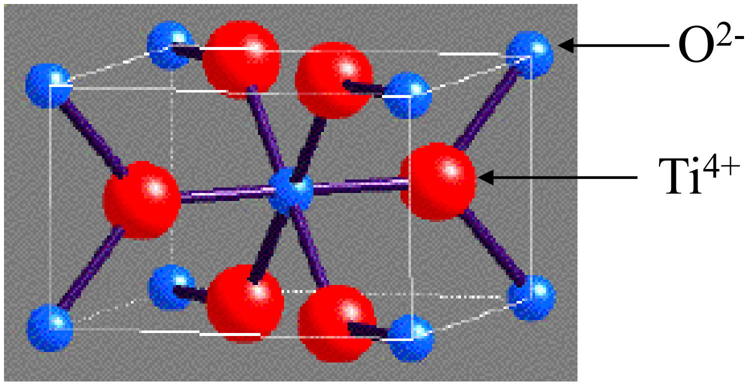
$$31\ Na_2SiO_3 + Al(OH)_3 \xrightarrow[\text{100-200 °C followed by heating at 500 °C}]{(nPr)_4NOH} \text{Zeolite ZSM-5}$$

TRANSITION METAL OXIDES

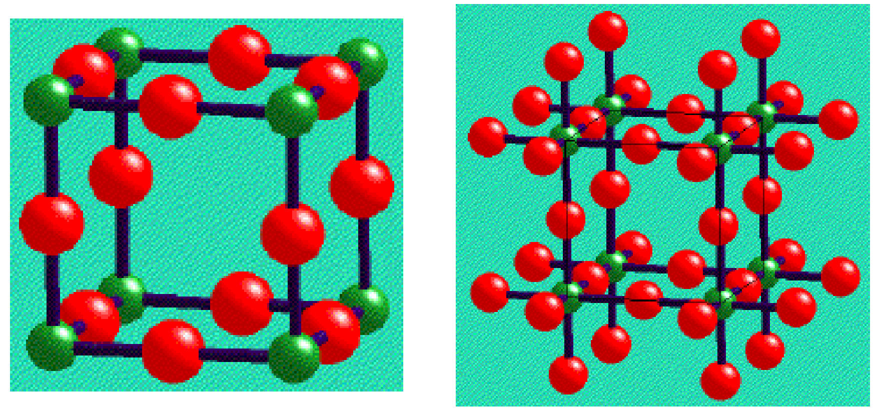
AKG – 14 5

Rock Salt Structure (NaCl-type)

TiO ………… NiO (First row transition metal oxides)



ReO_3



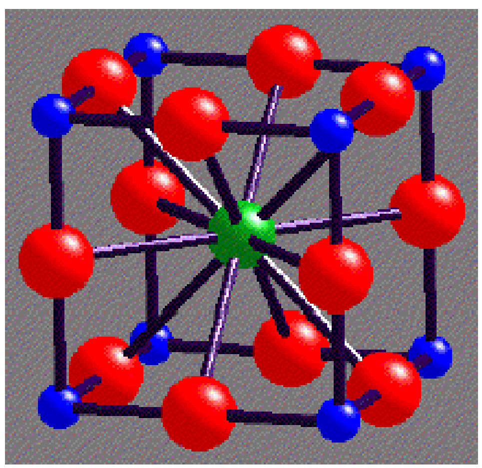
ReO_6 octahedra; corner connected

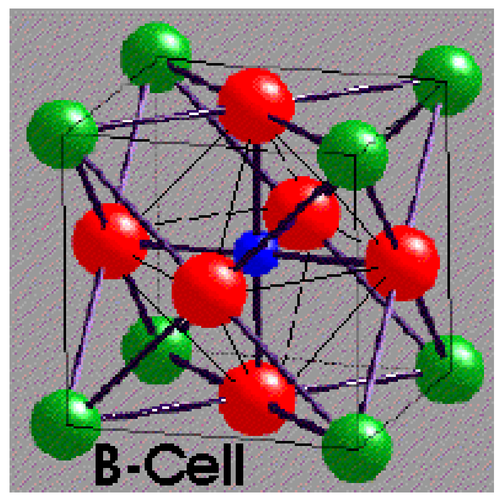
Perovskite Structure

(ABO_3)

A – 12 coordinated
B – 6 coordinated

$BaTiO_3$
$CaTiO_3$
$LaMnO_3$

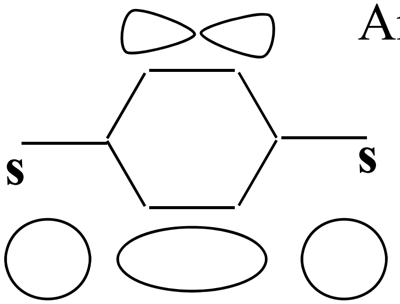


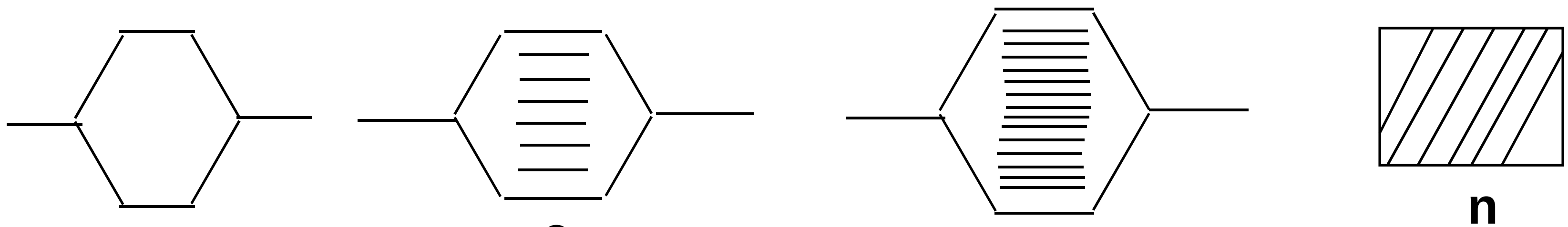


BO_6 octahedra;
(T. metal ion - B)

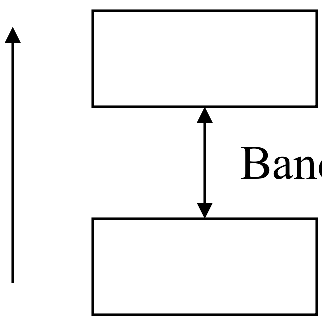
From Bonds (Molecules) to Bands (Solids)

AKG - 146





Formation of ‘n’ molecular orbitals from n atomic orbitals



material	Band gap (eV)
C (diamond)	6
NaCl	9
Si	1
Ge	0.7
GaAs	1.4

Insulators (High band gap): C (diamond), NaCl

Semi-conductors: Si, Ge, GaAs (Metals partially filled bands)

300K

Copper : 10^{7} Ohm^{-1} cm^{-1}

Doped silicon (n or p) : 10^{2} Ohm^{-1} cm^{-1}

Silicon : 10^{-7} Ohm^{-1} cm^{-1}

Diamond : 10^{-9} Ohm^{-1} cm^{-1}

Nylon : 10^{-9} Ohm^{-1} cm^{-1}

Mica : 10^{-11} Ohm^{-1} cm^{-1}

PVC : 10^{-13} Ohm^{-1} cm^{-1}

Metal

Resistivity

Insulator

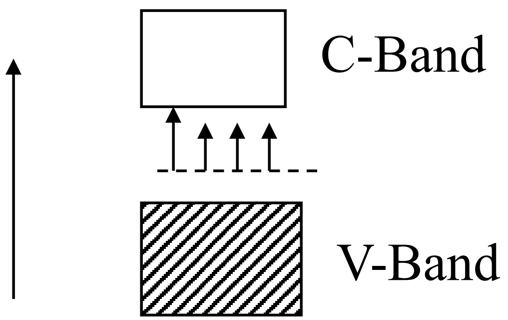
Metals/ Semiconductors/ Insulators

AKG - 147

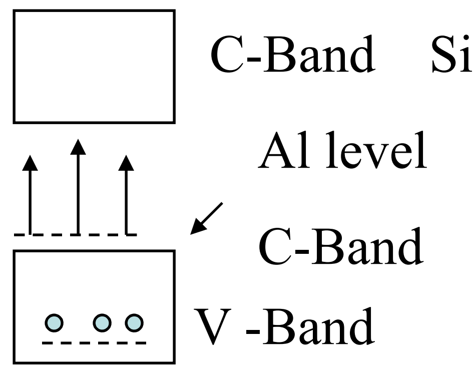
- Ability to conduct electricity → Flow of electrons (holes)
- Band gap low (intrinsic semiconductor)

  Doping → ‘P’ in Si (n- type)

  ‘Al’ in Si (p- type) | Extrinsic semiconductor

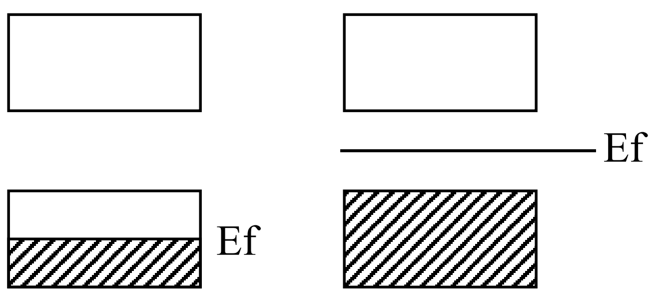


‘p’ – doped in Si
n-type



(Al C-Band is lower than Si)
— p-type

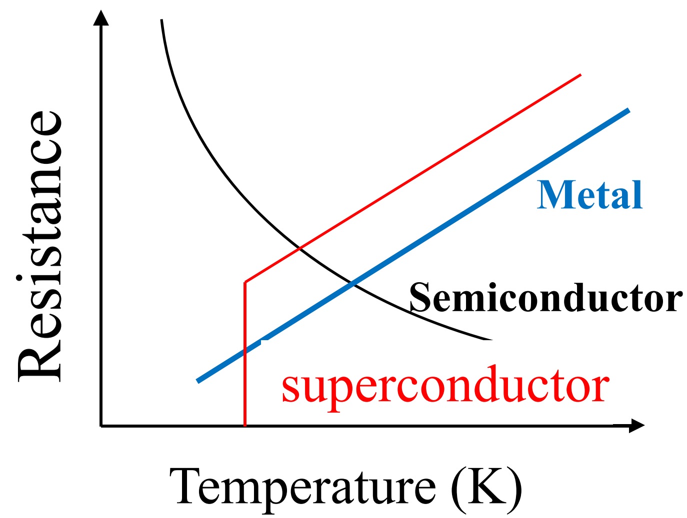
Ef = Fermi energy
(Fermi edges)



Metal
(Partially filled band)

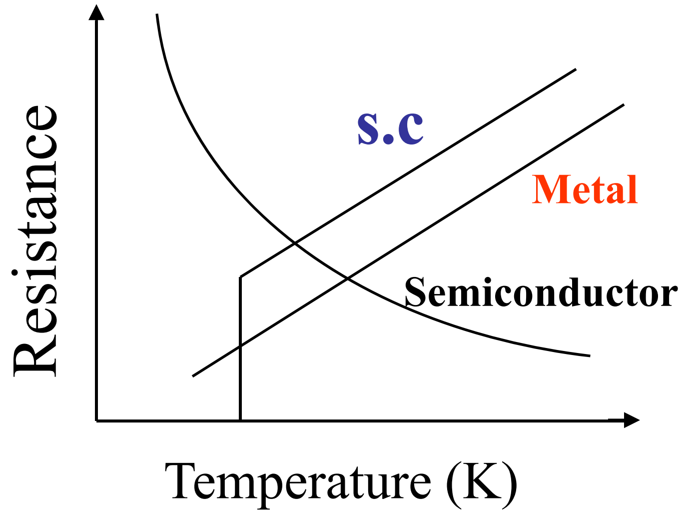
Semiconductor

$R = \rho l/A$



SUPERCONDUCTIVITY

Kammerlingh Onnes 1911 (Nobel 1)

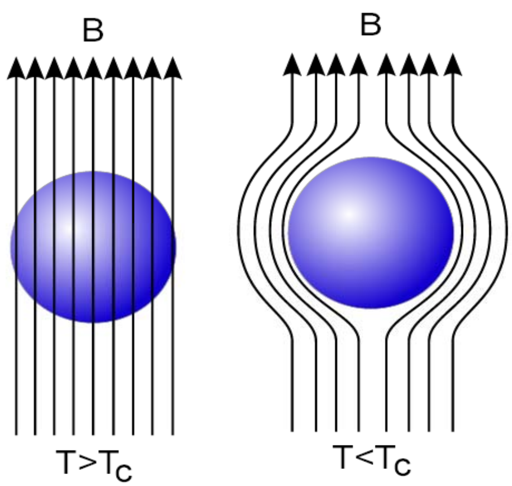


Ideal Superconductors

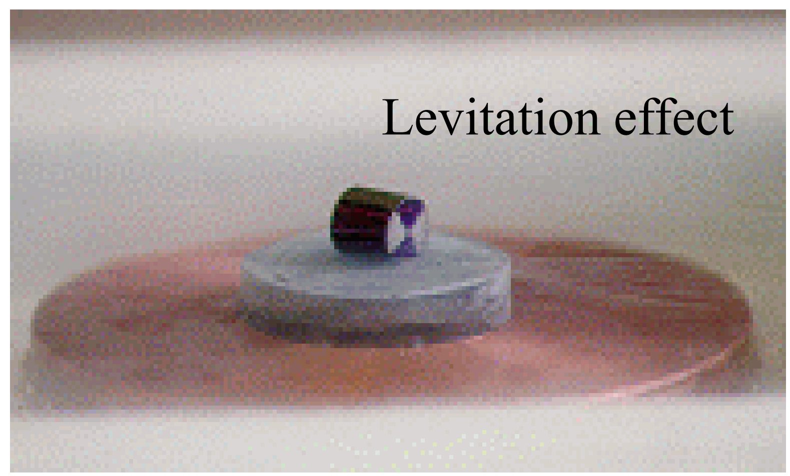
Zero Electrical Resistance (Perfect Conductor)
Zero Magnetic Induction (Perfect Diamagnet)

Macroscopic quantum phenomena

Superconductivity electrical resistance
Superfluidity viscosity



Meissner effect



100 years of superconductivity

APPLICATIONS OF SUPERCONDUCTORS

1. Medical Industry

MRI Exploits the high magnetic fields expelled by superconducting wires for medical applications

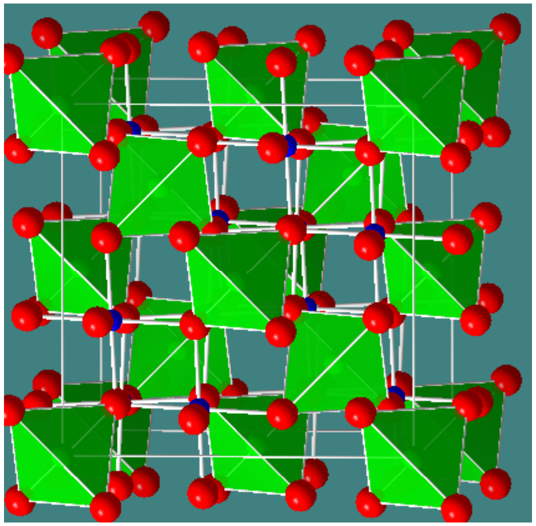
2. Transportation Industry

Superconductor coils create strong magnetic fields that produce the effect of levitation 500 miles per hour / small consumption of energy

3. Electric Power Industry

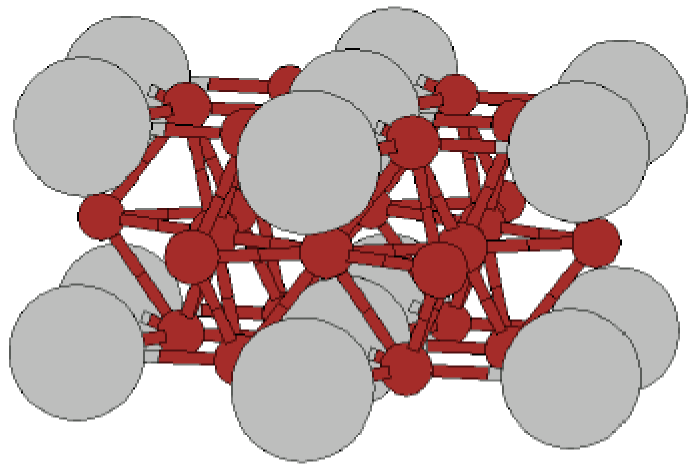
HTS power cables can carry two to ten times more power in equally or smaller sized cables

Applications of Inorganic Solids



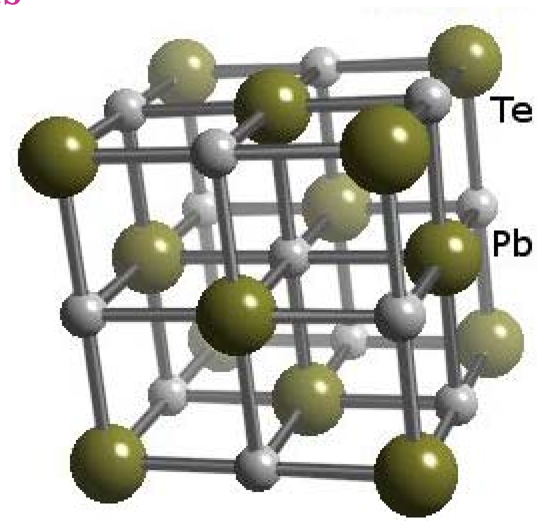
$LiMn_2O_4$ Spinel

Battery material



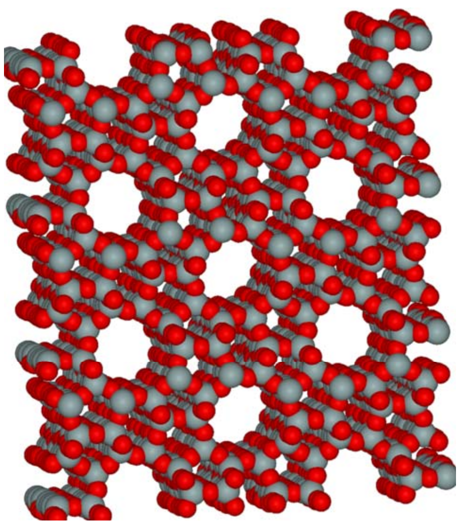
$LaNi_5$

Hydrogen storage material



PbTe

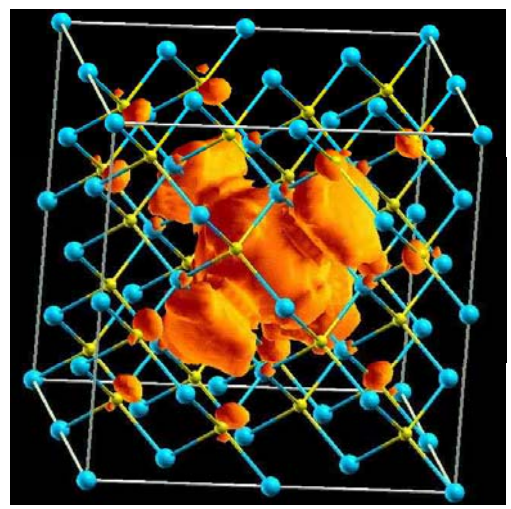
Thermoelectric



Zeolite

Catalysts

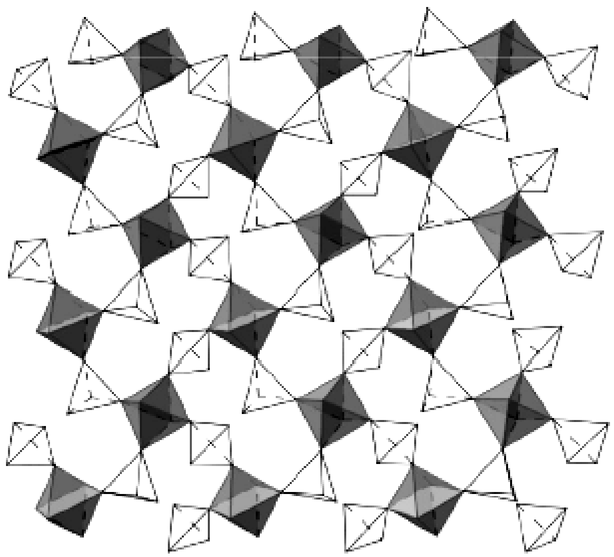
Mol. sieves



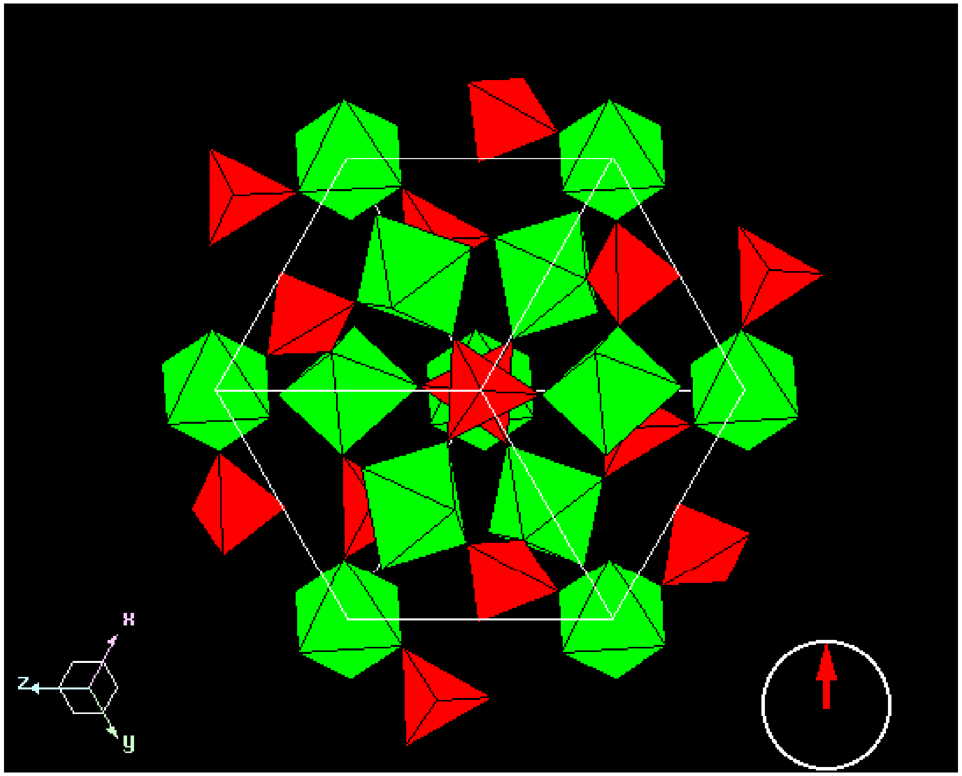
$Cu_{1-X}S$ (spintronics)

ZrW_2O_8 (0.3K to 1050K)

- Strong isotropic thermal expansion from 20 to 425K.
- NTE is based on the transverse thermal motion of oxygen in M-O-M linkages.
- Some polyhedra corners are linkage free



Network of corner-sharing $ZrO_{6/2}$ octahedra and $WO_{4/2}$ tetrahedra.

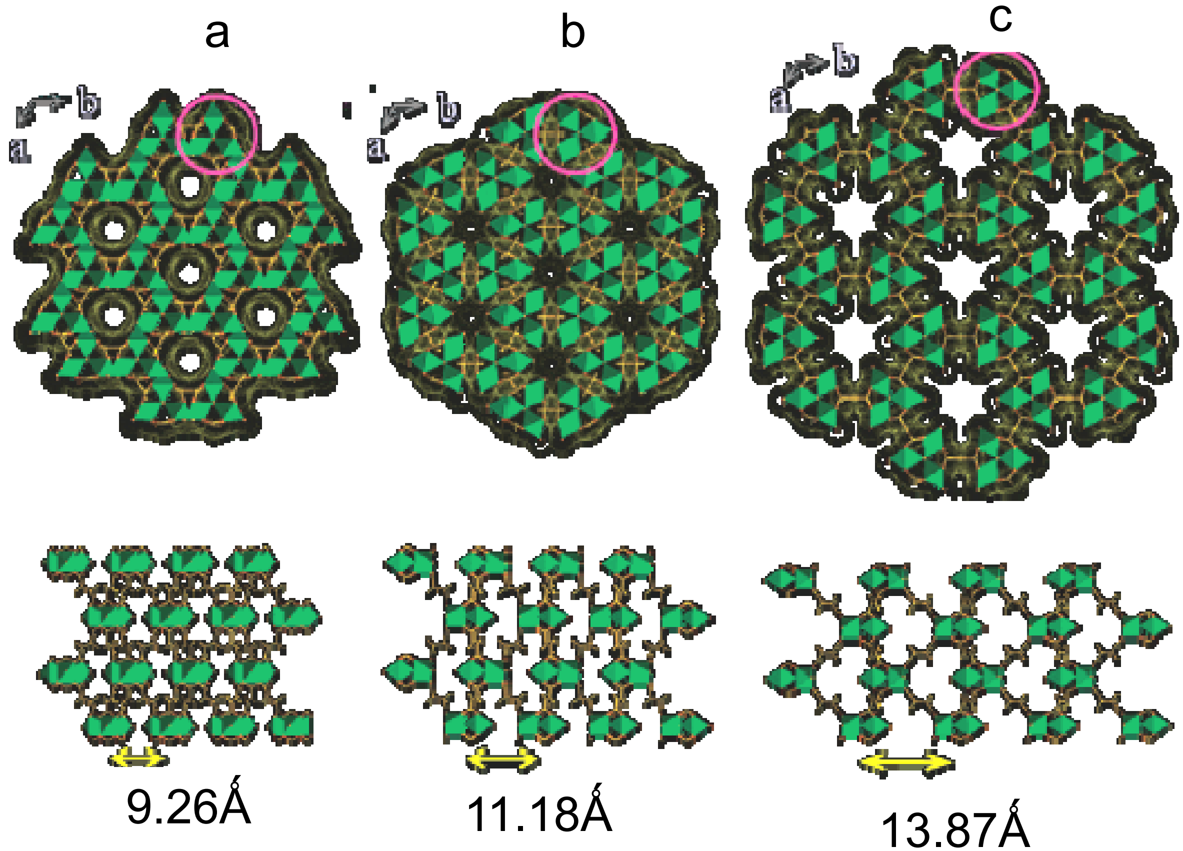


A. W. Sleight et al. J Solid State Chem, (2003)

Can Solid Breathe???

Nanoporous iron(III) carboxylate (MIL-88)

Exhibits almost a reversible doubling (85%) of its cell volume while fully retaining its open-framework topology.



Contracted **as-synthesized** **open forms**

Atomic displacements larger than 4 Å are observed when water or various alcohols are adsorbed in the porous structure.

Displacive transition occurs during the swelling phenomenon (X-ray thermodiffractometry).

G. Ferey et al. JACS (2005)