

## Chemistry of materials

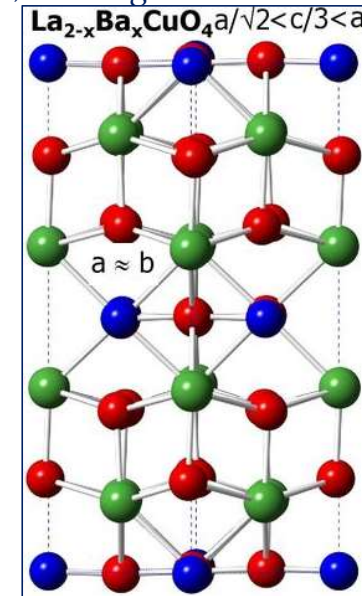
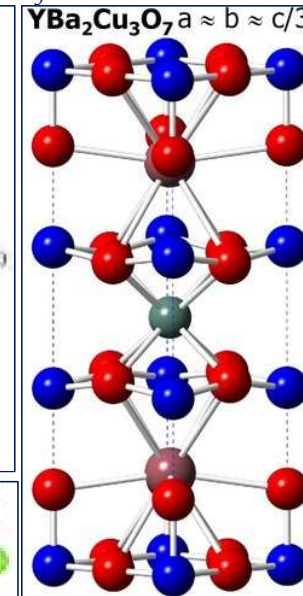
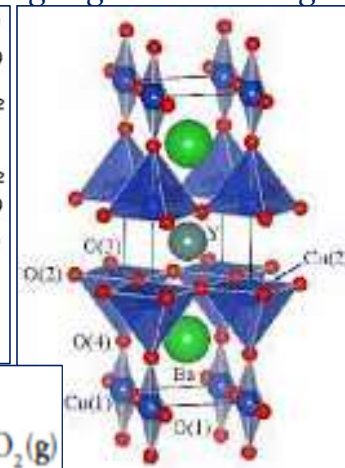
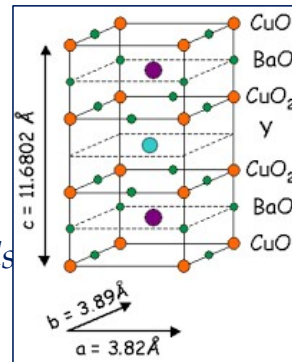
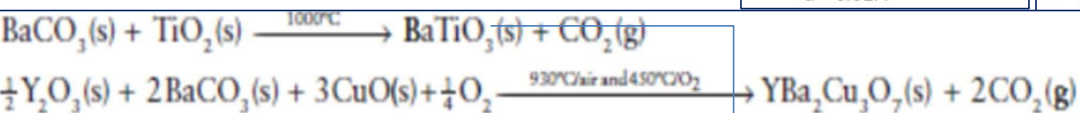
Inorganic materials are synthesized as bulk solids & on substrates. The role of defects in controlling structure, ion migration in solids is very important. Microporous solids are used in molecular separations and heterogeneous catalysis. Computer modelling is used to develop numerical models of the structures, properties of materials and predict how atomic, electronic structure control their physical properties.

Reaction of solids for formation of solid materials involves overcoming high lattice energies of extended structures, ion migration in solid state is slow except at elevated temps.

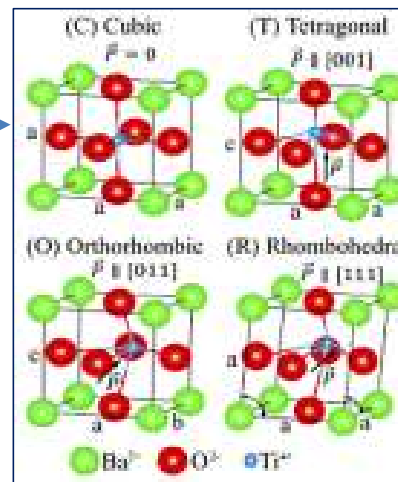
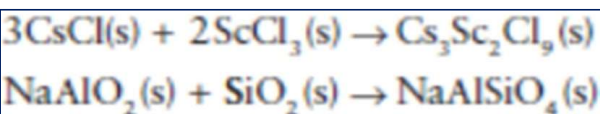
Bulk material can be synthesized by 2 methods:

**Direct synthesis:** at high temps to overcome high Coulombic attractions, yield complex solids

E.g. ternary and quaternary oxides



E.g. syntheses of complex chlorides and dense, anhydrous metal aluminosilicates:



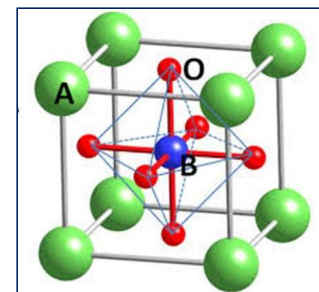
The tetragonal polymorph is the most widely used because of its excellent ferroelectric, piezoelectric, and thermoelectric properties

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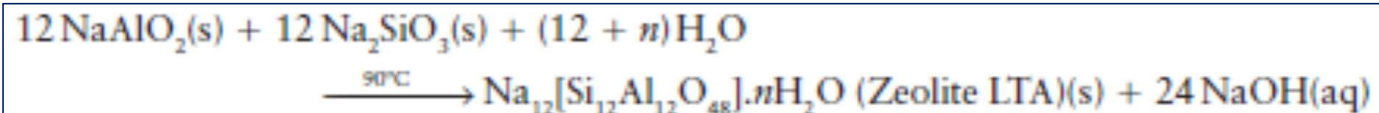
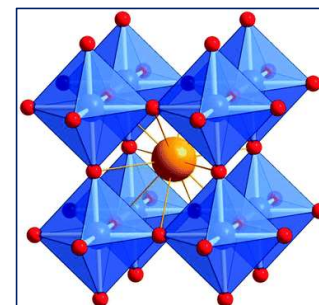
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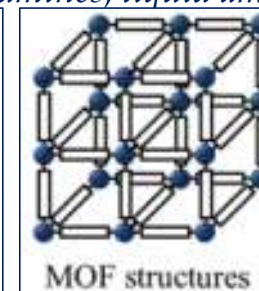
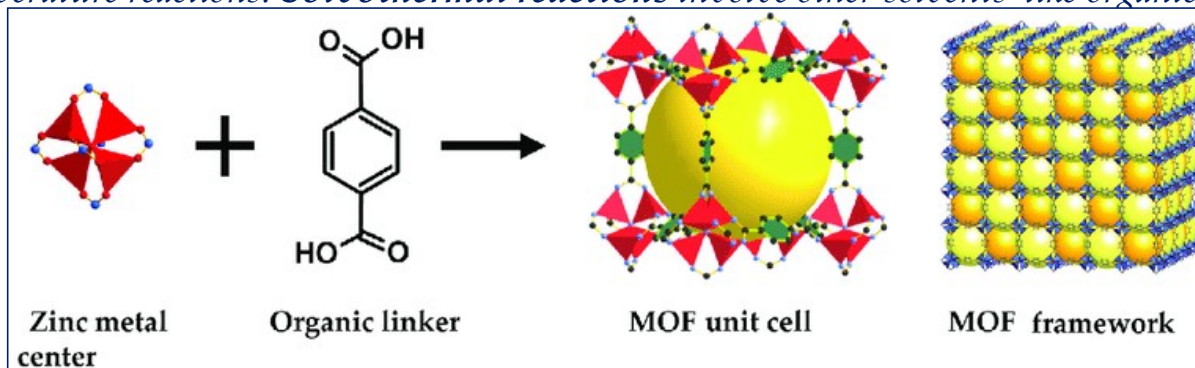
High pressures are used to control the composition of the reaction product and to affect the outcome of a solid-state chemical reaction. Reactions carried out under such conditions promote the formation of dense, higher coordination number structures. An example is the production of  $\text{MgSiO}_3$ , with a perovskite-like structure and six-coordinate Si in an octahedral  $\text{SiO}_6$  unit, rather than the normal tetrahedral  $\text{SiO}_4$  unit.



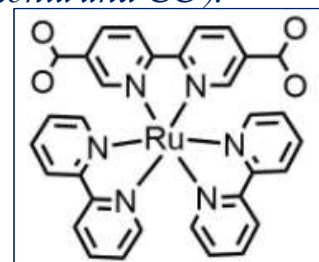
**Solution methods:** Condensation reactions in solution can give rise to polyhedral species. Many inorganic materials are synthesized by crystallization from solution using **hydrothermal techniques**, in which reacting soln is heated above its normal bp in a sealed vessel, in case of aluminosilicates (zeolites aluminosilicates have large open aperture/ cavities and act as molecular sieves used for gas absorption, ion exchange & heterogeneous catalysis). Sodium aluminosilicate zeolite  $\text{Na}_{12}[\text{Si}_{12}\text{Al}_{12}\text{O}_{48}]\cdot n\text{H}_2\text{O}$  formed in soln converts on heating above  $800^\circ\text{C}$  to the dense aluminosilicate  $\text{NaSiAlO}_4$ .



**Metal-organic frameworks (MOF)** in which metal ions are linked by coordinating organic species, such as carboxylates cannot be made by direct high-temperature reactions. **Solvothermal reactions** involve other solvents like organic amines, liquid ammonia and  $\text{CO}_2$ .



MOF structures



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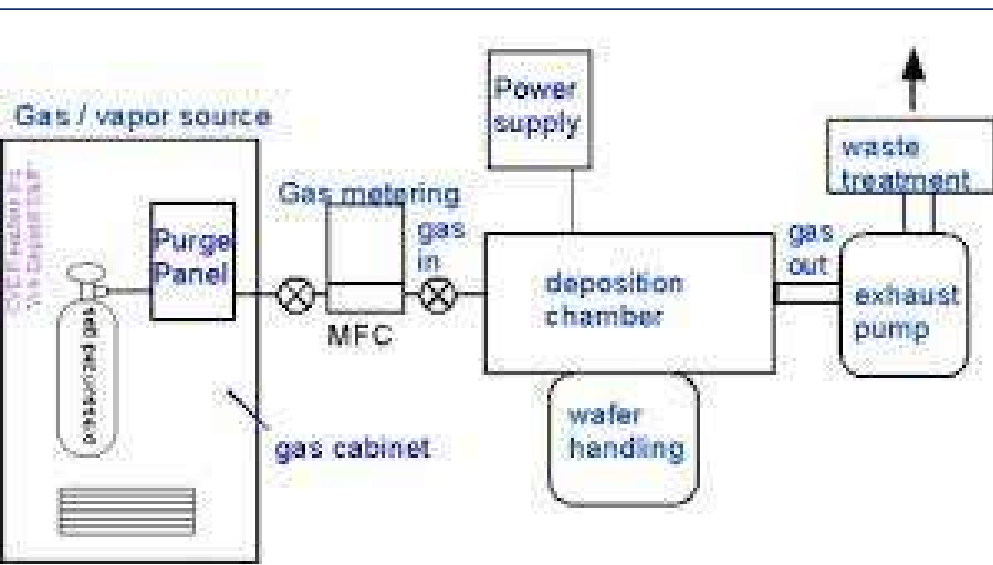
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Group 13/15 (III/V) semiconductors

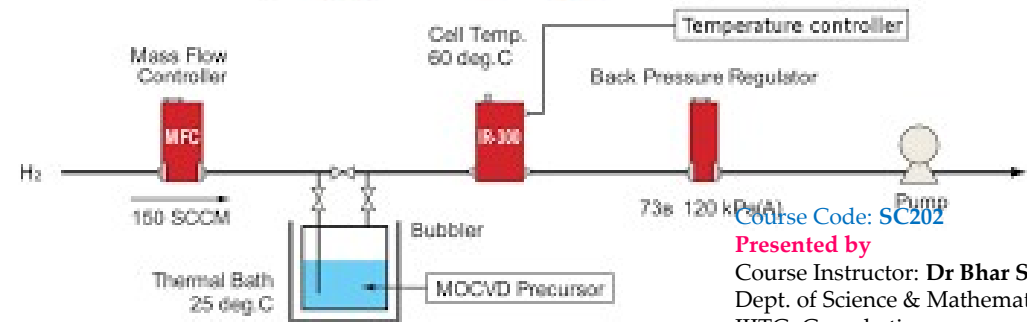
**Deposition:** In order to develop techniques to deposit films of many inorganic materials, the principal method is **chemical vapour deposition (CVD)**, in which a volatile inorganic compound is decomposed above the substrate. When the compound is a metallo-organic complex (that is, a complex of a metal atom with organic ligands), this route is known as **metallo-organic chemical vapour deposition (MOCVD)**. E.g.  $\text{Me}_2\text{Zn}$ , which has a vapour pressure of 0.3 bar at room temperature, can react with  $\text{H}_2\text{S}$  above a substrate to generate the Group 12/16 (II/VI) semiconductor  $\text{ZnS}$  (and methane). Another approach to molecules that can be used for CVD involves incorporating into a single-molecule precursor more than one of the atom types to be deposited. E.g. zinc sulfide can be deposited from a variety of zinc thiocomplexes, such as  $\text{Zn}(\text{S}_2\text{PMe}_2)_2$ .

Compound	Structure
AlN	wurtzite
AlP	zinc blende
AlAs	zinc blende
AlSb	zinc blende
GaN	wurtzite
GaP	zinc blende
GaAs	zinc blende
InN	wurtzite
InP	zinc blende
InAs	zinc blende
InSb	zinc blende



The **vapor pressure** of the MO source is an important consideration in MOCVD, since it determines the concentration of source material in the reactor and the deposition rate. Too low a vapor pressure makes it difficult to transport the source into the deposition zone and to achieve reasonable growth rates. Too high a vapor pressure may raise safety concerns if the compound is toxic.

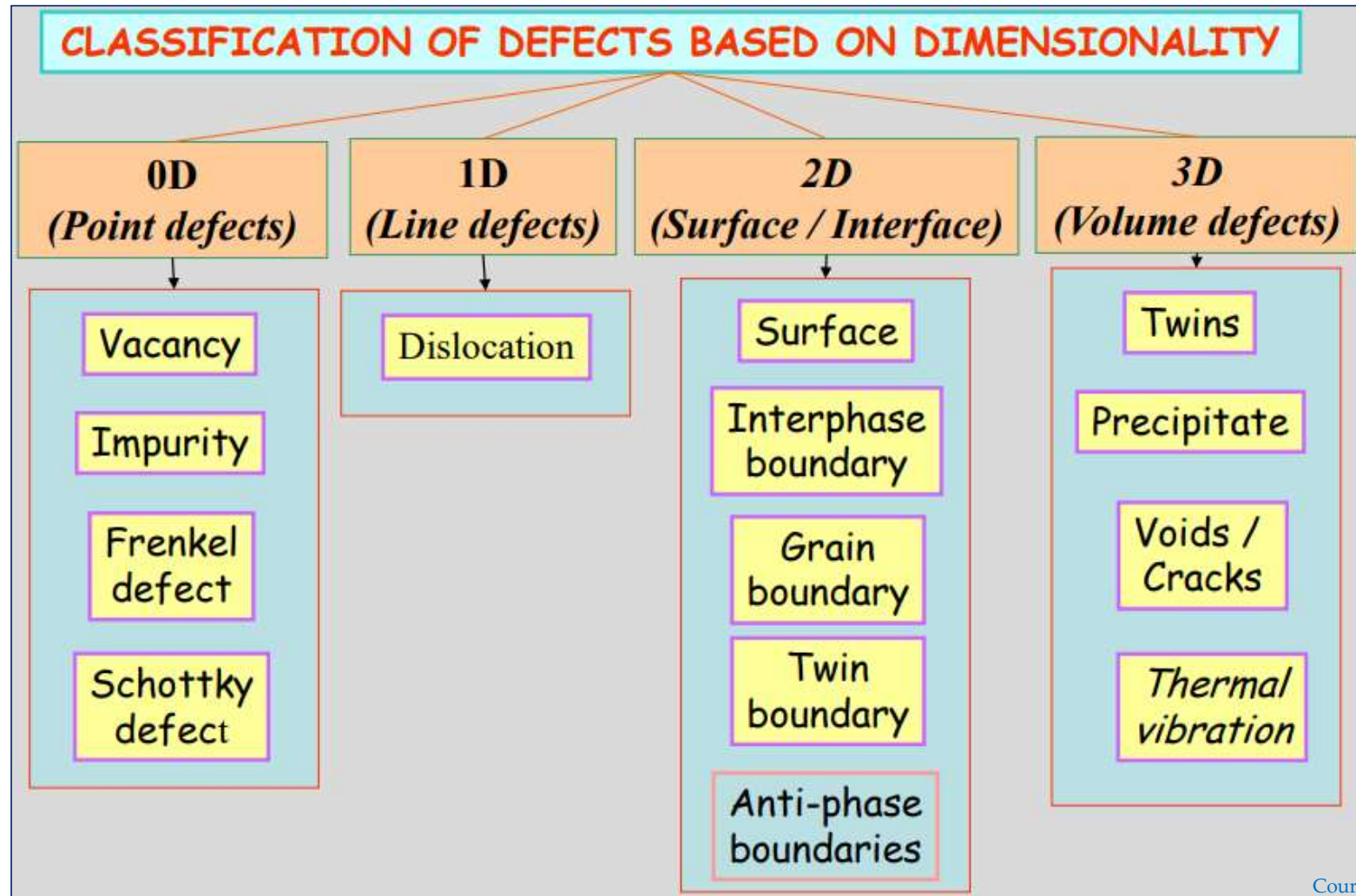
examples are  $\text{ZnS}_x\text{Se}_{1-x}$  and  $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$



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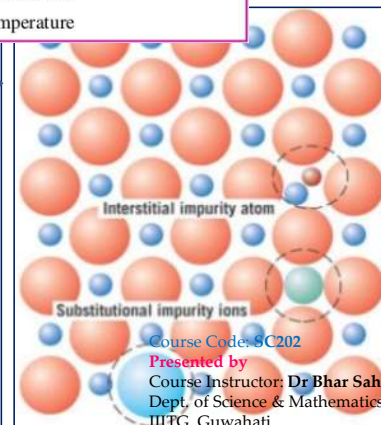
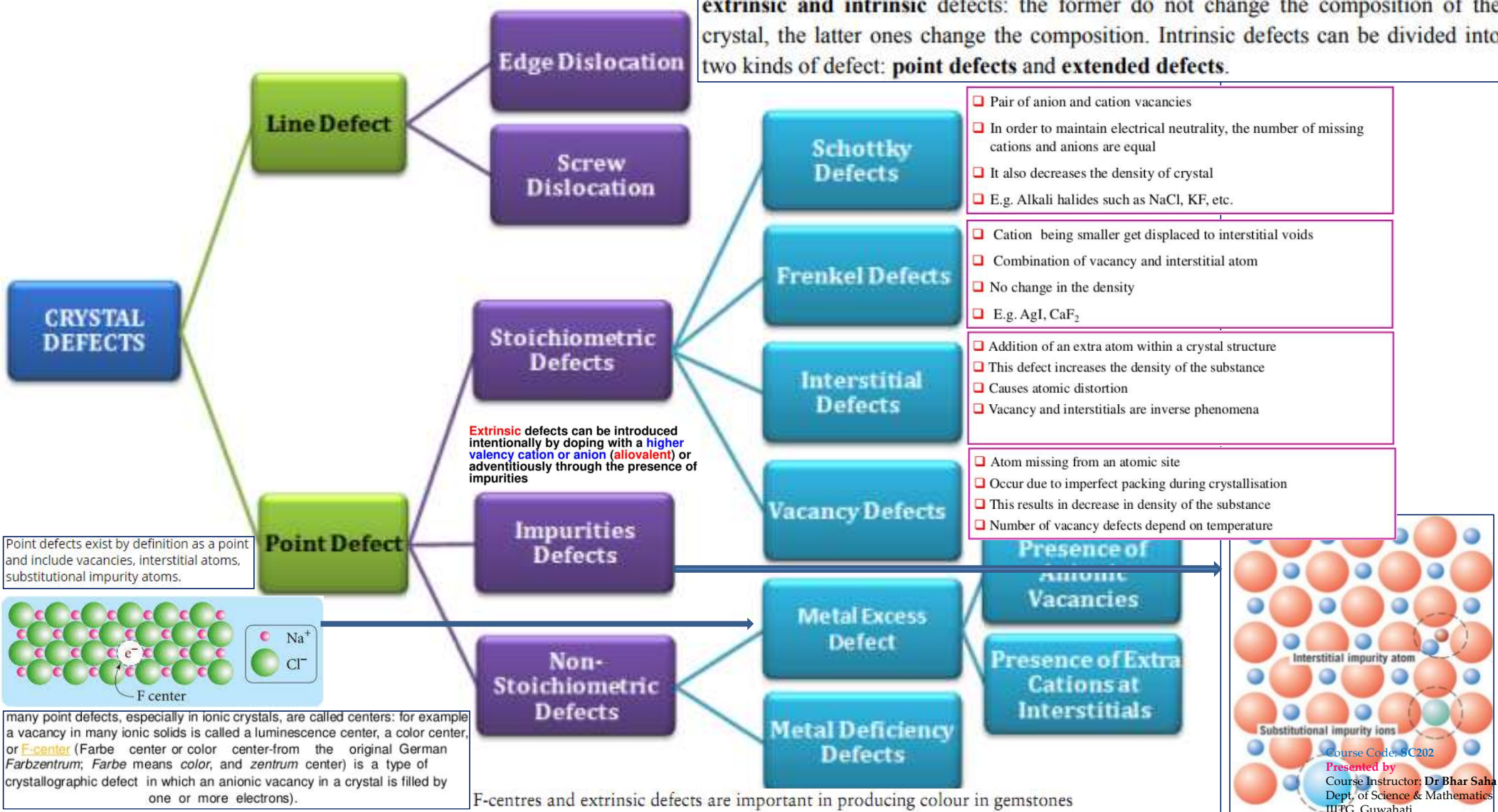
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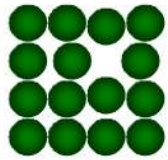
Every solid has a thermodynamic tendency to acquire point defects, as they introduce disorder and therefore increase entropy.

The formation of defects needs energy,  $\Delta H > 0$ . Defects lead to a gain in entropy,  $\Delta S > 0$ . According to the equation:  $\Delta G = \Delta H - T\Delta S$ , all solids tend to acquire defects, because defects increase their entropy and reduce the free energy. They can be classified as **extrinsic and intrinsic defects**: the former do not change the composition of the crystal, the latter ones change the composition. Intrinsic defects can be divided into two kinds of defect: **point defects and extended defects**.

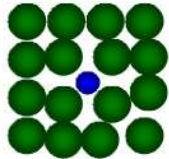




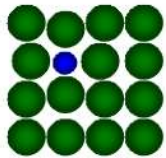
### Point defects of crystals



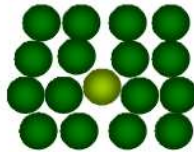
Vacancy



Interstitial impurity

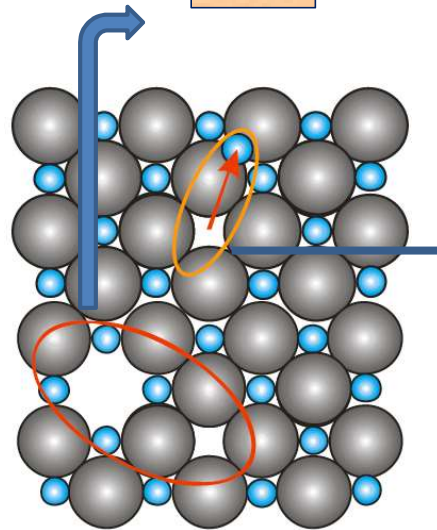


Substitution impurity



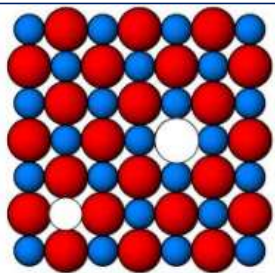
Self-interstitial

0D

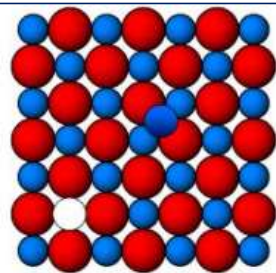


defect type	compound	$\Delta H$ ( $10^{-13}$ J)	$\Delta H$ (eV)
Schottky	MgO	10.57	6.60
	CaO	9.77	6.10
	LiF	3.75	2.34
	LiCl	3.40	2.12
	LiBr	2.88	1.80
	LiI	2.08	1.30
	NaCl	3.69	2.30
	KCl	3.62	2.26
Frenkel	UO <sub>2</sub>	5.45	3.40
	ZrO <sub>2</sub>	6.57	4.10
	CaF <sub>2</sub>	4.49	2.80
	SrF <sub>2</sub>	1.12	0.70
	AgCl	2.56	1.60
	AgBr	1.92	1.20
	beta-AgI	1.12	0.70

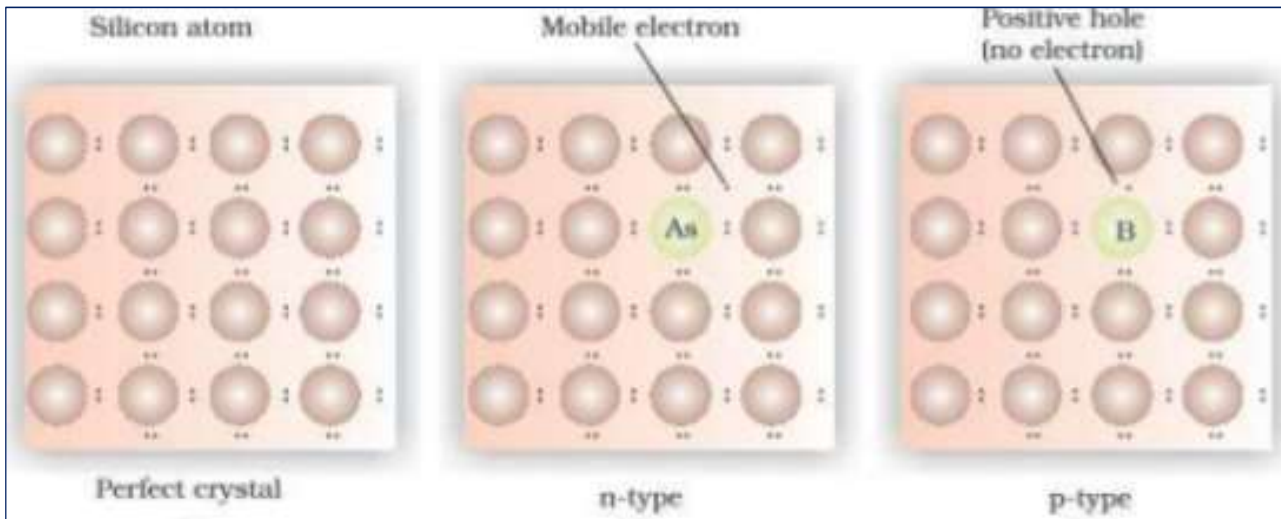
Enthalpy of formation scale with lattice energy and size of sites  
Controlled by electrostatic interactions



Schottky Defect  
(i.e. NaCl)  
 $\text{Na}^+ + \text{Cl}^- \rightarrow V_{\text{Na}} + V_{\text{Cl}}$



Frenkel Defect  
(i.e. AgCl)  
 $\text{Ag}^+ \rightarrow V_{\text{Ag}} + \text{Ag}^+_{\text{interstitial}}$



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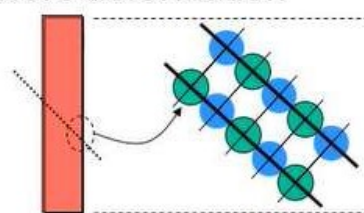
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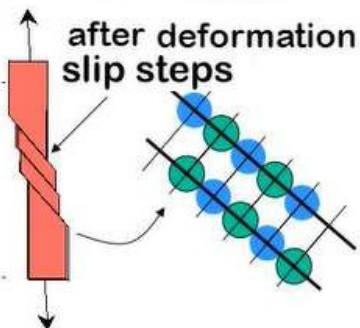
# 1D

## Dislocations Zinc Crystal (HCP)

before deformation

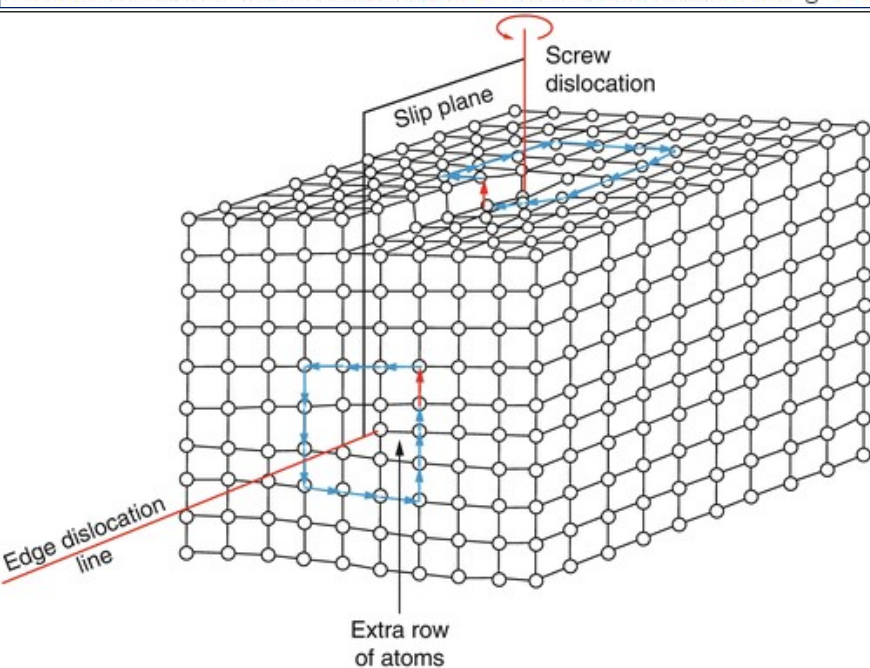


after deformation  
slip steps



FCC metals are in general more ductile;  
plastically deform well before failure  
HCP metals are in general less ductile  
BCC metals are stronger due to intersecting  
slip planes; limited dislocation activity;  
work harden very quickly

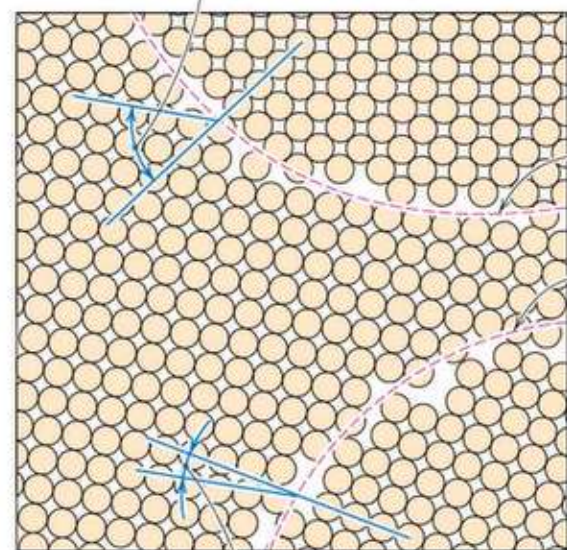
One-dimensional or linear defects are called dislocations. An *edge dislocation* is when a half plane of atoms disrupts the overall crystal structure. A *screw dislocation* is when a half twist disrupts the overall crystal structure. A *mixed dislocation* is a dislocation that combines both an edge and screw dislocation together.



Grain boundaries are regions between different grains within a material. They are classified as an interfacial defect and are two-dimensional.

# 2D

Angle of misalignment



High-angle  
grain  
boundary

Small-angle  
grain  
boundary

Angle of misalignment

One grain orientation can be obtained by rotation of another grain across the grain boundary about an axis through an angle

If the axis of rotation lies in the boundary plane it is called **tilt boundary**  
If the angle of rotation is perpendicular to the boundary plane it is called a **twist boundary**

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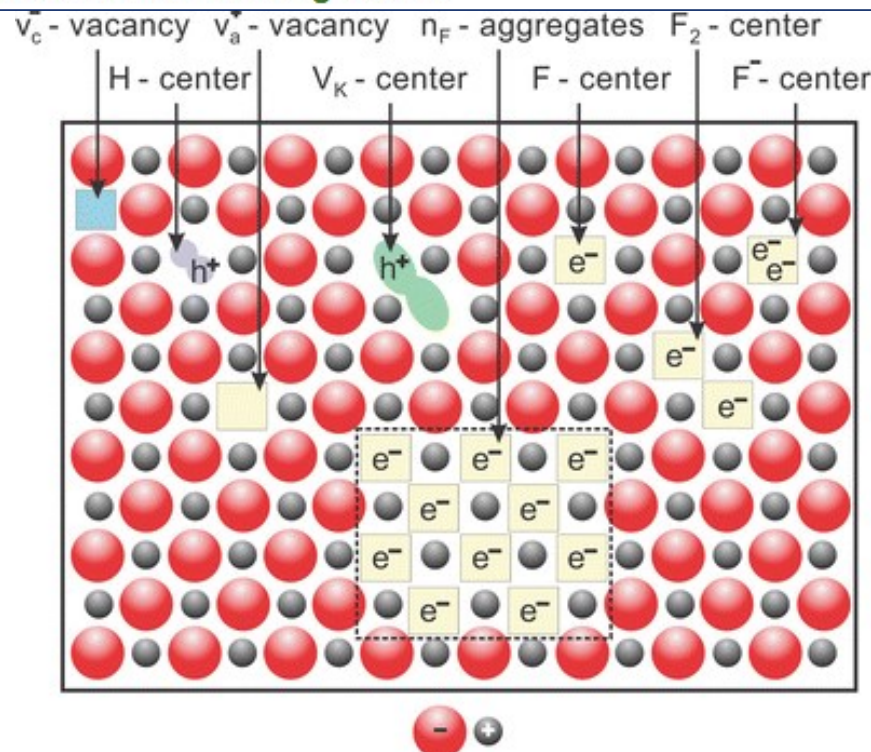
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## Metal Excess Defects

The anion may be missing from its lattice site leaving an electron behind so that the charge remains balanced. The sites containing the electrons are called as F-centres because they are responsible for imparting colour to the crystals; F stands for **F**arbenzenter meaning colour.



It has been observed that if a crystal of NaCl is heated in sodium vapour, it acquires a yellow colour. This yellow colour is due to the formation of a non-Stoichiometric compound of sodium chloride in which there is a slight excess of sodium ions.

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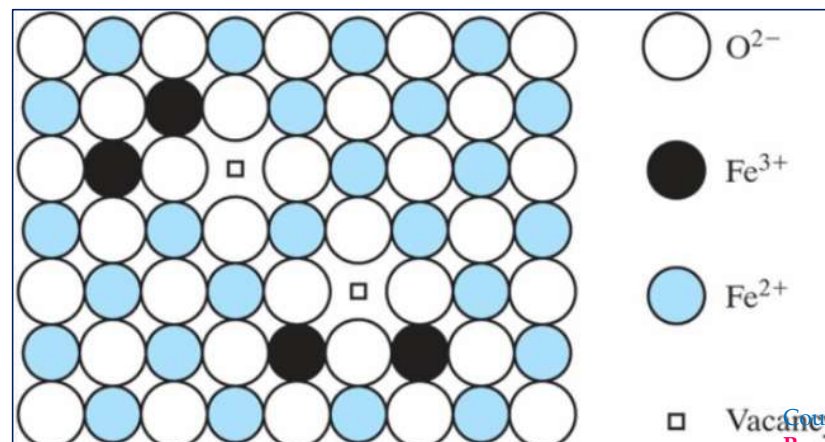
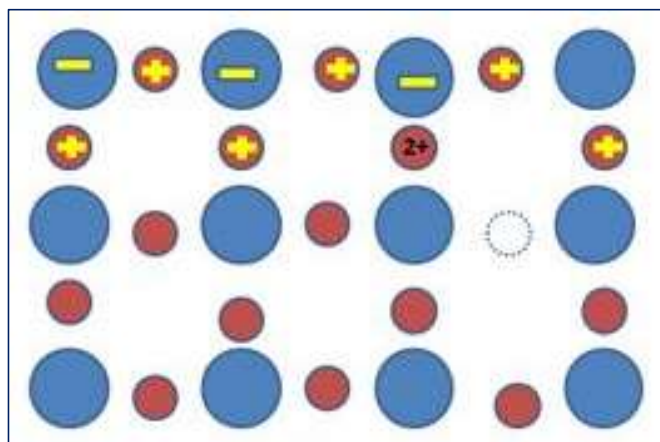
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## Metal Deficiency Defects

This type of defect is generally found amongst the compounds of transition metals which can exhibit variable oxidation state. In this defect cases, one of the positive ions is missing from its lattice site and the extra negative charge is balanced by some nearby metal ion acquiring two charges instead of one. There is evidently, a deficiency of the metal ions although the crystal as a whole is neutral. Crystals of FeO, FeS and NiO show this type of defects.



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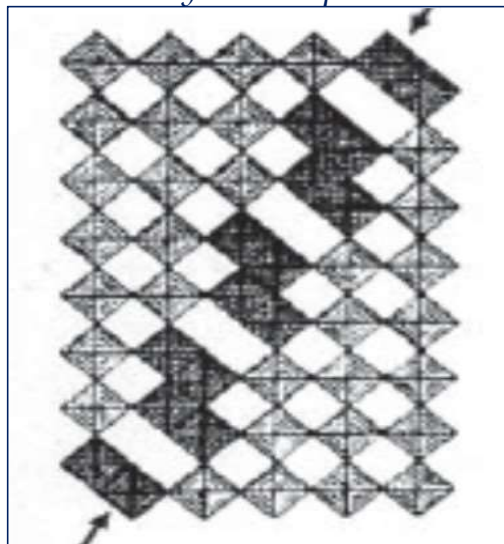
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### **Defects and ion transport:**

All solids above  $T = 0$  contain defects [point defects of type interstitial (Frenkel-type) or vacancies (Schottky-type)], which are important because they influence properties such as electrical conductivity and chemical reactivity. In addition, Wadsley defects are shear planes that collect defects along certain crystallographic directions. E.g. In  $\text{WO}_3$ , if shared O atoms are removed along a diagonal, then adjacent slabs slip over each other resulting in the vacant coordination sites around each tungsten atom. This shearing motion gives rise to edge-shared octahedra along a diagonal. The resulting structure is a **crystallographic shear plane** randomly distributed in the solid called **Wadsley defect**.

The shear planes provide stability to the overall structure by decreasing the structural degrees of freedom and preventing the tilts and distortions common to lithiated, unstabilized  $\text{ReO}_3$  and  $\text{WO}_3$ . Conducting tunnels vs. stabilizing shear planes decides the high-rate of electrochemical performance of the battery but the optimal shear structure is not yet known. The relationship between synthesis  $\rightarrow$  structure  $\rightarrow$  defect  $\rightarrow$  electrochemistry with superconductivity and high power energy storage is a nascent field of study.



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## Atom and ion diffusion

The presence of defects is required for the diffusion of ions in solids. The lowest energy pathway generally involves defect sites. Materials that show high rates of diffusion at moderate temperatures have the following characteristics:

1. **Low-energy barriers:** so temperatures at (or a little above) 300 K are sufficient to permit ions to jump from site to site.
2. **Low charges, small radii:** Most mobile cation (apart  $H^+$ ) & anion are  $Li^+$  &  $F^-$  respectively.  $Na^+$  &  $O^{2-}$  also exhibit reasonable mobility.

More highly charged ions form stronger electrostatic interactions and are less mobile.

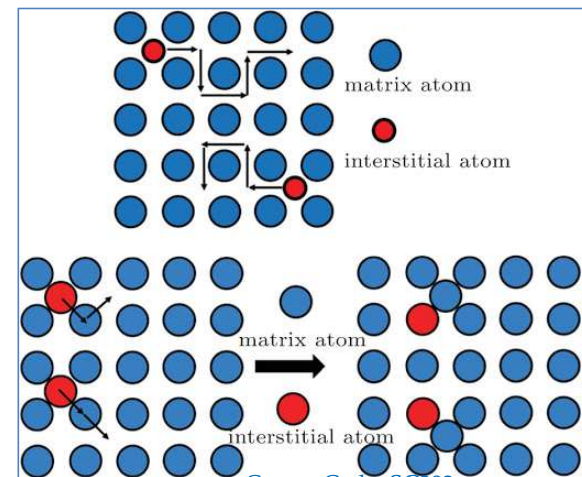
3. **High concentrations of intrinsic or extrinsic defects:** defects typically provide a low energy pathway for diffusion through a structure that does not involve the energy penalties associated with continuously displacing ions from normal, favourable ion sites. These defects should not be ordered, as for crystallographic shear planes, because such ordering removes the diffusion pathway.

4. **Mobile ions** are present as a significant proportion of the total no of ions. **TYPES of DIFFUSION:**

- ❑ **Self-diffusion** - The random movement of atoms within an essentially pure material. By using radioactive tracers.
- ❑ **Vacancy diffusion** - Diffusion of atoms when an atom leaves a regular lattice position to fill a vacancy in the crystal.
- ❑ **Interstitial diffusion** - Diffusion of small atoms from one interstitial position to another in the crystal structure.
- ❑ **Inter-diffusion** - In an alloy, atoms tend to migrate from regions of large concentration

Activation energies are usually lower for atoms diffusing through open structures than for closed-packed crystal structures.

Because the activation energy depends on the strength of atomic bonding, it is higher for diffusion of atoms in materials with a high melting temperature.



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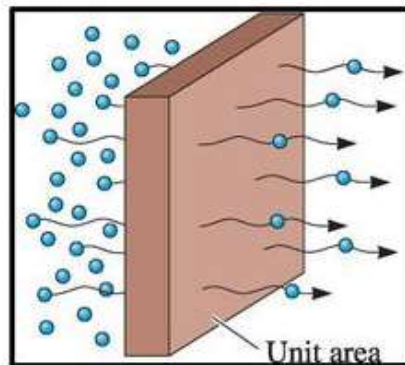
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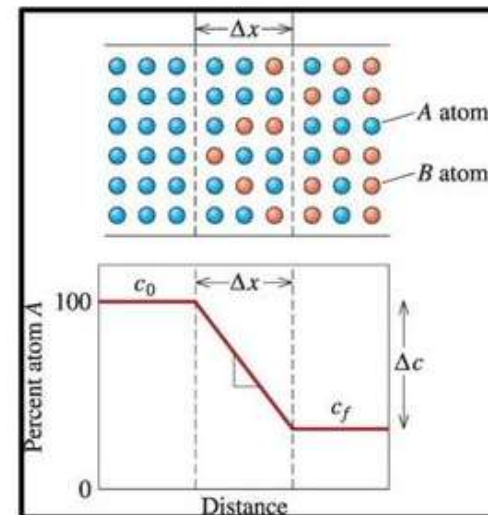
## Rate of Diffusion (Fick's First Law)

- **Fick's first law** - The equation relating the flux (atoms/cm<sup>2</sup> sec) of atoms by diffusion to the diffusion coefficient and the concentration gradient.
- **Diffusivity, Diffusion coefficient (D, cm<sup>2</sup>/sec)** - A temperature-dependent coefficient related to the rate at which atoms, ions, or other species diffuse.
- **Concentration gradient (dc/dx; atoms/cm<sup>3</sup>.cm or at%/cm)** - The rate of change of composition with distance in a nonuniform material.

$$J = -D \frac{dc}{dx}$$



The flux during diffusion is defined as the number of atoms passing through a plane of unit area per unit time



concentration gradient

- **Fick's second law** – the dynamic or nonsteady state, diffusion of atoms. The partial differential equation that describes the rate at which atoms are redistributed in a material by diffusion.

$$D \left( \frac{\partial^2 c}{\partial x^2} \right) = \frac{\partial c}{\partial t}$$

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## Vegard's law

# Non-stoichiometric compounds

For most of the non-stoichiometric compounds, *their unit cell size varies smoothly with composition but the symmetry is unchanged*. This is known as **Vegard's Law**.

❑ This law simply states that when you combine elements to form an alloy, the lattice constant will follow a linear trend with the element concentrations, provided that there is no *phase change* and *lattice parameters* do not differ by more than 5%.

➤ Mathematical expression for Vegard's law for a binary system A-B is:

$$\alpha = \alpha_A^0(1 - X) + \alpha_B^0(X)$$

- where  $X$  is the mole fraction of component B and  $\alpha$  = lattice parameters of pure components

**Superconductivity:** Many superconductors are non-stoichiometric.  $Y_xBa_2Cu_3O_{7-x}$ , arguably the most notable high temperature superconductor, is a non-stoichiometric solid with the formula  $Y_xBa_2Cu_3O_{7-x}$ . The critical temperature of the superconductor depends on the exact value of  $x$ .

Non-stoichiometric compounds are found to exist over a range of composition. It is possible to determine whether the non-stoichiometry is accommodated by vacancy or interstitial defects using **density measurements**.

## NS crystals

COMPOUND	COMPOSITION RANGE
TiO <sub>x</sub>	0.65 < x < 1.25
TiO <sub>x</sub>	1.998 < x < 2.00
VO <sub>x</sub>	0.79 < x < 1.29
FeO <sub>x</sub>	0.833 < x < 0.957
NiO <sub>x</sub>	0.999 < x < 1.000
ZnO <sub>x</sub>	1.000 < x < 0.999
UO <sub>x</sub>	1.65 < x < 2.25
H <sub>x</sub> MoO <sub>3</sub>	0.23 < x < 2.00
WO <sub>3-x</sub>	0.1 < x < 0.25
Li <sub>x</sub> WO <sub>3</sub>	0.0 < x < 0.50
TiS <sub>x</sub>	1.143 < x < 1.600

If  $Fe_{0.945}O_1$   $d_{cv} = 5.742 \times 10^3 \text{ kg m}^{-3}$

If  $Fe_1O_{1.058}$   $d_{ia} = 6.076 \times 10^3 \text{ kg m}^{-3}$

Experimental density  $d = 5.728 \text{ kg m}^{-3}$

✓ Thus, FeO has cation vacancy

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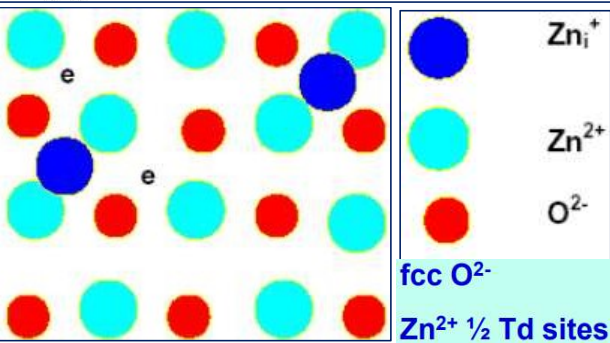
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## DIFFERENCE: NS ZINC OXIDE AND NICKEL OXIDE

**$\text{Zn}_{1+x}\text{O}$  made by adding 0.033 Zn atom% excess over stoichiometric**

**ZnO white, wide bandgap insulator**

**$\text{Zn}_{1+x}\text{O}$  orange, n-type semiconductor**



**NS zinc oxide**  
 $\text{Zn}^+$  Frenkel defects  
 Zn behaves as n-type dopant  
 Simple band model  
 Semiconductor behavior

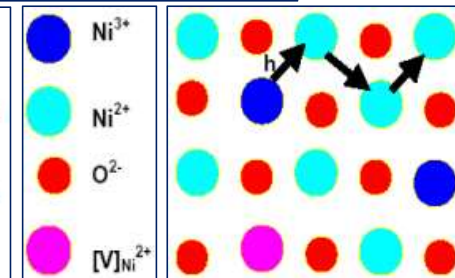
**$\text{Ni}_{1-x}\text{O}$  made by heating NiO in  $\text{O}_2$  introducing 0.001 Ni atom% deficiency over stoichiometric**

**NiO green, semiconducting anti-ferromagnet**

**$\text{Ni}_{1-x}\text{O}$  black, p-type hopping semiconductor**

NiO rock salt structure type  
 $\text{Ni(II) Oh } d^8$   
 $t_{2g}^6 (dxz, yz, xy)^6 e_g^2 (dz^2, x^2-y^2)^2$   
 RHS of 1<sup>st</sup> transition series  
 High effective nuclear charge  $Z^*$   
 Contracted d-orbitals  
**Narrow localized  $e_g^2 (dz^2, x^2-y^2)^2$  d-band**

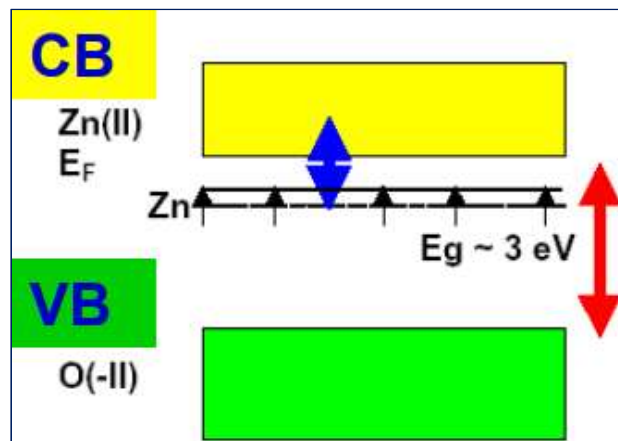
Overlap of  $dz^2, x^2-y^2$  with  $\text{O(-II) } 2p$  sigma-orbitals  
 UPEs **super-exchange coupled**  
**Behaves as antiferromagnetic semiconductor**



**Migration of Holes** (proved by Hall and Seebeck measurements) by mixed valence activated hopping process, hence origin of high  $E_a$   $\sigma = \sigma_0 \exp(-E_a/2kT)$

**NOT** migration of  $\text{Ni}^{3+}$ , instead **HOPPING SEMICONDUCTOR**, with activated diffusion of holes from  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$

**NOT** p-Si type electronic band model with excitation of e- into  $\text{Ni}^{3+}$  dopant levels above VB



**p-Type Hopping Semiconductor**



$$K = [\text{Ni}^{3+}]^2 [\text{V}_c] / p(\text{O}_2)^{1/2}$$

Assuming constant  $[\text{O}^{2-}] \sim [\text{Ni}^{2+}]$

$$[\text{V}_c] = 1/2[\text{Ni}^{3+}]$$

$$K \propto [\text{Ni}^{3+}]^3 / p(\text{O}_2)^{1/2}$$

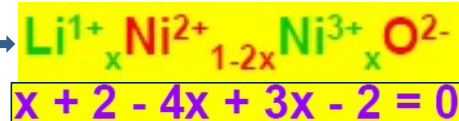
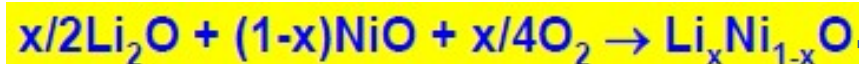
$$\sigma \propto N e \mu \propto [\text{Ni}^{3+}] \propto p(\text{O}_2)^{1/6}$$

Oh  $\text{Ni}^{2+}$  adjacent sites in rock salt lattice,  $d^8 (t_{2g}^6 e_g^2)$   
 Unpaired  $e_g$  electrons occupy symmetry equivalent  $d_{z^2} / d_{x^2-y^2}$   
 Couple electronically via p-type electrons of bridging oxygens, "super-exchange"  
 Give antiferromagnetic coupled  $e_g$  electrons

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$x = 0.125$ , consisting of 16 lattice sites in the primitive fcc cell



**Conductivity** - good semiconductor for all  $[\text{Li}^+]$

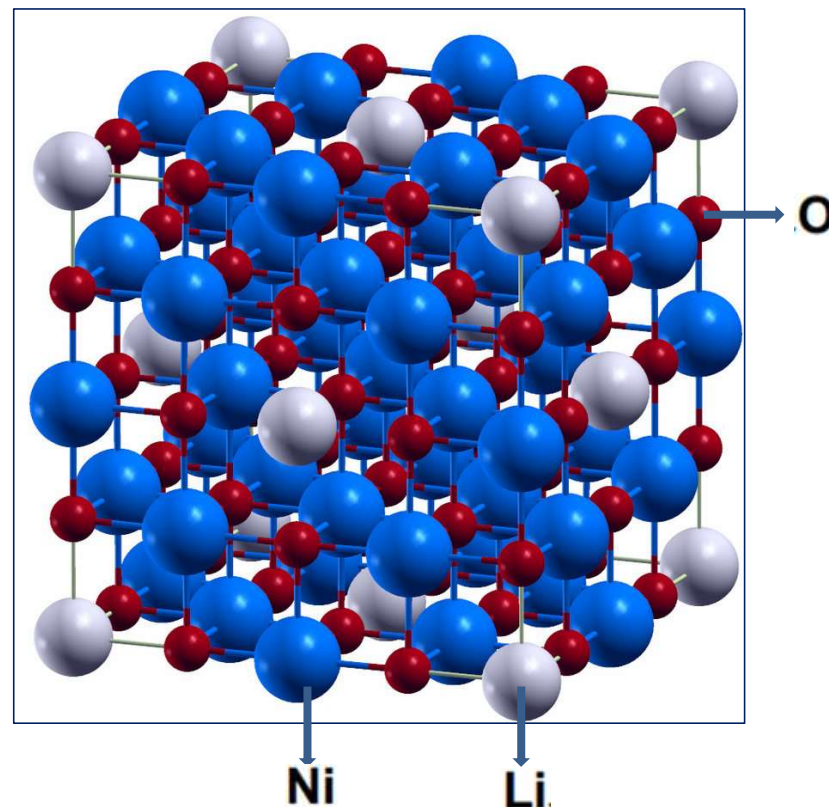
**Seebeck** shows hole p-type migration

**Activated**  $\text{Ni}^{3+}/\text{Ni}^{2+}$  hopping escaping  $\text{Li}^+$  neighboring sites

**Polaronic** motion of  $\text{Ni}^{3+}/\text{Ni}^{2+}$

**Wave like** behavior of O coordination sphere

**Hopping** motion



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Solid electrolytes are used to avoid a liquid phase due to possible spillage. Solid electrolytes with mobile cations like silver tetraiodomercurate (II),  $\text{Ag}_2\text{HgI}_4$ , and sodium–alumina  $\text{Na}_{1+x}\text{Al}_{11}\text{O}_{17+x/2}$ , NASICON (Na Superionic Conductor)  $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ , proton conductors that operate at or a little above room temperature, such as  $\text{CsHSO}_4$  above  $160^\circ\text{C}$ .

Metals	Solid Electrolytes
Conductivity Range = $10 \text{ S/cm} < \sigma < 10^5 \text{ S/cm}$	Conductivity Range = $10^{-3} \text{ S/cm} < \sigma < 10 \text{ S/cm}$
Electrons carry the current	Ions carry the current
Conductivity Increases linearly as temperature decreases (phonon scattering decreases as $T \downarrow$ )	Conductivity decreases exponentially as temperature decreases (activated transport)

## 1. Solid cationic electrolytes

Solid inorganic electrolytes often have a low-temperature form in which the ions are ordered on a subset of sites in the structure; at higher temperatures the ions become disordered over the sites and the ionic conductivity increases. E.g. NASICON (Na Superionic Conductor)  $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ .

### **Ag<sup>+</sup> Ion Conductors**

-AgI &  $\text{RbAg}_4\text{I}_5$

### **Na<sup>+</sup> Ion Conductors**

-Sodium  $\beta$ -Alumina (i.e.  $\text{NaAl}_{11}\text{O}_{17}$ ,  $\text{Na}_2\text{Al}_{16}\text{O}_{25}$ )

-NASICON ( $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$ )

### **Li<sup>+</sup> Ion Conductors**

- $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$

- $\text{LiMnO}_2$

### **O<sup>2-</sup> Ion Conductors**

-Cubic stabilized  $\text{ZrO}_2$  ( $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ ,  $\text{Ca}_x\text{Zr}_{1-x}\text{O}_{2-x}$ )

- $\delta\text{-Bi}_2\text{O}_3$

-Defect Perovskites ( $\text{Ba}_2\text{In}_2\text{O}_5$ ,  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3-y}$ )

### **F<sup>-</sup> Ion Conductors**

- $\text{PbF}_2$  &  $\text{AF}_2$  (A = Ba, Sr, Ca)

## 2. Solid anionic electrolytes

Anion mobility can occur at high temperatures in certain structures that contain high levels of anion vacancies. E.g. Zirconia,  $\text{ZrO}_2$ , at high temperature has a fluorite structure, but on cooling the pure material to room temperature it distorts to a monoclinic polymorph. The cubic fluorite structure may be stabilized at room temperature by replacing some  $\text{Zr}^{4+}$  with other ions, such as the similarly sized  $\text{Ca}^{2+}$  and  $\text{Y}^{3+}$  ions. Doping with these ions of lower oxidation number results in the introduction of vacancies on the anion sites to preserve the charge neutrality of the material and produce, for example,  $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2-x/2}$ , the material mentioned previously as 'yttrium stabilized zirconia' (YSZ).

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## General Characteristics

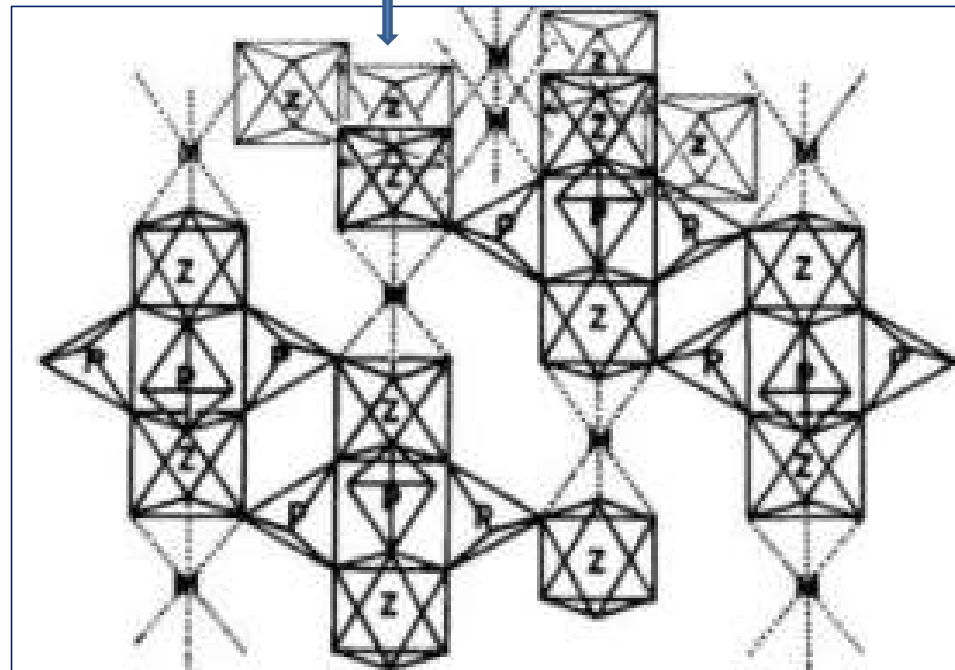
1. A large number of the ions of one species should be mobile. This requires a large number of empty sites, either vacancies or accessible interstitial sites.
  - Empty sites are needed for ions to move through the lattice.
2. The empty and occupied sites should have similar potential energies with a low activation energy barrier for jumping between neighboring sites.
  - High activation energy decreases carrier mobility, very stable sites (deep potential energy wells) lead to carrier localization.
3. The structure should have solid framework, preferable 3D, permeated by open channels.
  - The migrating ion lattice should be "molten", so that a solid framework of the other ions is needed in order to prevent the entire material from melting.
4. The framework ions (usually anions) should be highly polarizable.
  - Such ions can deform to stabilize transition state geometries of the migrating ion through covalent interactions.

### RbAg<sub>4</sub>I<sub>5</sub>

- Highest known conductivity at room temperature
- BCC Arrangement of I<sup>-</sup>, molten/disordered Ag<sup>+</sup>
- $\sigma \sim 0.25 \text{ S/cm (25 } ^\circ\text{C)}$ ,  $E_A = 0.07 \text{ eV}$

### Na<sub>3</sub>Zr<sub>2</sub>PSi<sub>2</sub>O<sub>12</sub> (NASICON)

- Framework of corner sharing ZrO<sub>6</sub> octahedra and PO<sub>4</sub>/SiO<sub>4</sub> tetrahedra
- Na<sup>+</sup> ions occupy trigonal prismatic and octahedral sites,  $\frac{1}{4}$  of the Na<sup>+</sup> sites are empty
- $E_A \sim 0.3 \text{ eV}$



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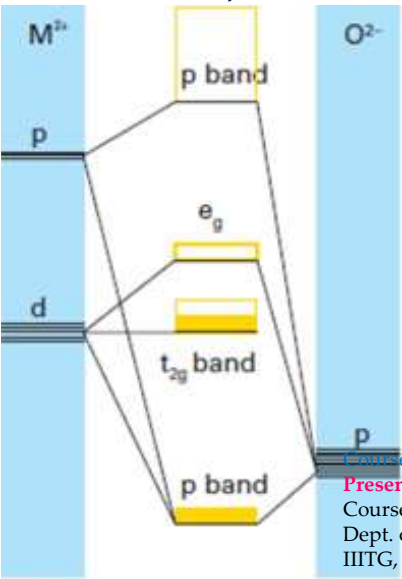
**Mixed ionic-electronic conductors**

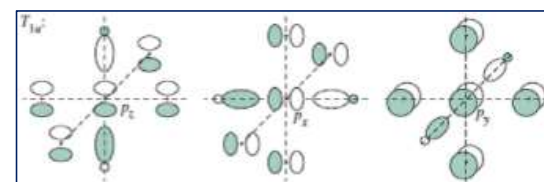
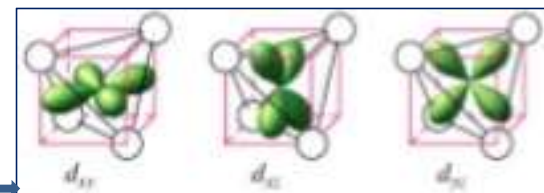
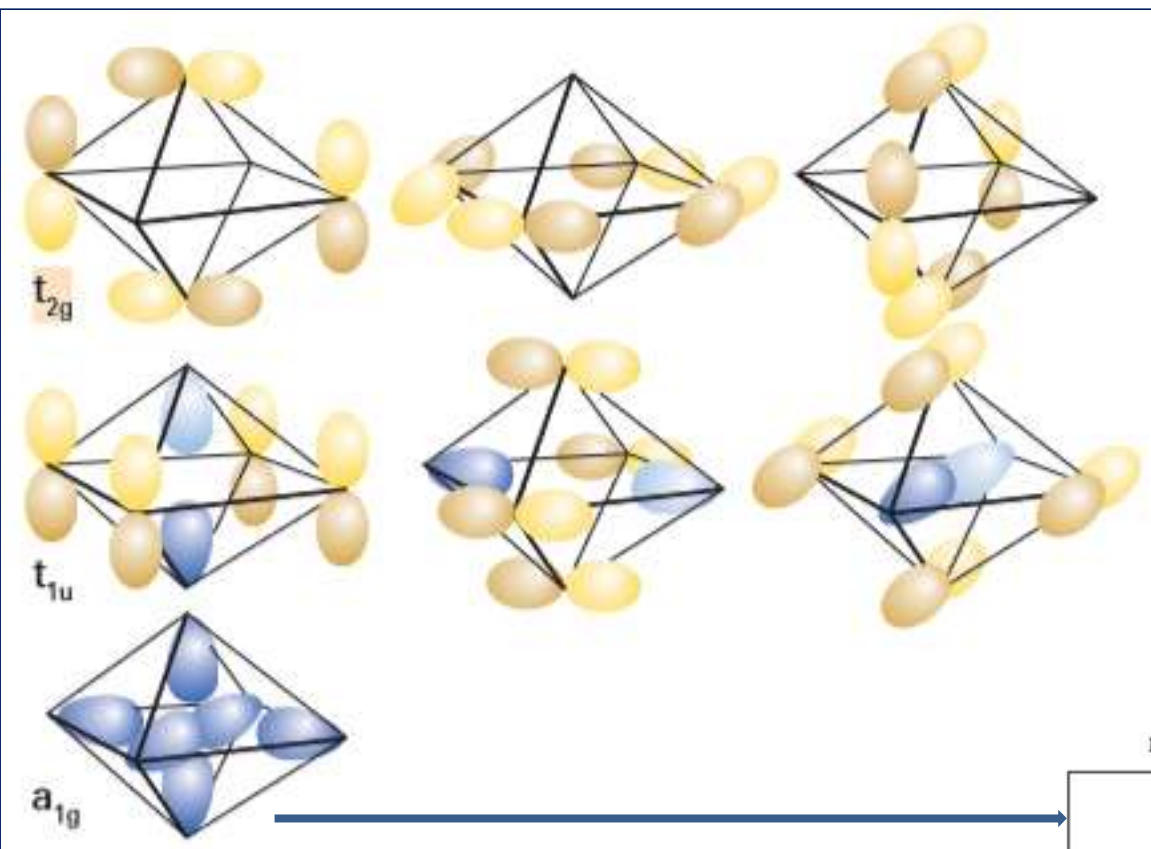
Solid materials can exhibit both ionic and electronic conductivity. E.g.  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$  and  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-y}$ . These oxide systems are good electronic conductors with partially filled bands as a result of the nonintegral d-metal oxidation number and can conduct by  $\text{O}^{2-}$  migration through the perovskite  $\text{O}^{2-}$  ion sites.

**Metal oxides, nitrides, and fluorides:** Monoxides of the 3d metals adopt the rock-salt structures. Mixed oxidation states and defects lead to nonstoichiometry for solids in TiO, VO, FeO, CoO, and NiO.

**Electronic properties:** The 3d-metal monoxides MnO, FeO, CoO, and NiO are semiconductors; TiO and VO are metallic conductors. The 3d-metal monoxides MnO,  $\text{Fe}_{1-x}\text{O}$ , CoO, and NiO have low electrical conductivities that increase with temperature (corresponding to semiconducting behaviour) or have such large band gaps that they are insulators. The electron or hole hops from one localized metal atom site to the next until it is thermally activated to migrate into another nearby site. When NiO is doped with  $\text{Li}_2\text{O}$  in an  $\text{O}_2$  atmosphere a solid solution

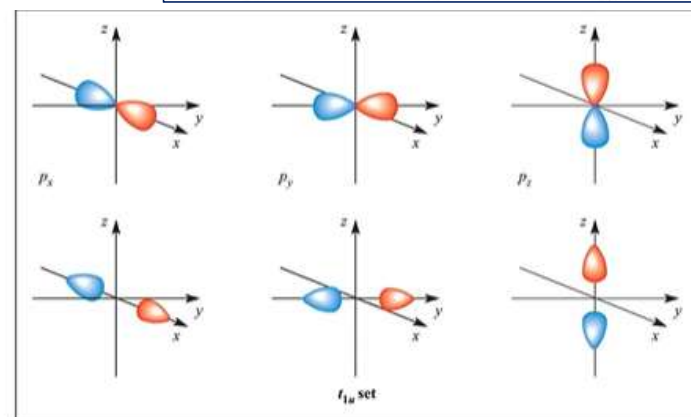
$\text{Li}_x(\text{Ni}^{2+})_{1-2x}(\text{Ni}^{3+})_x\text{O}$  is obtained, which has greatly increased conductivity for reasons similar to the increase in conductivity of Si when doped with B. TiO and VO have high electronic conductivities that decrease with increasing temperature. Here, a conduction band is formed by the overlap of the  $t_{2g}$  orbitals of metal ions in neighbouring octahedral sites that are oriented towards each other.





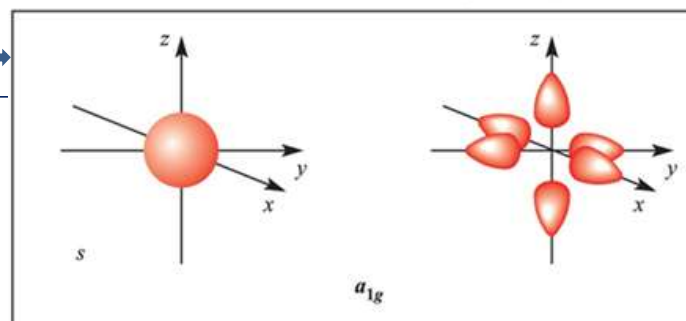
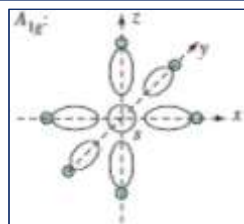
Metal Atomic Orbital

Ligand Group Orbital



Metal Atomic Orbital

Ligand Group Orbital



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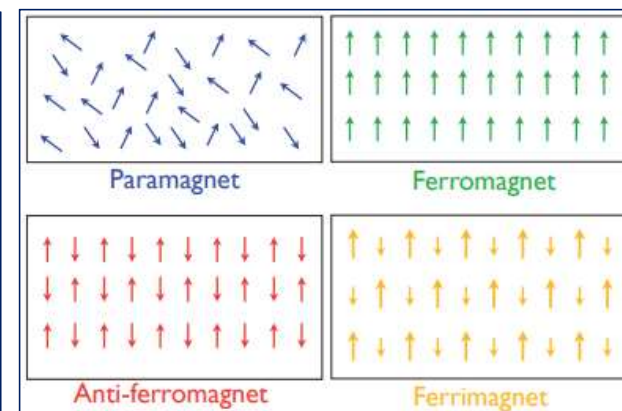
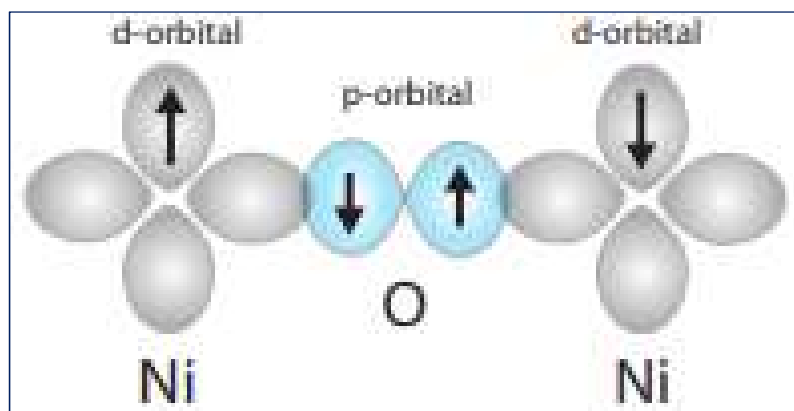


## Magnetic properties

The 3d-metal monoxides MnO, FeO, CoO, and NiO order antiferromagnetically with Neel temperatures that increase from Mn to Ni.

3- d-metal monoxides have magnetic properties that derive from cooperative interaction of the individual atomic magnetic moments. The Neel temperatures ( $T_N$ : the temperature of the paramagnetic/antiferromagnetic transition), of the series of d-metal oxides are as follows:

Compound	$\Theta_N$
MnO	116 K
FeO	198 K
CoO	293 K
NiO	523 K



This reflects the strength of the superexchange spin interactions along the M-O-M directions, which in the rock-salt type structure propagate in all three unit cell directions. As the size of the  $M^{2+}$  ion decreases from Mn to Ni, the superexchange mechanism becomes stronger due to the increased metal–oxygen orbital overlap and  $T_N$  increases.

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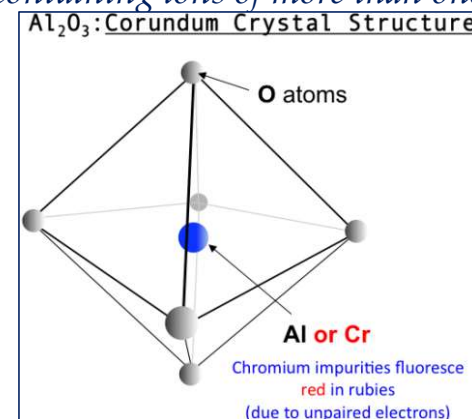
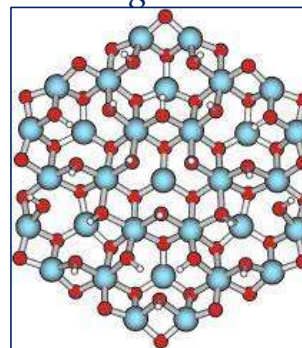
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## Higher oxides and complex oxides

Binary metal oxides that do not have a 1:1 metal : oxygen ratio are known as **higher oxides**. Compounds containing ions of more than one metal are often termed **complex oxides** or **mixed oxides** and include compounds containing three elements, ternary oxides, eg.  $\text{LaFeO}_3$ , and quaternary  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

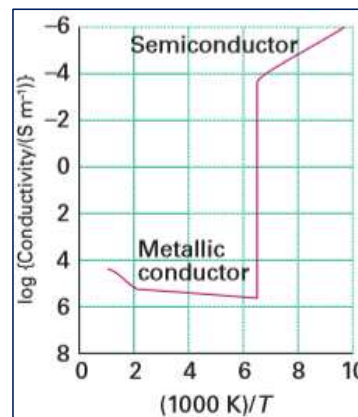
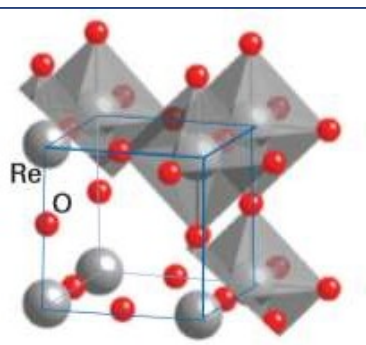
**1. The  $\text{M}_2\text{O}_3$  Corundum structure:** is adopted by many oxides of stoichiometry  $\text{M}_2\text{O}_3$ , including Cr-doped aluminium oxide (ruby).



$\alpha$ -Aluminium oxide (the mineral corundum) adopts a structure that can be modelled as a hexagonal close-packed array of  $\text{O}^{2-}$  ions with the cations in two-thirds of the octahedral holes.  $\text{Ti}_2\text{O}_3$  and  $\text{V}_2\text{O}_3$ , also have corundum structure and exhibit metallic-to-semiconducting transitions below 410 and 150 K, respectively. The two insulators  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  also display antiferromagnetic ordering.

**2. Rhenium trioxide:** The rhenium trioxide structure can be constructed from  $\text{ReO}_6$  octahedra sharing all vertices in three dimensions.

A cubic unit cell with Re atoms at the corners and O atoms at the mid-point of each edge. Rhenium trioxide is a bright red lustrous solid with electrical conductivity at room temperature.



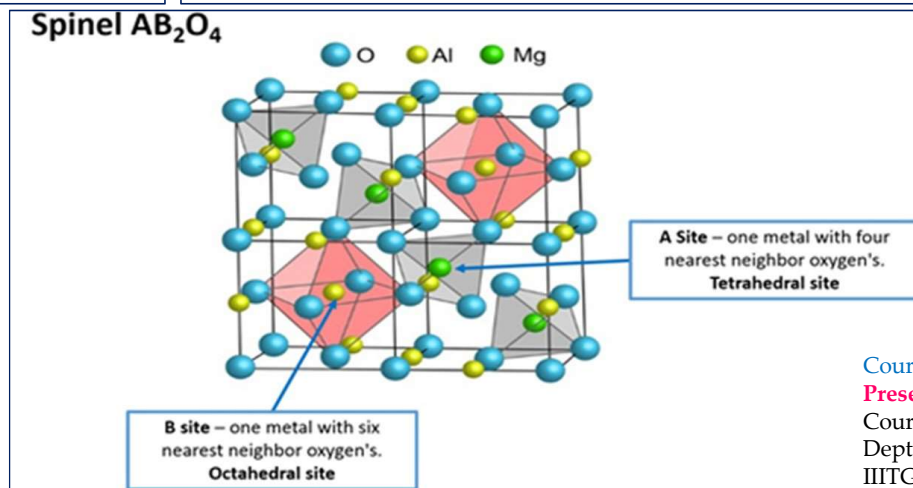
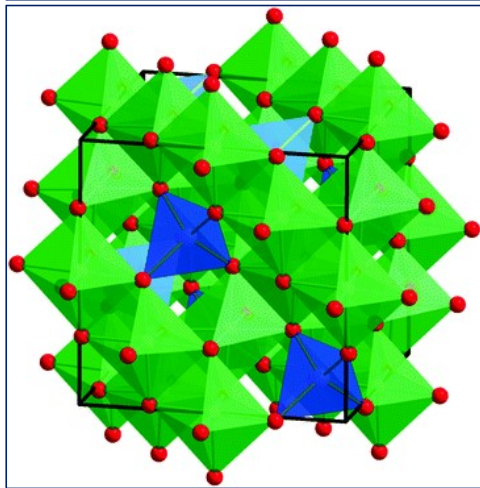
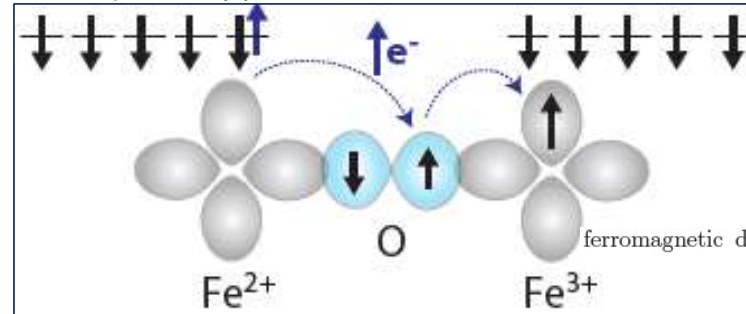
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3. **Spinel:** The observation that many *d*-metal spinels do not have the normal spinel structure is related to the effect of ligand-field stabilization energies on the site preferences of the ions. The spinel structure consists of an fcc array of  $O^{2-}$  ions in which the *A* ions reside in one-eighth of the tetrahedral holes and the *B* ions inhabit half the octahedral holes,  $A[B_2]O_4$ . *d*-metal spinels do not conform to this expectation because of the effect of ligand-field stabilization energies on the site preferences of the ions. The **occupation factor**,  $\lambda$ , of a spinel is the fraction of *B* atoms in the tetrahedral sites: 0 for a normal spinel and 12 for an inverse spinel,  $B[AB]O_4$ ; intermediate values indicate a level of disorder in the distribution, where *B*-type cations occupy that portion of the tetrahedral sites. When  $A^{2+}$  is a  $d_6$ ,  $d_7$ ,  $d_8$ , or  $d_9$  ion and  $B^{3+}$  is  $Fe^{3+}$ , the inverse structure is generally favoured. The inverse spinels of formula  $AFe_2O_4$  are sometimes classified as **ferrites**.

Another important interaction in inverse spinel ferrites is *double exchange*, where two cations of different charge occupy the same type of lattice site and are thus capable of exchanging an electron. The electron that hops from the  $Fe^{2+}$  ion must be the one that is anti-aligned with the other five electrons on the ion (to preserve Hund's rules) — say it is spin-up. It must displace a spin-up electron on the oxygen, which then hops onto the  $Fe^{3+}$  ion, which it can only do if those electrons are all spin-down, or in other words the same as the electrons on the  $Fe^{2+}$  ion. This leads to a ferromagnetic interaction.



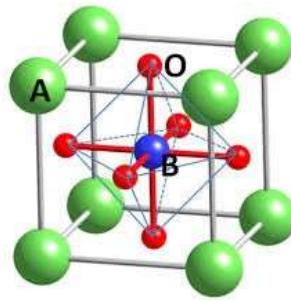
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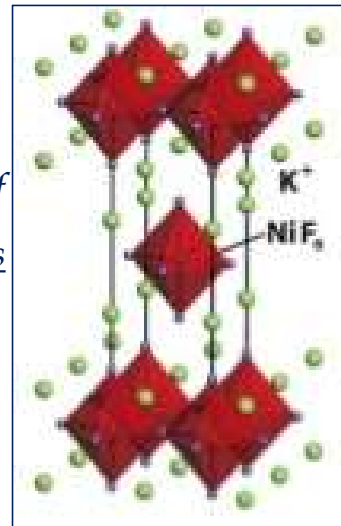
#### 4. Perovskites and related phases

The perovskites have the general formula  $ABX_3$ , in which the 12-coordinate hole of a  $ReO_3$ -type  $BX_3$  structure is occupied by a large  $A$  ion; the perovskite barium titanate,  $BaTiO_3$ , exhibits ferroelectric and piezoelectric properties associated with cooperative displacements of the ions. Application of an external electric field aligns these dipoles throughout the material, resulting in a bulk polarization in a particular direction, which can persist after removal of the electric field.



The temperature below which this spontaneous polarization can occur and the material behaves as a ferroelectric is called the **Curie temperature** (TC). For  $BaTiO_3$  TC is  $120^\circ\text{C}$ . A characteristic of many crystals, including a number of perovskites that lack a centre of symmetry, is **piezoelectricity**: the generation of an electrical field when the crystal is under stress or the change in dimensions of the crystal when an electrical field is applied.

The  $K_2NiF_4$  structure has been introduced as being derived from a single slice of the perovskite structure. Structures with  $K_2NiF_4$  at one end of the range (a single perovskite layer) and perovskite itself at the other (an infinite number of such layers) are known as **Ruddlesden–Popper phases**. They include  $Sr_3Fe_2O_7$  with double layers and  $Ca_4Mn_3O_{10}$  with triple layers.



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5. **High-temperature cuprate superconductors** have structures related to perovskite.

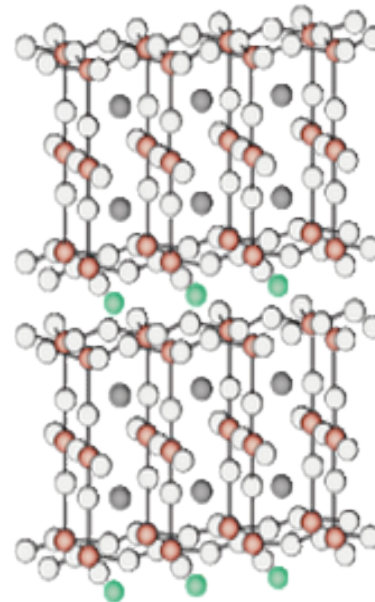
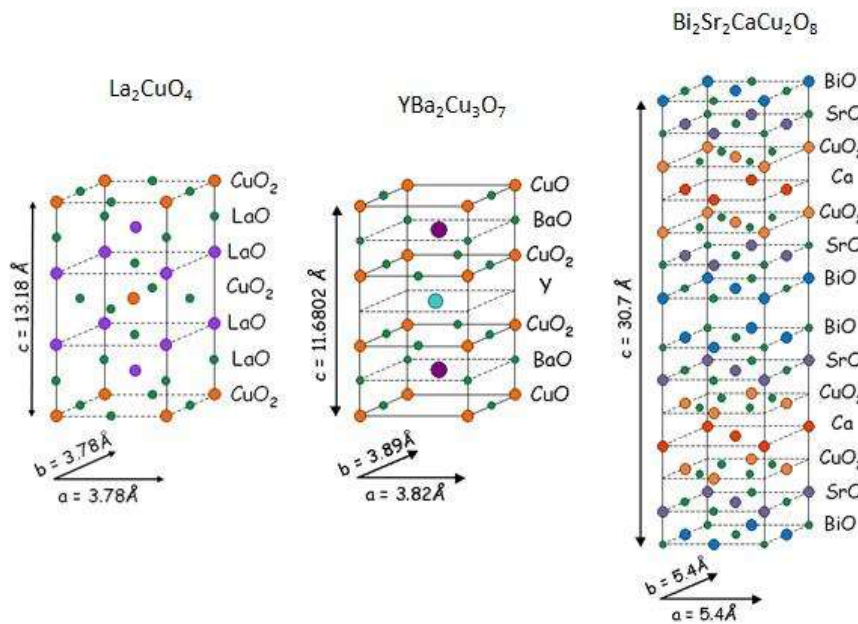
Superconductors have two striking characteristics:

1. Below a critical temperature,  $T_c$  (not to be confused with Curie temperature of a ferroelectric,  $T_C$ ), they enter the superconducting state and have zero electrical resistance.
2. In this superconducting state they also exhibit the **Meissner effect**, the exclusion of a magnetic field. The Meissner effect is the basis of the common demonstration of superconductivity in which a pellet of superconductor levitates above a magnet.

Two types of superconductors are known:

**Type I** show abrupt loss of superconductivity when an applied magnetic field exceeds a value characteristic of the material.

**Type II** superconductors, including high-temperature materials, show gradual loss of superconductivity above a critical field denoted  $H_c$ .



Complex structures and behavior characterize the high temperature superconductors.

	$T_c (\text{K})$
$\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$	30
$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$	38
$\text{La}_{2-x}\text{Sr}_x\text{CaCuO}_4$	60
$\text{YBa}_2\text{Cu}_3\text{O}_7$	92
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	110
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	125

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## Chalcogenides, intercalation compounds, and metal-rich phases

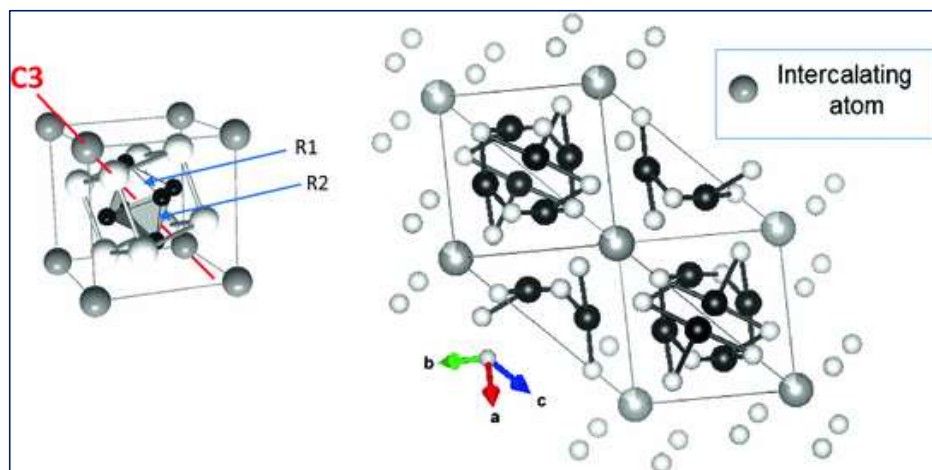
The soft chalcogens S, Se, and Te form binary compounds with metals that generally have very different structures from the corresponding oxides, nitrides, and fluorides. The d-block monosulfides generally adopt the more characteristically covalent nickel-arsenide structure rather than the rock-salt structure of alkaline-earth oxides such as MgO. However,  $\text{Ti}_2\text{S}$ ,  $\text{Pd}_4\text{S}$ ,  $\text{V}_2\text{O}$ , and  $\text{Fe}_3\text{N}$ , and even the alkali metal suboxides, such as  $\text{Cs}_3\text{O}$  do not conform to an ionic model.

## Layered $\text{MS}_2$ compounds and intercalation

**Synthesis:** d-Metal disulfides are synthesized by the direct reaction of the elements in a sealed tube and purified by using chemical vapour transport with iodine.



**Structure:** Elements on the left of the d block form sulfides consisting of sandwich-like layers of the metal coordinated to six S ions; the bonding between the layers is very weak. These sandwich-like slabs form a three-dimensional crystal by stacking in sequences such as AXBAXBAXB..., where the strongly bound AXB slabs are held to their neighbours by weak dispersion forces.



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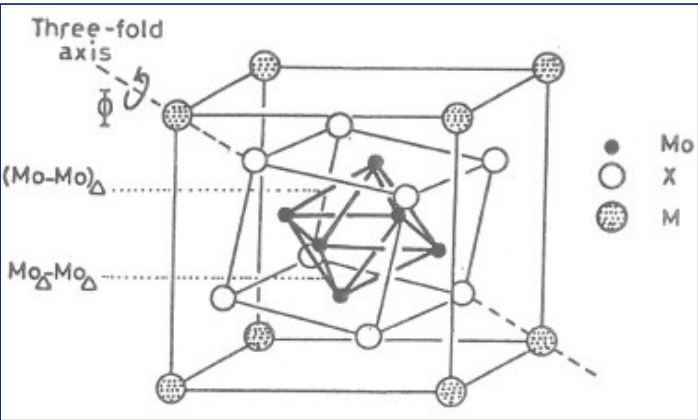


**Intercalation and insertion:** Insertion compounds can be formed from the d-metal disulfides either by direct reaction or electrochemically; insertion compounds can also be formed with molecular guests. For a reaction to qualify as an intercalation, or as an **insertion reaction**, the basic structure of the host should not be altered when it occurs. Reactions in which the structure of one of the solid starting materials is not radically altered are called **topotactic reactions**. The insertion of alkali metal ions into host structures can be achieved by direct combination of the alkali metal and the disulfide:



Insertion may also be achieved by using a highly reducing alkali metal compound, such as butyllithium, or the electrochemical technique of **electrointercalation**.

**Chevreton phases and chalcogenide thermoelectrics:** A Chevreton phase has a formula such as  $\text{Mo}_6\text{X}_8$  or  $\text{AXMo}_6\text{S}_8$ , where Se or Te may take the place of S and the intercalated A atom may be a variety of metals such as Li, Mn, Fe, Cd, and Pb. These compounds, which illustrate three-dimensional intercalation, have formulas such as  $\text{Mo}_6\text{X}_8$  and  $\text{A}_x\text{Mo}_6\text{X}_8$ . The parent compounds  $\text{Mo}_6\text{X}_8$  and  $\text{Mo}_6\text{Te}_8$  are prepared by heating the elements at about  $1000^\circ\text{C}$ . A structural unit common to this series is  $\text{Mo}_6\text{X}_8$ .

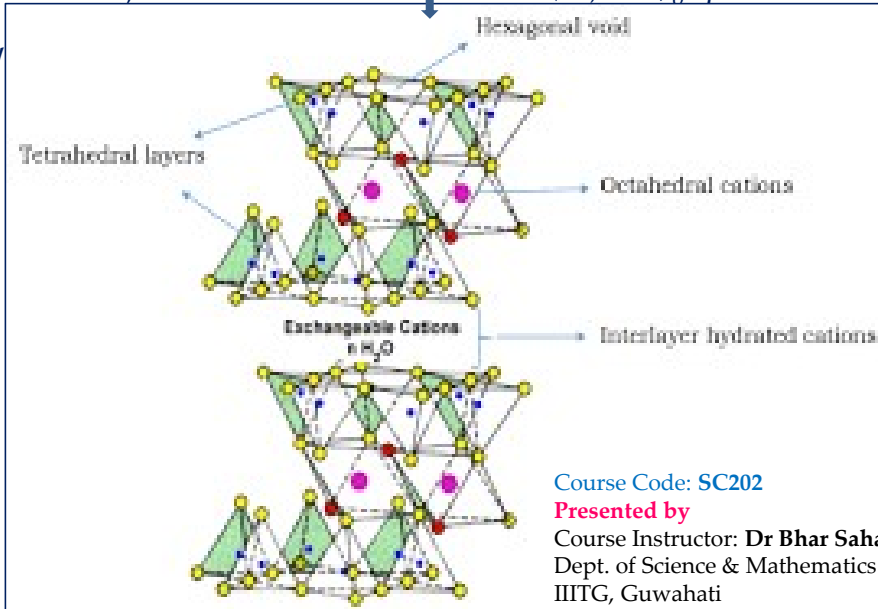
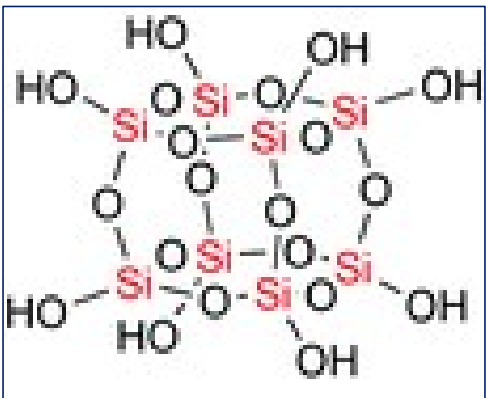


Superconductivity in Chevrel phases persists up to 14 K in  $\text{PbMo}_6\text{X}_8$ , Chevrel phases are also used in the thermoelectric devices used to convert heat into electrical energy or in devices that use electrical energy directly for cooling purposes.

Structures based on octahedra and tetrahedra: The  $\text{MO}_6$  polyhedral building unit may also be incorporated into framework-type structures, often in combination with tetrahedral oxo species.

**Clays, pillared clays, and layered double hydroxides:** Many metal hydroxides and clays having sheet-like structures, can be built from linked metal oxo tetrahedra and octahedra. Naturally occurring clays such as kaolinite, hectorite and montmorillonite have layer structures. Small singly and doubly charged ions, such as  $\text{Li}^+$  and  $\text{Mg}^{2+}$ , occupy sites between the layers. These interlayer cations are often hydrated and can readily be replaced by ion exchange. In the pillaring of clays, the species exchanged into the interlayer region is selected for size. The most widely used pillaring species are of the polynuclear hydroxide type and include  $\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{3+}$  and  $\text{Si}_8\text{O}_{12}(\text{OH})_8$ , the first consists of a central  $\text{AlO}_4$  tetrahedron surrounded by octahedrally coordinated  $\text{Al}^{3+}$  ions as  $\text{Al}(\text{O},\text{OH})_6$  species.

Once an ion has been incorporated between the layers, heating the modified clay results in its dehydration and the linking of the ion to the layers.



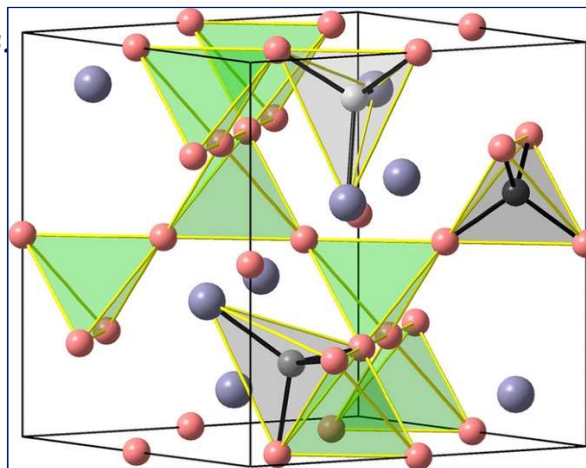
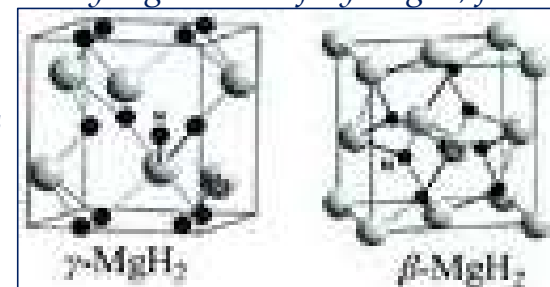
## Hydrides and hydrogen-storage materials

Many metal hydrides and complex metal hydrides such as alanates (hydridoaluminates), amides, and borohydrides release  $H_2$  when heated and are therefore potential materials for hydrogen storage. Hydrogen forms metal hydrides by reaction with many metals and metal alloys.

### Magnesium-based metal hydrides

Magnesium hydride,  $MgH_2$  (rutile structure type) potentially offers a high capacity of 7.7 per cent hydrogen by mass combined with the low cost of magnesium and good reversibility for hydrogen uptake and evolution at high temperatures. However, its decomposition temperature of  $300^\circ C$  under 1 atm of hydrogen gas is uneconomically high. Complex hydrides: include the tetrahydridoaluminates (containing  $AlH_4^-$ ), amides,  $NH_2^-$ , and boranates (hydridoborates containing  $BH_4^-$ ), which can contain very high levels of hydrogen, for example  $LiBH_4$  is 18 per cent hydrogen by mass.

**Intermetallic compounds:** A series of alloys termed **Laves phases** are adopted by some intermetallics of the stoichiometry  $AB_2$  where A is Ti, Zr, or Ln and B is a 3d metal such as V, Cr, Mn, or Fe. These materials have high capacities and good kinetics for hydrogen adsorption, forming compounds such as  $ZrFe_2H_{3.5}$  and  $ErFe_2H_5$  with up to 2 per cent hydrogen by mass.



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**Inorganic pigments:** Intense colour in inorganic solids can arise through d-d transitions, charge transfer (and the analogous interband electron transfer), or intervalence charge transfer. Pigments are of two types:

White pigments: e.g. Titanium dioxide

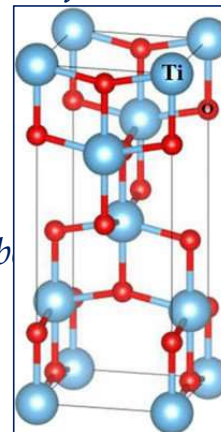
Black, absorbing, and specialist pigments: Special colour, light absorbing, and interference effects can be induced in inorganic materials used as pigments. The most important black pigment is carbon black, which is a better defined, industrially manufactured form of soot.

**Semiconductors:**

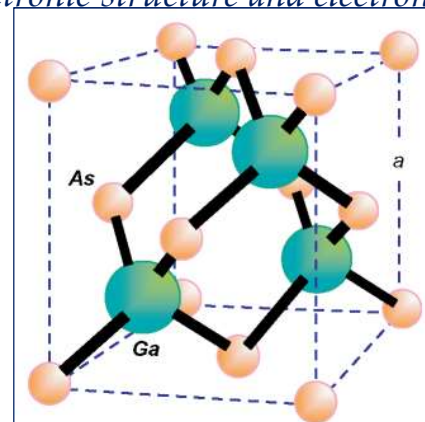
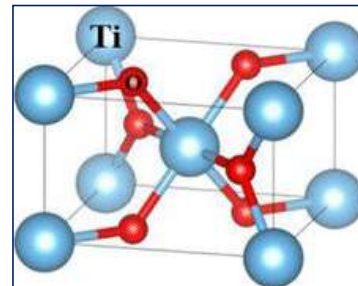
Group 14 semiconductors: Crystalline and amorphous silicon are cheap semiconducting materials and are widely used in electronic devices. The most important semiconducting material is Si, which in its pure crystalline form (with a diamond structure) has a band gap of 1.1 eV. As would be expected from considerations of atomic radii, orbital energies, and the extent of orbital overlap, Ge has a smaller band gap, 0.66 eV, and C as diamond has a band gap of 5.47 eV.

Semiconductor systems isoelectronic with silicon: Semiconductors formed from equal amounts of Group 13/15 or Group 12/16 elements are isoelectronic with silicon and can have enhanced properties based on changes in the electronic structure and electron motion. E.g. Gallium arsenide, GaAs.

Anatase



Rutile



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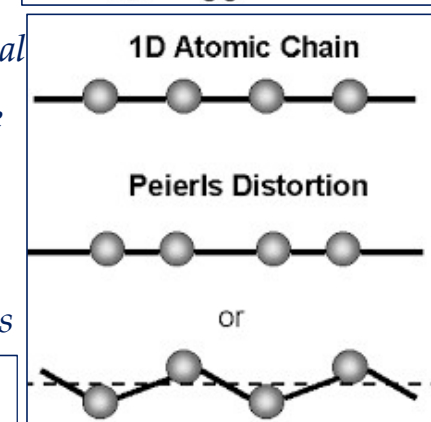
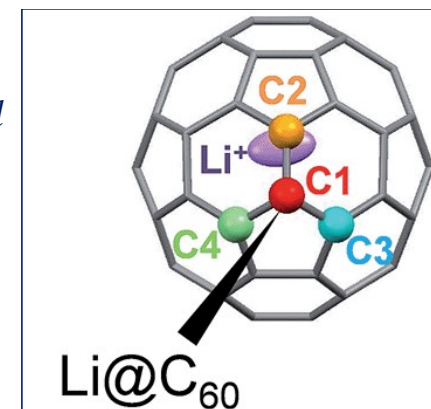
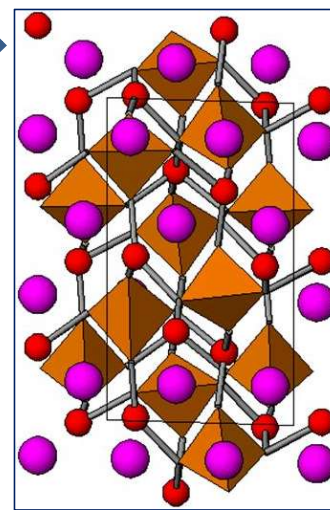
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**Molecular materials and fullerenes** : Solid  $C_{60}$  can be considered as a close-packed array of fullerene molecules interacting only weakly through van der Waals forces; holes in arrays of  $C_{60}$  molecules may be filled by simple and solvated cations and small inorganic molecules.

### Molecular materials chemistry

**One-dimensional metals**: A stack of molecules that interact with each other along one dimension, as occurs in a number of crystalline platinum complexes, can show conductivity in that direction; a Peierls distortion ensures that no one-dimensional solid is a metallic conductor below a critical temperature. In a one-dimensional solid at  $T = 0$ , there always exists a distortion, a **Peierls distortion**, which leads to a lower energy than in the perfectly regular solid.

**Molecular magnets**: Molecular solids containing individual molecules, clusters, or linked chains of molecules can show bulk magnetic effects such as ferromagnetism.



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1 H	<div> <div>Ferromagnetic</div> <div>Antiferromagnetic</div> <div>Paramagnetic</div> <div>Diamagnetic</div> </div>																2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	

**Superparamagnetism (SPM)** is a type of magnetism that occurs in small ferromagnetic or ferrimagnetic nanoparticles.

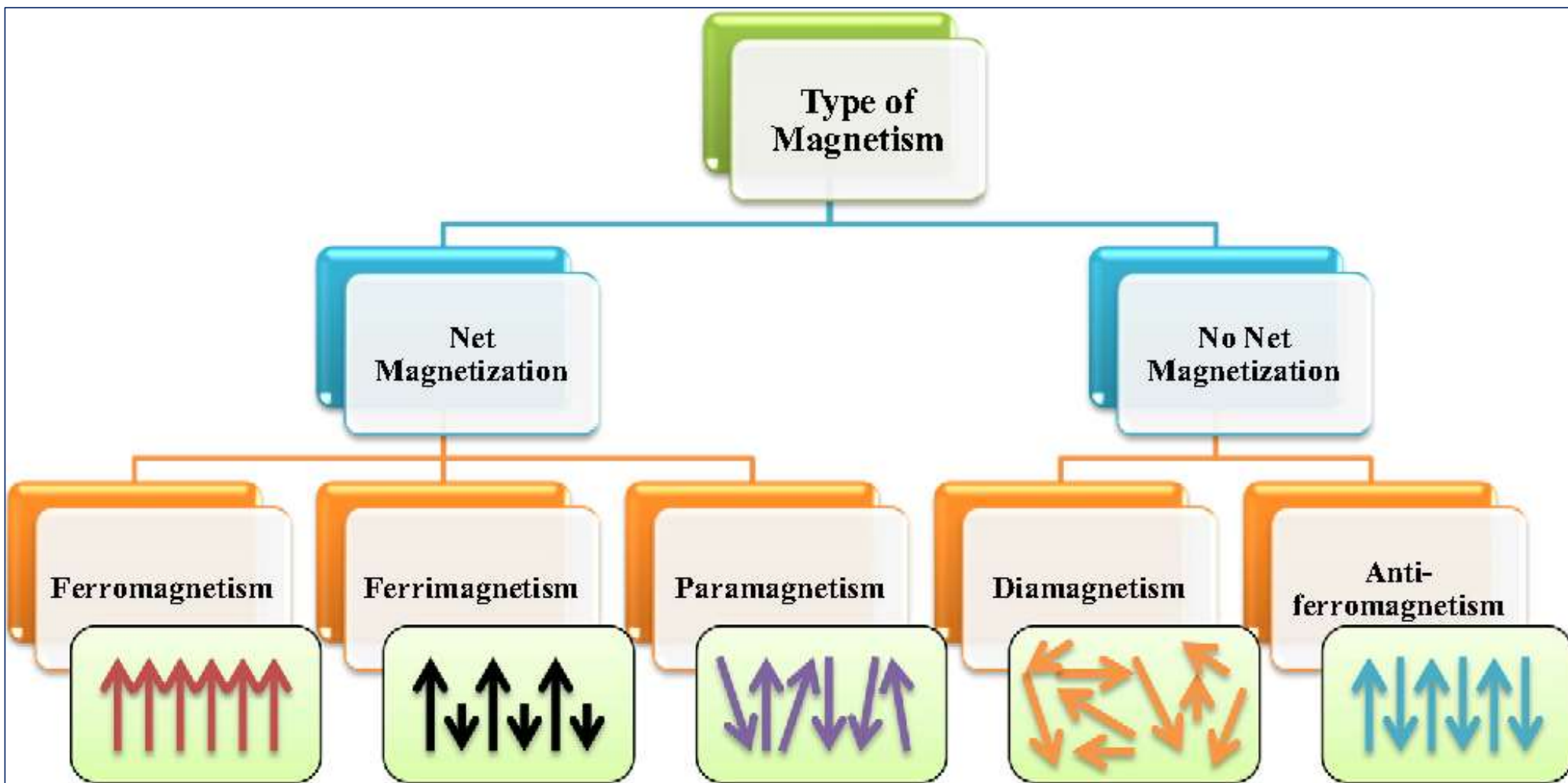
This implies sizes around a few nanometers to a couple of tenth of nanometers, depending on the material.

Additionally, these nanoparticles are single-domain particles.

In a simple approximation, the **total magnetic moment of the nanoparticle can be regarded as one giant magnetic moment**, composed of all the individual magnetic moments of the atoms which form the nanoparticle.

Type	Example	Atomic/Magnetic Behaviour	
Diamagnetism	Inert gases; many metals eg Au, Cu, Hg; non-metallic elements e.g. B, Si, P, S; many ions e.g. $\text{Na}^+$ , $\text{Cl}^-$ & their salts; diatomic molecules e.g. $\text{H}_2$ , $\text{N}_2$ ; $\text{H}_2\text{O}$ ; most organic compounds	Atoms have no magnetic moment. Susceptibility is small & negative, $-10^{-6}$ to $-10^{-5}$	
Paramagnetism	Some metals, e.g. Al; some diatomic gases, e.g. $\text{O}_2$ , NO; ions of transition metals and rare earth metals, and their salts; rare earth oxides.	Atoms have randomly oriented magnetic moments. Susceptibility is small & positive, $+10^{-5}$ to $+10^{-3}$	
Ferromagnetism	Transition metals Fe, H, Co, Ni; rare earths with $64 \leq Z \leq 69$ ; alloys of ferromagnetic elements; some alloys of Mn, e.g. MnBi, $\text{Cu}_2\text{MnAl}$ .	Atoms have parallel aligned magnetic moments. Susceptibility is large (below $T_C$ )	
Antiferromagnetism	Transition metals Mn, Cr & many of their compound, e.g. MnO, CoO, NiO, $\text{Cr}_2\text{O}_3$ , MnS, MnSe, $\text{CuCl}_2$ .	Atoms have anti-parallel aligned magnetic moments. Susceptibility is small & positive, $+10^{-5}$ to $+10^{-3}$	
Ferrimagnetism	$\text{Fe}_3\text{O}_4$ (magnetite); $\gamma\text{-Fe}_2\text{O}_3$ (maghemite); mixed oxides of iron and other elements such as Sr ferrite.	Atoms have mixed parallel and anti-parallel aligned magnetic moments. Susceptibility is large (below $T_C$ )	





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### Diamagnetism

In a diamagnetic material the atoms have no net magnetic moment when there is no applied field. Under the influence of an applied field ( $H$ ) the spinning electrons precess and this motion, which is a type of electric current, produces a magnetisation ( $M$ ) in the opposite direction to that of the applied field. All materials have a diamagnetic effect, however, it is often the case that the diamagnetic effect is masked by the larger paramagnetic or ferromagnetic term. The value of susceptibility is independent of temperature.

### Paramagnetism

There are several theories of paramagnetism, which are valid for specific types of material. The Langevin model, which is true for materials with non-interacting localised electrons, states that each atom has a magnetic moment which is randomly oriented as a result of thermal agitation. The application of a magnetic field creates a slight alignment of these moments and hence a low magnetisation in the same direction as the applied field. As the temperature increases, then the thermal agitation will increase and it will become harder to align the atomic magnetic moments and hence the susceptibility will decrease. This behaviour is known as the Curie law

### Ferromagnetism

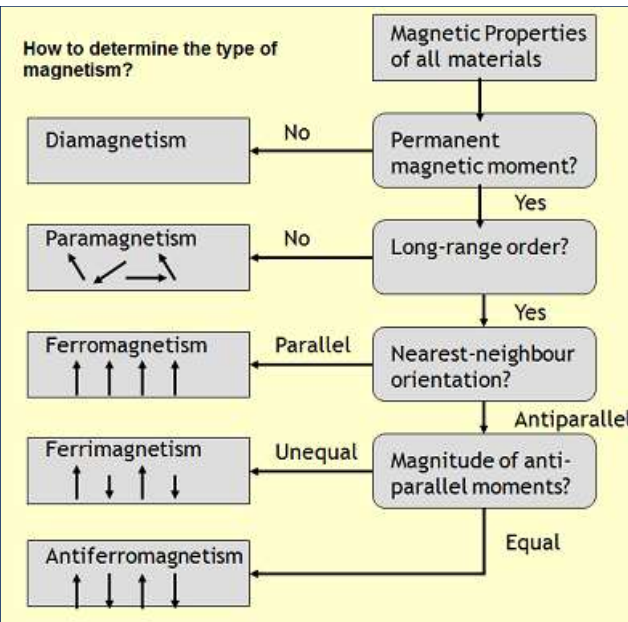
Ferromagnetism is only possible when atoms are arranged in a lattice and the atomic magnetic moments can interact to align parallel to each other. This effect is explained in classical theory by the presence of a molecular field within the ferromagnetic material, which was first postulated by Weiss in 1907. This field is sufficient to magnetise the material to saturation. In quantum mechanics, the Heisenberg model of ferromagnetism describes the parallel alignment of magnetic moments in terms of an exchange interaction between neighbouring moments.

### Antiferromagnetism

In the periodic table the only element exhibiting antiferromagnetism at room temperature is chromium. Antiferromagnetic materials are very similar to ferromagnetic materials but the exchange interaction between neighbouring atoms leads to the anti-parallel alignment of the atomic magnetic moments. Therefore, the magnetic field cancels out and the material appears to behave in the same way as a paramagnetic material. Like ferromagnetic materials these materials become paramagnetic above a transition temperature, known as the Néel temperature,  $T_N$ . (Cr:  $T_N=37^\circ\text{C}$ ).

### Ferrimagnetism

Ferrimagnetism is only observed in compounds, which have more complex crystal structures than pure elements. Within these materials the exchange interactions lead to parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others. The material breaks down into magnetic domains, just like a ferromagnetic material and the magnetic behaviour is also very similar, although ferrimagnetic materials usually have lower saturation magnetisations. For example in Barium ferrite ( $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$ ) the unit cell contains 64 ions of which the barium and oxygen ions have no magnetic moment, 16  $\text{Fe}^{3+}$  ions have moments aligned parallel and 8  $\text{Fe}^{3+}$  aligned anti-parallel giving a net magnetisation parallel to the applied field, but with a relatively low magnitude as only  $\frac{1}{6}$  of the ions contribute to the magnetisation of the material.



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**Inorganic liquid crystals:** Inorganic metal complexes with disc- or rod-like geometries can show liquid crystalline properties. Liquid crystalline, or **mesogenic**, compounds possess properties that lie between those of solids and liquids and include both. For instance, they are fluid, but with positional order in at least one dimension. Such materials have become widely used in displays. The molecules that form liquid crystalline materials are generally **calamitic** (rod-like) or **discotic** (disc-like), and these shapes lead to the ordered liquid-type structures in which the molecules align in a particular direction.

The phase which is intermediate of solid and liquid and which has properties in between true crystalline solid and true liquid (clear liquid) is called liquid crystal

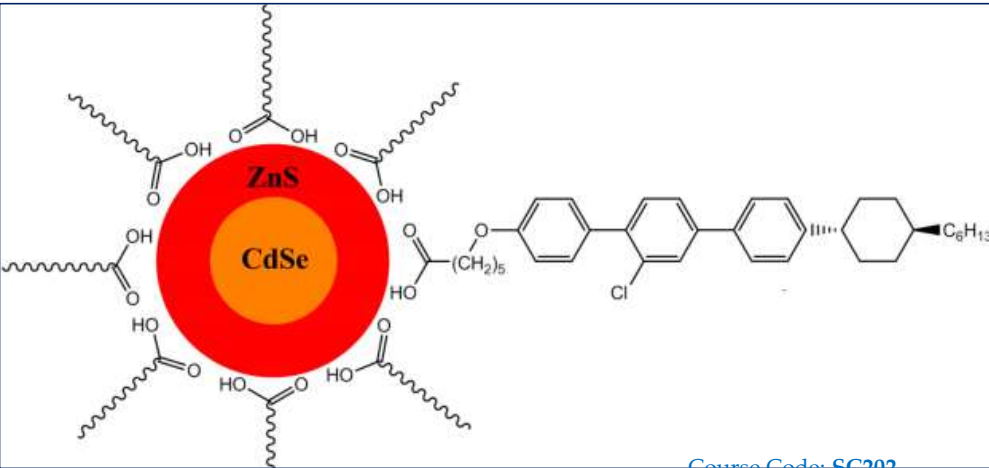
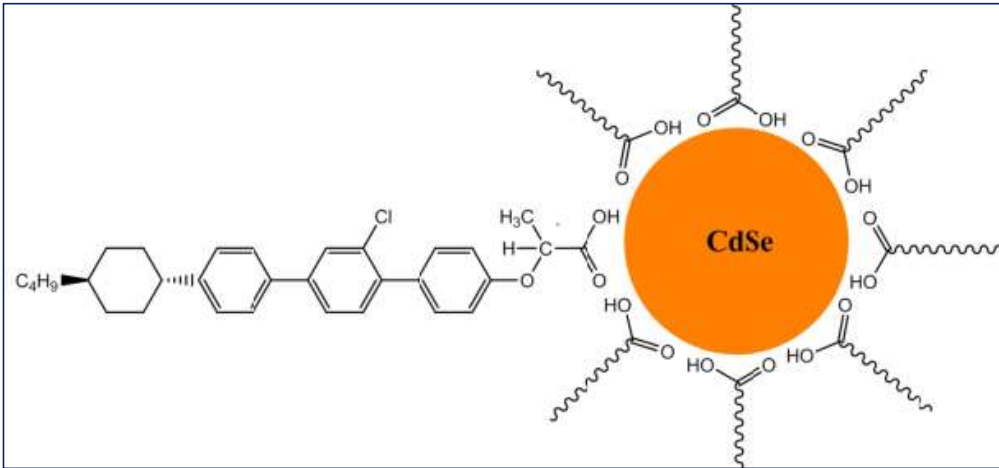
Properties of Liquid Crystals like solids:  
 orderly arrangement of particles  
 optical activity

Properties of Liquid Crystals like liquids:  
 fluidly  
 viscosity  
 surface tension

Rod-like / Calamitic



Disc-like / Discotic



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