

Chemistry of materials

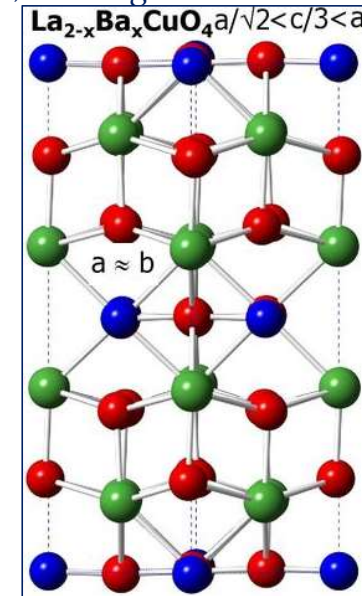
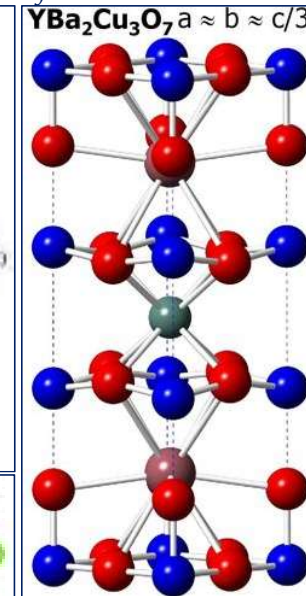
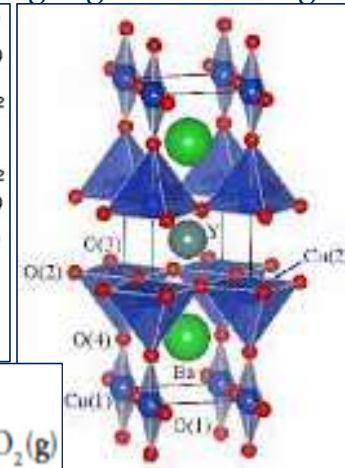
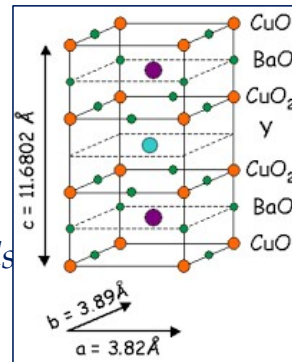
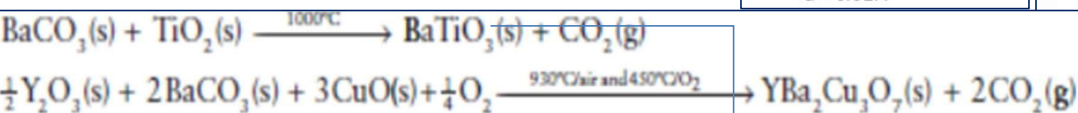
Inorganic materials are synthesized as bulk solids & on substrates. The role of defects in controlling structure, ion migration in solids is very important. Microporous solids are used in molecular separations and heterogeneous catalysis. Computer modelling is used to develop numerical models of the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

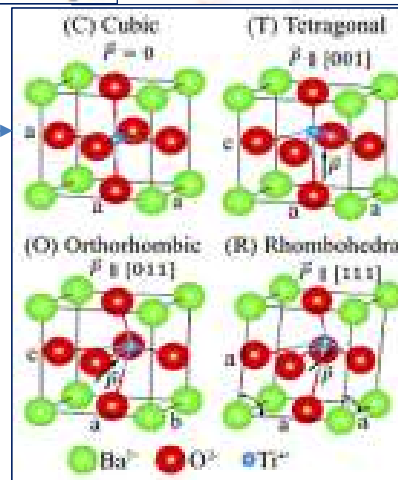
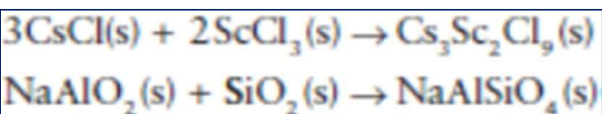
Bulk material can be synthesized by 2 methods:

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:



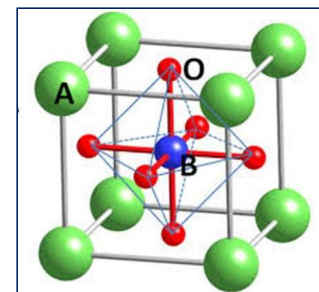
The tetragonal polymorph is the most widely used because of its excellent ferroelectric, piezoelectric, and thermoelectric properties

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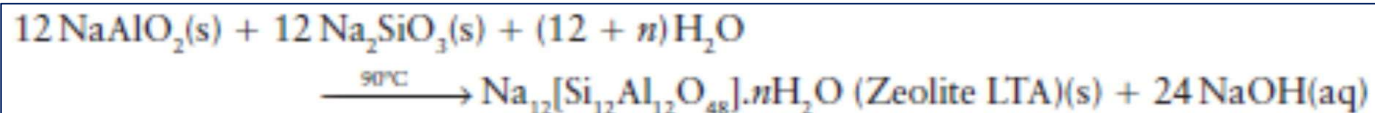
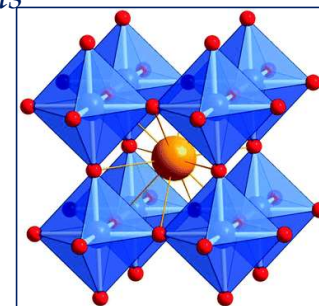
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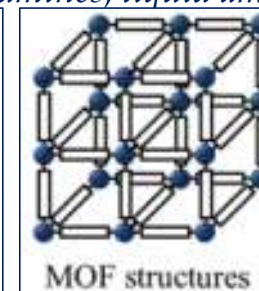
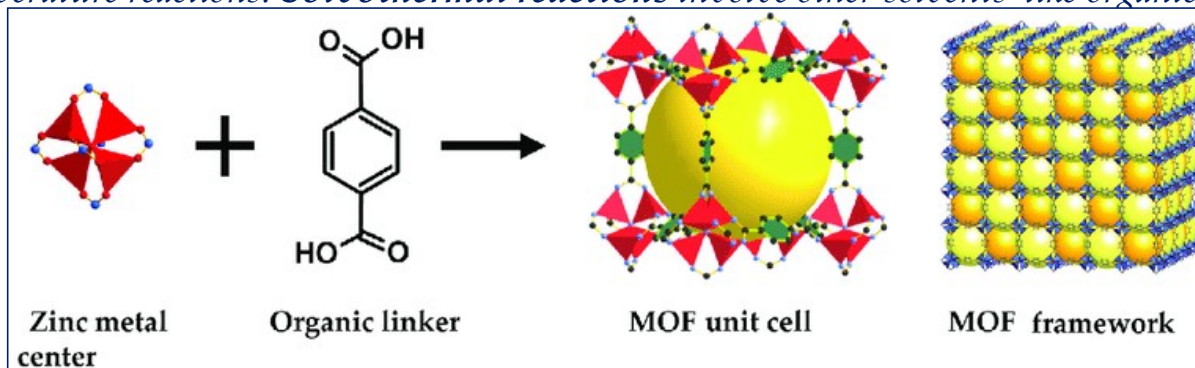
High pressures are used to control the composition of the reaction product and to affect the outcome of a solid-state chemical reaction. Reactions carried out under such conditions promote the formation of dense, higher coordination number structures. An example is the production of MgSiO_3 , with a perovskite-like structure and six-coordinate Si in an octahedral SiO_6 unit, rather than the normal tetrahedral SiO_4 unit.



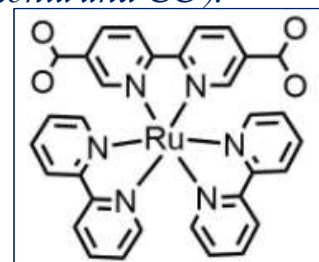
2. Solution methods: Condensation reactions in solution can give rise to polyhedral species. Many inorganic materials are synthesized by crystallization from solution using **hydrothermal techniques**, in which reacting soln is heated above its normal bp in a sealed vessel, in case of aluminosilicates (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°C to the dense aluminosilicate 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 CO_2 .



MOF structures



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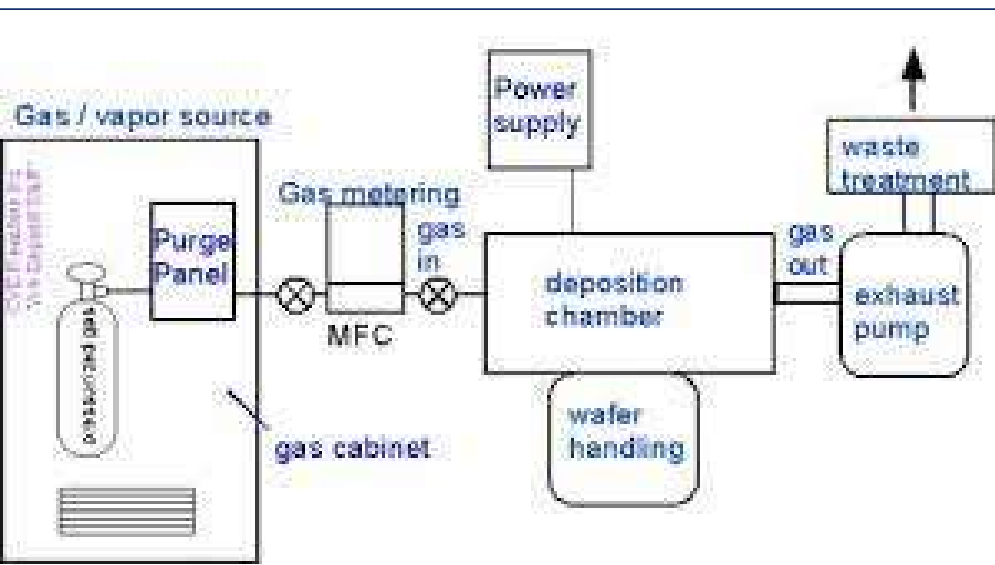
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Group 13/15 (III/V) semiconductors

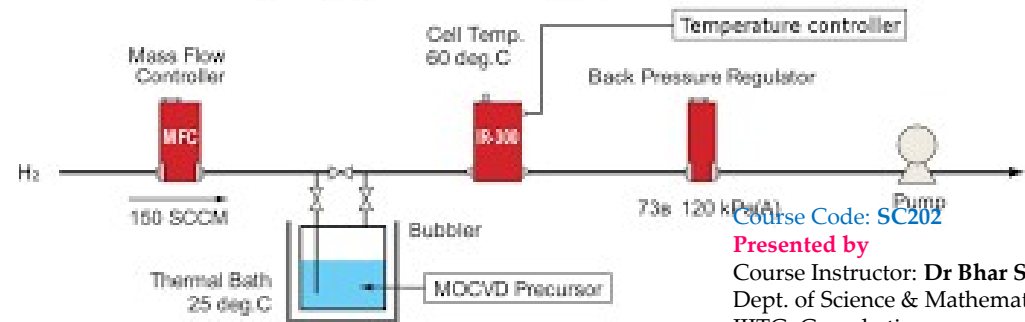
Deposition: In order to develop techniques to deposit films of many inorganic materials, the principal method is **chemical vapour deposition (CVD)**, in which a volatile inorganic compound is decomposed above the substrate. When the compound is a metallo-organic complex (that is, a complex of a metal atom with organic ligands), this route is known as **metallo-organic chemical vapour deposition (MOCVD)**. E.g. Me_2Zn , which has a vapour pressure of 0.3 bar at room temperature, can react with H_2S above a substrate to generate the Group 12/16 (II/VI) semiconductor 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.

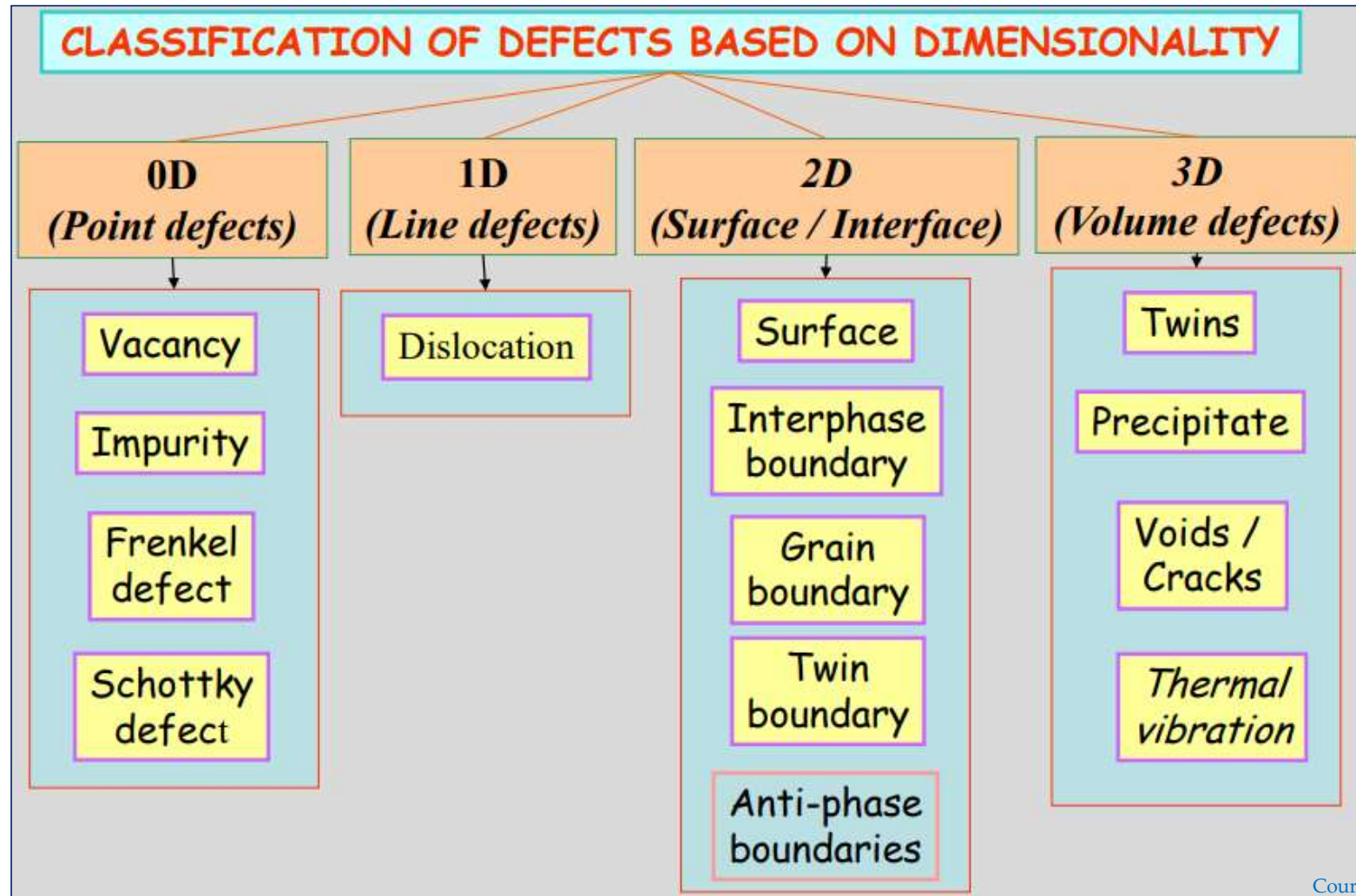
examples are $\text{ZnS}_x\text{Se}_{1-x}$ and $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$



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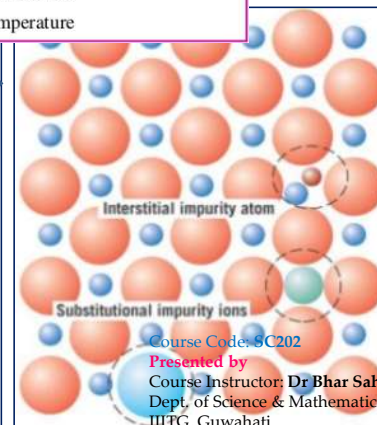
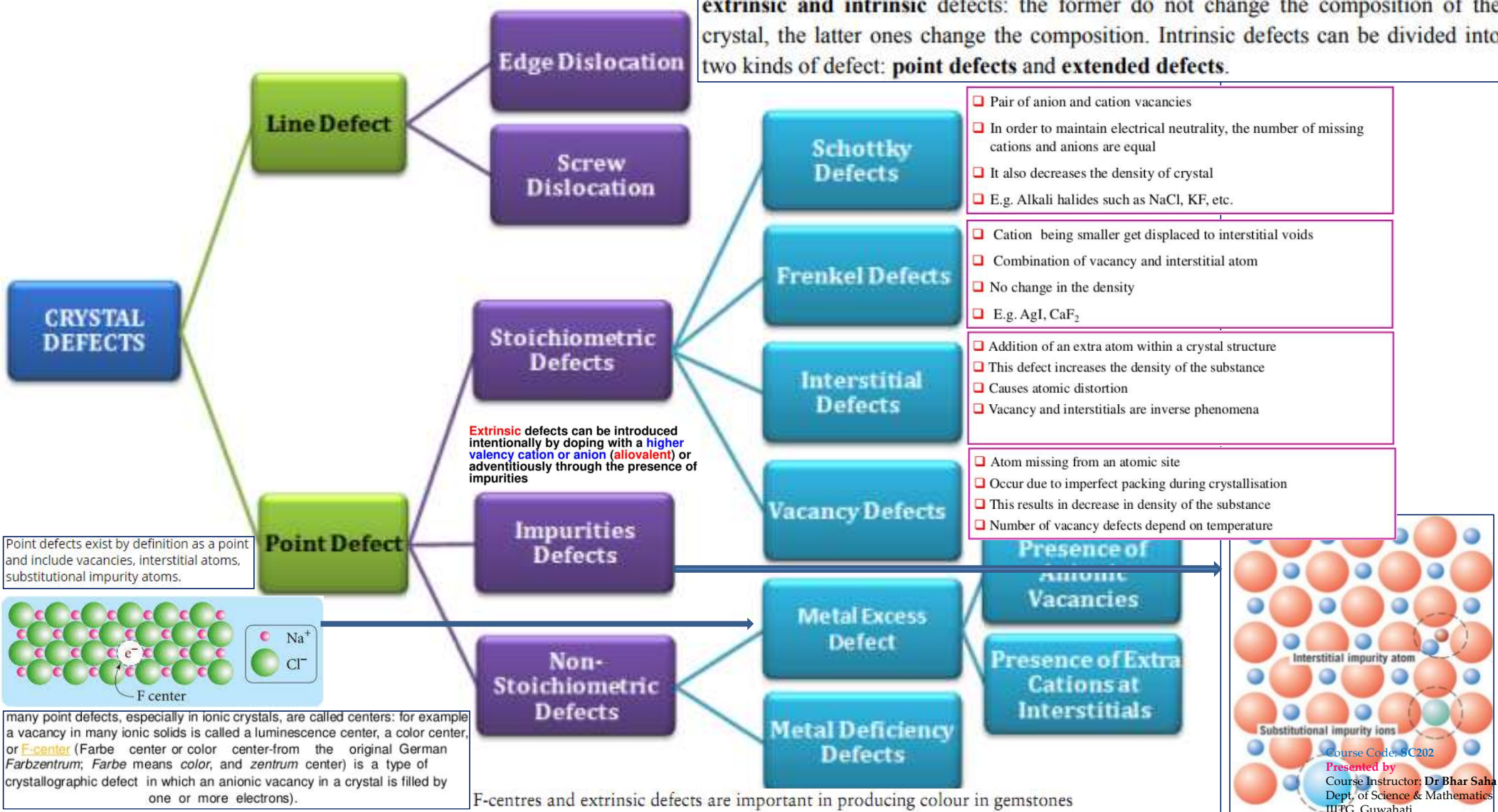
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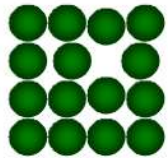
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Every solid has a thermodynamic tendency to acquire point defects, as they introduce disorder and therefore increase entropy.

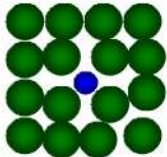
The formation of defects needs energy, $\Delta H > 0$. Defects lead to a gain in entropy, $\Delta S > 0$. According to the equation: $\Delta G = \Delta H - T\Delta S$, all solids tend to acquire defects, because defects increase their entropy and reduce the free energy. They can be classified as **extrinsic 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**.



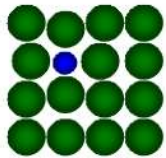
Point defects of crystals



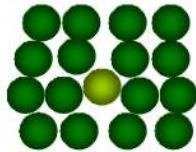
Vacancy



Interstitial impurity

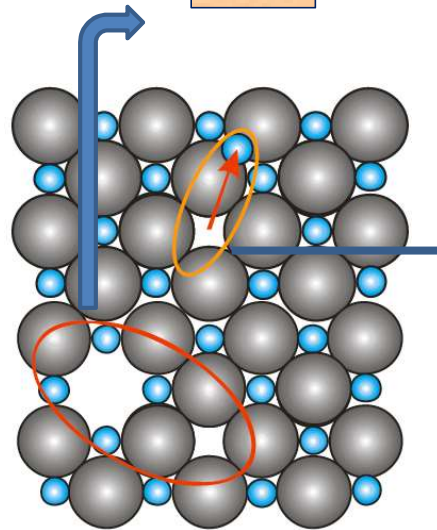


Substitution impurity



Self-interstitial

0D



defect type

compound

ΔH (10^{-19} J)

ΔH (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
UO ₂	5.45	3.40
ZrO ₂	6.57	4.10
CaF ₂	4.49	2.80
SrF ₂	1.12	0.70
AgCl	2.56	1.60
AgBr	1.92	1.20
beta-Agl	1.12	0.70

Frenkel

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

Silicon atom



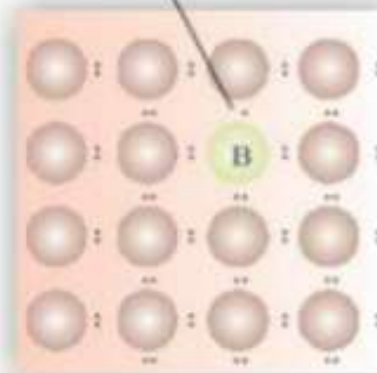
Perfect crystal

Mobile electron



n-type

Positive hole
(no electron)



p-type

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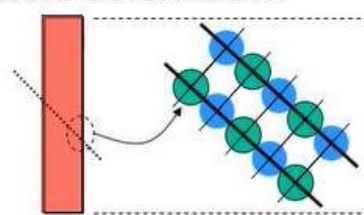
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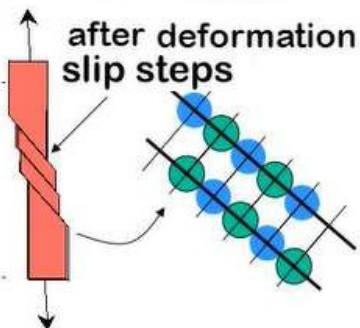
1D

Dislocations Zinc Crystal (HCP)

before deformation

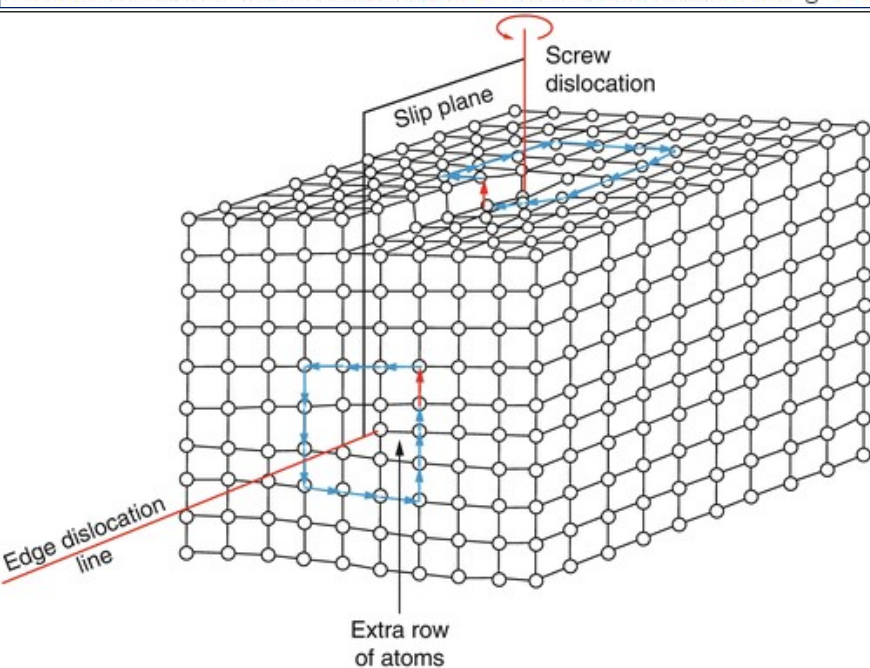


after deformation
slip steps



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

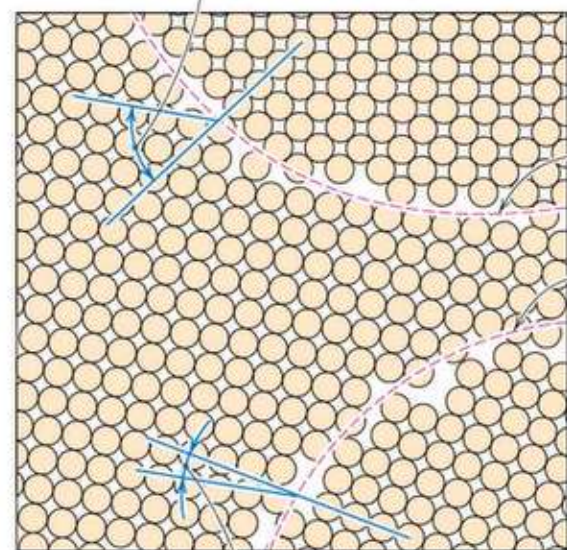
One-dimensional or linear defects are called dislocations. An *edge dislocation* is when a half plane of atoms disrupts the overall crystal structure. A *screw dislocation* is when a half twist disrupts the overall crystal structure. A *mixed dislocation* is a dislocation that combines both an edge and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

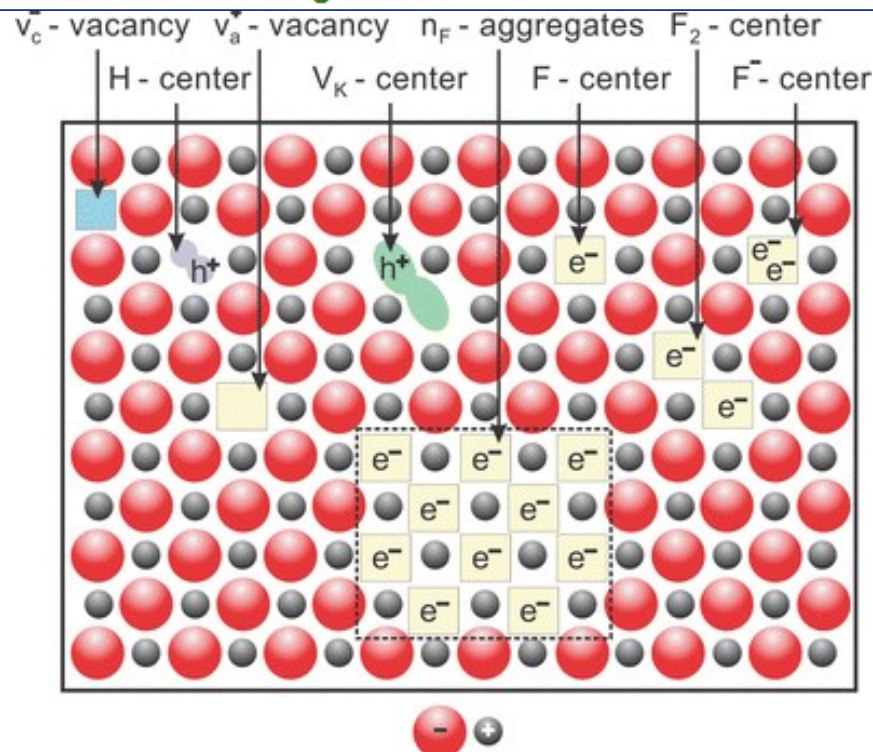
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Metal Excess Defects

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.

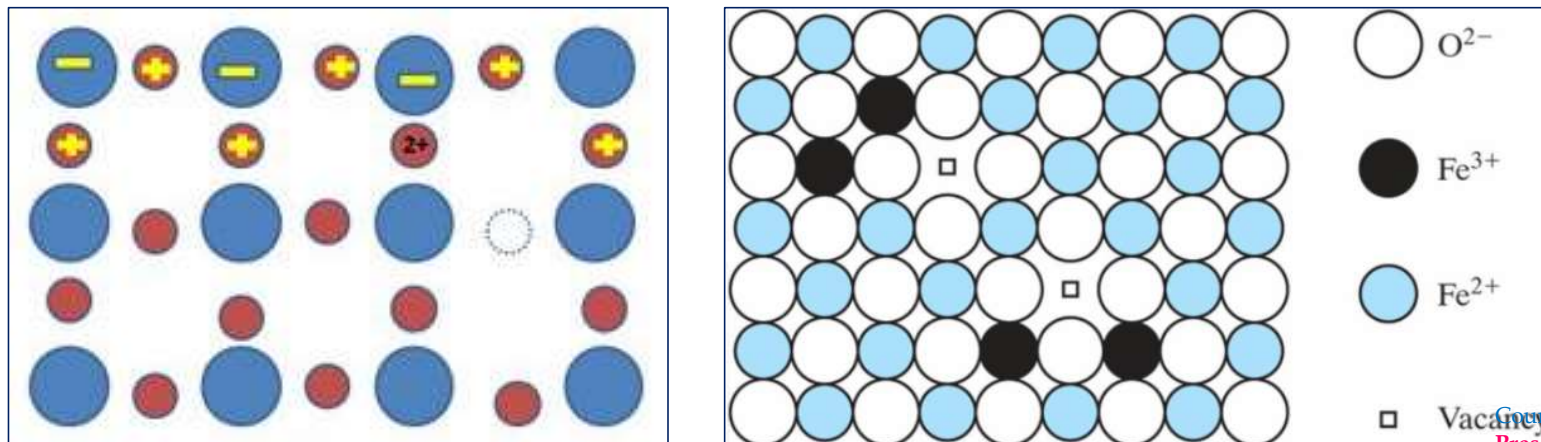
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Metal Deficiency Defects

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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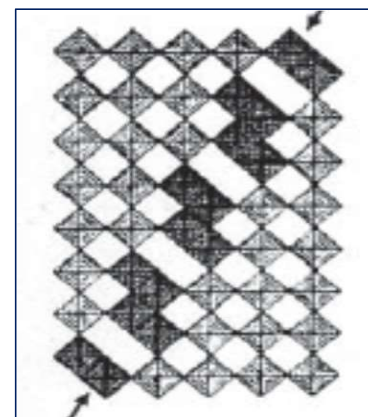
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Defects and ion transport:

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 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 ReO_3 and 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 and small radii:*** *The most mobile cation (other than the proton) and anion are Li^+ and F^- respectively. Na^+ and 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 number of ions.*

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 α = 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 _x	0.65 < x < 1.25
TiO _x	1.998 < x < 2.00
VO _x	0.79 < x < 1.29
FeO _x	0.833 < x < 0.957
NiO _x	0.999 < x < 1.000
ZnO _x	1.000 < x < 0.999
UO _x	1.65 < x < 2.25
H _x MoO ₃	0.23 < x < 2.00
WO _{3-x}	0.1 < x < 0.25
Li _x WO ₃	0.0 < x < 0.50
TiS _x	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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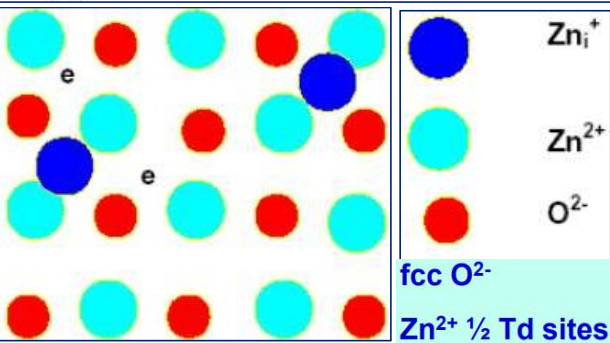
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DIFFERENCE: NS ZINC OXIDE AND NICKEL OXIDE

Zn_{1+x}O made by adding 0.033 Zn atom% excess over stoichiometric

ZnO white, wide bandgap insulator

Zn_{1+x}O orange, n-type semiconductor



NS zinc oxide
 Zn^+ Frenkel defects
 Zn behaves as n-type dopant
 Simple band model
 Semiconductor behavior

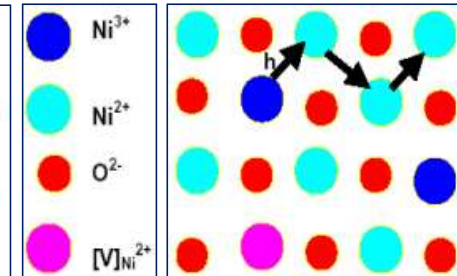
Ni_{1-x}O made by heating NiO in O_2 introducing 0.001 Ni atom% deficiency over stoichiometric

NiO green, semiconducting anti-ferromagnet

Ni_{1-x}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 1st transition series
 High effective nuclear charge Z^*
 Contracted d-orbitals
Narrow localized $e_g^2 (dz^2, x^2-y^2)^2$ d-band

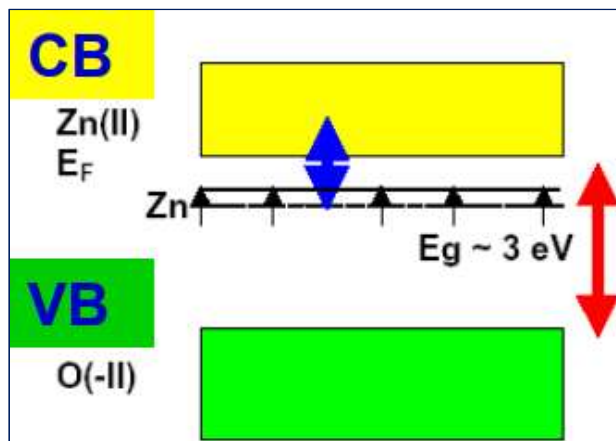
Overlap of dz^2, x^2-y^2 with $\text{O(-II) } 2p$ sigma-orbitals
 UPEs **super-exchange coupled**
Behaves as antiferromagnetic semiconductor



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 Ni^{3+} , instead **HOPPING SEMICONDUCTOR**, with activated diffusion of holes from Ni^{3+} to Ni^{2+}

NOT p-Si type electronic band model with excitation of e- into 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 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 antiferromagnetically coupled e_g electrons

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