4th year undergraduate course **Lecture 1**

Solid State Chemistry

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READING LIST

Principal textbook….

- **Basic Solid State Chemistry, A. R. West. (NUIG library)**

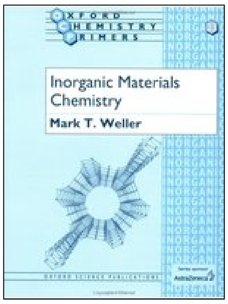
May also want to look in:

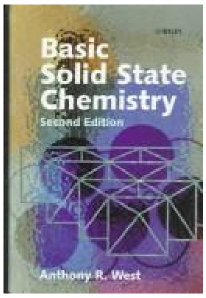
- ***Inorganic Chemistry*. Shriver, Atkins and Langford**
- ***Inorganic Chemistry*, Housecroft & Sharpe.**

- **A. K. Cheetham and P. Day, *Solid state chemistry techniques*. Oxford Science publications, 1987.**

Another helpful book (but does not contain all information needed)

"Inorganic Materials Chemistry", Mark T. Weller.
Oxford Chemistry Primer, Oxford Publications.





Lecture 1: Outcomes

• *Introduction to solid state chemistry*

Inorganic solids and their applications (various)

•*Introduction to structure of solids*

Amorphous ***crystalline***

•*Introduction to new functional materials from everyday life*

Transition metal oxides (inc. Perovskites) ***Silicates / Aluminosilicates***

• *Recap of 2/3rd year work on structural characterisation*

X-ray crystallography
The unit cell
Atom counting inside unit cell

SOLID STATE CHEMISTRY

Definition:
The study of the preparation, characterisation and physical properties of solids

Why study solids?

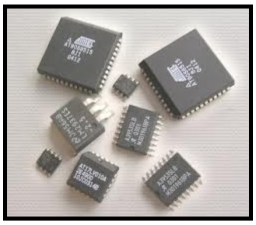
- Solids are of immense technological importance
- The study of solids leads to the preparation of new solids with improved/new technological properties

Strong overlap with:

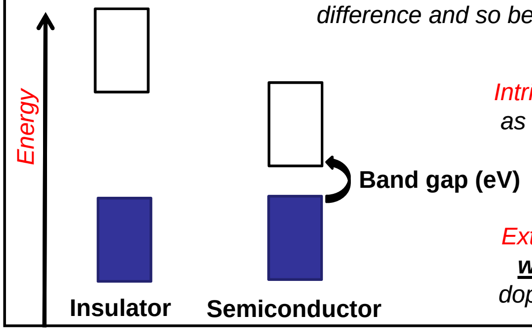
- Molecular Structure *(X-ray Crystallography, powder diffraction)*
- Solid-state Physics *(Conductivity, Electronic properties, ionic conductors)*
- Ceramics *(durable materials, heat resistant materials)*
- Metallurgy *(synthesis of new metal based solids towards conductors etc)*

PROPERTIES OF SOLIDS

- ELECTRICAL PROPERTIES
  - Conductors (Cu, Ag) (worse at high T)
  - Semiconductors (Si, GaAs) (better at high T)
  - Superconductors ($Y_2BaCu_3O_7$)



Semiconductors



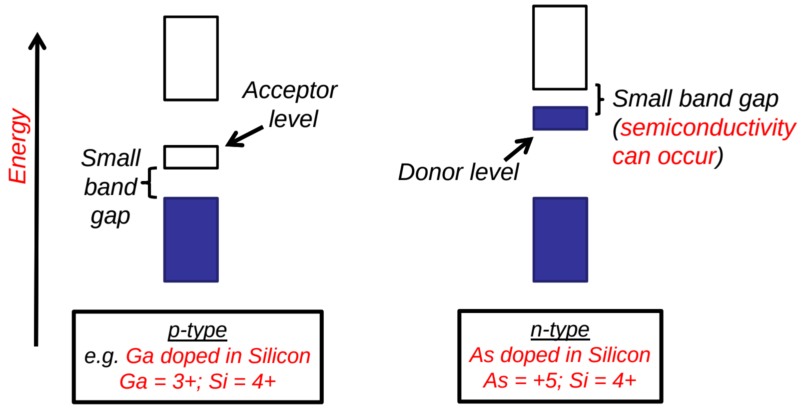
Band theory: *Group of MOs with minimal energy difference and so behave as continuous band of energy*

Intrinsic semiconductor: *Material behaves as semiconductor without the addition of dopants*

Extrinsic semiconductor: *Semiconductor* ***when doped*** *with minute amounts of dopant to enhance electrical conductivity*

PROPERTIES OF SOLIDS (2)

Extrinsic semiconductors (n and p-type):



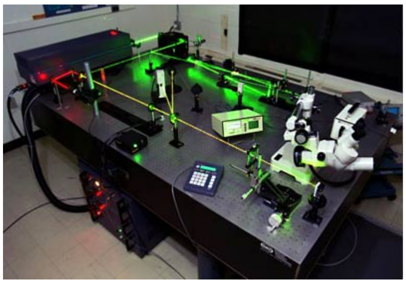
MAGNETIC PROPERTIES: CrO_2, $MgFe_2O_4$ for information recording (see 4th yr. magnetism notes)

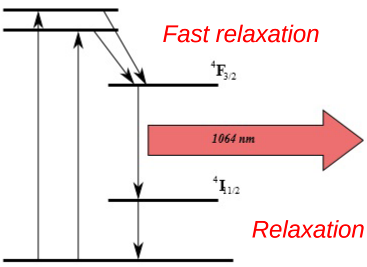
OPTICAL PROPERTIES: TiO_2 for pigments, Cr^{3+} doped into Al_2O_3 is ruby (gives colour)….ruby solid state lasers (now a little dated!)

PROPERTIES OF SOLIDS (3)

Nd-YAG High Powered Lasers

- Neodimium (Nd^{3+}) doped into a rod of Yttrium Aluminium Garnet (YAG; $Al_5Y_3O_{12}$)





Applications

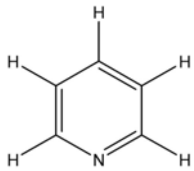
- *Hair removal and vascular defect removal*
- *Etching, cutting and welding metals*
- *Eye surgery*
- *Oncology: Removal of skin cancers*
- *Military Defence: Range Finders*

Inorganic Solids vs. Molecules

Differ greatly from one another:

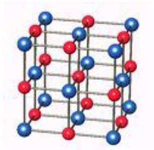
MOLECULES	INORGANIC SOLIDS
• *Single units*	*Infinite lattices*
• *Fixed formulae*	*Variable stoichiometry*
• *Defects not allowed*	*Defects unavoidable*
• *Properties are fixed*	*Properties vary with composition*

For example:



Pyridine

For example:



Sodium Chloride

Two forms of solid

Definitions:

A **crystalline solid**
is a solid in which the atoms, ions or molecules lie in an orderly array
(NaCl)

An **amorphous solid**
is a solid in which the atoms, ions or molecules lie in random positions
(glass, rubber).

STRUCTURE OF SOLIDS

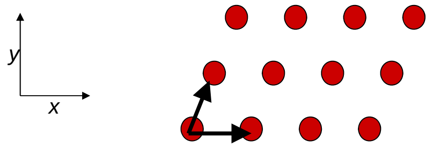
The structure of crystals influences their physical properties strongly

Structure of a crystalline solid: how atoms, ions, molecules are arranged with respect to one another.

• We use spheres to conveniently represent atoms or ions in solids

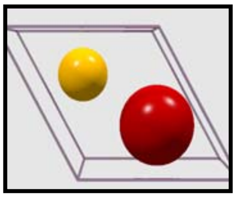
A **crystalline solids** is viewed as built from atoms or ions, which repeat with precise regularity.

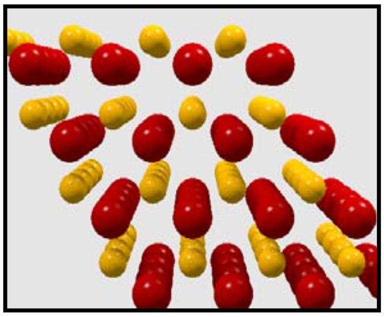
Lattice : an infinite array of points in space (lattice points), in which each point has identical surroundings to all of the other lattice points

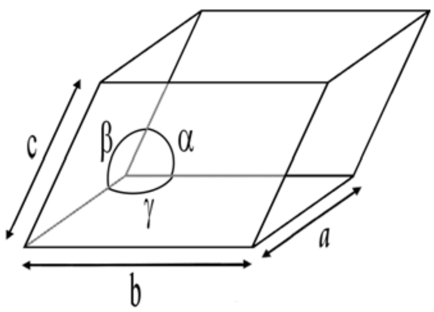


lattice

Unit cell: The smallest unit of a crystal that reproduces the crystal by translation along x, y, z





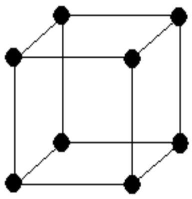


The parameters that define a unit cell are:

a, ***b***, ***c*** = unit cell dimensions along x, y, z respectively

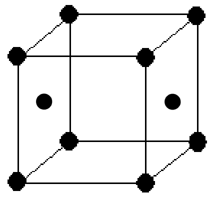
α, β, γ = angles between *b*,*c* (α); *a*,*c* (β); *a*,*b* (γ).

Types of Unit Cells

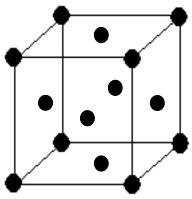


P (primitive cell)

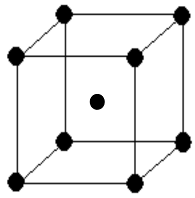
(A, or B, or C)



- *The end centred cells*



F (face centred cell)



I (body centred)

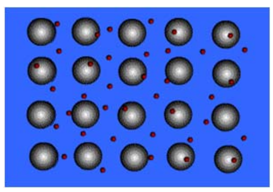
TYPES OF SOLIDS

Solids are classified according to the type of interactions between the particles forming the crystal
There are: **METALLIC, IONIC,** covalent and molecular solids

METALLIC SOLIDS

Metals (Ti, Ca)

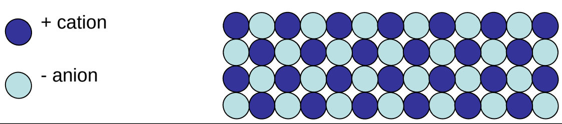
Metallic bond



IONIC CRYSTALS

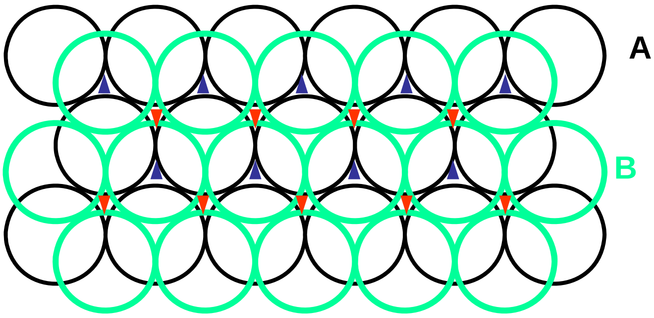
Oxides, halides etc (CaO, NaCl)

Ionic bond



IONIC COMPOUNDS: MX_n TYPE LATTICES

- Anions and cations are represented by spheres of different size.
- The anion is <u>larger</u> than the cation.
- The anion forms a close- packed or non-close packed lattice and the <u>cation fits into the holes.</u>

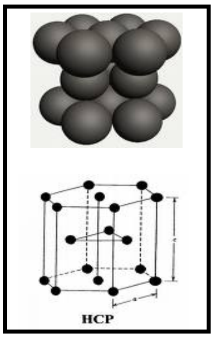


Only 2 types of holes In a ***close-packed*** arrangement

NOTE: non-close packed arrangements show more types of holes

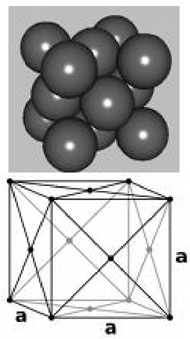
REMEMBER: *<u>Hexagonal Close Packing (HCP)</u>*

- *Packing = ABABAB (every other layer are the same*
- *Gives a Hexagonal unit cell = HCP system*



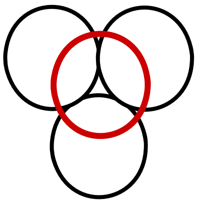
<u>Cubic Close Packed (CCP) (or Face-centred cubic (FCC)</u>

- *Spheres of third layer placed above the gaps in the first layer = ABCABC*
- *Gives a Face-centred cubic unit cell = FCC system*



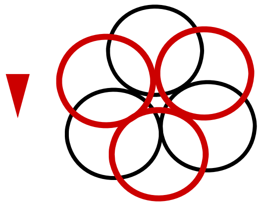
In either HCP or CCP arrangements there are two types of holes

1)



***Tetrahedral holes**:* CN (cation)=**4** as the cation is surrounded by **4** anions

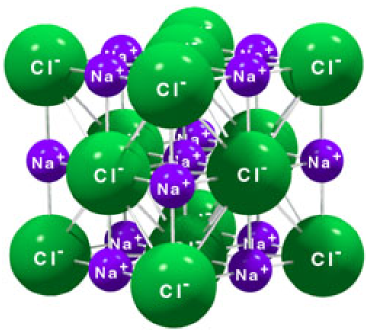
2)



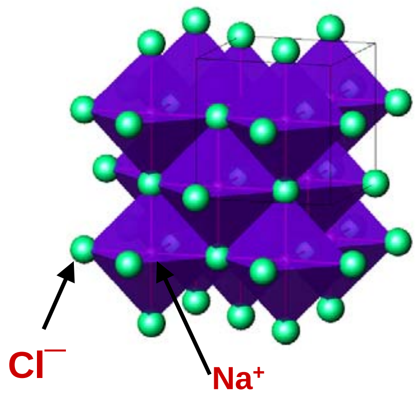
Octahedral holes: CN (cation)=**6** as the cation is surrounded by **6** anions

NOTE:
In a 3D close-packed array of *n* spheres, there are 2*n* tetrahedral holes and *n* octahedral holes

COMPOUND WITH CCP LATTICES



'Balls and sticks' representation



Polyhedral representation

NaCl (Rock-Salt)

Oxidation states

Need to know these to understand structure and physical properties of functional inorganic solids

Group	Oxidation State
1	+1 (Li)
2	+2 (Be)
3	+3 (Sc)
4	+4 (Ti)
13	+3 (B)
14	+4 (Si)

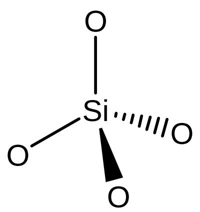
2,3,4,5	2,3,6	2,3,4,5,6,7	2,3	2,3	2,3	1,2	2
V	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**

All Ln ions = +3

Silicates – minerals comprising Si & O

Minerals = ~90% earth's crust
3D materials containing SiO_4^{4-} tetrahedra & M^+ ions, e.g. K^+, Na^+, Mg^{2+}

Basic building blocks:



Si = 4+, O = 2-

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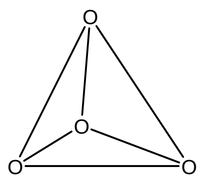

SiO_4^{4-}

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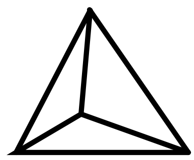
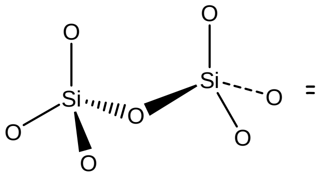
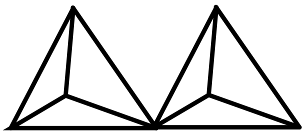


SiO_4^{4-}

atom	*charge*
Terminal O	1-
Shared O	0



$Si_2O_7^{6-}$



$Si_2O_7^{6-}$

- If all O-atoms shared = 3D lattice = silica, SiO_2; mineral **Quartz**
- Transparent, hard, stable material

Similar to structure of diamond

APPLICATIONS

a) *Gemstones*

b) *Glass & lenses, optical fibres, telecommunications…*

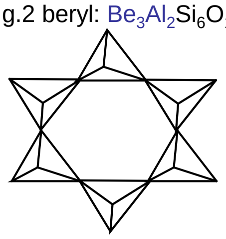
c) *Building materials – Quartz is a common constituent of granite, sandstone, limestone*

Aluminosilicates

Partial substitution of Si^{4+} by Al^{3+};

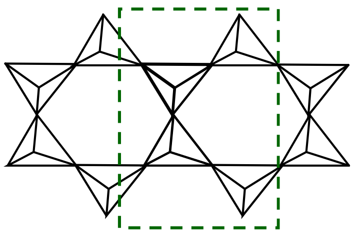
e.g.1 orthoclase: $KAlSi_3O_8$ - This mineral forms igneous rock. Main component of “moonstone”

e.g.2 beryl: $Be_3Al_2Si_6O_{18}$ colourless/white – main source of Be metal



$Si_6O_{18}^{12-}$

Emerald = beryl silicate 2% Al^{3+} replaced with **Cr^{3+}**



Asbestos (Tremolite)
$[Ca_2Mg_5(Si_4O_{11})(OH)_2]$
Fibrous - ionic bonds between sheets of silicate anions and Ca^{2+}/Mg^{2+} ions in between sheets = weak.

$Si_4O_{11}^{6-}$

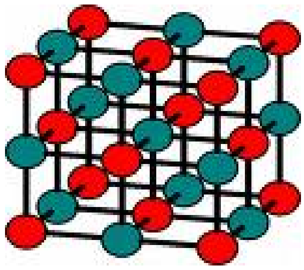
Also known as cyclosilicates

Metal oxides

MO

Transition metal oxides

- *NiO and TiO possess the Rocksalt (NaCl) structure*
- *Mainly formed from 1st row TMs (very few formed from 2/3 rd row TMs)*
- *Many of these materials are non-stoichometric and show a range of compositions* ***(i.e. TiOx (0.65 < X < 1.25)-described in Lecture 4***
- *The electronic properties of such materials vary from insulators to metallic conductors*



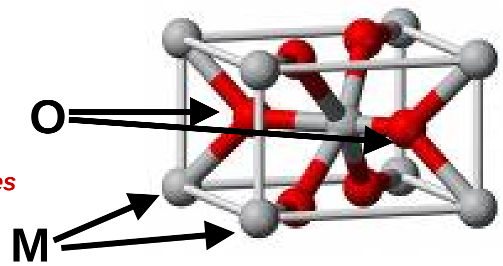
NaCl

Transition metal oxides (2)

MO_2

- *MO_2 (M = Ti, Cr, V, Mn, Zr-Pd and Hf-Pt) all crystallise in the Rutile (TiO_2) structure*

The rutile structure (unit cell)
O^{2-} ions pack in HCP
Ti^{4+} ions lie in octahedral holes



Atom counting

2 x O atoms fully inside cell = 2
4 x O atoms sharing with another cell face = 4 x 0.5 = ***2***
TOTAL O = ***4***
1 x M atom fully inside cell = ***1***
8 x M at corners (sharing with other 8 cells) 8 x 1/8 = ***1***
TOTAL M = ***2***

→ **M/O ratio 1:2** → **MO_2**

Ternary metal oxides (2)

(possessing 2 diff metal centres and therefore 3 different elements)

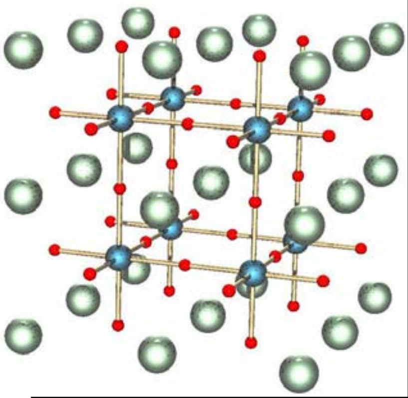
- *Most common type of ternary solid is the perovskite*
- *General Formula* ***ABO_3***
- *Structure frequently seen for ternary ABO_3 oxides formed from one large cation (A) and one smaller cation (B)*
- *First one* ***$CaTiO_3$****; discovered by L. V. Perovski*

Perovskites: General structure

- *Ideally have cubic symmetry*
- *The B cations are 6CN O_h*
- *Each A cation sits in the centre of unit cell*
- *The A cations are 12 coordinate (i.e they are larger)*
- *Distortions in perovskites can occur thus forming lower symmetry versions with lower CN numbers on both A and B*
- *The cations may be +2, +3, or +4 as long as A+B = +6. For example:*

Charge on A	Charge on B	Example
+3	+3	$LaCrO_3$
+2	+4	$SrTiO_3$
+1	+5	$NaWO_3$

$CaTiO_3$



Cation A (i.e. Ca in $CaTiO_3$)

Cation B (Ti in $CaTiO_3$)

O anions