Solid State Chemistry-I

Lecture-1,2

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Contents

- Introduction to Solid
- Structure of simple solids
- Metals, alloys and compounds
- Common structure types.

General Introduction

Two types

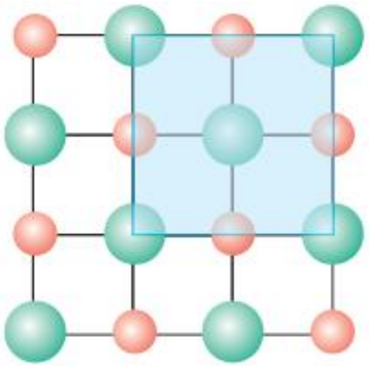
- Crystalline/true solids: Constituent units are arranged in ordered manner
- Amorphous/pseudo solids: Constituent units are not arranged in ordered manner

Solid state refers to a crystalline state. Crystalline solids can be classified as

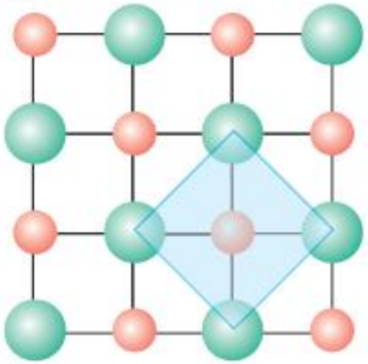
- Ionic solid: Constituent ions are held together by ionic forces
- Covalent solid: Constituent atoms are held together by covalent bonds
- Metallic solid: Constituent positively charged kernels are held together by metallic bonds
- Molecular solid: Constituent units are molecules and held together by hydrogen bonding or van der Waal’s forces
- Isomorphism: Similar crystalline form and similar chemical composition
- Polymorphism: More than one crystalline forms

Unit Cell and Crystal lattice

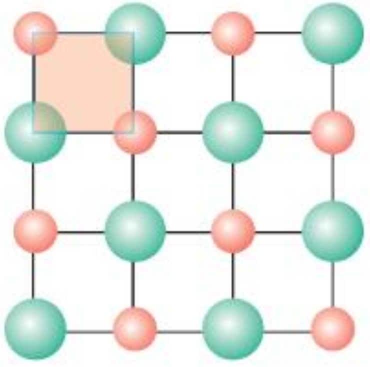
- A crystal of an element or compound can be regarded as regularly repeating structural elements/ atoms/molecules/ions
- The smallest building block of the crystal lattice is called the *Unit cell*
- A unit cell is a subdivision of a crystal that when stacked together following translations reproduces the crystal
- (b) would be preferred to (a) because it is smaller
- A *lattice* is a three-dimensional, infinite array of points, the *lattice points*, each of which is surrounded in an identically by neighboring points.
- The lattice defines the repeating nature of the crystal.
- The *crystal structure* itself is obtained by associating one or more identical structural units.



(a) Possible unit cell



(b) Preferred unit cell choice



(c) Not a unit cell

- The relationship between the lattice parameters in three dimensions as a result of the symmetry of the structure gives rise to the seven *crystal systems*, called *Bravais lattices*
- The corresponding unit cells are referred to as *Bravais unit cells.*
- The unit cells may be characterized by the following unit cell parameters
- relative lengths of the edges along the three axes (*a*, *b*, *c*).
- the three angles between the edges (α, β, γ)

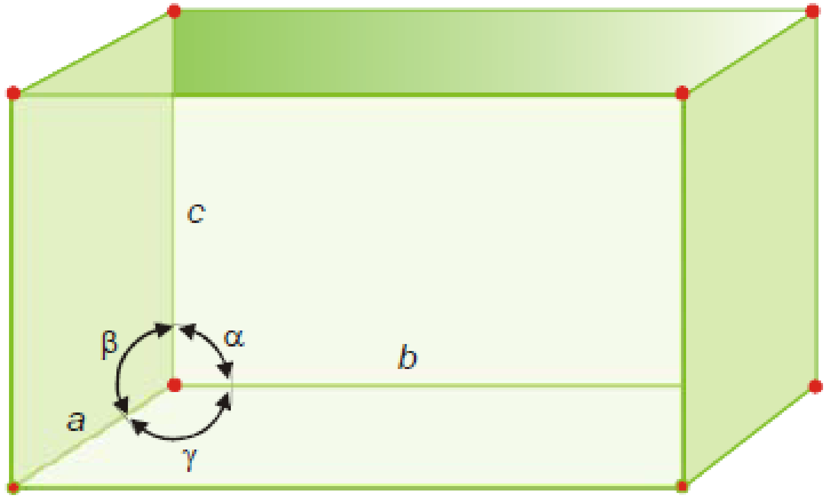
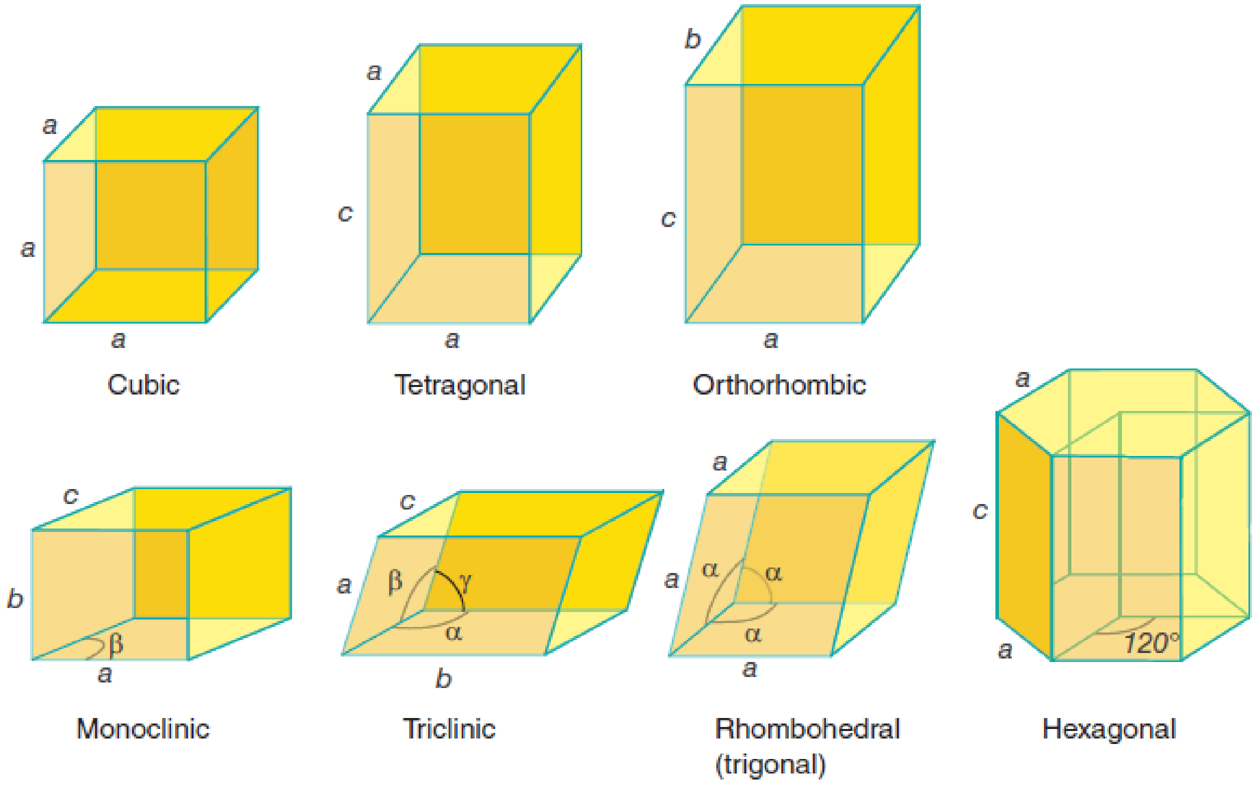


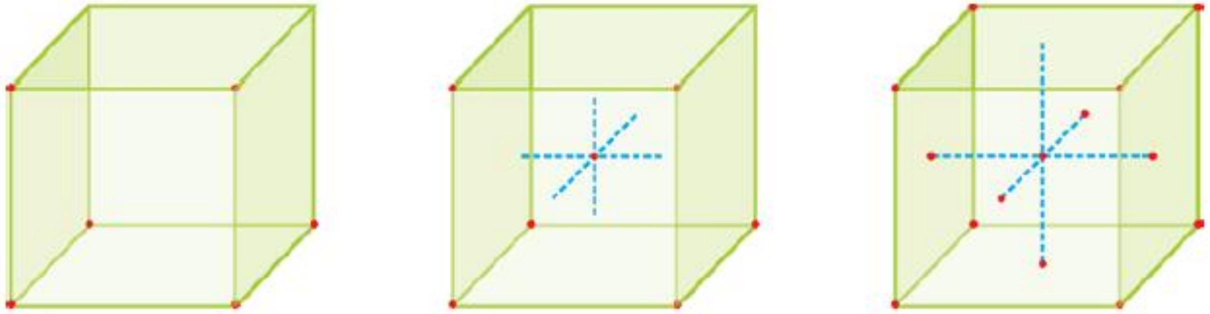
Illustration of parameters of a unit cell.



Crystal system	**Length**	**Angles**	**Unit cell defined by**	**Examples**
Cubic (isometric)	a = b = c	α = β = γ =90º	a	NaCl, CsCl
Tetragonal	a = b ≠ c	α = β = γ =90º	a, c	NH_4Br
Orthorhombic	a ≠ b ≠ c	α = β = γ =90º	a, b, c	KNO_3
Rhombohedral (trigonal)	a = b = c	α = β = γ ≠ 90º	a, α	$CaCO_3$, $NaNO_3$
Hexagonal	a = b ≠ c	α = β = 90º, γ = 120º	a, c	AgI, SiC
Monoclinic	a ≠ b ≠ c	α = β = 90º, γ ≠ 90º	a, b, c, β	$CaSO_4.2H_2O$
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90º	a, b, c, α, β, γ	$CuSO_4.5H_2O$

Cubic unit cells

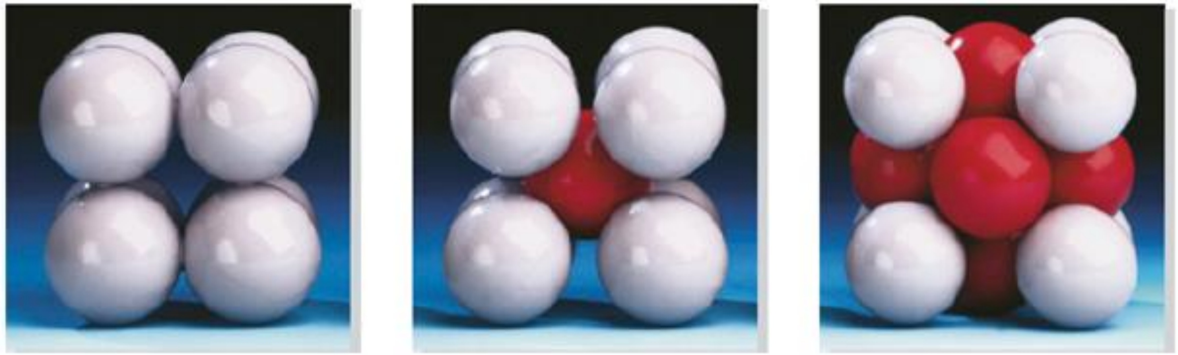
- There are three types of cubic unit cells
- A *simple cubic unit cell* is one in which the atoms or ions are occupying only the corners of the cube.
- A *body-centered cubic* unit cell has one particle at the center of the cube in addition to particles at the corners.
- A *face-centered cubic* unit cell has one particle at each of the six faces of the cube apart from the particles at the corners

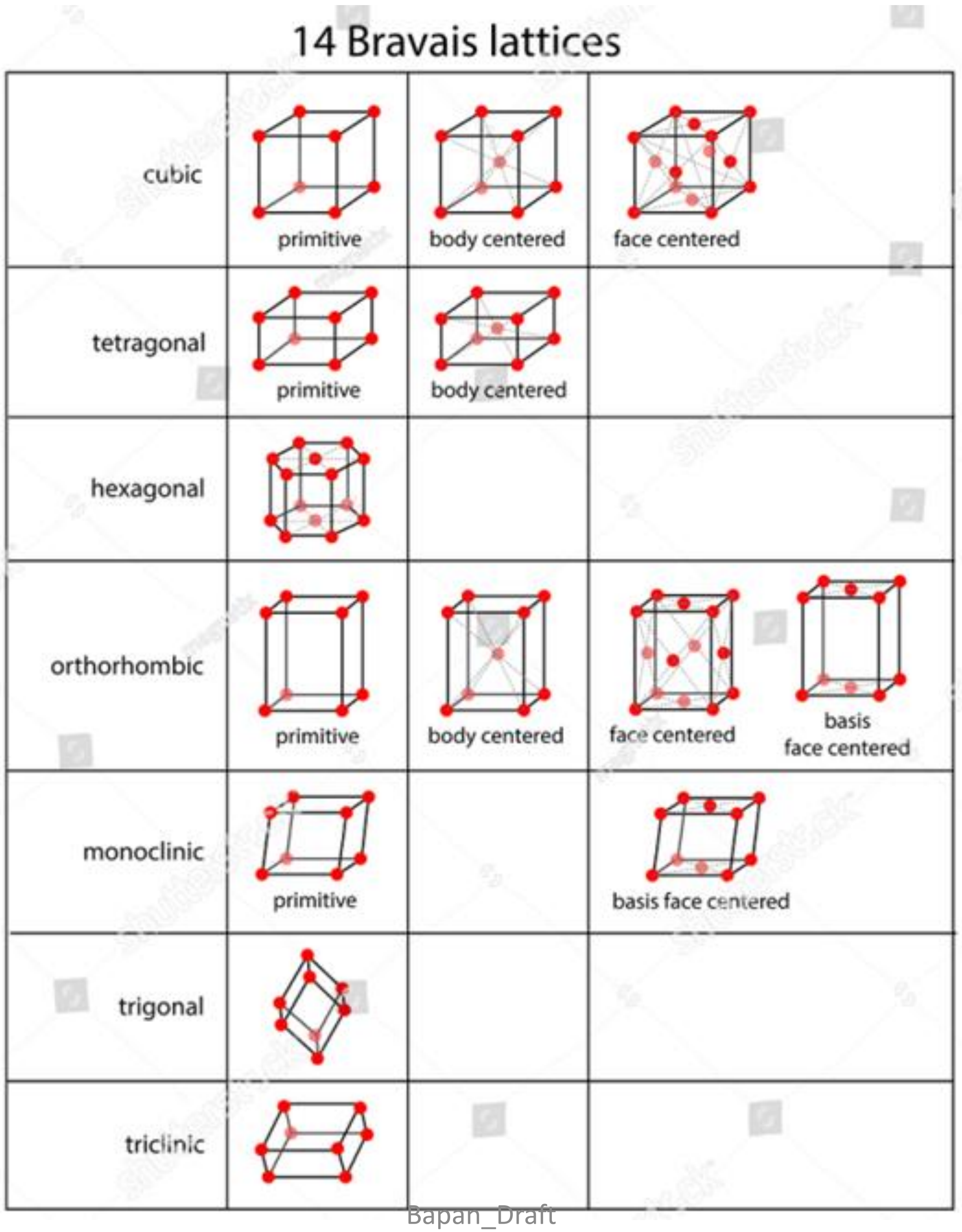


Simple cube

Body-centred cube

Face-centred cube



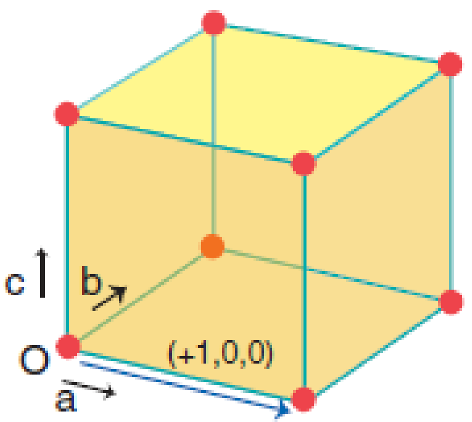


14 Bravais lattices

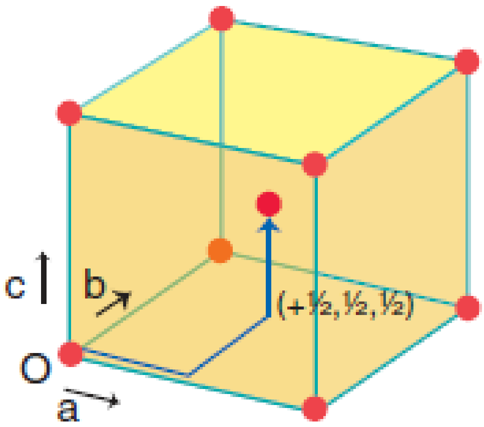
cubic	primitive	body centered	face centered
tetragonal	primitive	body centered	
hexagonal			
orthorhombic	primitive	body centered	face centered basis face centered
monoclinic	primitive		basis face centered
trigonal			
triclinic			

How to Compute Atoms or Points in a Unit Cell ?

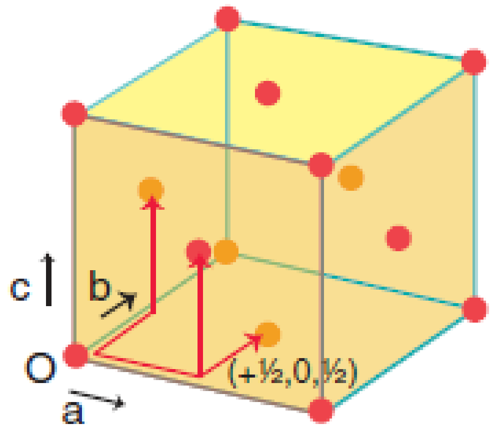
- A lattice point in the body (fully inside) belongs entirely to that cell and counts as 1.
- A lattice point on a face is shared by two cells and contributes 1/2 to the cell.
- A lattice point on an edge is shared by four cells and hence contributes 1/4.
- A lattice point at a corner is shared by eight cells that share the corner, and so contributes 1/8
- For the face-centered cubic lattice the total number of lattice points in the unit cell is (8 x 1/8) (6 x 1/2) = 4
- For the body-centered cubic lattice the number of lattice points is (1 x 1) (8 x 1/8) = 2



Lattice point at the origin (O) translates by (+1,0,0) to another corner of the primitive cubic unit cell.



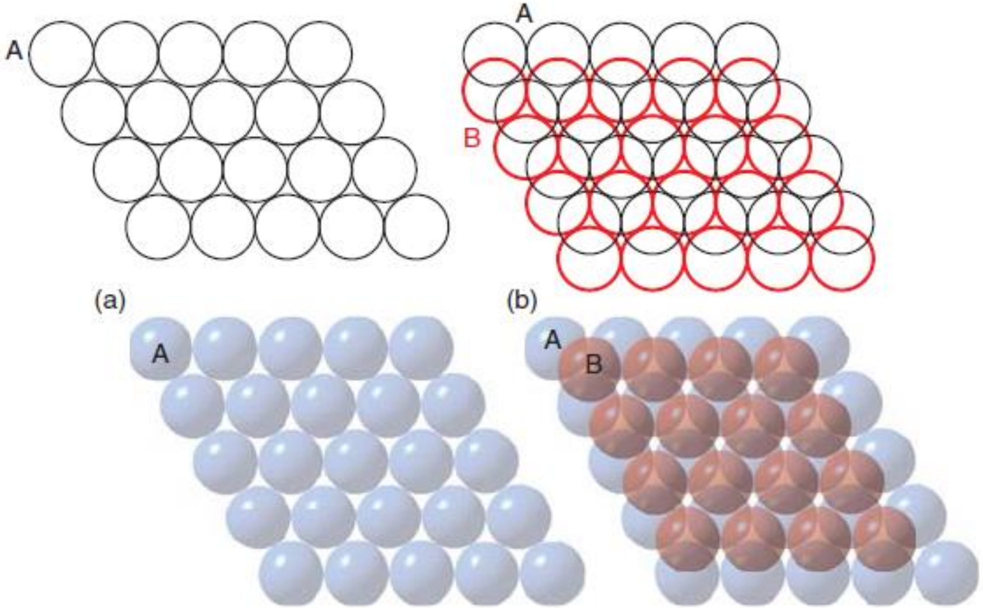
Lattice point at the origin (O) translates by (+½,+½,+½) to the body center of the unit cell.



Lattice point at the origin (O) translates by (+½,+½,0), (+½,0,+½), and (0,+½,+½) to points in the centers of each of the faces (in fcc)

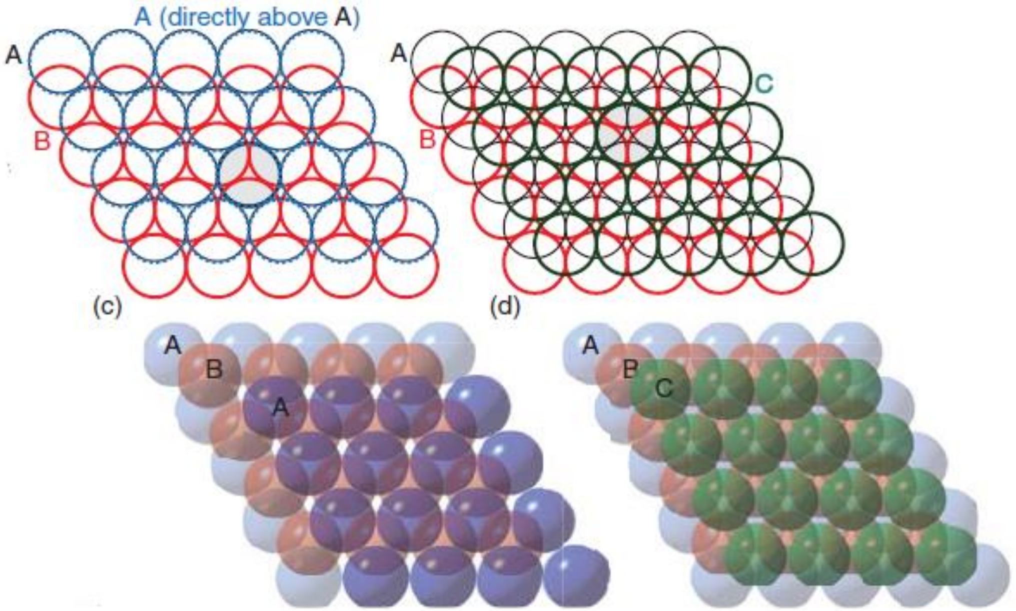
The close packing of spheres

- A close-packed structure is a structure with minimum unfilled space.
- The close packing of identical spheres results in a variety of polytypes
- Hexagonal and cubic close-packed structures are the most common.
- In a single layer (A) of identical spheres, maximum number of immediate neighbors is six and they can only be arranged in hexagonal close-packed layer (a).
- A second close-packed layer of spheres is formed by placing spheres in the dips between the spheres of the first layer, each sphere in this layer touches three spheres in the layer below (b).
- The arrangement of spheres in this second layer is identical to that in the first (slightly displaced horizontally) (b).

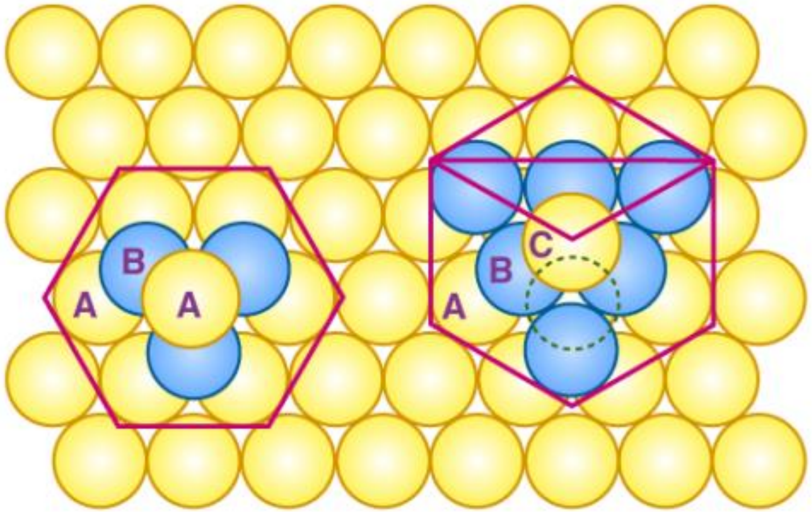


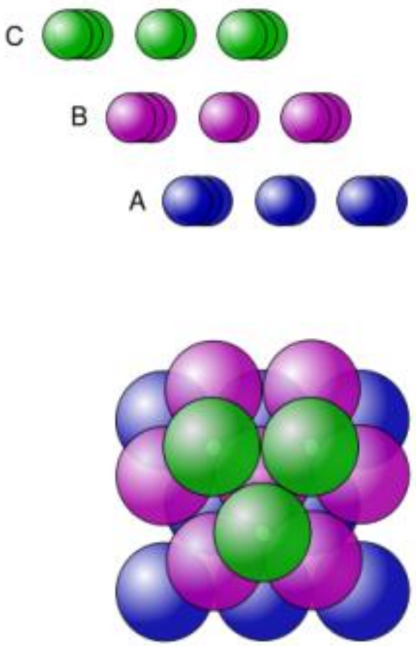
Polytypes - structures which are same in the layers (in 2D) but different in 3D

- The third layer of sphere may be placed on the second layer (B) in either of two ways.
- First, the center of spheres in the third layer lie vertically above the centers of spheres in the first layer (A). The third layer will be a repetition of A and the stack can be extended upward in the sequence ABABAB……..giving hexagonal close-packing (hcp) (c).
- Second, the spheres of the third layer are placed above the dips that were not occupied in the first layer. The second layer fits into half the dips in the first layer & the third layer lies above the remaining dips. This ABCABC…pattern (layer C has spheres that are not directly above spheres of the A or the B layer & will be directly above another C-type layer) results in *cubic close-packing (ccp)* (d)

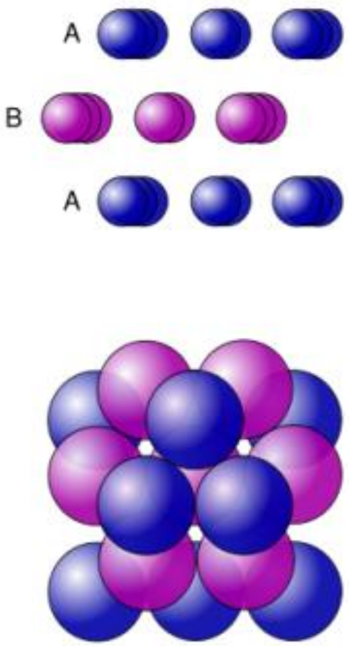


- The ccp and hcp arrangements are the most efficient ways of filling space with identical spheres.
- The occupied space in a close-packed structure amounts to 74 % of the total volume
- Each *ccp* unit cell has a sphere at one corner and one at the center of each face, a ccp unit cell is sometimes referred to as face-centered cubic (fcc).
- The CN of a sphere in a close-packed arrangement is 12 (formed from 6 touching spheres in the original close-packed layer & 3 from each layer above and below it).
- When directional bonding is important, the resulting structures are no longer close-packed and the coordination number is less than 12





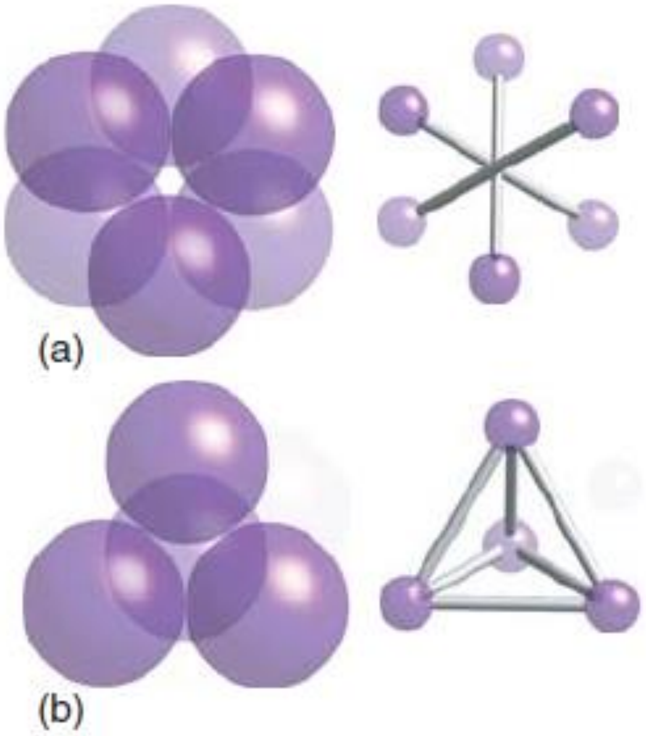
Cubic Close Packing (CCP)



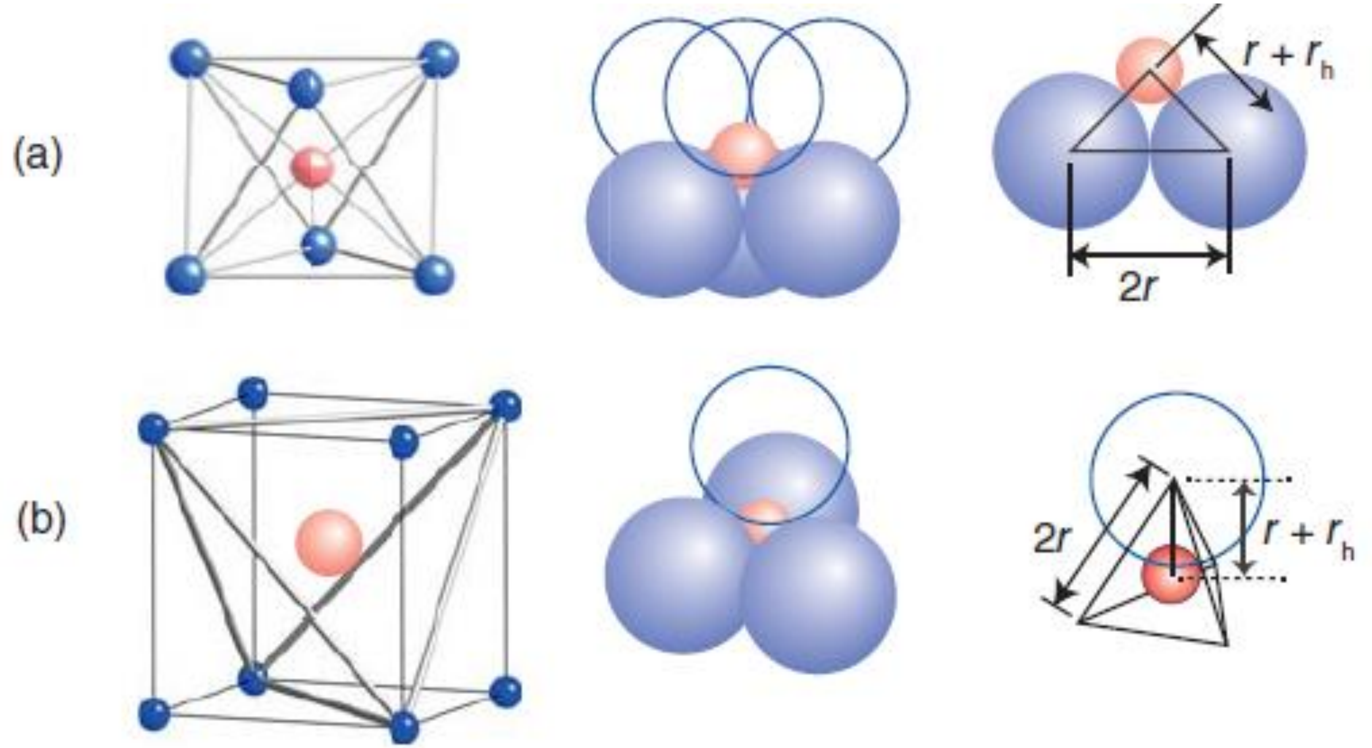
Hexagonal close packing (HCP)

Holes in close-packed structures

- The structures solid can be discussed in terms of close-packed arrangements of atoms of one type with Td or Oh (unoccupied space) occupied by other atoms/ions
- An **octahedral hole** lies between two triangles of spheres on adjoining layers (a).
- For a crystal consisting of *N* spheres in a close packed structure, there are *N* octahedral holes (O_h symmetry).
- A **tetrahedral hole** is formed by a planar triangle of touching spheres capped by a single sphere lying in the dip between them (b).
- In an arrangement of *N* close-packed spheres there are *N* tetrahedral holes of each set and 2*N* tetrahedral holes in all.
- The limiting size of an Oh and Td hole is determined by the ratio of the radii of the ions (smaller/larger)



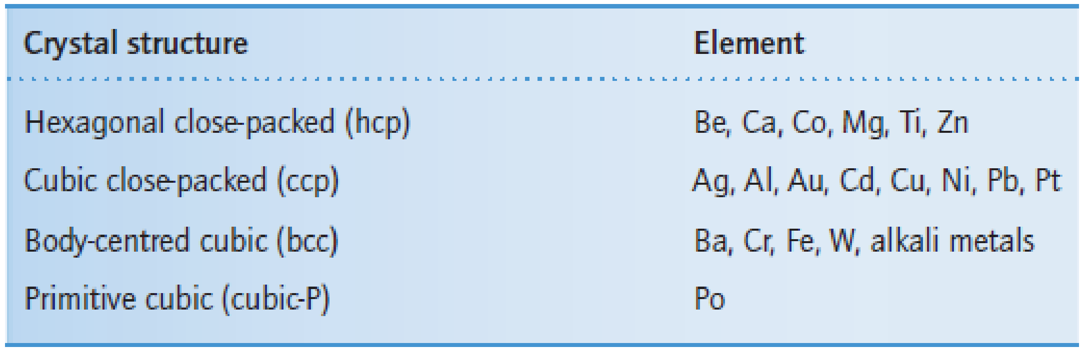
- An octahedral hole cannot accommodate any ion larger than 0.414*r* (r=radius of larger ion)
- A tetrahedral hole cannot accommodate any ions with radius greater than 0.225 *r*
- Where two sphere of different radius pack together (like cation-anion stacking), the larger spheres (anions) can form a close packed array and the smaller spheres (cations) occupy the octahedral or tetrahedral holes.
- The simple ionic structures is described in terms of the occupation of holes in close-packed arrays



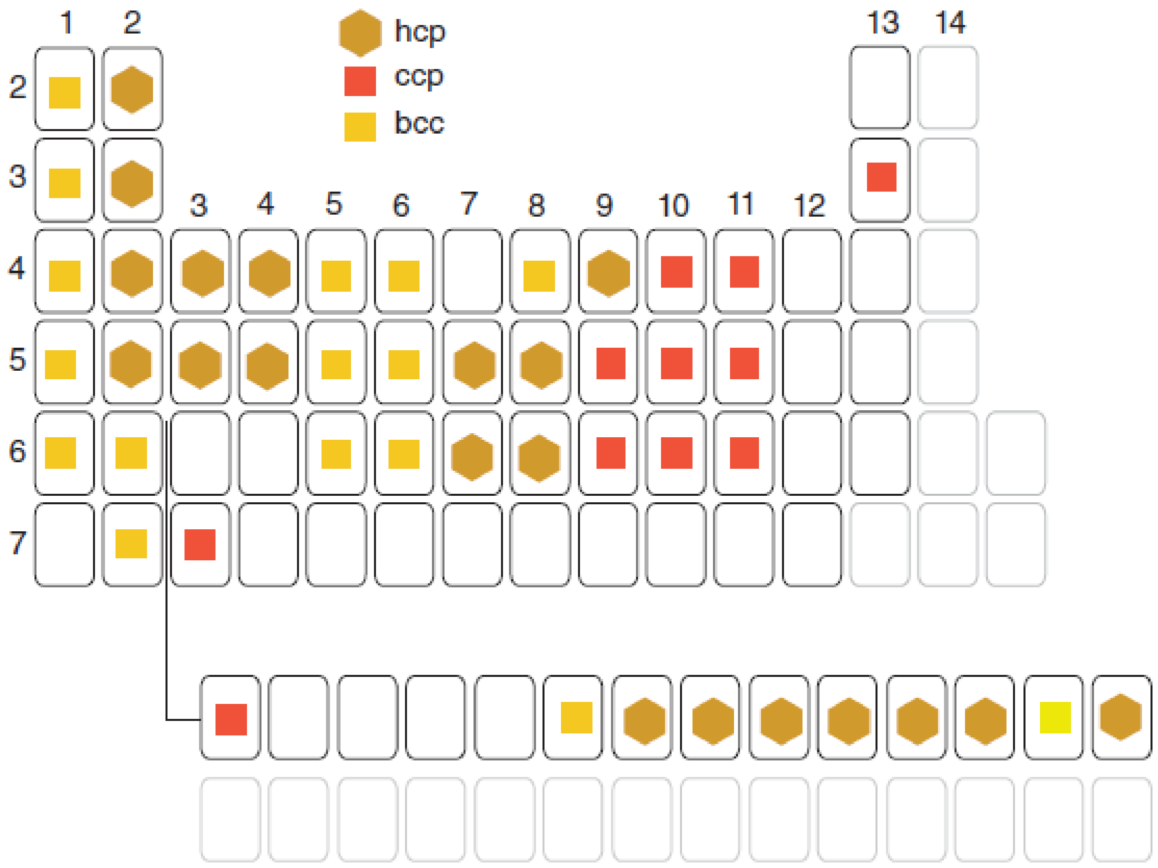
The structures of metals and alloys

- X-ray diffraction studies reveal that many metallic elements have close packed structures
- The bonds between the atoms have little directional covalent character.
- Due to this close-packing metals often have high densities, packed into the smallest volume.
- Osmium has the highest density of all the elements at 22.61 $\mathrm{g\,cm^{-3}}$

The crystal structures adopted by metals under normal conditions



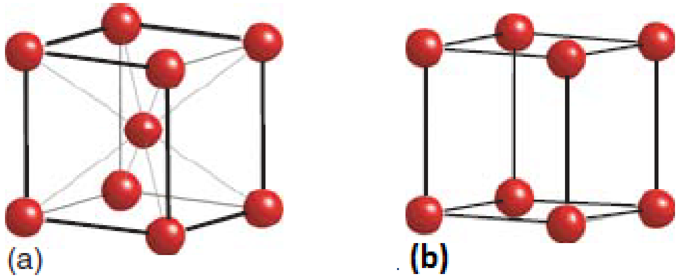
Crystal structure	Element
Hexagonal close-packed (hcp)	Be, Ca, Co, Mg, Ti, Zn
Cubic close-packed (ccp)	Ag, Al, Au, Cd, Cu, Ni, Pb, Pt
Body-centred cubic (bcc)	Ba, Cr, Fe, W, alkali metals
Primitive cubic (cubic-P)	Po

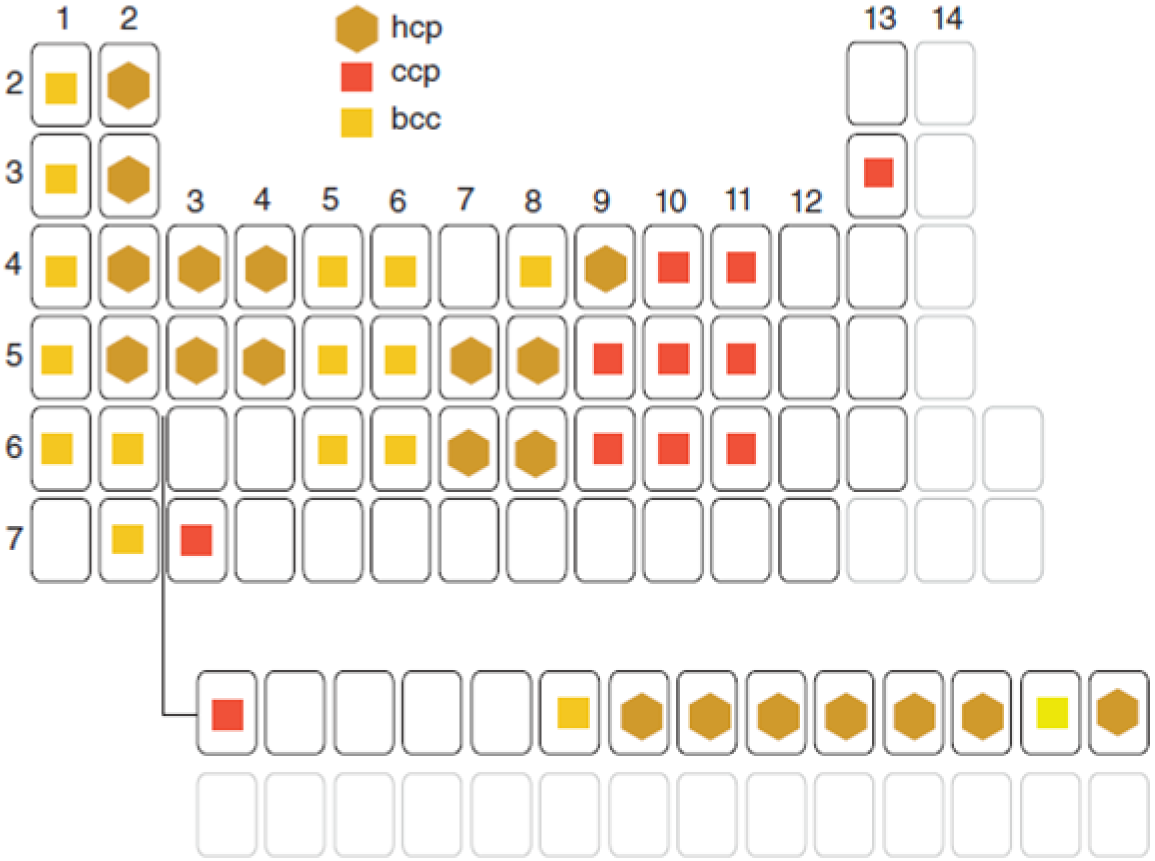


Polytypism

- Most metals adopt closed-packed (hcp/ccp) structures.
- Nature of adopted polytypes for a metal depends on the electronic structure of its atoms, the extent of interaction between second nearest neighbors, and the directional character in the bonding.
- Softer and more malleable metals (Cu and Au) adopt the ccp arrangement while harder and more brittle metals (Co and Mg) possess hcp arrangement.
- All elemental metals do not have close-packing structures (Non-close-packed structures)
- In body-centered cubic structure (cubic-I or bcc), a sphere is at the center of a cube with spheres at each corner (a).
- Metals with this structure have a coordination number of 8 because the central atom is in contact with the atoms at the corners of the unit cell.
- Some common metals also adopt less compact body centered cubic structure (CN=8, packing 68% of total volume)
- This type of arrangement is sometimes referred to as the ‘tungsten type

- Po is the only metal known to adopt the least compact simple cubic (P) structure.
- In primitive cubic (cubic-P) structure, the spheres are located at the lattice points of a primitive cubic lattice, taken as the corners of the cube. The coordination number of a cubic-P structure is 6. (b)





The crystal structures adopted by metals under normal conditions

Crystal structure	Element
Hexagonal close-packed (hcp)	Be, Ca, Co, Mg, Ti, Zn
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Body-centred cubic (bcc)	Ba, Cr, Fe, W, alkali metals
Primitive cubic (cubic-P)	Po

Polymorphism of metals

- The lack of directionality in the interactions between metal atoms accounts for the wide occurrence of **polymorphism**,
- Polymorphism is the ability to adopt different crystal forms under different conditions of pressure and temperature.
- It is often found that the most closely packed phases are thermodynamically favored at low temperatures and the less closely packed structures are favored at high temperatures.
- Similarly, the application of high pressure leads to structures with higher packing densities, such as ccp and hcp.
- The polymorphs of metals are generally labelled α, β, γ,… with increasing temperature.
- Some metals revert to a low-temperature form at higher temperatures.
- The bcc structure of Fe at room temperature called α-Fe changes to γ-Fe (ccp) at 906 ºC. Above 1401 ºC, it reverts back to α-Fe. Polymorph β-Fe (hcp) is formed at high pressure.

- Polymorphism is a common consequence of the low directionality of metallic bonding.
- At high temperatures a bcc structure is common for metals that are close-packed at low temperatures on account of the increased amplitude of atomic vibrations
- For many metals (among them Ca, Ti, and Mn) the transition temperature is above room temperature; for others (among them Li and Na), the transition temperature is below room temperature.
- It is also found empirically that a bcc structure is favored by metals with a small number of valence electrons per orbital.

Alloys and interstitials

- An **alloy** is a blend of metallic elements prepared by mixing the molten components and then cooling the mixture to produce a metallic solid.
- Alloys may be homogeneous solid solutions, in which the atoms of one metal are distributed randomly among the atoms of the other, or they may be compounds with a definite composition and internal structure.
- Alloys typically form from two electropositive metals.
- The majority of simple alloys can be classified as either ‘substitutional’ or ‘interstitial’.
- A substitutional solid solution is a solution in which atoms of the solute metal replace some of the parent pure metal atoms.
- Some of the classic examples of alloys are brass (38% Zn & 64% Cu), bronze (88% Cu & 12% Zn with trace amounts of Al, Zn, Ni), and stainless steel (12% Cr & 88 % Fe with trace amount of C, Ni, Mo, Ti, Nb, Mn).
- **Interstitial solid solutions** are often formed between metals and small atoms (B, C and N) that can occupy interstices (Oh & Td holes) at low levels in a parent metal maintaining its crystal structure. Example: carbon steels.

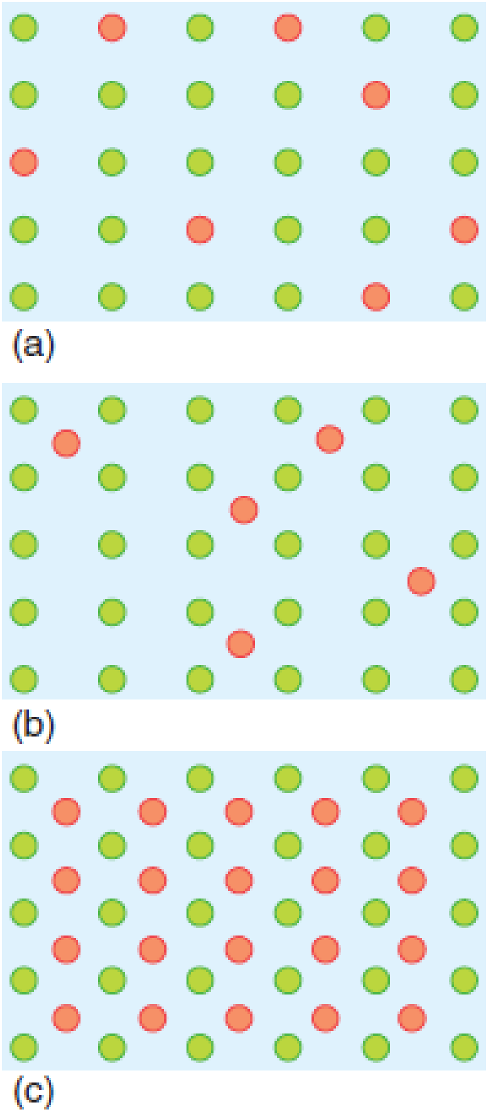
Substitutional alloys

- A substitutional solid solution or alloy involves the replacement of one type of metal atom in a structure by another
- Criteria for substitutional solid solutions
  - The atomic radii of the elements are within about 15 % of each other.
  - The crystal structures of the two pure metals are the same i.e., the directional forces between the two types of atom are compatible with each other.
  - The electropositive characters of the two components are similar (otherwise electron transfer would be more likely)
- For instance, Na and K are chemically similar and have bcc structures, the atomic radius of Na (191 pm) is 19 % smaller than that of K (235 pm), and the two metals do not form a solid solution.
- Cu and Ni have similar electropositive character, have both ccp structures, and similar atomic radii (Ni 125 pm, Cu 128 pm, differs by only 2.3 %), and can form a series of solid solutions (ranging from pure Ni to pure Cu)
- Intermetallics are the compounds where alloys adopt different crystal structure than those of pure metals.

Interstitial atoms in metals

- In an interstitial solid solution, additional small atoms occupy holes/interstices within the lattice of the original metal structure
- The small atoms enter the host solid with preservation of the crystal structure of the original metal and without the transfer of electrons and formation of ionic species.
- These are either in simple whole-number ratio of metal and interstitial atoms (WC) or the small atoms are distributed randomly in the available spaces or holes in the structure between the packed atoms.
- The former substances are true compounds and the latter can be considered as interstitial solid solutions or nonstoichiometric compounds.
- Size factor plays a deciding role whether the formation of an interstitial solid solution is likely to occur or not.
- For example, the largest solute atom that can enter a close-packed solid without distorting the structure appreciably is one that just fits an octahedral hole, which as has the radius 0.414 r.

- For small atoms such as B, C, or N the atomic radii of the possible host metal atom structures include those of the d metals such as Fe, Co, and Ni.
- One important class of materials of this type consists of carbon steels in which C atoms occupy some of the octahedral holes in the Fe bcc lattice.
- Carbon steels typically contain between 0.2 and 1.6 atom per cent C and with increasing carbon content they become harder and stronger but less malleable.



(a) Substitutional and (b) interstitial alloys. (c) A regular arrangement of interstitial atoms can lead to a new structure.

Intermetallic compounds

- Intermetallic compounds are the alloys in which the adopted structure differs from the structures of either component metal
- When some liquid mixtures of metals are cooled, they form phases with definite structures that are often unrelated to the parent structure. These phases are called **intermetallic compounds**
- For example, β-brass (CuZn) and compounds of the compositions $MgZn_2$, Cu_3Au, NaTl, & Na_5Zn_{21}. β-brass with the composition $Cu_{0.52}Zn_{0.48}$ adopts a bcc structure type at high temperature and a hcp structure at lower temperatures.
- Hume-Rothery rule (the electron-per atom ratio (e/a)) allows the prediction of the most stable structure (bcc/hcp/fcc) for a chosen alloy composition.
- Hume-Rothery rules predict that a Cu:Zn alloy with $e/a < 1.4$ (α-brass, $Cu_{1-x}Zn_x$ with $0 \leq x \leq 0.38$) should have a ccp lattice, and an alloy with e/a of 1.5 (CuZn, β-brass) a bcc lattice.

- Pure Cu ($3d^{10}4s^1$) as contributing one electron and Zn ($3d^{10}4s^2$) as contributing two electrons, so the alloys between pure Cu and pure Zn span e/a values from 1 to 2. On this basis the β-brass composition close to $Cu_{0.5}Zn_{0.5}$ (e/a = 1.5) is predicted to have a bcc structure (at high temperatures)
- Some alloys, including γ-brass in the Cu/Zn system of the stoichiometry $Cu_{0.39}Zn_{0.61}$, form very complex structures due to the arrangements of Cu and Zn atoms and some vacant sites; the unit cell of γ-brass is 27 times the size of that of β-brass.
- Other alloys such as $Al_{0.88}Mn_{0.12}$ form structures which include elements of five-fold symmetry and therefore do not repeat perfectly when translated as a unit cell. These materials are known as quasicrystals (Shechtman was awarded the 2011 Nobel Prize).
- Intermetallic compounds are normally high-melting, hard, and more brittle than most metals and alloys. Examples include alnico, A_3B Nb-Sn and Nb-Ge superconducting compounds, A_{15} systems such as $LaNi_5$ which can be used as hydrogen storage materials, NiAl and Ni_3Al superalloys, and TiNi shape-memory alloys.

- Some of these intermetallic compounds contain a very electropositive metal (K or Ba) in combination with a less electropositive metal or metalloid (Ge or Zn). Such combinations are called Zintl phases, and in a Ketelaar triangle lie above the true alloys.
- Although Zintl phases are brittle and have metallic properties (including lustre), they are not fully ionic. They can be considered as containing metal or complex metal cations and anions such as Cs^+ or $[Tl_4]^{8-}$. A classic example of a Zintl phase is KGe (K_4Ge_4)

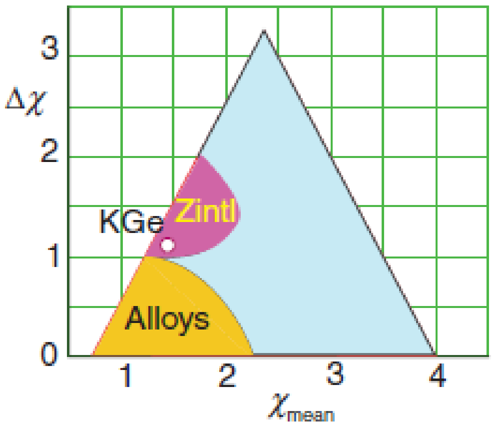


Figure 3.27 The approximate locations of Zintl phases in a Ketelaar triangle. The point marks the location of one exemplar, KGe.

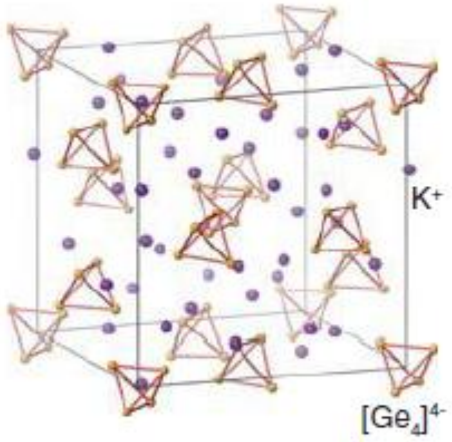
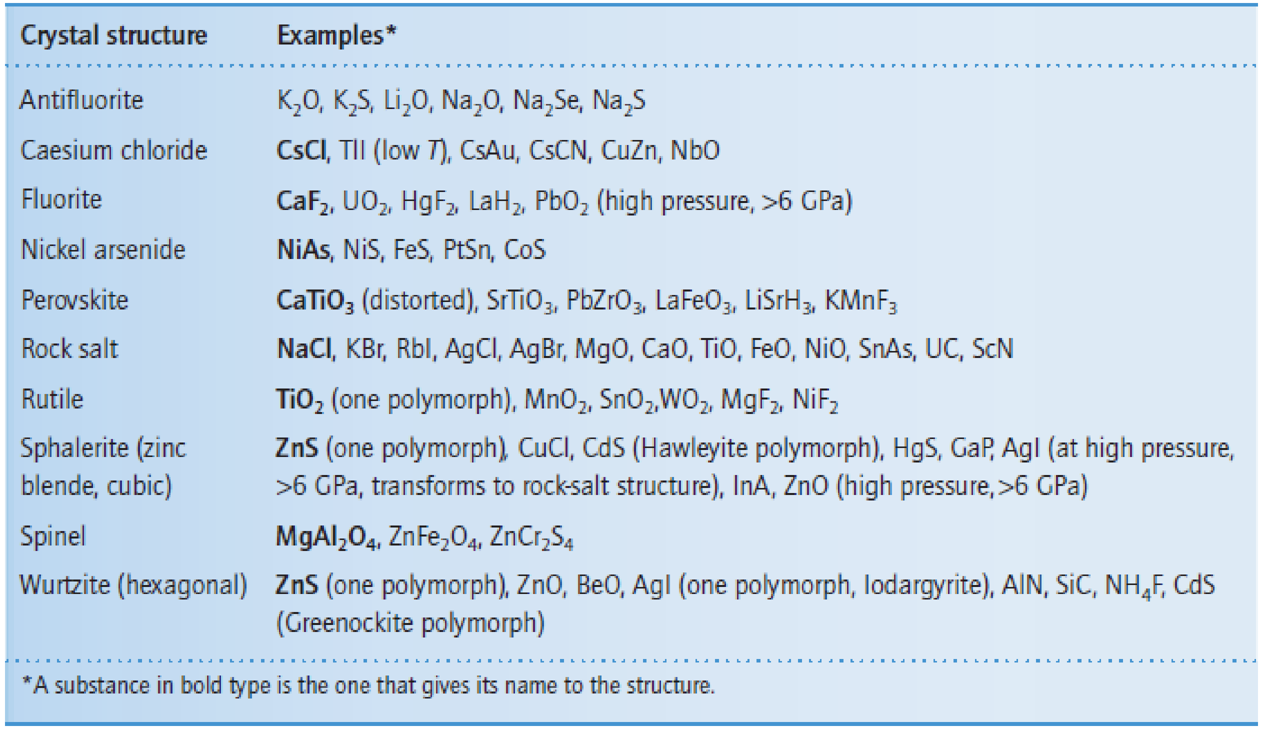


Figure 3.28* The structure of the Zintl phase KGe showing the $[Ge_4]^{4-}$ tetrahedral units and interspersed K^+ ions.

Ionic solids

- Ionic model treats a solid as an assembly of oppositely charged spheres that interact via nondirectional electrostatic forces
- Structures are derived from arrays in which the larger ions (anions) stack together in ccp/hcp patterns and the smaller counter-ions (cations) occupy the Oh/Td holes in the lattice
- The close-packed layers usually need to expand (minor perturbation) to accommodate the counter-ions
- This expansion avoids some of the strong repulsion between the identically charged ions and also allows larger species to be inserted into the holes between larger ions.
- The simplest ionic compounds with just one type of cation (A) and one type of anion (X), present in various ratios may be of AX and AX_2 type compositions.
- Several structures may exist for each of these compositions, depending on the relative size of the cations and anions, and which holes are filled and to what degree in the close-packed array

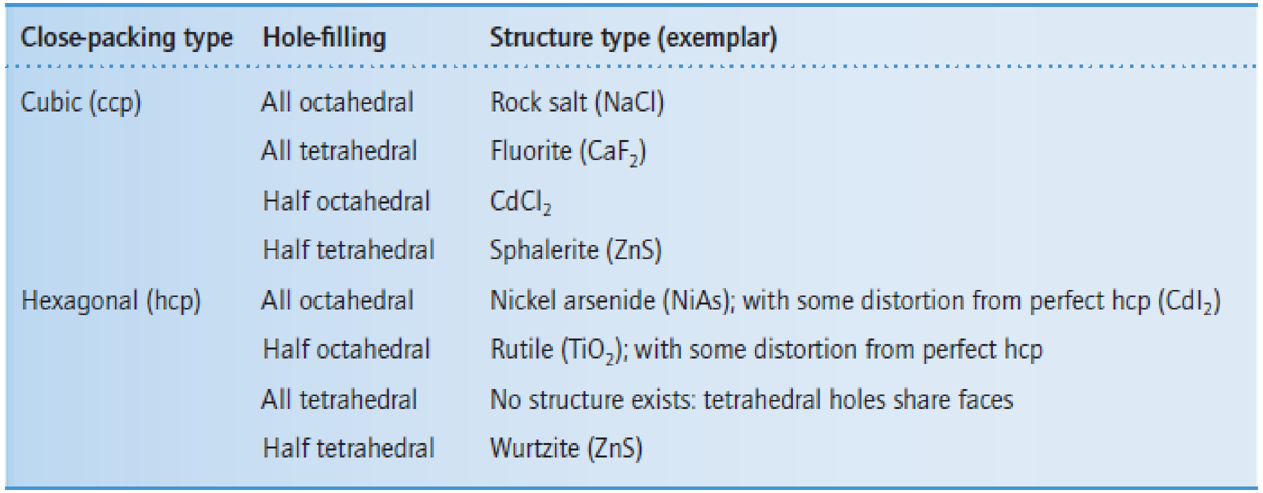
The crystal structures of compounds, at standard conditions unless otherwise stated



Crystal structure	Examples*
Antifluorite	K_2O, K_2S, Li_2O, Na_2O, Na_2Se, Na_2S
Caesium chloride	**CsCl**, TlI (low *T*), CsAu, CsCN, CuZn, NbO
Fluorite	**CaF_2**, UO_2, HgF_2, LaH_2, PbO_2 (high pressure, >6 GPa)
Nickel arsenide	**NiAs**, NiS, FeS, PtSn, CoS
Perovskite	**$CaTiO_3$** (distorted), $SrTiO_3$, $PbZrO_3$, $LaFeO_3$, $LiSrH_3$, $KMnF_3$
Rock salt	**NaCl**, KBr, RbI, AgCl, AgBr, MgO, CaO, TiO, FeO, NiO, SnAs, UC, ScN
Rutile	**TiO_2** (one polymorph), MnO_2, SnO_2,WO_2, MgF_2, NiF_2
Sphalerite (zinc blende, cubic)	**ZnS** (one polymorph), CuCl, CdS (Hawleyite polymorph), HgS, GaP, AgI (at high pressure, >6 GPa, transforms to rock-salt structure), InA, ZnO (high pressure, >6 GPa)
Spinel	**$MgAl_2O_4$**, $ZnFe_2O_4$, $ZnCr_2S_4$
Wurtzite (hexagonal)	**ZnS** (one polymorph), ZnO, BeO, AgI (one polymorph, Iodargyrite), AlN, SiC, NH_4F, CdS (Greenockite polymorph)

*A substance in bold type is the one that gives its name to the structure.

The relation of structure to the filling of holes

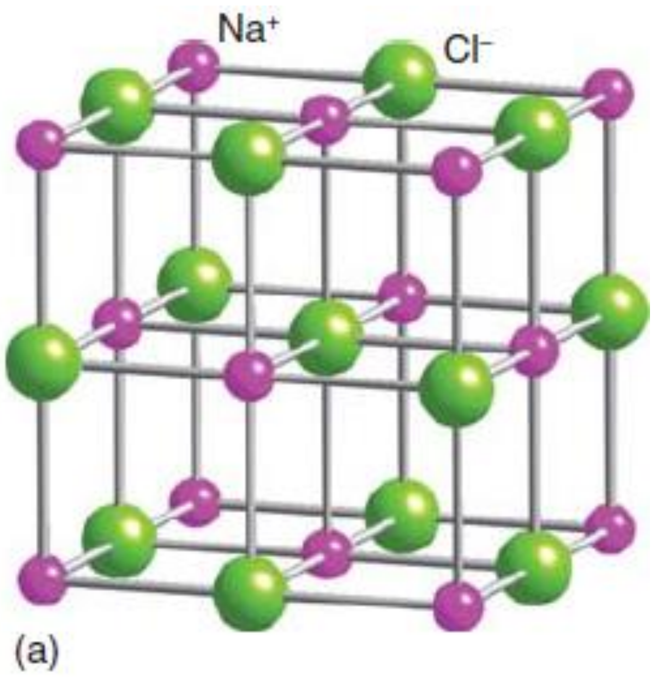


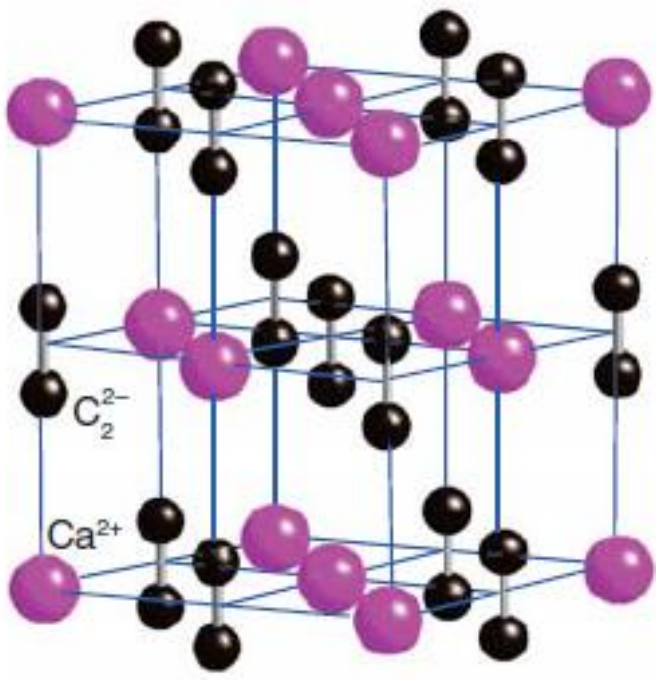
Close-packing type	Hole-filling	Structure type (exemplar)
Cubic (ccp)	All octahedral	Rock salt (NaCl)
	All tetrahedral	Fluorite (CaF_2)
	Half octahedral	$CdCl_2$
	Half tetrahedral	Sphalerite (ZnS)
Hexagonal (hcp)	All octahedral	Nickel arsenide (NiAs); with some distortion from perfect hcp (CdI_2)
	Half octahedral	Rutile (TiO_2); with some distortion from perfect hcp
	All tetrahedral	No structure exists: tetrahedral holes share faces
	Half tetrahedral	Wurtzite (ZnS)

Rock-salt structure

- The **rock-salt structure** is based on a ccp array of bulky anions with cations in all the octahedral holes.
- Alternatively, the anions occupy all the octahedral holes in a ccp array of cations.
- The number of octahedral holes in a close-packed array is equal to the number of anions forming the array (AX)
- Each ion is surrounded by an octahedron of six counter-ions, said to have 6:6 coordination.
- The rock-salt structure (NaCl) can be described as a face-centered cubic lattice.
- All six neighbors have a charge opposite to that of the central ion.
- The 12 second-nearest neighbors of the central ion are at the centers of the edges of the cell, and all have the same charge as the central ion.
- The eight third-nearest neighbors are at the corners of the unit cell, and have a charge opposite to that of the central ion.

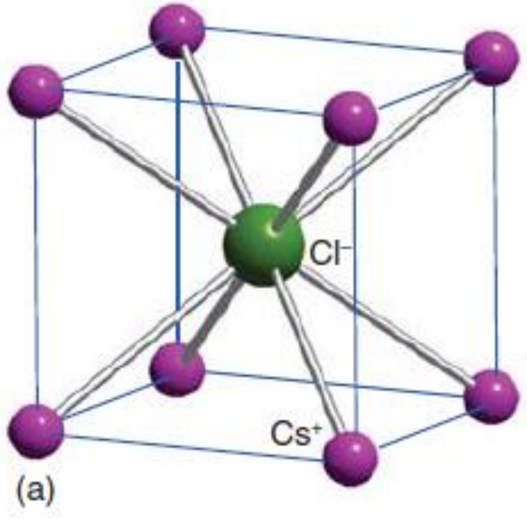
- The rock-salt arrangement is also observed for $[Co(NH_3)_6][TlCl_6]$, an array of close packed octahedral $[TlCl_6]^{3-}$ anions with $[Co(NH_3)_6]^{3+}$ cations in all the octahedral holes.
- Compounds such as CaC_2, CsO_2, KCN, and FeS_2 all adopt structures closely related to the rock-salt structure, with alternating cations and complex anions (C_2^{2-}, O^{2-}, CN^-, and S_2^{2-}, respectively), leading to elongation of the unit cell and elimination of the cubic symmetry

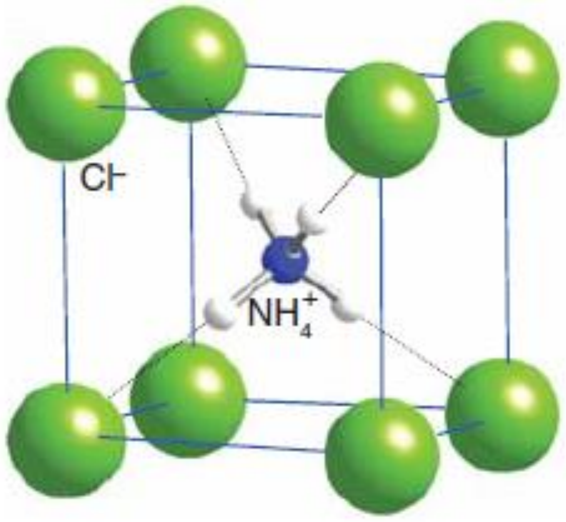




Cesium-chloride structure

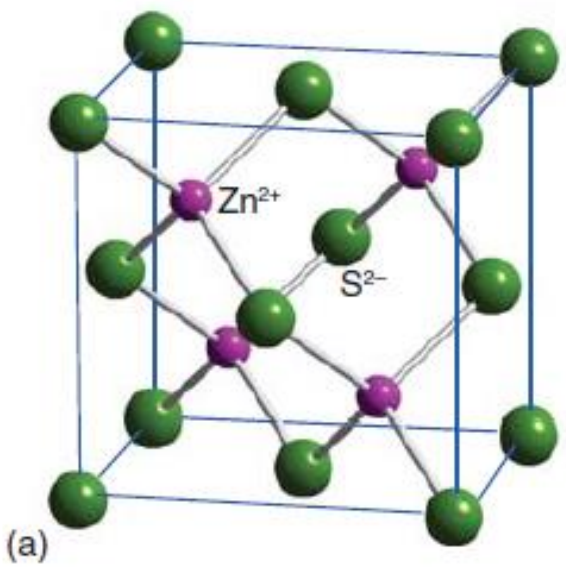
- **Cesium-chloride structure** is exhibited by CsCl, CsBr, CsI, and compounds of other ions of similar radii (TlI). It has 8:8 coordination.
- It has a primitive cubic unit cell structure, with each corner occupied by an anion and a cation occupying the 'cubic hole' at the cell center (or vice versa); as a result, $Z = 1$.
- Alternatively, it is a two interpenetrating primitive cubic cells, one of Cs^+ and the other of Cl^-.
- The radii are so similar that this energetically highly favorable coordination is feasible, with numerous counter-ions adjacent to a given ion.
- Despite small NH_4^+ ion, NH_4Cl also show this structure because the cation can form hydrogen bonds with four of the Cl^- ions at the corners of the cube.
- Many 1:1 alloys (AlFe and CuZn) have a cesium-chloride arrangement of the two metal atom types.





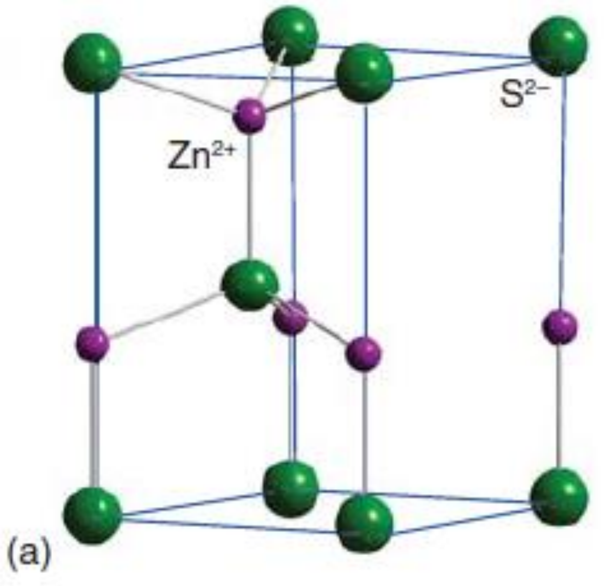
Sphalerite structure

- The **sphalerite structure (zinc-blende structure**) takes its name from one of the mineral forms of ZnS.
- Like the rock-salt structure, it is based on an expanded ccp anion arrangement
- The cations occupy one type of tetrahedral hole, one-half the tetrahedral holes present in a close-packed structure.
- Each ion is surrounded by four neighbors & so the structure has 4:4 coordination and $Z = 4$.



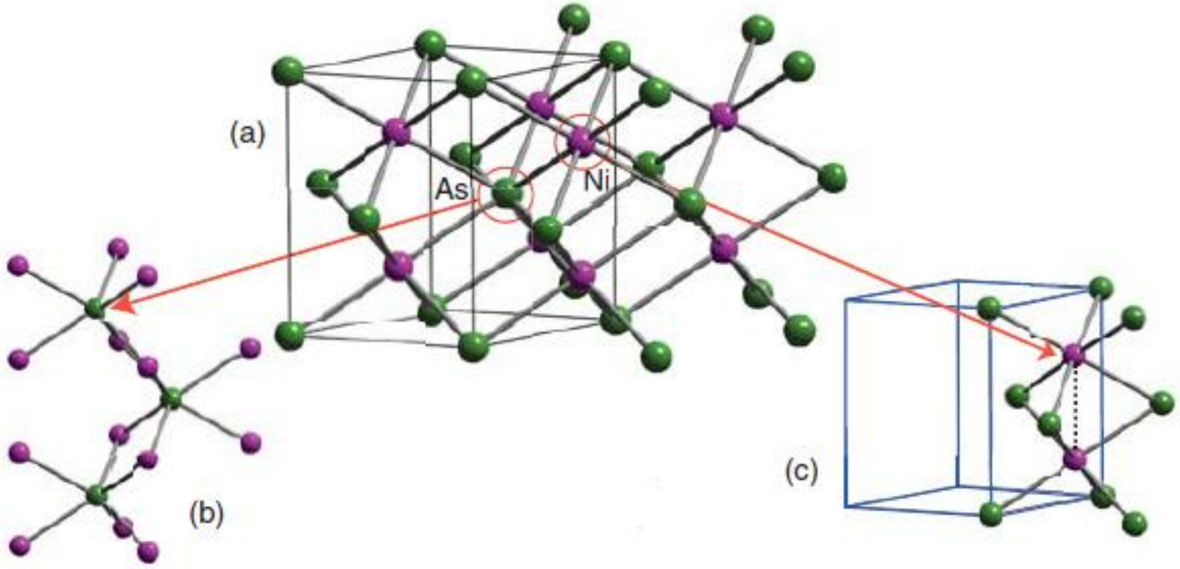
Wurtzite structure

- The **wurtzite structure** is another polymorph of zinc sulfide that occurs naturally as a mineral (4:4 coordination).
- It differs from the sphalerite structure, an expanded hcp anion array rather than a ccp array.
- This structure is adopted by ZnO, one form of AgI, and one polymorph of SiC, as well as several other compounds.
- The local symmetries of the cations and anions are identical with respect to their nearest neighbors in wurtzite and sphalerite but differ at the second-nearest neighbors.
- Many compounds show polymorphism and crystallize with both sphalerite and wurtzite structure types depending on the conditions under which they were formed, and temperature and pressure to which they are subjected.



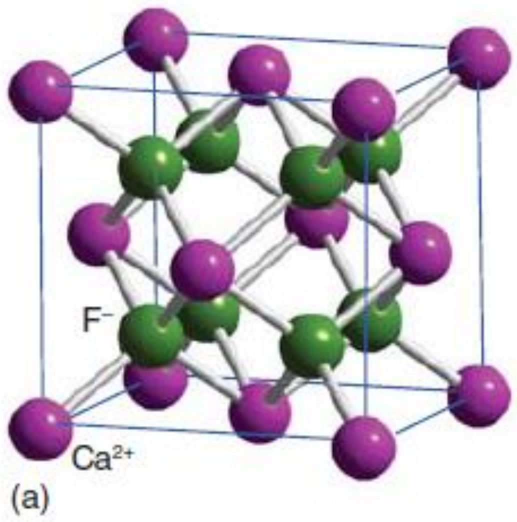
Nickel-arsenide structure

- The **nickel-arsenide structure** (NiAs) is also based on an expanded, distorted hcp anion array (NiS, FeS)
- The Ni atoms occupy the octahedral holes and each As atom lies at the center of a trigonal prism of Ni atoms (a).
- NiAs structure is typical for compounds with polarizable ions and elements with small electronegativity differences.
- Compounds that form this structure type lie in the ‘polarized ionic salt area’ of a Ketelaar triangle.
- There is also potential for some degree of metal-metal bonding between metal atoms in adjacent layers (c)
- This structure type (or its distorted forms) is also common for alloys of d- and p-block elements.



Fluorite structure

- **Fluorite structure** (common for AX type), name is derived from the naturally occurring mineral fluorite, CaF_2.
- In fluorite, the Ca^{2+} ions lie in an expanded ccp array and the F^- ions occupy all the tetrahedral holes.
- In this description it is the cations that are close-packed because the F^- anions are small.
- The lattice has 8:4 coordination, which is consistent with there being twice as many anions as cations.
- The anions in their tetrahedral holes have four nearest neighbors
- The cation site is surrounded by a cubic array of eight anions.



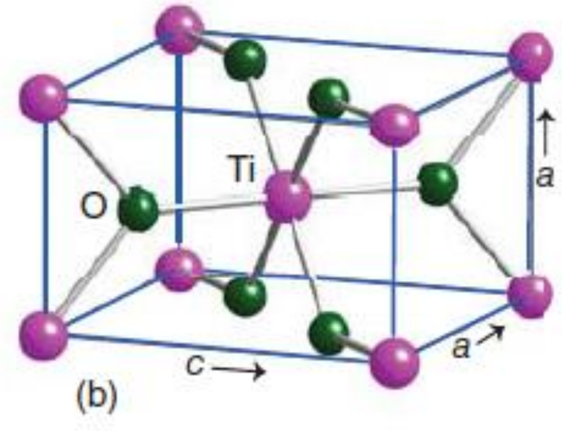
Antifluorite structure

- The **antifluorite** structure is the inverse of the fluorite structure.
- The locations of cations and anions are reversed
- This reflects the fact that the structure is adopted in compounds with the smallest cations such as Li^+ (r = 59 pm in four-fold coordination).
- The structure is shown by some alkali metal oxides, including Li_2O.
- In it, the cations (which are twice as numerous as the anions) occupy all the tetrahedral holes of a ccp array of anions.
- The coordination is (4:8) rather than the (8:4) of fluorite itself.

Insert image

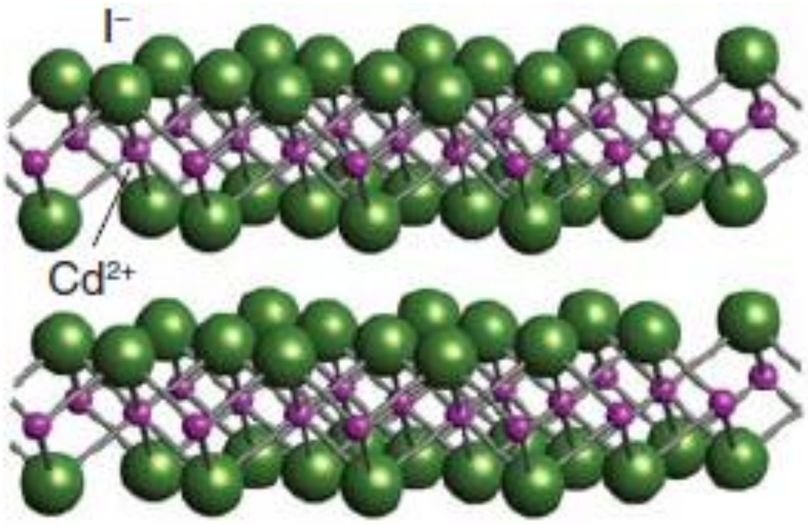
Rutile structure

- The **rutile structure** takes its name from rutile, a mineral form of titanium(IV) oxide, TiO_2.
- The structure can also be considered an example of hole-filling in an hcp anion arrangement
- The cations occupy only half the octahedral holes and there is considerable buckling of the close-packed anion layers.
- Each Ti^{4+}-ion is surrounded by six O-atoms
- Each O-atom is surrounded by three Ti^{4+} ions
- The rutile structure has 6:3 coordination.
- The principal ore of tin, cassiterite SnO_2, has the rutile structure, as do a number of metal difluorides.



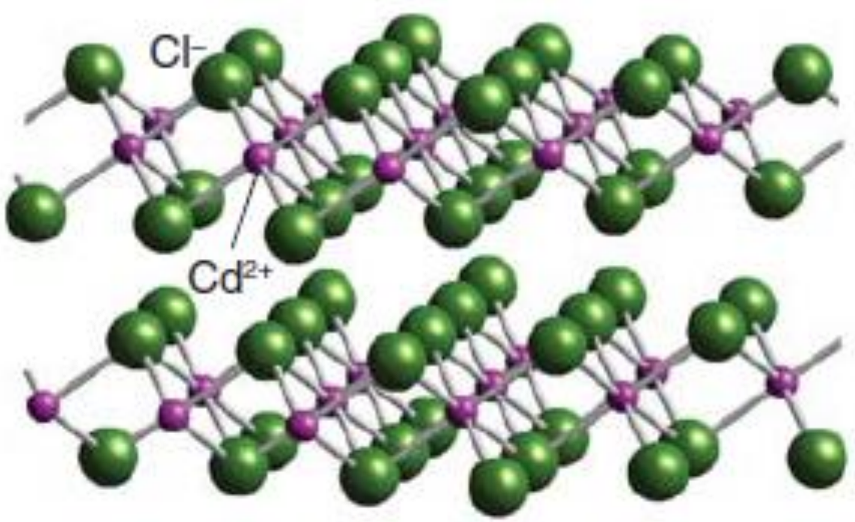
Cadmium-iodide structure

- In the **cadmium-iodide structure** (as in CdI_2), the octahedral holes between every other pair of hcp layers of I^- ions (half of the total number of octahedral holes) are filled by Cd^{2+} ions.
- The CdI_2 structure is also known as 'layer structure', - the repeating layers of atoms perpendicular to the close-packed layers form the sequence I-Cd-I…I-Cd-I with weak van der Waals interactions between the I-atoms in adjacent layers.
- The structure has (6:3)-coordination, being octahedral for the cation and trigonal pyramidal for the anion.
- The structure type is found commonly for many d-metal halides and chalcogenides ($FeBr_2$, MnI_2, ZrS_2, and $NiTe_2$).



Cadmium-chloride structure

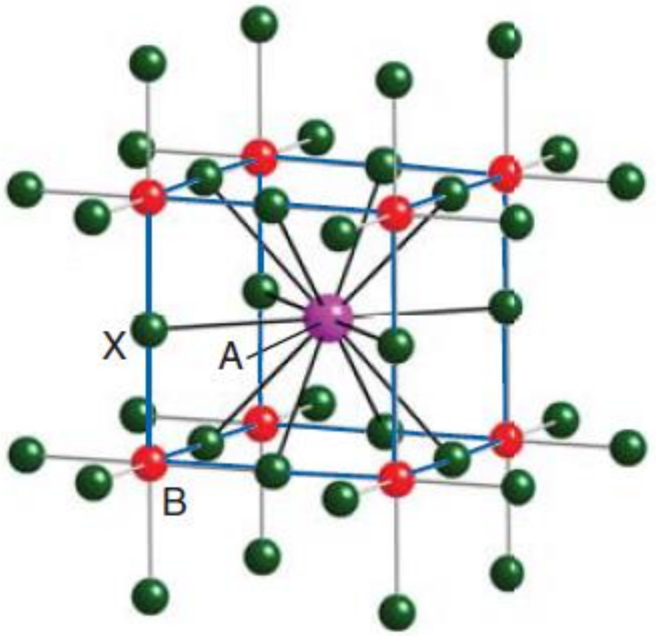
- The **cadmium-chloride structure** (as in $CdCl_2$) is analogous to the CdI_2 structure but with a ccp arrangement of anions; half the octahedral sites, those between alternate anion layers, are occupied.
- This layer structure has identical coordination numbers (6:3) and geometries for the ions to those found for the CdI_2 structure type.
- The structure is preferred for a number of d-metal dichloride, such as $MnCl_2$ and $NiCl_2$.



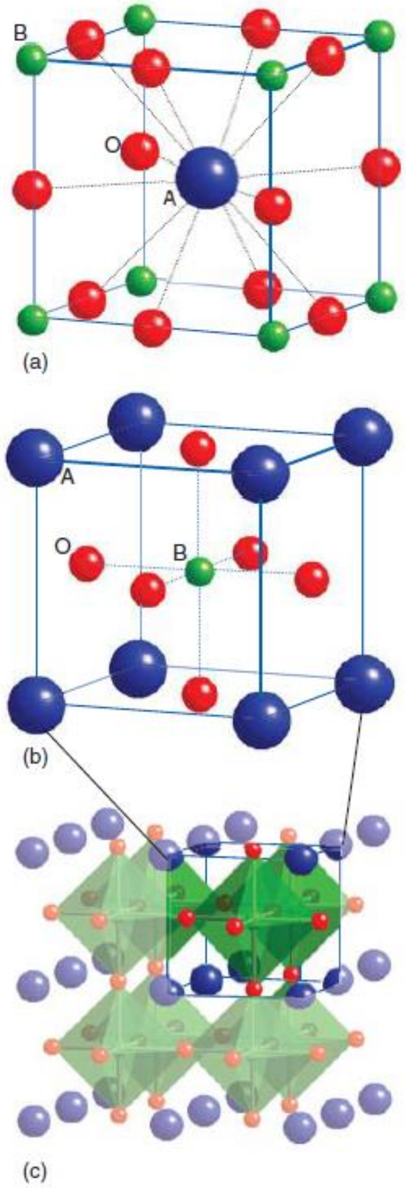
Perovskite structures

- The mineral perovskite bears the general formula of ABX_3 ($X = O^{2-}, F^-, N^{3-}, H^-$)
- The name ‘perovskite’ comes from the naturally occurring oxide mineral $CaTiO_3$, and the largest class of perovskites are those with the anion as oxide
- P**erovskite structure** is cubic with each A cation surrounded by 12 X anions and each B cation surrounded by 6 X anions.
- The perovskite structure may also be described as a close-packed array of A cations and O^{2-} anions (arranged in such a way that each A cation is surrounded by 12 O^{2-} anions from the original close-packed layers), with B cations in all the octahedral holes that are formed from six of the O^{2-} ions, giving $B_{n/4}[AO_3]_{n/4}$, which is equivalent to ABO_3.
- In oxides, X = O and the sum of the charges on the A and B ions must be +6. That sum can be achieved in several ways ($A^{2+}B^{4+}$ and $A^{3+}B^{3+}$ among them), including the possibility of mixed oxides of formula $A(B_{0.5}B'_{0.5})O_3$, as in $La(Ni_{0.5}Ir_{0.5})O_3$.
- The A-type cation in perovskites is therefore usually a large ion (of radius greater than 110 pm) of lower charge, such as

- The solid solutions and nonstoichiometry are also common features of the perovskite structure, as in $Ba_{1-x}Sr_xTiO_3$ and $SrFeO_{3-y}$.
- Materials adopting the perovskite structure often show interesting and useful electrical properties, such as piezoelectricity, ferroelectricity, and high-temperature superconductivity



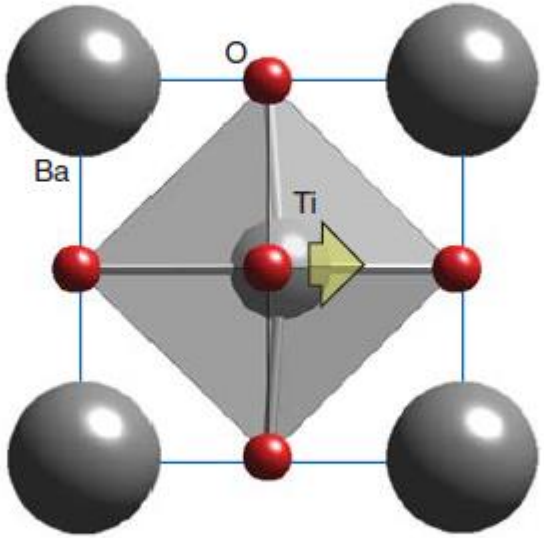
The perovskite structure, ABX_3: the cubic unit cell outlined in blue, emphasizing the coordination geometry of the A (12-fold) and B (6-fold octahedral) cations to X



Perovskite (ABO_3) structure (a) emphasizing the 12-fold coordination of the larger A cation, (b) highlighting the octahedral coordination of the B cation.(c) A polyhedral representation accentuating the BO_6 octahedra.

- The perovskite structure is often distorted (the unit cell is no longer centrosymmetric), and a portion of the crystal can acquire an overall permanent electric polarization as a result of aligning the directions of ion displacements within that part of the crystal.
- Some polar crystals are **ferroelectric** in the sense that they resemble ferromagnets, but instead of the electron spins being aligned over a region of the crystal (often termed a *domain*), the electric dipole moments of many unit cells are aligned.
- As a result, the relative permittivity, which reflects the polarity of a compound, for a ferroelectric material often exceeds 1×10^3 and can be as high as 1.5×10^4

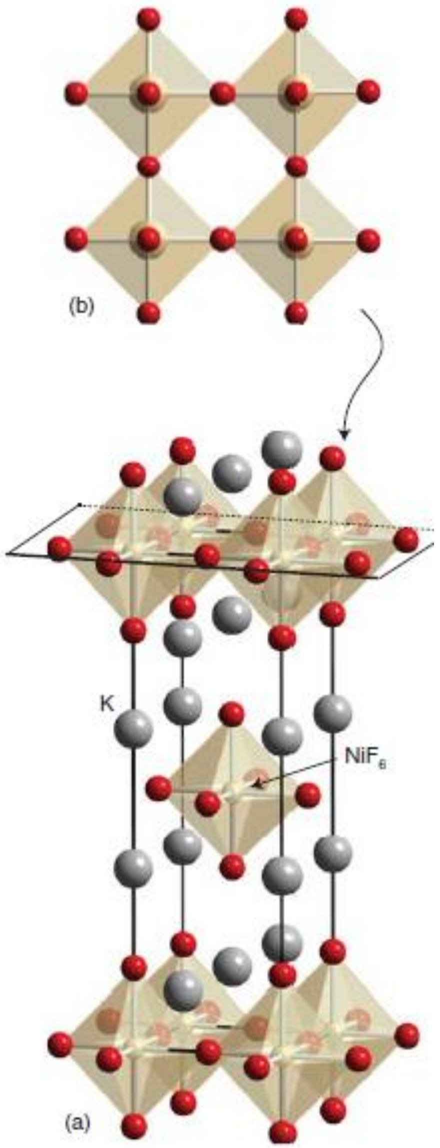
- Barium titanate, $BaTiO_3$, is the most extensively studied example.
- At temperatures above 120°C, it has perfect cubic perovskite structure.
- At room temperature, it adopts a lower-symmetry tetragonal unit cell in which the various ions can be considered as having been displaced from their normal high-symmetry sites. This displacement results in a spontaneous polarization of the unit cell and formation of an electric dipole; coupling between these ion displacements, and therefore the induced dipoles, is very weak.
- 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** (T_C).
- For $BaTiO_3$, $T_C = 120°C$. Its high relative permittivity leads to its use in capacitors, where its presence allows up to 1000 times the charge to be stored in comparison with a capacitor with air between the plates.
- Presence of dopants into $BaTiO_3$ structure, forming solid solutions is useful in tunning its properties (the replacement of Ba by Sr or of Ti by Zr causes a sharp lowering of T_C.



The tetragonal $BaTiO_3$ structure, showing the local Ti^{4+} ion displacement that leads to the ferroelectric behaviour of this material.

- Another characteristic, Perovskites that lack a center 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.
- Piezoelectric materials are used for a variety of applications, such as pressure transducers (in mechanical ignition devices for gas cookers and fires), ultra-micromanipulators (where very small movements can be controlled), sound detectors, and as the probe support in scanning tunnelling microscopy. Some examples are $BaTiO_3$, $NaNbO_3$, $NaTaO_3$, and $KTaO_3$.
- High-temperature cuprate superconductors have structures related to perovskite.

- The structure adopted by K_2NiF_4, is related to perovskite.
- It is believed to contain individual slices from the perovskite structure that share the four F-atoms from the octahedra within the layer, but have terminal F-atoms above and below the layer. These layers are displaced relative to each other and separated by the K^+ ions (which are nine-coordinate, to eight F^- ions of one layer and one terminal F^- ion from the next).
- Some high-temperature superconductors ($La_{1.85}Sr_{0.15}CuO_4$) also known to crystallize with K_2NiF_4 structure type.
- Apart from superconductivity, compounds with the K_2NiF_4 structure also provide an opportunity to investigate two-dimensional magnetic domains, as coupling between electron spins is much stronger within the layers of linked octahedra than between the layers.
- The K_2NiF_4 structure has been introduced as being derived from a single slice of the perovskite structure; other related structures are possible where two or more perovskite layers are displaced horizontally relative to each other.
- 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.



K_2NiF_4 structure: (a) the displaced layers of NiF_6 octahedra interspersed with K^+ ions, (b) a view of one layer of composition NiF_4 showing the corner-sharing octahedra linked through F

Spinel structure

- Spinels have the general formula AB_2O_4 ; A = +2 metal ions and B = +3 metal ions

- The d-block higher oxides Fe_3O_4, Co_3O_4, and Mn_3O_4, and related mixed-metal compounds such as $ZnFe_2O_4$ and $MgAl_2O_4$ have spinel structure

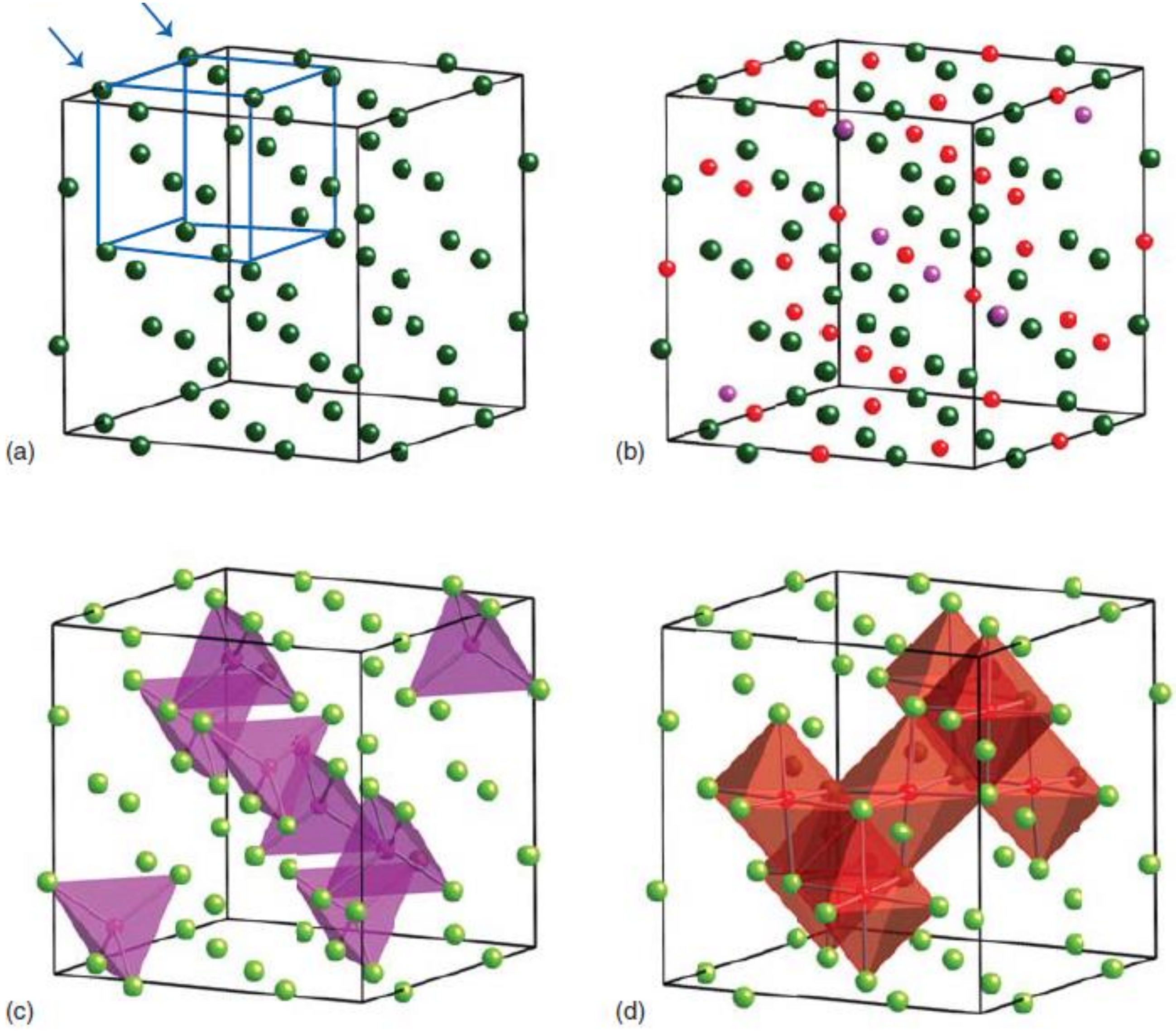
- The **spinel structure** consists of a ccp array of O^{2-} ions in which the A cations occupy one-eighth of the tetrahedral holes and the B cations occupy half of the octahedral holes.

- Spinel formulas are sometimes written $A[B_2]O_4$, the square brackets denoting the cation type (normally the smaller, higher-charged ion of A and B) that occupies the octahedral holes. So, for example, $ZnAl_2O_4$ can be written $Zn[Al_2]O_4$ to show that all the Al^{3+} cations occupy octahedral sites.

- Examples of compounds that have spinel structures include many ternary oxides with the stoichiometry AB_2O_4 that contain a 3d-series metal, such as $NiCr_2O_4$ and $ZnFe_2O_4$, and some simple binary d-block oxides, such as Fe_3O_4, Co_3O_4, and Mn_3O_4

- In these structures A and B are the same element but in different oxidation states, as in $Mn^{2+}[Mn^{3+}]_2O_4$.

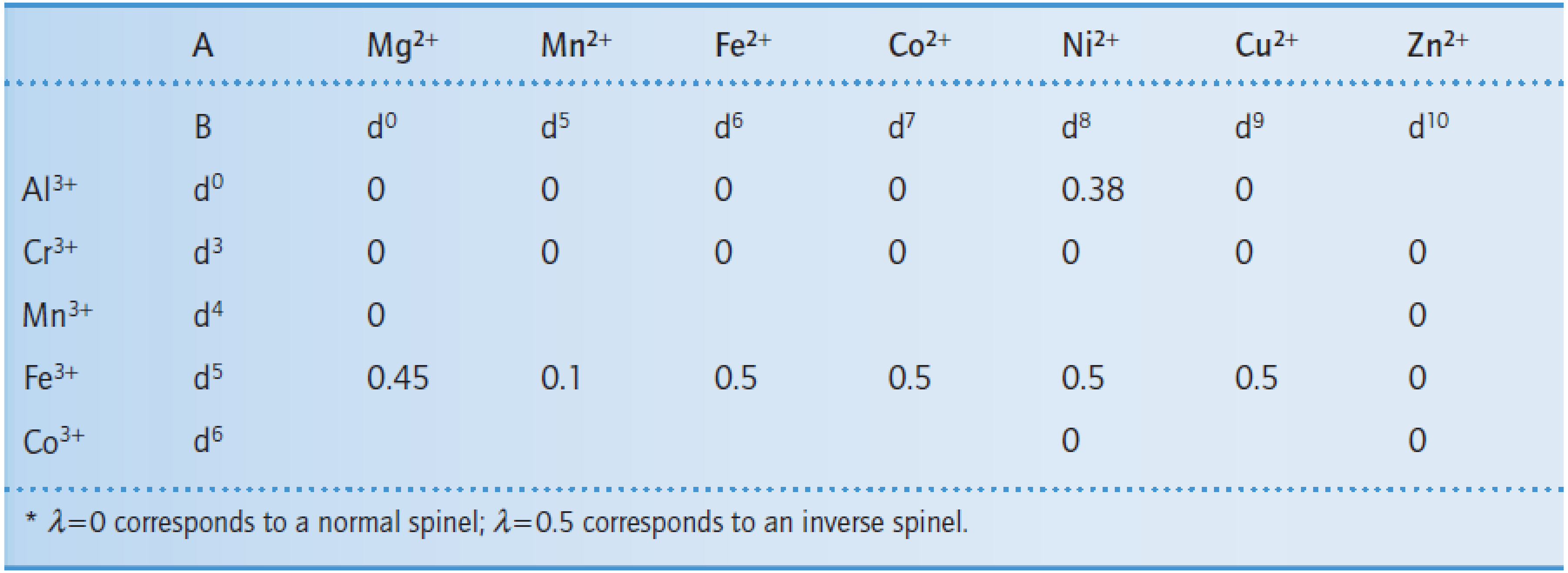
- There are also a number of compositions termed **inverse spinel**, in which the cation distribution is B[AB]O_4 and in which the more abundant cation is distributed over both tetrahedral and octahedral sites.
- Lattice-enthalpy calculations indicate that, for A^{2+} and B^{3+}, the normal spinel structure, A[B_2]O_4 , should be the more stable.
- Effect of ligand-field stabilization energies plays the deciding factor on the site preferences of the ions



The spinel structure AB_2O_4: (a) the close-packed arrangement of anions (O^{2-}) in the full unit cell (close-packed layers are arrowed); the smaller simple ccp unit cell is outlined in blue; (b) the arrangement of cations and anions within the full unit cell with the A cations shown in magenta & B cations in red; (c)* and (d) the polyhedral coordination of A (tetrahedral) & B (octahedral) by oxide for cation sites fully within the unit cell.

- The **occupation factor** , λ , of a spinel is the fraction of B atoms in the tetrahedral sites: $\lambda = 0$ for a normal spinel and $\lambda = 0.5$ for an inverse spinel, $B[AB]O_4$
- Intermediate λ values indicate a level of disorder in the distribution, where B-type cations occupy that portion of the tetrahedral sites.
- For d^0 (A^{2+}, B^{3+}) A and B ions, the normal structure is preferred, as predicted by electrostatic considerations.
- When A^{2+} is a d^6, d^7, d^8, or d^9 ion and B^{3+} (Fe^{3+}), the inverse structure is generally favored. This preference can be traced to the lack of ligand-field stabilization of the high-spin d^5 Fe^{3+} ion in either the octahedral or the tetrahedral site and the ligand-field stabilization of the other d^n ions in the octahedral site.
- For other combinations of d-metal ions on the A and B sites the relative ligand-field stabilization energies of the different arrangements of the two ions on the octahedral and tetrahedral sites need to be calculated.
- Simple ligand-field stabilization appears to work over this limited range of cations.
- More detailed analysis is necessary when cations of different radii are present or any ions that are present do not adopt the

Table 24.3 Occupation factor, λ, in some spinels*



	A	Mg^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
	B	d^0	d^5	d^6	d^7	d^8	d^9	d^{10}
Al^{3+}	d^0	0	0	0	0	0.38	0	
Cr^{3+}	d^3	0	0	0	0	0	0	0
Mn^{3+}	d^4	0						0
Fe^{3+}	d^5	0.45	0.1	0.5	0.5	0.5	0.5	0
Co^{3+}	d^6					0		0

* $\lambda=0$ corresponds to a normal spinel; $\lambda=0.5$ corresponds to an inverse spinel.

Q. Is $MnCr_2O_4$ likely to have a normal or inverse spinel structure?

Answer We need to consider whether there is a ligand-field stabilization. Because Cr^{3+} (d^3) has a large ligand-field stabilization energy ($1.2\Delta_O$) in the octahedral site (but a much smaller one in a tetrahedral field), whereas the high-spin d^5 Mn^{2+} ion does not have any LFSE, a normal spinel structure is expected.

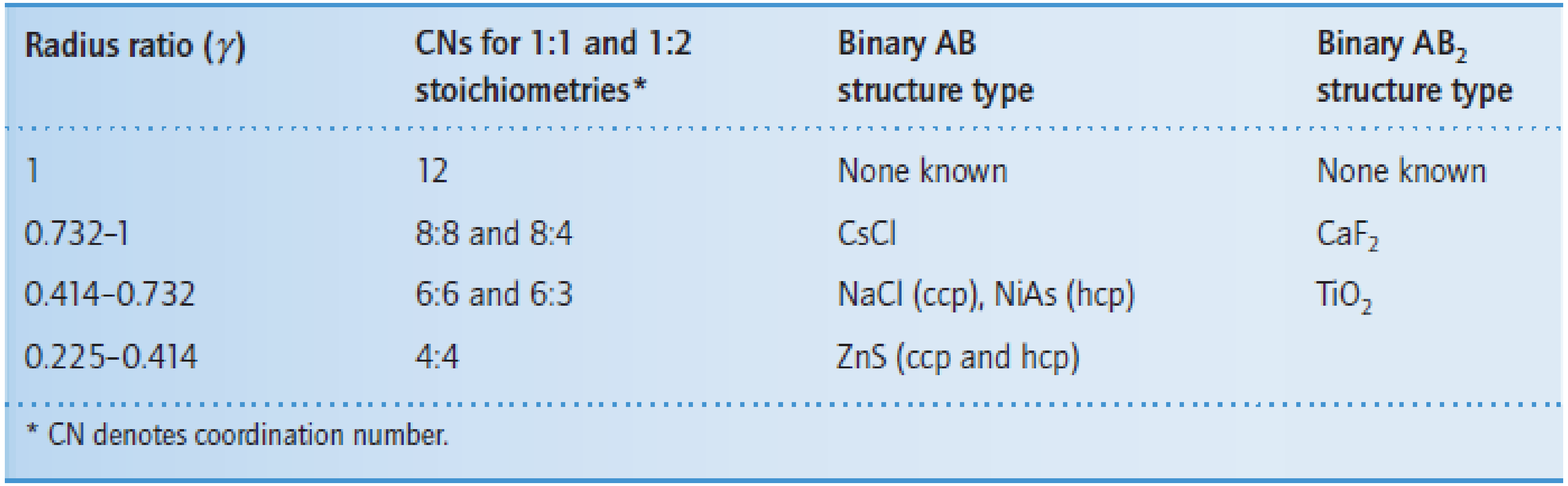
Q. $FeCr_2O_4$ is a normal spinel. Rationalize this observation

- The inverse spinels of formula AFe_2O_4 are sometimes classified as **ferrites**.
- When $RT > J$, where J is the energy of interaction of the spins on different ions, ferrites are paramagnetic.
- However, when $RT < J$, a ferrite may be either ferrimagnetic or antiferromagnetic.
- The antiparallel alignment of spins characteristic of antiferromagnetism is illustrated by $ZnFe_2O_4$, which has the cation distribution $Fe[ZnFe]O_4$. In this compound the Fe^{3+} ions (with $S = 5/2$) in the tetrahedral and octahedral sites are antiferromagnetically coupled, through a superexchange mechanism, below 9.5 K to give nearly zero net magnetic moment to the solid as a whole; note that Zn^{2+} as a d^{10} ion makes no contribution to the magnetic moment of the material.
- The compound $CoAl_2O_4$ is among the normal spinels with $\lambda = 0$ and thus has the Co^{2+} ions at the tetrahedral sites. The color of $CoAl_2O_4$ (an intense blue) is that expected of tetrahedral Co^{2+}. This property, coupled with the ease of synthesis and stability of the spinel structure, has led to cobalt aluminate being used as a pigment (‘cobalt blue’).
- Other mixed d-metal spinels that exhibit strong colors - for example $CoCr_2O_4$ (green), $CuCr_2O_4$ (black), and $(Zn,Fe)Fe_2O_4$ (orange-brown) - are also used as pigments

The radius ratio

- The radius ratio indicates the likely coordination numbers of the ions in a binary compound
- The **radius ratio,** γ is the ratio of the radius of the smaller ion (cation radius) to that of the larger (anion radius)

Table 3.6 The correlation of structural type with radius ratio



Radius ratio (γ)	CNs for 1:1 and 1:2 stoichiometries*	Binary AB structure type	Binary AB_2 structure type
1	12	None known	None known
0.732–1	8:8 and 8:4	CsCl	CaF_2
0.414–0.732	6:6 and 6:3	NaCl (ccp), NiAs (hcp)	TiO_2
0.225–0.414	4:4	ZnS (ccp and hcp)	

* CN denotes coordination number.

- Cation of radius 0.225*r* or below will fit into a tetrahedral hole.
- Cations of radius between 0.225 *r* and 0.414*r* will push the anions slightly apart, will only occupy a tetrahedral hole in a slightly expanded close-packed array of anions of radius *r*, (energetically favorable arrangement)

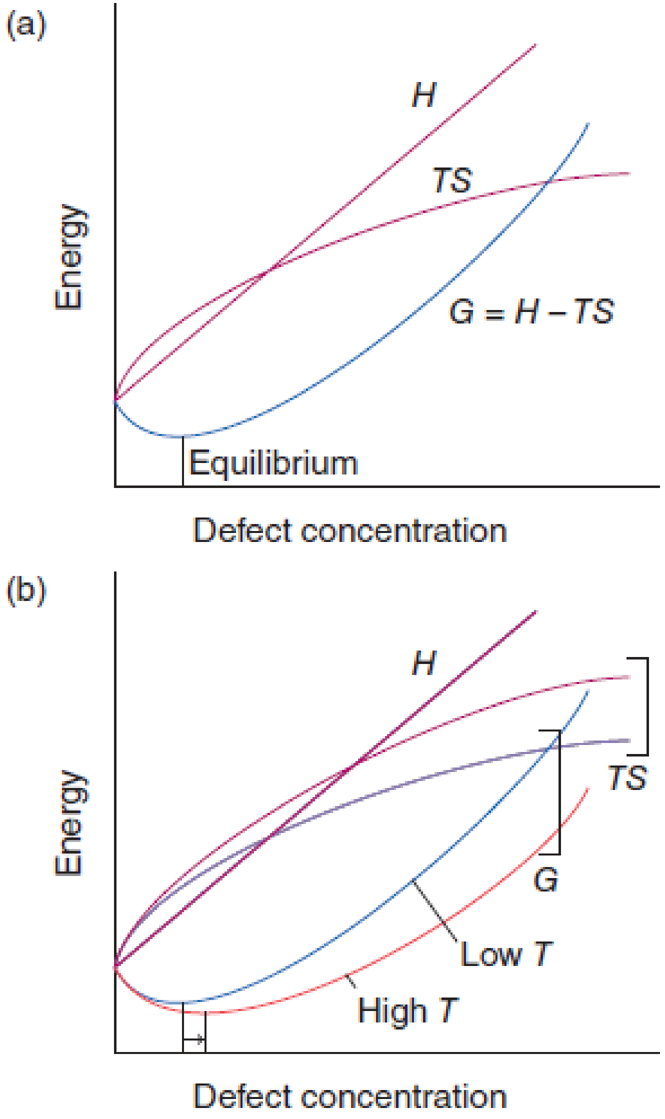
- Once the radius of a cation reaches 0.414 r, the anions are forced so far apart that octahedral coordination (CN=6) becomes more favorable. 6-coordination will be the preferred arrangement for $0.414 < \gamma < 0.732$.
- When cation radius reaches 0.732r, eight anions around the cation can get fit.
- The radius ratio is most reliable when the cation CN = 8, and less reliable with CN = 4, 6 (because directional covalent bonding becomes more important in lower CN)
- Polarization effects are also important for larger ions.
- The use of radius-ratio rules only predicts the experimental structure for about 50 % of compounds

Defects and nonstoichiometry

- All solids contain **defects**, or imperfections of structure or composition.
- Defects are important because they influence properties such as mechanical strength, electrical conductivity, and chemical reactivity.
- I**ntrinsic defects** occur in the pure substance and **extrinsic defects** stem from the presence of impurities.
- It is also common to distinguish **point defects**, which occur at single sites, from **extended defects**, which are ordered in one, two, and three dimensions.
- Point defects are random errors in a periodic lattice, such as the absence of an atom at its usual site or the presence of an atom at a site that is not normally occupied.
- Extended defects involve various irregularities in the stacking of the planes of atoms.

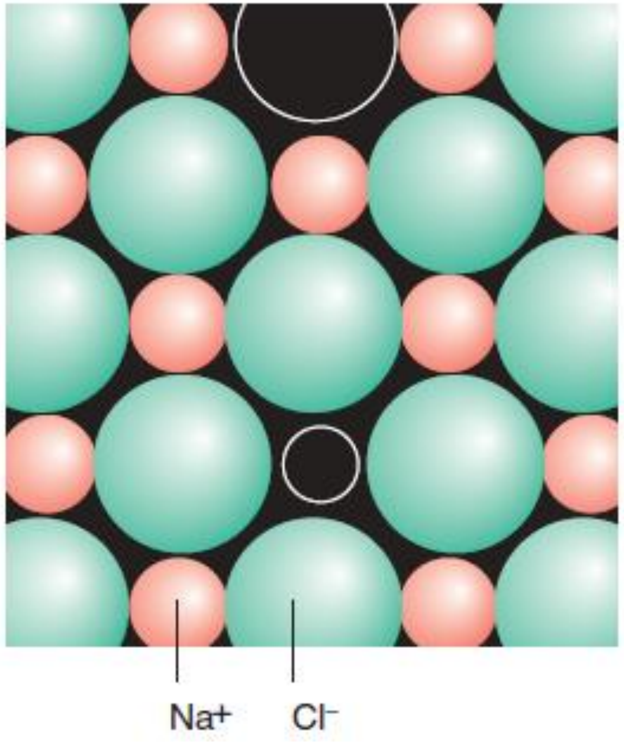
The origins and types of defects

- Solids contain defects because they introduce disorder into a perfect structure and hence increase its entropy.
- Gibbs energy (G = H – TS) of a solid with defects depends on H & S of the sample.
- Defect formation is normally endothermic (the lattice is disrupted so H increases)
- The term – TS becomes more negative as defects are formed because they introduce disorder into the lattice and the entropy rises.
- At T > 0, the Gibbs energy will have a minimum at a nonzero concentration of defects and their formation will be spontaneous (a) Moreover, as the temperature of the solid is raised, the minimum in *G* shifts to higher defect concentrations (b) so solids have a greater number of defects as their melting points are approached.

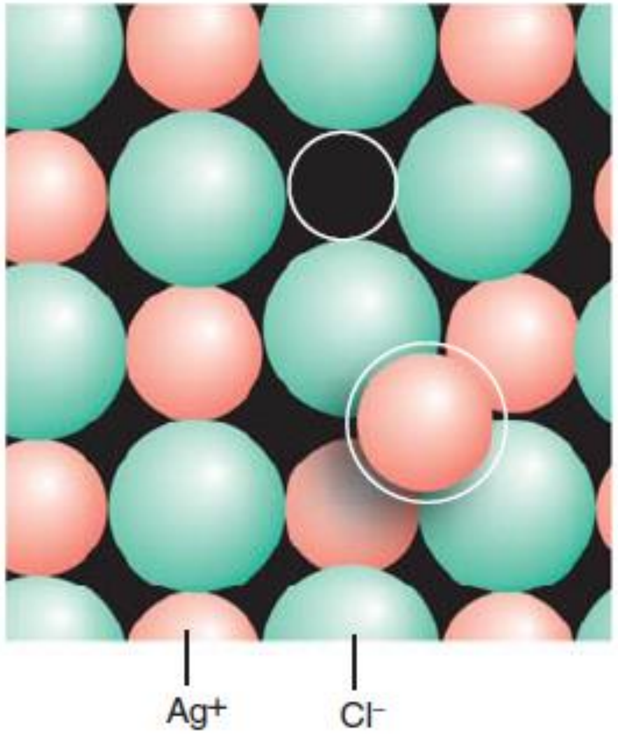


Intrinsic point defects (W. Schottky and J. Frenkel)

- A **Schottky defect** is a vacancy in a perfect arrangement of atoms or ions in a structure
- It is a point defect in which an atom or ion is missing from its normal site in the structure.
- The overall stoichiometry of a solid is not affected by the presence of Schottky defects
- To ensure charge balance, the defects occur in pairs in a compound of stoichiometry MX and there are equal numbers of vacancies at cation and anion sites.
- In solids of different composition, for example MX_2, the defects must occur with balanced charges, so two anion vacancies must be created for each cation lost.
- Schottky defects occur at low concentrations in purely ionic solids (NaCl) and in structures with high coordination numbers.

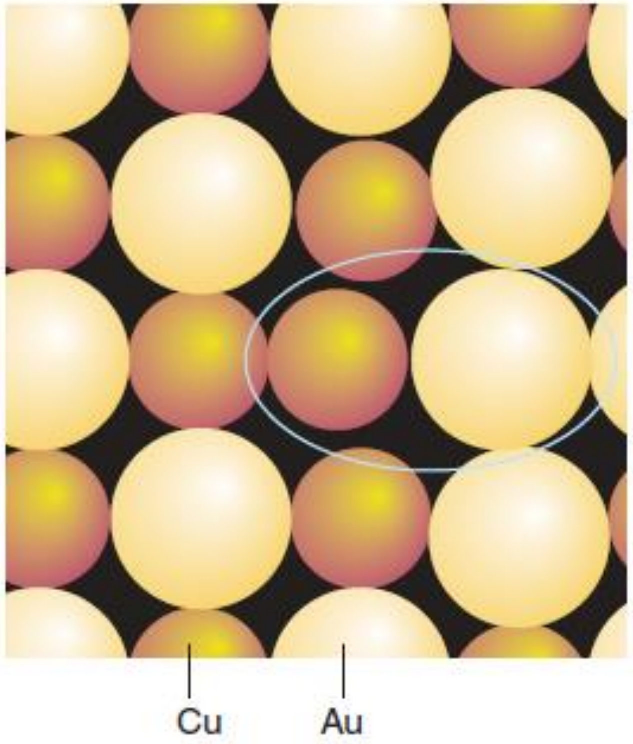


- A **Frenkel defect** is a point defect in which an atom or ion has been displaced onto an interstitial site.
- In AgCl (rock-salt structure), a small number of Ag^+ ions reside in tetrahedral sites, leaving vacancies elsewhere on octahedral sites normally occupied.
- The stoichiometry of the compound is unchanged when a Frenkel defect forms
- It is possible to have Frenkel defects involving either one (M or X displaced) or both (some M and some X interstitials) of the ion types in a binary compound, MX.
- Frenkel defects that occur in PbF_2 involve the displacement of a small number of F^- ions from their normal sites in the fluorite structure, on the tetrahedral holes in the close-packed Pb^{2+} ion array, to sites that correspond to the octahedral holes.
- Frenkel defects is found in solids with lower CN and more covalency



- Frenkel defects are most common in wurtzite (4:4) & sphalerite (4:4) in which coordination numbers are low (CN = 6 or less) and the more open structure provides sites that can accommodate the interstitial atoms.
- Frenkel defects are also observed in fluorite (8:4) structure which can accommodate such interstitials
- The concentration of Schottky defects varies considerably from one type of compound to the next.
- The concentration of vacancies is very low in the alkali metal halides while some d-metal oxides, sulfides, and hydrides have very high concentrations (the high-temperature form of TiO - one defect per seven formula units) of vacancies.
- Defects, when present in large numbers, may affect the density of a solid.
- Significant numbers of Schottky defects, as vacancies, will lead to a decrease in density.
- Frenkel defects have little effect on density as they involve displaced atoms or ions, leaving the number of species in the unit cell unchanged

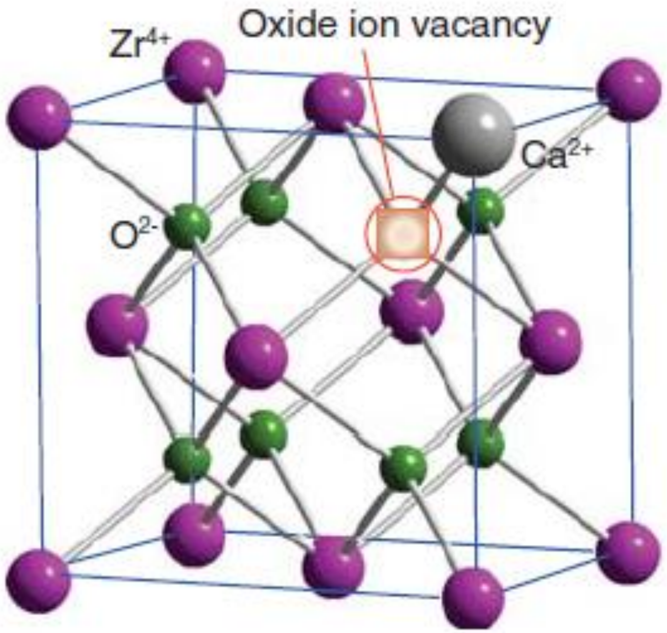
- Another possible type of defect is an **atom-interchange** or **anti-site defect**, which consists of an interchanged pair of atoms.
- This type of defect is common in metal alloys with exchange of neutral atoms.
- It is expected to be very unfavorable for binary ionic compounds on account of the introduction of strongly repulsive interactions between neighboring similarly charged ions.
- For example, a Cu/Au alloy of exact overall composition Cu-Au has extensive disorder at high temperatures, with a significant fraction of Cu and Au atoms interchanged.
- The interchange of similarly charged species on different sites in ternary and compositionally more complex compounds is common; thus in spinel the partial swapping of the metal ions between tetrahedral and octahedral sites is often observed.



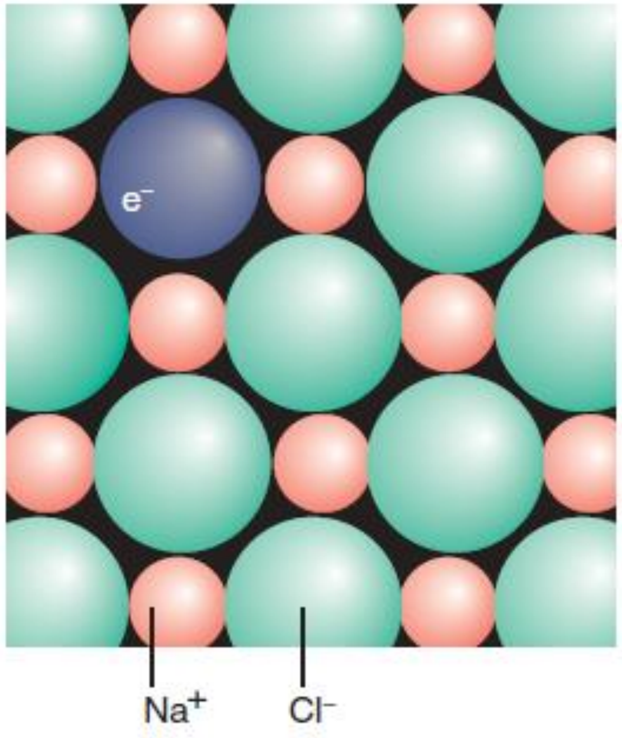
Extrinsic point defects

- Extrinsic defects are defects introduced into a solid as a result of doping with an impurity atom.
- For example, the incorporation of low levels of Cr into the Al_2O_3 structure produces the gemstone ruby, whereas replacement of some Al by Fe and Ti results in the blue gemstone sapphire (natural, synthetic equivalent is also possible).
- The substituting species normally has a similar atomic or ionic radius to the species which it replaces (Cr^{3+} ~ Al^{3+})
- Impurities can also be introduced intentionally by doping one material with another.
- A **dopant** is a small level, typically 0.1–5 %, of an element that replaces another in a structure.
- An example is the introduction of As into Si to modify the latter’s semiconducting properties.
- When the dopant species is introduced into the host the latter’s structure remains essentially unchanged.
- If attempts are made to introduce high levels of the dopant species, a new structure often forms or the dopant species is not incorporated. This behavior usually limits the level of extrinsic point defects to low levels.

- Dopants often modify the electronic structure of the solid. Thus, when an As atom replaces a Si atom, the additional electron from each As atom can be thermally promoted into the conduction band, improving the overall conductivity of the semiconductor.
- In the more ionic substance ZrO_2, the introduction of Ca^{2+} dopant ions in place of Zr^{4+} ions is accompanied by the formation of an O^{2-} ion vacancy to maintain charge neutrality. The induced vacancies allow oxide ions to migrate through the structure, increasing the ionic conductivity of the solid.
- Another example of an extrinsic point defect is a **color center**, a generic term for defects responsible for modifications to the IR, visible, or UV absorption characteristics of solids that have been irradiated or exposed to chemical treatment.



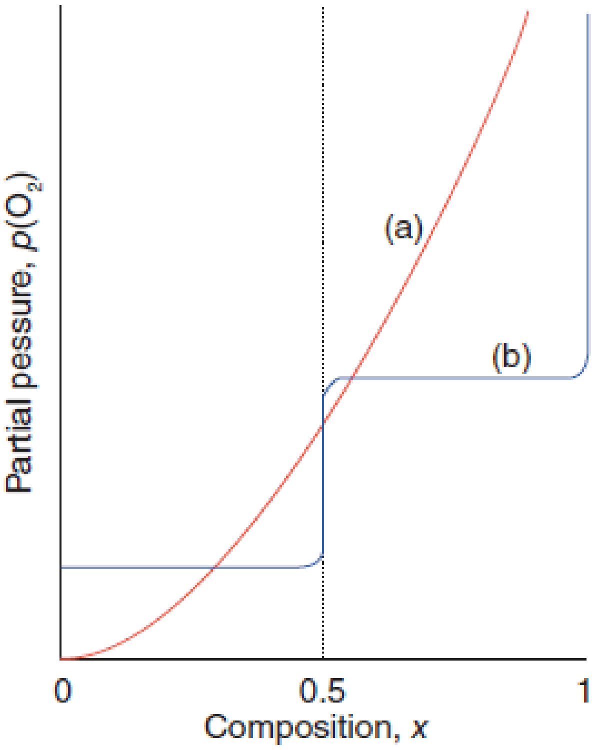
- One type of color center is produced by heating an alkali metal halide crystal in the vapor of the alkali metal, and gives a material with a color characteristic of the system: NaCl becomes orange, KCl violet, and KBr blue-green.
- The process results in the introduction of an alkali metal cation at a normal cation site and the associated electron from the metal atom occupies a halide ion vacancy.
- A color center consisting of an electron in a halide ion vacancy is called an **F-center**. The color results from the excitation of the electron in the localized environment of its surrounding ions.
- An alternative method of producing F-centers involves exposing a material to an X-ray beam that ionizes electrons into anion vacancies. F-centers and extrinsic defects are important in producing color in gemstones.

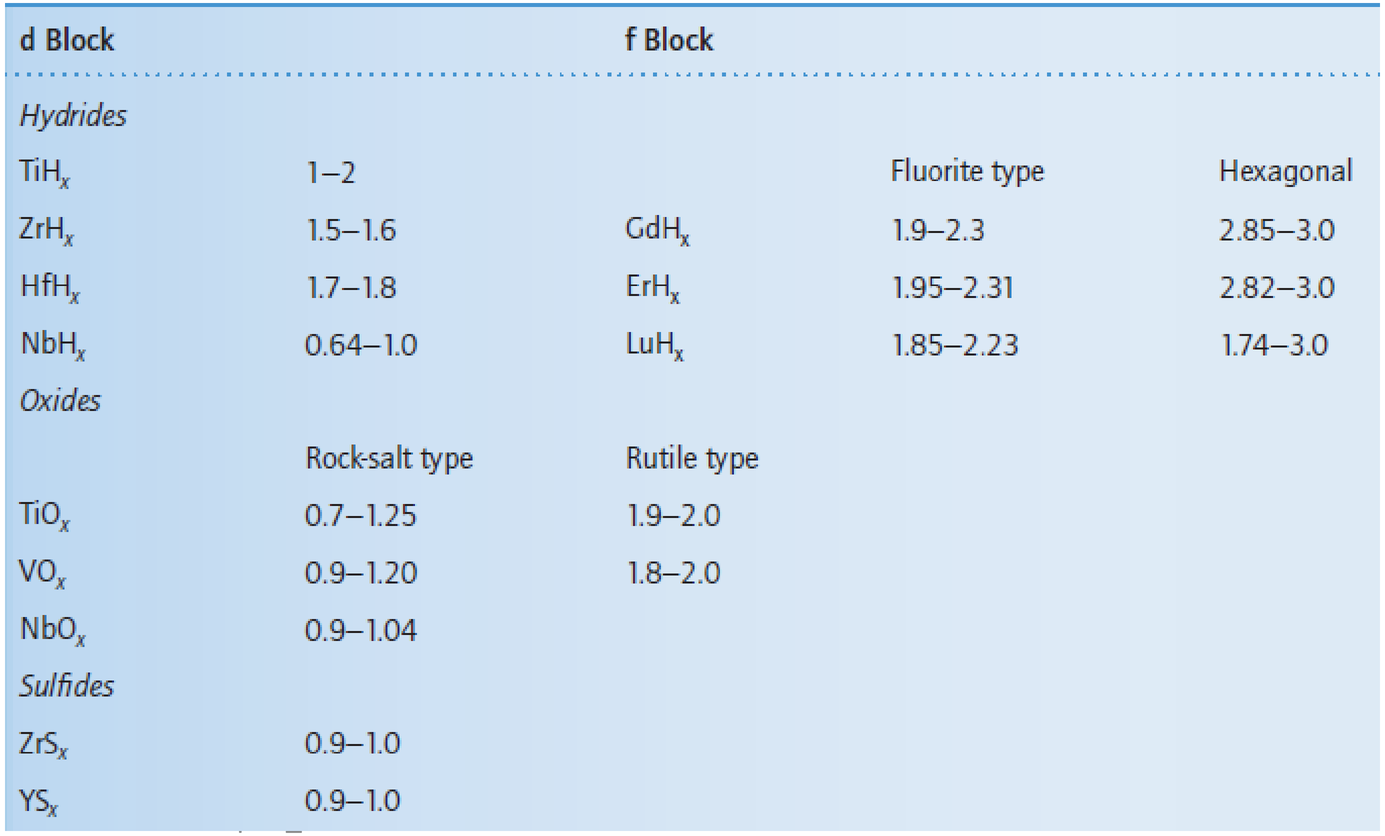


Nonstoichiometric compounds and solid solutions

- A **nonstoichiometric compound** is a substance that exhibits variable composition but retains the same structure type
- Deviations from ideal stoichiometry are common in the solid-state compounds of the d-, f-, and heavier p-block elements
- For example, at 1000°C the composition of ‘iron monoxide’, which is sometimes referred to as wustite, $Fe_{1-x}O$, varies from $Fe_{0.89}O$ to $Fe_{0.96}O$. Gradual changes in the size of the unit cell occur as the composition is varied, but all the features of the rock-salt structure are retained throughout this composition range
- The lattice parameter of the compound varies smoothly with composition is a defining criterion of a nonstoichiometric compound because a discontinuity in the value of the lattice parameter indicates the formation of a new crystal phase.
- Moreover, the thermodynamic properties of nonstoichiometric compounds also vary continuously as the composition changes.
- The formation of a nonstoichiometric compound requires overall changes in composition, it also requires at least one element to exist in more than one oxidation state.

- For example, as the partial pressure of oxygen above a metal oxide is varied, both the lattice parameter and the equilibrium composition of the oxide change continuously.
- The gradual change in the lattice parameter of a solid as a function of its composition is known as **Vegard's rule**
- In wustite, $Fe_{1-x}O$, as x increases some iron(II) must be oxidized to iron(III) in the structure.





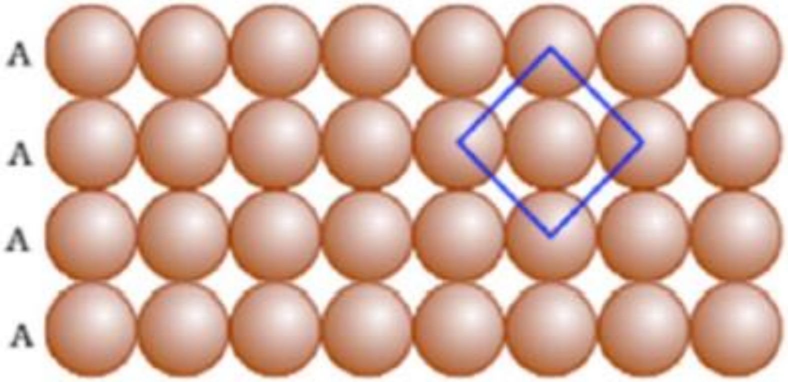
d Block		f Block		
Hydrides				
TiH_x	1–2		Fluorite type	Hexagonal
ZrH_x	1.5–1.6	GdH_x	1.9–2.3	2.85–3.0
HfH_x	1.7–1.8	ErH_x	1.95–2.31	2.82–3.0
NbH_x	0.64–1.0	LuH_x	1.85–2.23	1.74–3.0
Oxides				
	Rock-salt type	Rutile type		
TiO_x	0.7–1.25	1.9–2.0		
VO_x	0.9–1.20	1.8–2.0		
NbO_x	0.9–1.04			
Sulfides				
ZrS_x	0.9–1.0			
YS_x	0.9–1.0			

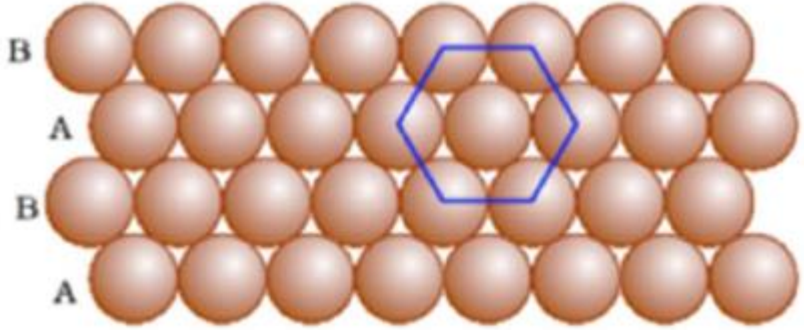
Solid solutions in compounds

- A solid solution occurs where there is a continuous variation in compound stoichiometry without a change in structural type.
- This behavior can occur in many ionic solids such as metal oxides.
- Zn/Cu brass exists in range of compositions $Cu_{1-x}Zn_x$ with $0 < x < 0.38$, where Cu atoms in the structure are gradually and randomly replaced by Zn atoms throughout the solid (individual unit cells contain an arbitrary number of Cu and Zn atoms)
- Another example, composition of many perovskites of stoichiometry ABX_3 (with A^{n+}, B^{m+} and X^{x-} ions) can be varied continuously by varying the ions that occupy some or all of the A, B, and X sites.
- Both $LaFe(III)O_3$ and $SrFe(IV)O_3$ adopt the perovskite structure and has randomly distributed, half $SrFeO_3$ unit cells (with Sr^{2+} on the A-type cation site) and half $LaFeO_3$ unit cells (with La^{3+} on the A-site). The overall compound stoichiometry is $(La_{0.5}Sr_{0.5})FeO_3$, to reflect the normal ABO_3 perovskite stoichiometry.
- Other proportions of these unit cells with stoichiometry $La_{1-x}Sr_xFeO_3$ with $0 \leq x \leq 1$ can also be prepared. This system is called a **solid solution** because all the phases formed as x is varied have the same perovskite structure.

- In a solid solution all the sites in the structure remain fully occupied, the overall compound stoichiometry remains constant, and there is a smooth variation in lattice parameter over its composition range.
- Solid solutions occur most frequently for d-metal compounds because the change in one component might require a change in the oxidation state of another component to preserve the charge balance. Thus, as x increases in $La_{1-x}Sr_xFeO_3$ and La(III) is replaced by Sr(II), the oxidation state of iron must change from Fe(III) to Fe(IV). This change can occur through a gradual replacement of one exact oxidation state, here Fe(III), by another, Fe(IV), on a proportion of the cation sites within the structure.
- Some other solid solutions include the high-temperature superconductors of composition $La_{2-x}Ba_xCuO_4$ $(0 \leq x \leq 0.4)$, which are superconducting for $0.12 \leq x \leq 0.25$, and the spinel $Mn_{1-x}Fe_{2+x}O_4$ $(0 \leq x \leq 1)$.

type of packing in solids is
known as hexagonal close packing in two dimensions. It has
lesser free space and hence
higher packing efficiency in comparison to square close
packing.


A
A
A
A


B
A
B
A

objects with sharp boundaries. The outer part of an atom is composed of electrons in bound orbits; the average number of electrons decreases gradually with increasing distance from the nucleus. There is no point that can be assigned as the precise radius of the atom. Scientists have discovered, however, that each atom in a solid has a characteristic radius that determines its preferred separation from neighbouring atoms. For most types of atom this radius is constant, even in different solids.

An empirical radius is assigned to each atom for bonding considerations, which leads to the concept of atomic size. Atoms readily make crystalline alloys when the radii of the two types of atoms agree to within roughly 15 percent.

Two kinds of ordering are found in crystalline alloys. Most alloys at low temperature are binary crystals with perfect ordering. An example is the alloy of copper and zinc. Copper is fcc, whereas zinc is hcp. A 50-percent-zinc–50-percent-copper alloy has a different structure—β-brass. At low temperatures it has the cesium chloride structure: a bcc lattice with alternating atoms of copper and