

COURSE CODE: SC202(CHEMISTRY)

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LECTURE-IONIC SOLIDS

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Ionic Solids and their Structure

Types of Bonding

1. Metallic Bonding 2. Ionic Bonding

- **Metallic Bonding** can be defined as the bonding that occurs in metals when each atom loses one or more electrons to a common 'sea' or that occurs by the overlap of atomic orbitals of metals to produce molecular orbitals extending throughout the sample.
- Metallic bonding is characteristic of elements with low ionization energies.
- Metals are malleable (easily deformed by the application of pressure) and ductile (able to be drawn into a wire) because the electrons can adjust rapidly to relocation of the metal atom nuclei and there is no directionality in the bonding.
- They are lustrous because the electrons can respond almost freely to an incident wave of electromagnetic radiation and reflect it.
- In **ionic bonding** ions of different elements are held together in rigid, symmetrical arrays as a result of the attraction between their opposite charges.
- Ionic bonding also depends on electron loss and gain, so it is found typically in compounds of metals with electronegative elements.

Unit cells and the description of crystal structures

(a) Lattices and unit cells

A **lattice** is a three-dimensional, infinite array of points, the **lattice points**, each of which is surrounded in an identical way by neighbouring points, and which defines the basic repeating structure of the crystal.

The **crystal structure** itself is obtained by associating one or more identical structural units (such as molecules or ions) with each lattice point.

A **unit cell** of the crystal is an imaginary parallel-sided region (a ‘parallelepiped’) from which the entire crystal can be built up by purely translational displacements

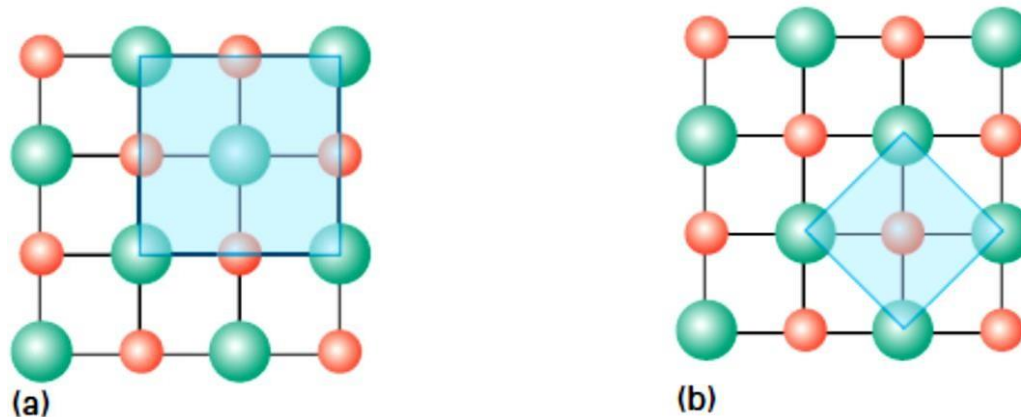


Fig. 1 A two-dimensional solid and two choices of a unit cell. The entire crystal is reproduced by translational displacements of either unit cell, but (b) is generally preferred to (a) because it is smaller.

- The angles (α , β , γ) and lengths (a , b , c) used to define the size and shape of a unit cell are the **unit cell parameters** (the ‘**lattice parameters**’).
- The angle between a and b is denoted γ , that between b and c is α , and that between a and c is β .

Table. 1 The seven crystal systems

System	Relationships between lattice parameters	Unit cell defined by	Essential symmetries
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	$a b c \alpha \beta \gamma$	None
Monoclinic	$a \neq b \neq c$ $\alpha \neq \gamma \neq 90^\circ$ $\beta = 90^\circ$	$a b c \alpha \gamma$	One twofold rotation axis and/or a mirror plane
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	$a b c$	Three perpendicular twofold axes and/or mirror planes
Rhombohedral	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	α	One threefold rotation axis
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	$a c$	One fourfold rotation axis
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	$a c$	One sixfold rotation axis
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	a	Four threefold rotation axes tetrahedrally arranged

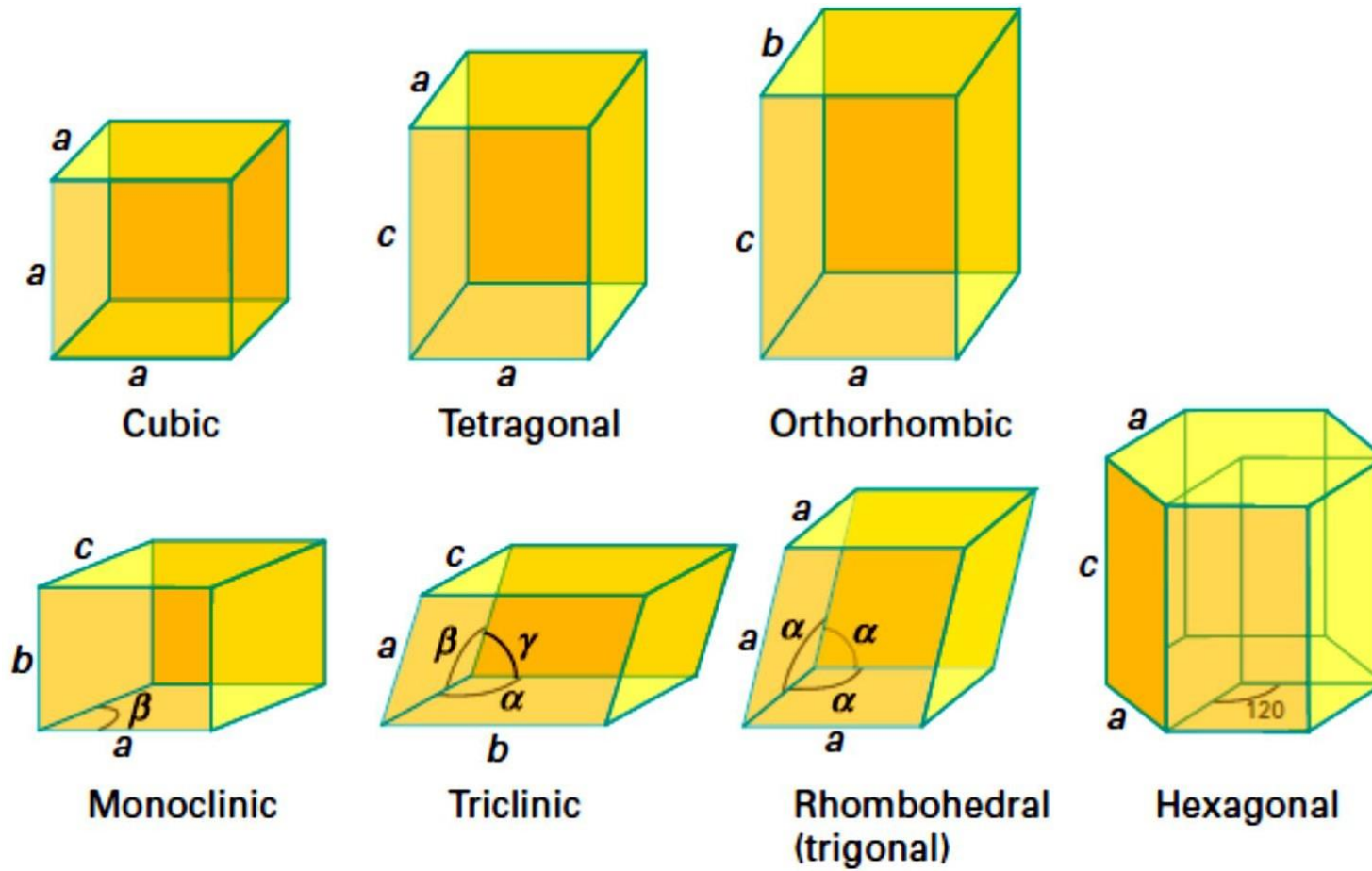


Fig. 2 The seven crystal systems.

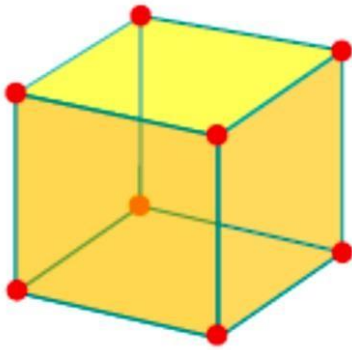


Fig. 3 Lattice points describing the translational symmetry of a primitive cubic unit cell.

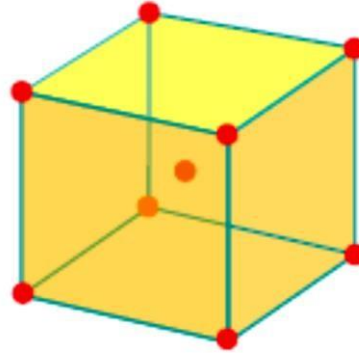


Fig. 4 Lattice points describing the translational symmetry of a body-centred cubic unit cell.

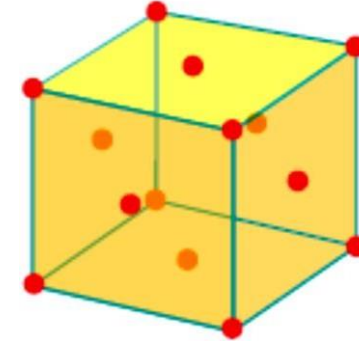


Fig. 5 Lattice points describing the translational symmetry of a face-centred cubic unit cell.

1. A lattice point in the body of, that is fully inside, a cell belongs entirely to that cell and counts as 1.
 2. A lattice point on a face is shared by two cells and contributes $\frac{1}{2}$ to the cell.
 3. A lattice point on an edge is shared by four cells and hence contributes $\frac{1}{4}$.
 4. A lattice point at a corner is shared by eight cells that share the corner, and so contributes $\frac{1}{8}$.
- Thus, for the face-centred cubic lattice depicted in Fig.5 the total number of lattice points in the unit cell is $(8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$.
 - For the body-centred cubic lattice depicted in Fig. 4, the number of lattice points is $(1 \times 1) + (8 \times \frac{1}{8}) = 2$.

Fractional atomic coordinates and projections

- The position of an atom in a unit cell is normally described in terms of **fractional coordinates**, coordinates expressed as a fraction of the length of a side of the unit cell. Thus, the position of an atom located at xa parallel to a , yb parallel to b , and zc parallel to c is denoted (x,y,z) , with $0 \leq x, y, z \leq 1$.
- View the unit cell down one direction, typically one of the axes of the unit cell.
- The positions of the atoms relative to the projection plane are denoted by the fractional coordinate above the base plane and written next to the symbol defining the atom in the projection.
- If two atoms lie above each other, then both fractional coordinates are noted in parentheses.

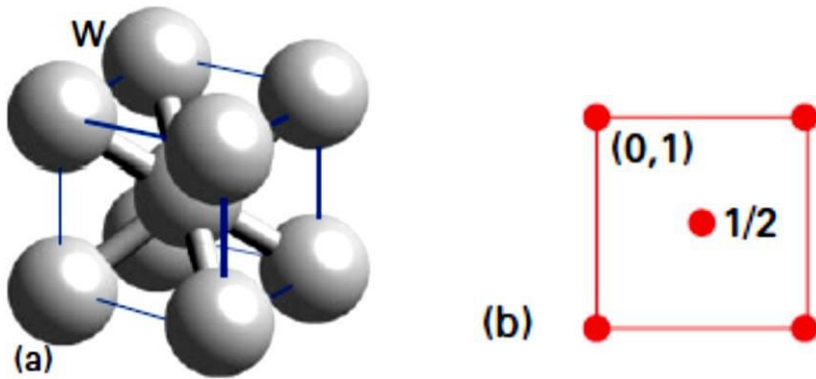


Fig.6 (a) The structure of metallic tungsten and (b) its projection representation.

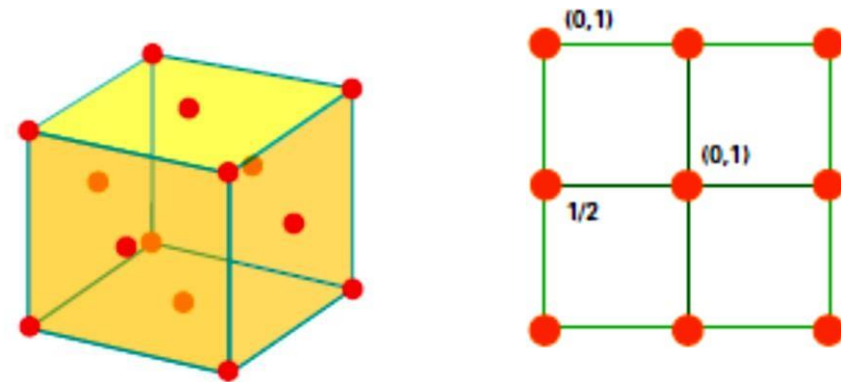


Fig.7 The projection representation of an fcc unit cell.

The close packing of spheres

- A **close-packed structure** is a structure in which there is least unfilled space.
- The **coordination number** (CN) of a sphere in a close-packed arrangement (the ‘number of nearest neighbours’) is 12.

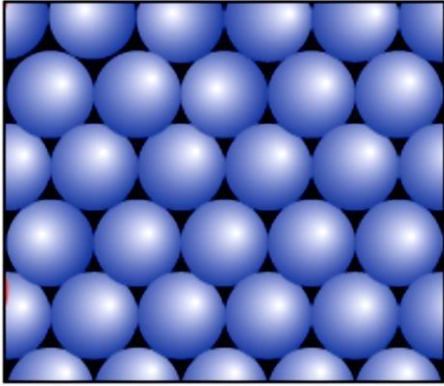
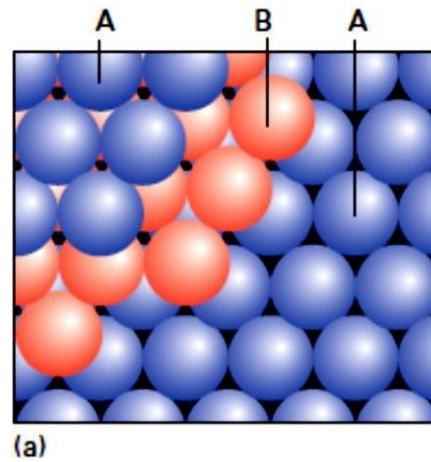
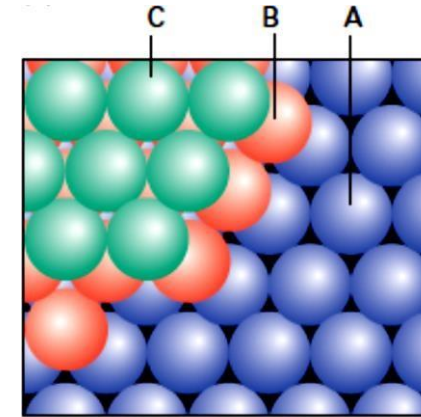


Fig.8 A close-packed layer of hard spheres.



(a)



(b)

Fig. 9 The formation of two close-packed polytypes. (a) The third layer reproduces the first to give an ABA structure.

(b) The third layer lies above the gaps in the first layer, giving an ABC structure. The different colours identify the different layers of identical spheres.

- Consider first a single layer of identical spheres (Fig. 8). The greatest number of immediate neighbours is 6 and there is only one way of constructing this close-packed layer.
- A second close-packed layer of spheres is formed by placing spheres in the dips between the spheres of the first layer.
- The third close-packed layer can be laid in either of two ways and hence can give rise to either of two **polytypes**.

(a) hexagonally close-packed (hcp, Figs 9a and 10).

(b) cubic close-packed (ccp, Figs 9b and 11). Because each ccp unit cell has a sphere at one corner and one at the centre of each face, a ccp unit cell is sometimes referred to as **face-centred cubic** (fcc).

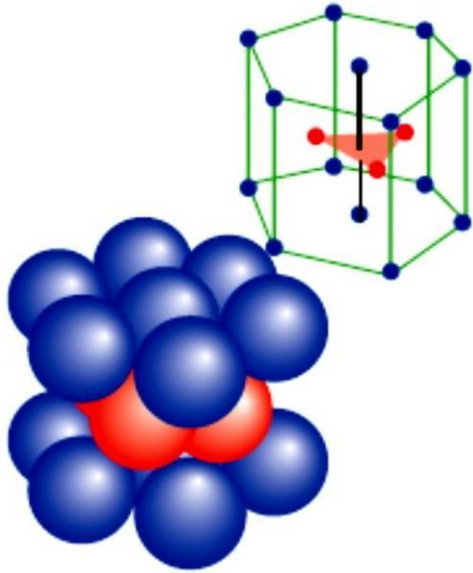


Fig. 10 The hexagonal close-packed (hcp) unit cell of the ABAB . . . polytype.

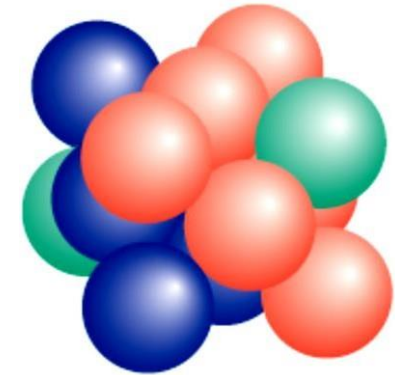
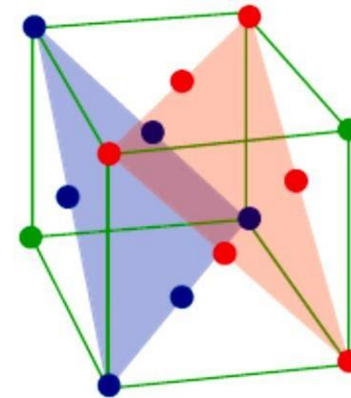


Fig. 11 The cubic close-packed (fcc) unit cell of the ABC . . . polytype. The colours of the spheres correspond to the layers in Fig 12b.

Problem 1. Calculate the percentage of unoccupied space in a close-packed arrangement of identical spheres.

Answer Because the space occupied by hard spheres is the same in the ccp and hcp arrays, we can choose the geometrically simpler structure, ccp, for the calculation.

- Consider Fig. 12. The spheres of radius r are in contact across the face of the cube and so the length of this diagonal is $r+2r+r = 4r$.
- The side of such a cell is $8^{1/2}r$ from Pythagoras' theorem (the square of the length of the diagonal $(4r)^2$ equals the sum of the squares of the two sides of length a , so $2 \times a^2 = (4r)^2$ giving $a = 8^{1/2}r$), so the cell volume is $(8^{1/2}r)^3 = 8^{3/2}r^3$.
- The unit cell contains $1/8$ of a sphere at each corner (for $8 \times 1/8 = 1$ in all) and half a sphere on each face (for $6 \times 1/2 = 3$ in all), for a total of 4. Because the volume of each sphere is $4/3 \pi r^3$, the total volume occupied by the spheres themselves is $4 \times 4/3 \pi r^3 = 16/3 \pi r^3$.
- The occupied fraction is therefore $(16/3 \pi r^3)/(8^{3/2}r^3) = 16/3 \pi/8^{3/2}$, which evaluates to 0.740. The unoccupied fraction is therefore 0.260, corresponding to 26.0 per cent.

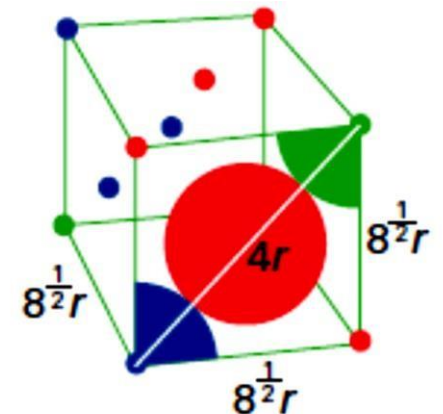


Fig. 12

Holes in close-packed structures

In a close-packed structure there are two types of **holes**, or unoccupied space between the spheres.

- An **octahedral hole** lies between two triangles of spheres on adjoining layers (Fig. 13).
- For a crystal consisting of N spheres in a close-packed structure, there are N octahedral holes.
- The distribution of these holes in an hcp unit cell is shown in Fig. 14a and those in a ccp unit cell Fig. 14b.

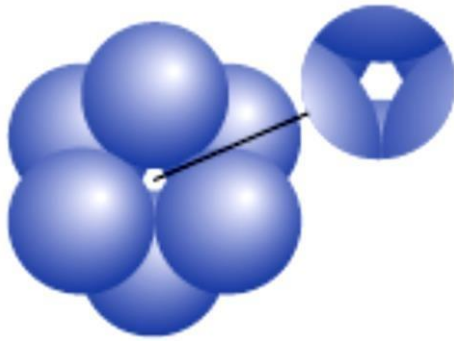


Fig. 13 An octahedral hole formed in an arrangement of close-packed spheres

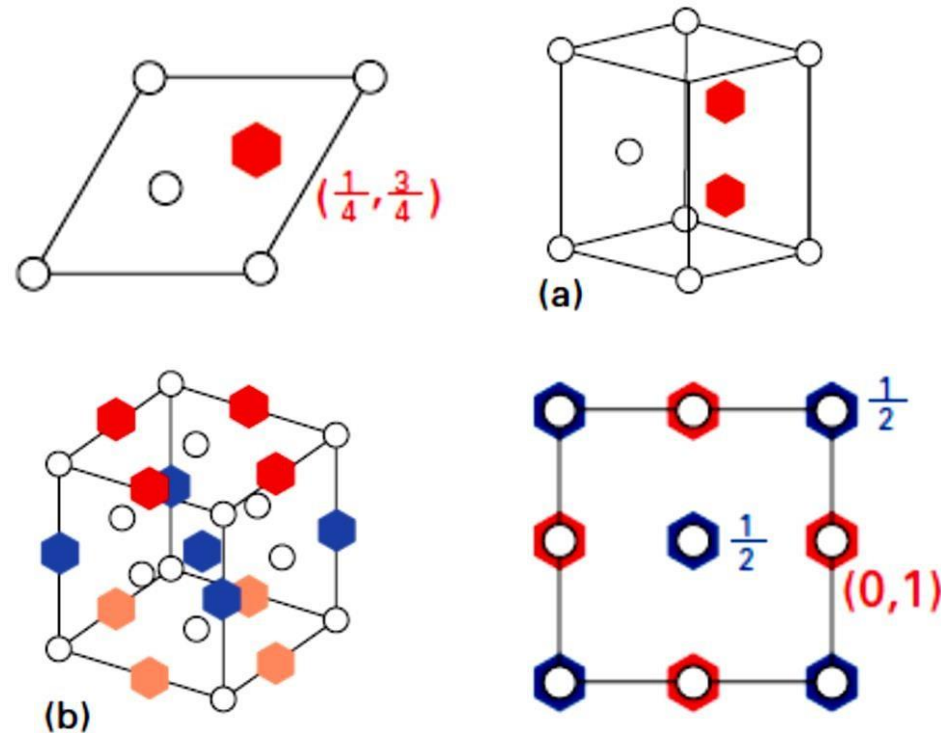


Fig. 14 (a) The location (represented by a hexagon) of the two octahedral holes in the hcp unit cell and (b) the locations (represented by hexagons) of the octahedral holes in the ccp unit cell.

- A **tetrahedral hole**, T, Figs 15 and Fig 16a and b is formed by a planar triangle of touching spheres capped by a single sphere lying in the dip between them.
- In an arrangement of N close-packed spheres there are N tetrahedral holes of each set and $2N$ tetrahedral holes in all.
- In a close-packed structure of spheres of radius r , a tetrahedral hole can accommodate another hard sphere of radius no greater than $0.225r$.

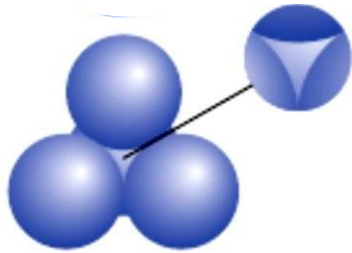


Fig. 15 .a tetrahedral hole formed in an arrangement of close-packed spheres

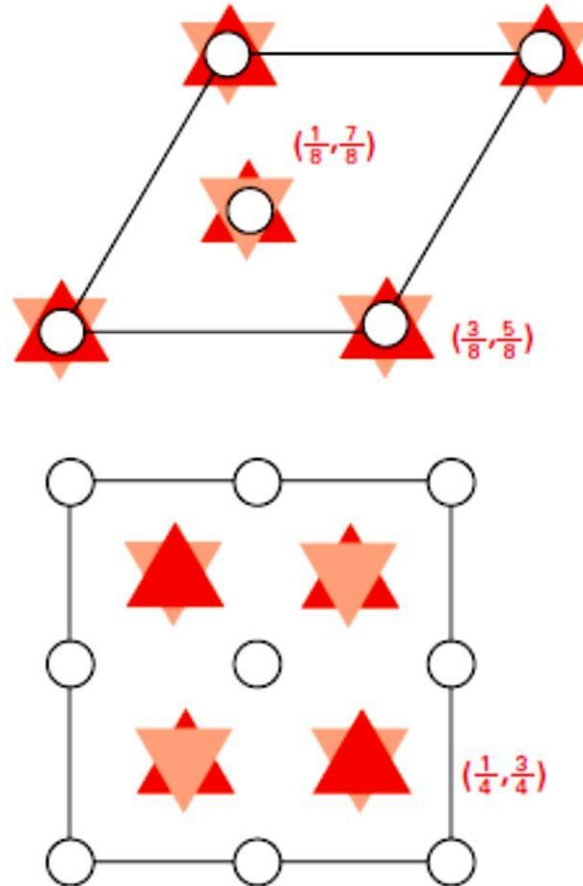
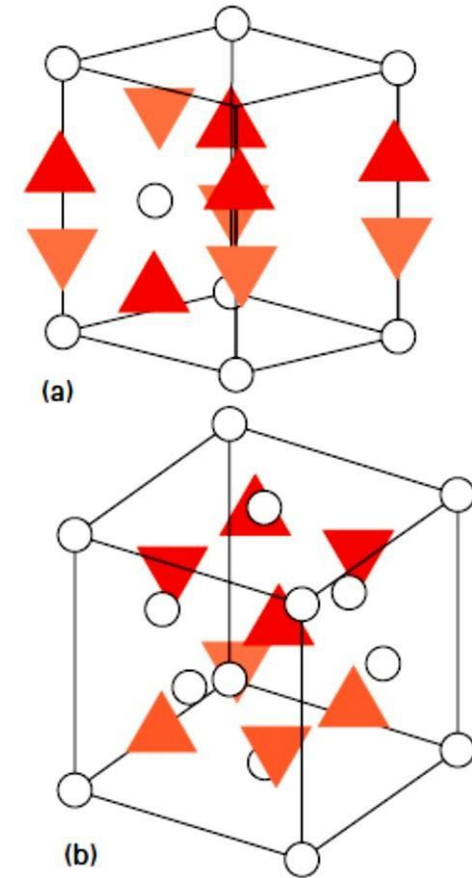


Fig.16 (a) The locations (represented by triangles) of the tetrahedral holes in The hcp unit cell and (b) the locations of the tetrahedral holes in the ccp unit cell.



Calculating the size of an octahedral hole

Problem 2: Calculate the maximum radius of a sphere that may be accommodated in an octahedral hole in a close-packed solid composed of spheres of radius r .

Answer The structure of a hole, with the top spheres removed, is shown in Fig. 17a. If the radius of a sphere is r and that of the hole is r_h , it follows from Pythagoras' theorem that $(r + r_h)^2 + (r + r_h)^2 = (2r)^2$ and therefore that $(r + r_h)^2 = 2r^2$, which implies that $r + r_h = 2^{1/2}r$. That is, $r_h = (2^{1/2} - 1)r = 0.414r$.

Each octahedral hole can accommodate a hard sphere representing another type of atom with a radius no larger than $0.414r$.

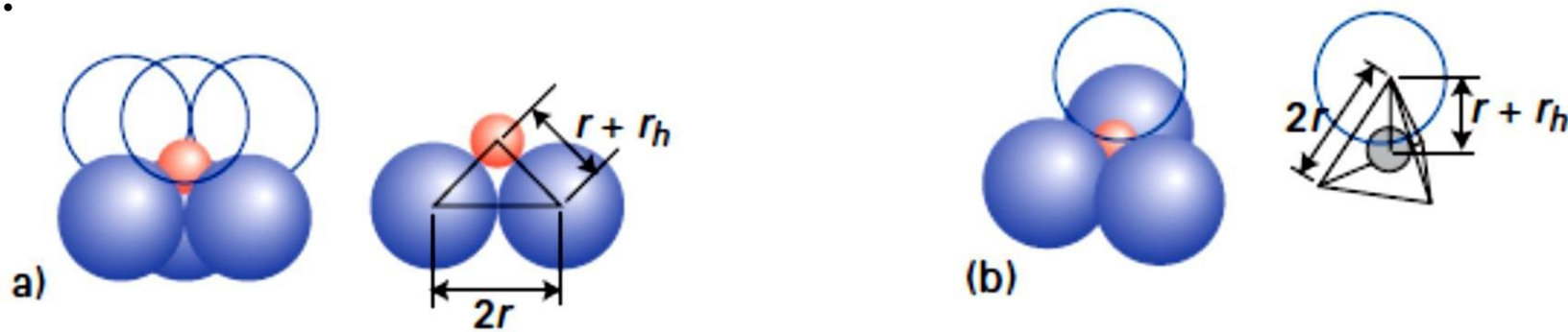


Fig.17 The distances used to calculate the size of (a) an octahedral hole and (b) a tetrahedral hole.

The maximum radius of a sphere that can fit into a tetrahedral hole is r_h $0.225r$;

Calculating the density of a substance from a structure

Problem 3: Calculate the density of gold, with a cubic close-packed array of atoms of molar mass $M = 196.97 \text{ g mol}^{-1}$ and a cubic lattice parameter $a = 409 \text{ pm}$.

Density is an intensive property; therefore the density of the unit cell is the same as the density of any macroscopic sample. In a ccp arrangement there are four spheres associated with the unit cell. The mass of each atom is M/N_A , where N_A is Avogadro's constant, and the total mass of the unit cell is $4M/N_A$. The volume of the cubic unit cell is a^3 . The mass density of the cell is $4M/N_A a^3$.

$$\rho = \frac{4 \times (196.97 \times 10^{-3} \text{ kg mol}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (409 \times 10^{-12} \text{ m})^3} = 1.91 \times 10^4 \text{ kg m}^{-3}$$

That is, the density of the unit cell, and therefore of the bulk metal, is 19.1 g cm^{-3} . The experimental value is 19.2 g cm^{-3} , in good agreement with this calculated value.

Problem 4: Calculate the lattice parameter of silver assuming that it has the same structure as elemental gold but a density of 10.5 g cm^{-3} .

Polytypism

- Cobalt is an example of a metal that displays complex polytypism. Above 500 °C, cobalt is ccp but it undergoes a transition when cooled. The structure that results is a nearly randomly stacked set (for instance, ABACBABABC...) of close-packed layers of Co atoms.

Polymorphism of metals

- **Polymorphism** is the ability to adopt different crystal forms under different conditions of pressure and temperature.
- The polymorphs of metals are generally labelled $\alpha, \beta, \gamma, \dots$ with increasing temperature.
- Iron, for example, shows several solid–solid phase transitions; α -Fe, which is bcc, occurs up to 906°C, γ -Fe, which is ccp, occurs up to 1401°C, and then α -Fe occurs again up to the melting point at 1530°C.

Alloys

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.

Solid solutions are classified as either ‘substitutional’ or ‘interstitial’.

A **substitutional solid solution** is a solid solution in which atoms of the solute metal occupy some of the locations of the solvent metal atoms (Fig. 18a).

An **interstitial solid solution** is a solid solution in which the solute atoms occupy the interstices (the holes) between the solvent atoms (Fig. 18b).

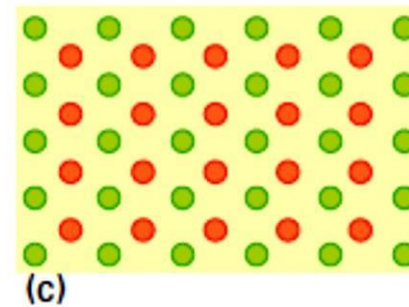
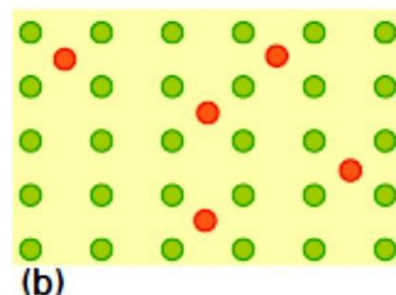
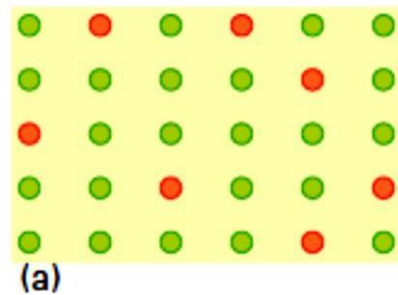


Fig. 18 (a) Substitutional and (b) interstitial alloys. (c) In some cases, an interstitial alloy may be regarded as a substitutional alloy derived from another lattice.

(a) Substitutional solid solutions

Substitutional solid solutions are generally formed if three criteria are fulfilled:

1. The atomic radii of the elements are within about 15 per cent of each other.
2. The crystal structures of the two pure metals are the same; this similarity indicates that the directional forces between the two types of atom are compatible with each other.
3. The electropositive characters of the two components are similar; otherwise compound formation, where electrons are transferred between species, would be more likely.

For eg. sodium and potassium are chemically similar and have bcc structures, the atomic radius of Na (191 pm) is 19 per cent smaller than that of K (235 pm), and the two metals do not form a solid solution. Copper and nickel, however, have similar electropositive character, similar crystal structures (both ccp), and similar atomic radii (Ni 125 pm, Cu 128 pm, only 2.3 per cent different), and form a continuous series of solid solutions, ranging from pure nickel to pure copper

A substitutional solid solution involves the replacement of one type of metal atom in a structure by another.

(b) Interstitial solid solutions of nonmetals

- Interstitial solid solutions are often formed between metals and small atoms (such as boron, carbon, and nitrogen) that can inhabit the interstices in the structure.
- 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. With increasing carbon content they become harder and stronger but less malleable.

(c) Intermetallic compounds

- 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.

They include β -brass (CuZn) and compounds of composition MgZn_2 , Cu_3Au , NaTl , and $\text{Na}_5\text{Zn}_{21}$.

Symmetry operations, elements and point groups

- **Symmetry operation** is defined as an action, such as rotation through a certain angle, that leaves the molecule apparently unchanged. Eg. rotation of a H₂O molecule by 180° around the bisector of the HOH angle (Fig. 1).
- Associated with each symmetry operation there is a **symmetry element**, a point, line, or plane with respect to which the symmetry operation is performed.
- All these operations leave at least one point unchanged (the centre of the molecule), and hence they are referred to as the operations of **point-group symmetry**.
- The **identity operation**, *E*, consists of doing nothing to the molecule. Every molecule has at least this operation.

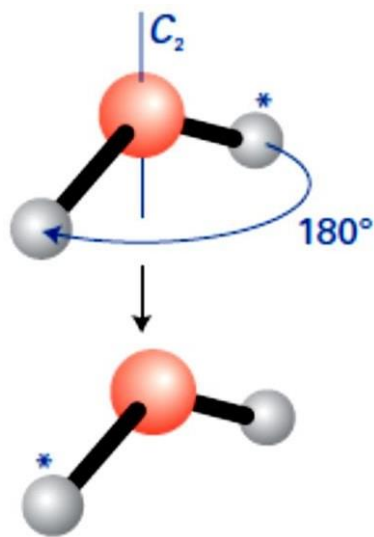


Fig 1. In H₂O molecule, rotation of 180° (the *C*₂ operation) leaves it apparently unchanged. There is only one rotation operation associated with a *C*₂ axis (as in H₂O) because clockwise and anticlockwise rotations by 180° are identical.

- In general, an ***n*-fold rotation** is a symmetry operation if the molecule appears unchanged after rotation by $360^\circ/n$.
- The corresponding symmetry element is a line, an ***n*-fold rotation axis**, C_n , about which the rotation is performed.
- The trigonal-pyramidal NH_3 molecule has a threefold rotation axis, denoted C_3 , but there are now two operations associated with this axis, one a clockwise rotation by 120° and the other an anticlockwise rotation by 120° .
- The two operations are denoted C_3 and C_3^2 (because two successive clockwise rotations by 120° are equivalent to an anticlockwise rotation by 120°), respectively.

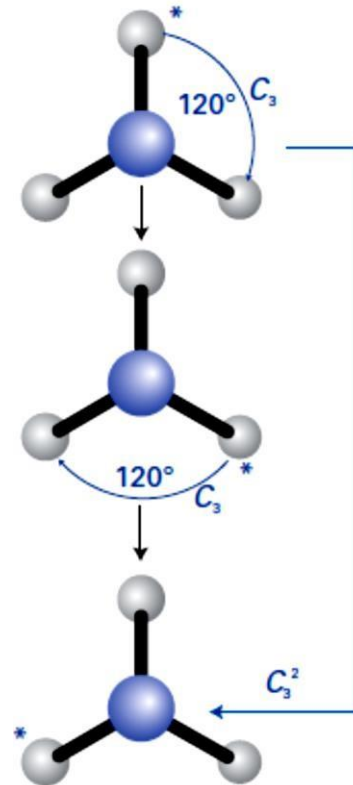


Fig 2. A threefold rotation and the corresponding C_3 axis in NH_3 . There are two rotations associated with this axis, one through 120° (C_3) and one through 240° (C_3^2).

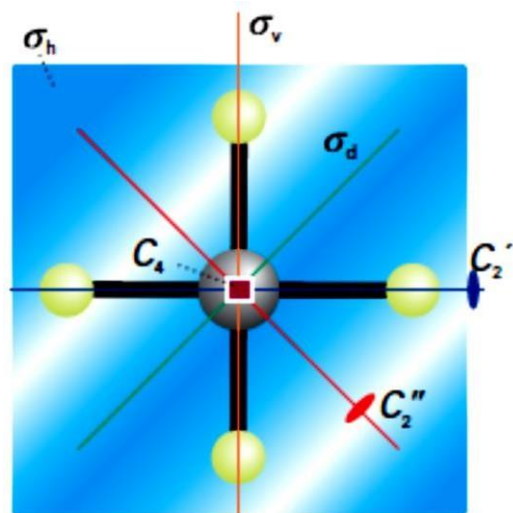


Fig 3. Some of the symmetry elements of a square-planar molecule such as XeF_4 .

- The square-planar molecule XeF_4 has a fourfold C_4 axis, but in addition it also has two pairs of twofold rotation axes that are perpendicular to the C_4 axis: one pair (C_2) passes through each *trans*-FXeF unit and the other pair (C_2) passes through the bisectors of the FXeF angles (Fig.3).
- By convention, the highest order rotational axis, which is called the **principal axis**, defines the z -axis (and is typically drawn vertically).

- The reflection of an H_2O molecule in either of the two planes shown in Fig. 4 is a symmetry operation; the corresponding symmetry element, the plane of the mirror, is a **mirror plane**, σ . The H_2O molecule has two mirror planes that intersect at the bisector of the HOH angle. Because the planes are ‘vertical’, in the sense of containing the rotational (z) axis of the molecule, they are labelled with a subscript v , as in σ_v and σ_v' .
- The XeF_4 molecule in Fig.3 has a mirror plane σ_h in the plane of the molecule. The subscript h signifies that the plane is ‘horizontal’ (the vertical principal rotational axis of the molecule is perpendicular to it). This molecule also has two more sets of two mirror planes that intersect the fourfold axis.
- The symmetry elements (and the associated operations) are denoted σ_v for the planes that pass through the F atoms and σ_d for the planes that bisect the angle between the F atoms. The d denotes ‘dihedral’ and signifies that the plane bisects the angle between two C_2 axes (the FXeF axes).

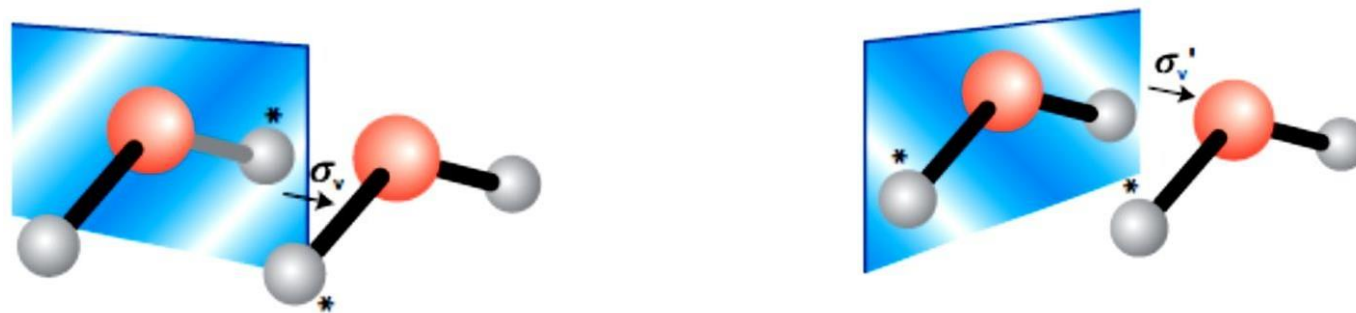


Fig 4. The two vertical mirror planes σ_v and σ_v' in H_2O . Both planes cut through the C_2 axis.

- In **inversion operation**, i , we need to imagine that each atom is projected in a straight line through a single point located at the centre of the molecule and then out to an equal distance on the other side (Fig.5).
- The symmetry element, the point through which the projections are made, is called the **centre of inversion**, i . For SF_6 , the centre of inversion lies at the nucleus of the S atom. Likewise, the molecule CO_2 has an inversion centre at the C nucleus. However, there need not be an atom at the centre of inversion: a N_2 molecule has a centre of inversion midway between the two nitrogen nuclei.

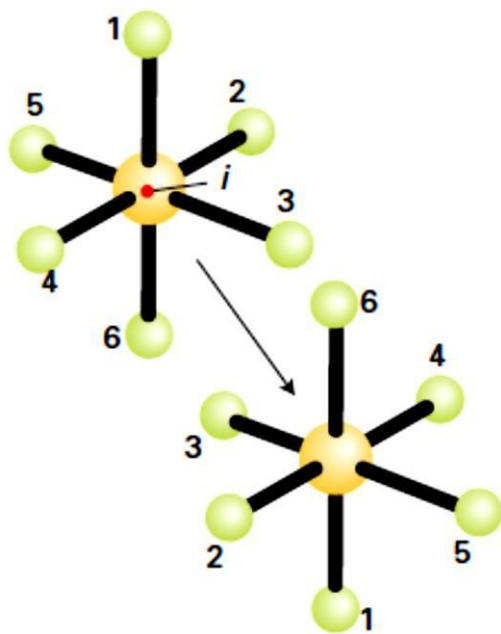


Fig 5. The inversion operation and the centre of inversion i in SF_6 .

- An **improper rotation** consists of a rotation of the molecule through a certain angle around an axis followed by a reflection in the plane perpendicular to that axis (Fig. 6).
- Eg. Consider CH_4 molecule. In this case, the operation consists of a 90° (that is, $360^\circ/4$) rotation about an axis bisecting two HCH bond angles, followed by a reflection through a plane perpendicular to the rotation axis. A fourfold improper rotation is denoted S_4 .
- The symmetry element, the **improper-rotation axis**, S_n (S_4 in the example), is the corresponding combination of an n -fold rotational axis and a perpendicular mirror plane.

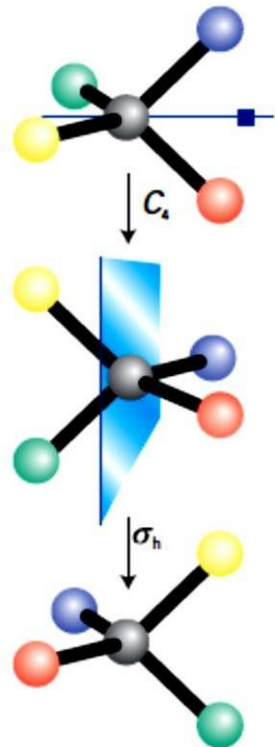


Fig 6. A fourfold axis of improper rotation S_4 in the CH_4 molecule.

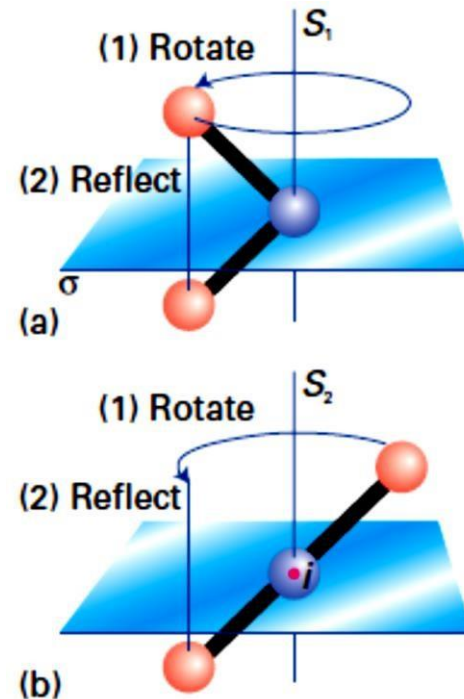
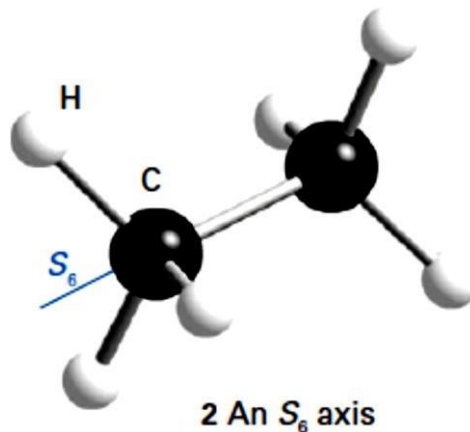
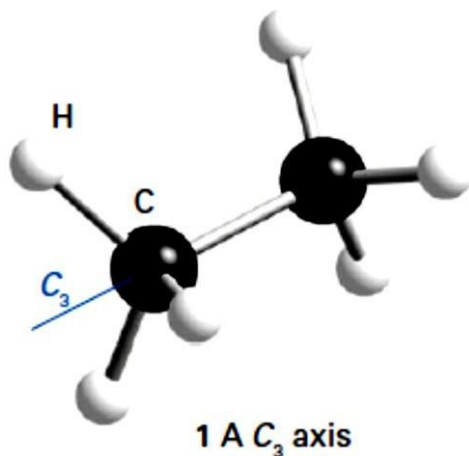


Fig 7. (a) An S_1 axis is equivalent to a mirror plane and (b) an S_2 axis is equivalent to a centre of inversion.

Problem: Identify the symmetry elements in the eclipsed and staggered conformations of an ethane molecule.

Answer We need to identify the rotations, reflections, and inversions that leave the molecule apparently unchanged.

The eclipsed conformation of a CH_3CH_3 molecule (1) has the elements E , C_3 , C_2 , σ_h , σ_v , and S_3 . The staggered conformation (2) has the elements E , C_3 , σ_d , i , and S_6 .



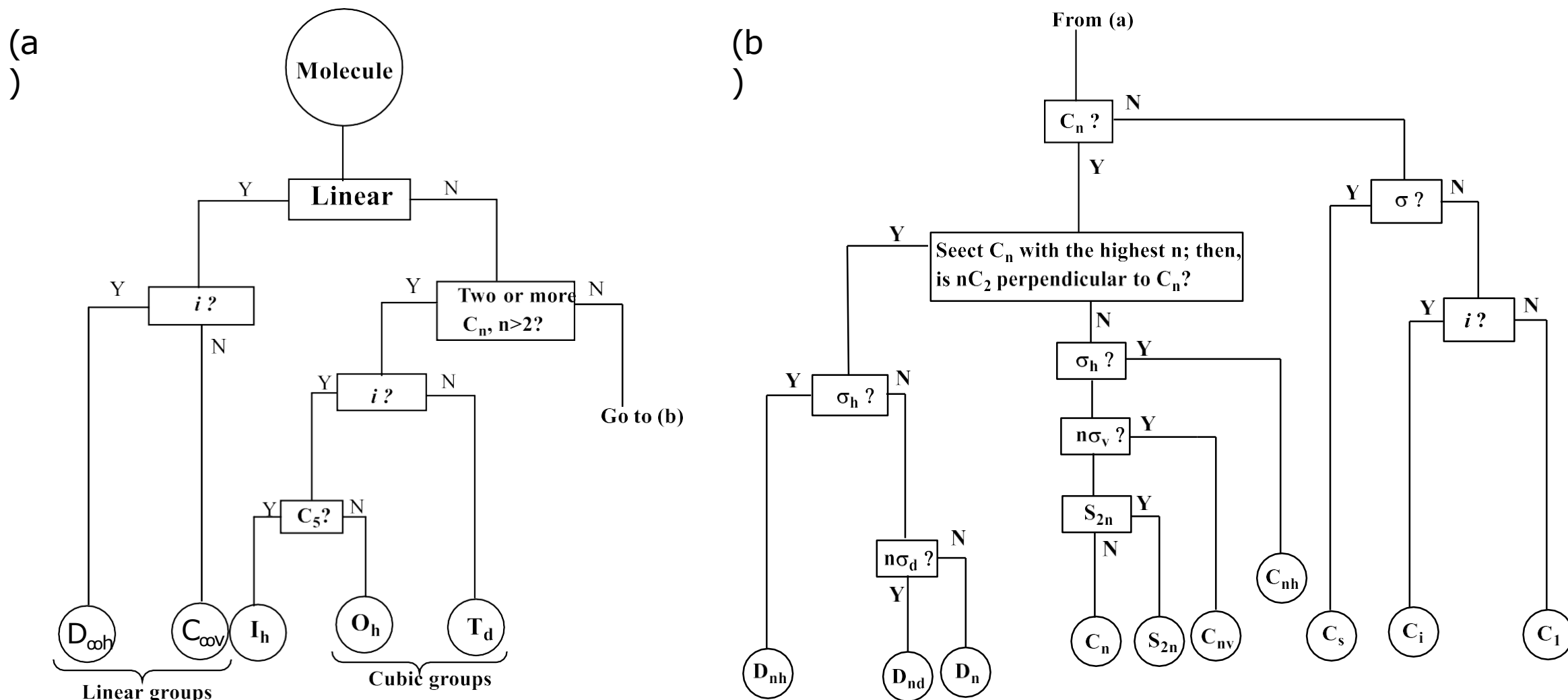


Fig 8. The decision tree for identifying a molecular point group. The symbols of each point refer to the symmetry elements.

The name of the point group is normally its **Schoenflies symbol**, such as C_{2v} for a water molecule.

Problem: To what point groups do H_2O and XeF_4 belong?

Answer : (a) The symmetry elements of H_2O are shown in Fig. 9. H_2O possesses the identity (E), a twofold rotation axis (C_2), and two vertical mirror planes (σ_v and σ_v'). The set of elements ($E, C_2, \sigma_v, \sigma_v'$) corresponds to the group C_{2v} . (b) The symmetry elements of XeF_4 are shown in Fig. 10. XeF_4 possesses the identity (E), a fourfold axis (C_4), two pairs of twofold rotation axes that are perpendicular to the principal C_4 axis, a horizontal reflection plane σ_h in the plane of the paper, and two sets of two vertical reflection planes, σ_v and σ_d . This set of elements identifies the point group as D_{4h} .

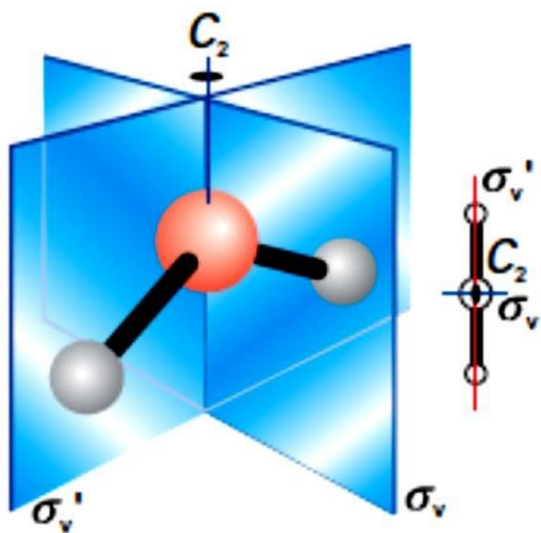


Fig 9. The symmetry elements of H_2O .

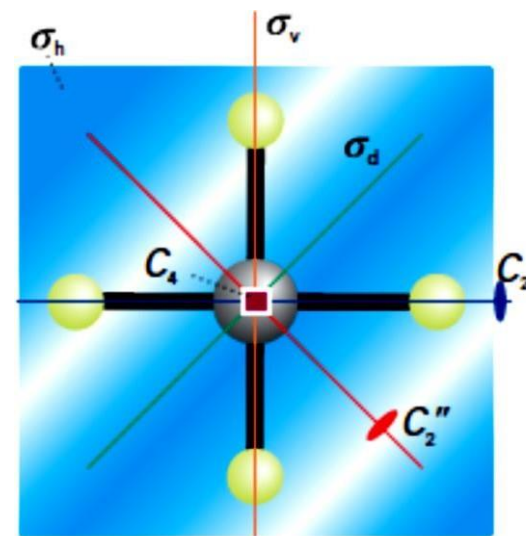
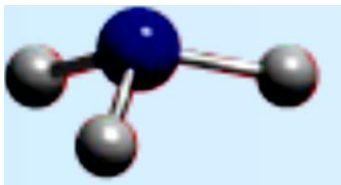
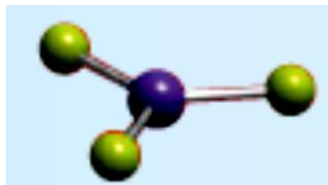


Fig 10. Symmetry elements of XeF_4 .

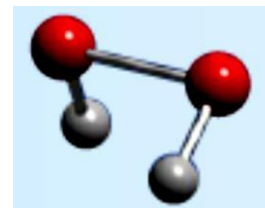
Problem: Find out the point group of (a) NH_3 (b) BF_3 (c) H_2O_2 (d) PCl_5 (e) OCS (f) CO_2 (g) CH_4 (h) SF_6



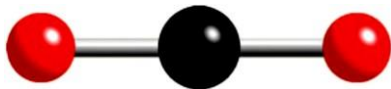
$E, 2C_3, 3\sigma_v$
 C_{3v}



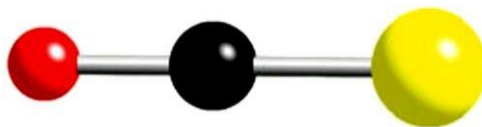
$E, 2C_3, 3C_2, \sigma_h, 2S_3, 3\sigma_v$
 D_{3h}



E, C_2



$\text{CO}_2 (D_{\infty h})$



$\text{OCS} (C_{\infty v})$

Ionic solids

Characteristic structures of ionic solids

(a) Binary phases, AX_n

- The simplest ionic compounds contain just one type of cation (A) and one type of anion (X) present in various ratios covering compositions such as AX and AX_2 .
- The **rock-salt structure** is based on a ccp array of bulky anions with cations in all the octahedral holes (Fig. 11).
- The structure is said to have **(6,6)-coordination**. In this notation, the first number in parentheses is the coordination number of the cation, and the second number is the coordination number of the anion.
- The rock-salt structure can be described as having a face-centred cubic lattice.
- In the unit cell of NaCl, there are the equivalent of $8 \times 1/8 + 6 \times 1/2 = 4$ Na^+ ions and $12 \times 1/4 + 1 = 4$ Cl^- ions. Hence, each unit cell contains four NaCl formula units.
- The number of formula units present in the unit cell is commonly denoted Z, so in this case $Z = 4$.

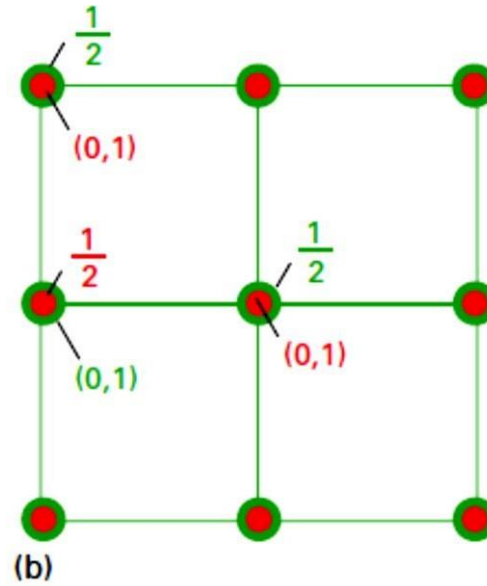
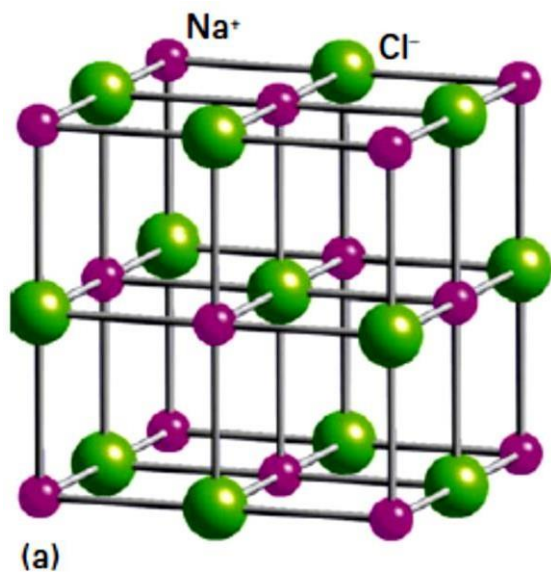


Fig 11. (a) The rock-salt structure and (b) its projection representation

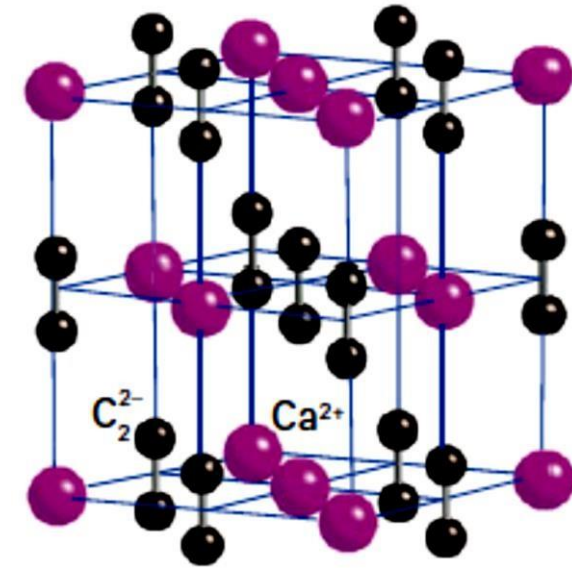


Fig 12. The structure of CaC_2 is based on the rock-salt structure but is elongated in the direction parallel to the axes of the C_2^{2-} ions.

- 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).

Caesium-chloride structure

- Compounds with **caesium-chloride structure** possess stoichiometry of AX (Fig. 13), eg. CsCl, CsBr, and CsI.
- The caesium-chloride structure has a cubic unit cell with each corner occupied by an anion and a cation occupying the ‘cubic hole’ at the cell centre (or vice versa); as a result, $Z = 1$.
- The coordination number of both types of ion is 8, so the structure is described as having **(8, 8)-coordination**.
- Many 1:1 alloys, such as AlFe and CuZn, have a caesium-chloride arrangement of the two metal atom types.

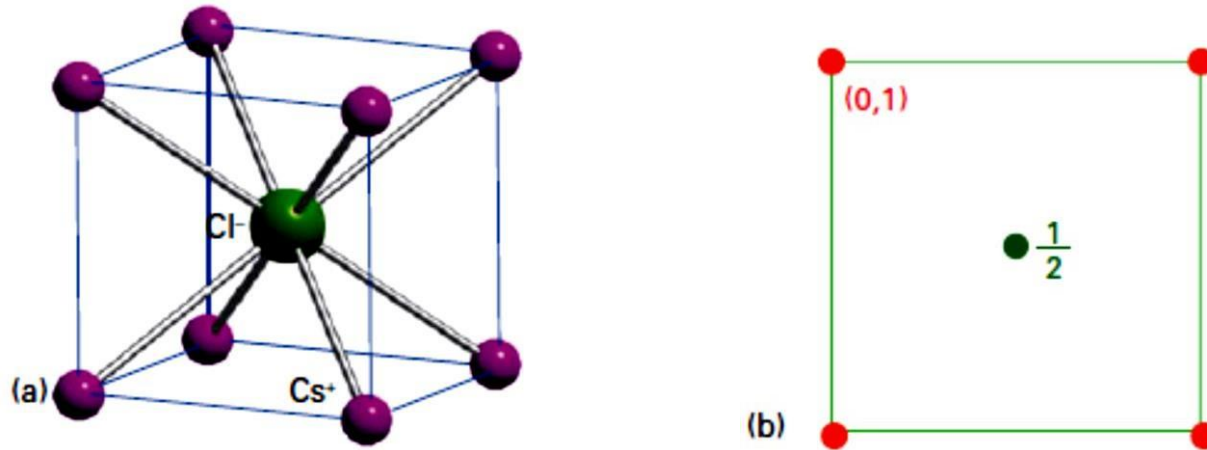


Fig 13. (a) The caesium-chloride structure. The corner lattice points, which are shared by eight neighbouring cells, are surrounded by eight nearest-neighbour lattice points. The anion occupies a cubic hole in a primitive cubic lattice. (b) Its projection.

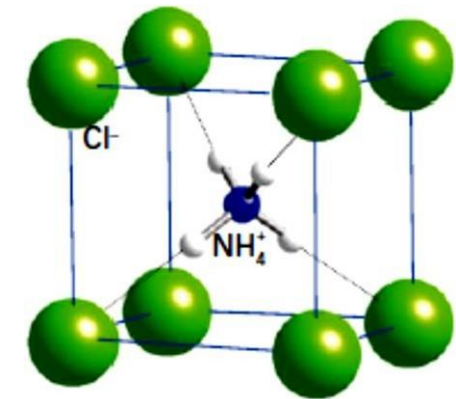


Fig 14. The structure of ammonium chloride, NH_4Cl , reflects the ability of the tetrahedral NH_4^+ ion to form hydrogen bonds to the tetrahedral array of Cl^- ions around it.

Sphalerite structure

- The **sphalerite structure** (Fig. 15), also known as the **zinc-blende structure**, takes its name from ZnS.
- It is based on an expanded ccp anion arrangement where 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 neighbours and so the structure has **(4, 4)-coordination and $Z = 4$** .

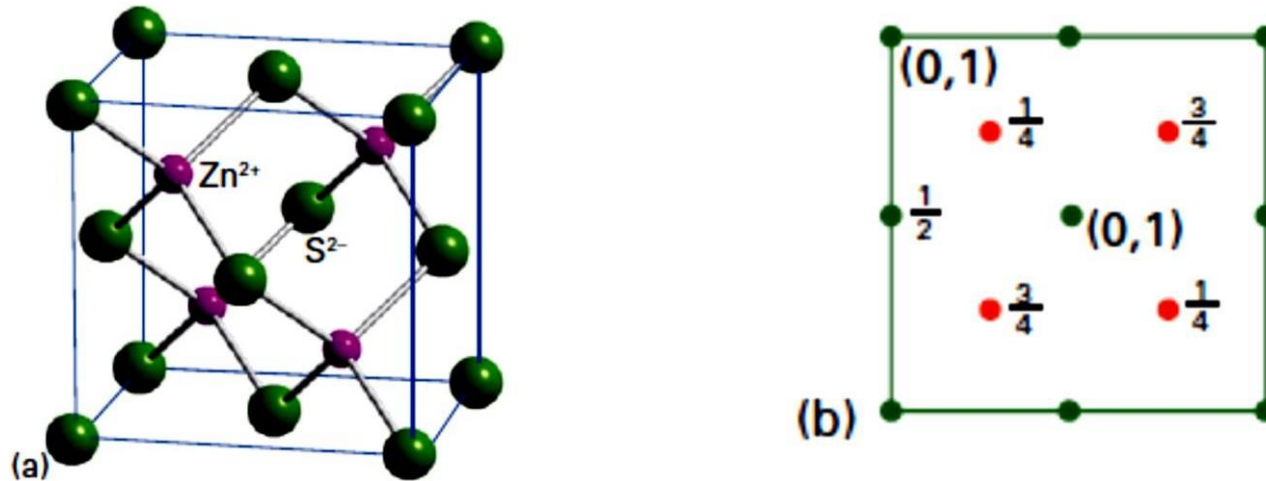


Fig. 15 (a) The sphalerite (zinc-blende) structure and (b) its projection representation.

- The **wurtzite structure** (Fig. 16) takes its name from another polymorph of zinc sulfide.
- It differs from the sphalerite structure in being derived from an expanded hcp anion array rather than a ccp array, but as in sphalerite the cations occupy half the tetrahedral holes.
- This structure has **(4,4)-coordination**, eg. ZnO, AgI, and one polymorph of SiC.



Fig 16. (a) The wurtzite structure and (b) its projection representation

- The **nickel-arsenide structure** (NiAs, Fig.17) is based on an expanded, distorted hcp anion array, but the Ni atoms now occupy the octahedral holes and each As atom lies at the centre of a trigonal prism of Ni atoms.
- This structure is adopted by NiS, FeS, and a number of other sulfides.

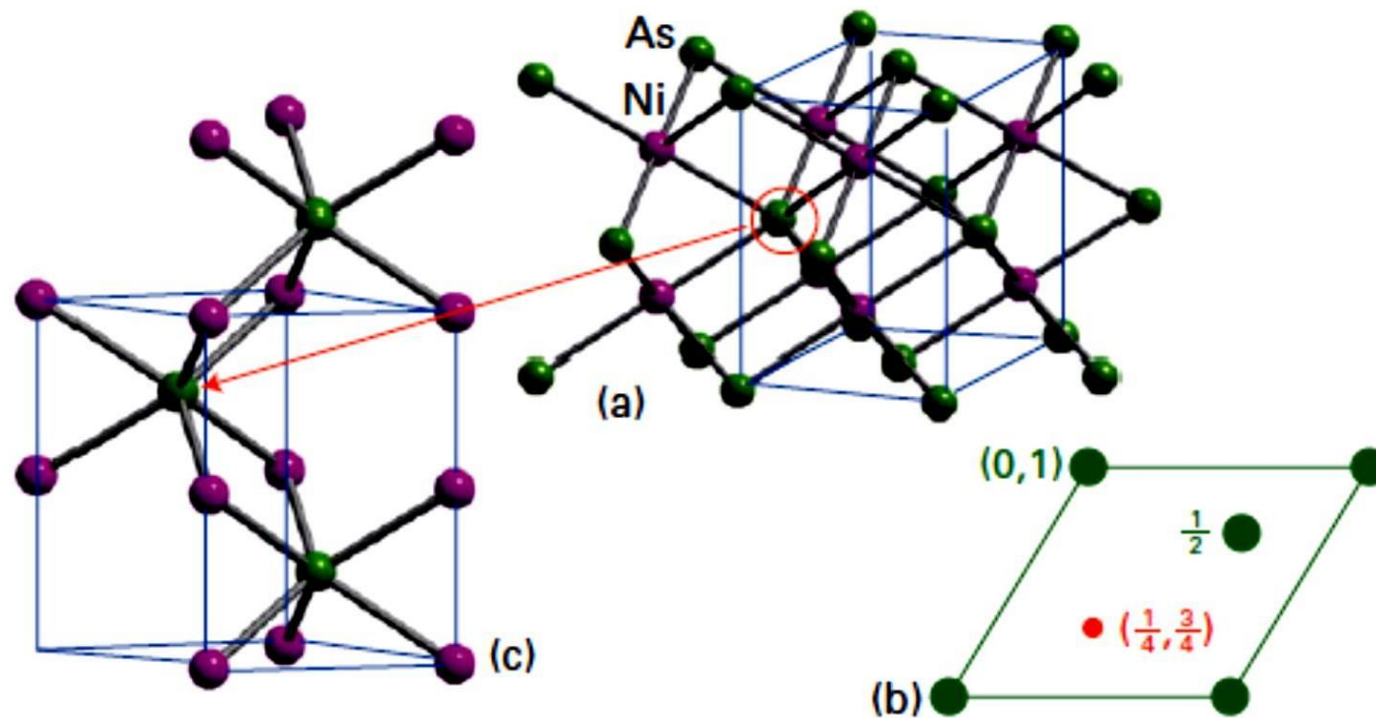


Fig. 17 (a) The nickel-arsenide structure, (b) the projection representation of the unit cell, and (c) the trigonal prismatic coordination around As.

- A common AX_2 structural type is the **fluorite structure**, which takes its name from 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 (Fig. 18).
- The lattice has **(8,4)-coordination**, which is consistent with there being twice as many anions as cations.
- The anions form a non close-packed, primitive cubic lattice and the cations occupy half the cubic holes in this lattice.

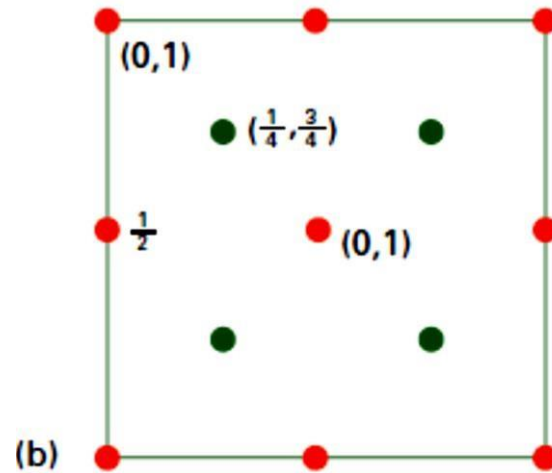
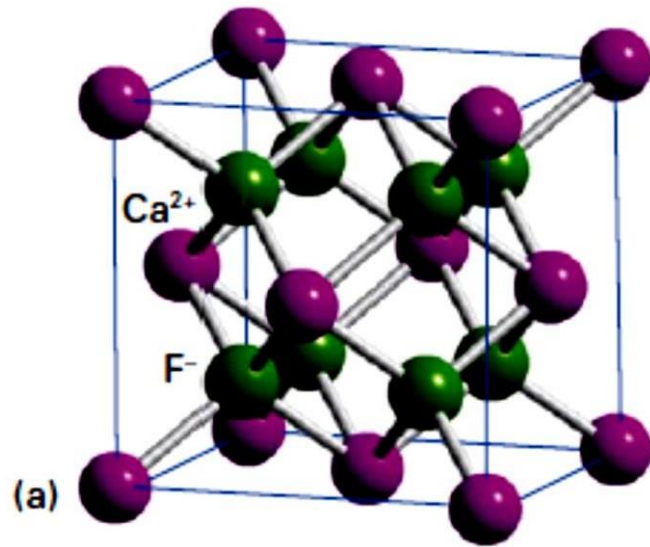


Fig. 18 (a) The fluorite structure and (b) its projection representation. This structure has a ccp array of cations and all the tetrahedral holes are occupied by anions.

- The **antifluorite** structure is the inverse of the fluorite structure in the sense that the locations of cations and anions are reversed. Eg. 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.

- The **rutile structure** (Fig. 19) takes its name from rutile, a mineral form of titanium(IV) oxide, TiO_2 .
- The structure has hcp arrangement of anions in which the cations occupy only half the octahedral holes.
- Each Ti^{4+} atom is surrounded by six O atoms and each O atom is surrounded by three Ti^{4+} ions; hence 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.

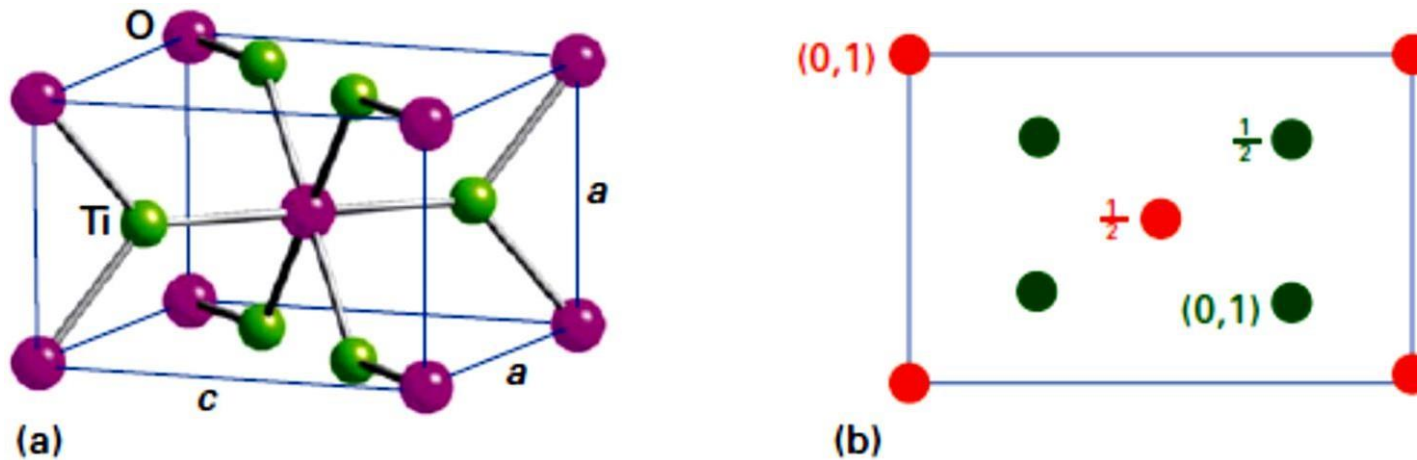


Fig. 19 (a) The rutile structure and (b) its projection representation. Rutile itself is one polymorph of TiO_2 .

- In the **cadmium-iodide structure** (as in CdI_2 , Fig. 20), the octahedral holes between every other pair of hcp layers of I^- ions (that is half of the total number of octahedral holes) are filled by Cd^{2+} ions.

The structure has (6,3)- coordination. The structure type is found commonly for many d-metal halides and chalcogenides (for example, FeBr_2 , MnI_2 , ZrS_2 , and NiTe_2).

- The **cadmium-chloride structure** (as in CdCl_2 , Fig. 21) is analogous to the CdI_2 structure but with a ccp arrangement of anions.

This layer structure has coordination numbers (6,3) and geometries for the ions to those found for the CdI_2 structure-type, although it is preferred for a number of d-metal dichlorides, such as MnCl_2 and NiCl_2 .

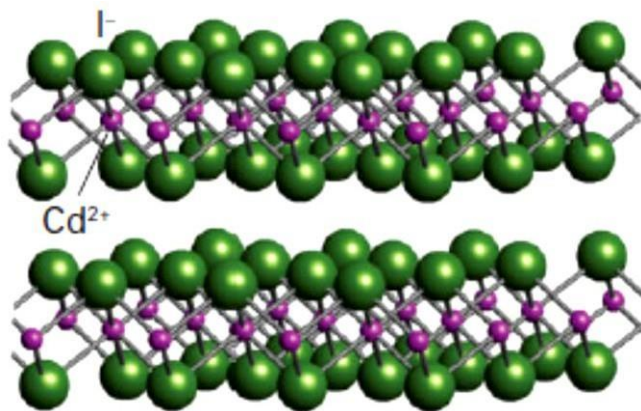


Fig. 20 The CdI_2 structure (left).

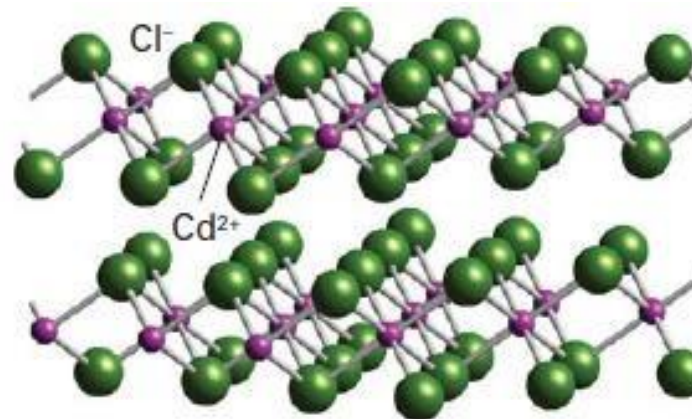


Fig. 21 The CdCl_2 structure (right).

Ternary phases $A_aB_bX_n$

- The mineral perovskite, CaTiO_3 , is the structural prototype of many ABX_3 solids, particularly oxides. In its ideal form, the **perovskite structure** is cubic with each A cation surrounded by 12 X anions and each B cation surrounded by six X anions (Fig. 22). There are six O^{2-} ions around the central Ti^{4+} ion, so the coordination number of Ti in perovskite is 6.

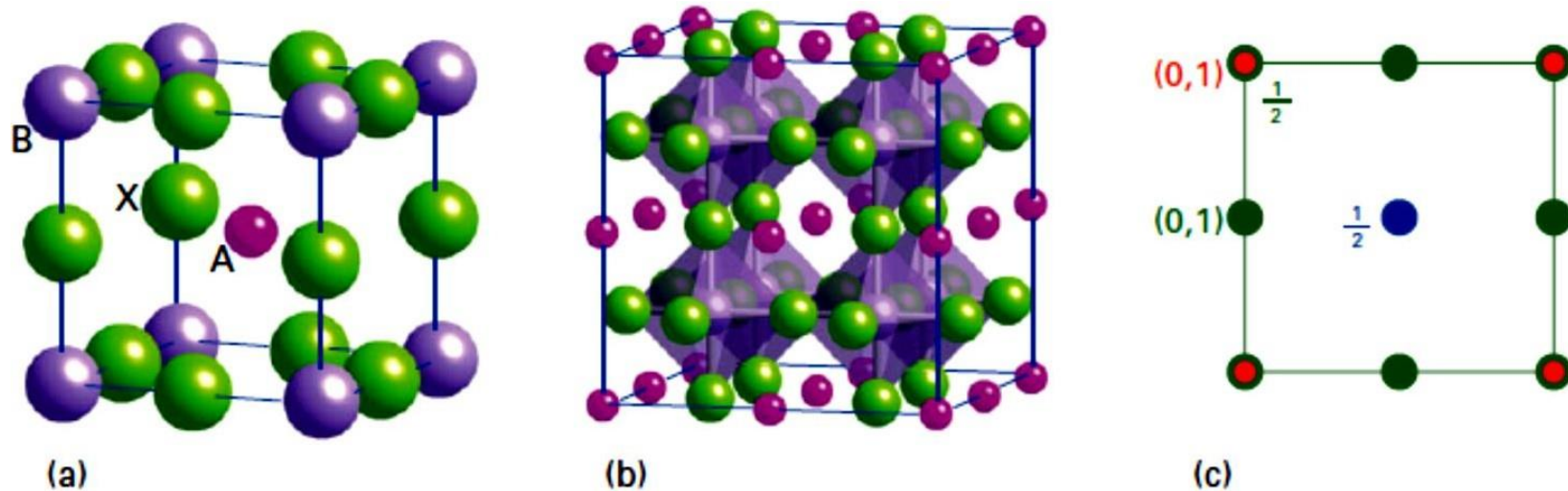


Fig. 22 (a) The perovskite structure, ABX_3 , (b) a display that emphasizes the octahedral shape of the B sites, and (c) its projection representation.

- The perovskite structure is closely related to the materials that show interesting electrical properties, such as piezoelectricity, ferroelectricity, and high-temperature superconductivity.

Spinel

- Spinel itself is MgAl_2O_4 , and oxide spinels, in general, have the formula AB_2O_4 .
- 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 the octahedral holes (Fig. 23).
- Spinel is sometimes denoted $\text{A}[\text{B}_2]\text{O}_4$, 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 $\text{Zn}[\text{Al}_2]\text{O}_4$ to show that all the Al^{3+} cations occupy octahedral sites.
- Examples 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 $\text{Fe}^{2+}[\text{Fe}^{3+}]_2\text{O}_4$).
- There are also a number of compositions termed **inverse spinels**, in which the cation distribution is $\text{B}[\text{AB}]\text{O}_4$ and in which the more abundant cation is distributed over both tetrahedral and octahedral sites.

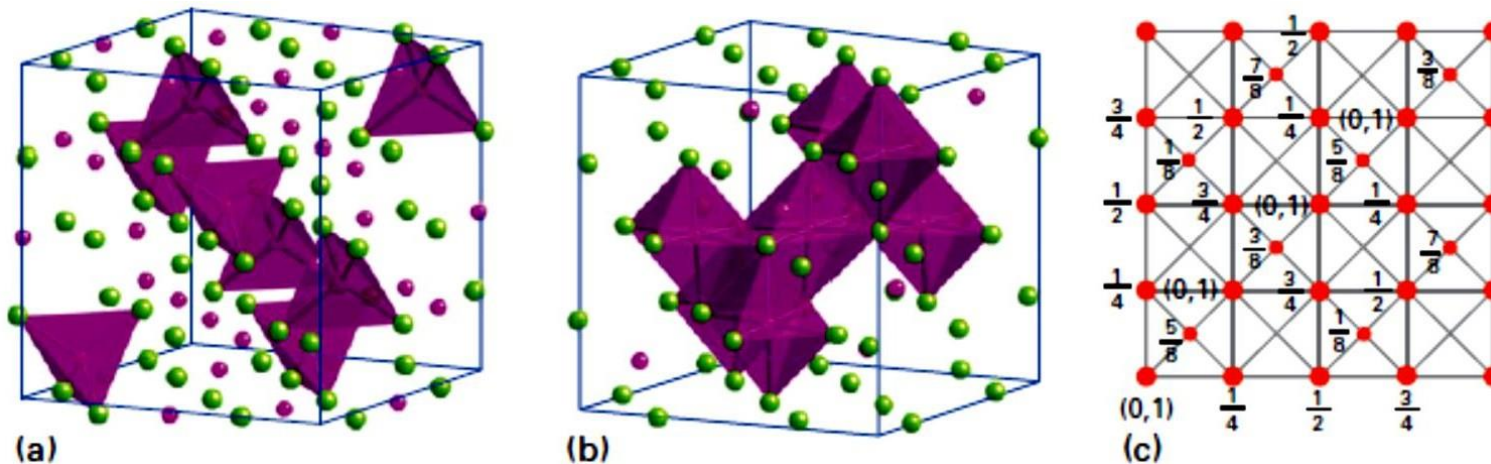


Fig. 23 (a) The spinel structure showing the tetrahedral oxygen environment around the B cations, (b) showing the octahedral oxygen environment around the A cations, and (c) its projection representation with only the cation locations specified.

Defects and nonstoichiometry

The origins and types of defects

The Gibbs energy, $G = H - TS$, of a solid with defects has contributions from the enthalpy and the entropy of the sample. The formation of defects is normally endothermic because, as the lattice is disrupted, the enthalpy of the solid rises. However, the term $-TS$ becomes more negative as defects are formed because they introduce disorder into the lattice and the entropy rises. Provided $T > 0$, therefore, the Gibbs energy will have a minimum at a nonzero concentration of defects and their formation will be spontaneous.

(a) Intrinsic point defects

- The solid-state physicists W. Schottky and J. Frenkel identified two specific types of point defect.
- A **Schottky defect** (Fig. 24) 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 because, 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 , two anion vacancies must be created for each cation lost. Schottky defects occur at low concentrations in purely ionic solids, such as NaCl; **they occur most commonly in structures with high coordination numbers.**

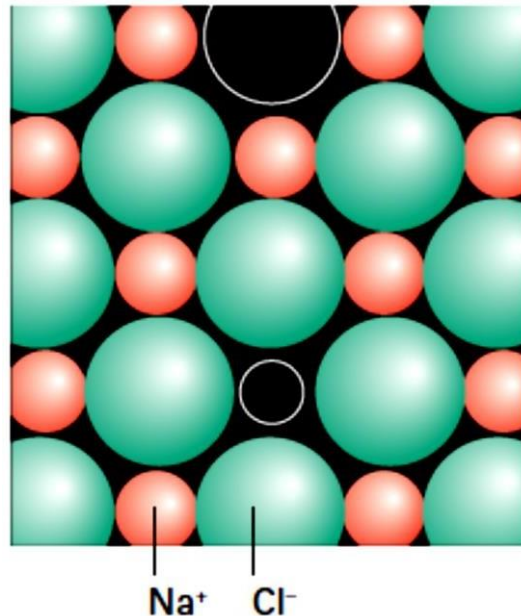
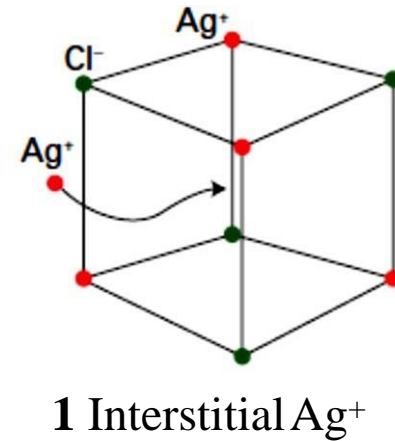
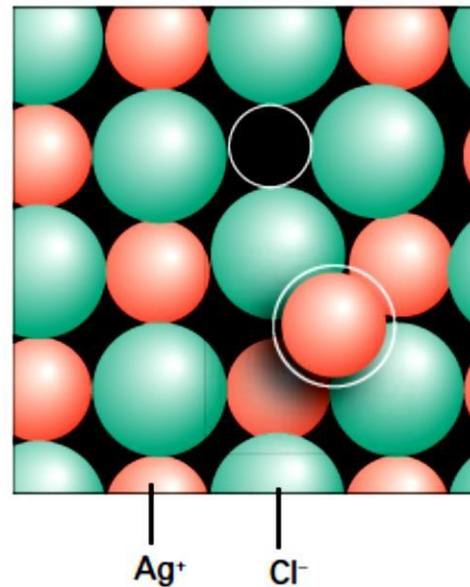


Fig. 24 A Schottky defect is the absence of ions on normally occupied sites; for charge neutrality there must be equal numbers of cation and anion vacancies in a 1:1 compound.

- A **Frenkel defect** (Fig. 25) is a point defect in which an atom or ion has been displaced onto an interstitial site. For example, in silver chloride, which has the rock-salt structure, a small number of Ag^+ ions reside in tetrahedral sites (1). The stoichiometry of the compound is unchanged when a Frenkel defect forms.
- Frenkel defects are most often encountered in structures such as wurtzite and sphalerite in which coordination numbers are low (6 or less) and the more open structure provides sites that can accommodate the interstitial atoms.



Problem: What type of intrinsic defect would you expect to find in (a) MgO and (b) CdTe?

Answer The type of defect formed depends on factors such as the coordination numbers and the level of covalency in the bonding with high coordination numbers and ionic bonding favouring Schottky defects and low coordination numbers and partial covalency in the bonding favouring Frenkel defects.

(a) MgO has the rock-salt structure and the ionic bonding in this compound generally favours Schottky defects.

(b) CdTe adopts the wurtzite structure with (4,4)-coordination, favouring Frenkel defects.

Schottky defects are site vacancies, formed in cation/anion pairs, and Frenkel defects are displaced, interstitial atoms; the structure of a solid influences the type of defect that occurs, with Frenkel defects forming in solids with lower coordination numbers and more covalency and Schottky defects in more ionic materials.

(b) Extrinsic point defects

- **Extrinsic defects** are those resulting from the presence of impurities in crystals.
- 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 .
- The dopant species normally has a similar atomic or ionic radius to the species which it replaces. Thus Cr^{3+} in ruby and Fe^{3+} in sapphire have similar ionic radii to Al^{3+} .
- Another example of an extrinsic point defect is a **colour centre**, a generic term for defects responsible for modifications to the IR, visible, and UV absorption characteristics of solids that have been irradiated or exposed to chemical treatment.

One type of colour centre is produced by heating an alkali metal halide crystal in the vapour of the alkali metal and gives a material with a colour characteristic of the system: NaCl becomes orange, KCl violet, and KBr blue-green.

- A colour centre consisting of an electron in a halide ion vacancy is called an **F-centre** (Fig. 26). The colour results from the excitation of the electron in the localized environment of its surrounding ions.

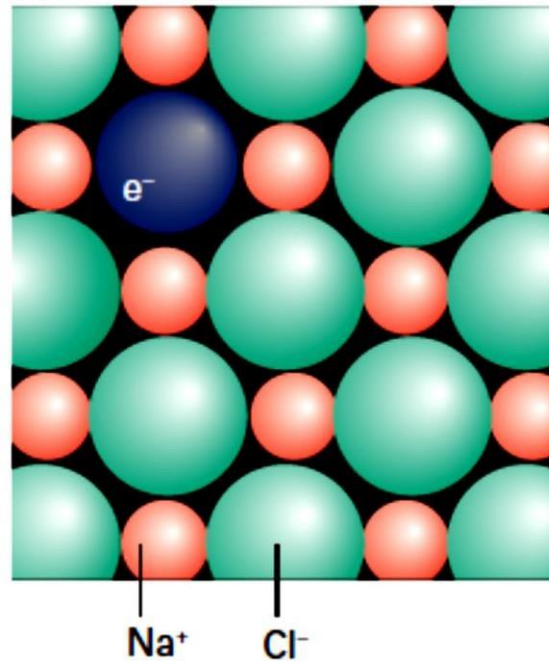


Fig. 26 An F-centre is an electron that occupies an anion vacancy. The energy levels of the electron resemble those of a particle in a three-dimensional square well.

The conductivities of inorganic solids

- Electronic conduction is also a characteristic of semiconductors. The criterion for distinguishing between a metallic conductor and a semiconductor is the temperature dependence of the electric conductivity:
- A **metallic conductor** is a substance with an electric conductivity that *decreases* with increasing temperature.
- A **semiconductor** is a substance with an electric conductivity that increases with increasing temperature.
- A solid **insulator** is a substance with a very low electrical conductivity.
- **Superconductors** are a special class of materials that have zero electrical resistance below a critical temperature.

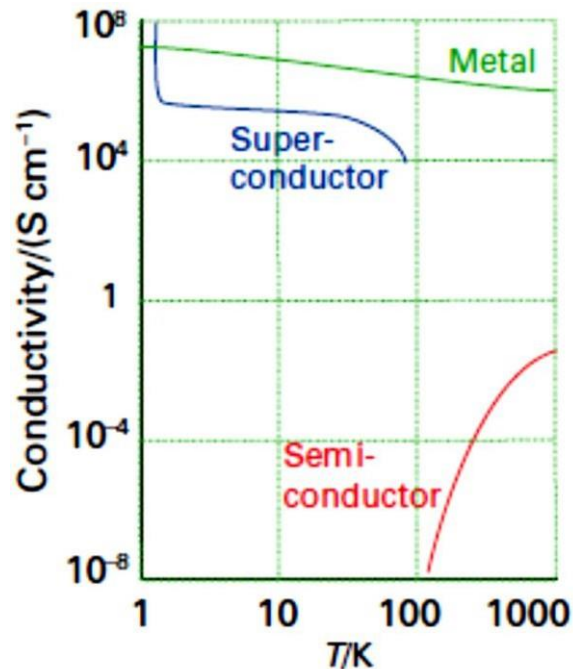


Fig. 27 The variation of the electrical conductivity of a substance with temperature is the basis of the classification of the substance as a metallic conductor, a semiconductor, or a superconductor.

Bands formed from overlapping atomic orbitals

(a) Band formation by orbital overlap

The overlap of a large number of atomic orbitals in a solid leads to a large number of molecular orbitals that are closely spaced in energy and so form an almost continuous **band** of energy levels (Fig. 29). Bands are separated by **band gaps**, which are values of the energy for which there is no molecular orbital.

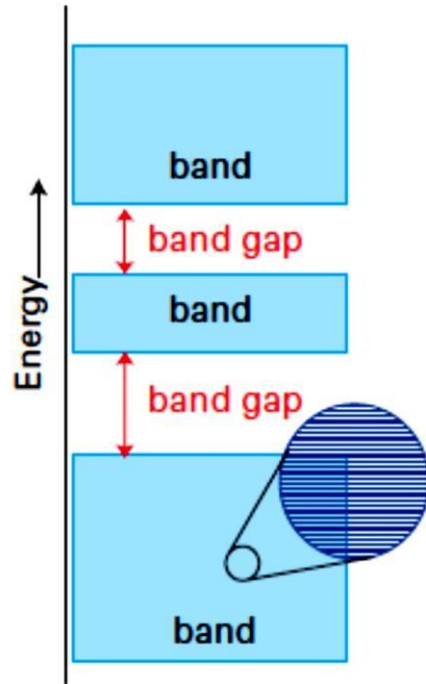


Fig. 28 The electronic structure of a solid is characterized by a series of bands of orbitals separated by gaps at energies where orbitals do not occur.

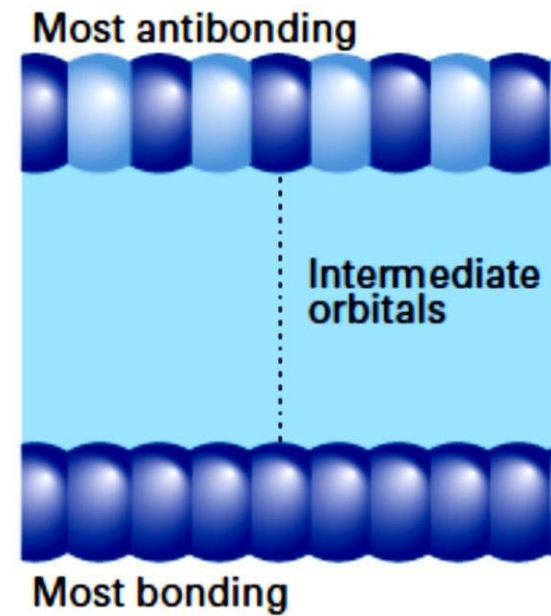


Fig. 29 A band can be thought of as formed by bringing up atoms successively to form a line of atoms. (s-band)

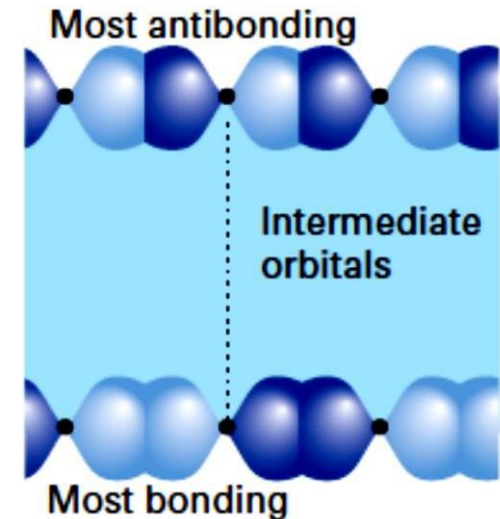


Fig. 30 An example of a p band in a one-dimensional solid.

Because p orbitals lie higher in energy than s orbitals of the same valence shell, there is often an energy gap between the s band and the p band (Fig. 31).

However, if the bands span a wide range of energy and the atomic s and p energies are similar (as is often the case), then the two bands overlap.

The d **band** is similarly constructed from the overlap of d orbitals.

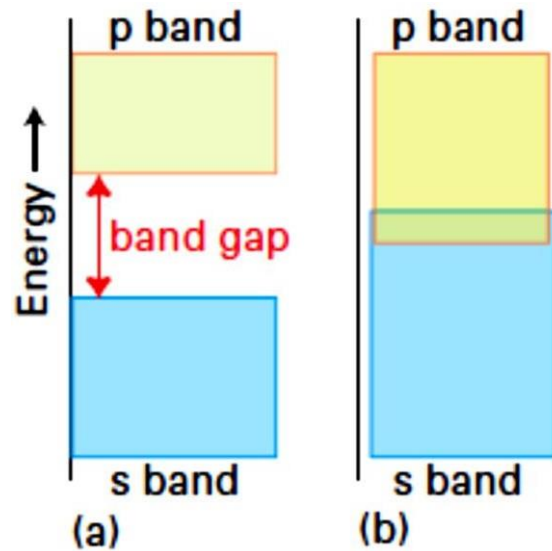


Fig. 31 (a) The s and p bands of a solid and the gap between them. The gap depends on the separation of the s and p orbitals of the atoms and the strength of the interaction between them in the solid. (b) If the interaction is strong, the bands are wide and may overlap.

The Fermi level

- At $T = 0$, the lowest N orbitals are occupied if each atom supplies one s electron.
- The highest occupied orbital at $T = 0$ is called the **Fermi level**; it lies near the centre of the band (Fig. 32).
- When the band is not completely full, the electrons close to the Fermi level can easily be promoted to nearby empty levels. As a result, they are mobile and can move freely through the solid, and the substance is an electrical conductor.

Insulators

- A solid insulator is a semiconductor with a large band gap. Eg. NaCl
- In an insulator the band of highest energy that contains electrons (at $T = 0$) is normally termed the **valence band**. There next higher band (which is empty at $T = 0$) is called the **conduction band**.
- In NaCl the band derived from the Cl orbitals is the valence band and the band derived from the Na orbitals is the conduction band.

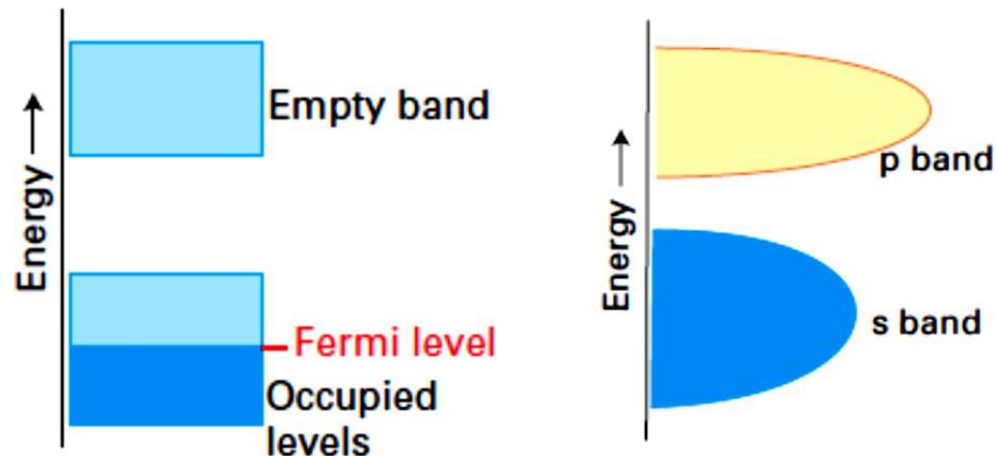


Fig.32 If each of the N atoms supplies one s electron, then at $T = 0$ the lower $\frac{1}{2}N$ orbitals are occupied and the Fermi level lies near the centre of the band.

Fig. 33 The structure of a typical insulator: there is a significant gap between the filled and empty bands.

Semiconduction

The characteristic physical property of a semiconductor is that its electrical conductivity increases with increasing temperature.

Intrinsic semiconductors

- In an **intrinsic semiconductor**, the band gap is so small that the energy of thermal motion results in some electrons from the valence band populating the empty upper band (Fig. 34). This occupation of the conduction band introduces **positive holes**, equivalent to an absence of electrons, into the lower band, and as a result the solid is conducting because both the holes and the promoted electrons can move.

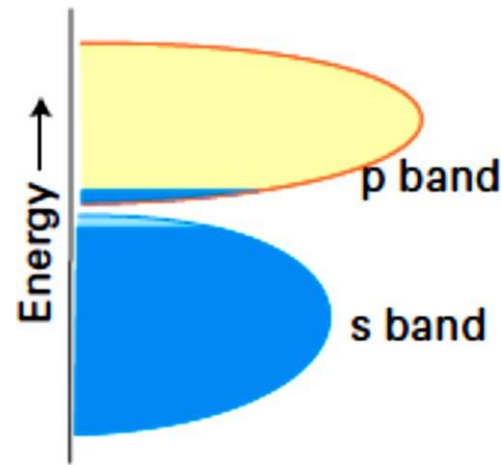


Fig. 34 In an intrinsic semiconductor, the band gap is so small that the Fermi distribution results in the population of some orbitals in the upper band.

Extrinsic semiconductors

An **extrinsic semiconductor** is a substance that is a semiconductor on account of the presence of intentionally added impurities. The number of electron carriers can be increased if atoms with more electrons than the parent element can be introduced by the process called **doping**.

- If arsenic atoms ($[\text{Ar}]4s^24p^3$) are introduced into a silicon crystal ($[\text{Ne}]3s^23p^2$), one additional electron will be available for each dopant atom that is substituted. The foreign atom levels will lie at higher energy than the valence electrons of the host structure and the filled dopant band is commonly near the empty conduction band (Fig. 35a)..
- For $T > 0$, some of its electrons will be thermally promoted into the empty conduction band. From there it will be able to migrate through the structure in the band formed by Si–Si overlap. This process gives rise to **n-type semiconductivity**, the ‘n’ indicating that the charge carriers are negatively charged (that is, electrons).
- Typical n-type semiconductors include Fe_2O_3 , MnO_2 , and CuO .

- An alternative substitutional procedure is to dope the silicon with atoms of an element with fewer valence electrons on each atom, such as gallium ($[\text{Ar}]4s^24p^1$). A dopant atom of this kind effectively introduces holes into the solid. More formally, the dopant atoms form a very narrow, empty **acceptor band** that lies above the full Si band (Fig. 35b).

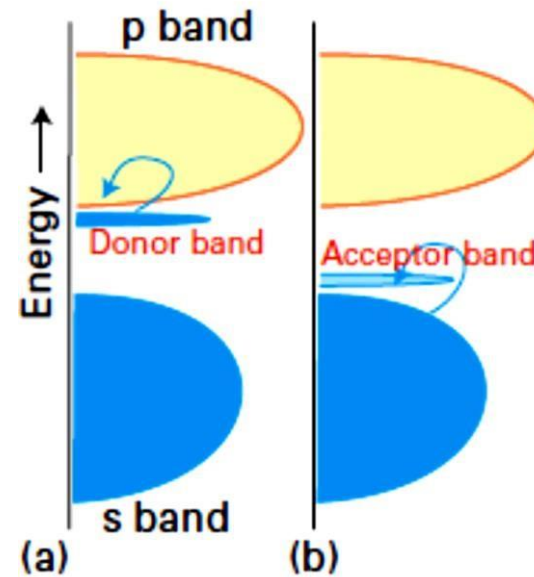


Fig. 35 The band structure in (a) an n-type semiconductor and (b) a p-type semiconductor.

- At $T = 0$ the acceptor band is empty but at higher temperatures it can accept thermally excited electrons from the Si valence band. By doing so, it introduces holes into the latter and hence allows the remaining electrons in the band to be mobile. Because the charge carriers are now positive holes in the lower band, this type of semiconductivity is called **p-type semiconductivity**. Eg. MnO and Cr₂O₃.

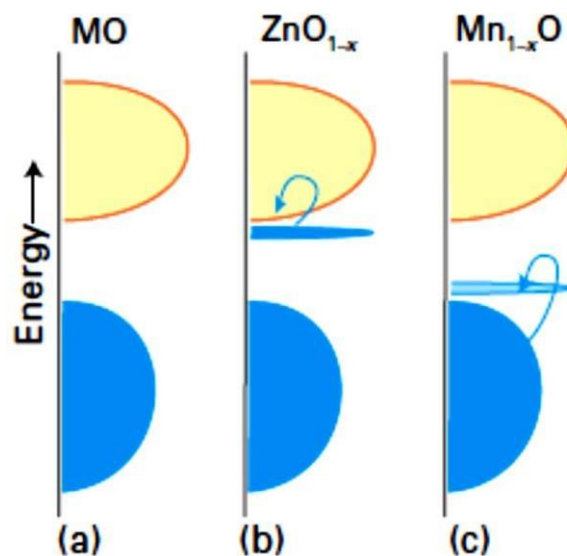


Fig. 36 The band structure in (a) a stoichiometric oxide, (b) an anion-deficient oxide, and (c) an anion-excess oxide.

Reference

Peter Atkins, Tina Overton, Jonathan Rourke, Mark Weller, Fraser Armstrong, Mike Hagerman; Shriver & Atkins' Inorganic Chemistry, 5th Ed. 2012