

(ii) Relative sizes of tetrahedral and octahedral sites

— A general guideline for the relative size of sites:

tetrahedra < octahedra < polyhedra of higher coordination number

— In ionic structures, cations M occupy those sites of suitable sizes.

— Cations may occupy sites which appear too small by pushing apart anions and expanding the structure (as in eutectic structures).

— Cations tend not to occupy sites that are too large, unless the structure can adjust itself, by twisting or distorting the anion array so as to reduce the size of the sites.

— In many distorted perovskite structures in which cations are too small to occupy large 12-coordinate site and a partial structure collapse occurs.

— In some cases, a cation site is marginally too large, the cation can then undergo small displacements giving rise to high polarizability, high permittivity and the phenomenon of ferroelectricity.

(iii) Location of tetrahedral and octahedral sites in an *fcc* unit cell; bond length calculations; fractional atomic coordinates

Fig. 1.20 An *fcc* anion array (cation sites 1–12)

— The  $T_+$ ,  $T_-$  and O sites are located within an *fcc* unit cell that has anions, X, at corners and face centers.

— The octahedral sites are easiest to locate: at edge-center 1, 2, 3 and body-center 4 positions.

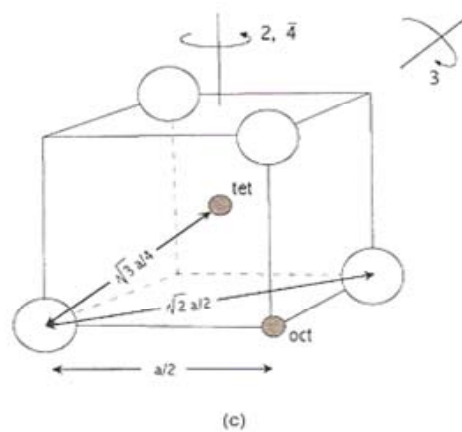
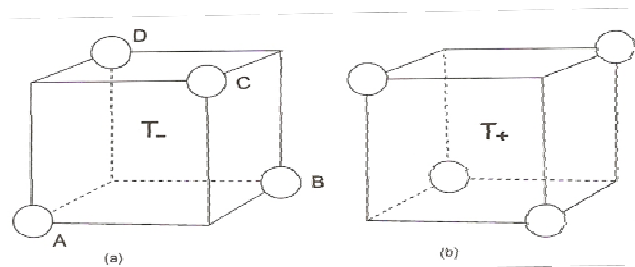
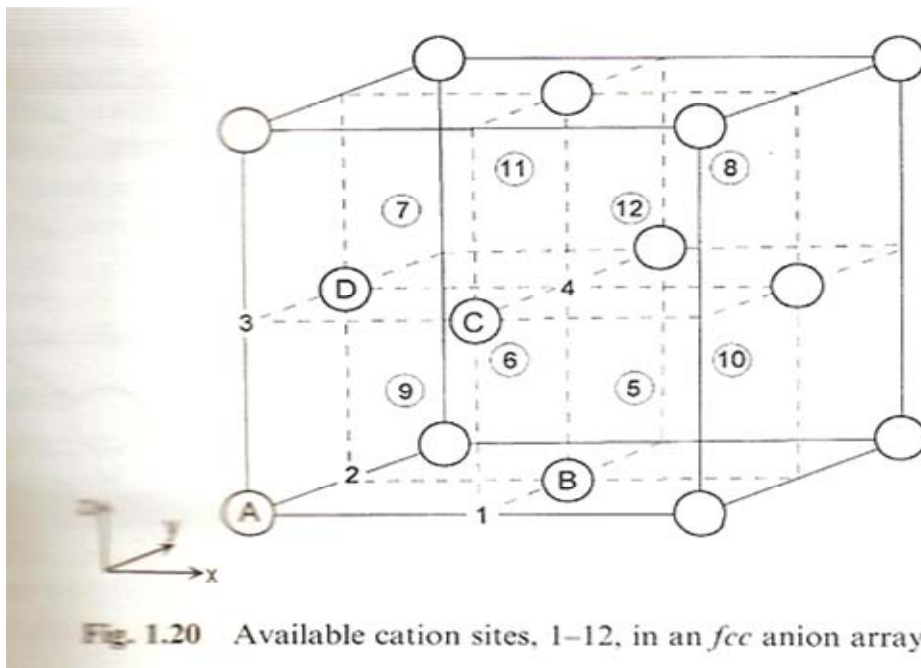


Fig. 1.21 (a, b) Tetrahedral sites  $T_+$ ,  $T_-$  and their relation to a cube. (c) Bond length calculations and some symmetries of a tetrahedron

- In order to see the  $T_+$ ,  $T_-$  sites, we divide the unit cell into eight minicubes, which contain anions at only **four** of the eight corners. In the middle of each minicube is a tetrahedral site.
- There are two orientations for the minicubes, as shown in Fig.1.21.
- In Fig.1.21a, the  $T_-$  tetrahedra have their apices pointing in the  $[\bar{1}\bar{1}\bar{1}]$  and in Fig.1.21b the  $T_+$  sites in the  $[111]$  direction.
- It is exceptionally useful to regard a tetrahedral site as occupying the center of a cube with alternate corners absent, Fig.1.21a,b.
- Fig.1.21c, the minicube
  - \*edge dimension =  $a/2$
  - \*M–X = bond length =  $\frac{1}{2}\sqrt{(\sqrt{2}\frac{a}{2})^2 + (\frac{a}{2})^2} = \frac{1}{2}\sqrt{3(\frac{a}{2})^2} = \frac{\sqrt{3}}{4}a$
  - \*2-fold rotation axes and  $\bar{4}$  (fourfold inversion) axes run parallel to minicube edges but pass through pairs of opposite faces; three of these in total.
  - \*mirror planes occur parallel to the set of lattice planes with indices  $\{110\}$ ; six of these in total.
  - \*3-fold axes run parallel to  $\langle 111 \rangle$  directions; four in total.
- The fractional coordinates of the atoms in Fig.1.20
  - \*an *fcc* unit cell has effectively 4 anions in the cell:
    - One at the corner and three at face centers, A, B, C, D
    - i.e.  $000 \quad \frac{1}{2} \frac{1}{2} 0 \quad \frac{1}{2} 0 \frac{1}{2} \quad 0 \frac{1}{2} \frac{1}{2}$
- $000$  : eight equivalents,  $\frac{1}{8}$  of each belongs to the cell

$\frac{1}{2} \frac{1}{2} 0, \frac{1}{2} 0 \frac{1}{2}, 0 \frac{1}{2} \frac{1}{2}$  : six equivalents,  $\frac{1}{2}$  of each belongs to the cell

— Cation positions

Octahedral      1:  $\frac{1}{2} 0 0$     2:  $0 \frac{1}{2} 0$     3:  $0 0 \frac{1}{2}$     4:  $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

Tetrahedral,  $T_+$     5:  $\frac{3}{4} \frac{1}{4} \frac{1}{4}$     6:  $\frac{1}{4} \frac{3}{4} \frac{1}{4}$     7:  $\frac{1}{4} \frac{1}{4} \frac{3}{4}$     8:  $\frac{3}{4} \frac{3}{4} \frac{3}{4}$

Tetrahedral,  $T_-$     9:  $\frac{1}{4} \frac{1}{4} \frac{1}{4}$     10:  $\frac{3}{4} \frac{3}{4} \frac{1}{4}$     11:  $\frac{1}{4} \frac{3}{4} \frac{3}{4}$     12:  $\frac{3}{4} \frac{1}{4} \frac{3}{4}$

— four of each type of cation site, O,  $T_+$ ,  $T_-$  in the unit cell together with four anions

— When different sites are fully or partially occupied by cations, different structures are generated.

#### (d) Covalent network structures

Materials such as diamond and silicon carbide, which have very strong, directional, covalent bonds, can also be described as *cp* structures or eutectic structures.

e.g. a polymorph of SiC having the wurtzite structure

it is immaterial whether Si or C is regarded as the packing atom; since the net result, a 3D framework of corner-sharing tetrahedra, is the same.

e.g. diamond

- can be regarded as a sphalerite structure in which half the C atoms form a *ccp* array and the other half occupy  $T_+$  sites.
- the two types of atom are equivalent
- diamond should be classified as a eutectic structure; it is unrealistic distinguish between packing atoms and interstitial atoms

Many structures have mixed ionic-covalent bonding, e.g. ZnS and  $CrCl_3$ , and they can be described in terms of *cp* without reference to the type of bonding that is present.

### (e) Molecular structures

Many molecular compounds crystallize as *cp* structures even though the forces between adjacent molecules are weak van der Waals forces.

If the molecules are roughly spherical or become spherical because they can rotate or occupy different orientations at random, then simple *hcp* or *ccp* structures result (e.g. crystalline  $H_2$ ,  $CH_4$  and  $HCl$ ).

Non-spherical molecules, especially if they are built of tetrahedra or octahedra, can also fit into a *cp* arrangement.

**Ex.  $Al_2Br_6$ :** a dimer with two  $AlBr_4$  tetrahedra sharing a common

each Br has  $T_+$  T. (2) sites edge (Fig 1.22a). Br atoms 3 and 5 are common to both  
Al occupied 1/6 T-sites tetrahedra and are the bridging atoms.

$\rightarrow (\frac{1}{6} * 2) Br$  atoms

$\rightarrow Al : Br = \frac{1}{3} : 1$

In crystalline  $Al_2Br_6$ , the Br atoms form an *hcp* array and Al atoms occupy 1/6 of the tetrahedral sites (Fig 1.22b).

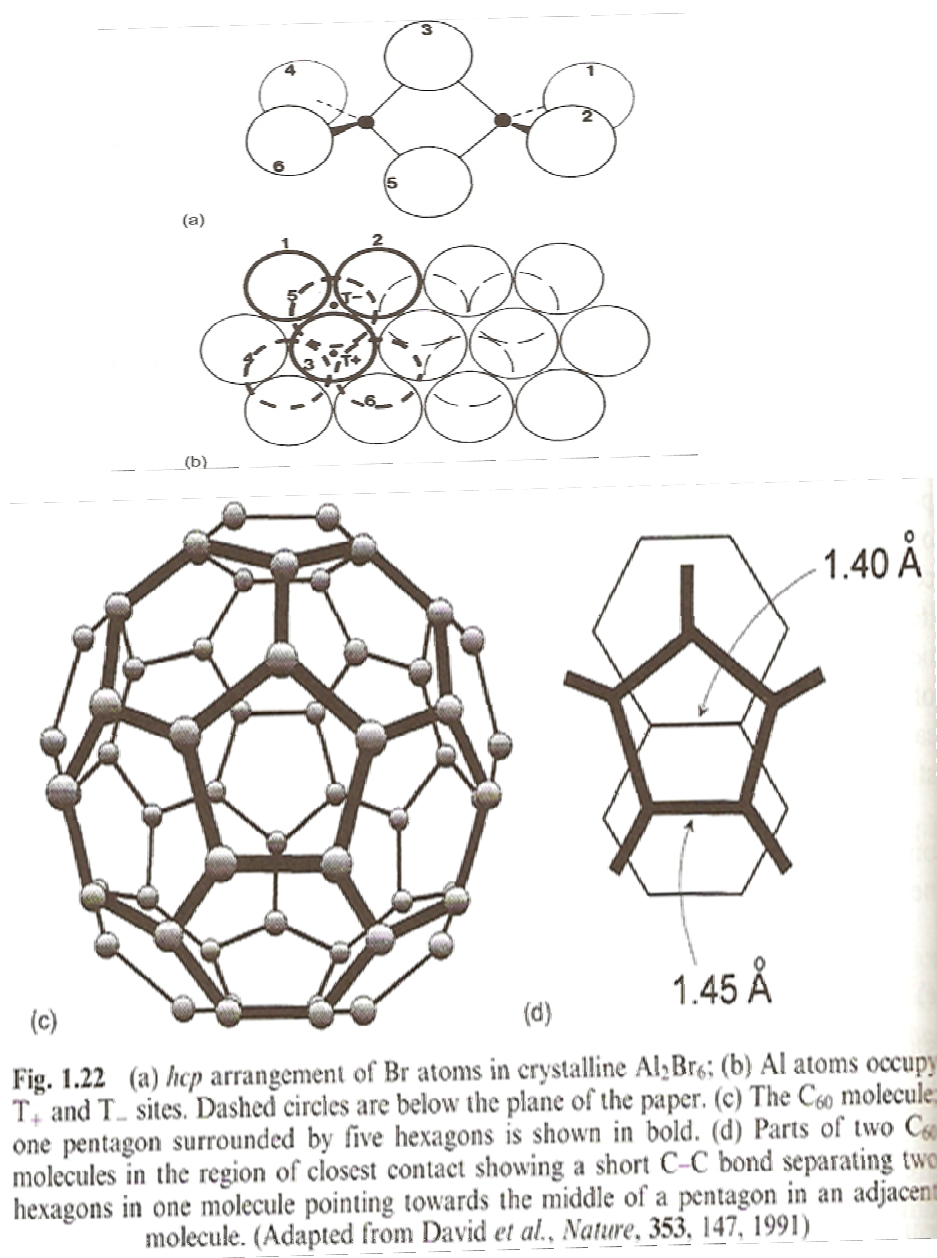


Fig 1.22b shows one molecule  $\text{Al}_2\text{Br}_6$  (Br in heavy outline) in a *cp* array. Al atoms occupy one pair of adjacent  $T_+$  and  $T_-$  sites.

Adjacent  $\text{Al}_2\text{Br}_6$  molecules are arranged so that each Br in the *hcp* array belongs to only one molecule.

$\text{SnBr}_4$ : a tetrahedral molecule and crystallize with an *hcp* Br array.  
1/8 of the tetrahedral sites are occupied.

#### (f) Fullerenes and fullerides

Simplest, most well-known and symmetrical fullerene is  $\text{C}_{60}$   
Fig 1.22c — a hollow, spherical cage of diameter 7.1Å  
— formed from 3-coordinate C atoms (approximately  $\text{sp}^2$  hybridized)  
— a network of 12 pentagons and 20 hexagons  
— match the pattern on a soccer ball, American name “buckyball”  
 (“fullerene” is in honor of Buckminster Fuller who designed the geodesic dome that has the same network structure as  $\text{C}_{60}$ )

Crystalline  $\text{C}_{60}$ :  $\text{C}_{60}$  molecules are arranged in close packing at room temperature

— face centered cubic,  $Z = 4(\text{C}_{60})$ ,  $a = 14.17\text{Å}$

$\text{C}_{60}$  molecules are orientationally disordered **at room temp.**

- Fig.1.18(a)  $2r = \sqrt{2} a = 20\text{\AA}$ 
  - $r =$  distance between centers of adjacent  $C_{60} = 10\text{\AA}$
  - $\text{gap} = 10\text{\AA} - 7.1\text{\AA} = 2.9\text{\AA}$

At  $T < 249\text{K}$ , ordered arrangement of  $C_{60}$  molecules

- driving force for this ordering
    - the short electron-rich C-C bond that links two hexagons in one  $C_{60}$  points directly at the center of an electron-deficient pentagon (Fig.1.22(d))
  - this arrangement minimizes direct C-C overlap but maximizes donor-acceptor interactions
  - two groups of bonds in  $C_{60}$ :
    - 1.40 $\text{\AA}$  for C-C bonds linking two hexagons
    - 1.45 $\text{\AA}$  for C-C bonds linking one hexagon and one pentagon
- ps. Single and double bond length of C-C in organics are 1.54 and 1.33 $\text{\AA}$ , respectively.

Other fullerenes, such as  $C_{70}$

- also form *cp*, even though they are not spherical
- $C_{70}$  is an ellipsoid (rugby ball, long axis = 8.34 $\text{\AA}$ , short axis = 7.66 $\text{\AA}$ )
- at room temperature, the ellipsoids rotate freely to give quasi-spherical molecules and form an *fcc* structure,  $a = 15.01\text{\AA}$



Fullerides: tetrahedral and octahedral interstitial sites of  $C_{60}$  occupied by large alkali cations (like Rb, rubidium)

$A_3C_{60}$  (as in  $Rb_3C_{60}$  or  $K_2RbC_{60}$ )

- all  $T_+$ ,  $T_-$  and O sites are occupied
- they are metallic since alkali metals ionize and donate  $e^-$  to the conduction band of the  $C_{60}$  network, which is half-full in  $A_3C_{60}$ .
- at low temperatures, many fullerides become superconducting.

$AC_{60}$  (rock salt or zinc blende analogues)

$A_2C_{60}$  (fluorite analogues)

$A_4C_{60}$  ( $A = Na$ ,  $A_4$  clusters form in the octahedral sites)

$A_6C_{60}$  (the packing of  $C_{60}$  changes from *ccp* to *bcc*)

- *bbc* has a large number of interstitial sites
- 6 distorted tetrahedral sites distributed over the cube faces

The excitement in  $C_{60}$  chemistry

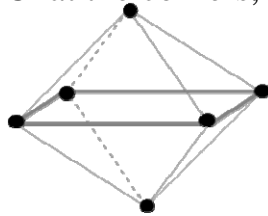
- $C_{60}$  can accept a number of  $e^-$  to give anions  $C_{60}^{n-}$
- electronic properties range from insulating to metallic/superconducting, depending on the value of  $n$ .

## 1.16 Structures built of space-filling polyhedra

This approach emphasizes the coordination number of cations; structures

are built of polyhedra (cation + anionic neighbors); polyhedra link by sharing corners, edges, or faces.

Example: NaCl (Na has six Cl nearest neighbors arranged octahedrally)  
 an octahedron: Cl at the corners, Na at the center



A 3D overview of NaCl, each octahedron edge is shared between two octahedra (Fig.1.26, see later), resulting in an infinite framework.

Example: Perovskite SrTiO<sub>3</sub>

TiO<sub>6</sub> octahedra link by corner-sharing to form a 3D framework (Fig.1.36, see later)

Very many other crystals involve mainly tetrahedra and octahedra, leading to a wide diversity of structures (Table 1.5)

Table 1.5 *Some structures built of space-filling polyhedra*

<i>Octahedra only</i>	
12 edges shared	NaCl
6 corners shared	ReO <sub>3</sub>
3 edges shared	CrCl <sub>3</sub> , BiI <sub>3</sub>
2 edges and 6 corners shared	TiO <sub>2</sub>
4 corners shared	KAlF <sub>4</sub>
<i>Tetrahedra only</i>	
4 corners shared (between 4 tetrahedra)	ZnS
4 corners shared (between 2 tetrahedra)	SiO <sub>2</sub>
1 corner shared (between 2 tetrahedra)	Si <sub>2</sub> O <sub>7</sub> <sup>6-</sup>
2 corners shared (between 2 tetrahedra)	(SiO <sub>3</sub> ) <sub>n</sub> <sup>2n-</sup> , chains or rings

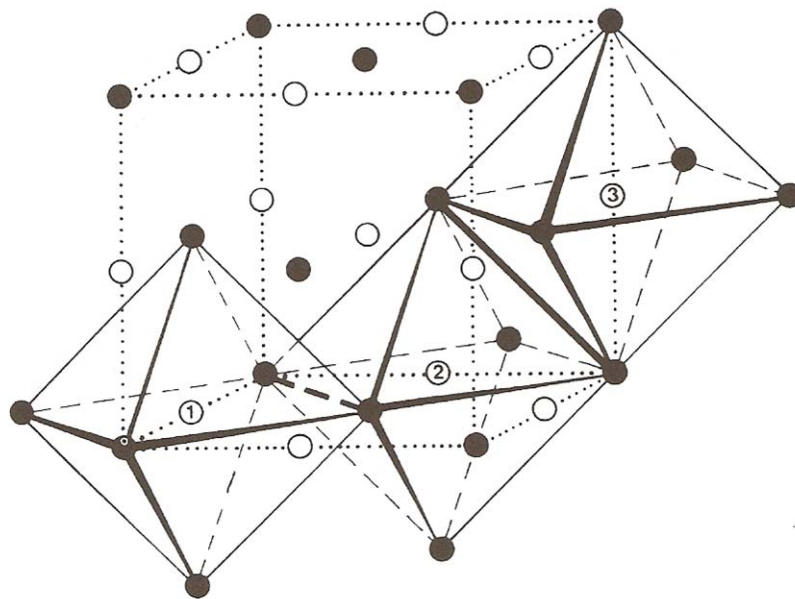


Fig. 1.26 Unit cell of the rock salt structure showing edge-sharing octahedra

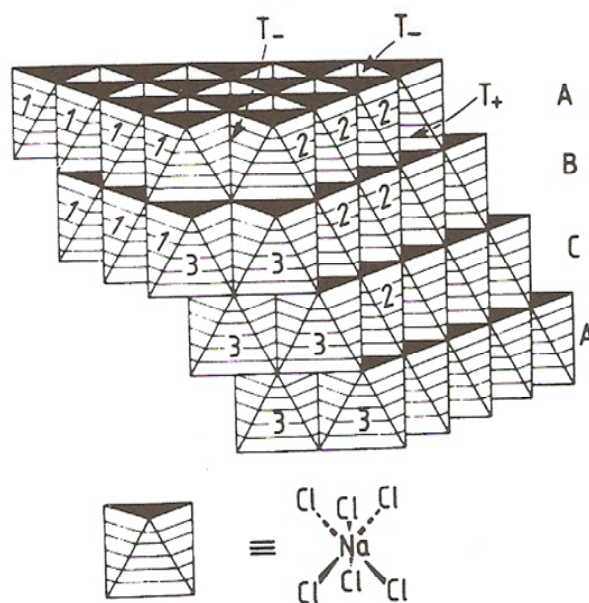
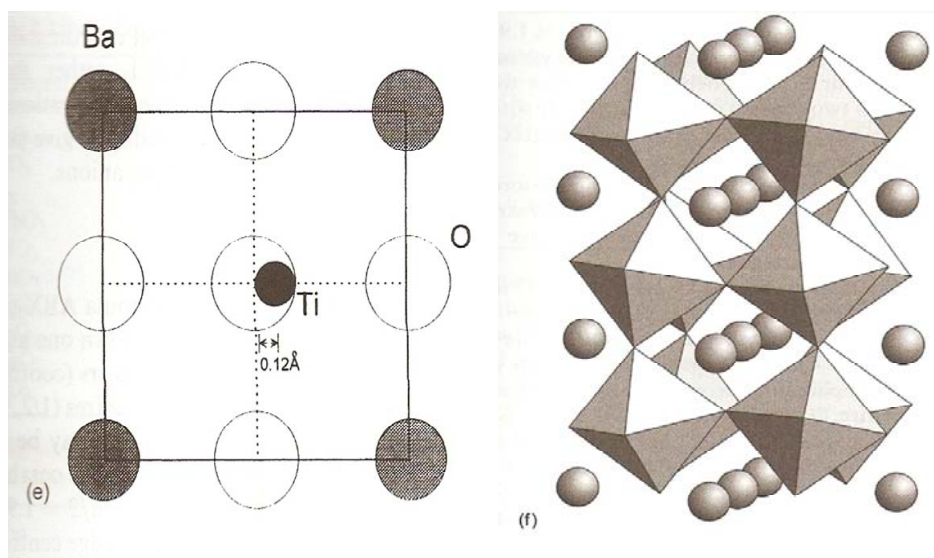
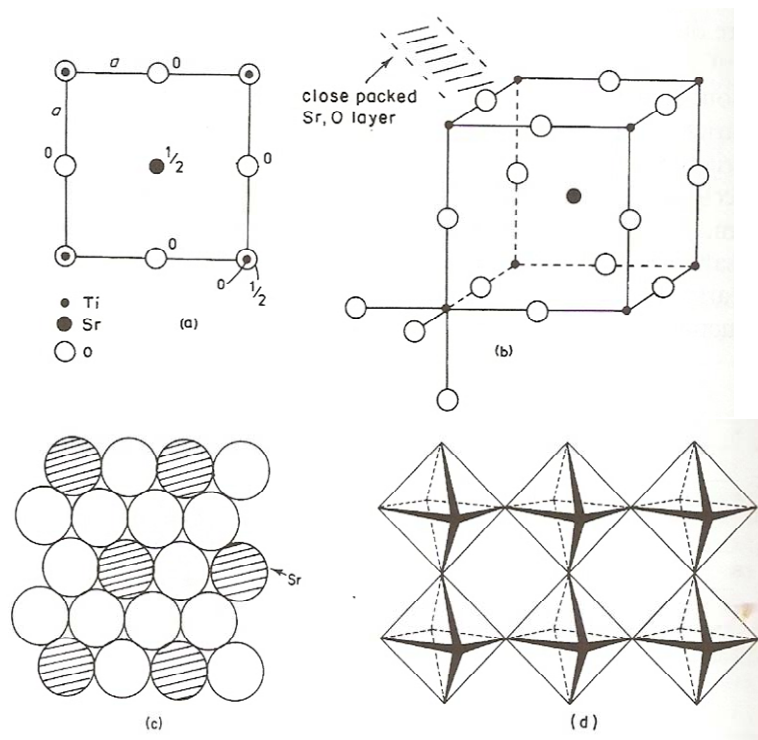


Fig. 1.27 The rock salt structure as an array of edge-sharing octahedra



**Fig. 1.36** (a–d) The perovskite structure of  $\text{SrTiO}_3$ . (e) Structure of tetragonal  $\text{BaTiO}_3$  projected onto the  $ac$  plane. (From Weller, *Inorganic Materials Chemistry*, 1994.) Note, the origin of the unit cell is shifted to coincide with Ba rather than with Ti as in (a). (f)  $\text{GdFeO}_3$  structure

We cannot estimate the efficiency of packing spheres for space-filling polyhedra since the anions (usually the largest) are represented by points. However, the space-filling polyhedron approach shows the topology or connectivity of a framework and indicates clearly the location of interstitial sites.

### **The Variables for Space-Filling Polyhedron Approach**

Polyhedra: tetrahedra, octahedra, trigonal prisms, ...

Link: share some or all of their corners, edges and faces with adjacent polyhedra. Corners and edges may be common to two or more polyhedra, but only two can share a common face.

Some important points:

1) The bonding forces between atoms or ions are not taken into account for topological approach to arrange polyhedra.

2) The polyhedron entities do not necessarily exist.

e.g.  $\text{NaCl}_6$  in NaCl ionic network and  $\text{SiC}_4$  in covalent SiC network not exist

e.g. molecular  $\text{Al}_2\text{Br}_6$  (containing pairs of edge-sharing tetrahedral) exist; complex ions  $\text{SiO}_4$  tetrahedra range from monomers to infinite chains.

### **Principles for Polyhedral linkages**

Shared edges and faces decrease the stability of a structure, particularly for cations of high valence and small coordination number.

1) Decrease in the cation-cation distance (i.e. distances between the centers of polyhedra) due to sharing can lead to the cations repelling each other electrostatically.

- 2) Fig. 1.23 (a and b). The cation-cation distance is less in edge sharing than in corner sharing.
- 3) Fig. 1.23 (b and c). The cation-cation distance M–M is less between tetrahedra than between octahedral because the MXM bridge angle is  $71^\circ$  for the former ( $M-M = 1.16 M-X$ ) and  $90^\circ$  for the latter ( $M-M = 1.414 M-X$ ).
- 4) Table 1.6 shows the maximum possible M–M distances for various polyhedral linkages (as a function of M–X). The M–M distance is greatest for corner-sharing and least for face-sharing octahedra.
- 5) Reduced distance occurs if the polyhedra are rotated about the shared corner or edge (e.g. the MXM angle between corner-shared polyhedra is less than  $180^\circ$ ).
- 6) Table 1.6, face-shared tetrahedra: M–M is less than M–X, this unstable situation does not normally occur.
- 7) Tetrahedra containing cations of high charge, edge sharing is energetically unstable and only corner sharing occurs. e.g. in silica built of  $\text{SiO}_4$  tetrahedra, edge sharing never occurs.

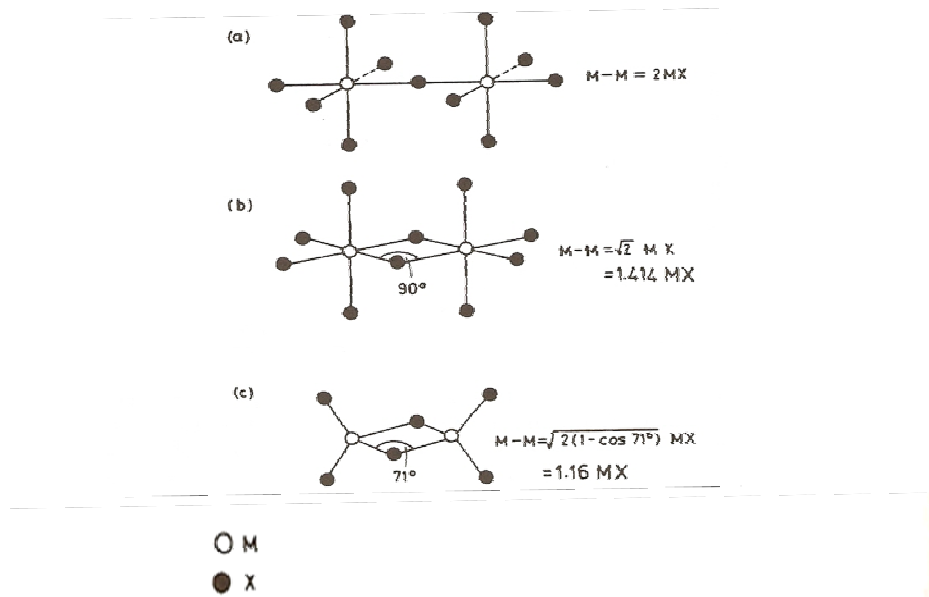


Fig. 1.23 Cation-cation separation in octahedra which share (a) corners and (b) edges and in (c) tetrahedra which share edges

Table 1.6 The distance  $M-M$  between  $MX_4$  or  $MX_6$  groups sharing  $X$  atom(s)

	Corner sharing	Edge sharing	Face sharing
Two tetrahedra	$2.00 MX(\text{tet.})^*$	$1.16 MX(\text{tet.})^*$	$0.67 MX(\text{tet.})$
Two octahedra	$2.00 MX(\text{oct.})^*$	$1.41 MX(\text{oct.})^*$	$1.16 MX(\text{oct.})$

\* Maximum possible value.