1.9 Description of crystal structures

The most common way for describing crystal structure is to refer the structure to the unit cell. The structure is given by the size and shape of the cell and the position of atoms (i.e. atomic coordinates). However, this is insufficient to <u>visualize</u> the whole crystal structures in 3D. Referring to a larger part of the structure (comprising perhaps several unit cells) and considering the arrangement relative to each other, their coordination numbers, interatomic distances, types of bonding, etc are more important.

Two of the most useful ways of describing structures are based on <u>close packing</u> and <u>space-filling</u> polyhedra. They provide greater insight into the crystal chemistry than is obtained using unit cells alone.

1.10 Close packed structures – cubic and hexagonal close packing

Many crystal structures can be described using the concept of close packing.

※Structures are usually arranged to have the maximum density.

※Consider the most efficient way of packing equal-sized spheres in 3D.

Fig. 1.12 shows the most efficient way to pack spheres in 2D.

Each sphere, Ⓐ is surrounded by, and is in contact with, six others; i.e.

Ⓐ has six nearest neighbors. The coordination number of six is the

maximum possible for a planar arrangement of contacting, equal-sized spheres.

1

Fig. 1.12 A *cp* layer of equal-sized spheres. Inset shows a non-*cp* layer with co-ordination number 4
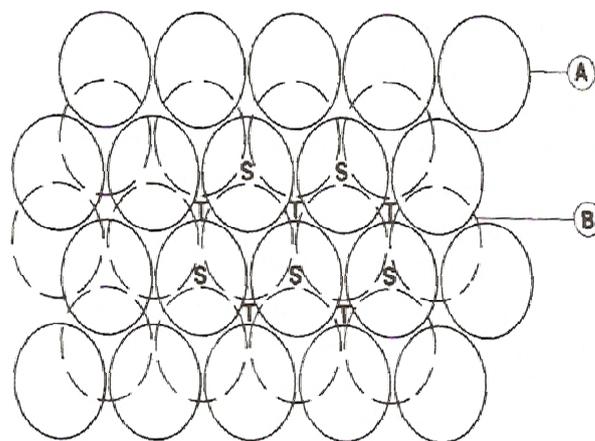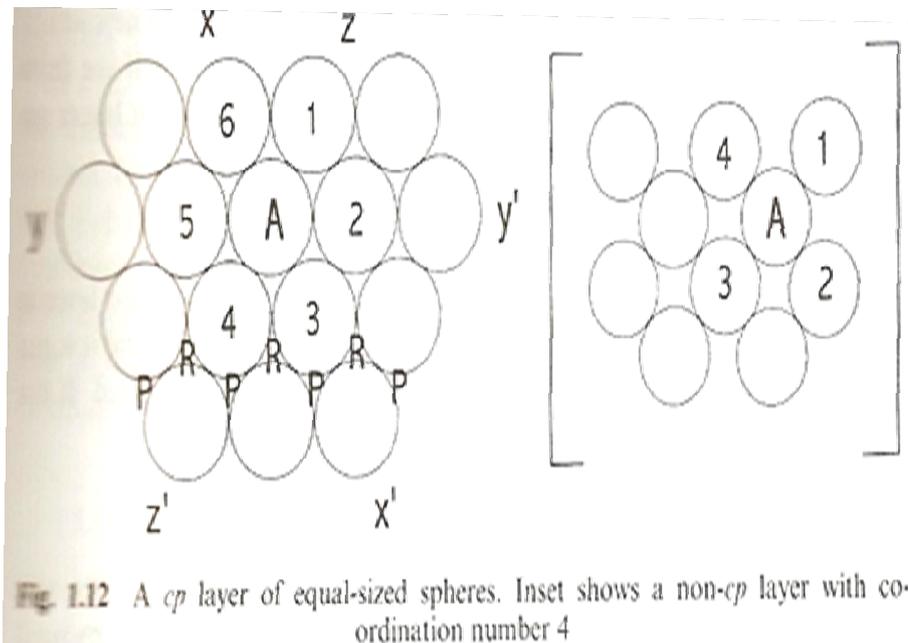
Fig. 1.13 Two *cp* layers arranged in A and B positions. The B layer occupies the P positions of Fig. 1.12

Regular repetition

⇨ Close packed layer (cp layer)

The cp layer has three close packed directions: XX', YY', ZZ' (spheres are in contact in the directions).

A non-cp layer is shown in the inset of Fig. 1.12; a lower coordination number is observed (4 for Ⓐ).

※The most efficient way to pack spheres in 3D is to stack cp layers on top of each other: [hexagonal close packed] and [cubic close packed].

- The most efficient way for two cp layers **A** and **B** to be in contact
    Each sphere of one layer to rest in a hollow between three spheres in the other layer, e.g. at **P** or **R** in Fig. 1.12

- Fig. 1.13 shows such a position for 2 layers.
    Atoms in second layer may occupy either **P** or **R** (Fig. 1.12), not both, nor a mixture of the two.

Hexagonal Close Packing (*hcp*)
- Fig. 1.13, suppose that A lies underneath the B layer.
    A third layer on top of B: positions S or T
    For S position, the third layer directly over the A layer. As subsequent layers are added, the following sequence arises:
        …ABABAB…
        This is known as hexagonal close packing (*hcp*)

Cubic Close Packing (*ccp*)

- In Fig. 1.13, the third layer is placed at T, then all three layers are staggered relative to each other and it is not until the fourth layer is positioned (at A) that the sequence is repeated..

    The third layer is called C, and it gives

    …ABCABCABC…

    i.e. cubic close packing (*ccp*)   Fig. 1.14

hcp and ccp are two simplest stacking sequences and are by far the most important in structure chemistry.

Other more complex sequences with larger repeat units, e.g. ABCACB or ABAC are related to the phenomenon of polytypism （多樣型）.

In 3D cp structures, each sphere is in contact with twelve others and this is the maximum coordination number possible for contacting and equal-sized spheres. (A common non-cp structure is body centered cube, with CN = 8, Fig. 1.9c for α–Fe)

6 of these neighbors are coplanar (Fig. 1.12)

Two groups
of 3 spheres   One group in the plane above   Fig. 1.13 and 1.14
                 One group in the plane below
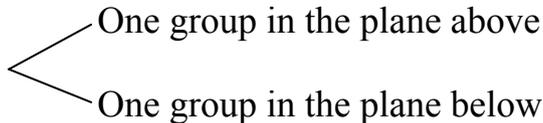
Fig. 1.15: hcp and ccp differ only in the relative orientations of these two groups of 3 spheres.
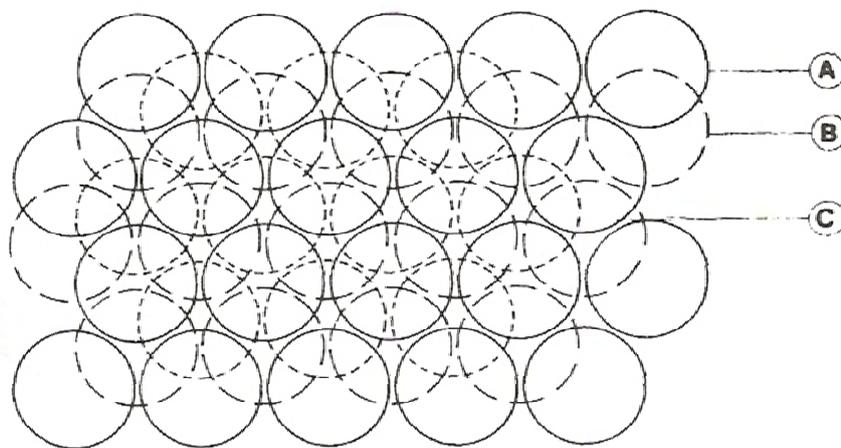
Fig. 1.14 Three close packed layers in *ccp* sequence
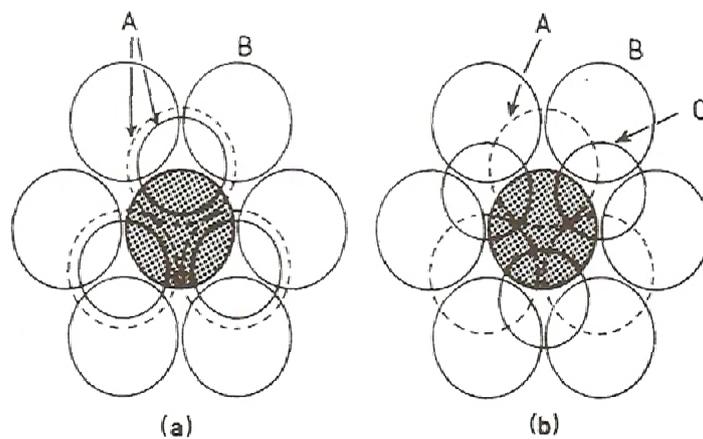
Fig. 1.15 Coordination number 12 of shaded sphere in (a) *hcp* and (b) *ccp* structures. The shaded sphere is in the B layer, the layer underneath is A and the layer above is either (a) A or (b) C

1.11 Relationship between cubic close packed and face centered cubic

The unit cell of a *ccp* arrangement is the face centered (*fcc*) unit cell (Fig. 1.9(a) with spheres at the corners and face centers).

- The relationship between *ccp* and *fcc* is not obvious since the faces of the *fcc* unit cell do not correspond to *cp* layers.

- The *cp* layers are parallel to the {111} planes of the *fcc* unit cell (Fig. 1.16, the spheres labeled 2–7 in (a) and (b) form part of a *cp* layer, revealed by removing sphere **1**)

- In an *fcc* structure, *cp* layers occur in four orientations and are perpendicular to the body diagonals. (the *fcc* cube has four body diagonals, originating from 8 corners)

- Fig. 1.16(c), the *cp* layers in one orientation are seen edge-on.
  從側邊看

- Fig. 1.16(d), the *cp* layers are seen perpendicular to the layers.
  (對角 corner 的 atoms 剛剛好對到, 均為 A layers)
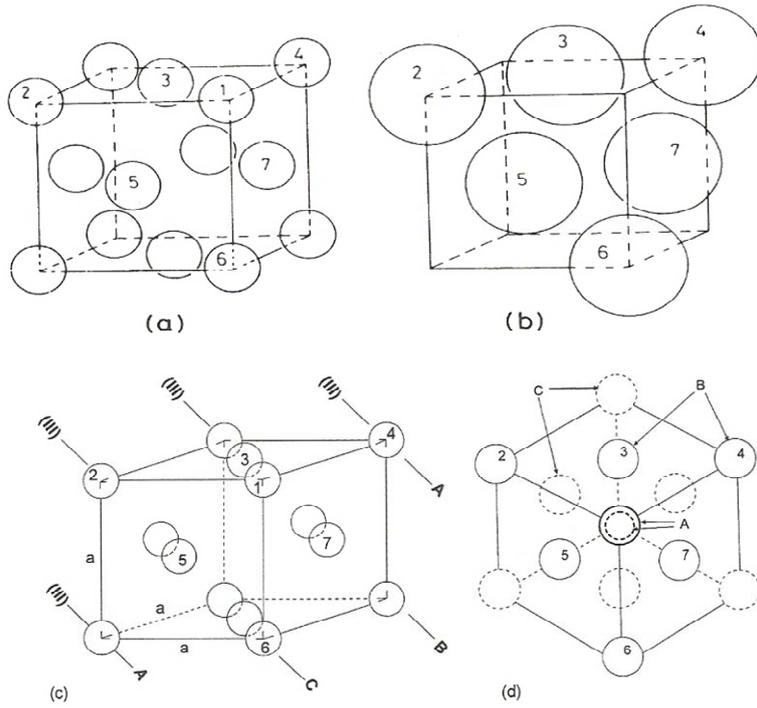
Fig. 1.16 Face centred cubic unit cell of a *ccp* arrangement of spheres
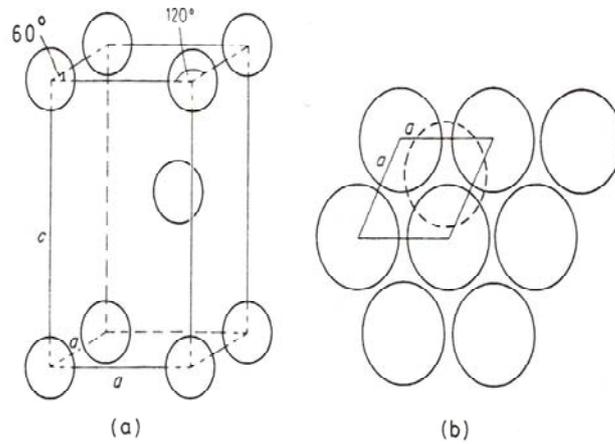
Fig. 1.17 Hexagonal unit cell of a *hcp* arrangement of spheres

1.12 Hexagonal unit cell and close packing

An *hcp* arrangement of spheres has a hexagonal unit cell.

- The basal plane of the cell coincides with a *cp* layer of spheres (Fig, 1.17b)

- The unit cell centains two spheres

    One at the origin (and hence at all corners)

    One inside the cell at position $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ (dashed circle in b).

- *cp* Layers occur in only <u>one orientation</u> in a *hcp* structure (hexagonal unit cell).

- Fig. 1.17 shows that the two axes in the basal plane are of equal length (a = 2r, if the spheres of radius *r* touch)

- The angle γ is 120°, c-axis is a sixfold rotation axis.

See further from the auxiliary materials

1.13　Density of close packed structures

In *cp* structures, 74.05% of the total volume is occupied by spheres. This is the maximum density possible if structures constructed of spheres of only one size.

Ex: the *fcc* unit cell (4 spheres in one unit cell).

One at a corner and three at face centers

The *cp* directions (XX', YY', ZZ' in Fig. 1.12) occur parallel to the face diagonal of the unit cell, i.e. spheres 2,5,6 in Fig. 1.16b.

The length of the face diagonal: $4r$

The length of the cell edge: $2\sqrt{2}\, r$　　　　$\sqrt{\left(2\sqrt{2}\gamma\right)^2 + \left(2\sqrt{2}\gamma\right)^2} = 4\gamma$

The volume of the cell: $16\sqrt{2}\, r^3$　　　　$\left(2\sqrt{2}\gamma\right)^3 = 16\sqrt{2}\gamma^3$

$$\therefore \frac{total\ sphere\ volume}{unit\ cell\ volume} = \frac{4 \times \frac{4}{3}\pi\gamma^3}{16\sqrt{2}\gamma^3} = 0.7405$$

Similar results are obtained for *hcp*.

In non-cp structures, densities lower than 0.7405 are obtained

- Body centered cubic, *bcc*, is 0.6802 (the *cp* directions (Fig. 1.12) in *bcc* are parallel to the body diagonals of the cube).

1.14   Unit cell projections and atomic coordinates

To give 3D perspective to crystal structures, they are often drawn as oblique projections (Fig, 1.16a).

For accurate and unambiguous descrriptionm, it is necessary to project them down particular crystallographic directions and/or on to crystallographic faces.

     Ex. Fig. 1.18b (Unit Cell Projections), a face centered cube projected down the *z*-axis onto the *ab* unit cell face.

- All sense of vertical perspective is lost
- To restore vertical perspective, their vertical height in the cell is given as a fraction of *c*, beside each atom.
- It is not necessary to specify the x, y coordinates if the structure is drawn to scale.
- The origin is often taken as the top left hand corner.
- Two atoms at each corners and two at top and bottom face centers, with *z*-coordinates of 0 and 1.
- The four side face centers, each with $z = 1/2$

Fig. 1.18c (Atomic Coordinates): It is important to use Fig. 1.18b to relate the fractional atomic coordinates.

- A face centered cube contains, effectively, four positions: one corner and three face centers, i.e. $000, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}\frac{1}{2}$
- Each coordinates specifies the fractional distance of the atom from the origin in the directions *a, b*, and *c*.
- The more complete structure shown in Fig. 1.18b is obtained by

addition of extra, equivalent positions. (to Fig. 1.18c)
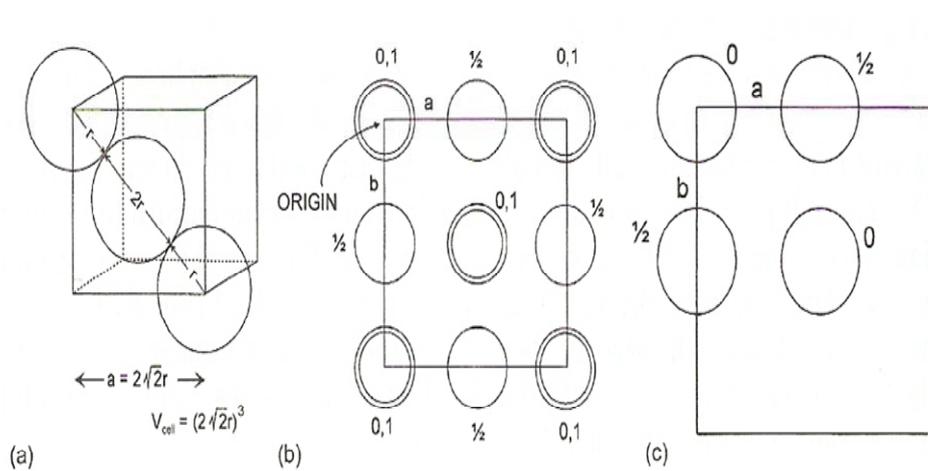
Fig. 1.18 (a) Unit cell dimensions for a face centred cubic unit cell with spheres of radius, r in contact along face diagonals. (b, c) Projection of a face centred cubic structure onto a unit cell face

Table 1.3 *Structures and unit cell dimensions ($\overset{\circ}{A}$) of some common metals*

ccp, a		hcp, a, c			bcc, a	
Cu	3.6147	Be	2.2856	3.5842	Fe	2.8664
Ag	4.0857	Mg	3.2094	5.2105	Cr	2.8846
Au	4.0783	Zn	2.6649	4.9468	Mo	3.1469
Al	4.0495	Cd	2.9788	5.6167	W	3.1650
Ni	3.5240	Ti	2.9506	4.6788	Ta	3.3026
Pb	4.9502	Zr	3.2312	5.1477	Ba	5.019

1.15 Materials that can be described as close packed

a) Metals

Most metals crystallize in one of the three arrangements:

  ccp, *hcp*, and *bcc* (Table 1.3)

- No clear-cut trends are observed (reason for preferred structure not well understood)
- Lattice energies of *hcp* and *ccp* metal structures are comparable
- The structure observed probably depends on fine details of the bonding requirements or band structure of the metal.
- Appendix 4: structure details of elements.

b) Alloys

Alloys are intermetallic phases or solid solutions.

Many of them have *cp* structures.

  Ex: Cu and Au

  - both have *ccp* structures as pure elements

    Cu−Au alloys have *ccp* structures

  - At high temperatures, a complete range of solid solutions between Cu and Au forms; the Cu and Au atoms are distributed statistically over the lattice points of the *fcc* unit cell, i.e. a random mixture of Cu and Au.

  - On annealing the compositions AuCu and $AuCu_3$ at lower temperatures, the Au and Cu atoms order themselves; *ccp* layers still occur but the arrangement is no longer statistical. (Such order-disorder phenomena are outside the scope of this introduction to crystal structures but occur commonly in both metallic and ionic structures).

c) Ionic structures

Ionic compounds: such as NaCl, Al_2O_3, Na_2O, ZnO,……

- The anion is larger than the cation; the structures are built of *cp* layers of anions with the cations placed in the interstitial sites.

- Many structures are possible: structural variables: 1) anion stacking sequence (either *hcp* or *ccp*); 2) number and type of interstitial sites occupied by cations.

- To accommodate large cations, expanding the anion array is necessary. The anions in *cp* may not be in contact (eutactic). In the following discussions, use of the terms hcp and ccp for anion arrays may include the structures being in contact or eutactic.

(i) Tetrahedral and octahedral sites

Two types of interstitial sites in *cp*: tetrahedral and octahedral, the nature of the interstitial space between any pair of adjacent *cp* layers.

Tetrahedral sites, T

— 3 anions that form the base of the tetrahedron belong to one cp layer

the apex of the tetrahedron in the layer **above** the base (Fig.1.19a)

the apex of the tetrahedron in the layer **below** the base (Fig.1.19b)

the apex is **up**, giving the T_+ tetrahedral site

the apex is **down**, giving the T_- tetrahedral site

— Because the center of gravity of a tetrahedron is nearer to the base than the apex

→cations in tetrahedral sites are not located midway between

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adjacent ion layers but are nearer one layer than the other (the layers seen edge-on in Fig.19c,d).
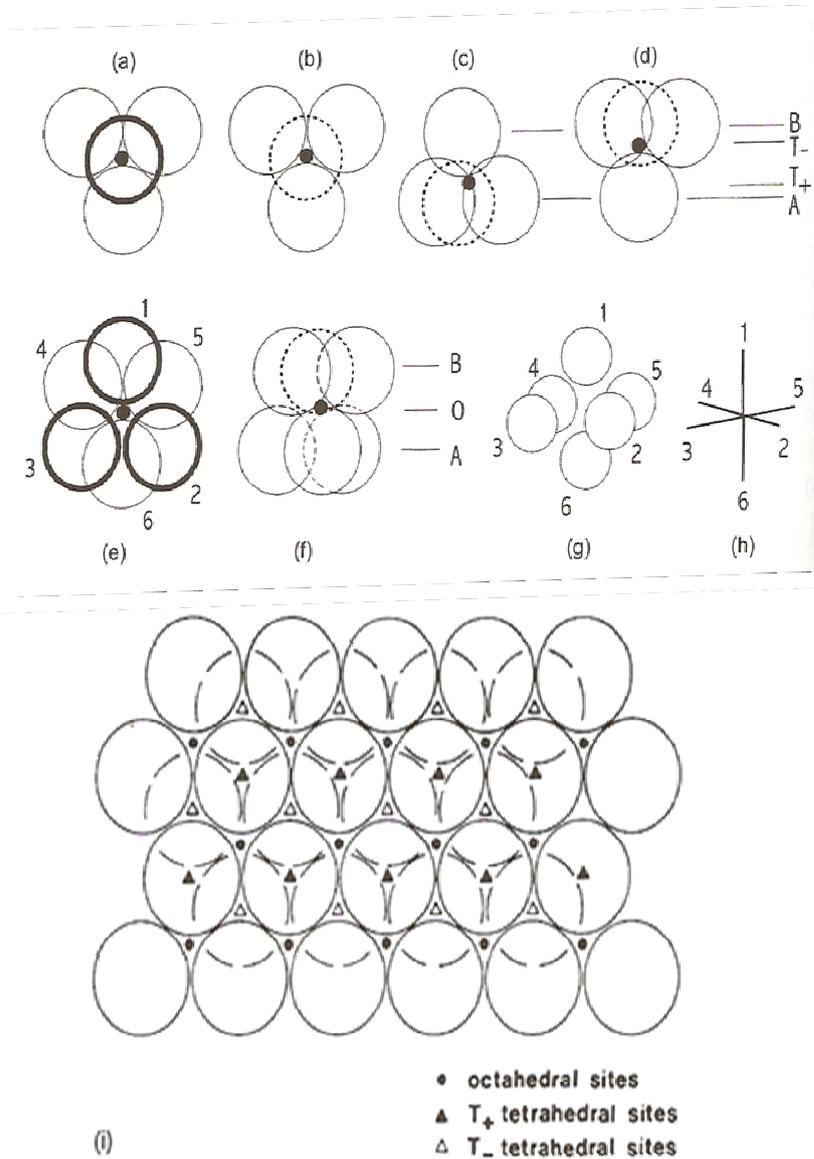
Fig. 1.19 Tetrahedral and octahedral sites between two close packed anion layers, seen from different perspectives. (a, b) Projection down threefold axis of T_+, T_- sites. (c, d) Tetrahedral sites edge-on. (e) Projection down threefold axis of octahedral site and (f) seen edge on. (g, h) Conventional representation of octahedral site. (i) Distribution of T_+, T_-, O sites between two cp layers

Octahedral sites, O

－these sites are coordinated to 3 anions in both adjacent anion layers.
(Fig.1.19e)

－these sites are midway between the anion layers (Fig.1.19f edge-on)

－A more common way to regard octahedral coordination is as 4
coplanar atoms with one atom at each apex above and below the
plane. In Fig.1.19e, atoms 1,2,4,6 are coplanar. Also, atoms 2,3,4,5
and 1,3,5,6 are coplanar.

－Fig.1.19g,h are more conventional perspective.

Fig.1.19i :

The distribution of interstitial sites between any two adjacent layers of
cp anions:

－below every sphere in the upper layer (solid line) is a T_+

－above every sphere in the lower layer (dashed line) is a T_-

－many O sites

－counting up the number of each, for every anion there is one
octahedral site and two tetrahedral sites, one T_+ and one T_-.
site number distribution $\rightarrow$ anion : octahedral : T_+ : $T_- = 1 : 1 : 1 : 1$

Table 1.4:

－It is rare that all the interstitial sites in a *cp* structure are occupied;
often one set is full or partly occupied and the remaining sets are
empty.

－*cp* ionic structures, classified according to the anion layer stacking

sequence and the occupancy of the interstitial sites (Table 1.4)

— how a wide range of structures are grouped into one large family; this
  helps to bring out similarities and differences between them.

For example:

(a) rock salt and nickel arsenide (NiAs) structures both have
    octahedrally coordinated cations and differ only in the anion
    stacking sequence; similar relationships for olivine and spinel,
    wurtzite and blende, CdI_2 and $CdCl_2$.

(b) rutile TiO_2 and CdI_2 both have *hcp* anions with half the octahedral
    sites occupied by cations; in rutile, half the octahedral sites between
    any pair of *cp* anion layers are occupied by Ti; in CdI_2, layers of
    fully occupied octahedral site alternate with layers in which all sites
    are empty (this gives CdI_2 a layered structure).

(c) In a few structures, it is useful to regard cations as forming the *cp*
    layers with the anions occupying the interstitial sites.
    — The fluorite structure, CaF_2, may be regarded as *ccp* Ca with all T_+
    and T_- sites occupied by F.
    — The antifluorite structure of K_2O is the exact inverse of fluorite
    with *ccp* layers of O and K in T_+, T_- sites.

(d) The *cp* concept may be extended to structures in which a mixture of
    anions and large cations form the packing layers and smaller cations
    occupy interstitial sites.
       In perovskite, $BaTiO_3$, *ccp* layers of composition 'BaO_3' occur
       and one quarter of the octahedral sites are occupied by Ti (only

those sites in which all six corners are O^{2-} ions).

(e) Some structures are anion-deficient *cp* structures in which the anions form an incomplete *cp* array.

 − ReO$_3$: has *ccp* oxide layers with 1/4 of O sites empty.

   It is analogous to perovskite in which Ti is replaced by Re and Ba sites are left vacant.

 − β-alumina (NaAl$_{11}$O$_{17}$): *cp* oxide layers in which every fifth layer has approximately three quarters of the O^{2-} ions missing. (NaAl$_{11}$O$_{17}$□$_3$)

Table 1.4 *Some close packed structures*

Anion arrangement	Interstitial sites			Examples
	T_+	T_-	O	
ccp	—	—	1	NaCl, rock salt
	1	—	—	ZnS, blende or sphalerite
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	MgAl$_2$O$_4$, spinel
	—	—	$\frac{1}{2}$	CdCl$_2$
	—	—	$\frac{1}{3}$	CrCl$_3$
	1	1	—	K$_2$O, antifluorite
hcp	—	—	1	NiAs
	1	—	—	ZnS, wurtzite
	—	—	$\frac{1}{2}$	CdI$_2$
	—	—	$\frac{1}{2}$	TiO$_2$, rutile*
	—	—	$\frac{2}{3}$	Al$_2$O$_3$, corundum
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	Mg$_2$SiO$_4$, olivine
ccp 'BaO$_3$' layers	—	—	$\frac{1}{4}$	BaTiO$_3$, perovskite

* The *hcp* oxide layers in rutile are not planar but are buckled; the oxide ion arrangement may alternatively be described as *tetragonal packed* (*tp*).

Table 1.8   *Some compounds with the NaCl structure, a ($\overset{\circ}{A}$)*

MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	αMnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	4.64	RbCl	6.5810
FeO	4.307	CaSe	5.924	NaCl	5.6402	RbBr	6.889
CoO	4.260	SrSe	6.246	NaBr	5.9772	RbI	7.342
NiO	4.1769	BaSe	6.600	NaI	6.473	AgF	4.92
CdO	4.6953	CaTe	6.356	TiN	4.240	AgCl	5.549
TiC	4.3285	LaN	5.30	UN	4.890	AgBr	5.7745

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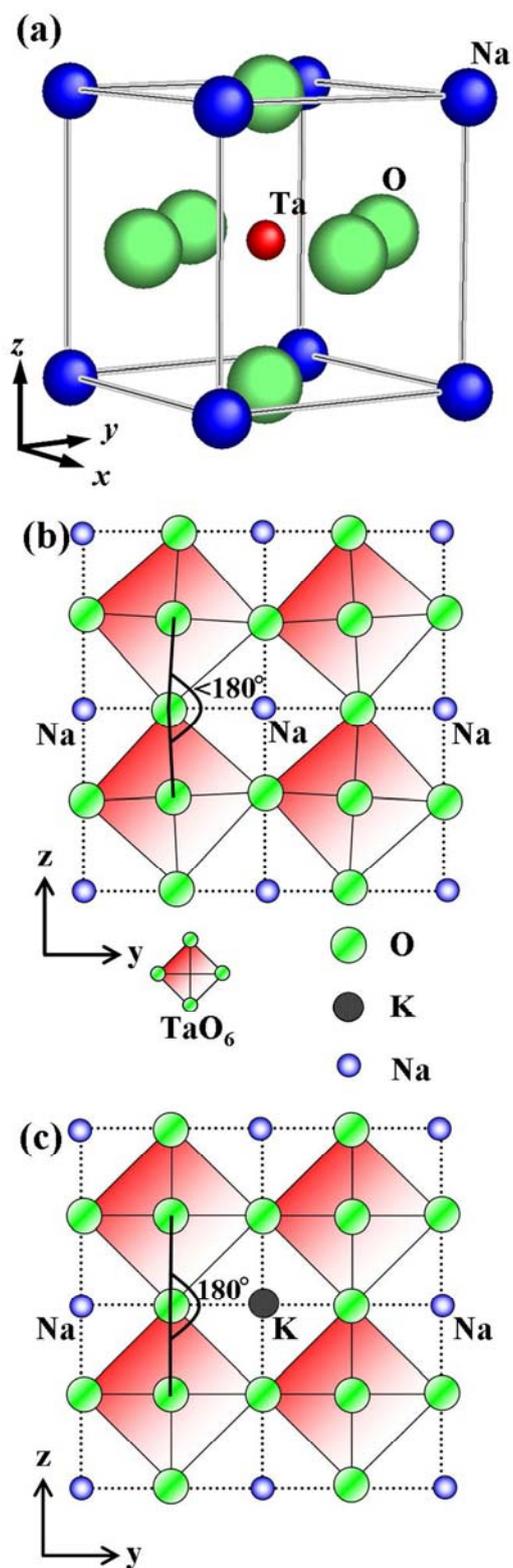
Figure 2 (a) The unit cell of monoclinic NaTaO$_3$; (b) the refined structure of monoclinic phase NaTaO$_3$ with a Ta–O–Ta bond angle less than 180°; (c) the refined structure of K-doped monoclinic NaTaO$_3$ with a Ta–O–Ta bond angle of approximately 180°.
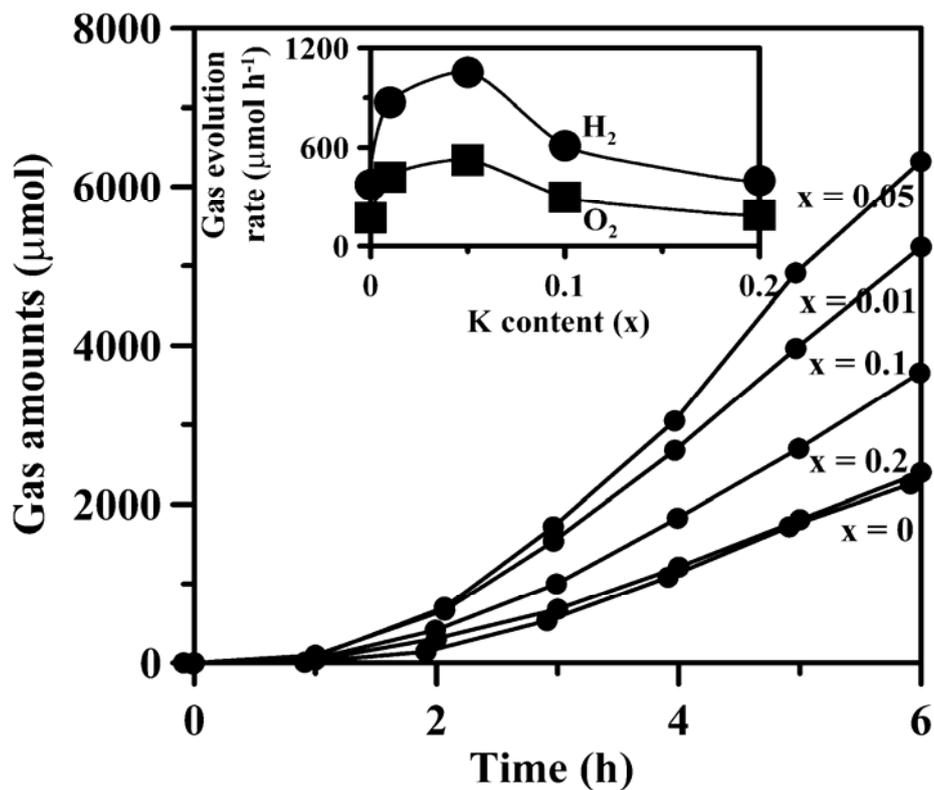
Figure 6 Time course of photocatalytic H_2 evolution from 1100 mL pure water suspended with 0.1 g of the $Na_{1-x}K_xTaO_3$ catalysts under mercury lamp irradiation. The inset shows the dependence of the H_2 and O_2 evolution rates on the K content.

Reference:

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