

HEXAGONAL CLOSE-PACKED STRUCTURE

An HCP crystal is a close-packed structure with the stacking sequence ...ABABAB...

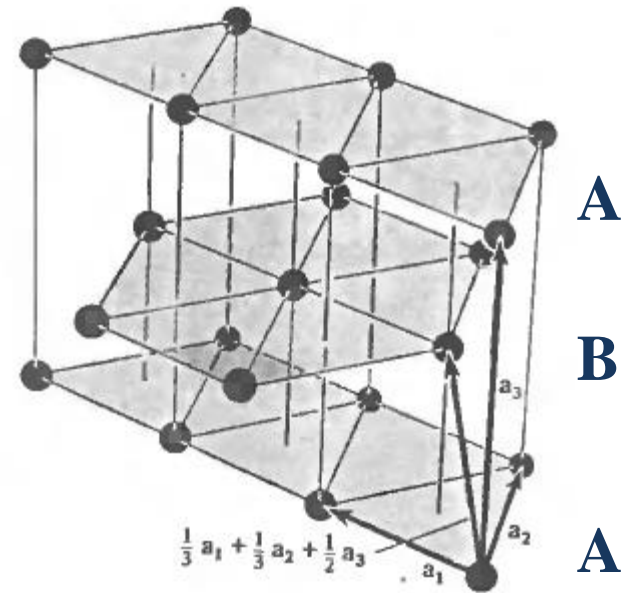
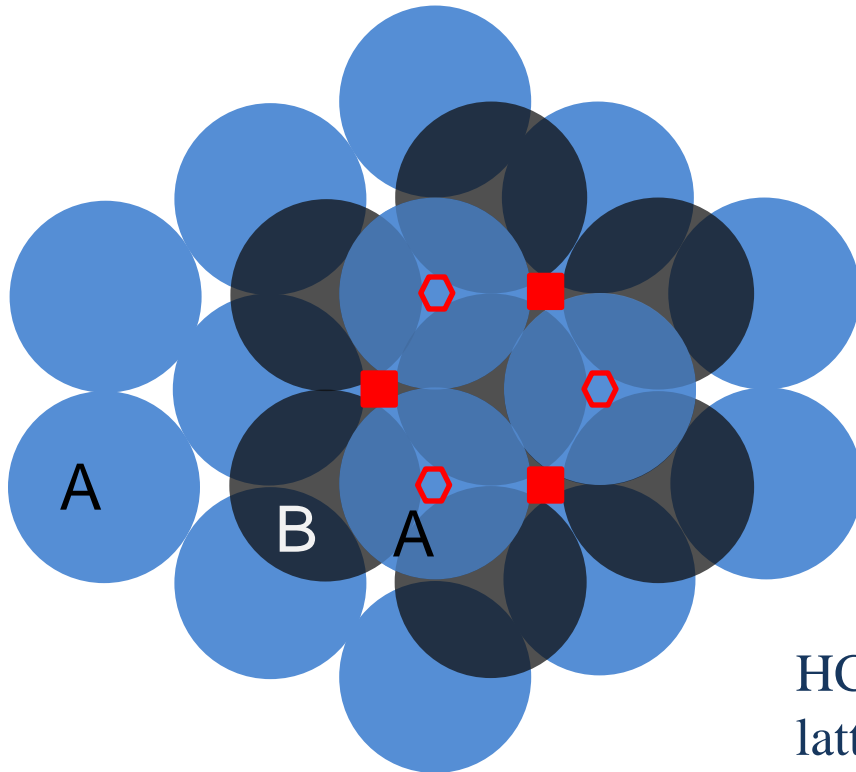
To construct:

1st layer: 2D HCP array (layer A)

2nd layer: HCP layer with each sphere placed in alternate interstices in 1st layer (B)

3rd layer: HCP layer positioned directly above 1st layer (repeat of layer A)

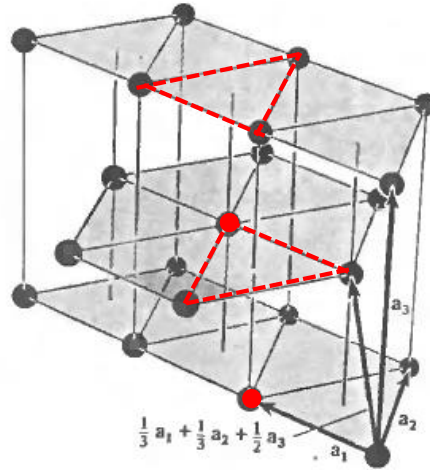
...ABABABAB...



HCP is two interpenetrating simple hexagonal lattices displaced by $\mathbf{a}_1/3 + \mathbf{a}_2/3 + \mathbf{a}_3/2$

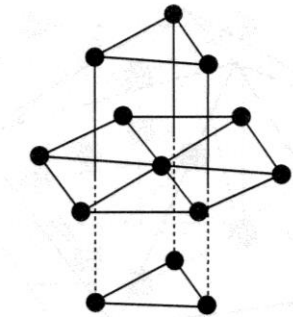
HCP STRUCTURE

- *not a Bravais lattice*



**Orientation alternates
with each layer**

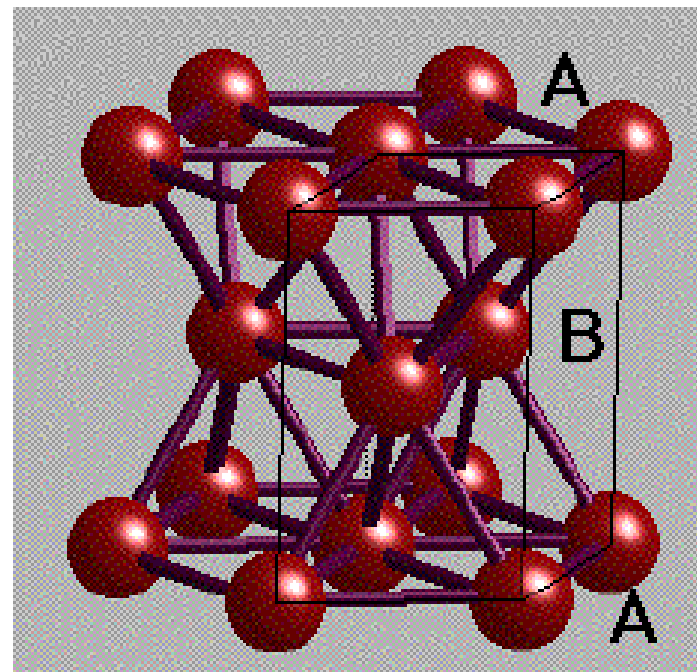
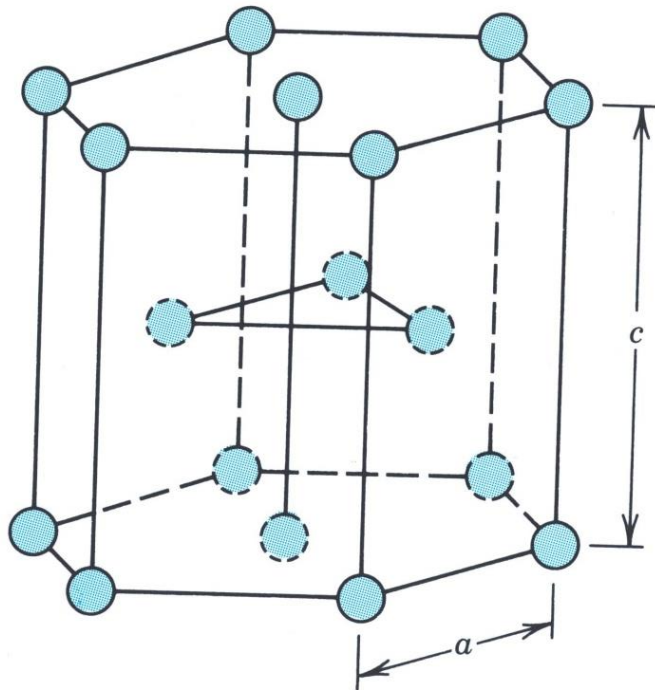
- *each sphere touches 12 equidistant nearest neighbors (CN = 12)*



Six in plane, six out-of-plane

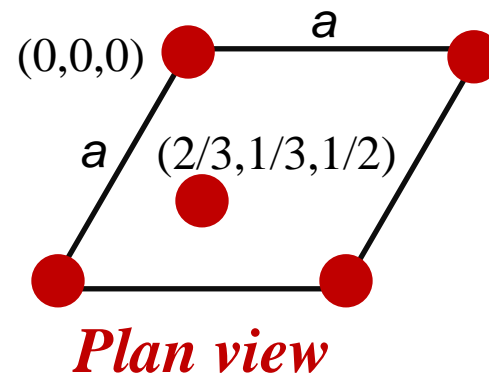
- *structure has maximum packing fraction possible for single-sized spheres (0.74)*

HCP STRUCTURE



- *unit cell is a simple hexagonal lattice with a two-point basis*

- *ideal ratio c/a of $\sqrt{8/3} = 1.633$*
- *$\{0002\}$ planes are close packed*
- *ranks in importance with FCC and BCC Bravais lattices*



HCP STRUCTURE

- *about 30 elements crystallize in the HCP form*

Table 4.4
ELEMENTS WITH THE HEXAGONAL CLOSE-PACKED CRYSTAL
STRUCTURE

ELEMENT	a (Å)	c	c/a	ELEMENT	a (Å)	c	c/a
Be	2.29	3.58	1.56	Os	2.74	4.32	1.58
Cd	2.98	5.62	1.89	Pr	3.67	5.92	1.61
Ce	3.65	5.96	1.63	Re	2.76	4.46	1.62
α -Co	2.51	4.07	1.62	Ru	2.70	4.28	1.59
Dy	3.59	5.65	1.57	Sc	3.31	5.27	1.59
Er	3.56	5.59	1.57	Tb	3.60	5.69	1.58
Gd	3.64	5.78	1.59	Ti	2.95	4.69	1.59
He (2 K)	3.57	5.83	1.63	Tl	3.46	5.53	1.60
Hf	3.20	5.06	1.58	Tm	3.54	5.55	1.57
Ho	3.58	5.62	1.57	Y	3.65	5.73	1.57
La	3.75	6.07	1.62	Zn	2.66	4.95	1.86
Lu	3.50	5.55	1.59	Zr	3.23	5.15	1.59
Mg	3.21	5.21	1.62		—	—	
Nd	3.66	5.90	1.61	"Ideal"			1.63

CUBIC CLOSE-PACKED STRUCTURE

A CCP crystal is a close-packed structure with the stacking sequence ...ABCABC...

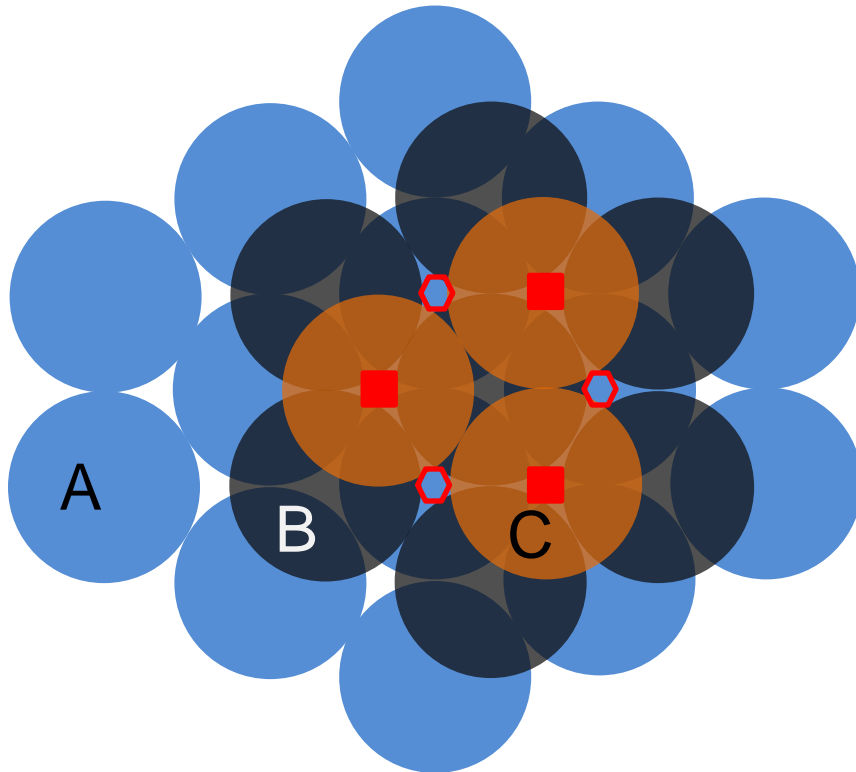
To construct:

1st layer: 2D HCP array (layer A)

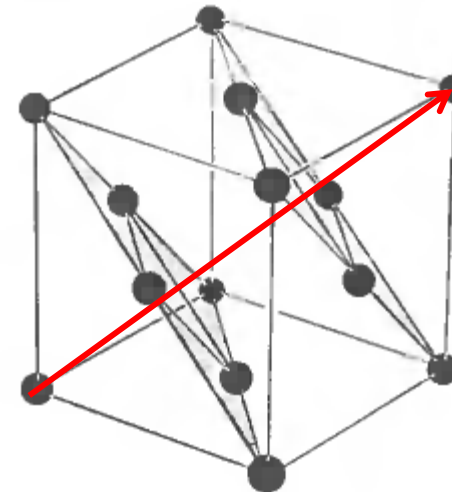
2nd layer: HCP layer with each sphere placed in alternate interstices in 1st layer (B)

3rd layer: HCP layer placed in the *other* set of interstitial depressions (squares, C)

4th layer: repeats the 1st layer (A)



...ABCABCABC...

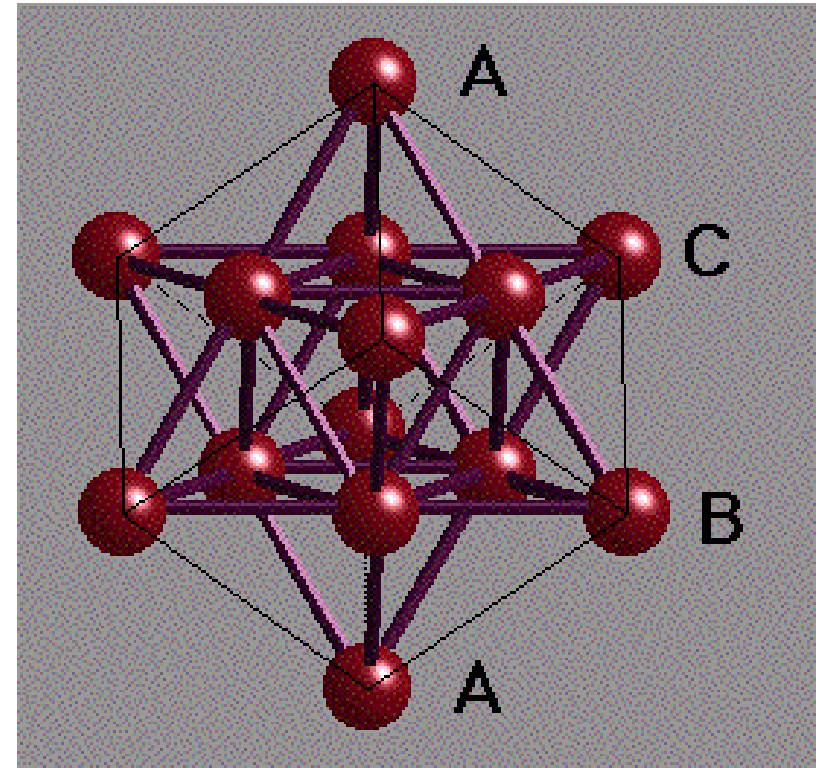
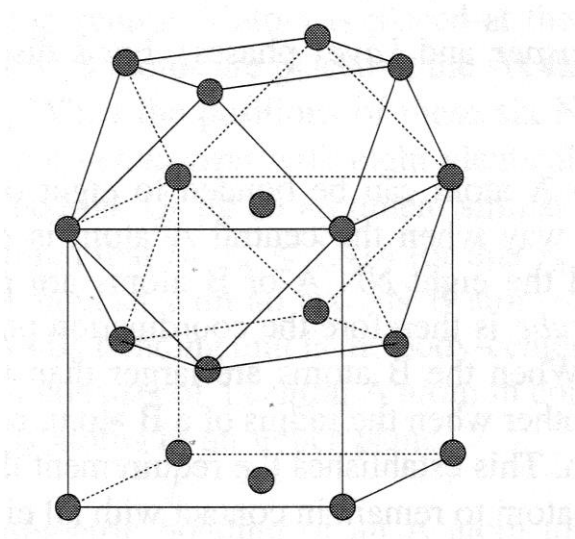


stacking
of HCP layers
along
body diagonals

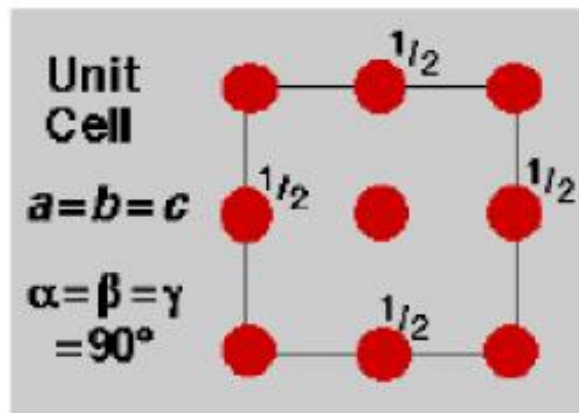
It turns out that the CCP structure is just the FCC Bravais lattice!

CCP STRUCTURE

- $CN = 12$, packing fraction 0.74



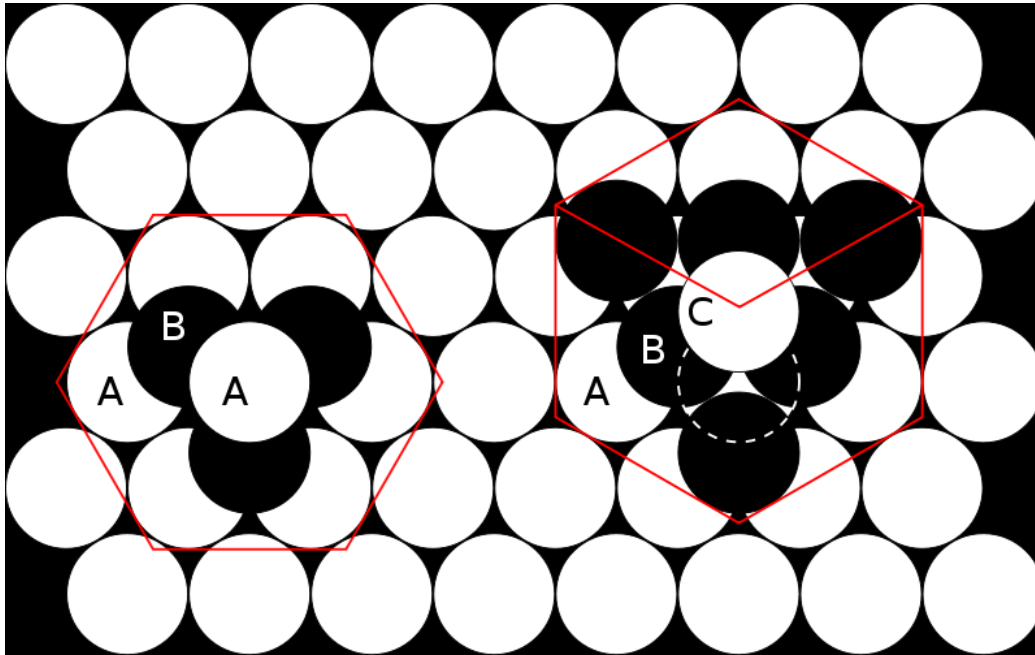
- $\{111\}$ planes are close packed
- 4 atoms in unit cell



Plan view

CLOSE-PACKED STRUCTURES

- *most common are HCP and CCP*



- *an infinite # of alternative stacking sequences exist*

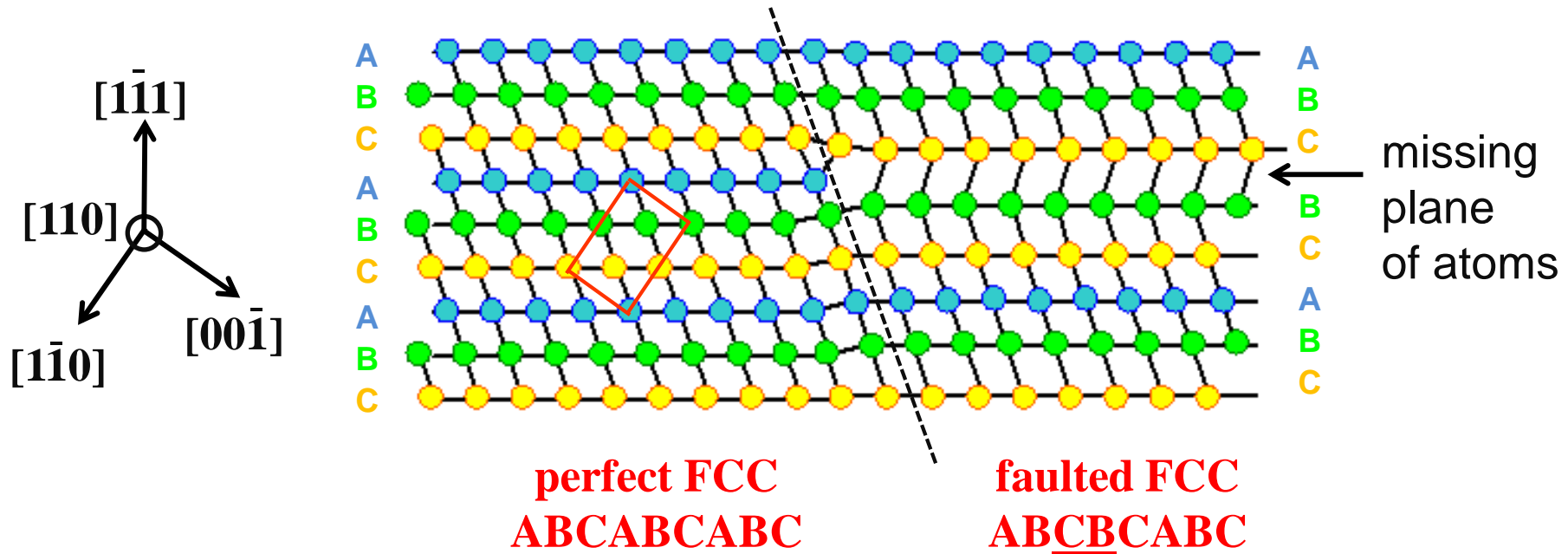
Example: silicon carbide has over 250 polytypes
e.g., 6H-SiC
stacking sequence ...ABCACB...



STACKING FAULTS

Stacking faults are one or two layer interruptions in the stacking sequence that destroy lattice periodicity

e.g., an $\langle 110 \rangle$ projection of an FCC lattice:

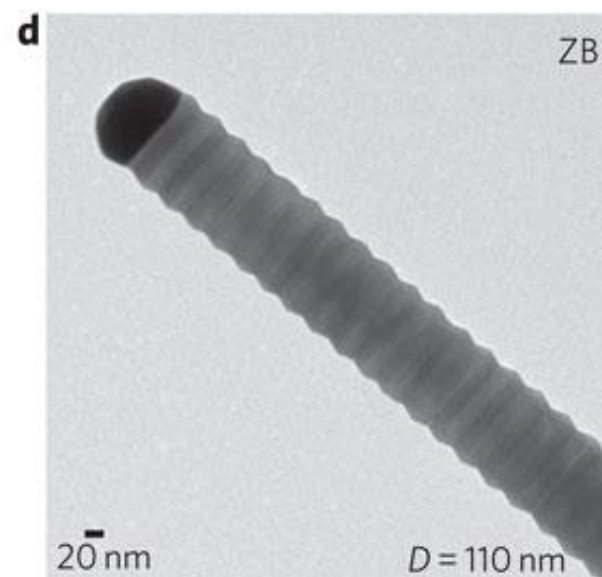
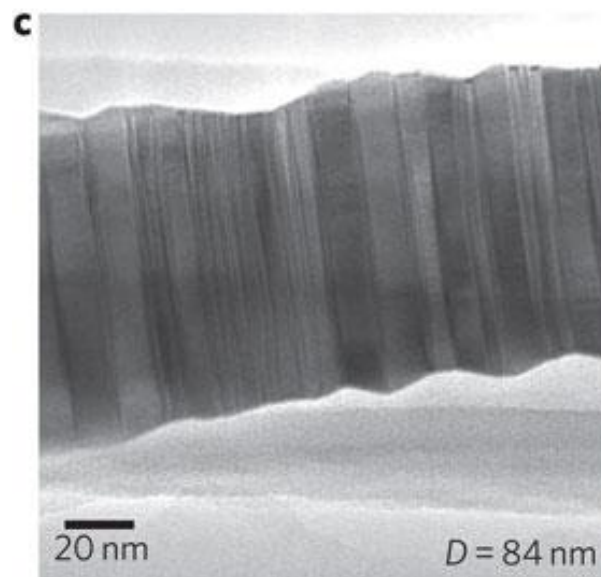
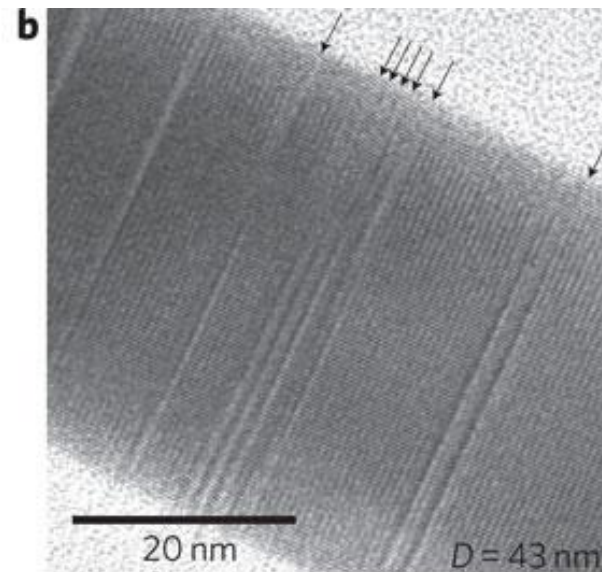
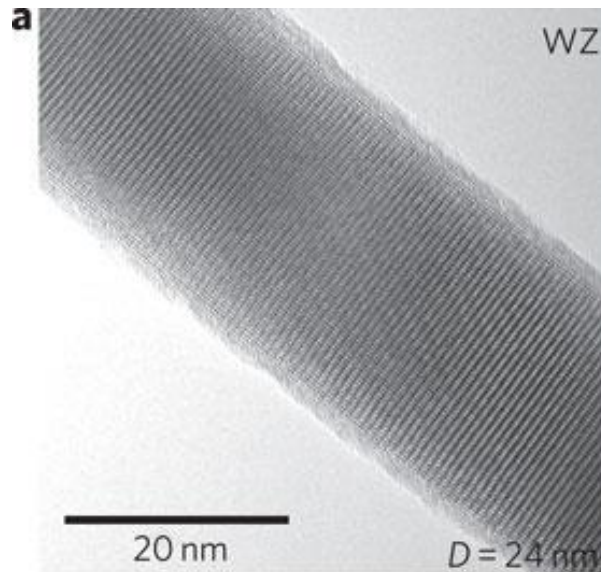


The stacking fault is an example of a **planar defect**

- stacking fault energy $\gamma \sim 100 \text{ mJ m}^{-2}$
- also results in a linear defect called a **dislocation**

EXAMPLE

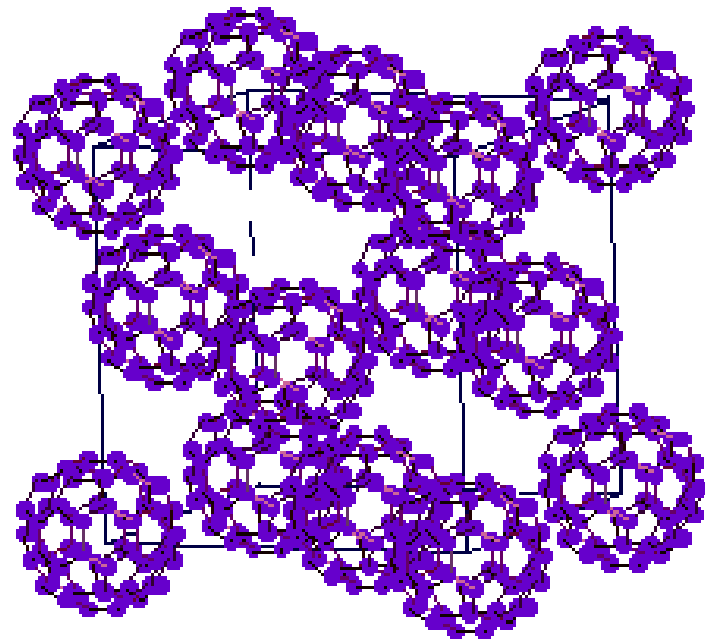
InAs nanowires - $\langle 110 \rangle$ projection



1 1A	2 2A	Hexagonal close-packed		Face-centered cubic		Body-centered cubic				Other structures (see caption)				13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
		3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9	10	11 1B	12 2B								
Li	Be																		
Na	Mg	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al							
K	Ca	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ga							
Rb	Sr											In	Sn						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb						

- *CCP and HCP have very similar lattice energies*
- *no clear cut trends*

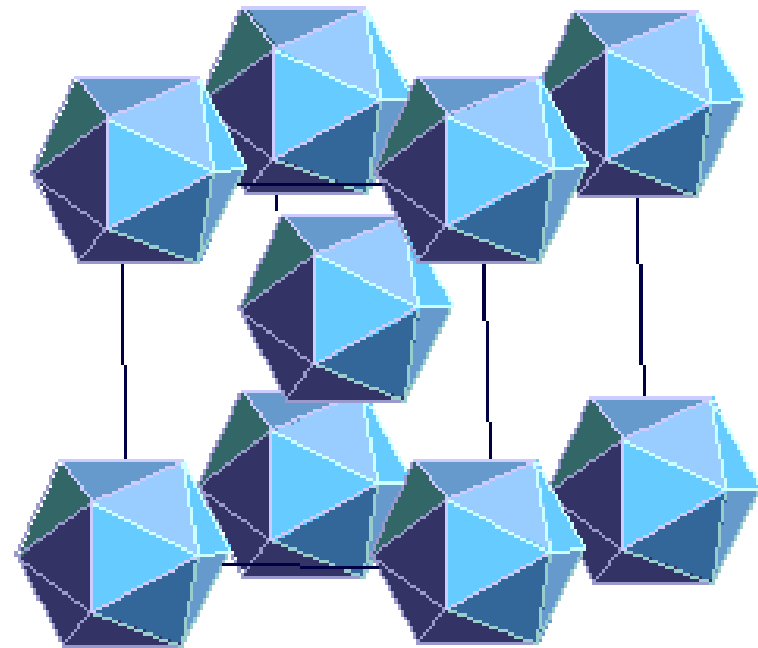
BUCKMINSTERFULLERENE



FCC

Nature 353, 147 - 149 (12 Sep 1991)

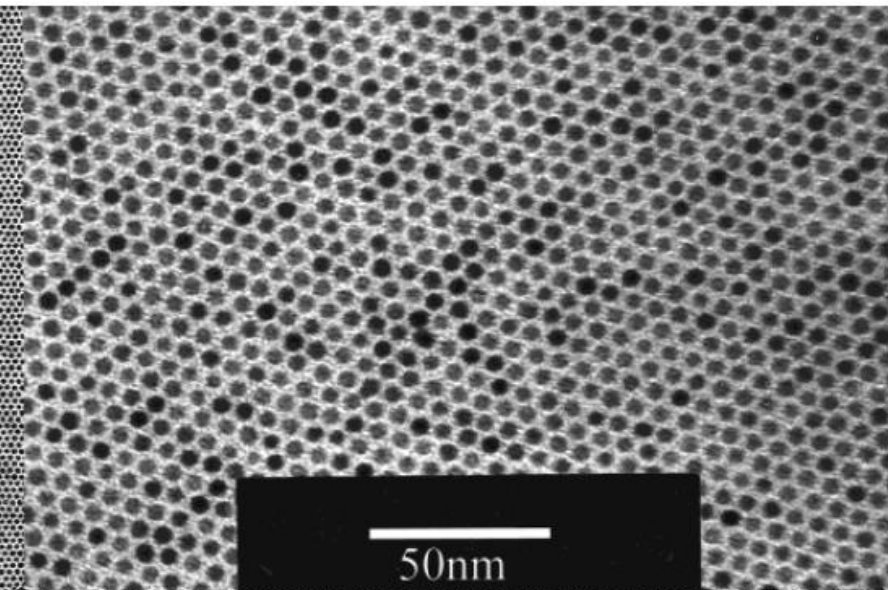
FOOT & MOUTH VIRUS



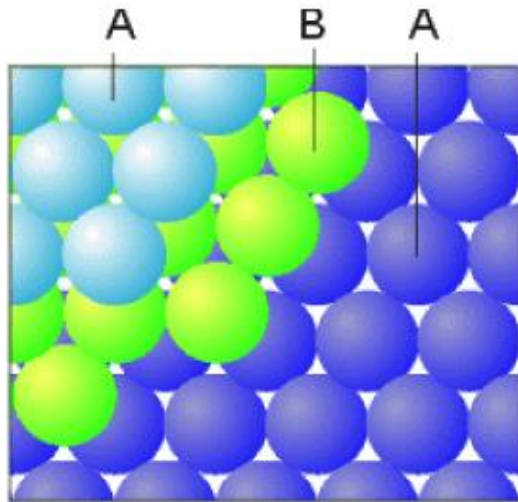
BCC

Rare Gases: Ne, He, Ar, Kr, Xe (CCP)

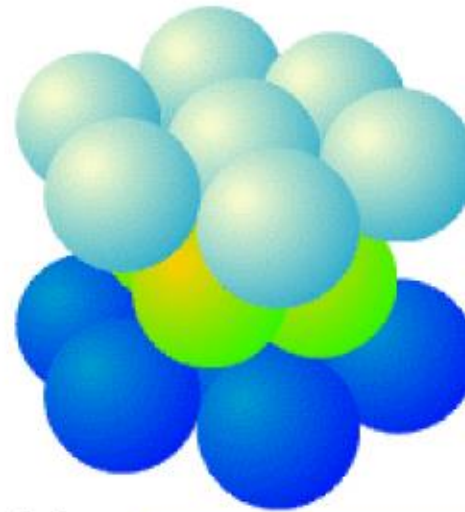
gold nanocrystals
X. M. Lin



ANOTHER VIEW OF CLOSE PACKING

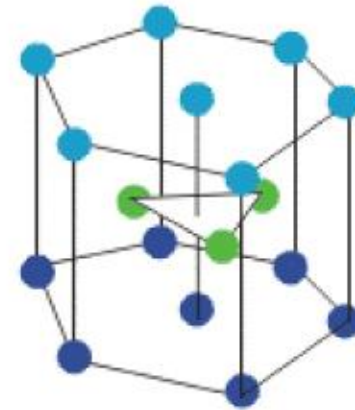


(a)



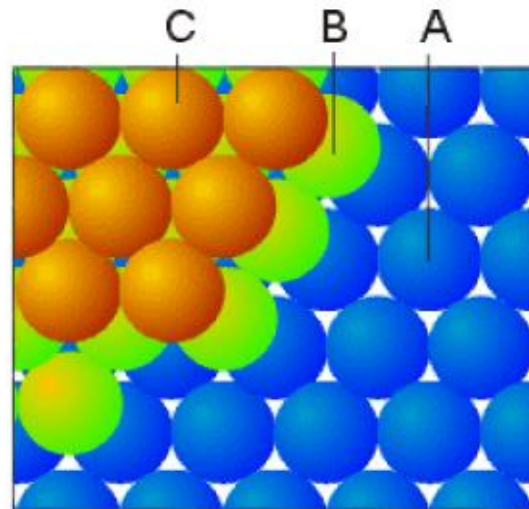
(a)

Hexagonal Close Packing



hcp

Mg, Be, Sc, Ti...

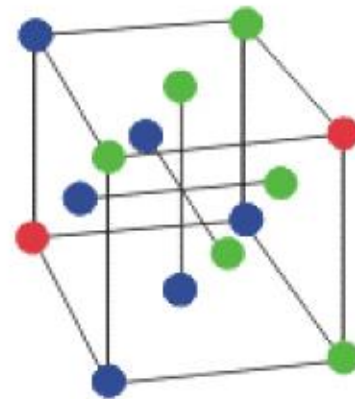


(b)



(b)

Cubic Close Packing



ccp/fcc

Cu, Ca, Sr, Ag, Au, ...

Close Packing of Spheres

The most efficient way to fill space with spheres

Is there another way of packing spheres that is more space-efficient?

In 1611 Kepler asserted that there was no way of packing equivalent spheres at a greater density than that of a face-centred cubic arrangement. This is now known as the **Kepler Conjecture**.

This assertion has long remained without rigorous proof. In 1998 Hales announced a computer-based solution. This proof is contained in over 250 manuscript pages and relies on over 3 gigabytes of computer files. It was reviewed by a panel of 12 referees; the panel reported in 2003, after 4 years of work, that it was “99% certain” of the correctness of the proof, but couldn’t verify all of the computer calculations. Hales and Ferguson (his student) received the Fulkerson Prize for outstanding papers in the area of discrete mathematics in 2009.

In 2003, Hales announced that he would pursue a formal proof of the Conjecture that could be verified by computer. He estimated that the proof would be finished by 2023...but it was announced complete on Aug 10, 2014!!!!

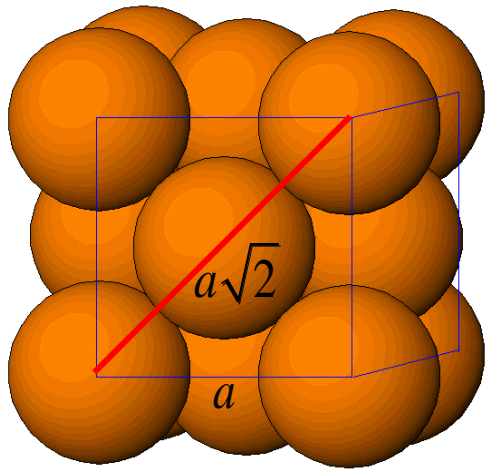
In January 2015 Hales and 21 collaborators published "A formal proof of the Kepler conjecture". The proof was accepted in 2017.

http://en.wikipedia.org/wiki/Kepler_conjecture

PACKING FRACTIONS

The fraction of the total crystal volume that is occupied by spheres

CCP (and HCP)

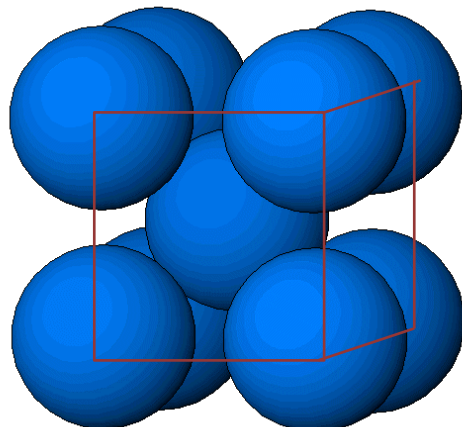


$$\text{radius} = \frac{a\sqrt{2}}{4}$$

$$\text{fraction} = \frac{V_{\text{atoms}}}{V_{\text{cell}}} = \frac{4 \times \frac{4}{3} \pi \left(\frac{a\sqrt{2}}{4}\right)^3}{a^3} = \frac{\pi}{6} \sqrt{2} = 0.7405$$

74%

BCC



$$\text{radius} = \frac{a\sqrt{3}}{4}$$

$$\text{fraction} = \frac{2 \times \frac{4}{3} \pi \left(\frac{a\sqrt{3}}{4}\right)^3}{a^3} = 0.6802$$

68%

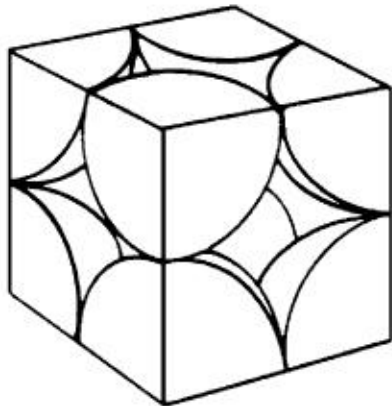
SC

$$\text{fraction} = \frac{\frac{4}{3} \pi \left(\frac{a}{2}\right)^3}{a^3} = 0.5236$$

52%

Close Packing of Spheres

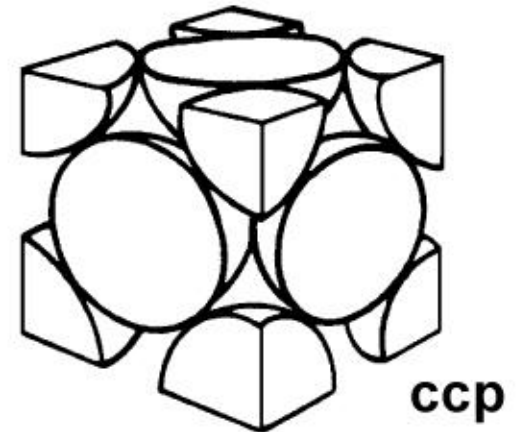
Comparison of Packing Efficiencies



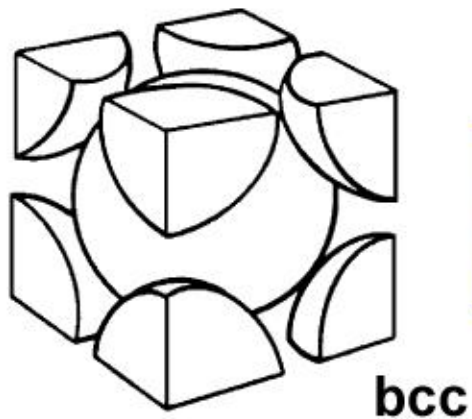
Primitive Cubic [α -Po]
Coordination Number 6
52% Packing Efficiency

$$V_{\text{atoms}}/V_{\text{cell}} = 0.52, \text{ since}$$
$$V_{\text{cell}} = a^3 \text{ and}$$
$$V_{\text{atoms}} = Z \frac{4}{3} \pi r^3$$

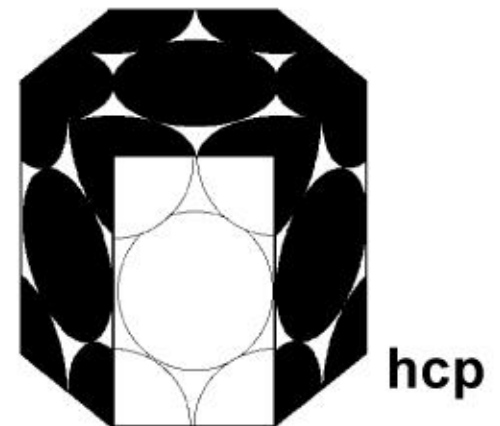
with $a = 2r$ and $Z = 1$



Close-Packed (ccp or hcp)
Coordination Number 12
74% Packing Efficiency



Body-Centered Cubic [W]
Coordination Number 8
68% Packing Efficiency



(increased pressure favors higher packing efficiency)

DENSITY CALCULATION

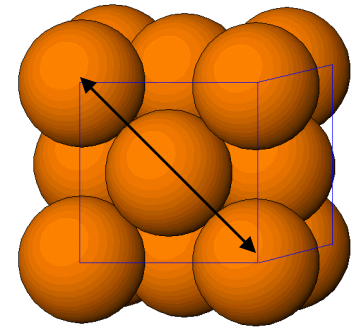
$$\rho = \frac{m_{atoms}}{V_{cell}} = \left(\frac{nA}{N_A} \right) \frac{1}{V_C}$$

n : number of atoms/unit cell

A : atomic mass

V_C : volume of the unit cell

N_A : Avogadro's number
(6.023×10^{23} atoms/mole)



Calculate the density of copper.

$R_{Cu} = 0.128 \text{ nm}$, Crystal structure: FCC, $A_{Cu} = 63.5 \text{ g/mole}$

$$n = 4 \text{ atoms/cell}, \quad V_C = a^3 = (2\sqrt{2}R)^3 = 16\sqrt{2}R^3$$

$$\rho = \frac{(4)(63.5)}{[16\sqrt{2}(1.28 \times 10^{-8})^3 \times (6.023 \times 10^{23})]} = 8.89 \text{ g/cm}^3$$

8.96 g/cm³ in the literature

INTERSTITIAL SITES IN CP STRUCTURES

A large number of ionic structures can be regarded as built of CP layers of anions with the cations placed in interstitial sites

for every anion, there is 1 Octahedral site and 2 Tetrahedral sites

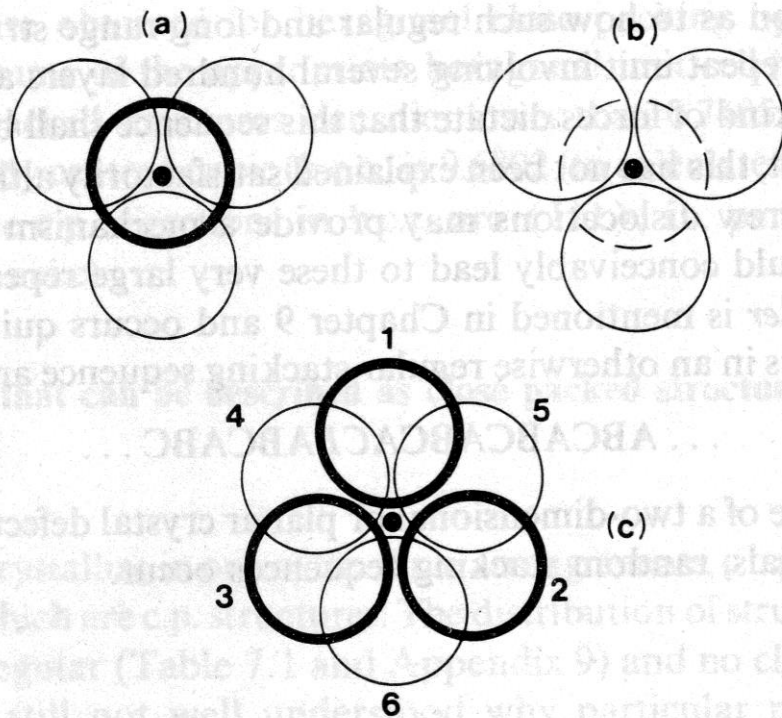
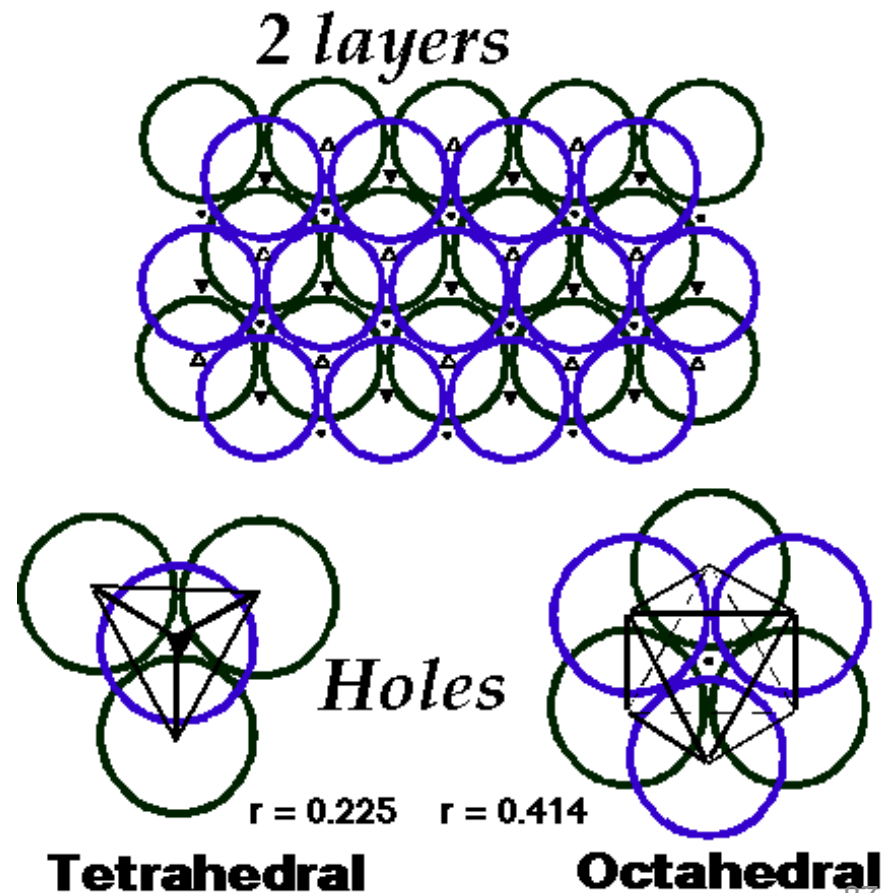


Fig. 7.7 Interstitial sites in a c.p. structure. Heavy circles are above and the dashed circles below the plane of the paper: (a) T_+ site, (b) T_- site, (c) O site





Octahedral holes

coordinates:

$\frac{1}{2}00$

$0\frac{1}{2}0$

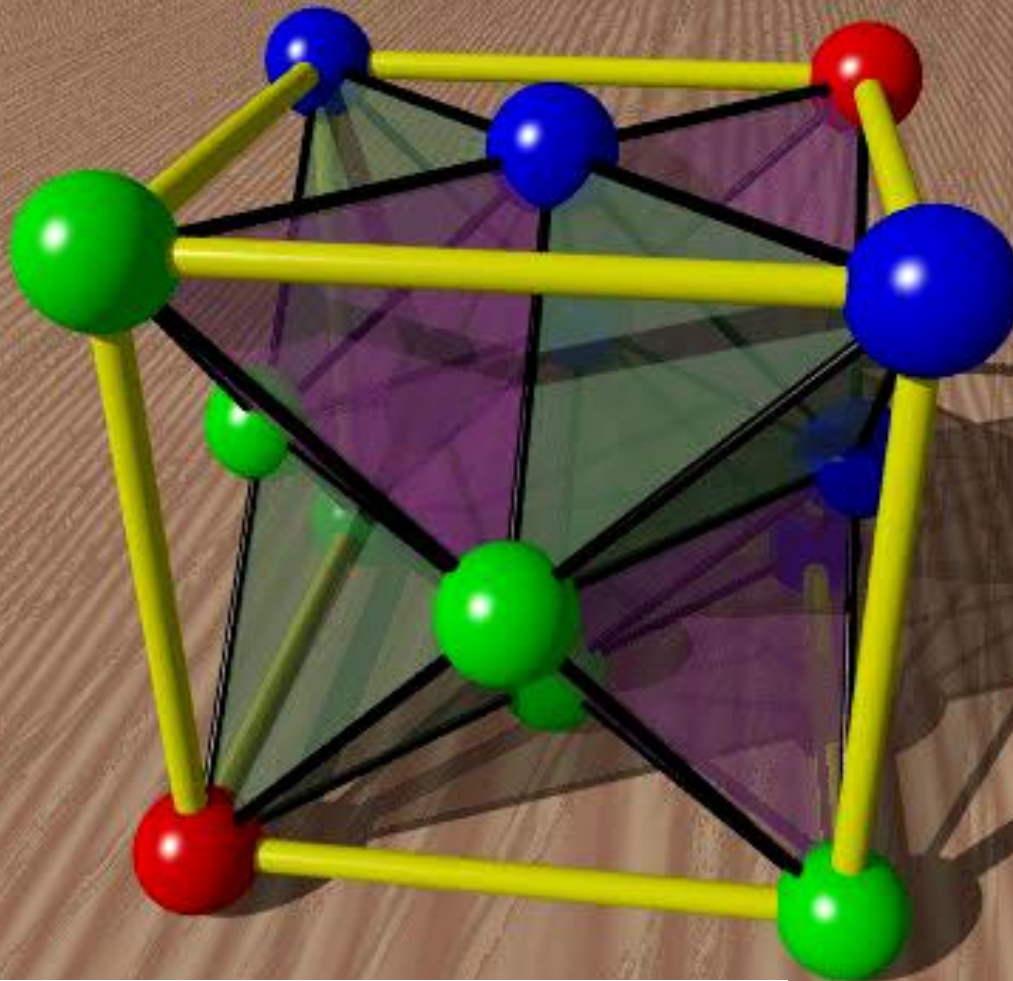
$00\frac{1}{2}$

$\frac{1}{2}\frac{1}{2}\frac{1}{2}$

+ = O site

**cavities have $\langle 100 \rangle$
orientation**

Tetrahedral holes in CCP



T₊ sites:

$$\frac{3}{4}\frac{1}{4}\frac{1}{4}$$

$$\frac{1}{4}\frac{3}{4}\frac{1}{4}$$

$$\frac{1}{4}\frac{1}{4}\frac{3}{4}$$

$$\frac{3}{4}\frac{3}{4}\frac{3}{4}$$

T₋ sites:

$$\frac{1}{4}\frac{1}{4}\frac{1}{4}$$

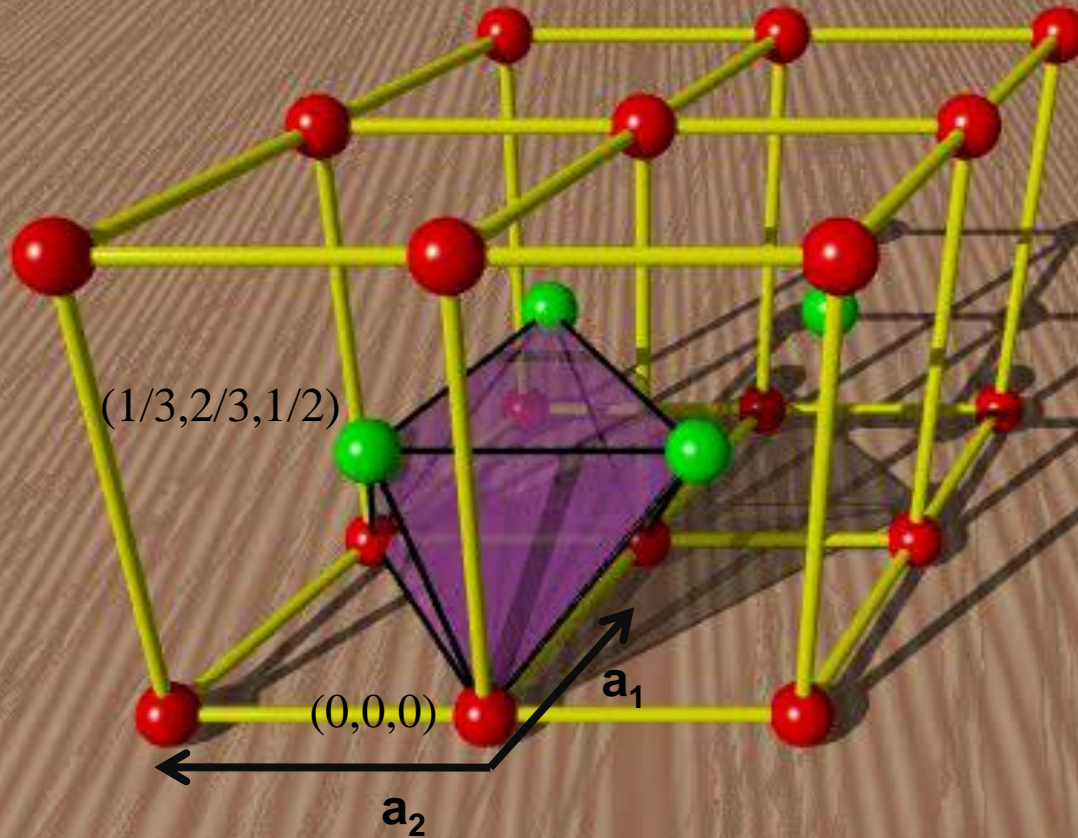
$$\frac{3}{4}\frac{3}{4}\frac{1}{4}$$

$$\frac{1}{4}\frac{3}{4}\frac{3}{4}$$

$$\frac{3}{4}\frac{1}{4}\frac{3}{4}$$

cavities have $\langle 111 \rangle$ orientation

Holes in HCP



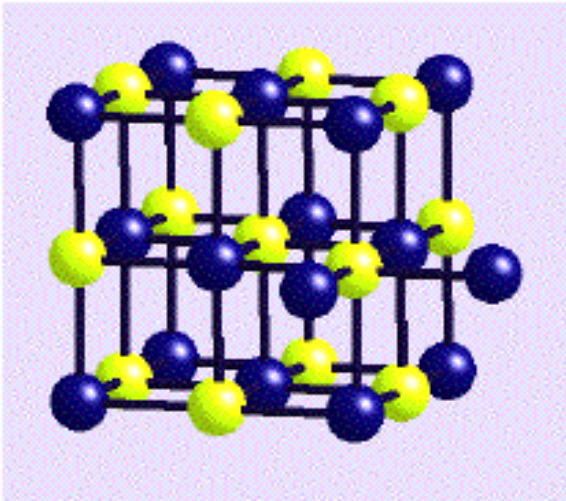
O sites:
 $2/3, 1/3, 1/4$
 $2/3, 1/3, 3/4$

T_+ sites:
 $1/3, 2/3, 1/8$
 $0, 0, 5/8$

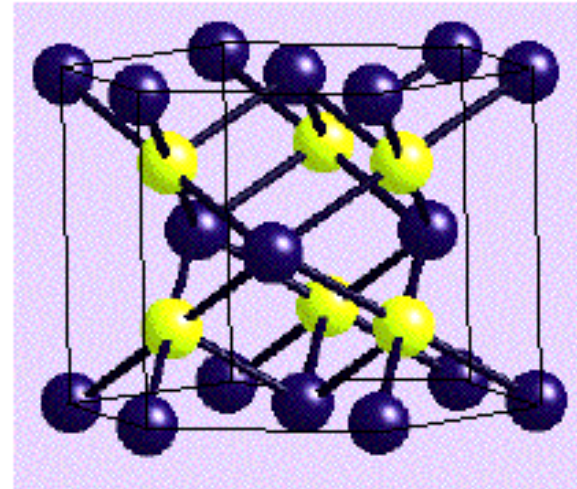
T_- sites:
 $0, 0, 3/8$
 $1/3, 2/3, 7/8$

LOCATION OF OCTAHEDRAL HOLES

CCP



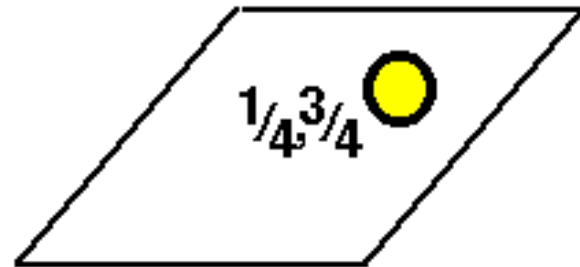
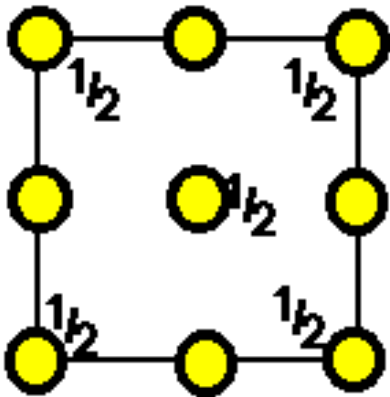
HCP



Location
of

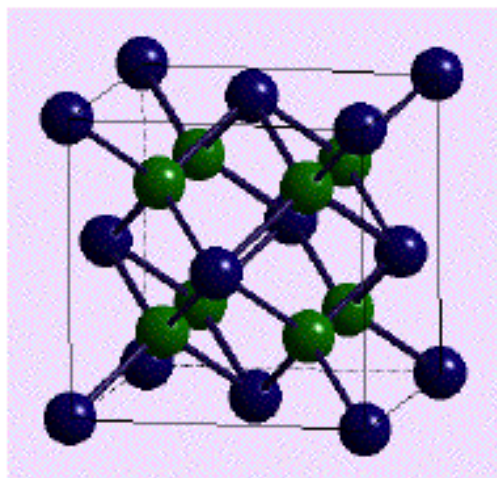
OCTAHEDRAL
Interstitial
Holes

1 per sphere

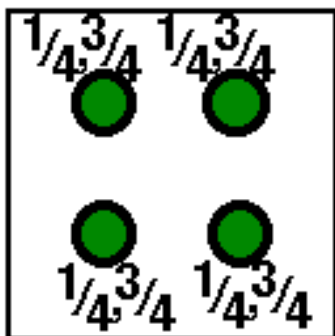
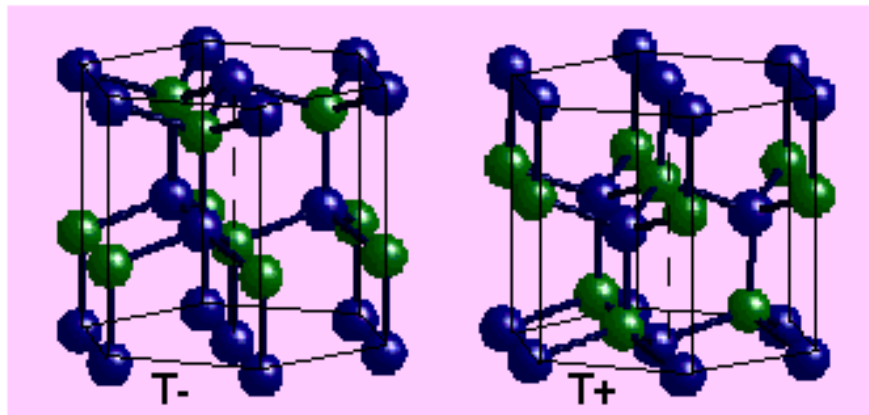


LOCATION OF TETRAHEDRAL HOLES

CCP

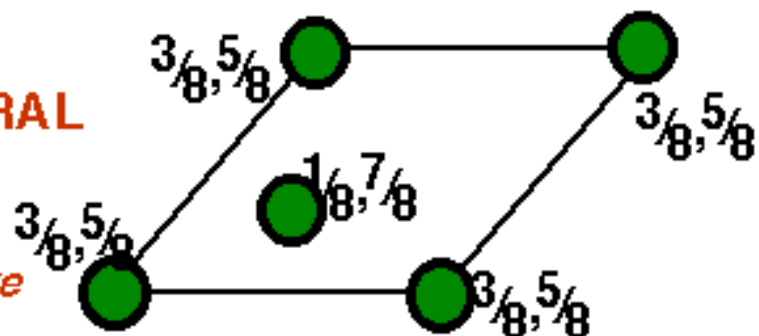


HCP



Location
of
TETRAHEDRAL
Interstitial
Holes

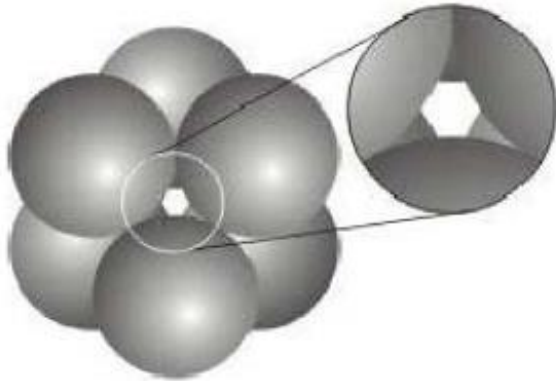
2 per sphere



(3/8 of a unit cell directly
above/below each anion)

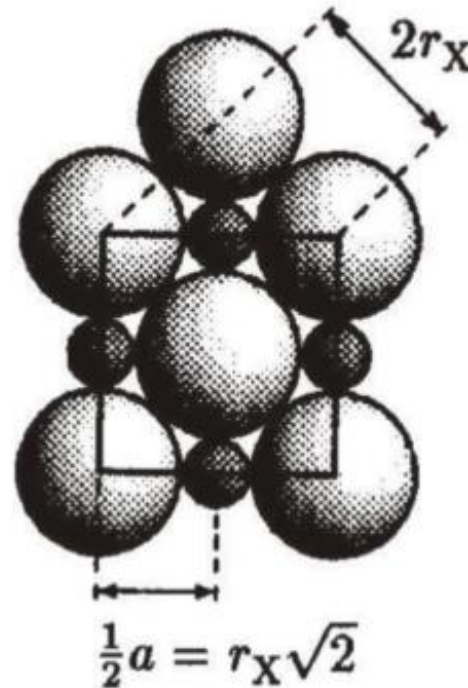
SIZE OF OCTAHEDRAL CAVITY

Only cations smaller than the diameter of the cavity can fit without forcing the anion lattice to expand



M = cation
X = anion

face of unit cell



from cell edge

$$a = 2r_M + 2r_X$$

from face diagonal

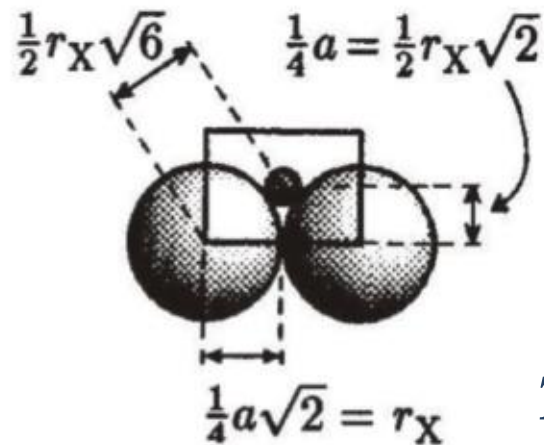
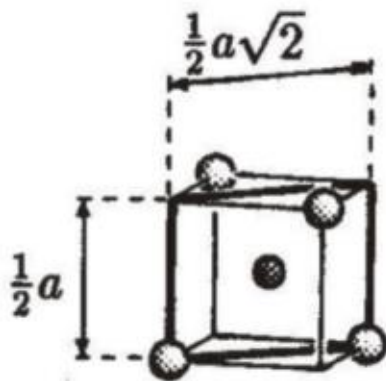
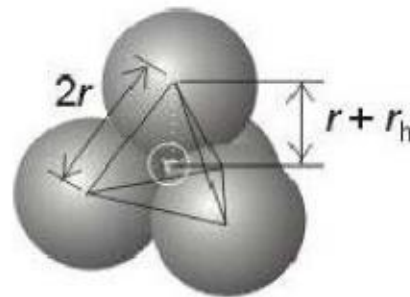
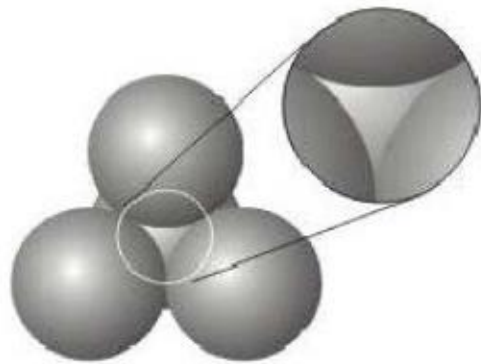
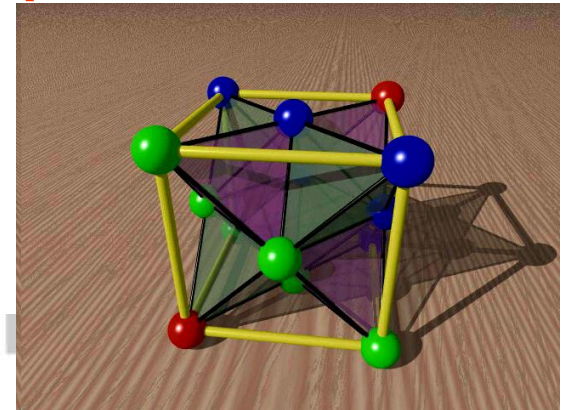
$$a = 2\sqrt{2}r_X$$

$$\begin{aligned}r_M + r_X &= r_X\sqrt{2} \\ r_M/r_X &= \sqrt{2} - 1 \\ &= 0.414\end{aligned}$$

The cavity radius is 41% of the anion radius

SIZE OF TETRAHEDRAL CAVITY

The tetrahedral holes are twice as numerous but six times smaller in volume



$$r_M + r_X = r_X \cdot \frac{1}{2}\sqrt{6}$$

$$r_M/r_X = \frac{1}{2}\sqrt{6} - 1$$

$$= 0,225$$

The cavity radius is 22.5% of the anion radius

EUTACTIC STRUCTURES

Structures in which the arrangement of ions is the same as in a close packed array but the ions are not necessarily touching

Within certain loose limits (given by the *radius ratio rules*), cations too large to fit in the interstices can be accommodated by an expansion of the anion array

- *anions don't like to touch anyway*
- *modern techniques show that, in many cases, anions (cations) are not as large (small) as previously thought*
- *we still describe eutactic structures as CCP or HCP lattices with ions in some fraction of the interstitial sites*

CRYSTALS THAT CAN BE DESCRIBED IN TERMS OF INTERSTITIAL FILLING OF A CLOSE-PACKED STRUCTURE

SOME EUTACTIC CRYSTAL STRUCTURES

Variables:

- 1) anion layer stacking sequence: CCP or HCP array?
- 2) occupancy of interstitial sites

Anion arrangement	Interstitial sites			Examples
	T_+	T_-	Oct	
c.c.p.	—	—	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
	1	—	—	CuFeS ₂
	—	—	$\frac{1}{3}$	CrCl ₃
h.c.p.	1	1	—	K ₂ O antifluorite
	—	—	1	NiAs ←
	1	—	—	ZnS, wurtzite
	—	—	$\frac{1}{2}$	CdI ₂
	—	—	$\frac{1}{2}$	TiO ₂ *, rutile
	—	—	$\frac{2}{3}$	Al ₂ O ₃
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{3}{2}$	Mg ₂ SiO ₄ , olivine ←
	1	—	—	β -Li ₃ PO ₄
$\frac{1}{2}$	$\frac{1}{2}$	—	γ -Li ₃ PO ₄ *	
c.c.p. 'CaO ₃ ' layers	—	—	$\frac{1}{4}$	CaTiO ₃ perovskite

* The h.c.p. oxide layers in rutile and γ -Li₃PO₄ are not planar but are buckled. The oxide ion arrangement in these may alternatively be described as tetragonal packed (t.p.).

Structures obtained by filling Octahedral Holes

Structure	Fraction Holes Filled	Packing
NaCl	1	ccp
NiAs	1	hcp
CdCl ₂	1/2	ccp
CdI ₂	1/2	hcp
TiO ₂ [†]	1/2	hcp
Al ₂ O ₃	2/3	hcp

[†] The hcp anion layers are buckled in rutile.

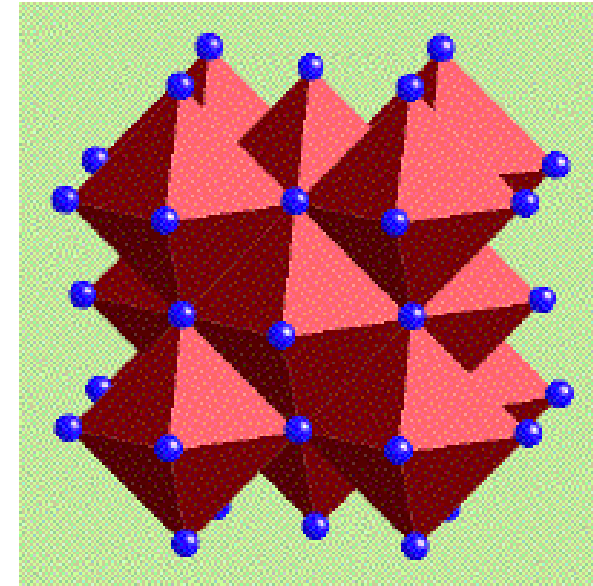
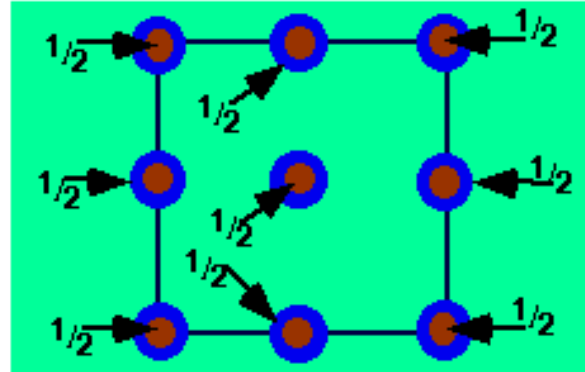
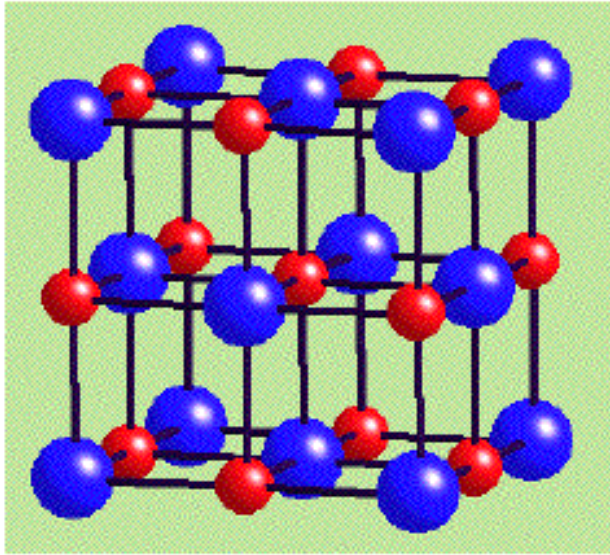
Structures obtained by filling Tetrahedral Holes

Structure	Fraction Holes Filled	Packing
Fluorite [‡]	1	ccp
Sphalerite	1/2	ccp
Wurtzite	1/2	hcp

[‡]In fluorite (i.e. CaF₂) the cations are close packed and the anions fill the tetrahedral holes. The opposite is true of the antifluorite structure (Na₂O)

NaCl (ROCK SALT, HALITE) STRUCTURE

(CCP, 100% Oct. Holes Filled)



Space Group = $Fm\bar{3}m$

Lattice = FCC

Basis = Cl (0,0,0), Na ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$)

Coordination = 6, 6

Cation Coord. → Octahedron

Anion Coord. → Octahedron

Connectivity → Edge sharing octahedra
with faces parallel to {111}

4 NaCl in unit cell

Table 7.5 Some compounds with the NaCl structure

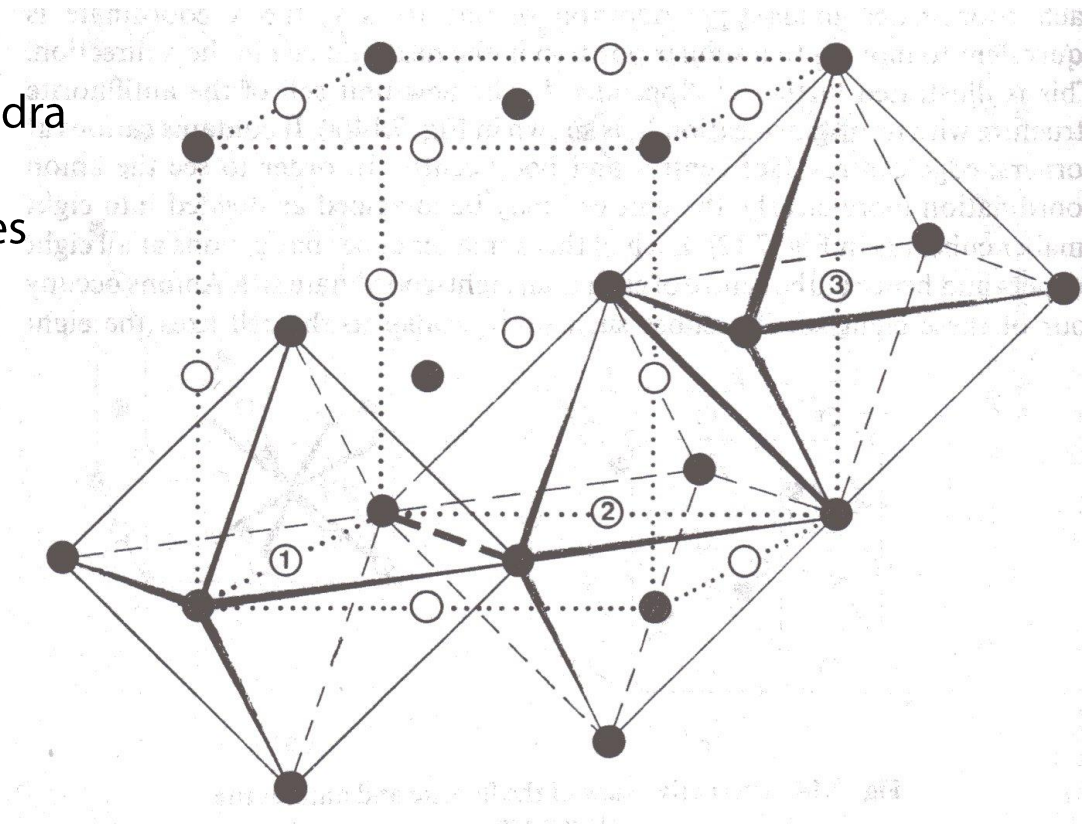
	$a(\text{\AA})$		$a(\text{\AA})$		$a(\text{\AA})$		$a(\text{\AA})$
MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	α MnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	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	NaH	4.890	AgCl	5.549
SnAs	5.7248	SrTe	6.660	ScN	4.44	AgBr	5.7745
TiC	4.3285	BaTe	7.00	TiN	4.240	CsF	6.014
UC	4.955	LaN	5.30	UN	4.890		

POLYHEDRAL REPRESENTATION

- *shows the topology and indicates interstitial sites*
- *tetrahedra and octahedra are the most common shapes*

Rock Salt:

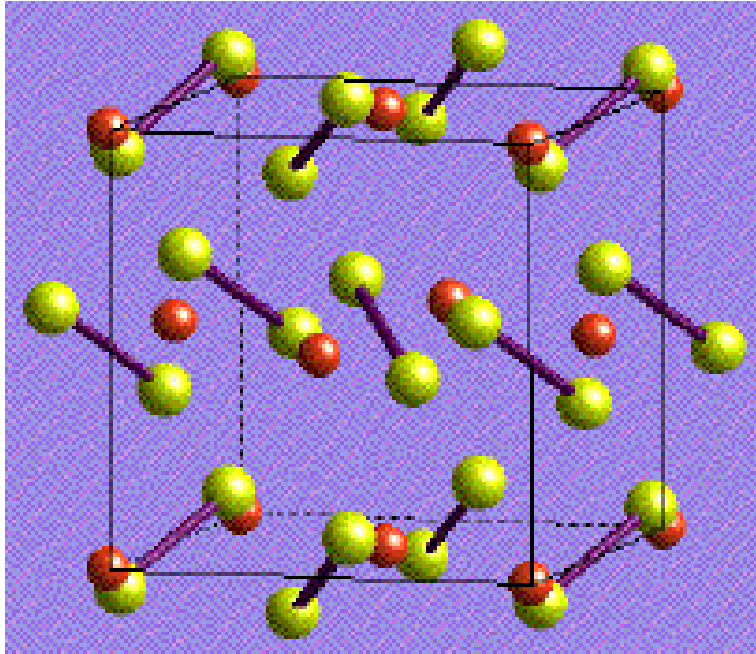
- Array of edge sharing NaCl_6 octahedra
- Each octahedron shares all 12 edges
- Tetrahedral interstices



ROCK SALT - OCCURANCE

- Very common (inc. 'ionics', 'covalents' & 'intermetallics')
- Most alkali halides (CsCl , CsBr , CsI excepted)
- Most oxides / chalcogenides of alkaline earths
- Many nitrides, carbides, hydrides (e.g. ZrN , TiC , NaH)

COMPLEX ION VARIANT OF ROCK SALT



FeS₂

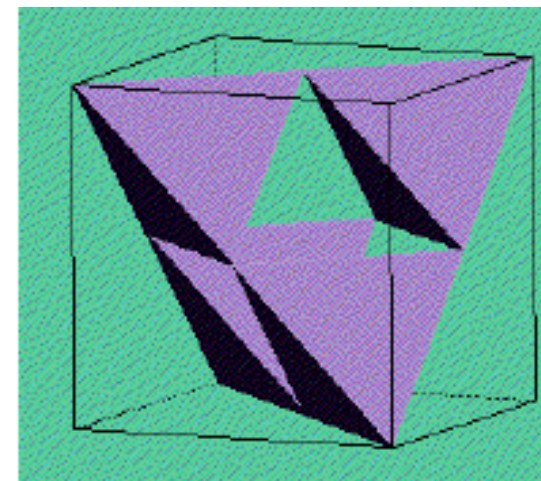
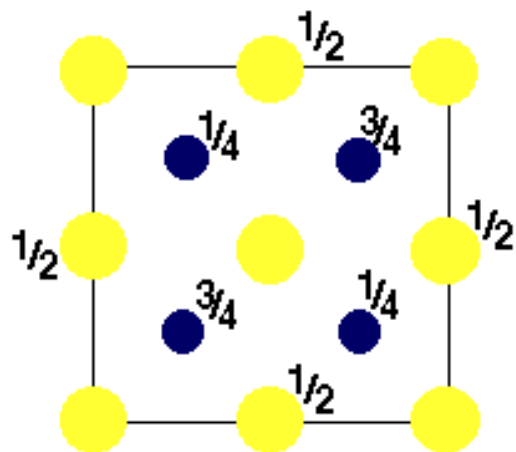
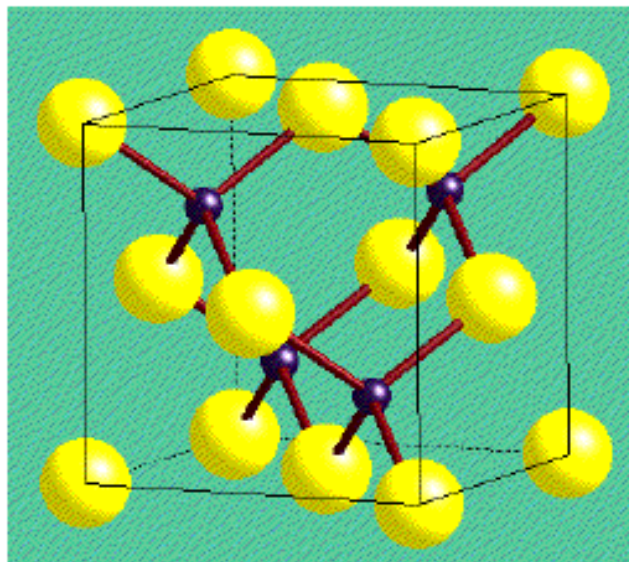
Pyrite

- space group = $\text{Pa}\bar{3}$
- S_2^{2-} dimers oriented along $\langle 111 \rangle$



ZINC BLENDE (ZnS, SPHALERITE)

(CCP, T+ Holes Filled)



Space Group = $F\bar{4}3m$

Lattice = FCC

Basis = S (0,0,0), Zn ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)

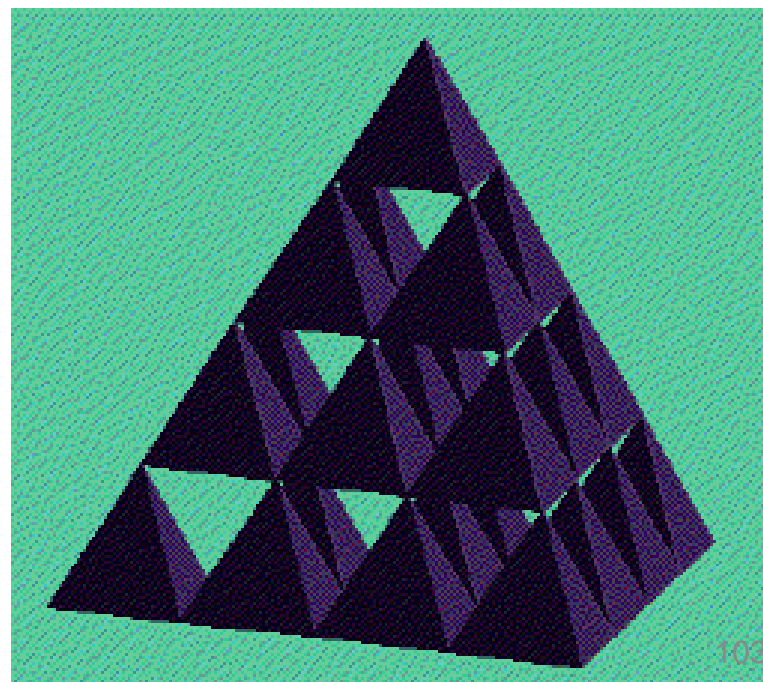
Coordination = 4, 4

Cation Coord. → Tetrahedron

Anion Coord. → Tetrahedron

Connectivity → Corner sharing Tetra.

4 ZnS in unit cell



ZINC BLENDE



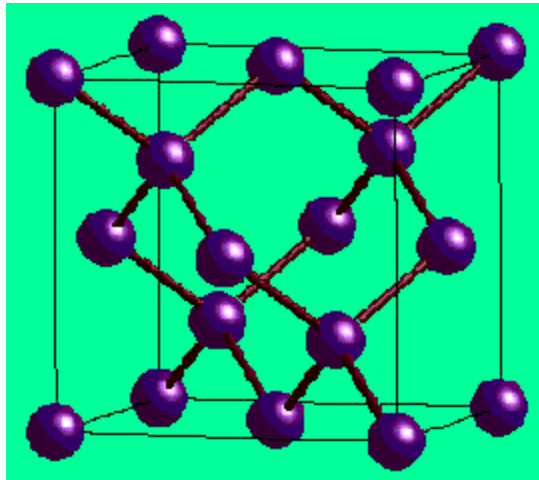
- *bonding is less ionic than in rock salt*
- *common for Be, Zn, Cd, Hg chalcogenides (i.e., ZnS, ZnSe, ZnTe)*
- *common for III-V compounds (B, Al, Ga, In with N, P, As, Sb)*

Table 7.6 Some compounds with the zinc blende (sphalerite) structure

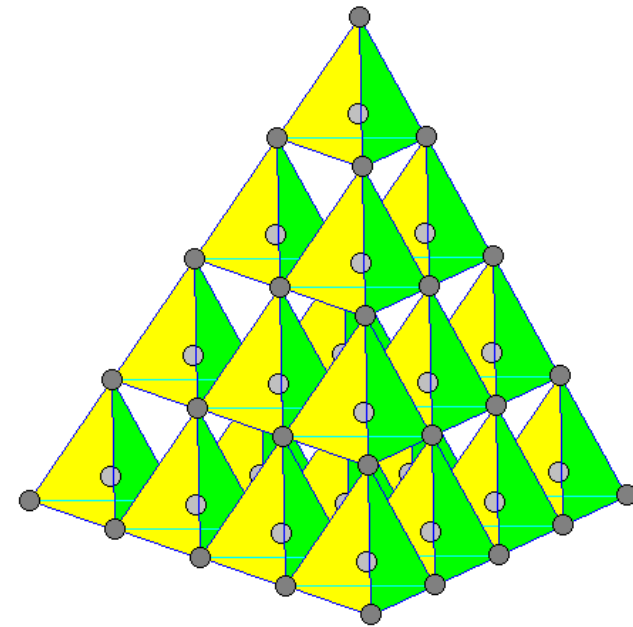
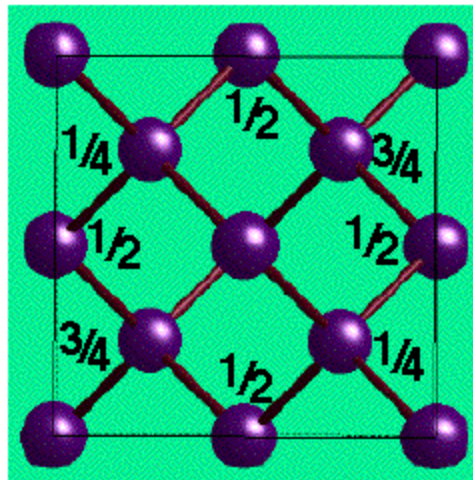
	$a(\text{\AA})$		$a(\text{\AA})$		$a(\text{\AA})$		$a(\text{\AA})$		$a(\text{\AA})$
CuF	4.255	BeS	4.8624	β -CdS	5.818	BN	3.616	GaP	5.448
CuCl	5.416	BeSe	5.07	CdSe	6.077	BP	4.538	GaAs	5.6534
γ -CuBr	5.6905	BeTe	5.54	CdTe	6.481	BA _s	4.777	GaSb	6.095
γ -CuI	6.051	β -ZnS	5.4060	HgS	5.8517	AlP	5.451	InP	5.869
γ -AgI	6.495	ZnSe	5.667	HgSe	6.085	AlAs	5.662	InAs	6.058
β -MnS, red	5.600	ZnTe	6.1026	HgTe	6.453	AlSb	6.1347	InSb	6.4782
β -MnSe	5.88	β -SiC	4.358						

DIAMOND STRUCTURE

Same as sphalerite, but with identical atoms in all positions



Unit Cell



Space Group = $Fd\bar{3}m$

Lattice = FCC

Basis = C (0,0,0), C ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)

Coordination = 4

Connectivity → Corner sharing Tetra.

8 C atoms per unit cell

TABLE 1.9 Elemental Crystals with the Diamond Crystal Structure

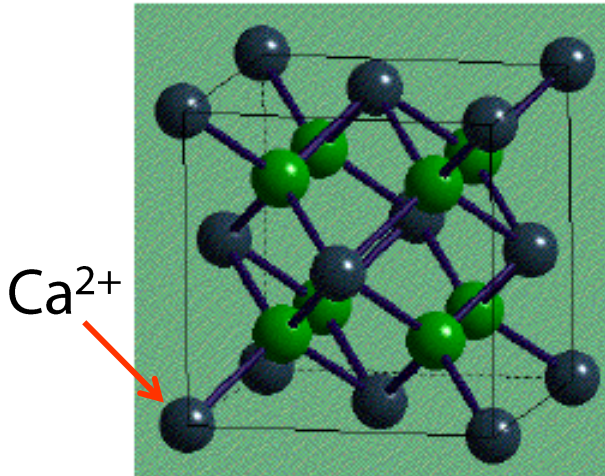
Element	a (nm) ^a	Element	a (nm) ^a
C	0.3567	Si	0.543
Ge	0.5657	Sn (gray)	0.649

^aLattice constants are values at room temperature.

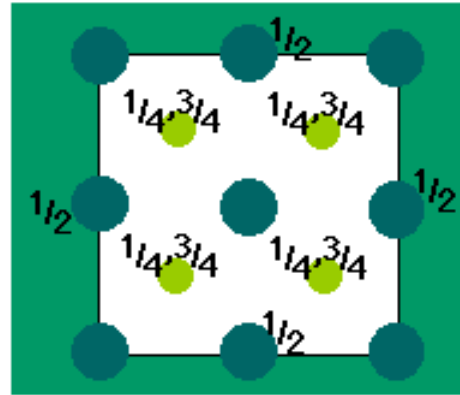
FLUORITE (CaF_2) & ANTIFLUORITE (Na_2O)

Fluorite : CCP of Ca^{2+} , 100% Tetra. Holes Filled with F^-

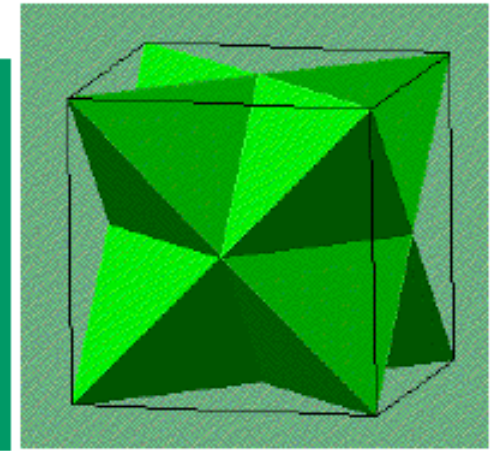
Anti-fluorite : cation and anion positions are reversed



Fluorite A-cell



Plan view



FCa_4 Tetrahedra

Space Group = $\text{Fm}\bar{3}\text{m}$

Lattice = FCC

Basis = Ca^{2+} (0,0,0), F^- ($1/4, 1/4, 1/4$) & ($3/4, 3/4, 3/4$)

Coordination = 8, 4 (fluorite)

Cation Coord. \rightarrow Cubic

Anion Coord. \rightarrow Tetrahedral

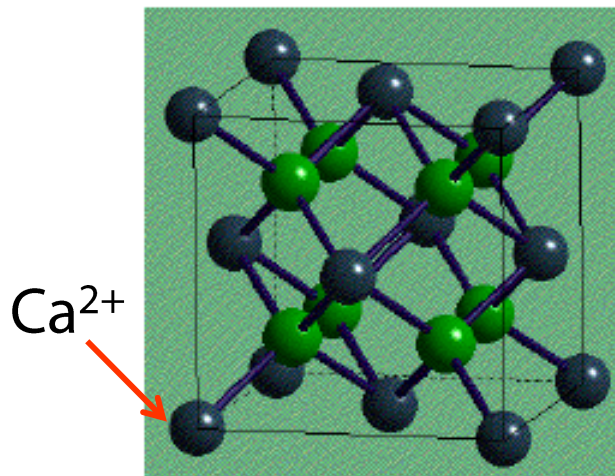
Connectivity \rightarrow Edge sharing FCa_4 tetrahedra or edge sharing CaF_8 cubes

4 CaF_2 in unit cell

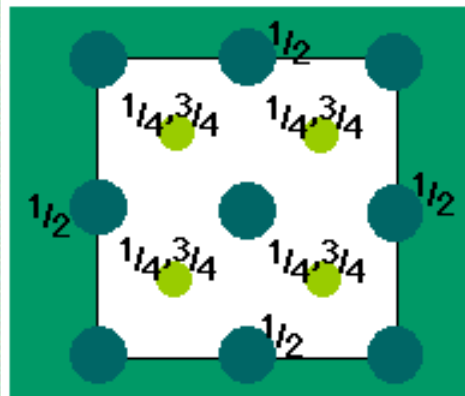
Table 7.7 Some compounds with fluorite and antifluorite structure

Fluorite structure		Antifluorite structure					
$a(\text{\AA})$	$a(\text{\AA})$	$a(\text{\AA})$	$a(\text{\AA})$				
CaF_2	5.4626	PbO_2	5.349	Li_2O	4.6114	K_2O	6.449
SrF_2	5.800	CeO_2	5.4110	Li_2S	5.710	K_2S	7.406
SrCl_2	6.9767	PrO_2	5.392	Li_2Se	6.002	K_2Se	7.692
BaF_2	6.2001	ThO_2	5.600	Li_2Te	6.517	K_2Te	8.168
BaCl_2	7.311	PaO_2		Na_2O	5.55	Rb_2O	6.74
CdF_2	5.3895	UO_2	5.372	Na_2S	6.539	Rb_2S	7.65
HgF_2	5.5373	NpO_2	5.4334	Na_2Se	6.823		
EuF_2	5.836	PuO_2	5.386	Na_2Te	7.329		
$\beta\text{-PbF}_2$	5.940	AmO_2	5.376				
		CmO_2	5.3598				

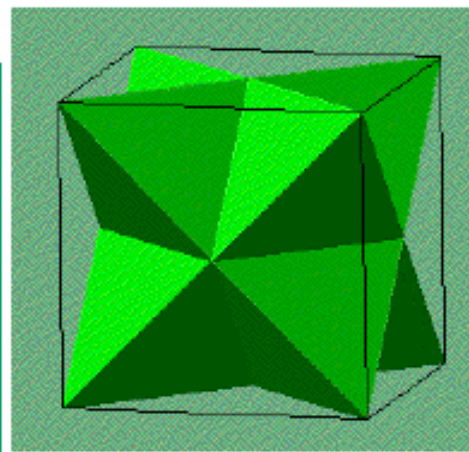
ALTERNATIVE REPRESENTATIONS



Fluorite A-cell

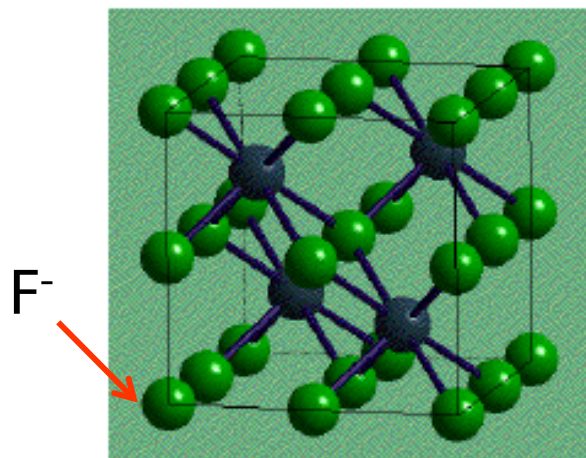


Plan view

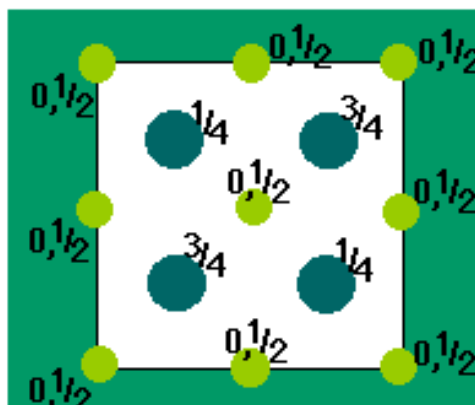


FCa₄ Tetrahedra

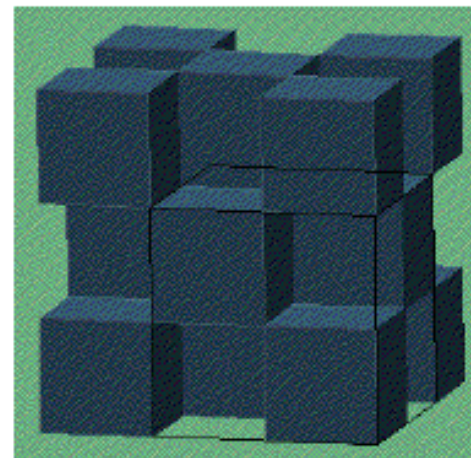
Displacing the unit cell by $\frac{1}{4}$ of a body diagonal emphasizes the cubic cation coordination:



Fluorite B-cell

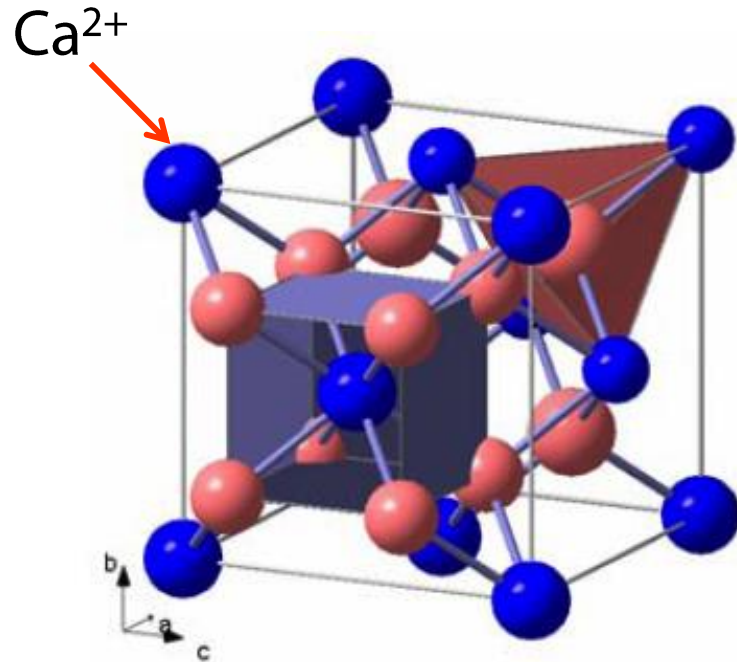


Plan view

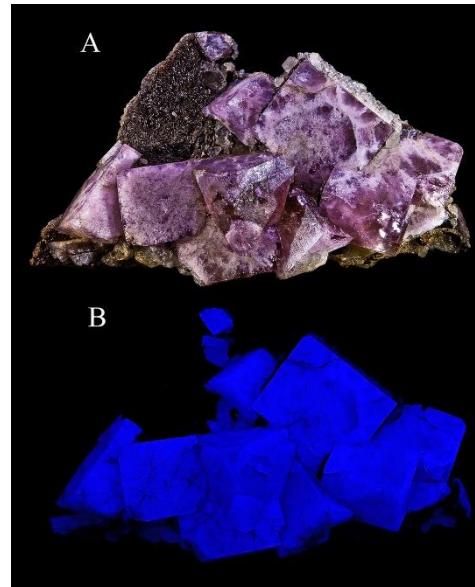


CaF₈ Cubes

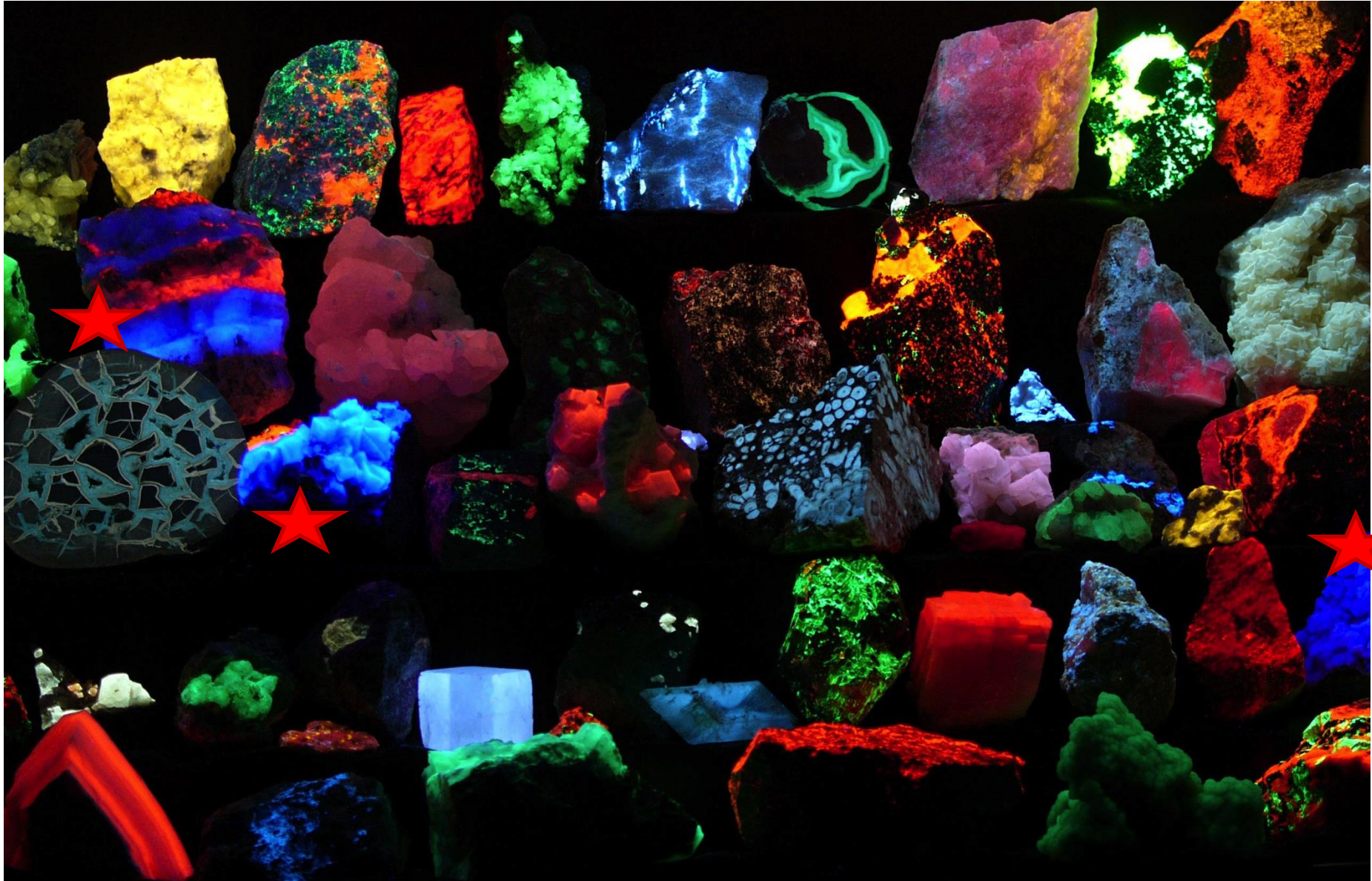
FLUORITE / ANTIFLUORITE



- *origin of the term “fluorescence”* (George Stokes, 1852)
- *fluorite common for fluorides of large, divalent cations and oxides of large tetravalent cations (M^{2+}F_2 and M^{4+}O_2)*
- *antifluorite common for oxides/chalcogenides of alkalis (M_2O)*



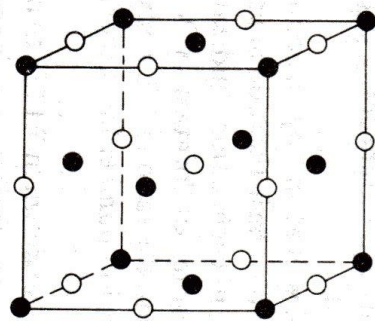
FLUORESCENT MINERALS



★ = fluorite

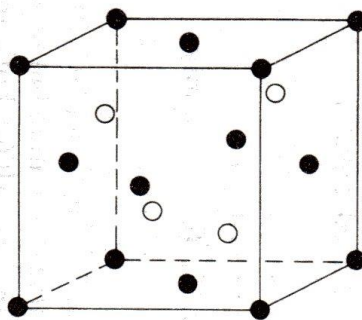
COMPARING NaCl, ZnS, Na₂O

NaCl



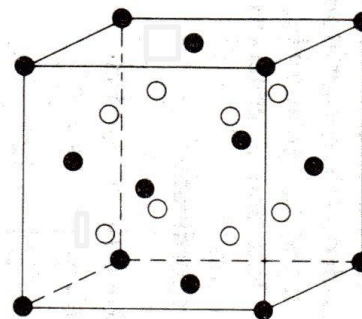
(a)

ZnS

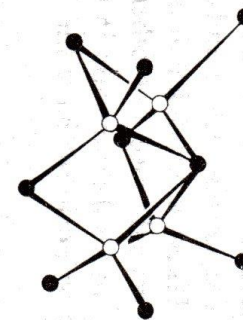
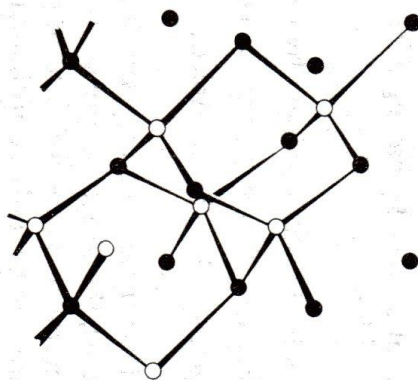
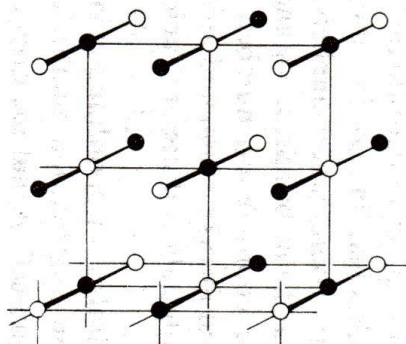


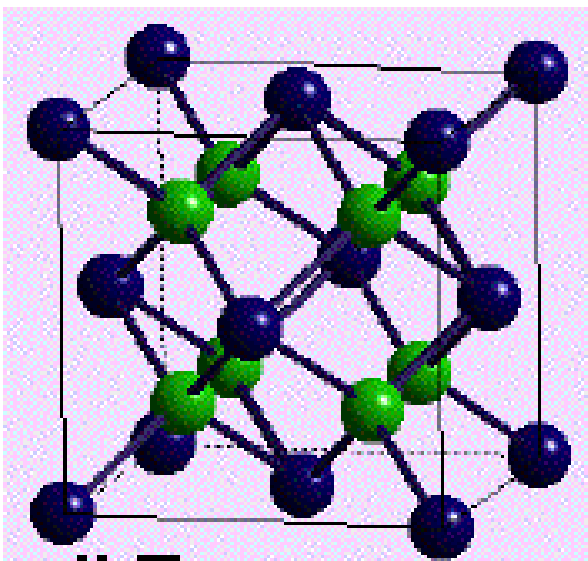
(b)

Na₂O



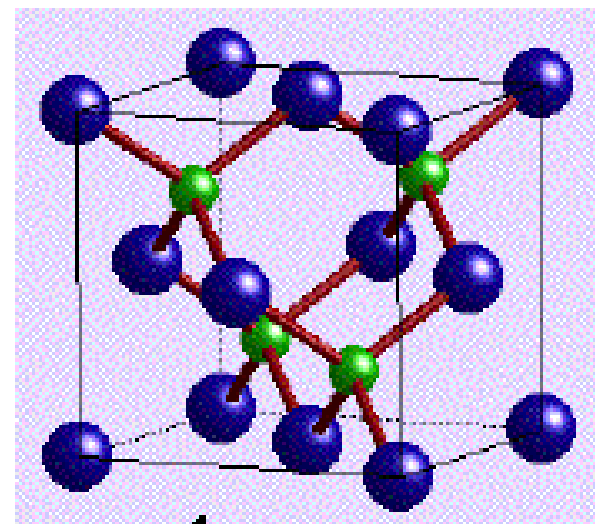
(c)





CaF₂

ZnS

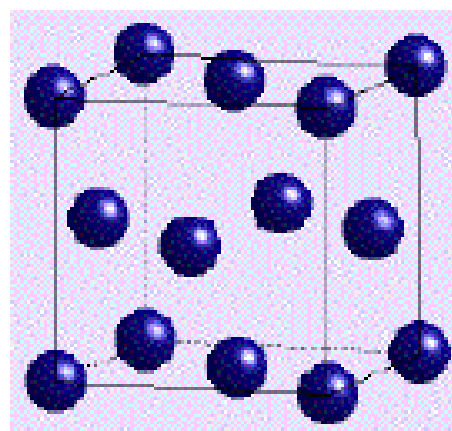


all T

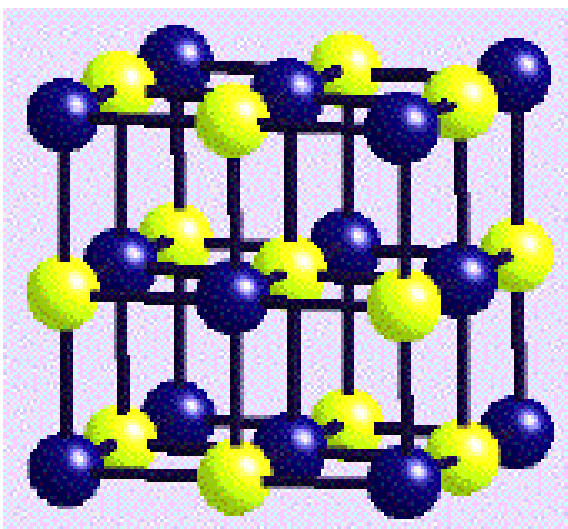
$\frac{1}{2}$ T (T+ only)

all O

all O & T

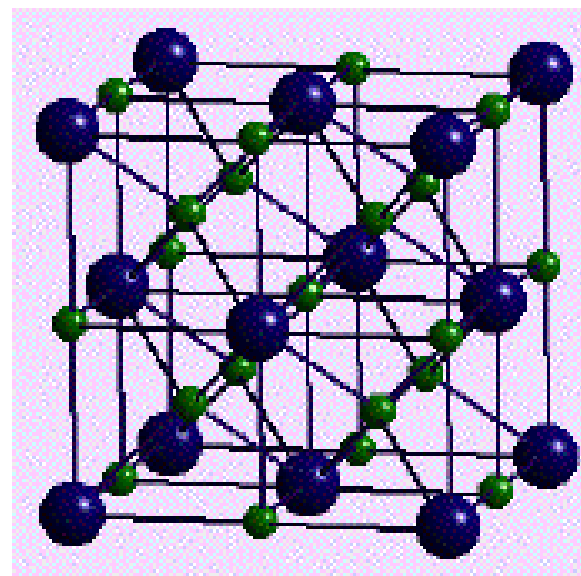


CCP



NaCl

Li₃Bi



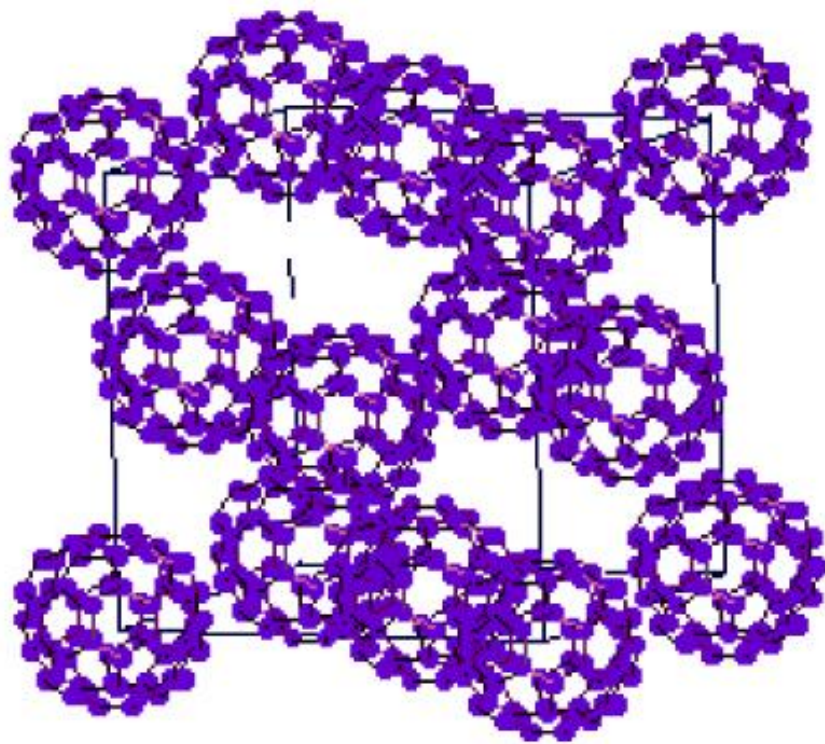
Li₃Bi EXAMPLE

ccp

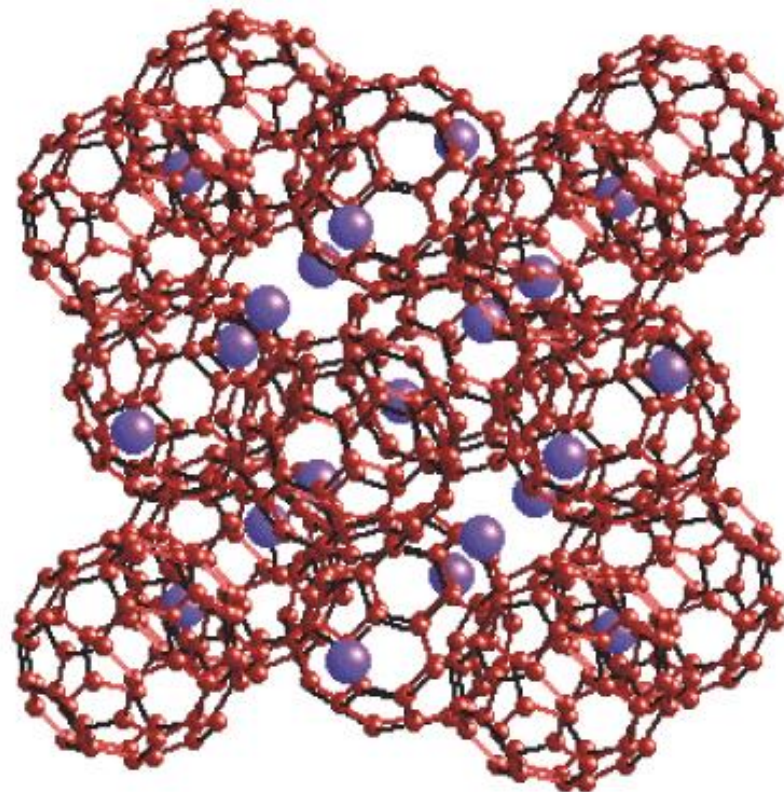


Li₃Bi type

filling of all O_h and T_d voids



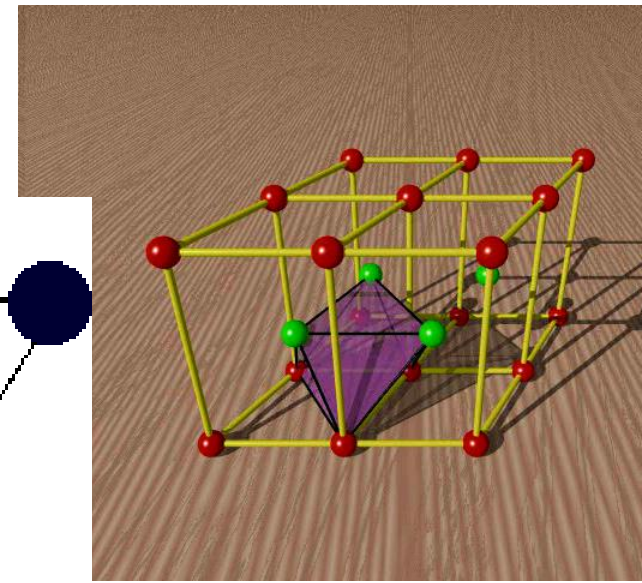
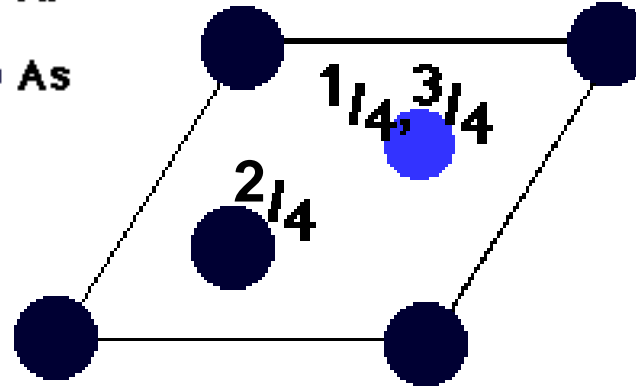
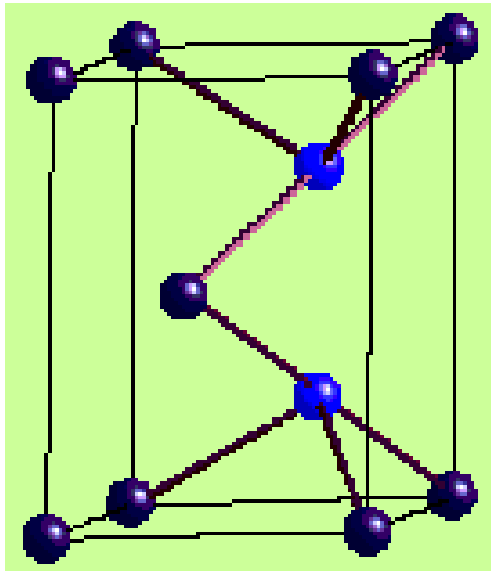
C₆₀



K₃C₆₀

NiAs STRUCTURE

(HCP, 100% Oct. Holes Filled)



Space Group = $P6_3/mmc$

Lattice = Primitive hexagonal

Basis = As (0,0,0) & (2/3,1/3,1/2)

Ni (1/3,2/3,1/4) & (1/3,2/3,3/4)

Coordination = 6, 6

Cation Coord. → Octahedron

Anion Coord. → Trigonal prism

Connectivity → Edge/face sharing Oct.
or edge-sharing trigonal prisms

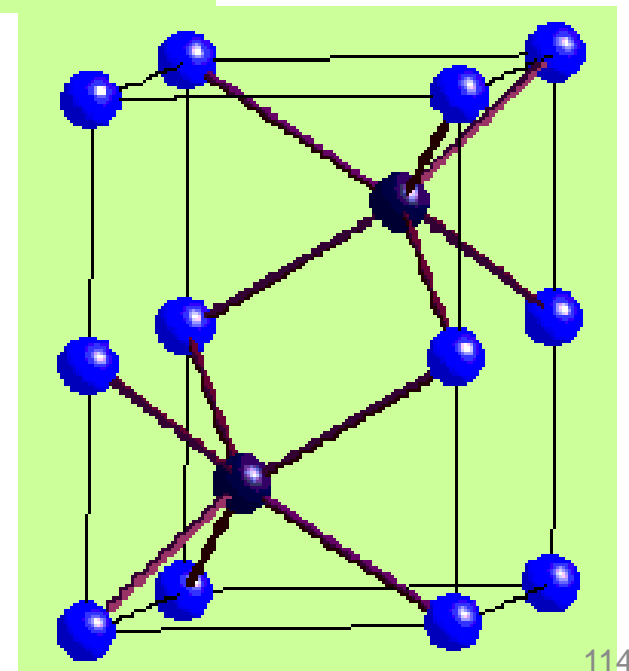
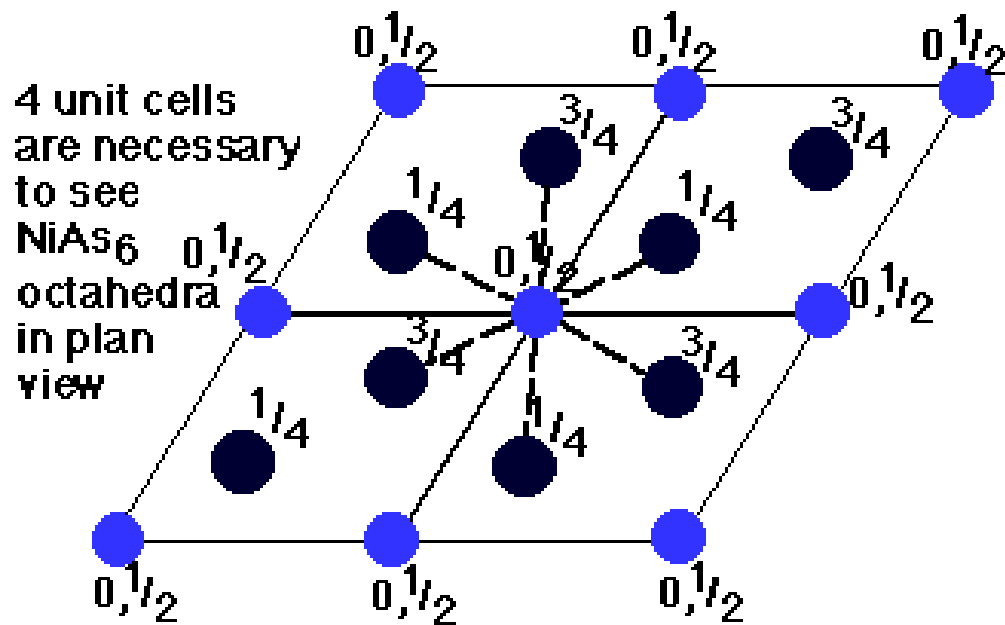
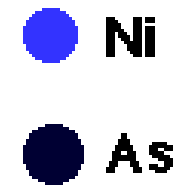
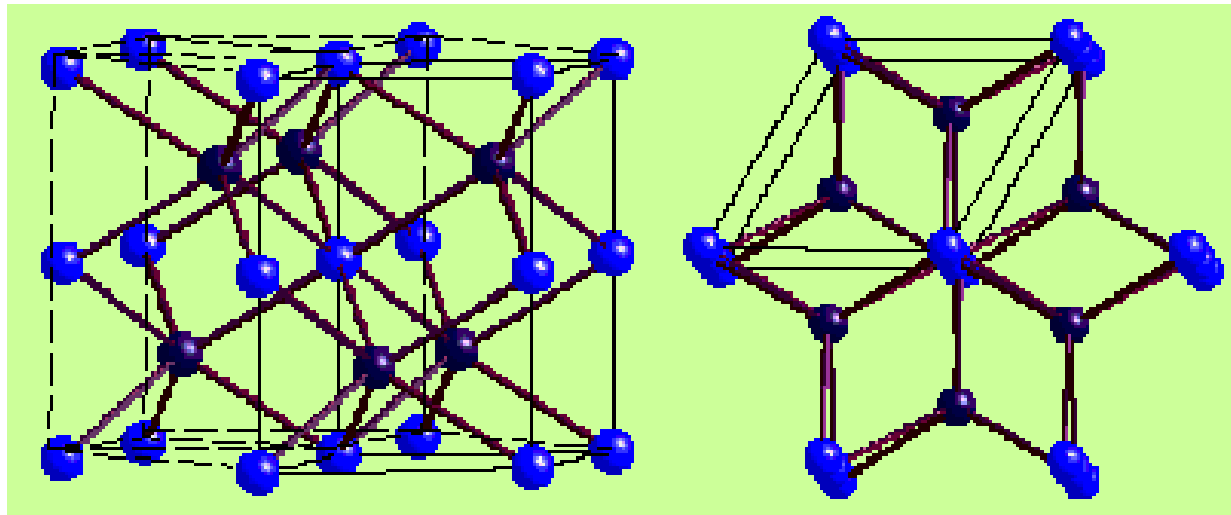
2 NiAs in unit cell

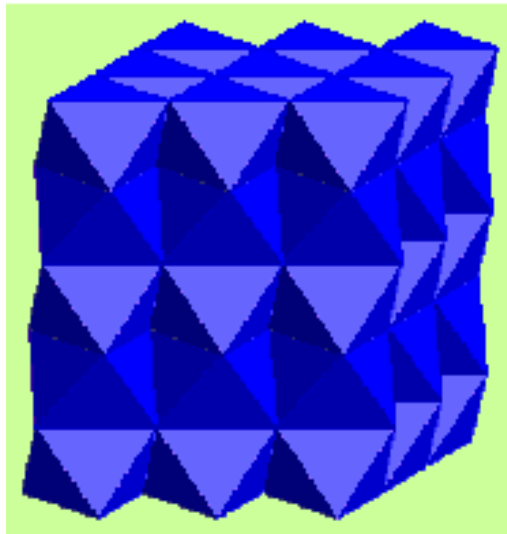
Table 7.10 Some compounds with the NiAs structure. (Data taken from Wyckoff, 1971, Vol. 1)

	$a(\text{\AA})$	$c(\text{\AA})$	c/a		$a(\text{\AA})$	$c(\text{\AA})$	c/a
NiS	3.4392	5.3484	1.555	CoS	3.367	5.160	1.533
NiAs	3.602	5.009	1.391	CoSe	3.6294	5.3006	1.460
NiSb	3.94	5.14	1.305	CoTe	3.886	5.360	1.379
NiSe	3.6613	5.3562	1.463	CoSb	3.866	5.188	1.342
NiSn	4.048	5.123	1.266	CrSe	3.684	6.019	1.634
NiTe	3.957	5.354	1.353	CrTe	3.981	6.211	1.560
FeS	3.438	5.880	1.710	CrSb	4.108	5.440	1.324
FeSe	3.637	5.958	1.638	MnTe	4.1429	6.7031	1.618
FeTe	3.800	5.651	1.487	MnAs	3.710	5.691	1.534
FeSb	4.06	5.13	1.264	MnSb	4.120	5.784	1.404
δ' -NbN*	2.968	5.549	1.870	MnBi	4.30	6.12	1.423
PtB*	3.358	4.058	1.208	PtSb	4.130	5.472	1.325
PtSn	4.103	5.428	1.323	PtBi	4.315	5.490	1.272

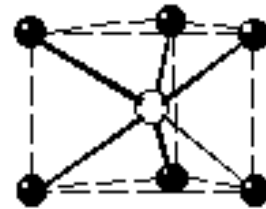
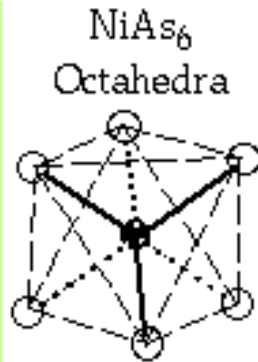
* Anti-NiAs structure.

Alternative unit cell with Ni at the origin:

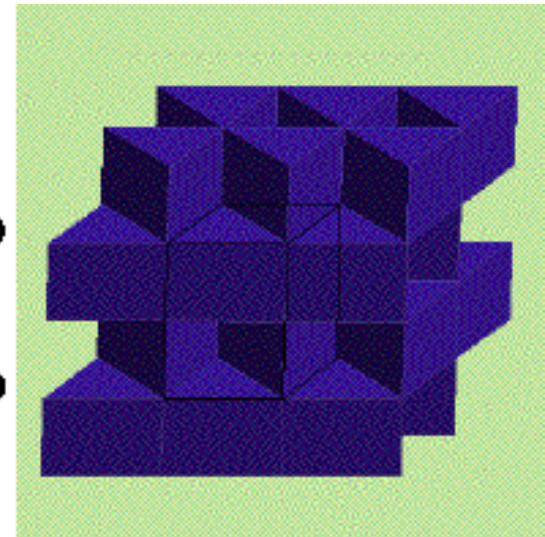




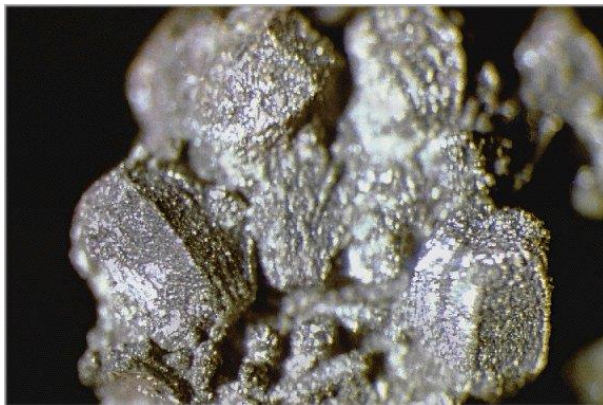
NiAs₆ Octahedra



AsNi₆
Trigonal
Prisms



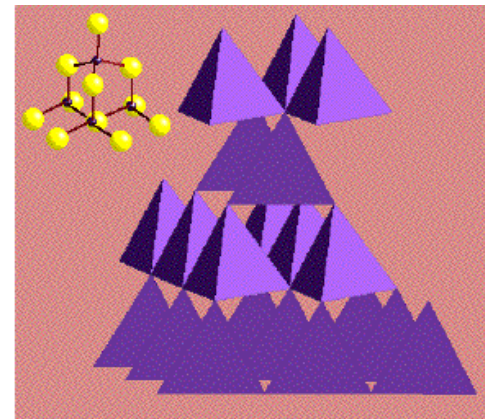
AsNi₆ Trigonal Prisms



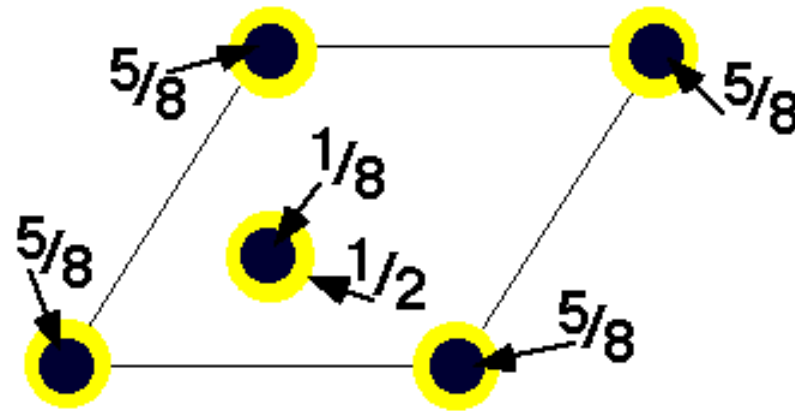
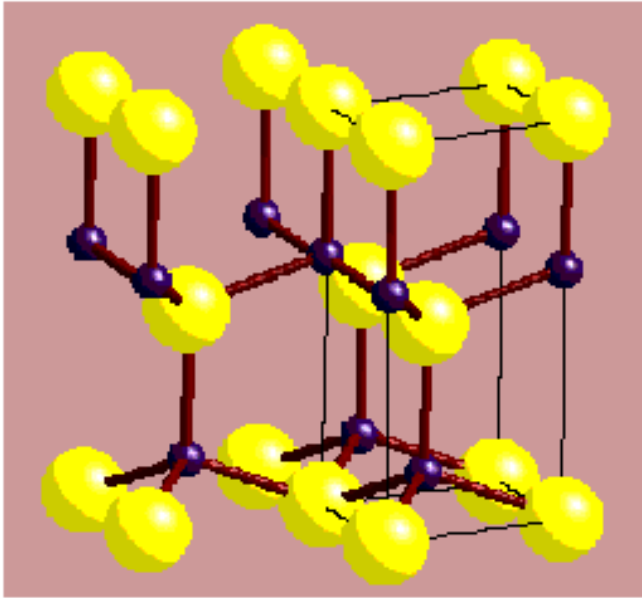
NiAs

- **Transition metals** with chalcogens, As, Sb, Bi
 e.g. Ti(S, Se, Te);
 Cr(S, Se, Te, Sb);
 Ni(S, Se, Te, As, Sb, Sn)

WURTZITE (ZnS) STRUCTURE



(HCP, T+ Holes Filled)



Space Group = $P6_3mc$

Lattice = Primitive hexagonal

Basis = S (0,0,0) & (2/3,1/3,1/2)

Zn (0,0,5/8) & (2/3,1/3,1/8)

Coordination = 4, 4

Cation Coord. → Tetrahedron

Anion Coord. → Tetrahedron

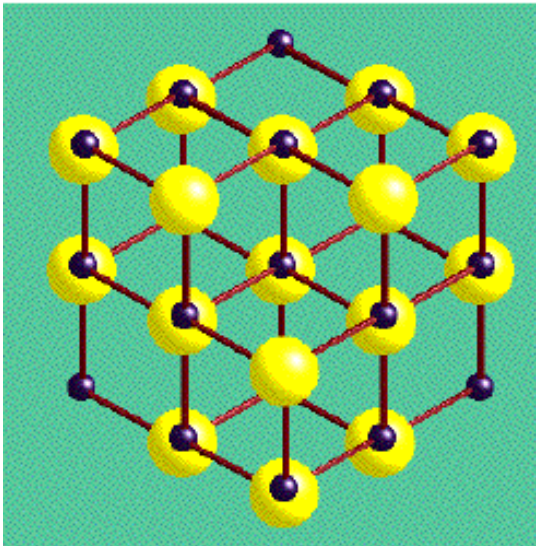
Connectivity → Corner sharing Tetra.

2 ZnS in unit cell

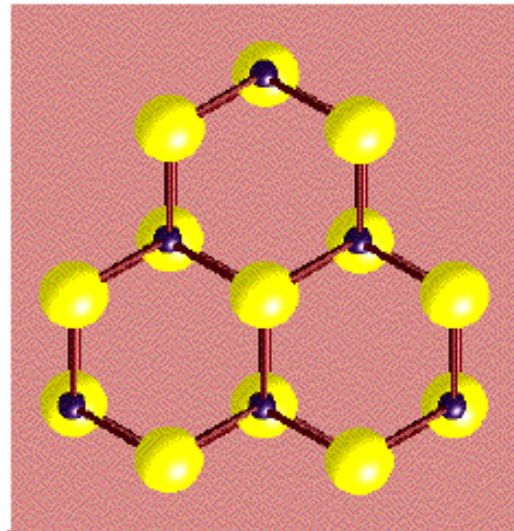
Table 7.9 Some compounds with the wurtzite structure. (Data taken from Wyckoff, 1971, Vol. 1)

	$a(\text{Å})$	$\alpha(\text{Å})$	u	c/a		$a(\text{Å})$	$\alpha(\text{Å})$	u	c/a
ZnO	3.2495	5.2069	0.345	1.602	AgI	4.580	7.494		1.636
ZnS	3.811	6.234		1.636	AlN	3.111	4.978	0.385	1.600
ZnSe	3.98	6.53		1.641	GaN	3.180	5.166		1.625
ZnTe	4.27	6.99		1.637	InN	3.533	5.693		1.611
BeO	2.698	4.380	0.378	1.623	TaN	3.05	4.94		1.620
CdS	4.1348	6.7490		1.632	NH ₄ F	4.39	7.02	0.365	1.600
CdSe	4.30	7.02		1.633	SiC	3.076	5.048		1.641
MnS	3.976	6.432		1.618					
MnSe	4.12	6.72		1.631					

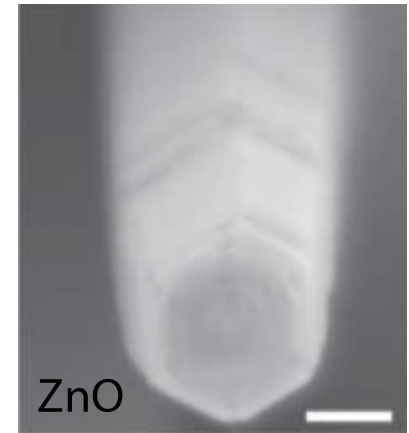
PLAN VIEWS



Zinc Blende
CCP ABC repeat

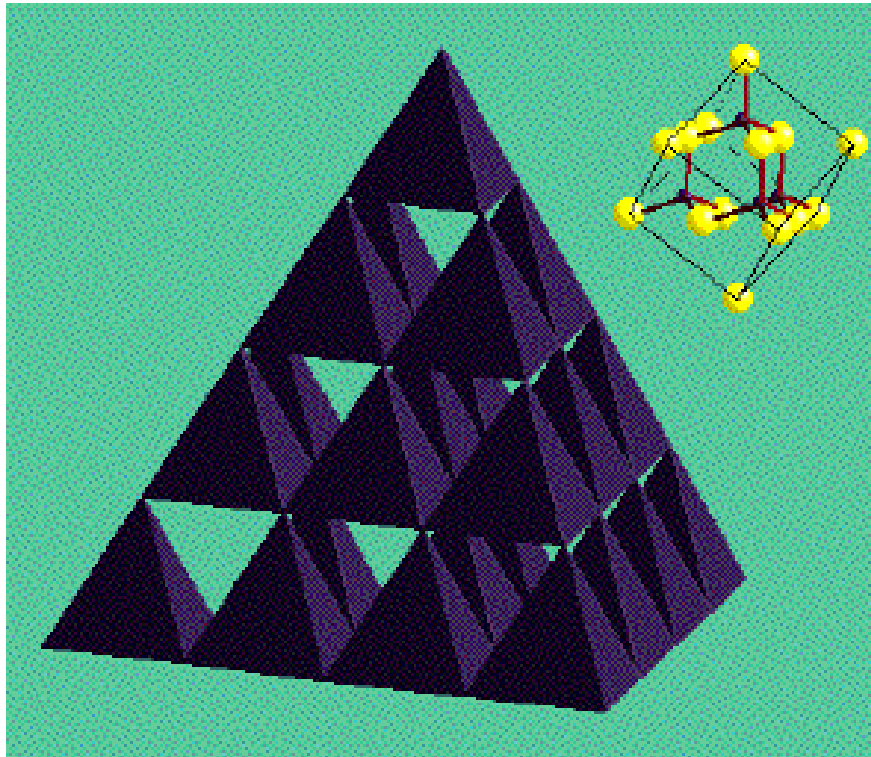


Wurtzite
HCP AB repeat

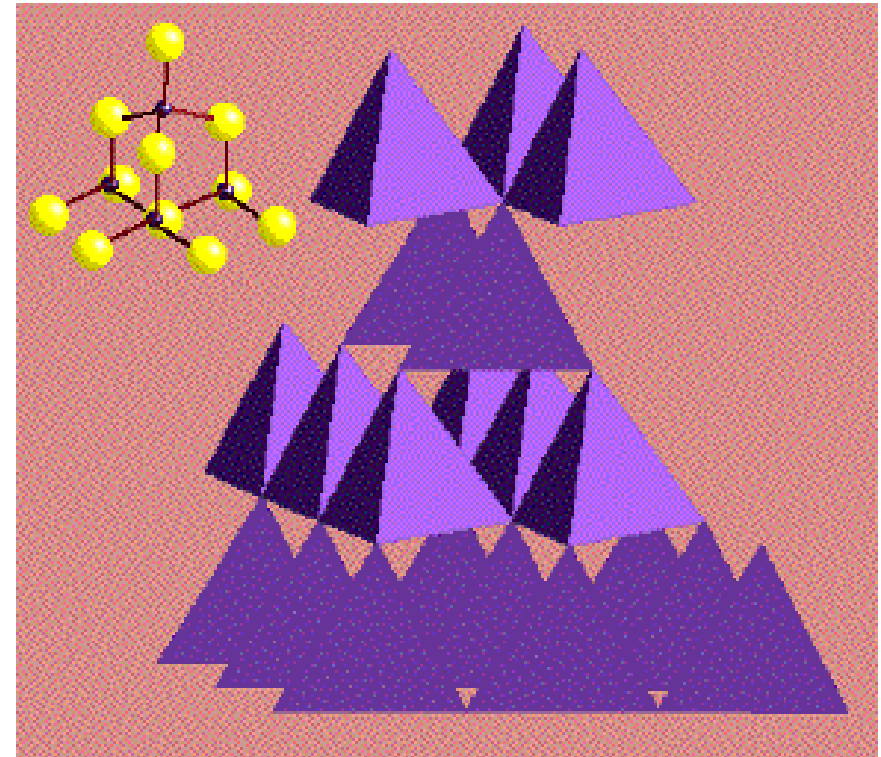


Projections perpendicular to close-packed planes

POLYHEDRAL REPRESENTATIONS



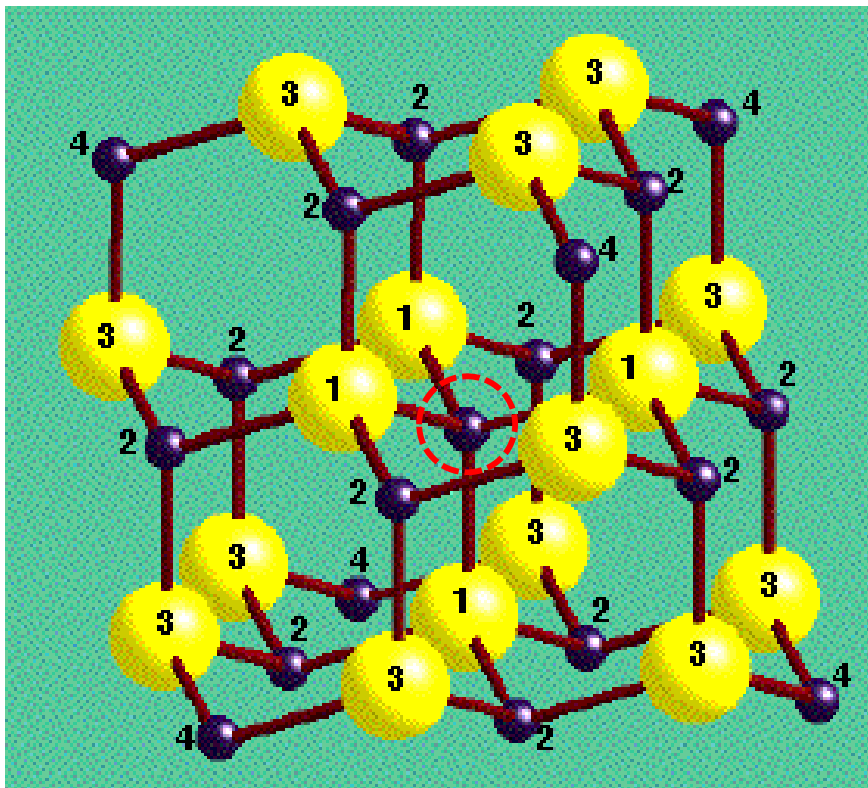
Zinc Blende



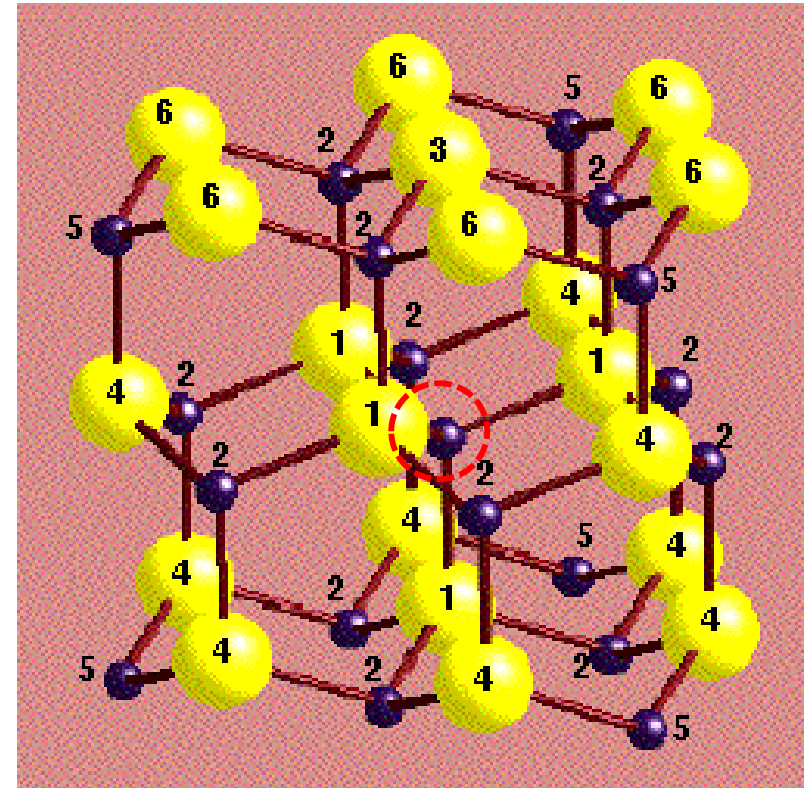
Wurtzite

Vertex-linked tetrahedra only, but layers skewed in Wurtzite, & not in Blende

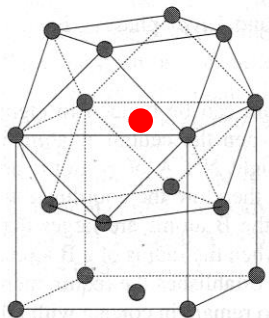
COORDINATION ENVIRONMENTS



Zinc Blende



Wurtzite

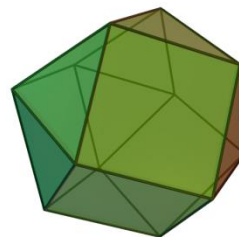


4 Nearest Neighbours (*Tetrahedral*)
 12 Next-Nearest Neighbours

Cuboctahedral ←

→ *Anti-Cuboctahedral*

Very different next-nearest neighbor coordinations & beyond

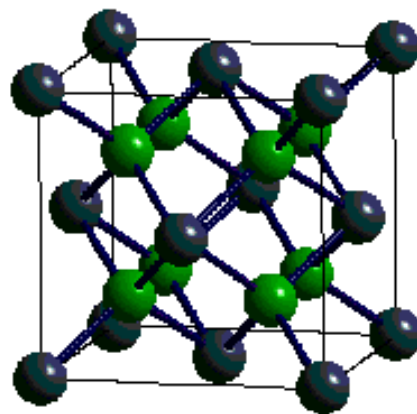


HCP VERSION OF CaF_2 ?

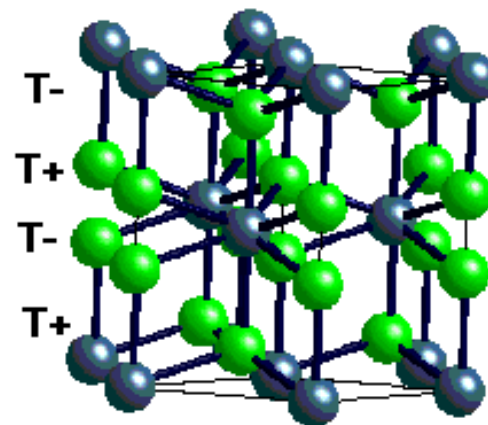
No structures are known with all Tetra. sites ($T+$ and $T-$) filled in HCP - i.e. there is no HCP analogue of the *Fluorite / Anti-Fluorite* structure

Why?

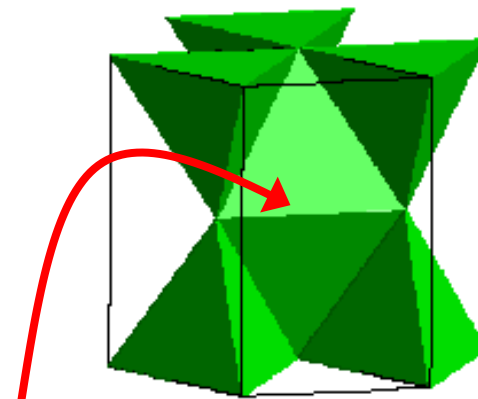
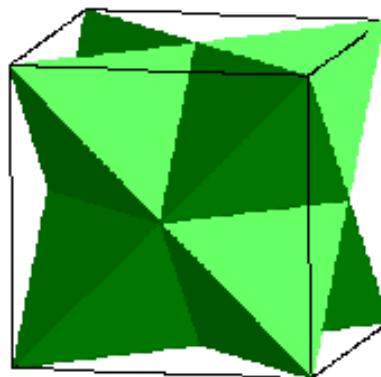
The $T+$ and $T-$ interstitial sites above and below a layer of close-packed spheres in HCP are too close to each other (distance = $0.25c$) to tolerate the coulombic repulsion generated by filling with like-charged ions.



Fluorite



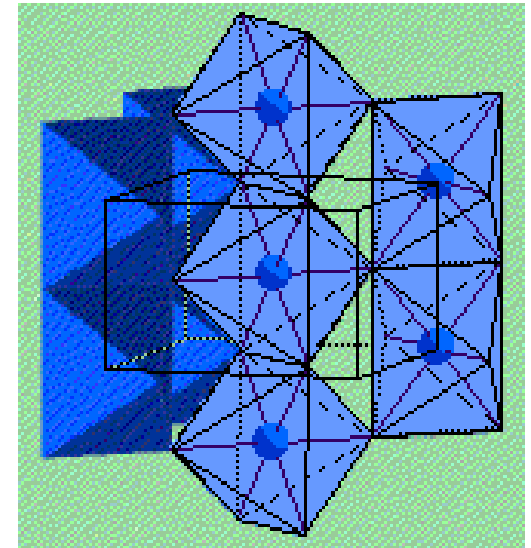
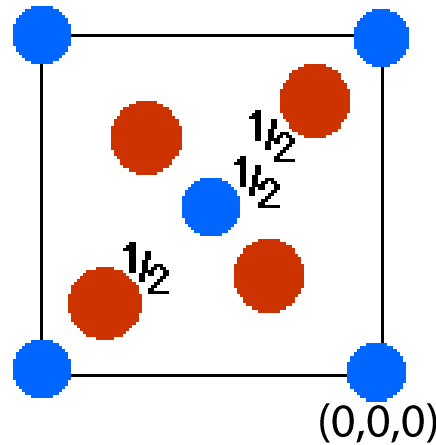
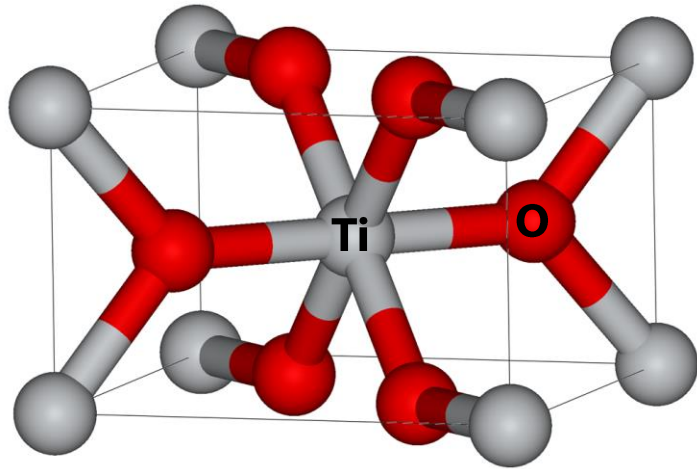
*unknown
HCP Fluorite*



Face-linking is unfavorable

RUTILE STRUCTURE (TiO₂)

(distorted HCP, 50% Oct. Holes Filled)



Space Group = $P4_2/mnm$

Lattice = Primitive tetragonal

Basis = Ti (0,0,0) & $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

O (0.3,0.3,0), (0.7,0.7,0), (0.8,0.2,0.5), (0.2,0.8,0.5)

Coordination = 6, 3

Cation Coord. → Octahedral

Anion Coord. → Trigonal planar

Connectivity → chains of edge-sharing Oct. along c axis, linked by vertices

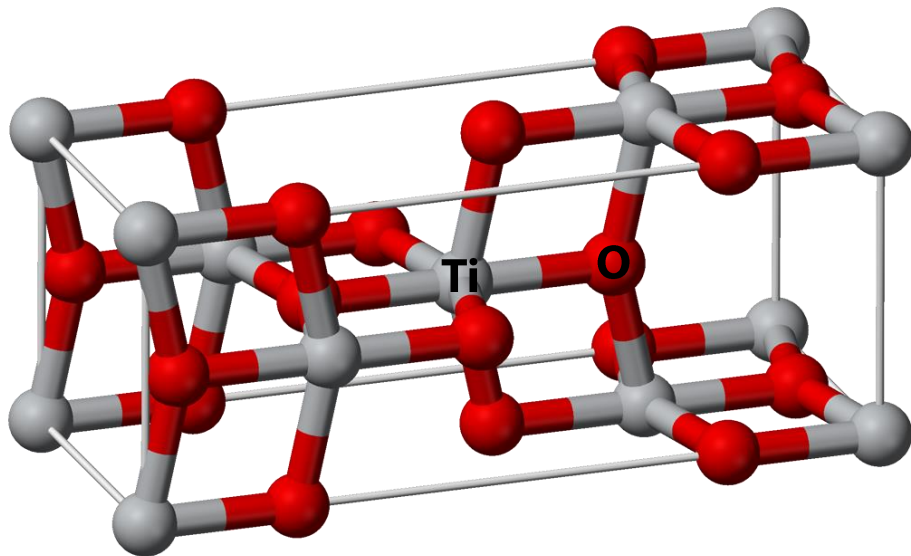
2 TiO₂ per unit cell

Table 7.12 Some compounds with the rutile structure. (Data taken from Wyckoff, 1971, Vol. 1)

	$a(\text{Å})$	$c(\text{Å})$	x		$a(\text{Å})$	$c(\text{Å})$	x
TiO ₂	4.5937	2.9581	0.305	CoF ₂	4.6951	3.1796	0.306
CrO ₂	4.41	2.91		FeF ₂	4.6966	3.3091	0.300
GeO ₂	4.395	2.859	0.307	MgF ₂	4.623	3.052	0.303
IrO ₂	4.49	3.14		MnF ₂	4.8734	3.3099	0.305
β -MnO ₂	4.396	2.871	0.302	NiF ₂	4.6506	3.0836	0.302
MoO ₂	4.86	2.79		PdF ₂	4.931	3.367	
NbO ₂	4.77	2.96		ZnF ₂	4.7034	3.1335	0.303
OsO ₂	4.51	3.19					
PbO ₂	4.946	3.379					
RuO ₂	4.51	3.11					
SnO ₂	4.7373	3.1864	0.307				
TaO ₂	4.709	3.065					
WO ₂	4.86	2.77					

ANATASE STRUCTURE (TiO₂)

(distorted CCP, 50% Oct. Holes Filled)



$$\begin{aligned}a &= 3.776 \text{ \AA} \\b &= 3.776 \text{ \AA} \\c &= 9.486 \text{ \AA}\end{aligned}$$



Volume anatase TiO₂ cell: 136.25 Å³
rutile TiO₂ cell: 62.07 Å³

Space Group = I4₁/amd

Lattice = body-centered tetragonal

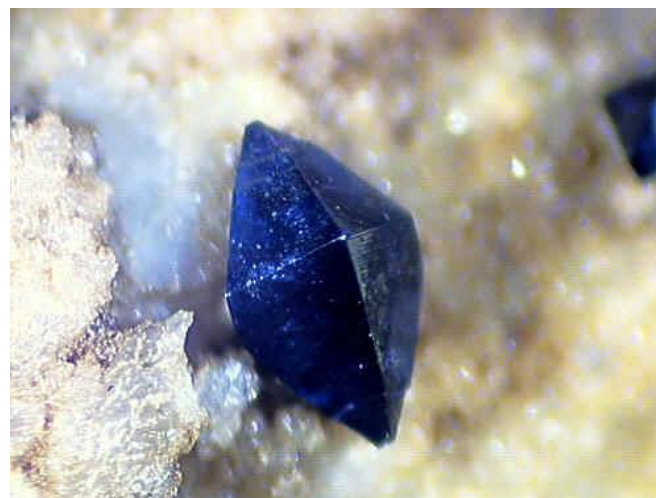
Coordination = 6, 3

Cation Coord. → Octahedral

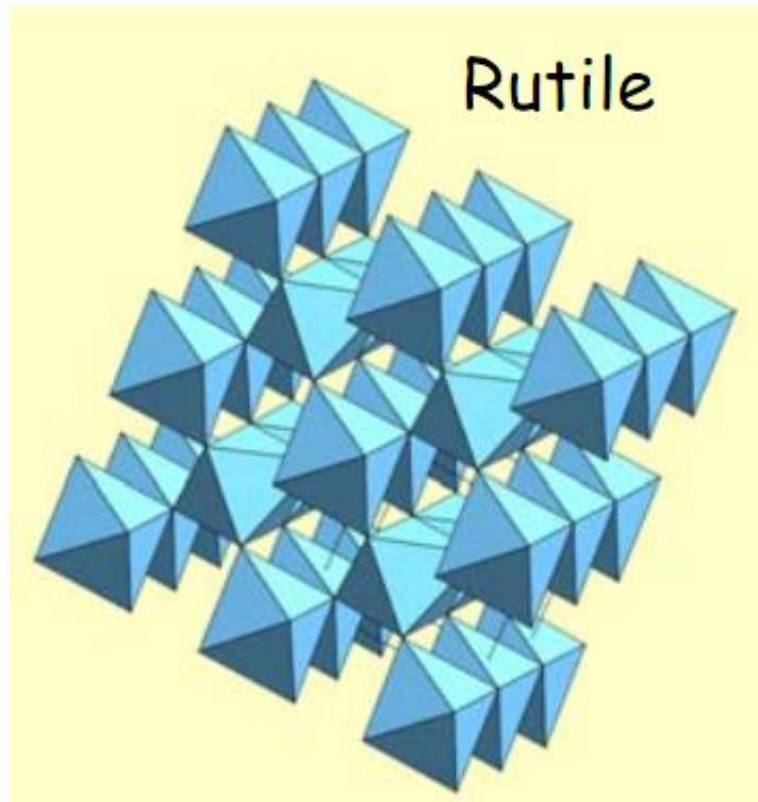
Anion Coord. → Trigonal planar

Connectivity → chains of edge-sharing Oct.
along c axis, linked by vertices and edges

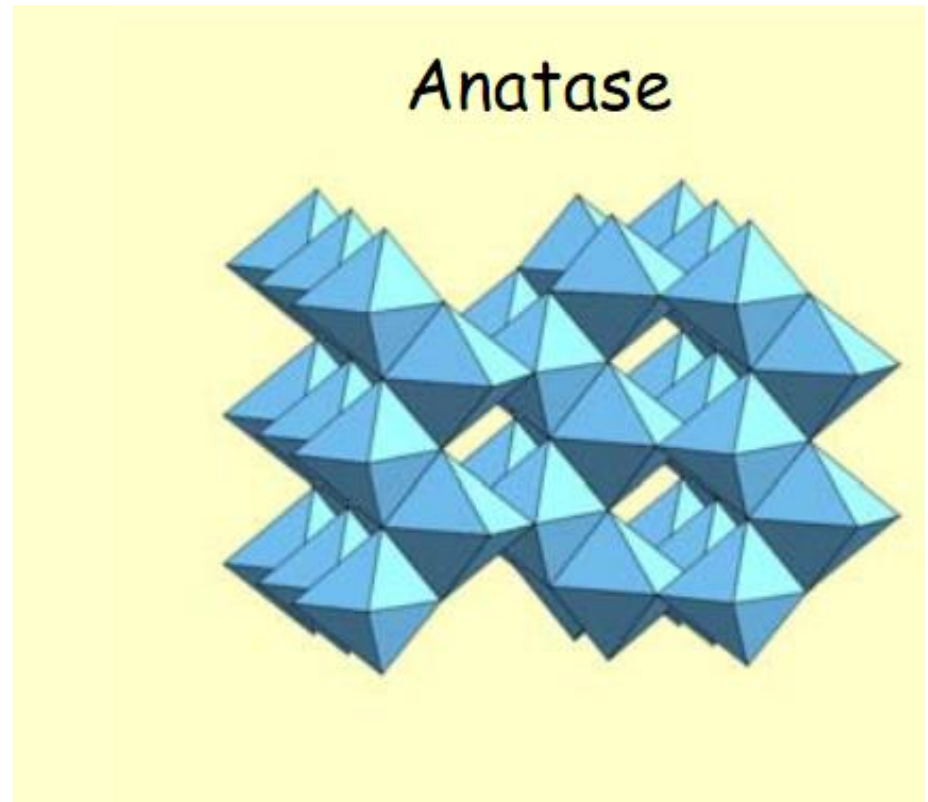
4 TiO₂ per unit cell



RUTILE AND ANATASE



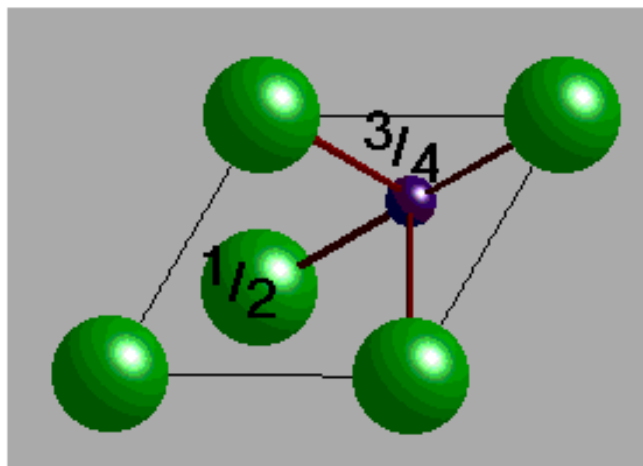
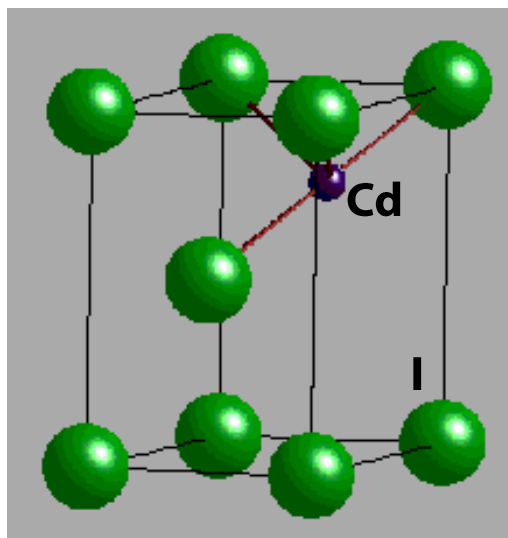
chains of edge sharing oct.,
linked at corners



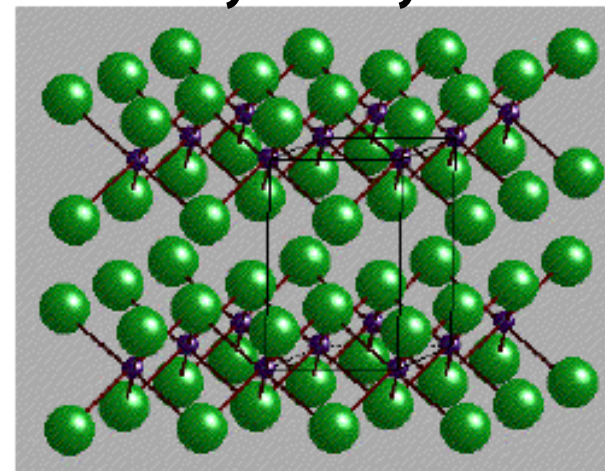
greater density of edge sharing
→ a bit less stable

CdI₂ STRUCTURE

(HCP, with Cd in Oct. Holes of *alternate layers*)



A layered crystal



Space Group = $\bar{P}3m1$

Lattice = Primitive trigonal

Basis = Cd (0,0,0)

I (2/3,1/3,1/4) & (1/3,2/3,3/4)

Coordination = 6, 3

Cation Coord. → Octahedron

Anion Coord. → Trigonal pyramid

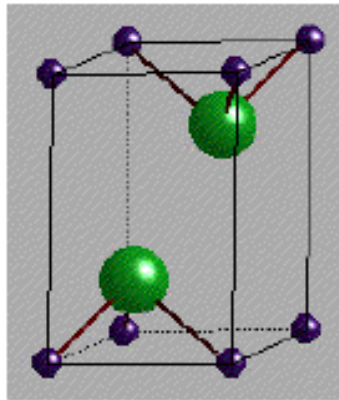
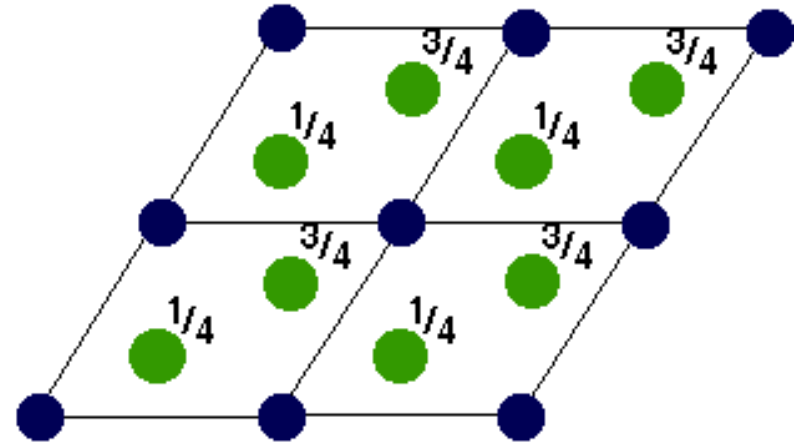
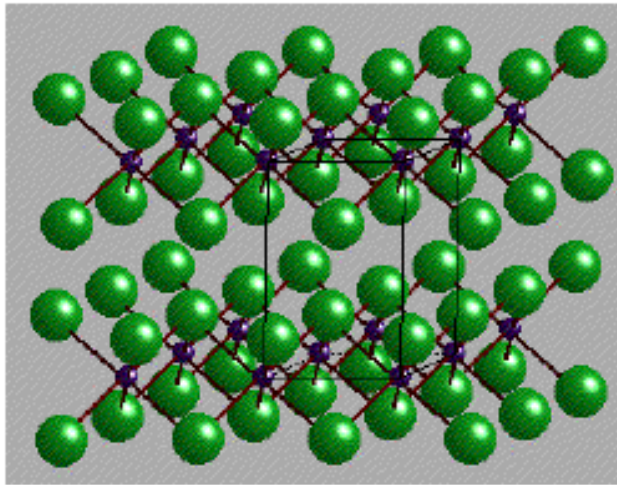
Connectivity → sheets of edge-sharing Oct.

1 CdI₂ per unit cell

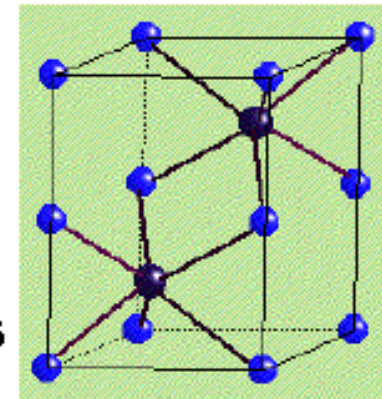
Table 7.13 Some compounds with the CdI₂ structure. (Data taken from Wyckoff, 1971, Vol. 1)

	a(Å)	c(Å)		a(Å)	c(Å)
CdI ₂	4.24	6.84	VBr ₂	3.768	6.180
CaI ₂	4.48	6.96	TiBr ₂	3.629	6.492
CoI ₂	3.96	6.65	MnBr ₂	3.82	6.19
FeI ₂	4.04	6.75	FeBr ₂	3.74	6.17
MgI ₂	4.14	6.88	CoBr ₂	3.68	6.12
MnI ₂	4.16	6.82	TiCl ₂	3.561	5.875
PbI ₂	4.555	6.977	VCl ₂	3.601	5.835
ThI ₂	4.13	7.02	Mg(OH) ₂	3.147	4.769
TiI ₂	4.110	6.820	Ca(OH) ₂	3.584	4.896
TmI ₂	4.520	6.967	Fe(OH) ₂	3.258	4.605
VI ₂	4.000	6.670	Co(OH) ₂	3.173	4.640
YbI ₂	4.503	6.972	Ni(OH) ₂	3.117	4.595
ZnI ₂ (l)	4.25	6.54	Cd(OH) ₂	3.48	4.67

Alternative
unit cell
with Cd at
the origin:

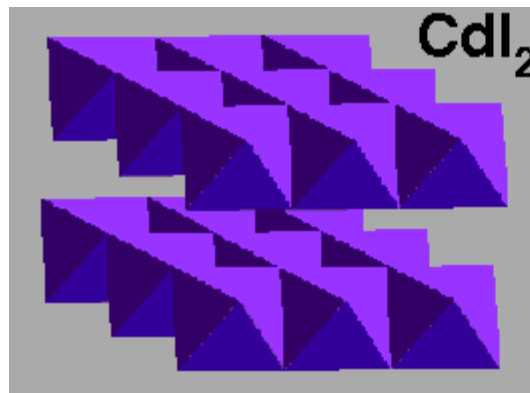


Comparison
 CdI_2 vs

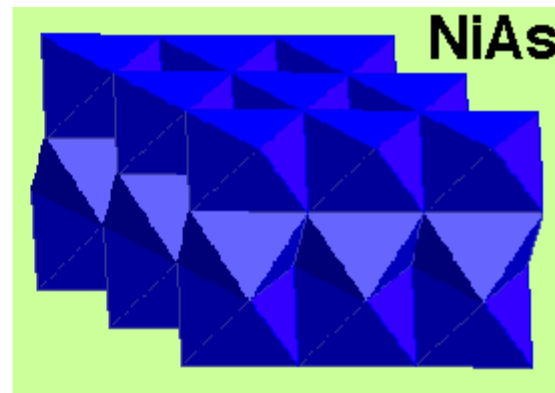


NiAs

CdI_6 units



NiAs



NiAs_6 units

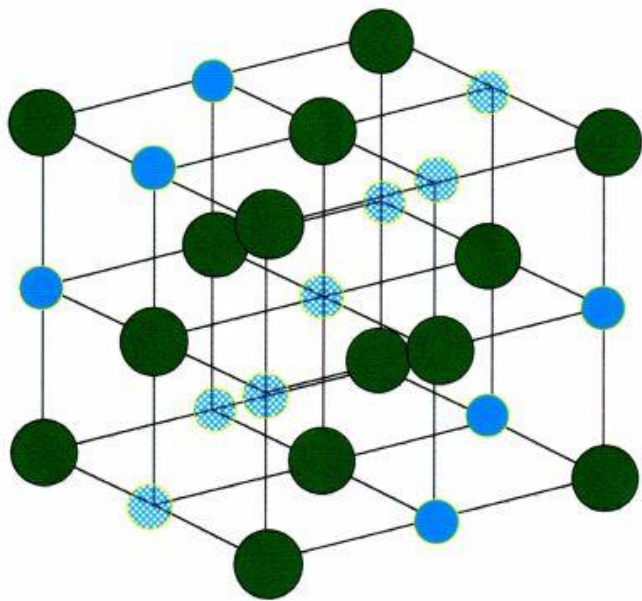
CdI₂ - OCCURRENCE

- Iodides of moderately polarizing cations; bromides and chlorides of strongly polarizing cations;
e.g. PbI₂, FeBr₂, VCl₂
- Hydroxides of many divalent cations
e.g. (Mg,Ni)(OH)₂
- Di-chalcogenides of many quadrivalent cations
e.g. TiS₂, ZrSe₂, CoTe₂

CdCl₂ STRUCTURE

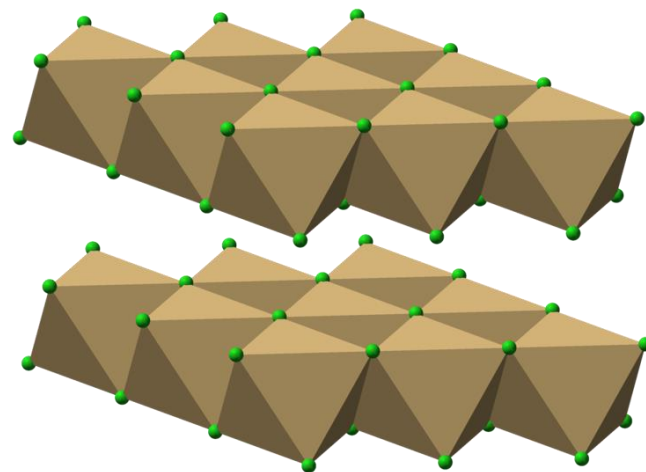
The CCP analogue of CdI₂

(CCP, with Cd in Oct. Holes of alternate layers along [111])



The cadmium chloride crystal structure. The structure is identical to the NaCl structure, but with half of the cations removed as a sheet (shown with hatched lines).

Solid light blue = Cd²⁺
Hatched light blue = no ion
Dark green = Cl⁻



CdCl₆ octahedra

Space Group = $\bar{R}32/m$

Chlorides of moderately polarizing cations

e.g. MgCl₂, MnCl₂

Di-sulfides of quadrivalent cations

e.g. TaS₂, NbS₂ (CdI₂ form as well)

Table 7.14 Some compounds with the CdCl₂ structure. (Data taken from Wyckoff, 1971, Vol. 1)

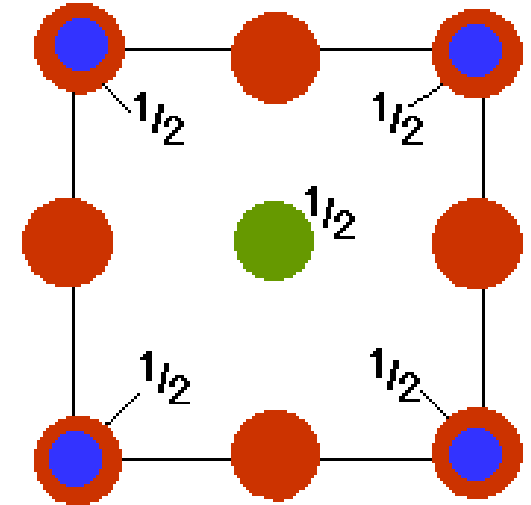
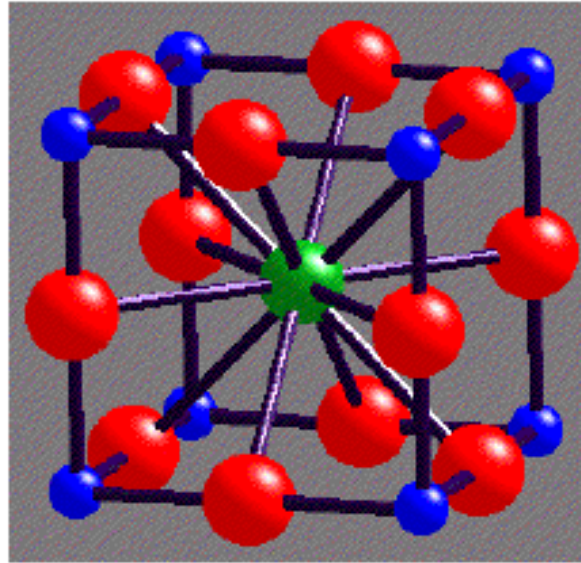
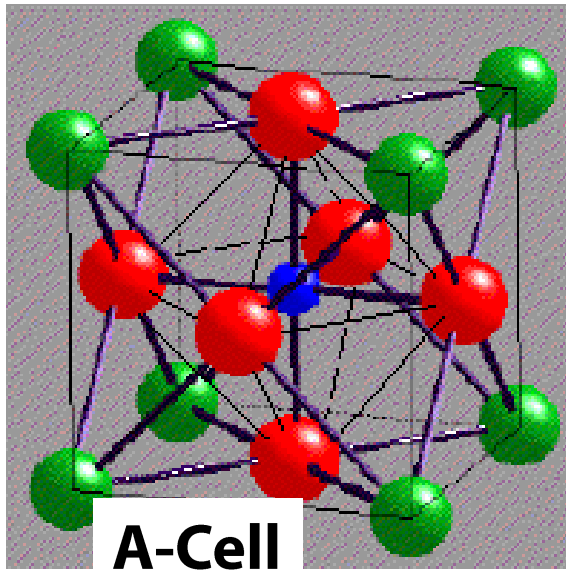
	<i>a</i> (Å)	<i>c</i> (Å)		<i>a</i> (Å)	<i>c</i> (Å)
CdCl ₂	3.854	17.457	NiCl ₂	3.543	17.335
CdBr ₂	3.95	18.67	NiBr ₂	3.708	18.300
CoCl ₂	3.544	17.430	NiI ₂	3.892	19.634
FeCl ₂	3.579	17.536	ZnBr ₂	3.92	18.73
MgCl ₂	3.596	17.589	ZnI ₂	4.25	21.5
MnCl ₂	3.686	17.470	Cs ₂ O*	4.256	18.99

*Cs₂O has an anti-CdCl₂ structure.

Formula	Type and fraction of sites occupied	CCP	HCP
AB	All octahedral	NaCl <i>Rock Salt</i>	NiAs <i>Nickel Arsenide</i>
	Half tetrahedral (T+ or T-)	ZnS <i>Zinc Blende</i>	ZnS <i>Wurtzite</i>
A₂B	All tetrahedral	Na₂O <i>Anti-Fluorite</i> CaF₂ <i>Fluorite</i>	not known
A₃B	All octahedral & tetrahedral	Li₃Bi	not known
AB₂	Half octahedral (Alternate layers full/empty)	CdCl₂ (<i>Cadmium Chloride</i>)	CdI₂ (<i>Cadmium Iodide</i>)
	Half octahedral (Ordered framework arrangement)	TiO₂ (<i>Anatase</i>)	CaCl₂ TiO₂ (<i>Rutile</i>)
AB₃	Third octahedral Alternate layers 2/3 full/empty	YCl₃	BiI₃

PEROVSKITE STRUCTURE ABX_3 ($CaTiO_3$)

(CCP of Ca & O, 25% Oct. Holes Filled by Ti)



● Ca ● Ti ● O

B-Cell

Space Group = $Pm\bar{3}m$

Lattice = Primitive cubic

Basis = Ti (0,0,0), Ca ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$),
O ($\frac{1}{2}, 0, 0$), (0, $\frac{1}{2}$, 0) & (0, 0, $\frac{1}{2}$)

Coordination = Ca-12 ; Ti-6; O-6

Ca Coord. → Cuboctahedron

Ti Coord. → Octahedron

O Coord. → distorted octahedron (4 Ca, 2 Ti)

1 $CaTiO_3$ per unit cell

An extremely rich, important class of compounds:

Magnetoresistance

Ferroelectricity

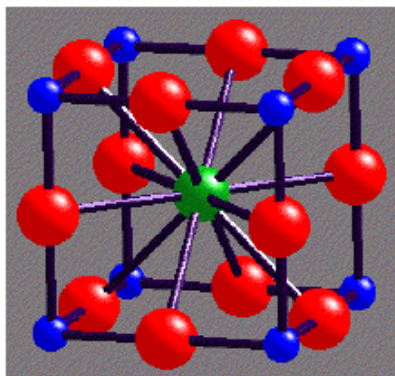
Multiferroics

Superconductivity

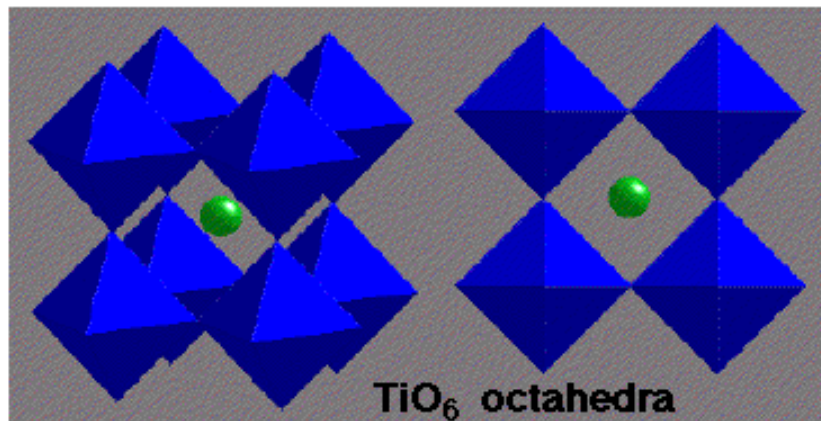
Catalysis (fuel cells)

Spin transport

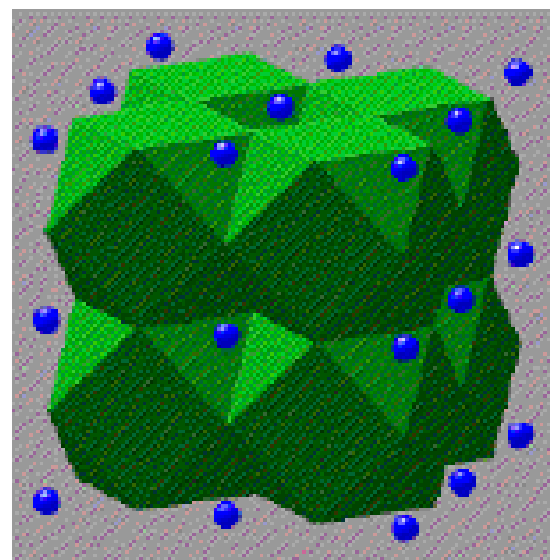
PEROVSKITE CONNECTIVITY



B-Cell



3D network of corner-sharing octahedra



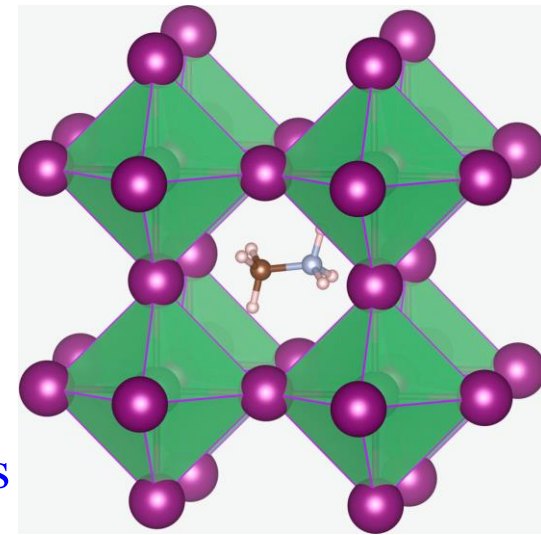
CaO_{12} cuboctahedra
Network of face-sharing cuboctahedra

Perovskites: the most widely studied oxide structure

- Wide range of chemistries possible
 - thousands of examples known
- Cubic, tetragonal, and orthorhombic symmetries are common

Unique properties of perovskites

- high T_c cuprate superconductors
- Colossal Magneto-Resistance (La,SrMnO₃)
- fast ion conduction (Li⁺, O²⁻ in SrSnO₃), batteries, fuel cells
- mixed electronic/ionic conduction, fuel cells
- oxidation/reduction catalysts
- ferroelectric / piezoelectric ceramics (BaTiO₃, Pb(ZrTi)O₃)
- important mineral structure in lower mantle (MgSiO₃, pyroxene)
- frequency filters for wireless communications : Ba(Zn_{1/3}Ta_{2/3})O₃

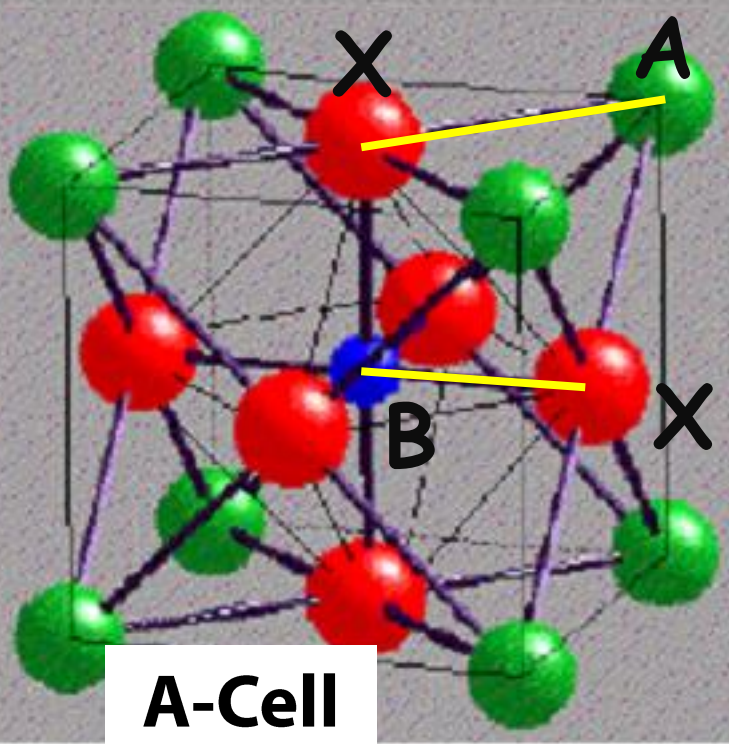


(CH₃NH₃)PbI₃
organic-inorganic

Perovskite Structure: ABX_3

Tolerance factor (t):

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$



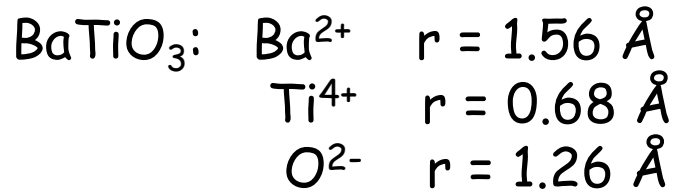
A-Cell

t	Effect	Likely structure
> 1	A cation too large to fit in interstices	Hexagonal perovskite
0.9 - 1.0	ideal	Cubic perovskite
0.71 - 0.9	A cation too small	Orthorhombic perovskite
< 0.71	A cation same size as B cation	Possible close packed lattice

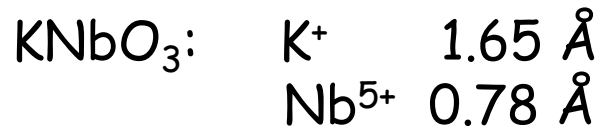
PEROVSKITES

Most perovskites contain distorted octahedra and are not cubic, at least at lower temperatures. These distortions give perovskites a rich physics.

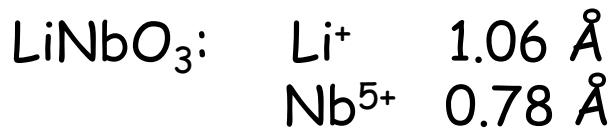
symmetry at 25°C



$t = 1.03$ - tetragonal

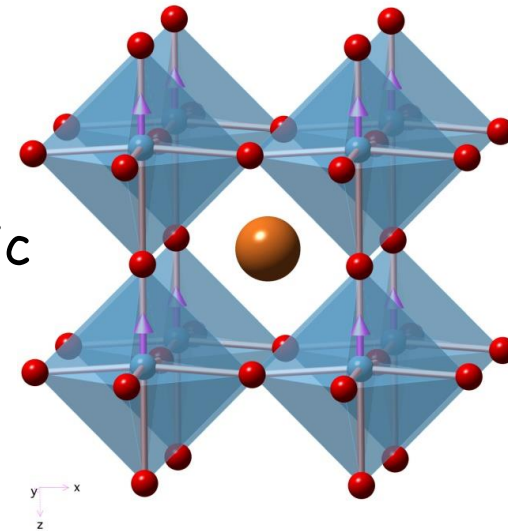


$t = 1.01$ - orthorhombic

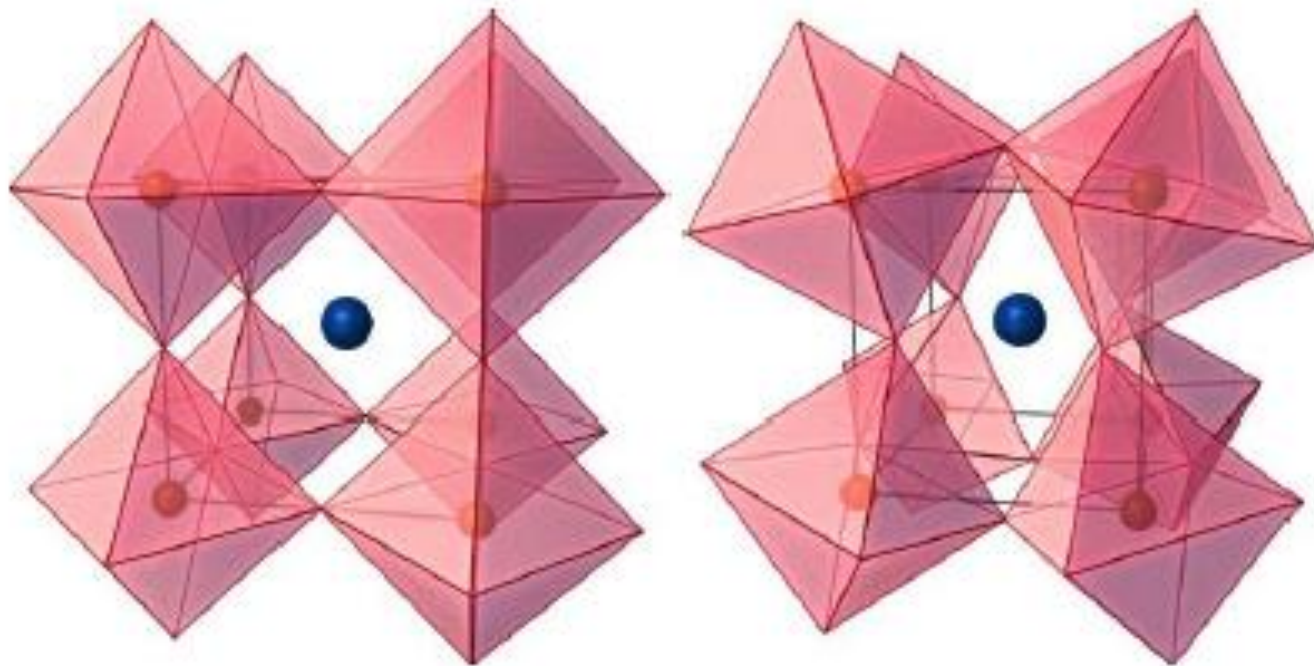


$t = 0.81$ - trigonal

Barium Titanate - Perovskite Structure



LiNbO₃ : ferroelectricity, Pockels effect, piezoelectricity, photoelasticity, nonlinear optical polarizability



(a) Cubic

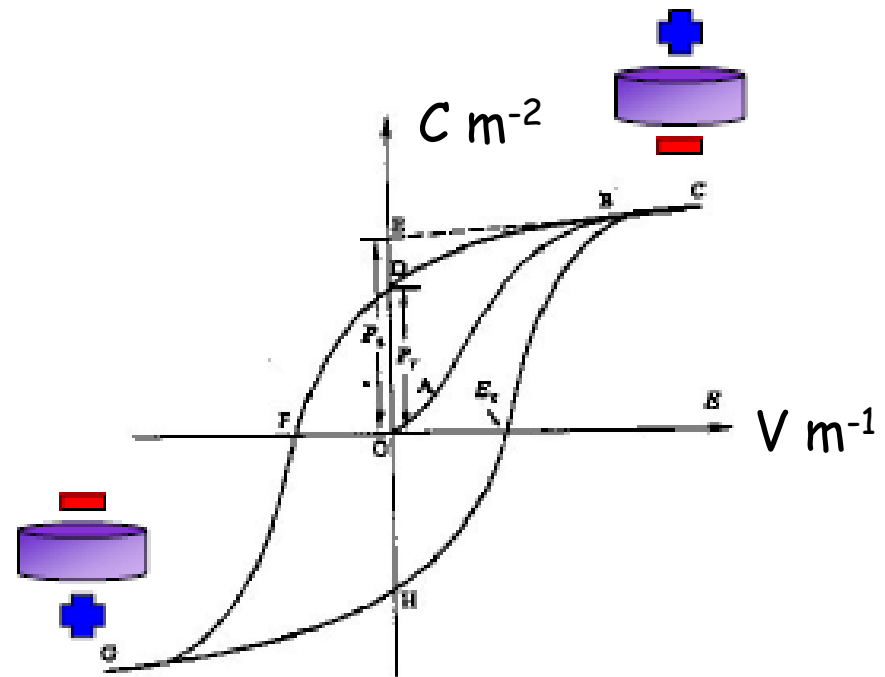
(b) Orthorhombic

Figure 3.7: Perovskite distortion from (a) cubic to (b) orthorhombic.

What is a Ferroelectric

A ferroelectric material develops a spontaneous polarization (builds up a charge) in response to an external electric field.

- The polarization does not go away when the external field is removed.
- The direction of the polarization is reversible.

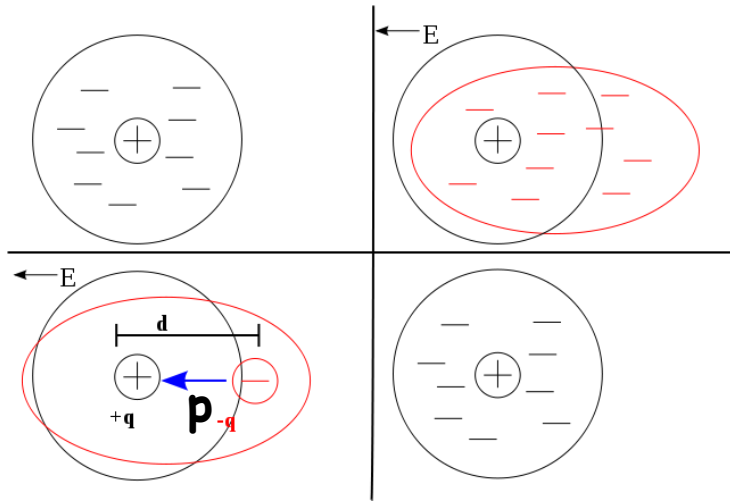


Applications of Ferroelectric Materials

- Multilayer capacitors
- Non-volatile FRAM (Ferroelectric Random Access Memory)

DI-, PARA-, AND FERROELECTRICS

response of atom to applied \mathbf{E} field



dipole moment: $\mathbf{p} = q\mathbf{d} = \alpha\mathbf{E}$

polarization: $\mathbf{P} = \Sigma\mathbf{p}/V$

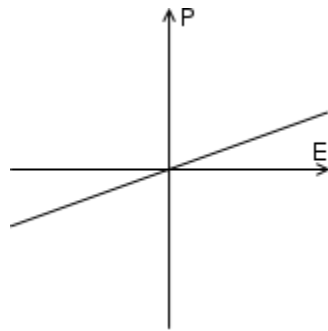
$$\mathbf{P} = \epsilon_0\chi_e\mathbf{E}$$

\mathbf{P} : polarization (C/m^2)

ϵ_0 : vacuum permittivity - $8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$

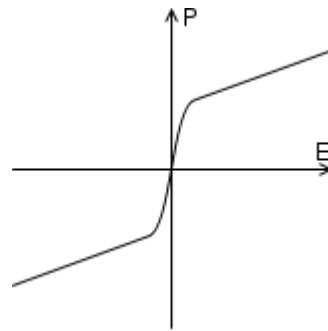
χ_e : electric susceptibility (unitless)

\mathbf{E} : electric field (V/m , or N/C)



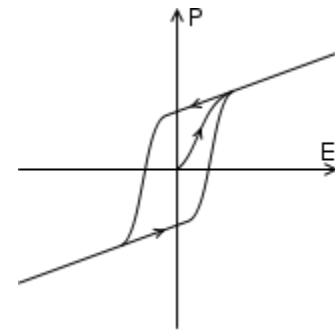
dielectric polarization

- linear: $\mathbf{P} = \epsilon_0\chi_e\mathbf{E}$
- no \mathbf{P} without \mathbf{E}



paraelectric polarization

- nonlinear
- no \mathbf{P} without \mathbf{E}

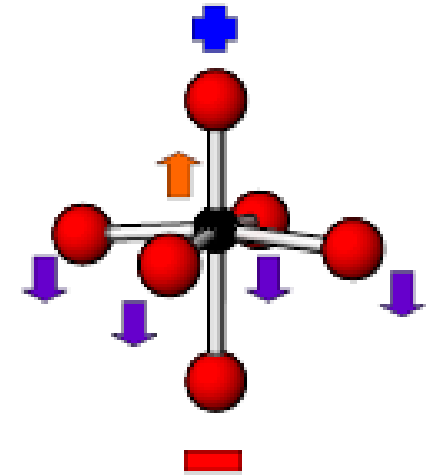


ferroelectric polarization

- residual (zero-field) polarization
- reversible direction of residual \mathbf{P}
- very large susceptibilities

WHY IS BaTiO₃ FERROELECTRIC

- Ba²⁺ is larger than the vacancy in the octahedral network tolerance factor > 1.
- This expands the octahedron, which leads to a shift of Ti⁴⁺ toward one of the corners of the octahedron.
- The direction of the shift can be altered through application of an electric field.

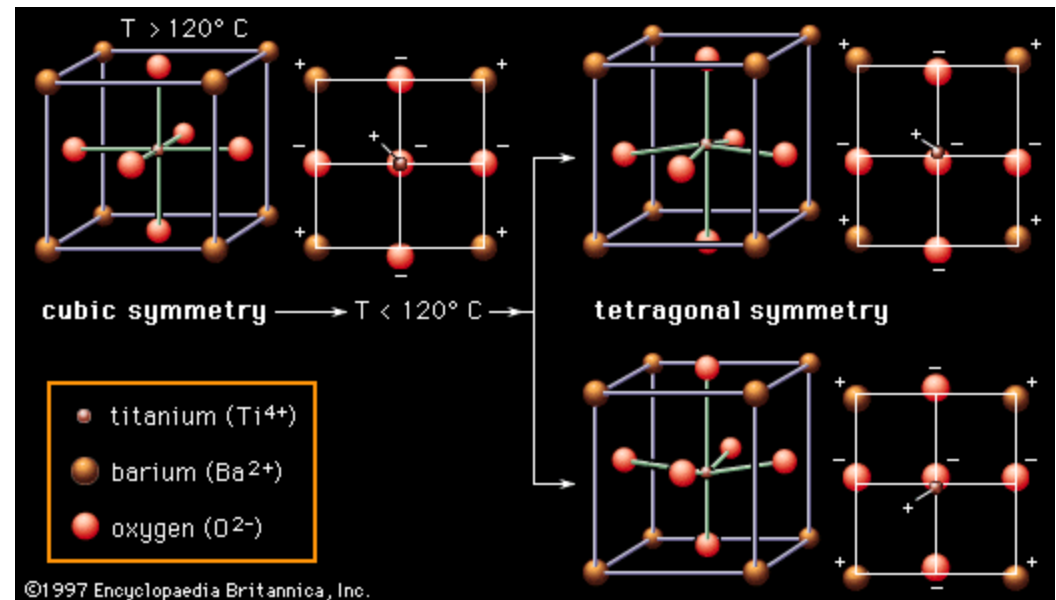


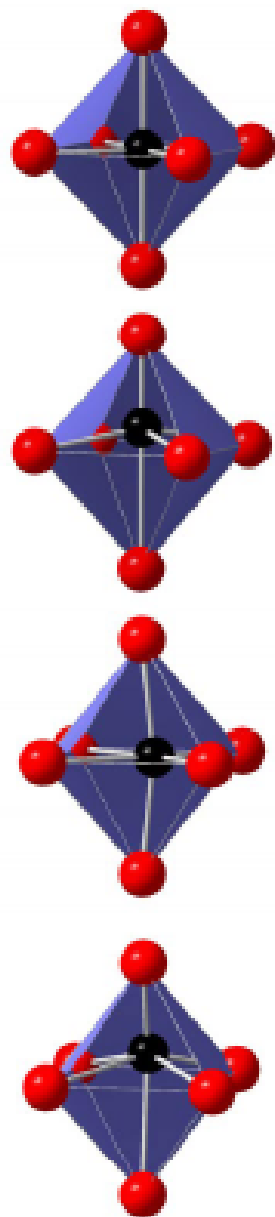
~0.1 Å displacement

ferroelectric phase transition

- > 120°C cubic, not FE
- < 120°C tetragonal, FE

transition occurs at the
Curie temperature, T_c





Cubic (Pm3m)

$T > 393 \text{ K}$

Ti-O Distances (Å)

6x2.00

Tetragonal (P4mm)

$273 \text{ K} < T < 393 \text{ K}$

Ti-O Distances (Å)

1.83, 4x2.00, 2.21

Toward a corner

Orthorhombic (Amm2)

$183 \text{ K} < T < 273 \text{ K}$

Ti-O Distances (Å)

2x1.87, 2x2.00, 2x2.17

Toward an edge

Rhombohedral (R3m)

$183 \text{ K} < T < 273 \text{ K}$

Ti-O Distances (Å)

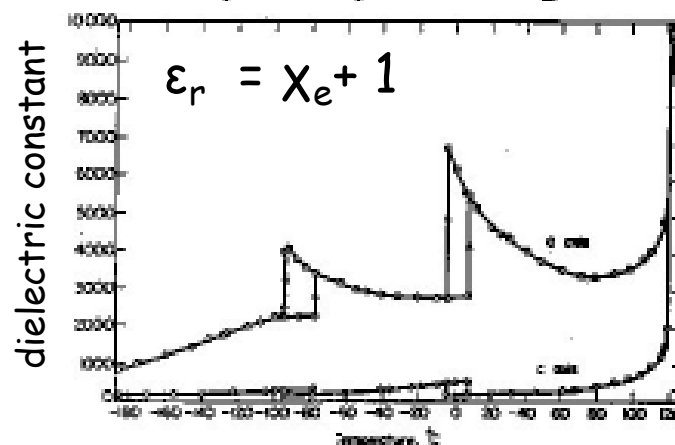
3x1.88, 3x2.13

Toward a face

BaTiO₃ Phase Transitions

In the cubic structure BaTiO₃ is paraelectric. That is to say that the orientations of the ionic displacements are not ordered and dynamic.

Below 393 K BaTiO₃ becomes ferroelectric and the displacement of the Ti⁴⁺ ions progressively displace upon cooling.



See Kwei et al. *J. Phys. Chem.* **97**, 2368 (1993).

FERROELECTRIC HYSTERESIS LOOPS

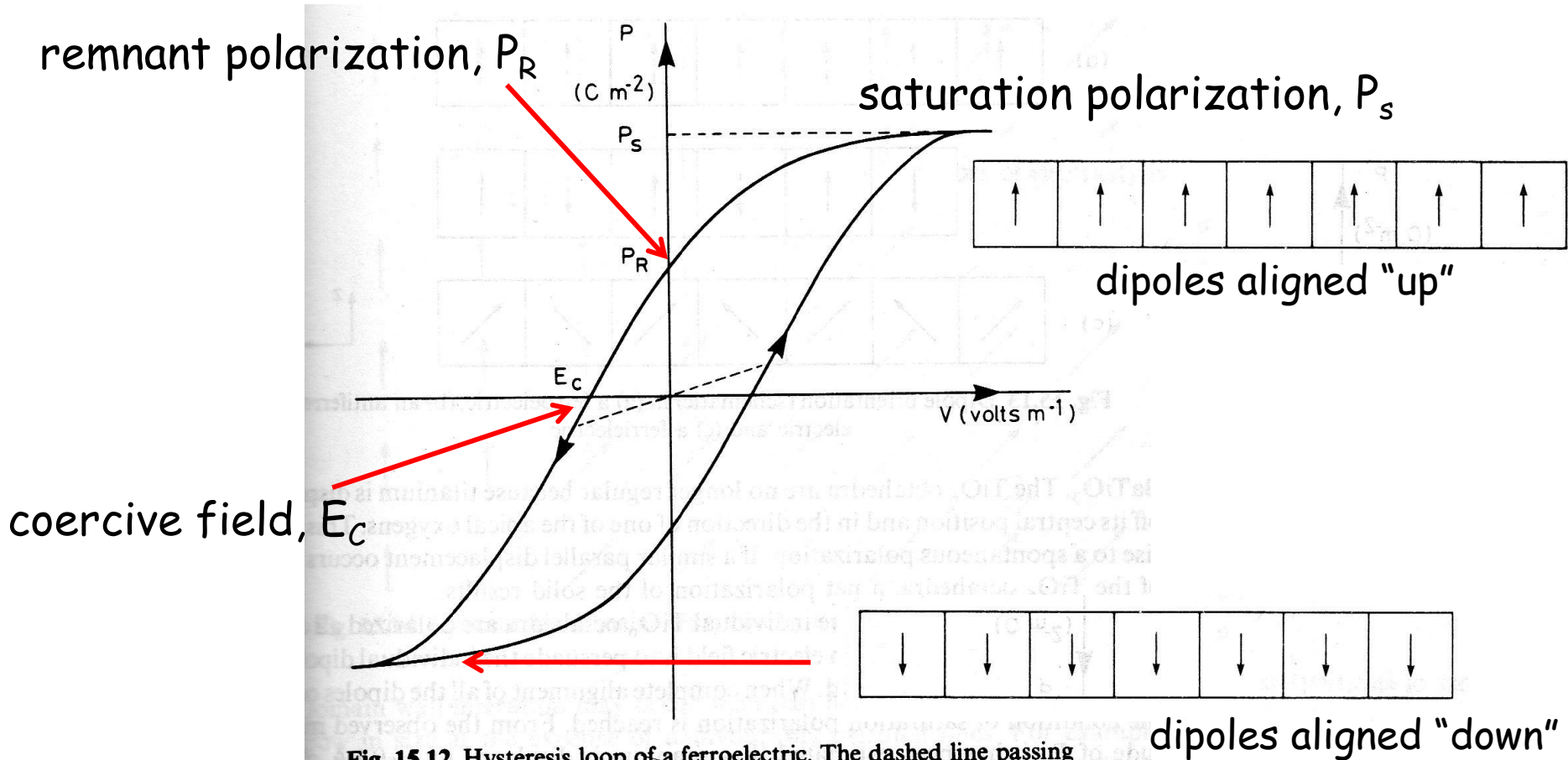
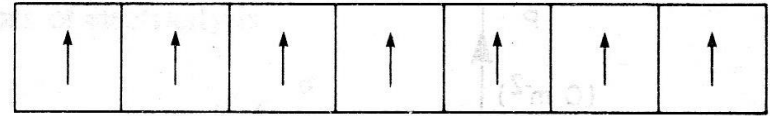


Fig. 15.12 Hysteresis loop of a ferroelectric. The dashed line passing through the origin represents the behaviour of normal dielectric materials

ORDERED ELECTRIC DIPOLE PHASES

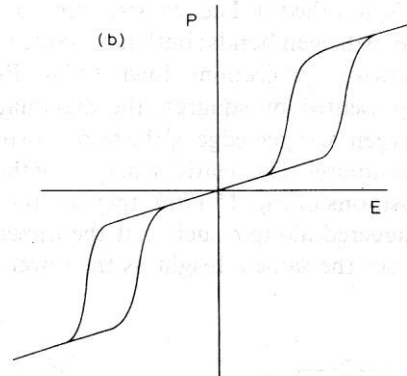
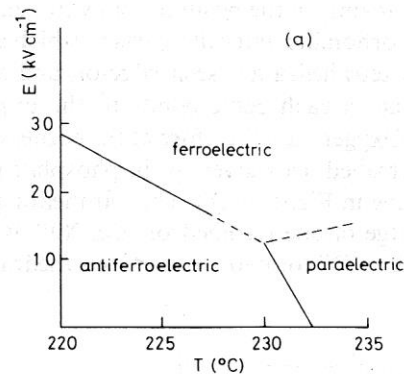
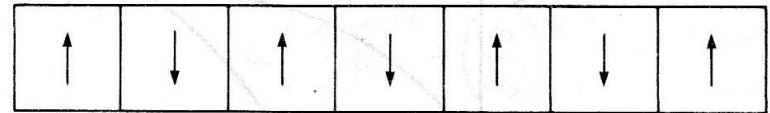
ferroelectric (BaTiO_3)

- parallel ordering below T_c



antiferroelectric (PbZrO_3)

- antiparallel ordering below T_c

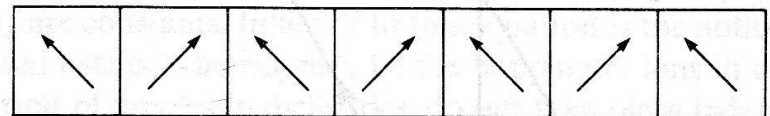


E field can induce ferroelectric state

Fig. 15.16 (a) Antiferroelectric-ferroelectric transition in PbZrO_3 as a function of the applied field, E . (b) Polarization behaviour across this transition

ferrielectric ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$)

- net spontaneous polarization in only certain direction(s)



CURIE TEMPERATURE

Thermal energy destroys the ordered electric dipole state. The temperature above which this *order-disorder phase transition* occurs is the *Curie temperature, T_c* .

Above T_c , the material is often paraelectric.

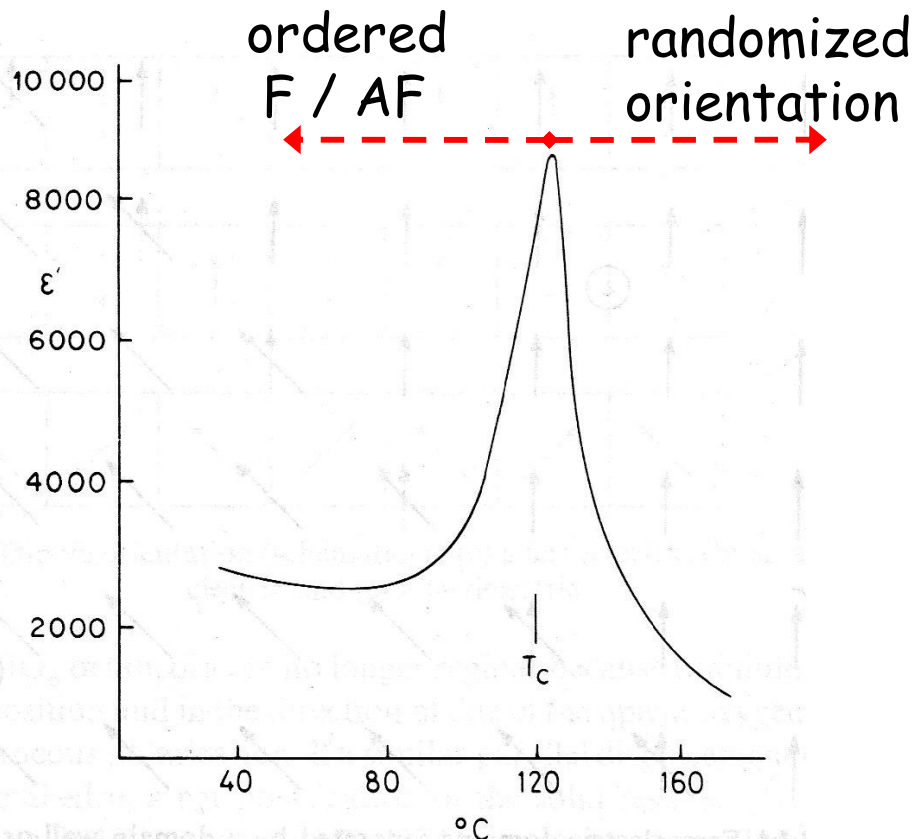
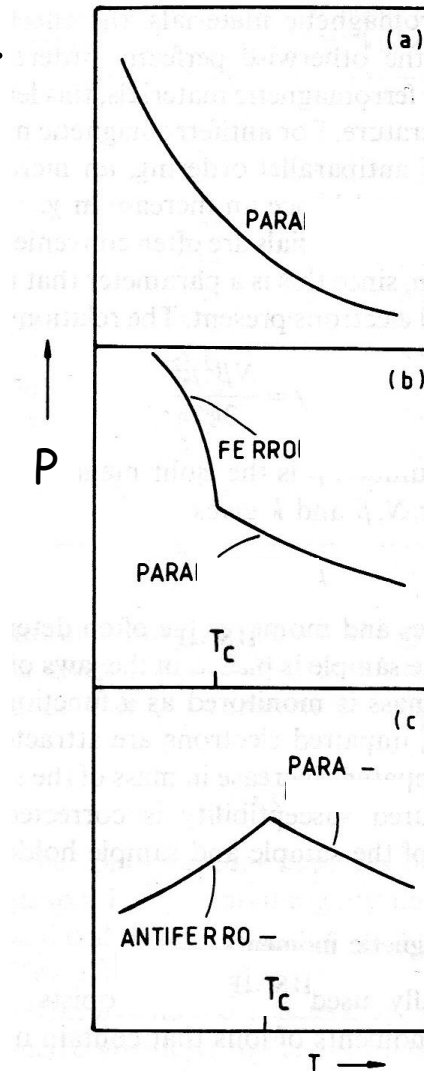


Fig. 15.15 Dielectric constant of BaTiO_3 ceramic



Note:
These curves omit the "spikes" in P at T_c

PHASE DIAGRAMS

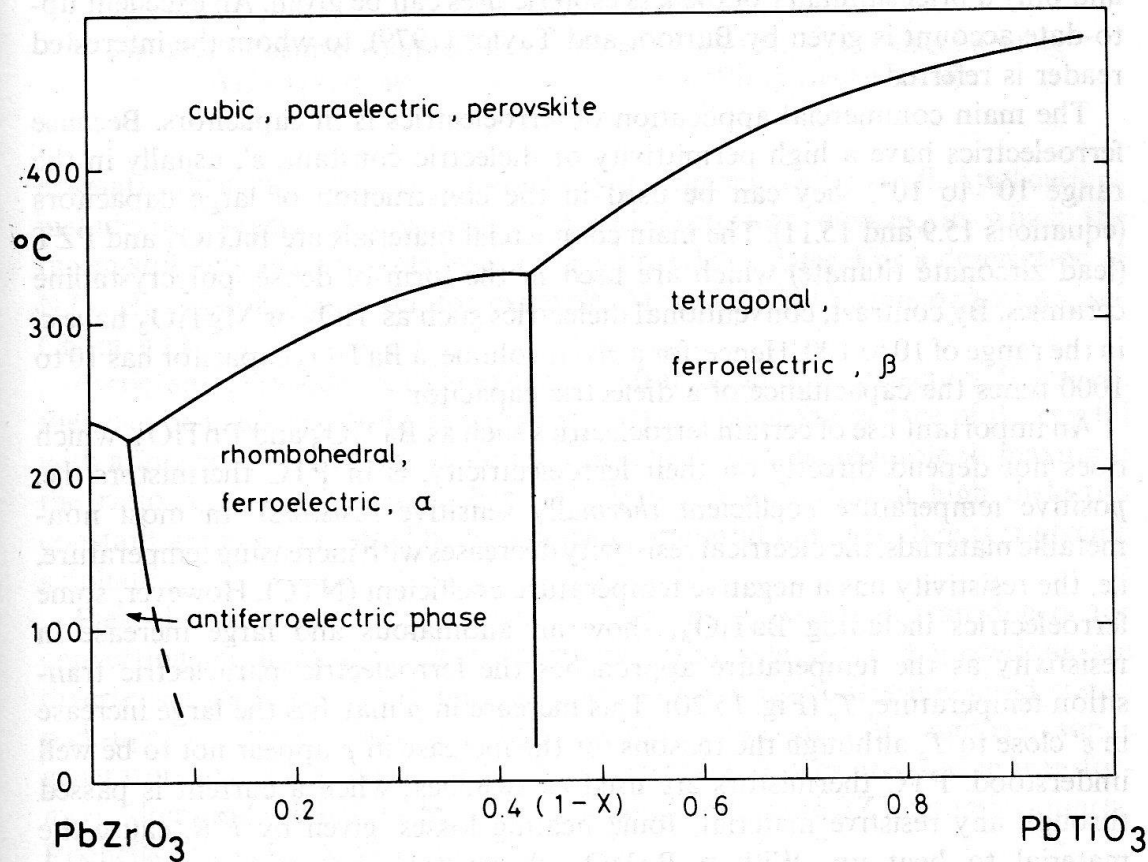


Table 15.2 Some ferroelectric materials

	$T_c(^{\circ}\text{C})$
Barium titanate, BaTiO_3	120
Rochelle salt, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	Between -18 and $+24$
Potassium niobate, KNbO_3	434
Potassium dihydrogen phosphate, KDP, KH_2PO_4	-150
Lead titanate, PbTiO_3	490
Lithium niobate, LiNbO_3	1210
Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$	675
Gadolinium molybdate, GMO, $\text{Gd}_2(\text{MoO}_4)_3$	159
Lead zirconate titanate, PZT, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$	Depends on x

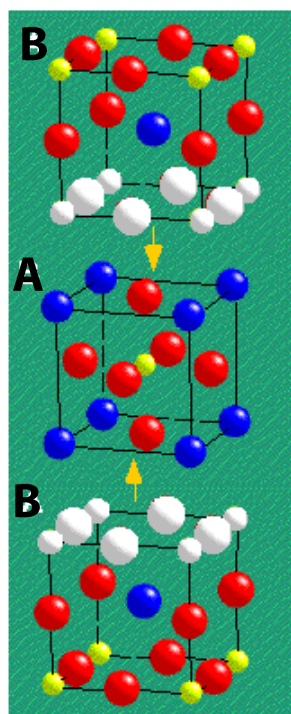
K_2NiF_4 STRUCTURE (La_2CuO_4)

Many “complex” structures are composed of simple, familiar building blocks.
The high- T_c copper oxide superconductors are an example.

Doped La_2CuO_4 was the first (1986) **High- T_c Superconducting Oxide** ($T_c \sim 40$ K)

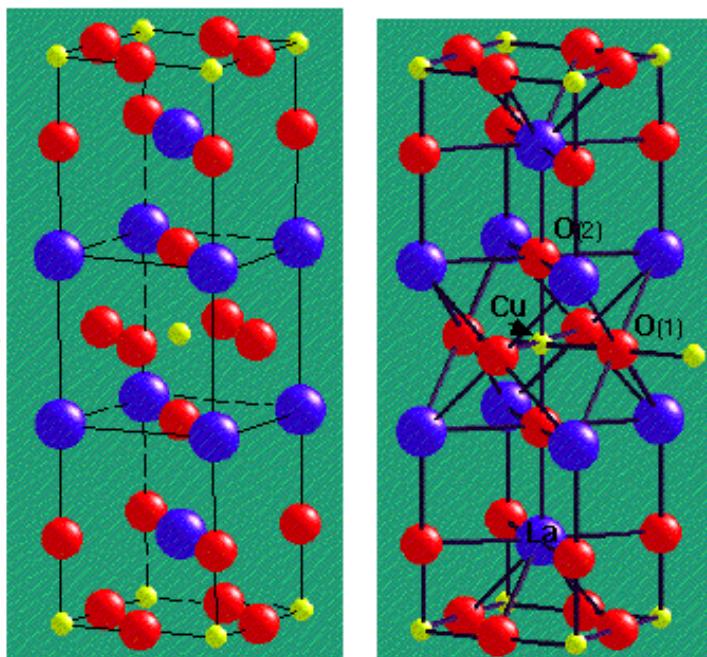
Bednorz & Müller were awarded a Nobel Prize

La_2CuO_4 may be viewed as if constructed from an ABAB... arrangement of Perovskite cells - *known as an AB Perovskite!*

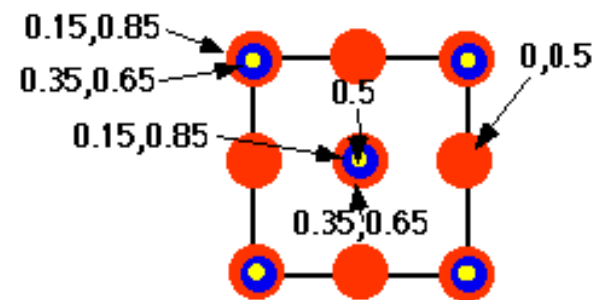


Stacked Perovskites
(\circ = missing atom)

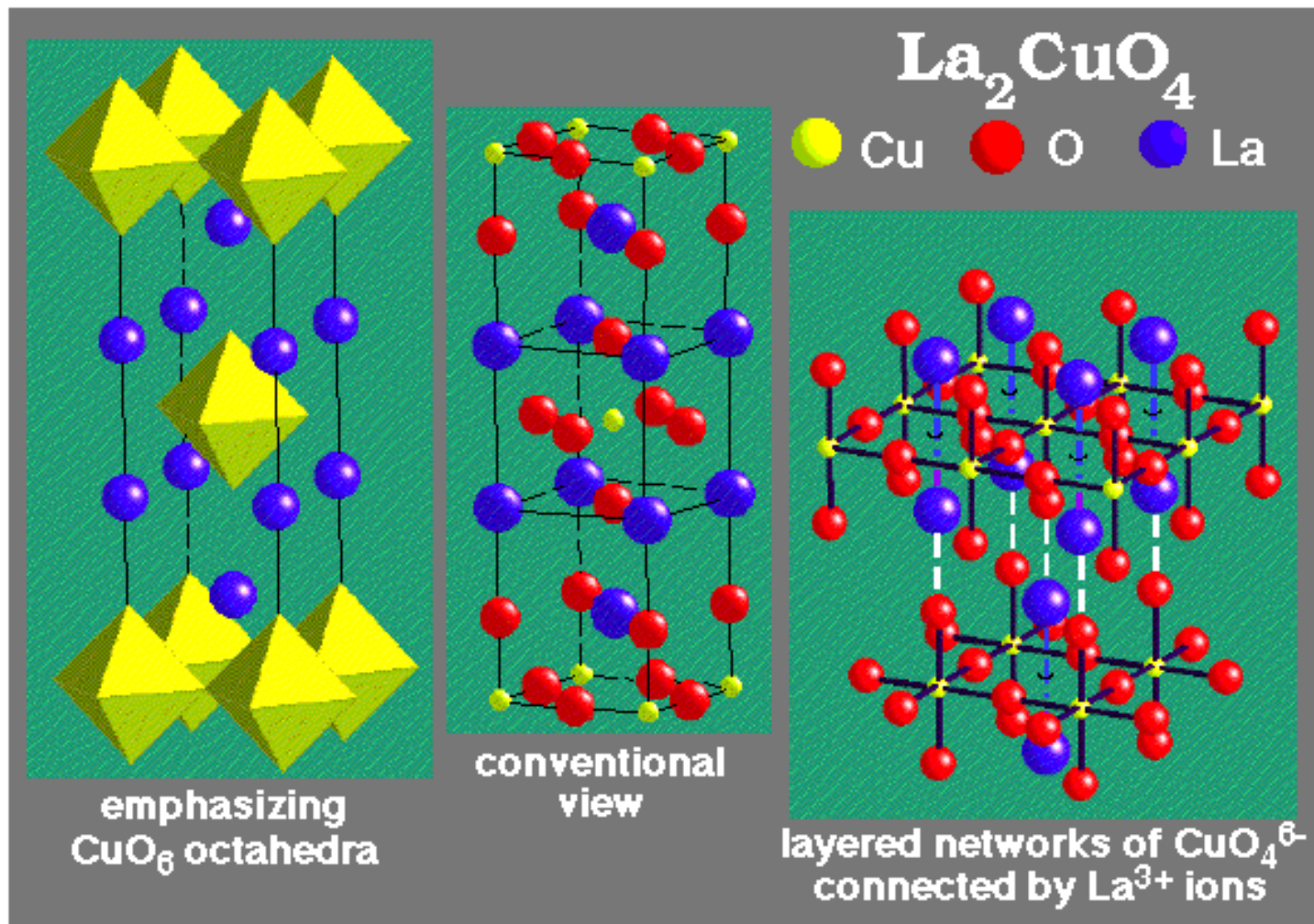
La_2CuO_4



2 La_2CuO_4 per unit cell



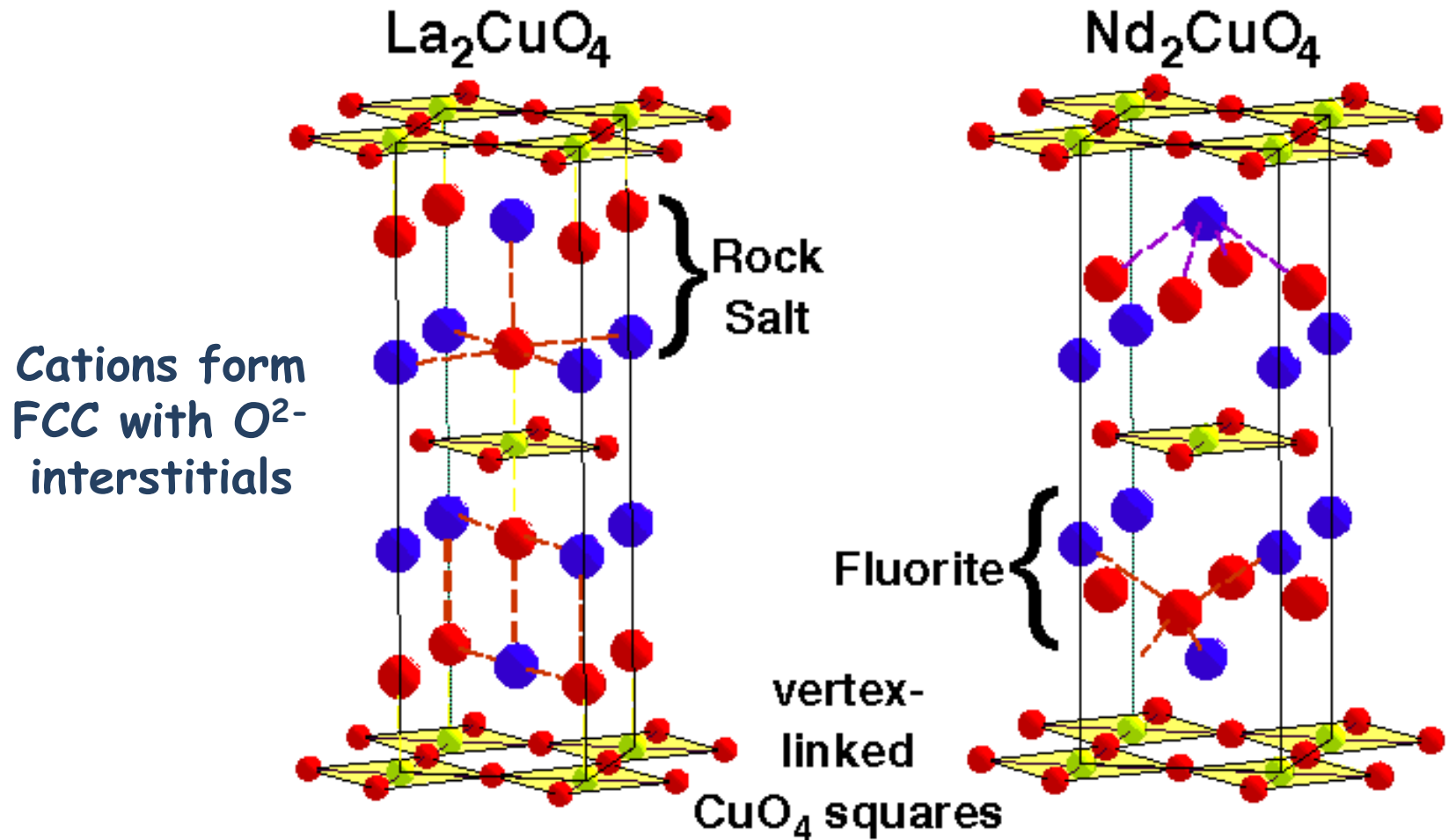
ALTERNATE VIEWS OF La_2CuO_4



We may view the structure as based on:

1. Sheets of elongated CuO_6 octahedra, sharing only vertices
2. Layered networks of CuO_4^{6-} , connected by La^{3+} ions

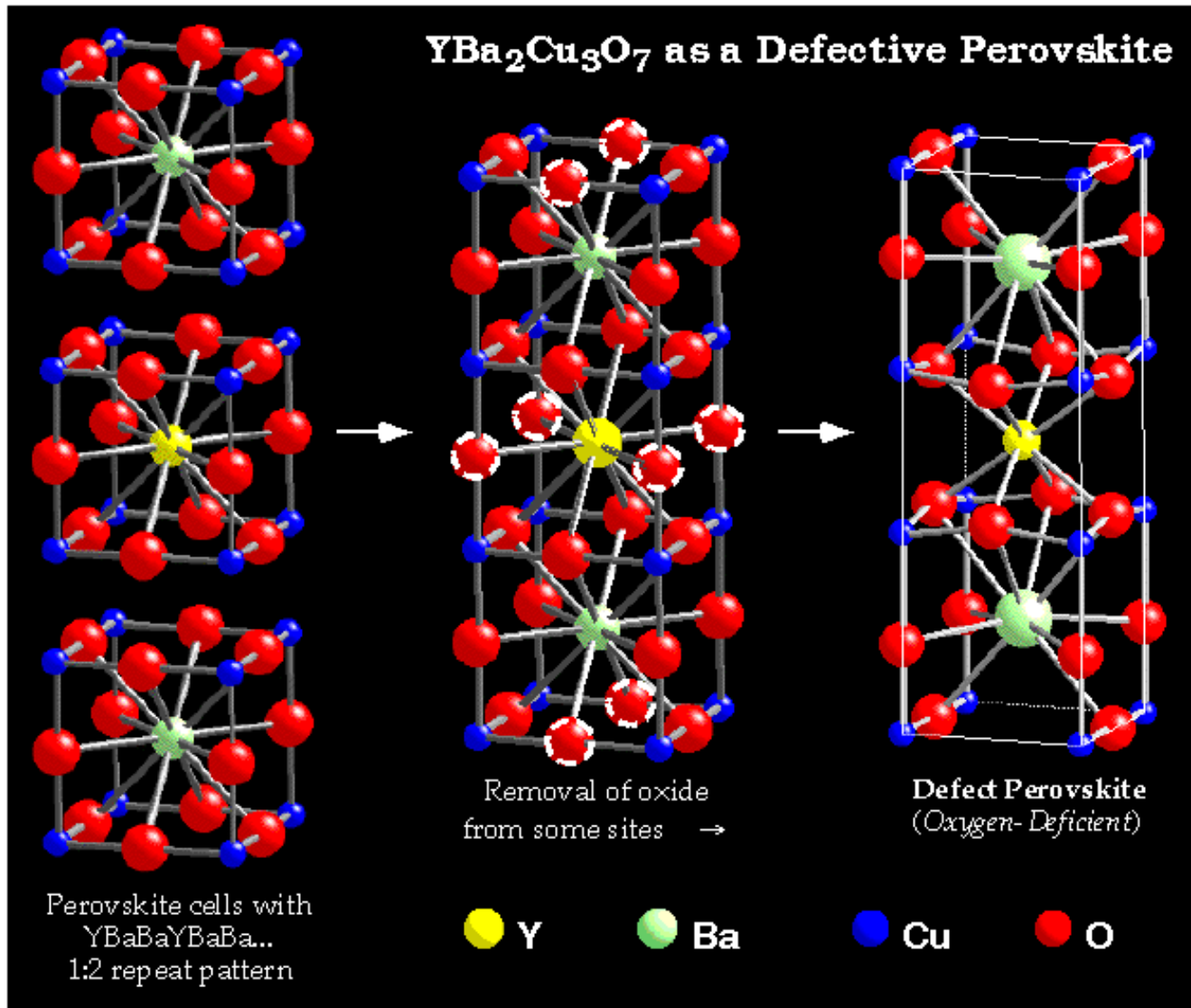
COMMON STRUCTURAL FORM



- Common structural motif of **vertex-linked CuO_4 squares**
- This motif occurs in all the high- T_c superconducting copper oxides
- The structures differ in the structure of the 'filling' in the 'sandwich' of copper oxide layers - known as ***Intergrowth Structures***

$Y_1Ba_2Cu_3O_7$: THE 1,2,3 SUPERCONDUCTOR

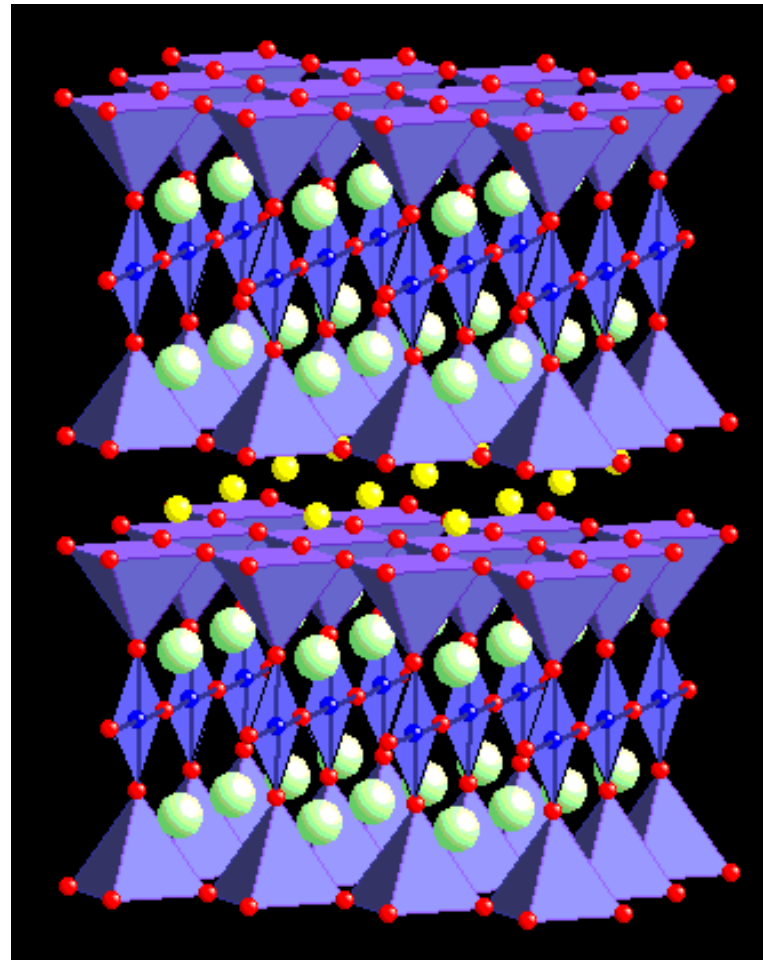
- the first material to superconduct at LN₂ temperature, $T_c > 77$ K
- $YBa_2Cu_3O_7$ can be viewed as an Oxygen-Deficient Perovskite



POLYHEDRAL REPRESENTATION OF YBCO

Two types of Cu sites:

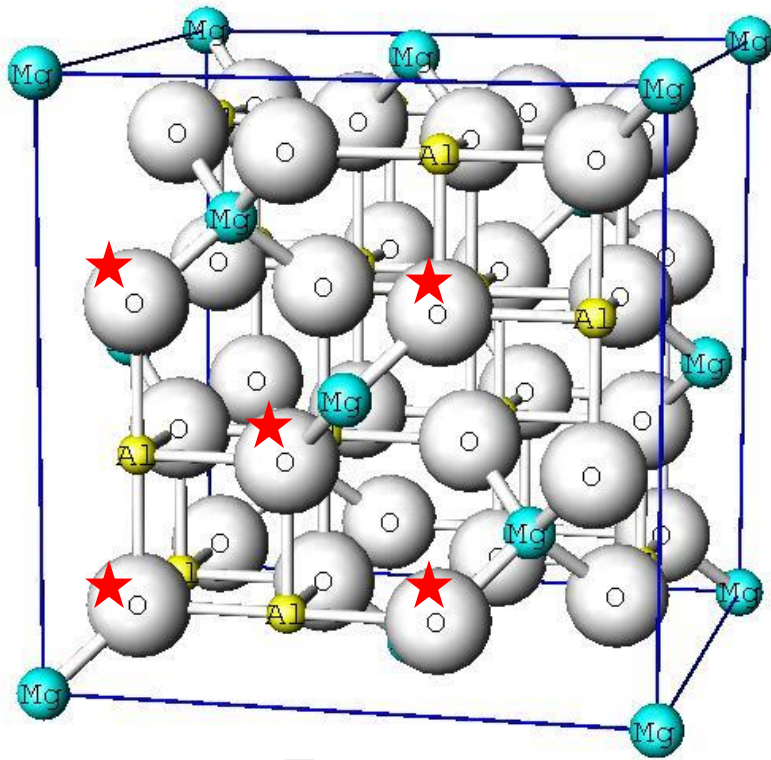
- 1) Layers of CuO_5 square pyramids
- 2) Chains of vertex-linked CuO_4 squares



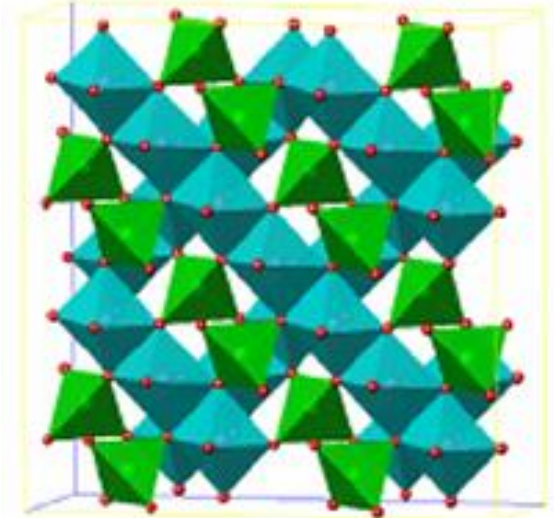
CuO_2
BaO
CuO
BaO
 CuO_2
Y
 CuO_2

SPINEL STRUCTURE AB_2O_4 ($MgAl_2O_4$)

(CCP, Mg in 1/8th of Tetra. Holes and Al in 50% of Oct. Holes)



$a = 8.08 \text{ \AA}$



Space Group = $Fd\bar{3}m$

Lattice = FCC

Coordination = Mg-4; Al-6; O-4

Mg Coord. → Tetrahedron

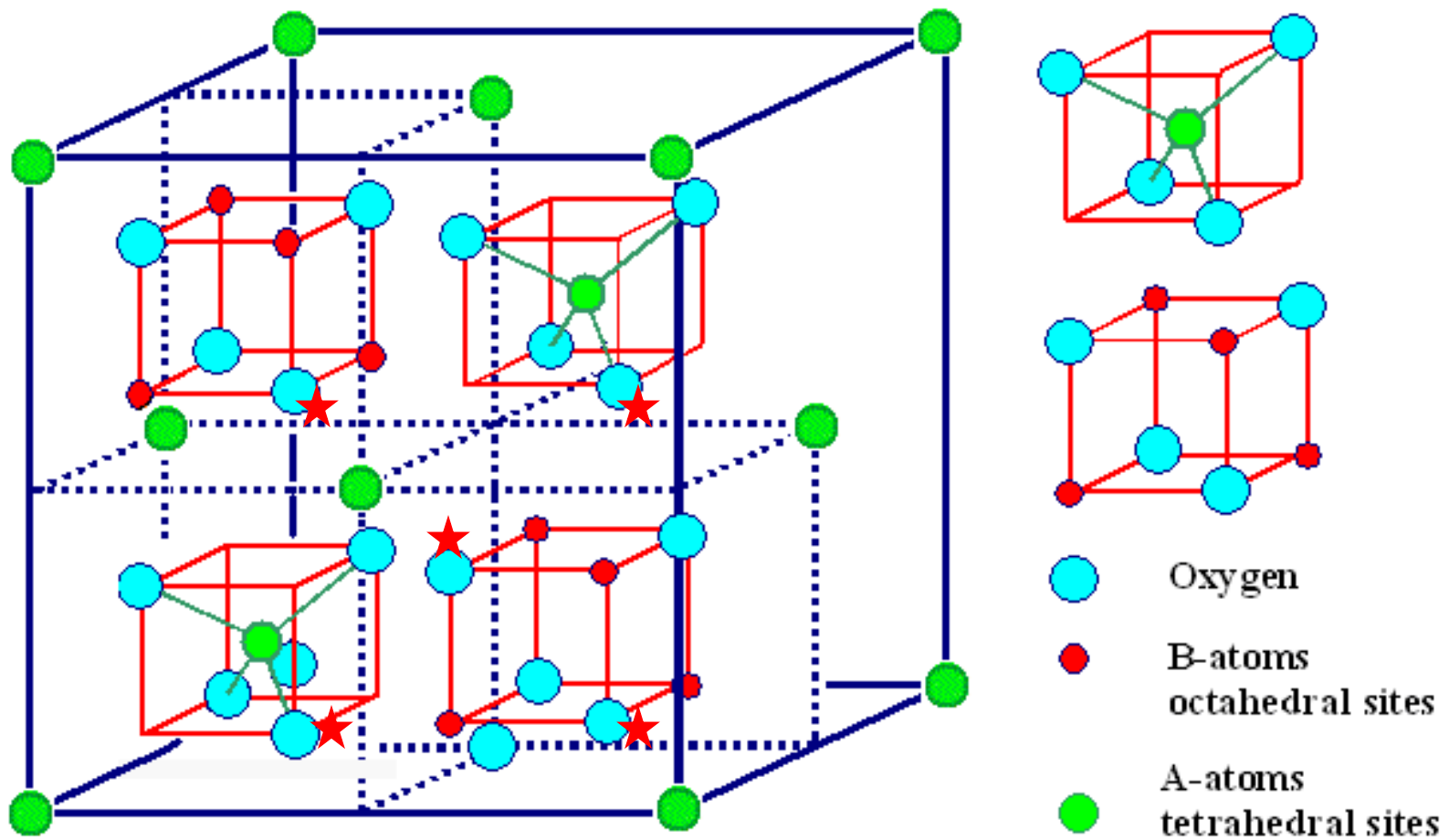
Al Coord. → Octahedron

Connectivity → chains of edge-sharing AlO_6 octahedra, linked by MgO_4 tetra.

8 $MgAl_2O_4$ per unit cell (56 atoms)

- extremely flexible structure, adopted by 100s of compounds
- **normal spinel**: 8 A in Tetra., 16 B in Oct.
- **inverse spinel**: 8 B in Tetra, 8 A and 8 B in Oct. intermediate cations distributions also occur.

The unit cell of the spinel structure formula



AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell

SPINELS - OCCURANCE

Aluminium spinels:

Spinel - $MgAl_2O_4$, after which this class of minerals is named

Gahnite - $ZnAl_2O_4$

Hercynite - $FeAl_2O_4$

Iron spinels:

Magnetite - Fe_3O_4

Franklinite - $(Fe,Mn,Zn)(Fe,Mn)_2O_4$

Ulvöspinel - $TiFe_2O_4$

Jacobsite - $MnFe_2O_4$

Trevorite - $NiFe_2O_4$

Chromium spinels:

Chromite - $FeCr_2O_4$

Magnesiochromite - $MgCr_2O_4$

Others with the spinel structure:

Ulvöspinel - Fe_2TiO_4

Ringwoodite - Mg_2SiO_4 , an abundant olivine polymorph within the Earth's mantle from about 520 to 660 km depth, and a rare mineral in meteorites

Table 5.2. Composition and cell size of the more common thiospinels

	Composition	Cell size a (Å)
Linnaeite	Co_3S_4	9.399
Polydymite	Ni_3S_4	9.480
Siegenite	$(Co,Ni)_3S_4$	9.418
Greigite	Fe_3S_4	9.876
Violarite	$FeNi_2S_4$	9.463
Carrollite	$CuCo_2S_4$	9.461
Daubréelite	$FeCr_2S_4$	9.989
Indite	$InFe_2S_4$	10.62

CRYSTAL FIELD STABILIZATION ENERGY

In transition metal compounds, d electron effects such as crystal field stabilization energy (CFSE) can be important in determining structure.

crystal field splitting diagrams

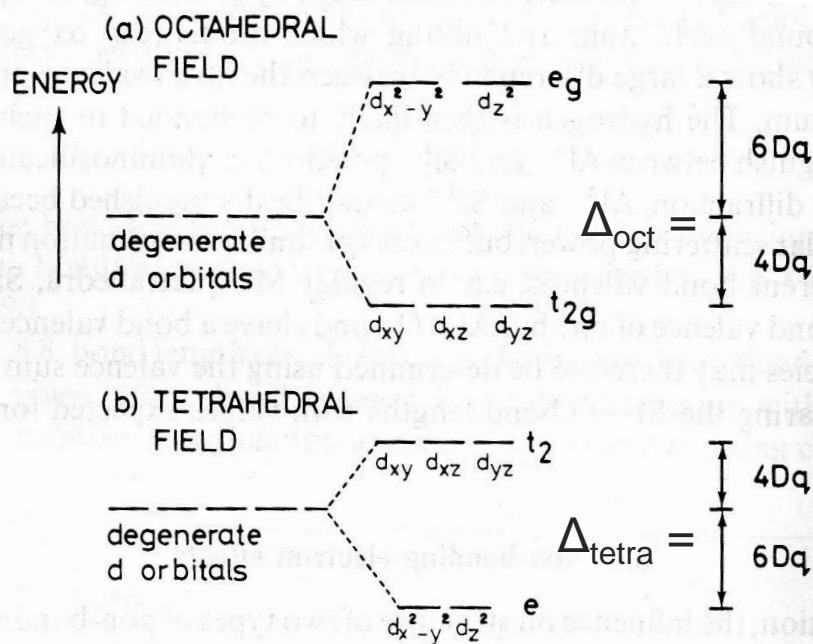
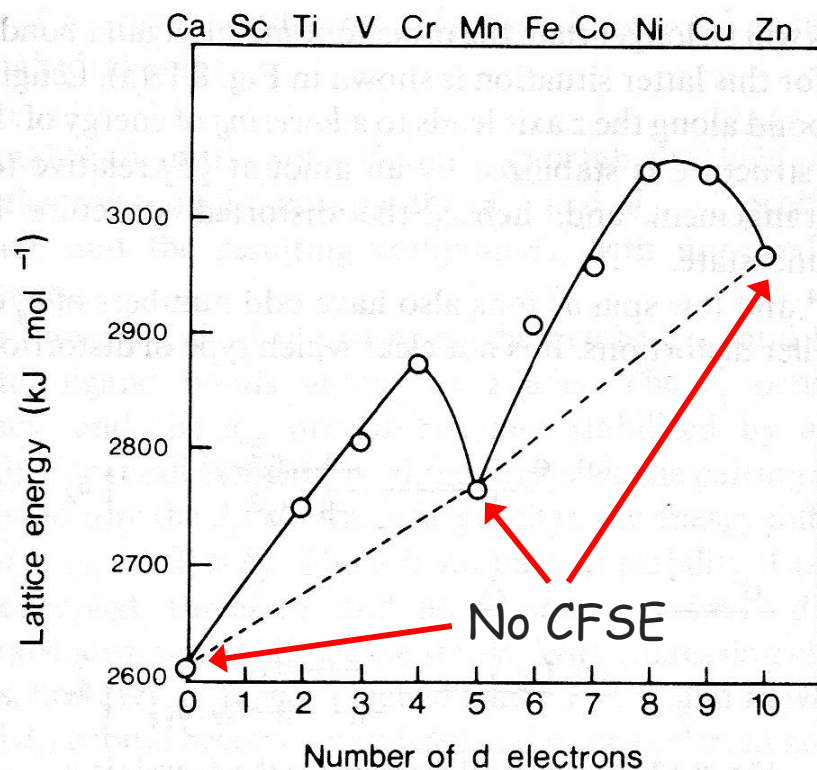


Fig. 8.9 Splitting of d energy levels in (a) an octahedral and (b) a tetrahedral field

$$CFSE_{oct} = (0.4 \times \#t_{2g} - 0.6 \times \#e_g) \Delta_{oct}$$

$$\Delta_{tetra} = (4/9)\Delta_{oct}$$

e.g. MF_2 compounds (high spin rutile)



CATION SITE PREFERENCES IN SPINELS

The larger CFSE of metal ions in octahedral sites is sometimes an important factor in determining spinel structures (normal vs inverse).



Table 8.15 Crystal field stabilization energies (kJ mol^{-1}) estimated for transition metal oxides. (Data from Dunitz and Orgel, 1960)

Ion		Octahedral stabilization	Tetrahedral stabilization	Excess octahedral stabilization
Ti ³⁺	d ¹	87.4	58.5	28.9
V ³⁺	d ²	160.1	106.6	53.5
Cr ³⁺	d ³	224.5	66.9	157.6
Mn ³⁺	d ⁴	135.4	40.1	95.3
Fe ³⁺	d ⁵	0	0	0
Mn ²⁺	d ⁵	0	0	0
Fe ²⁺	d ⁶	49.7	33.0	16.7
Co ²⁺	d ⁷	92.8	61.9	30.9
Ni ²⁺	d ⁸	122.1	35.9	86.2
Cu ²⁺	d ⁹	90.3	26.8	63.5

y = fraction of A in oct. sites
y = 0 is normal, y = 1 is inverse

Table 8.16 The γ parameters of some spinels. (Data from Greenwood, 1968 and Dunitz and Orgel, 1960)

M ³⁺	M ²⁺	Mg ²⁺	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
Al ³⁺		0	0.3	0	0	0.75	0.4	0
Cr ³⁺		0	0	0	0	0	0	0
Fe ³⁺		0.9	0.2	1	1	1	1	0
Mn ³⁺		0	0	0.67	0	1	0	0
Co ³⁺		—	—	—	0	—	—	0

In the absence of CFSE effects: 2,3 spinels tend to be normal (MgAl_2O_4)
4,2 spinels tend to be inverse (TiMg_2O_4)

In 2,3 spinels, CFSE favors the following:

- 1) Chromium spinels (Cr^{3+}) are normal
- 2) Magnetite (Fe_3O_4) is inverse b/c Fe^{3+} has zero CFSE, while Fe^{2+} prefers oct.
- 3) Mn_3O_4 is normal b/c Mn^{2+} has no CFSE

CORUNDUM STRUCTURE ($\alpha\text{-Al}_2\text{O}_3$)

(HCP, 2/3 of Oct. Holes filled)

Space Group = $\bar{R}3c$

Lattice = Primitive trigonal

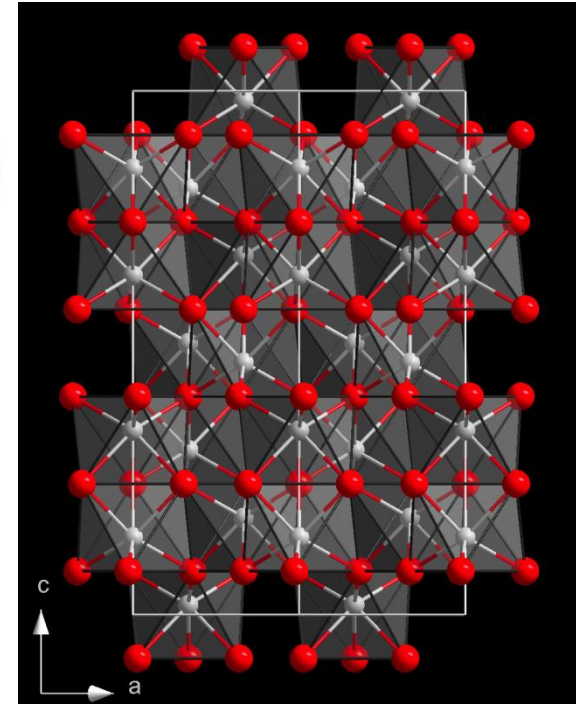
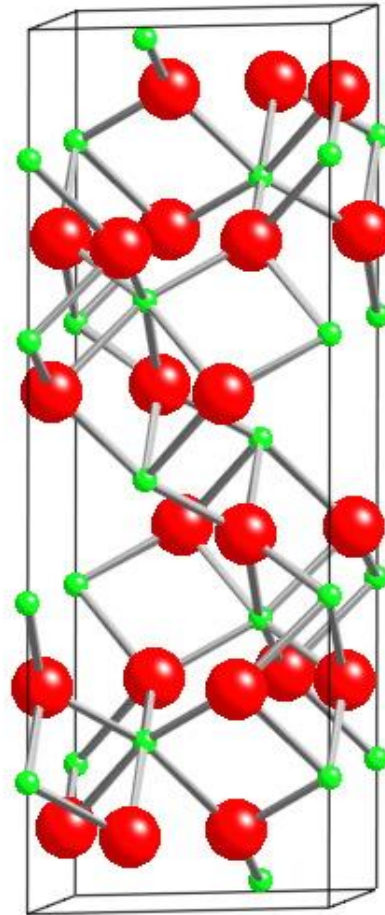
Coordination = 6, 4

Cation Coord. \rightarrow Octahedron

Anion Coord. \rightarrow distorted tetrahedron

Connectivity \rightarrow edge, face-sharing Oct.

6 Al_2O_3 per unit cell



• Ruby (Cr), sapphire (Fe, Ti, Cr), Fe_2O_3

