Crystal Structures

Chapter 7

Wednesday, October 21, 2015

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

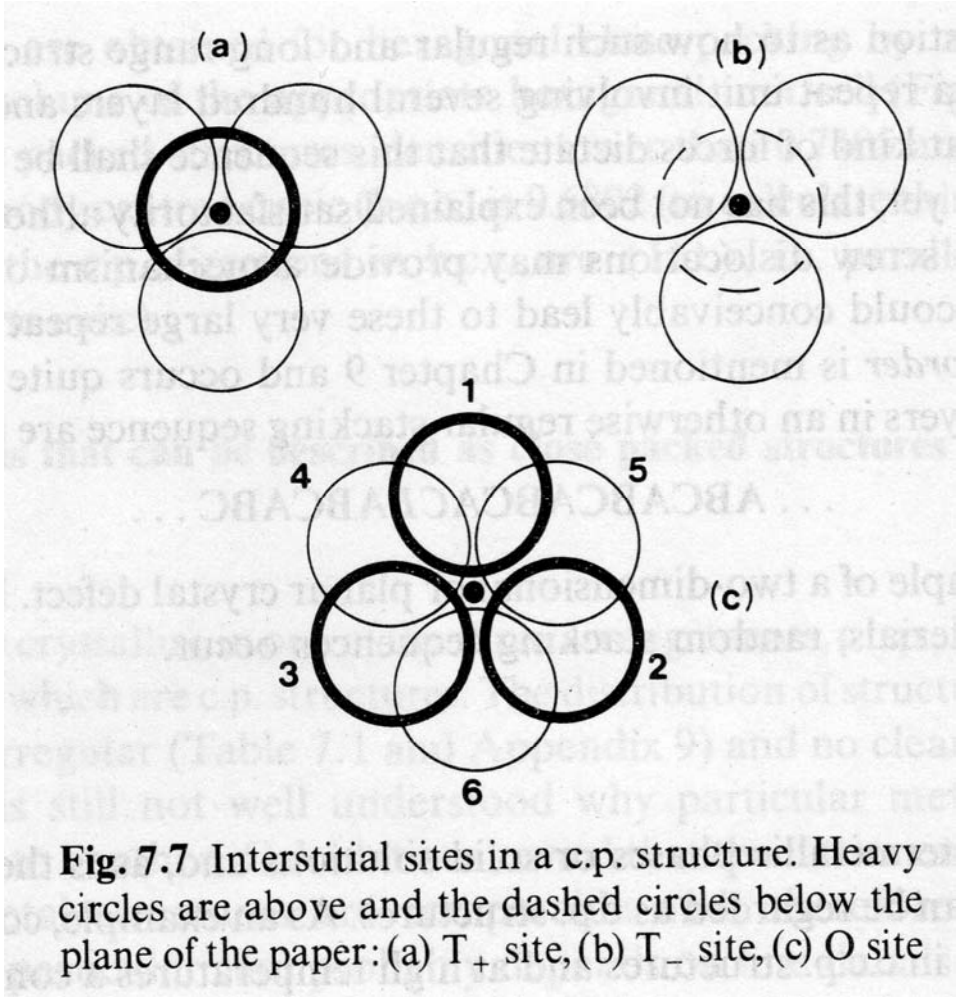
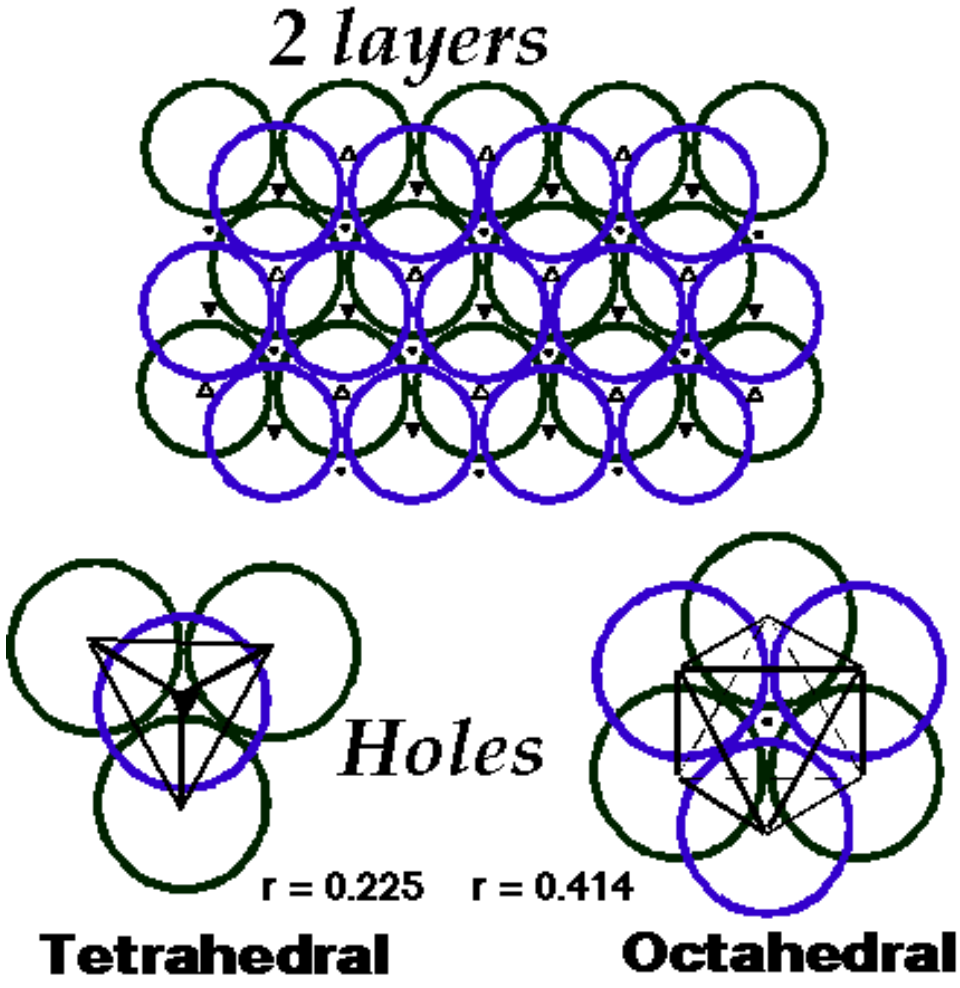
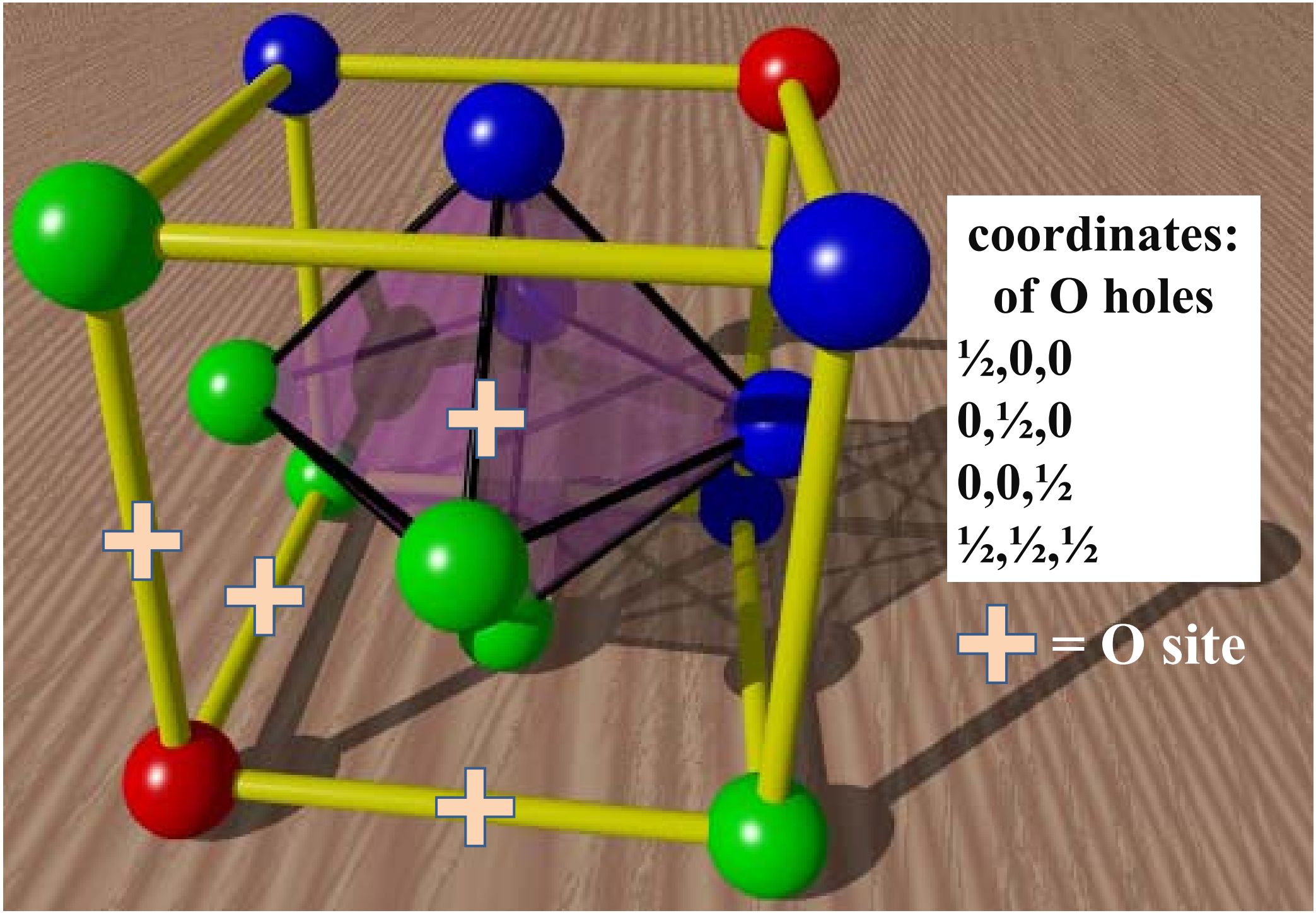


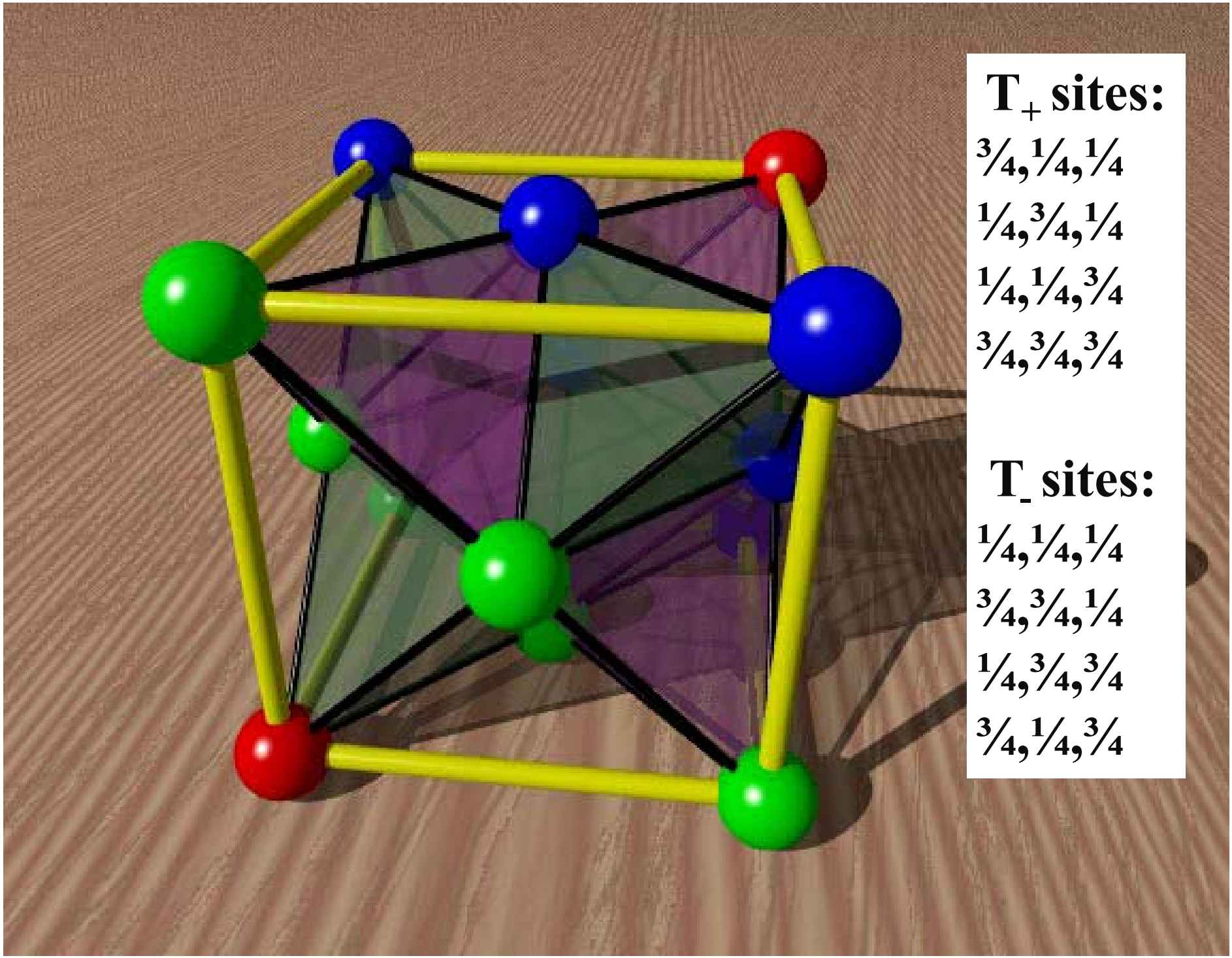
Fig. 7.7 Interstitial sites in a c.p. structure. Heavy circles are above and the dashed circles below the plane of the paper: (a) T_+ site, (b) T_- site, (c) O site



Octahedral Holes in CCP



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:

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

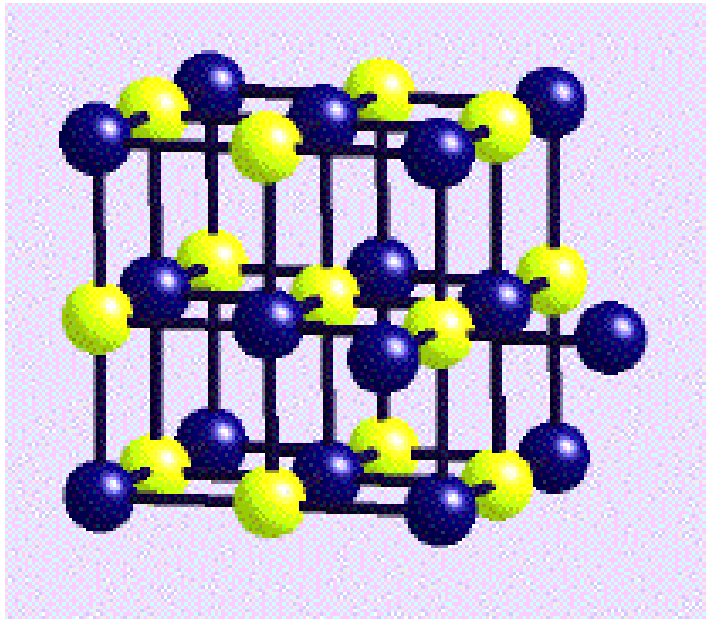
$\frac{3}{4},\frac{3}{4},\frac{1}{4}$

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

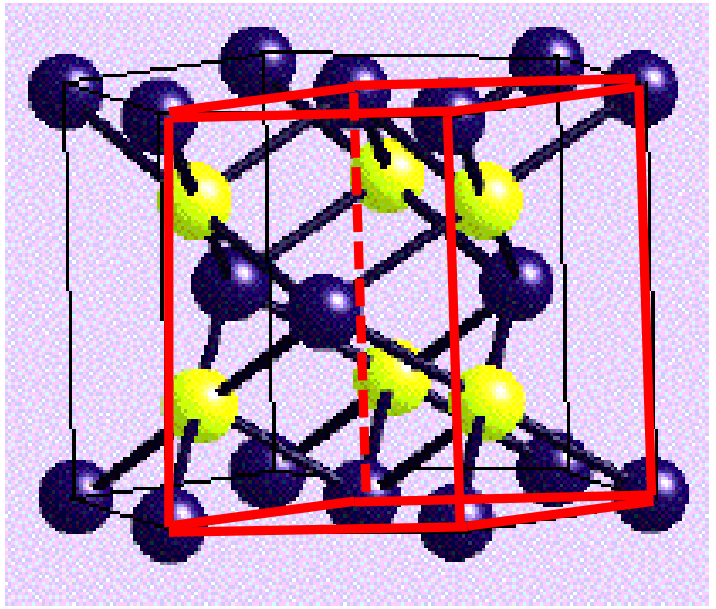
$\frac{3}{4},\frac{1}{4},\frac{3}{4}$

Octahedral Holes in CCP and HCP

CCP

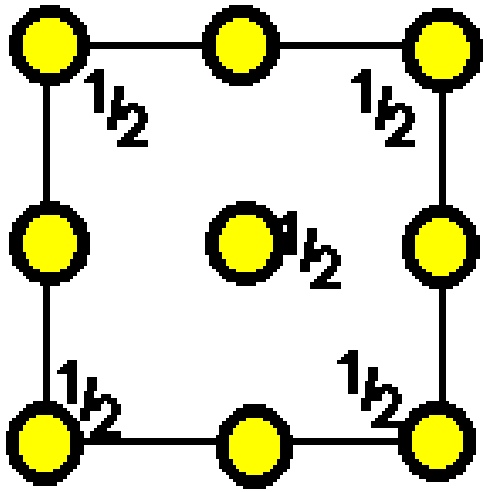


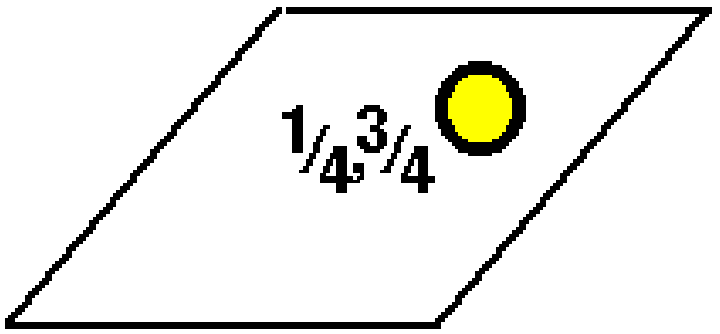
HCP



Location of **OCTAHEDRAL** Interstitial Holes

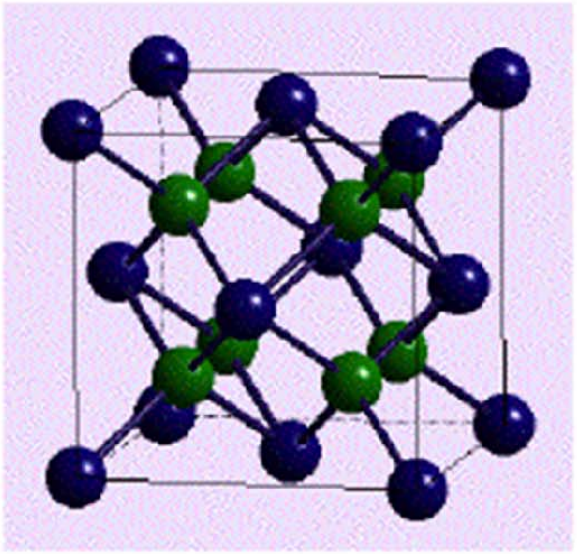
1 per sphere



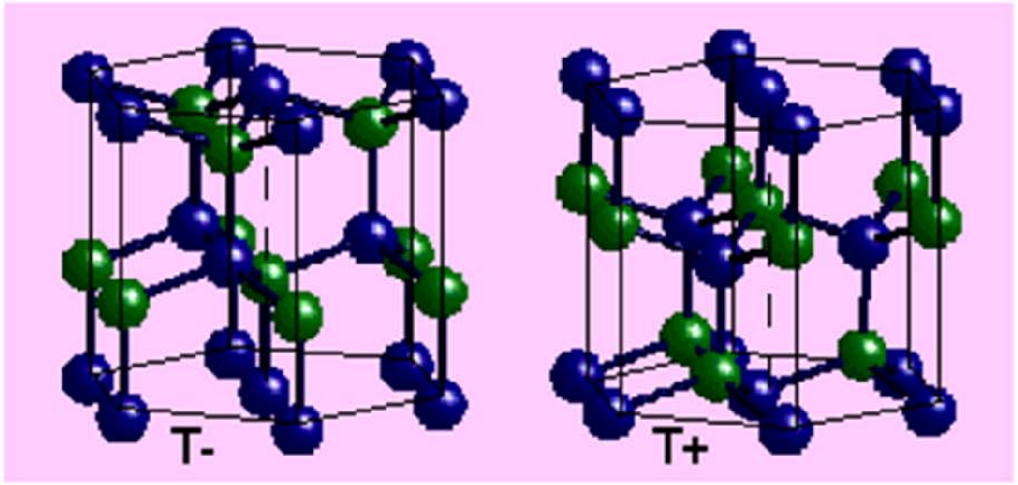


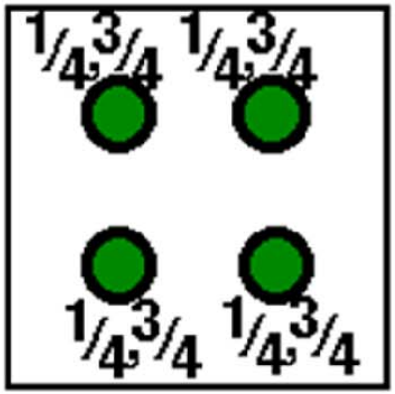
Tetrahedral Holes in CCP and HCP

CCP



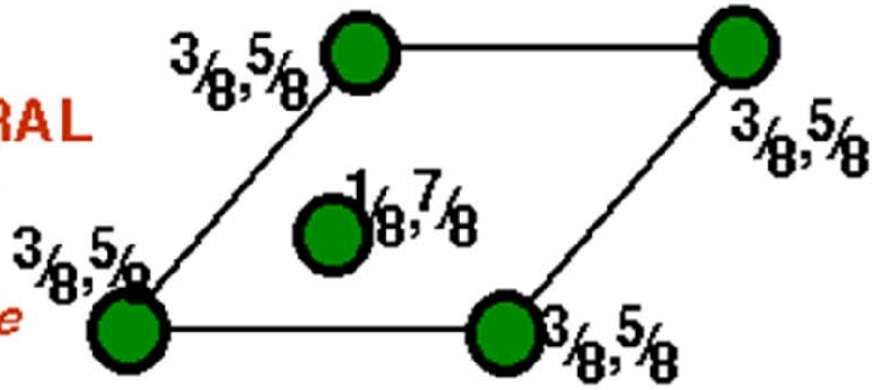
HCP





Location of **TETRAHEDRAL** Interstitial Holes

2 per sphere



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

Ionic Crystal Structures

Many ionic crystals consist of a close-packed lattice of the larger anions with the smaller cations occupying interstitial sites.

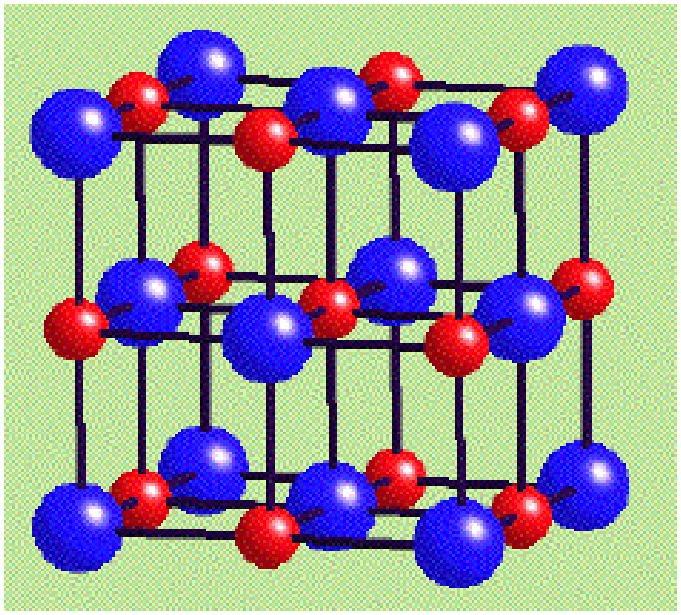
Anion arrangement	Interstitial sites T_+	T_-	Oct	Examples
c.c.p.	—	—	1	NaCl, rock salt
	1	—	—	ZnS blende or sphalerite
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	$MgAl_2O_4$, spinel
	—	—	$\frac{1}{2}$	$CdCl_2$
	1	—	—	$CuFeS_2$
	—	—	$\frac{1}{3}$	$CrCl_3$
	1	1	—	K_2O antifluorite
h.c.p.	—	—	1	NiAs
	1	—	—	ZnS, wurtzite
	—	—	$\frac{1}{2}$	CdI_2
	—	—	$\frac{1}{2}$	TiO_2*, rutile
	—	—	$\frac{2}{3}$	Al_2O_3
	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{2}$	Mg_2SiO_4, olivine
	1	—	—	β-Li_3PO_4
	$\frac{1}{2}$	$\frac{1}{2}$	—	γ-Li_3PO_4*
c.c.p. 'CaO_3' layers	—	—	$\frac{1}{4}$	$CaTiO_3$ perovskite

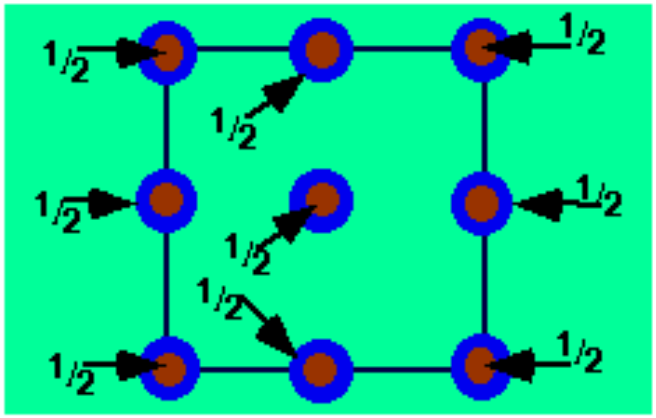
* The h.c.p. oxide layers in rutile and γ-Li_3PO_4 are not planar but are buckled. The oxide ion arrangement in these may alternatively be described as tetragonal packed (t.p.).

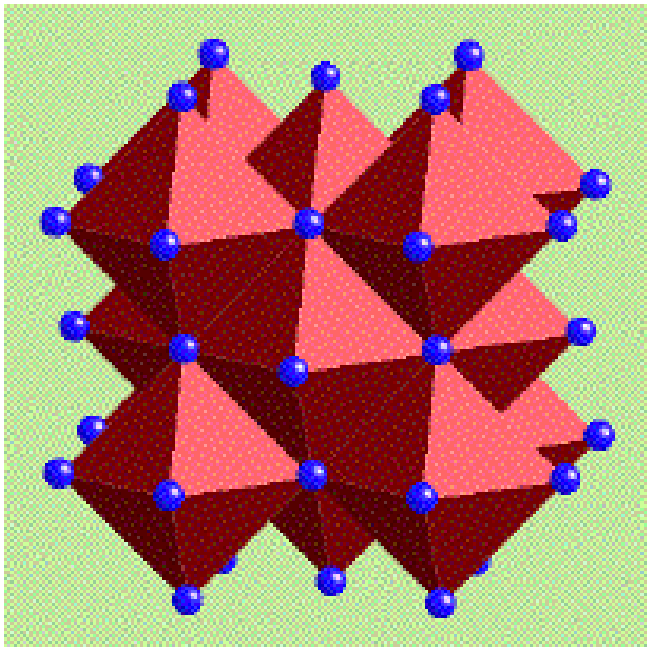
let's look at these structures

NaCl Structure

CCP with all octahedral holes filled







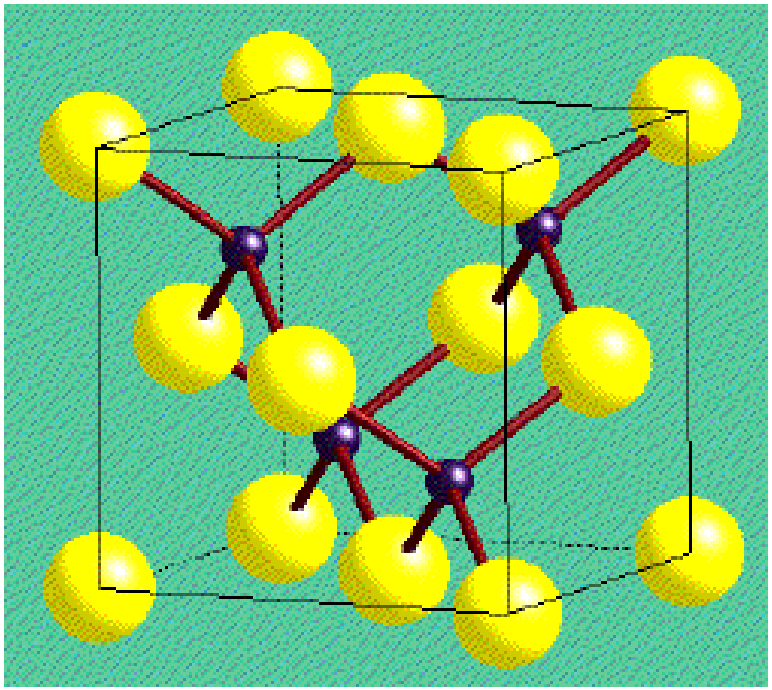
Coordination = 6, 6
Cation Coord. → Octahedron
Anion Coord. → Octahedron
Connectivity → Edge sharing octahedra
4 NaCl in unit cell

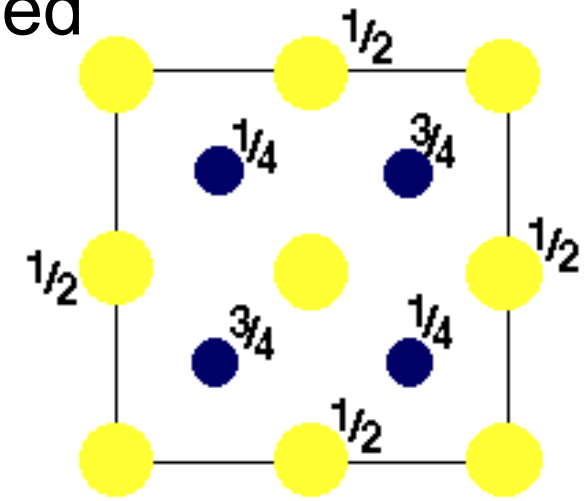
Table 7.5 *Some compounds with the NaCl structure*

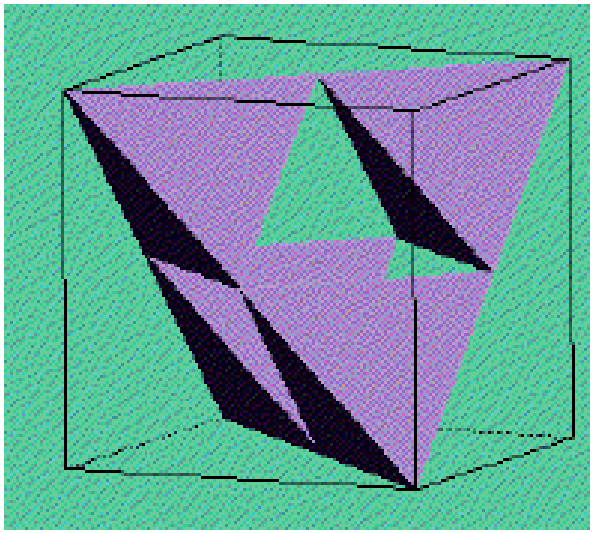
	a(Å)		a(Å)		a(Å)		a(Å)
MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	αMnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	4.64	RbCl	6.5810
FeO	4.307	CaSe	5.924	NaCl	5.6402	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	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		

Zinc Blende (ZnS) Structure

CCP with all T^+ holes filled







Coordination = 4, 4
Cation Coord. → Tetrahedron
Anion Coord. → Tetrahedron
Connectivity → Corner sharing Tetrahedra
4 ZnS in unit cell

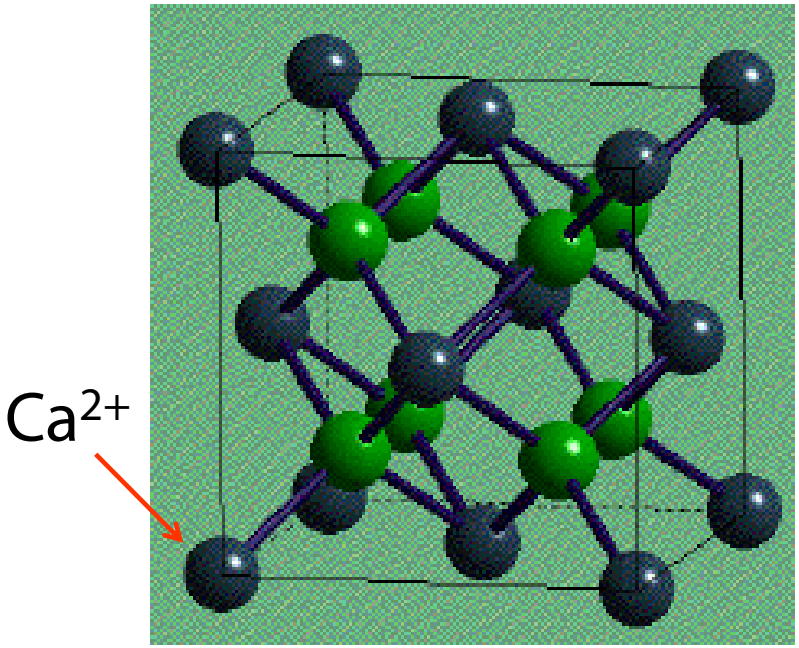
Table 7.6 *Some compounds with the zinc blende (sphalerite) structure*

	a(Å)		a(Å)		a(Å)		a(Å)		a(Å)
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	BAs	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						

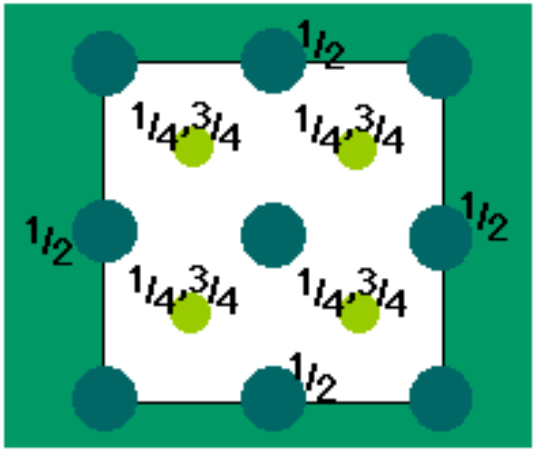
Fluorite (CaF_2) and Antifluorite (Li_2O)

Fluorite: CCP of Ca^{2+} with all T^+ and T^- holes filled with F^-

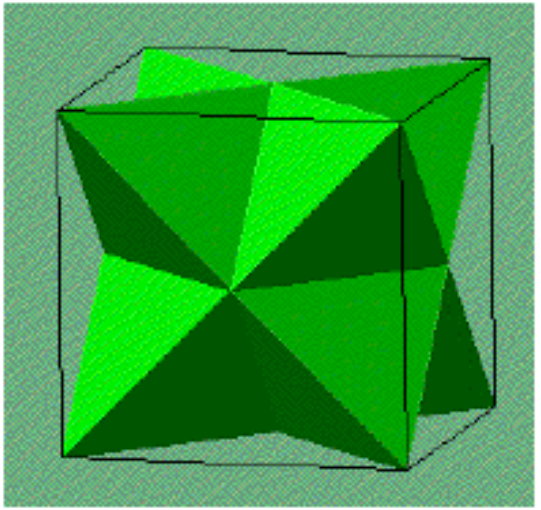
Antifluorite: CCP of O^{2-} with all T^+ and T^- holes filled with Li^+



Fluorite A-cell



Plan view



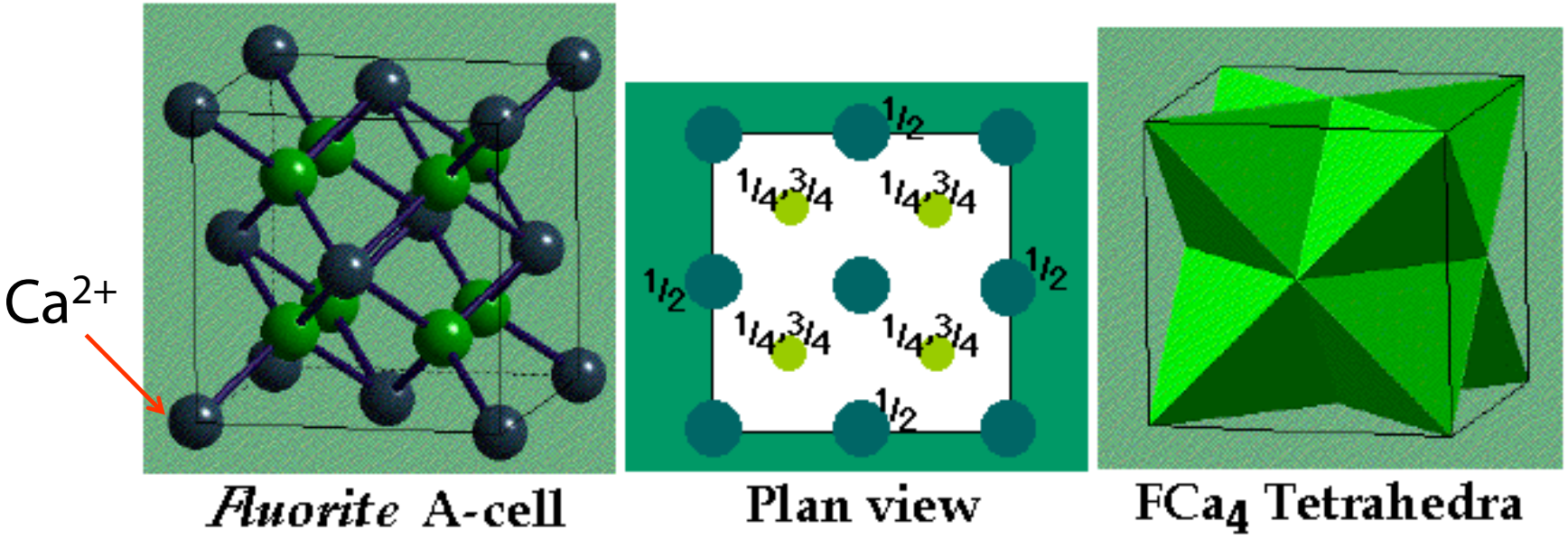
FCa_4 Tetrahedra

Coordination = 8, 4 (fluorite)
Cation Coord. → Cubic
Anion Coord. → Tetrahedral
Connectivity → 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*

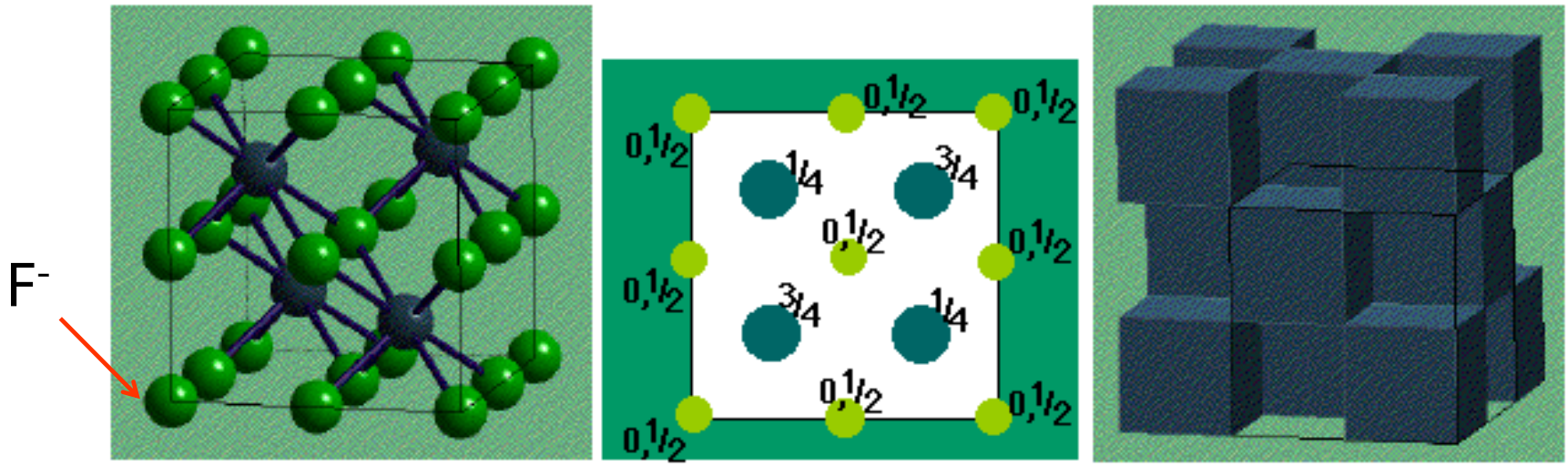
Fluorite structure				Antifluorite structure			
	a(Å)		a(Å)		a(Å)		a(Å)
CaF_2	5.4626	PbO_2	5.349	Li_2O	4.6114	K_2O	6.449
SrF_2	5.800	CeO_2	5.4110	Li_2S	5.710	K_2S	7.406
$SrCl_2$	6.9767	PrO_2	5.392	Li_2Se	6.002	K_2Se	7.692
BaF_2	6.2001	ThO_2	5.600	Li_2Te	6.517	K_2Te	8.168
$BaCl_2$	7.311	PaO_2		Na_2O	5.55	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		
β-PbF_2	5.940	AmO_2	5.376				
		CmO_2	5.3598				

Alternative Representations of Fluorite



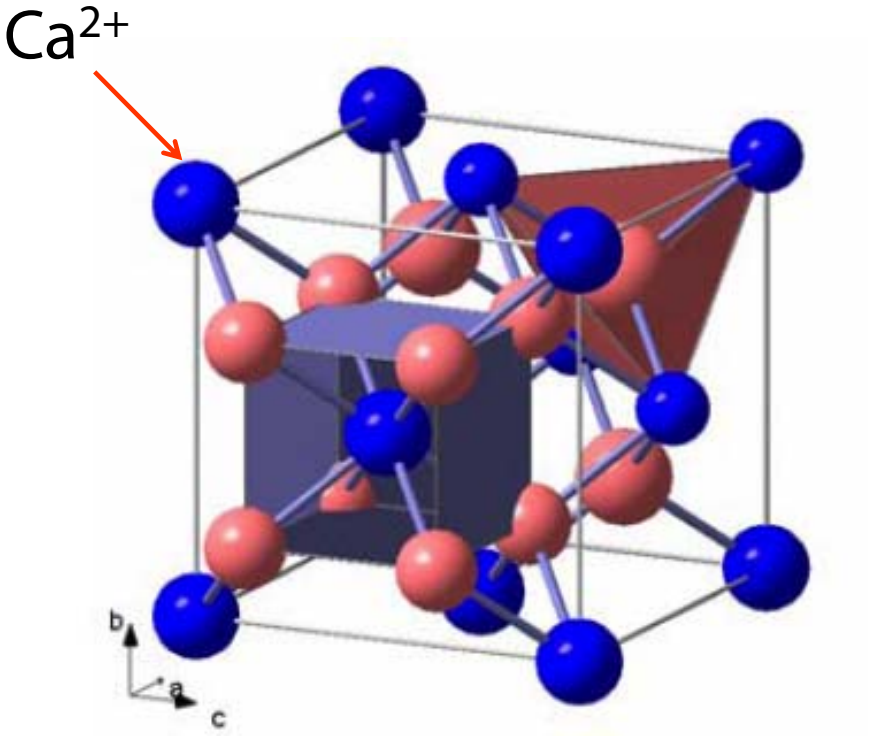
Fluorite A-cell | Plan view | FCa_4 Tetrahedra

Displacing the unit cell by ¼ of a body diagonal emphasizes the cubic cation coordination:

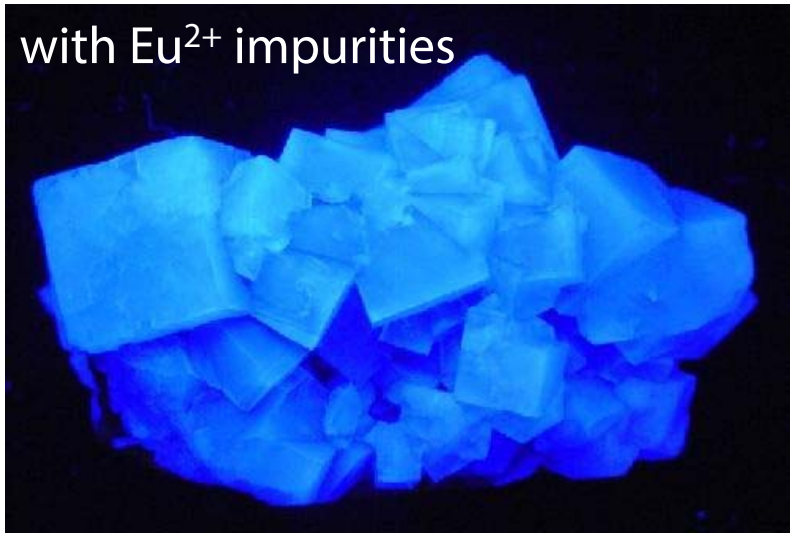


Fluorite B-cell | Plan view | CaF_8 Cubes

Fluorite (CaF_2) and Antifluorite (Li_2O)

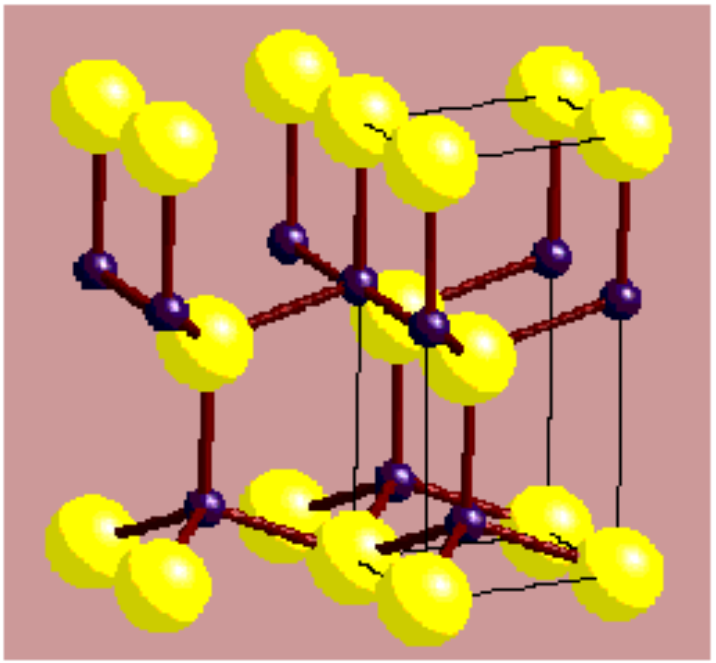


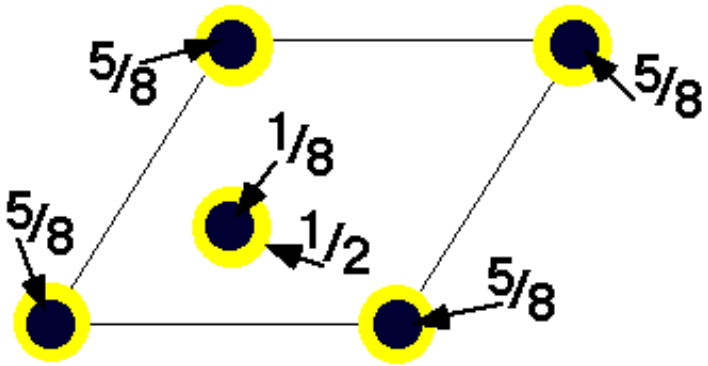
- *origin of the term "fluorescence"* (George Stokes, 1852)
- ***fluorite*** *common for fluorides of large, divalent cations and oxides of large tetravalent cations* ($M^{2+}F_2$ and $M^{4+}O_2$)
- ***antifluorite*** *common for oxides/chalcogenides of alkali earths* (M_2O)

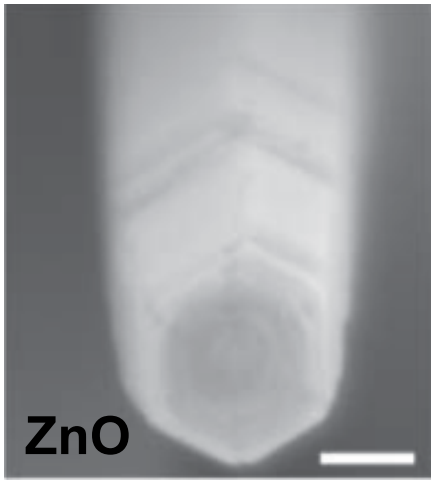


Wurtzite (ZnS) Structure

HCP with all T^+ holes filled







50 nm

Coordination = 4, 4
Cation Coord. → Tetrahedron
Anion Coord. → Tetrahedron
Connectivity → Corner sharing Tetra.
2 ZnS per unit cell

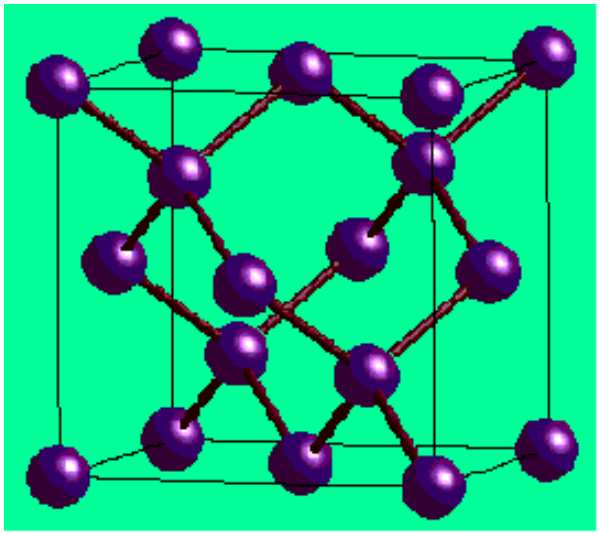
Table 7.9 *Some compounds with the wurtzite structure.* (Data taken from Wyckoff, 1971, Vol. 1)

	a(Å)	*c*(Å)	*u*	*c*/*a*		*a*(Å)	*c*(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_4F	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					

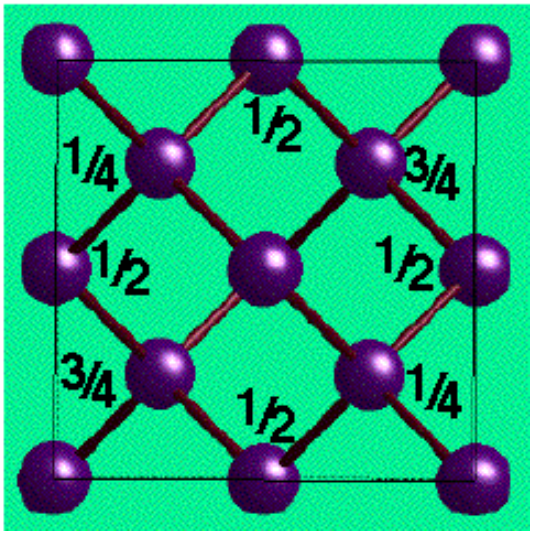
Diamond Structure

same as zinc blende, but with only one element

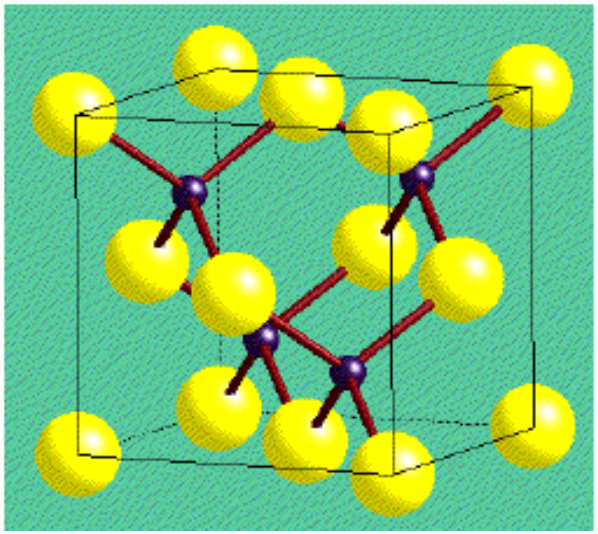
diamond



Unit Cell



zinc blende



Coordination = 4

Connectivity → Corner sharing Tetrahedra

8 C atoms per unit cell

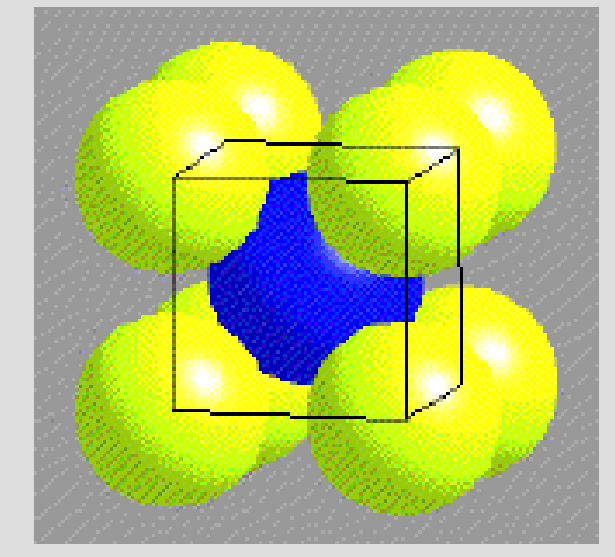
TABLE 1.9 Elemental Crystals with the Diamond Crystal Structure

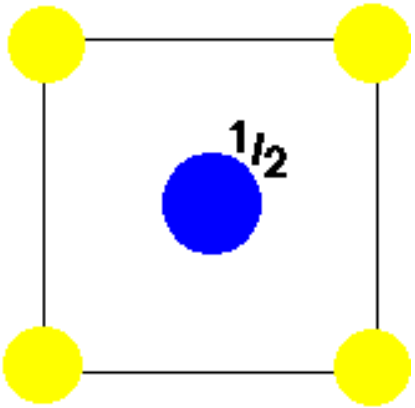
Element	a (nm)[a]	Element	a (nm)[a]
C	0.3567	Si	0.543
Ge	0.5657	Sn (gray)	0.649

[a]Lattice constants are values at room temperature.

CsCl Structure

simple cubic lattice with Cs^+ at cube center (not CP, not BCC!)





Coordination = 8, 8
Cation Coord. → Cubic
Anion Coord. → Cubic
Connectivity → face sharing cubes
1 CsCl per unit cell

Table 7.11 *Some compounds with the CsCl structure*

	a(Å)		*a*(Å)
CsCl	4.123	CuZn	2.945
CsBr	4.286	CuPd	2.988
CsI	4.5667	AuMg	3.259
CsCN	4.25	AuZn	3.19
NH_4Cl	3.8756	AgZn	3.156
NH_4Br	4.0594	LiAg	3.168
TlCl	3.8340	AlNi	2.881
TlBr	3.97	LiHg	3.287
TlI	4.198	MgSr	3.900

Adoption by chlorides, bromides and iodides of larger cations

Self Test

Identify the following crystal structures: