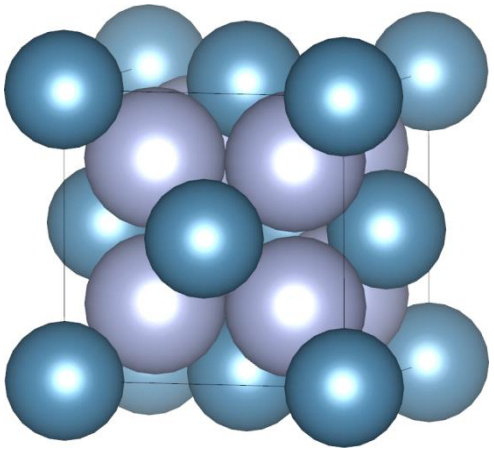
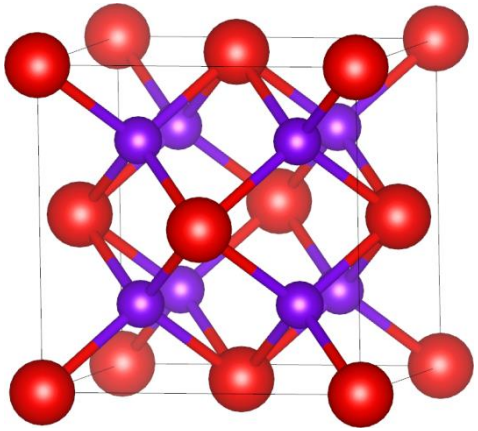




Structure types

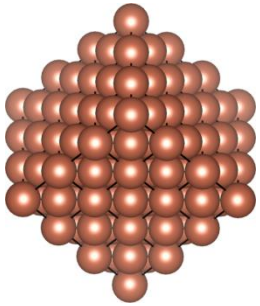
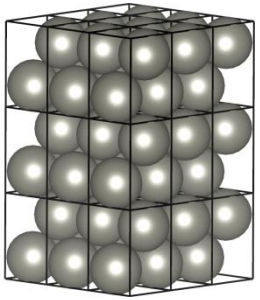
Please see Lecture 3 for definitions of close-packing and interstitial sites

Structure types in this document

Name	Crystal system	Space group
NaCl (rocksalt)	Cubic	*Fm*-3*m*
ZnS (zinc blende)	Cubic	*F*-43*m*
CaF_2 (fluorite)	Cubic	*Fm*-3*m*
Na_2O (antifluorite)	Cubic	*Fm*-3*m*
CsCl	Cubic	*Pm*-3*m*
ZnS (wurtzite)	Hexagonal	$P6_3mc$
NiAs	Hexagonal	$P6_3mc$
CdI_2	Trigonal	*P*-3*m*
Al_2O_3 (corundum)	Trigonal	*R*-3*c*
TiO_2 (rutile)	Tetragonal	$P4_2/mnm$
$CaTiO_3$ (perovskite)	Cubic	*Pm*-3*m*
$MgAl_2O_4$ (spinel)	Cubic	*Fd*-3*m*
Inverse spinel	Cubic	*Fd*-3*m*

Interstitial sites in close-packed lattices

Table 1.4 ***Some close packed structures***

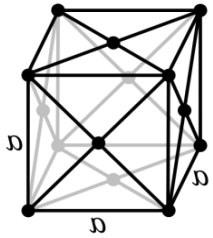
Anion arrangement	Interstitial sites T_+	Interstitial sites T_-	Interstitial sites O	Examples
ccp 	–	–	1	NaCl, rock salt
	1	–	–	ZnS, blende or sphalerite
	1/8	1/8	1/2	$MgAl_2O_4$, spinel
	–	–	1/2	$CdCl_2$
	–	–	1/3	$CrCl_3$
	1	1	–	K_2O, antifluorite
hcp 	–	–	1	NiAs
	1	–	–	ZnS, wurtzite
	–	–	1/2	CdI_2
	–	–	1/2	TiO_2, rutile[a]
	–	–	2/3	Al_2O_3, corundum
	1/8	1/8	1/2	Mg_2SiO_4, olivine
ccp 'BaO_3' layers	–	–	1/4	$BaTiO_3$, perovskite

[a]The *hcp* oxide layers in rutile are not planar but are buckled; the oxide arrangement may alternatively be described as *tetragonal* packed, tp.

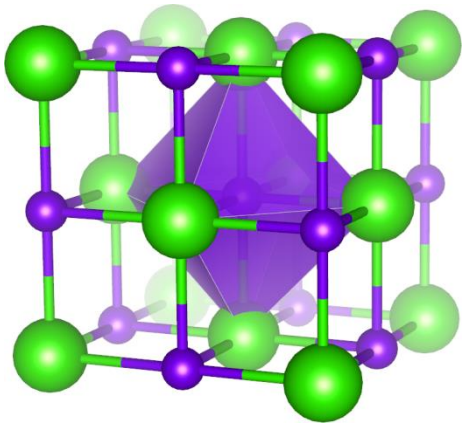
Ref: West p. 28

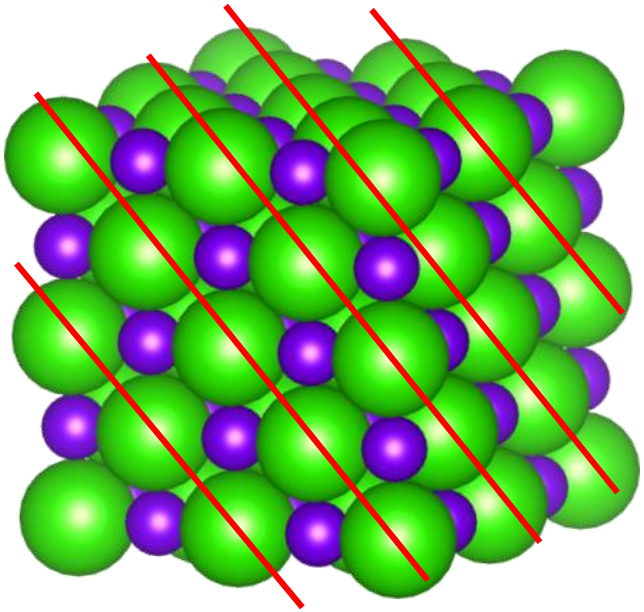
NaCl (rocksalt): *Fm*-3*m*

- Cubic close-packed layers of Cl^- anions (red lines in figure below)
- Na^+ cations in octahedral interstitials



F (fcc)





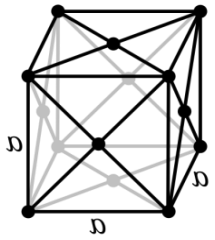
Figures: AJK

Table 1.8 ***Some compounds with the NaCl structure, a/Å***

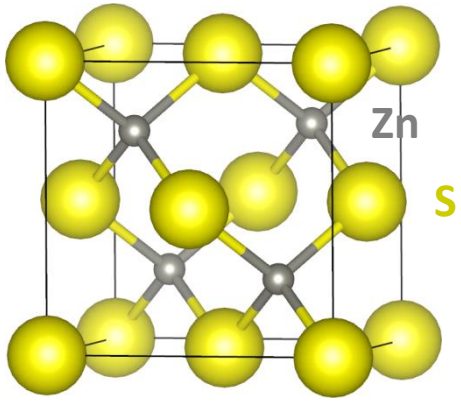
MgO	4.213	MgS	5.200	LiF	4.0270	KF	5.347
CaO	4.8105	CaS	5.6948	LiCl	5.1396	KCl	6.2931
SrO	5.160	SrS	6.020	LiBr	5.5013	KBr	6.5966
BaO	5.539	BaS	6.386	LiI	6.00	KI	7.0655
TiO	4.177	α-MnS	5.224	LiH	4.083	RbF	5.6516
MnO	4.445	MgSe	5.462	NaF	4.64	RbCl	6.5810
FeO	4.307	CaSe	5.924	NaCl	5.6402	RbBr	6.889
CoO	4.260	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	TiN	4.240	AgCl	5.549
TiC	4.3285	LaN	5.30	UN	4.890	AgBr	5.7745

ZnS (zinc blende): *F*-43*m*

- Zn at T^+ (or T^-) sites
- Anion and cation sites are interchangeable
- Diamond-like network with two atom types



F (fcc)



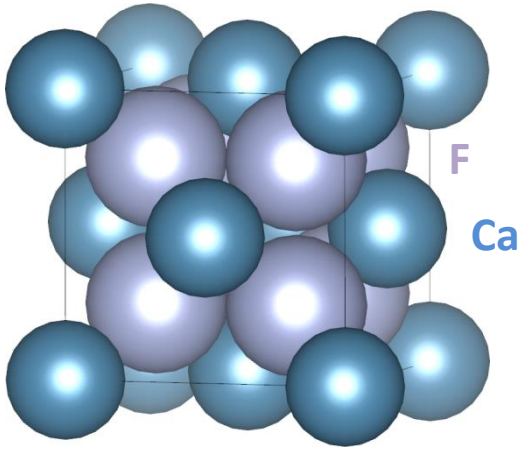
Figures: AJK

Table 1.9 ***Some compounds with the zinc blende (sphalerite) structure, a/Å***

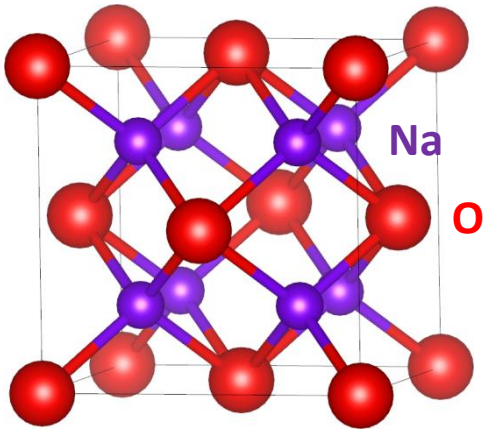
CuF	4.255	BeS	4.8624	β-CdS	5.818	BN	3.616	GaP	5.448
CuCl	5.416	BeSe	5.07	CdSe	6.077	BP	4.538	GaAs	5.6534
γ-CuBr	5.6905	BeTe	5.54	CdTe	6.481	BAs	4.777	GaSb	6.095
γ-CuI	6.051	β-ZnS	5.4060	HgS	5.8517	AlP	5.451	InP	5.869
γ-AgI	6.495	ZnSe	5.667	HgSe	6.085	AlAs	5.662	InAs	6.058
β-MnS, red	5.600	β-SiC	4.358	HgTe	6.453	AlSb	6.1347	InSb	6.4782
C[a]	3.5667	Si	5.4307	Ge	5.6574	α-Sn (grey)	6.4912		

[a]Diamond structure.

Fluorite and antifluorite (*Fm*-3*m*)



CaF_2 (*fluorite*)
F: tetrahedral, Ca: cube



Figures: AJK

Na_2O (*antifluorite*),
Na at T^+ and T^- sites

Table 1.10 ***Some compounds with fluorite or antifluorite structure, a/Å***

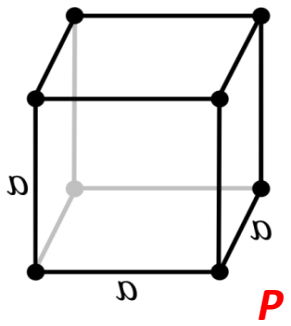
Fluorite structure				Antifluorite structure			
CaF_2	5.4626	PbO_2	5.349	Li_2O	4.6114	K_2O	6.449
SrF_2	5.800	CeO_2	5.4110	Li_2S	5.710	K_2S	7.406
$SrCl_2$	6.9767	PrO_2	5.392	Li_2Se	6.002	K_2Se	7.692
BaF_2	6.2001	ThO_2	5.600	Li_2Te	6.517	K_2Te	8.168
CdF_2	5.3895	UO_2	5.372	Na_2O	5.55	Rb_2O	6.74
β-PbF_2	5.940	NpO_2	5.4334	Na_2S	6.539	Rb_2S	7.65

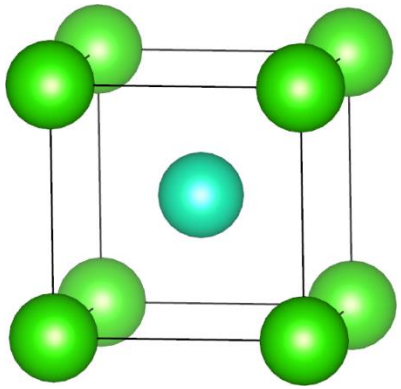
Ref: West p. 41

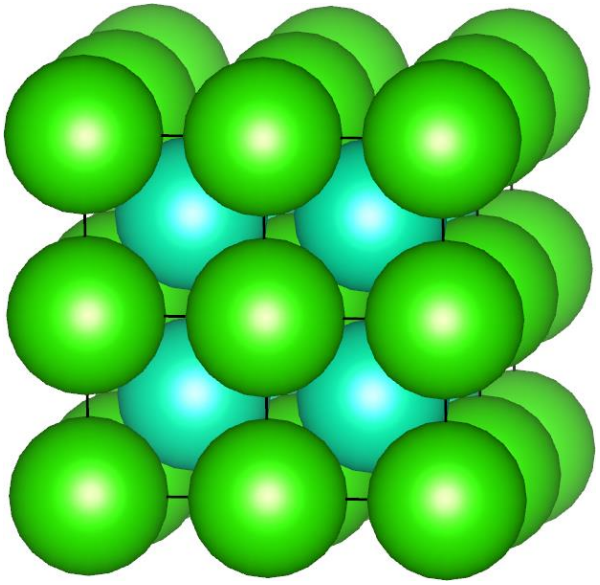
CsCl (*Pm*-3*m*)

Primitive cubic**, not** body centered cubic since there are different ions at corner and body-center positions!

The anion and cation sites are interchangeable







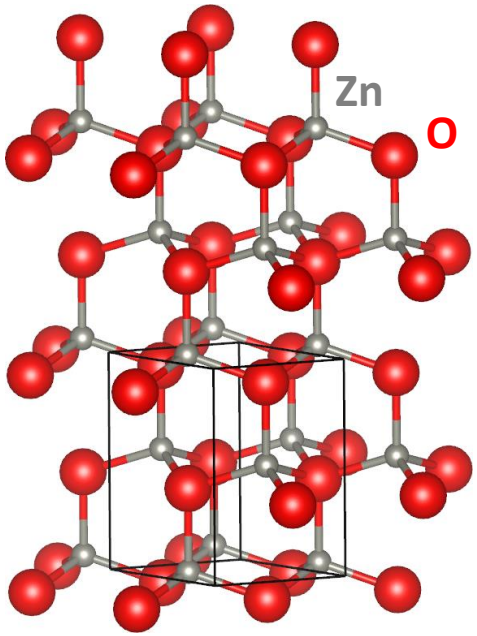
Figures: AJK

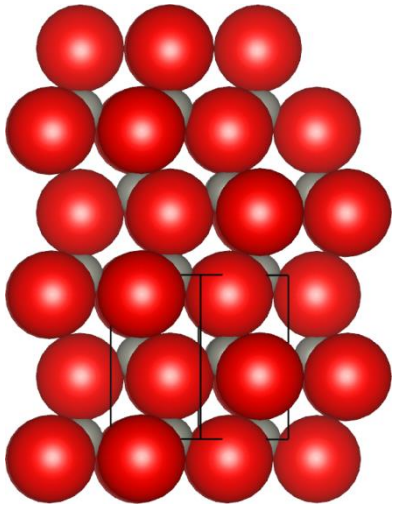
Table 1.14 ***Some compounds with the CsCl structure***

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

Ref: West p. 48

ZnS (wurtzite): $P6_3mc$





hcp anion array
Zn at T^+ (or T^-) sites
Both atoms have tetrahedral coordination

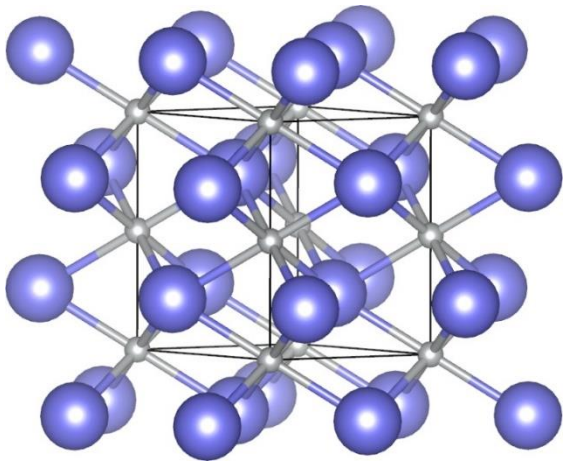
Figures: AJK

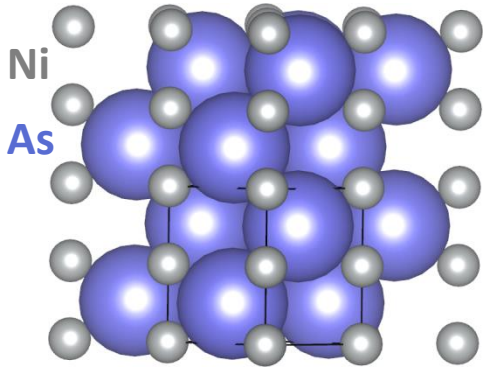
Table 1.12 ***Some compounds with the wurtzite structure***

Compound	a/Å	c/Å	u	c/a	Compound	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

NiAs ($P6_3mc$)

Figures: AJK





hcp anion array

NiAs: Ni at O sites. Coordination: Ni octahedral (6); As trigonal prism (6)

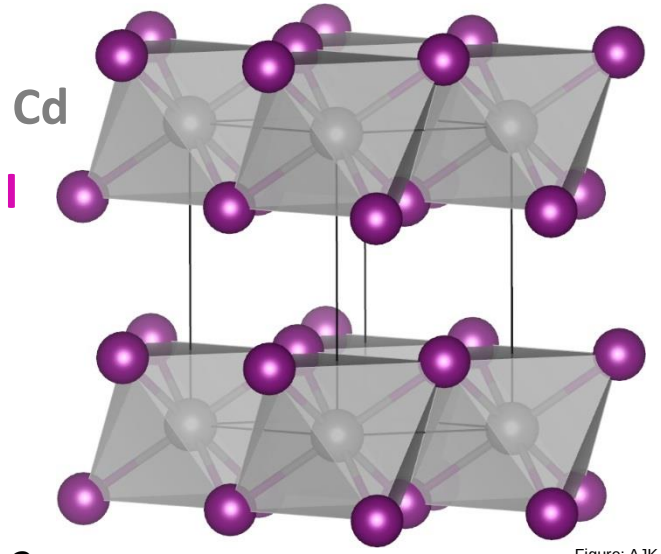
Table 1.13 ***Some compounds with the NiAs structure***

Compound	a/Å	c/Å	c/a	Compound	a/Å	c/Å	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[a]	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

[a] Anti-NiAs structure.

CdI_2 (*P*-3*m*)

- *hcp* anion array
- Cations at the O sites (1/2 occupation)



P-3*m*

Figure: AJK

Ref: West p. 53

Table 1.16 ***Some compounds with the CdI_2 structure***

Compound	*a*/Å	*c*/Å	Compound	*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

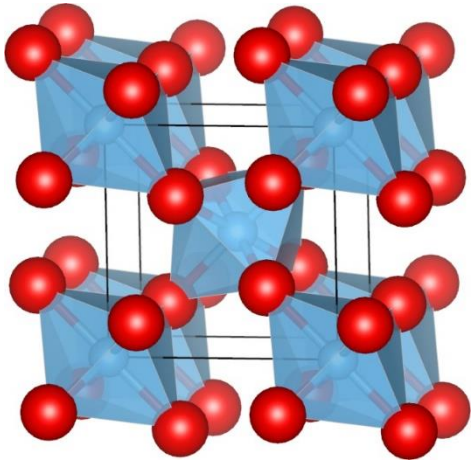
Interatomic distances in some simple structures

Table 1.11 ***Calculation of interatomic distances in some simple structures***

Structure type	Distance	Number of such distances	Magnitude of distance in terms of unit cell dimensions
Rock salt (cubic)	Na–Cl	6	$a/2 = 0.5a$
	Cl–Cl	12	$a/\sqrt{2} = 0.707a$
	Na–Na	12	$a/\sqrt{2} = 0.707a$
Zinc blende (cubic)	Zn–S	4	$a\sqrt{3}/4 = 0.433a$
	Zn–Zn	12	$a/\sqrt{2} = 0.707a$
	S–S	12	$a/\sqrt{2} = 0.707a$
Fluorite (cubic)	Ca–F	4 or 8	$a\sqrt{3}/4 = 0.433a$
	Ca–Ca	12	$a/\sqrt{2} = 0.707a$
	F–F	6	$a/2 = 0.5a$
Wurtzite[a] (hexagonal)	Zn–S	4	$a\sqrt{3}/8 = 0.612a = 3c/8 = 0.375c$
	Zn–Zn	12	$a = 0.612c$
	S–S	12	$a = 0.612c$
Nickel arsenide[a] (hexagonal)	Ni–As	6	$a/\sqrt{2} = 0.707a = 0.433c$
	As–As	12	$a = 0.612c$
	Ni–Ni	2	$c/2 = 0.5c = 0.816a$
	Ni–Ni	6	$a = 0.612c$
Caesium chloride (cubic)	Cs–Cl	8	$a\sqrt{3}/2 = 0.866a$
	Cs–Cs	6	a
	Cl–Cl	6	a
Cadmium iodide (hexagonal)	Cd–I	6	$a/\sqrt{2} = 0.707a = 0.433c$
	I–I	12	$a = 0.612c$
	Cd–Cd	6	$a = 0.612c$

[a]These formulae do not necessarily apply when c/a is different from the ideal value of 1.633.

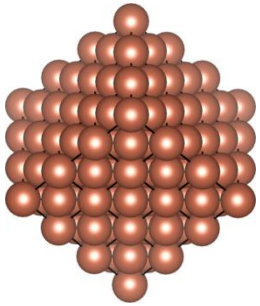
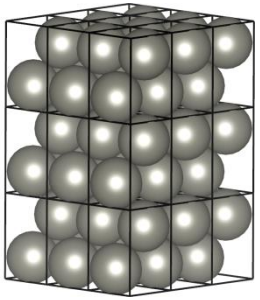
Ref: West p. 42



Metal oxide structure types

Interstitial sites in close-packed lattices of oxygen anions

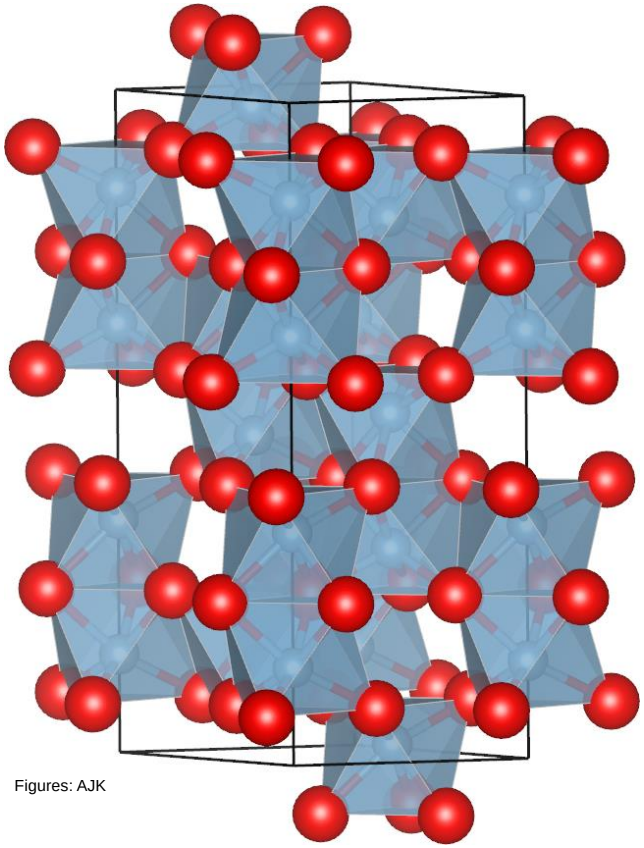
Table 1.4 ***Some close packed structures***

Anion arrangement	Interstitial sites T_+	Interstitial sites T_-	Interstitial sites O	Examples
ccp 	–	–	1	NaCl, rock salt
	1	–	–	ZnS, blende or sphalerite
	1/8	1/8	1/2	$MgAl_2O_4$, spinel
	–	–	1/2	$CdCl_2$
	–	–	1/3	$CrCl_3$
	1	1	–	K_2O, antifluorite
hcp 	–	–	1	NiAs
	1	–	–	ZnS, wurtzite
	–	–	1/2	CdI_2
	–	–	1/2	TiO_2, rutile[a]
	–	–	2/3	Al_2O_3, corundum
	1/8	1/8	1/2	Mg_2SiO_4, olivine
ccp 'BaO_3' layers	–	–	1/4	$BaTiO_3$, perovskite

[a]The *hcp* oxide layers in rutile are not planar but are buckled; the oxide arrangement may alternatively be described as *tetragonal* packed, tp.

Ref: West p. 28

Al_2O_3 (corundum): *R*-3*c*



Figures: AJK

hcp anion lattice
2/3 of O sites occupied by cations

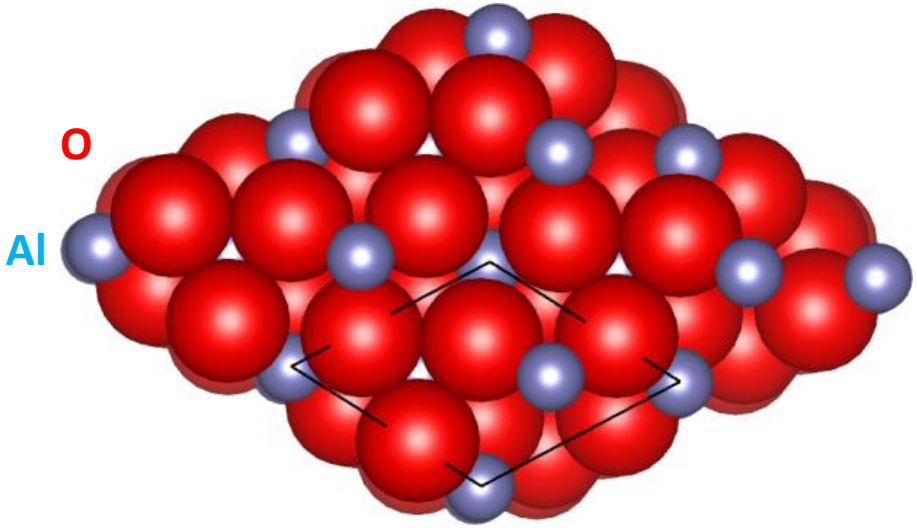
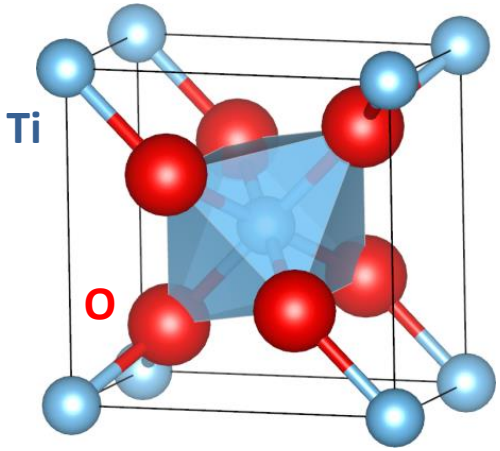


Table 1.24 ***Some compounds with corundum-related structures***

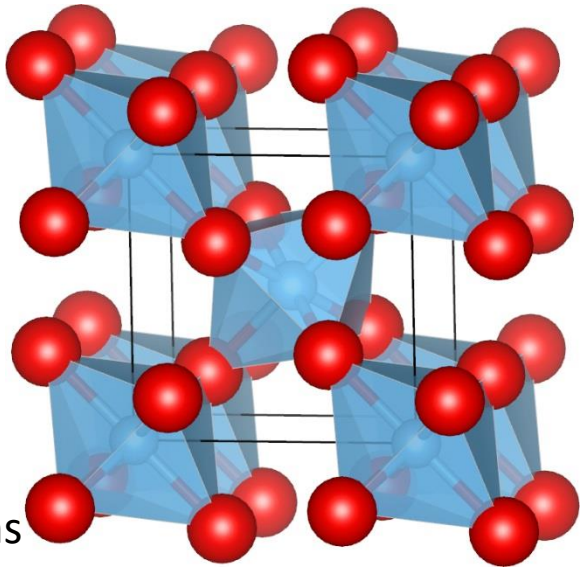
Corundum	M_2O_3: M = Al, Cr, Fe (hematite), Ti, V, Ga, Rh
(α-alumina)	Al_2O_3: with Cr dopant (ruby)
	Al_2O_3: with Ti dopant (sapphire)
Ilmenite	$MTiO_3$: M = Mg, Mn, Fe, Co, Ni, Zn, Cd
	$MgSnO_3$, $CdSnO_3$
	$NiMnO_3$
	$NaSbO_3$
$LiNbO_3$, $LiTaO_3$	

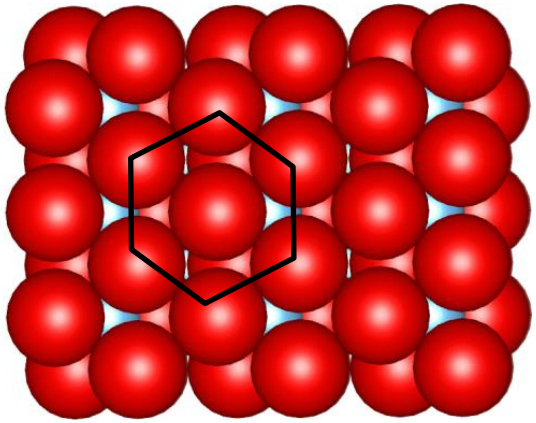
Figures: AJK

TiO_2 (rutile): $P4_2/mnm$



Distorted *hcp* anion lattice
1/2 of O sites occupied by cations





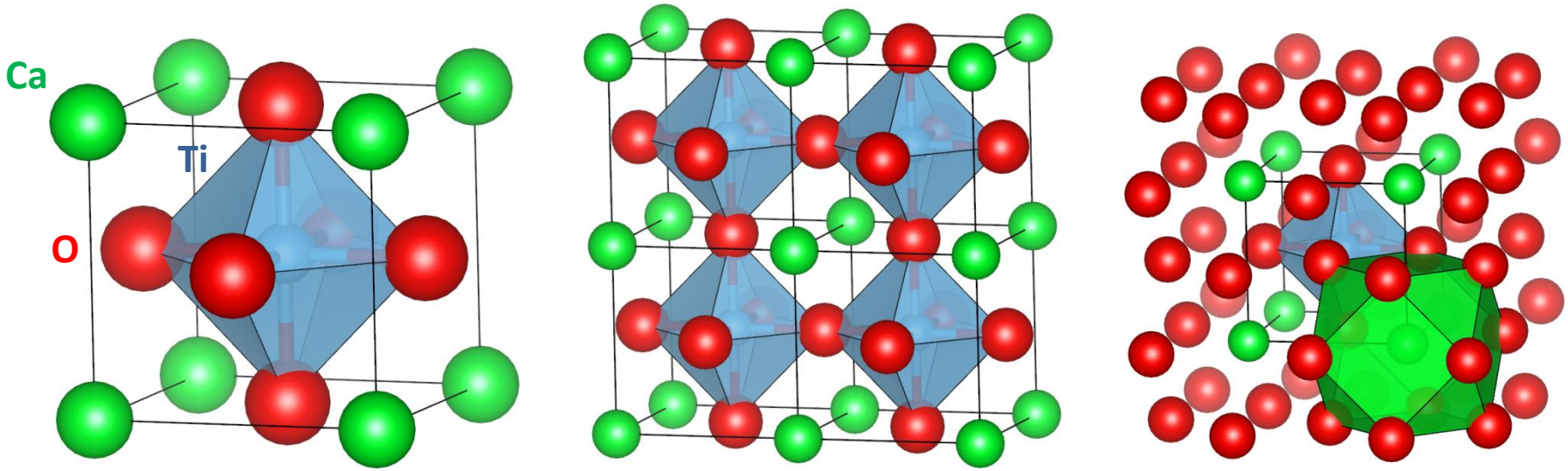
c

a

Table 1.15 ***Some compounds with the rutile structure***

Compound	*a*/Å	*c*/Å	*x*	Compound	*a*/Å	*c*/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		SnO_2	4.7373	3.1864	0.307
PbO_2	4.946	3.379		TaO_2	4.709	3.065	
RuO_2	4.51	3.11		WO_2	4.86	2.77	

$CaTiO_3$ (perovskite): *Pm*-3*m*



Figures: AJK

General formula ABX_3, where A and B are cations and X is anion
In oxides, ABO_3, for example $A^{2+}B^{4+}O_3$ in $CaTiO_3$
ccp anion array, B cations at octahedral sites

Table 1.18 ***Some compounds with the perovskite structure***

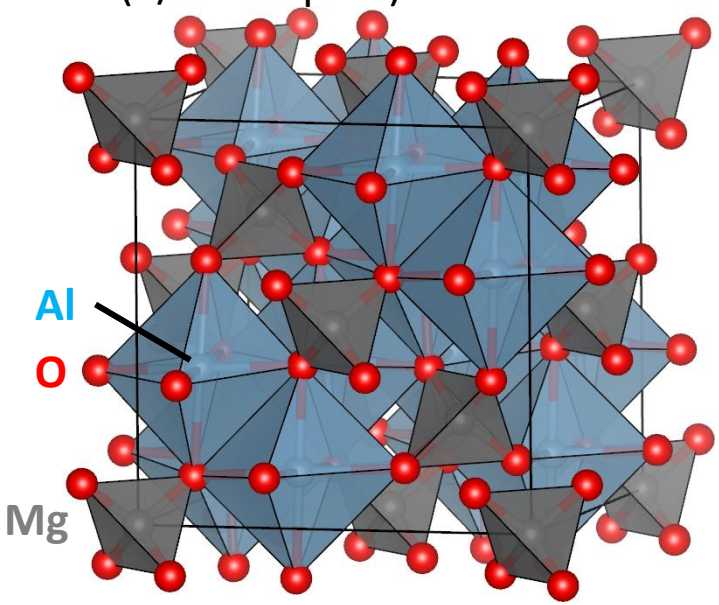
Compound	a/Å	Compound	a/Å	Compound	a/Å
$KNbO_3$	4.007	$LaFeO_3$	3.920		
$KTaO_3$	3.9885	$LaGaO_3$	3.875	$CsCaF_3$	4.522
KIO_3	4.410	$LaVO_3$	3.99	$CsCdBr_3$	5.33
$NaNbO_3$	3.915	$SrTiO_3$	3.9051	$CsCdCl_3$	5.20
$NaWO_3$	3.8622	$SrZrO_3$	4.101	$CsHgBr_3$	5.77
$LaCoO_3$	3.824	$SrHfO_3$	4.069	$CsHgCl_3$	5.44
$LaCrO_3$	3.874	$SrSnO_3$	4.0334		

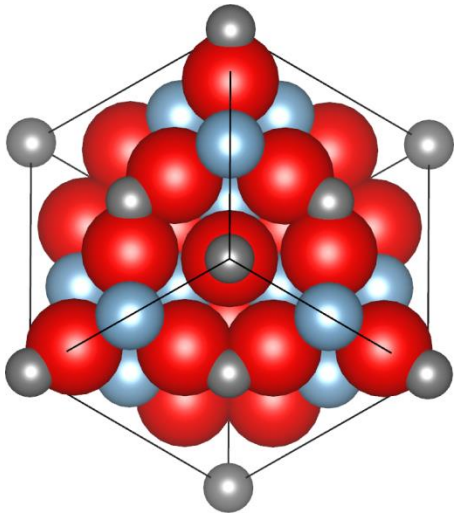
$MgAl_2O_4$ (spinel): *Fd*-3*m*

ccp anion array, general formula AB_2O_4
Mg (A cation) in tetrahedral interstitials (1/8 occupied)
Al (B cation) in octahedral interstitials (2/4 occupied)

AB_2O_4 structures with different cation charge combinations are possible:

2, 3	as in	$MgAl_2O_4$
2, 4	as in	Mg_2TiO_4
1, 3, 4	as in	$LiAlTiO_4$
1, 3	as in	$Li_{0.5}Al_{2.5}O_4$
1, 2, 5	as in	$LiNiVO_4$
1, 6	as in	Na_2WO_4





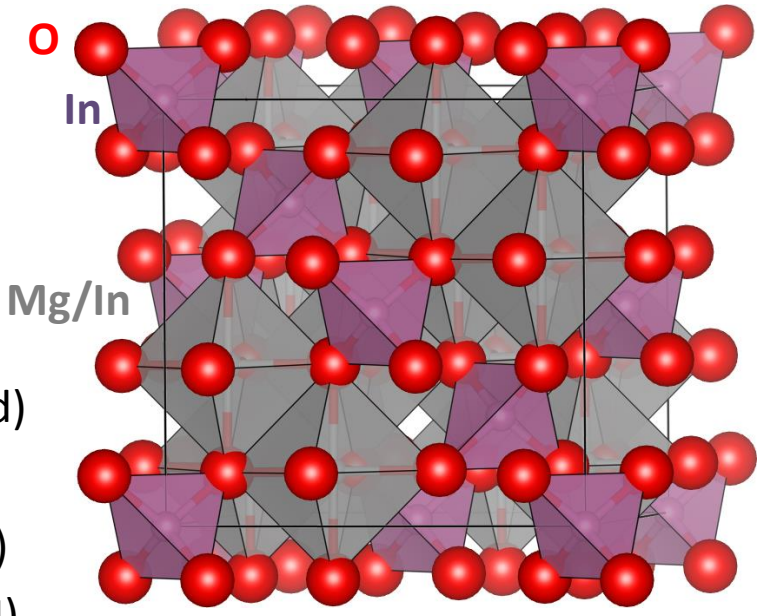
Figures: AJK

Table 1.22 ***Some compounds with the spinel structure***

Compound	Type	a/Å	Structure	Compound	Type	a/Å	Structure
$MgAl_2O_4$	2, 3	8.0800	Normal	$MgIn_2O_4$	2, 3	8.81	Inverse
$CoAl_2O_4$	2, 3	8.1068	Normal	$MgIn_2S_4$	2, 3	10.708	Inverse
$CuCr_2S_4$	2, 3	9.629	Normal	Mg_2TiO_4	2, 4	8.44	Inverse
$CuCr_2Se_4$	2, 3	10.357	Normal	Zn_2SnO_4	2, 4	8.70	Inverse
$CuCr_2Te_4$	2, 3	11.051	Normal	Zn_2TiO_4	2, 4	8.467	Inverse
$MgTi_2O_4$	2, 3	8.474	Normal	$LiAlTiO_4$	1, 3, 4	8.34	Li in tet
Co_2GeO_4	2, 4	8.318	Normal	$LiMnTiO_4$	1, 3, 4	8.30	Li in tet
Fe_2GeO_4	2, 4	8.411	Normal	$LiZnSbO_4$	1, 2, 5	8.55	Li in tet
$MgFe_2O_4$	2, 3	8.389	Inverse	$LiCoSbO_4$	1, 2, 5	8.56	Li in tet
$NiFe_2O_4$	2, 3	8.3532	Inverse				

Inverse spinel

- AB_2O_4, with all A cations at octahedral sites
- Half of the B cations at octahedral sites
- Other half of the B cations at tetrahedral sites
- $MgIn_2O_4$ (*Fd*-3*m*)
  - *fcc* anion lattice
  - Mg (A) in octahedral interstitials (1/4 occupied)
  - In (B) in octahedral interstitials (1/4 occupied)
  - In (B) in tetrahedral interstitials (1/8 occupied)
- With one metal: Fe_3O_4 with A = Fe(II) and B = Fe(III)



Figures: AJK

Table 1.22 ***Some compounds with the spinel structure***

Compound	Type	a/Å	Structure	Compound	Type	a/Å	Structure
$MgAl_2O_4$	2, 3	8.0800	Normal	$MgIn_2O_4$	2, 3	8.81	Inverse
$CoAl_2O_4$	2, 3	8.1068	Normal	$MgIn_2S_4$	2, 3	10.708	Inverse
$CuCr_2S_4$	2, 3	9.629	Normal	Mg_2TiO_4	2, 4	8.44	Inverse
$CuCr_2Se_4$	2, 3	10.357	Normal	Zn_2SnO_4	2, 4	8.70	Inverse
$CuCr_2Te_4$	2, 3	11.051	Normal	Zn_2TiO_4	2, 4	8.467	Inverse
$MgTi_2O_4$	2, 3	8.474	Normal	$LiAlTiO_4$	1, 3, 4	8.34	Li in tet
Co_2GeO_4	2, 4	8.318	Normal	$LiMnTiO_4$	1, 3, 4	8.30	Li in tet
Fe_2GeO_4	2, 4	8.411	Normal	$LiZnSbO_4$	1, 2, 5	8.55	Li in tet
$MgFe_2O_4$	2, 3	8.389	Inverse	$LiCoSbO_4$	1, 2, 5	8.56	Li in tet
$NiFe_2O_4$	2, 3	8.3532	Inverse				