Most well-known solid state structures with cp anion arrays

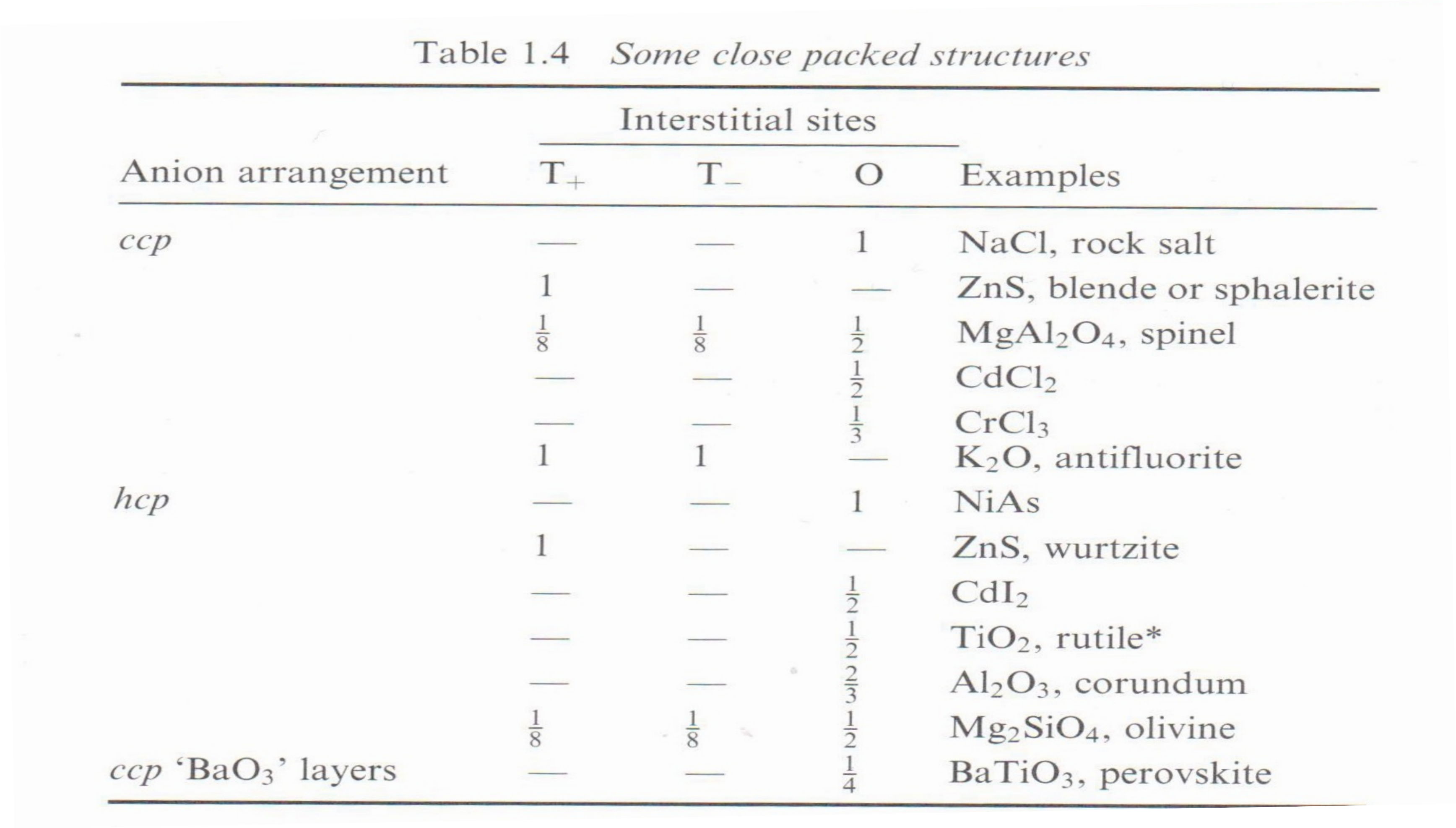


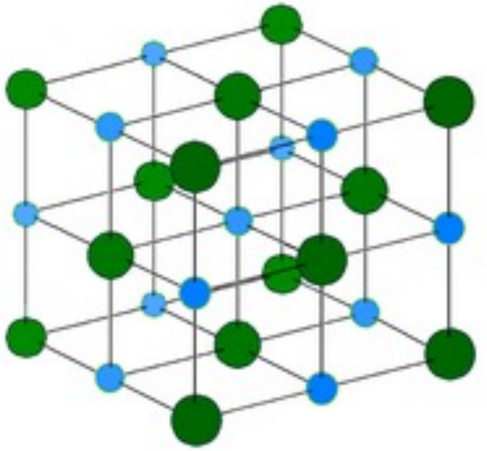
Table 1.4 *Some close packed structures*

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

NaCl Structure Type

1. Basics

Monoxides of the first transition series, except from CuO, adopt the rocksalt structure:



Green sphere = oxygen; blue sphere = metal

Space group Fm3m
Lattice parameter a ~ 5.64 Å; Z = 4

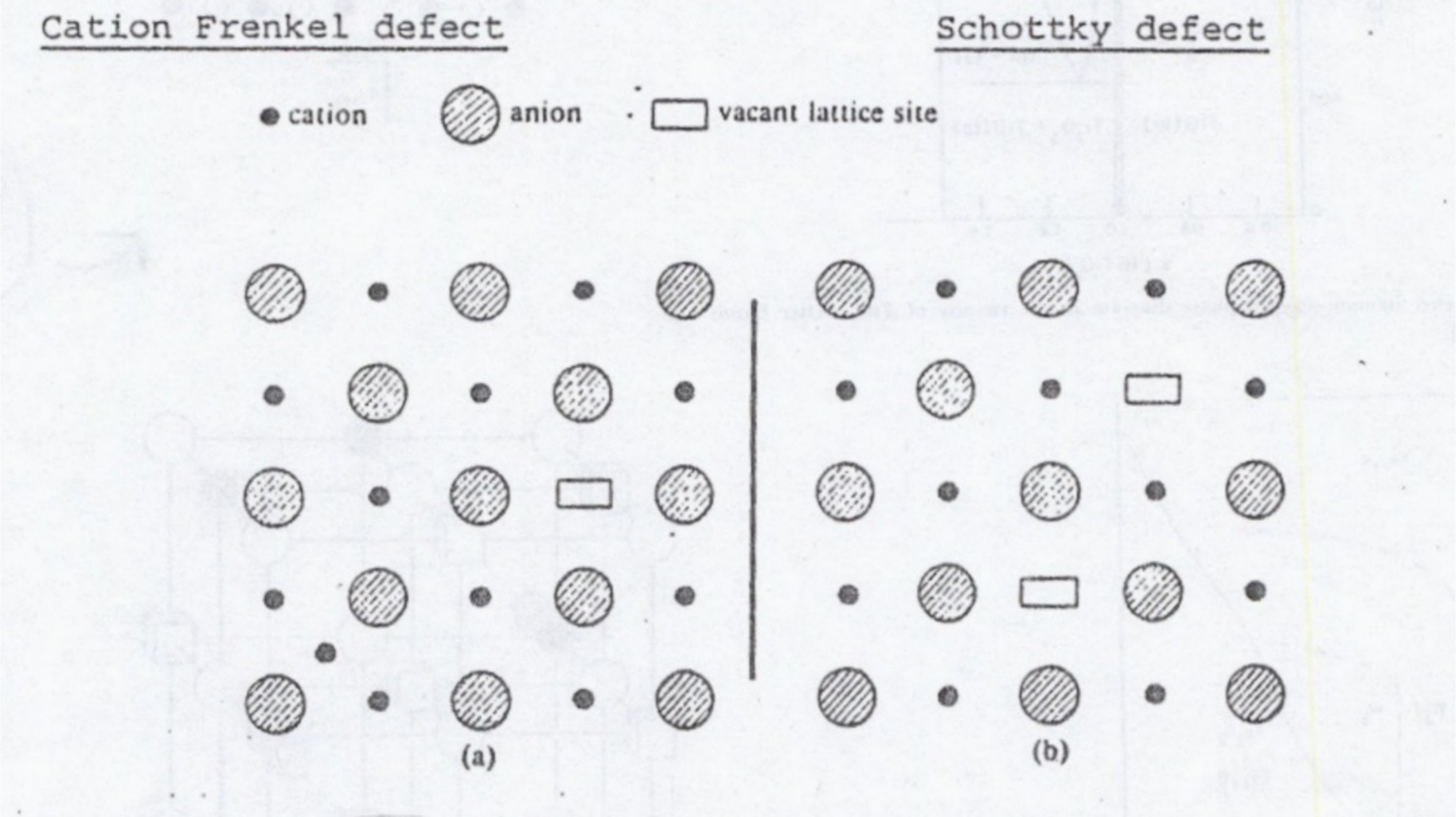
Atom	**Site**	**x**	**y**	**z**
O	4a	0	0	0
M	4b	½	0	0

2. Defects in rocksalt structures

Point defects in the NaCl structure are largely limited to Schottky defects, in which there are equal numbers of cation and anion vacancies.

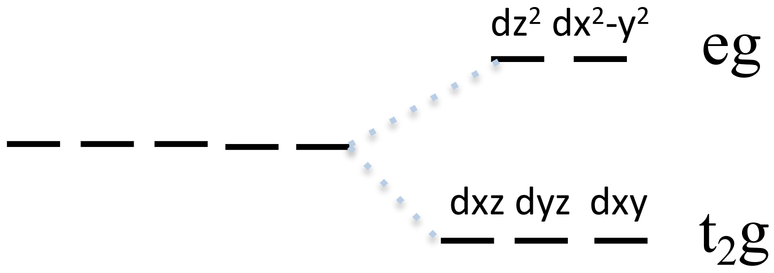
Point defects in ionic solids:

These usually comprise Frenkel or Schottky defects:



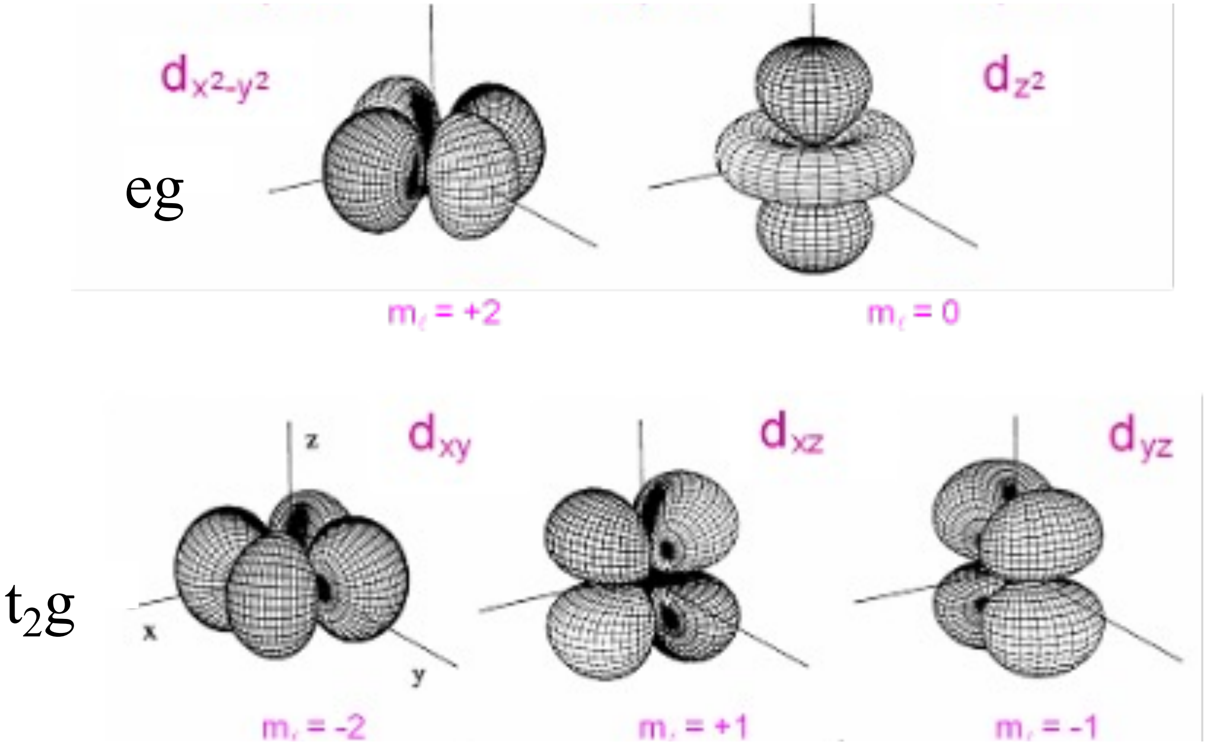
Exercise: Many early transition metal oxides having the rock salt structure, like TiO and VO, exhibit metallic level conductivity, while late transition metal oxides, like NiO, do not. Can you explain why?

Hint: You must know the rocksalt structure, crystal field theory (orientation of the d-orbitals in space) and d electron configurations of metals.



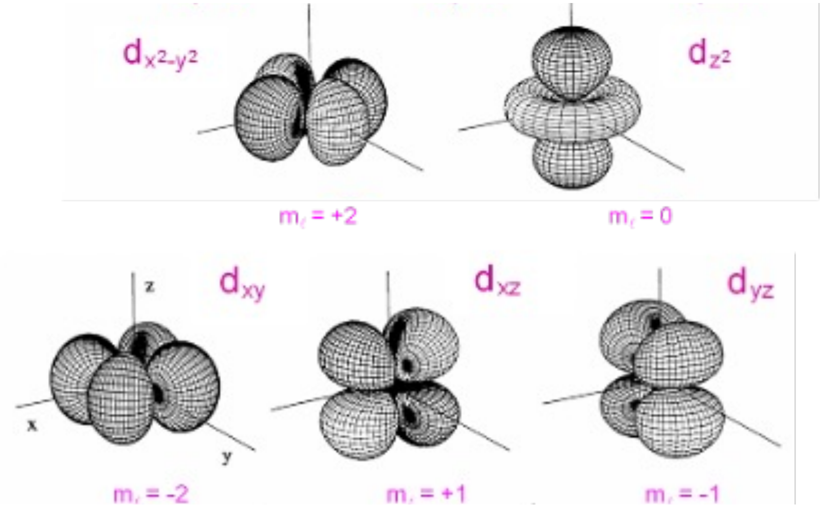
dz^2 dx^2-y^2 eg

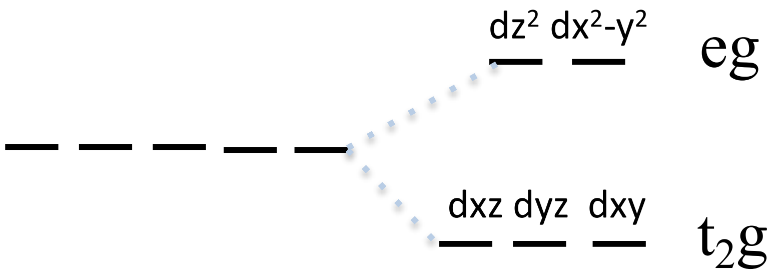
dxz dyz dxy t_2g



Exercise: Many early transition metal oxides having the rock salt structure, like TiO and VO, exhibit metallic level conductivity, while late transition metal oxides, like NiO, do not. Can you explain why?

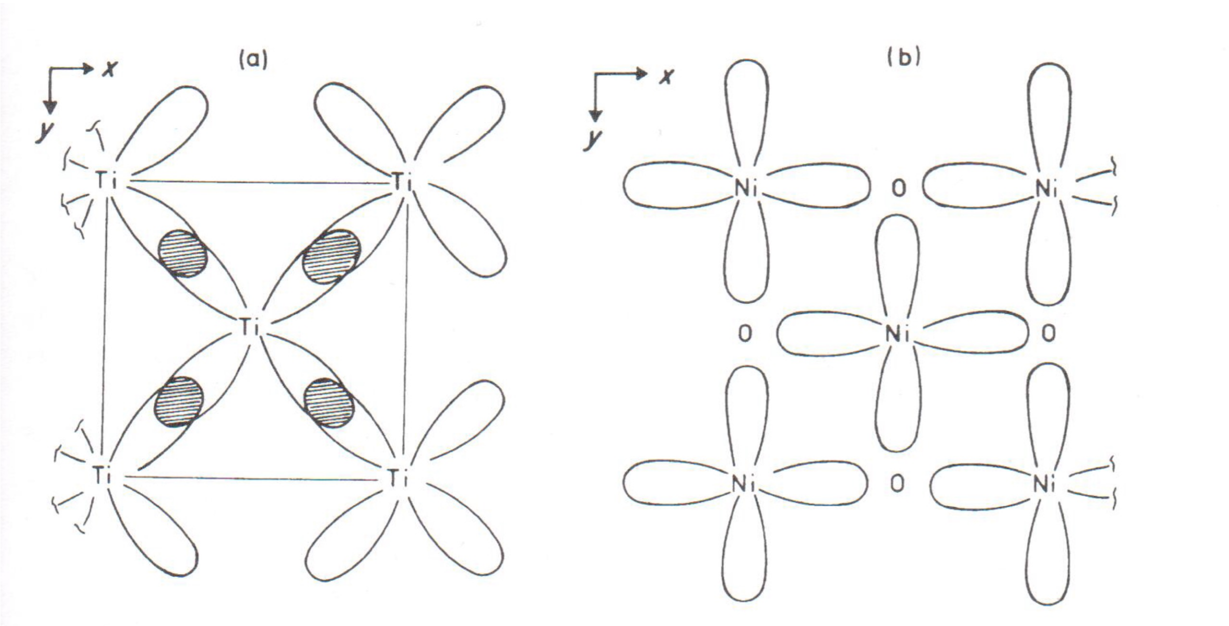
Hint: Considering the rocksalt structure, crystal field theory (orientation of d-orbitals in space) and d electron configurations of metals.





dz^2 dx^2-y^2 eg

dxz dyz dxy t_2g



Ni^{2+} is 3d^8

Ti^{2+} is 3d^2

Radius Ratio Rule

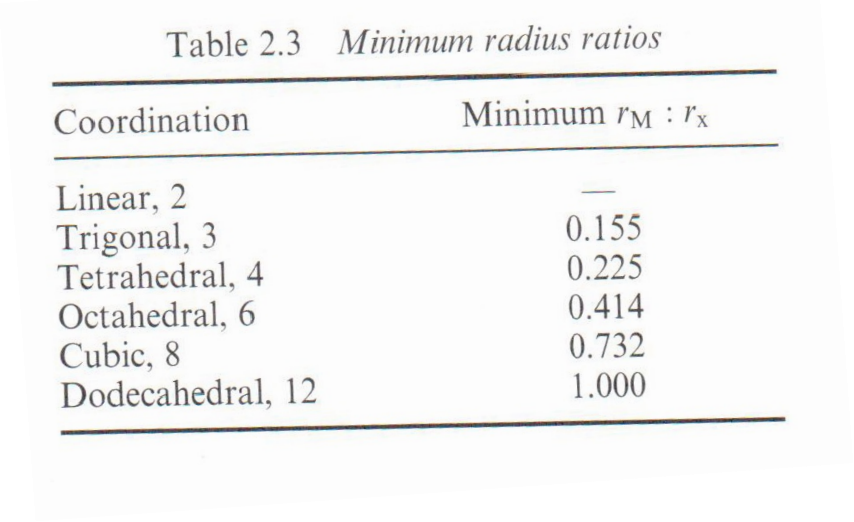


Table 2.3 *Minimum radius ratios*

Coordination	Minimum $r_M : r_x$
Linear, 2	—
Trigonal, 3	0.155
Tetrahedral, 4	0.225
Octahedral, 6	0.414
Cubic, 8	0.732
Dodecahedral, 12	1.000

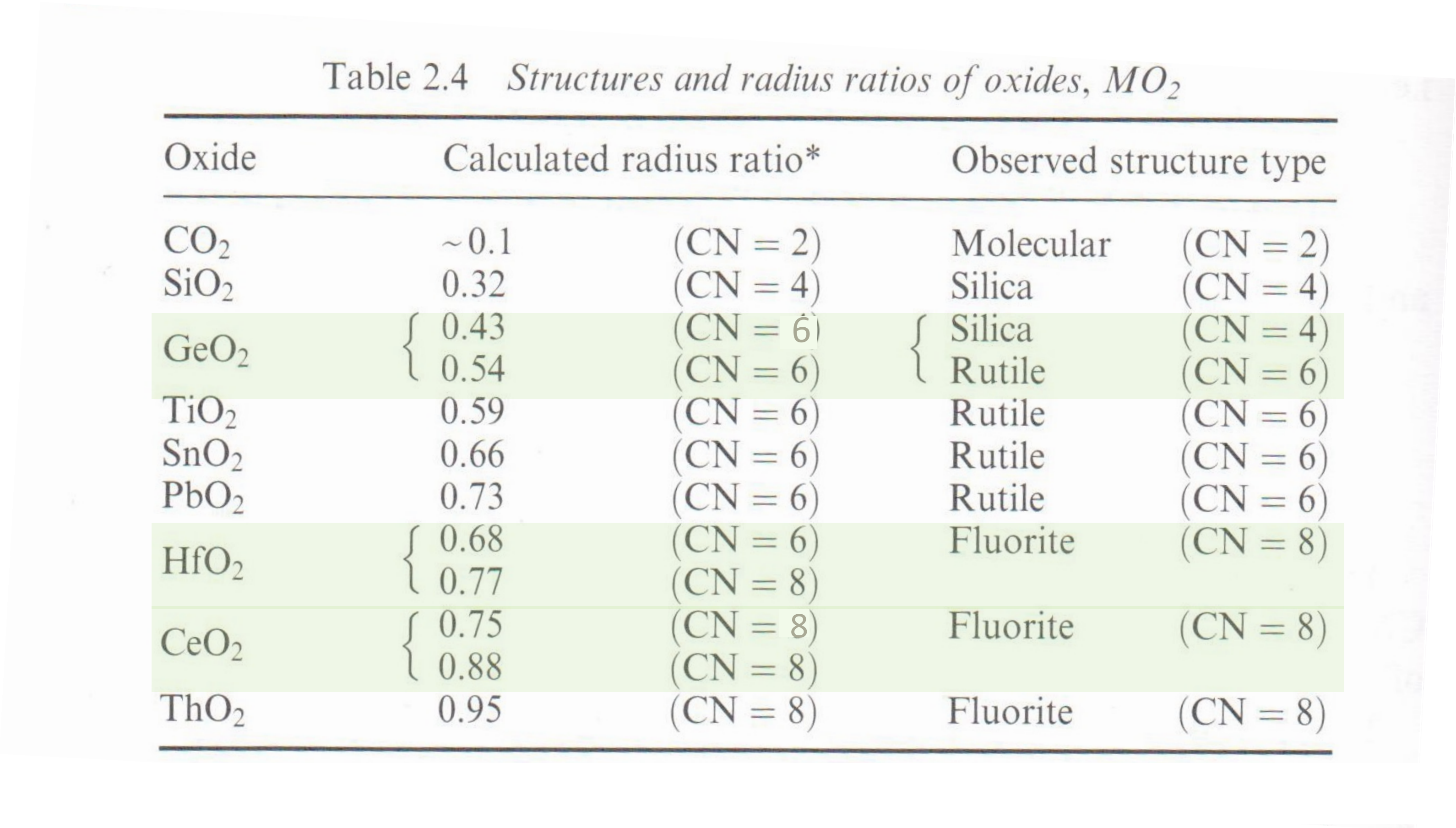


Table 2.4 *Structures and radius ratios of oxides,* MO_2

Oxide	Calculated radius ratio*		Observed structure type	
CO_2	~0.1	(CN = 2)	Molecular	(CN = 2)
SiO_2	0.32	(CN = 4)	Silica	(CN = 4)
GeO_2	0.43	(CN = 6)	Silica	(CN = 4)
	0.54	(CN = 6)	Rutile	(CN = 6)
TiO_2	0.59	(CN = 6)	Rutile	(CN = 6)
SnO_2	0.66	(CN = 6)	Rutile	(CN = 6)
PbO_2	0.73	(CN = 6)	Rutile	(CN = 6)
HfO_2	0.68	(CN = 6)	Fluorite	(CN = 8)
	0.77	(CN = 8)		
CeO_2	0.75	(CN = 8)	Fluorite	(CN = 8)
	0.88	(CN = 8)		
ThO_2	0.95	(CN = 8)	Fluorite	(CN = 8)

Exercise: Identify the Miller Indices for each plane.