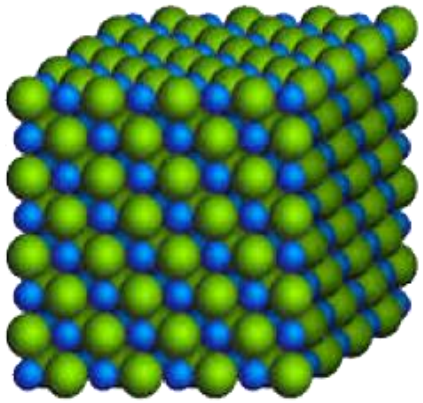
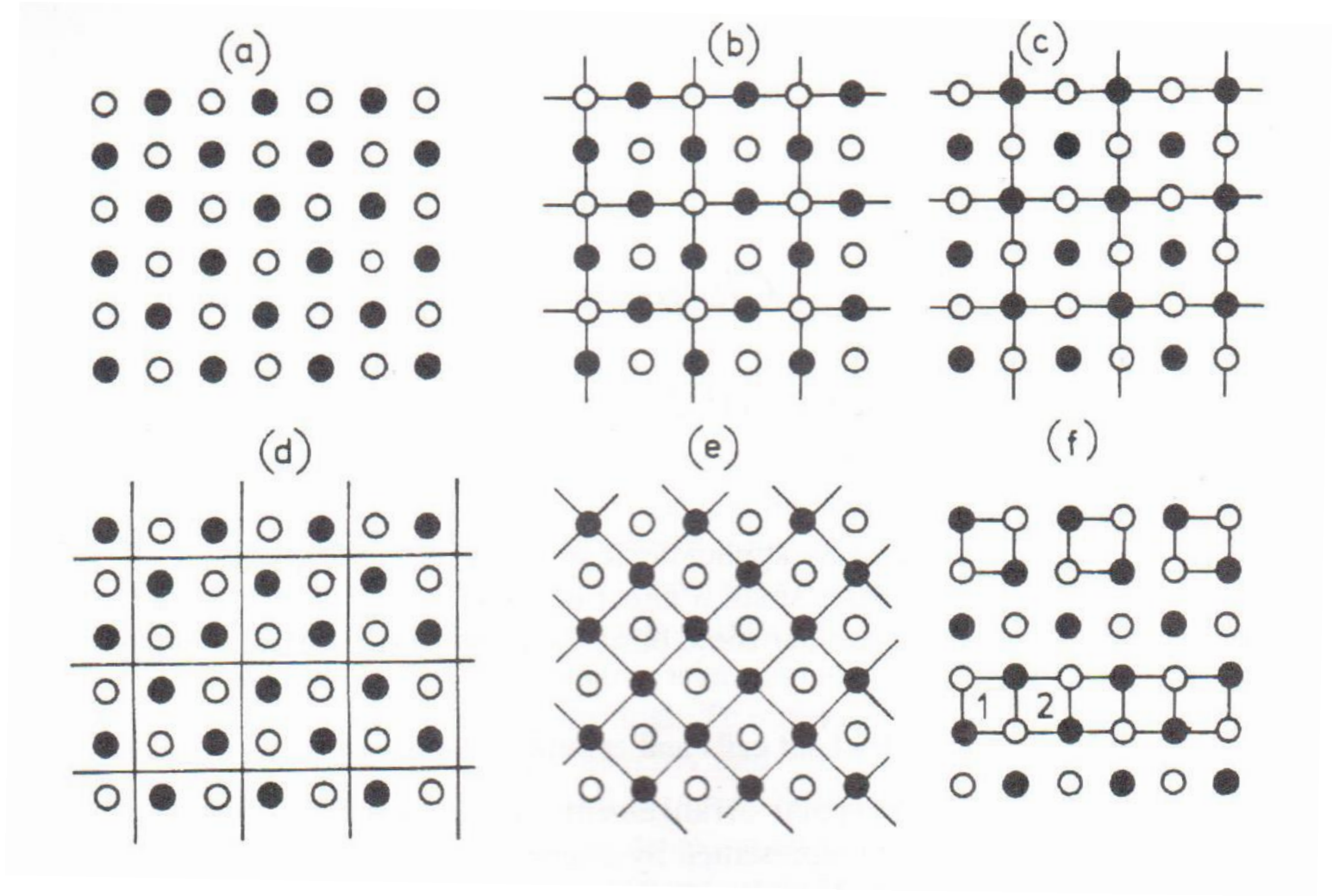
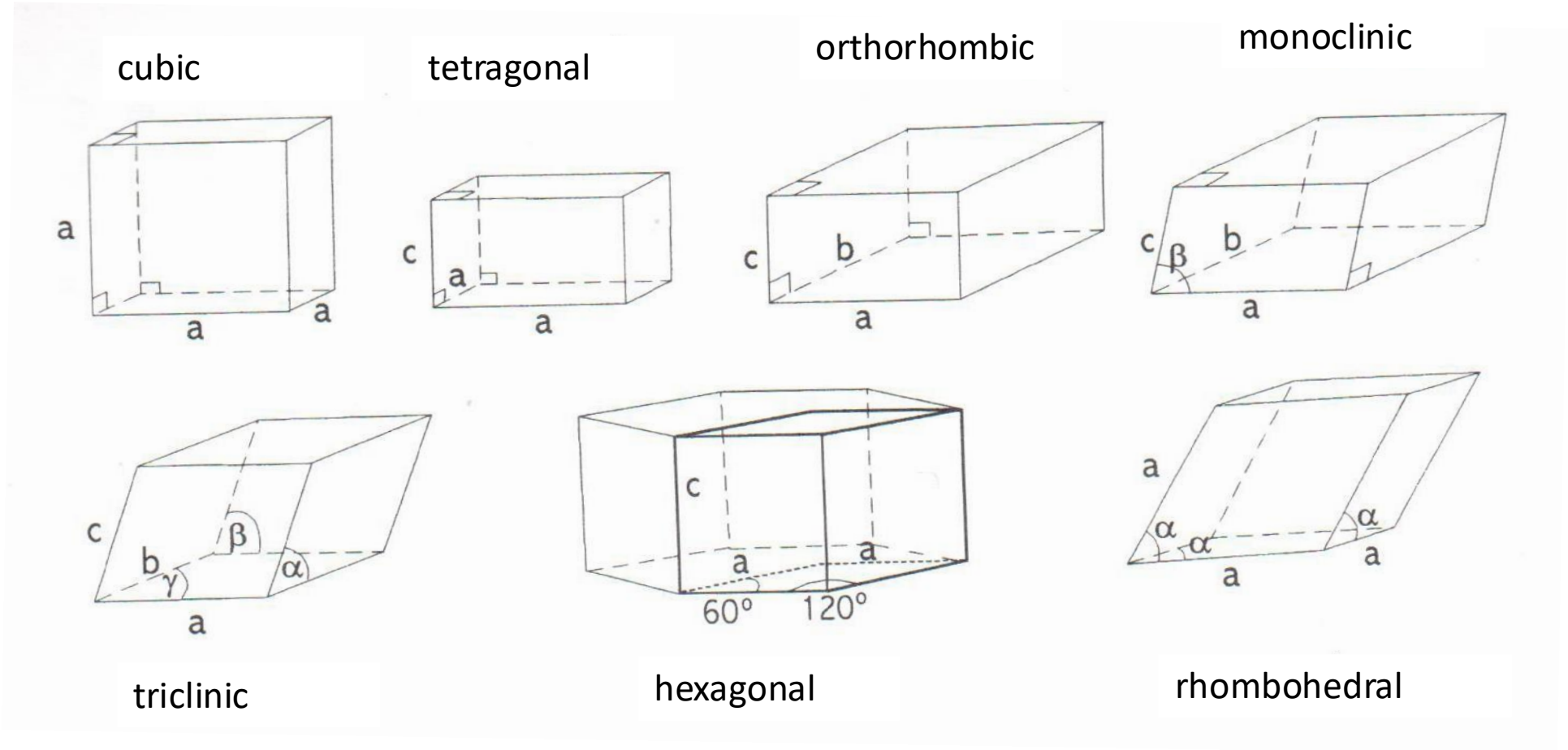
Unit Cells





Crystal systems



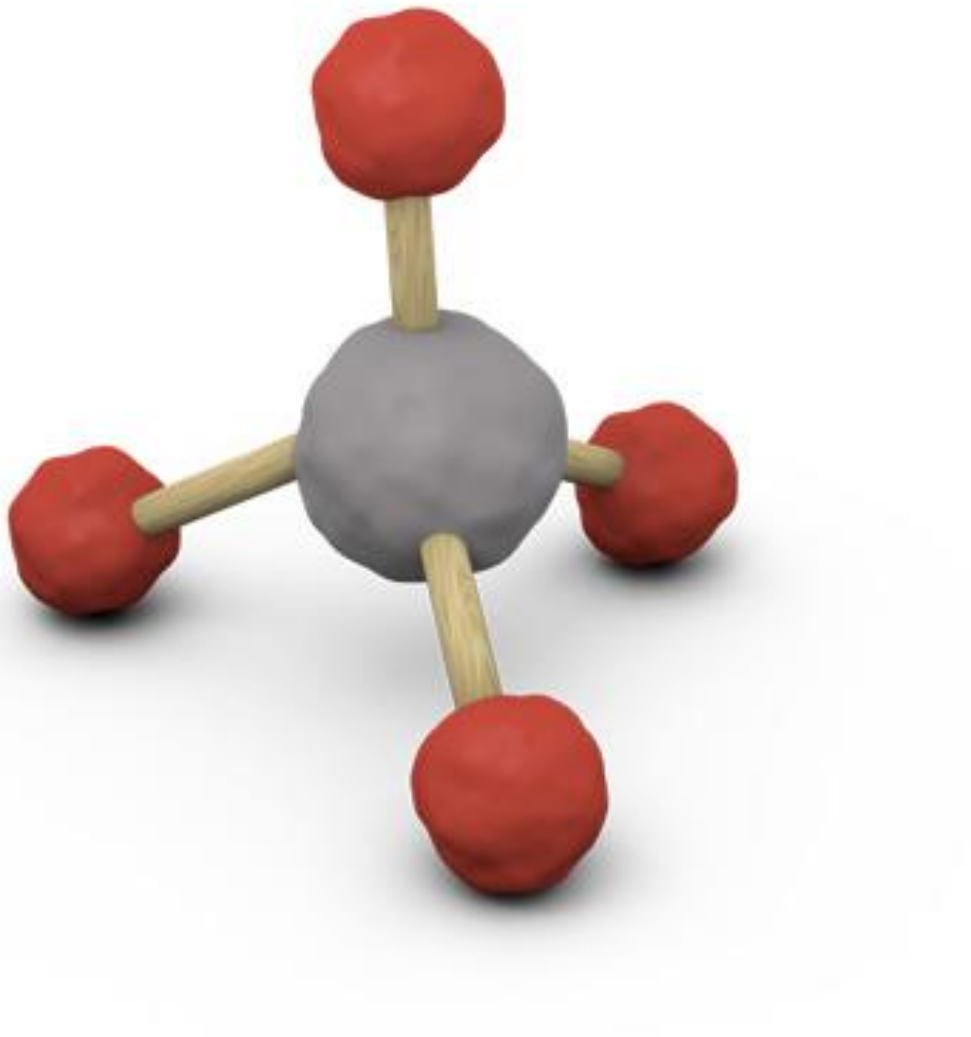
Point Symmetry Elements

Symmetry element	Symmetry operation	Schönflies Symbol (spectroscopy)	Herman-Maugin Symbol (crystallography)
Rotation axis	rotation by 360°/n	C_n	n = 2, 3, 4, 6
mirror plane	Reflection across a plane	σv, σh	m
center of inversion	Inversion -pull atoms through a center point	i	$\bar{1}$
improper axis of rotation aka alternating axis	rotation of 360°/n followed by mirror reflection that is perpendicular to the rotational axis.	S_n	2/m 4/m 6/m
inversion axis	Is an n fold rotation followed by an inversion center.	-	$\bar{n}$ = $\bar{3}$, $\bar{4}$, $\bar{6}$ etc

Exercise: No 5 and 7 Why is this?

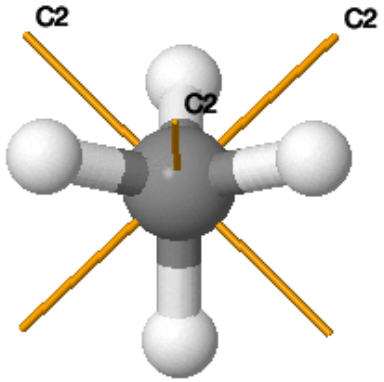
Exercise: Why is there no $\bar{2}$? 3/m

Question: What symmetry elements can you find in an MO_4 tetrahedron?

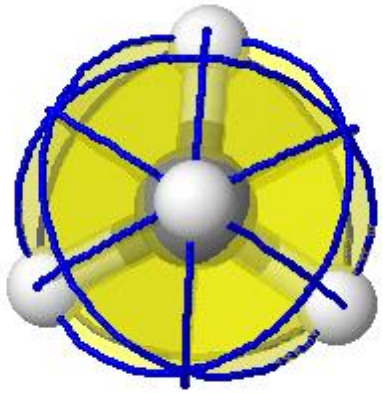


Question: What symmetry elements can you find in an MO_4 tetrahedron?

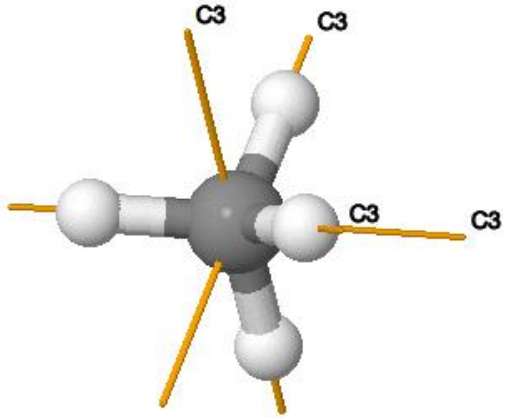
3 x C_2 rotations



6 x m planes

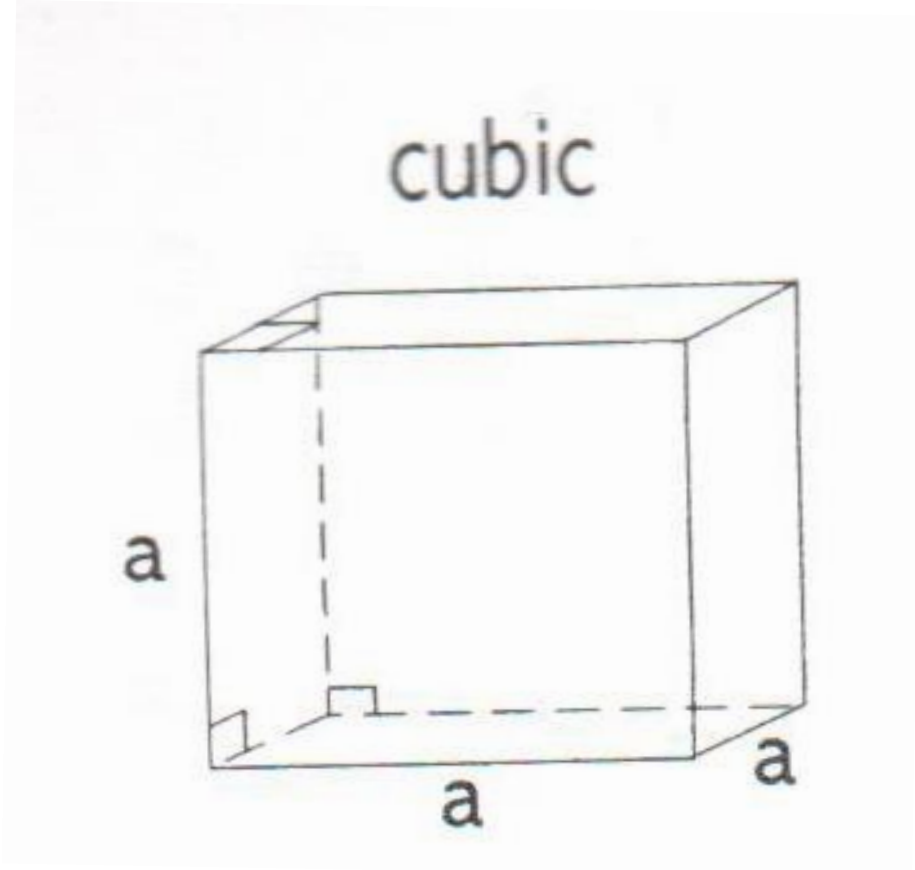


4 x C_3 rotations

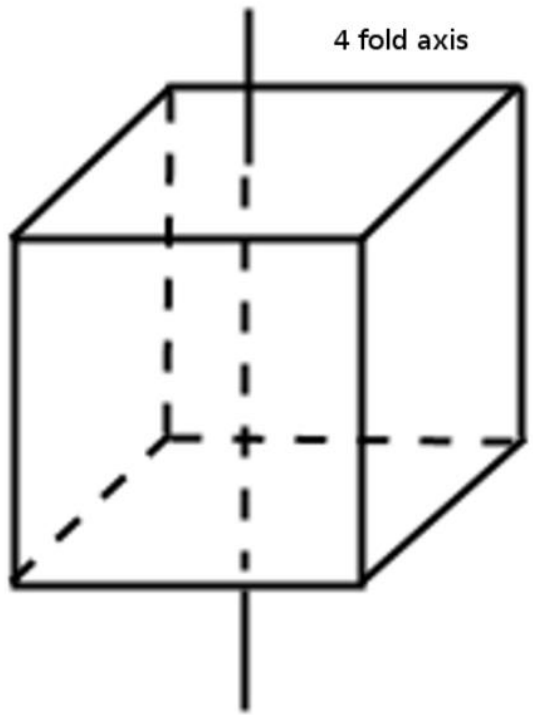


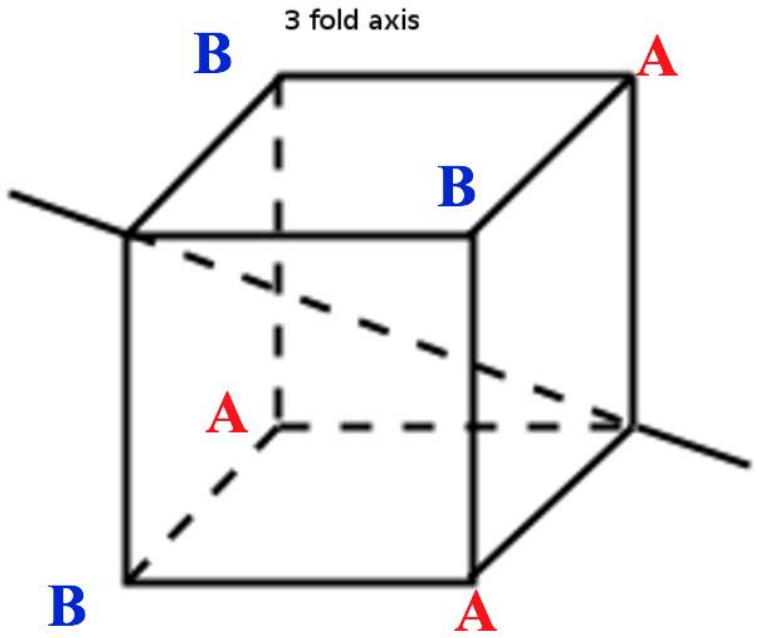
No inversion center but it has 3 x S_4 or -4. For the C_2 axis, instead rotate by 90 ^{0} (C_4) and then do a mirror perpendicular.

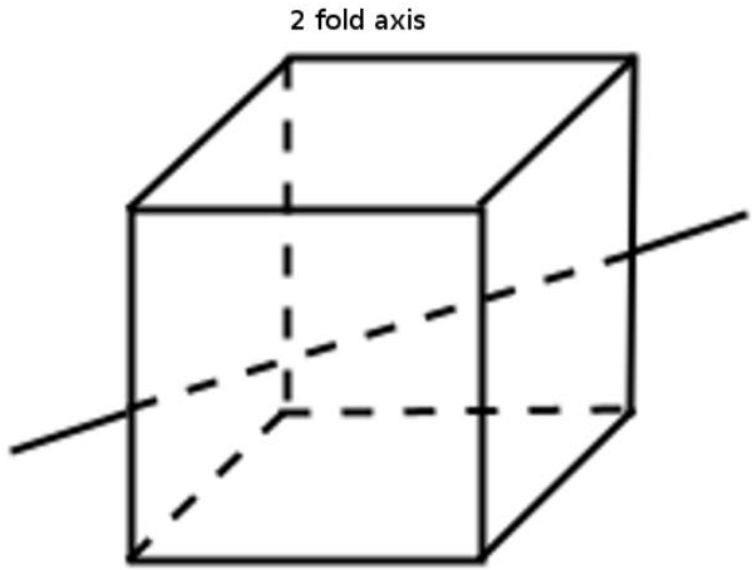
Question: What are the rotational axes of a cubic unit cell?



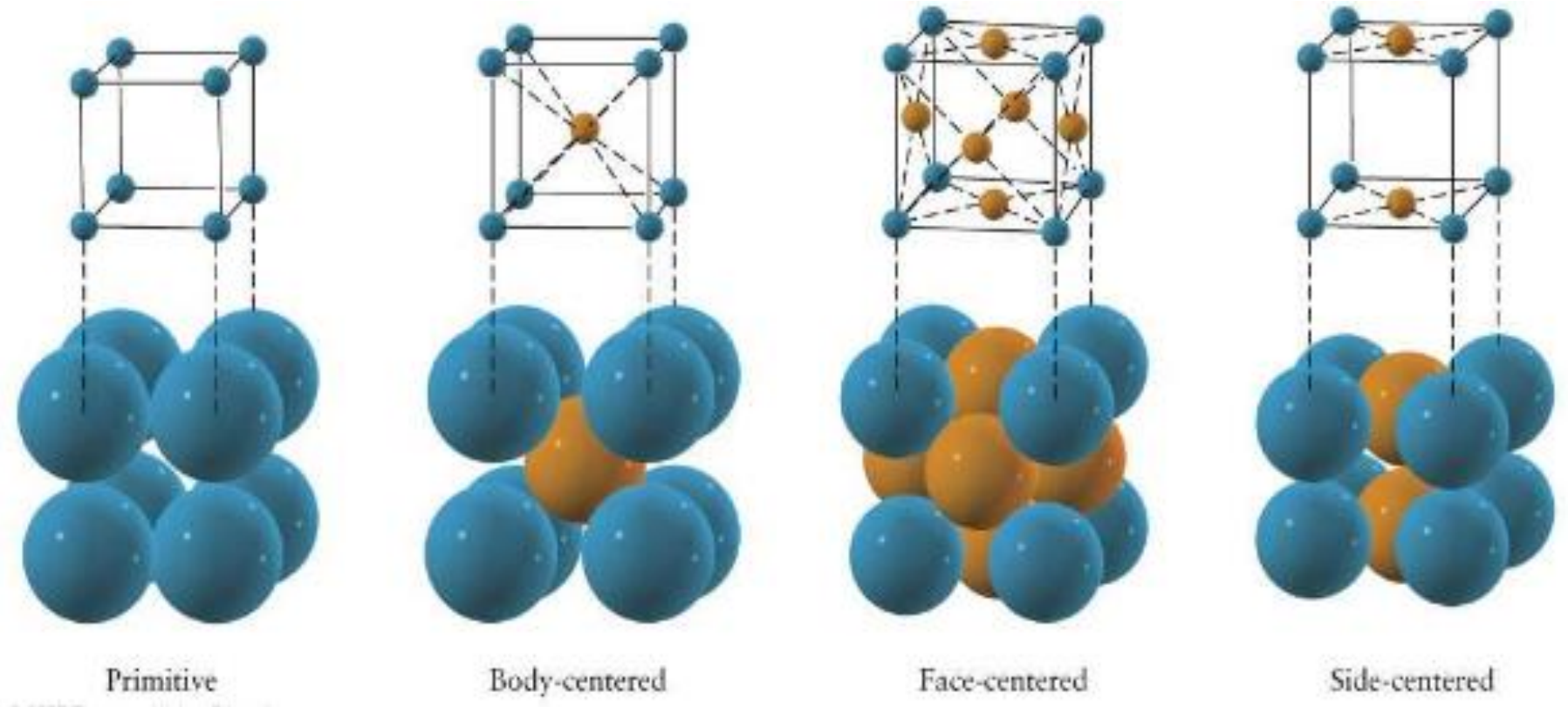
Rotational axes of symmetry in the cube





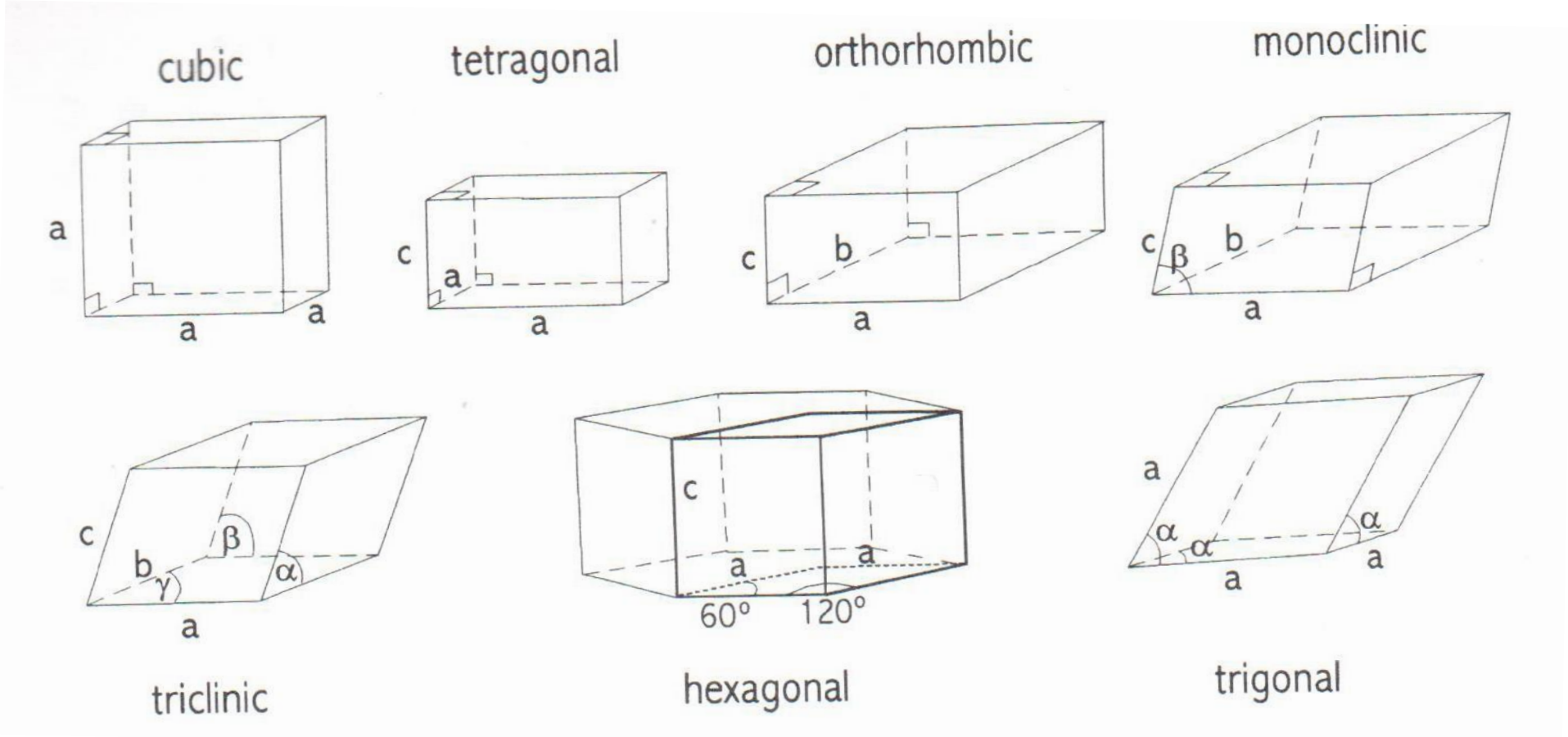


Cell centering



Crystal systems

Crystal system	Unit cell shape†	Essential symmetry
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	Four threefold axes
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	One fourfold axis
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Three twofold axes or mirror planes
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis
(b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis
Monoclinic*	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None



Exercises:

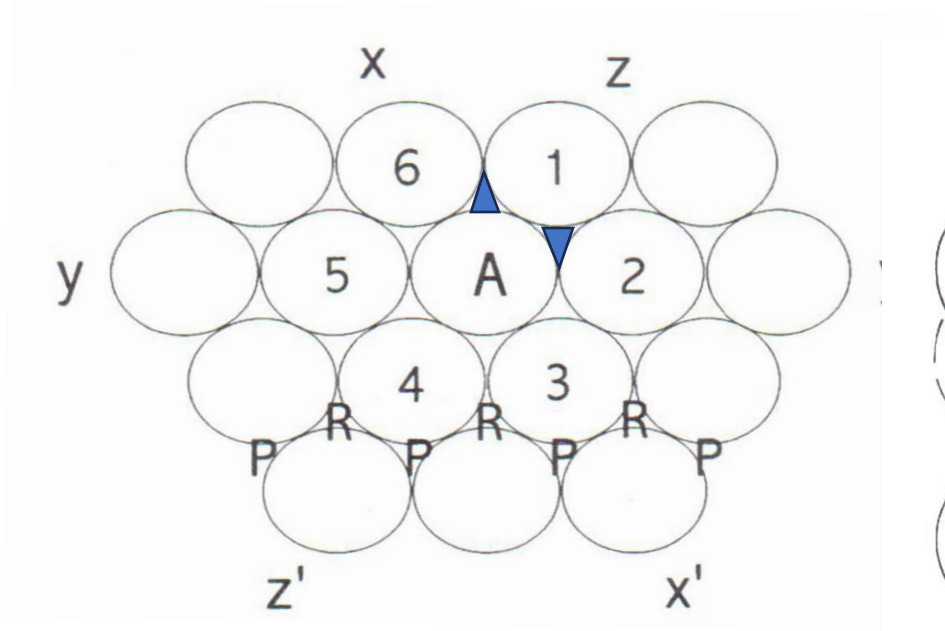
Why is there no F-centered tetragonal cell?
Recalculate the volume of the new unit cell in terms of a and c

Why there is no C-centered tetragonal?

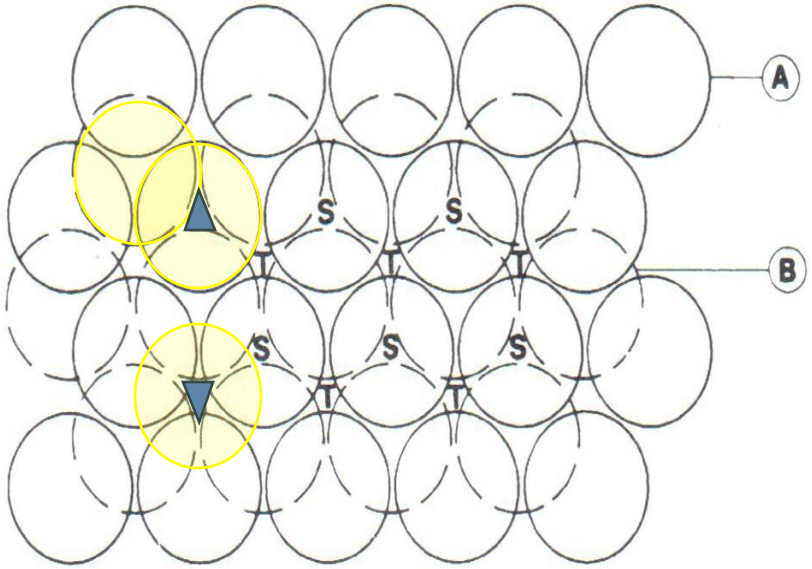
Why is there no C-centered cubic cell?

Close-Packed Systems

Close-packing



Layer 1



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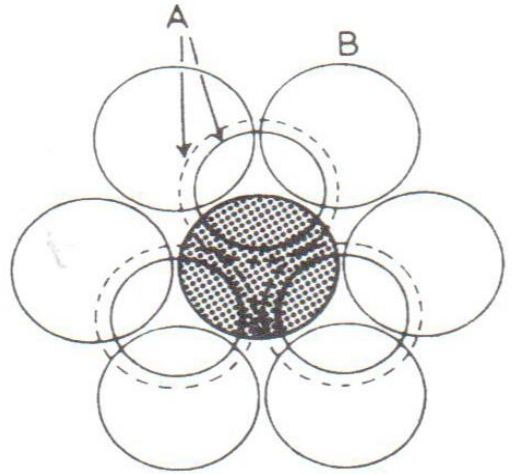
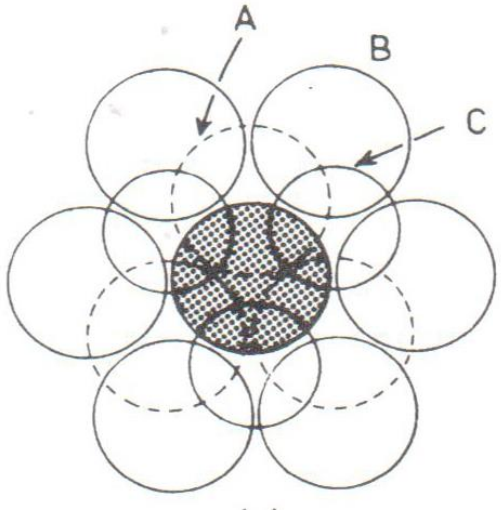
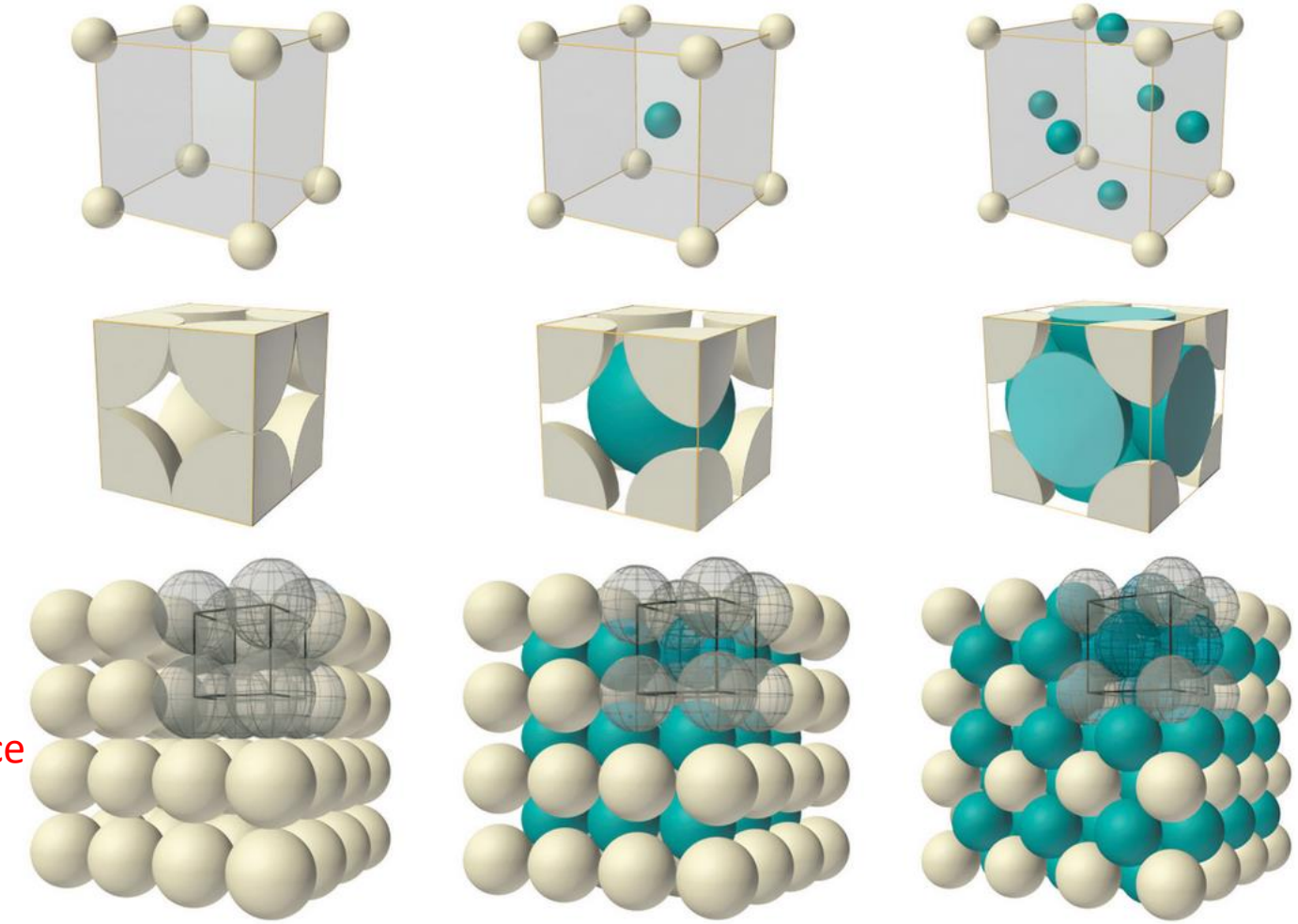


Layer 3 - ABA



Layer 3 - ABC

Exercise: Of these cubic structures, which shows a ccp structure type and which ccp structure is it?



Also # of lattice points

P

atoms per cell = 1
CN # = 6

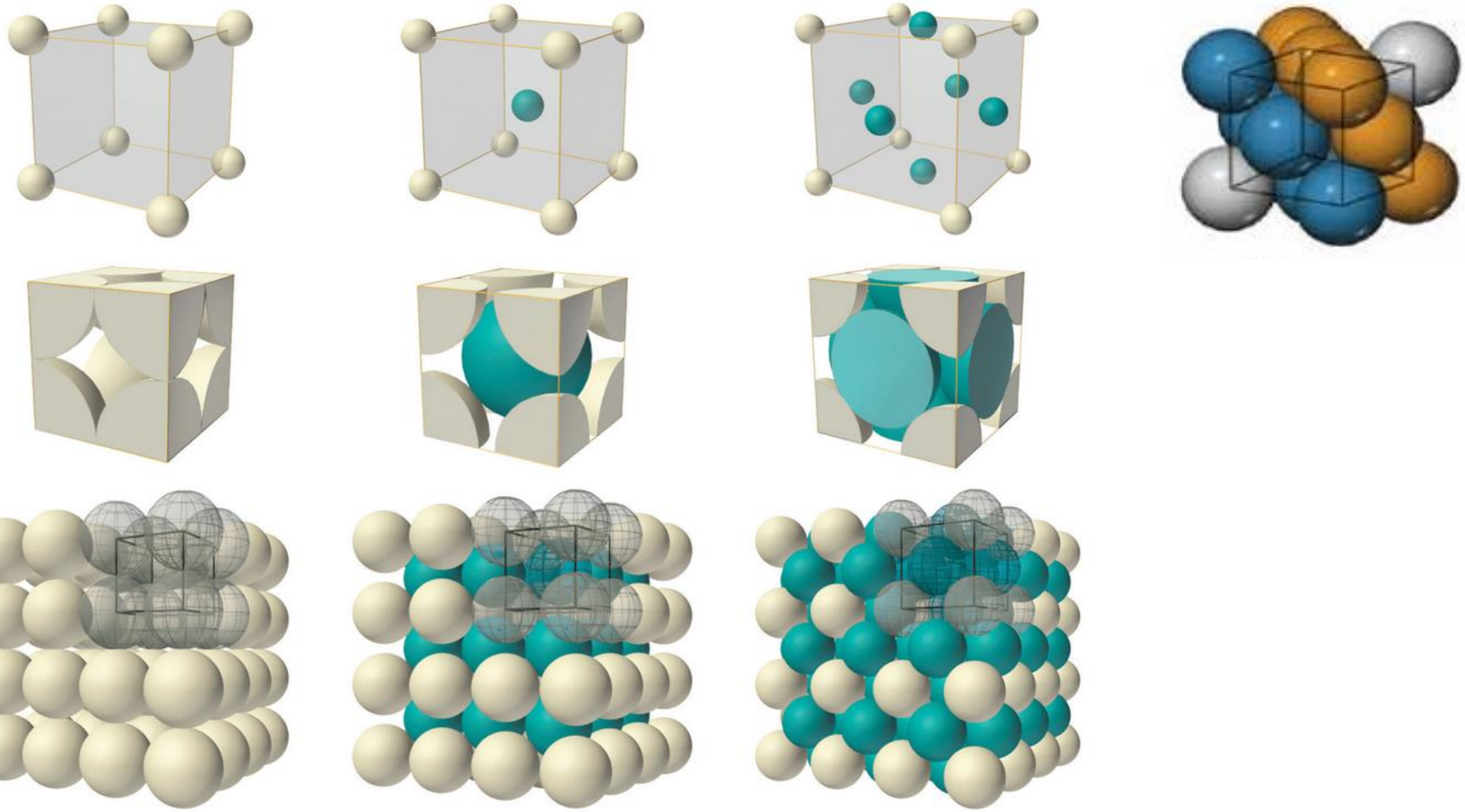
I

atoms per cell = 2
CN # = 8

F

atoms per cell = 4
CN # = 12

Exercise: Of these cubic structures, which shows a ccp structure type and which ccp structure is it?



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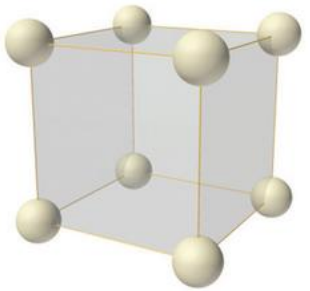
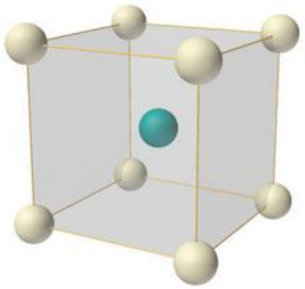
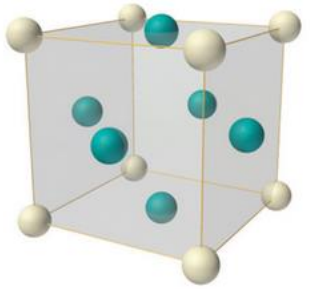
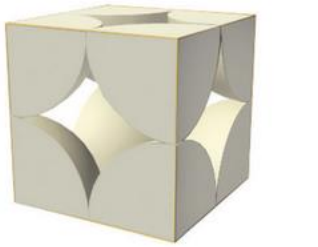
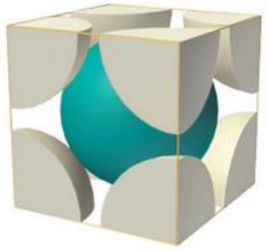
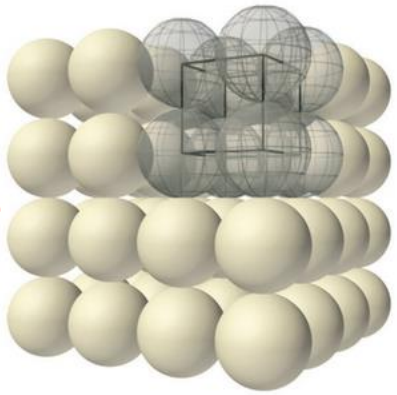
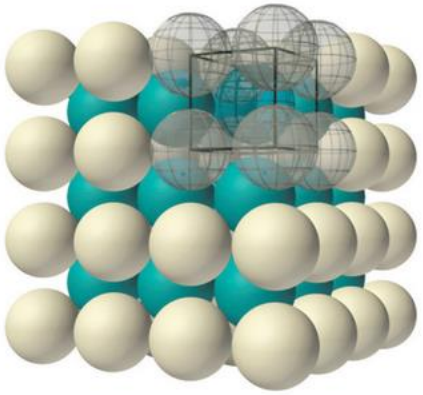
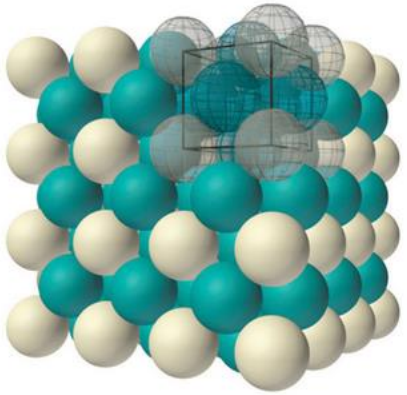
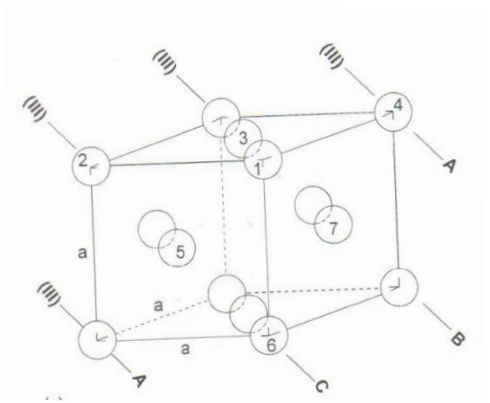
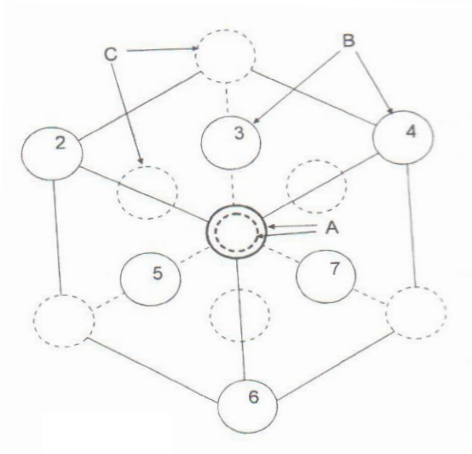




Also # of lattice points

P

atoms per cell = 1
Nearest neighbors (NN) = 6

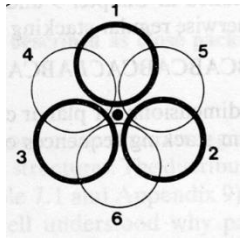
I

atoms per cell = 2
NN # = 8

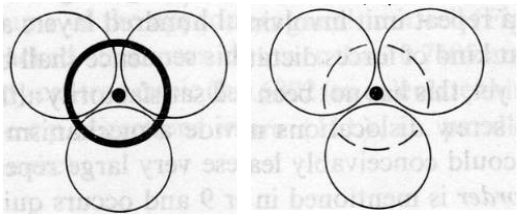
F

atoms per cell = 4
NN # = 12

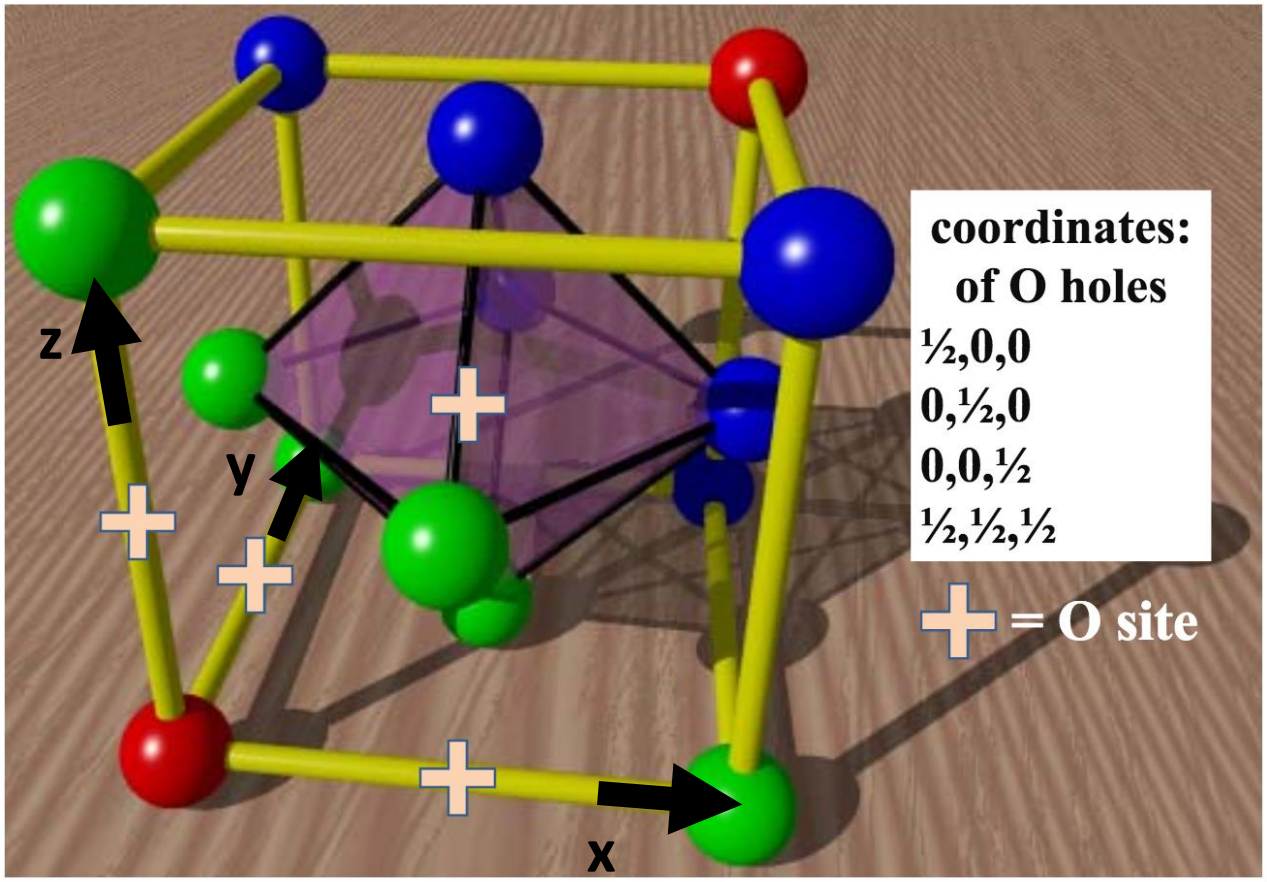
Octahedral and Tetrahedral holes in CCP structures

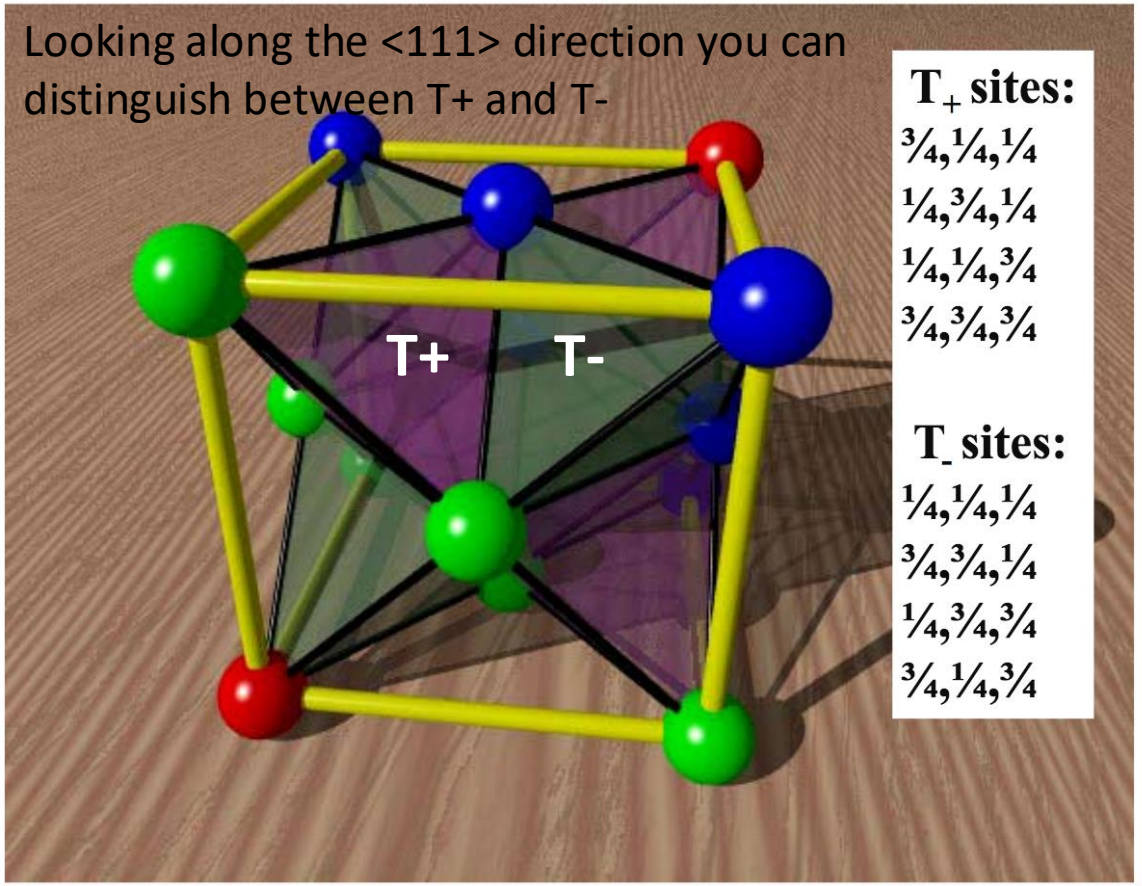


Exercise: How many lattice points per cell if all octahedral holes are filled?

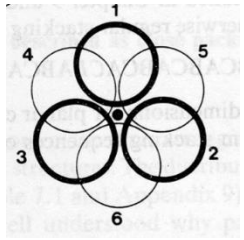


Exercise: How many lattice points per cell if all tetrahedral holes are filled?

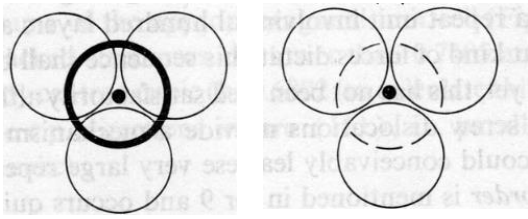




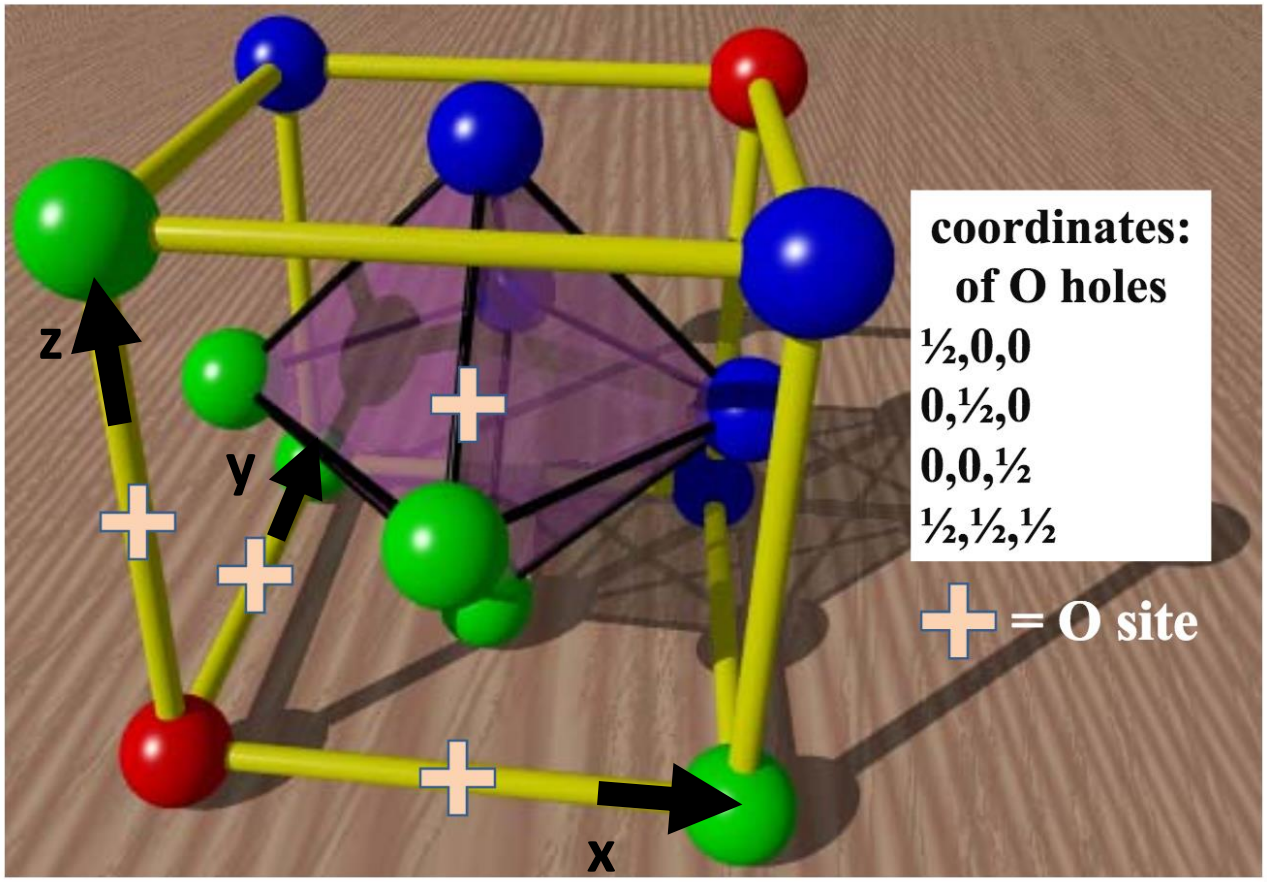
Octahedral and Tetrahedral holes in CCP structures

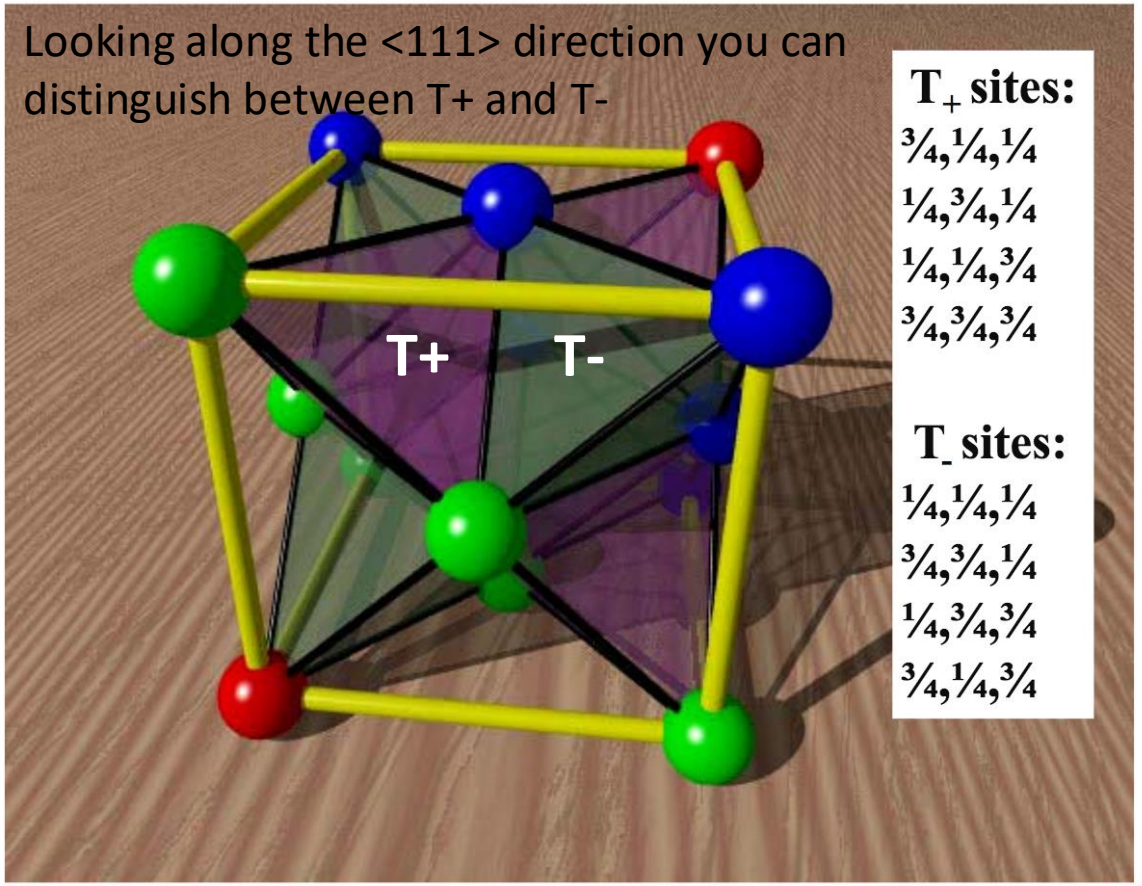


Exercise: How many lattice points per cell if all octahedral holes are filled? 4

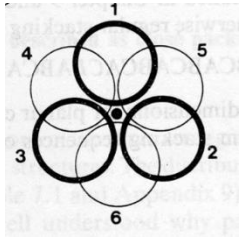


Exercise: How many lattice points per cell if all tetrahedral holes are filled? 8

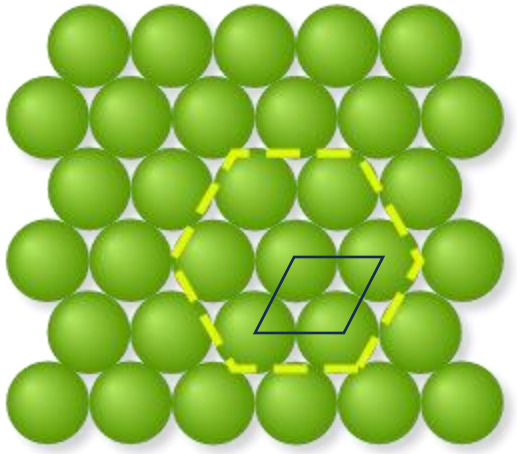


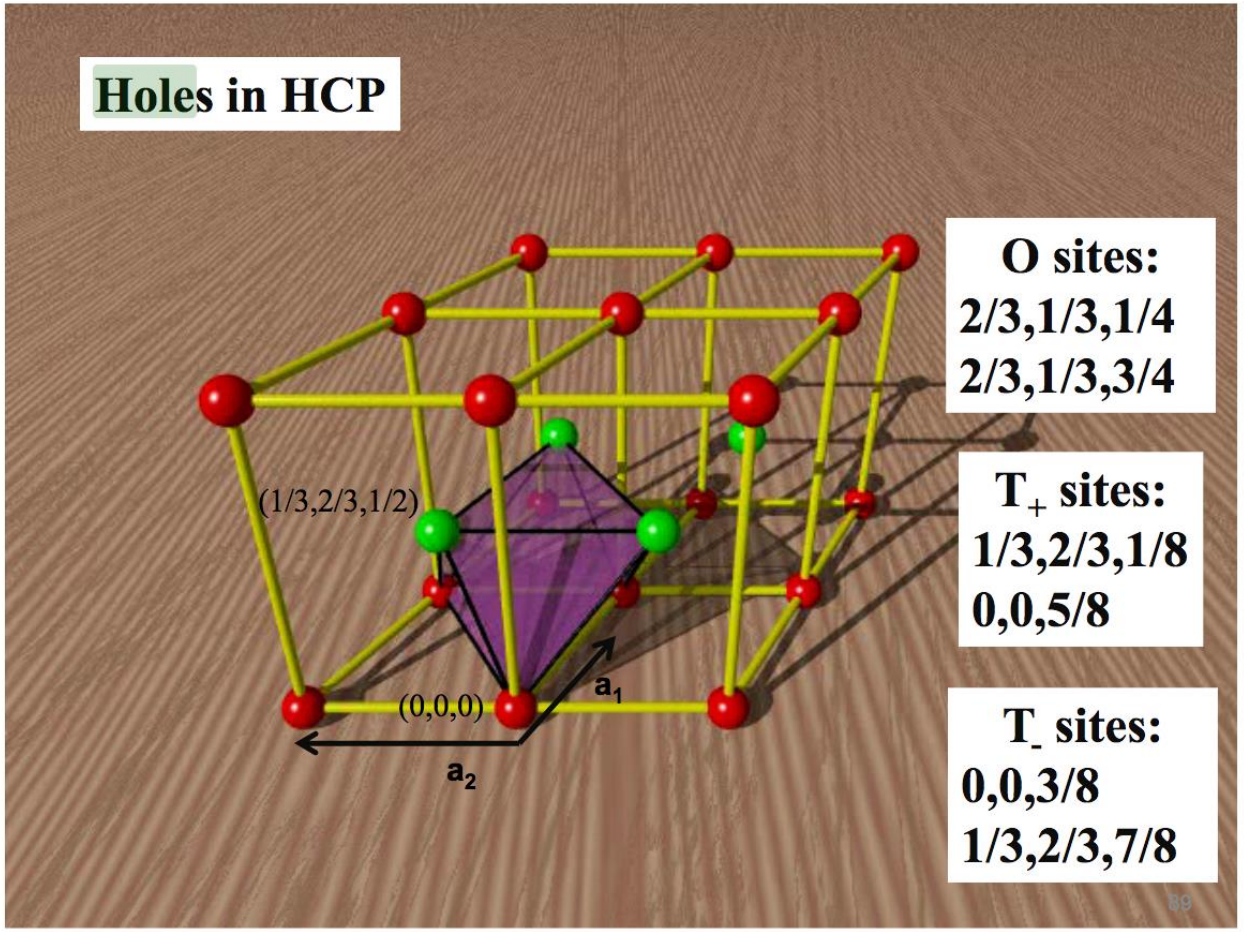


Octahedral and Tetrahedral holes in HCP structures

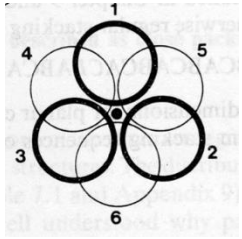


Exercise: How many lattice points per hexagon if all octahedral are filled?

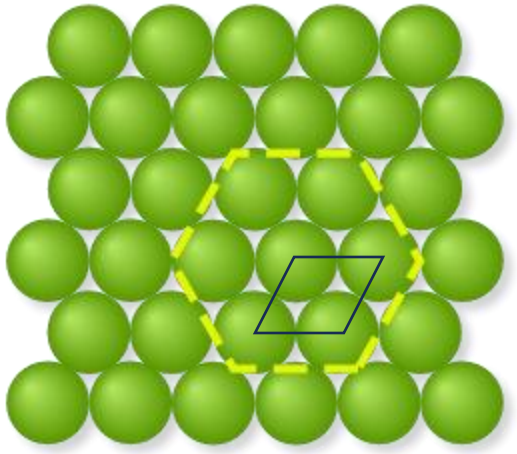


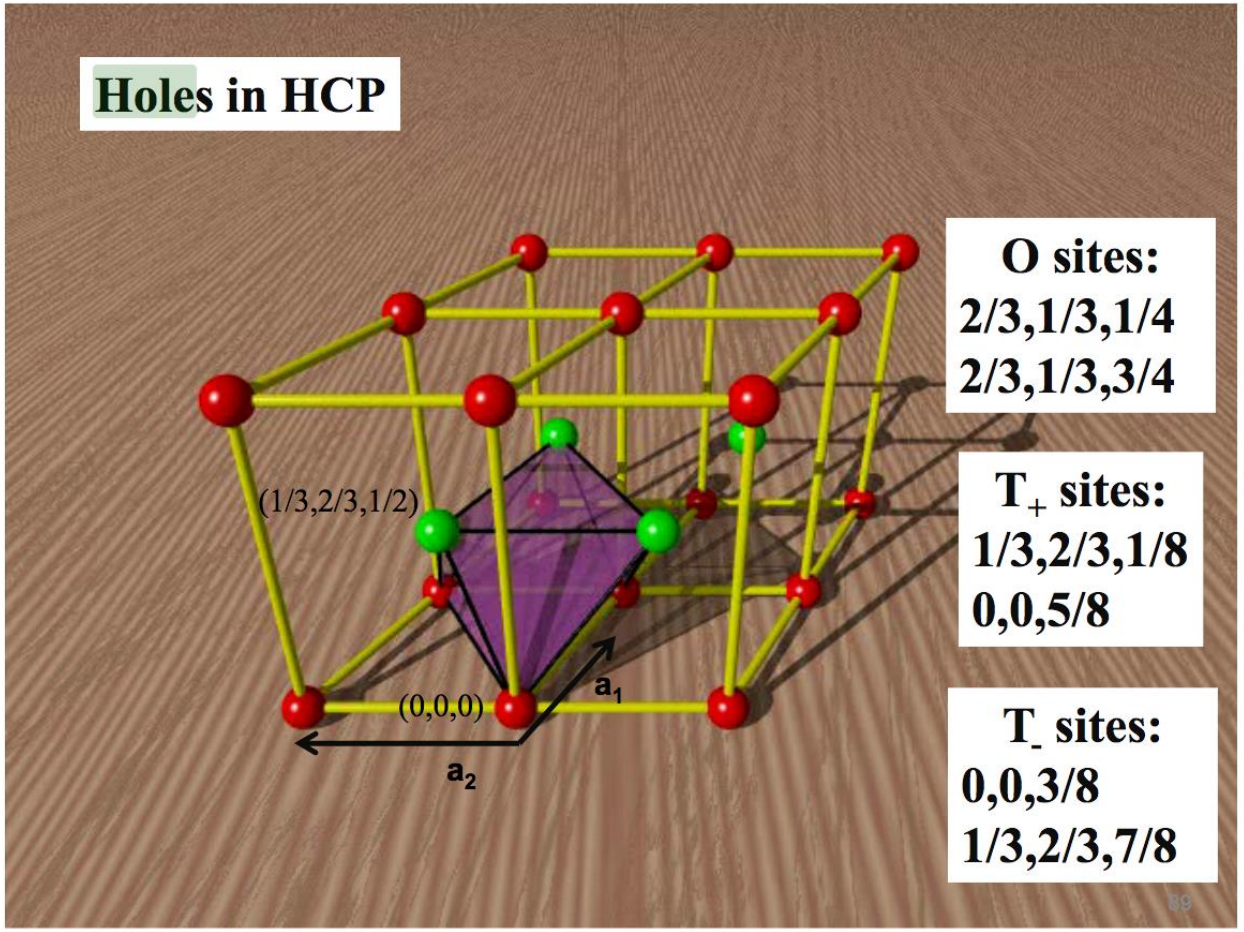


Octahedral and Tetrahedral holes in HCP structures



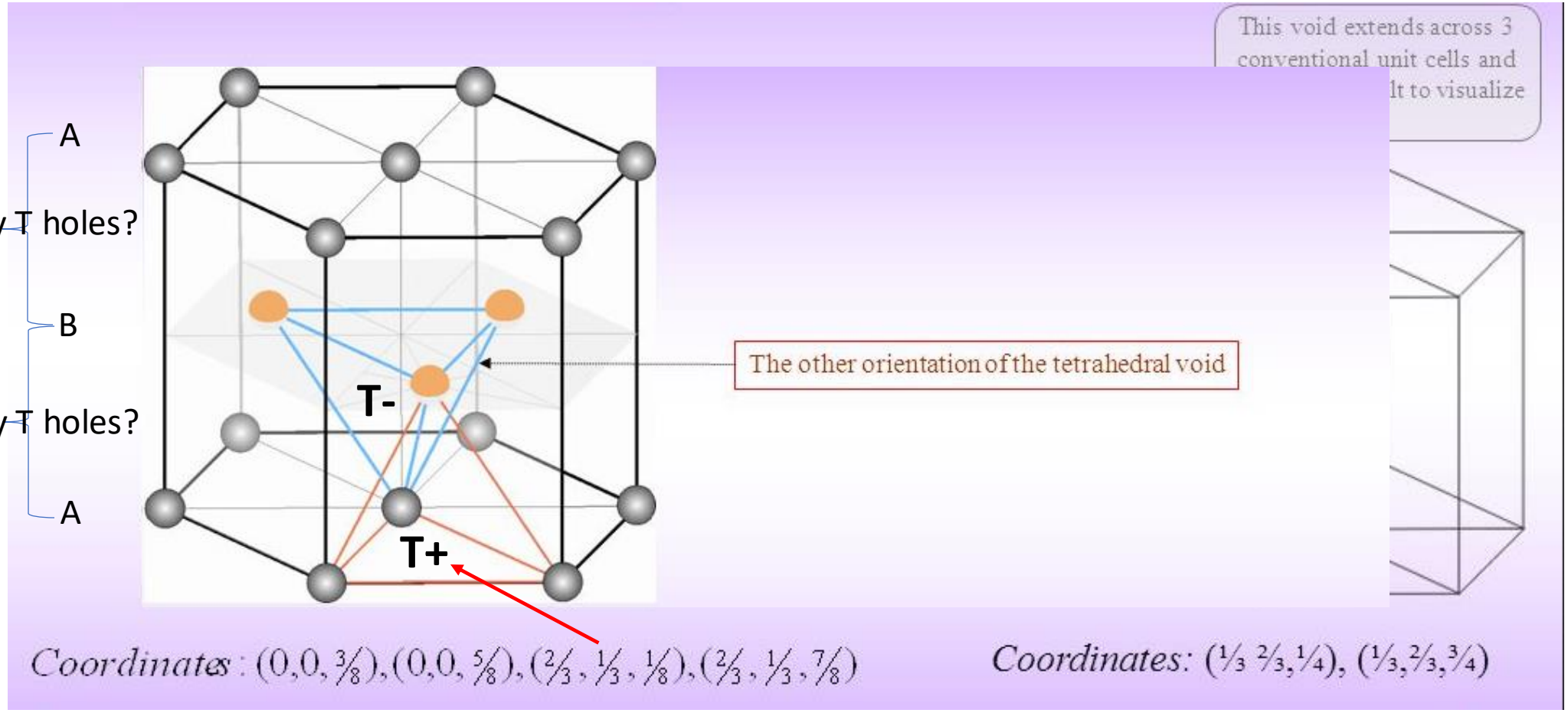
Exercise: How many lattice points per hexagon if all octahedral are filled? 6



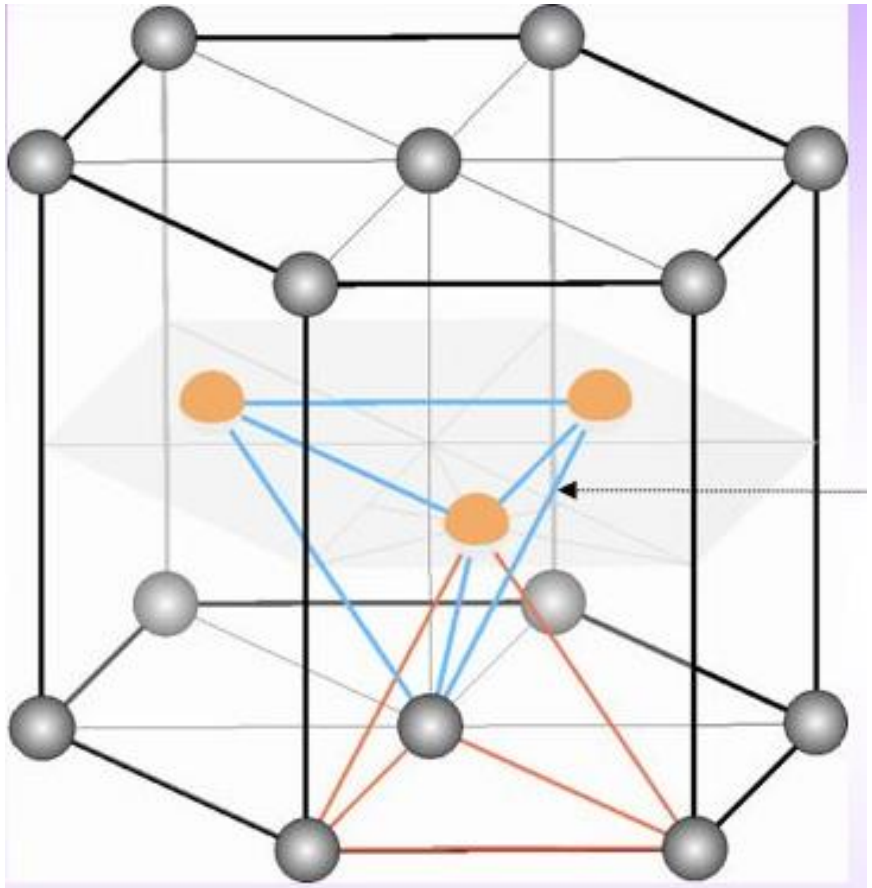


Tetrahedral and Octahedral holes in HCP

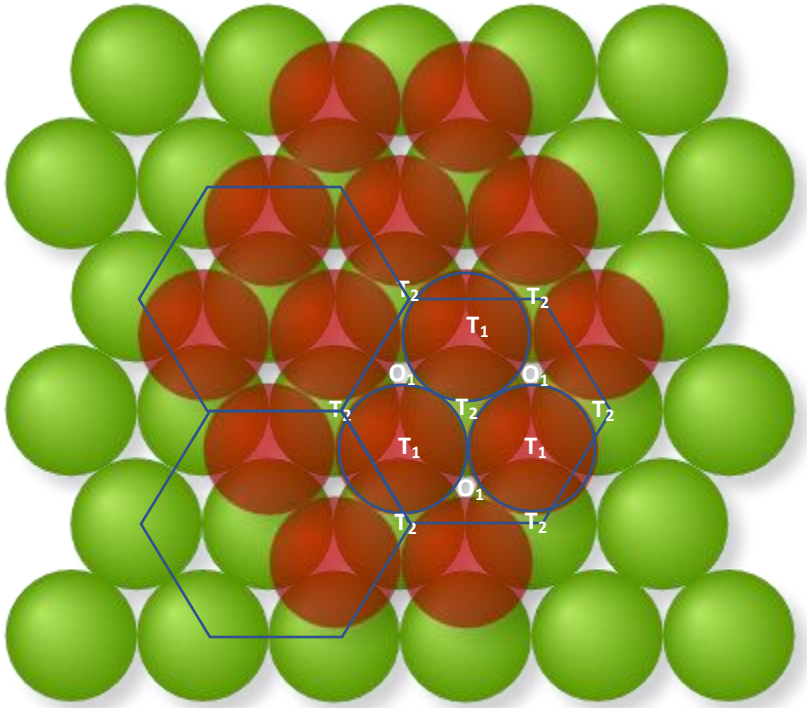
A B A…packing



Tetrahedral and Octahedral holes in HCP



A



B

A

O sites:

2/3,1/3,1/4 O_1 x 3

2/3,1/3,3/4 x 3

6

T_+ sites:

1/3,2/3,1/8 T_1 x 3

0,0,5/8 x 3

T_- sites:

0,0,3/8 T_2 x 3

1/3,2/3,7/8 x 3

12

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