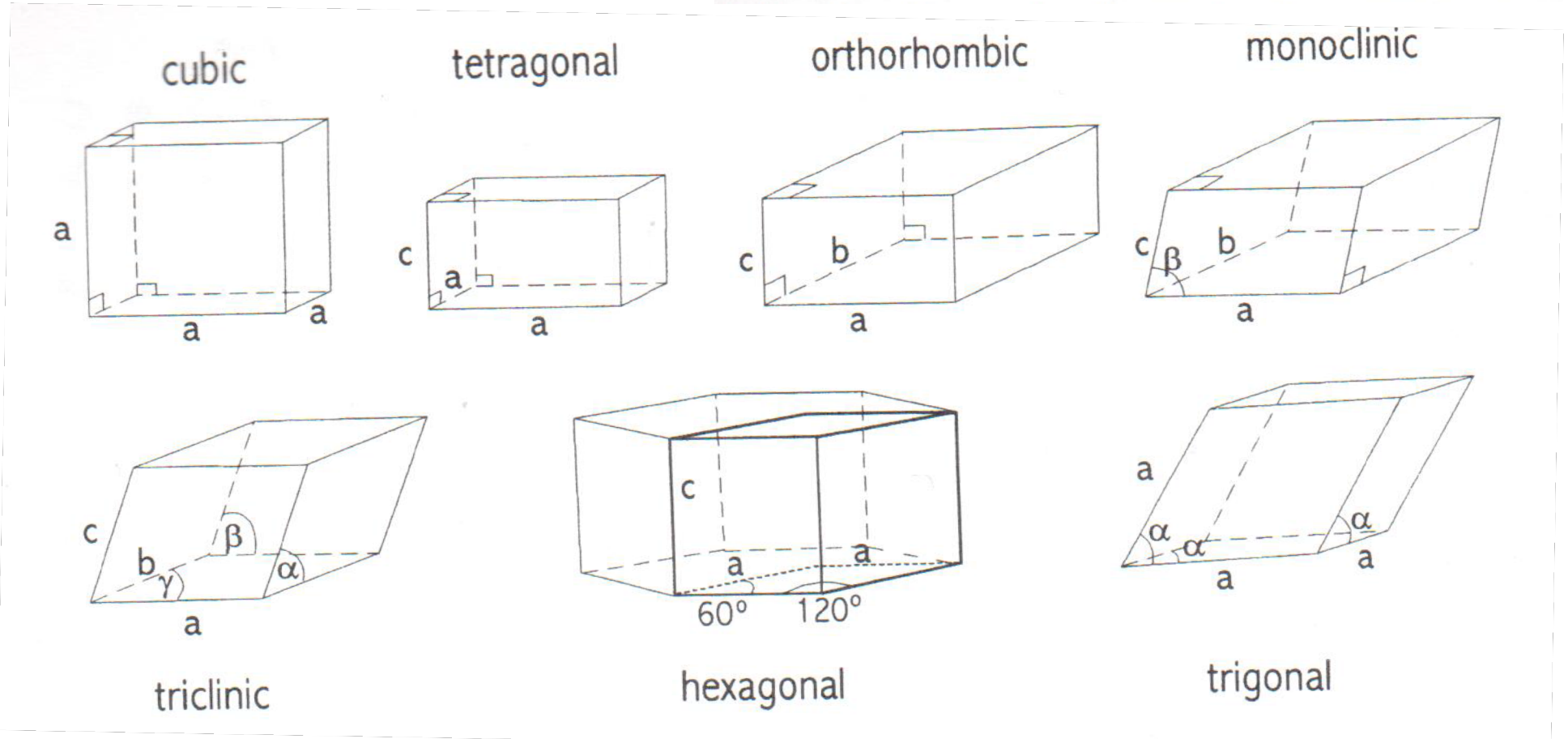
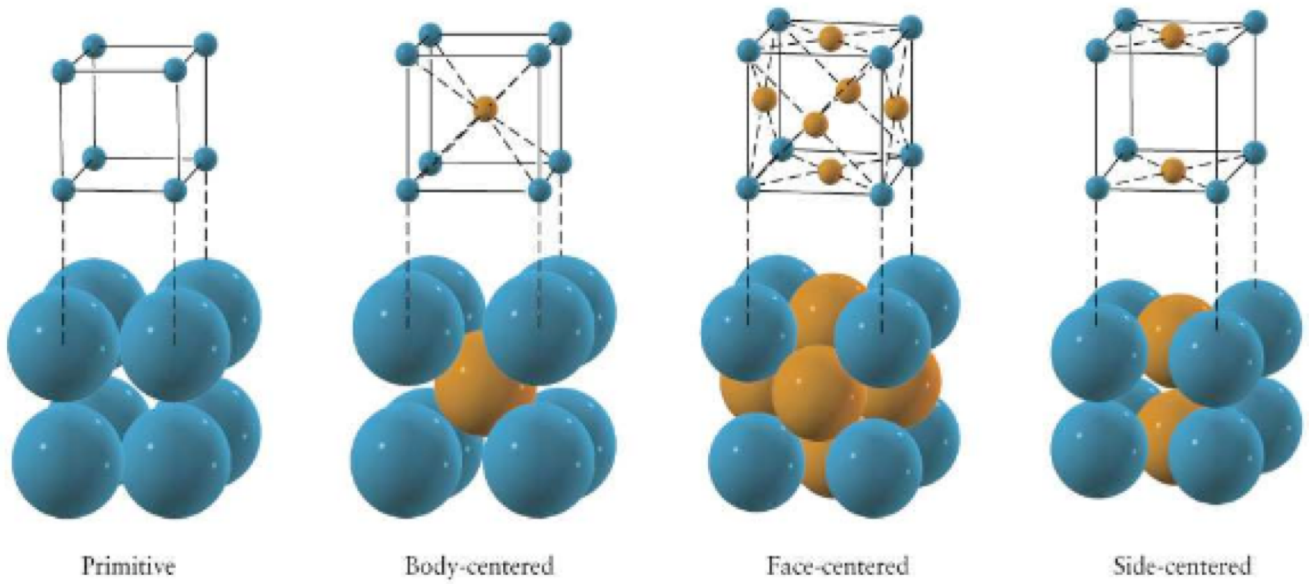
7 Crystal systems

Crystal system	Unit cell shape†
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$
(b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$
Monoclinic*	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$



14 Bravais Lattices

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



Primitive Body-centered Face-centered Side-centered

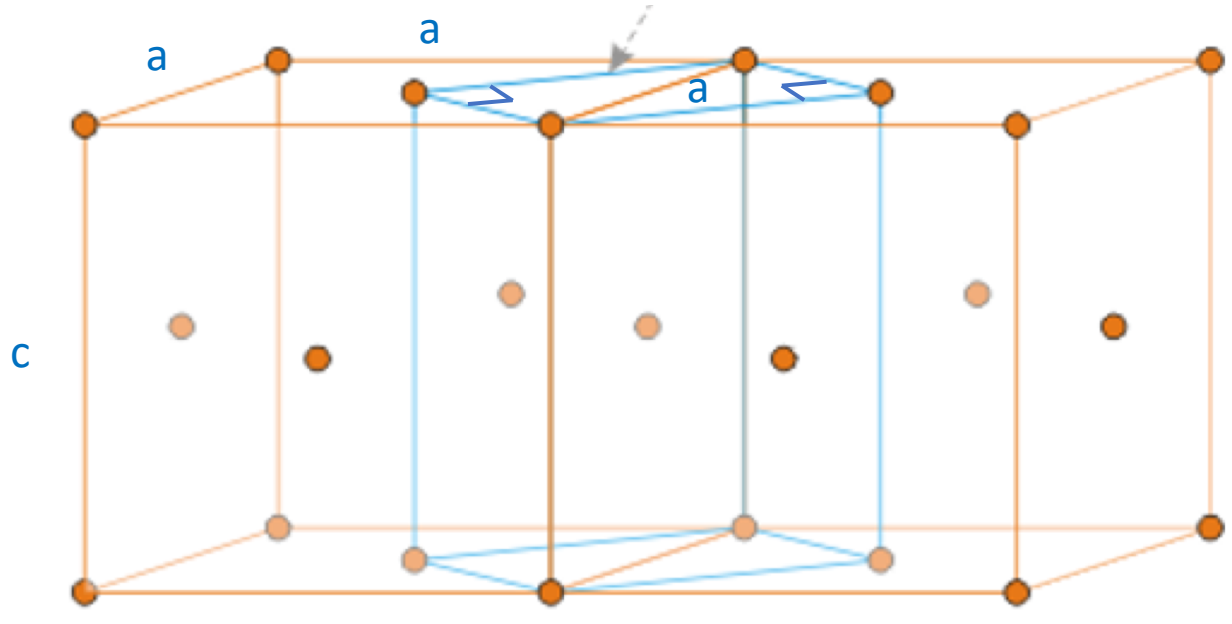
Exercises:

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

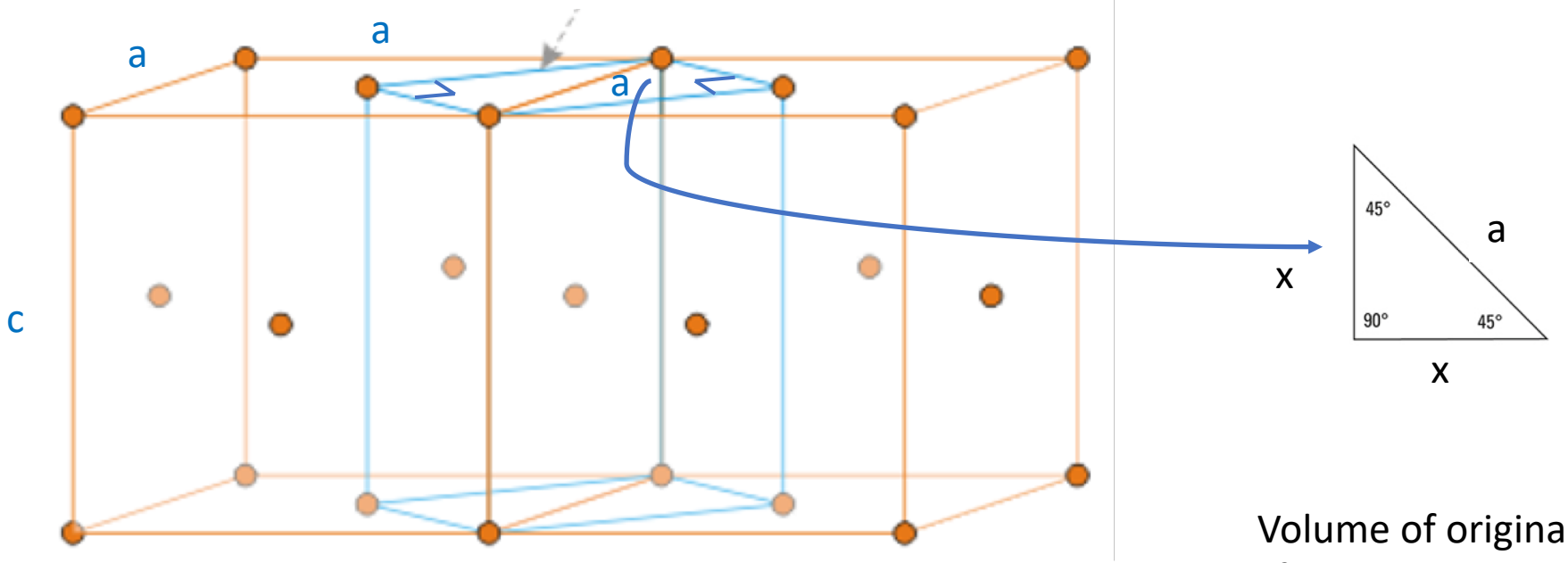
Why there is no C-centered tetragonal?

Why is there no C-centered cubic cell?

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



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

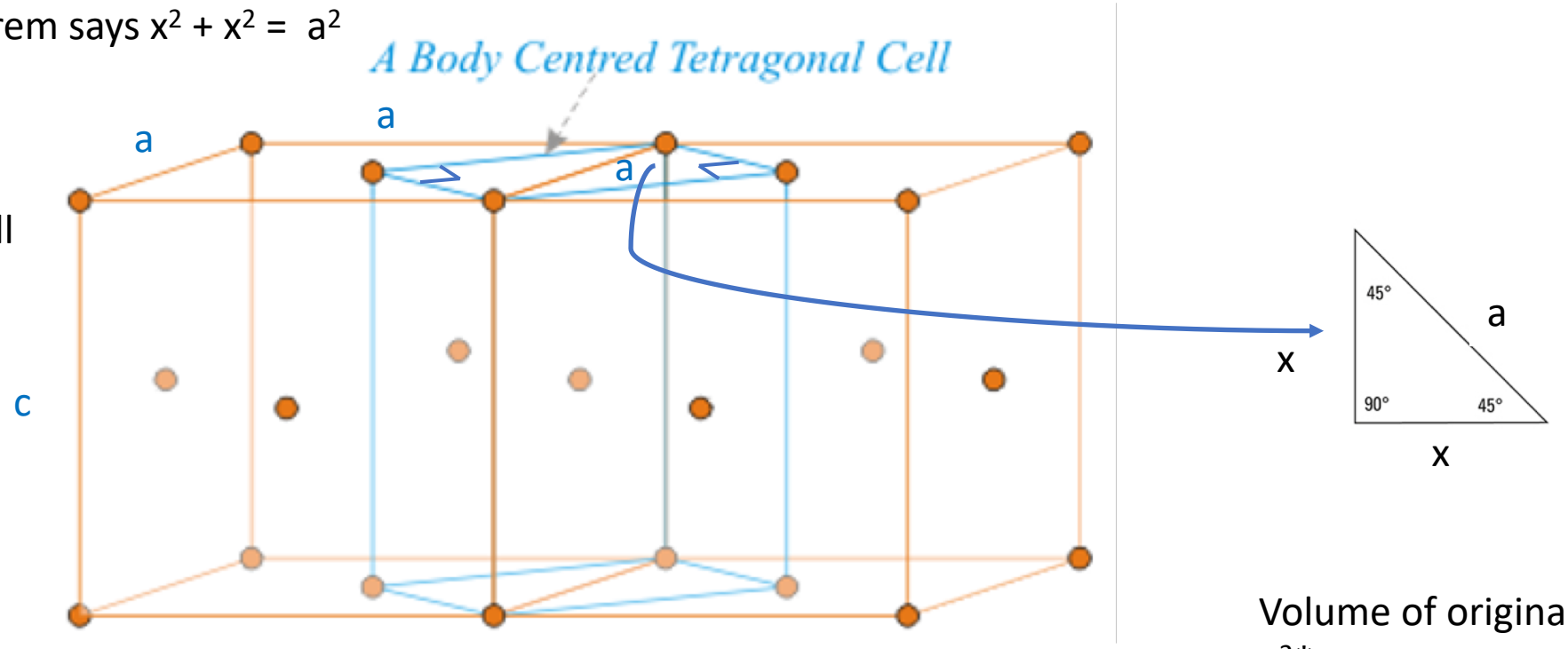


Volume of original unit cell
a^2*c

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

The Pythagorean theorem says $x^2 + x^2 = a^2$
Therefore, $2x^2 = a^2$
$x = a/2^{1/2}$ or $0.7071a$

Volume of new unit cell
$0.5\ a^2 * c$



Some **O**ld **H**ippie **C**aught **A** **H**igh **T**ripping **O**n **A**cid

sin 45 = o/h = x/a
cos 45 = a/h = x/a

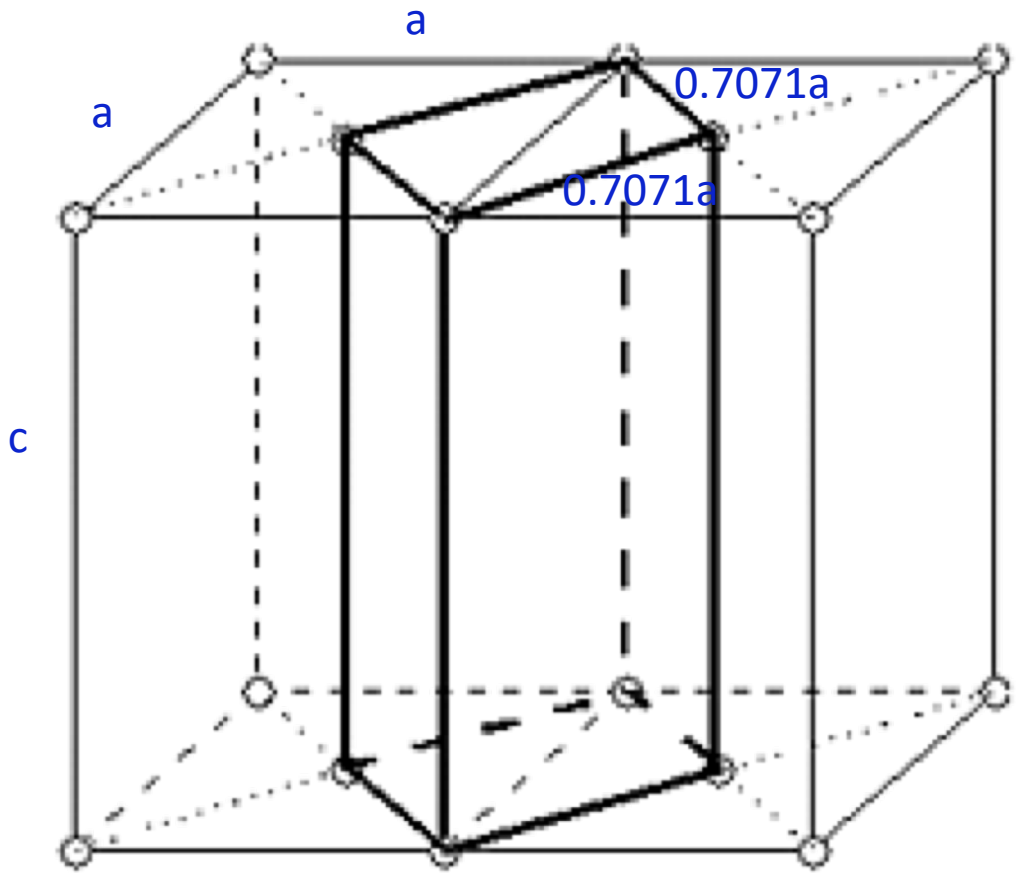
sin 45 = 0.7071a = x
cos 45 = 0.7071a = x

Volume of original unit cell
$a^2 * c$

Volume of new unit cell
$0.5a^2 * c$

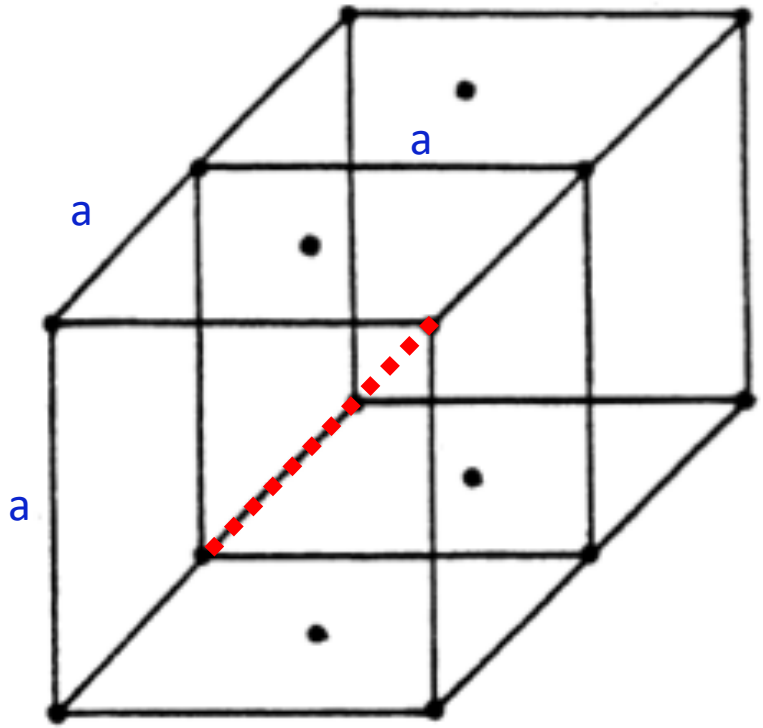
Answer: The better unit cell is body-centered tetragonal with half the volume of the original cell.

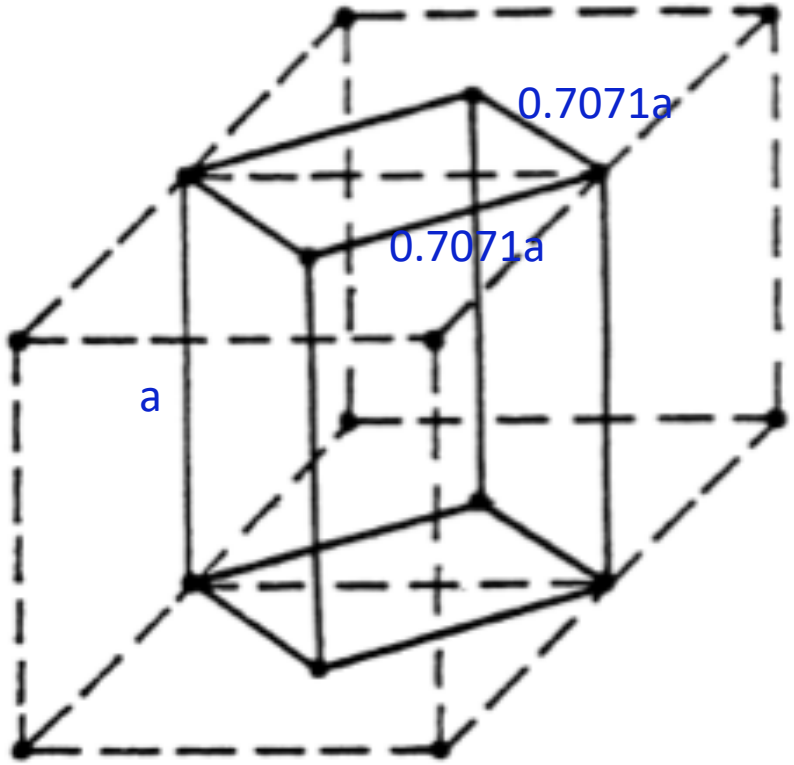
Exercise: Why there is no C-centered tetragonal?



Answer: The better unit cell that is primitive tetragonal. We know from the previous slide that the unit cell volume is half of the previous one.

Problem: Why is there no c-centered cubic cell?



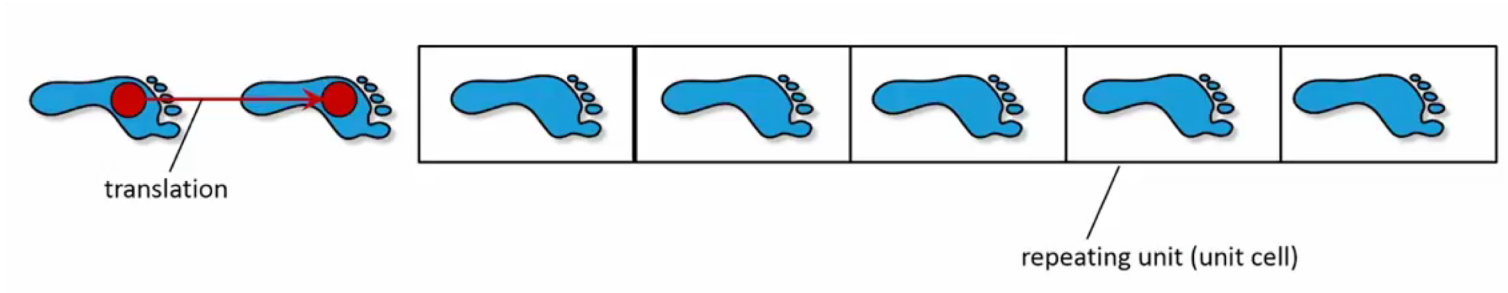


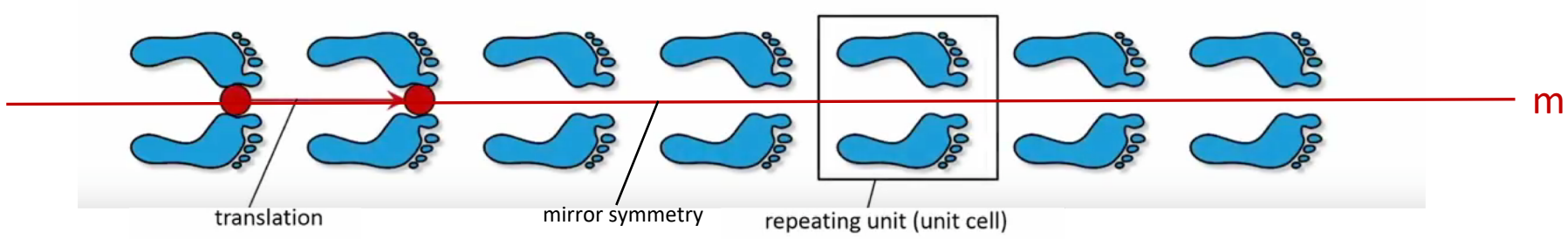
Answer: The better unit cell that is primitive tetragonal. We know from the previous slide that the unit cell volume is half of the previous one. But the better answer is that the initial cell is not cubic at all because it does not have a three-fold rotation axis along the body diagonal.

Point Symmetry Elements

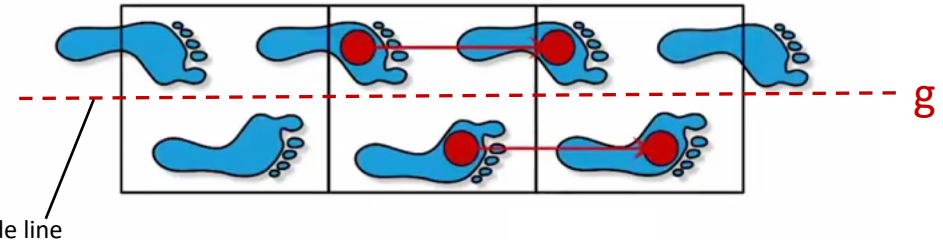
Symmetry element	Symmetry operation	Schönflies Symbol (spectroscopy)	Herman-Maugin Symbol (crystallography)
Rotation axis	rotation by 360°/n	C_n	n = 2, 3, 4, 6
mirror plane	Reflection across a plane	σv, σh	m
center of inversion	Inversion -pull atoms through a center point	i	$\bar{1}$
improper axis of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

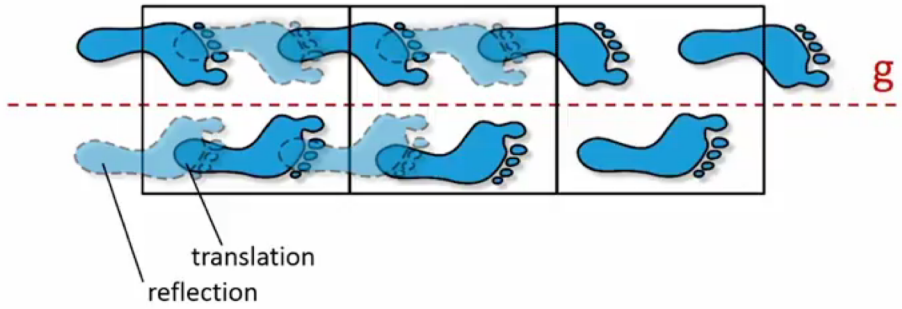
Translational symmetry



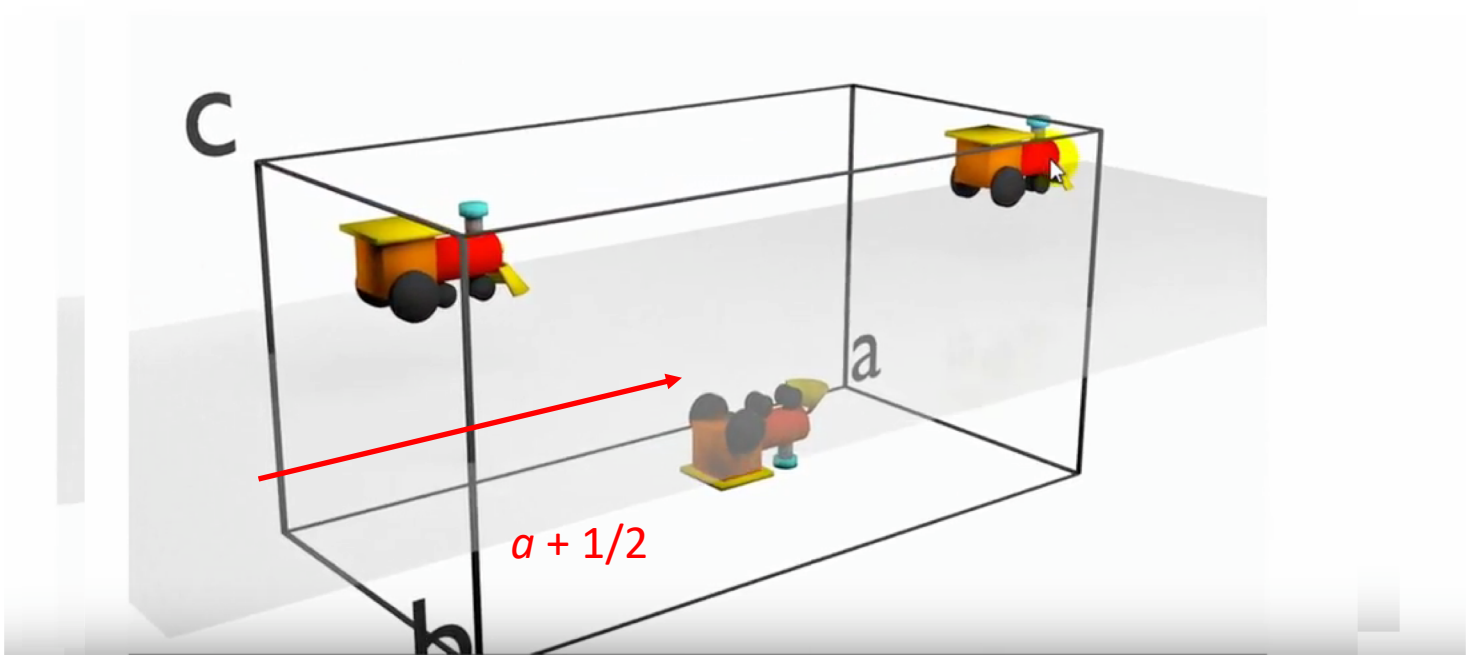


glide reflection → (a) reflection at a plane / line
(b) translation (usually by $^1/_2$ of the unit cell)

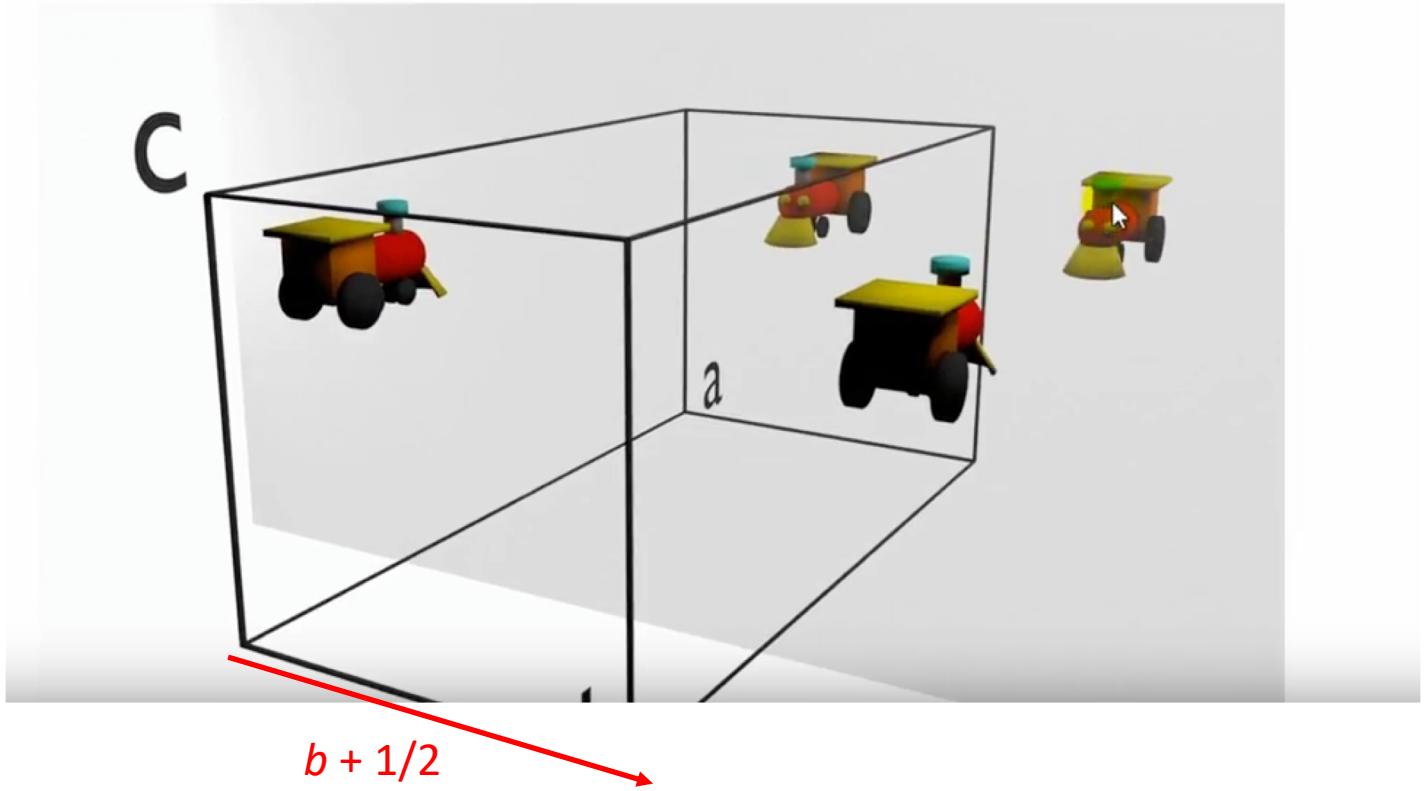




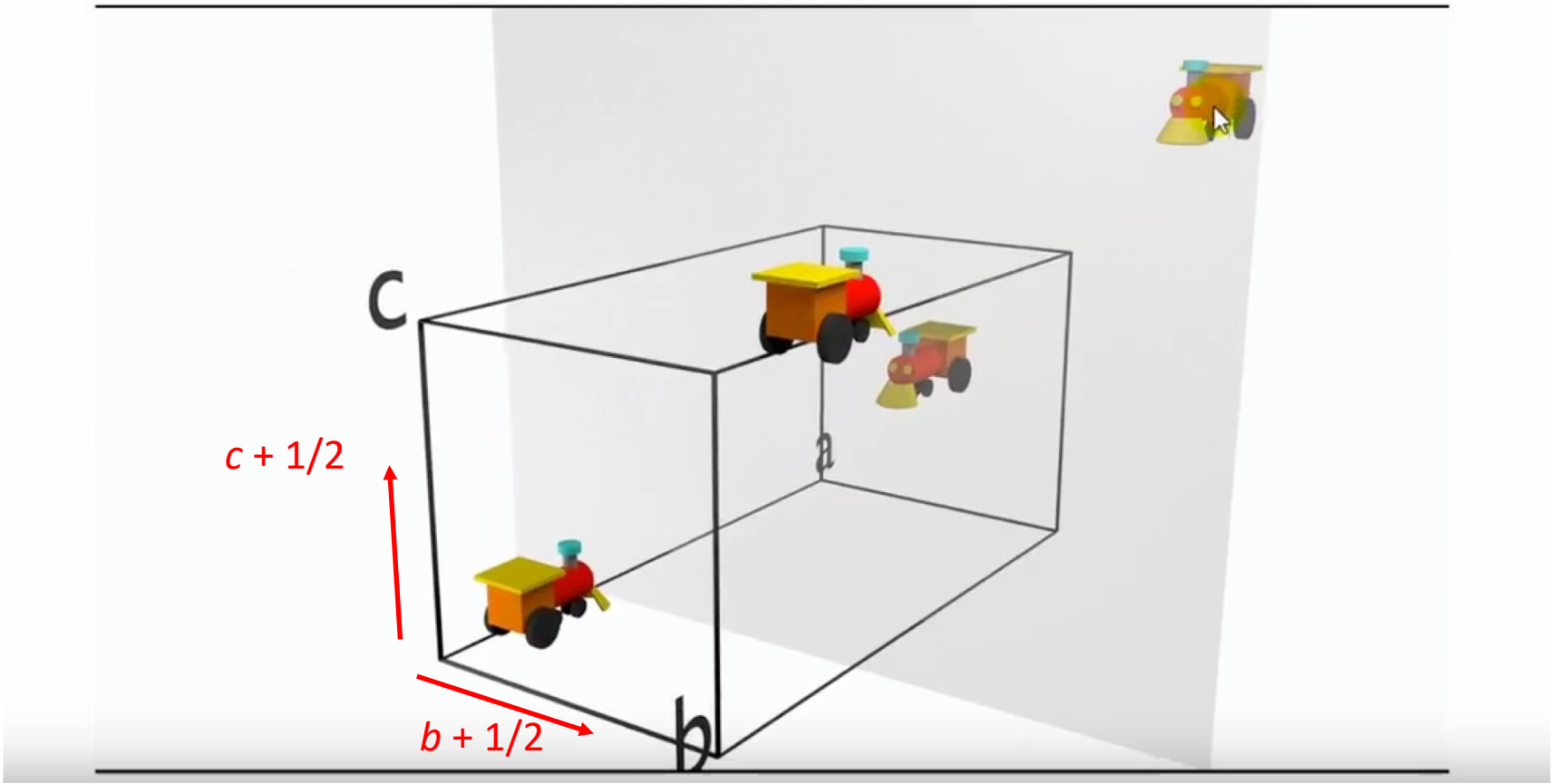
Glide plane in a crystal structure, a glide



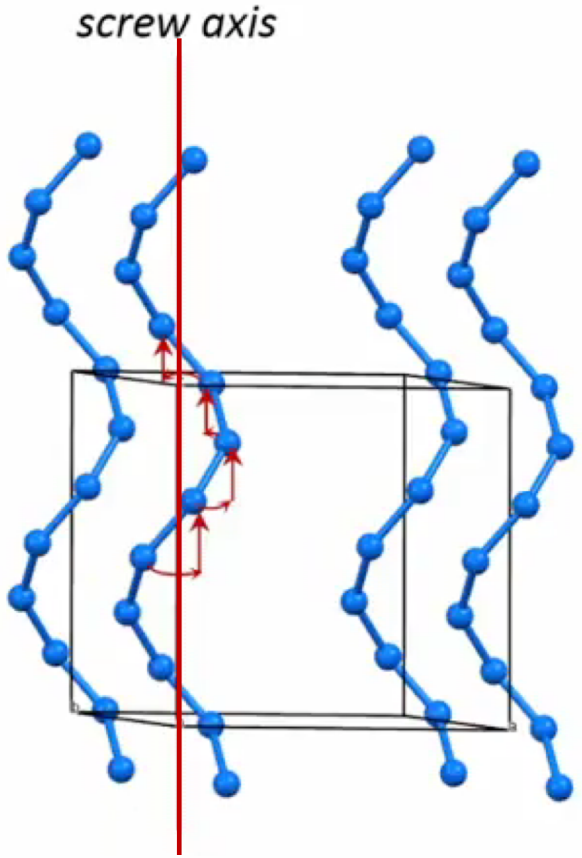
Glide plane in a crystal structure, b glide

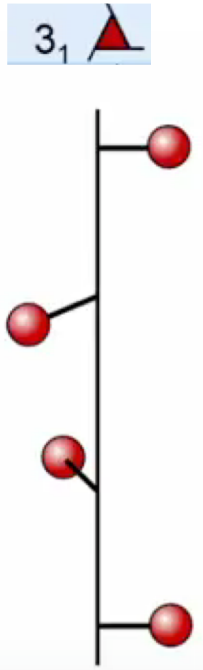


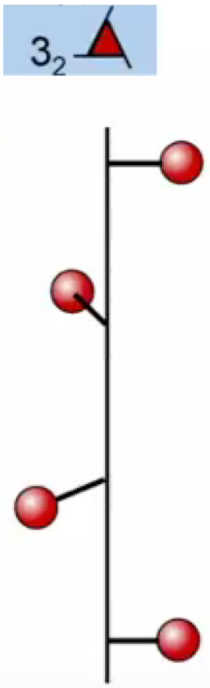
Glide plane in a crystal structure, n glide

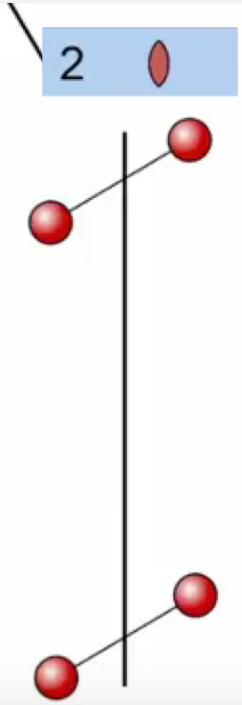


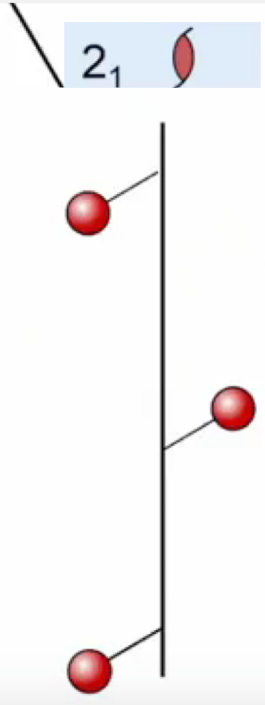
Screw Axis







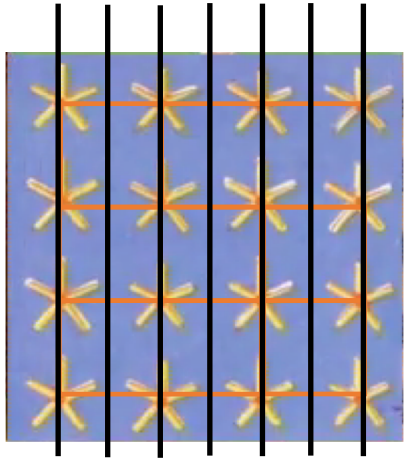


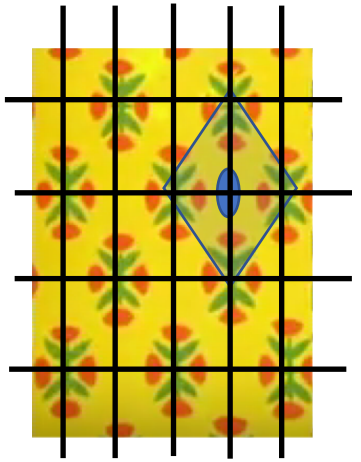


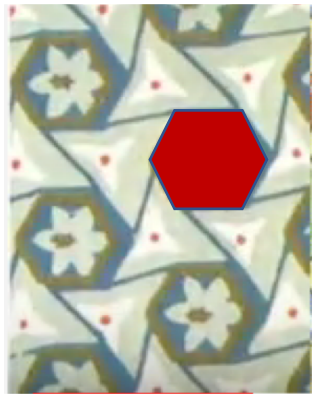
6_1 screw axis, n_m
Rotation by 360/n = 360/6 = 60
Translation by m/n = 1/6

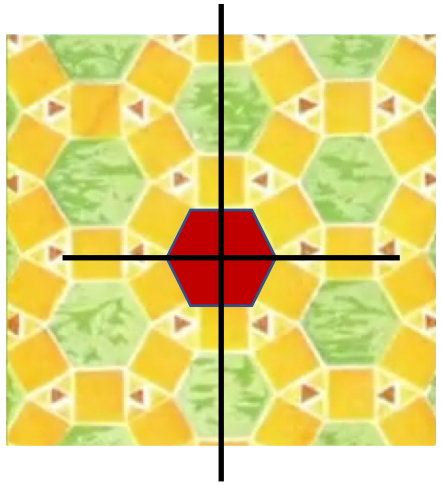
Identify the symmetry elements

Spotted newt









Symmetry in crystals

7 Crystal systems: Describes unit cell dimensions a,b,c, α, β, γ

14 Bravais Lattices: Includes potential centering conditions, PFIC

32 Point Groups: Includes point symmetry operations

230 Space groups: Includes translational symmetry operations

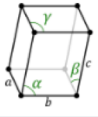
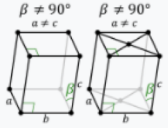
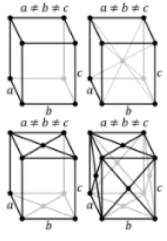
all compounds crystallize in one or more of these space groups
usually possible to find **P1**, but **always** try to find the
highest possible symmetry.

structures observed in all 230 space groups

~95% of all structures: **monoclinic, triclinic, orthorhombic**

~83% of all structures: **$P2_1/c$, $P\bar{1}$, $P2_12_12_1$, $C2/c$, $P2_1$, $Pbca$**

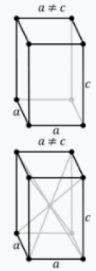
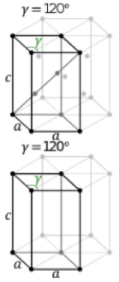
230 Possible Space Groups

#	Crystal system (count) Bravais lattice	Point Group		Space groups (international short symbol)
		Intl	Schön.	
1	Triclinic (2) 	1	C_1	P1
2		$\bar{1}$	C_i	$P\bar{1}$
3–5	Monoclinic (13) 	2	C_2	P2, $P2_1$ C2
6–9		m	C_s	Pm, Pc Cm, Cc
10–15		2/m	C_{2h}	P2/m, $P2_1/m$ C2/m, P2/c, $P2_1/c$ C2/c
16–24	Orthorhombic (59) 	222	D_2	P222, $P222_1$, $P2_12_12$, $P2_12_12_1$, $C222_1$, C222, F222, I222, $I2_12_12_1$
25–46		mm2	C_{2v}	Pmm2, $Pmc2_1$, Pcc2, Pma2, $Pca2_1$, $Pnc2$, $Pmn2_1$, Pba2, $Pna2_1$, Pnn2 Cmm2, $Cmc2_1$, Ccc2, Amm2, Aem2, Ama2, Aea2 Fmm2, Fdd2 Imm2, Iba2, Ima2
47–74		mmm	D_{2h}	Pmmm, Pnnn, Pccm, Pban, Pmma, Pnna, Pmna, Pcca, Pbam, Pccn, Pbcm, Pnnm, Pmmn, Pbcn, Pbca, Pnma Cmcm, Cmce, Cmmm, Cccm, Cmme, Ccce Fmmm, Fddd Immm, Ibam, Ibca, Imma

Monoclinic: Descriptor axis is the crystallographic b axis

Orthorhombic: Descriptor axes are a, b, c

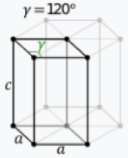
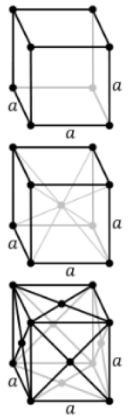
230 Possible Space Groups

#	Crystal system (count) Bravais lattice	Point Group		Space groups (international short symbol)
		Intl	Schön.	
75–80	Tetragonal (68) 	4	C_4	P4, $P4_1$, $P4_2$, $P4_3$, I4, $I4_1$
81–82		$\bar{4}$	S_4	$P\bar{4}$, $I\bar{4}$
83–88		4/m	C_{4h}	P4/m, $P4_2$/m, P4/n, $P4_2$/n I4/m, $I4_1$/a
89–98		422	D_4	P422, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_32_12$ I422, $I4_122$
99–110		4mm	C_{4v}	P4mm, P4bm, $P4_2$cm, $P4_2$nm, P4cc, P4nc, $P4_2$mc, $P4_2$bc I4mm, I4cm, $I4_1$md, $I4_1$cd
111–122		$\bar{4}$2m	D_{2d}	$P\bar{4}2$m, $P\bar{4}2$c, $P\bar{4}2_1$m, $P\bar{4}2_1$c, $P\bar{4}$m2, $P\bar{4}$c2, $P\bar{4}$b2, $P\bar{4}$n2 $I\bar{4}$m2, $I\bar{4}$c2, $I\bar{4}$2m, $I\bar{4}$2d
123–142		4/mmm	D_{4h}	P4/mmm, P4/mcc, P4/nbm, P4/nnc, P4/mbm, P4/mnc, P4/nmm, P4/ncc, $P4_2$/mmc, $P4_2$/mcm, $P4_2$/nbc, $P4_2$/nnm, $P4_2$/mbc, $P4_2$/mnm, $P4_2$/nmc, $P4_2$/ncm I4/mmm, I4/mcm, $I4_1$/amd, $I4_1$/acd
143–146	Trigonal (25) 	3	C_3	P3, $P3_1$, $P3_2$ R3
147–148		$\bar{3}$	S_6	$P\bar{3}$, $R\bar{3}$
149–155		32	D_3	P312, P321, $P3_112$, $P3_121$, $P3_212$, $P3_221$ R32
156–161		3m	C_{3v}	P3m1, P31m, P3c1, P31c R3m, R3c
162–167		$\bar{3}$m	D_{3d}	$P\bar{3}$1m, $P\bar{3}$1c, $P\bar{3}$m1, $P\bar{3}$c1 $R\bar{3}$m, $R\bar{3}$c

Tetragonal: Descriptor axes are c, b and a, and the face diagonal between b and a

Trigonal: Descriptor axes are c, a and b, and perpendicular to a and b.

230 Possible Space Groups

#	Crystal system (count) Bravais lattice	Intl	Schön.	Space groups (international short symbol)
168–173	Hexagonal (27) 	6	C_6	P6, P6$_1$, P6$_5$, P6$_2$, P6$_4$, P6$_3$
174		$\bar{6}$	C_{3h}	P$\bar{6}$
175–176		6/m	C_{6h}	P6/m, P6$_3$/m
177–182		622	D_6	P622, P6$_1$22, P6$_5$22, P6$_2$22, P6$_4$22, P6$_3$22
183–186		6mm	C_{6v}	P6mm, P6cc, P6$_3$cm, P6$_3$mc
187–190		$\bar{6}$m2	D_{3h}	P$\bar{6}$m2, P$\bar{6}$c2, P$\bar{6}$2m, P$\bar{6}$2c
191–194		6/mmm	D_{6h}	P6/mmm, P6/mcc, P6$_3$/mcm, P6$_3$/mmc
195–199	Cubic (36) 	23	T	P23, F23, I23 P2$_1$3, I2$_1$3
200–206		m$\bar{3}$	T_h	Pm$\bar{3}$, Pn$\bar{3}$, Fm$\bar{3}$, Fd$\bar{3}$, Im$\bar{3}$, Pa$\bar{3}$, Ia$\bar{3}$
207–214		432	O	P432, P4$_2$32 F432, F4$_1$32 I432 P4$_3$32, P4$_1$32, I4$_1$32
215–220		$\bar{4}$3m	T_d	P$\bar{4}$3m, F$\bar{4}$3m, I$\bar{4}$3m P$\bar{4}$3n, F$\bar{4}$3c, I$\bar{4}$3d
221–230		m$\bar{3}$m	O_h	Pm$\bar{3}$m, Pn$\bar{3}$n, Pm$\bar{3}$n, Pn$\bar{3}$m Fm$\bar{3}$m, Fm$\bar{3}$c, Fd$\bar{3}$m, Fd$\bar{3}$c Im$\bar{3}$m, Ia$\bar{3}$d

Hexagonal: Descriptor axes are c, a and b, and perpendicular to a and b.

Cubic: Descriptor axes are a b and c, body diagonal, and the face diagonals.

Symmetry in crystals

7 Crystal systems: Describes unit cell dimensions a,b,c, α, β, γ

14 Bravais Lattices: Includes potential centering conditions, PFIC

32 Point Groups: Includes point symmetry operations

230 Space groups: Includes translational symmetry operations

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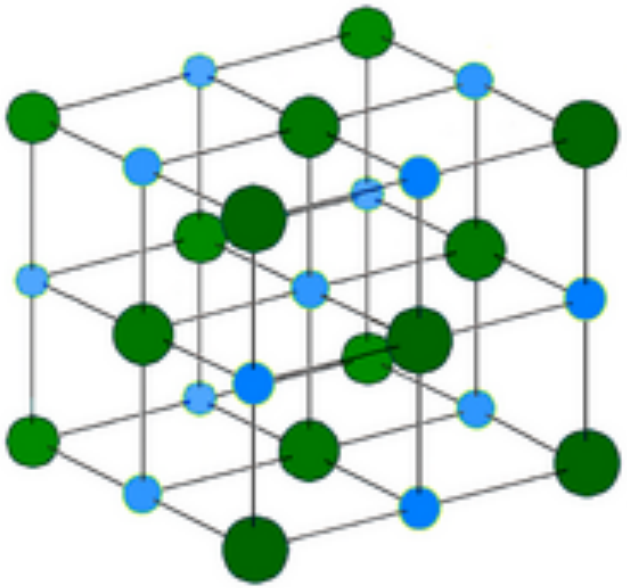
~95% of all structures: **monoclinic, triclinic, orthorhombic**

~83% of all structures: **$P2_1/c$, $P\bar{1}$, $P2_12_12_1$, $C2/c$, $P2_1$, $Pbca$**

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
				NaCl, rock salt
				ZnS, blende or sphalerite
				$MgAl_2O_4$, spinel
				$CdCl_2$
				$CrCl_3$
				K_2O, antifluorite
				NiAs
				ZnS, wurtzite
				CdI_2
				TiO_2, rutile*
				Al_2O_3, corundum
				Mg_2SiO_4, olivine
				$BaTiO_3$, perovskite

Green sphere = oxygen; blue sphere = metal

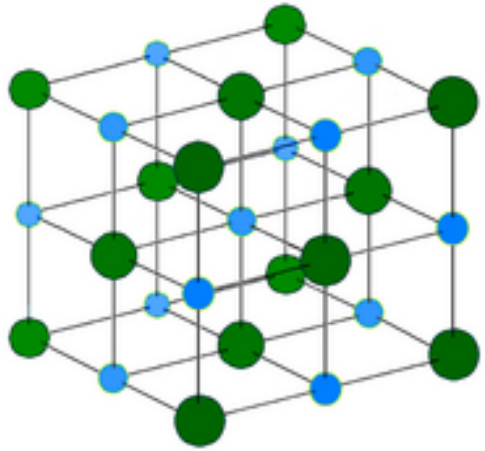
Space group Fm3m (cubic)
Lattice parameter a ~ 5.64 Å; Z = 4

Atom	Site	x	y	z
O	4a	0	0	0
M	4b	½	0	0

NaCl Structure Type

1. Basics

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



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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. The number per mole, n_s, is given by:

$$n_s = N.\exp(-e_s/2RT)$$

where e_s is the energy required to form such a defect. For NaCl, e_s ~ 192 kJ/mol. These defects are responsible for the transport properties of the oxides, i.e. ionic diffusion and conductivity, since they provide pathways for the ions to hop from one site to another.

Point defects in ionic solids:

These usually comprise Frenkel or Schottky defects: