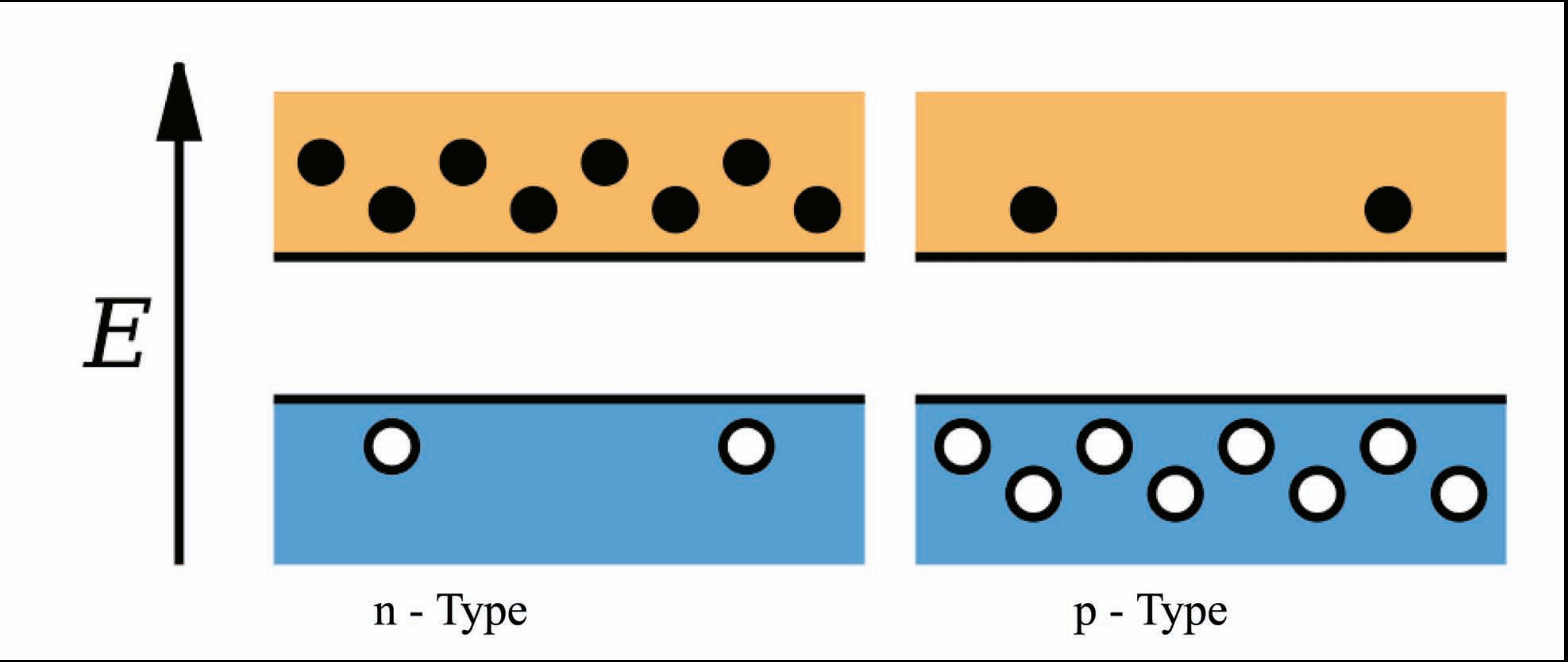
Welcome to 3.091

Lecture 15

October 14, 2009

Introduction to Crystallography



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The Big Picture

electronic structure ☞ ***bonding*** ☞ ***state of aggregation***

Bohr atom	primary:	gas
Bohr-Sommerfeld	❶ ionic	liquid
quantum numbers	❷ covalent	***solid***
Aufbau principle	❸ metallic	
multielectron atoms	❹ van der Waals	3.091 ☺
Periodic Table patterns		
octet stability	secondary:	
	❶ dipole-dipole	
	❷ London dispersion	
	❸ hydrogen	

solid: that which is dimensionally stable, i.e., has a volume of its own

classifications of solids:

❶ bonding type

❷ atomic arrangement

classifications of solids:
❶ bonding type
❷ atomic arrangement

❷ classifications of solids by atomic arrangement

	ordered	*disordered*
atomic arrangement	regular	random*
order	long-range	short-range*
name	crystalline	amorphous
	"crystal"	"glass"

Early Crystallography

Robert Hooke (1660): cannon balls

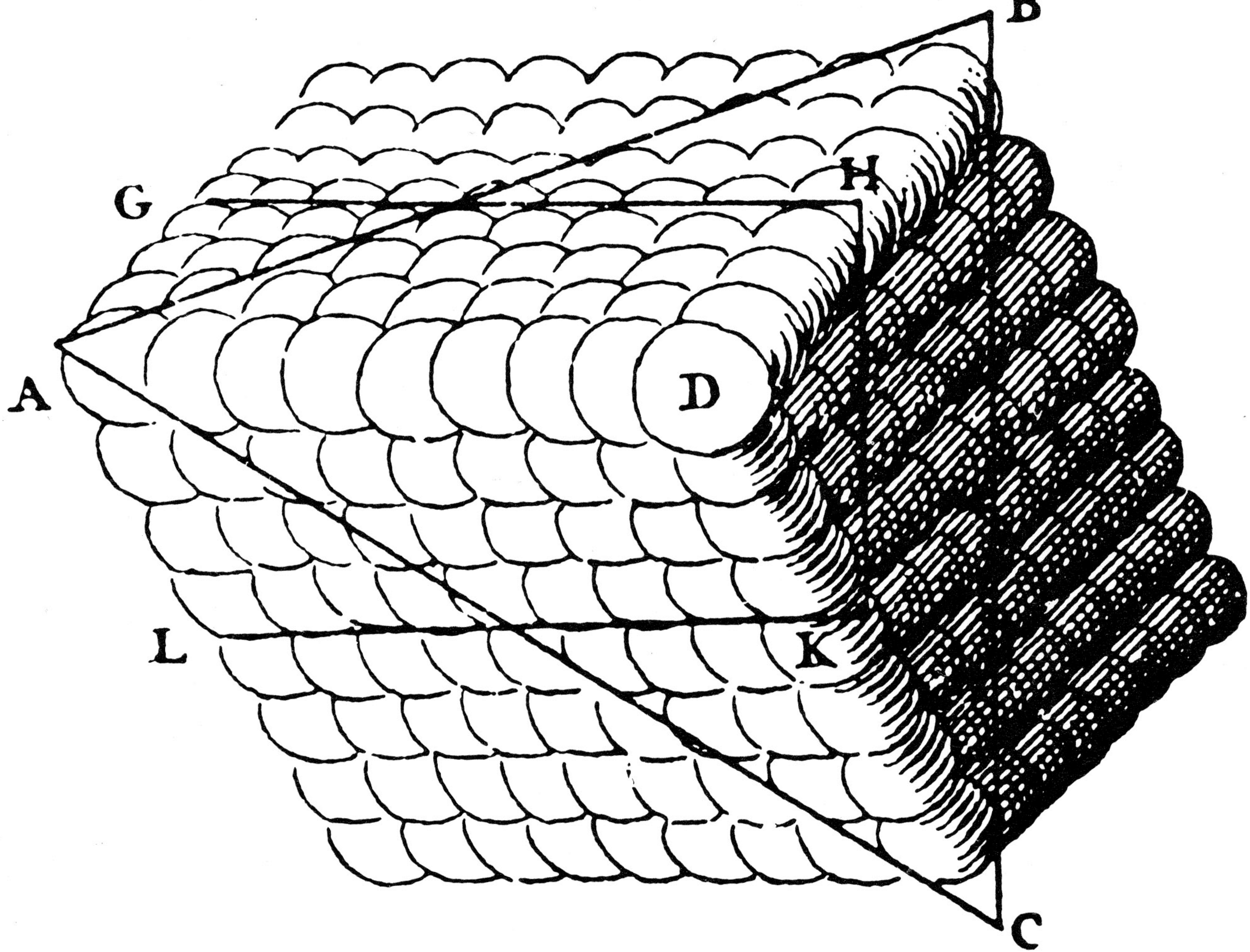
- crystal must owe its regular shape to the packing of spherical particles (balls)

Niels Steensen (1669): quartz crystals

- all crystals have the same angles between corresponding faces

Christian Huygens (1690): calcite crystals

- drawings of atomic packing & bulk shape


B
H
G
A
D
L
K
C

Sn^{white}

1.40	7.03
1.62	290.4
16.31	301.25
3.67/7.7	0.228
$11.5^{0°C}$	0.668

Tetragonal

$a = b \neq c, \ \alpha = \beta = \gamma = 90^o$

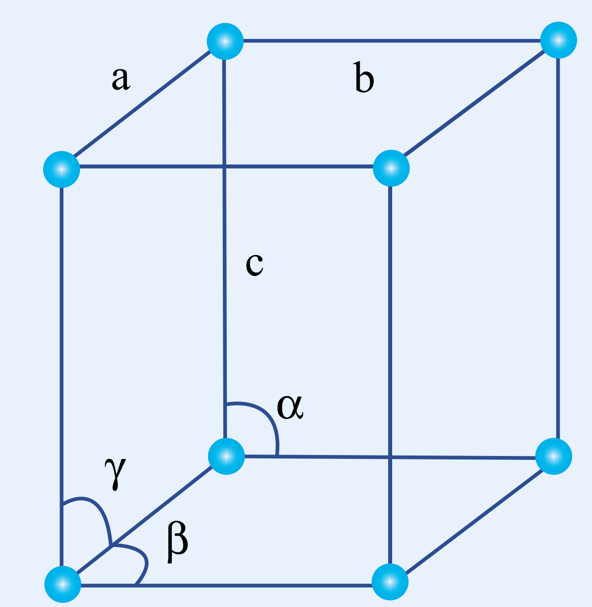


Image by MIT OpenCourseWare.

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Early Crystallography
(continued)

René-Just Haüy (1781): cleavage of calcite

- common shape to all shards: rhombohedral
- mathematically proved that there are only 7 distinct space-filling volume elements

☞☞☞ ***7 crystal systems***

~7 distinct shapes of “milk cartons”

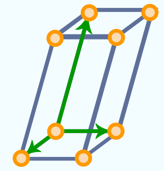
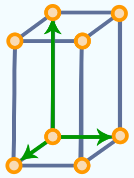
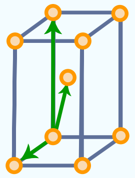
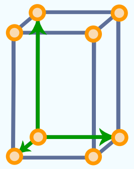
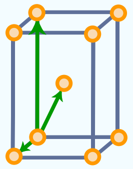
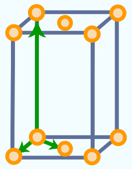
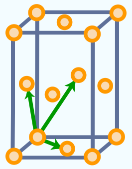
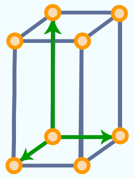
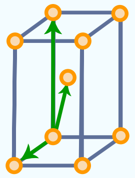
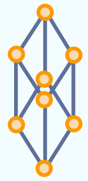
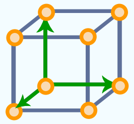
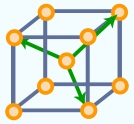
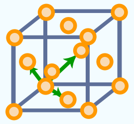
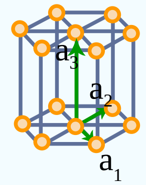
August Bravais (1848): more math

- mathematically proved that there are 14 distinct ways to arrange points in space

☞☞☞ ***14 Bravais lattices***

4 Lattice Types

7 Crystal Classes

Bravais Lattice	Parameters	Simple (P)	Volume Centered (I)	Base Centered (C)	Face Centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90^0$ $\alpha_{12} \neq 90^0$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120^0$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90^0$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120^0$ $\alpha_{23} = \alpha_{31} = 90^0$				

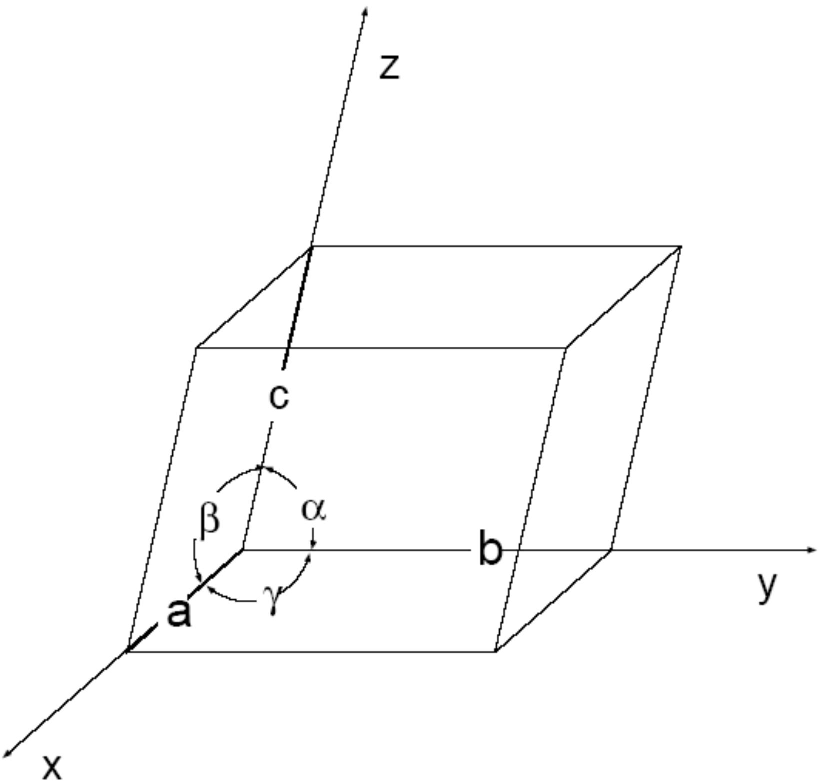
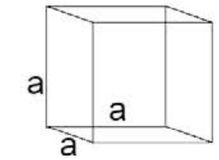


Table I. The Seven Crystal Systems

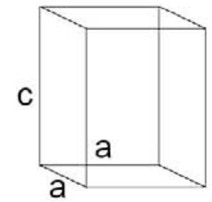
System	Parameters	Interaxial Angles
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$

7 Crystal systems

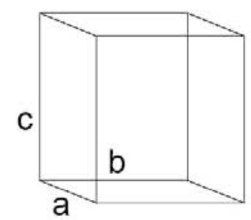
cubic
a=b=c
$\alpha=\beta=\gamma=90^{o}$



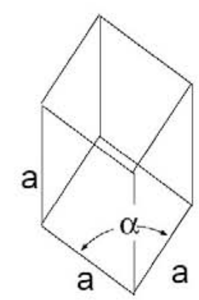
tetragonal
$a=b\neq c$
$\alpha=\beta=\gamma=90^{o}$



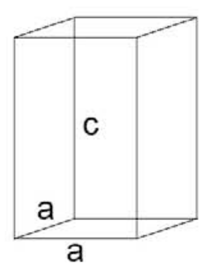
orthorhombic
$a\neq b\neq c$
$\alpha=\beta=\gamma=90^{o}$



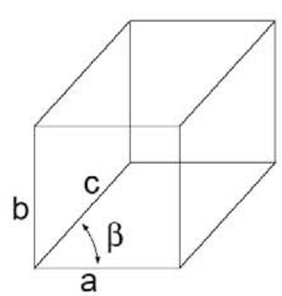
rhombohedral
a=b=c
$\alpha=\beta=\gamma\neq 90^{o}$



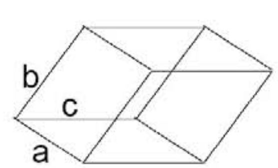
hexagonal
$a=b\neq c$
$\alpha=\beta=90^{o}$
$\gamma=120^{o}$

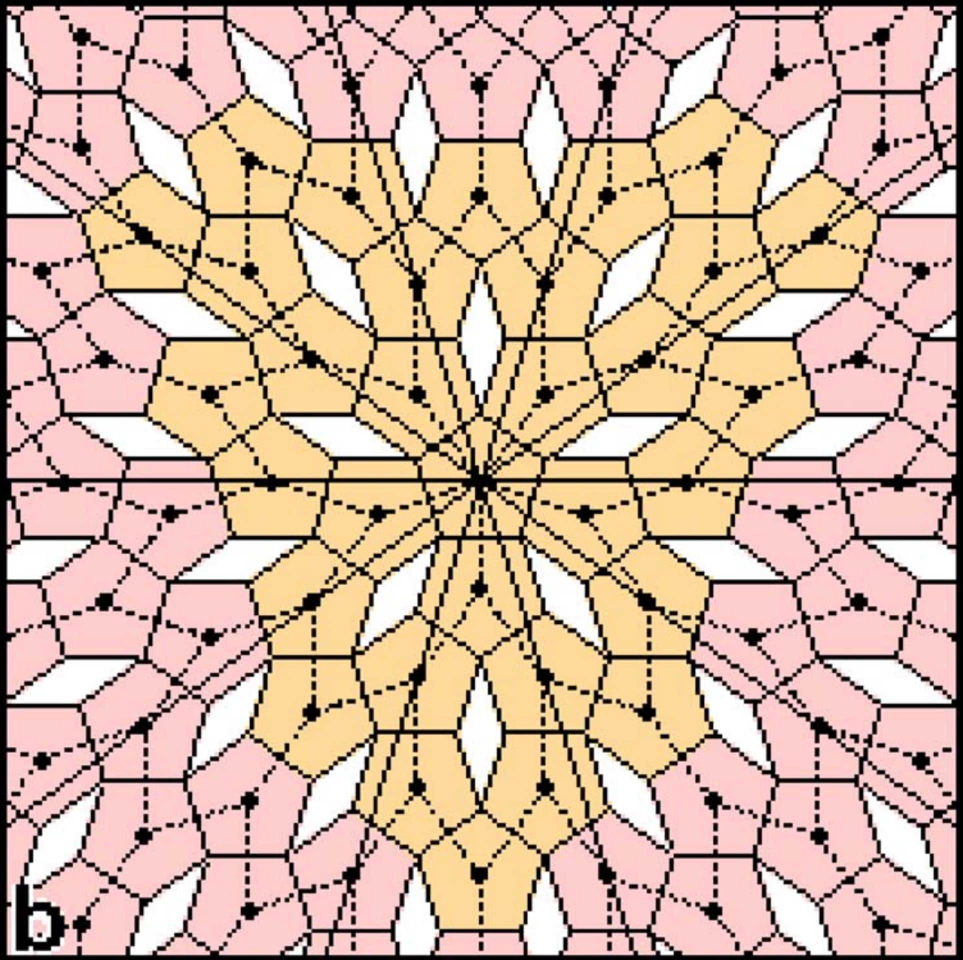


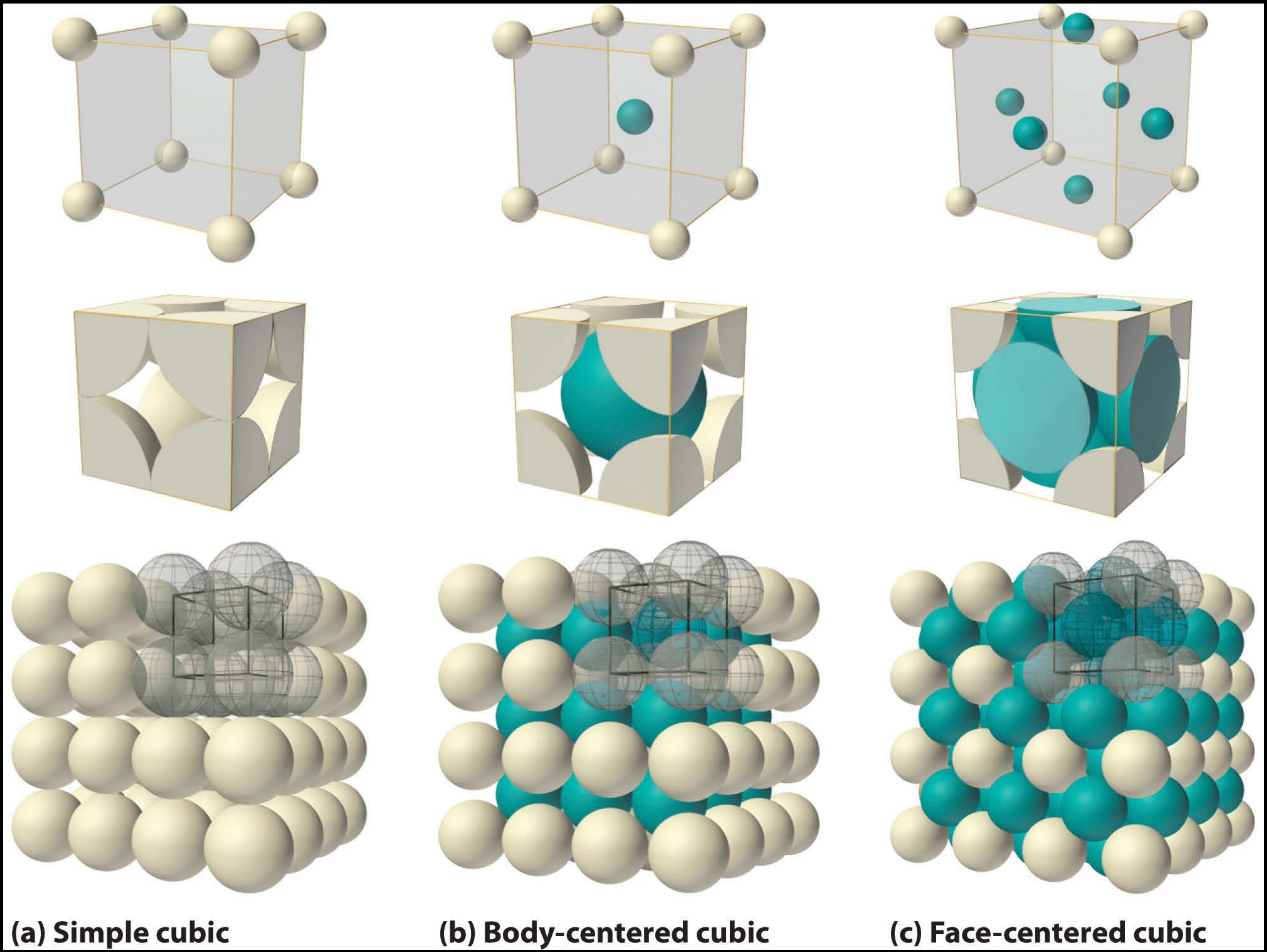
monoclinic
$a\neq b\neq c$
$\alpha=\gamma=90^{o}\neq\beta$



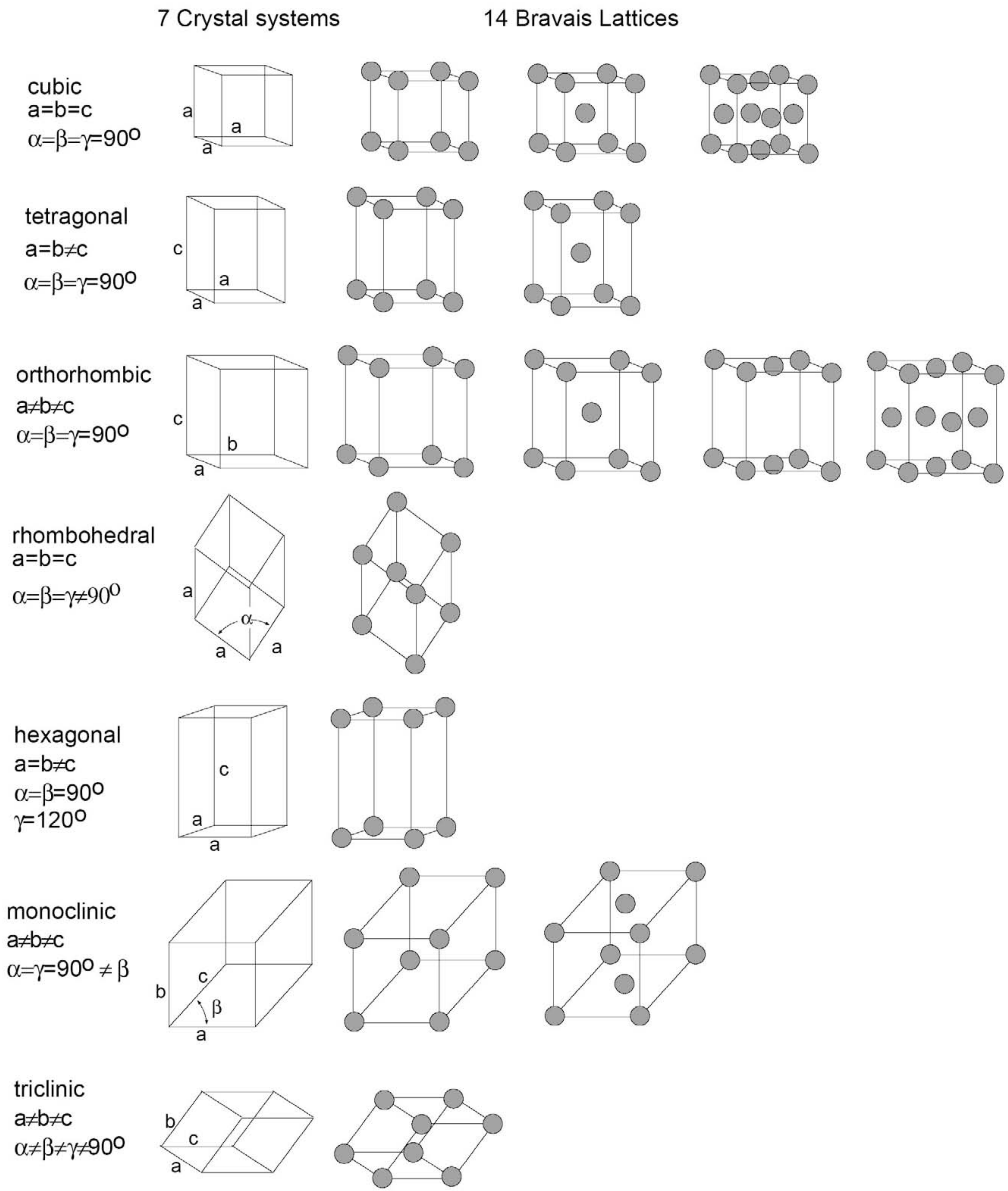
triclinic
$a\neq b\neq c$
$\alpha\neq\beta\neq\gamma\neq 90^{o}$

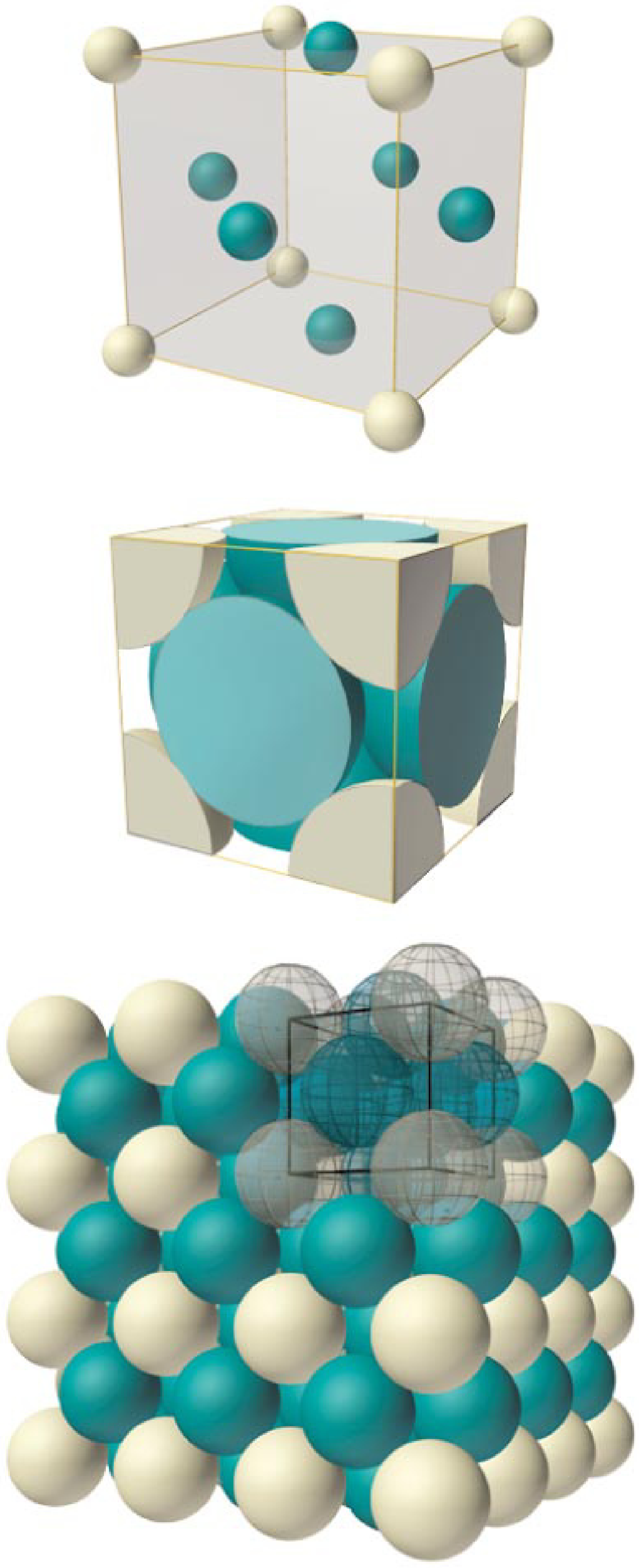



b



Averill, B., and P. Eldredge. *Chemistry: Principles, Patterns, and Applications.* Flat World Knowledge, 2011. ISBN: 9781453331224.


7 Crystal systems
14 Bravais Lattices
cubic
a=b=c
α=β=γ=90°
tetragonal
a=b≠c
α=β=γ=90°
orthorhombic
a≠b≠c
α=β=γ=90°
rhombohedral
a=b=c
α=β=γ≠90°
hexagonal
a=b≠c
α=β=90°
γ=120°
monoclinic
a≠b≠c
α=γ=90° ≠ β
triclinic
a≠b≠c
α≠β≠γ≠90°



(c) Face-centered cubic

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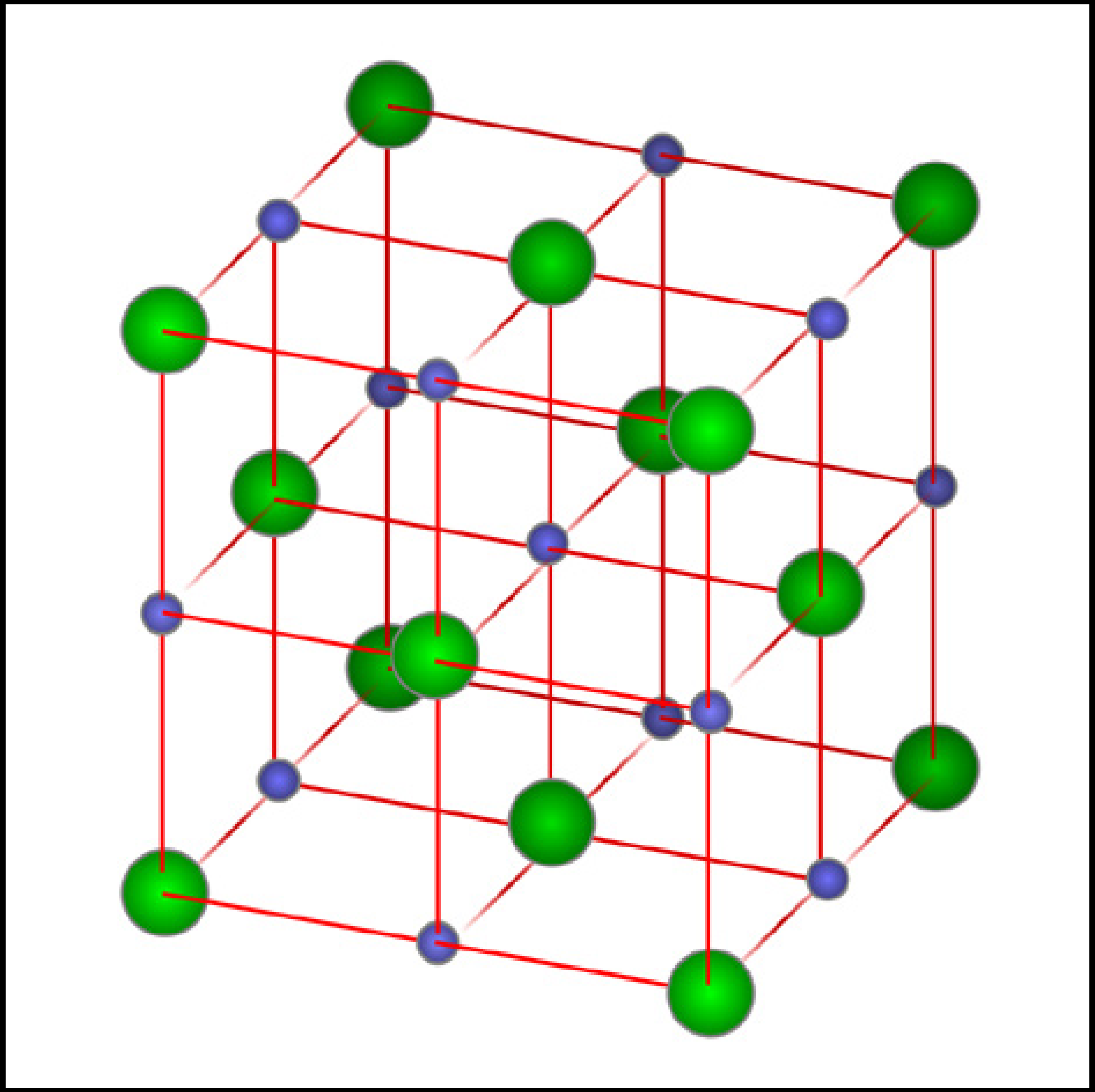
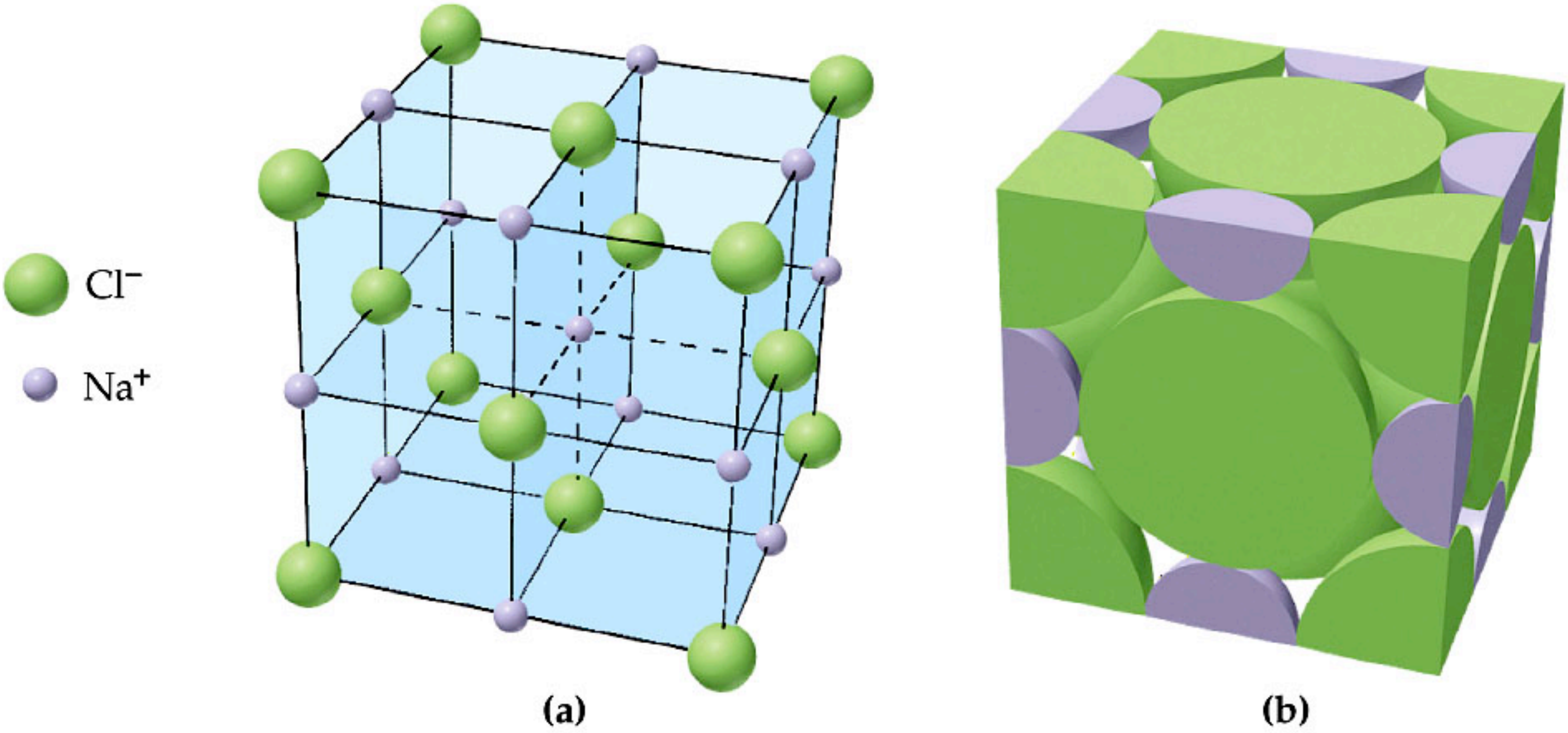
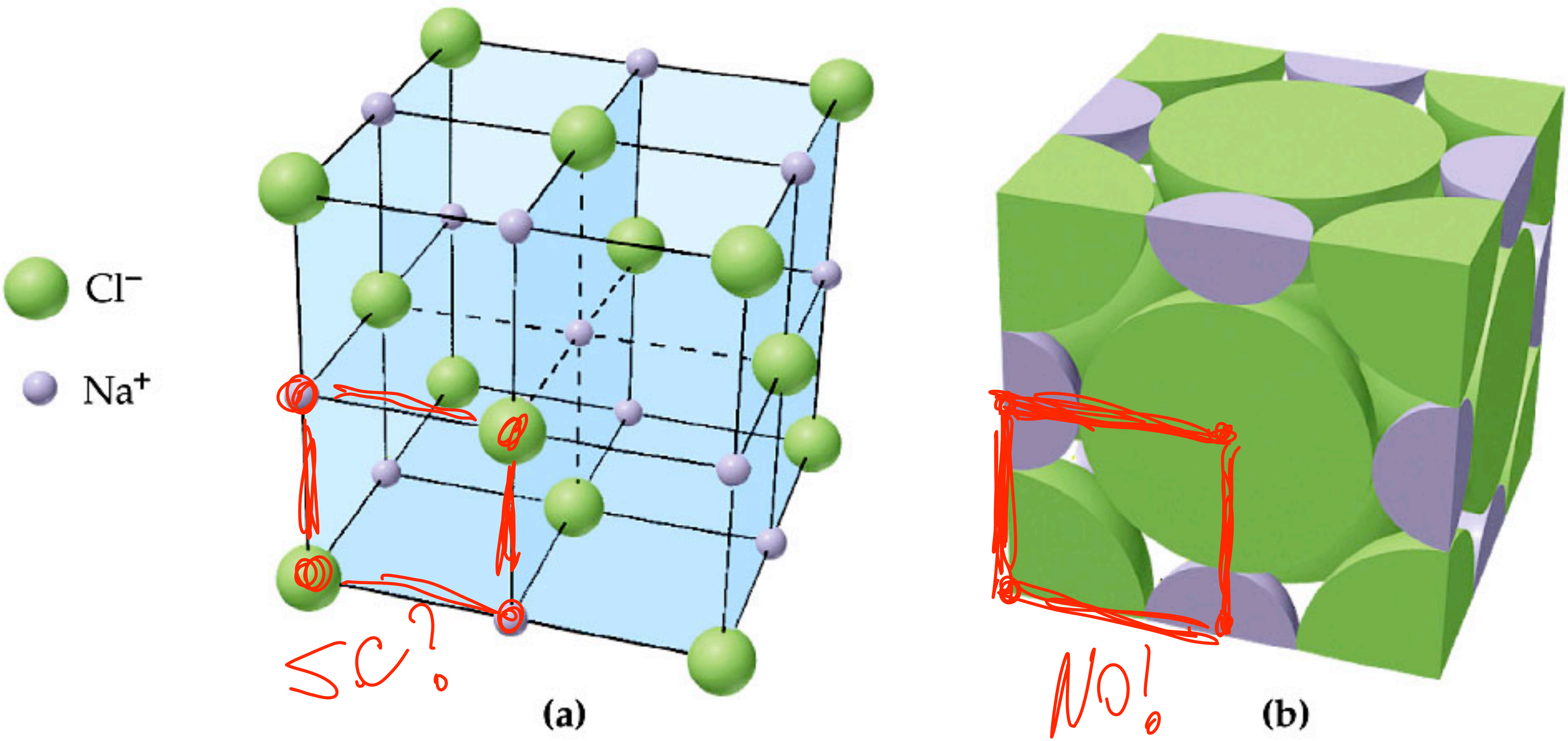


Image by Eloy at Wikipedia.



Source: Fig. 10.24 in McMurry, John, and Robert C. Fay. *Chemistry*. 4th ed. Upper Saddle River, NJ: Pearson/Prentice-Hall, 2004. ISBN: 0131402218.



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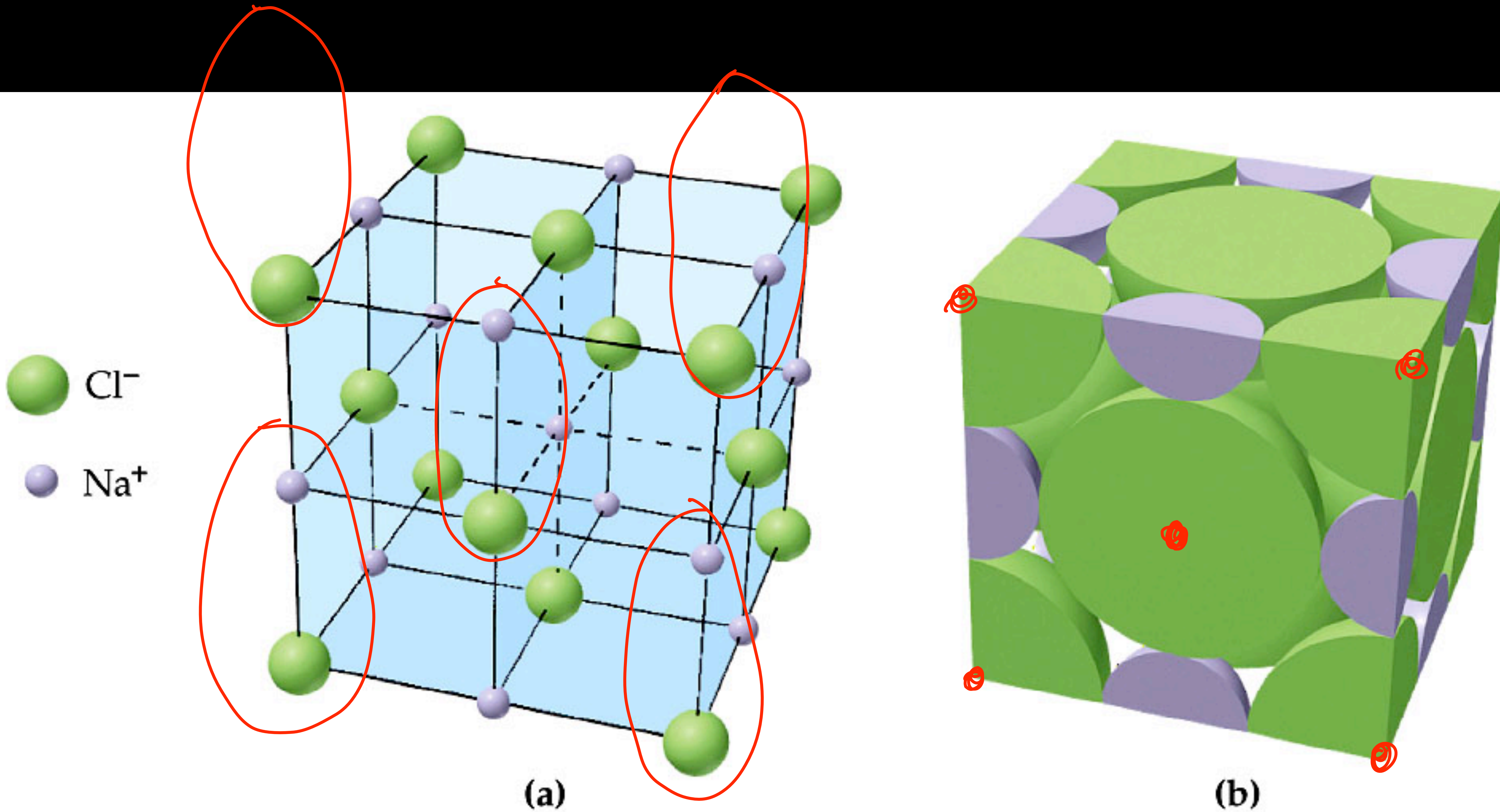

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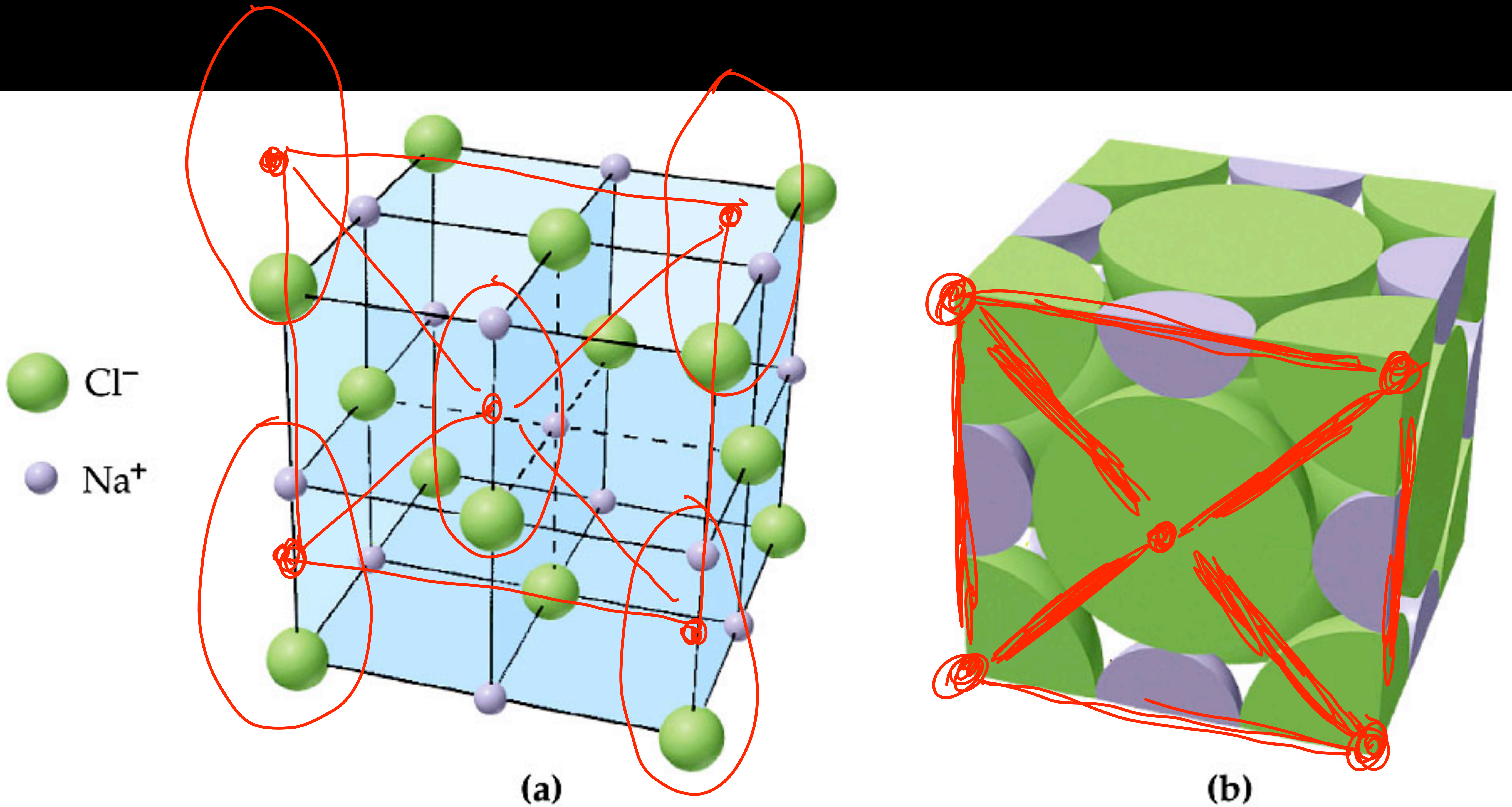

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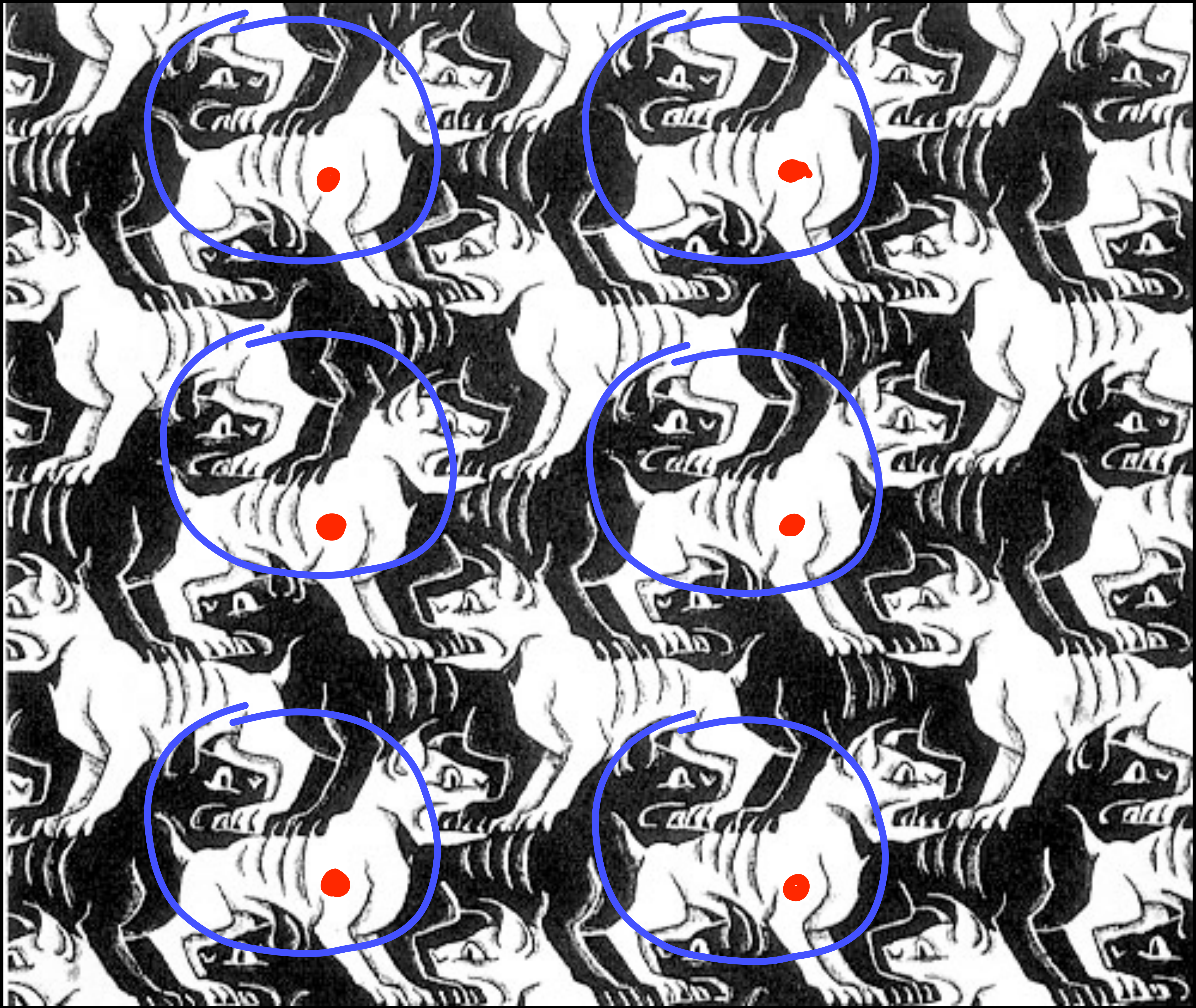

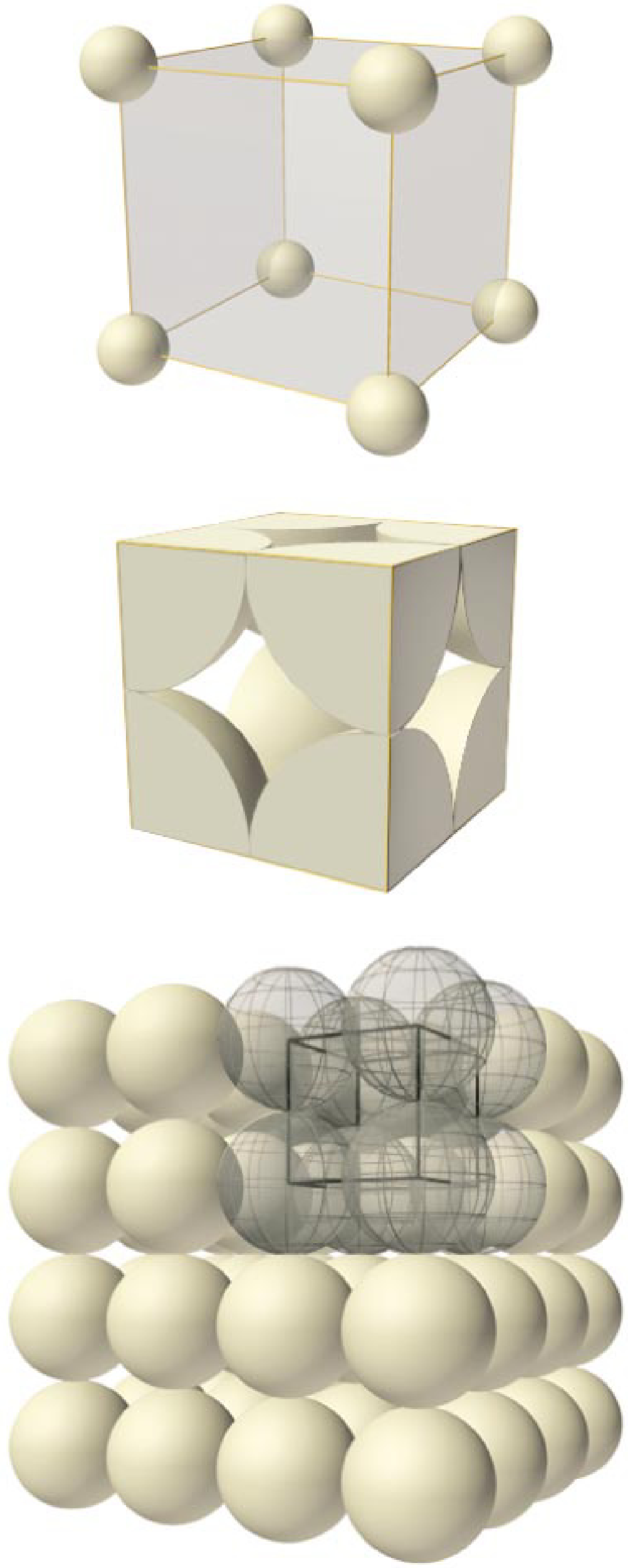

(a) Simple cubic

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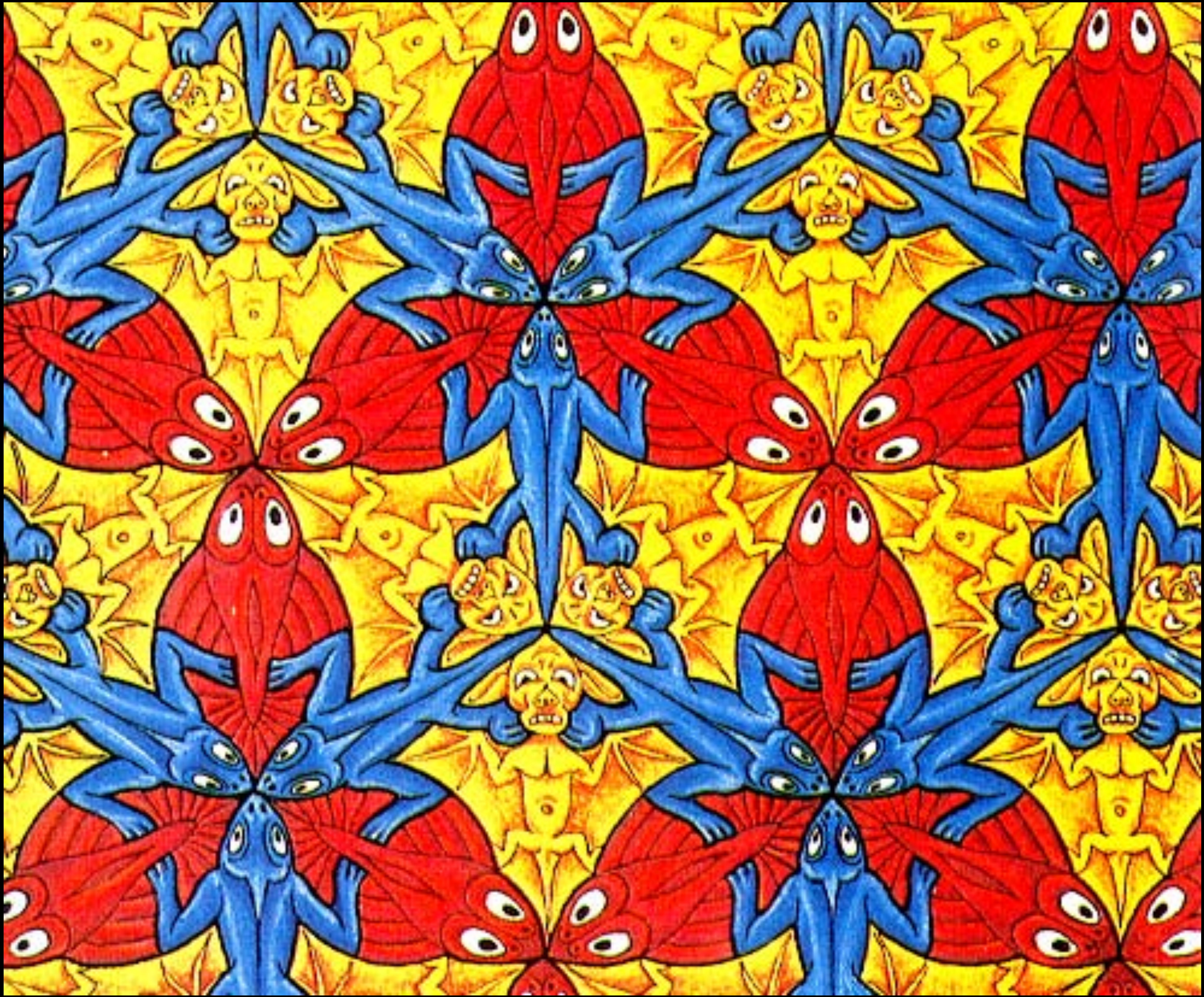
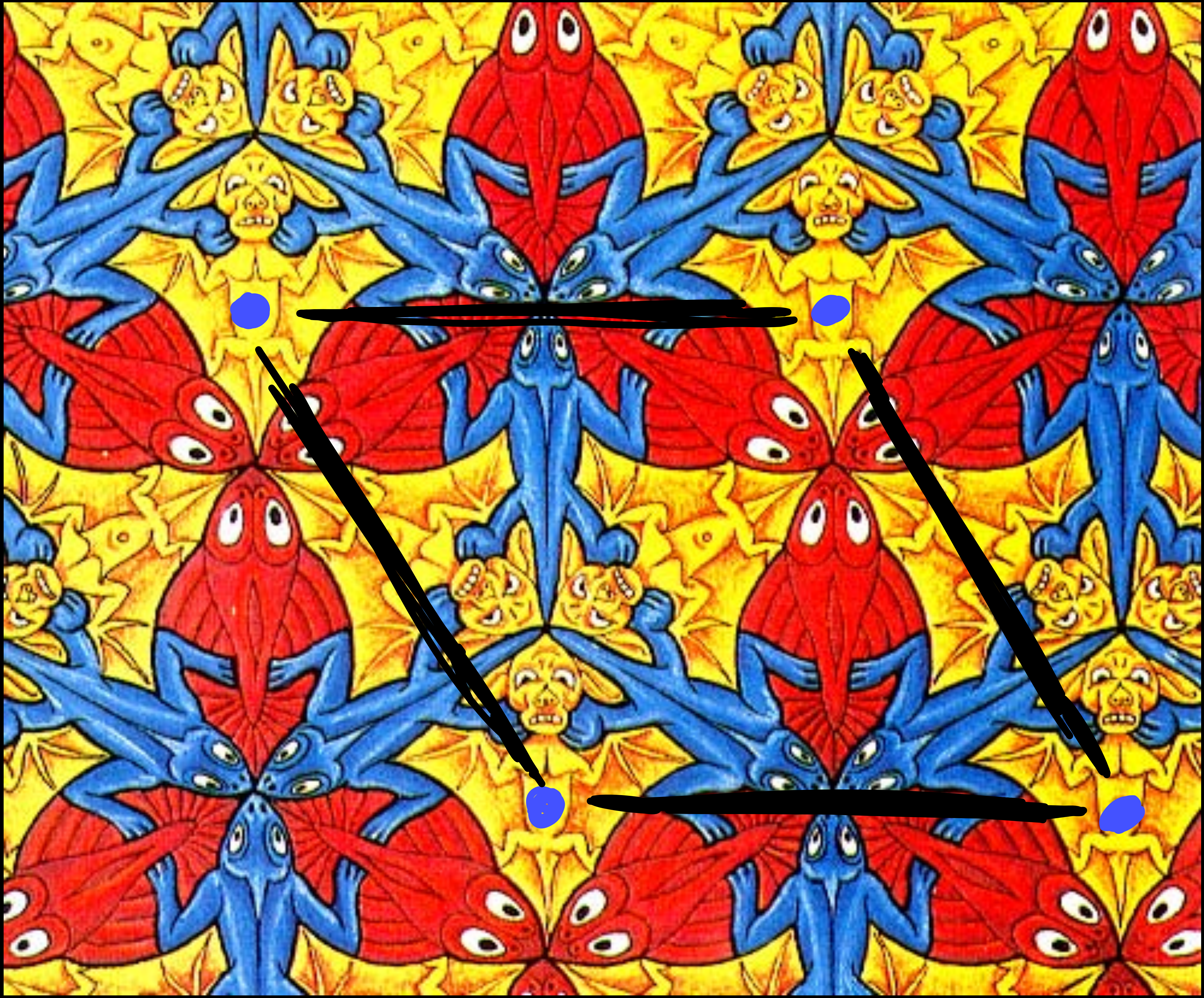




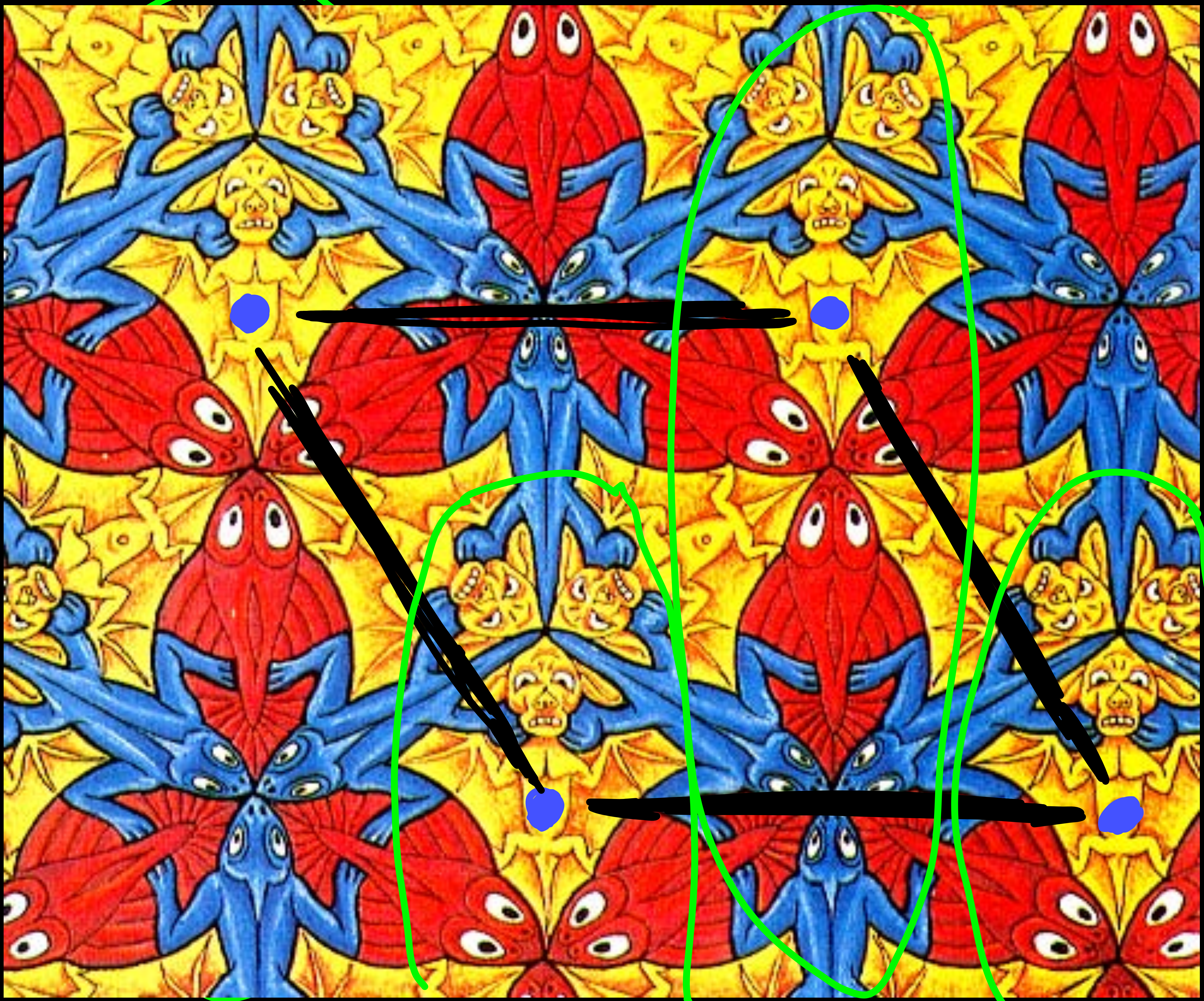
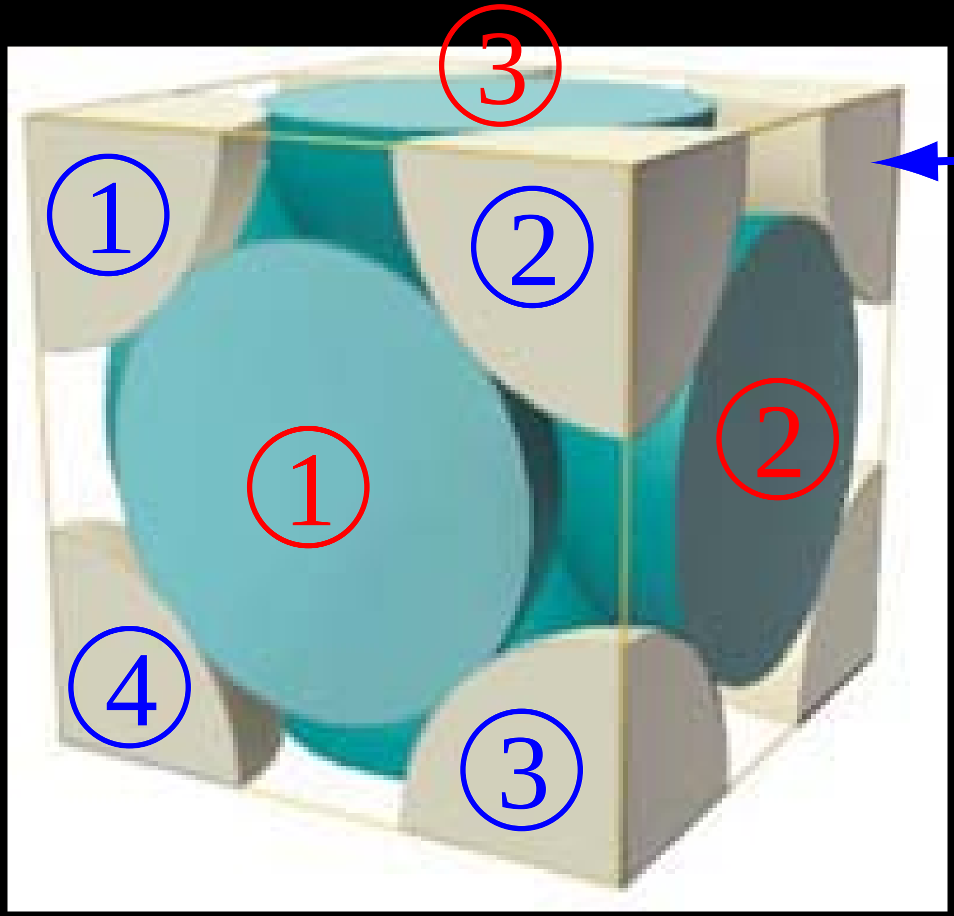


TABLE II. Characteristics of Cubic Lattices

	Simple	Body-Centered	Face-Centered
Unit Cell Volume	a^3	a^3	a^3
Lattice Points Per Cell	1	2	4
Nearest Neighbor Distance	a	$\frac{a\sqrt{3}}{2}$	$\frac{a}{\sqrt{2}}$
Number of Nearest Neighbors	6	8	12
Second Nearest Neighbor Distance	$a\sqrt{2}$	a	a
Number of Second Neighbors	12	6	6
a = f(r)	**2r**	**$4r/\sqrt{3}$**	**$2\sqrt{2}r$**
or 4r =	**$\sqrt{4}$ a**	**$\sqrt{3}$ a**	**$\sqrt{2}$ a**
packing density	**0.5**	**0.68**	**0.74**



FCC

$$8 \times \frac{1}{8} = 1$$

$$6 \times \frac{1}{2} = 3$$

= 4 lattice points/unit cell

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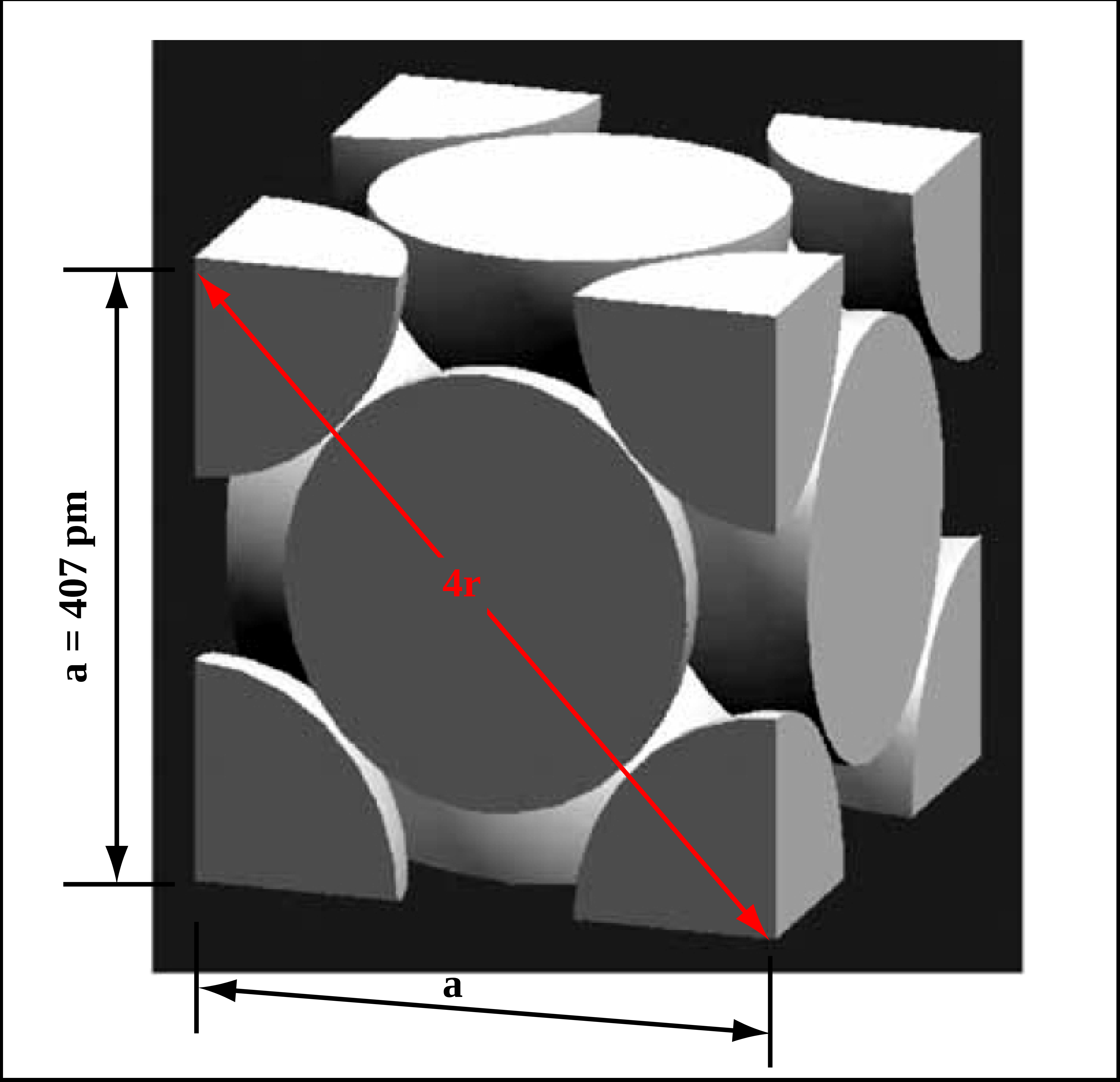
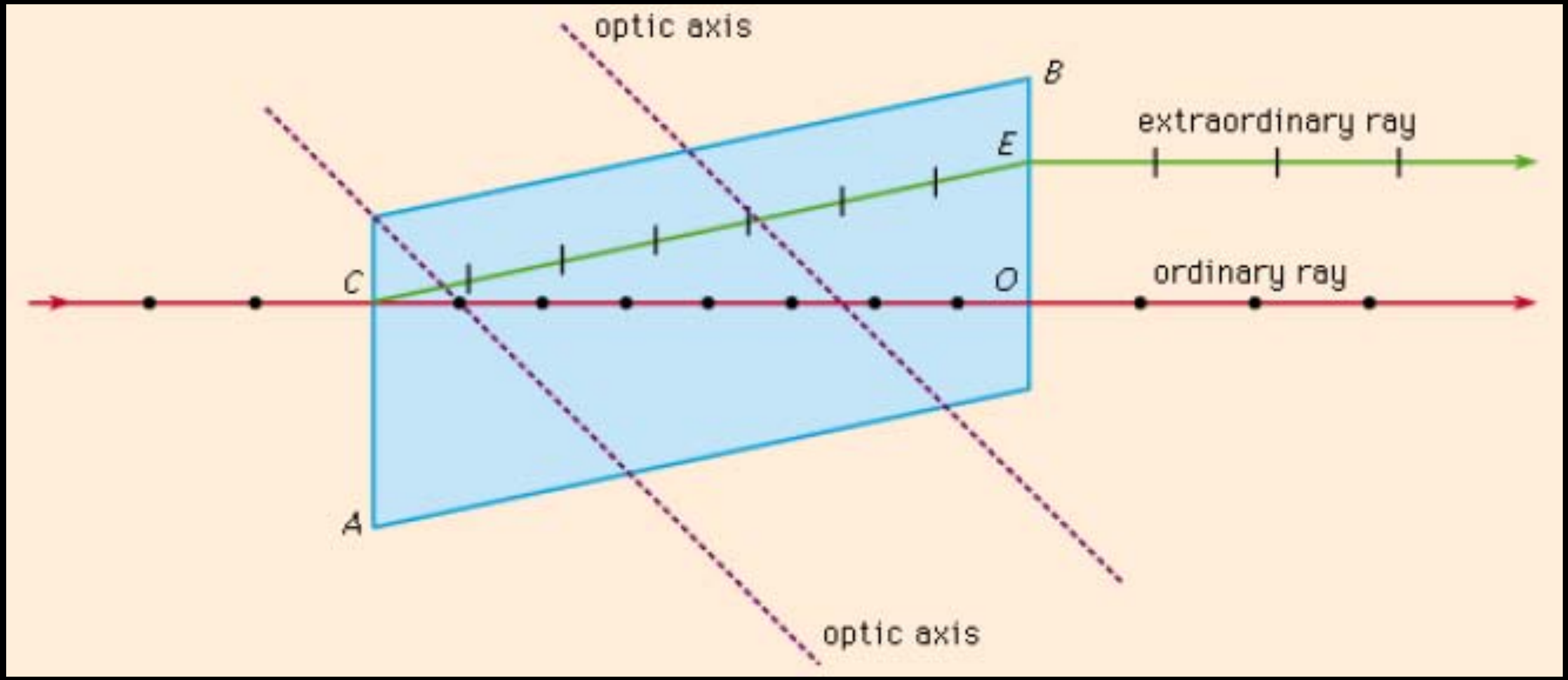

a = 407 pm
4r
a

Houses at L’Estaque

Georges Braque

1908


optic axis
B
extraordinary ray
E
C
O
ordinary ray
A
optic axis

Crystal	n_o	n_e
Tourmaline	1.669	1.638
Calcite	1.6584	1.4864
Quartz	1.5443	1. 5534
Sodium Nitrate	1.5854	1. 3369
Ice	1.309	1.313
Rutile (TiO2)	2.616	2.903

Colored Golds: FCC with zest

pure Au	yellow
$Cu_{(low)}$	yellow
$Cu_{(high)}$	pink
Ni	white
Al	purple
In	blue
Cr	green