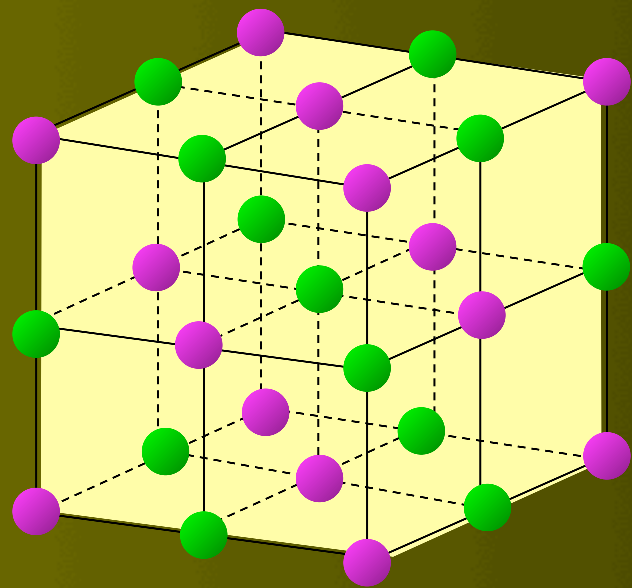
Dakar
January 23-28, 2012

Third African School
and Workshop

X-rays in Materials

Basic crystallography



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University of Trento, Italy

Overview

- X-rays, basic properties
- X-rays and materials structure
- Crystal lattices
- Some relevant crystal structures
- Crystal planes
- Reciprocal lattice

X-rays, basic properties

X-rays are electromagnetic waves

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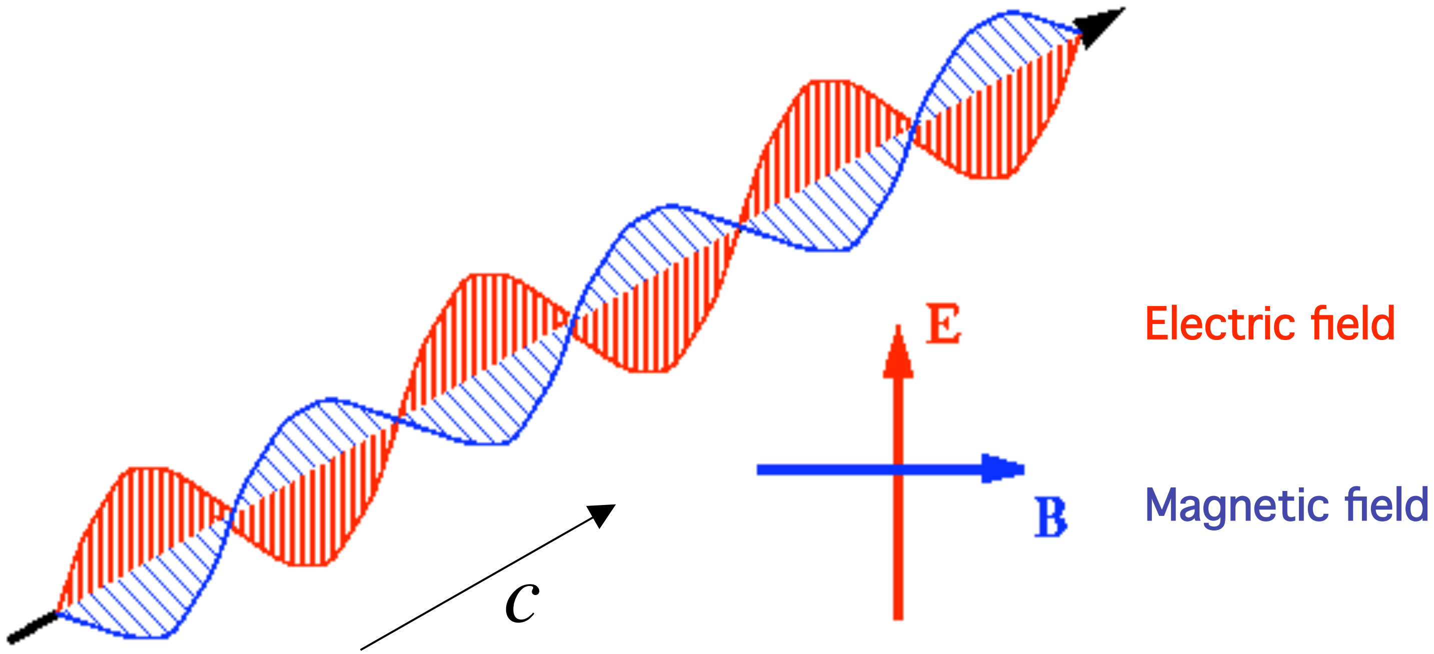

$\vec{B} \perp \vec{E}$

Speed (in vacuum):

$c \approx 3 \times 10^8$ m/s

$B = \dfrac{E}{c}$ (S.I. Units)

Periodicity of waves

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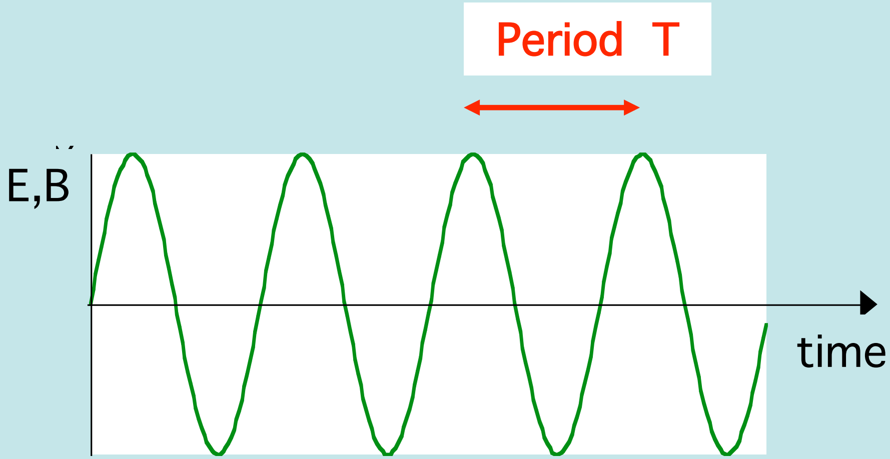
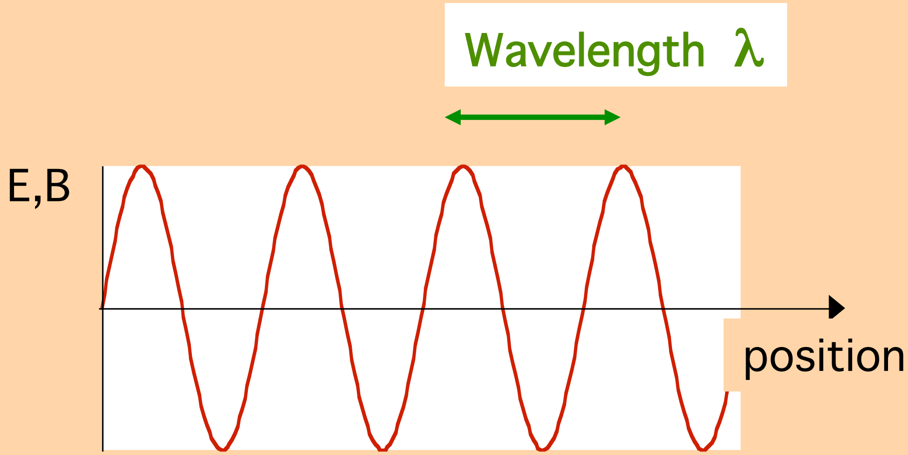
Time periodicity



Space periodicity



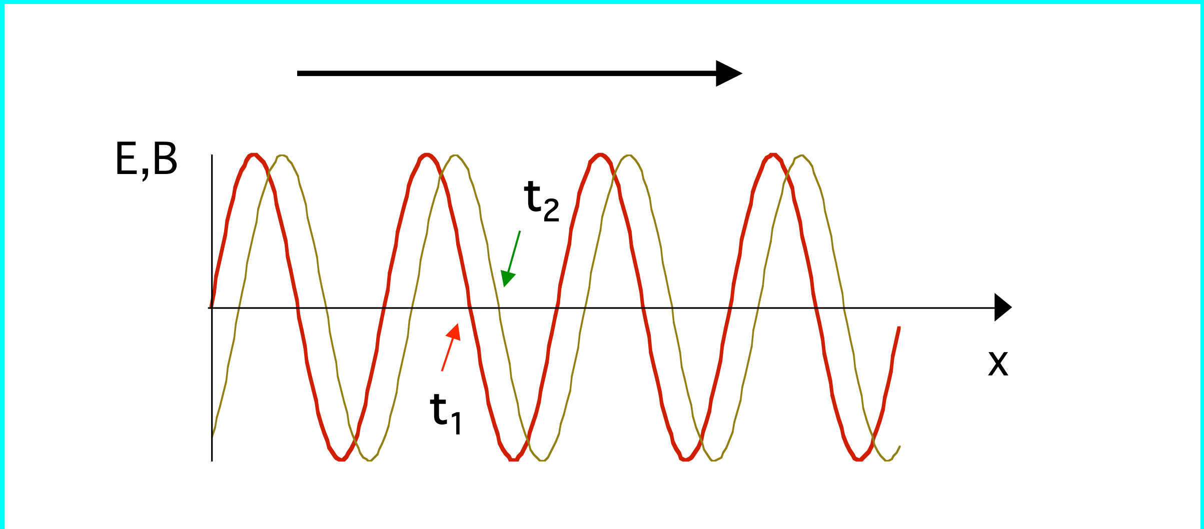
Period	T
Frequency	$\nu = 1/T$
Angular frequency	$\omega = 2\pi\nu = 2\pi/T$

$$T = \lambda/c$$
$$\nu = c/\lambda$$
$$\omega = c\,k$$

Wavelength	λ
Wavenumber	$1/\lambda$
Wavevector	$k = 2\pi/\lambda$

1 Å = 10^{-10} m
1 nm = 10^{-9} m

Propagating sinusoidal waves



Propagating wave (1- dimesion)

$$E = E_0 \cos(kx - \omega t) = E_0 \cos\left[2\pi\left(\frac{x}{\lambda} - \frac{t}{T}\right)\right]$$

Particle approach:

Photon energy

$$E = h\nu = \hbar\omega$$

3-D plane-waves: wave-vector

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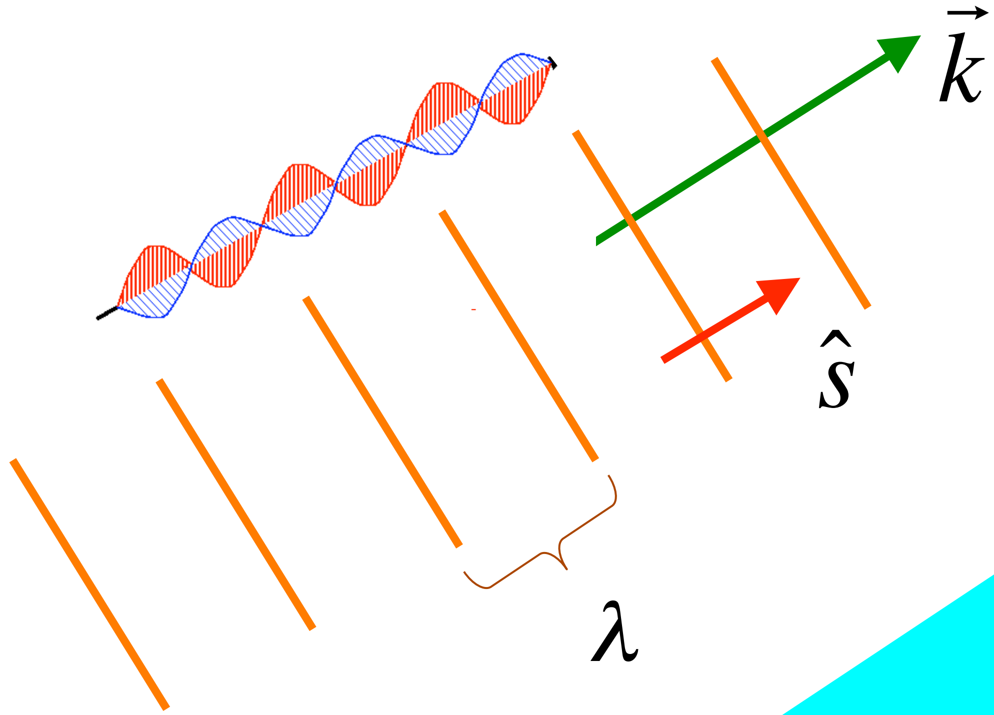
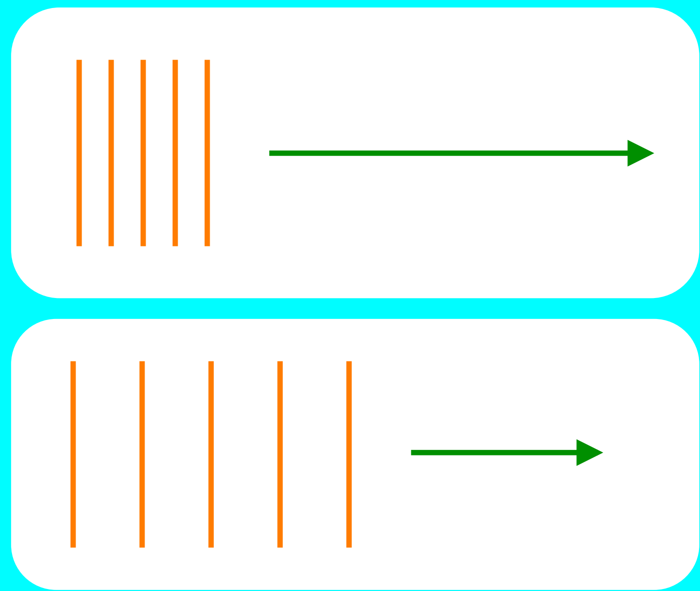


Plane wave

$$\vec{k} = \frac{2\pi}{\lambda}\,\hat{s}$$



Plane wave: complex notation

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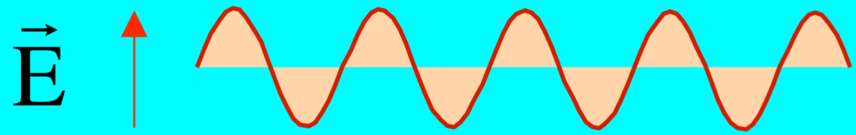

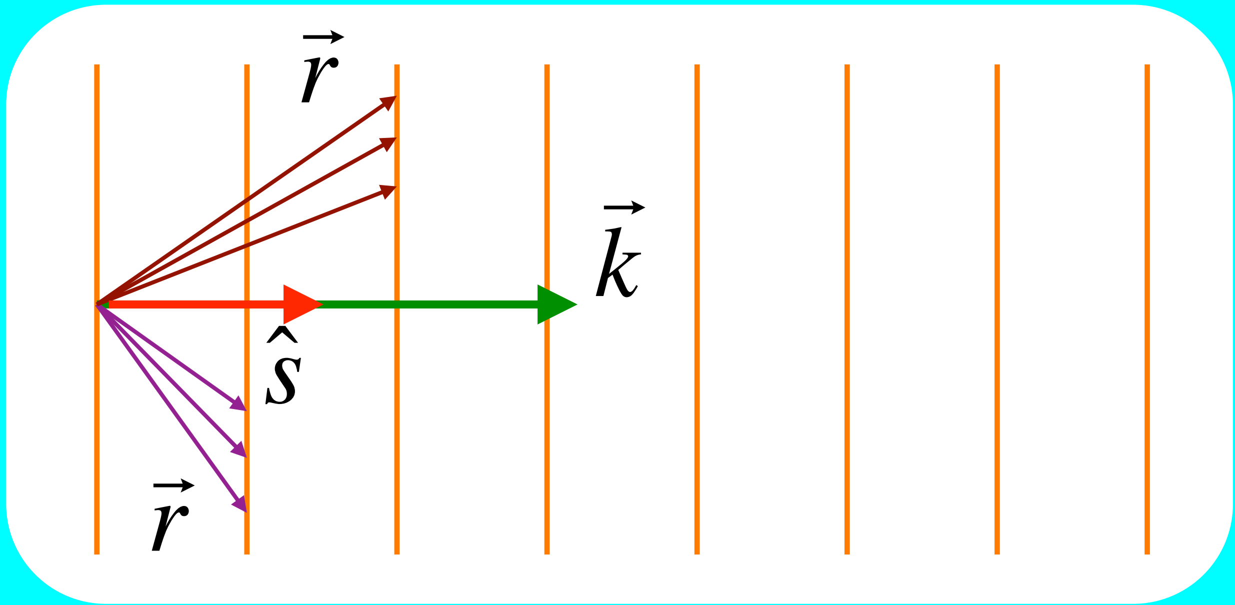

$$\vec{k} = \frac{2\pi}{\lambda}\,\hat{s}$$

Fixed time

$$\vec{\mathrm{E}}(\vec{r}) = \vec{\mathrm{E}}_0 \cos\left(\vec{k}\cdot\vec{r}\right) \quad = \vec{\mathrm{E}}_0 \quad \text{for} \quad \vec{k}\cdot\vec{r} = 2n\pi$$

$$\mathrm{Re}\left\{e^{i\vec{k}\cdot\vec{r}}\right\} = \mathrm{Re}\left\{e^{i(2\pi/\lambda)\hat{s}\cdot\vec{r}}\right\}$$

Complex notation

Electromagnetic spectrum

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Photon energy

Wavelength

$$E = h\nu = hc/\lambda$$

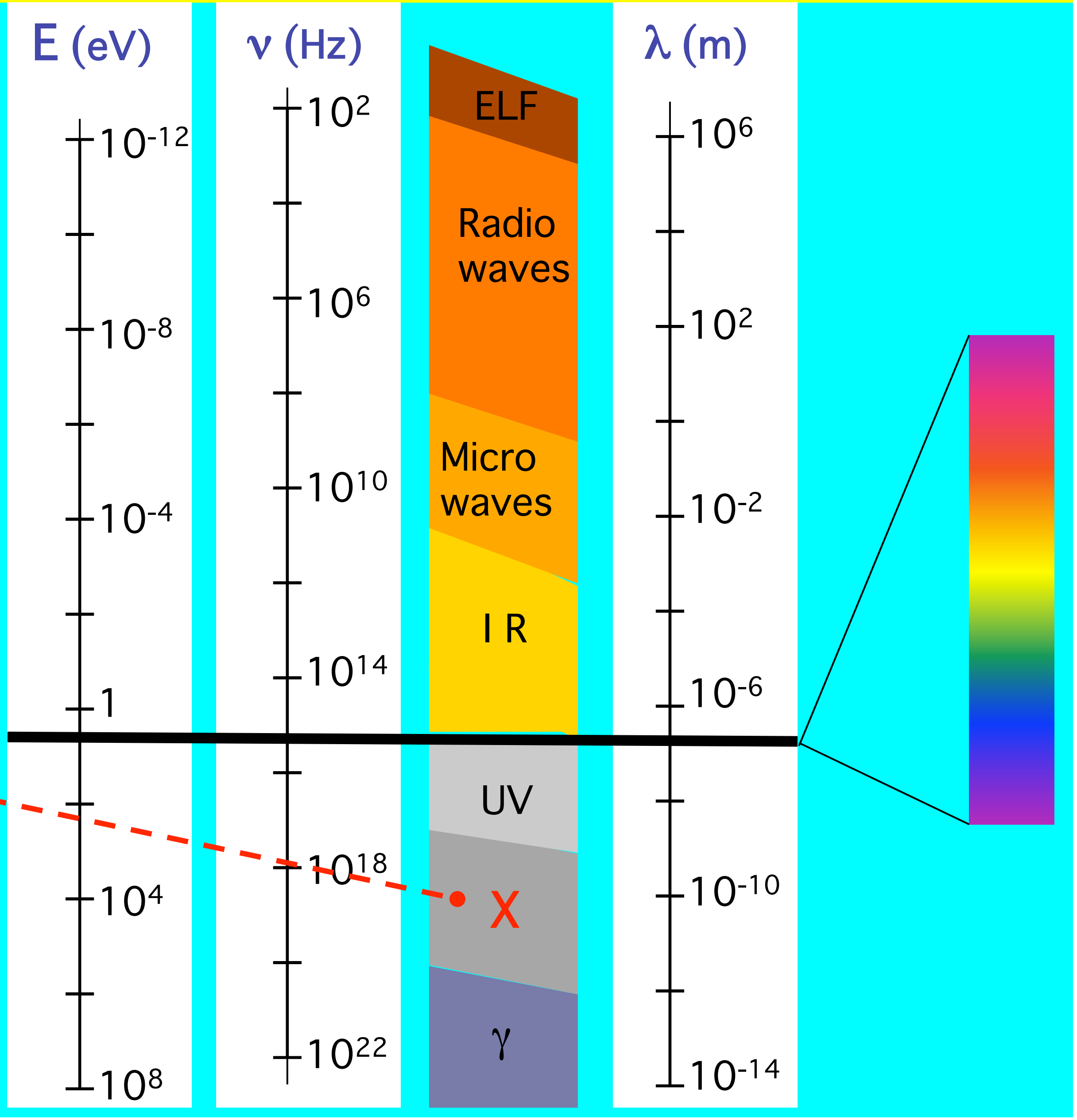
Frequency

X-rays

$$\lambda \approx 0.01 \div 10 \text{ Å}$$

$$\nu \approx 10^{17} \div 10^{20} \text{ Hz}$$

$$E \approx 0.4 \div 400 \text{ keV}$$



Interaction of x-rays with matter

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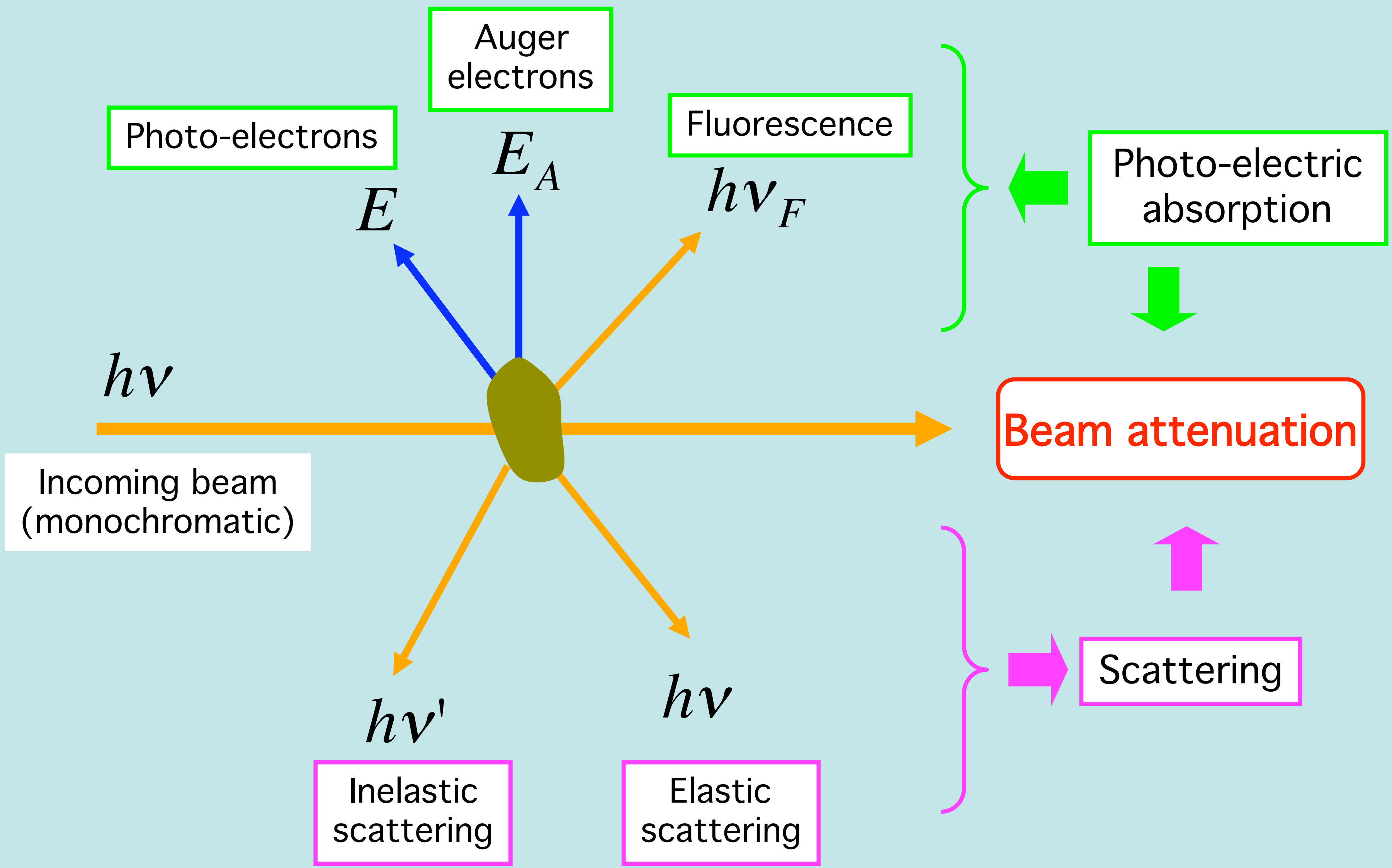

X-RAYS and X-ray techniques

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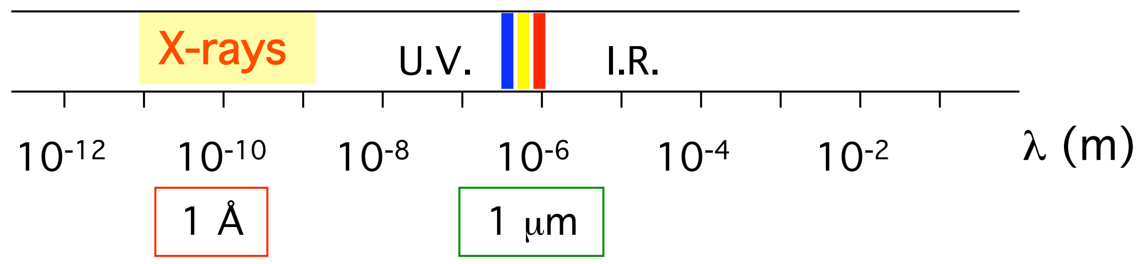
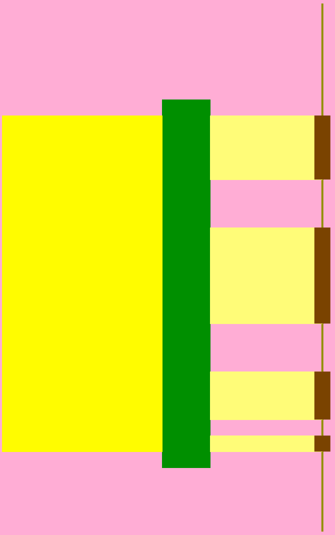


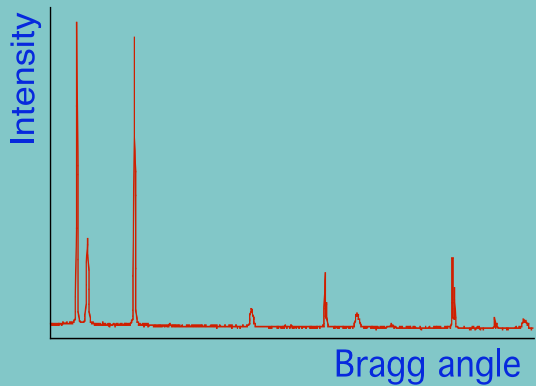
$$E[\mathrm{keV}] = \frac{12.4}{\lambda[\mathrm{Å}]}$$

Imaging

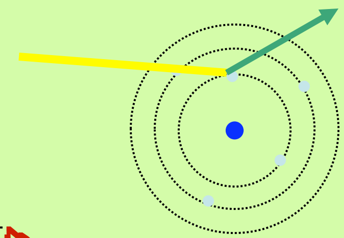


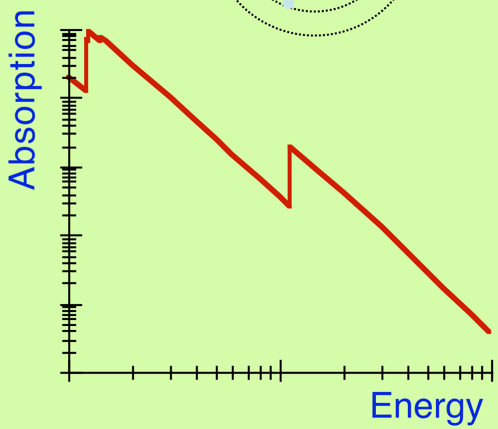
Scattering

$$\lambda = 2d\sin\theta$$



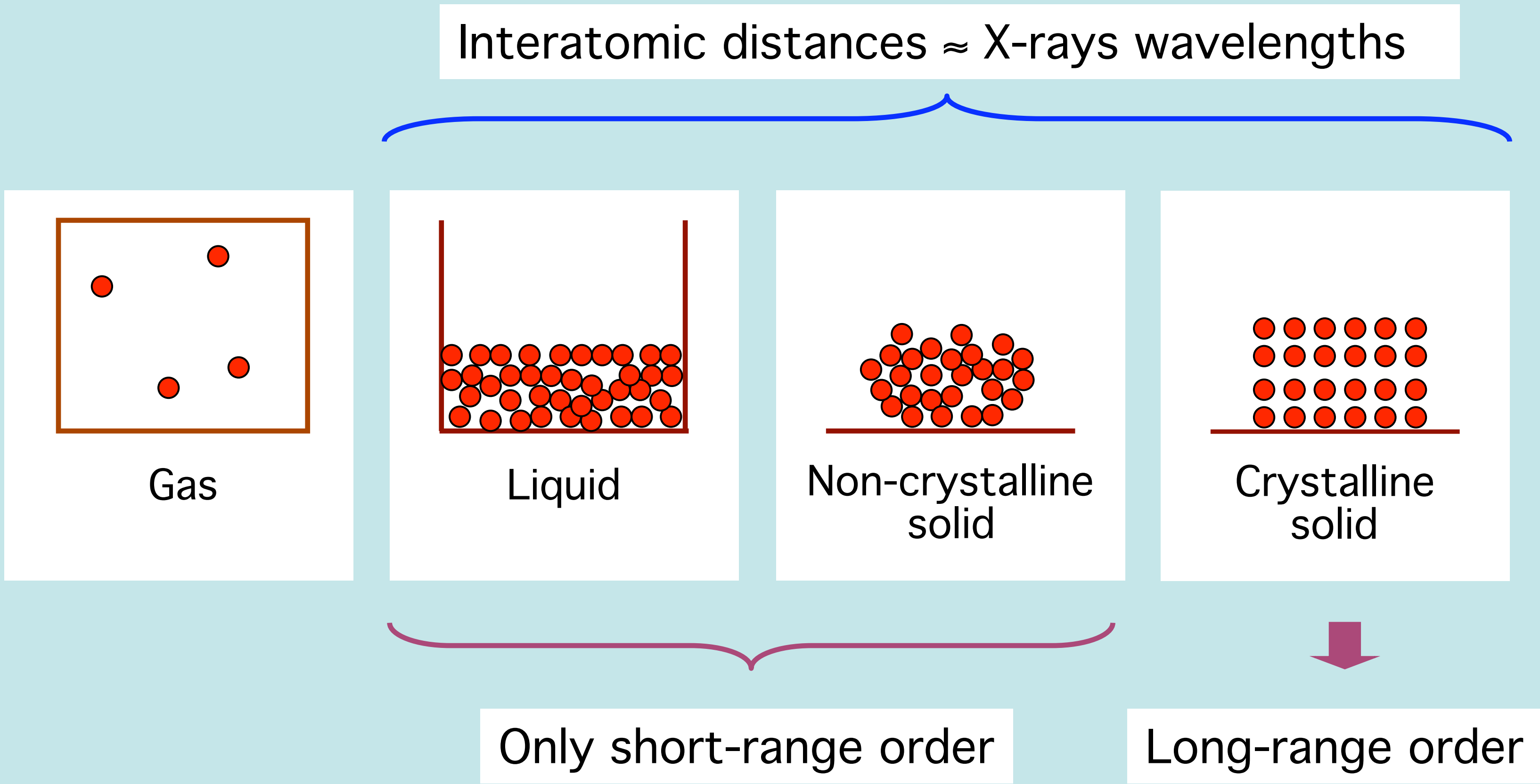
Spectroscopy





X-rays and materials structure

Aggregates of atoms



Crystals

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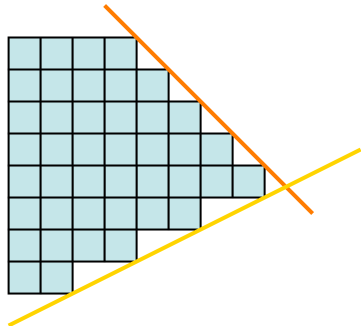
Quartz crystal (SiO_2)

Macroscopic regularities
(e.g. constancy of angles)

⇒ Classification of crystals

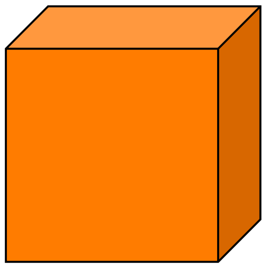
⇒



Regular packing
of microscopic structural units
R.J. Haüy (1743-1822)

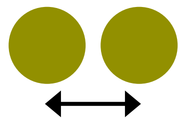
HYPOTHESIS: Structural units = atoms

Example: NaCl



Atomic masses: Na 38.12×10^{-24} g
Cl 58.85×10^{-24} g

Cubic structure
1 cm^3 m = 2.165 g
N = 44.6×10^{21} atoms



0.28 nm = 2.8 Å

CONCLUSION: Inter-atomic distances / Atomic dimensions ≈ X-ray wavelengths

X-ray diffraction from crystals

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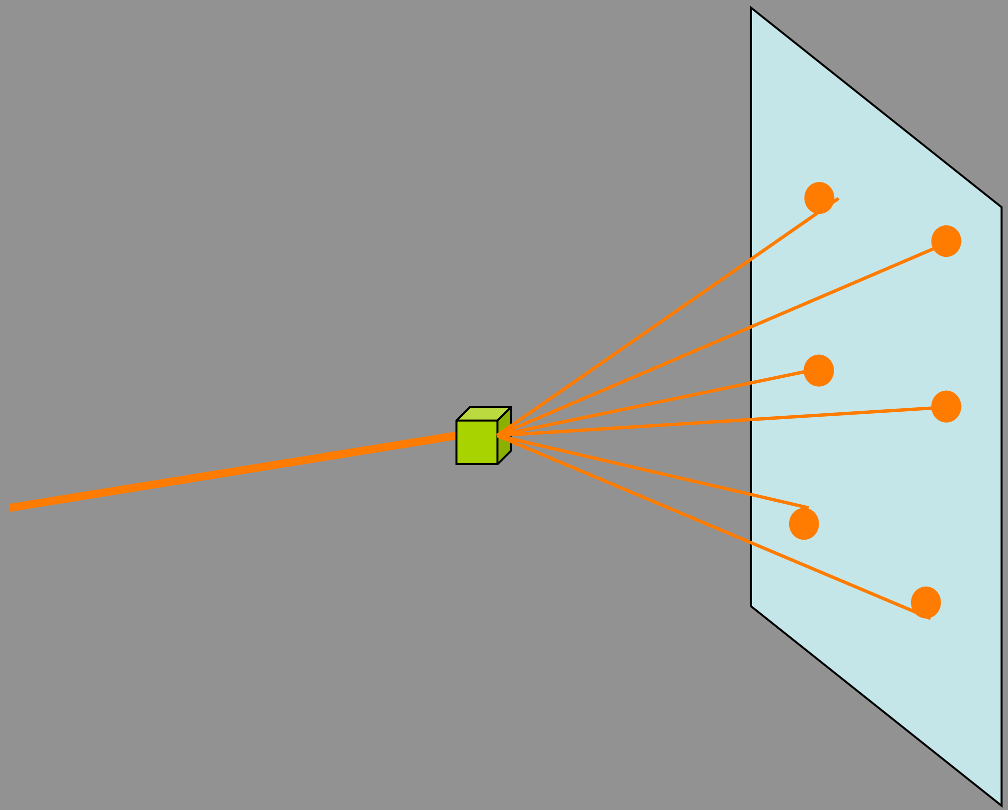

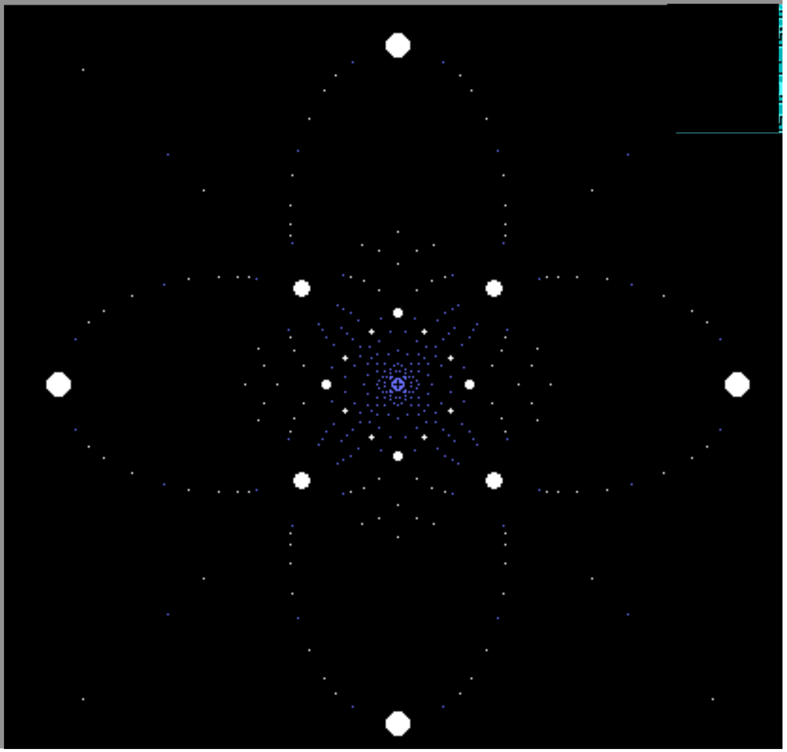

Munich, 1912:
- Max von Laue
- W. Friedrich & P.Knipping

Crystallography

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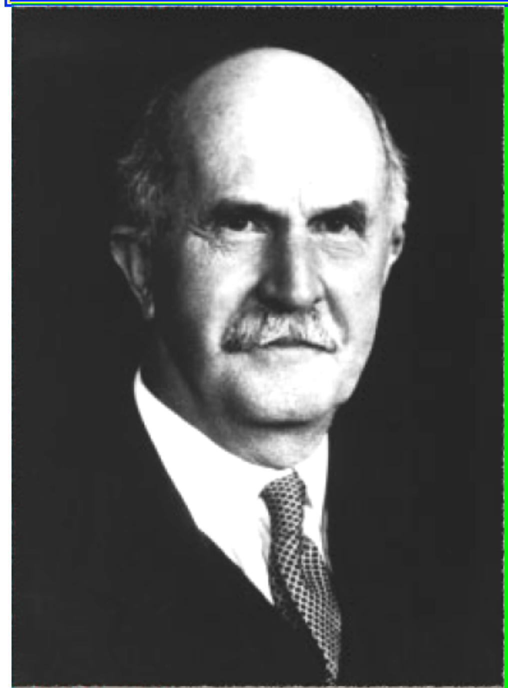
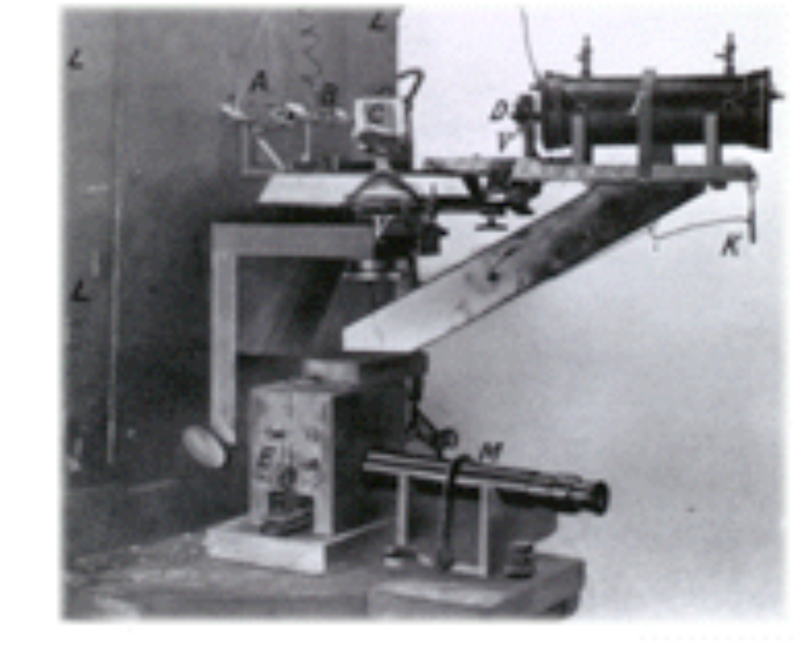


William Henry Bragg
(1862-1942)

Cambridge, 1912/13



Bragg spectrometer

William Lawrence Bragg
(1890-1971)

Crystal structure

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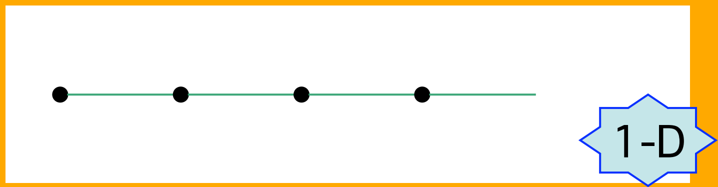
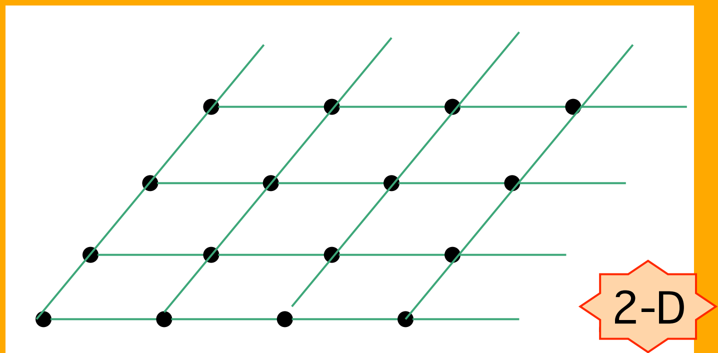
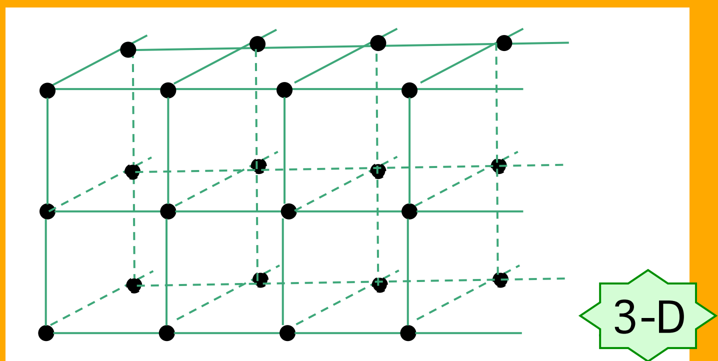
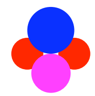
Bravais lattice + Basis

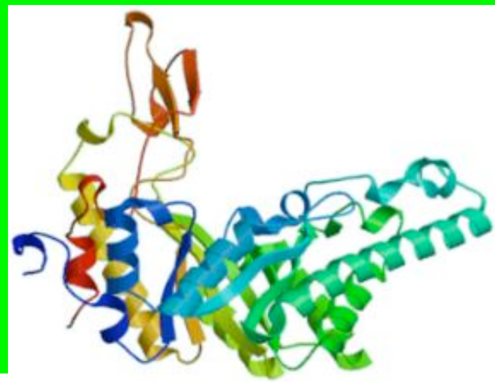







Atom


Molecule


Protein

Bravais lattice + basis

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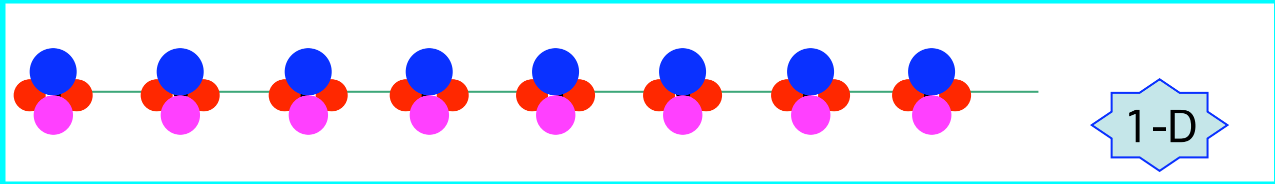

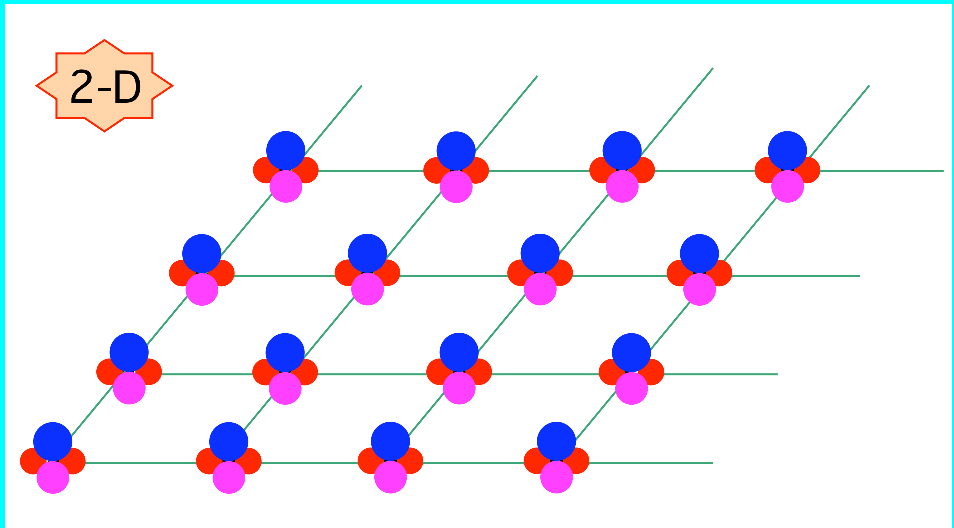

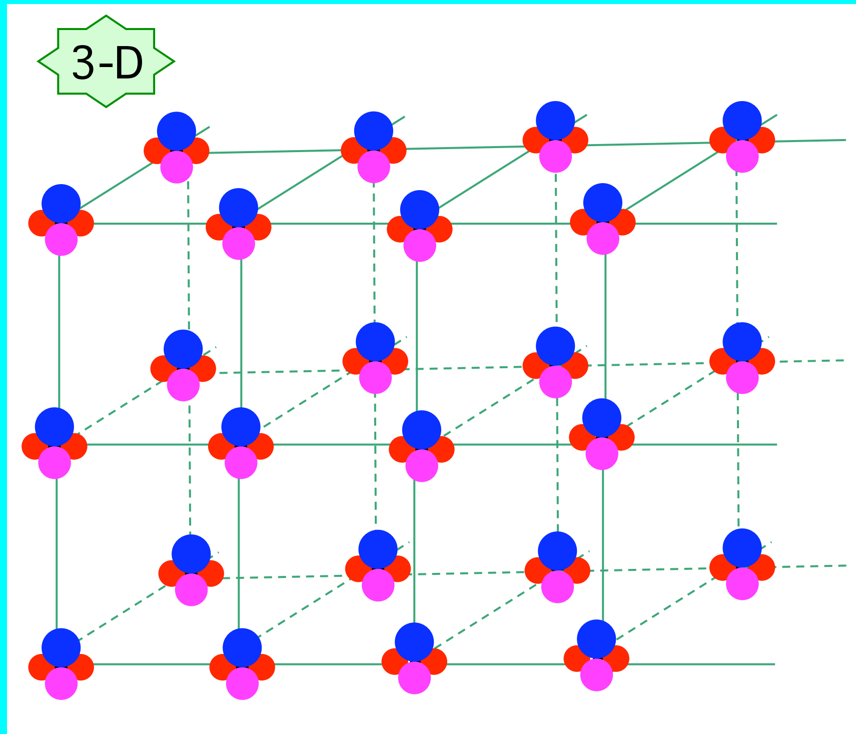

Macro and micro-crystals

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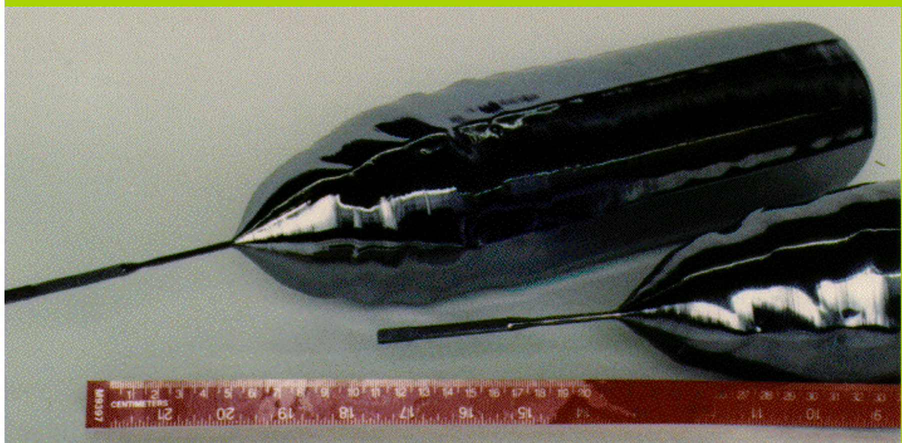
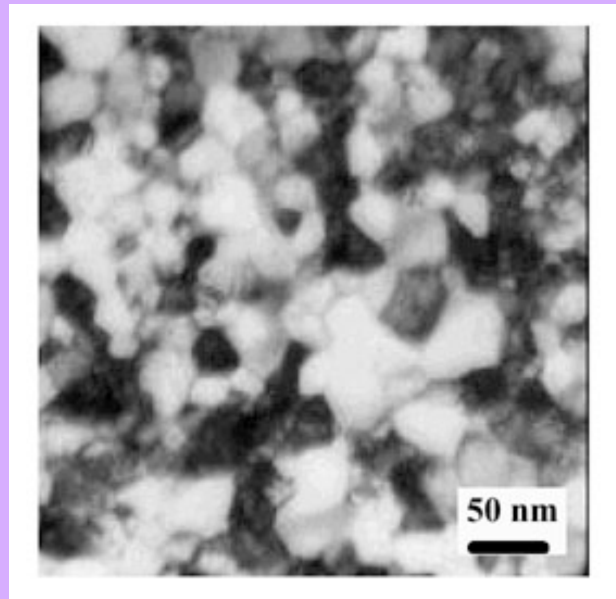
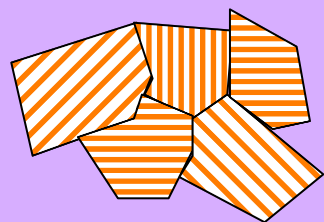
Monocrystalline silicon, ∅ 13 cm





Cr, electron microscopy



Grain structure

Effects of temperature

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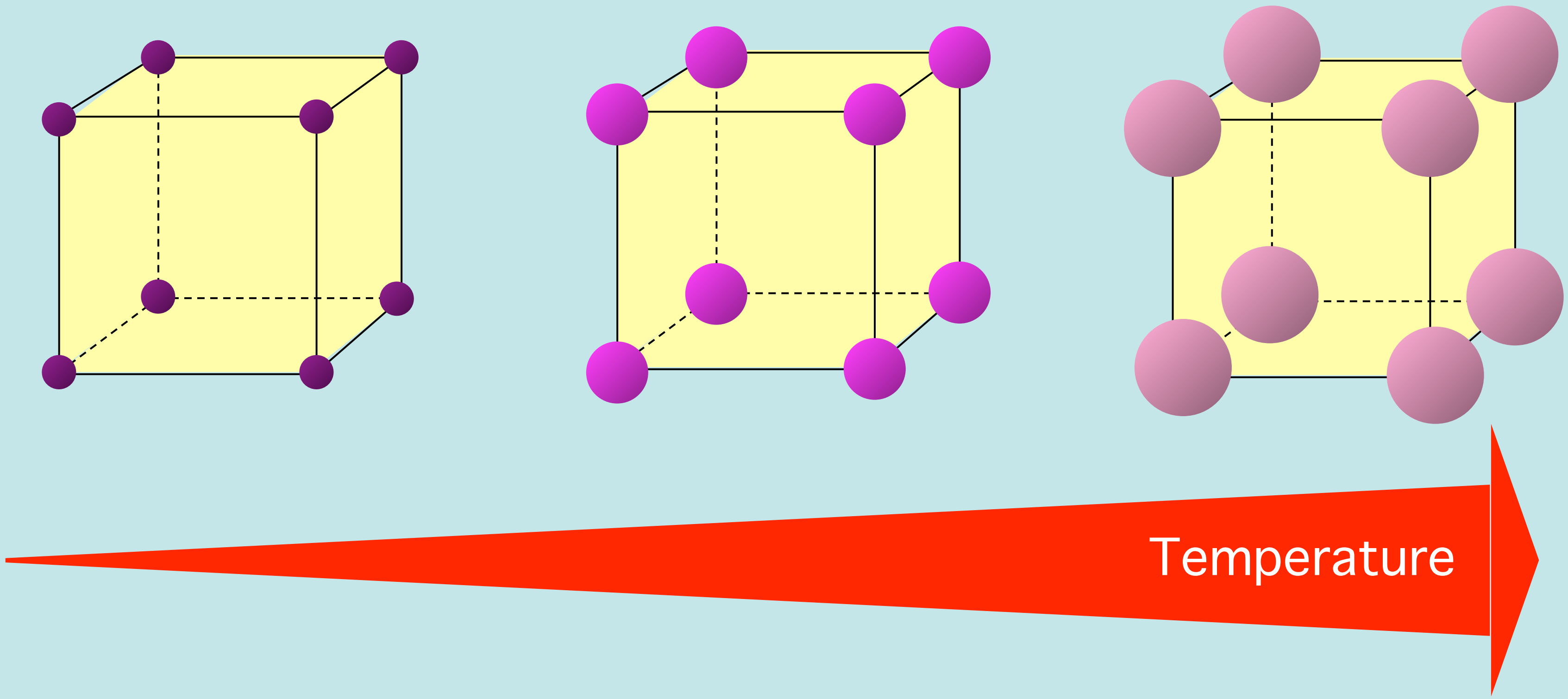

Thermal motion → Spread of atomic positions

Crystal lattices

Translation vectors (2D)

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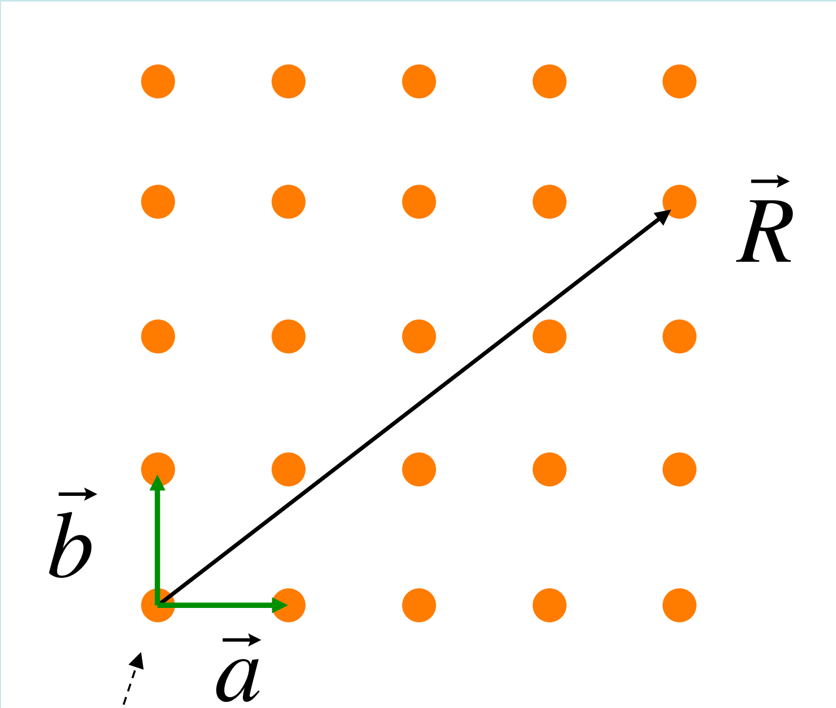
2-D



Arbitrary origin

For every lattice point

$$\vec{R} = n_1\vec{a} + n_2\vec{b}$$

integers

primitive vectors

Primitive vectors (2D)

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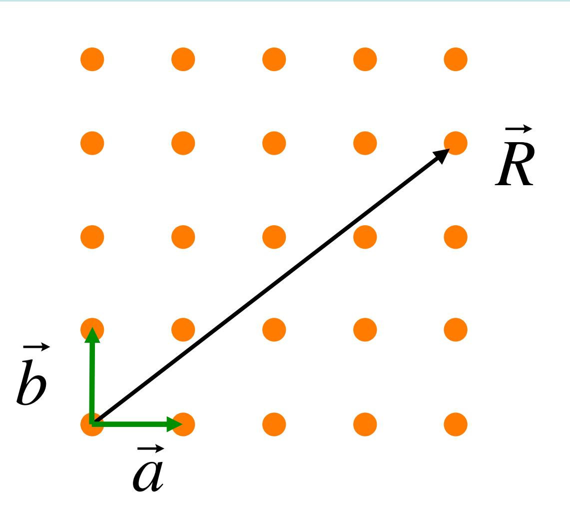
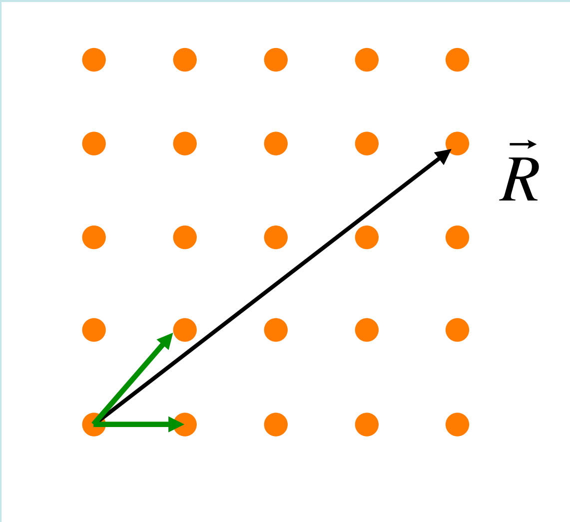
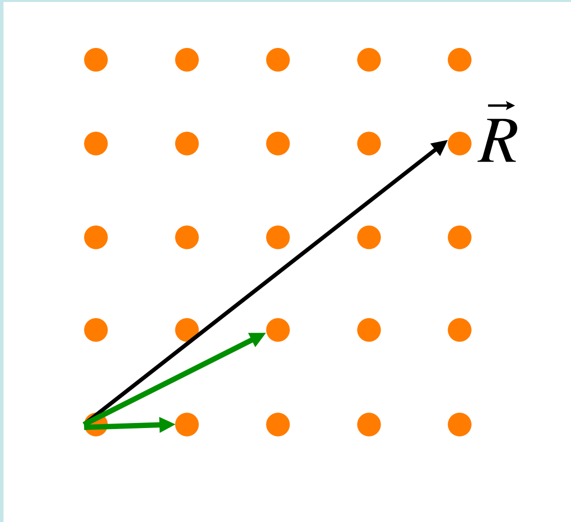
2-D

$$\vec{R} = n_1\vec{a} + n_2\vec{b}$$







Different choices of primitive vectors $\vec{a}, \vec{b}$

Non-primitive vectors (2D)

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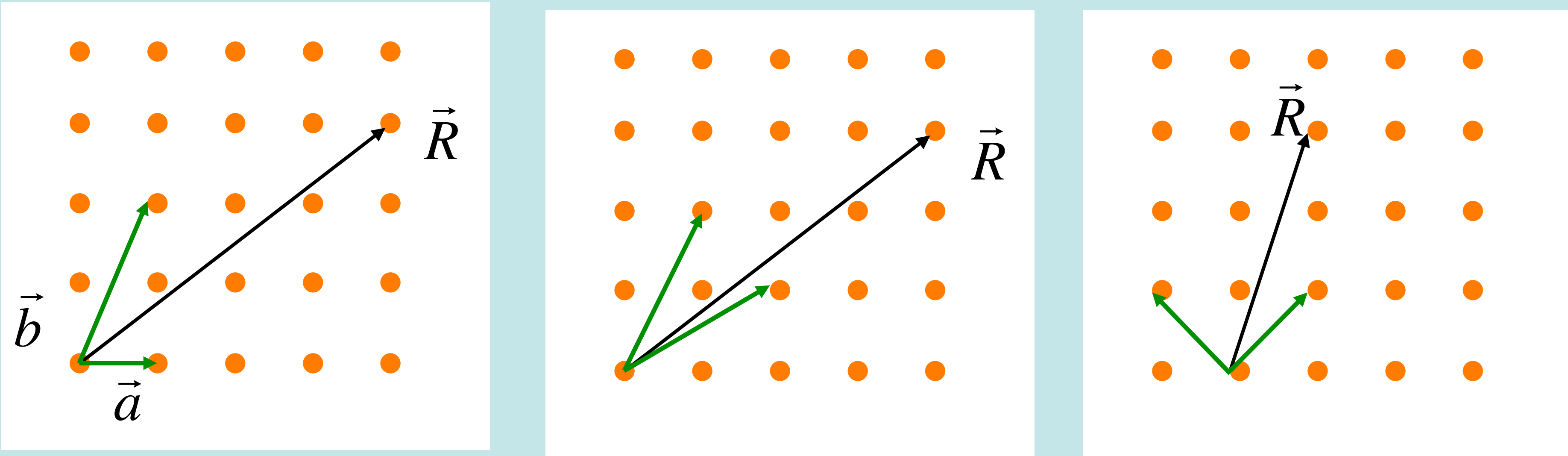
2-D

Not all $\vec{a},\vec{b}$ pairs are primitive



$$\vec{R} \neq n_1\vec{a} + n_2\vec{b}$$

Primitive vectors (3D)

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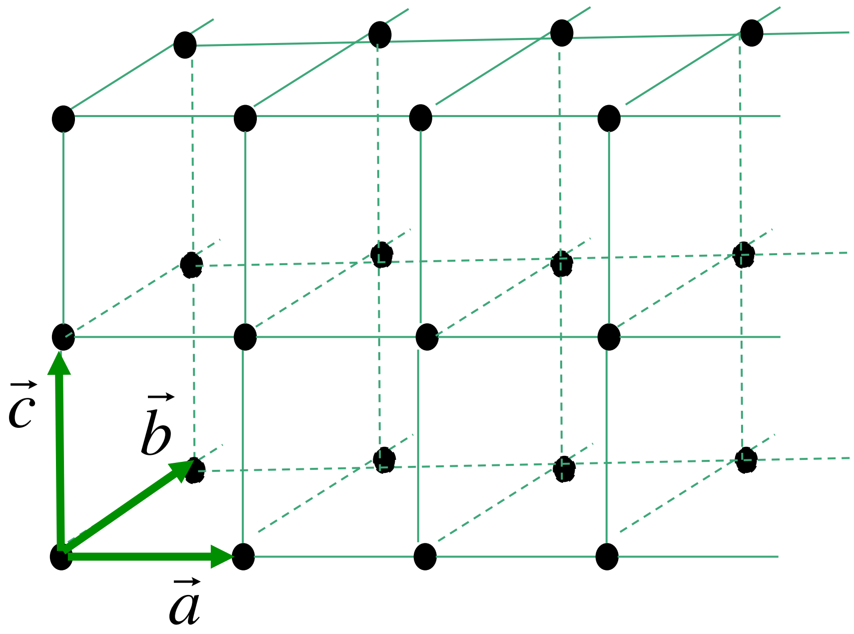
3-D

$$\vec{R} = n_1\vec{a} + n_2\vec{b} + n_3\vec{c}$$



Different choices of primitive vectors $\vec{a},\vec{b},\vec{c}$

Primitive unit cells (2D)

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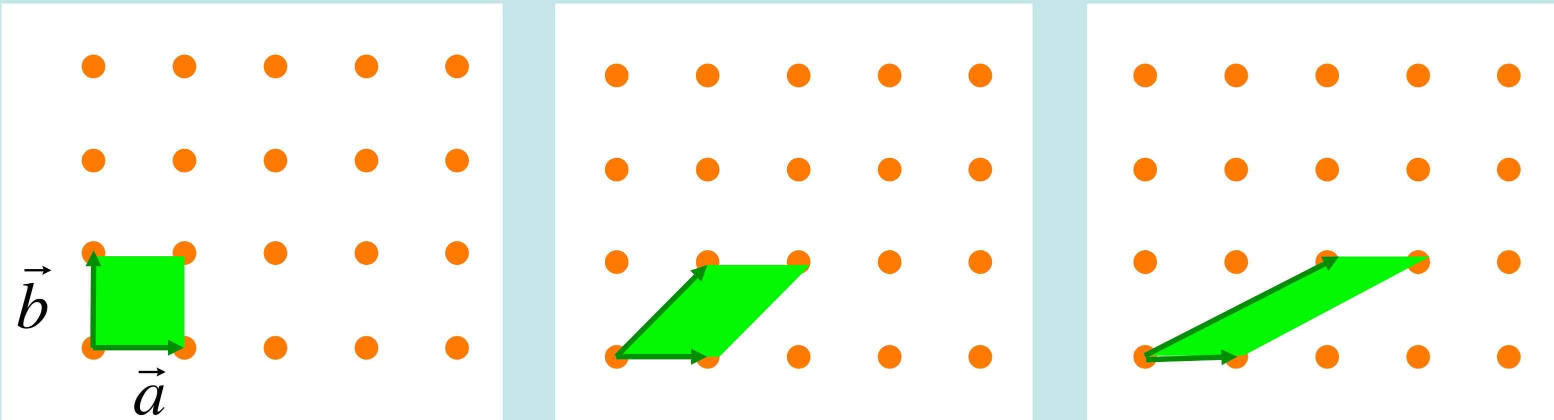
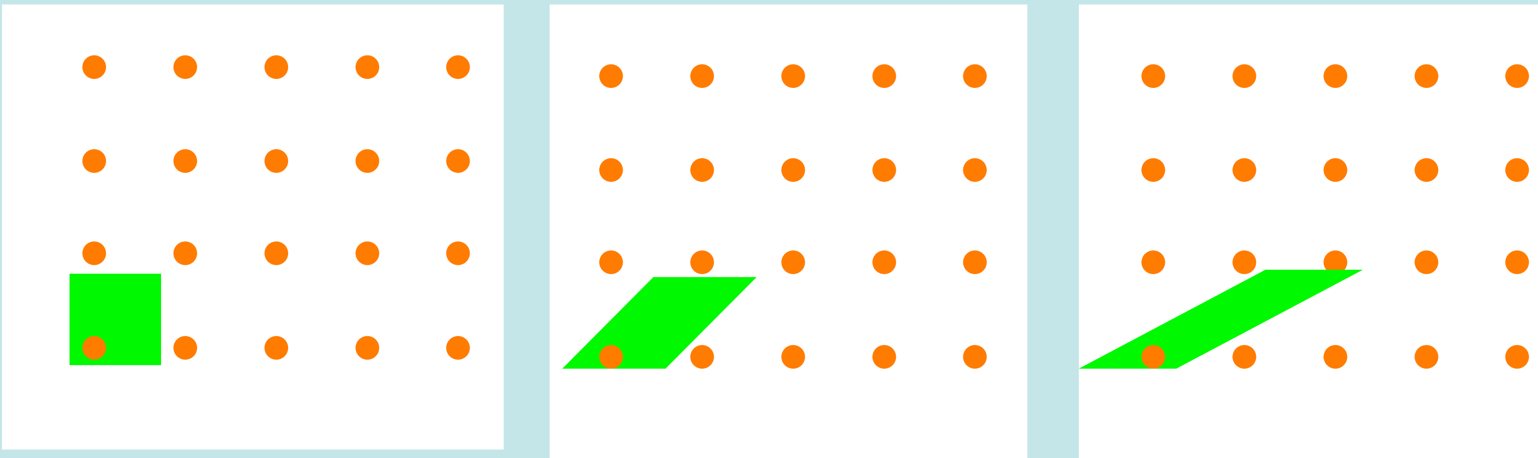
2-D



Different choices of primitive unit cells



Primitive cell = 1 lattice point

Conventional unit cells (2D)

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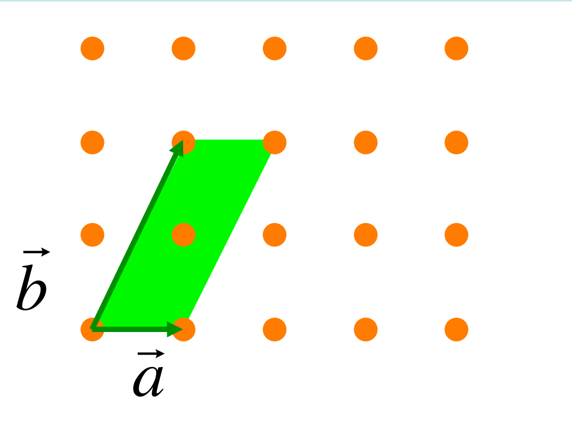
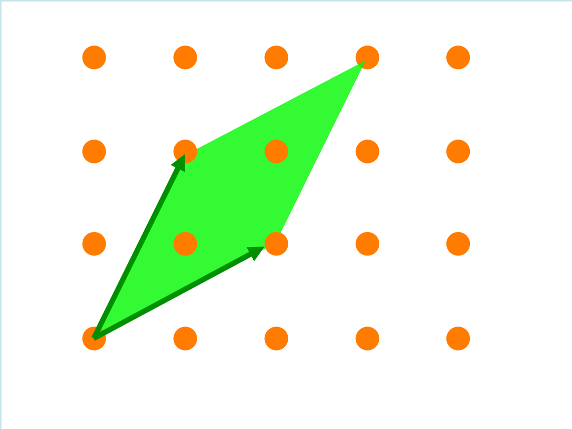
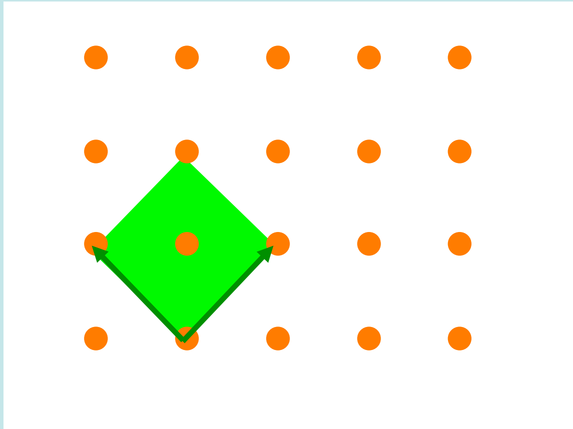
2-D







More than 1 lattice point per unit cell

Non-Bravais lattices

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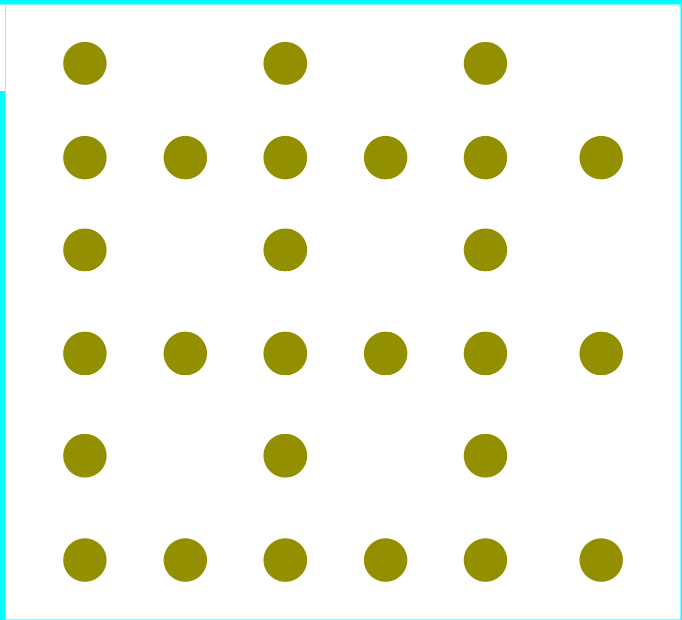
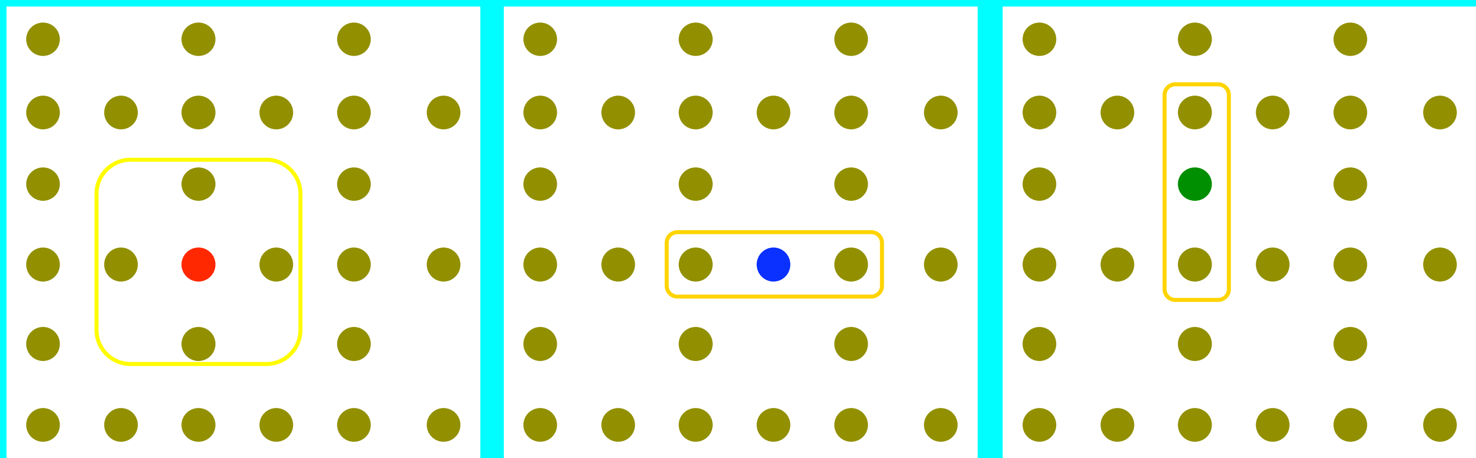
2-D

Atoms



$$\vec{R} \neq n_1\vec{a} + n_2\vec{b}$$

Un-equivalent sites



Bravais lattices

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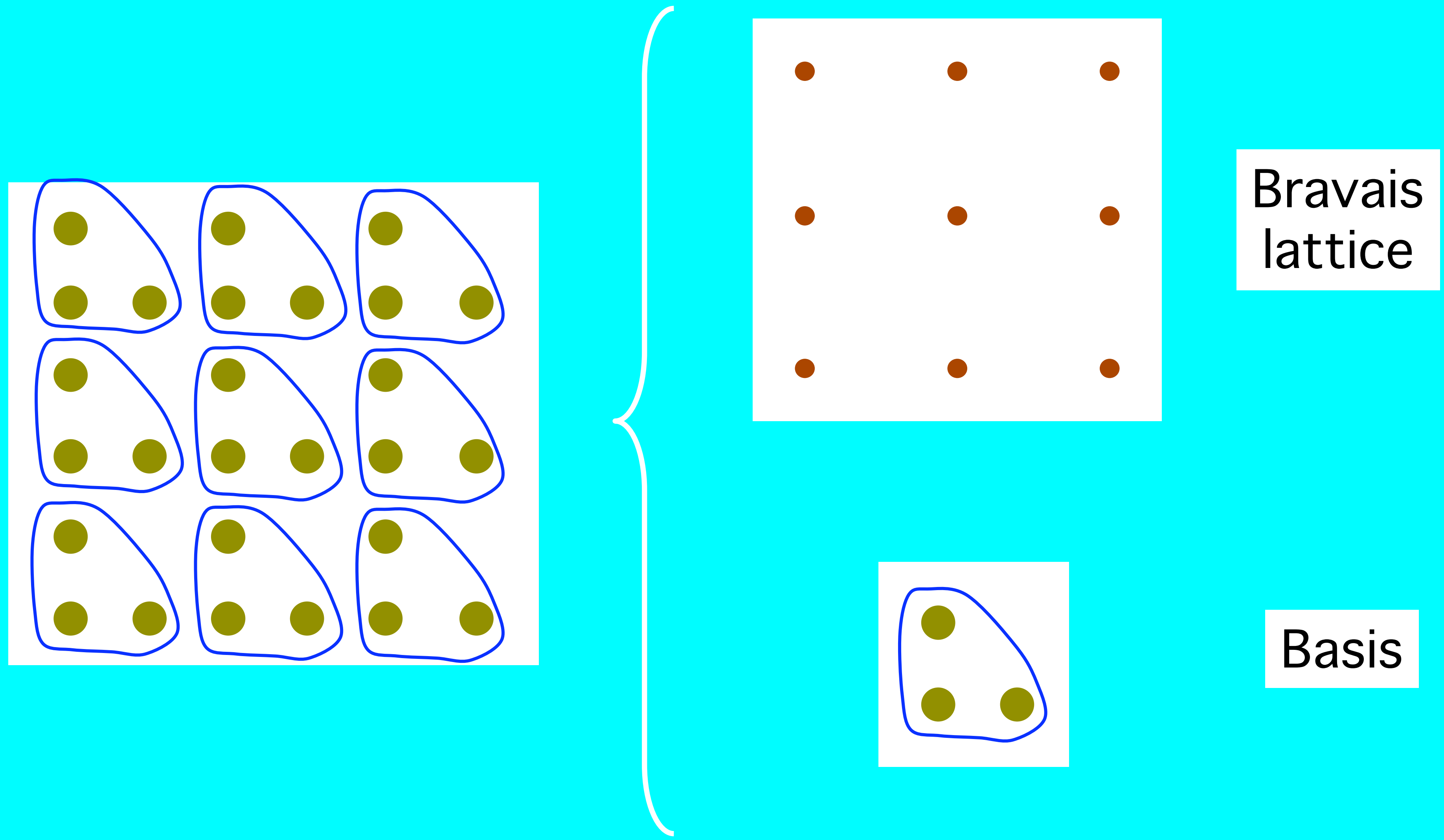
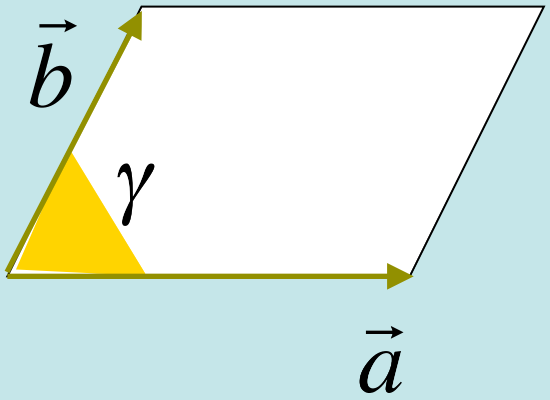
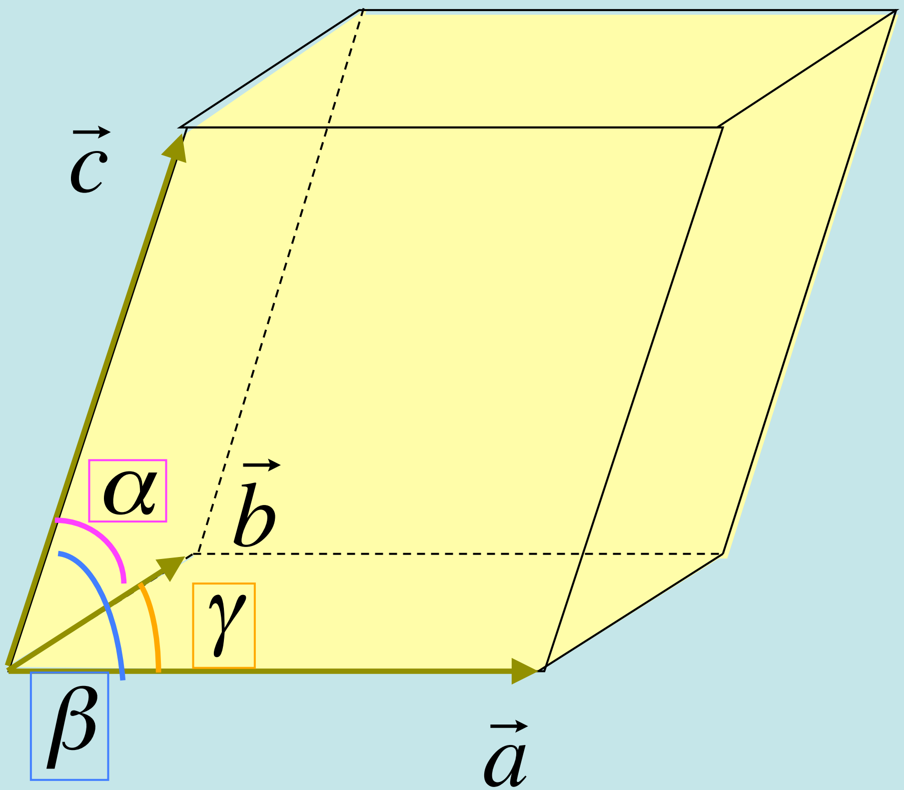


Characterization of unit cells

2-D



3-D



a	b	c	latin
α	β	γ	greek

7 crystal systems and 14 Bravais lattices

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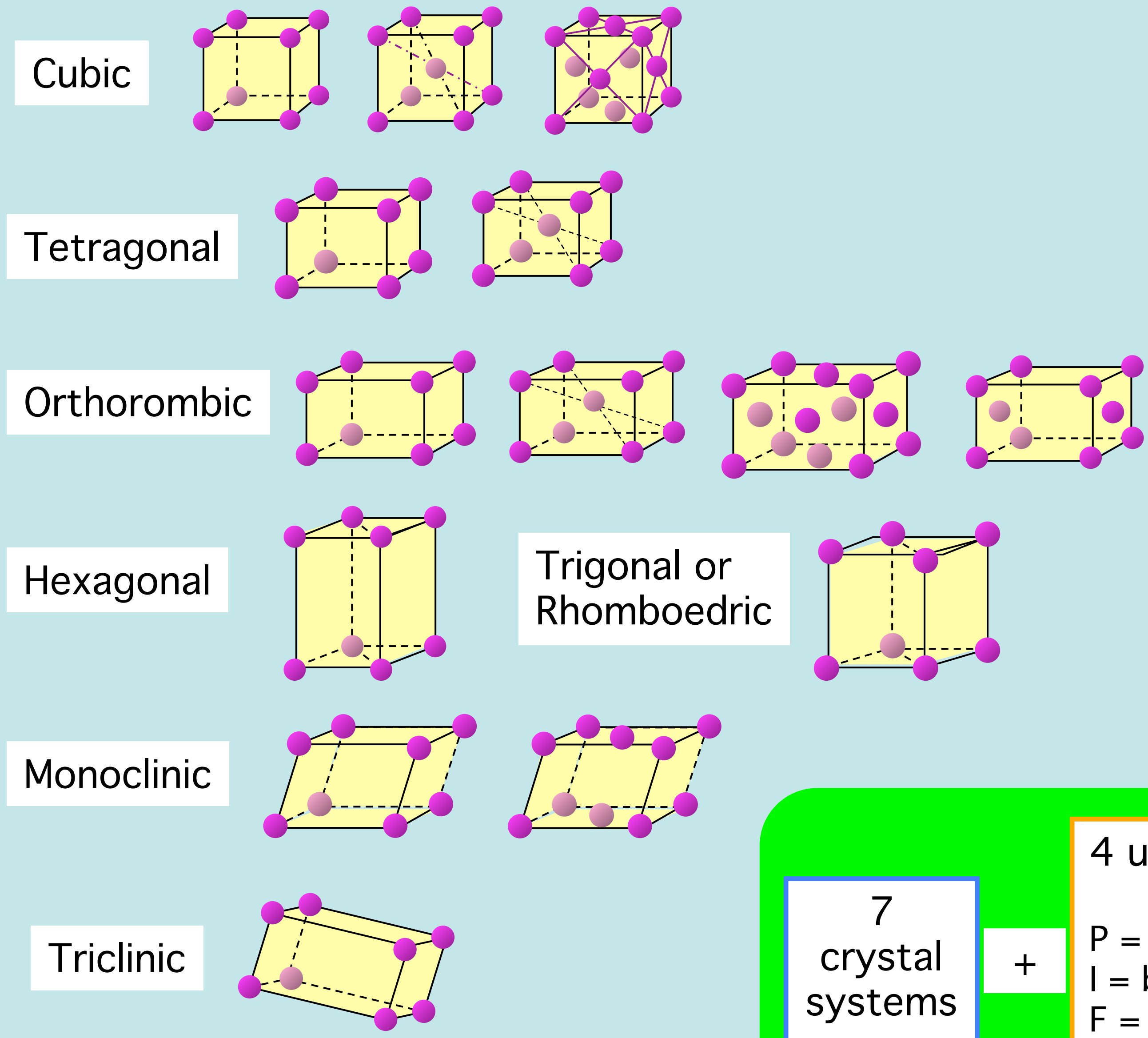
3-D



7 crystal systems + 4 unit cells = 14 Bravais lattices

4 unit cells

- P = primitive
- I = body centered
- F = face centered
- C = side centered

Internal coordinates

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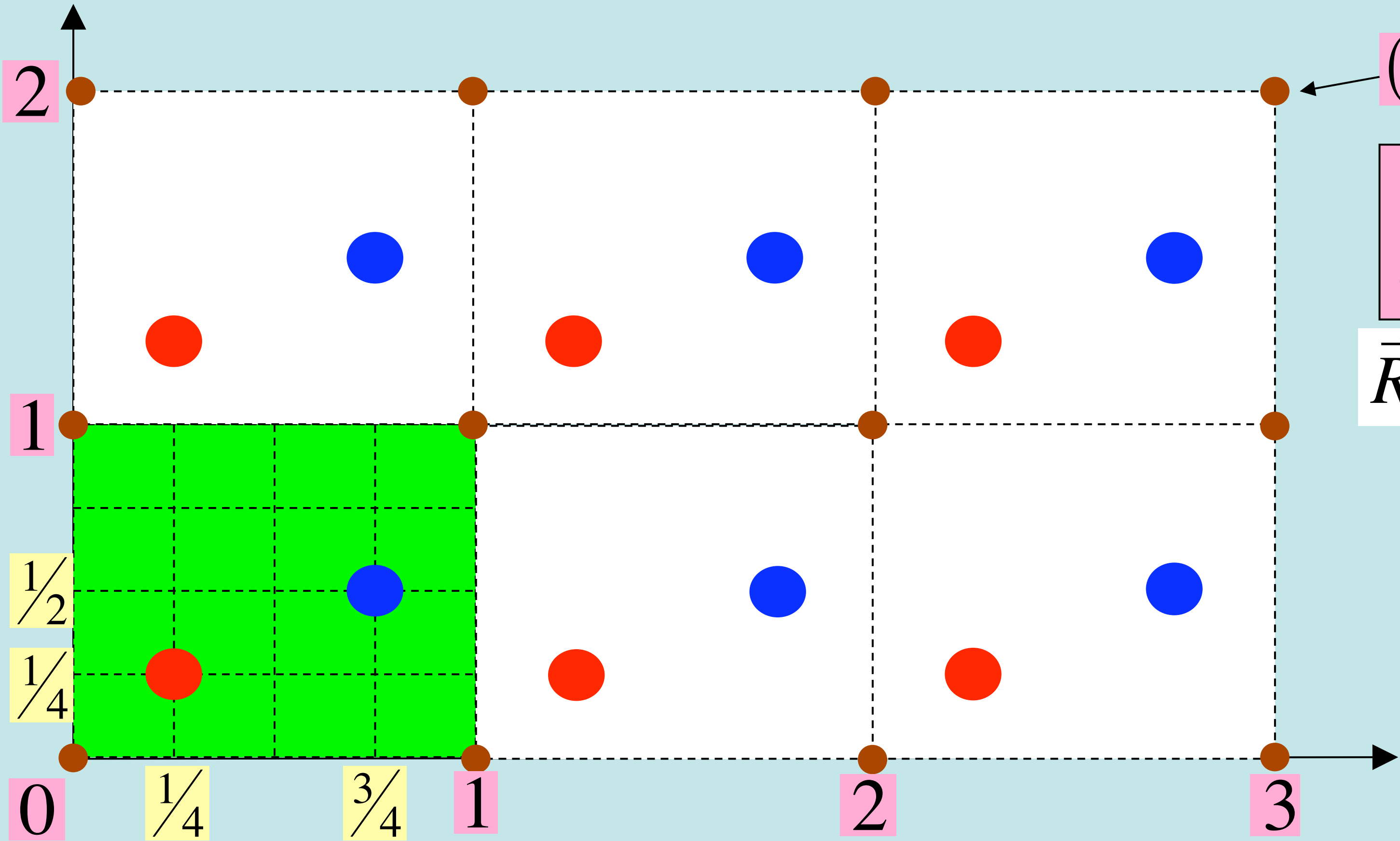

Lattice points: integer coordinates

$$\vec{R} = n_1\vec{a} + n_2\vec{b}$$

Inside cell: fractional coordinates

Red: $\left(\frac{1}{4},\frac{1}{4}\right)$ Blue: $\left(\frac{3}{4},\frac{1}{2}\right)$

- Some relevant crystal structures

Simple cubic lattice

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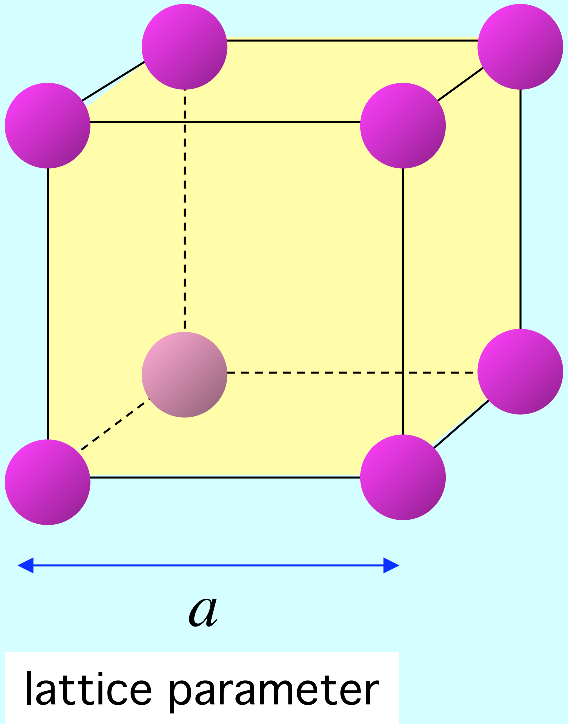
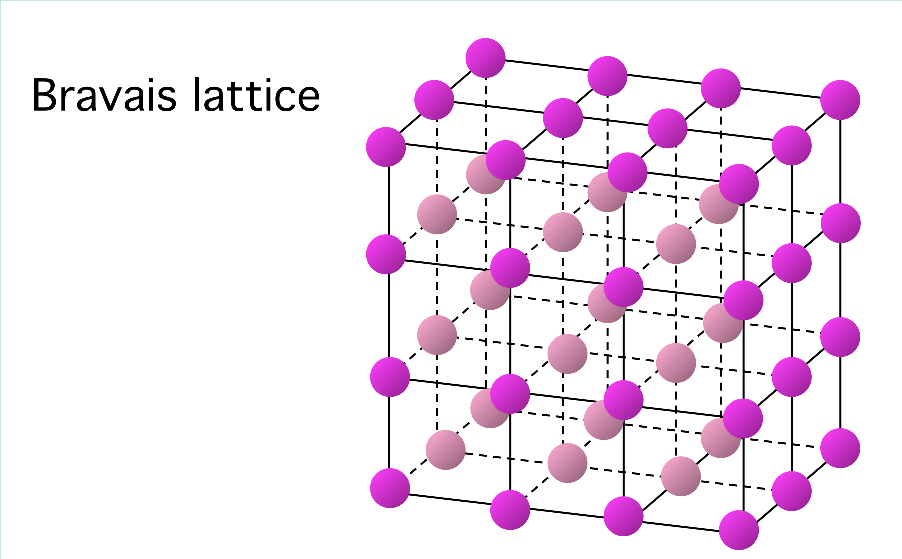
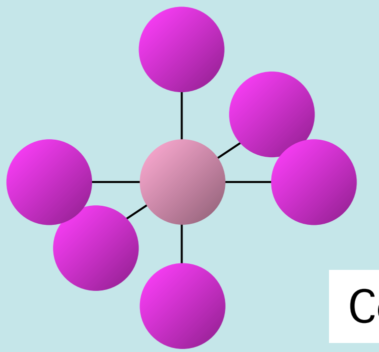
84-Po   a=3.35 Å



Primitive unit cell
(1 lattice point per cell)





Coordination number = 6

Body centered cubic lattice (bcc)

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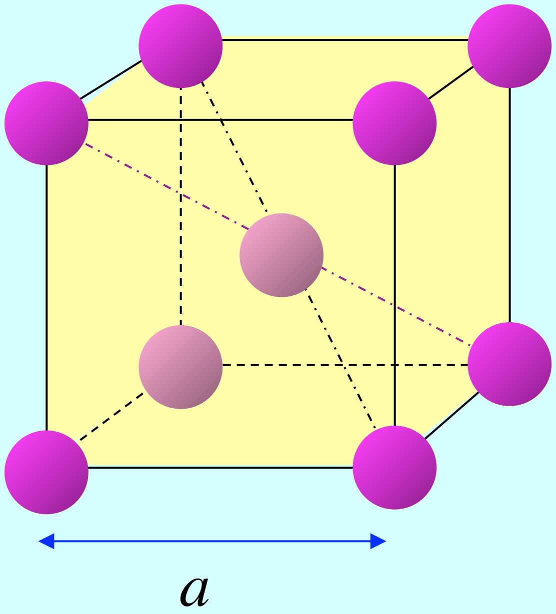
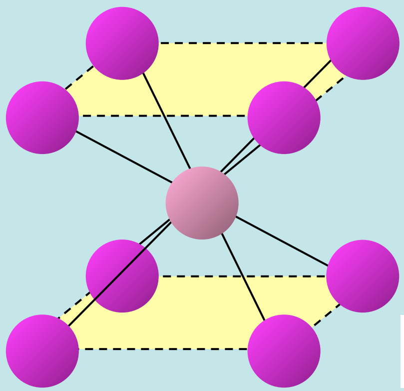
24-Cr	a=2.88 Å
26-Fe	a=2.87 Å
42-Mo	a=3.15 Å



lattice parameter

conventional unit cell
(2 lattice points per cell)

Bravais lattice



Coordination number = 8

Face centered cubic lattice (fcc)

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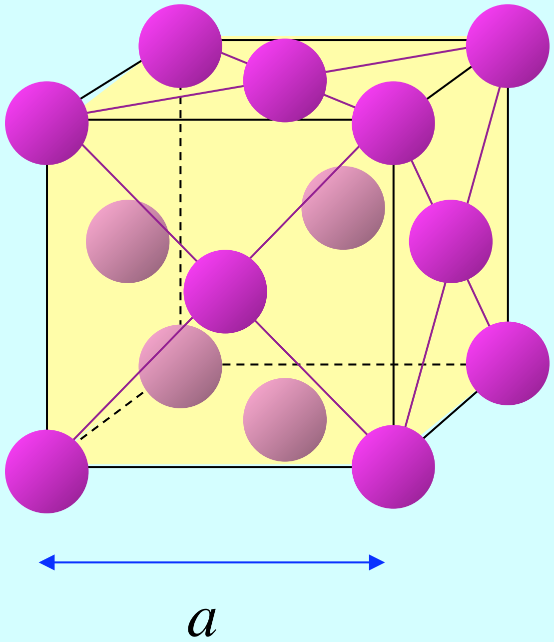
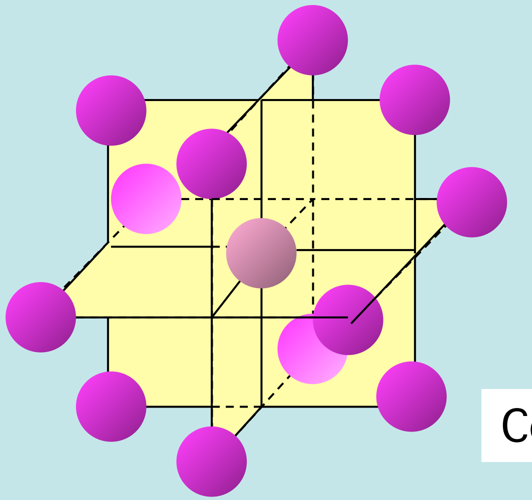


lattice parameter

conventional unit cell
(4 lattice points per cell)

29-Cu	a=3.61 Å
47-Ag	a=4.09 Å
79-Au	a=4.08 Å

Bravais lattice



Coordination number = 12

Diamond structure

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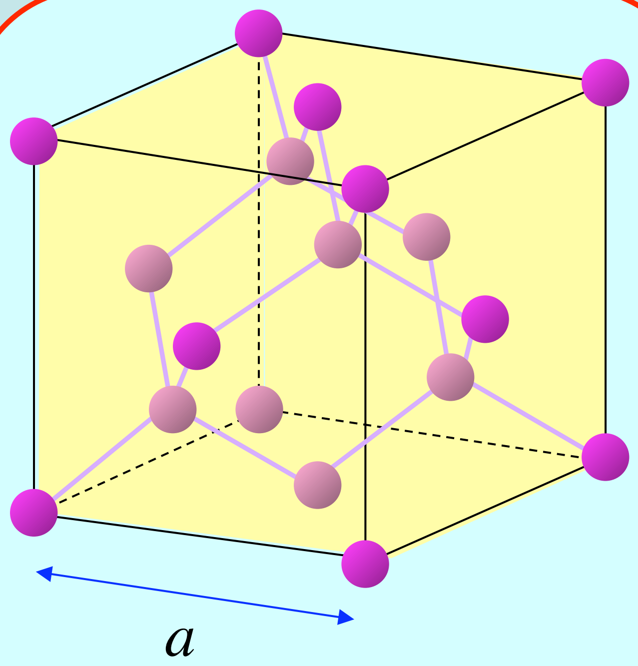
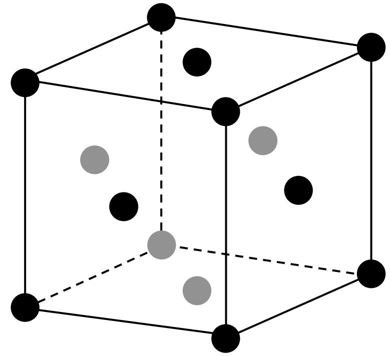


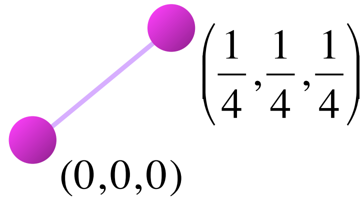
conventional unit cell
(8 atoms per cell)

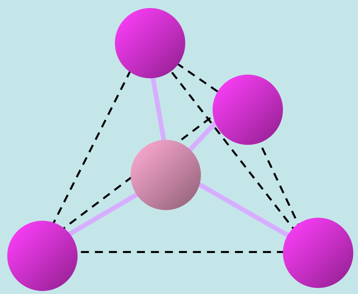
6-C	a=3.57 Å
14-Si	a=5.43 Å
32-Ge	a=5.66 Å

Non-Bravais lattice

fcc Bravais lattice + 2-atom basis







Coordination number = 4

Zincblende (sphalerite) structure

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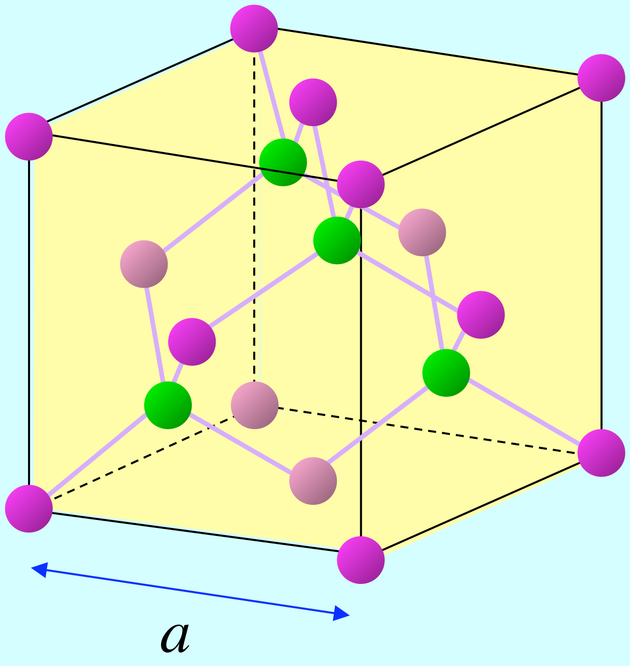
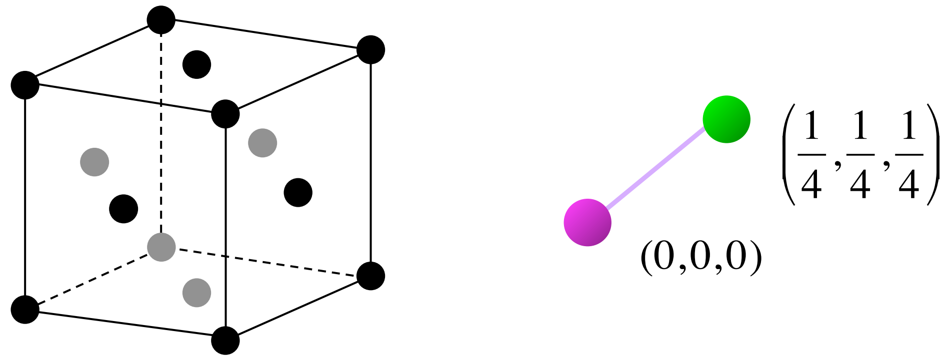


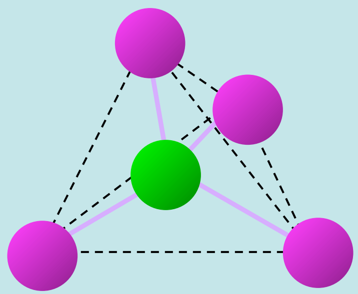
conventional unit cell
(8 atoms per cell)

ZnS	a=5.41 Å
GaAs	a=5.65 Å
SiC	a=4.35 Å

Non-Bravais lattice

fcc Bravais lattice + 2-atom basis





Cordination number = 4

Rock-salt (NaCl) structure

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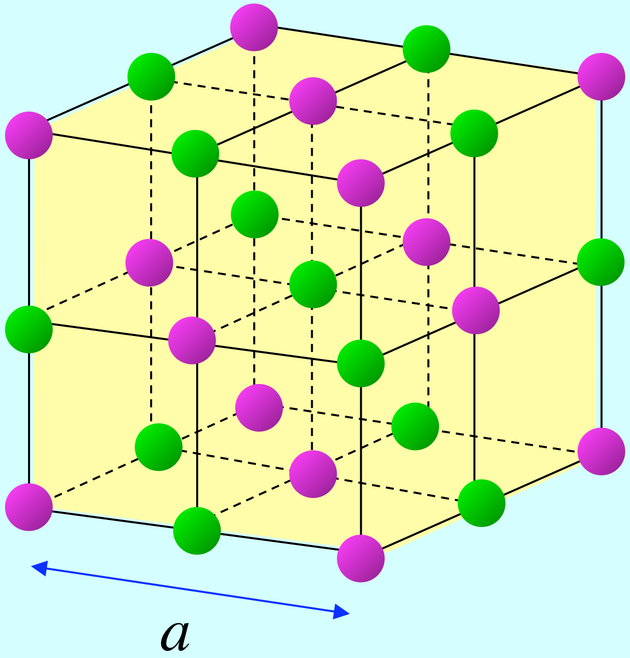
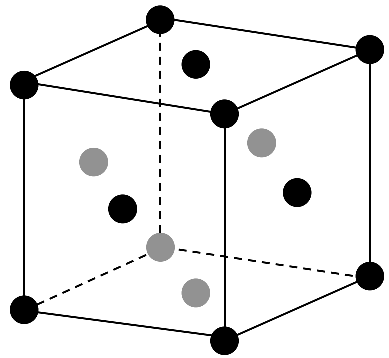


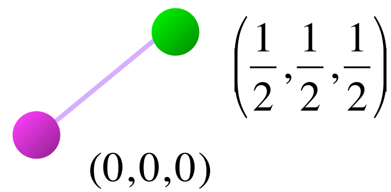
conventional unit cell
(8 atoms per cell)

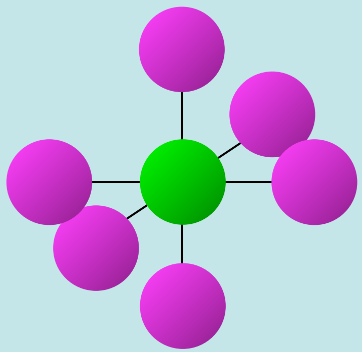
NaCl	a=5.64 Å
KBr	a=6.60 Å
CaO	a=4.81 Å

Non-Bravais lattice

fcc Bravais lattice + 2-atom basis







Cordination number = 6

Simple hexagonal structure

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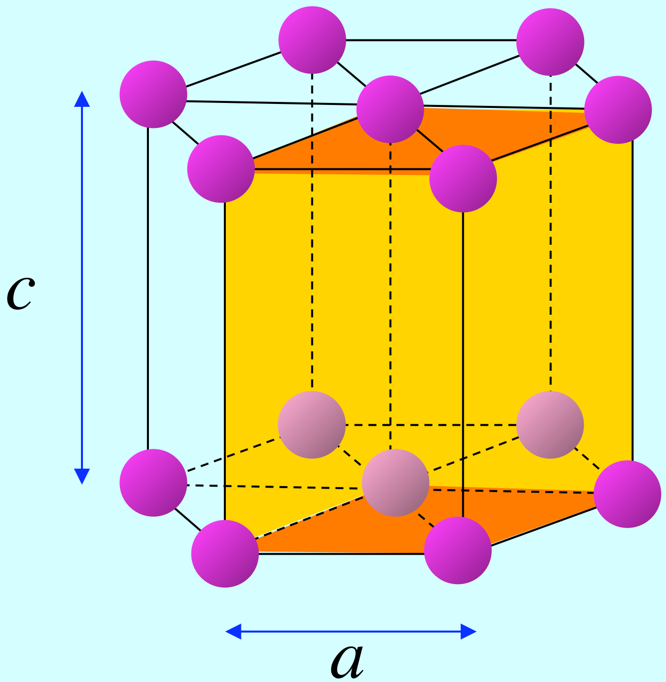
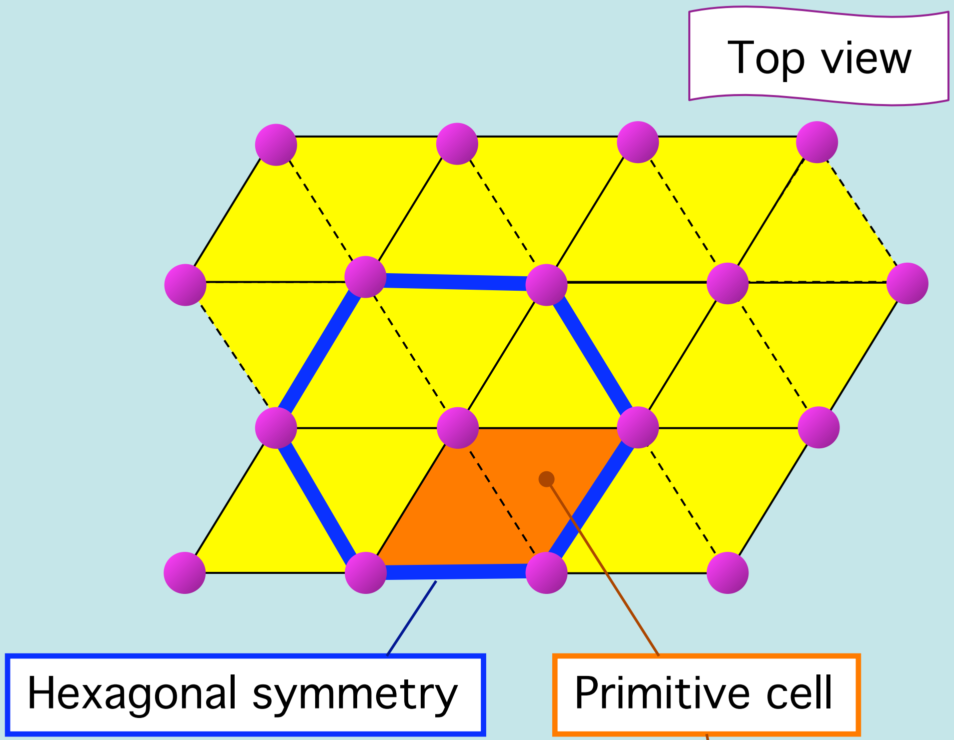
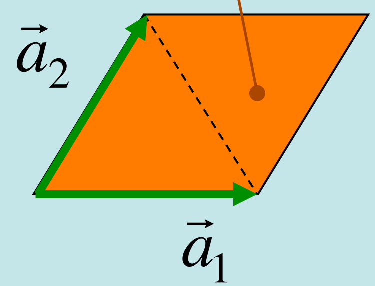


2 lattice parameters

Primitive unit cell
(1 lattice point per cell)



$$a_1 = a_2$$



Hexagonal close packed structure

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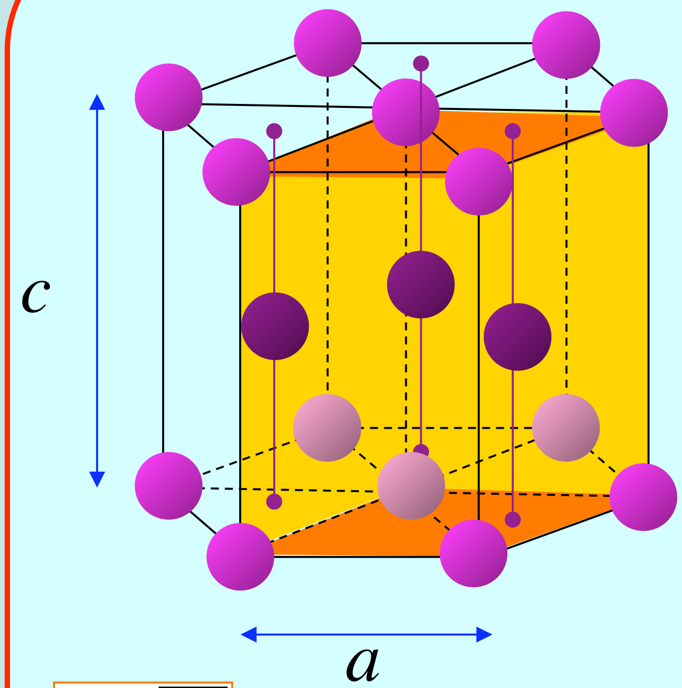


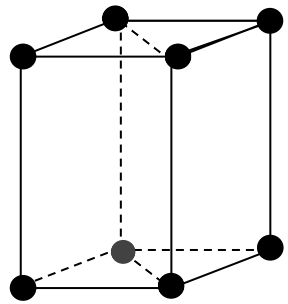
$$c = \sqrt{\frac{8}{3}}\, a$$

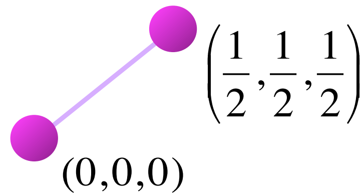
Conventional unit cell
(2 atoms per cell)

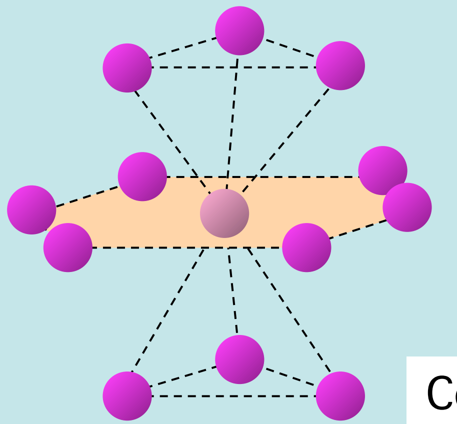
4-Be	a=2.29 Å
12-Mg	a=3.21 Å
48-Cd	a=2.98 Å

Non-Bravais lattice

primitive cell + 2-atom basis







Cordination number = 12

Coordination number

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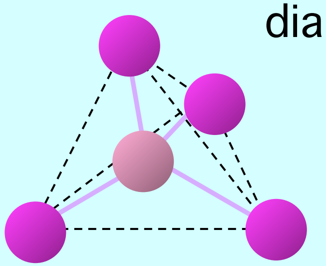
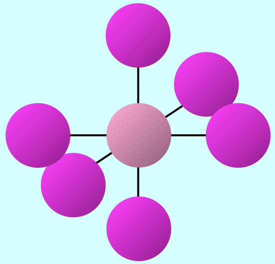
diamond



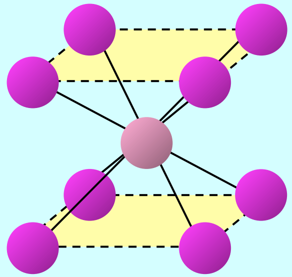
N=4

cubic



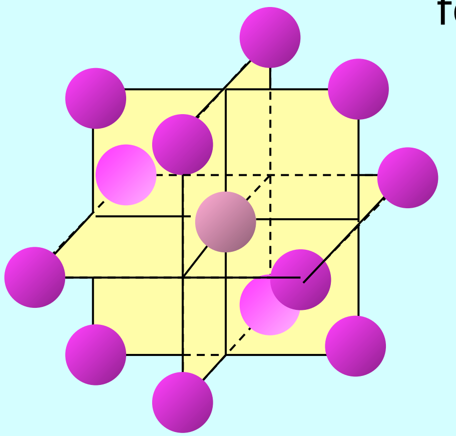
N=6

bcc

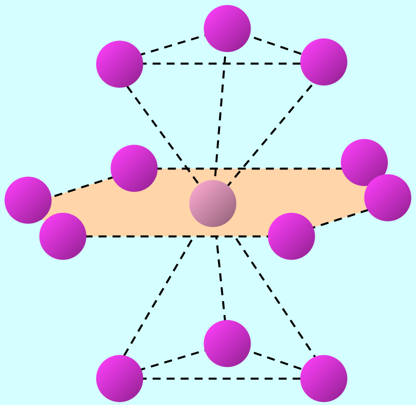


N=8

fcc



hcp



N=12

Close packing

Close-packing of spheres

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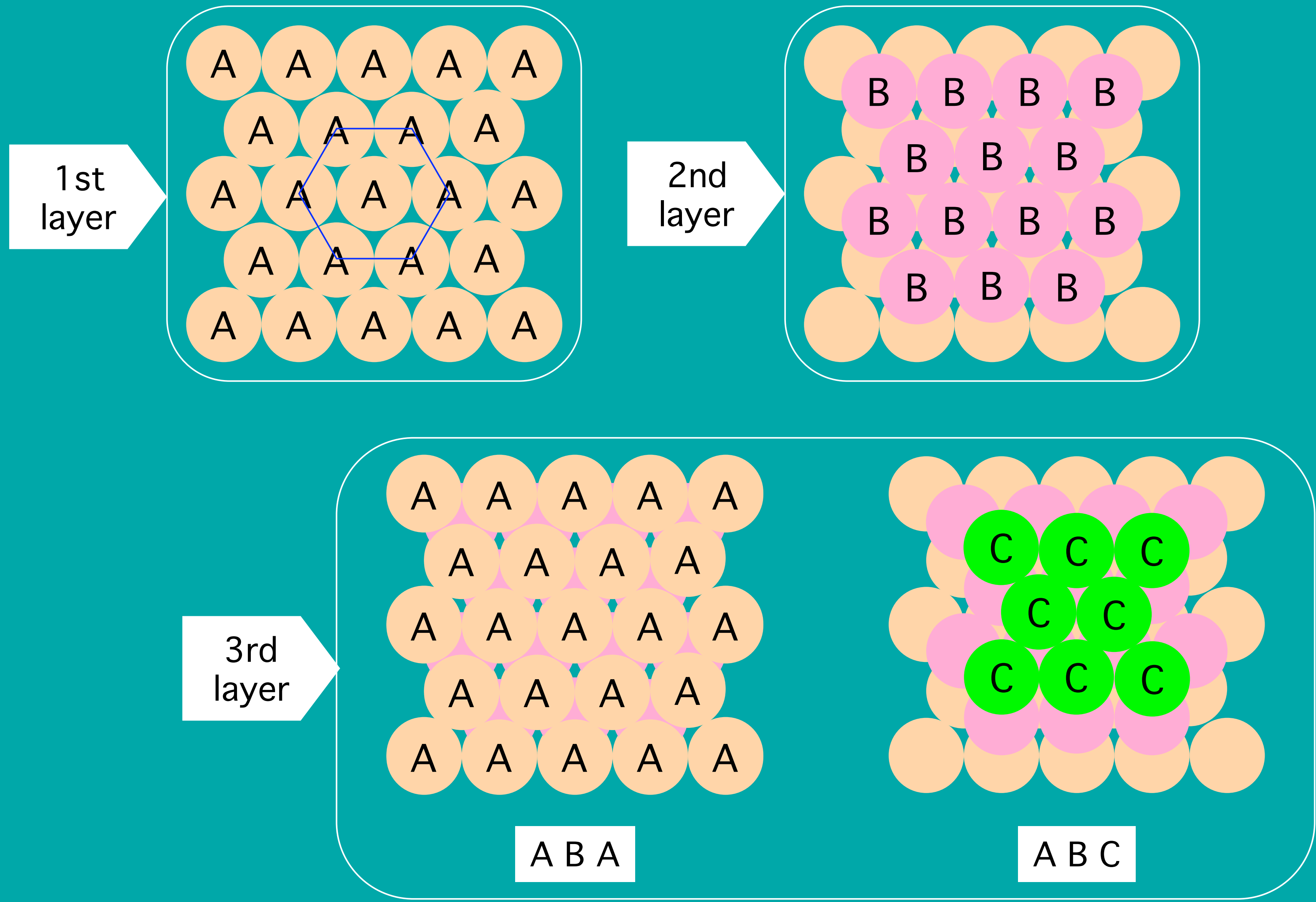

hcp versus fcc

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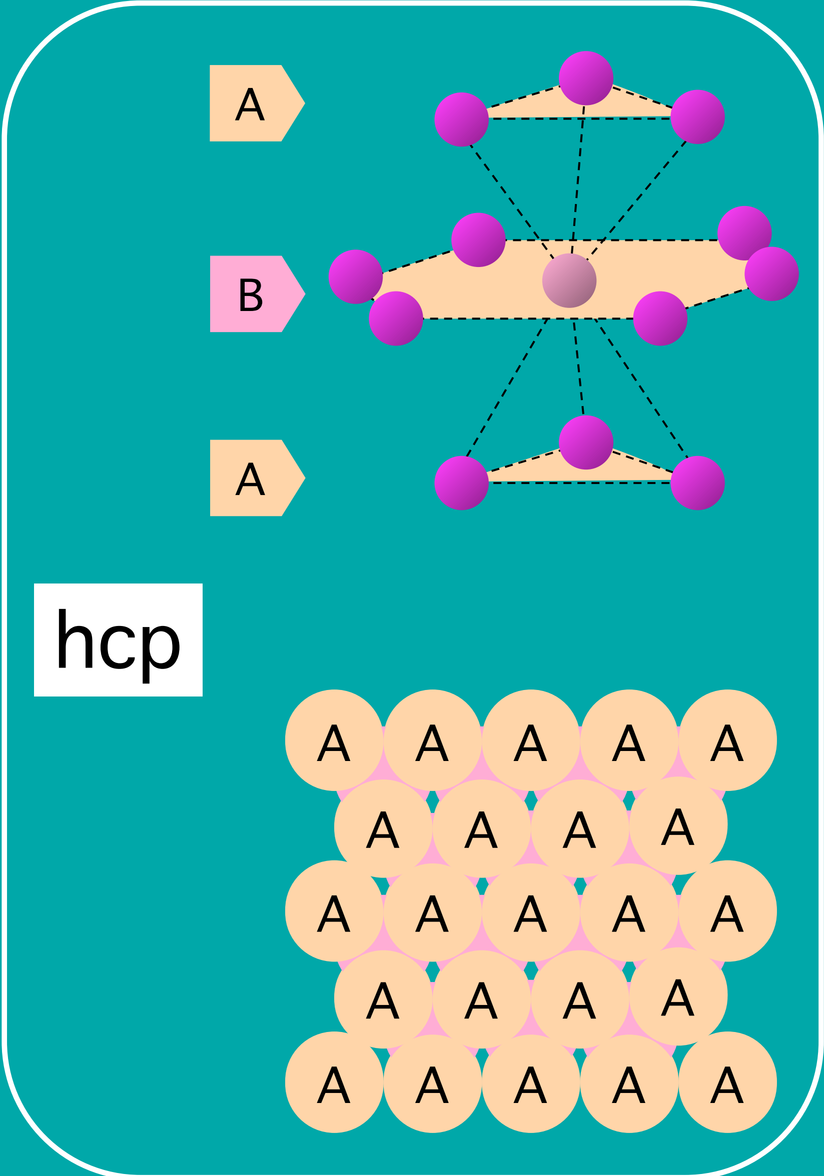

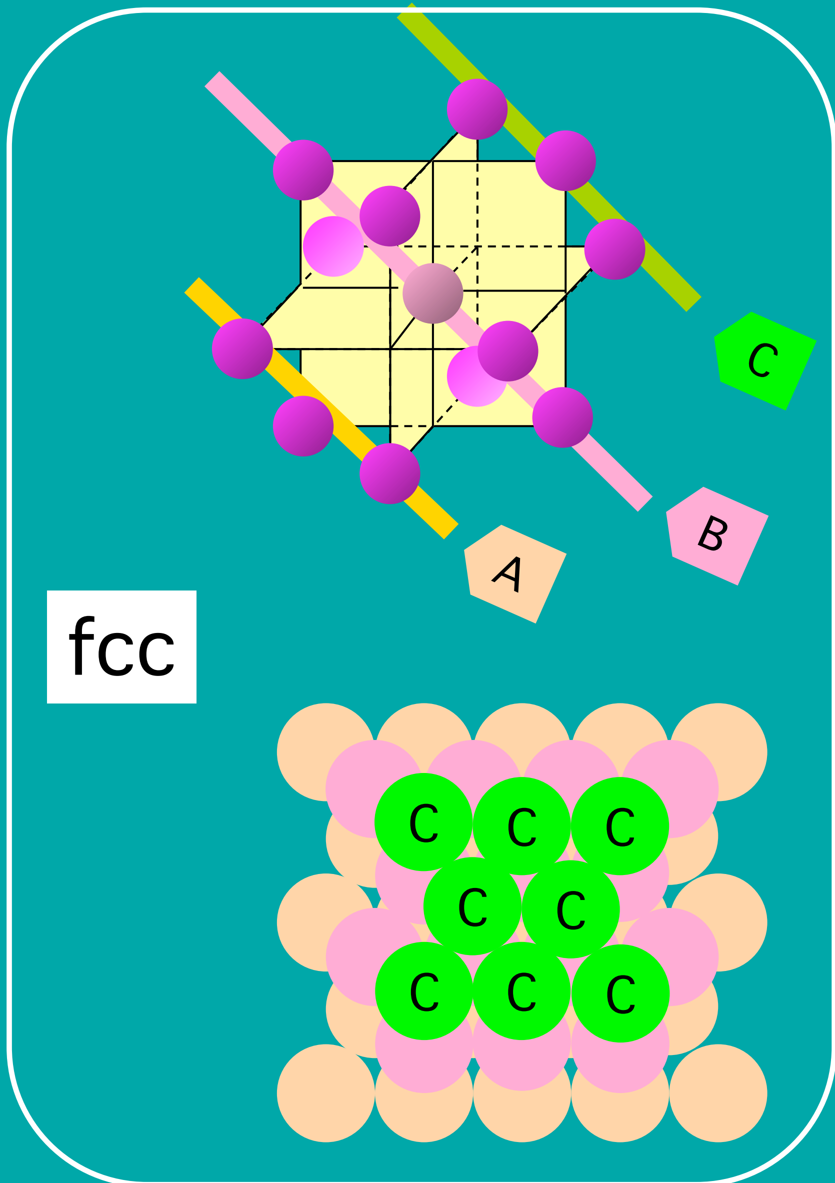

Crystal planes

Crystal planes in 2D

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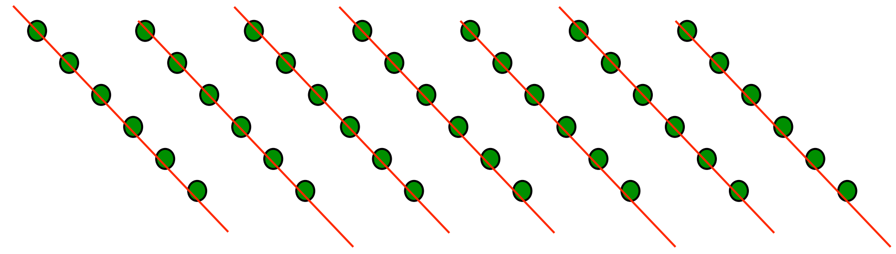
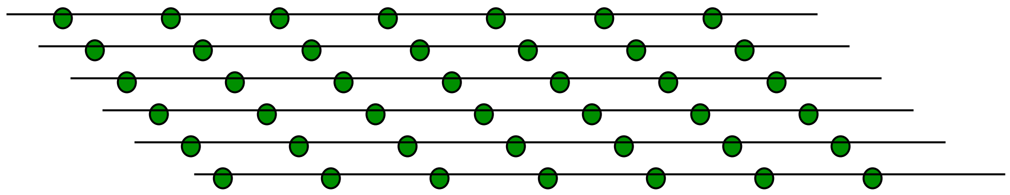
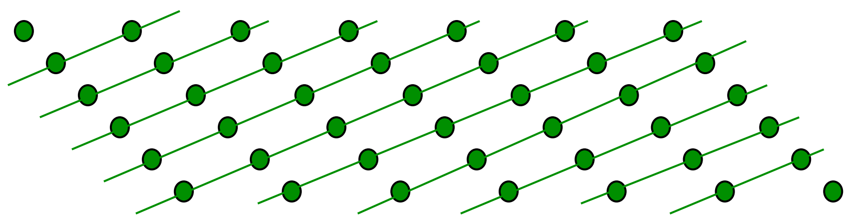
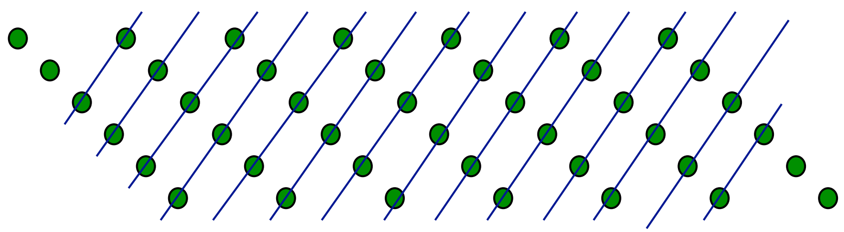
2-D









Miller indices, 2-D (a)

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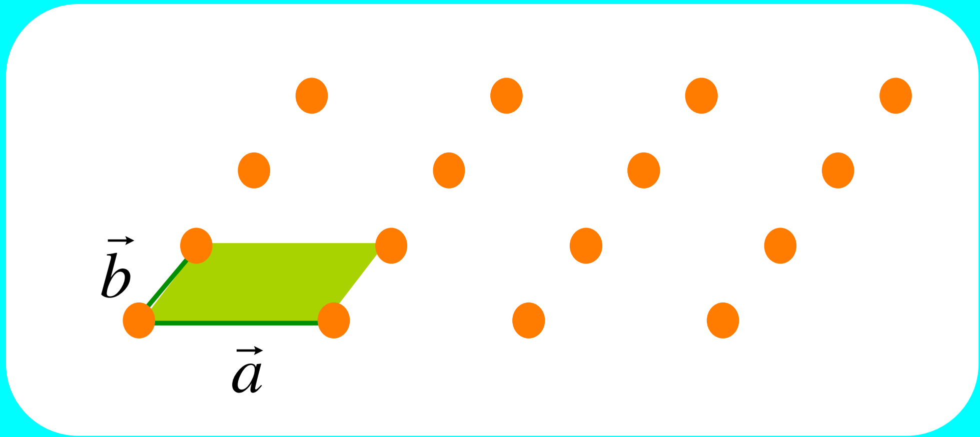
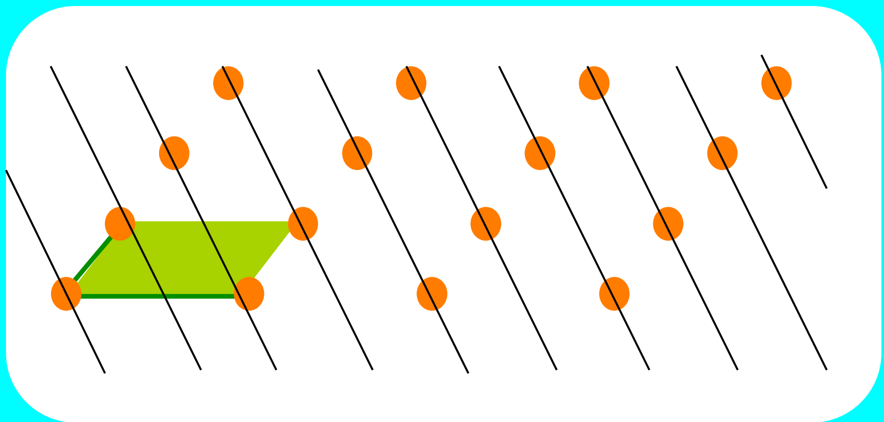
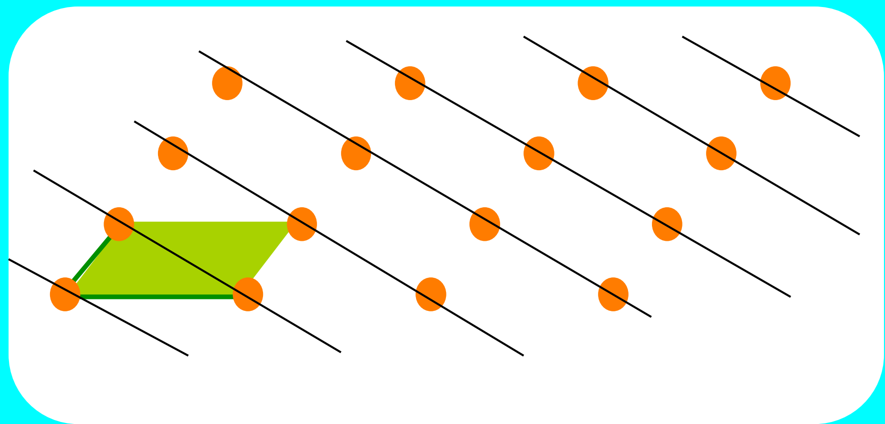
2-D





(hk) = (21)



(hk) = (11)

Miller indices, 2-D (b)

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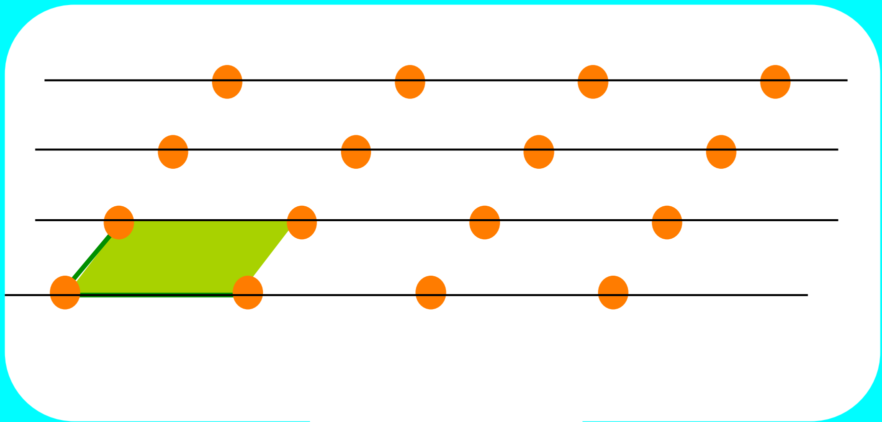
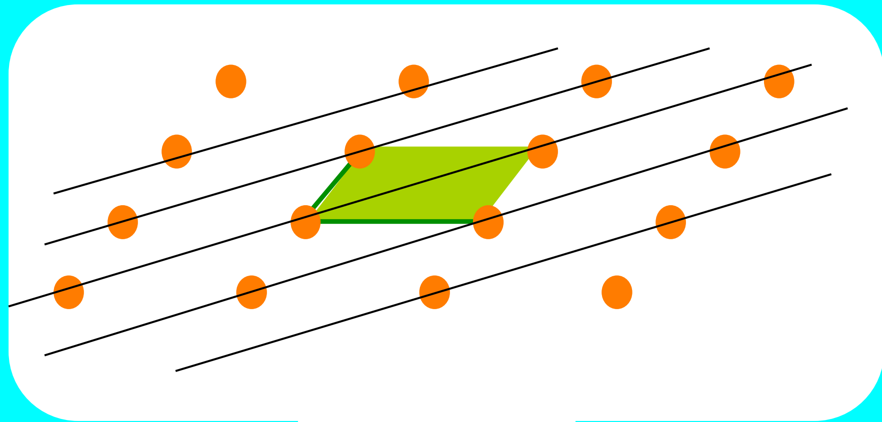
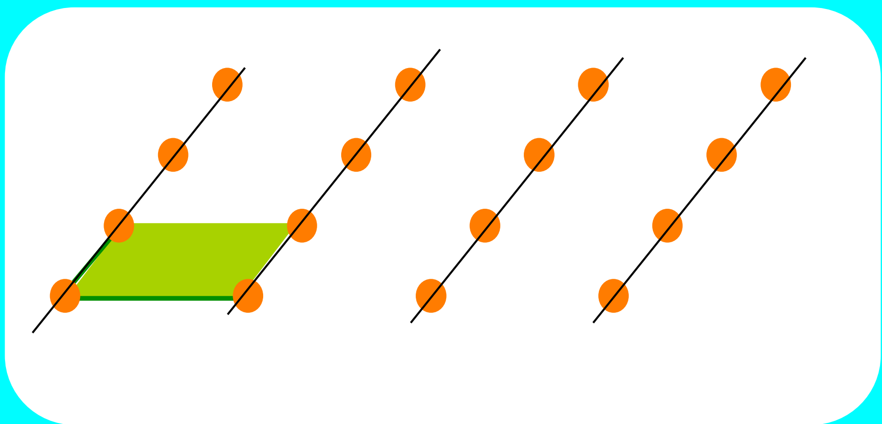


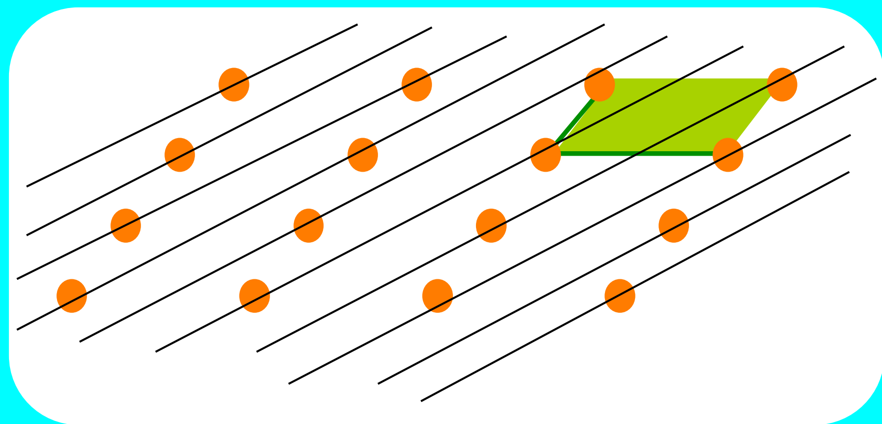
$(hk) = (01)$



$(hk) = (1\bar{1})$



$(hk) = (10)$



$(hk) = (2\bar{1})$

Miller indices, 3-D

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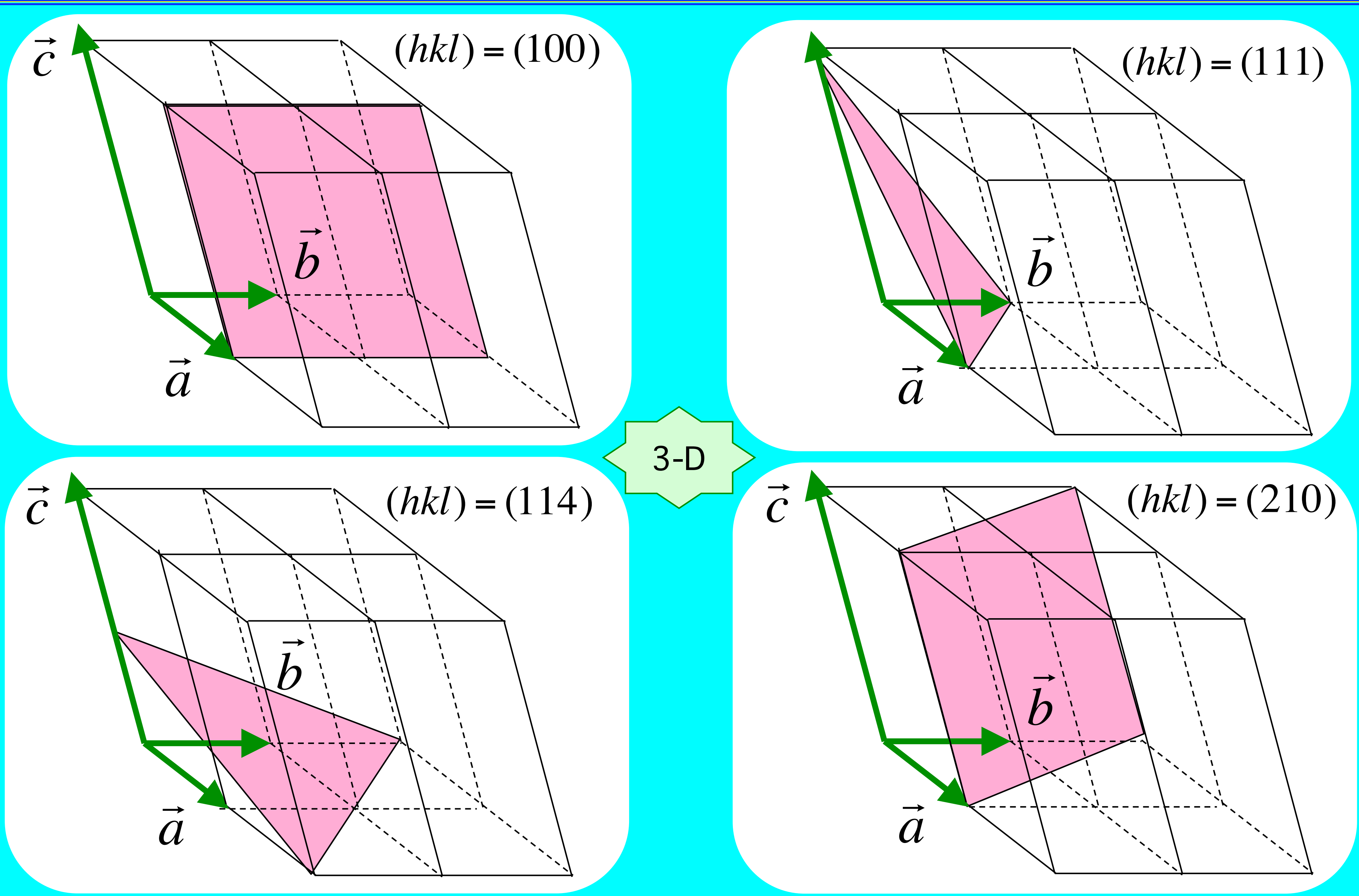

Miller indices, cubic lattices

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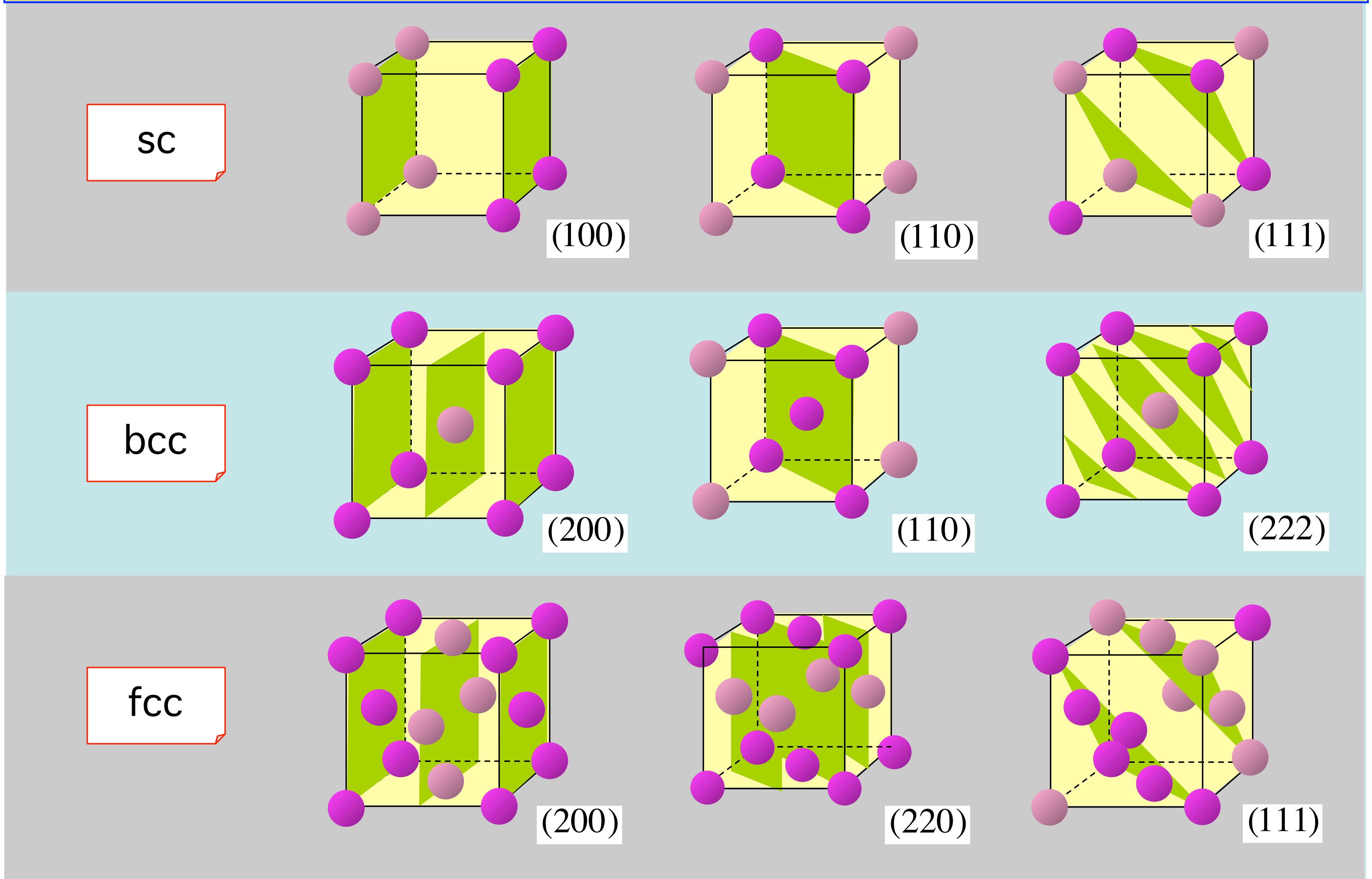

Interplanar distance

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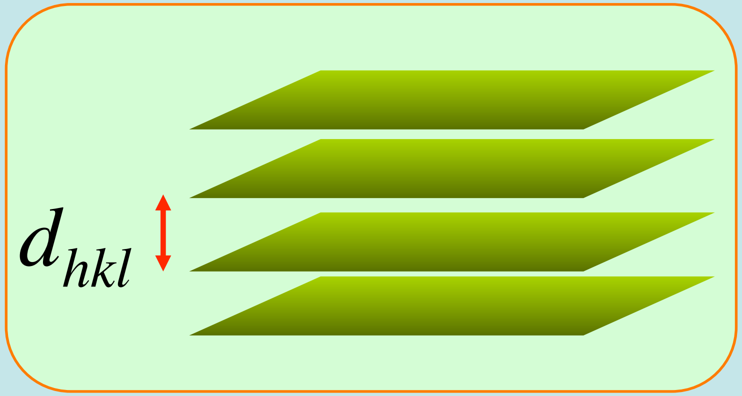
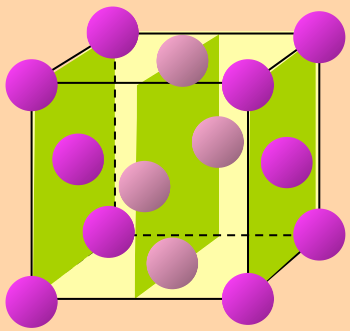


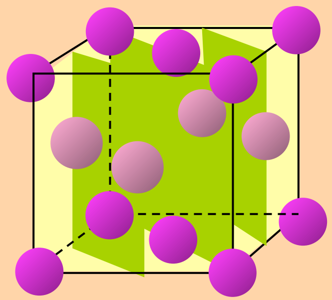
Cubic lattices

$$d_{hkl}^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

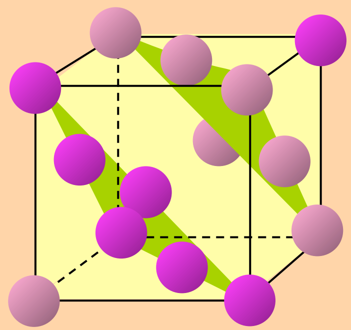
Copper, fcc, a=3.61 Å



$$d_{200} = \frac{a}{2} = 1.805 \text{ Å}$$



$$d_{220} = \frac{a}{2\sqrt{2}} = 1.276 \text{ Å}$$



$$d_{111} = \frac{a}{\sqrt{3}} = 2.084 \text{ Å}$$

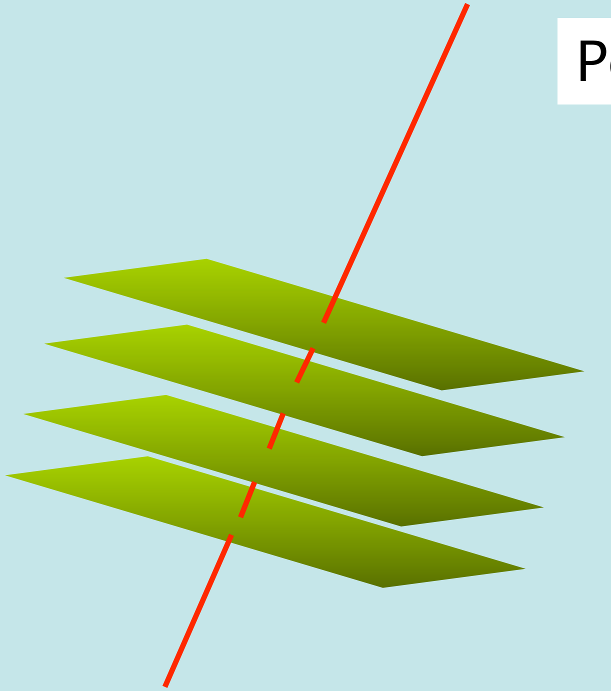
Planes and directions

Perpendicular direction

$[hkl]$

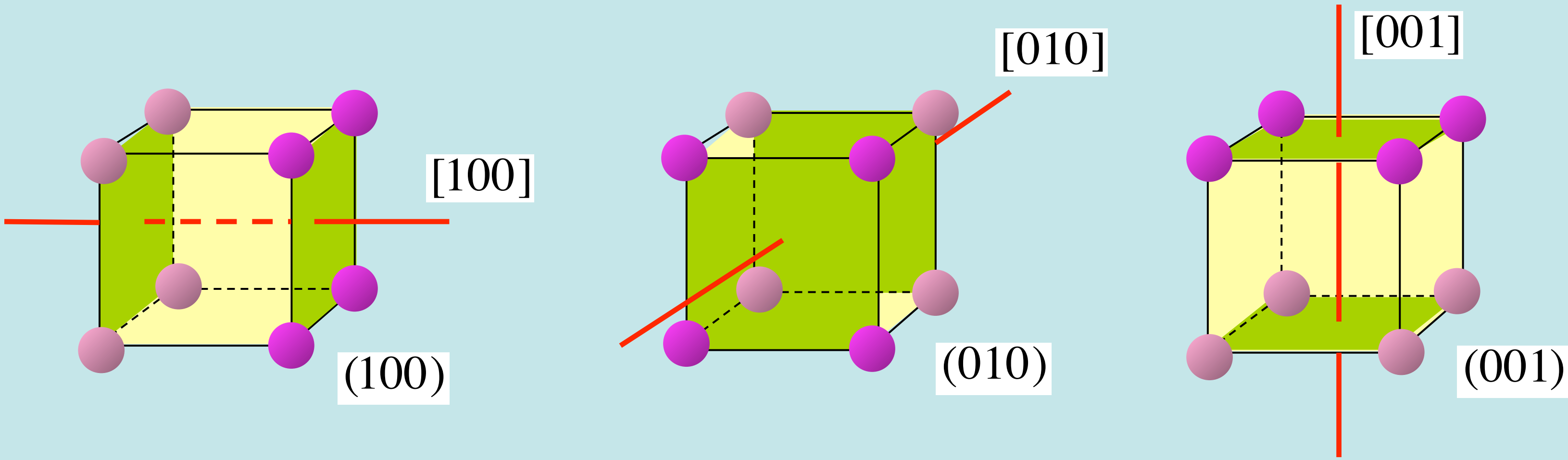
Family of planes

(hkl)



Equivalent planes and directions

Equivalent directions $< 100 >$



Equivalent planes $\{100\}$

Reciprocal lattice

X-ray diffraction patterns

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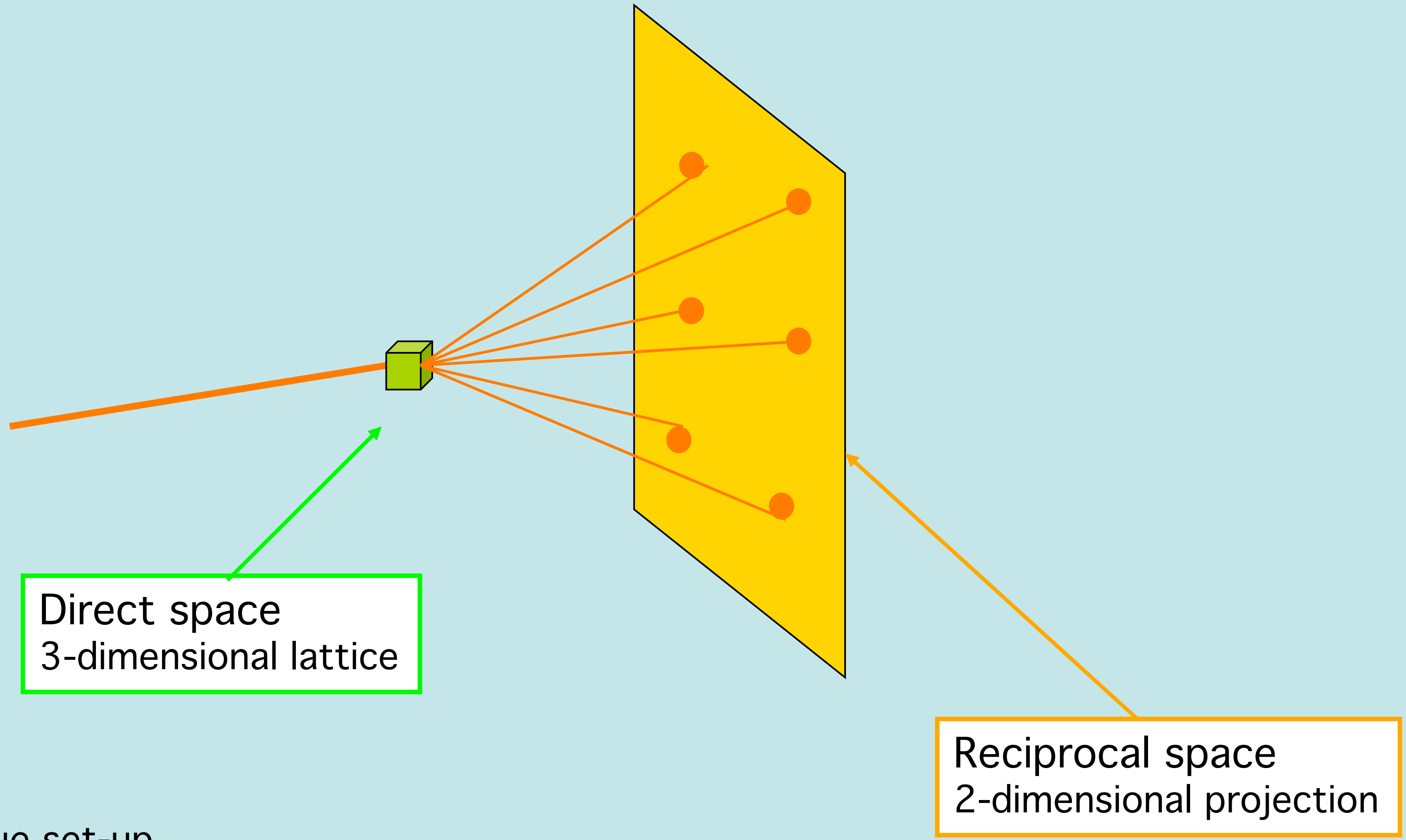

Laue set-up

Basic idea

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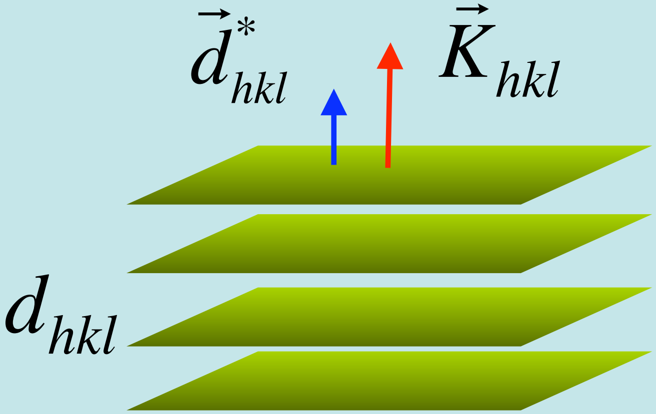
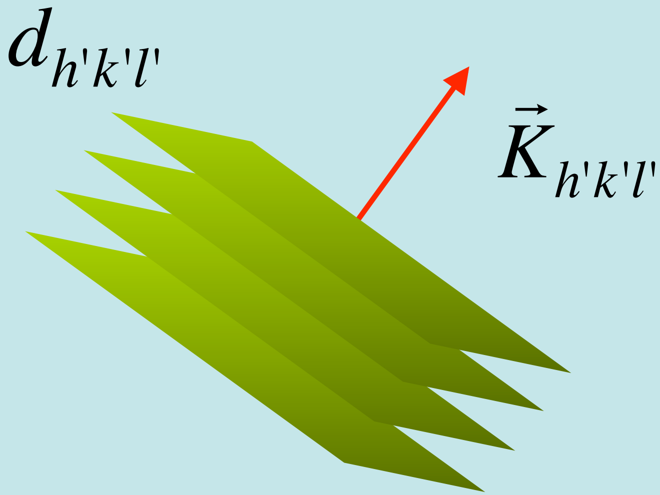
A) Family of planes → wave-vector



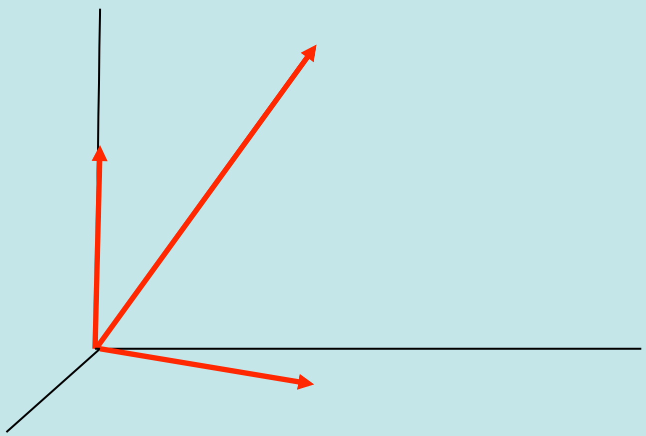
$$\vec{K}_{hkl} = \frac{2\pi}{d_{hkl}}\,\hat{s}$$

$$d^*_{hkl} = \frac{1}{d_{hkl}}$$



B) Wave-vectors → set of points

C) Set of points → lattice



Time periodicity

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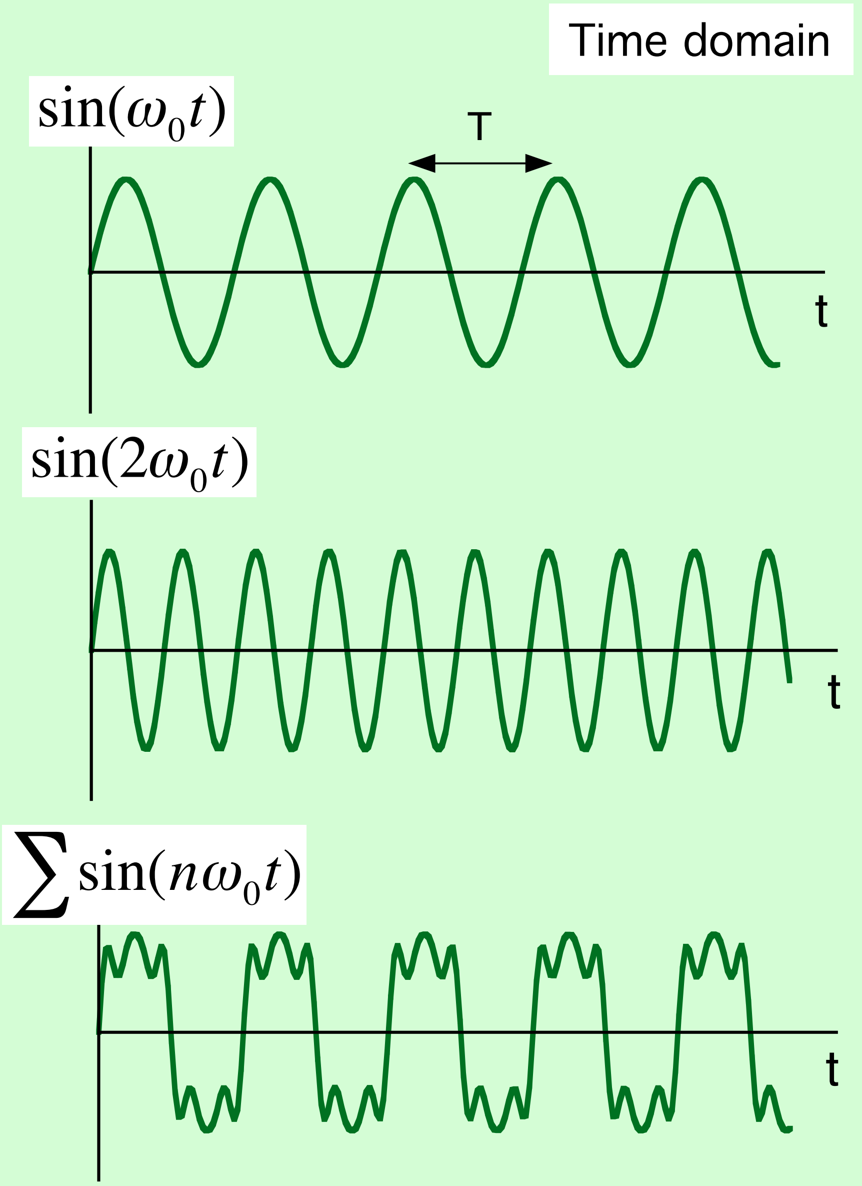

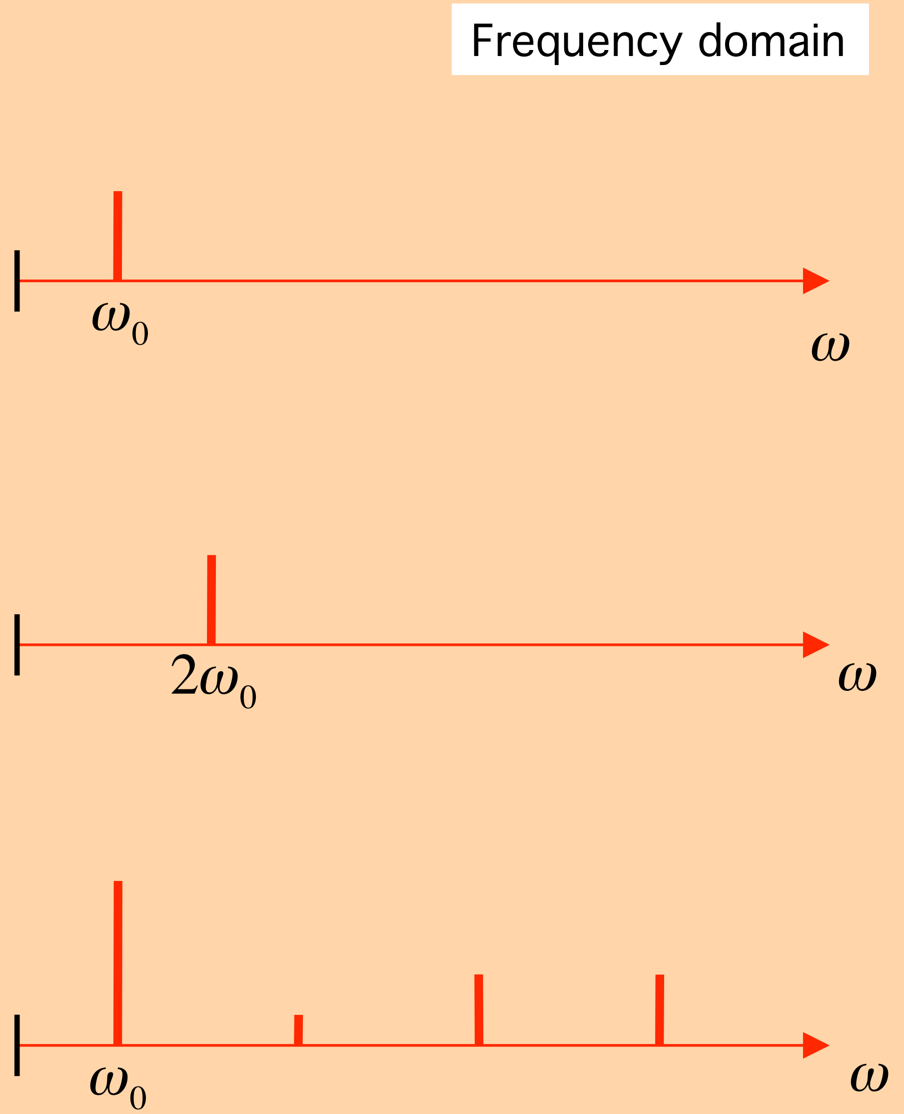

$$\omega = 2\pi\,\nu = 2\pi / T$$

Space periodicity (1D)

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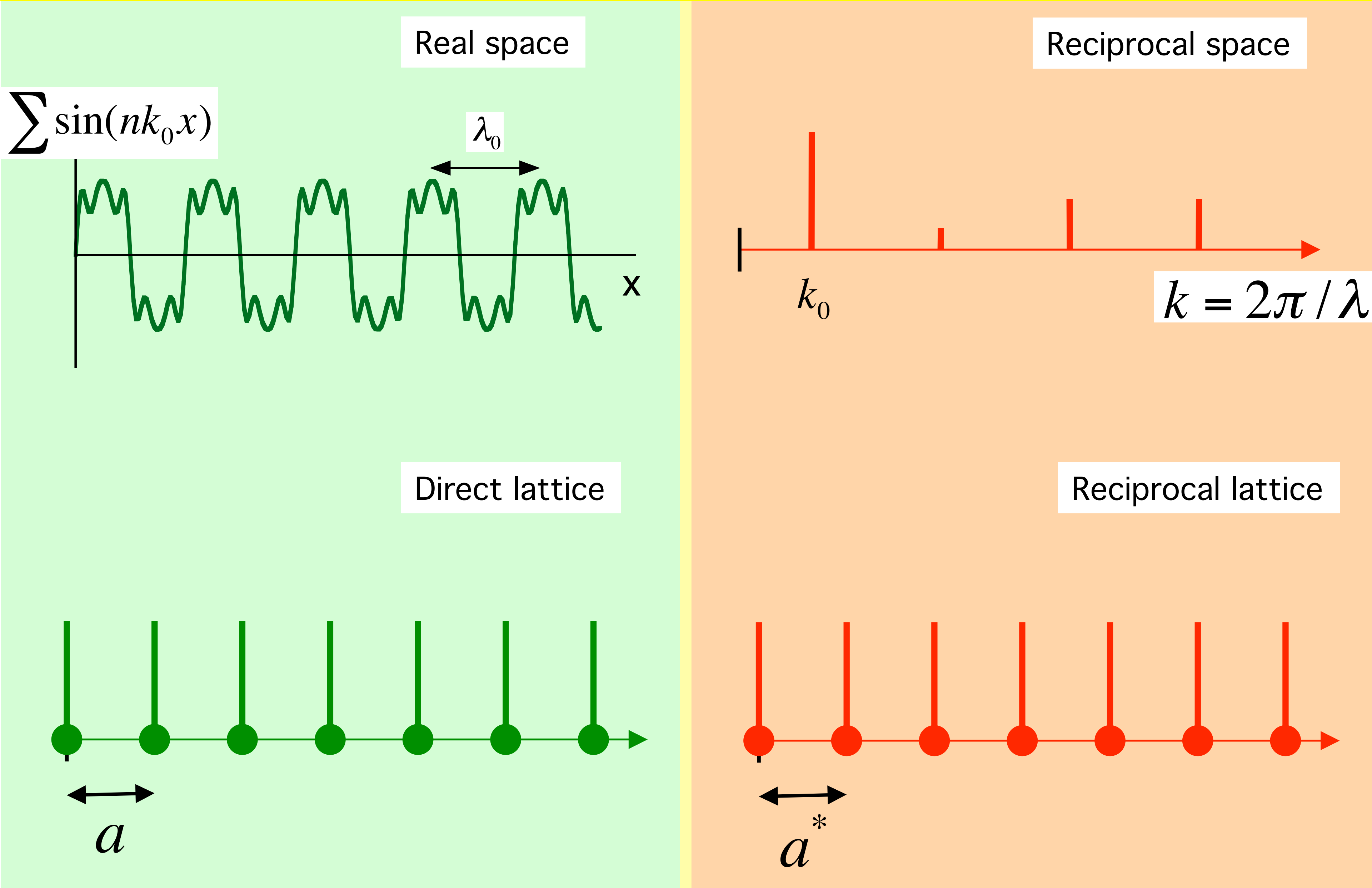

1-D

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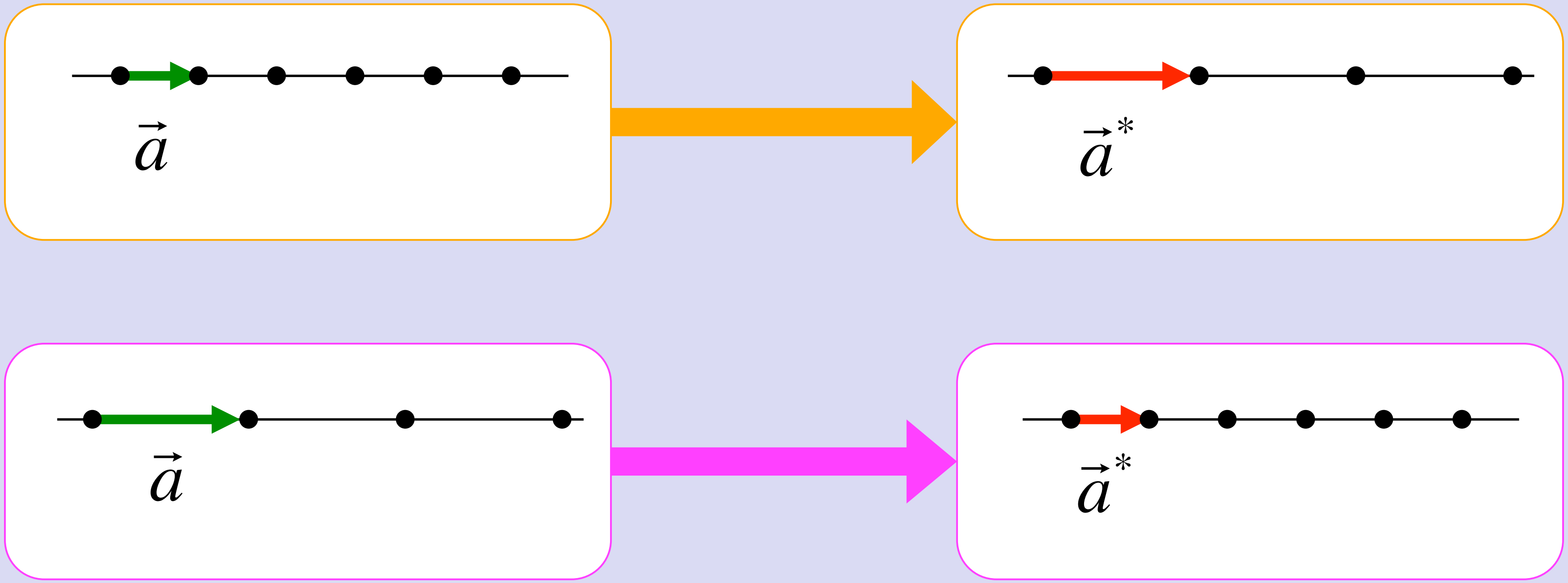
Direct space

Reciprocal space



Convention 1: $a^* = \dfrac{2\pi}{a}$

Convention 2: $a^* = \dfrac{1}{a}$

2-D, rectangular lattice

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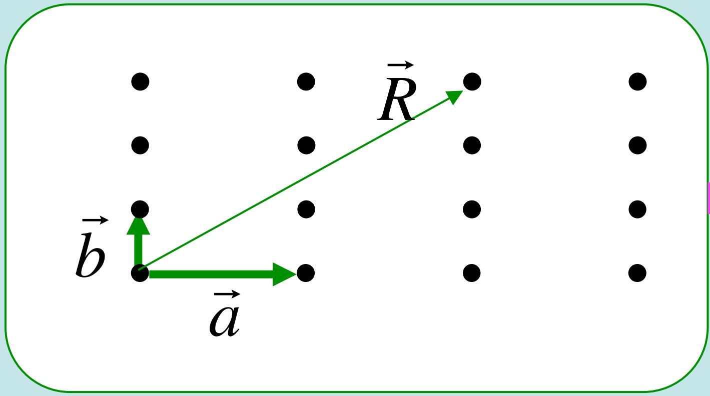
Direct space

Reciprocal space

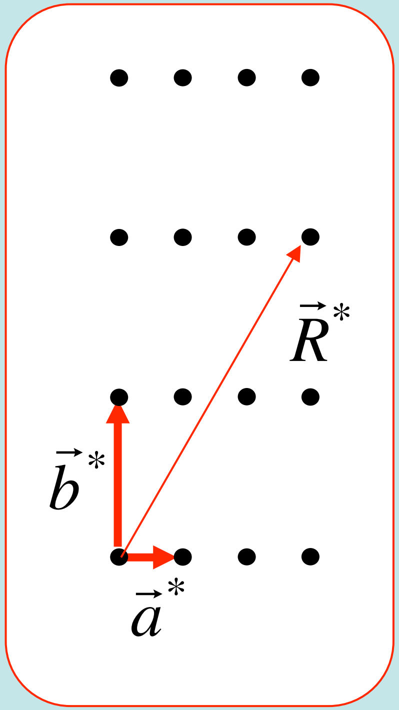


$$a^* = \frac{2\pi}{a} = \frac{2\pi b}{ab}$$

$$b^* = \frac{2\pi}{b} = \frac{2\pi a}{ab}$$

$$\vec{a}^* \perp \vec{b}$$

$$\vec{b}^* \perp \vec{a}$$



$$\vec{R} = n_1\vec{a} + n_2\vec{b}$$

$$\vec{R}^* = m_1\vec{a}^* + m_2\vec{b}^*$$

2-D, oblique lattice

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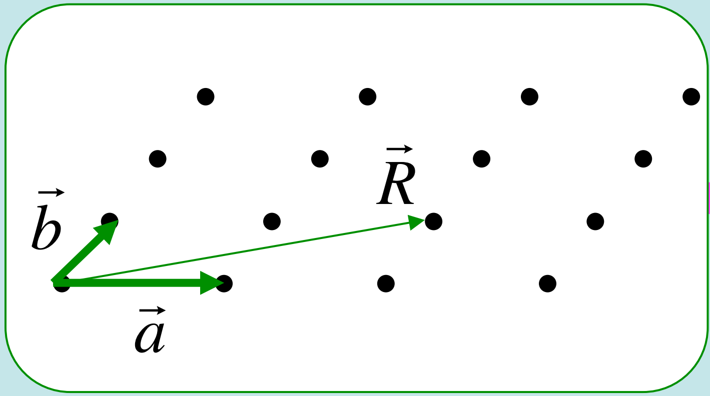
Direct space



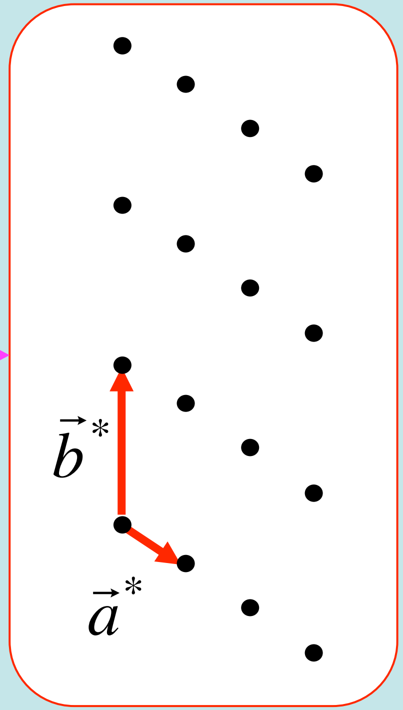
$$a^* = \frac{2\pi}{a\sin\theta} = \frac{2\pi b}{ab\sin\theta}$$

$$b^* = \frac{2\pi}{b\sin\theta} = \frac{2\pi a}{ab\sin\theta}$$

$$\vec{a}^* \perp \vec{b}$$

$$\vec{b}^* \perp \vec{a}$$

Reciprocal space



Cubic lattices (a)

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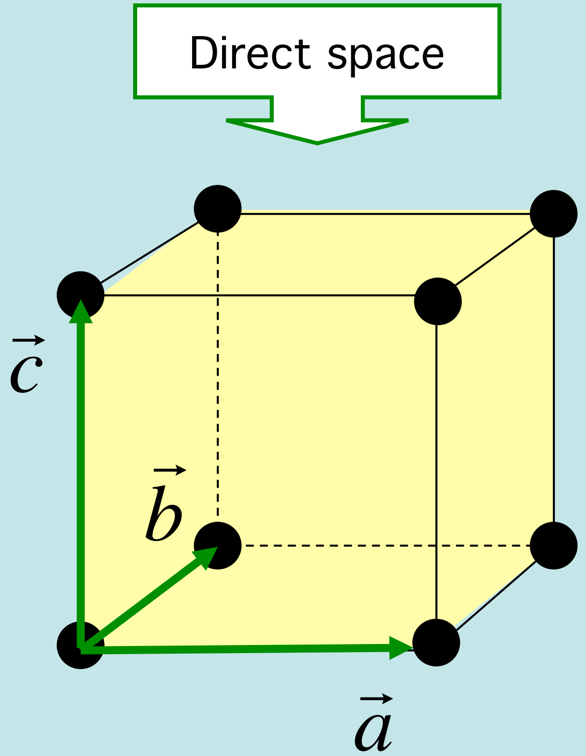

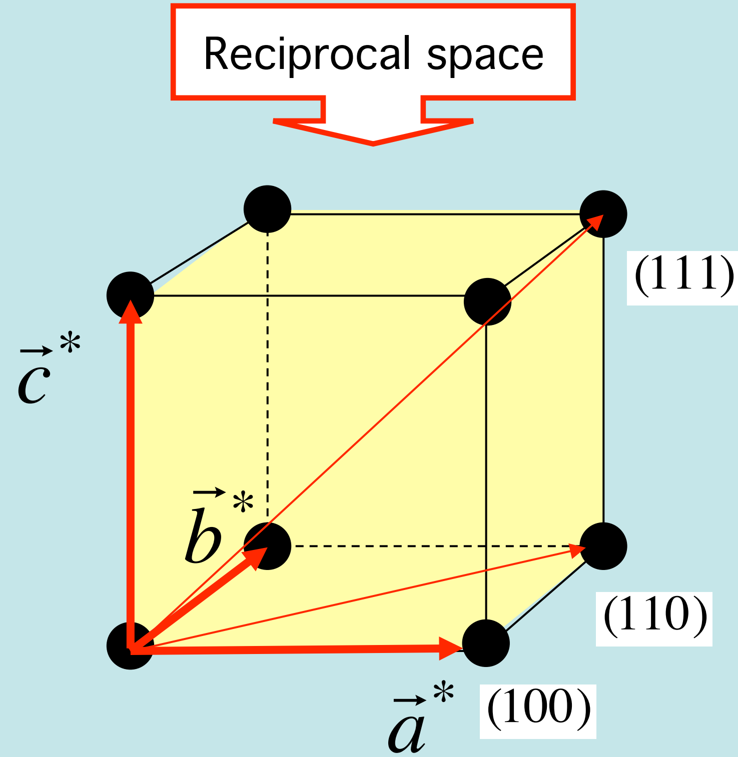

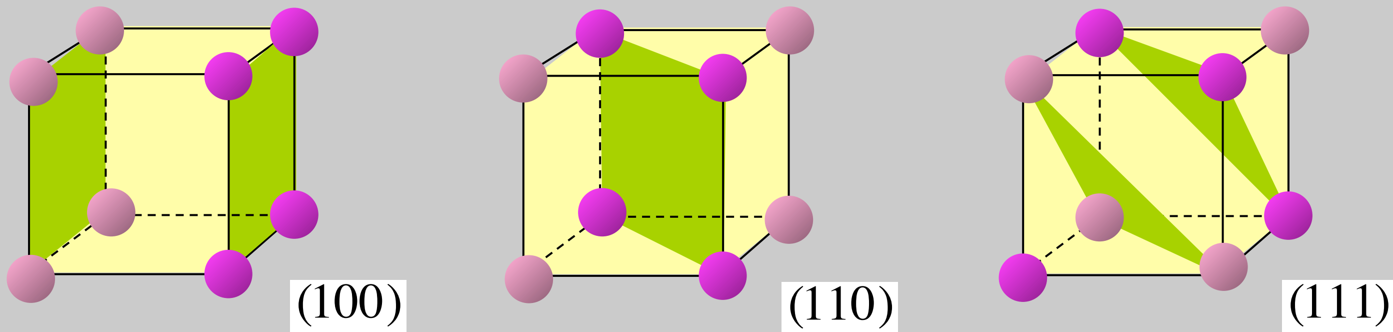

Cubic lattices (b)

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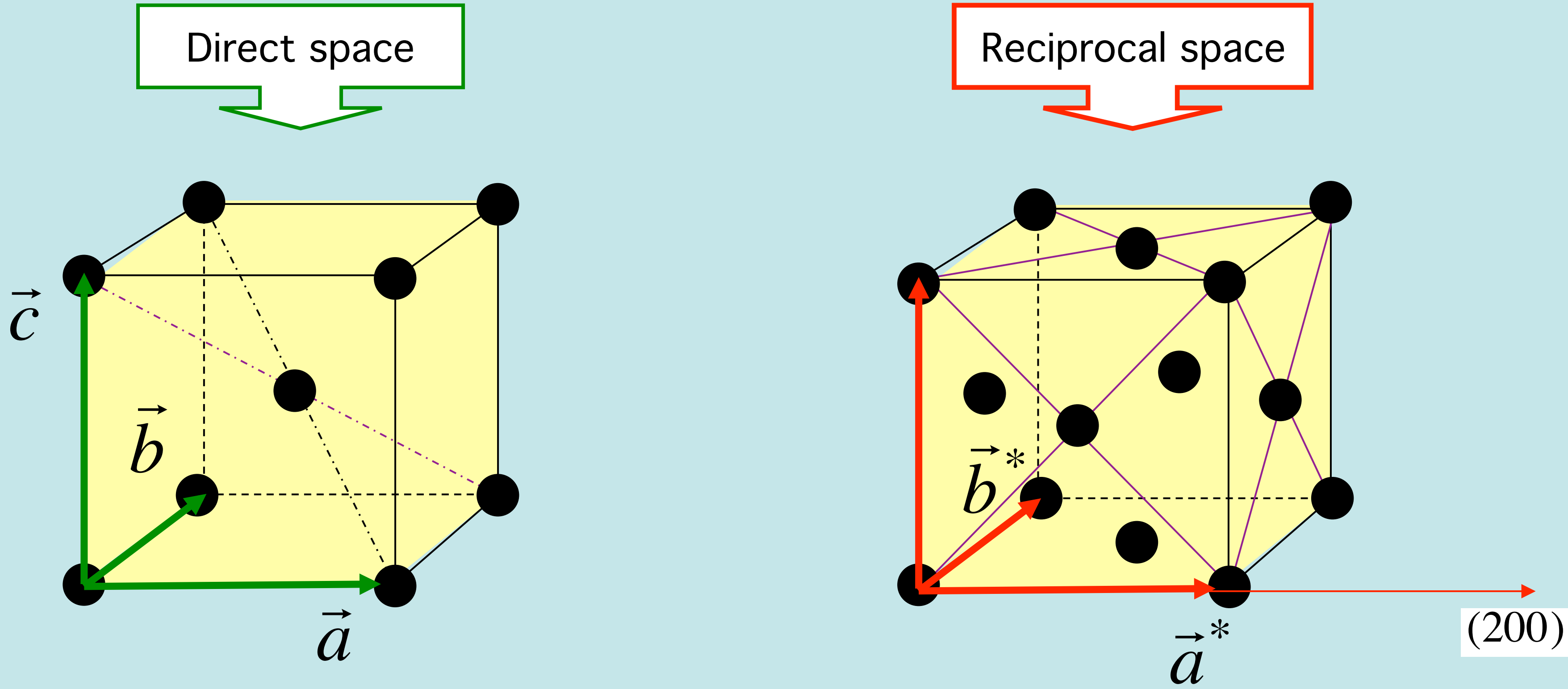

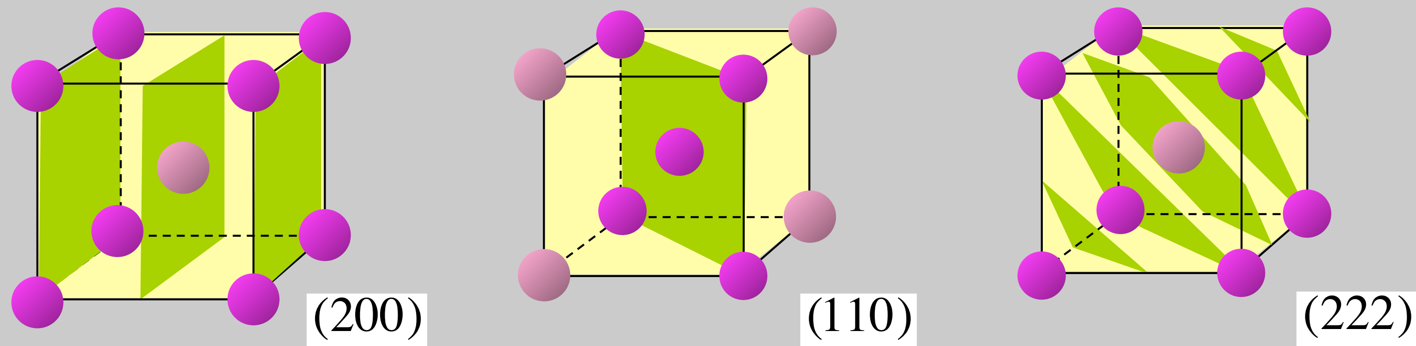

Cubic lattices (c)

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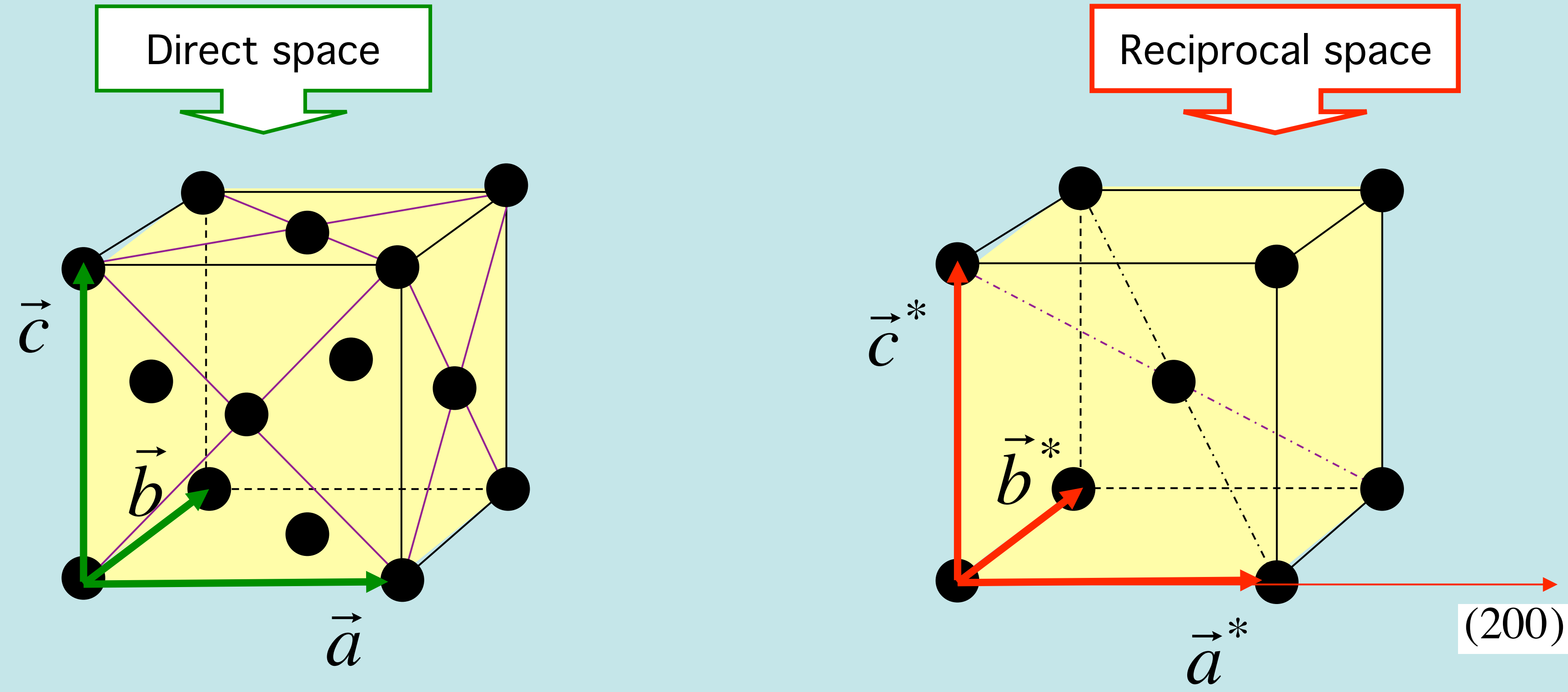

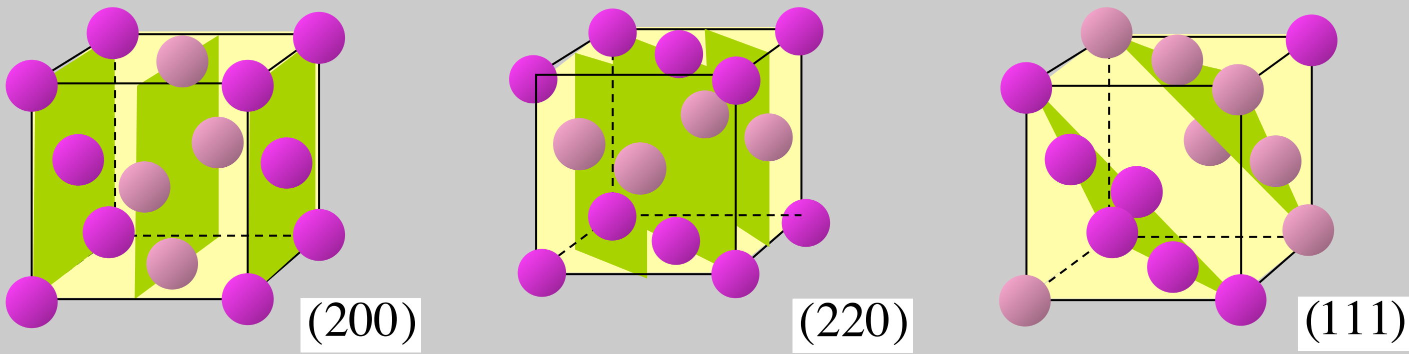

Primitive vectors: general rule

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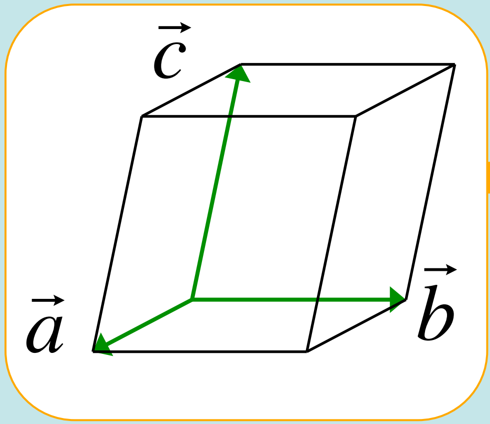
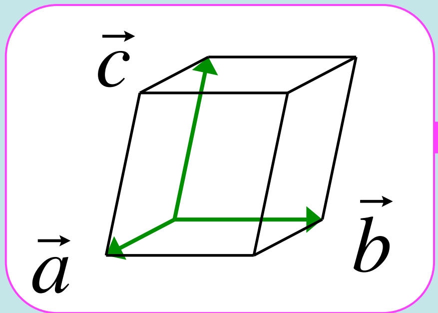
Direct space

Reciprocal space

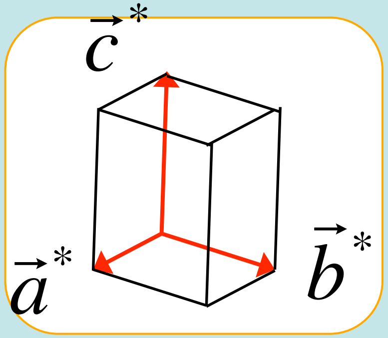


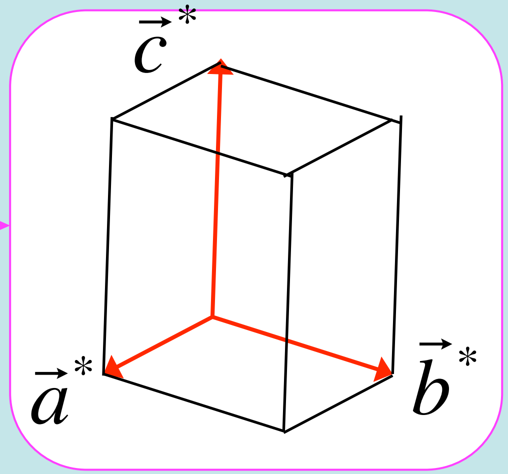


$$\vec{a}^* = 2\pi \frac{\vec{b}\times\vec{c}}{\vec{a}\cdot\left(\vec{b}\times\vec{c}\right)}$$

$$\vec{b}^* = 2\pi \frac{\vec{c}\times\vec{a}}{\vec{a}\cdot\left(\vec{b}\times\vec{c}\right)}$$

$$\vec{c}^* = 2\pi \frac{\vec{a}\times\vec{b}}{\vec{a}\cdot\left(\vec{b}\times\vec{c}\right)}$$





$$\vec{a}\cdot\left(\vec{b}\times\vec{c}\right)$$

Reciprocal lattice and lattice planes

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For any family of lattice planes separated by a distance d there are reciprocal lattice vectors perpendicular to the planes, the shortest of which have a length $2\pi/d$.

For any reciprocal lattice vector **R***,
there is a family of lattice planes normal to **R***
and separated by a distance d,
where $2\pi/d$ is the length of the shortest reciprocal lattice vector
parallel to **R***.

Summary

- Plane waves and wavevector
- Crystalline and non-crystalline materials
- Crystal structure = Bravais lattice + basis
- Bravais lattices: primitive vectors, unit cells (primitive and conventional), classifications
- Crystal structures (sc, bcc, fcc, hcp ...)
- Crystal planes and Miller indices
- Reciprocal lattice

Snow crystals
on an iced lake