Advanced Topics in Condensed Matter

Lecture 2: Crystal lattices and structures

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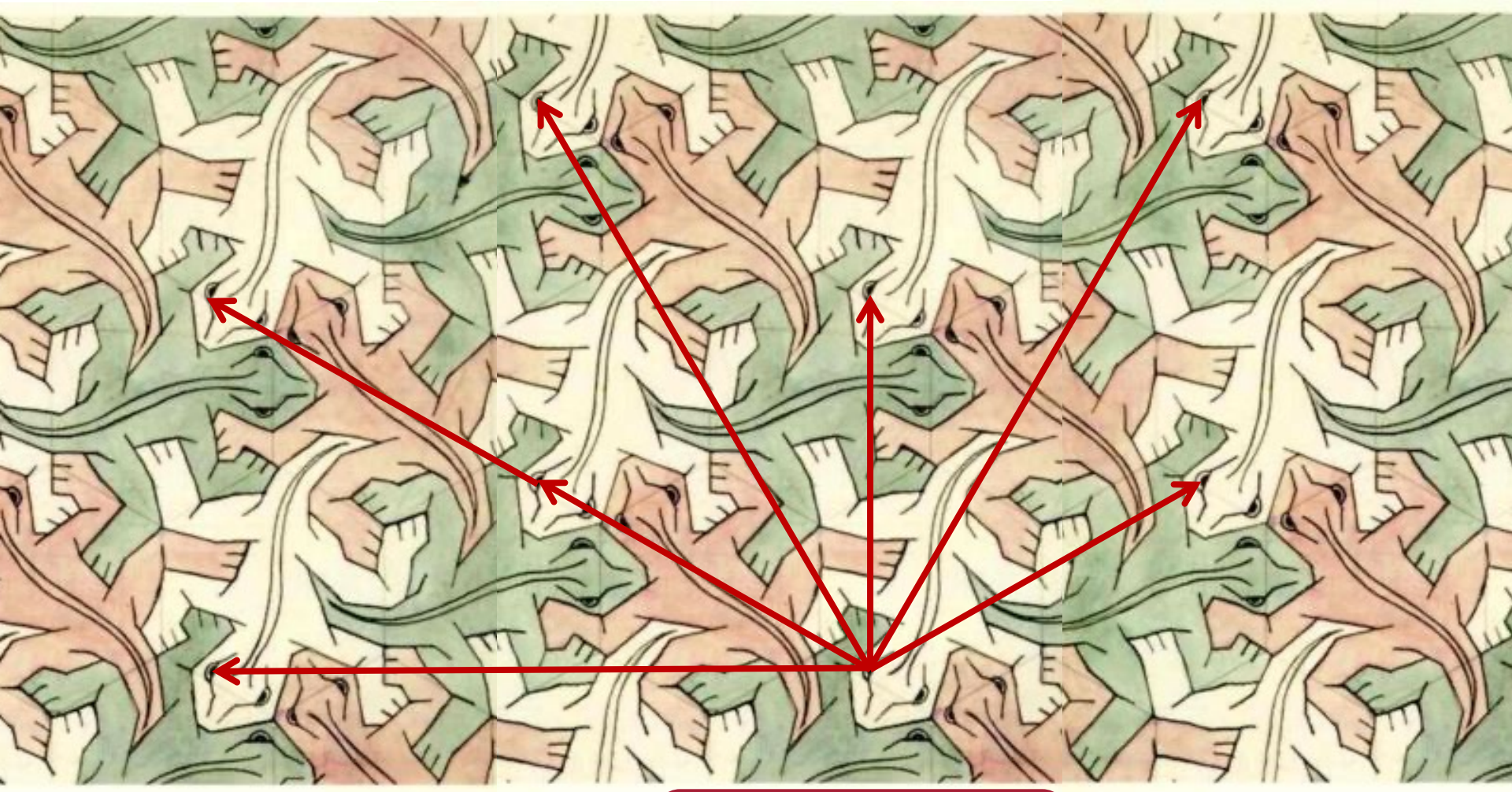
Periodicity

M. C. Escher, Regular Division of the Plane #25 (1939)

Periodicity



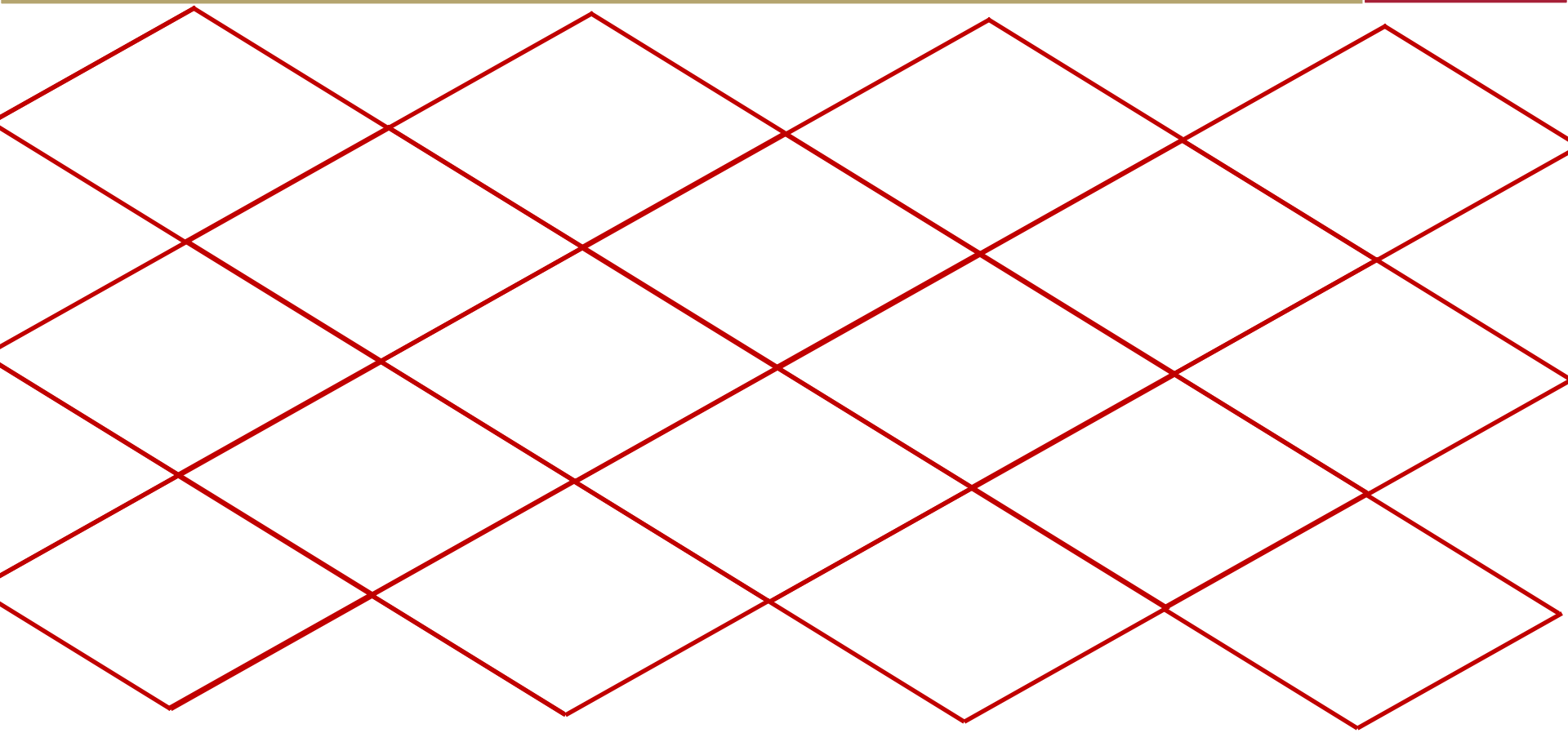
Translation symmetry

M. C. Escher, Regular Division of the Plane #25 (1939)

Periodicity

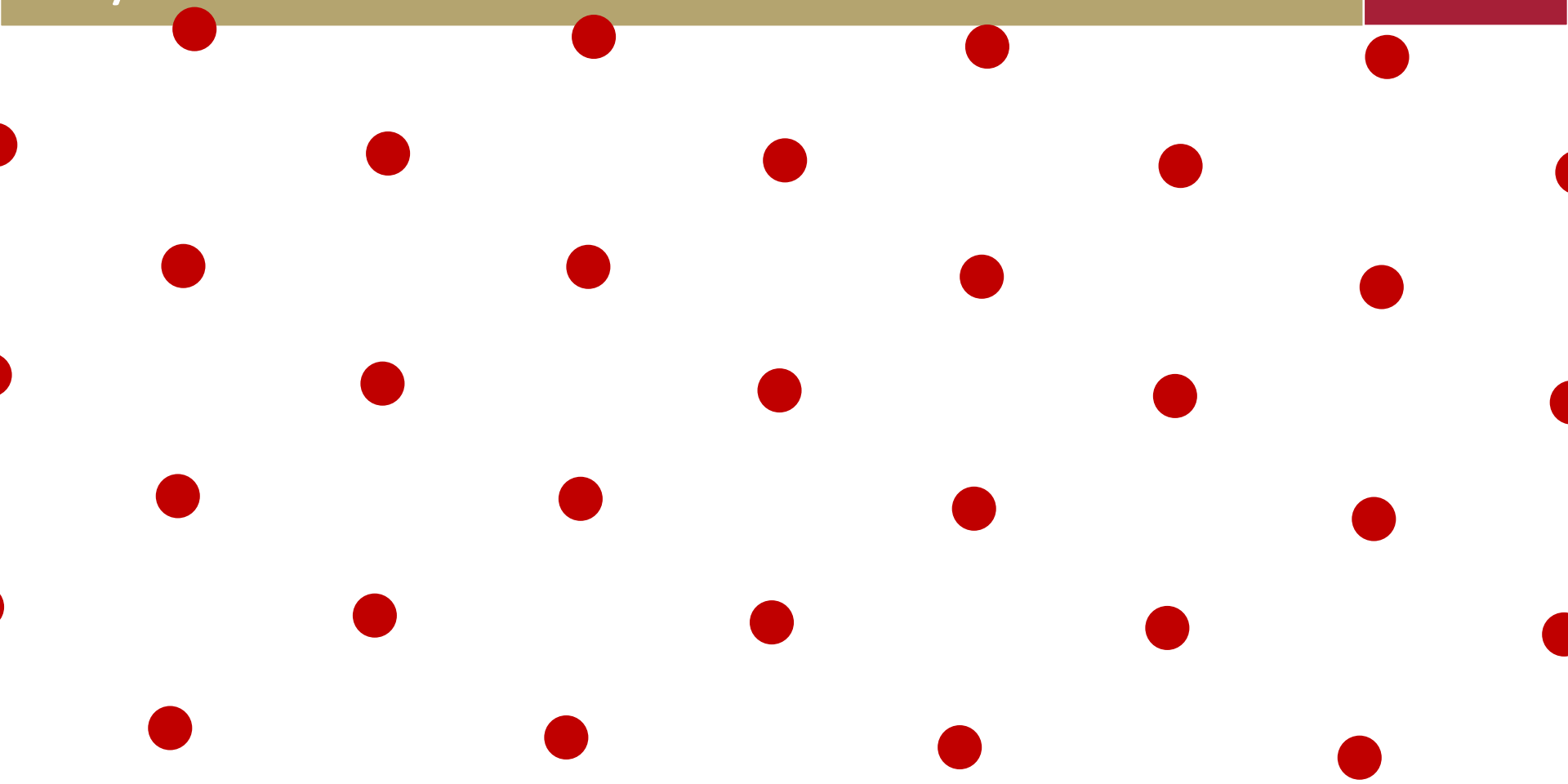
M. C. Escher, Regular Division of the Plane #25 (1939)

Crystal lattice



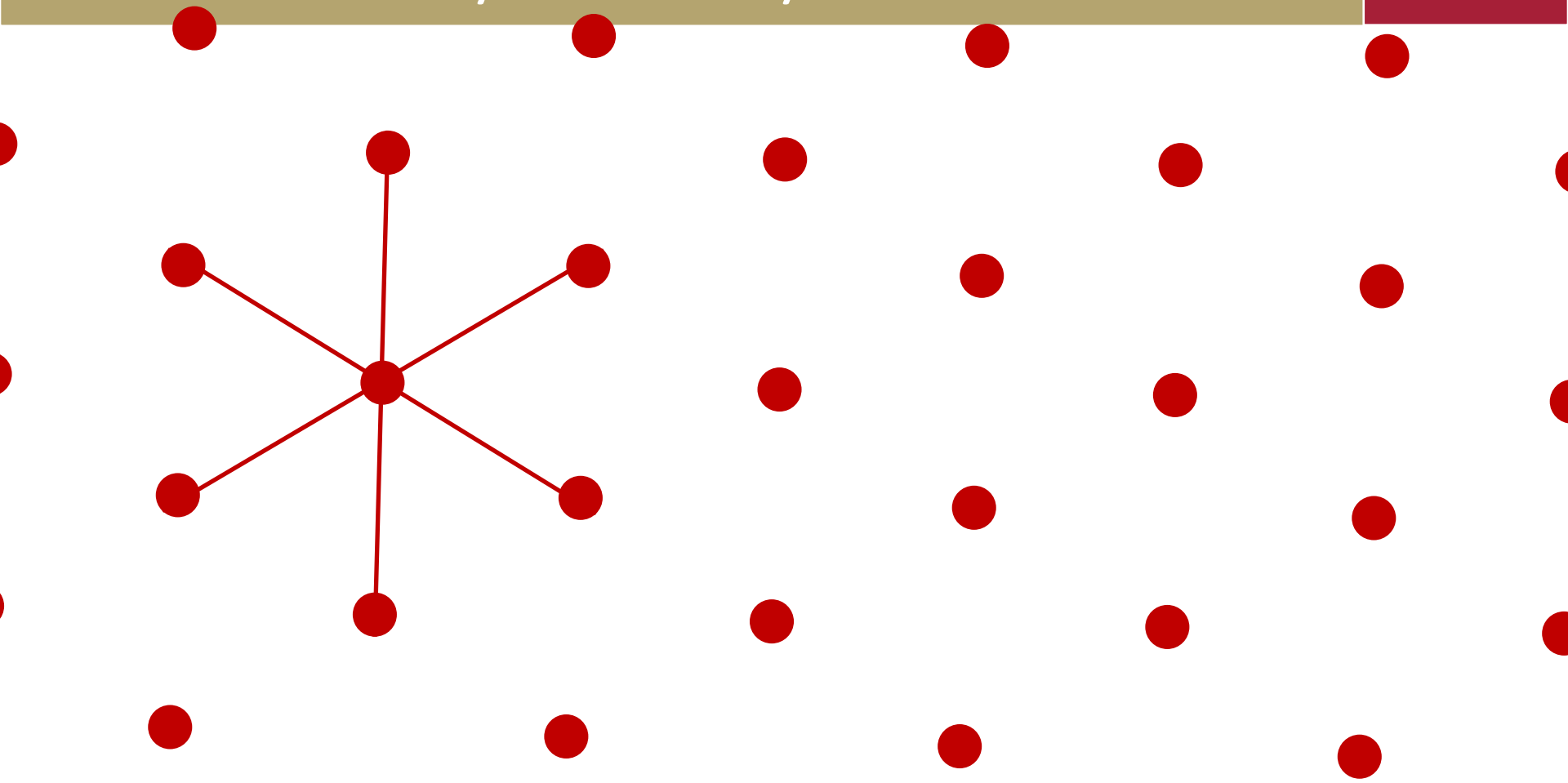
$$\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

Crystal lattice



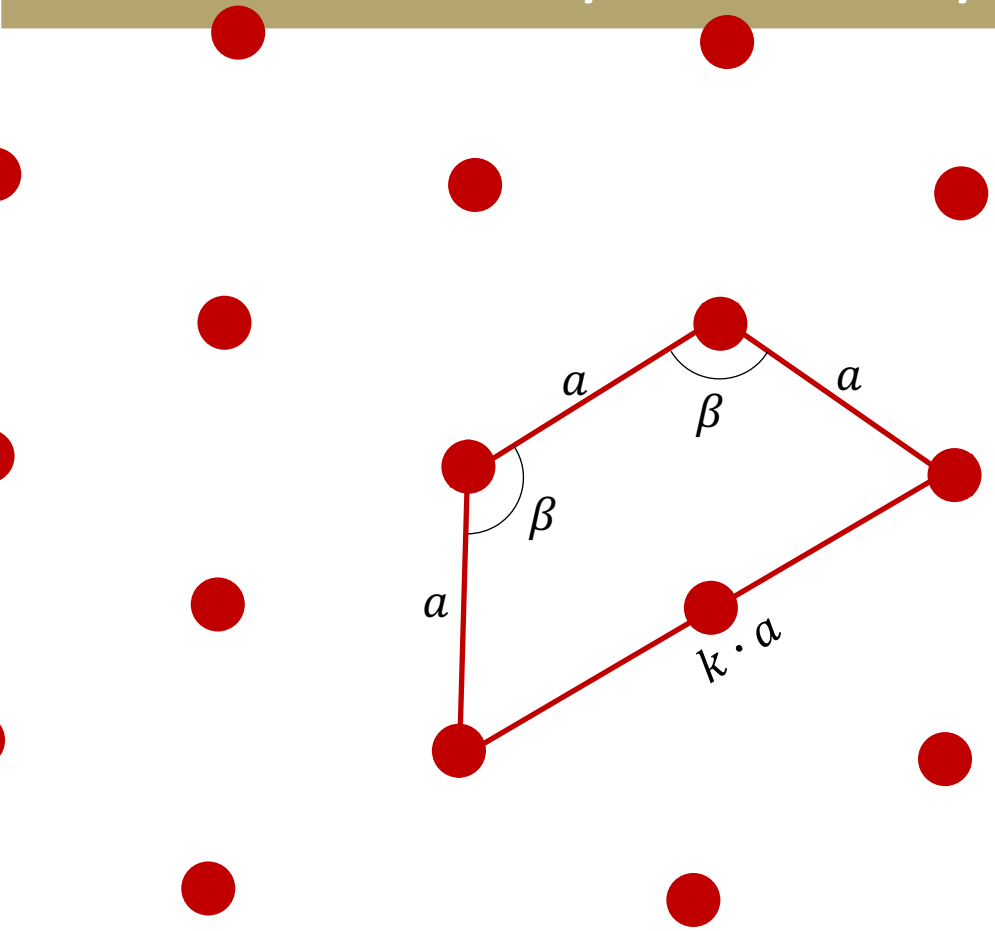
Lattice – an infinite array of discrete points, generated by a set of discrete translation operations: $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

Rotational symmetry



Only rotational axes of orders $n = 1, 2, 3, 4, 6$ are possible

Rotational symmetry



$$ka = a - 2a\cos\beta$$

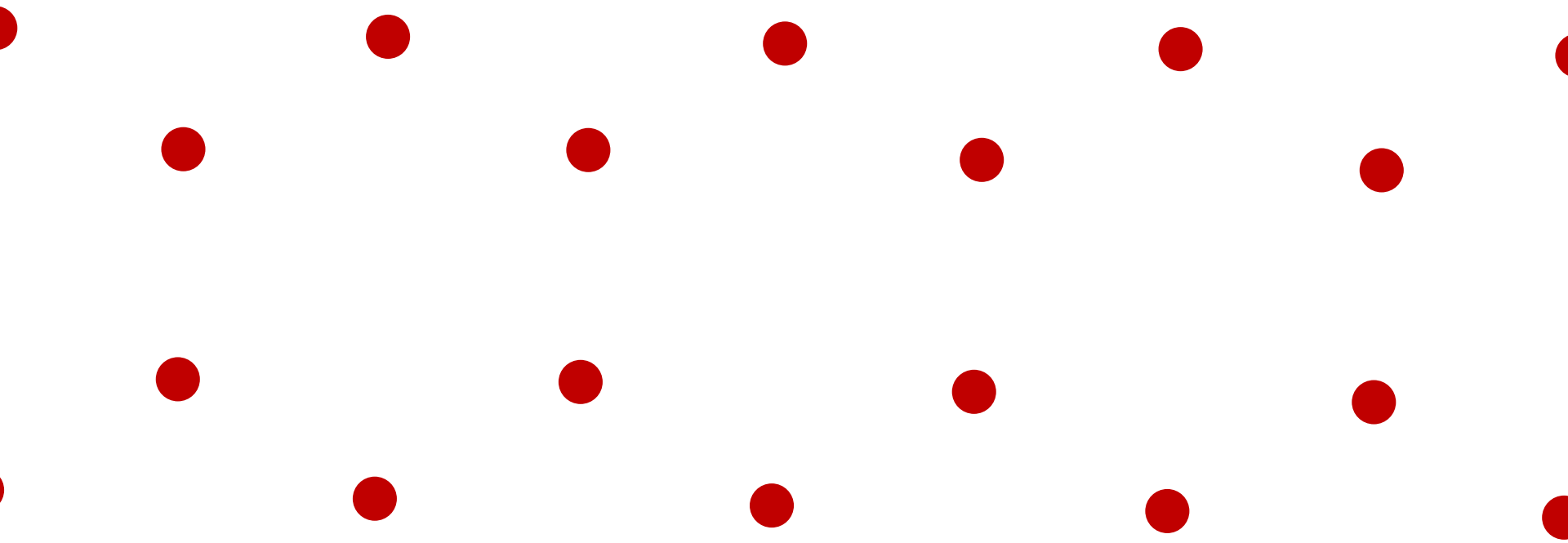
$$\cos\beta = \frac{1-k}{2}$$

$$k = -1, 0, 1, 2, 3$$

$$\beta = 0, \frac{\pi}{3}, \frac{\pi}{2}, \frac{2\pi}{3}, \pi$$

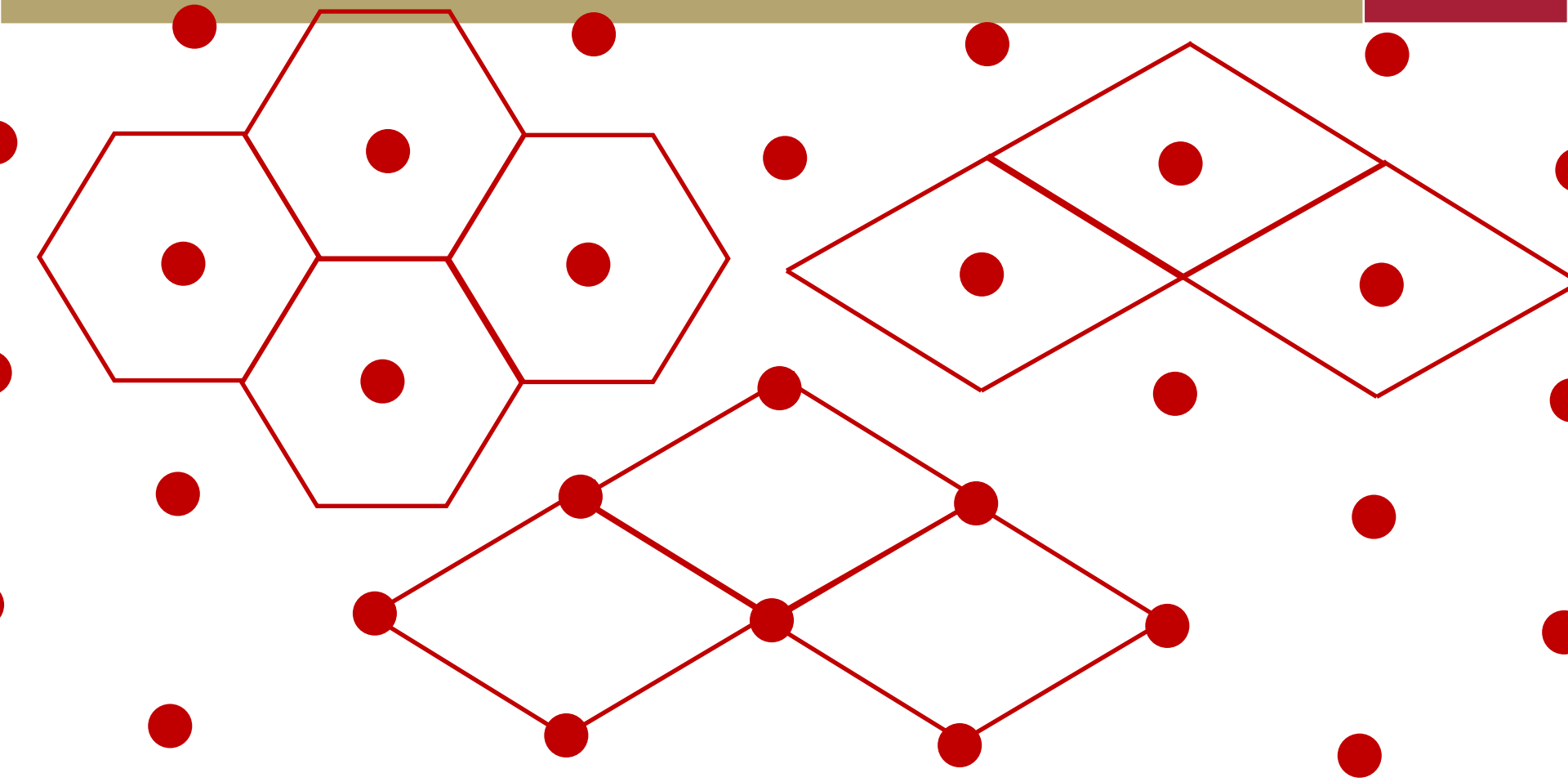
Only rotational axes of orders $n = 1, 2, 3, 4, 6$ are possible

Crystal lattice



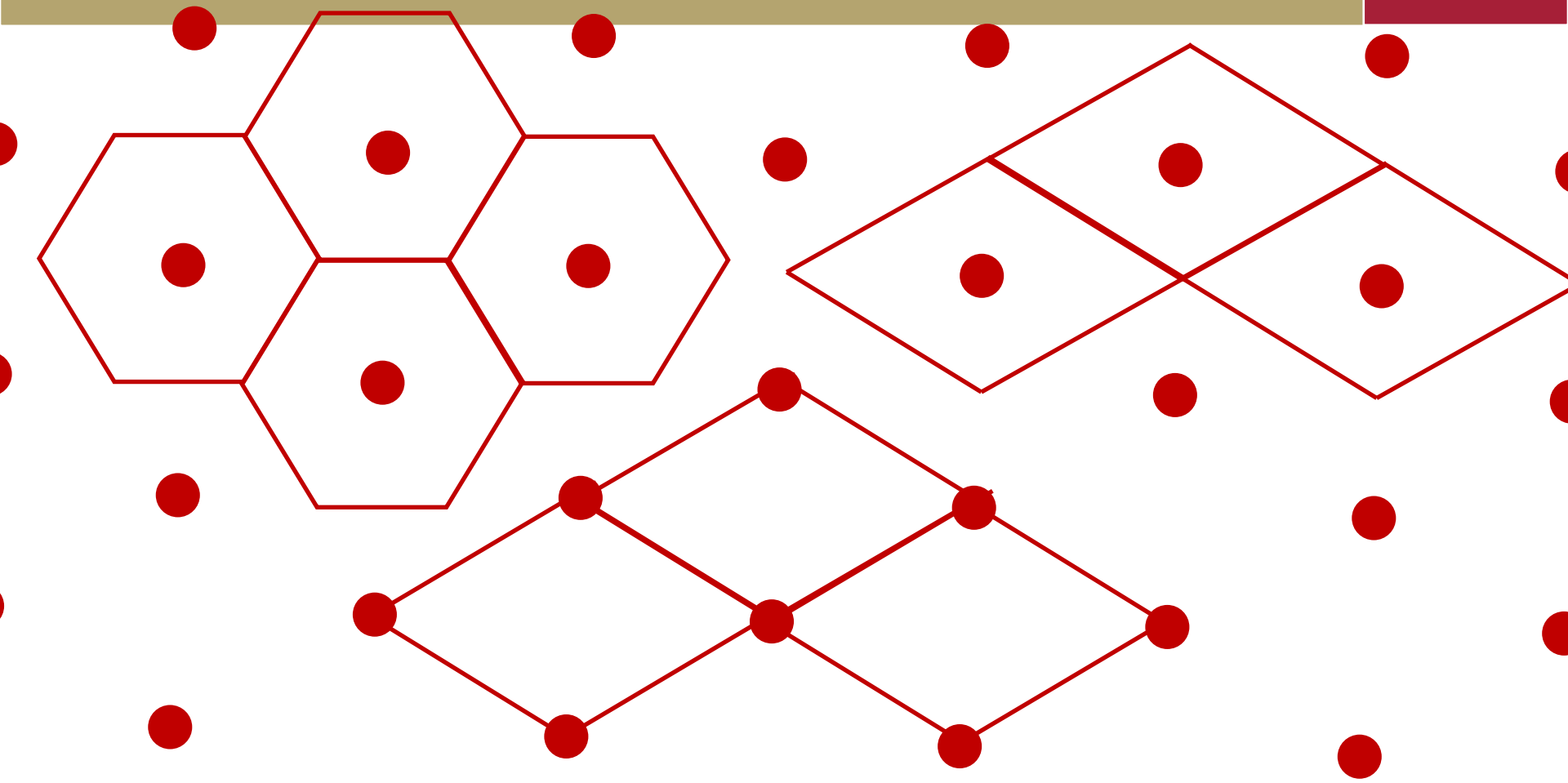
Lattice – an infinite array of discrete points, generated by a set of discrete translation operations: $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

Unit cell



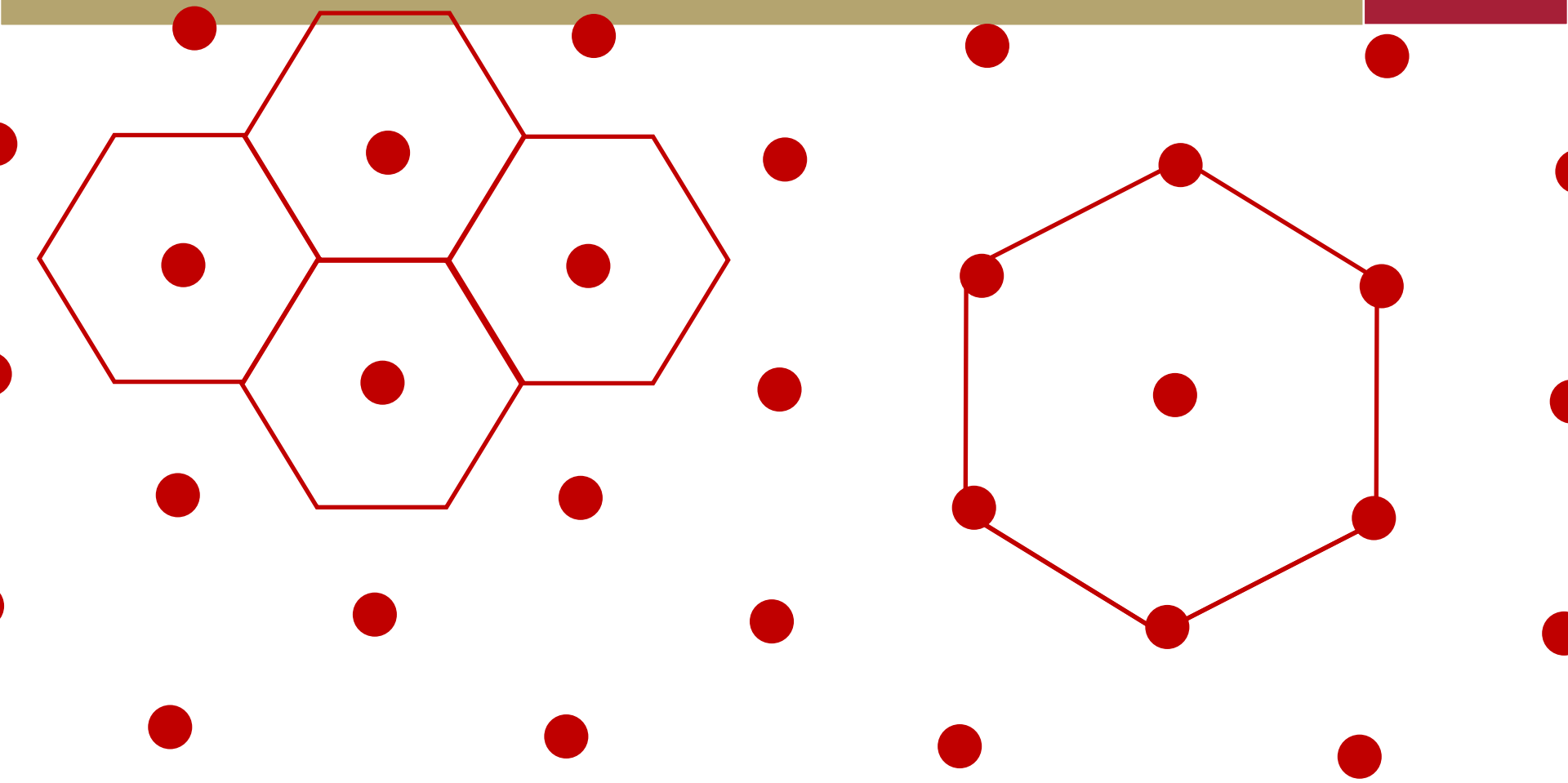
Unit cell – a volume, a repetitive arrangement of which (pure translations, i.e. $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$) can fill the whole space without overlaps and gaps.

Unit cell



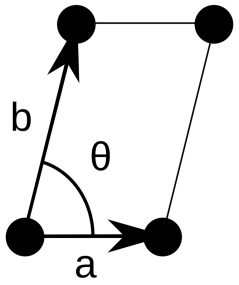
Primitive unit cell – one lattice cite per cell

Unit cell

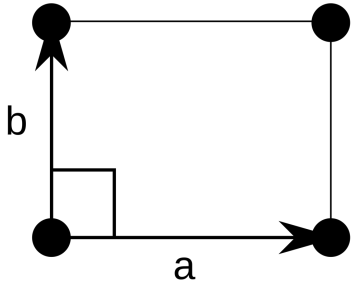


Conventional unit cell – contains the full symmetry of the lattice and may include more than one lattice point

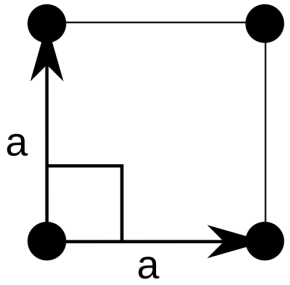
Crystal systems in 2D



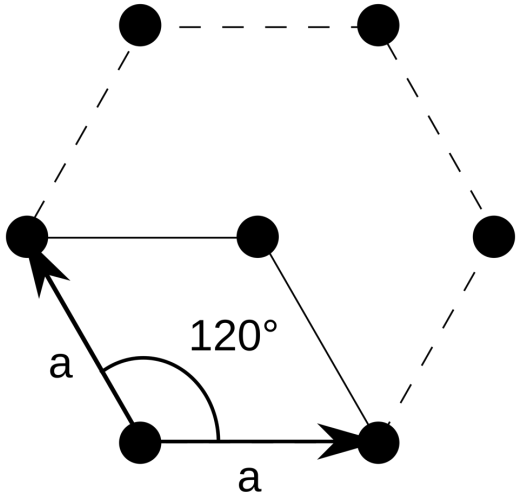
Monoclinic



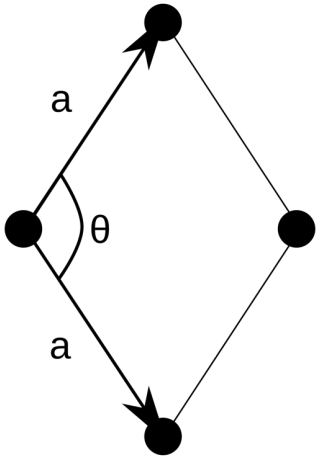
Orthorhombic



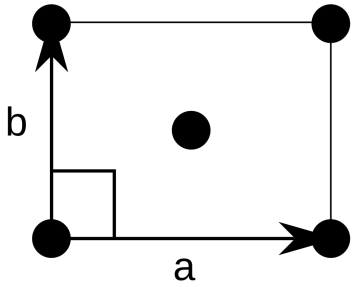
Tetragonal (Square)



Hexagonal



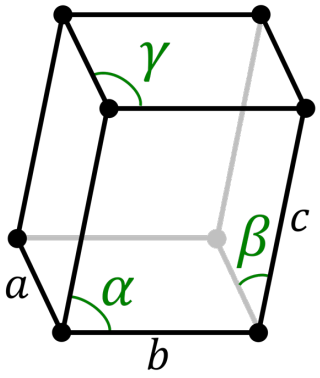
Rhombohedral (primitive)



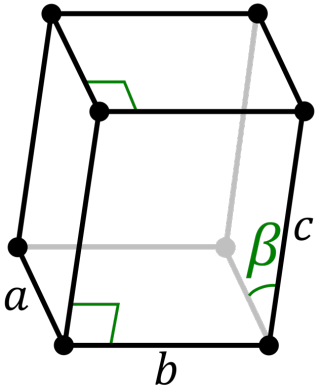
Centered rectangular (conventional)

5 Bravais lattices are possible in 2D.

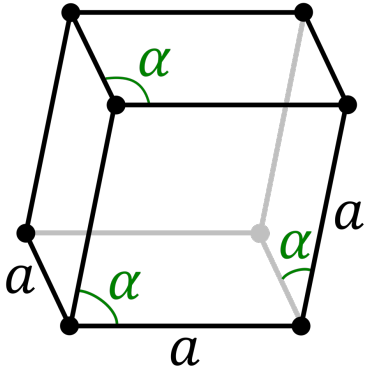
Crystal systems in 3D



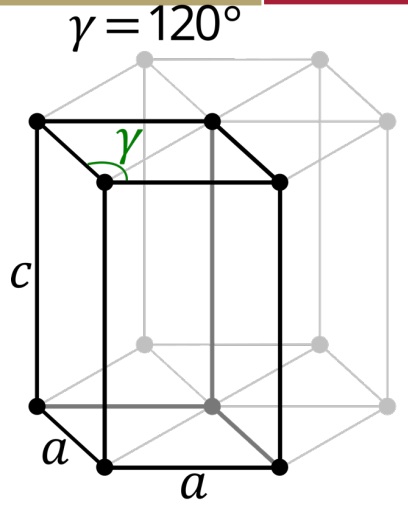
Triclinic



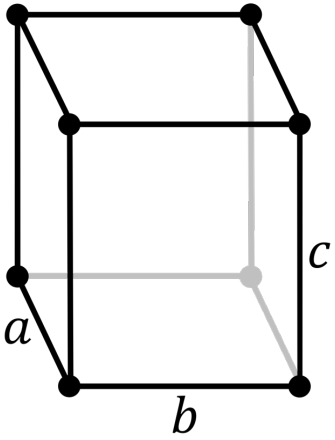
Monoclinic



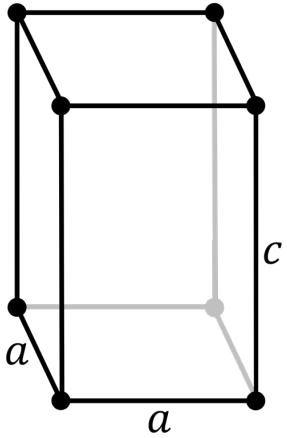
Rhombohedral



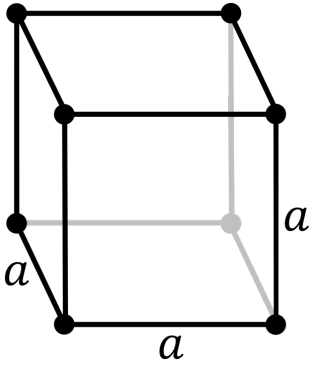
Hexagonal



Orthorhombic



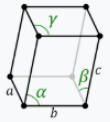
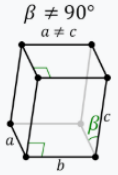
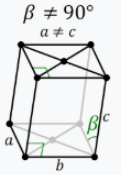
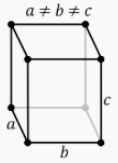
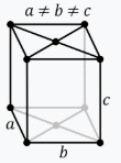
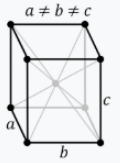
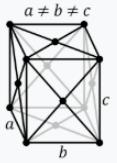
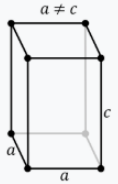
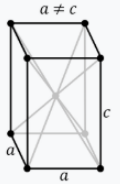
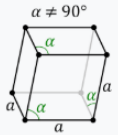
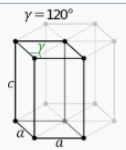
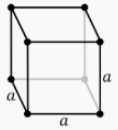
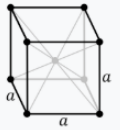
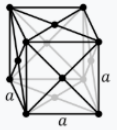
Tetragonal



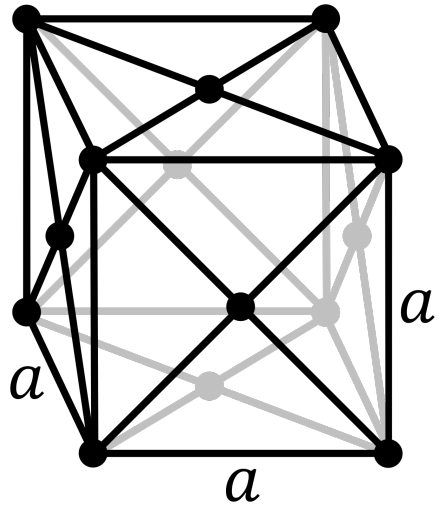
Cubic

Bravais lattices in 3D

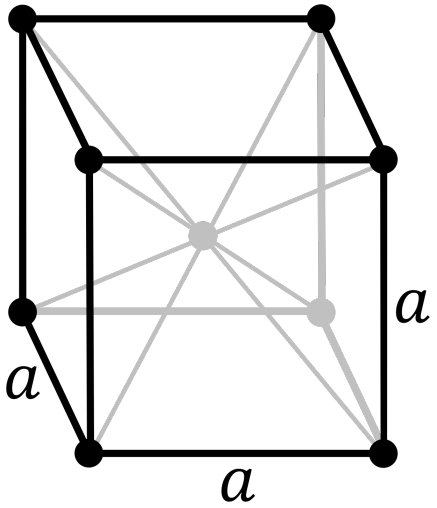
14 Bravais lattices are possible in 3D.

Crystal Family	Lattice System	Schönflies	14 Bravais Lattices			
			Primitive (P)	Base-centered (C)	Body-centered (I)	Face-centered (F)
Triclinic		C_i				
Monoclinic		C_{2h}				
Orthorhombic		D_{2h}				
Tetragonal		D_{4h}				
Hexagonal	Rhombohedral	D_{3d}				
	Hexagonal	D_{6h}				
Cubic		O_h				

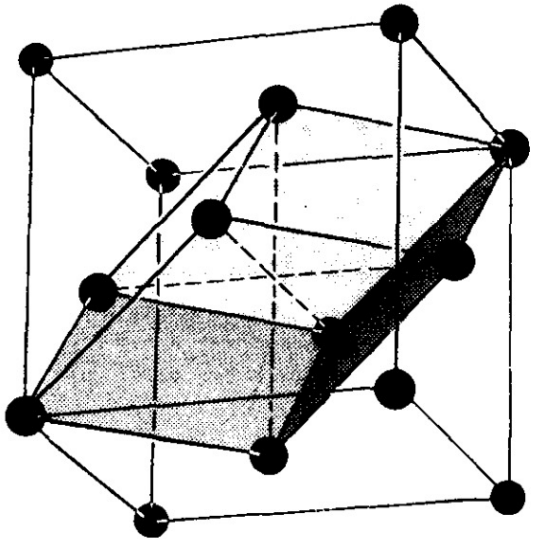
Primitive unit cells for cubic lattices

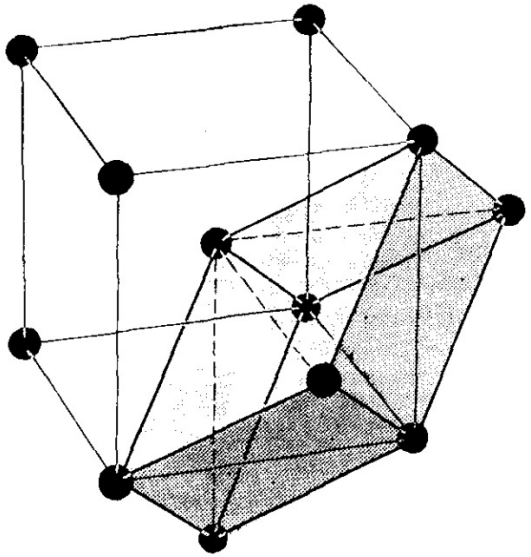


Face Centered Cubic (FCC)

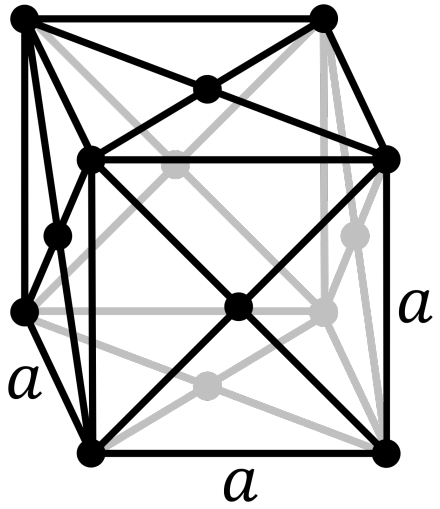


Body Centered Cubic (BCC)

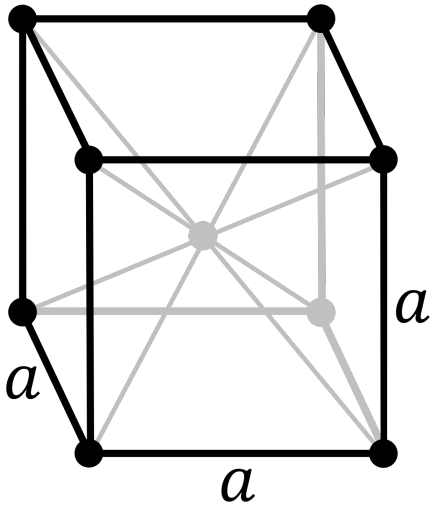




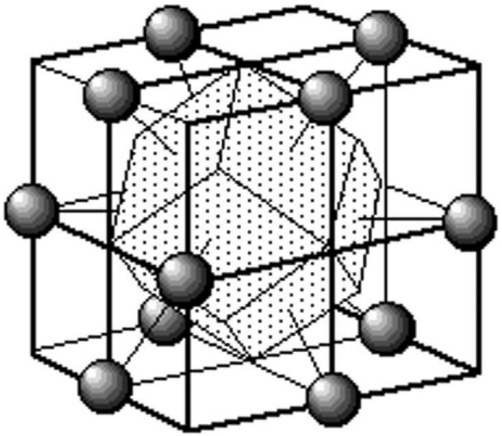
Primitive unit cells for cubic lattices



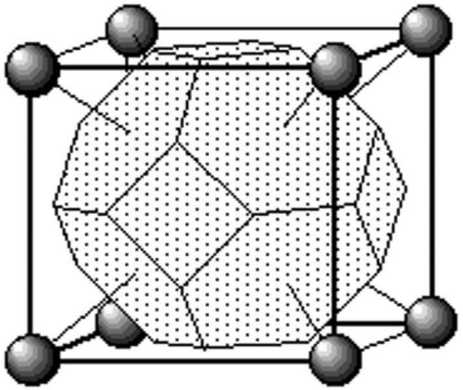
Face Centered Cubic (FCC)



Body Centered Cubic (BCC)



rhombic dodecahedron

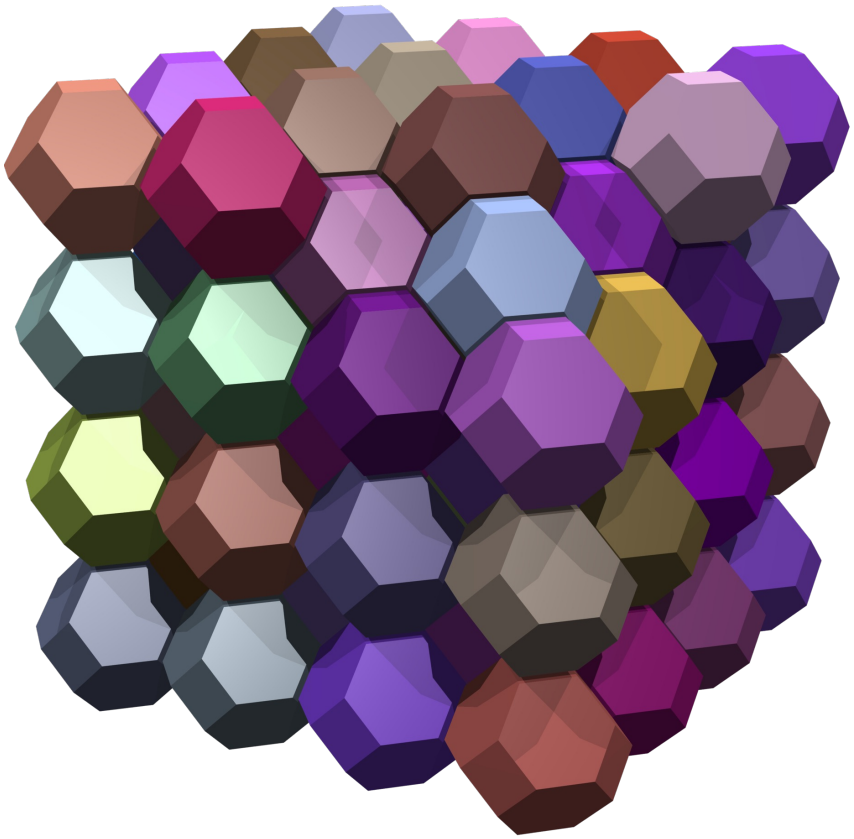


truncated octahedron

Primitive unit cells for cubic lattices

Face Centered Cubic (FCC)

Body Centered Cubic (BCC)

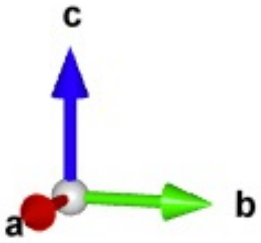


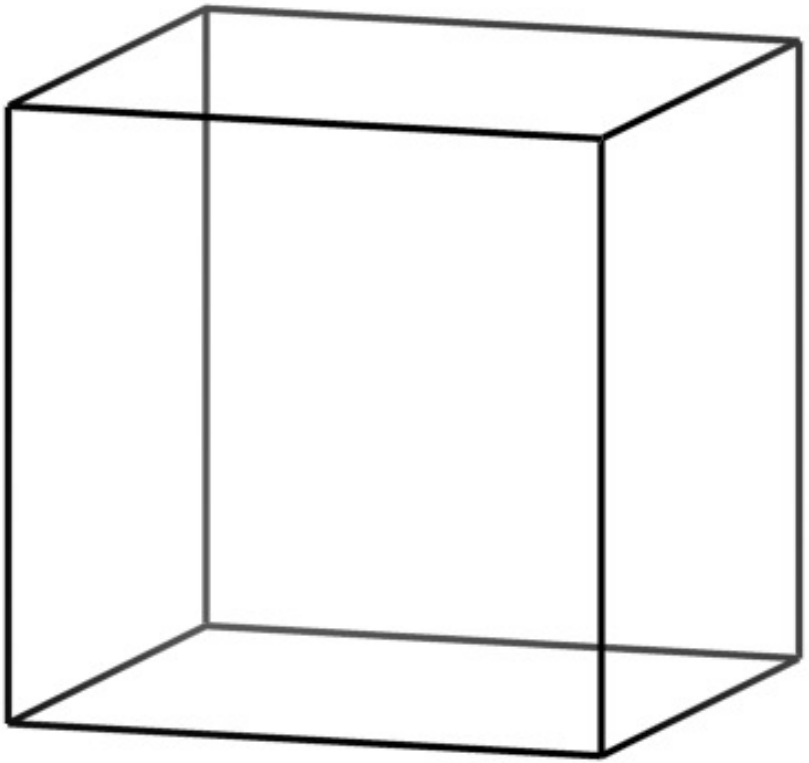
Building a crystal of LaB_6

1. Unit cell parameters

cubic unit cell: $a = b = c = 4.15$ Å

$\alpha = \beta = \gamma = 90°$



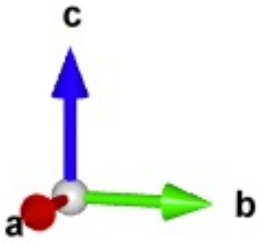


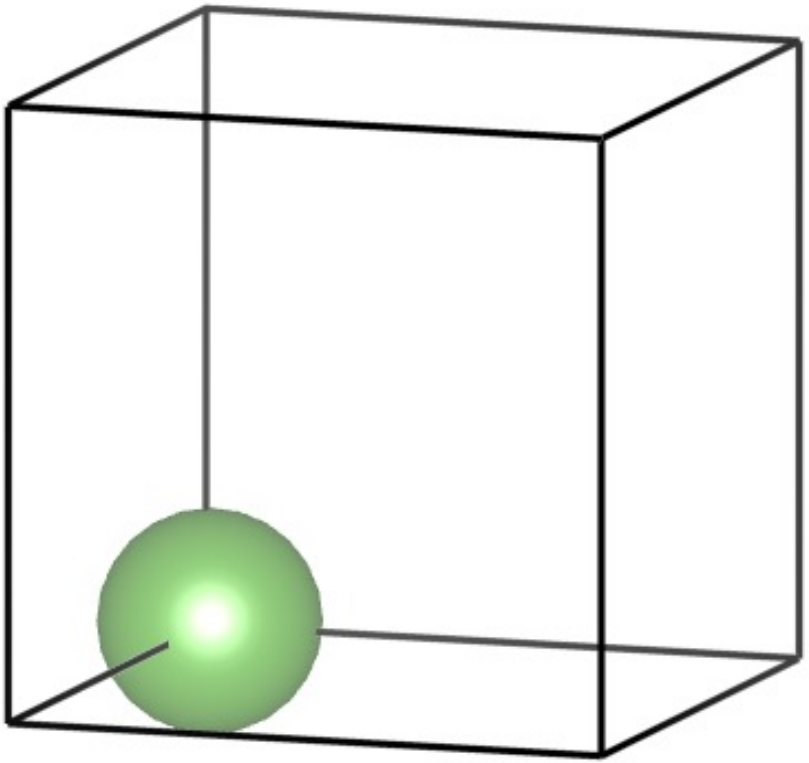
Building a crystal of LaB_6

2. Locating atoms within the unit cell

La:

$$\vec{r} = 0 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 0 \cdot \vec{a}_3 = (0,0,0)$$





Building a crystal of LaB_6

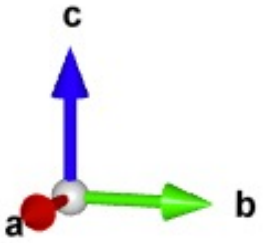
2. Locating atoms within the unit cell

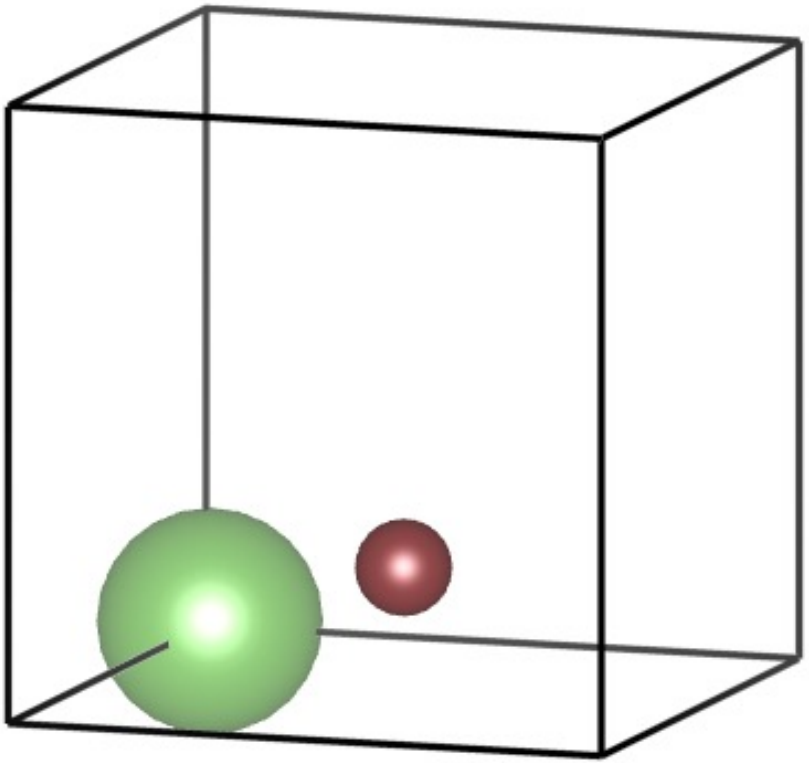
La:

$$\vec{r} = 0 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 0 \cdot \vec{a}_3 = (0,0,0)$$

B:

$$\vec{r}_1 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{5} \cdot \vec{a}_3 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{5})$$





Building a crystal of LaB_6

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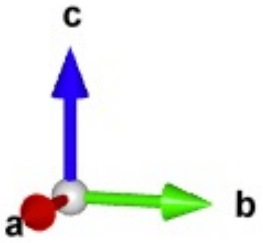
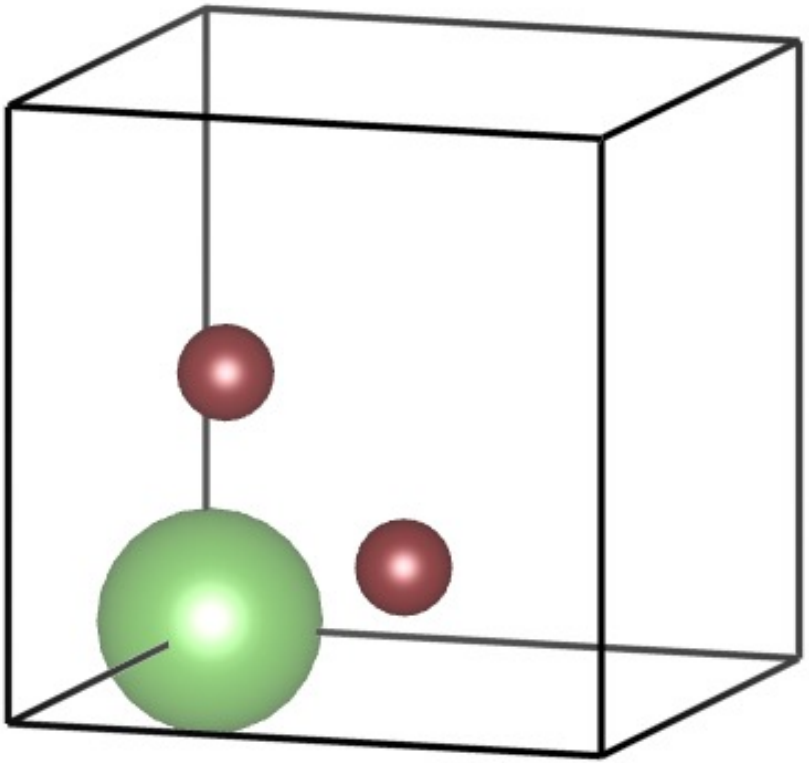
B:

$$\vec{r}_1 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{5} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{5}\right)$$

$$\vec{r}_2 = \frac{1}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{5}, \frac{1}{2}, \frac{1}{2}\right)$$





Building a crystal of LaB_6

2. Locating atoms within the unit cell

La:

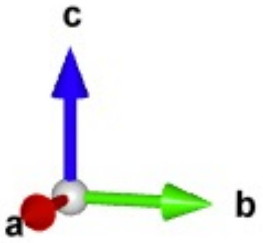
$$\vec{r} = 0 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 0 \cdot \vec{a}_3 = (0,0,0)$$

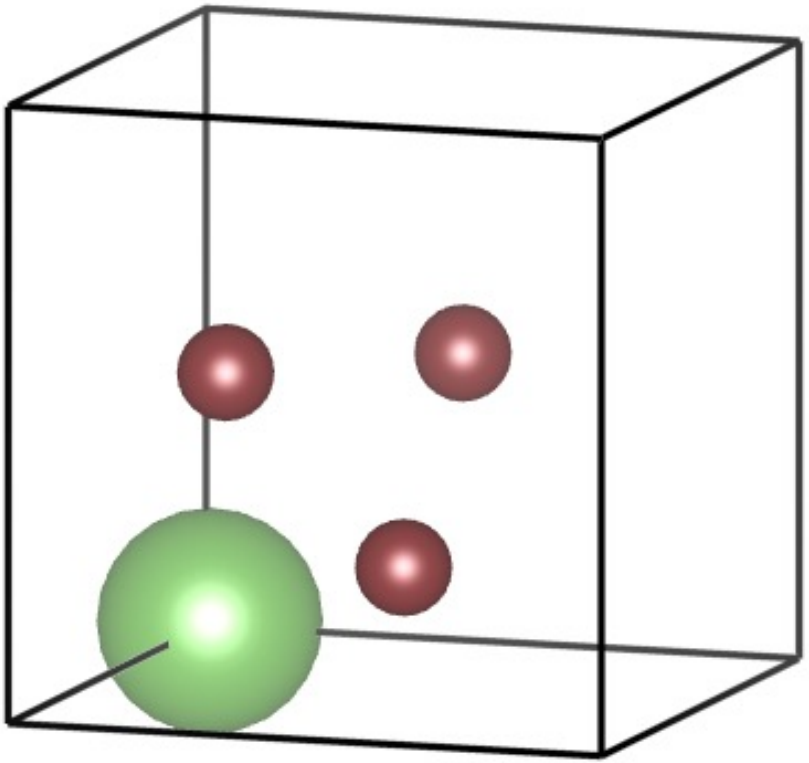
B:

$$\vec{r}_1 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{5} \cdot \vec{a}_3 = (\frac{1}{2}, \frac{1}{2}, \frac{1}{5})$$

$$\vec{r}_2 = \frac{1}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = (\frac{1}{5}, \frac{1}{2}, \frac{1}{2})$$

$$\vec{r}_3 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{5} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = (\frac{1}{2}, \frac{1}{5}, \frac{1}{2})$$





Building a crystal of LaB_6

2. Locating atoms within the unit cell

La:

$$\vec{r} = 0 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 0 \cdot \vec{a}_3 = (0,0,0)$$

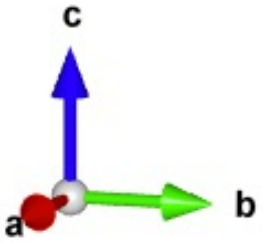
B:

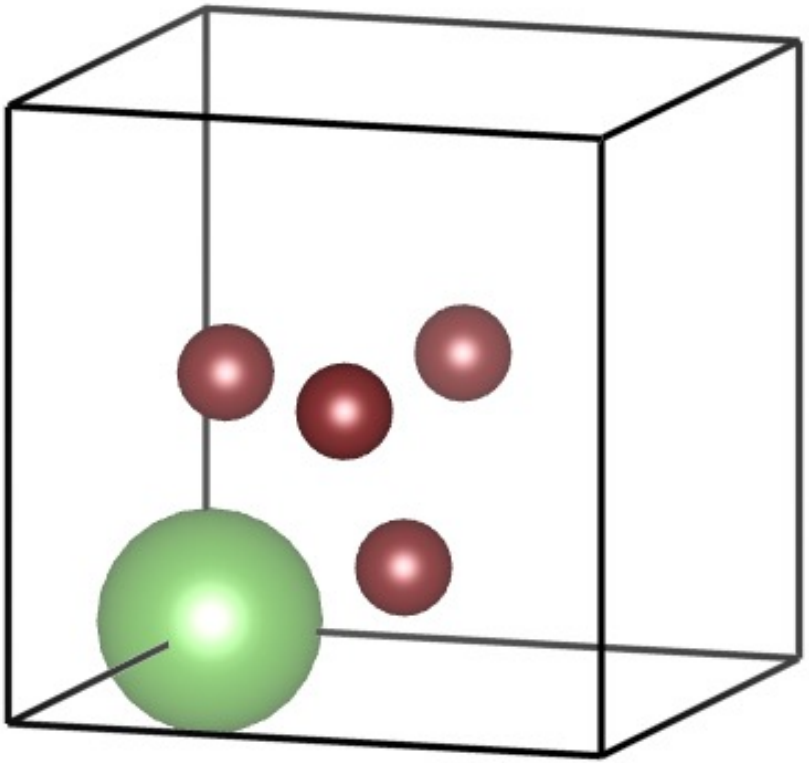
$$\vec{r}_1 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{5} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{5}\right)$$

$$\vec{r}_2 = \frac{1}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{5}, \frac{1}{2}, \frac{1}{2}\right)$$

$$\vec{r}_3 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{5} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{5}, \frac{1}{2}\right)$$

$$\vec{r}_4 = \frac{4}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{4}{5}, \frac{1}{2}, \frac{1}{2}\right)$$





Building a crystal of LaB_6

2. Locating atoms within the unit cell

La:

$$\vec{r} = 0 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 0 \cdot \vec{a}_3 = (0,0,0)$$

B:

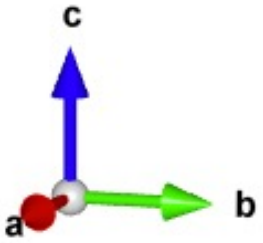
$$\vec{r}_1 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{5} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{5}\right)$$

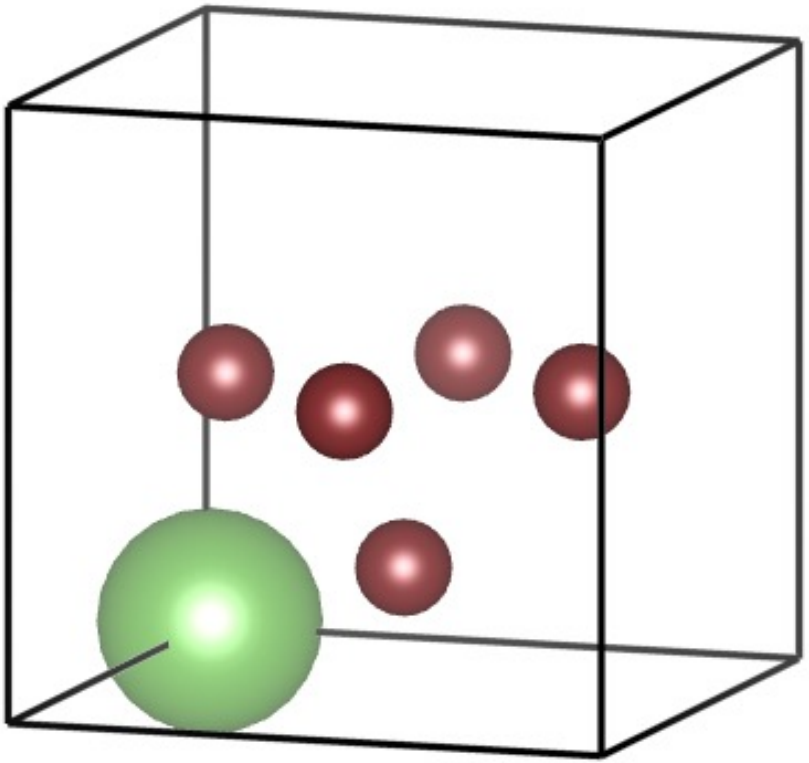
$$\vec{r}_2 = \frac{1}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{5}, \frac{1}{2}, \frac{1}{2}\right)$$

$$\vec{r}_3 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{5} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{5}, \frac{1}{2}\right)$$

$$\vec{r}_4 = \frac{4}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{4}{5}, \frac{1}{2}, \frac{1}{2}\right)$$

$$\vec{r}_5 = \frac{1}{2} \cdot \vec{a}_1 + \frac{4}{5} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{4}{5}, \frac{1}{2}\right)$$





Building a crystal of LaB_6

2. Locating atoms within the unit cell

La:

$$\vec{r} = 0 \cdot \vec{a}_1 + 0 \cdot \vec{a}_2 + 0 \cdot \vec{a}_3 = (0,0,0)$$

B:

$$\vec{r}_1 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{5} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{5}\right)$$

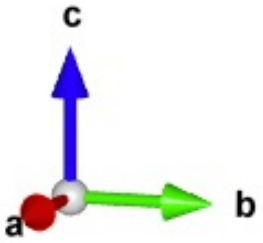
$$\vec{r}_2 = \frac{1}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{5}, \frac{1}{2}, \frac{1}{2}\right)$$

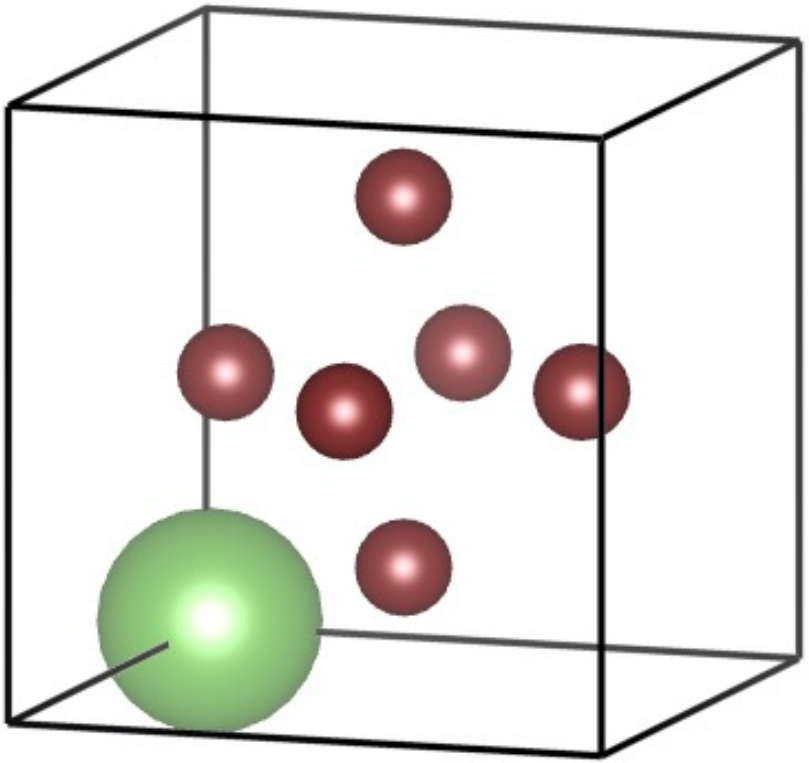
$$\vec{r}_3 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{5} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{5}, \frac{1}{2}\right)$$

$$\vec{r}_4 = \frac{4}{5} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{4}{5}, \frac{1}{2}, \frac{1}{2}\right)$$

$$\vec{r}_5 = \frac{1}{2} \cdot \vec{a}_1 + \frac{4}{5} \cdot \vec{a}_2 + \frac{1}{2} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{4}{5}, \frac{1}{2}\right)$$

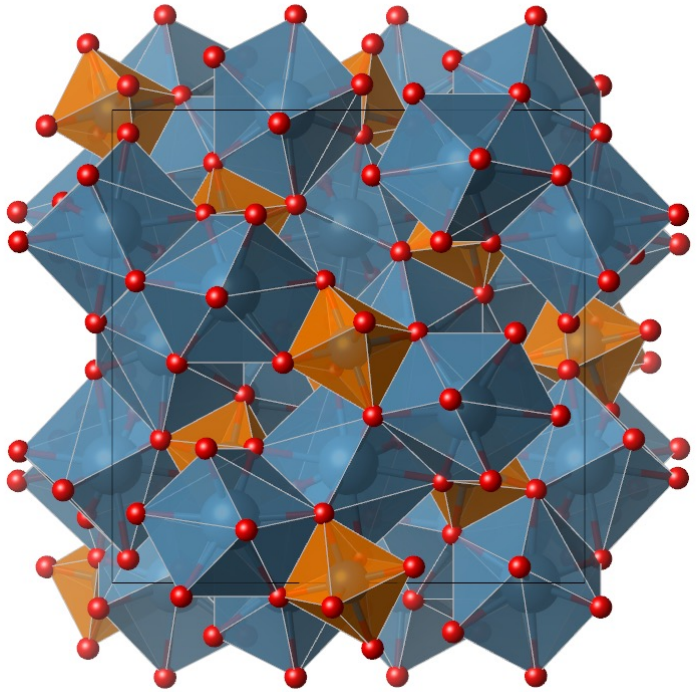
$$\vec{r}_6 = \frac{1}{2} \cdot \vec{a}_1 + \frac{1}{2} \cdot \vec{a}_2 + \frac{4}{5} \cdot \vec{a}_3 = \left(\frac{1}{2}, \frac{1}{2}, \frac{4}{5}\right)$$





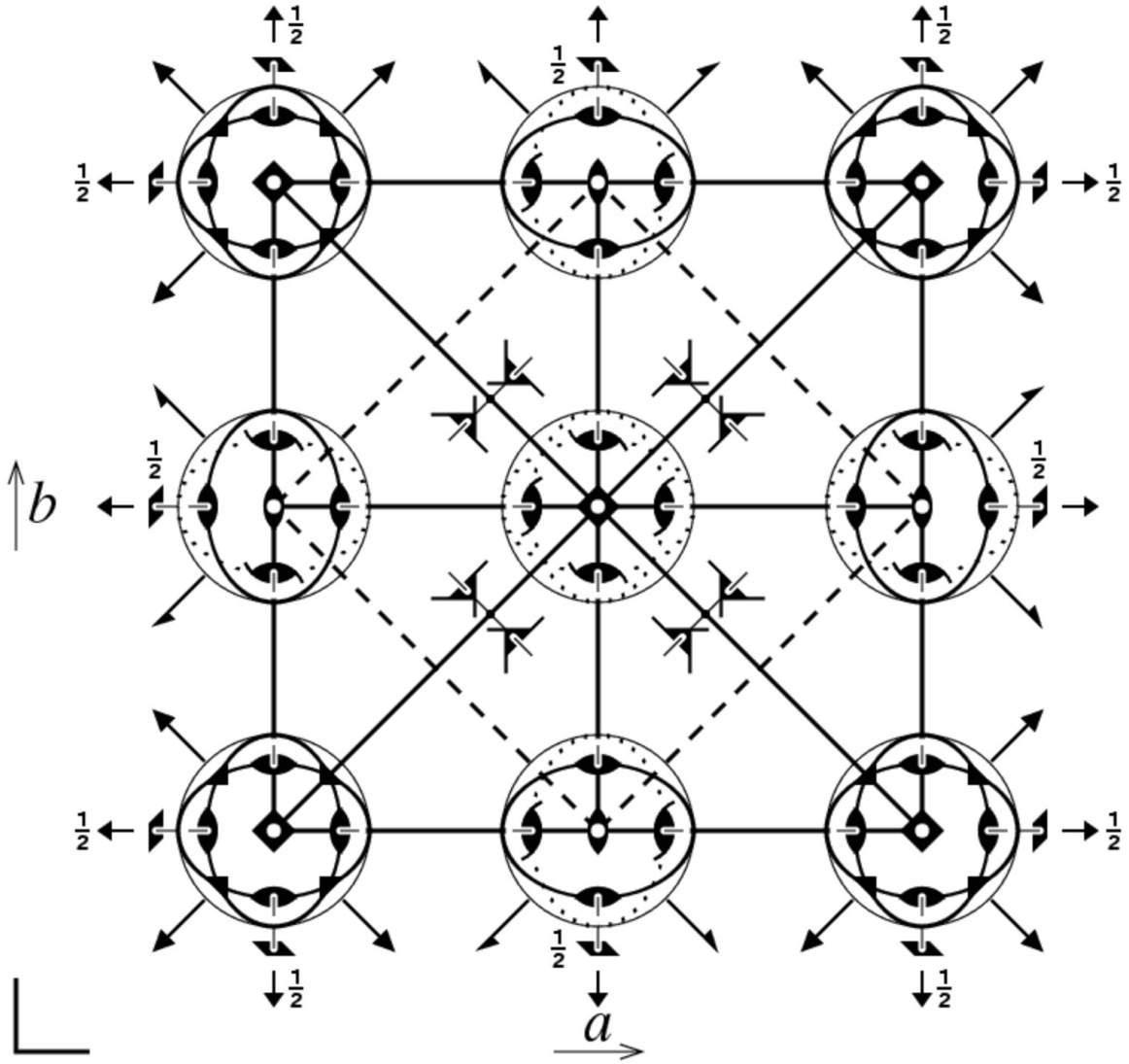
230 crystal families

#221
Pm-3m
Example – ZIF-71-RHO



Point symmetry of LaB_6

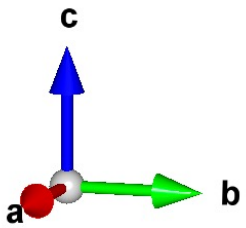
$Pm\bar{3}m$ $P\,4/m\,\bar{3}\,2/m$ $m\bar{3}m$ No. 221

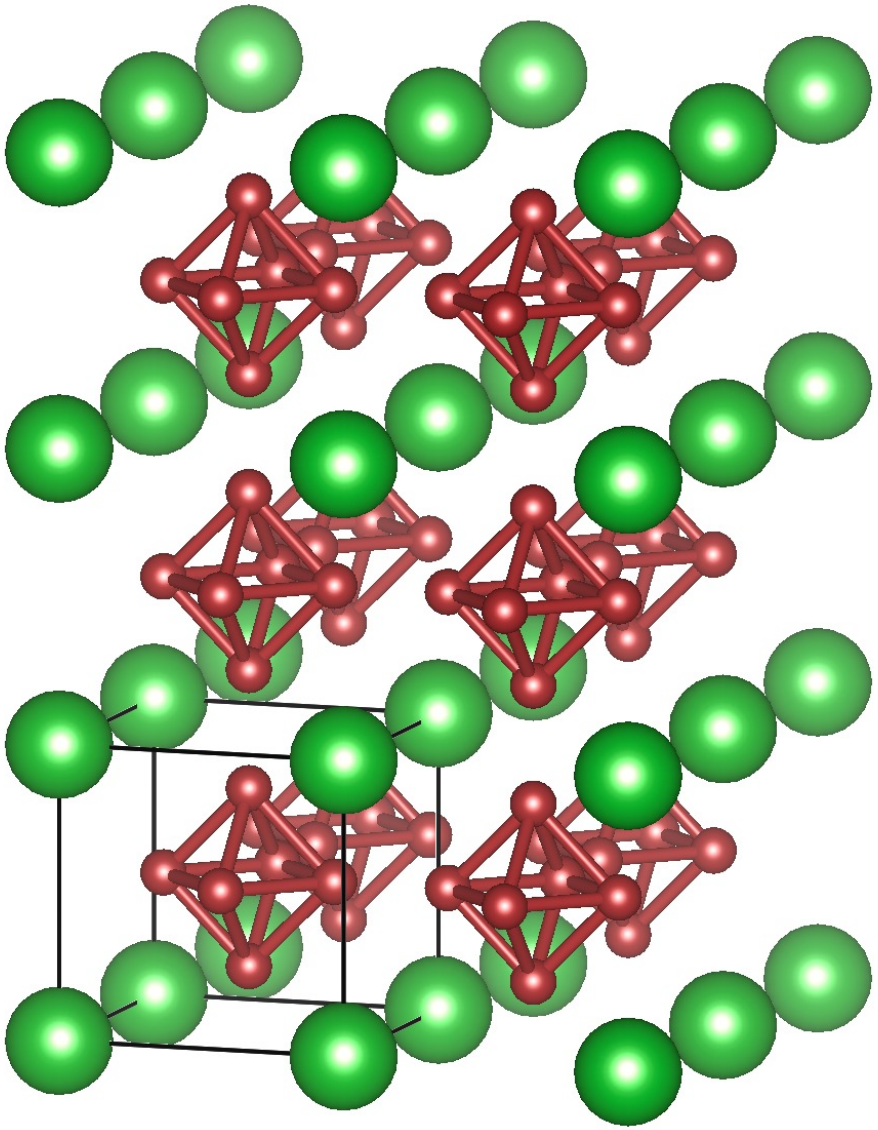


1	x, y, z	25	$\bar{x}, \bar{y}, \bar{z}$
2	$x, \bar{y}, \bar{z}$	26	$\bar{x}, y, z$
3	$\bar{x}, y, \bar{z}$	27	$x, \bar{y}, z$
4	$\bar{x}, \bar{y}, z$	28	$x, y, \bar{z}$
5	z, x, y	29	$\bar{z}, \bar{x}, \bar{y}$
6	$\bar{z}, \bar{x}, y$	30	$z, x, \bar{y}$
7	$z, \bar{x}, \bar{y}$	31	$\bar{z}, x, y$
8	$\bar{z}, x, \bar{y}$	32	$z, \bar{x}, y$
9	y, z, x	33	$\bar{y}, \bar{z}, \bar{x}$
10	$\bar{y}, z, \bar{x}$	34	$y, \bar{z}, x$
11	$\bar{y}, \bar{z}, x$	35	$y, z, \bar{x}$
12	$y, \bar{z}, \bar{x}$	36	$\bar{y}, z, x$
13	$x, \bar{z}, y$	37	$\bar{x}, z, \bar{y}$
14	$x, z, \bar{y}$	38	$\bar{x}, \bar{z}, y$
15	$\bar{x}, \bar{z}, \bar{y}$	39	x, z, y
16	$\bar{x}, z, y$	40	$x, \bar{z}, \bar{y}$
17	$z, y, \bar{x}$	41	$\bar{z}, \bar{y}, x$
18	$\bar{z}, y, x$	42	$z, \bar{y}, \bar{x}$
19	$\bar{z}, \bar{y}, \bar{x}$	43	z, y, x
20	$z, \bar{y}, x$	44	$\bar{z}, y, \bar{x}$
21	$\bar{y}, x, z$	45	$y, \bar{x}, \bar{z}$
22	$y, \bar{x}, z$	46	$\bar{y}, x, \bar{z}$
23	$\bar{y}, \bar{x}, \bar{z}$	47	y, x, z
24	$y, x, \bar{z}$	48	$\bar{y}, \bar{x}, z$

Building a crystal of LaB_6

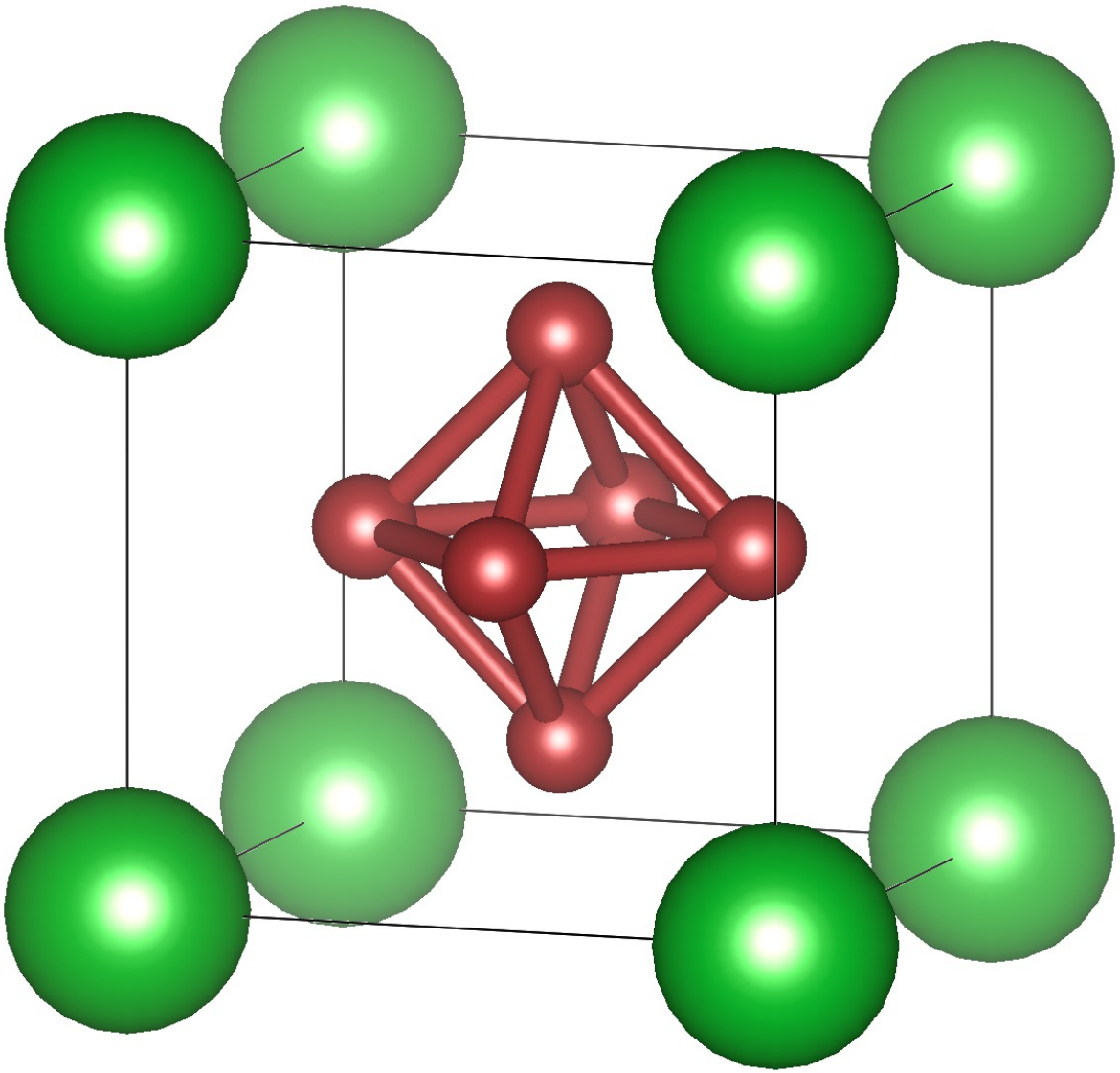
3. Applying translational symmetry

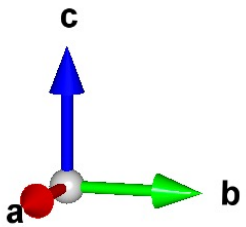




Building a crystal of LaB_6

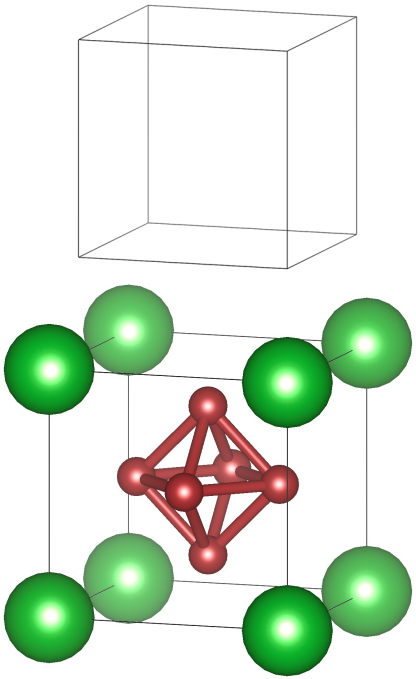
3. Applying translational symmetry





Crystal structure

Crystal structure = lattice + basis



Lattice describes periodicity of the structure. It is determined by the unit cell (3 lengths and 3 angles)

Basis describes arrangement of atoms within a unit cell

Position of any atom inside a crystal:

$$\vec{r} = \underbrace{n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3}_{\vec{R}_n} + \underbrace{x\vec{a}_1 + y\vec{a}_2 + z\vec{a}_3}_{\vec{r}_j}$$

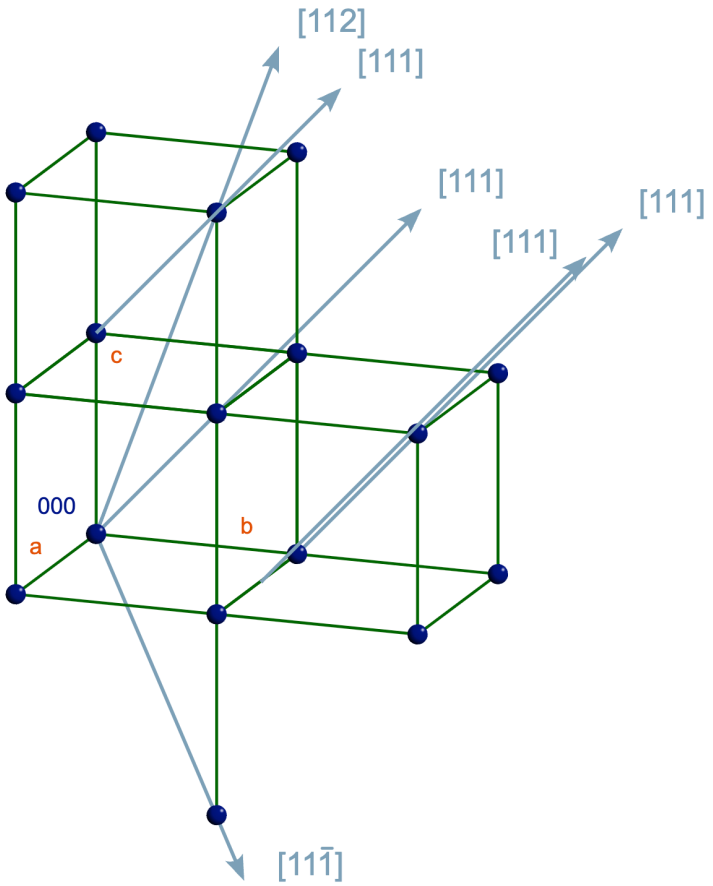
Crystallographic directions

In a lattice, each translation vector $\vec{R}_n = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ determines a direction

Directions are described with three integer Miller indices as $[uvw]$, where *u,v,w* – are three smallest integer numbers, proportional to the components of $\vec{R}_n$.

$[uvw]$ - direction

$\langle uvw \rangle$ - set of equivalent directions



Crystallographic planes

Lattice plane is defined by 3 non-collinear lattice points.

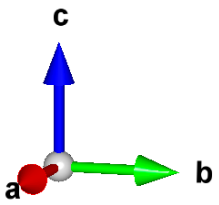
Lattice planes are described with three integer Miller indices as (hkl), where *h,k,l* – are three smallest integer numbers, proportional to $\frac{1}{u}, \frac{1}{v}, \frac{1}{w}$.

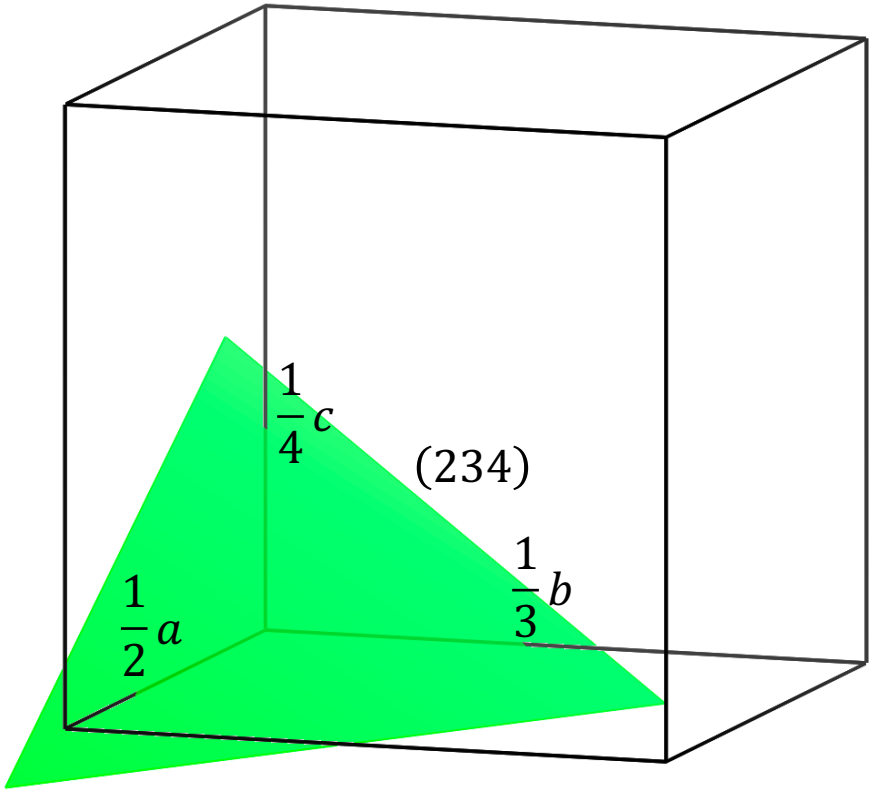
(hkl) - lattice plane

$\{hkl\}$ - set of equivalent planes

$$u = \frac{1}{2} \quad v = \frac{1}{3} \quad w = \frac{1}{4}$$

$$\frac{1}{u} = 2 \quad \frac{1}{v} = 3 \quad \frac{1}{w} = 4$$





Crystallographic planes

Lattice plane is defined by 3 non-collinear lattice points.

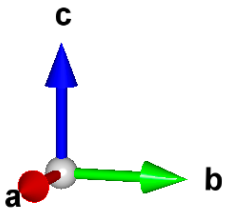
Lattice planes are described with three integer Miller indices as (hkl), where *h,k,l* – are three smallest integer numbers, proportional to $\frac{1}{u}, \frac{1}{v}, \frac{1}{w}$.

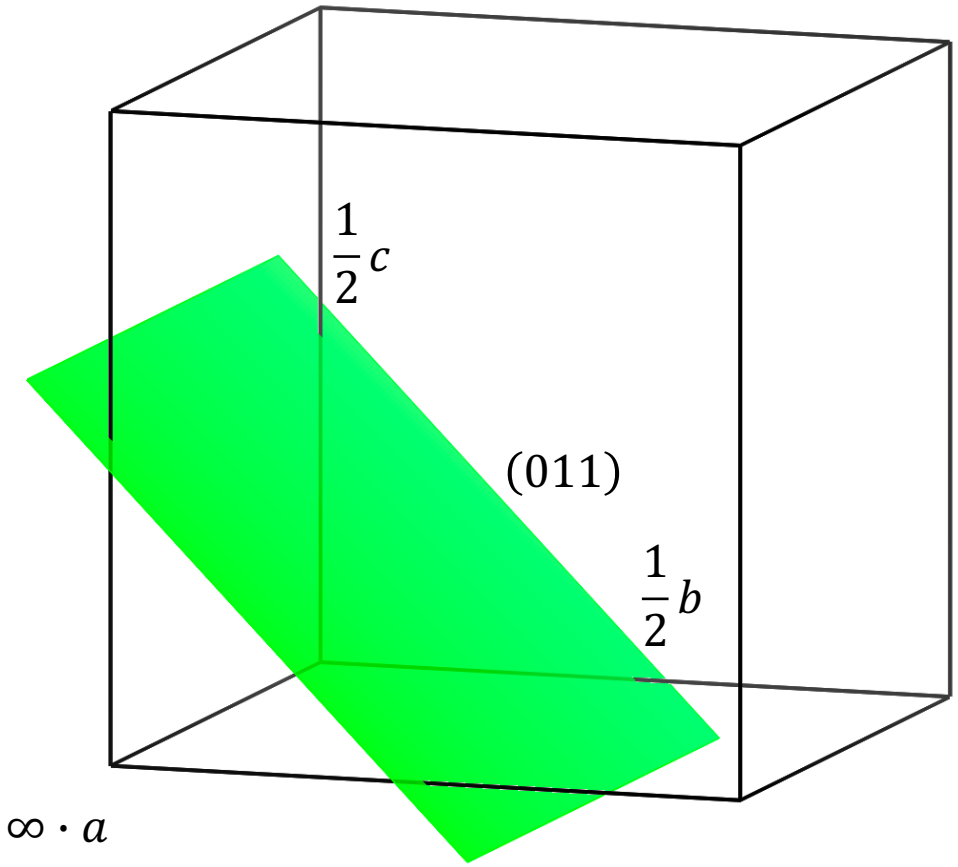
(hkl) - lattice plane

$\{hkl\}$ - set of equivalent planes

$$u = \frac{1}{\infty} \quad v = \frac{1}{2} \quad w = \frac{1}{2}$$

$$\frac{1}{u} = 0 \quad \frac{1}{v} = 2 \quad \frac{1}{w} = 2$$





Crystallographic planes

Lattice plane is defined by 3 non-collinear lattice points.

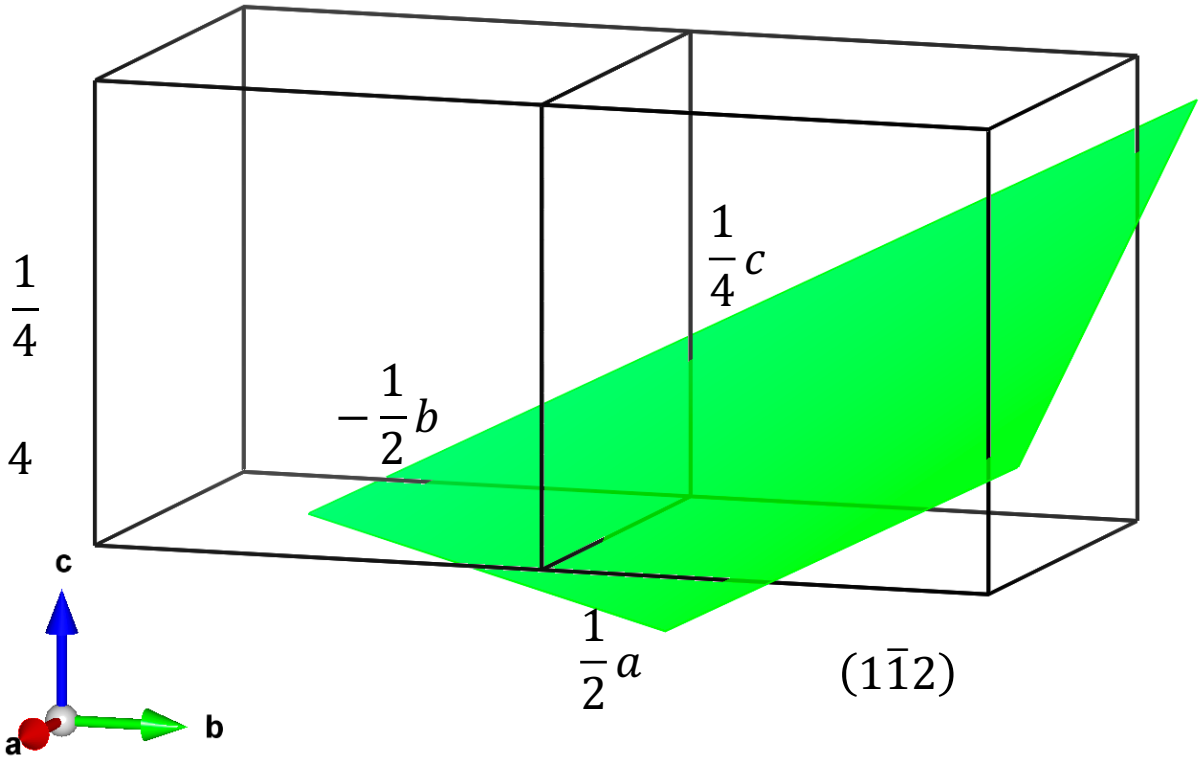
Lattice planes are described with three integer Miller indices as (hkl), where *h,k,l* – are three smallest integer numbers, proportional to $\frac{1}{u}, \frac{1}{v}, \frac{1}{w}$.

(hkl) - lattice plane

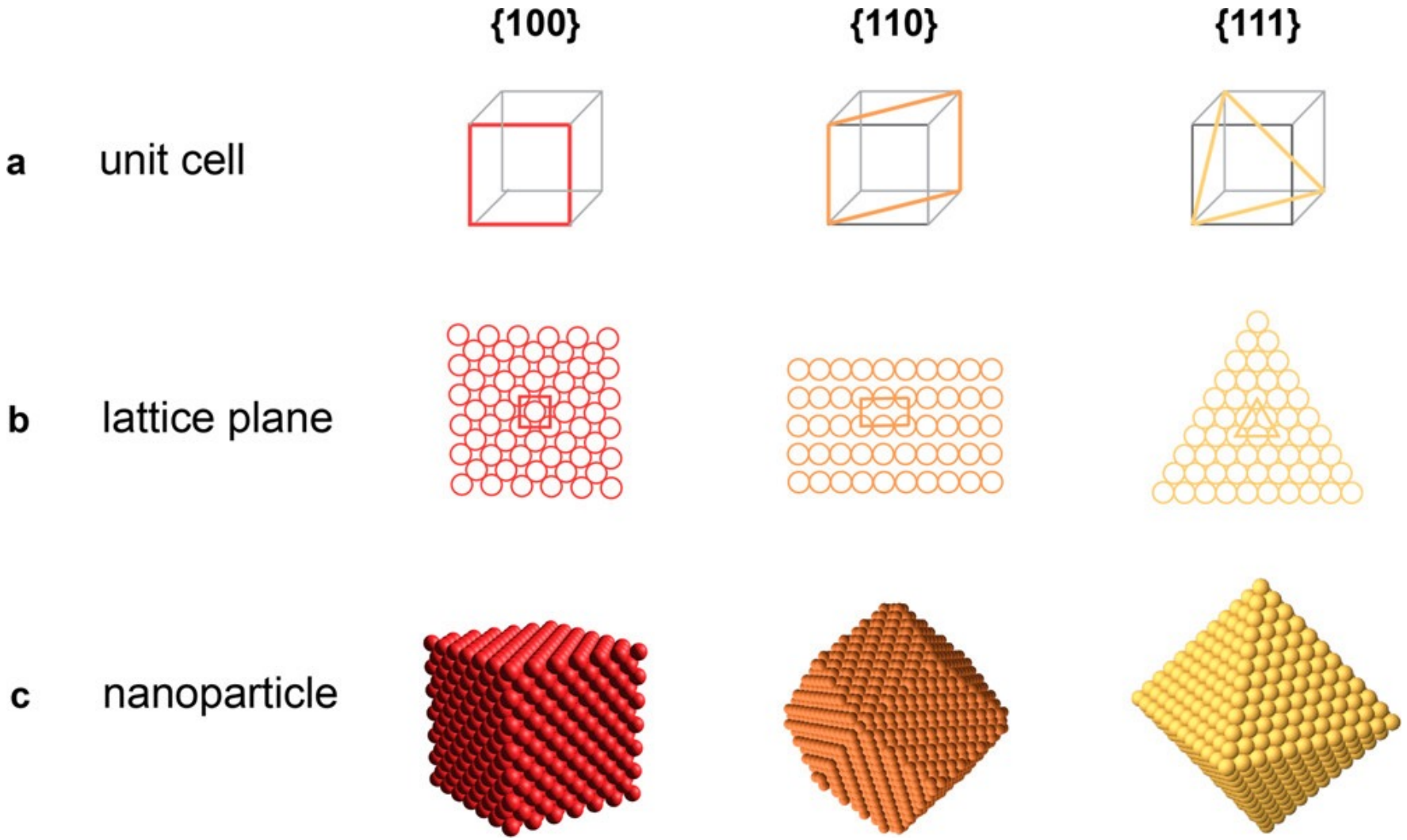
$\{hkl\}$ - set of equivalent planes

$$u = \frac{1}{2} \quad v = -\frac{1}{2} \quad w = \frac{1}{4}$$

$$\frac{1}{u} = 2 \quad \frac{1}{v} = -2 \quad \frac{1}{w} = 4$$



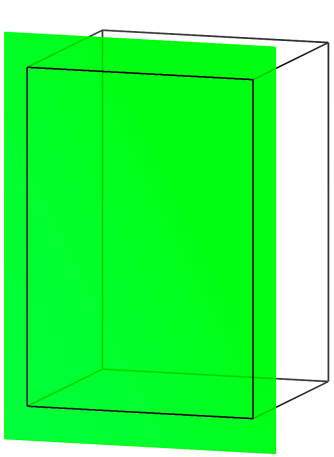
Why do we need lattice planes?



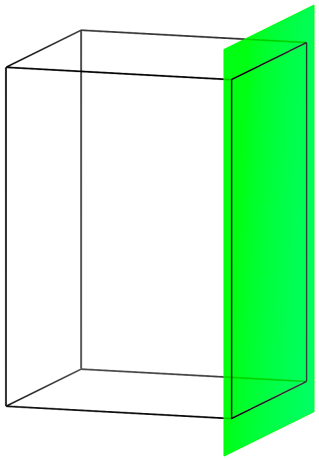
A.K. Bentley, S.E. Skrabalak. J. Chem. Educ. ***100****, 3425 (2023)*

Equivalent planes for tetragonal lattice

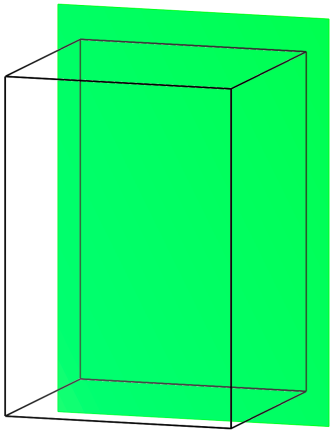
$$\{100\} \rightarrow (100), (010), (\bar{1}00), (0\bar{1}0)$$



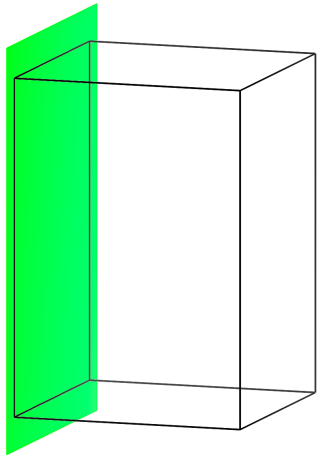
(100)



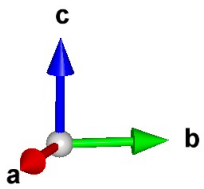
(010)



$(\bar{1}00)$



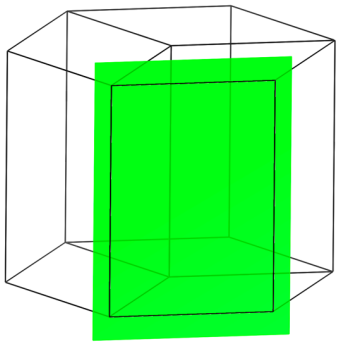
$(0\bar{1}0)$



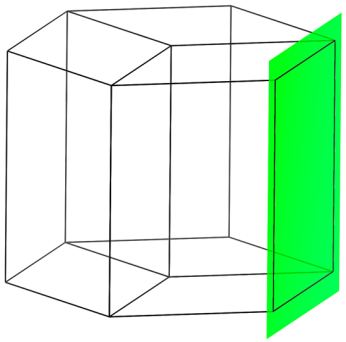
Miller indices of equivalent planes can be obtained as permutations

Miller indices for hexagonal lattice

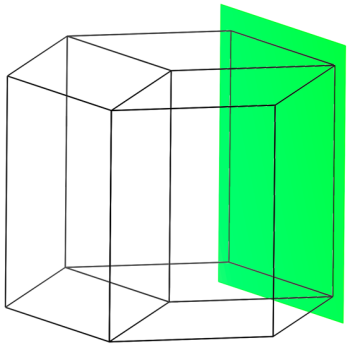
$$\{100\} \rightarrow (100), (010), (\bar{1}00), (0\bar{1}0), (\bar{1}10), (1\bar{1}0)$$



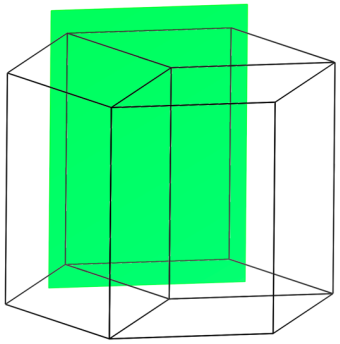
(100)



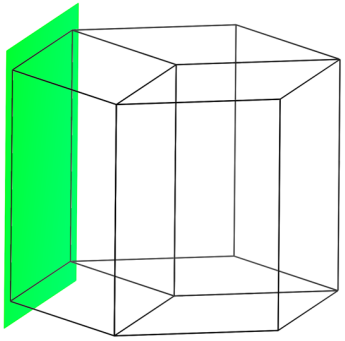
(010)



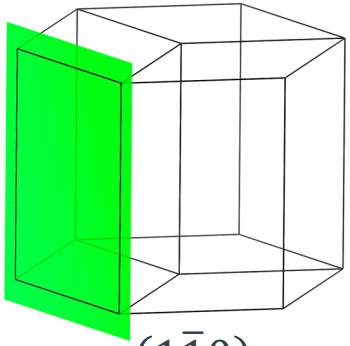
$(\bar{1}10)$



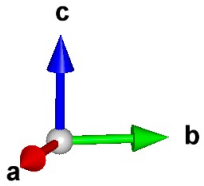
$(\bar{1}00)$



$(0\bar{1}0)$



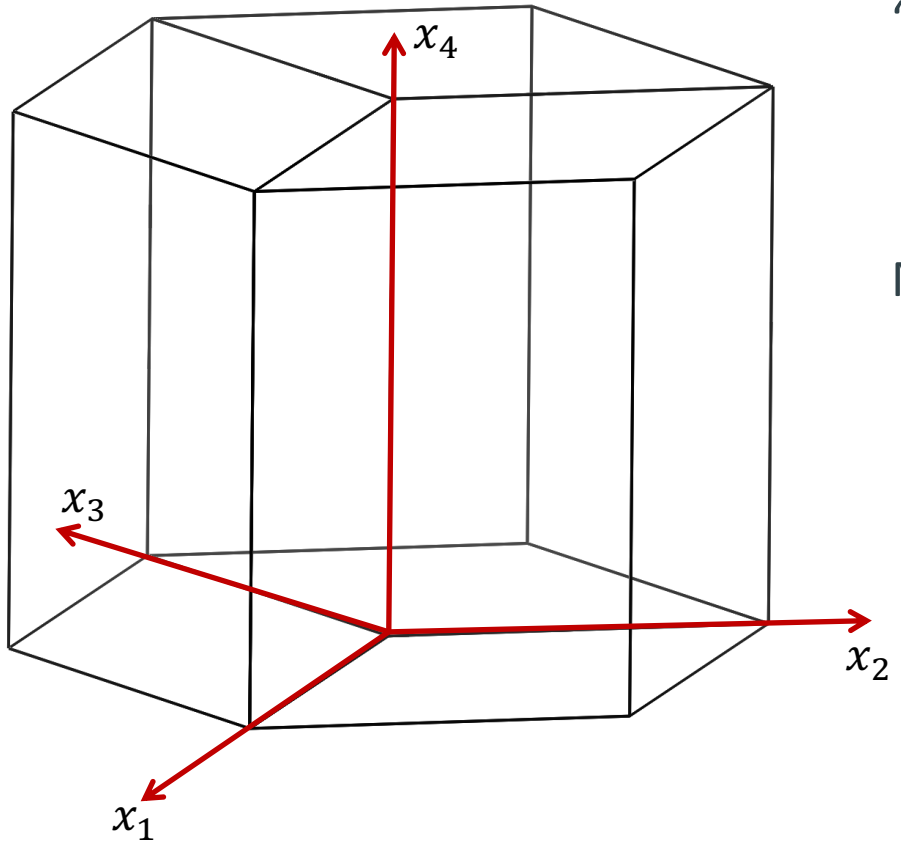
$(1\bar{1}0)$



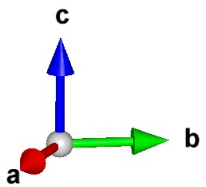
Miller indices of equivalent planes **cannot** be obtained as permutations

Miller indices for hexagonal lattice

x_1, x_2, x_3 - equivalent axis for the hexagonal symmetry



$$x_3 = -(x_1 + x_2)$$



"Usual" Miller indices:

(hkl)

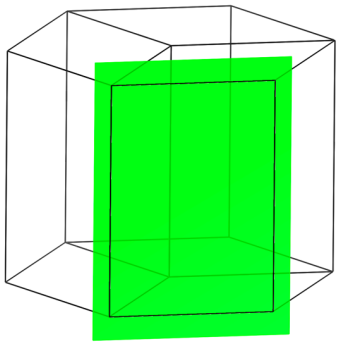
Miller-Bravais indices:

$(hkil)$

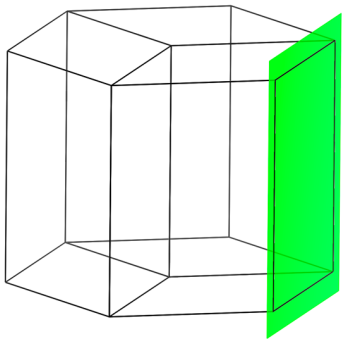
$$i = -(h + k)$$

Miller indices for hexagonal lattice

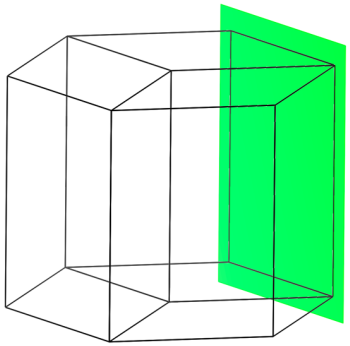
$$\{1\bar{1}00\} \rightarrow (10\bar{1}0), (01\bar{1}0), (\bar{1}100), (\bar{1}010), (0\bar{1}10), (1\bar{1}00)$$



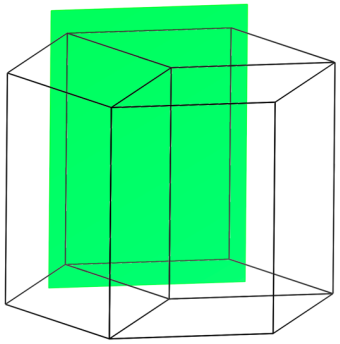
$(10\bar{1}0)$



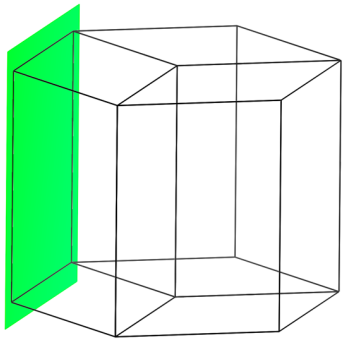
$(01\bar{1}0)$



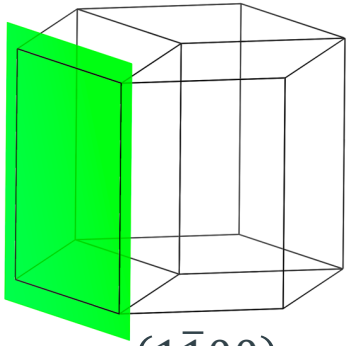
$(\bar{1}100)$



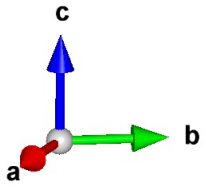
$(\bar{1}010)$



$(0\bar{1}10)$

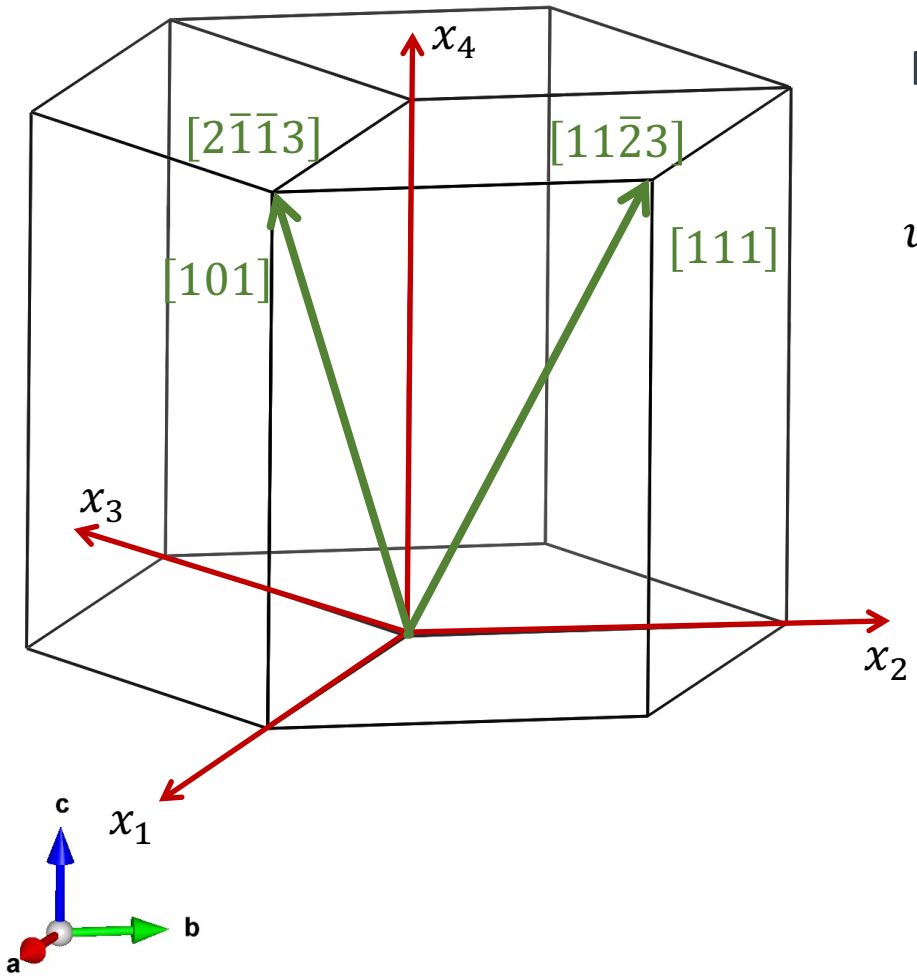


$(1\bar{1}00)$



Miller-Bravais indices of equivalent planes **can** be obtained as permutations

Miller indices for hexagonal lattice



Transformation from Miller indices to Miller-Bravais indices for directions

$$[uvw] \Longrightarrow [u'v't'w']$$

$$u\vec{a}_1 + v\vec{a}_2 + w\vec{c} = u'\vec{a}_1 + v'\vec{a}_2 + t'\vec{a}_3 + w'\vec{c}$$

$$\vec{a}_3 = -(\vec{a}_1 + \vec{a}_2)$$

$$\begin{cases} u = u' - t' \\ v = v' - t' \\ w = w' \\ t' = -(u' + v') \end{cases}$$

$$\begin{cases} u' = \frac{1}{3}(2u - v) \\ v' = \frac{1}{3}(2v - u) \\ t' = -\frac{1}{3}(u + v) \\ w' = w \end{cases}$$

Fourier series

In Fourier space (reciprocal space), description is done in terms of waves.

$$f(x) = \sum_{n=-\infty}^{+\infty} c_n \cdot exp(ik_n x)$$

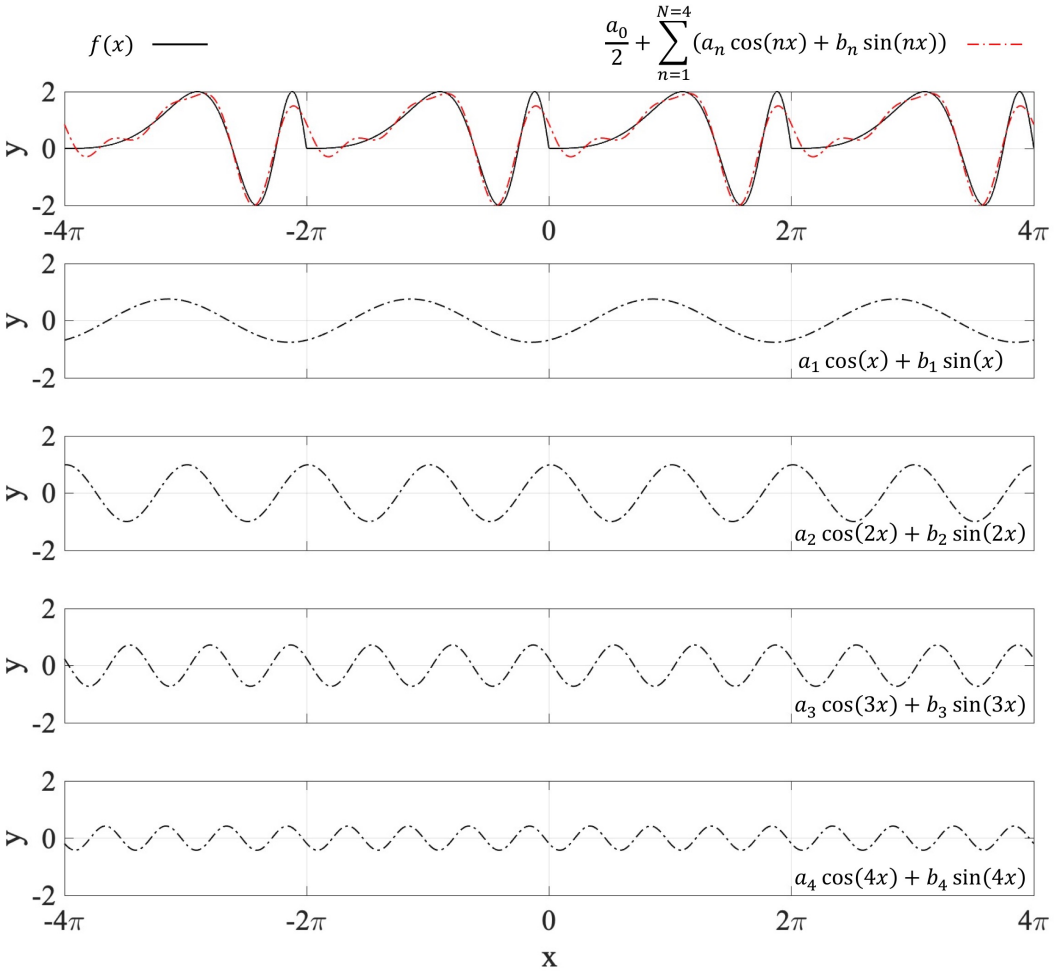
sum of waves with wavevectors

$$k_n = \frac{2\pi}{L} n$$

and complex amplitudes

$$c_n = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \cdot exp(-ik_n x) dx$$

periodic function with period L



Fourier transform

In Fourier space (reciprocal space), description is done in terms of waves.

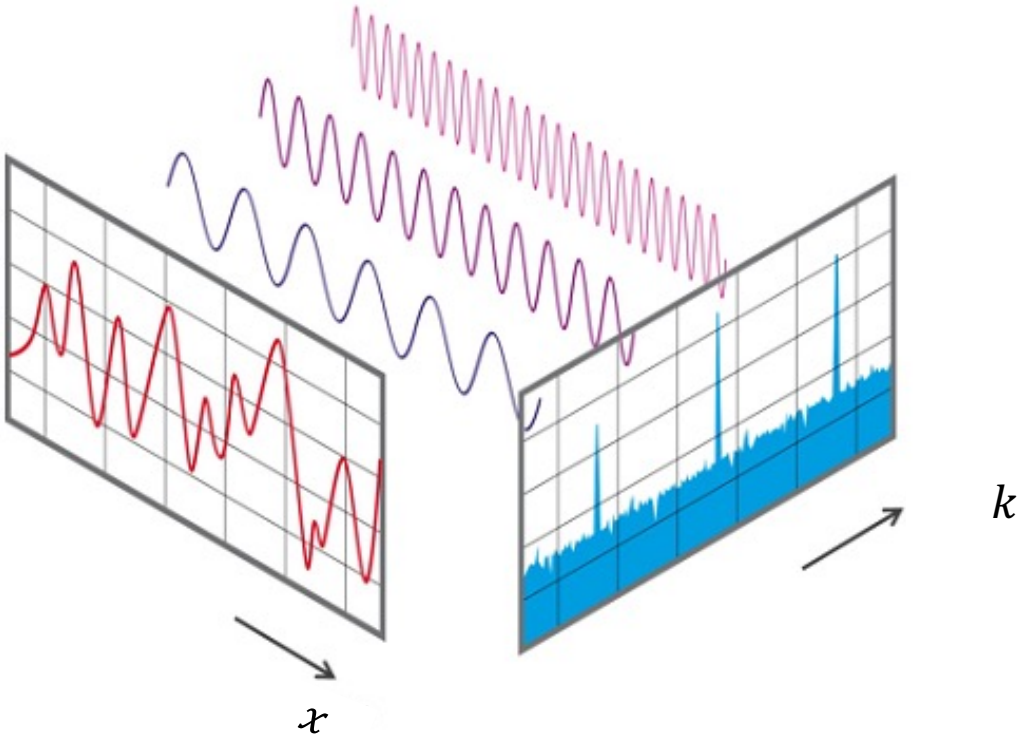
$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} c(k) \cdot exp(ikx) dx$$

integral of waves with wavevecto

$k \in (-\infty, +\infty)$

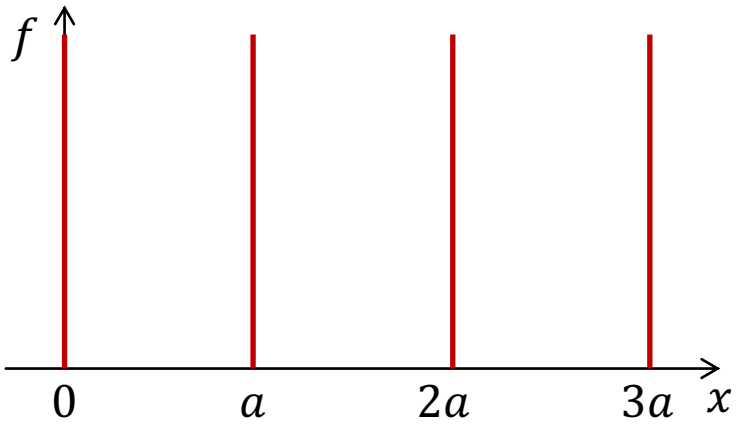
and complex amplitudes

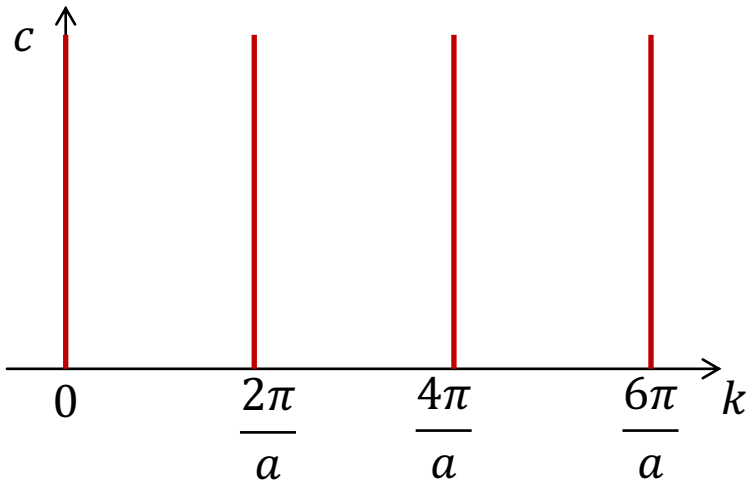
$$c(k) = \int_{-\infty}^{+\infty} f(x) \cdot exp(-ikx) dx$$



almost any function (not necessarily periodic)

Dirac comb





$$f(x) = \sum_{n=-\infty}^{+\infty} \delta(x - n \cdot a)$$

$$c_n = \frac{1}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} f(x) \cdot exp(-ik_n x)dx = \frac{1}{a} \sum_{n=-\infty}^{+\infty} \int_{-\frac{a}{2}}^{\frac{a}{2}} \delta(x - n \cdot a) \cdot exp(-ik_n x)dx = \frac{1}{a}$$

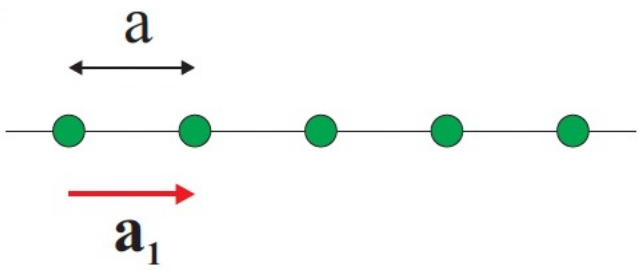
$$k_n = \frac{2\pi}{a} n$$

$$f(x) = \frac{1}{a} \sum_{n=-\infty}^{+\infty} exp(ik_n x)$$

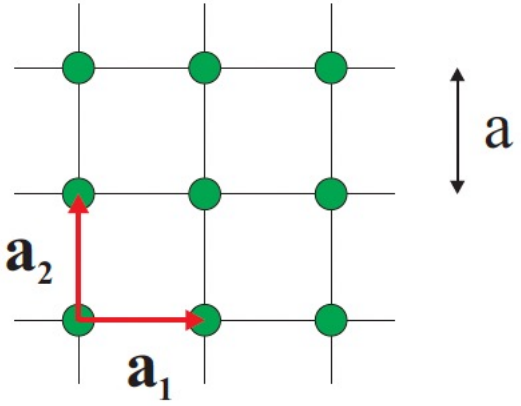
Fourier transform of a lattice

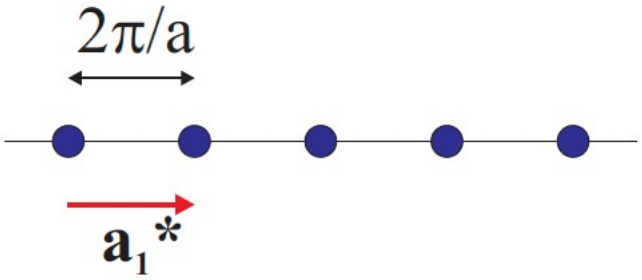
Real space

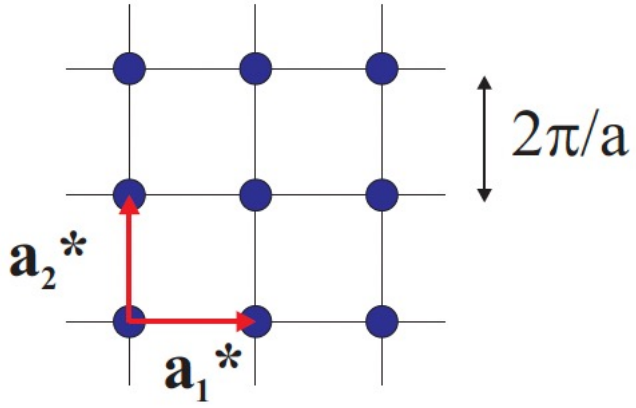
1D



2D







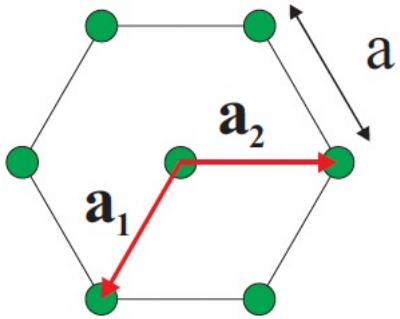
Reciprocal space

J. Als-Nielsen, D. McMorrow, Elements of Modern X-ray Scattering (2011)

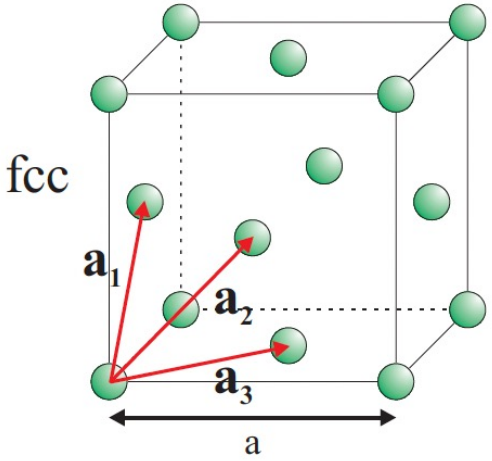
Fourier transform of a lattice

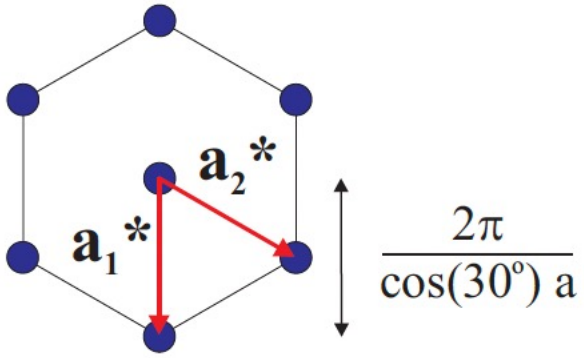
Real space

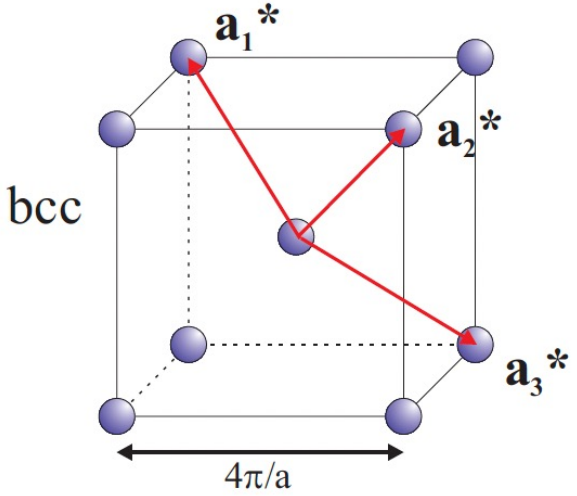
2D



3D







Reciprocal space

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