Ingredients for solid state physics

- The electromagnetic interaction
- Quantum Mechanics
- Many particles
- Symmetry to handle it all

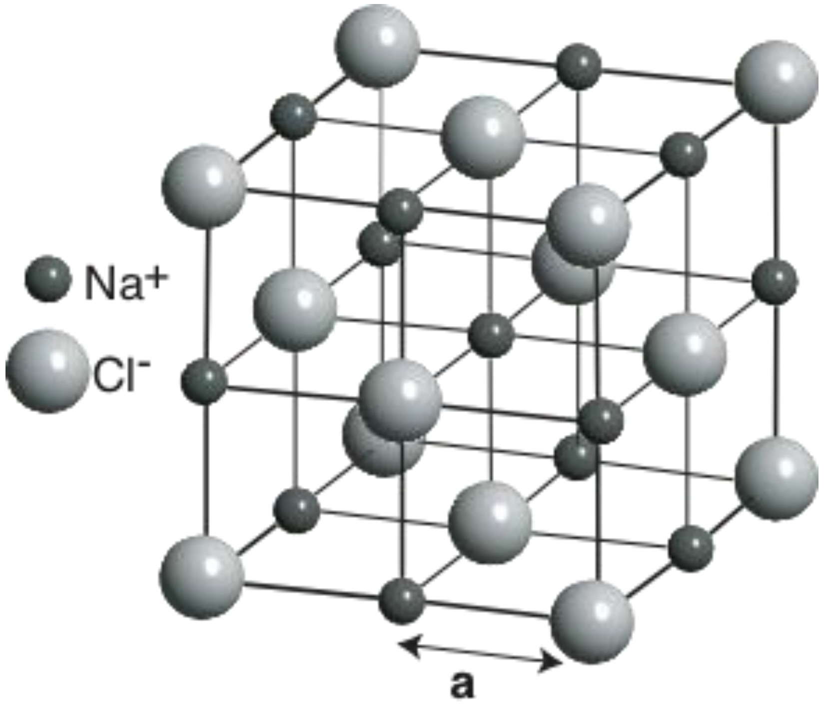
and what we get out

- Microscopic picture for a zoo of different phenomena: conductivity, superconductivity, mechanical properties, magnetism, optical properties.
- Funny new “quasi” particles: ‘electrons’ with unusual mass and charge, phonons, Cooper pairs, particles which are neither bosons or fermions, magnetic monopoles,....

Perfect Crystalline Solids

bismuth

NaCl



$$G = U + PV - TS$$

- solid made from small, identical building blocks (unit cells) which also show in the macroscopic shape

Crystals and crystalline solids: contents

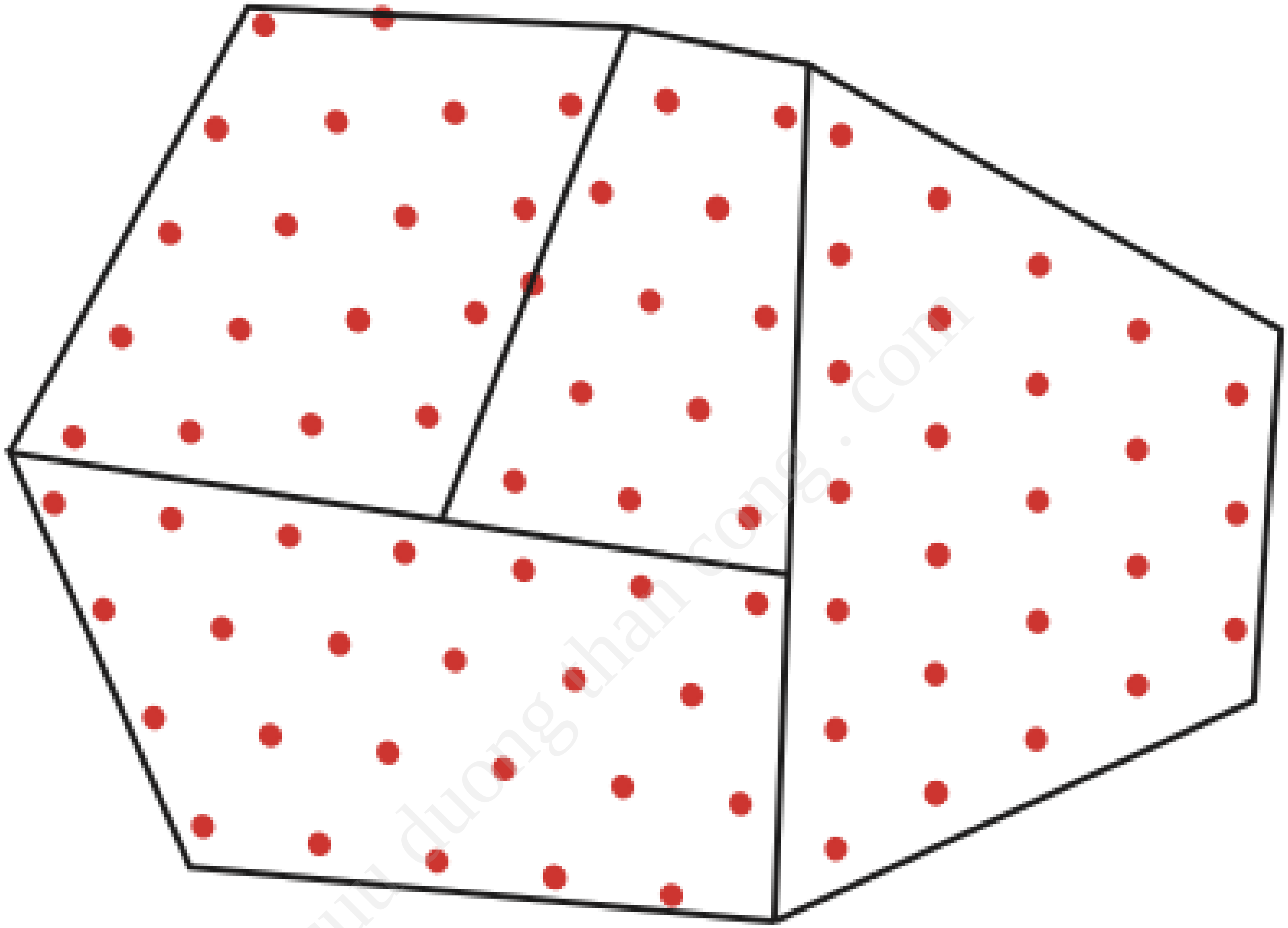
at the end of this lecture you should understand....

- Bravais lattice, unit cell and basis
- Miller indices
- Real crystal structures
- X-ray diffraction: Laue and Bragg conditions, Ewald construction
- The reciprocal lattice
- Electron microscopy and diffraction

Crystals and crystalline solids

- The total energy gain when forming crystals most be very big because the ordered states exists also at elevated temperatures, despite its low entropy.
- The high symmetry greatly facilitates the solution of the Schrödinger equation for the solid because the solutions also have to be highly symmetric.

Crystals and crystalline solids



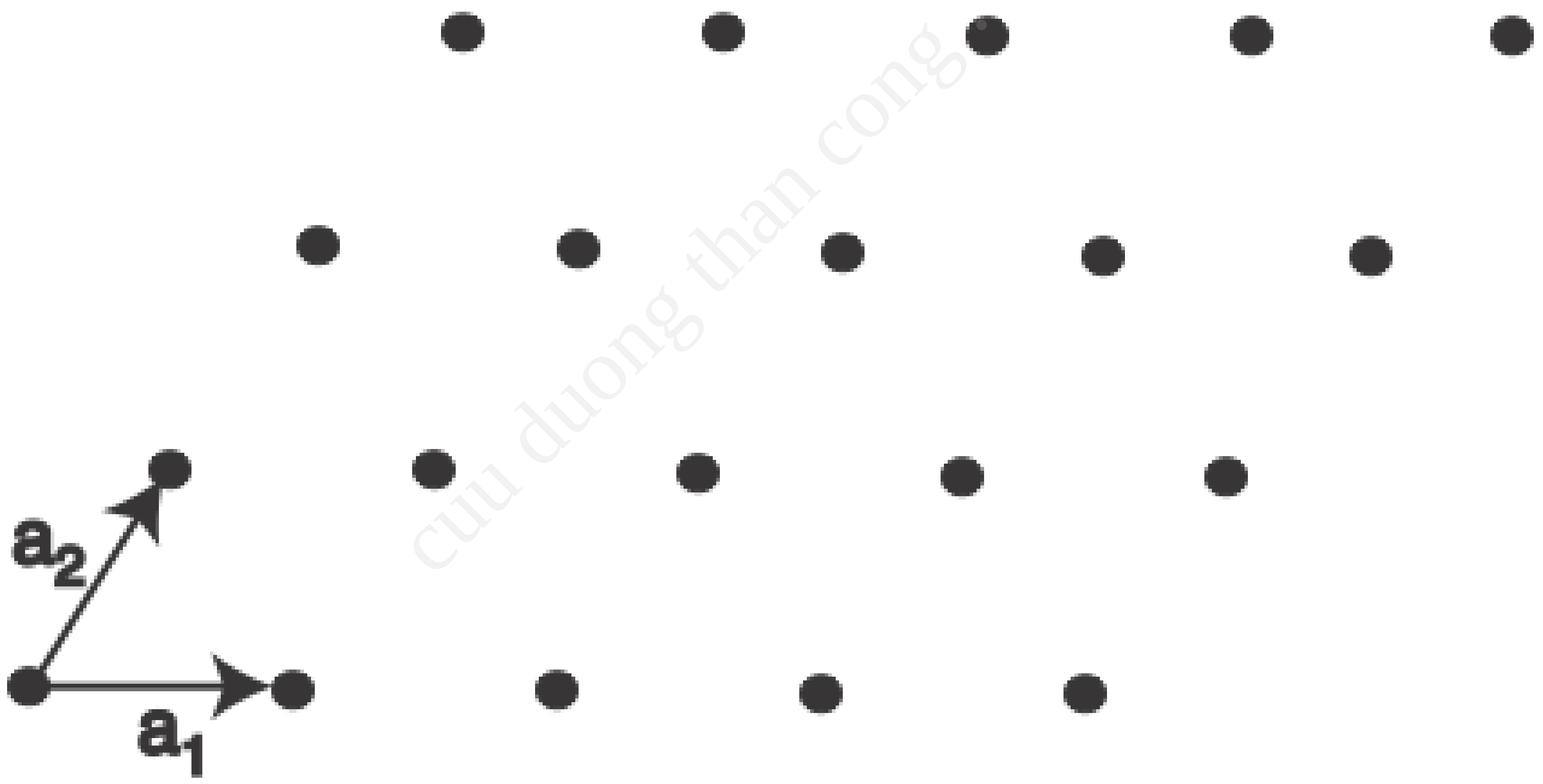
- most real solids are polycrystalline
- still, even if the grains are small, only a very small fraction of the atoms is close to the grain boundary
- the solids could also be amorphous (with no crystalline order)

Some formal definitions

The crystal lattice: Bravais lattice (2D)

A Bravias lattice is a lattice of points, defined by

$$\mathbf{R}_{mn} = m\mathbf{a}_1 + n\mathbf{a}_2$$



The lattice looks exactly the same from every point

The crystal lattice: Bravais lattice (2D)

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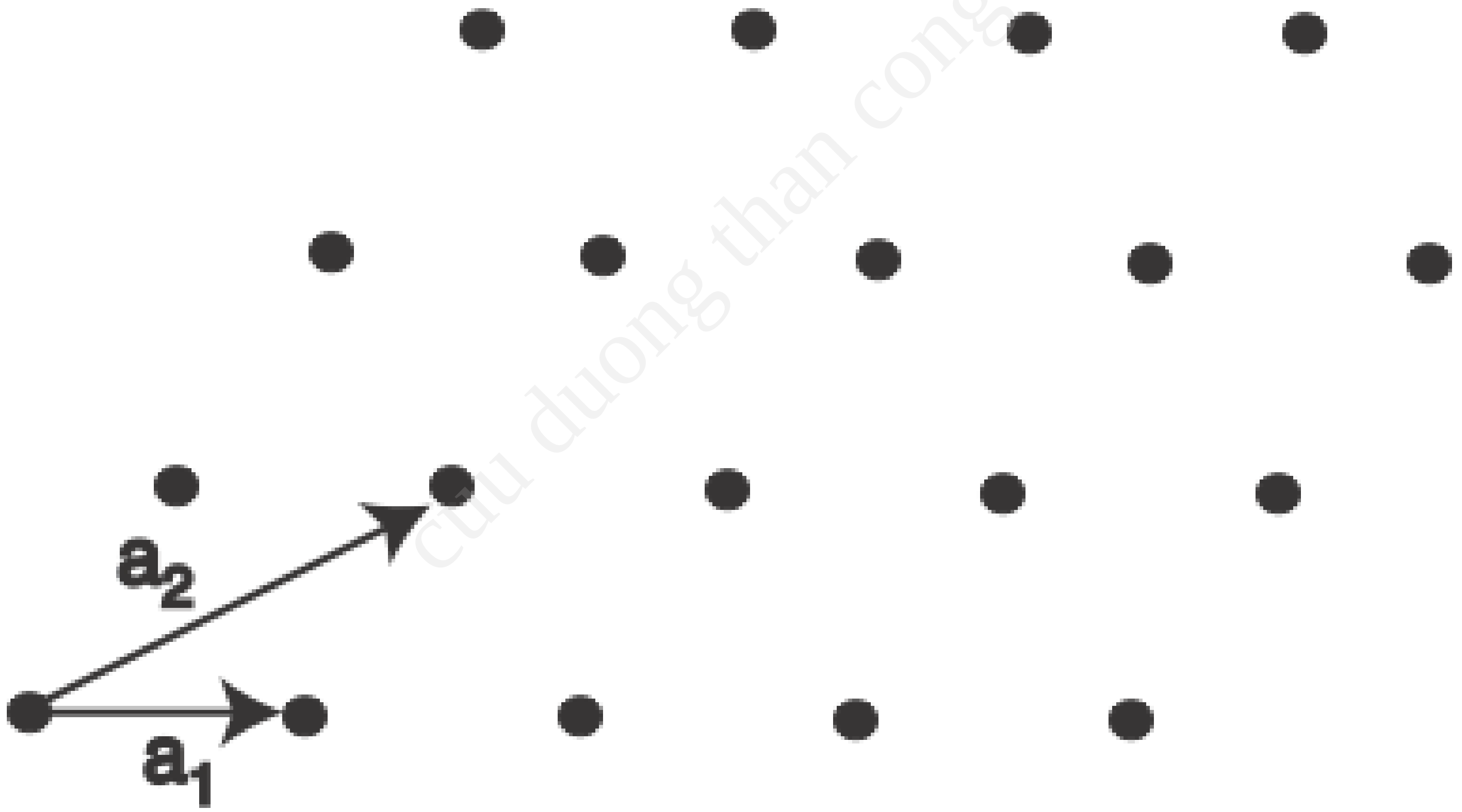
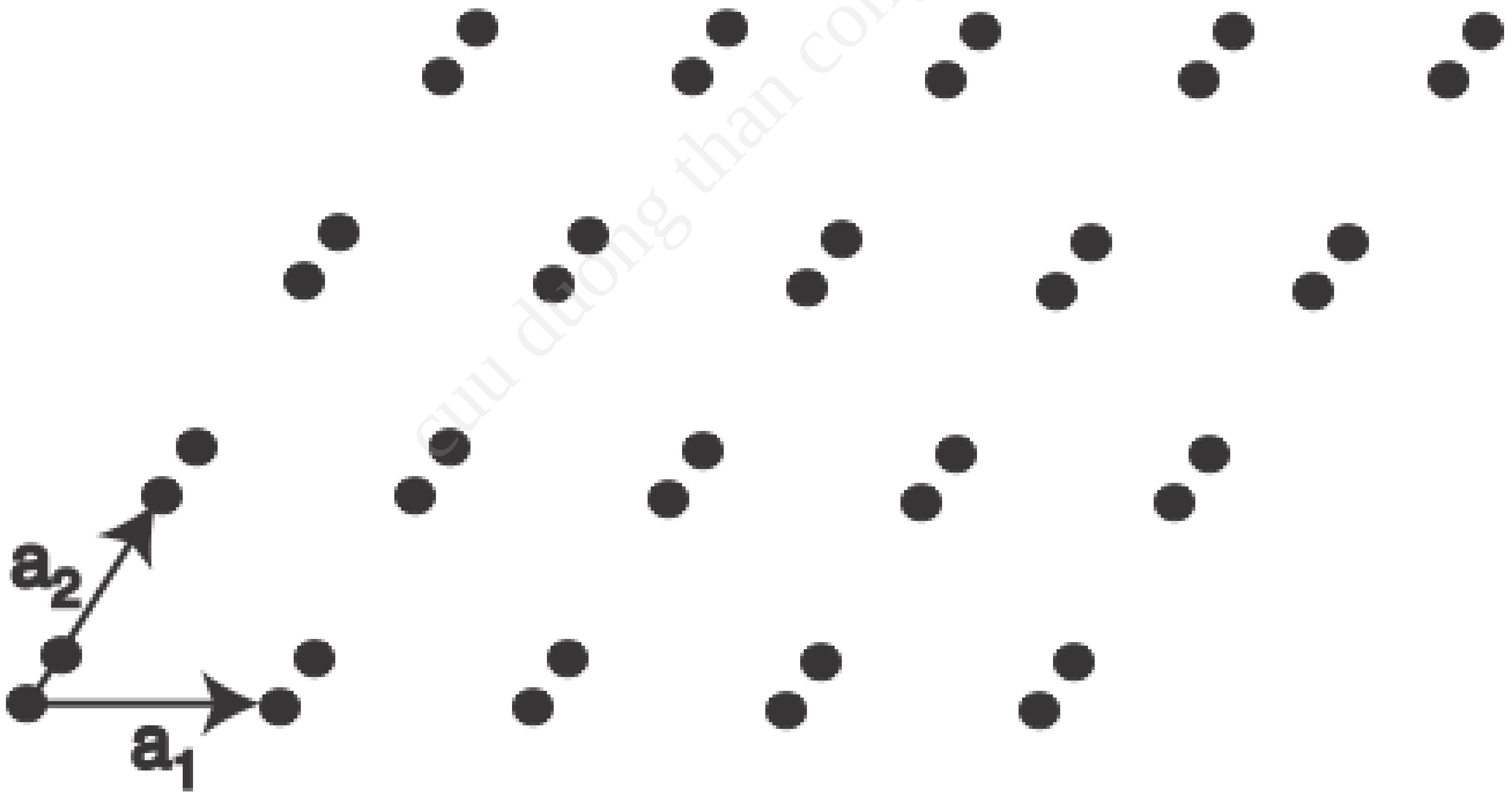


The lattice looks exactly the same from every point

The crystal lattice: Bravais lattice (2D)

Not every lattice of points is a Bravais lattice

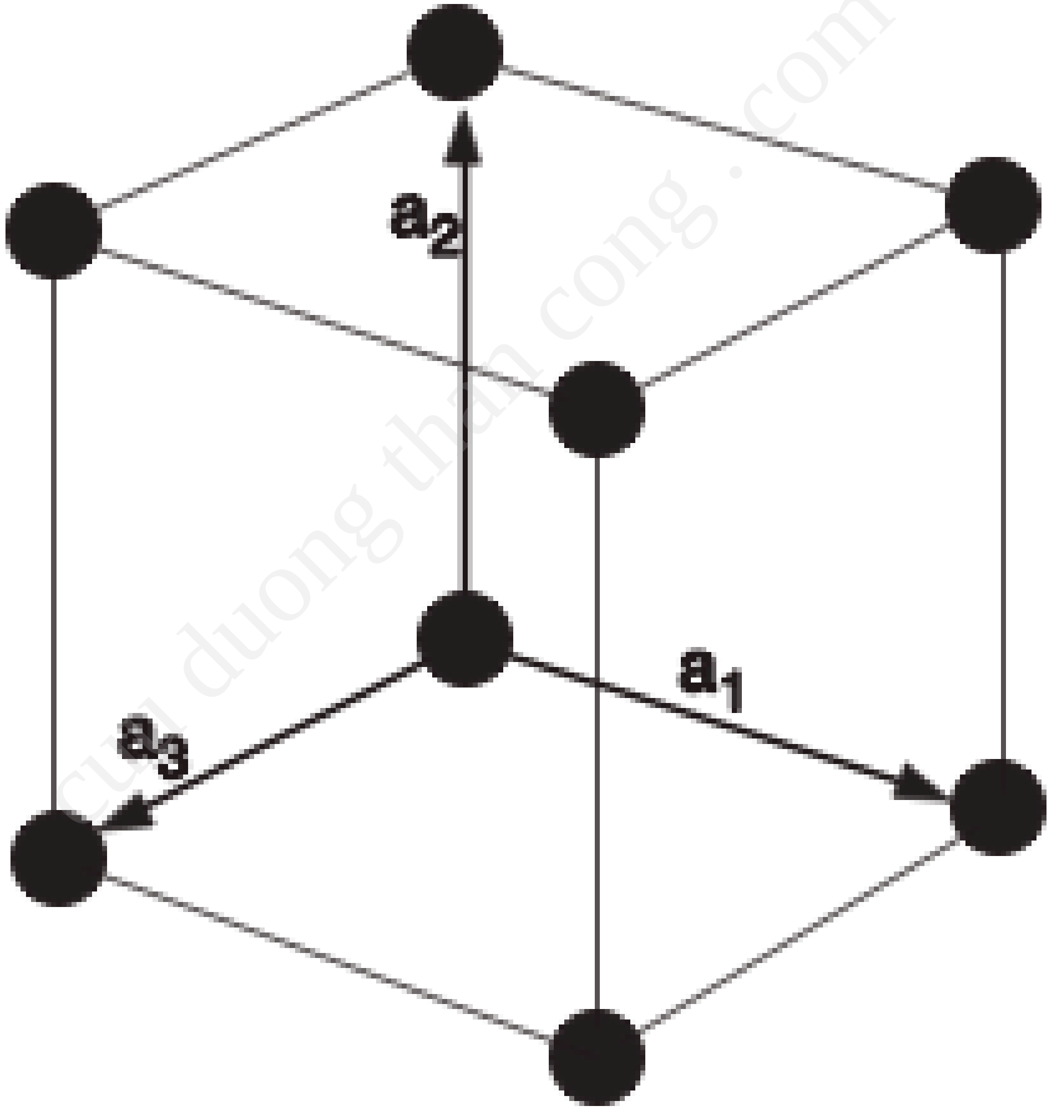
$$\mathbf{R}_{mn} = m\mathbf{a}_1 + n\mathbf{a}_2$$



The crystal lattice: Bravais lattice (3D)

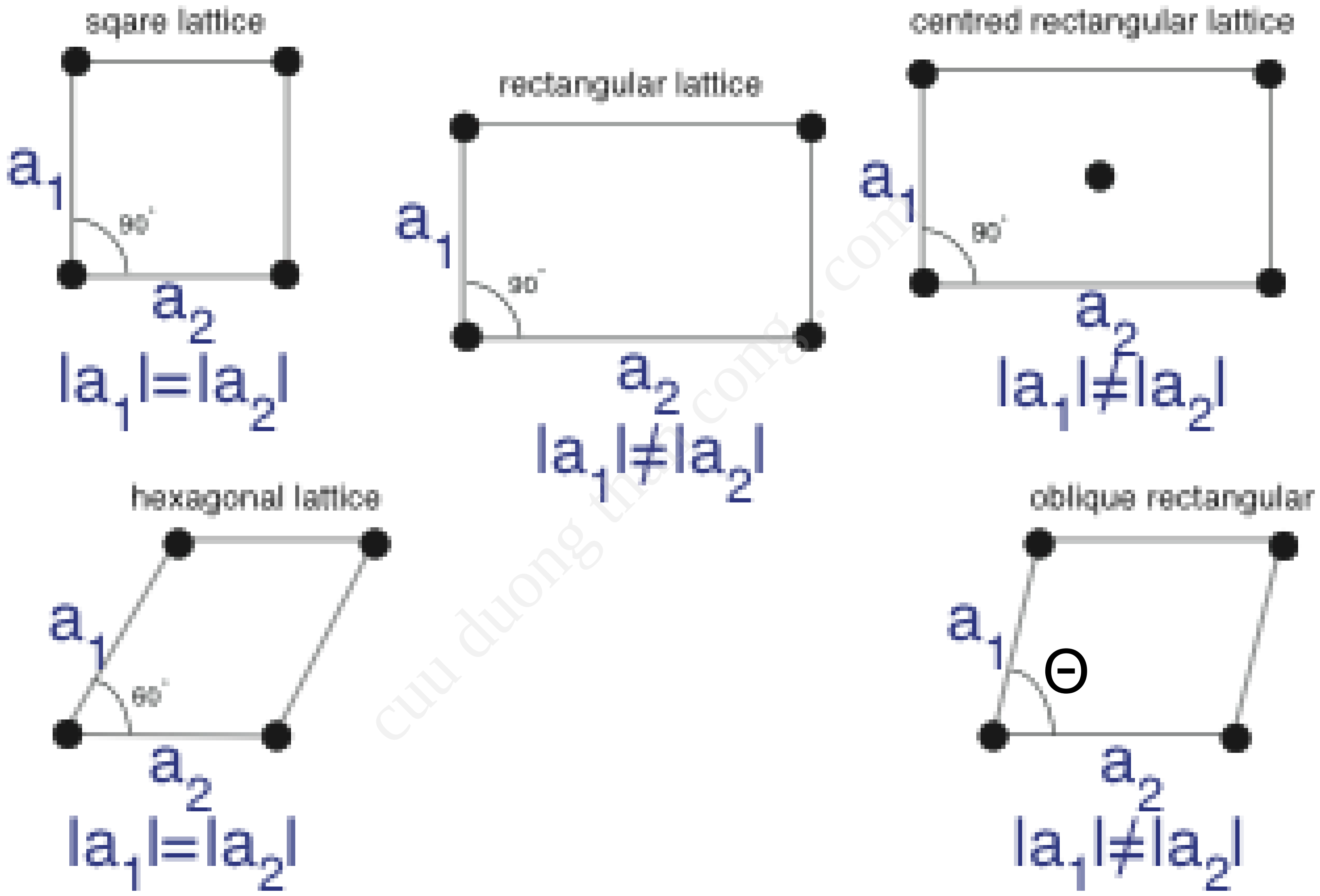
A Bravias lattice is a lattice of points, defined by

$$\mathbf{R} = m\mathbf{a_1} + n\mathbf{a_2} + o\mathbf{a_3}$$



This reflects the translational symmetry of the lattice

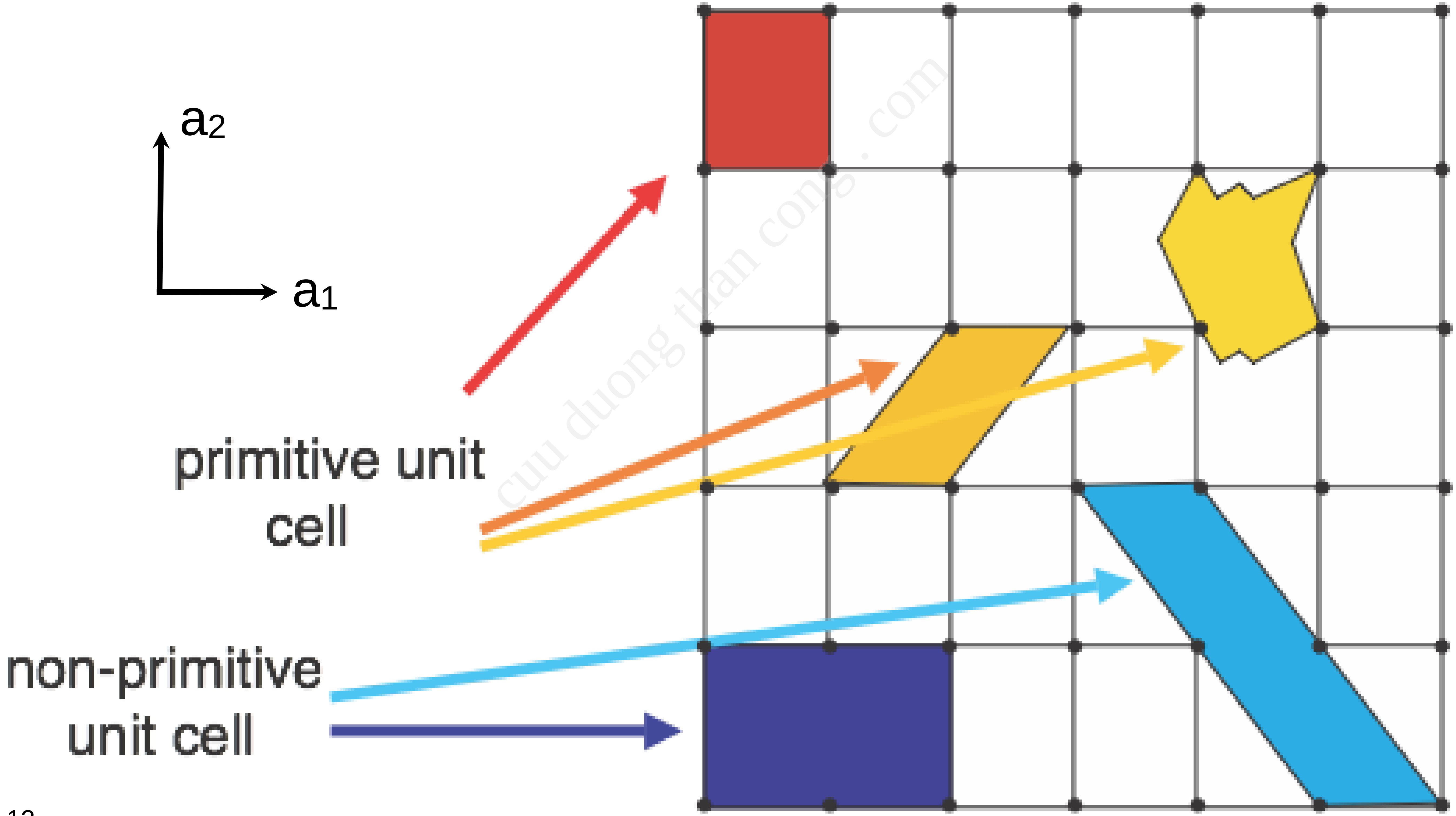
Bravais lattice (2D)



- The number of possible Bravais lattices (of fundamentally different symmetry) is limited to 5 (2D) and 14 (3D).

The crystal lattice: primitive unit cell

Primitive unit cell: any volume of space which, when translated through all the vectors of the Bravais lattice, fills space without overlap and without leaving voids



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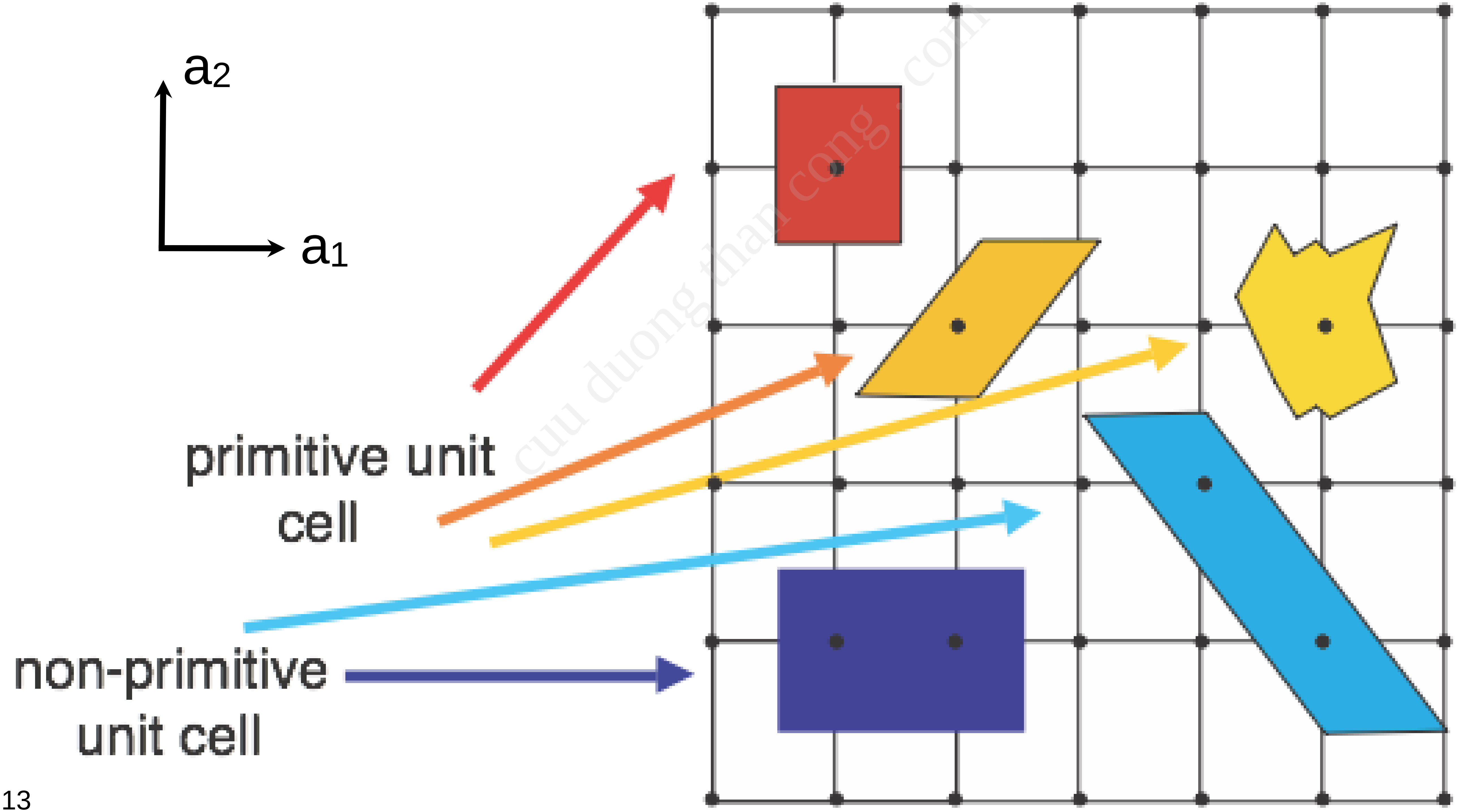
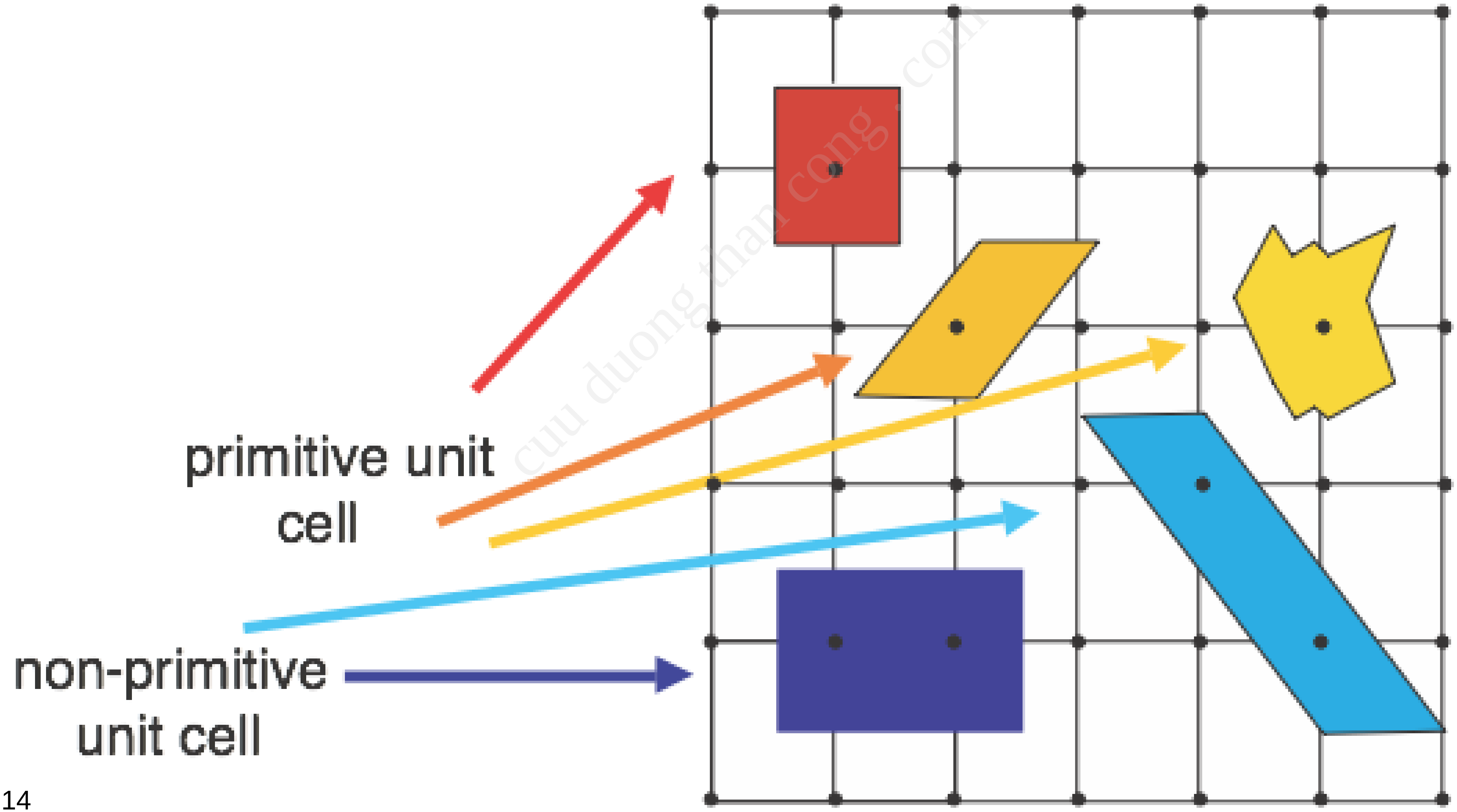


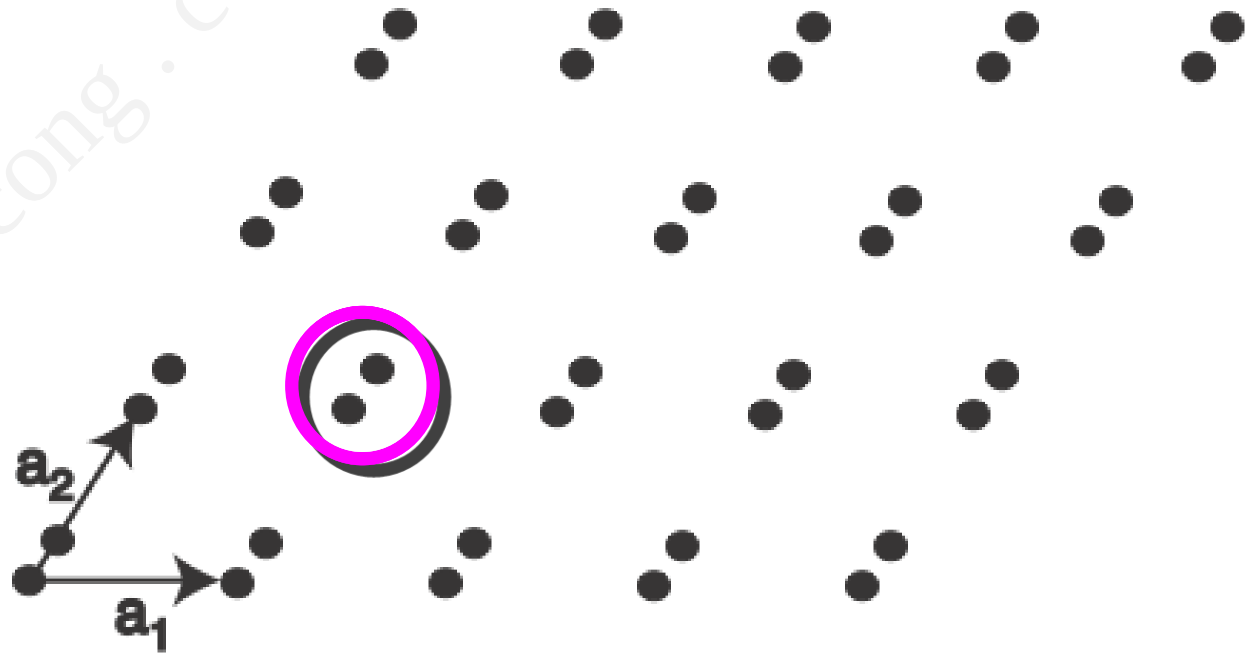
The crystal lattice: Wigner-Seitz cell

Wigner-Seitz cell: special choice of primitive unit cell: region of points closer to a given lattice point than to any other.



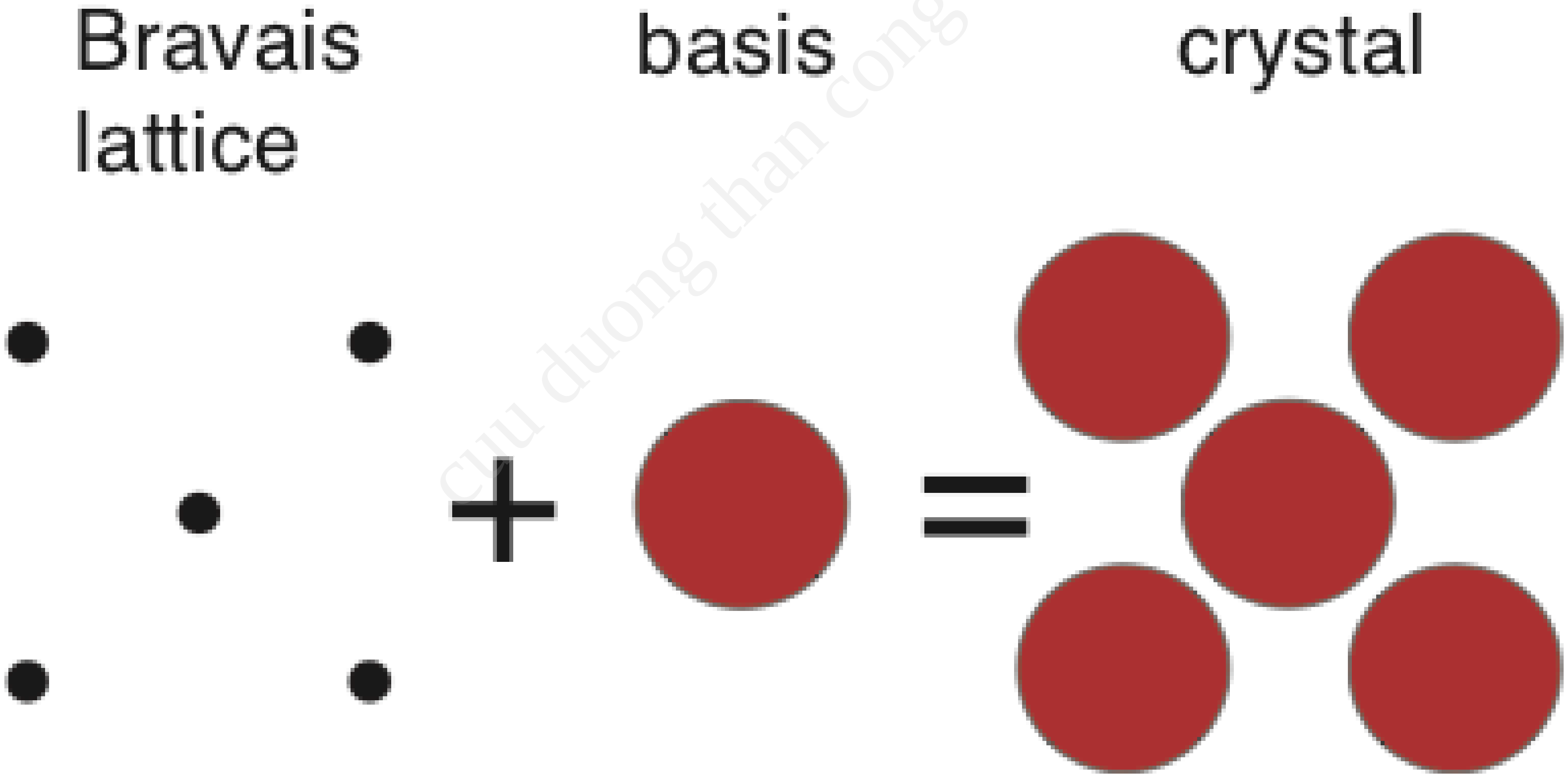
The crystal lattice: basis

- We could think: all that remains to do is to put atoms on the lattice points of the Bravais lattice.
- But: not all crystals can be described by a Bravais lattice (ionic, molecular, not even some crystals containing only one species of atoms.)
- BUT: all crystals can be described by the combination of a Bravais lattice and a basis. This basis is what one “puts on the lattice points”.



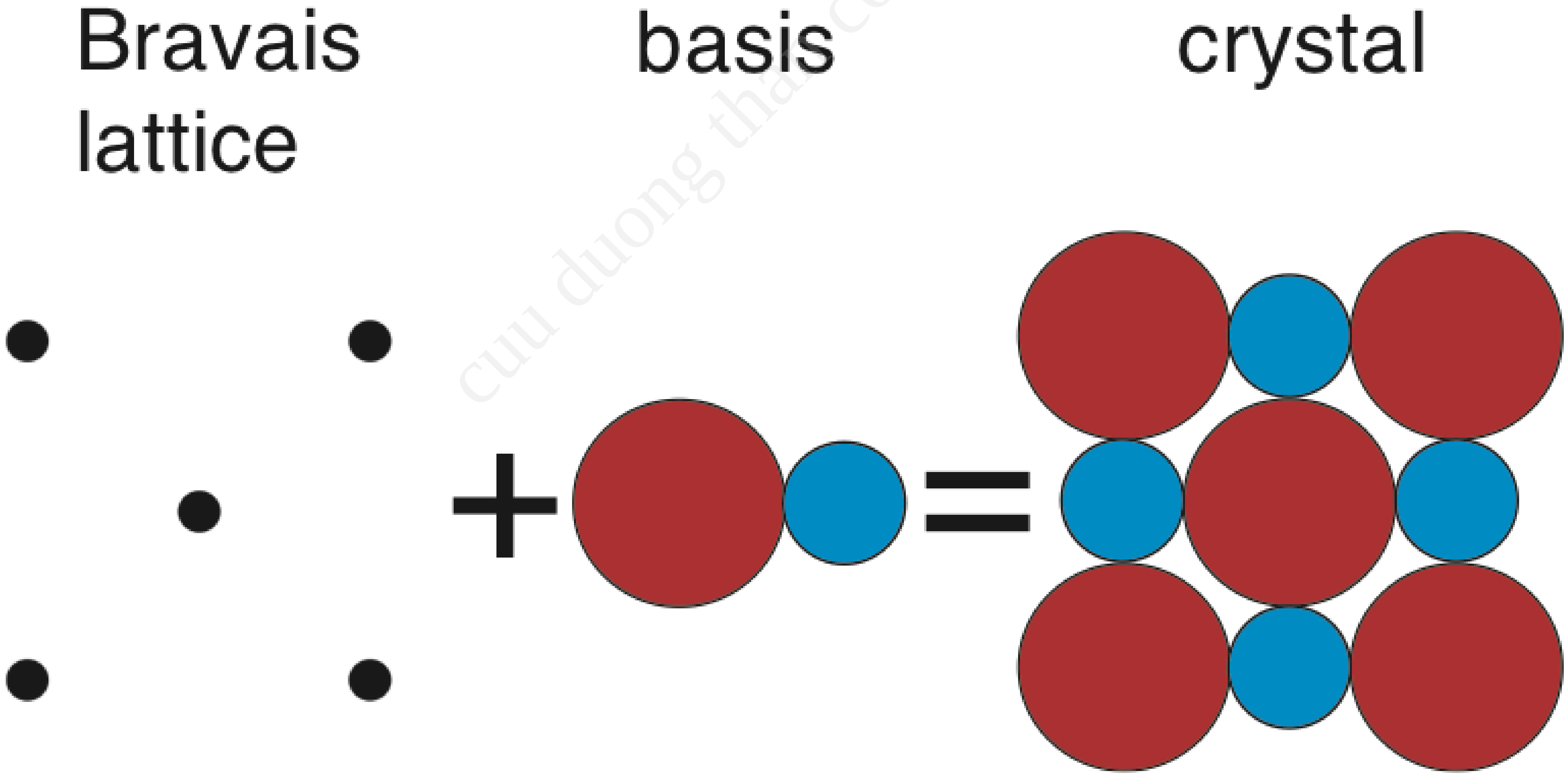
The crystal lattice: one atomic basis

- The basis can also just consist of one atom.



The crystal lattice: basis

- Or it can be several atoms.

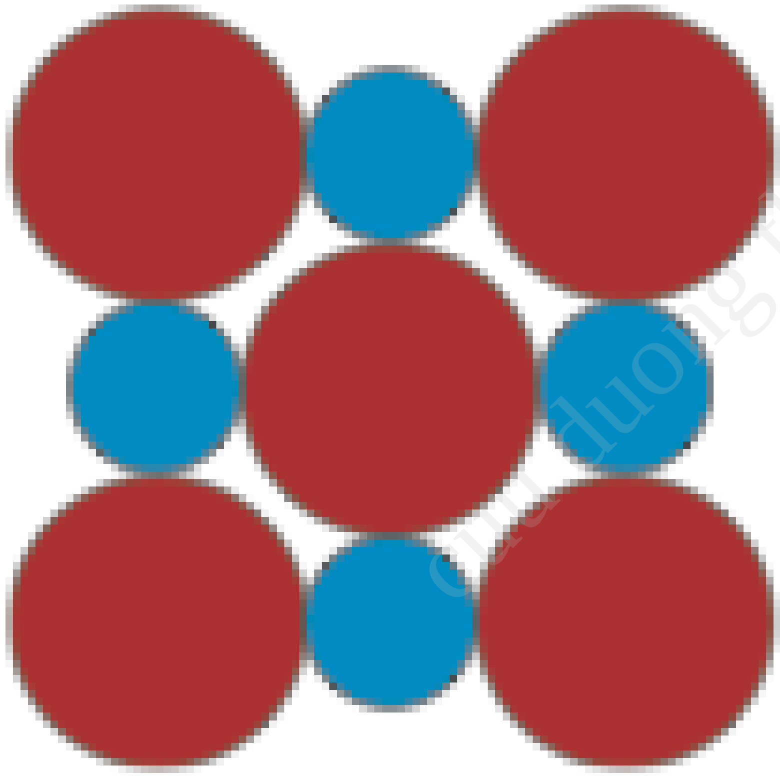


The crystal lattice: basis

- Or it can be molecules, proteins and pretty much anything else.

The crystal lattice: one more word about symmetry

- The other symmetry to consider is point symmetry. The Bravais lattice for these two crystals is identical:



four mirror lines
4-fold rotational axis
inversion

no additional
point symmetry

The crystal lattice: one more word about symmetry

The Bravais lattice vectors are

$$\mathbf{R}_{mno} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$$

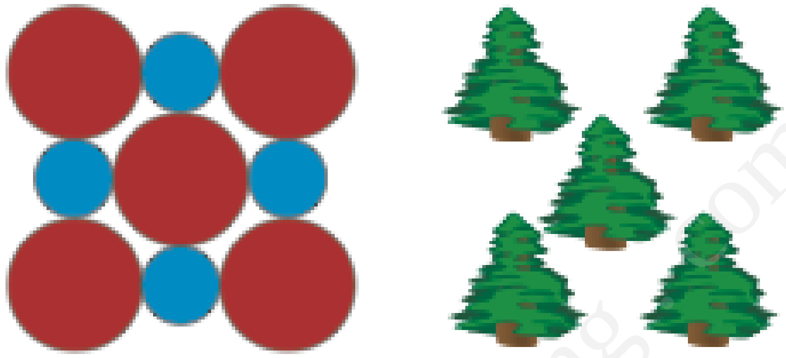
We can define a translation operator *T* such that

$$T_{\mathbf{R}_{mno}} F(\mathbf{r}) = F(\mathbf{r} + \mathbf{R}_{mno})$$

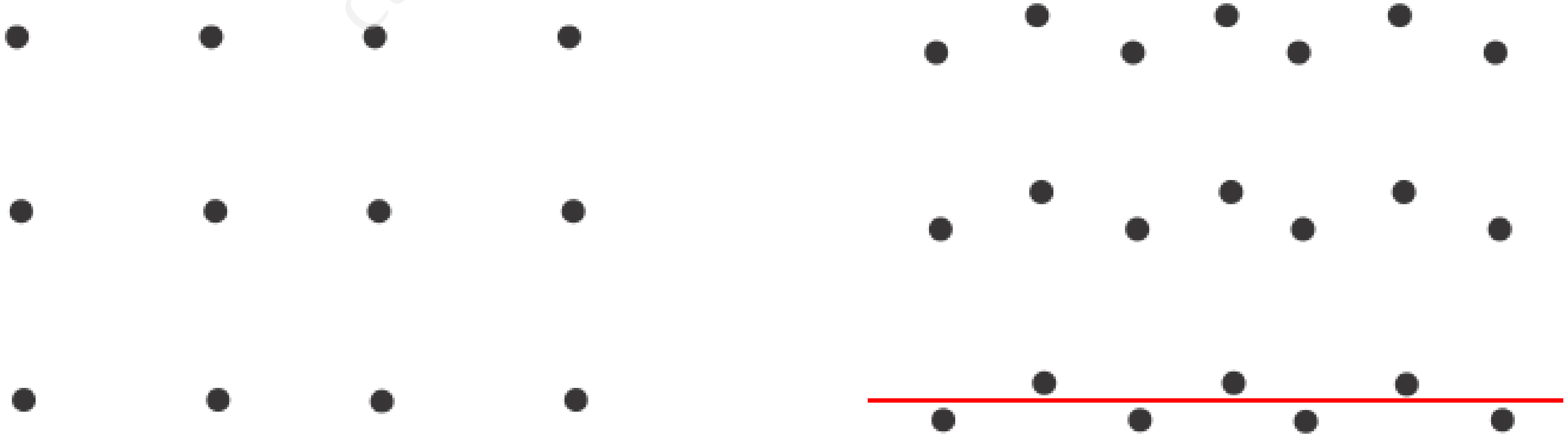
This operator commutes with the Hamiltonian of the solid and therefore we can choose the eigenfunctions of the Hamiltonian such that they are also eigenfunctions of the translation operator.

Nasty stuff...

adding the basis keeps translational symmetry but can reduce point symmetry

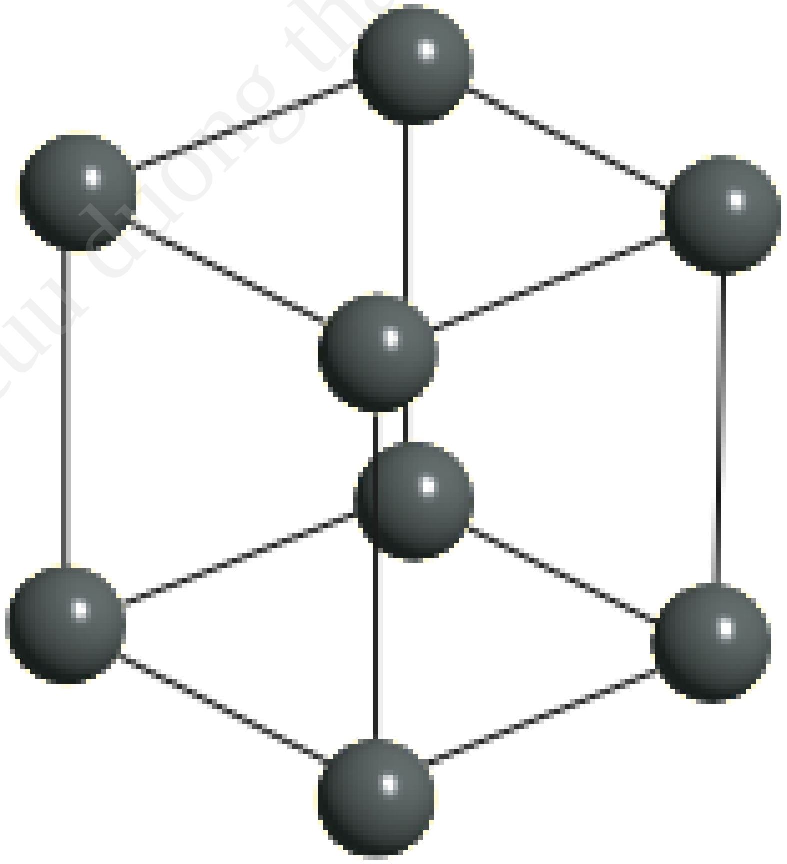


but it can also add new symmetries (like glide planes here)



Real crystal structures

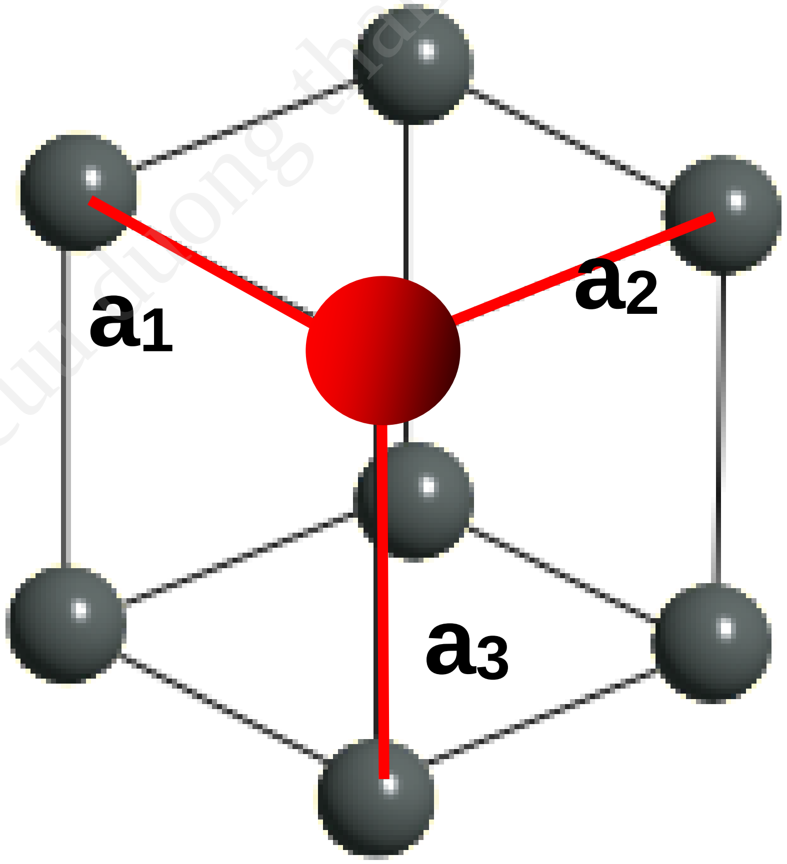
- What structure do the solids have? Can we predict it?
- Consider inert elements (spheres). This could be anything with no directional bonding (noble gases, simple and noble metals).
- Just put the spheres together in order to fill all space. This should have the lowest energy.
- A simple cubic structure?



Simple cubic

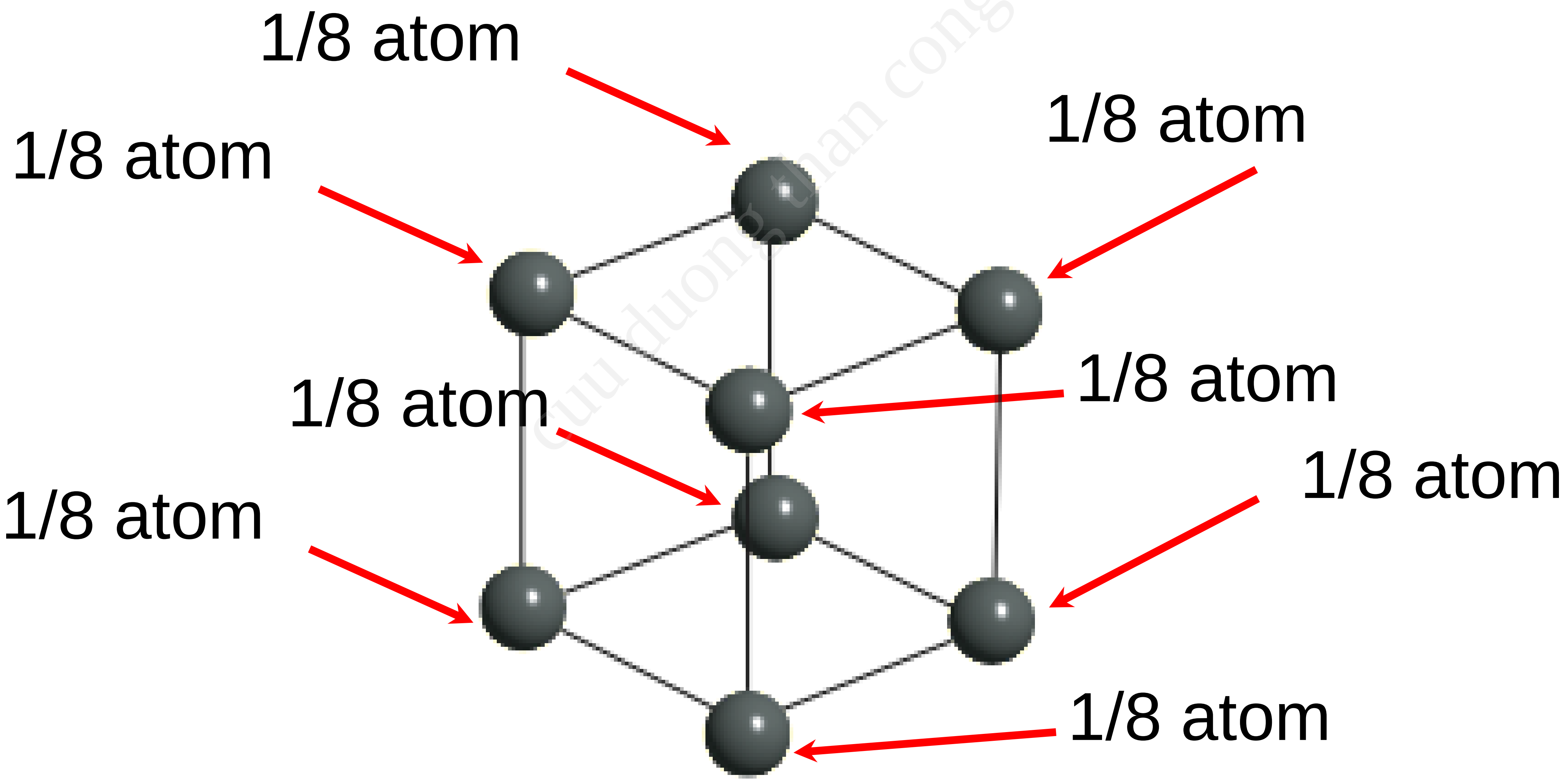
- The simple cubic structure is a Bravais lattice.
- The Wigner-Seitz cell is a cube
- The basis is one atom. So there is one atom per unit cell.

$$\mathbf{R}_{mno} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$$



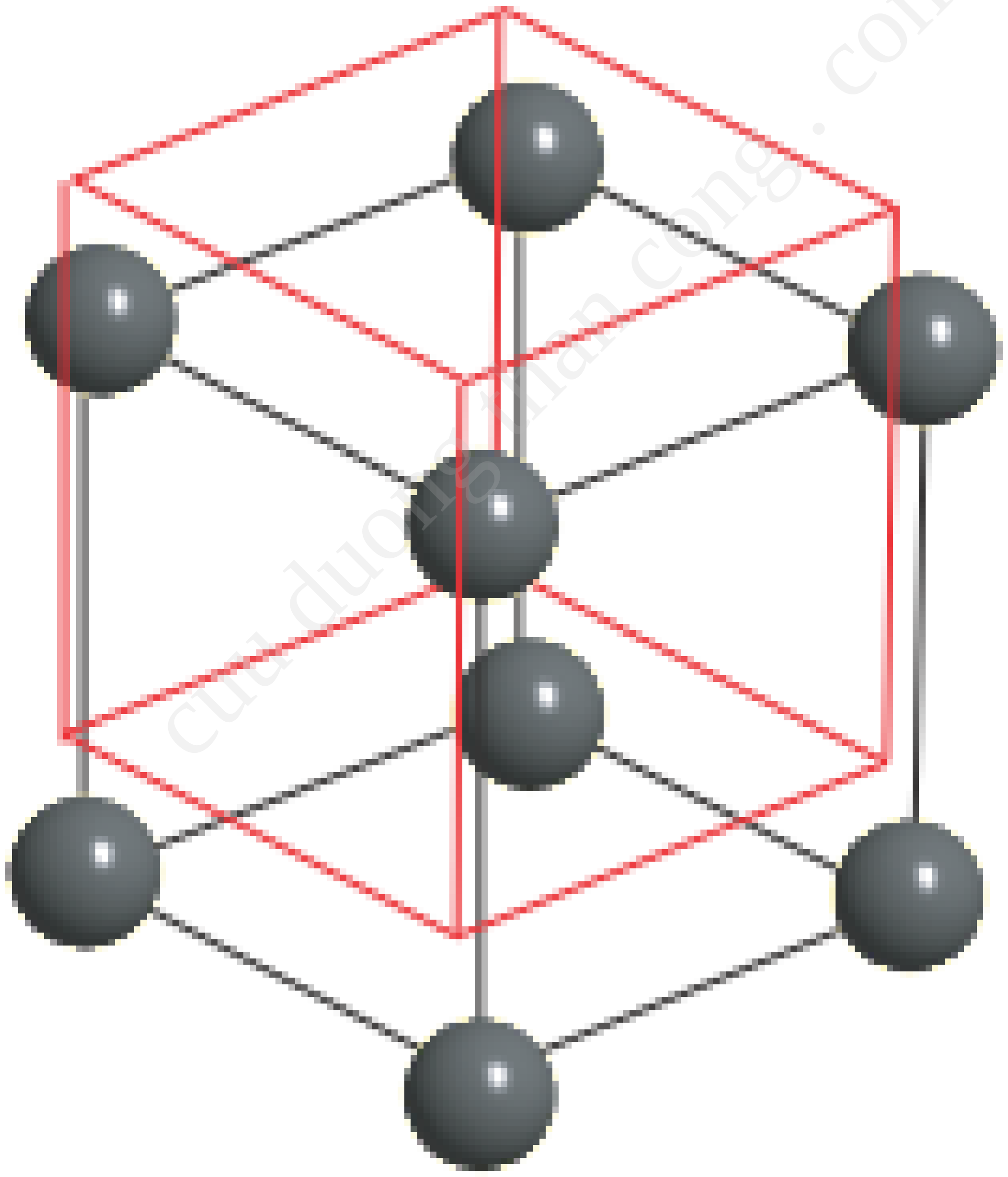
Simple cubic

- We can also simply count the atoms we see in one unit cell.
- But we have to keep track of how many unit cells share these atoms.



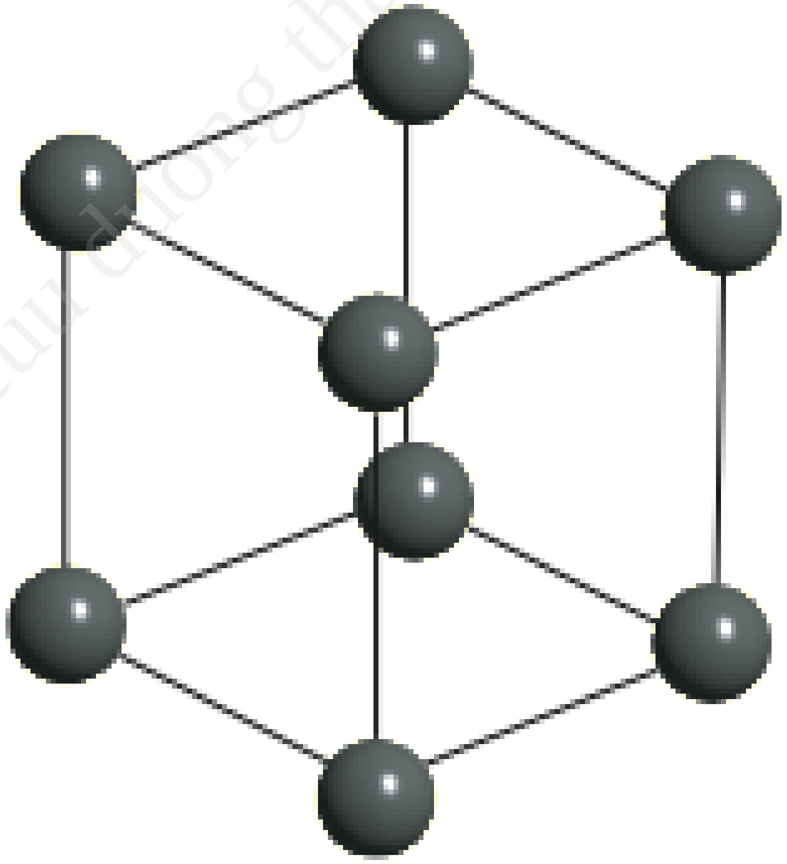
Simple cubic

- Or we can define the unit cell like this

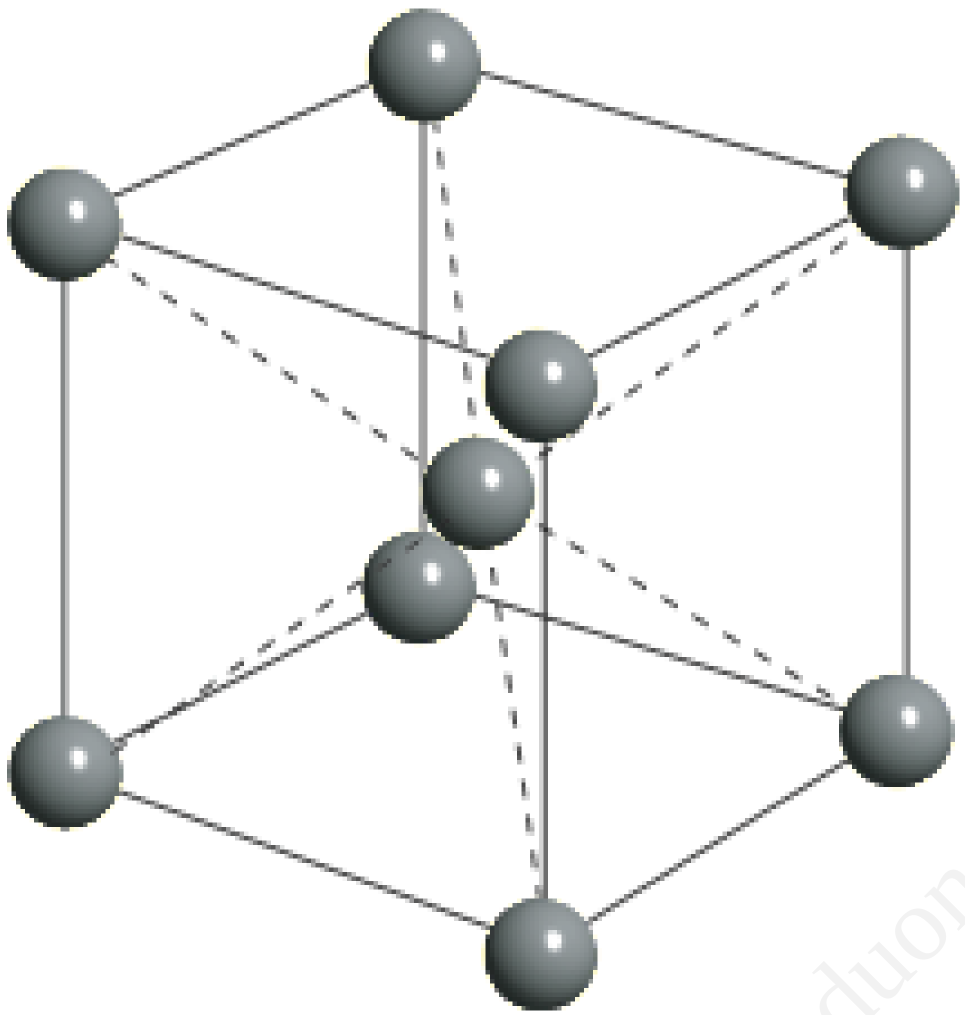


Simple cubic

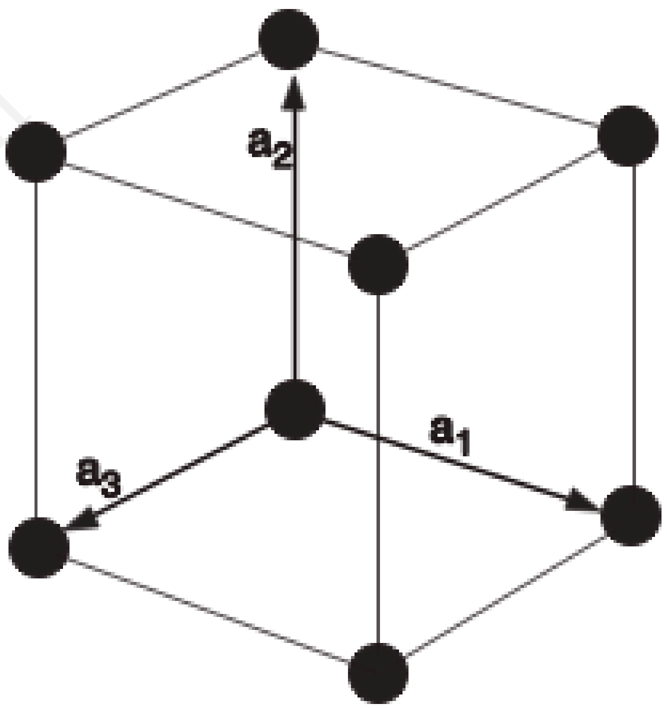
- A simple cubic structure is not a good idea for packing spheres (they occupy only 52% of the total volume).
- Only two elements crystallise in the simple cubic structure (F and O).



Better packing

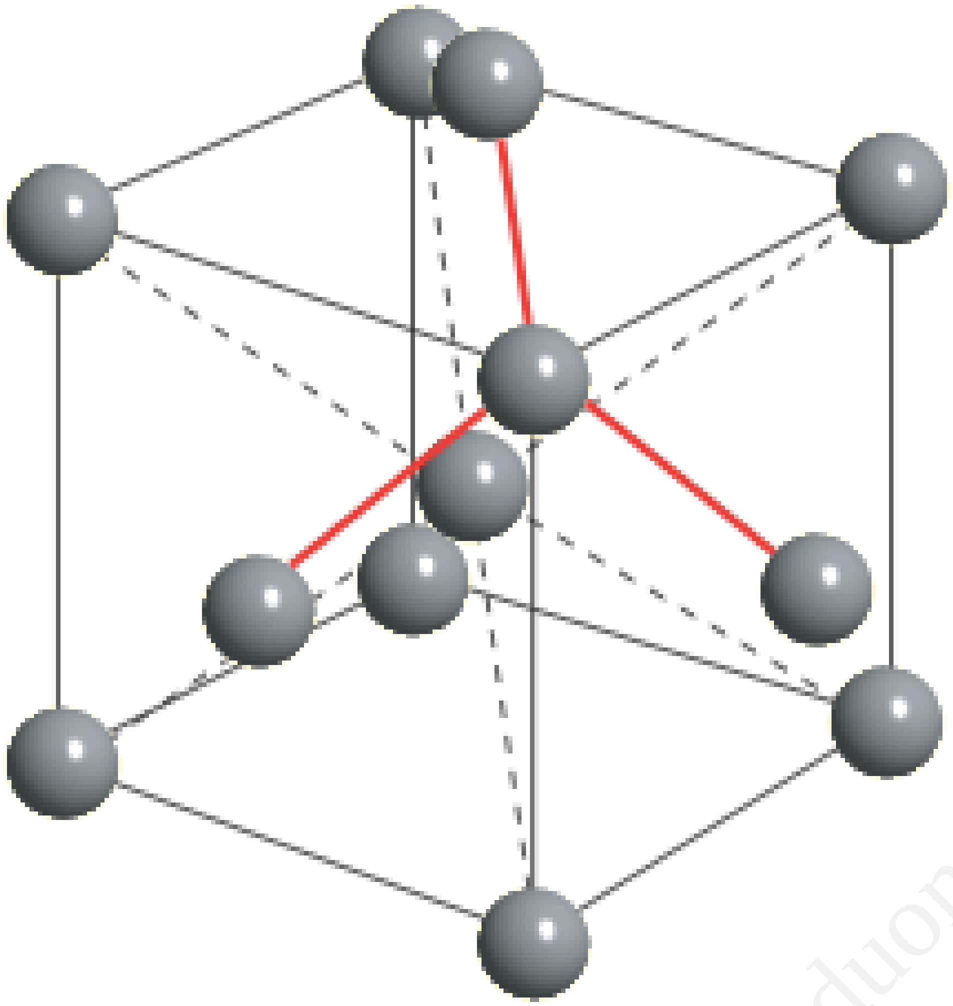


$$\mathbf{R} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$$



- In the body-centred cubic (bcc) structure 68% of the total volume is occupied.
- The bcc structure is also a Bravais lattice but the edges of the cube are (obviously) not the Bravais lattice vectors.

Better packing

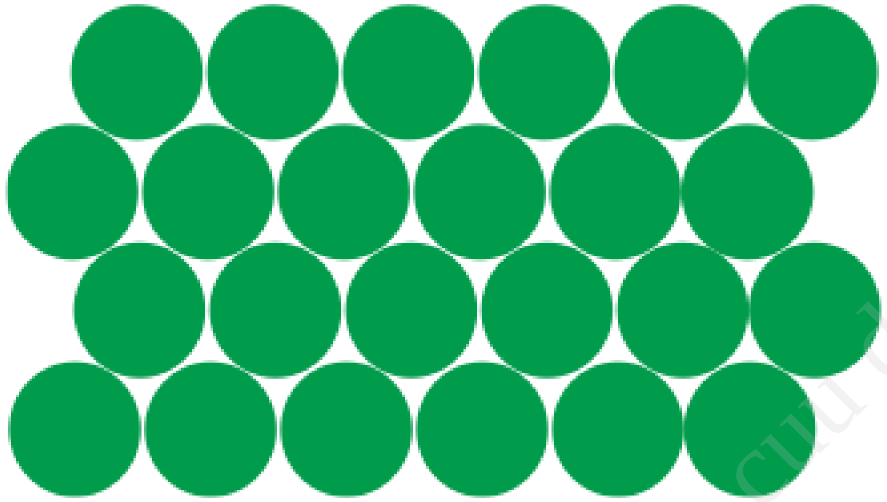


- In the body-centred cubic (bcc) structure 68% of the total volume is occupied.
- The bcc structure is also a Bravais lattice but the edges of the cube are not the correct lattice vectors.

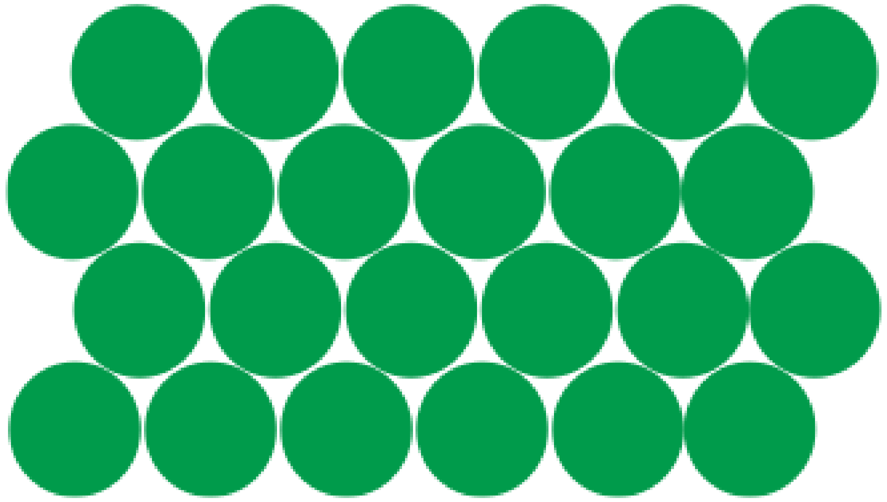
Close-packed structures

Close-packed structures: fcc and hcp

hcp
ABABAB...



fcc
ABCABCABC...



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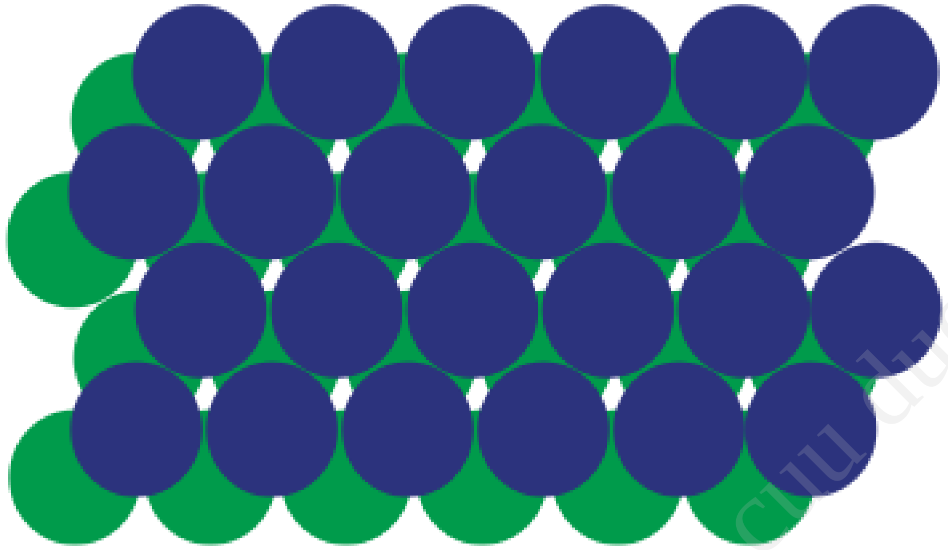
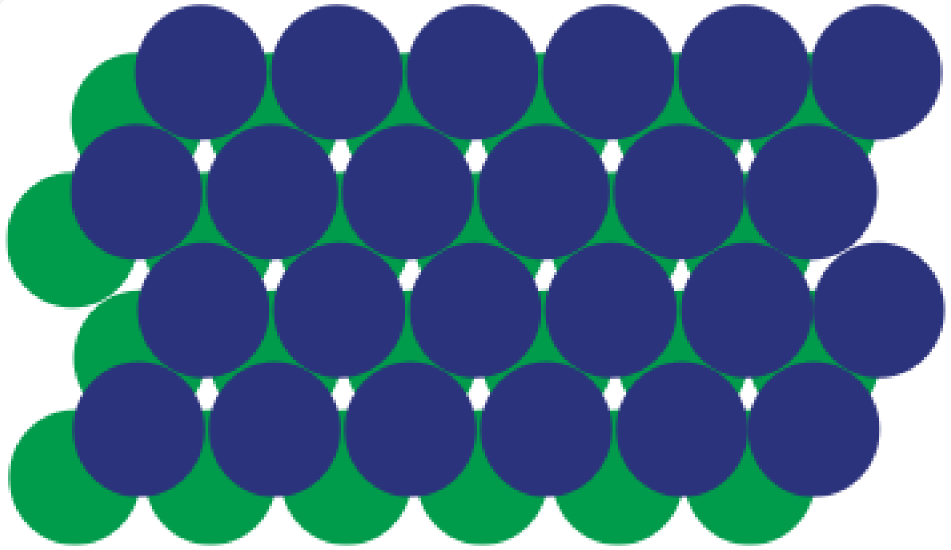
ABABAB...



fcc
ABCABCABC...



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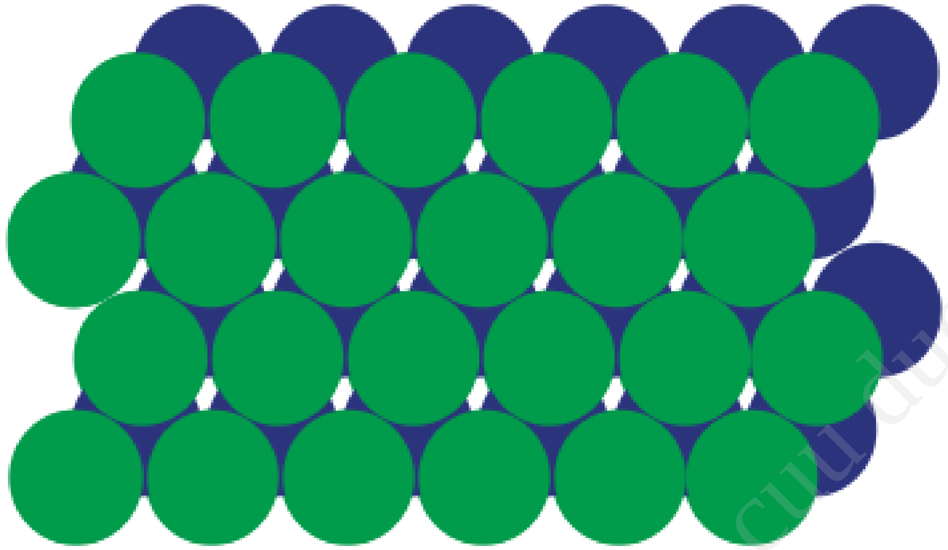
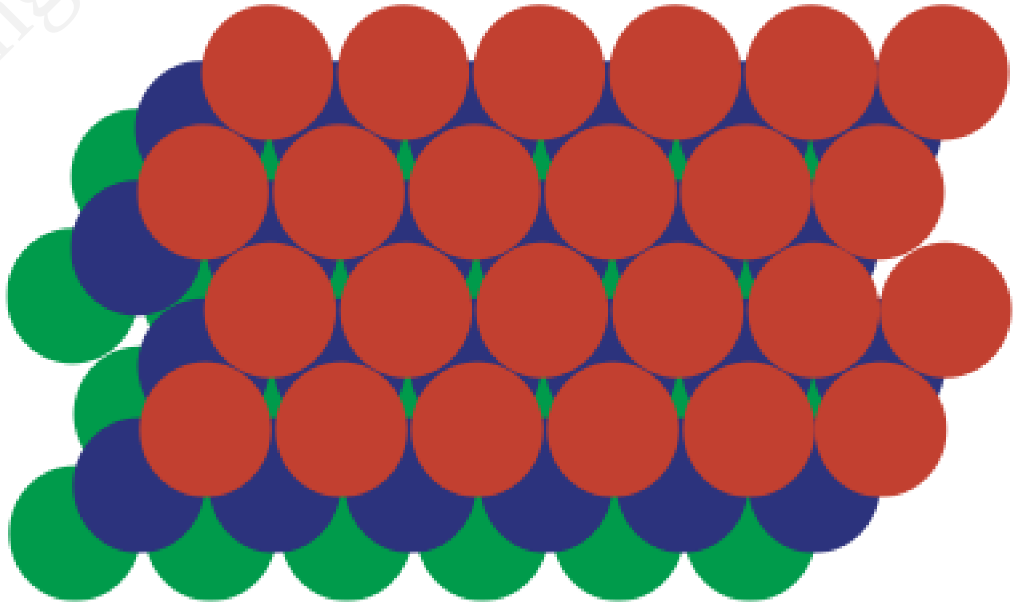
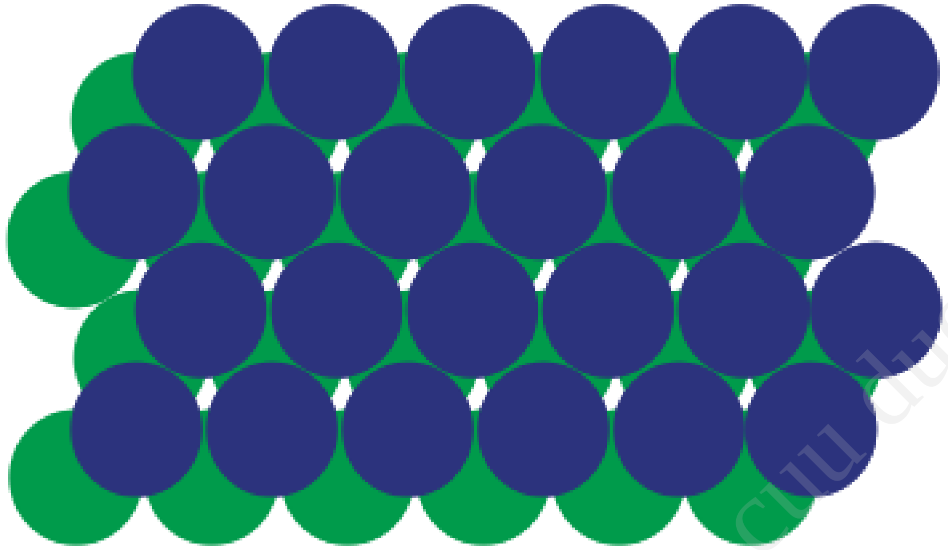


fcc
ABCABCABC...

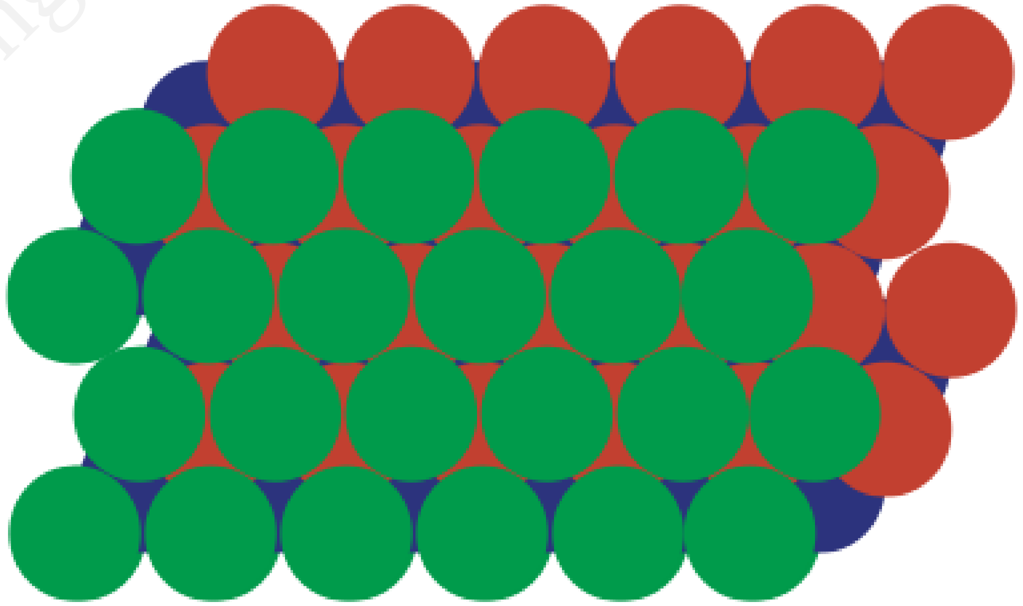


Close-packed structures: fcc and hcp

hcp
ABABAB...

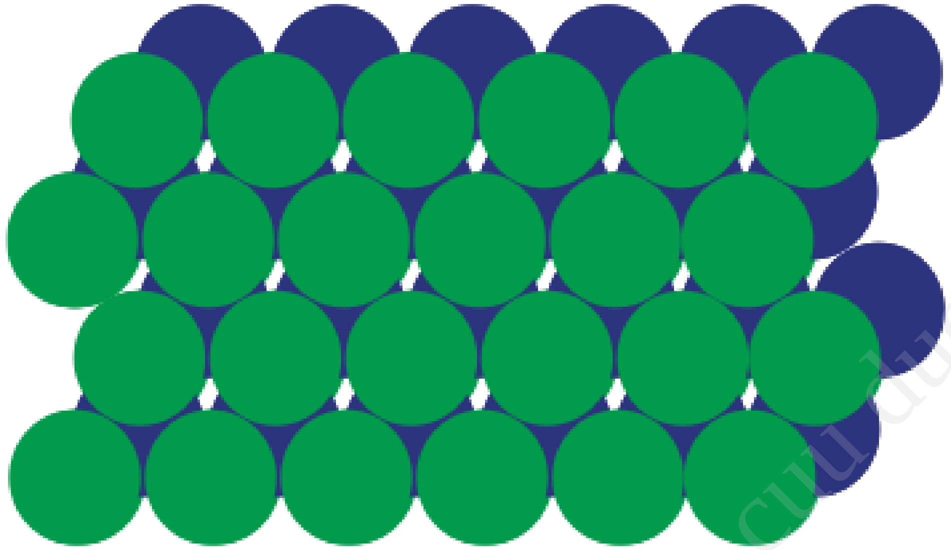


fcc
ABCABCABC...

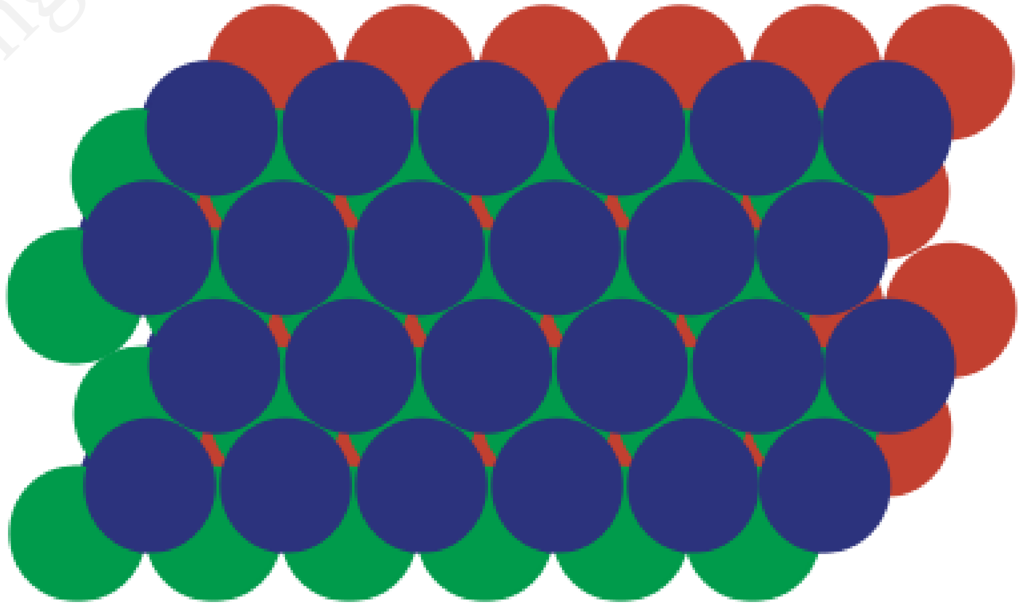


Close-packed structures: fcc and hcp

hcp
ABABAB...

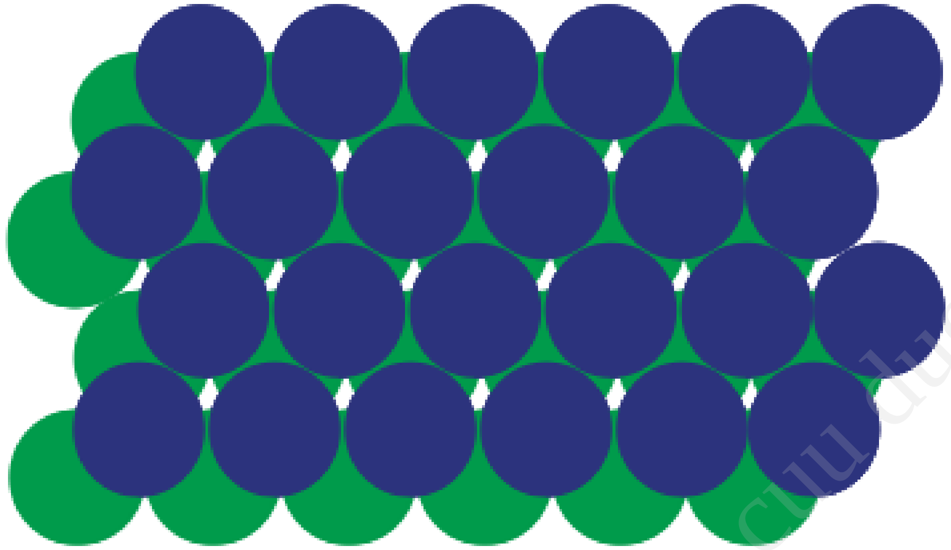


fcc
ABCABCABC...

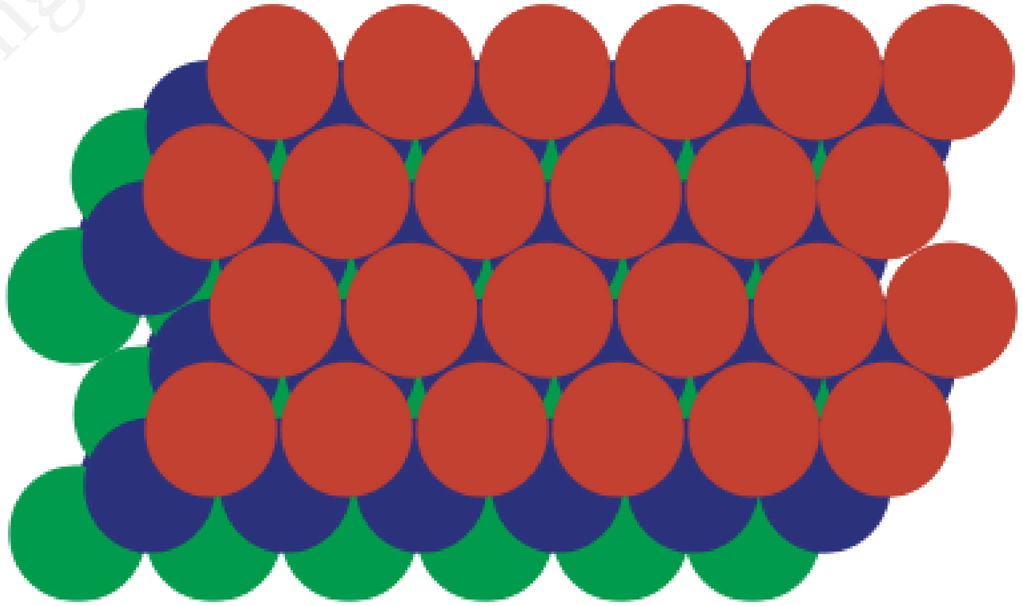


Close-packed structures: fcc and hcp

hcp
ABABAB...

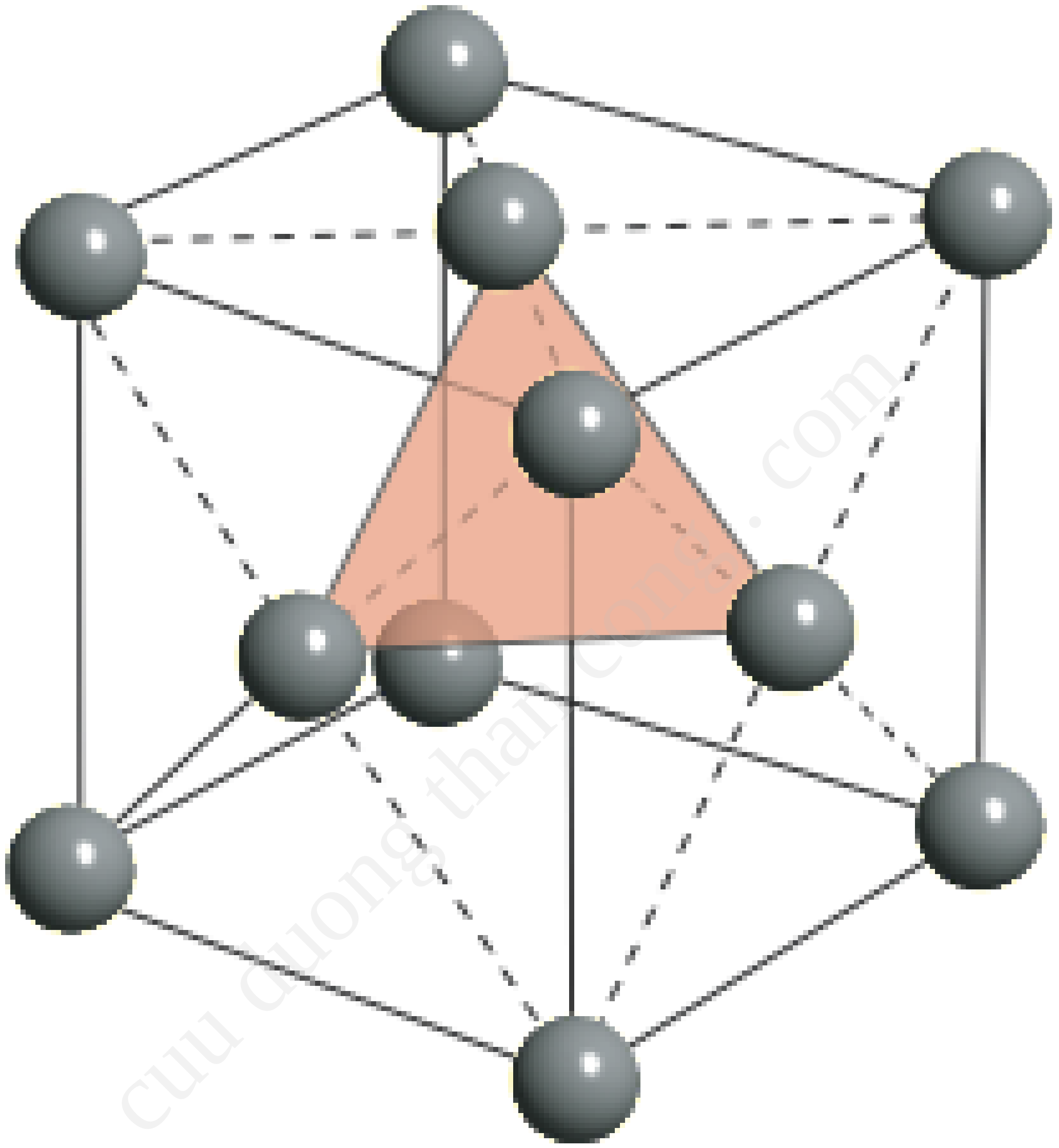


fcc
ABCABCABC...



- The hexagonal close-packed (hcp) and face-centred cubic (fcc) and structure have the same packing fraction

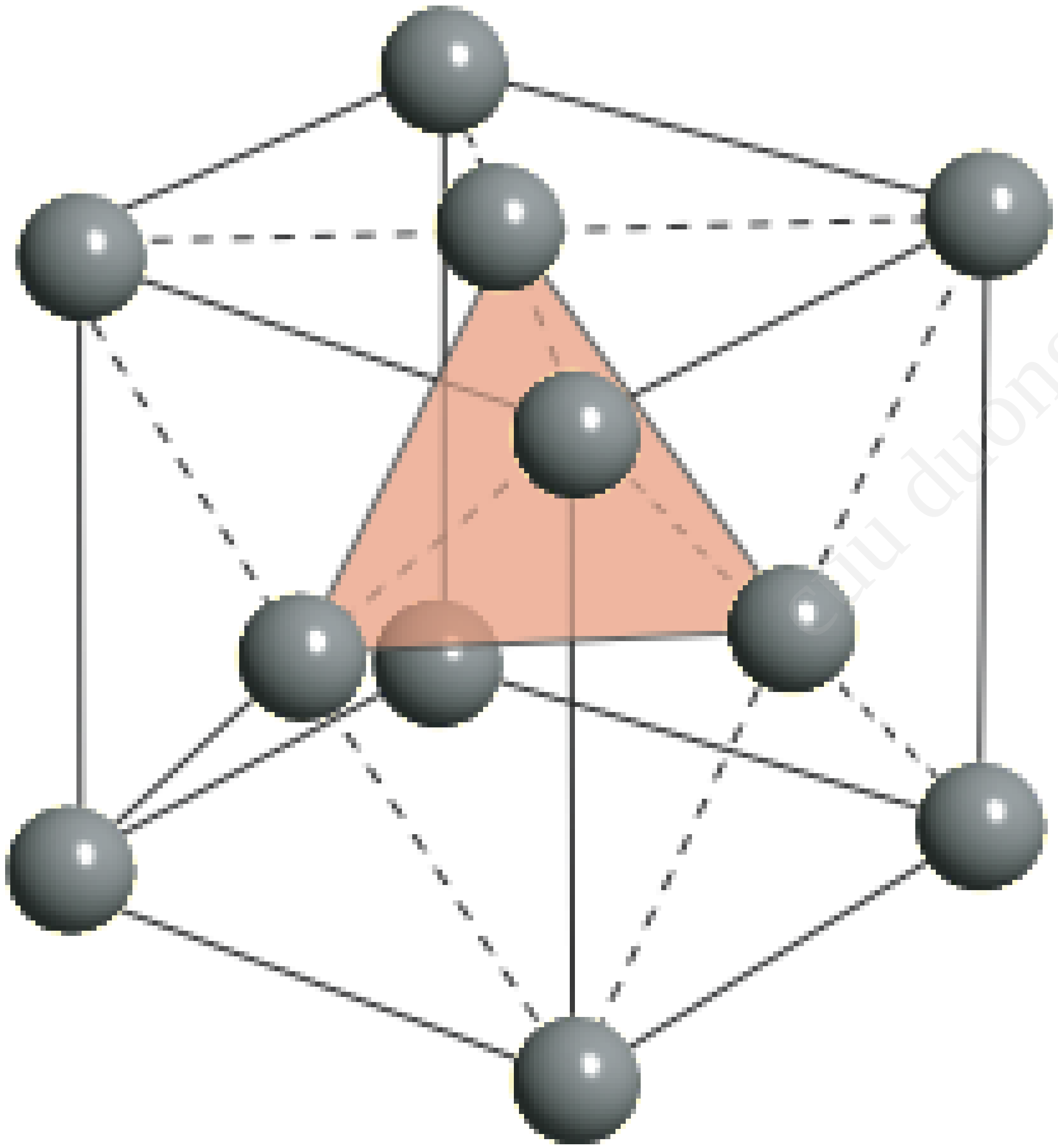
The fcc structure



- In the face-centred cubic (fcc) structure 74% of the total volume is occupied (slightly better than bcc with 68%)
- This is probably the optimum (Kepler, 1611) and grocers.

The fcc lattice: Bravais lattice (3D)

- The fcc lattice is also a Bravais lattice but the edges of the cube are not the correct lattice vectors.
- The cubic unit cell contains more than one atom.



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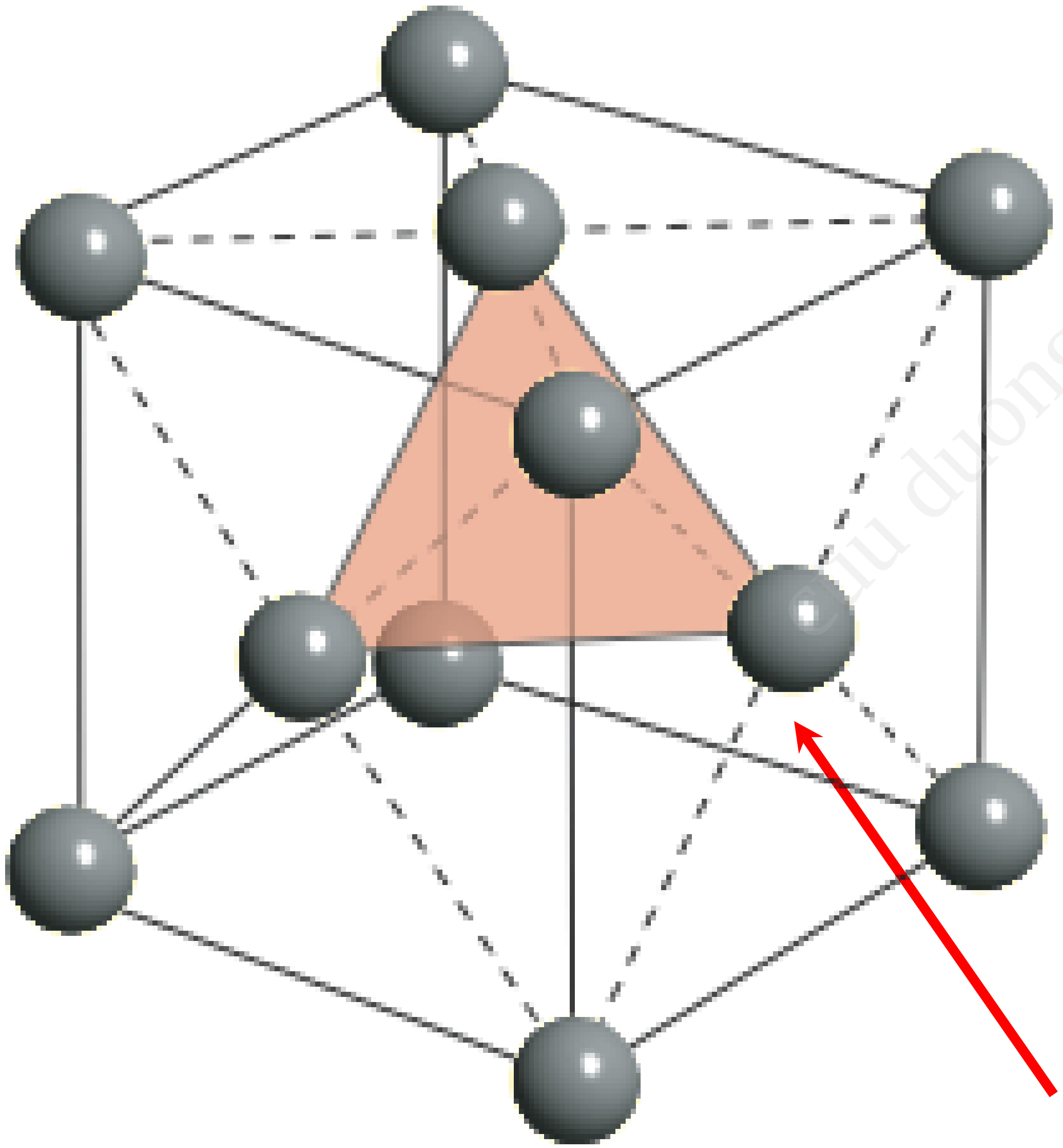


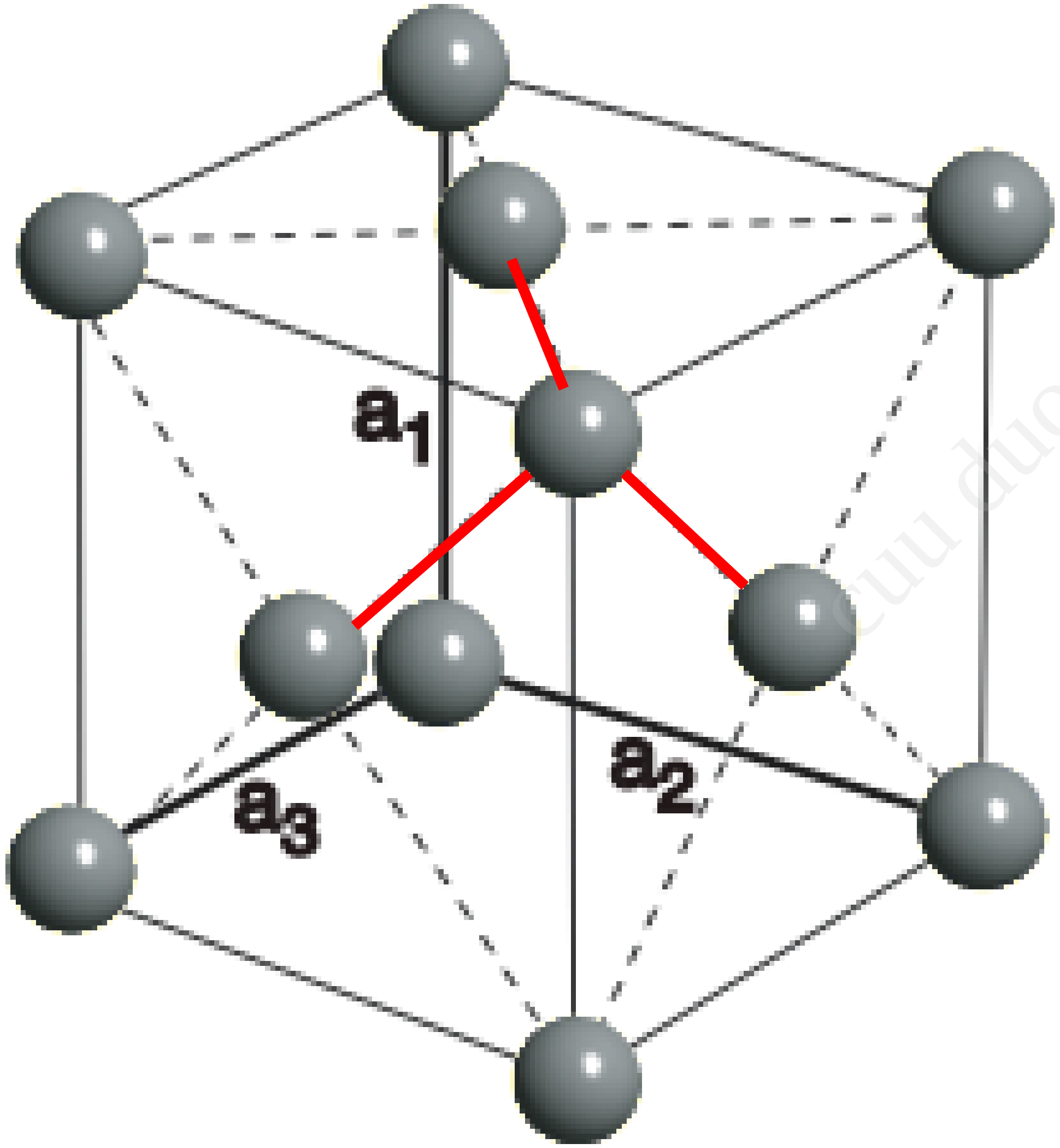
$$\mathbf{R}_{mno} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$$

1/8 atom

1/2 atom

The fcc lattice: Bravais lattice (3D)

- The fcc and bcc lattices are also Bravais lattices but the edges of the cube are not the correct lattice vectors.
- When choosing the correct lattice vectors, one has only one atom per unit cell.



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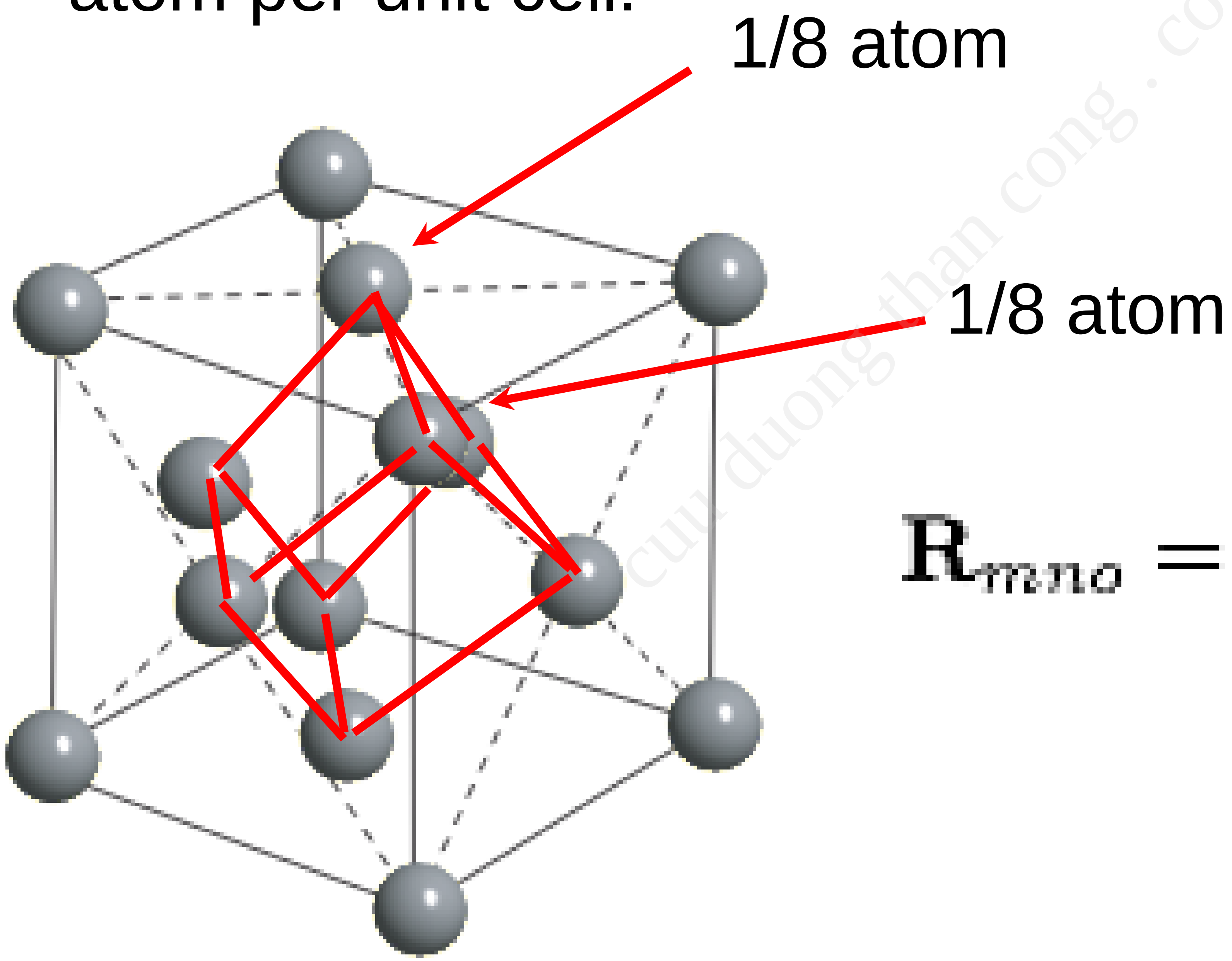
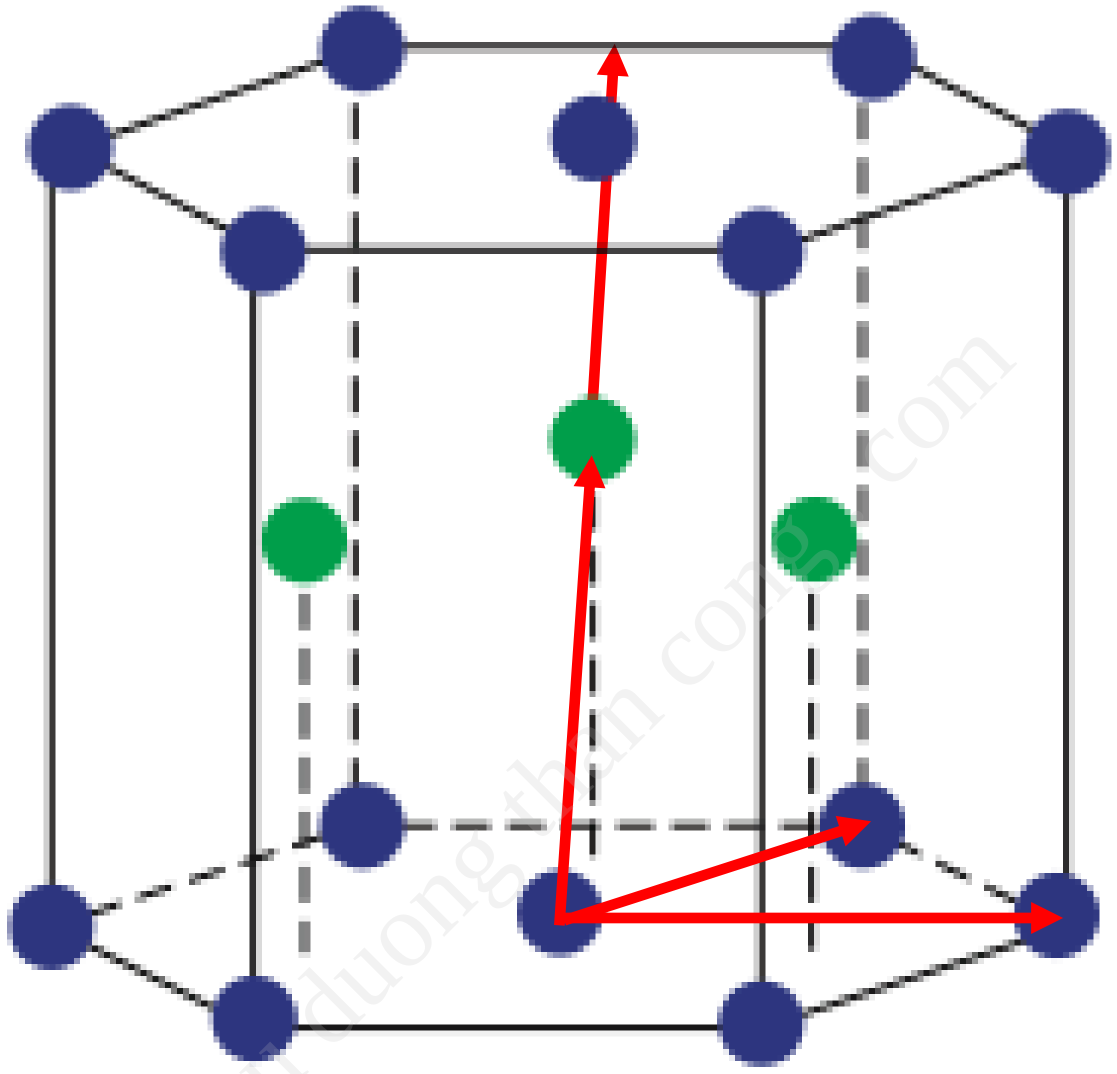


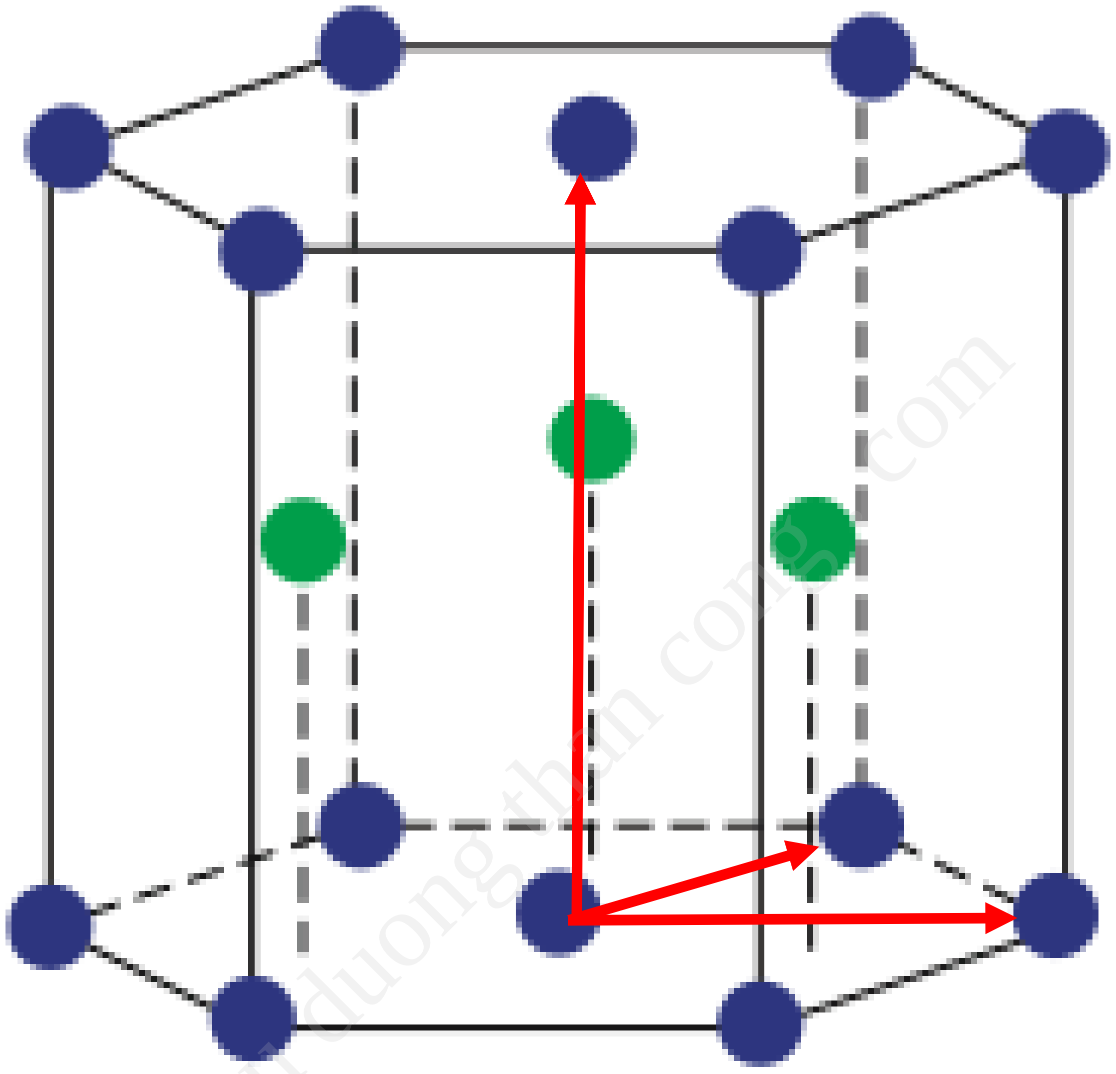
$$\mathbf{R}_{mno} = m\mathbf{a}_1 + n\mathbf{a}_2 + o\mathbf{a}_3$$

Close-packed structures: hcp



- The hcp lattice is NOT a Bravais lattice. It can be constructed from a Bravais lattice with a basis containing two atoms.
- the packing efficiency is of course exactly the same as for the fcc structure (74 % of space occupied).

Close-packed structures: hcp



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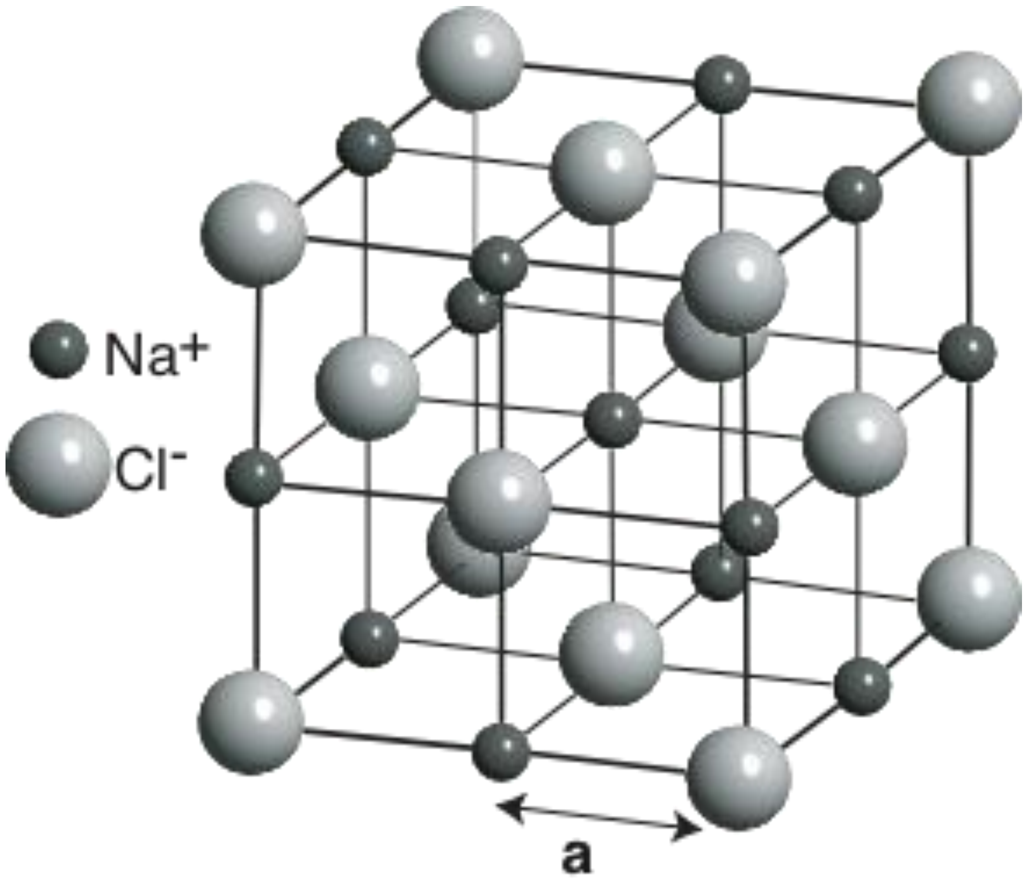
Close-packed structures

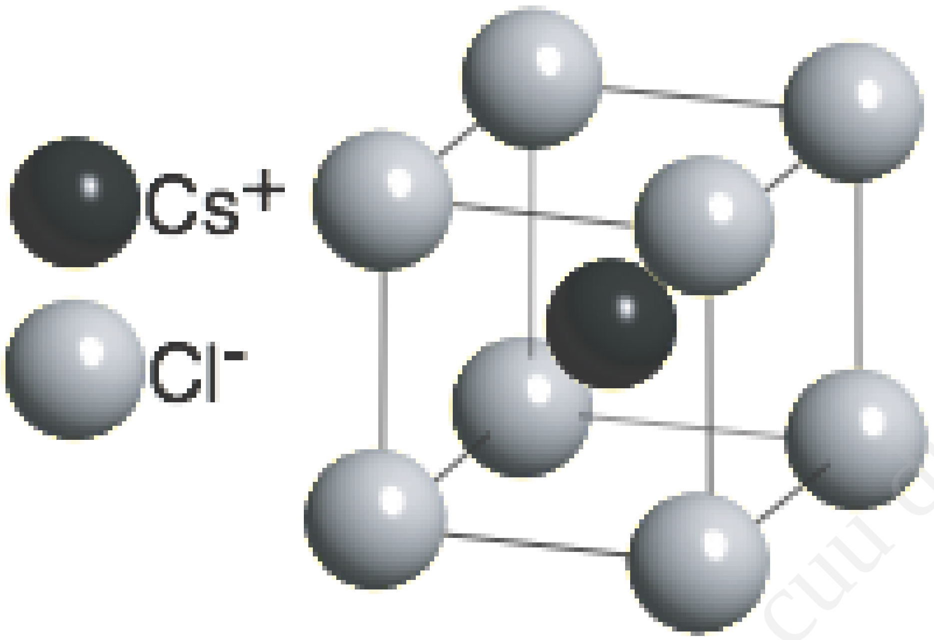
- Close-packed structures are indeed found for inert solids and for metals.
- For metals, the conduction electrons are smeared out and directional bonding is not important. Close-packed structures have a big overlap of the wave functions.
- Most elements crystallize as hcp (36) or fcc (24).

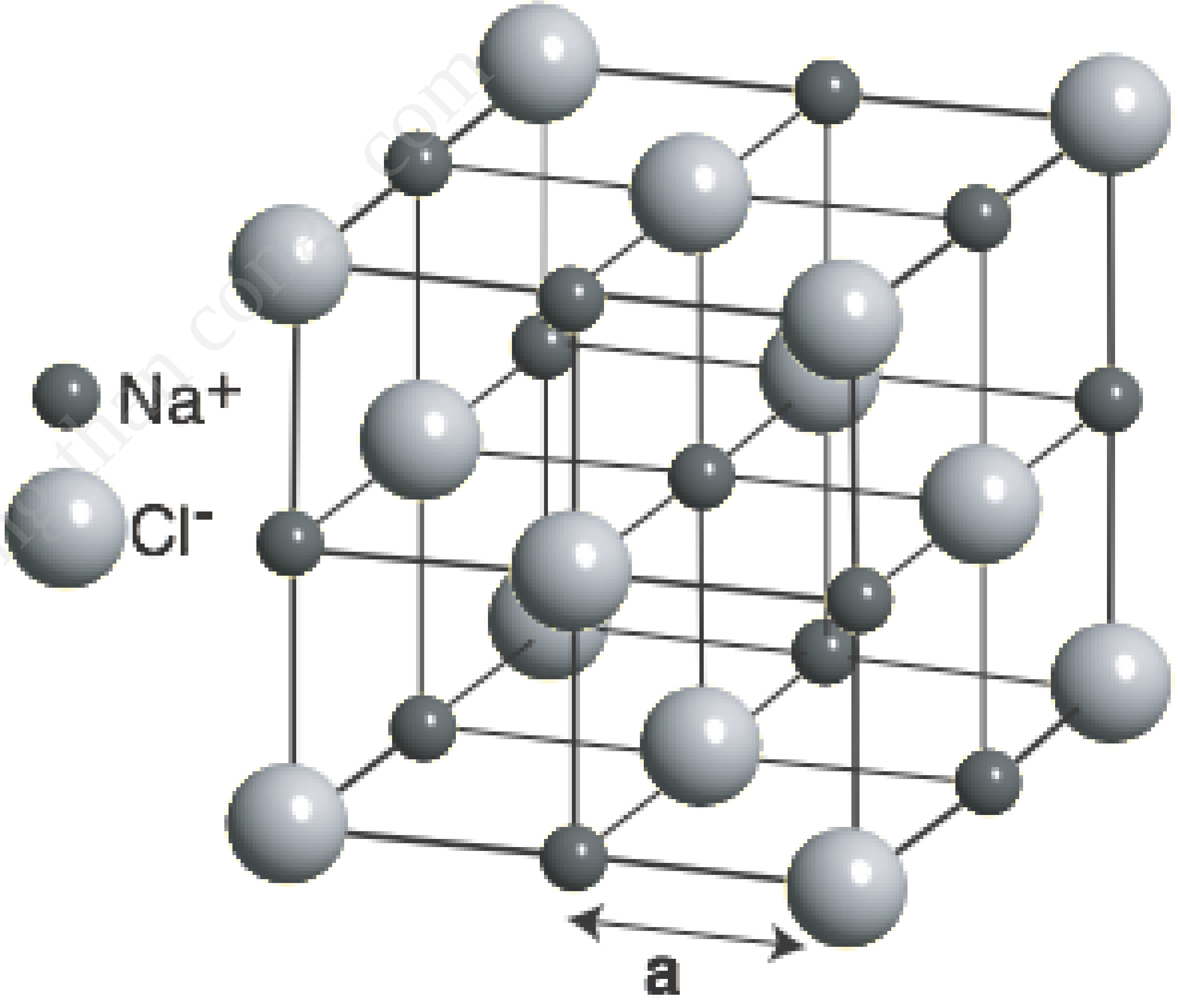
Close-packed structures: ionic materials

- In ionic materials, different considerations can be important (electrostatics, different size of ions)
- In NaCl the small Na are in interstitial positions of an fcc lattice formed by Cl ions (slightly pushed apart)



Close-packed structures: ionic materials

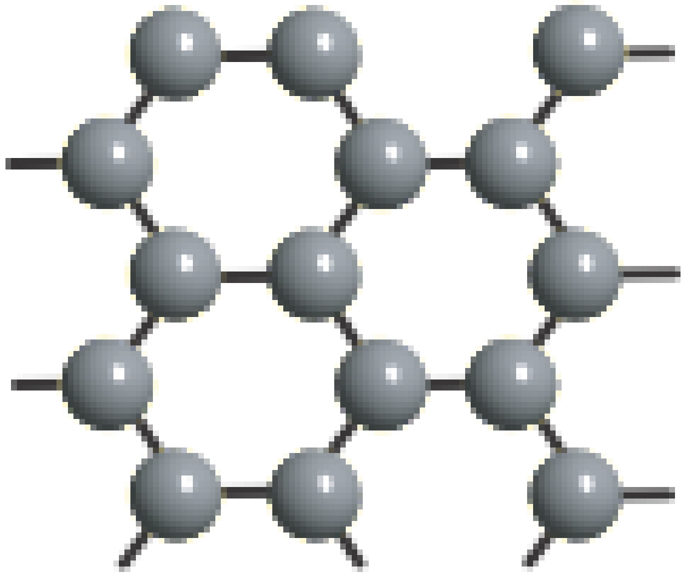




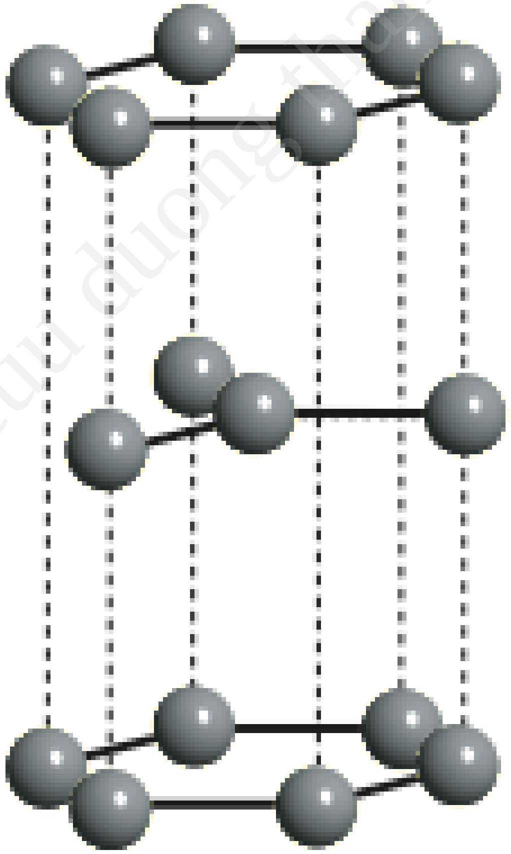
Non close-packed structures

- covalent materials (bond direction more important than packing)

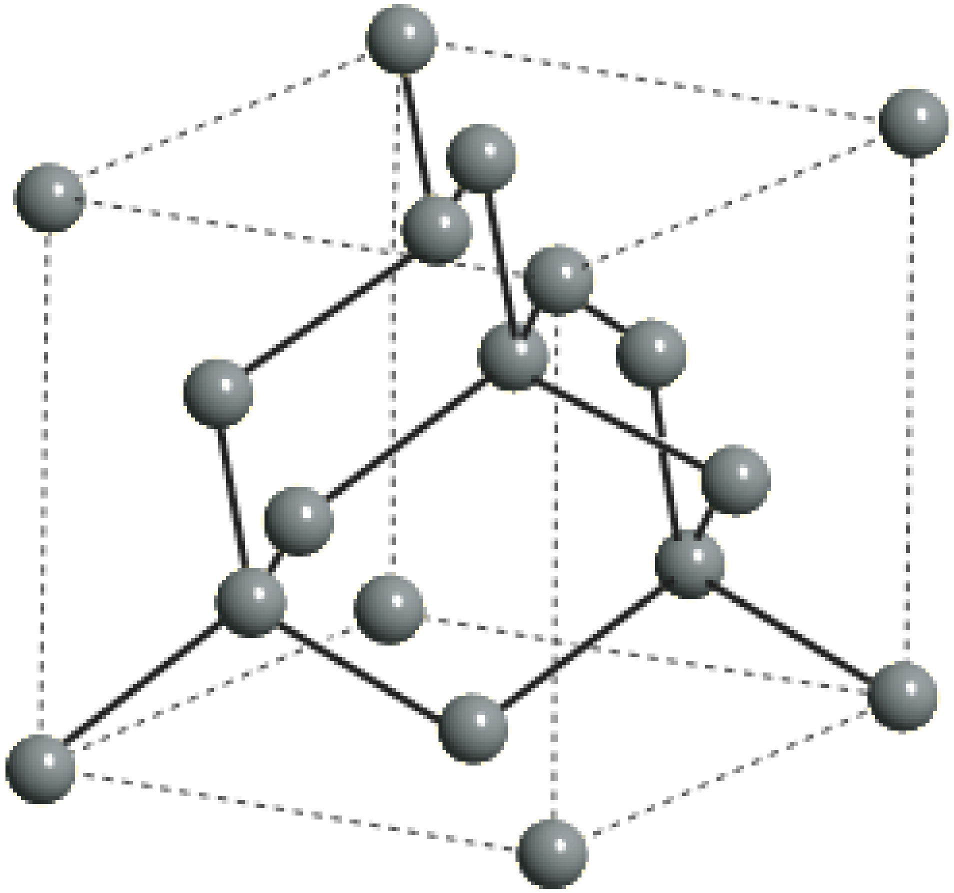
graphene



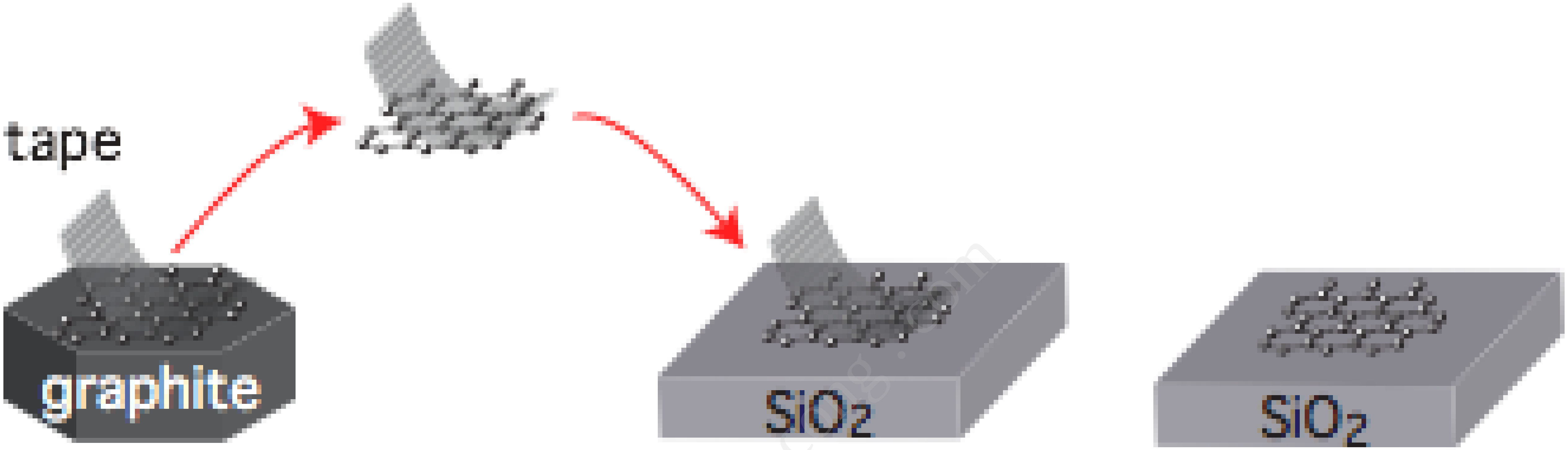
graphite



diamond (only 34 % packing)



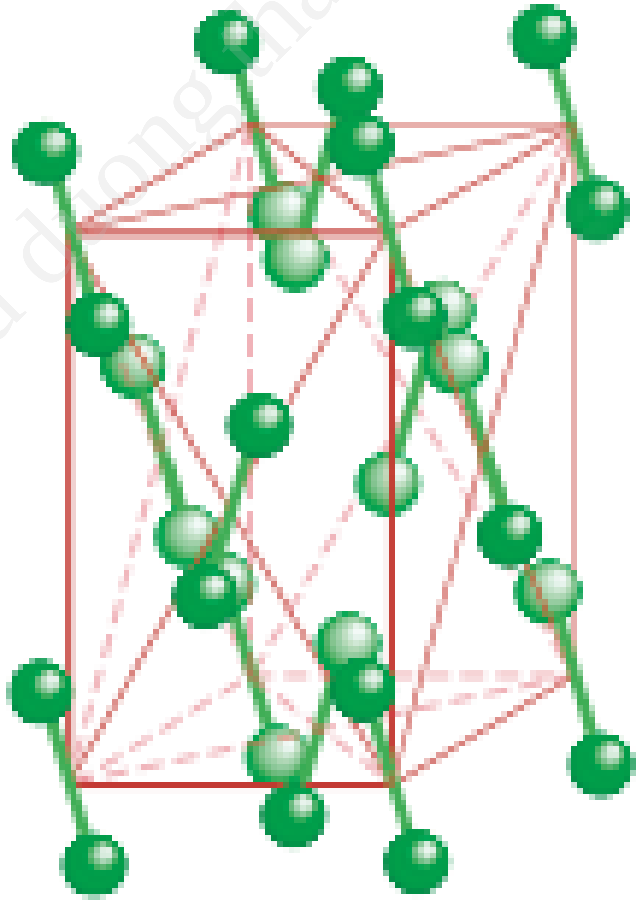
graphene



Non close-packed structures

- molecular crystals (molecules are not round, complicated structures)

α-Gallium, Iodine



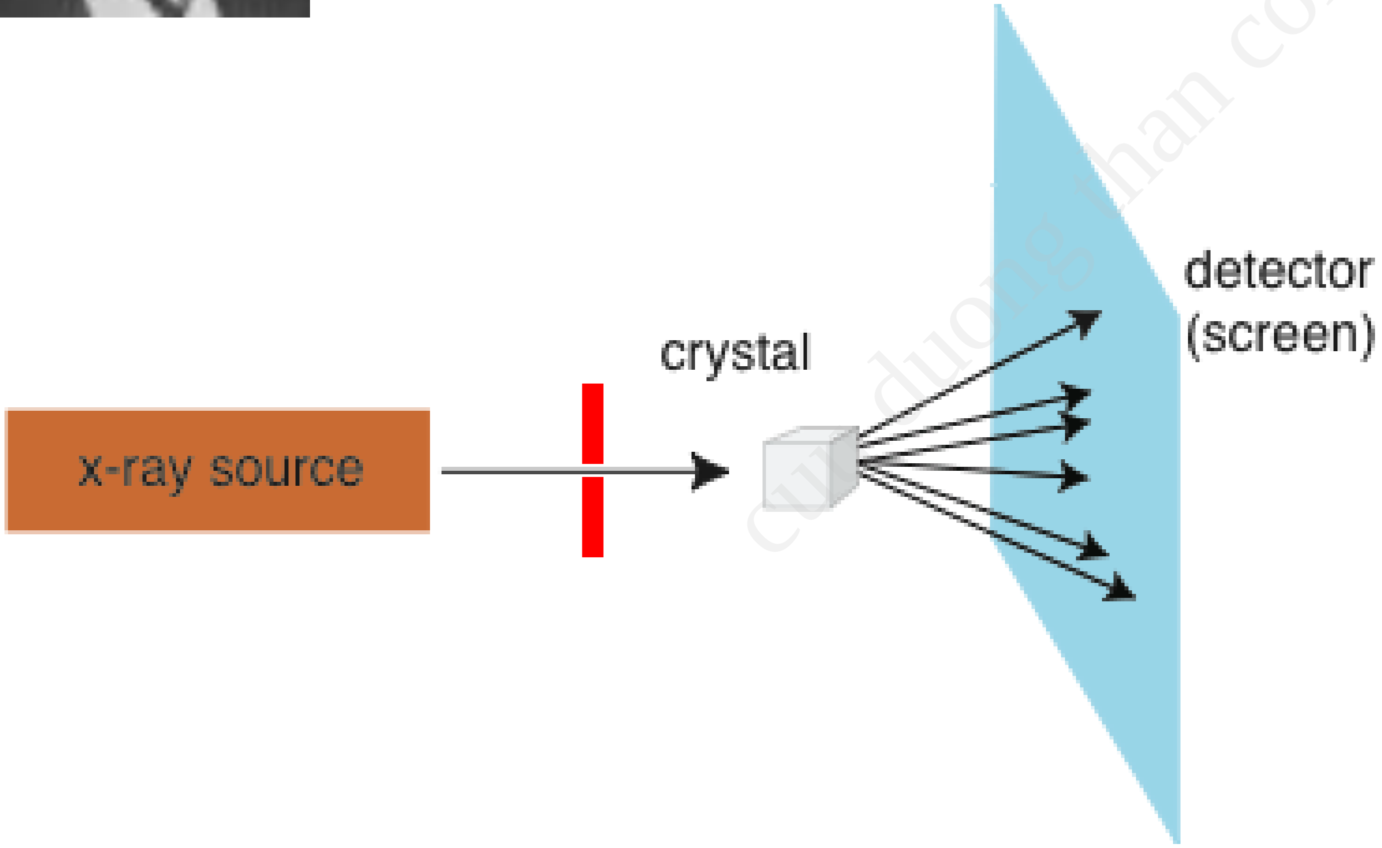
Crystal structure determination

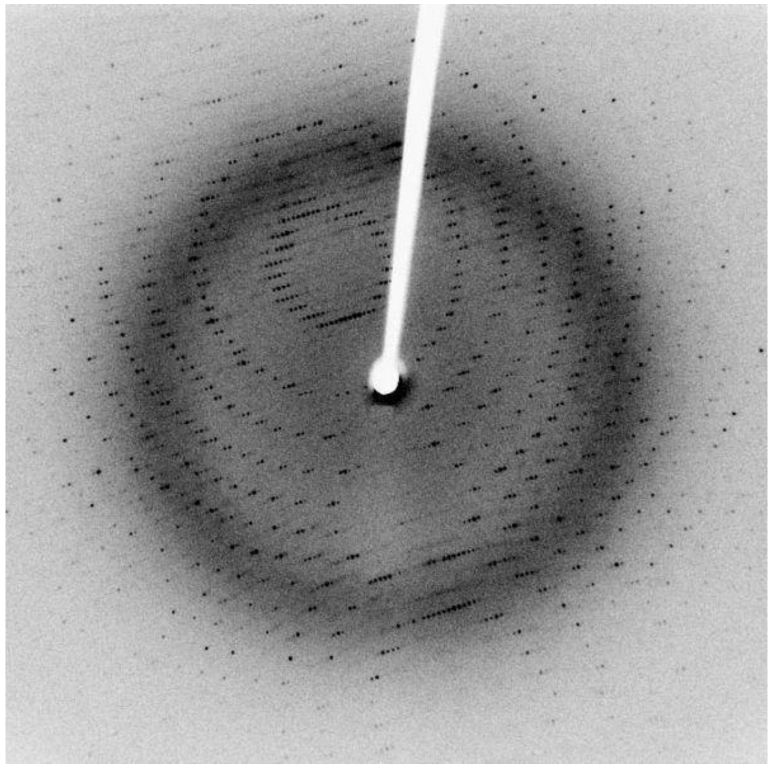
X-ray diffraction

- The atomic structure of crystals cannot be determined by optical microscopy because the wavelength of the photons is much too long (400 nm or so).
- So one might want to build an x-ray microscope but this does not work for very small wavelength because there are no suitable x-ray optical lenses.
- The idea is to use the diffraction of x-rays by a perfect crystal.
- Here: monochromatic x-rays, elastic scattering, kinematic approximation

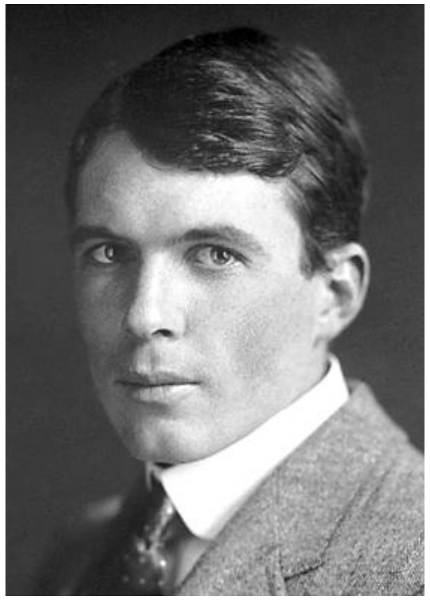
X-ray diffraction

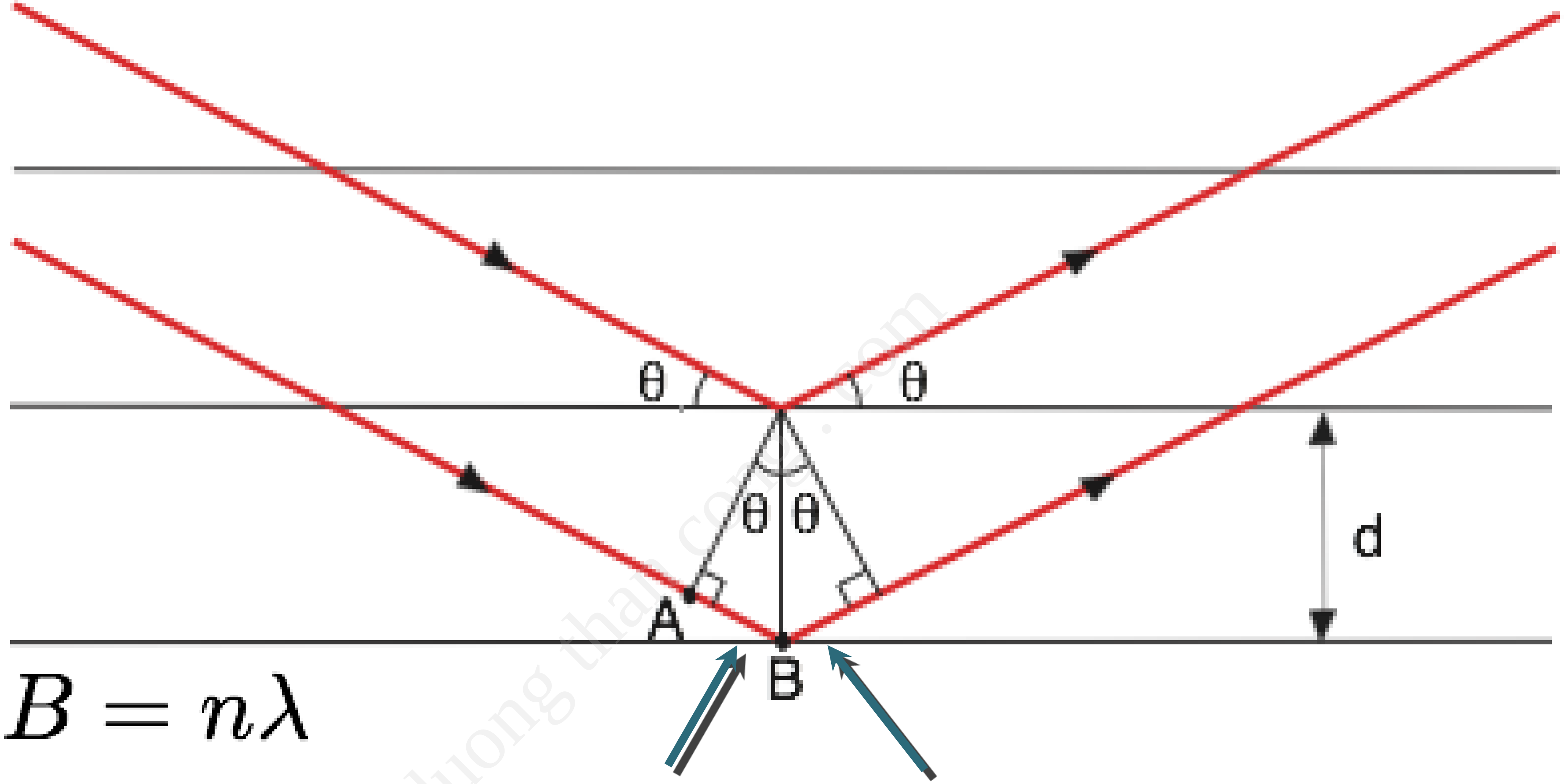
- The crystals can be used to diffract X-rays (von Laue, 1912).





The Bragg description (1912): specular reflection





$$d\sin\Theta \quad d\sin\Theta$$

$$2AB = n\lambda$$

$$\sin\Theta = \frac{AB}{d}$$

$$\boxed{n\lambda = 2d\sin\Theta}$$

and this only works for $\lambda < 2d$

- The Bragg condition for constructive interference holds for any number of layers, not only two (why?)

X-ray diffraction: the Bragg description

- The X-rays penetrate deeply and many layers contribute to the reflected intensity
- The diffracted peak intensities are therefore very sharp (in angle)
- The physics of the lattice planes is totally obscure!

A little reminder about waves and diffraction

$$\mathbf{A}(\mathbf{r},t) = \mathbf{A}_0 e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}$$

$$|\mathbf{k}| = \frac{2\pi}{\lambda}$$

$$\mathbf{A}_0 \cdot \mathbf{k} = 0$$

λ = 1 Å
hν = 12 keV

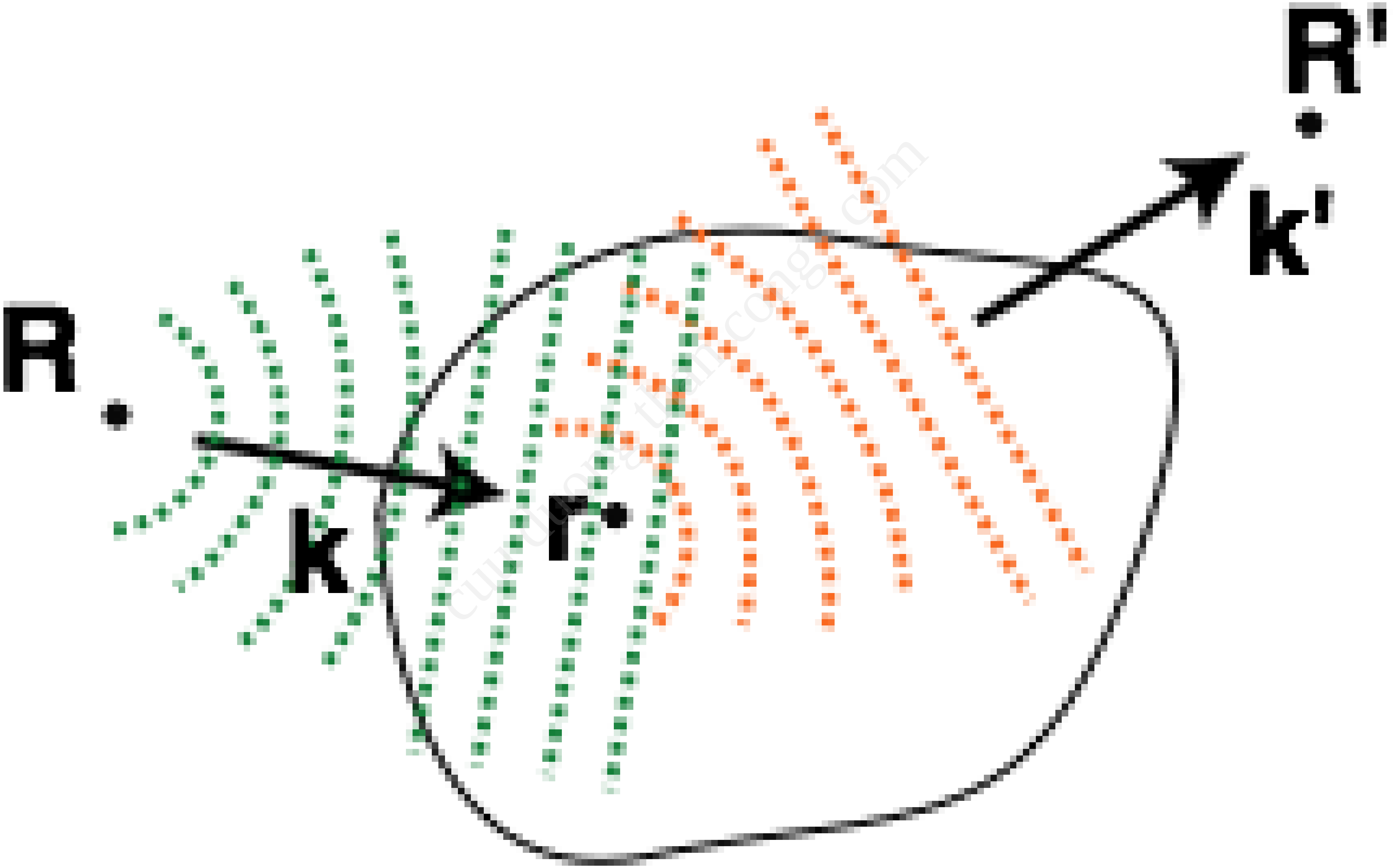
complex notations

$$\mathbf{A}(\mathbf{r},t) = \mathbf{A}_0 \cos(\mathbf{k}\cdot\mathbf{r} - \omega t) = \Re\left[\mathbf{A}_0 e^{i\mathbf{k}\cdot\mathbf{r} - i\omega t}\right]$$

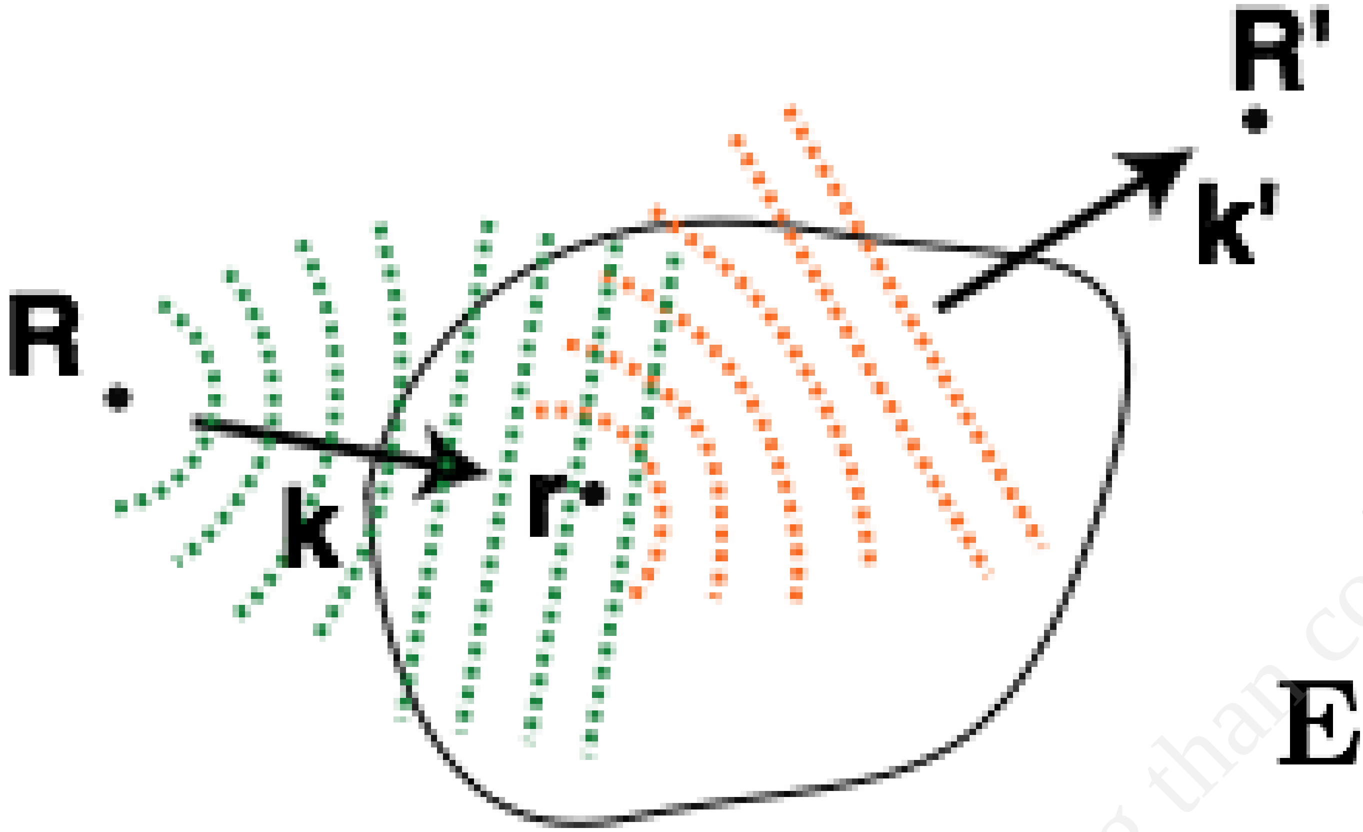
(for real $\mathbf{A}_0$)

$$e^{i\phi} = \cos\phi + i\sin\phi$$

X-ray diffraction, von Laue description



X-ray diffraction, von Laue description



incoming wave at **r**

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})-i\omega t}$$

absolute E_0 of no interest

$$\mathbf{E}(\mathbf{r},t) \propto e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})} e^{-i\omega t}$$

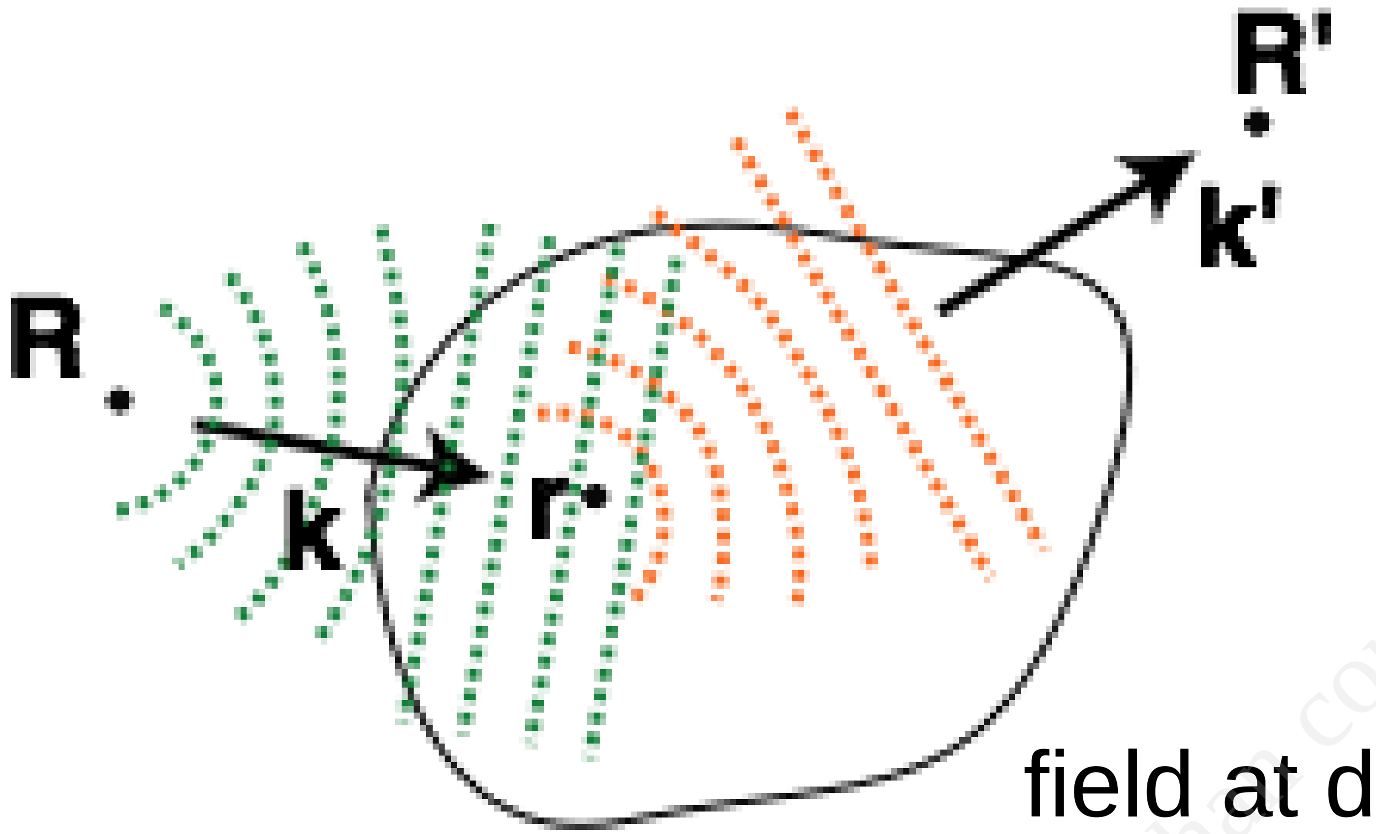
outgoing wave in detector direction

$$\mathbf{E}(\mathbf{R}',t) \propto \mathbf{E}(\mathbf{r},t)\rho(\mathbf{r}) e^{i\mathbf{k}'\cdot(\mathbf{R}'-\mathbf{r})}$$

$$\mathbf{E}(\mathbf{R}',t) \propto e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})}\rho(\mathbf{r}) e^{i\mathbf{k}'\cdot(\mathbf{R}'-\mathbf{r})} e^{-i\omega t}$$

$$= e^{i(\mathbf{k}'\cdot\mathbf{R}'-\mathbf{k}\cdot\mathbf{R})}\rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} e^{-i\omega t}$$

X-ray diffraction, von Laue description



field at detector for one point

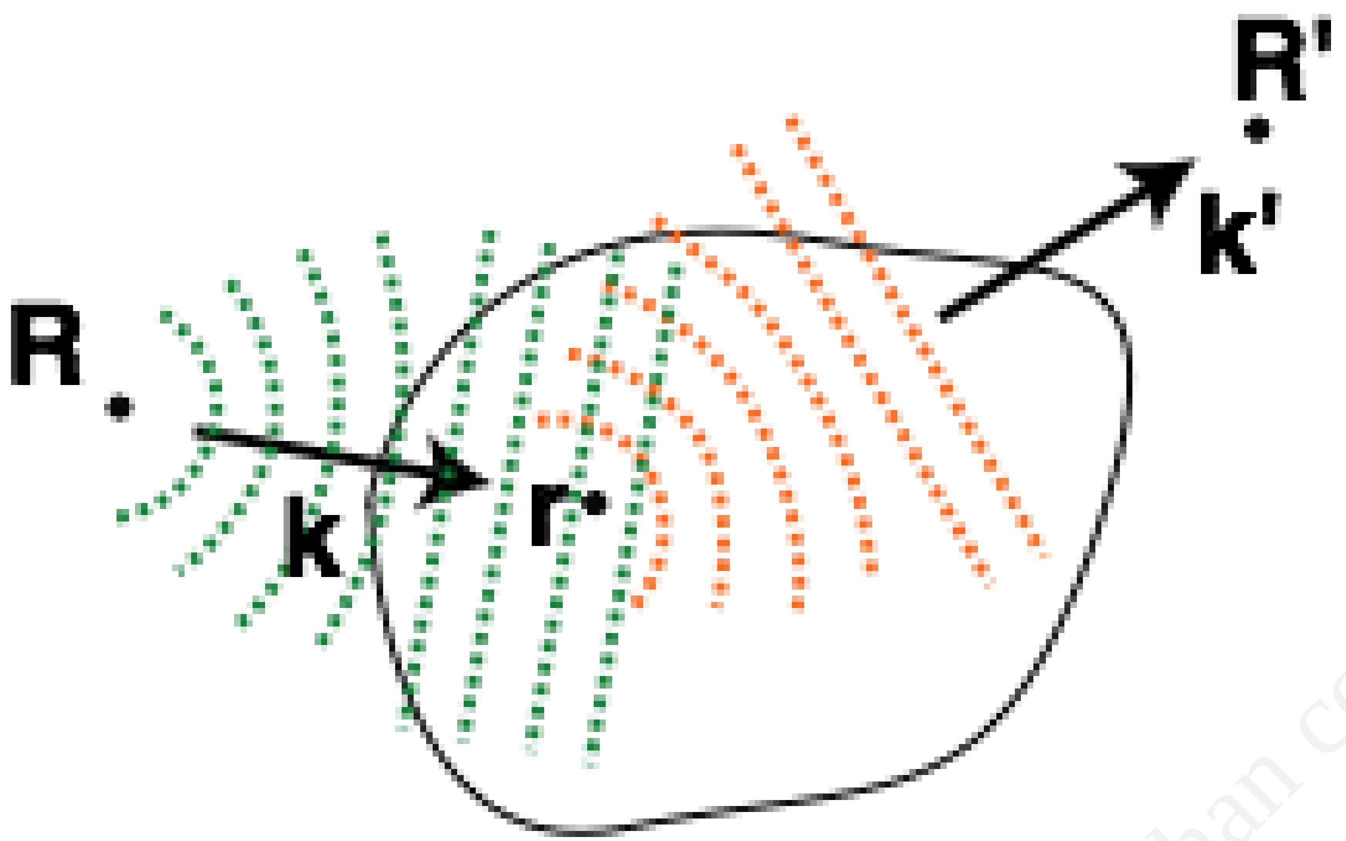
$$\mathbf{E}(\mathbf{R}',t) \propto e^{i(\mathbf{k}'\cdot\mathbf{R}'-\mathbf{k}\cdot\mathbf{R})}\rho(\mathbf{r})e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}e^{-i\omega t}$$

$$\mathbf{E}(\mathbf{R}',t) \propto \rho(\mathbf{r})e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}e^{-i\omega t}$$

and for the whole crystal

$$\mathbf{E}(\mathbf{R}',t) \propto e^{-i\omega t}\int_V \rho(\mathbf{r})e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}dV$$

X-ray diffraction, von Laue description



$$\mathbf{E}(\mathbf{R}', t) \propto e^{-i\omega t} \int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV$$

so the measured intensity is

$$I(\mathbf{K}) \propto |\int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV|^2 = |\int_V \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} dV|^2$$

with

$$\mathbf{K} = \mathbf{k}' - \mathbf{k}$$

X-ray diffraction, von Laue description

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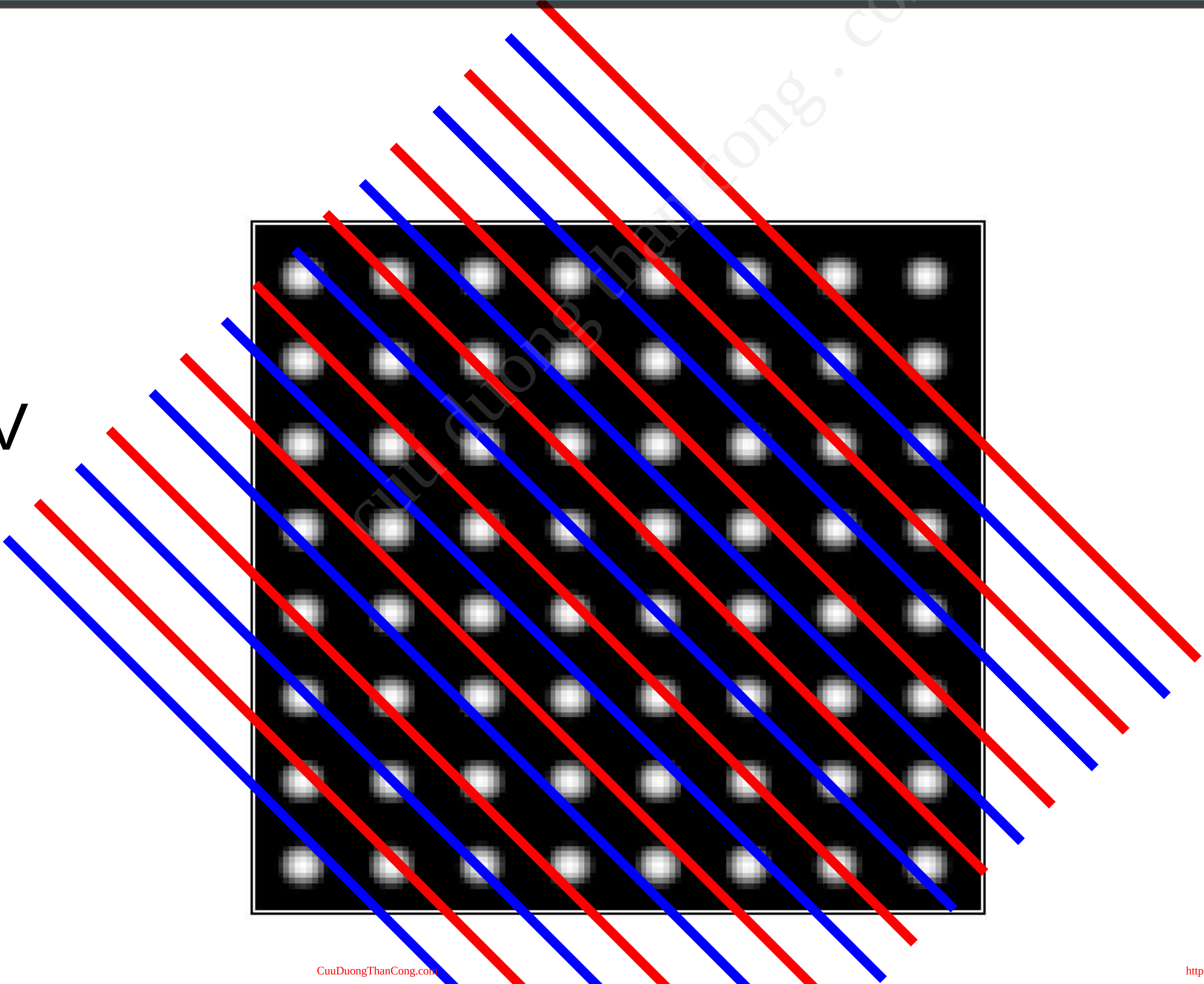
ρ(**r**) in
Volume V



X-ray diffraction, von Laue description

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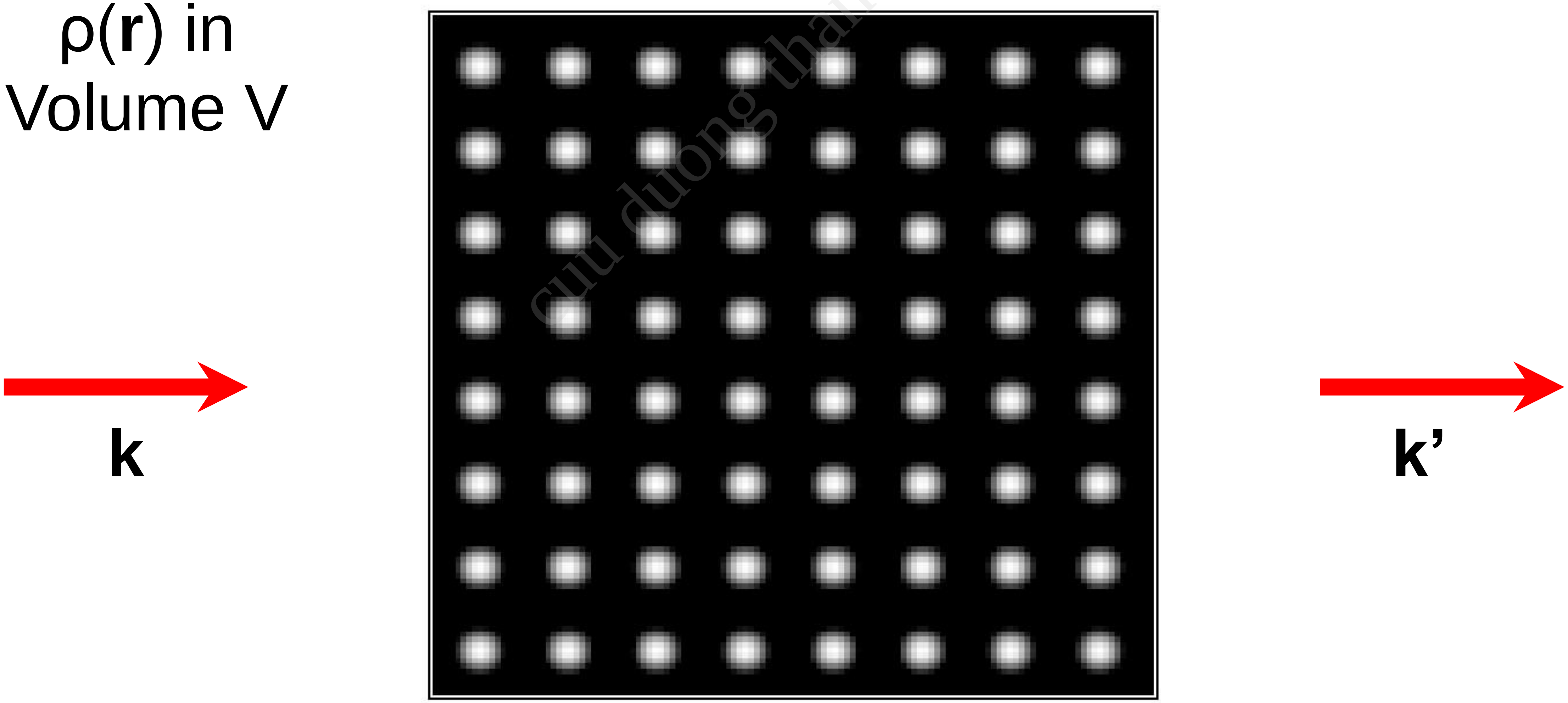

X-ray diffraction, von Laue description

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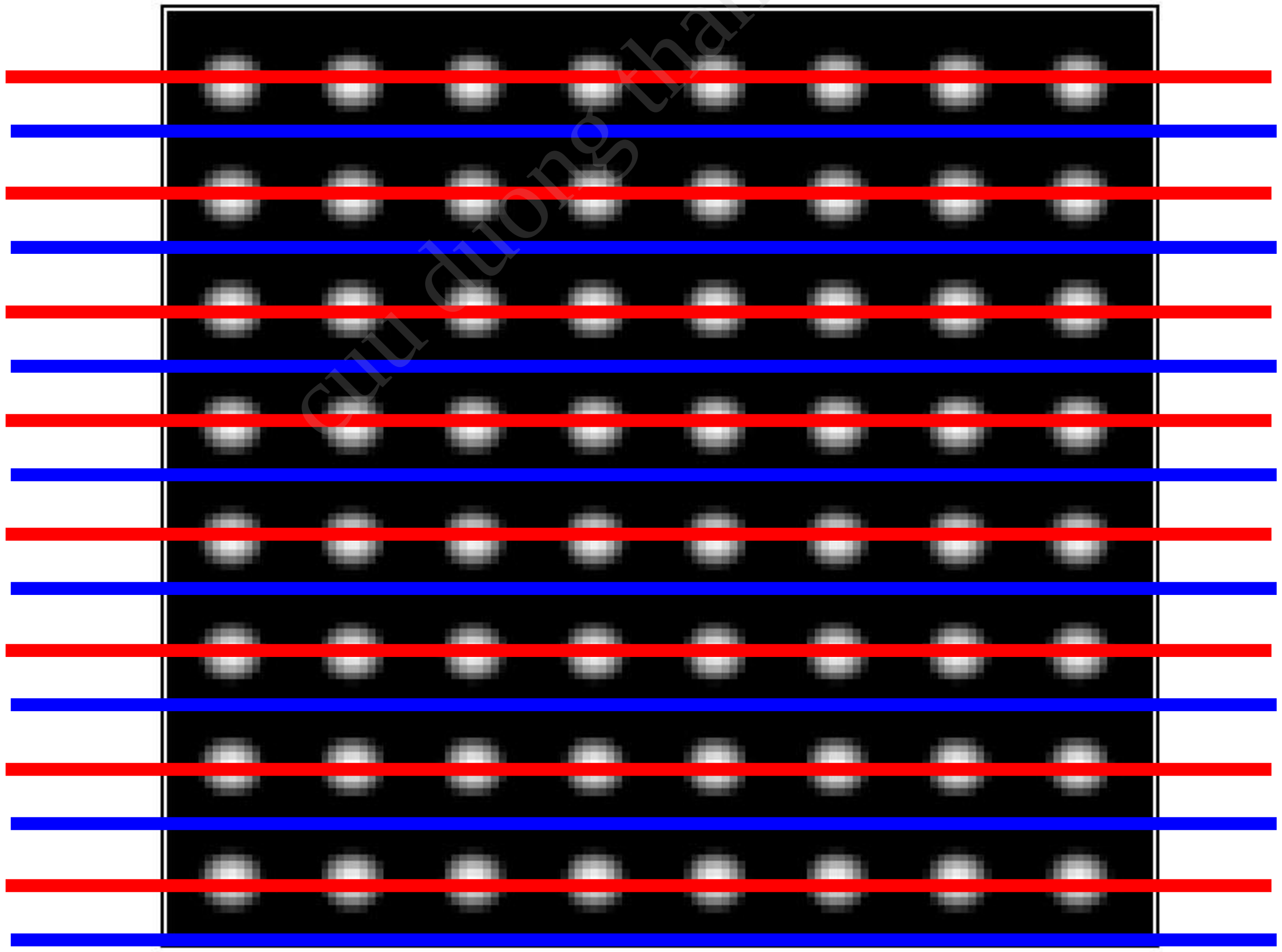


The reciprocal lattice

for a given Bravais lattice

$$\mathbf{R} = m\mathbf{a_1} + n\mathbf{a_2} + o\mathbf{a_3}$$

the reciprocal lattice is defined as the set of vectors **G** for which

$$\mathbf{R} \cdot \mathbf{G} = 2\pi l$$

or

$$e^{\mathbf{iG \cdot R}} = 1$$

The reciprocal lattice is also a Bravais lattice

$$\mathbf{G} = m'\mathbf{b_1} + n'\mathbf{b_2} + o'\mathbf{b_3}$$

The reciprocal lattice

construction of the reciprocal lattice

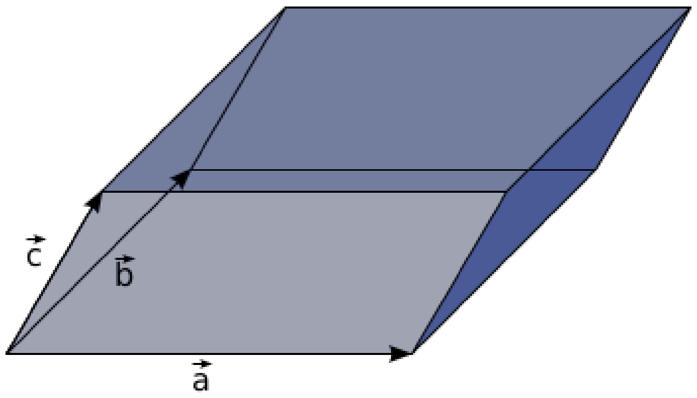
$$\mathbf{R} = m\mathbf{a_1} + n\mathbf{a_2} + o\mathbf{a_3}$$

$$\mathbf{G} = m'\mathbf{b_1} + n'\mathbf{b_2} + o'\mathbf{b_3}$$

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

a useful relation is

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$



with this it is easy to see why

$$\mathbf{R} \cdot \mathbf{G} = 2\pi l$$

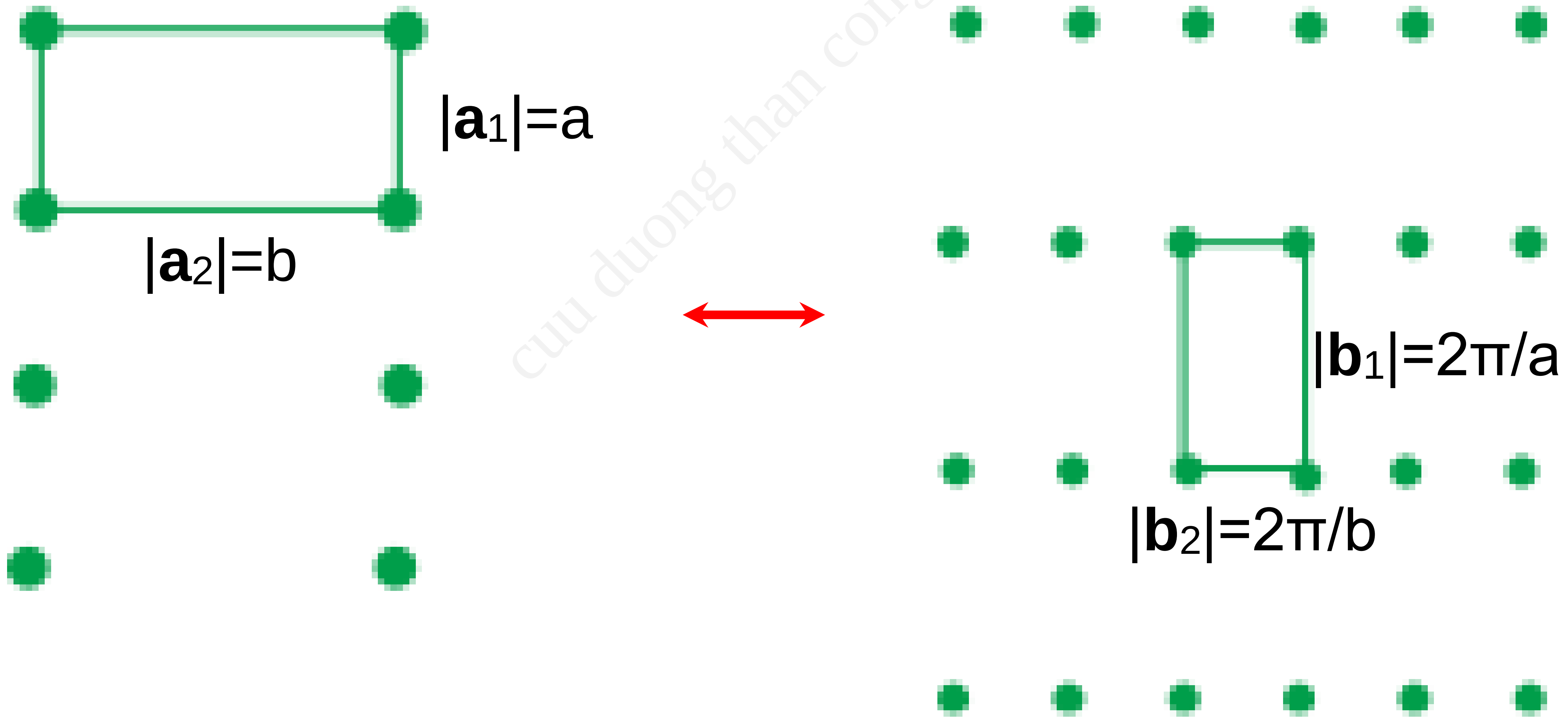
The reciprocal lattice

example 1: in two dimensions

$$\mathbf{R} = m\mathbf{a}_1 + n\mathbf{a}_2$$

$$\mathbf{G} = m\mathbf{b}_1 + n\mathbf{b}_2$$

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$



The reciprocal lattice

if we have

$$\mathbf{R}\cdot\mathbf{G} = 2\pi l \qquad e^{\mathbf{iG}\cdot\mathbf{R}} = 1$$

then we can write

$$e^{i\mathbf{G}\cdot\mathbf{r}} = e^{i\mathbf{G}\cdot\mathbf{r}}e^{i\mathbf{G}\cdot\mathbf{R}} = e^{i\mathbf{G}\cdot(\mathbf{r}+\mathbf{R})}$$

The vectors **G** of the reciprocal lattice give plane waves with the periodicity of the lattice.
In this case **G** is the wave vector and 2π/|**G**| the wavelength.

X-ray diffraction, von Laue description

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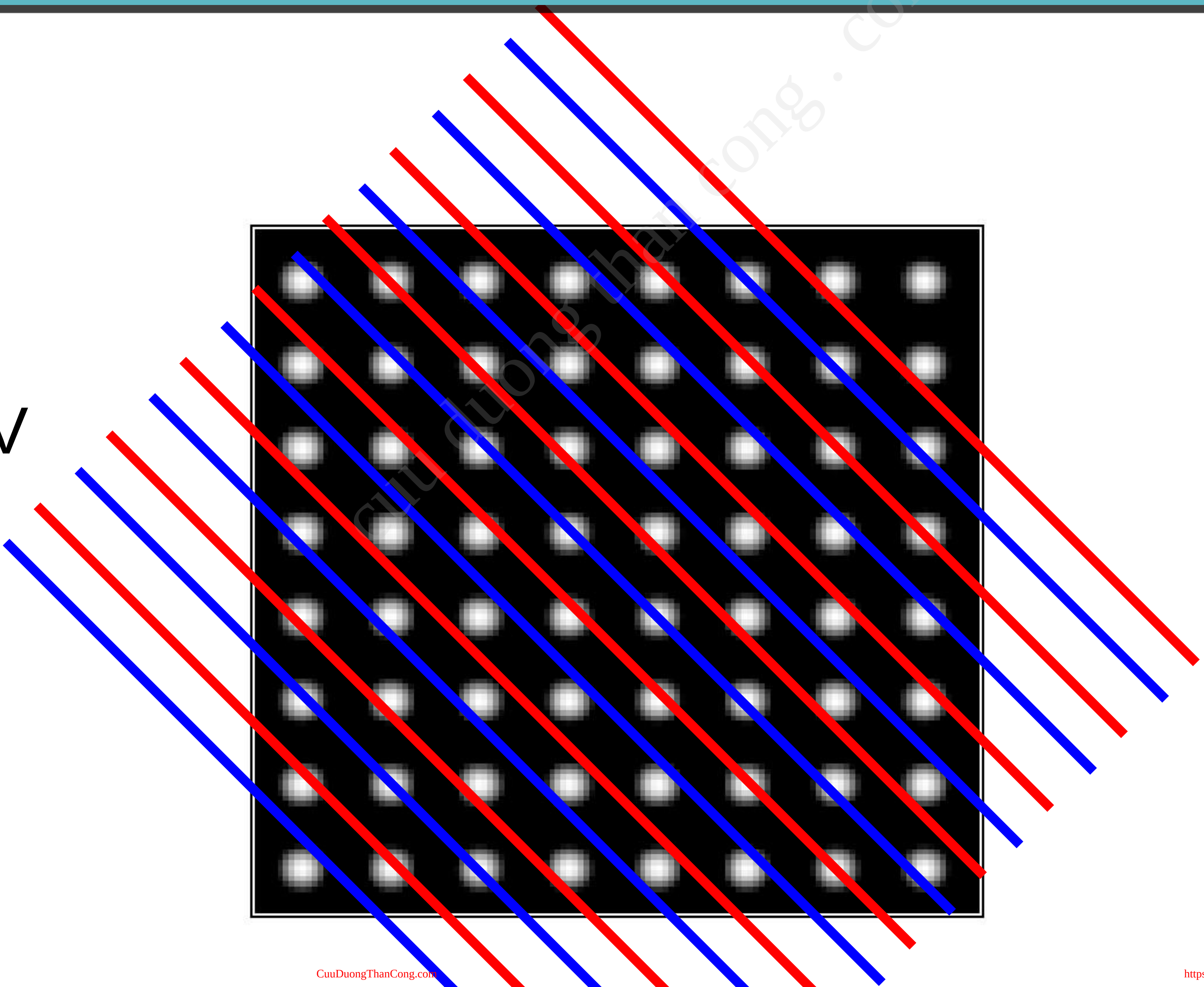
ρ(**r**) in
Volume V



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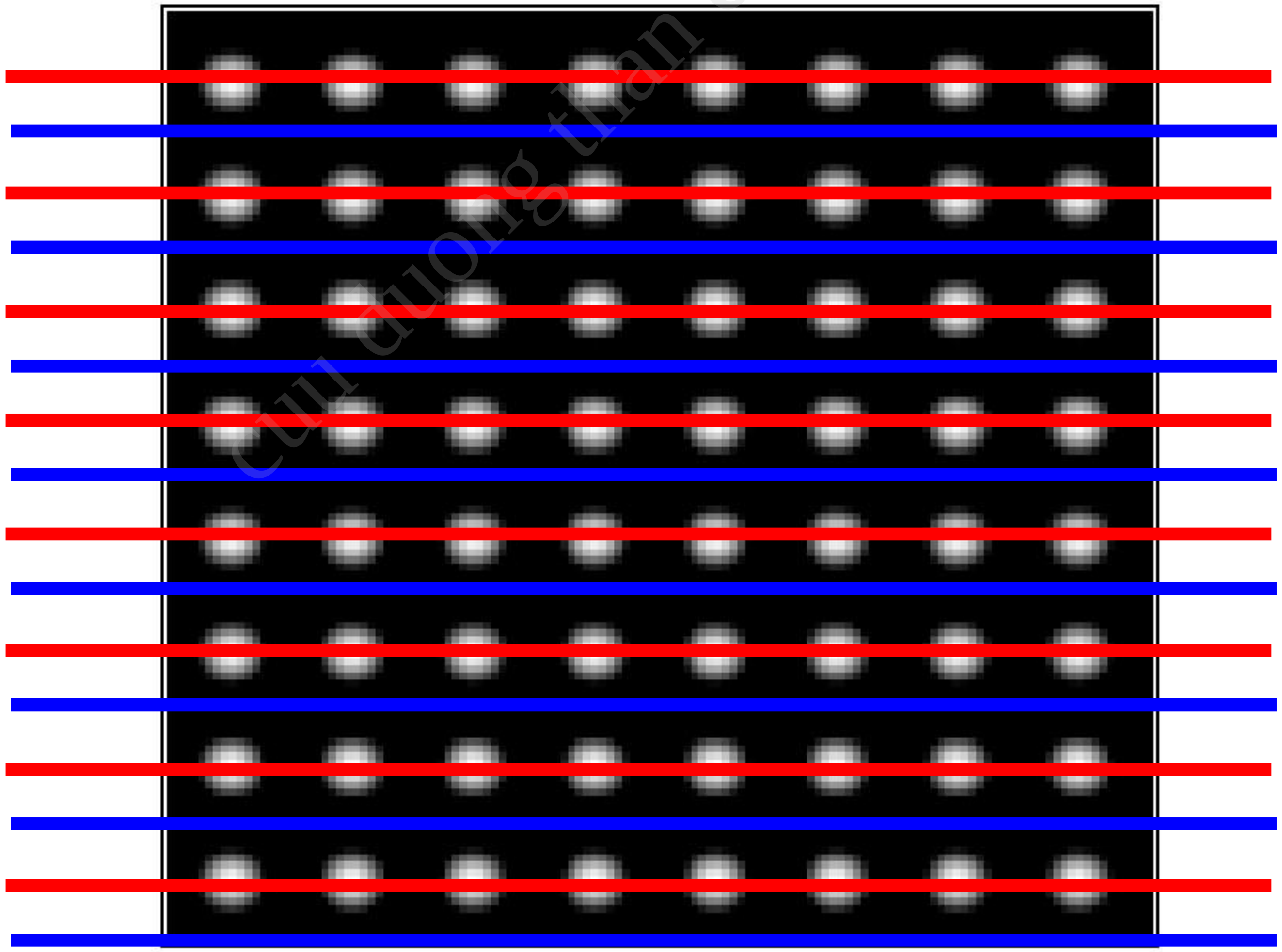
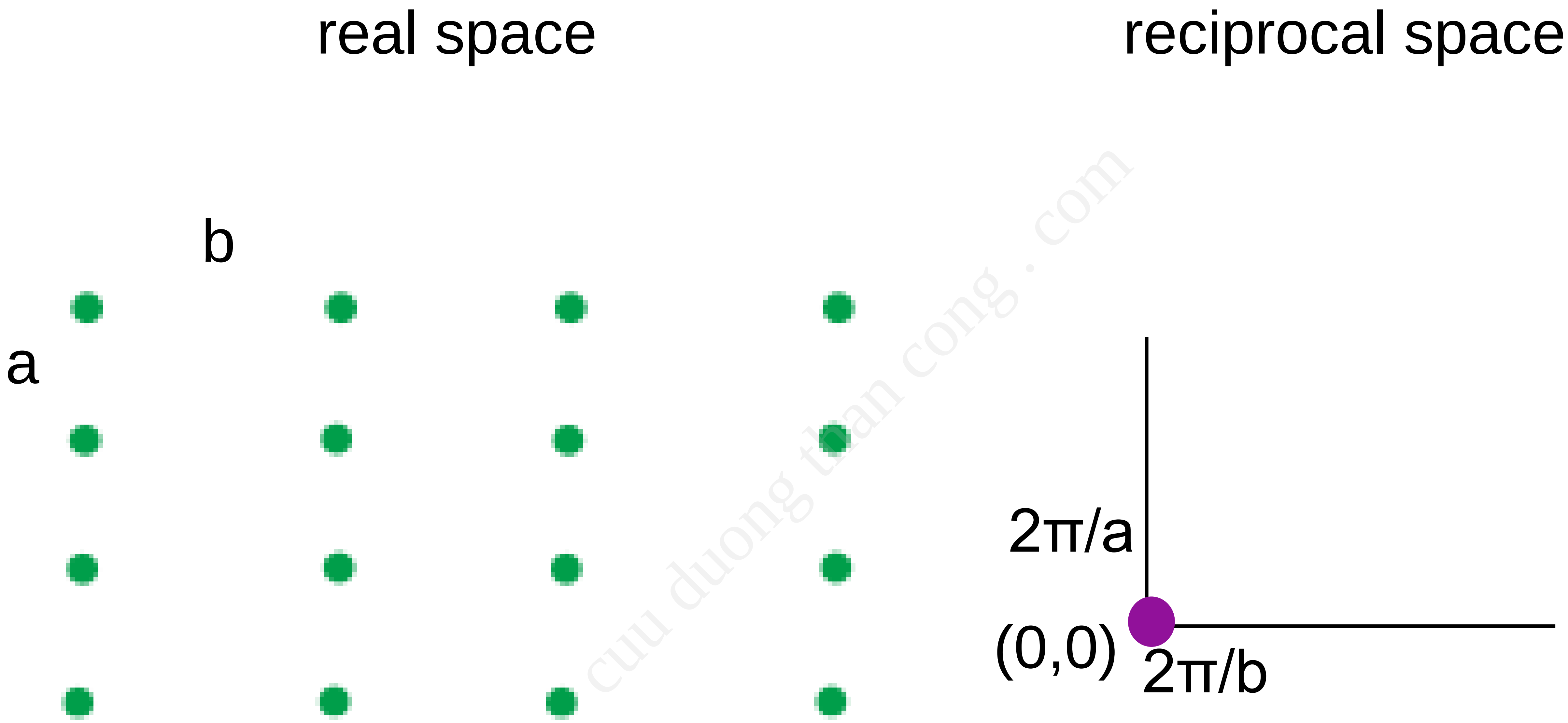


Volume V

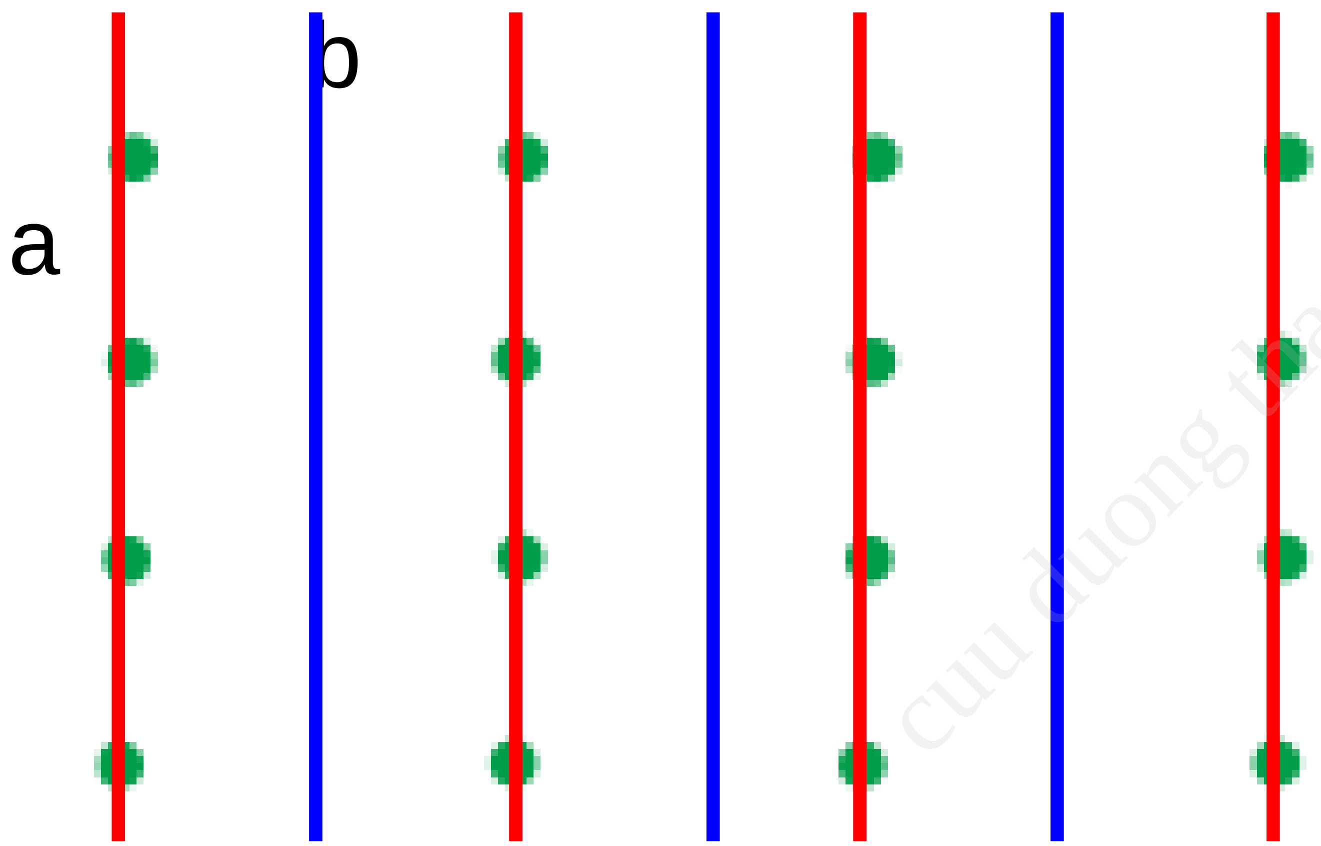
K=G

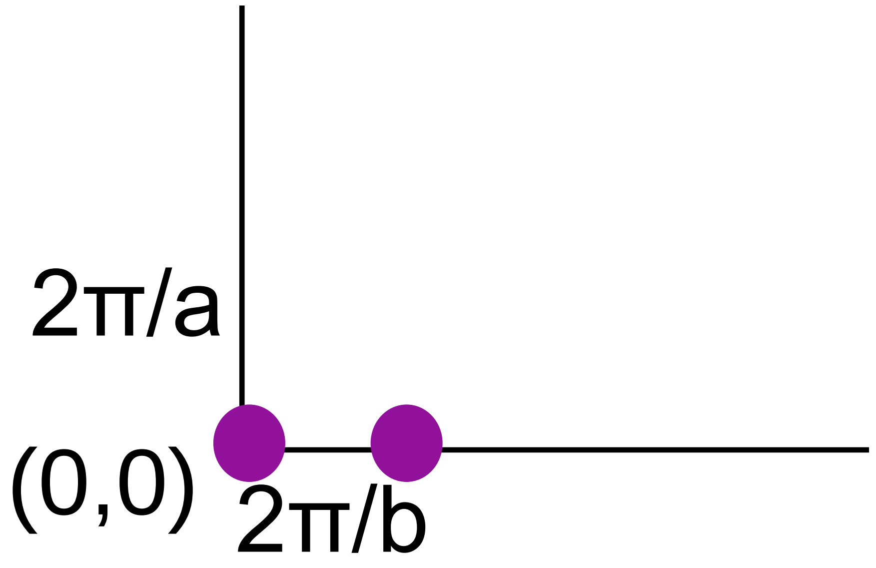
Lattice waves



$$e^{i\mathbf{G}\mathbf{r}} = e^{i\mathbf{G}\mathbf{r}} e^{i\mathbf{G}\mathbf{R}} = e^{i\mathbf{G}(\mathbf{r}+\mathbf{R})}$$

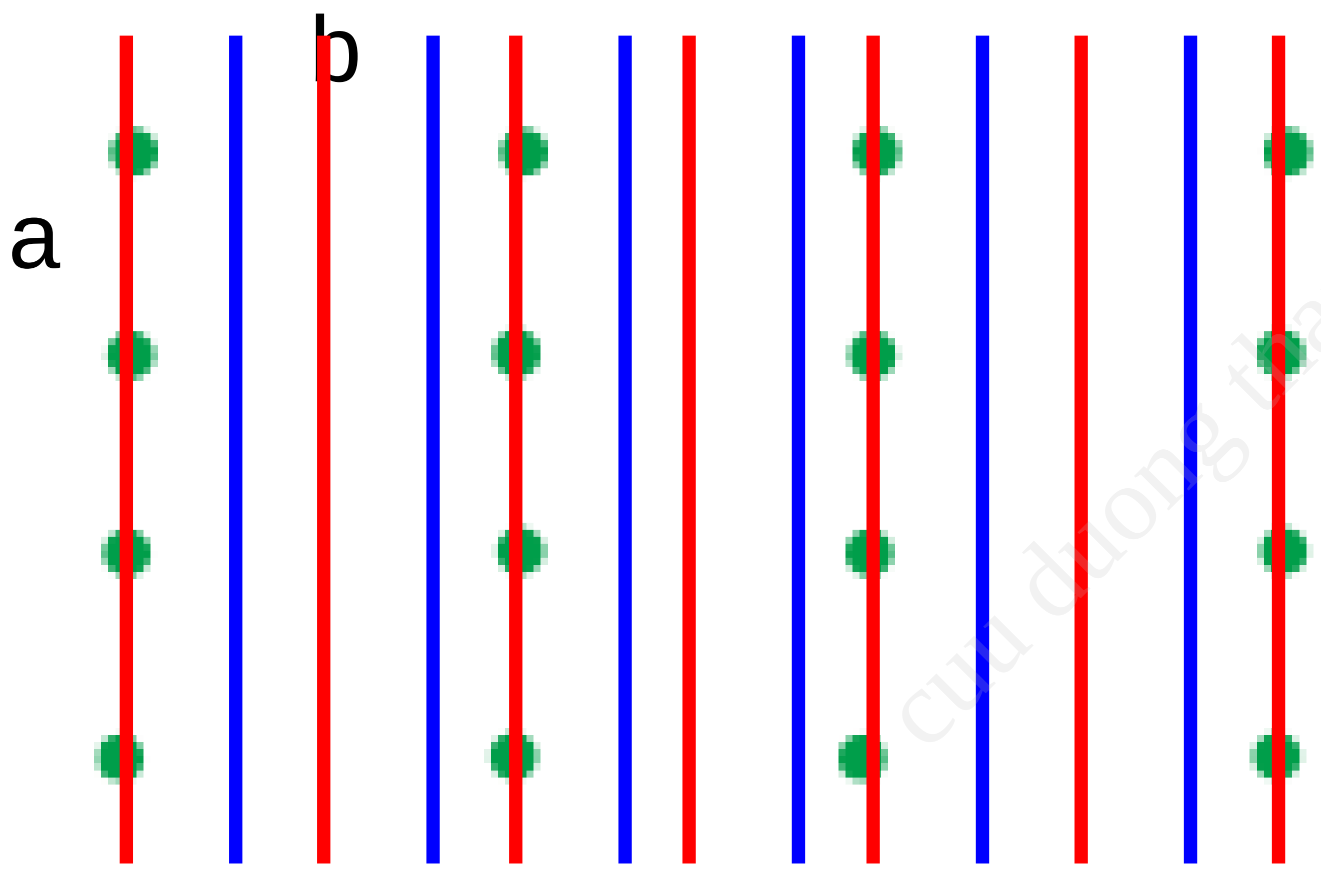
Lattice waves

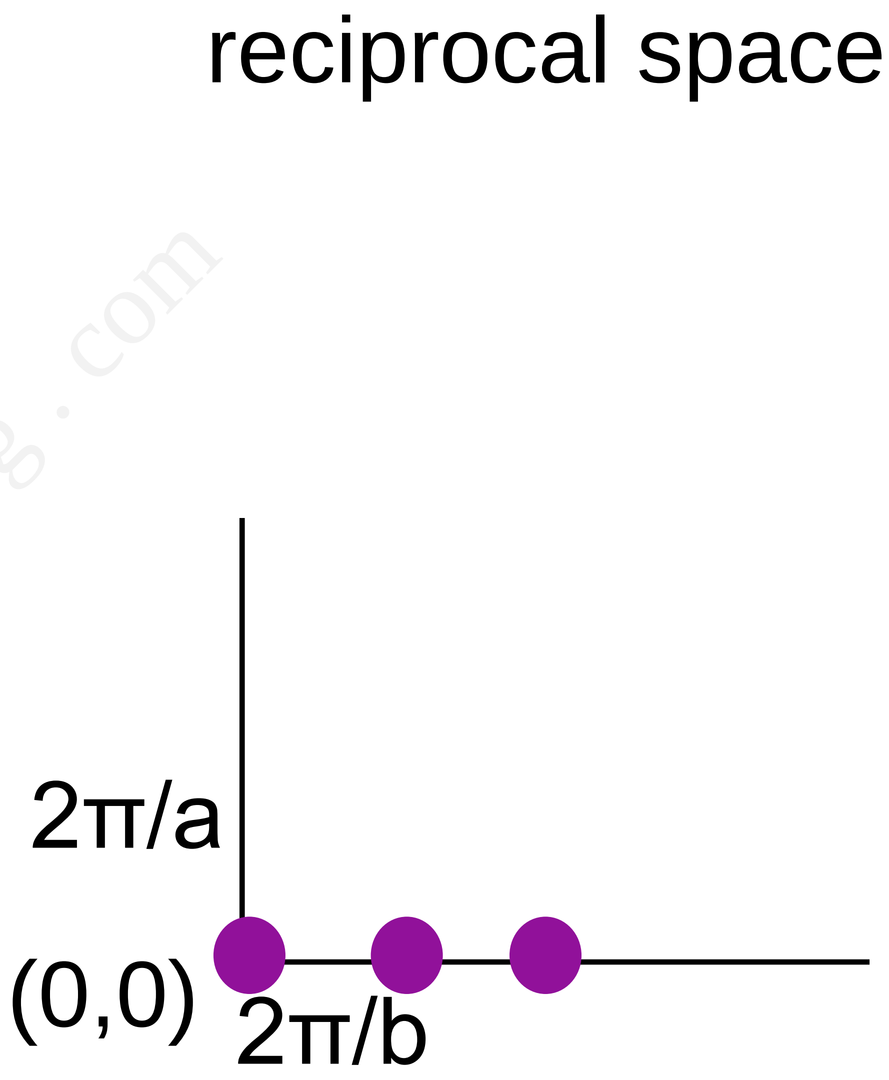




$$e^{i\mathbf{Gr}} = e^{i\mathbf{Gr}} e^{i\mathbf{GR}} = e^{i\mathbf{G}(\mathbf{r}+\mathbf{R})}$$

Lattice waves

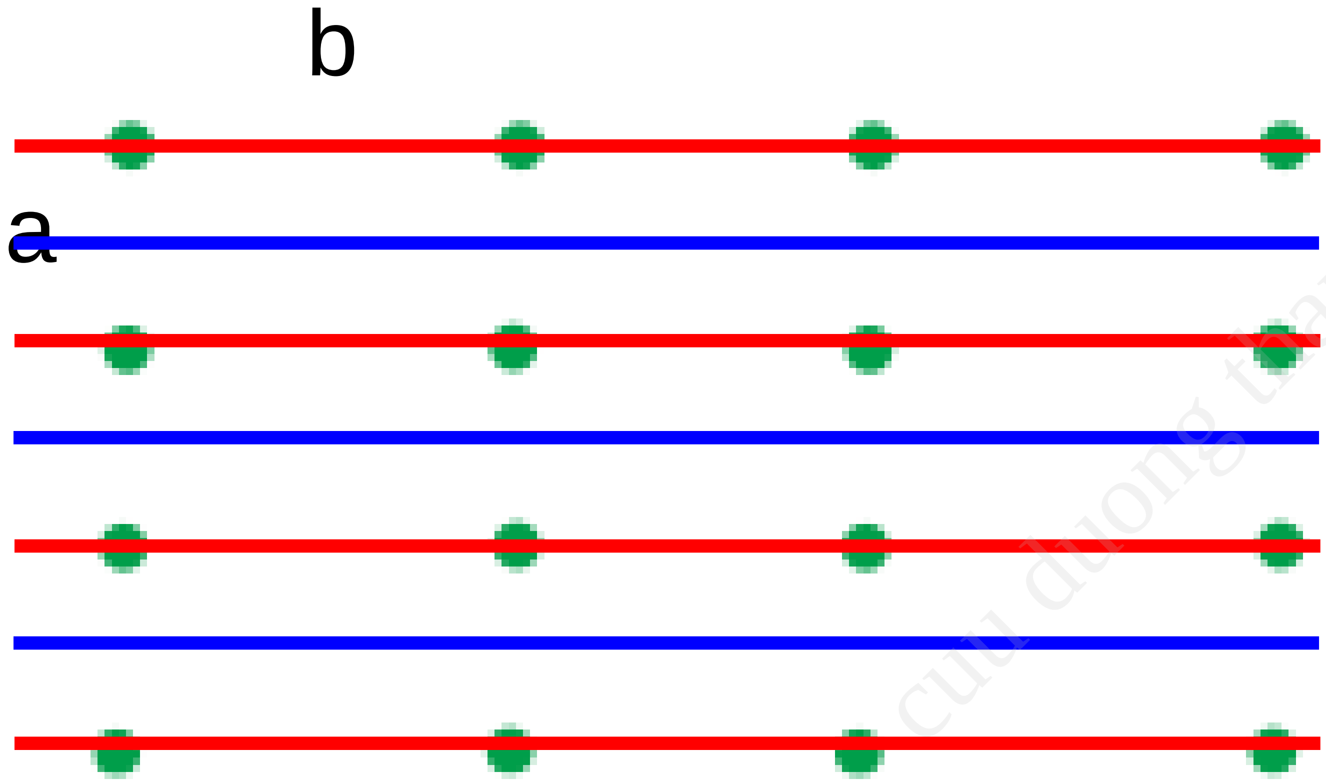




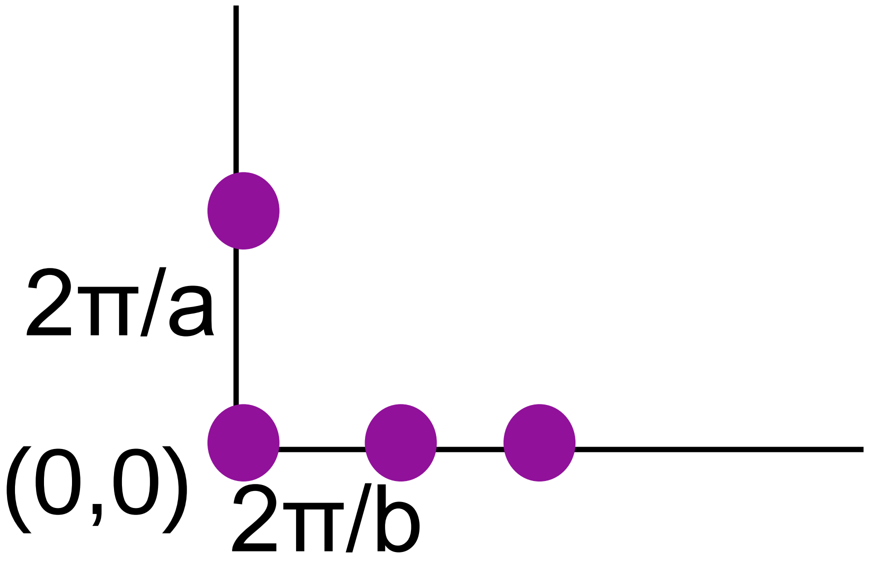
$$e^{i\mathbf{G}\mathbf{r}} = e^{i\mathbf{G}\mathbf{r}}e^{i\mathbf{G}\mathbf{R}} = e^{i\mathbf{G}(\mathbf{r}+\mathbf{R})}$$

Lattice waves

real space



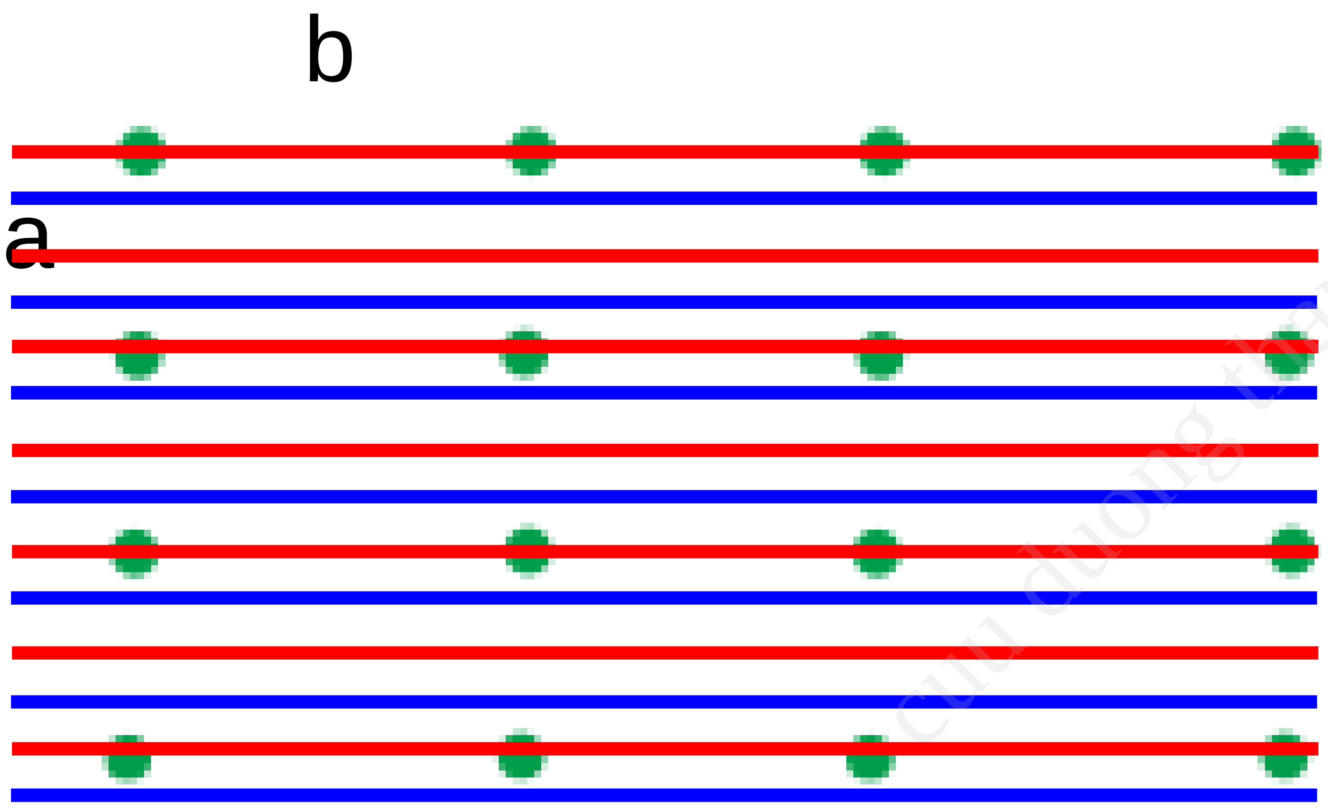
reciprocal space



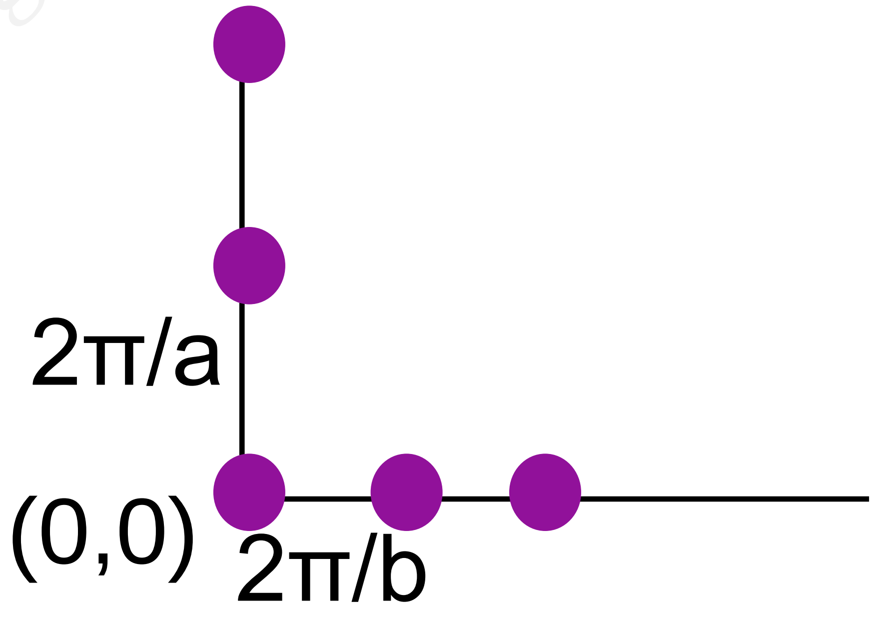
$$e^{i\mathbf{Gr}} = e^{i\mathbf{Gr}} e^{i\mathbf{GR}} = e^{i\mathbf{G}(\mathbf{r}+\mathbf{R})}$$

Lattice waves

real space



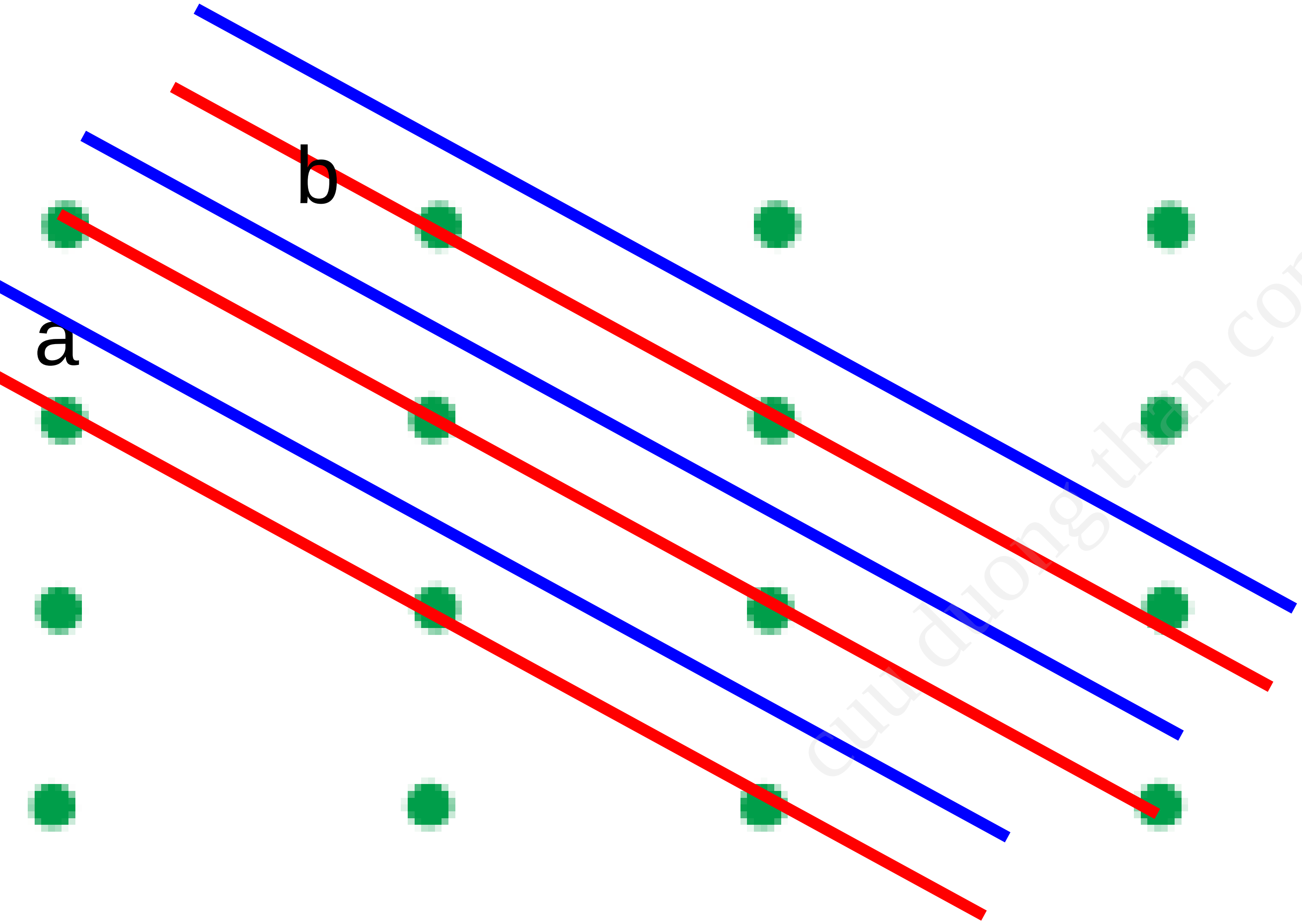
reciprocal space



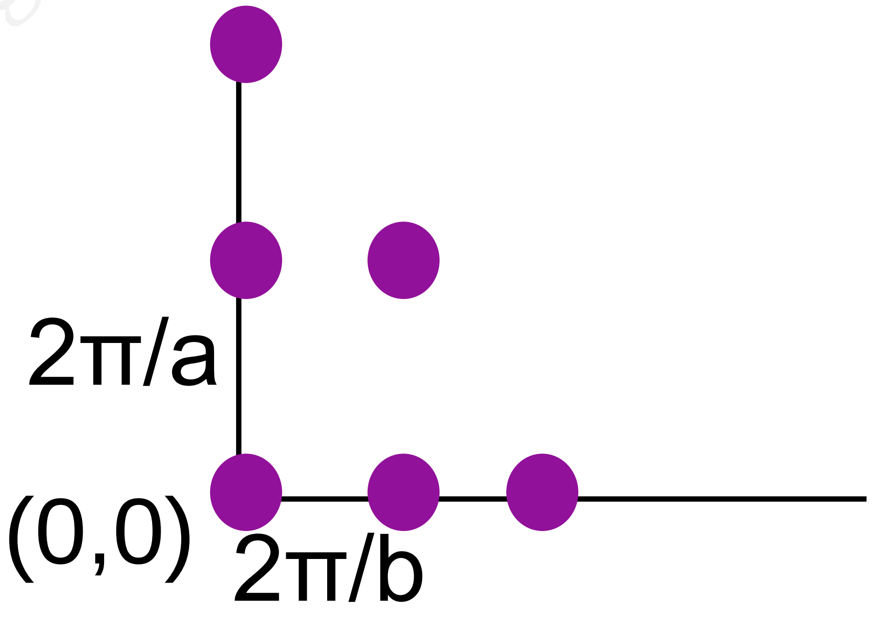
$$e^{i\mathbf{G}\mathbf{r}} = e^{i\mathbf{G}\mathbf{r}}e^{i\mathbf{G}\mathbf{R}} = e^{i\mathbf{G}(\mathbf{r}+\mathbf{R})}$$

Lattice waves

real space



reciprocal space



$$e^{i\mathbf{Gr}} = e^{i\mathbf{Gr}} e^{i\mathbf{GR}} = e^{i\mathbf{G}(\mathbf{r}+\mathbf{R})}$$

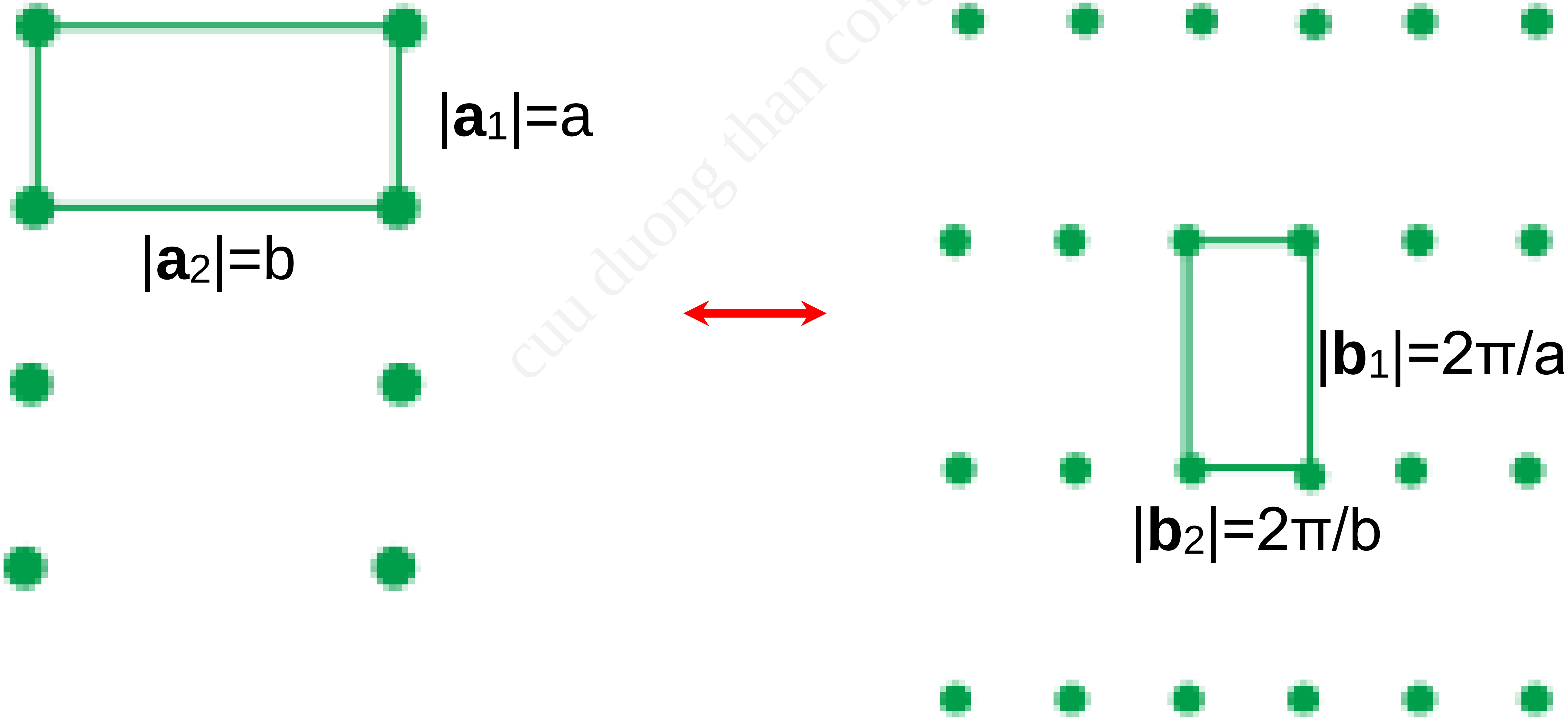
The reciprocal of the reciprocal lattice

is again the real lattice

$$\mathbf{R} = m\mathbf{a}_1 + n\mathbf{a}_2$$

$$\mathbf{G} = m\mathbf{b}_1 + n\mathbf{b}_2$$

$$\mathbf{a}_i\mathbf{b}_j = 2\pi\delta_{ij}.$$



|**a**$_1$|=a

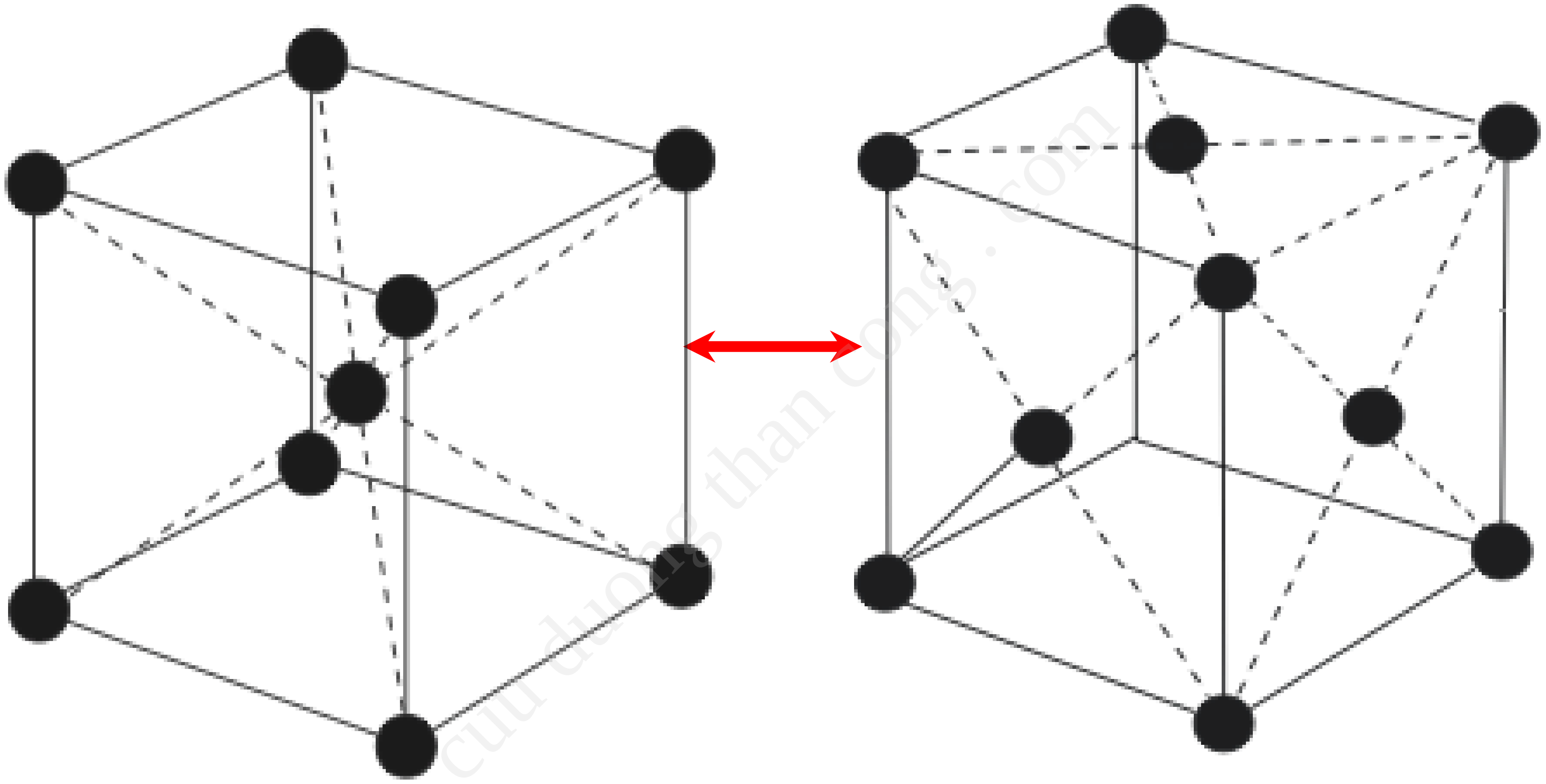
|**a**$_2$|=b

|**b**$_1$|=2π/a

|**b**$_2$|=2π/b

The reciprocal lattice in 3D

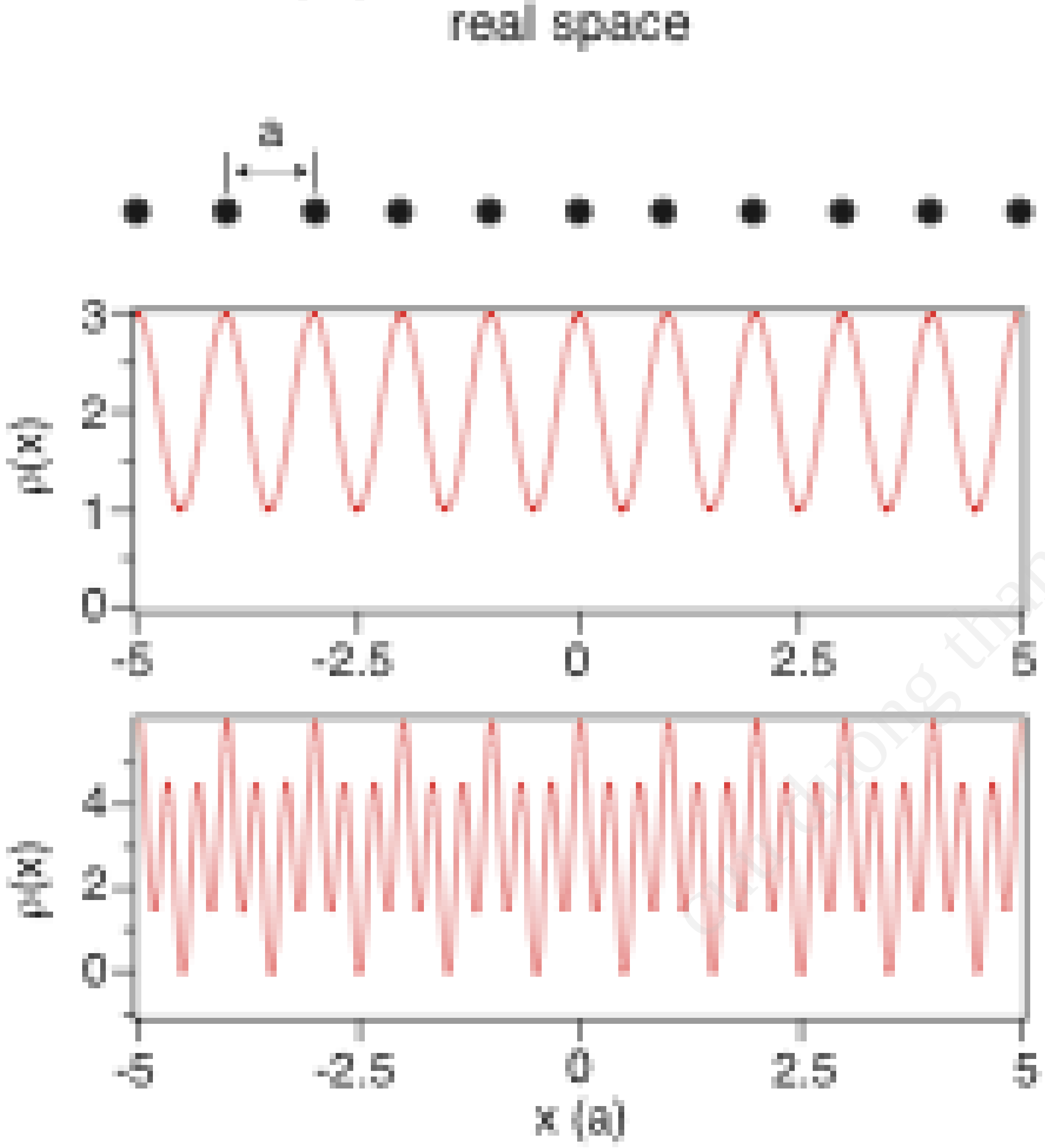
example 2: in three dimensions bcc and fcc lattice



$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1(\mathbf{a}_2\times\mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_1(\mathbf{a}_2\times\mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1\times\mathbf{a}_2}{\mathbf{a}_1(\mathbf{a}_2\times\mathbf{a}_3)}$$

The fcc lattice is the reciprocal of the bcc lattice and vice versa.

Applications of the reciprocal lattice



1D chain of atoms

example of charge density 1

example of charge density 2

- Greatly simplifies the description of lattice-periodic functions (charge density, one-electron potential...).

Applications of the reciprocal lattice

example: charge density in the chain

$$\rho(x) = \rho(x+a)$$

Fourier series

$$\rho(x) = \rho_0 + \sum_{n=1}^{\infty} \left\{ C_n cos(x 2\pi n/a) + S_n sin(x 2\pi n/a) \right\}$$

alternatively

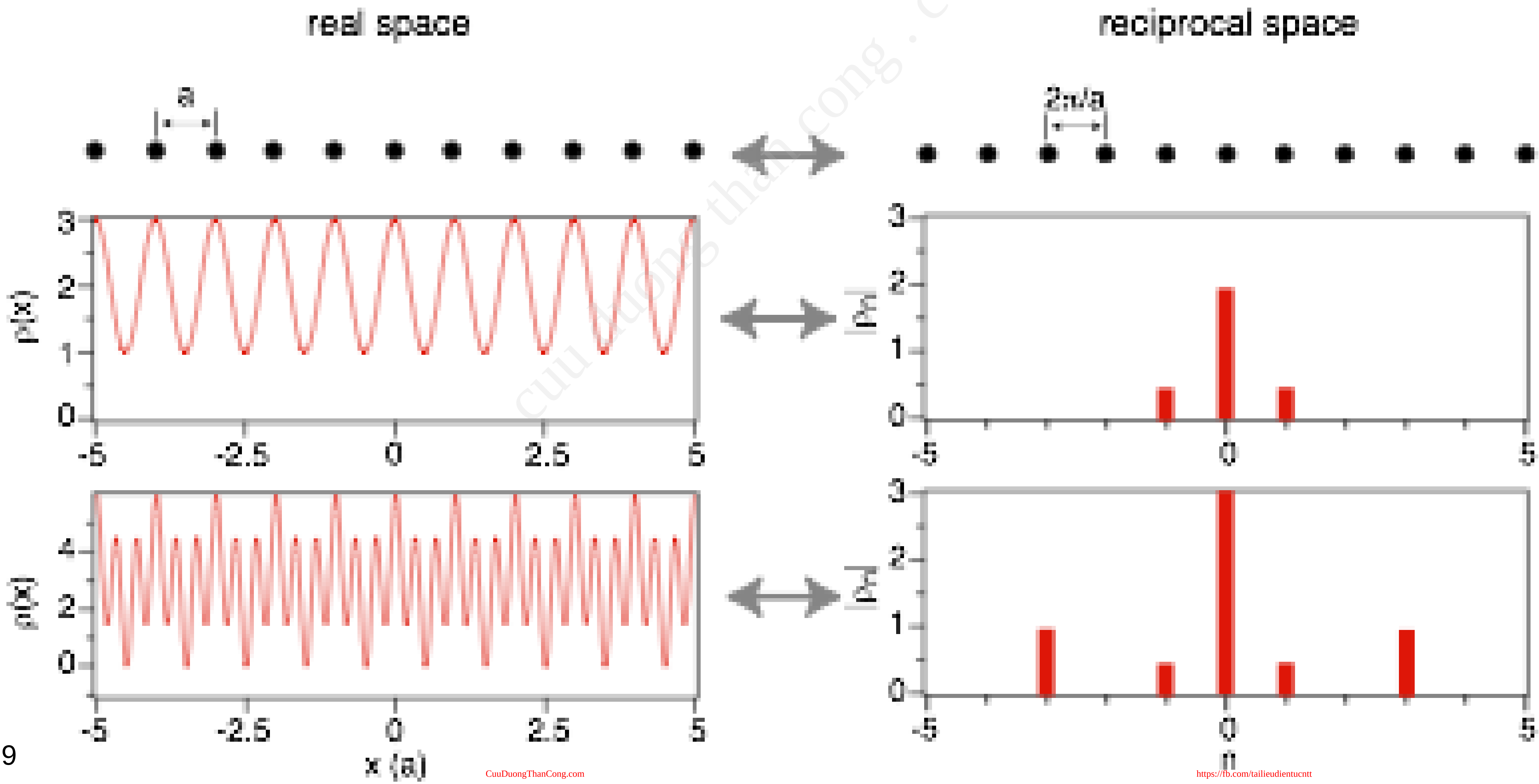
$$\rho(x) = \sum_{n=-\infty}^{\infty} \rho_n e^{ixn2\pi/a} \qquad \rho^*_{-n} = \rho_n$$

Applications of the reciprocal lattice

1D reciprocal lattice

$$\rho(x) = \sum_{n=-\infty}^{\infty} \rho_n e^{ixn2\pi/a}$$

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



Applications of the reciprocal lattice

1D

$$\rho(x) = \sum_{n=-\infty}^{\infty} \rho_n e^{ixn2\pi/a} = \sum_{n=-\infty}^{\infty} \rho_n e^{igx}$$

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

$$\rho^*_{-n} = \rho_n$$

3D

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$$

$$\rho^*_{-\mathbf{G}} = \rho_{\mathbf{G}}$$

X-ray diffraction, von Laue description

so the measured intensity is

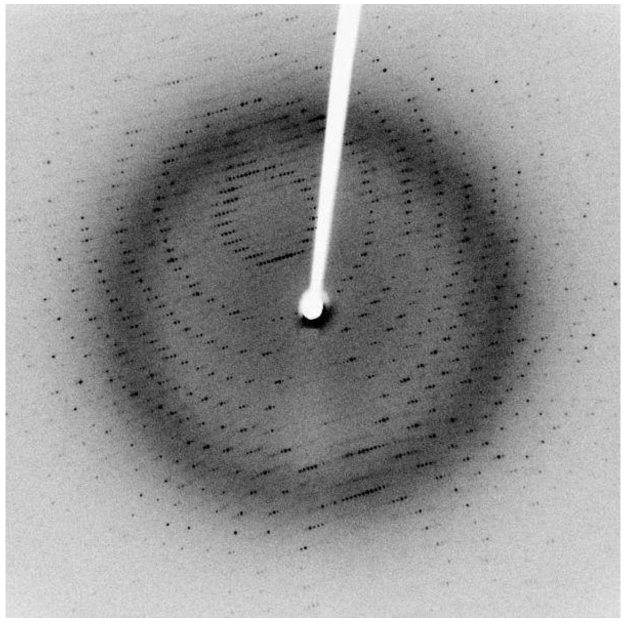
$$I(\mathbf{K}) \propto \left|\int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV\right|^2 = \left|\int_V \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} dV\right|^2$$

with

$$\mathbf{K} = \mathbf{k}' - \mathbf{k}$$

use

$$\rho(\mathbf{r}) = \sum_{\mathbf{G}} \rho_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}}$$



$$I(\mathbf{K}) \propto \left|\sum_{\mathbf{G}} \rho_{\mathbf{G}} \int_V e^{i(\mathbf{G}-\mathbf{K})\cdot\mathbf{r}} dV\right|^2$$

constructive interference when $\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$

Laue condition

X-ray diffraction, von Laue description

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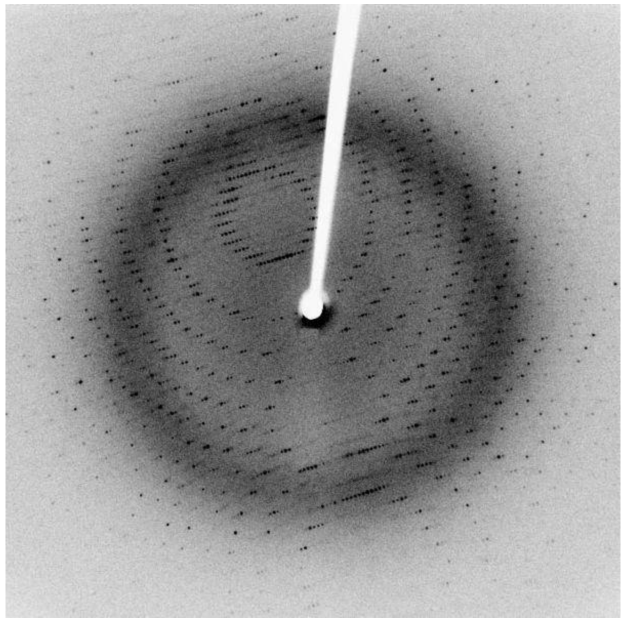


$$I(\mathbf{K}) \propto |\sum_{\mathbf{G}} \rho_{\mathbf{G}} \int_V e^{i(\mathbf{G}-\mathbf{K})\cdot\mathbf{r}} dV|^2$$

for a specific spot

$$I(\mathbf{K} = \mathbf{G}) \propto |\rho_{\mathbf{G}}|^2$$

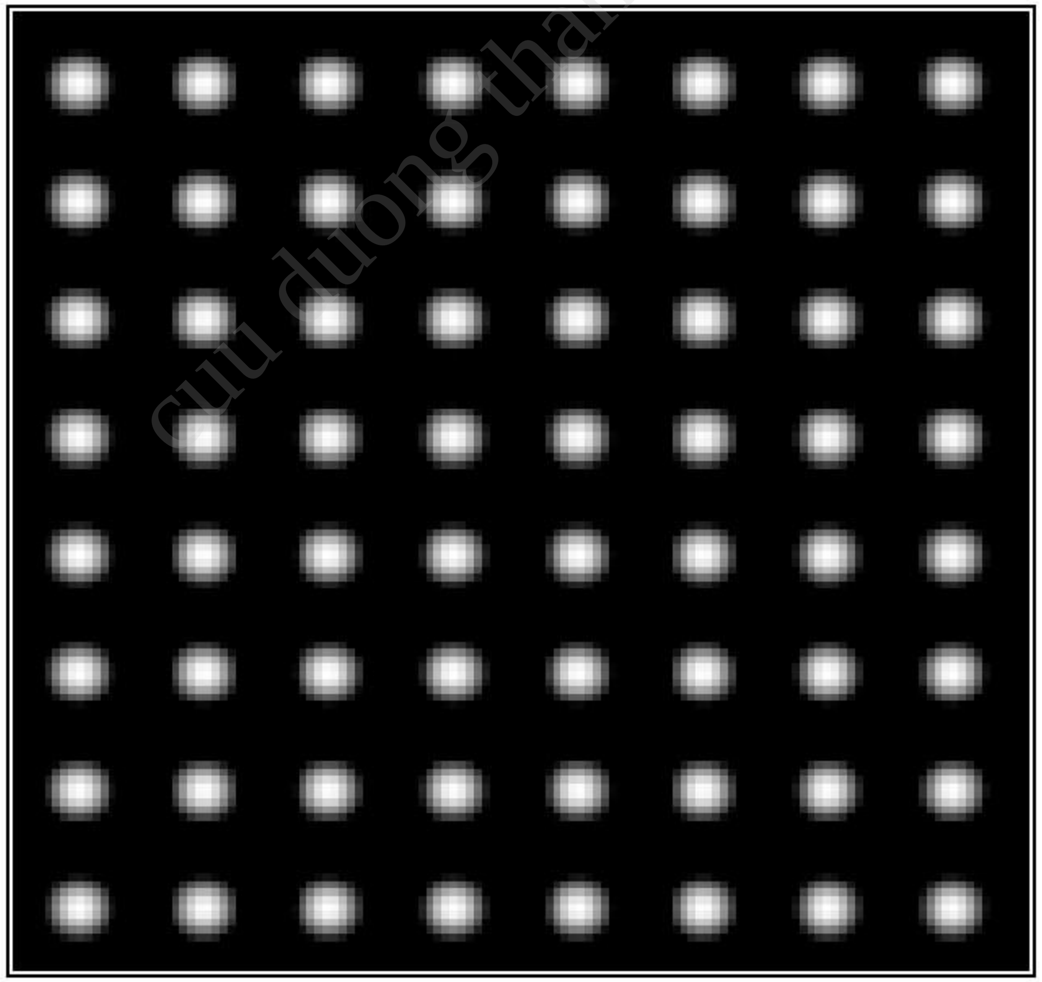
X-ray diffraction, von Laue description

so the measured intensity is

$$I(\mathbf{K}) \propto \left| \int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV \right|^2 = \left| \int_V \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} dV \right|^2$$

$$\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$$

Volume
V



X-ray diffraction, von Laue description

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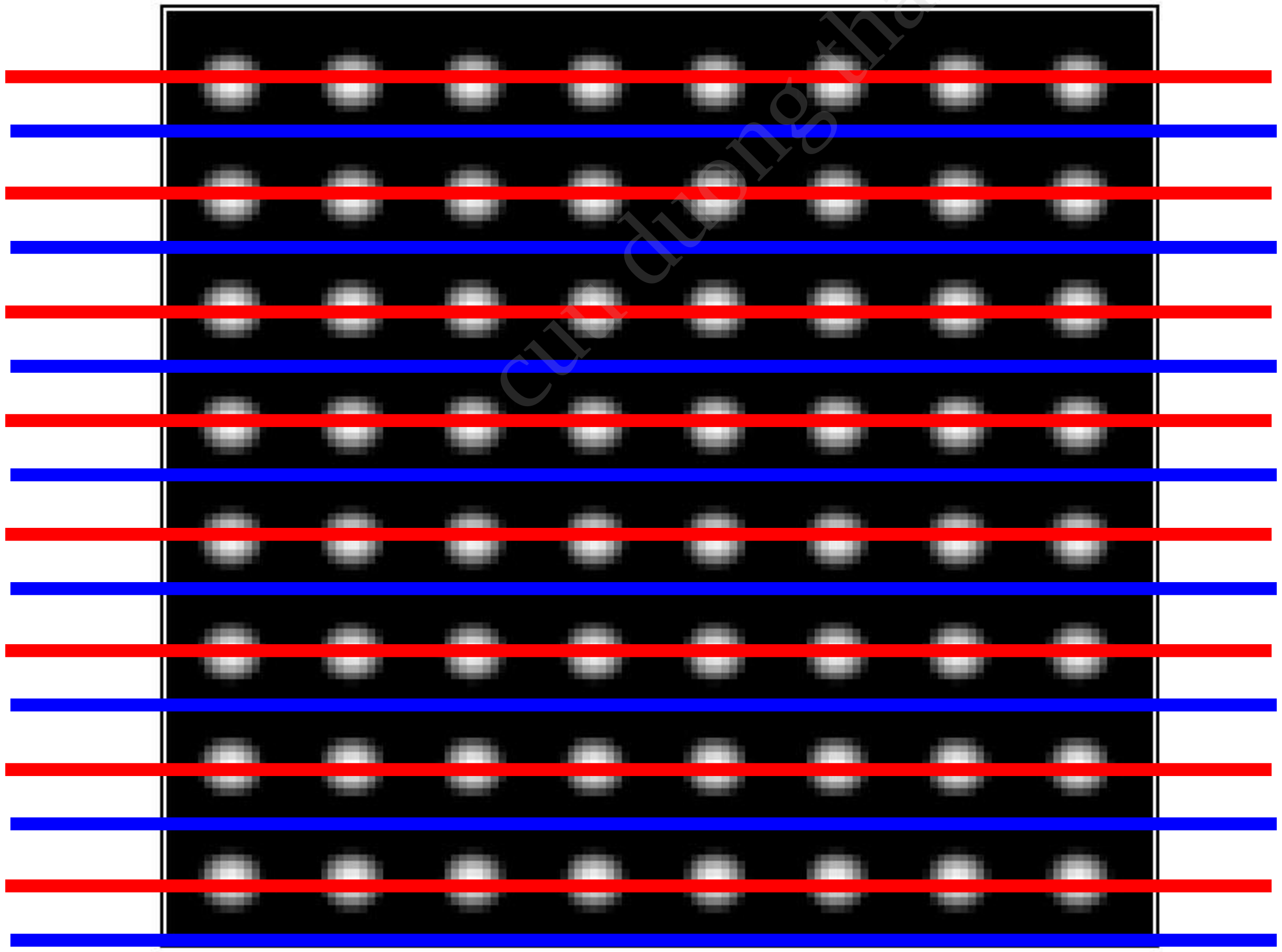
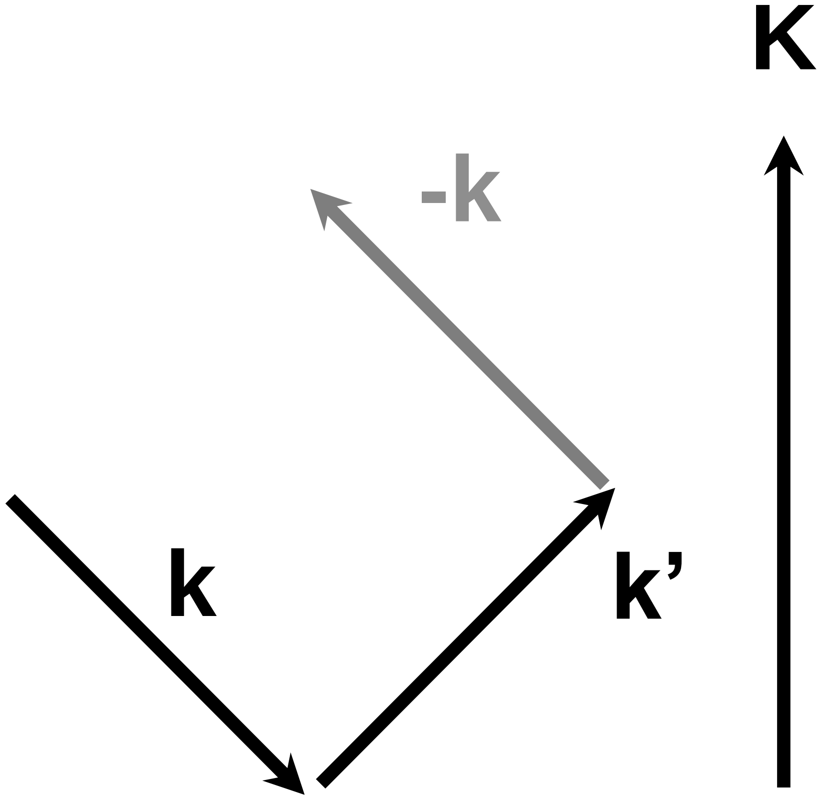
Volume V





X-ray diffraction, von Laue description

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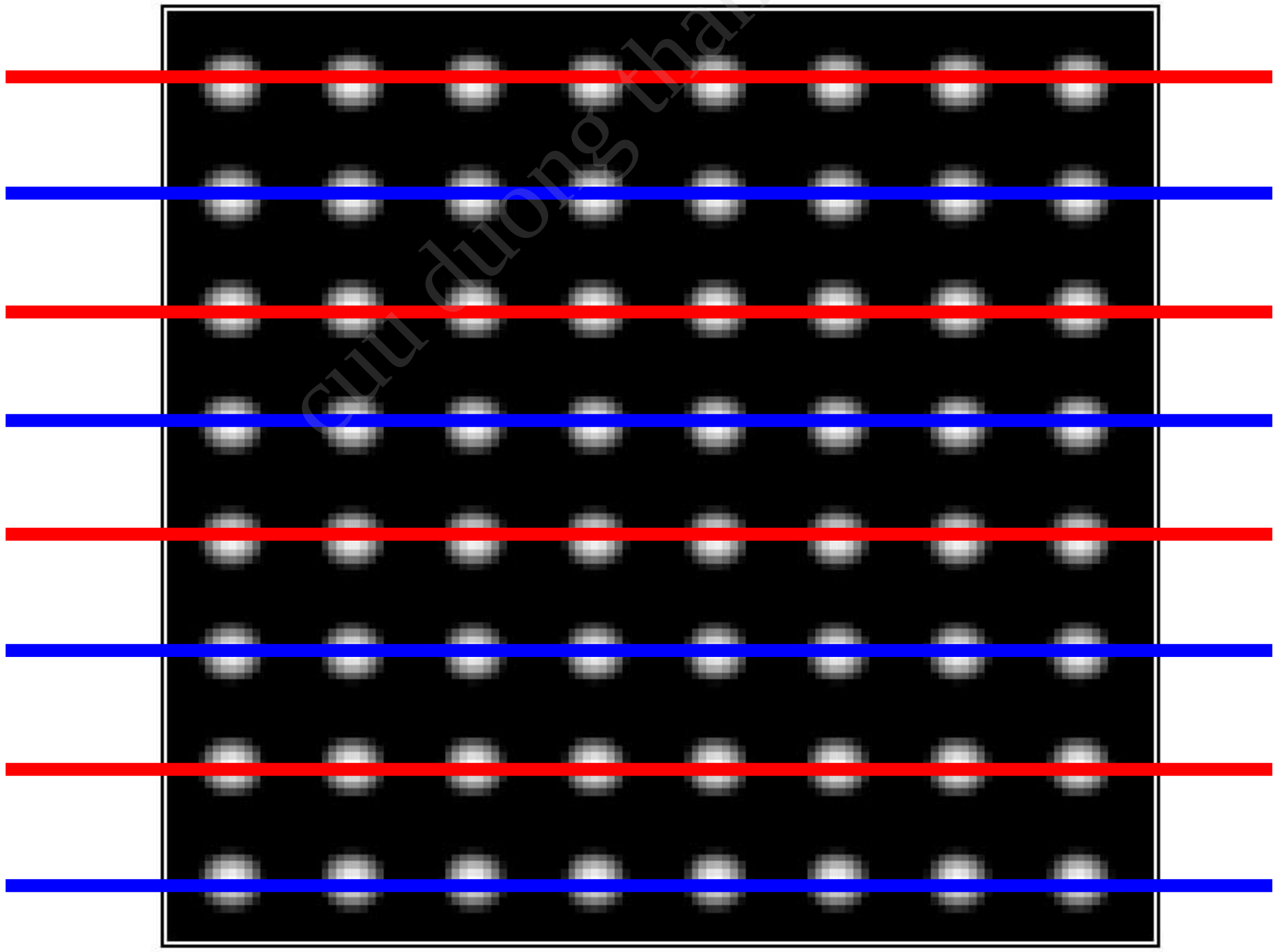
Volume
V



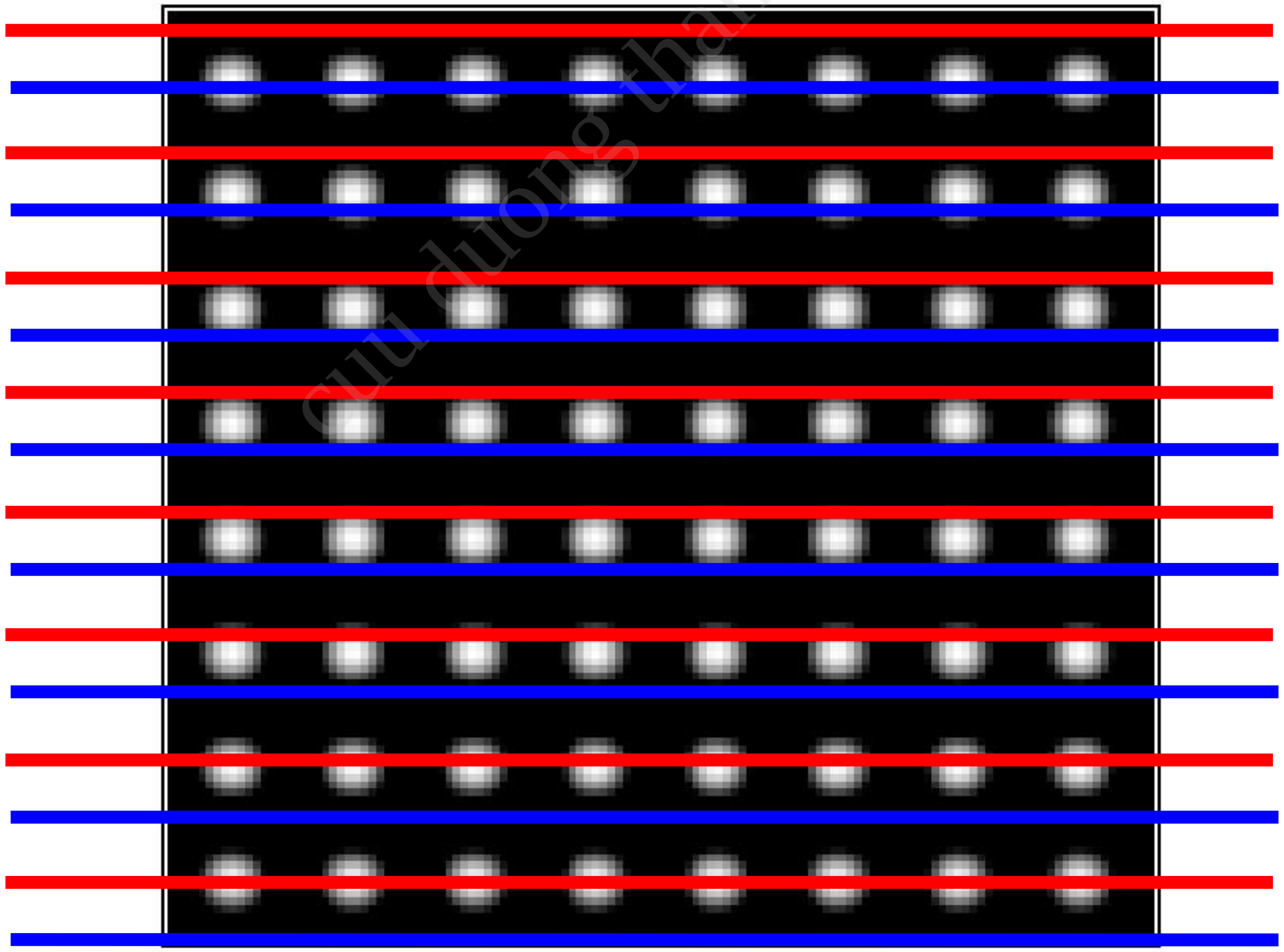
X-ray diffraction, von Laue description

so the measured intensity is

$$I(\mathbf{K}) \propto \left| \int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV \right|^2 = \left| \int_V \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} dV \right|^2$$

$$\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$$

Volume
V



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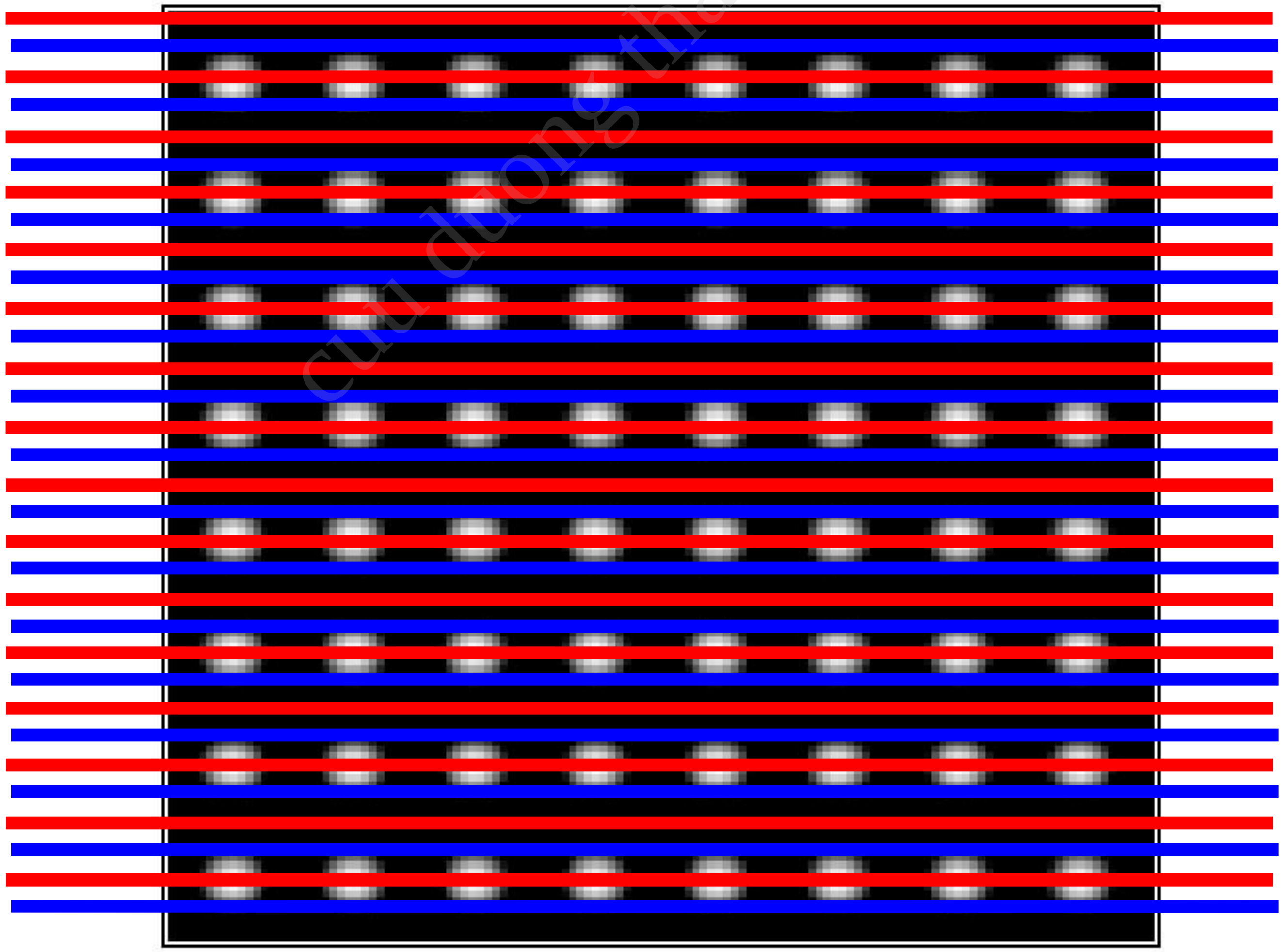
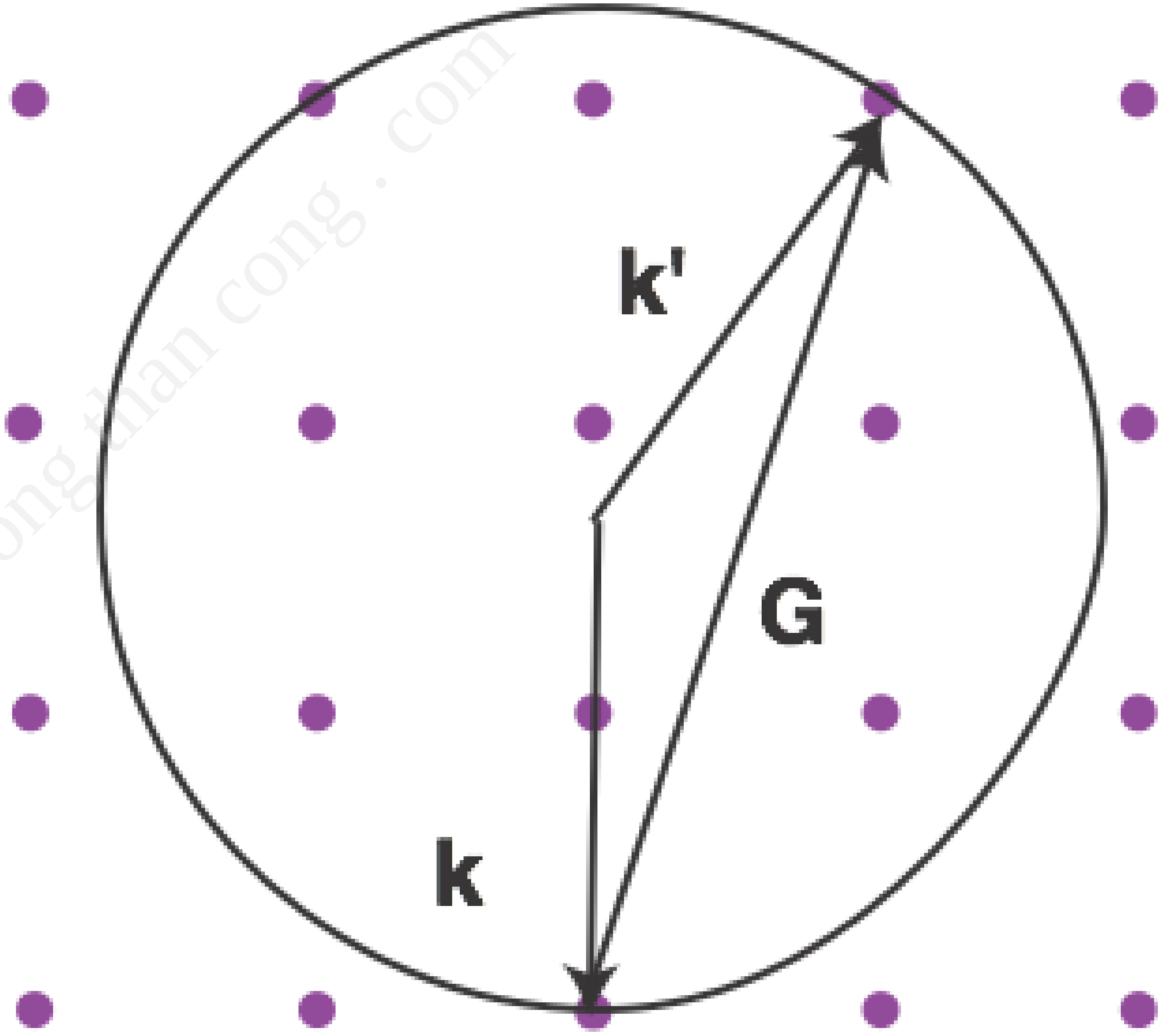


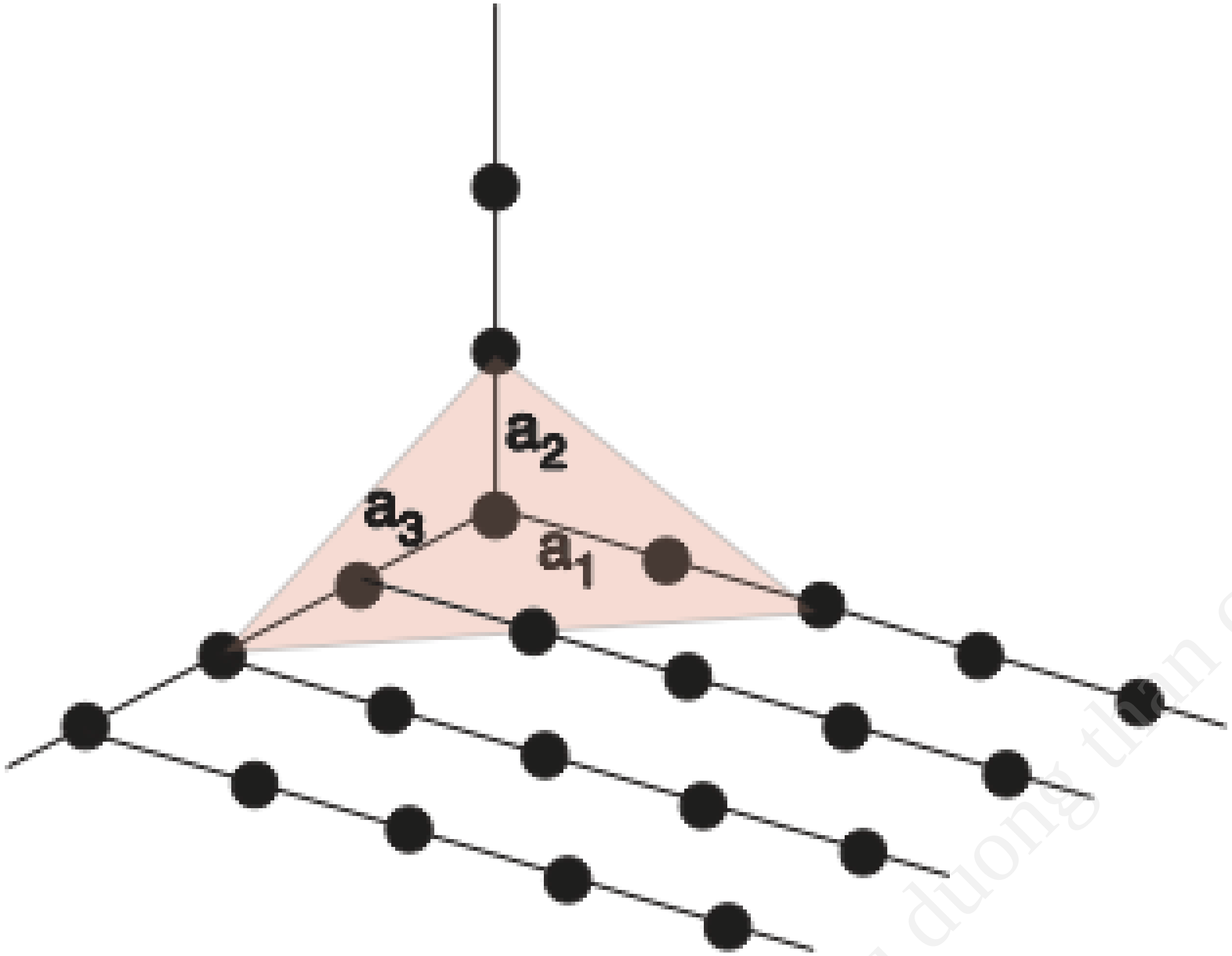
The Ewald construction

Laue condition $\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$ if **G** is a rec. lat. vec.

- Draw (cut through) the reciprocal lattice.
- Draw a **k** vector corresponding to the incoming x-rays which ends in a reciprocal lattice point.
- Draw a circle around the origin of the **k** vector.
- The Laue condition is fulfilled for all vectors **k’** for which the circle hits a reciprocal lattice point.



Labelling crystal planes (Miller indices)



step 1: (2,1,2)

step 2: ((1/2),1,(1/2))

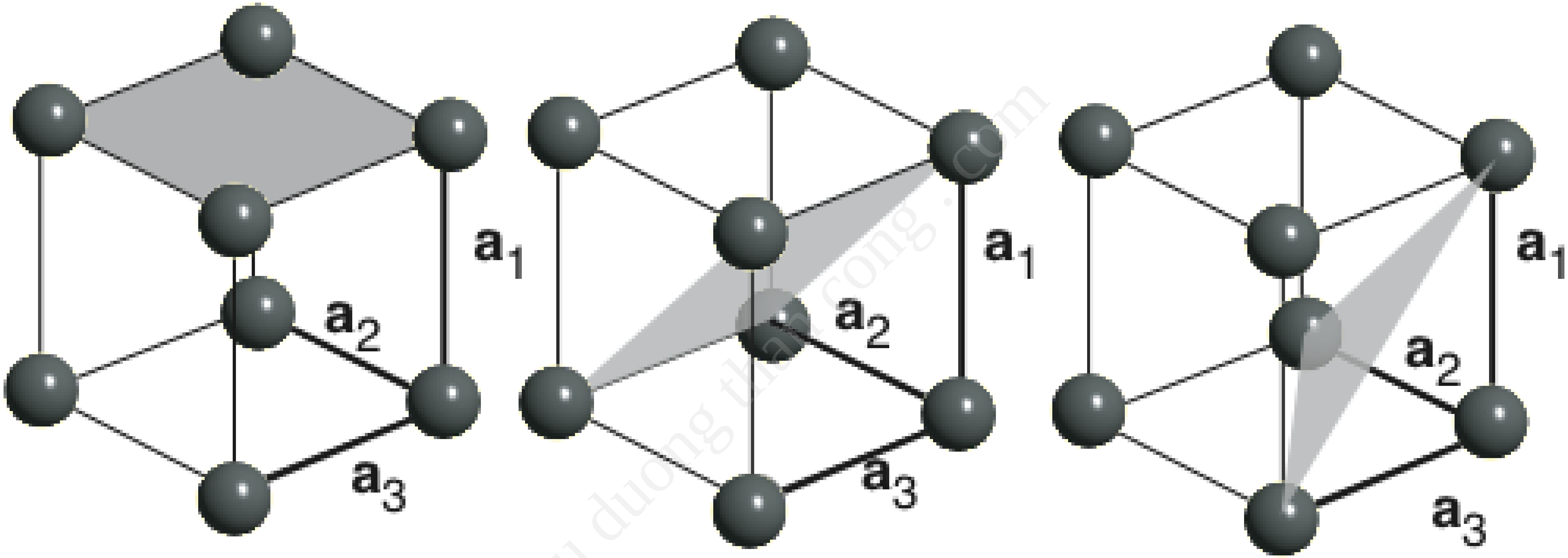
step 3: (1,2,1)

1. determine the intercepts with the axes in units of the lattice vectors

2. take the reciprocal of each number

3. reduce the numbers to the smallest set of integers having the same ratio. These are then called the Miller indices.

Example



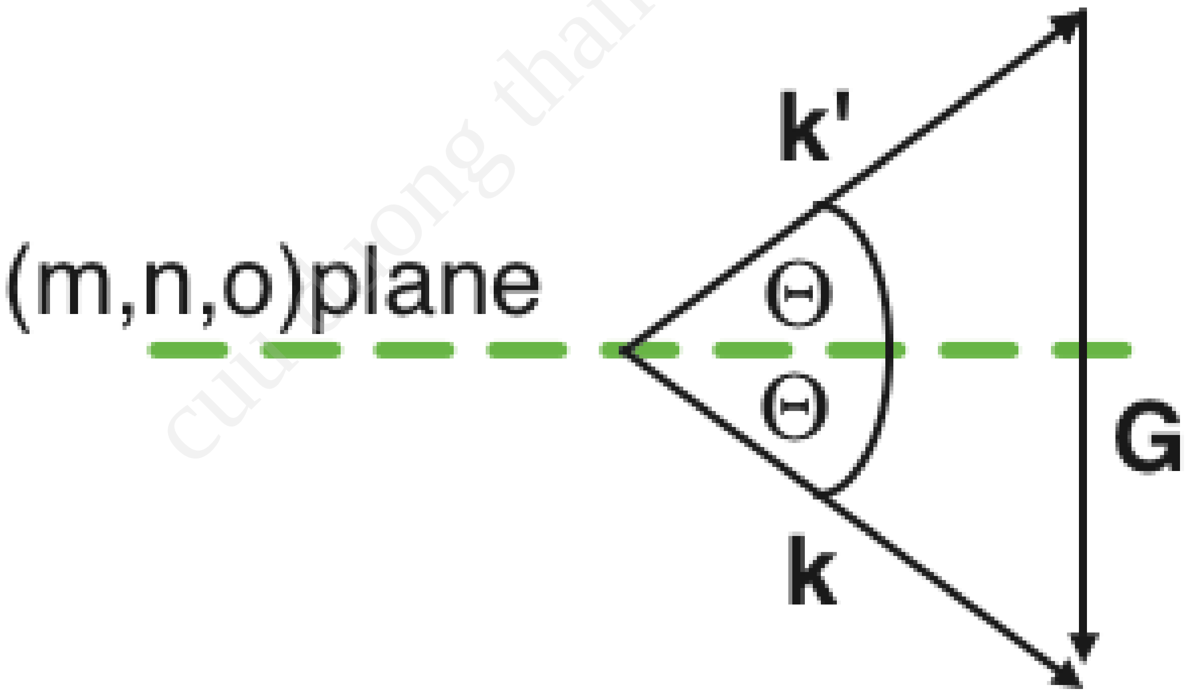
(1,0,0) (1,1,0) (1,1,1)

Relation to lattice planes / Miller indices

The vector

$$\mathbf{G} = m\mathbf{b_1} + n\mathbf{b_2} + o\mathbf{b_3}$$

is the normal vector to the lattice planes with Miller indices (m,n,o)



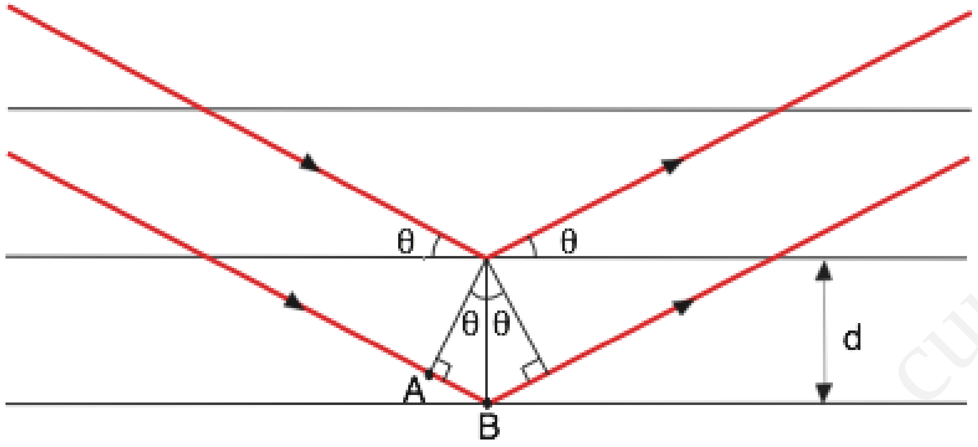
$$\mathbf{k} - \mathbf{k'} = \mathbf{G}$$

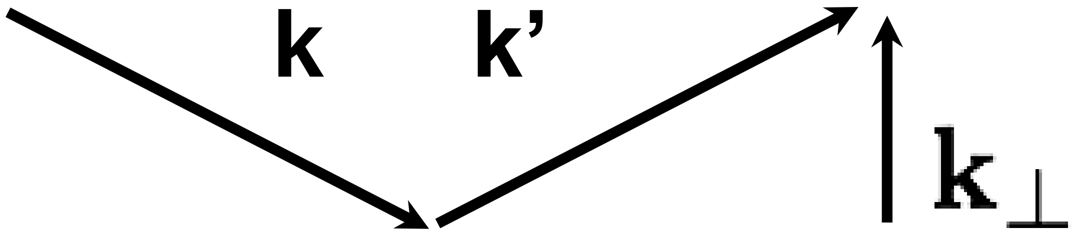
Why does the Bragg condition appear so much simpler?

Laue condition $\mathbf{K} = \mathbf{k}' - \mathbf{k} = \mathbf{G}$

automatically fulfilled parallel to the surface (choosing specular reflection)

$$k'_\perp - k_\perp = 2k_\perp = 2\frac{2\pi}{\lambda}\sin\Theta = G_\perp$$





define vector **d** connecting the planes

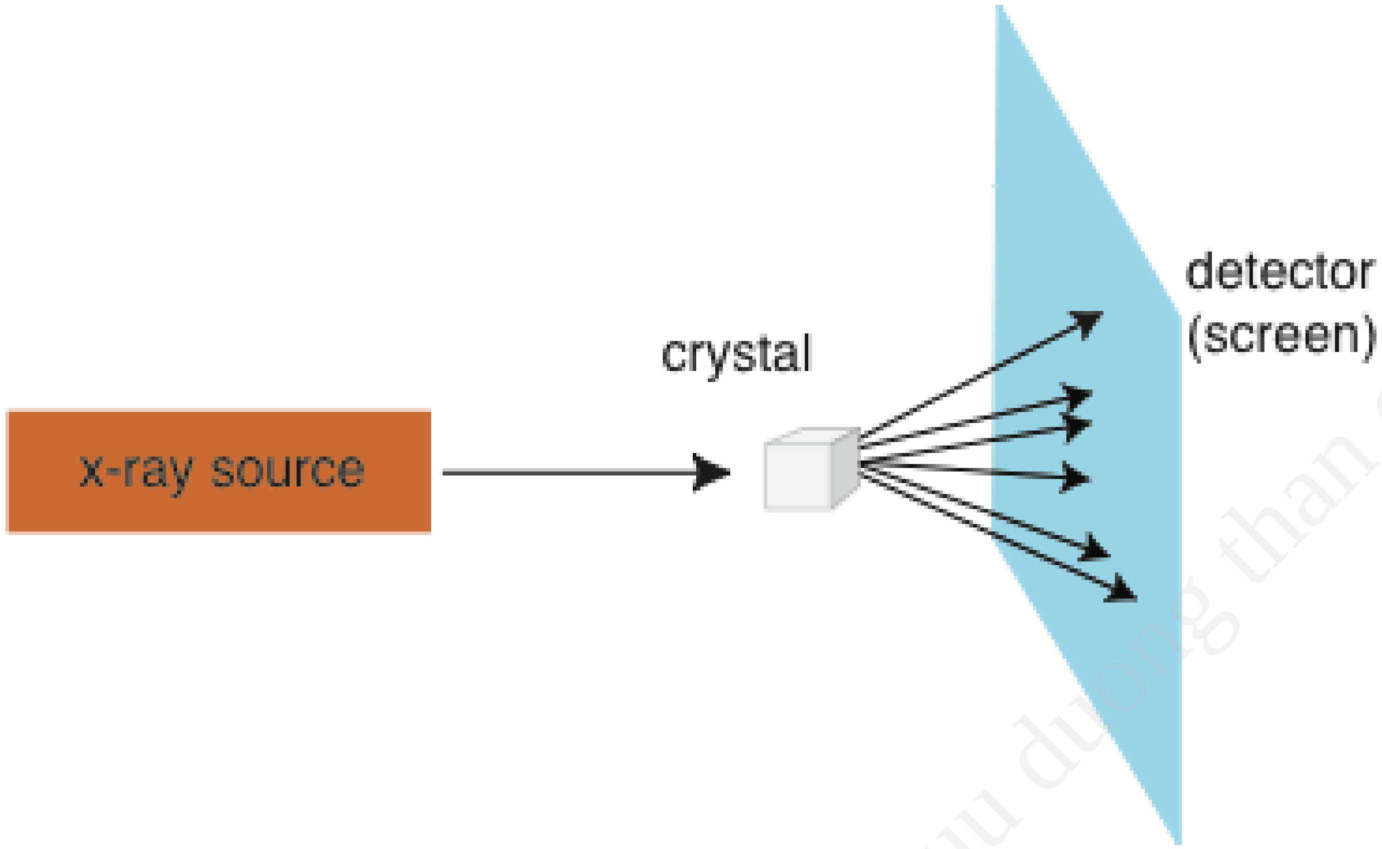
1D reciprocal lattice in this direction:

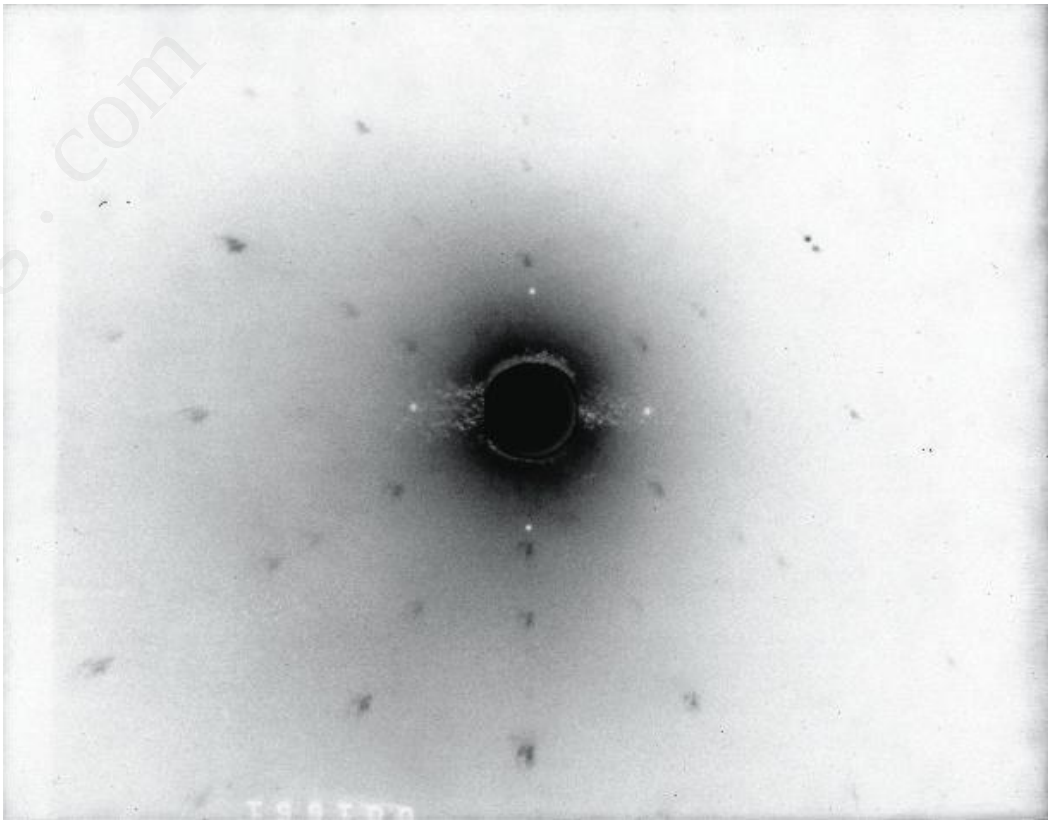
$$G_\perp = m\frac{2\pi}{d}$$

$$2d\sin\Theta = m\lambda$$

x-ray diffraction in practice

Laue Method

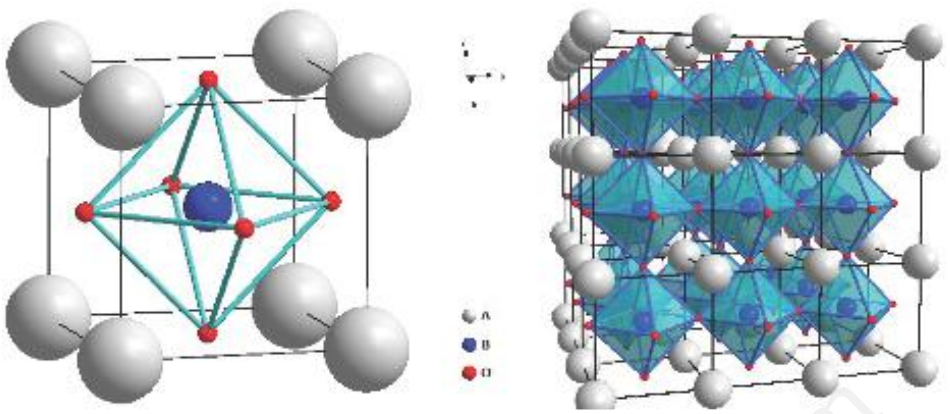




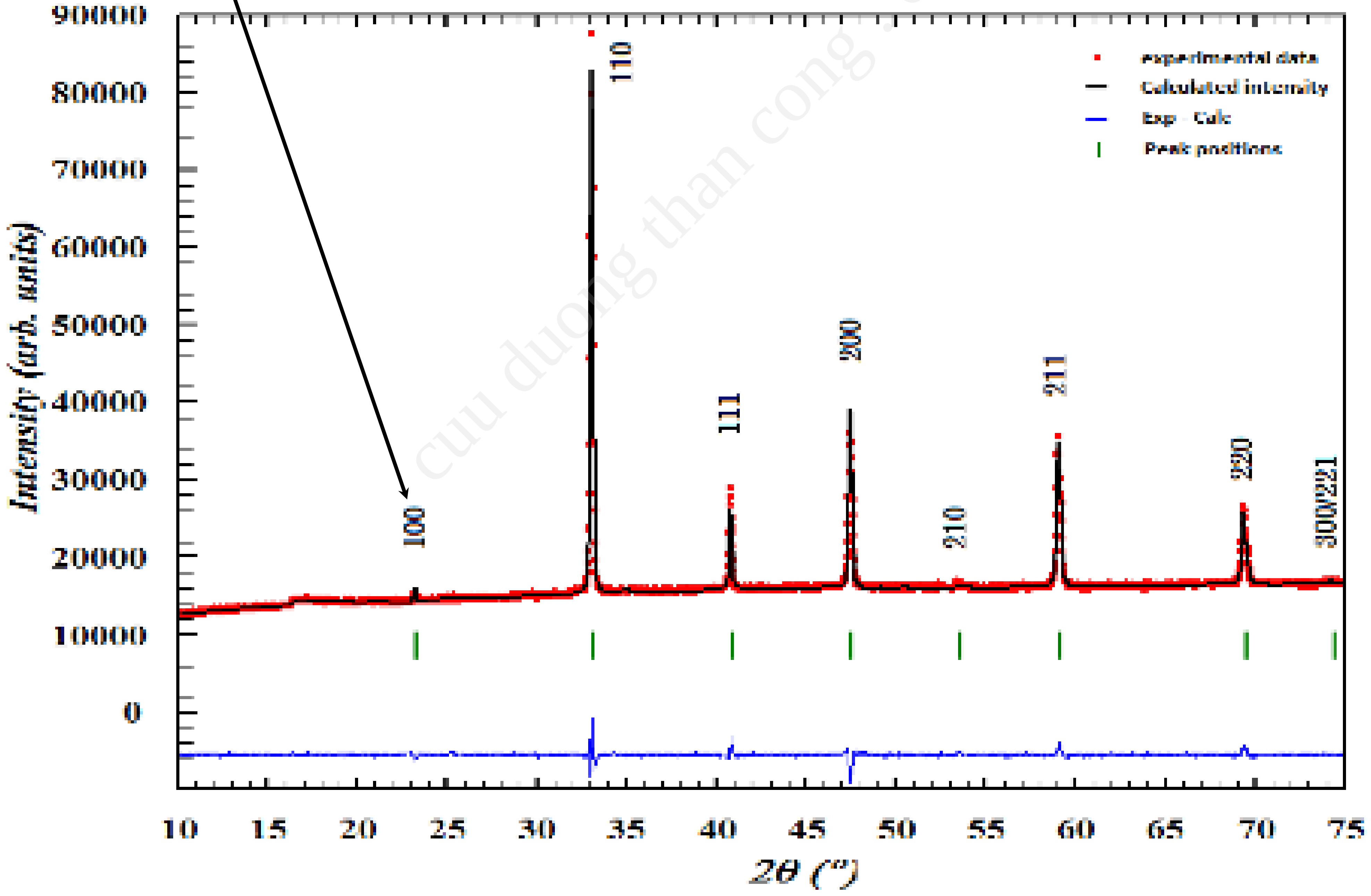
- Using white x-rays in transmission or reflection.
- Obtain the symmetry of the crystal along a certain axis.

Powder Diffraction

reciprocal lattice point



SrCoO3 chemically oxidized



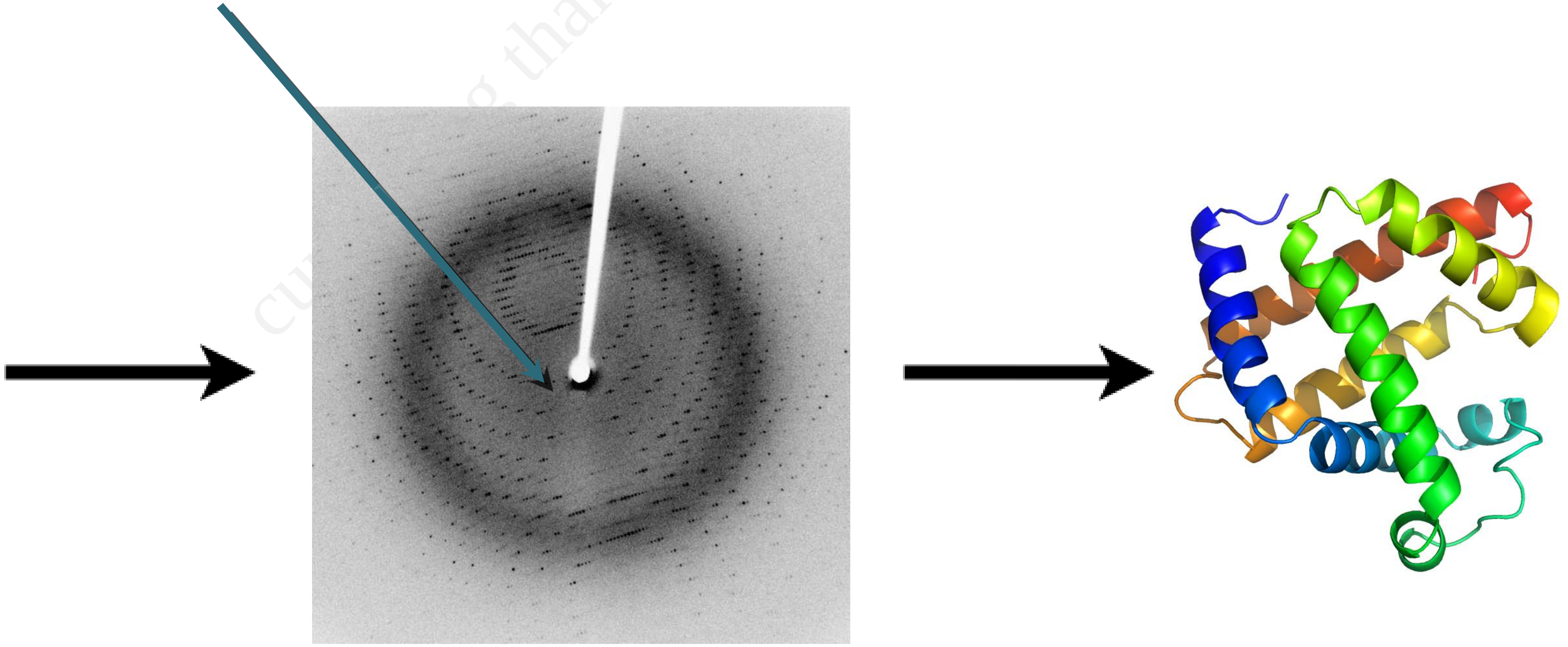
advanced X-ray diffraction

- The position of the spots gives information about the reciprocal lattice and thus the Bravais lattice.
- An intensity analysis can give information about the basis.
- Even the structure of a very complicated basis can be determined (proteins...)

every spot

$$I(\mathbf{K}=\mathbf{G}) \propto |\rho_{\mathbf{G}}|^2$$

crystallize protein



remember

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)} \qquad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1(\mathbf{a}_2 \times \mathbf{a}_3)}$$

advanced x-ray sources: synchrotron radiation

SPring-8

ASTRID

- A highly collimated and monochromatic beam is needed for protein crystallography.
- This can only be provided by a synchrotron radiation source.

What is in the basis?

$$I(\mathbf{K}) \propto |\int_V \rho(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} dV|^2 = |\int_V \rho(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} dV|^2$$

with $\mathbf{K} = \mathbf{G}$

$$I(\mathbf{G}) \propto |\int_V \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} dV|^2$$

we have N unit cells in the crystal and write this as sum over cells

$$I(\mathbf{G}) \propto |\sum_{\mathbf{R}} \int_{V_{cell}} \rho(\mathbf{r}-\mathbf{R}) e^{-i\mathbf{G}\cdot(\mathbf{r}-\mathbf{R})} dV|^2 = |\sum_{\mathbf{R}} \int_{V_{cell}} \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} e^{i\mathbf{G}\cdot\mathbf{R}} dV|^2$$

$$I(\mathbf{G}) \propto |N \int_{V_{cell}} \rho(\mathbf{r}) e^{-i\mathbf{G}\cdot\mathbf{r}} dV|^2$$

$$\rho(\mathbf{r}) \sum_j \rho_j(\mathbf{r} - \mathbf{r_j})$$

(sum over the *j* atoms in the unit cell, model this)

Inelastic scattering

- Gain information about possible excitations in the crystal (mostly lattice vibrations). Not discussed here.

Other scattering methods (other than x-rays)

- electrons (below)
- neutrons

Electron microscopes / electron diffraction

- Electrons can also have a de Broglie wavelength similar to the lattice constant in crystals.
- For electrons we get

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2m_e E_{kin}}}$$

This gives a wavelength of 5 Å for an energy of 6 eV.