Tutorial on crystallography

And how the hexagonal crystal is almost always different

Albes Koxhaj Elena Pascal

University of Strathclyde

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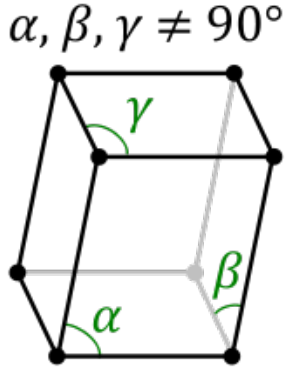
Outline

Crystallographic maths

Spoiler: It never happens in Cartesian frames

- Vector calculus in a rectilinear but not necessary orthonormal or even orthogonal reference frame.
- Need to define basic vector operation in non-Cartesian frames:



- Dot product
- Cross product
- Length of a vector
- Angle between two vectors

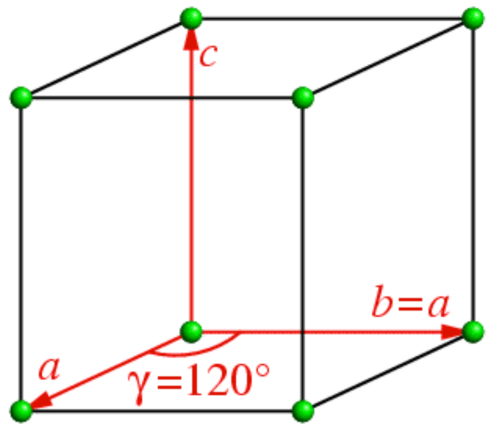
Basis vectors and unit cells

- A *lattice* is defined as a set of points which is created by all integer linear combination of three basis vectors **a, b, c.**

$$\mathbf{t} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$$

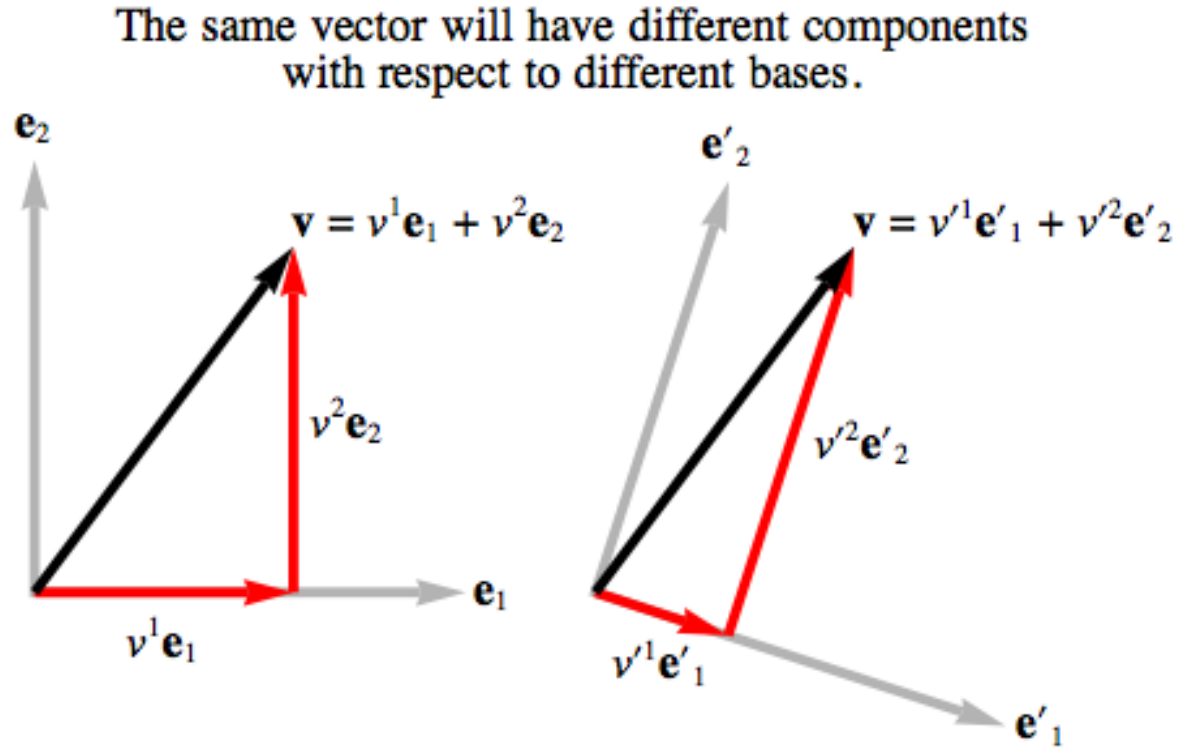
where u, v, w are arbitrary integers.

- A *crystal structure* is defined as a regular arrangement of atoms decorating a given lattice.



A vector is defined using a crystal's basis vectors

$$\mathbf{v} = v^1\mathbf{e_1} + v^2\mathbf{e_2} + v^3\mathbf{e_3} = \sum_{i=1}^{3} v^i\mathbf{e_i} = v_i\mathbf{e_i}$$



Dot product in a crystal frame

- Dot product definition:

$$\mathbf{p} \cdot \mathbf{q} = |\mathbf{p}||\mathbf{q}| \cos\theta$$

If same vector $\mathbf{p} = p_x\mathbf{a} + p_y\mathbf{b} + p_z\mathbf{c} = p_i\mathbf{a_i}$

$$\textit{then} \quad |\mathbf{p}| = \sqrt{\mathbf{p} \cdot \mathbf{p}} = \sqrt{p_i\mathbf{a_i} \cdot p_j\mathbf{a_j}} = \sqrt{p_i\,(\mathbf{a_i} \cdot \mathbf{a_j})\,p_j}$$

- If $\mathbf{p}$ is defined in a non-Orthogonal (or any) crystal frame:

$$|\mathbf{p}| = \sqrt{p_i\, g_{ij}\, p_j}$$

$$g_{ij} \equiv \mathbf{a_i} \cdot \mathbf{a_j} = |\mathbf{a_i}||\mathbf{a_j}| \cos\theta_{ij}$$

- g_{ij} is known as the direct metric tensor

Finally...

- The dot product between any two arbitrary vectors:

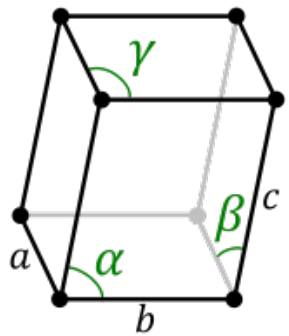
$$\begin{aligned}
\mathbf{p} \cdot \mathbf{q} &= \sum_{i,j=1}^{3} (p_i \mathbf{a_i}) \cdot (q_j \mathbf{a_j}) \\
&= \sum_{i,j=1}^{3} p_i \left(\mathbf{a_i} \cdot \mathbf{a_j}\right) q_j \\
&= \sum_{i,j=1}^{3} p_i g_{ij} q_j \\
&= p_i g_{ij} q_j
\end{aligned}$$

Direct Metric Tensor

- 3×3 matrix to define how distances are measured
- defined by the six lattice parameters:

$$g = \begin{bmatrix} \mathbf{a}\cdot\mathbf{a} & \mathbf{a}\cdot\mathbf{b} & \mathbf{a}\cdot\mathbf{c} \\ \mathbf{b}\cdot\mathbf{a} & \mathbf{b}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{c} \\ \mathbf{c}\cdot\mathbf{a} & \mathbf{c}\cdot\mathbf{b} & \mathbf{c}\cdot\mathbf{c} \end{bmatrix} = \begin{bmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ba\cos\gamma & b^2 & bc\cos\alpha \\ ca\cos\beta & cb\cos\alpha & c^2 \end{bmatrix} \quad (1)$$

- Each crystallographic reference frame has a unique one



Example

Find angle θ between [100] and [111] directions in GaN 2H

For GaN : $a = 3.19\text{Å}$, $c = 5.19\text{Å}$.

Let $p = [100]$, $q = [111]$, then $g_{ij} = \begin{bmatrix} a^2 & -\frac{a^2}{2} & 0 \\ -\frac{a^2}{2} & a^2 & 0 \\ 0 & 0 & c^2 \end{bmatrix}$

Using the dot product $\cos\theta = \frac{\mathbf{p}\cdot\mathbf{q}}{|\mathbf{p}||\mathbf{q}|}$:

where $\mathbf{p}\cdot\mathbf{q} = p_i g_{ij} q_j = \begin{bmatrix} 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} a^2 & -\frac{a^2}{2} & 0 \\ -\frac{a^2}{2} & a^2 & 0 \\ 0 & 0 & c^2 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} = \frac{a^2}{2}$,

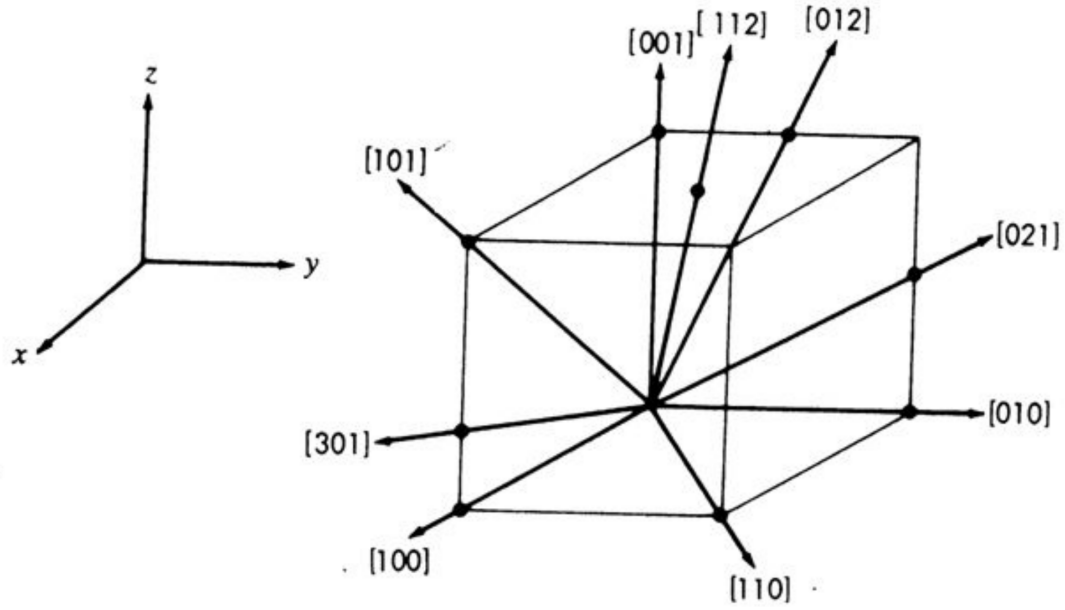
$$|\mathbf{p}| = \sqrt{p_i\, g_{ij}\, p_j} = \sqrt{a^2} = a, \;\; |\mathbf{q}| = \sqrt{q_i\, g_{ij}\, q_j} = \sqrt{a^2 + c^2}$$

$$\therefore \cos\theta = \frac{a^2}{2a\sqrt{a^2 + c^2}} = \frac{a}{2\sqrt{a^2 + c^2}}$$

For lattice parameters given: $\theta = 74.8^\circ$

Directions and distance between points

- Square brackets $[p_x\ p_y\ p_z]$.

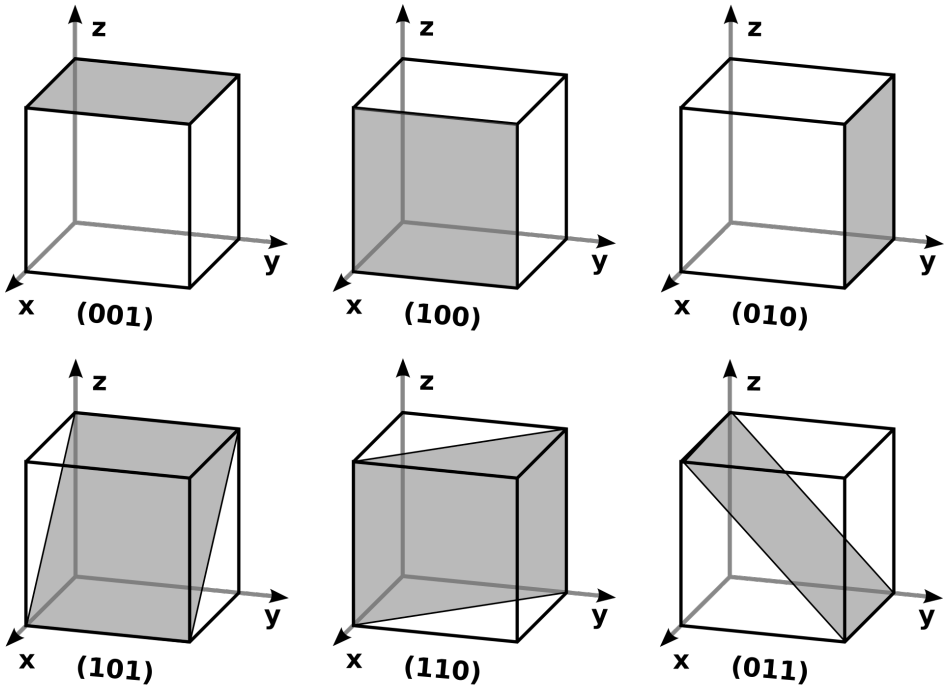


- Distance between points P ($OP = \mathbf{p}$) and Q ($OQ = \mathbf{q}$).

$$D^2 = (\mathbf{q} - \mathbf{p})_i \, g_{ij} \, (\mathbf{q} - \mathbf{p})_j$$

Lattice planes and Miller indices

- Describe lattice plane with a series of 3 integers written in round brackets $(h\,k\,l)$



- if the plane goes through origin displace it parallel to itself
- determine the intercepts with the 3 basis vectors
- invert the intercept $(\infty \rightarrow 0)$
- reduce to smallest integers

Question to ponder about

- the Miller indices (hkl) form a triplet of integer numbers that fully characterize a plane.
- But can we interpret the Miller indices as components of a vector?

Family of planes

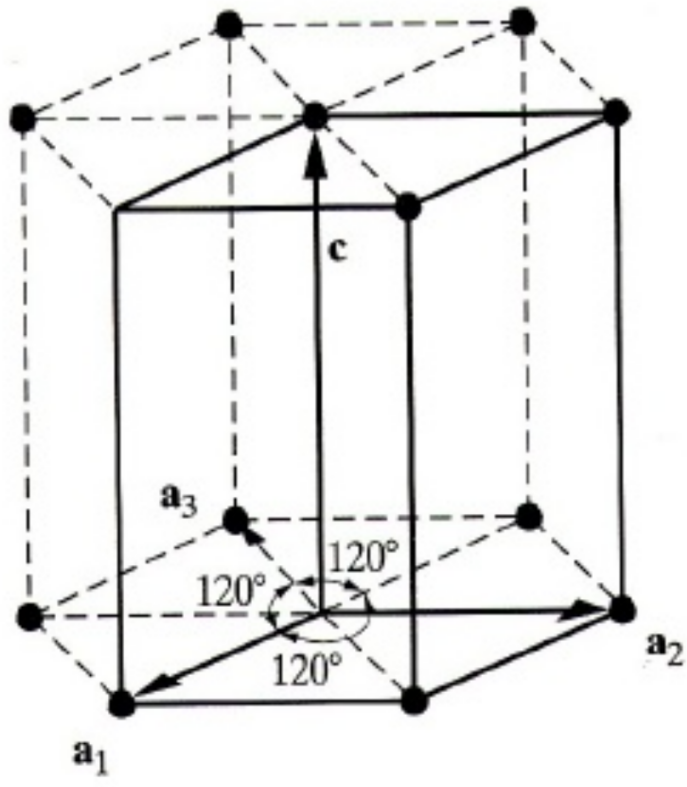
- all crystal planes equivalent to (hkl) form the family of planes $\{hkl\}$.
- the planes in a family can be obtained by permutation of their Miller indices (including negatives).
- the number of planes belonging to a family (multiplicity) is determined by the crystal symmetry
- the concept of family of planes is important when describing the external shape of a crystal – a form is a group of crystal faces that belong to the same family.

Family of directions

- all crystal directions equivalent to $[uvw]$ form the family of directions $\langle uvw \rangle$.
- the directions in a family can be obtained by permutation of their indices (including negatives).
- the number of directions belonging to a family (multiplicity) is determined by the crystal symmetry

Miller-Bravais indices

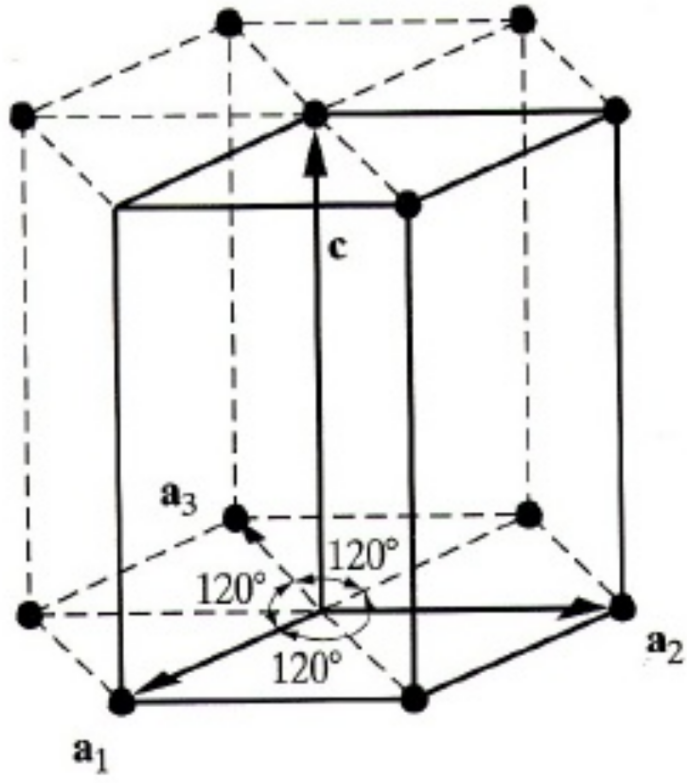
- the hexagonal crystal is more conveniently described by 4 basis vectors
- 3 of which are co-planar and not linearly independent
- Miller-Bravais index $(hkil)$ where third index $i = -(h + k)$ can be omitted $(hk.l)$



Miller-Bravais indices

good for families of planes

- the third index makes it easy to determine the equivalent planes
- by permuting the first 3 Miller-Bravais indices (including negative values)
- $\{11\bar{2}0\} = \{(11\bar{2}0), (1\bar{2}10), (\bar{2}110), (\bar{1}\bar{1}20), (\bar{1}2\bar{1}0), (2\bar{1}\bar{1}0)\}$
- as compared to Miller indices: $\{110\} = \{(110), (1\bar{2}0), (\bar{2}10), (\bar{1}\bar{1}0), (\bar{1}20), (2\bar{1}0)\}$



Miller-Bravais indices

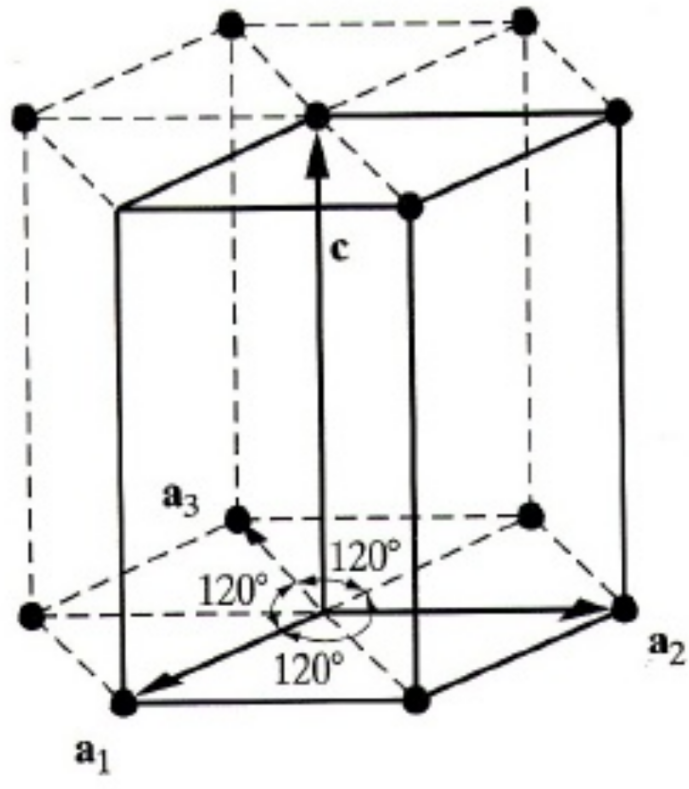
awkward for families of directions

- directions in Miller-Bravais indices are [uvtw]
- where $t = -(u + v)$ is the index corresponding to $\mathbf{a_3}$
- where $\mathbf{a_3} = -(\mathbf{a_1} + \mathbf{a_2})$
- So then:

$$u\mathbf{a_1}+v\mathbf{a_2}+t\mathbf{a_3}+w\mathbf{c} = U\mathbf{a_1}+V\mathbf{a_2}+W\mathbf{c}$$

- Such that:

$$U = 2u + v$$
$$V = 2v + u$$
$$W = w$$



Example

Miller direction [100] in Miller-Bravais

Going the other way we have for [UVW]≡[100]:

$$u = \frac{1}{3}(2U - V) = \frac{2}{3}, \;\; v = \frac{1}{3}(2V - U) = -\frac{1}{3},$$

$$t = -(u + v) = -\frac{1}{3}, \;\; w = W = 0$$

Thus we have the direction written in Miller-Bravais form to be:

$$[100] \equiv [\frac{2}{3}\frac{\bar{1}}{3}\frac{\bar{1}}{3}0]$$

Simplifying to:

$$[100] \equiv [2\bar{1}\bar{1}0]$$

Distances versus frequency

A dual view of the world

Real (Direct) space

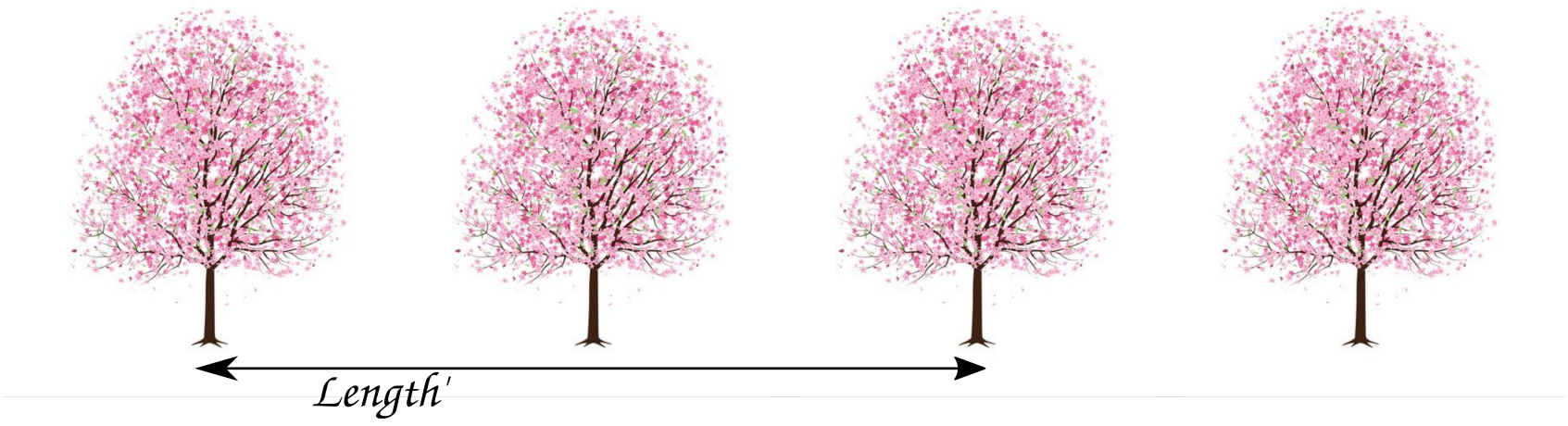
- distances between trees:
  $$d = 1\ \langle Length \rangle$$

Reciprocal space

- trees per unit $\langle Length \rangle$:
  $$r = 1\ \langle 1/Length \rangle$$

Distances versus frequency

A dual view of the world



$$Length' = 2\,Length$$

Real (Direct) space

- distances between trees:
  $$d = 1/2\ \langle Length' \rangle$$
- d is contravariant quantity

Reciprocal space

- trees per unit $\langle Length' \rangle$:
  $$r = 2\ \langle 1/Length' \rangle$$
- r is covariant quantity

A dual view of the world

- Real space and reciprocal space are complementary ways of looking at the crystal lattice.
- They are called spaces because they are described by different vector spaces
- ... even if these spaces are not spatially different
- Why do we need multiple views of the crystal ?
- Remember the pondering question.
- The reciprocal space is defined as the coordinate system in which the Miller indices of a plane are the components of the normal to that plane.

Reciprocal basis vectors

For any crystal structure the reciprocal lattice vector $\mathbf{g}$, with components (h, k, l) is by definition perpendicular to the plane with Miller indices (hkl).

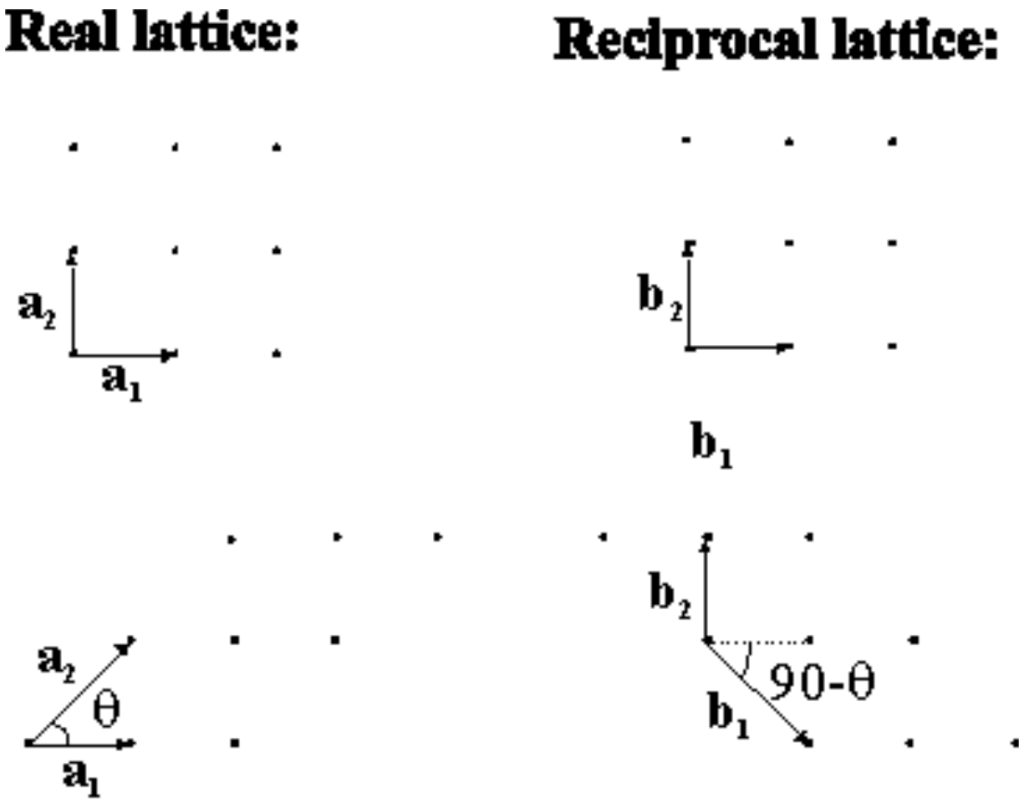
$$\mathbf{g}_{hkl} = h\mathbf{b_1}^* + k\mathbf{b_2}^* + l\mathbf{b_3}^*$$

where

$$\mathbf{b}_1^* = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{V}$$

$$\mathbf{b}_2^* = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{V}$$

$$\mathbf{b}_3^* = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{V}$$



Reciprocal space vector length

- The other awesome property of the reciprocal space vector $\mathbf{g}_{hkl}$ is that its length is equal to the inverse of the distance between the (hkl) planes:

$$|\mathbf{g}_{hkl}| = \frac{1}{d_{hkl}}$$

- But the reciprocal space is just a different basis vector and we know we can use the metric tensor formalism to compute vector lengths.

Reciprocal metric tensor

We've done this before:

$$|\mathbf{g}| = \sqrt{\mathbf{g}\cdot\mathbf{g}} = \sqrt{(g_i \mathbf{a^*}_i)\cdot(g_j \mathbf{a^*}_j)} = \sqrt{(g_i(\mathbf{a^*}_i\cdot\mathbf{a^*}_j)g_j} = \sqrt{g_i g^*_{ij} g_j}$$

where we call g^*_{ij} the reciprocal metric tensor:

$$g^* = \begin{bmatrix} \mathbf{a}^*\cdot\mathbf{a}^* & \mathbf{a}^*\cdot\mathbf{b}^* & \mathbf{a}^*\cdot\mathbf{c}^* \\ \mathbf{b}^*\cdot\mathbf{a}^* & \mathbf{b}^*\cdot\mathbf{b}^* & \mathbf{b}^*\cdot\mathbf{c}^* \\ \mathbf{c}^*\cdot\mathbf{a}^* & \mathbf{c}^*\cdot\mathbf{b}^* & \mathbf{c}^*\cdot\mathbf{c}^* \end{bmatrix}$$

$$= \begin{bmatrix} a^{*2} & a^*b^*\cos\gamma^* & a^*c^*\cos\beta^* \\ b^*a^*\cos\gamma^* & b^{*2} & b^*c^*\cos\alpha^* \\ c^*a^*\cos\beta^* & c^*b^*\cos\alpha^* & c^{*2} \end{bmatrix}$$

Reciprocal metric tensor

Nevermind the reciprocal basis

Quite conveniently we don't really have to do any reciprocal space maths because the matrices representing the direct and reciprocal space are each other's inverses:

$$g^*_{ij} = (g_{ij})^{-1}$$

For instance,

$$g^*_{hexagonal} = \begin{bmatrix} \frac{4}{3a^2} & \frac{2}{3a^2} & 0 \\ \frac{2}{3a^2} & \frac{4}{3a^2} & 0 \\ 0 & 0 & \frac{1}{c^2} \end{bmatrix}$$

Example

Expressions for the length $|\mathbf{g}_{hkl}| = 1/d_{hkl}$

System	$\lvert\mathbf{g}_{hkl}\rvert$ **expression**
Cubic	$g^c = \frac{1}{a}\left\{h^2 + k^2 + l^2\right\}^{1/2}$
Tetragonal	$g^t = \left\{\frac{1}{a^2}(h^2 + k^2) + \frac{1}{c^2}l^2\right\}^{1/2}$
Hexagonal	$g^h = \left\{\frac{4}{3a^2}(h^2 + k^2 + hk) + \frac{1}{c^2}l^2\right\}^{1/2}$

Angle between reciprocal vectors

Or between planes normals

As in real space the angle α between reciprocal vectors $\mathbf{g}$ and $\mathbf{h}$:

$$\alpha = \cos^{-1}\left(\frac{\mathbf{g}\cdot\mathbf{h}}{|\mathbf{g}|\ |\mathbf{h}|}\right) = \cos^{-1}\left(\frac{g_i g^*_{ij} h_j}{\sqrt{g_i g^*_{ij} g_j}\sqrt{h_i g^*_{ij} h_j}}\right)$$

For $\mathbf{g}_{h_1 k_1 l_1}$ and $\mathbf{h}_{h_2 k_2 l_2}$ in a hexagonal system:

$$\alpha = \frac{\frac{4}{3a^2}\left(h_1 k_1 + k_1 k_2 + \frac{1}{2}(h_1 k_1 + k_1 h_2)\right) + \frac{1}{c^2} l_1 l_2}{g_{h_1 k_1 l_1} h_{h_2 k_2 l_2}}$$

Reciprocal space vector in real space

And vice versa

- A vector exists independently of the reference frame.
- So for a vector $\mathbf{p}$ defined by components p_i in the direct lattice frame with basis vectors $\mathbf{a}_i$: $p = p_i \mathbf{a}_i$,
- we can find components p_j^* in the reciprocal space with basis vectors $\mathbf{a}_j^*$:

$$\mathbf{p} = p_i \mathbf{a}_i = p_j^* \mathbf{a}_j^*$$

So then:

$$p_m^* = p_i g_{im}$$

And:

$$p_i = p_m^* g_{mi}^*$$

For Further Reading I


M. De Graef, M. E. McHenry
Structure of materials; An introduction to crystallography, diffraction and symmetry.
Cambridge University Press, 2012.


M. De Graef
Introduction to conventional transmission electron microscopy.
Cambridge University Press, 2003.