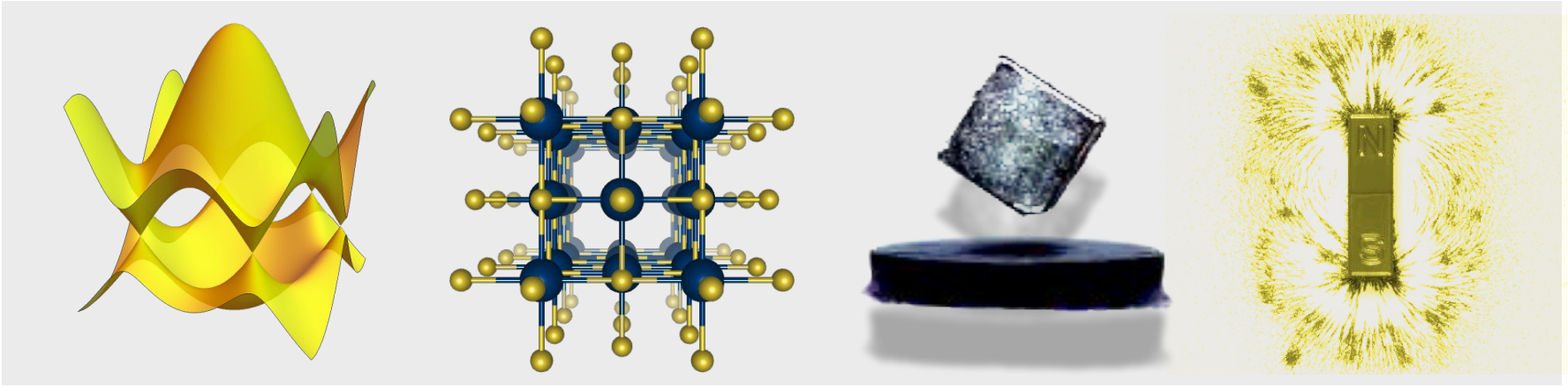
# ESCOLA SÉRGIO MASCARENHAS DE FÍSICA DA MATÉRIA CONDENSADA

Aula 1 - 15 de Julho

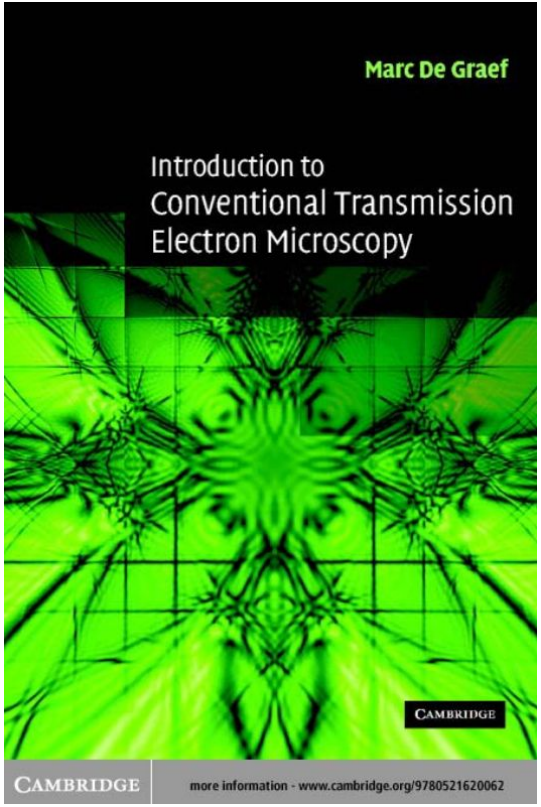
## Redes Cristalinas



# Redes Cristalinas

INTRODUCTION TO CONVENTIONAL TRANSMISSION ELECTRON MICROSCOPY

MARC DE GRAEF

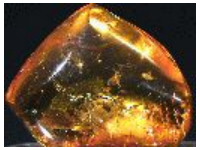


# Tópicos

1. Redes em 3D e 2D.
2. Simetrias.
3. Alguns materiais representativos e propriedades.

# Alguns Cristais e Minerais

- http://www.bestcrystals.com/crystals2.html
- http://www.galleries.com/minerals


âmbar


ametista


anatase


rutilo


apatita


gipsita


quartzo

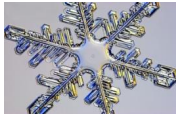

grafite


diamante


galena


bismuto


natrolita

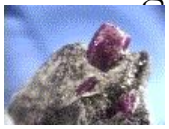

gelo


pirita


talco


magnetita


borax


rubi


lazulita


estibilita

# Breve Histórico

- Mineralogistas descobrem que as direções das faces dos cristais tem relação com números inteiros
  - cristais são formados por arranjos periódicos de elementos
    - *Essai d'une théorie sur la structure des cristaux*, R. J. Haüy, Paris, 1784
    - *Traité de cristalographie*, Paris, 1801
- Simetrias existentes nos cristais
  - Redes de Bravais
    - 14 tipos de redes tridimensionais para os sistemas cristalinos, A. Bravais, 1845

# Breve Histórico

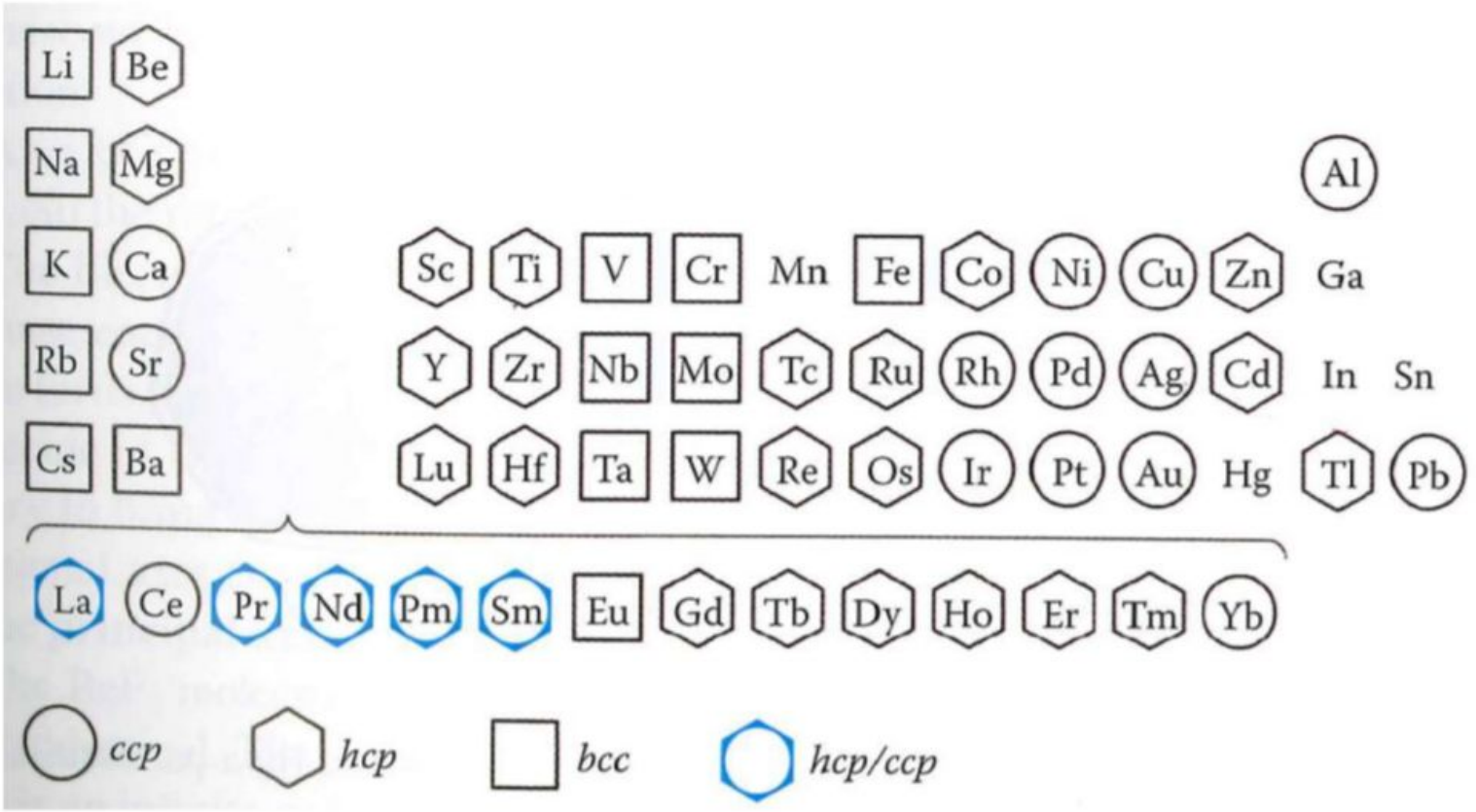
- Descoberta dos raios-x
  - Röntgen, 1895
    - Utilizados em radiografias humanas e de outros objetos, para estudo do interior dos mesmos.

- Teoria elementar da difração, e primeiros experimentos com difração em cristais
  - *Interference effects with Röntgen rays*, apresentado à Bavarian Academy of Sciences – Munique, 1912.
    - Von Laue: formalização de uma teoria elementar de difração, baseada nas propriedades geométricas da rede real e da rede recíproca.
    - Friedrich e Knipping: primeiras experiências de difração de raios-x por cristais.

# Breve Histórico

- Formalização alternativa para a difração:
  - W. H. Bragg e W. L. Bragg, 1913.
    - Teoria de difração considerando planos cristalinos e “reflexão” especular pelos planos.
    - Lei de Bragg.

# Occurrence of packing types assumed by elements

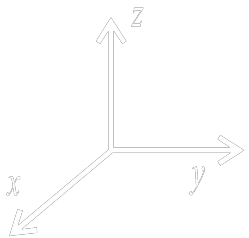


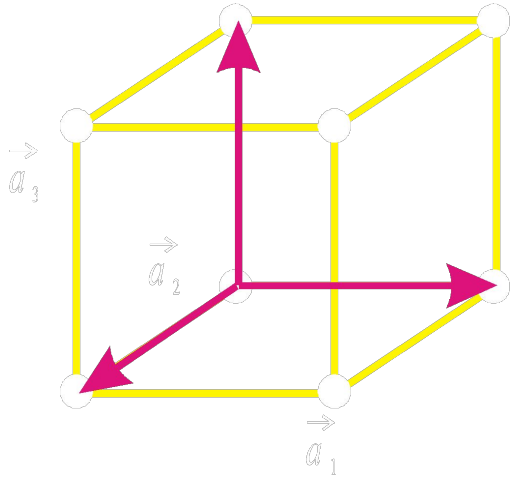

https://www.unf.edu/~michael.lufaso/chem4627/ch1_solid_state.pdf

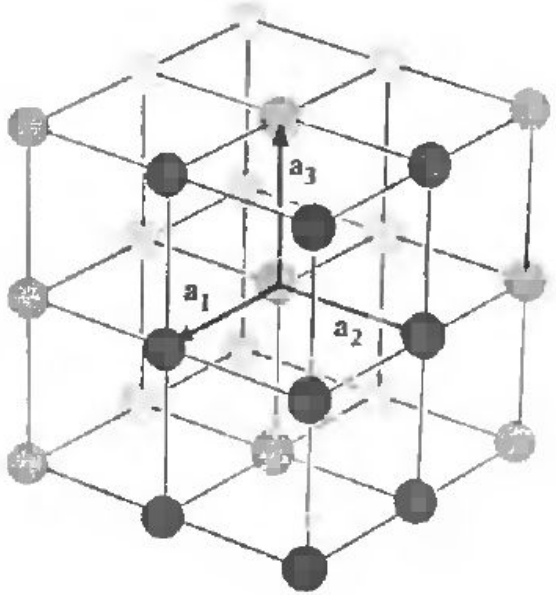
# Redes de Bravais

- Exemplos de redes de Bravais
  - Rede cúbica simples (SC – *simple cubic*).
  - Ex.: α-Po.

$$\vec{a}_1 = a\,\hat{x}$$
$$\vec{a}_2 = a\,\hat{y}$$
$$\vec{a}_3 = a\,\hat{z}$$



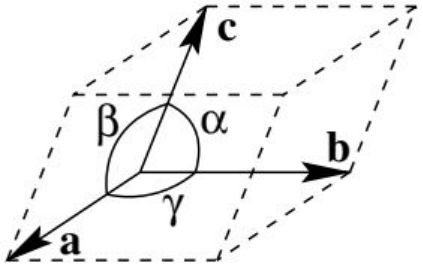
# Redes Cristalinas

## Basic crystallography

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

$$\mathbf{t} = \sum_{i=1}^{3} u_i \mathbf{a}_i$$

$$\mathbf{t} = u_i \mathbf{a}_i$$




The six numbers $\{a, b, c, \alpha, \beta, \gamma\}$ are known as the *lattice parameters*

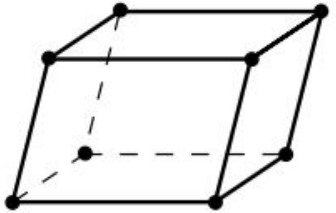
| | | |
|---|---|---|
| $\{a, b, c, \alpha, \beta, \gamma\}$ | $a \neq b \neq c; \alpha \neq \beta \neq \gamma$ | triclinic or anorthic (a); |
| $\left\{a, b, c, \frac{\pi}{2}, \beta, \frac{\pi}{2}\right\}$ | $a \neq b \neq c; \beta \neq \frac{\pi}{2}$ | monoclinic (m); |
| $\left\{a, a, c, \frac{\pi}{2}, \frac{\pi}{2}, \frac{2\pi}{3}\right\}$ | $a = b \neq c$ | hexagonal (h); |
| $\{a, a, a, \alpha, \alpha, \alpha\}$ | $a = b = c; \alpha \neq \frac{\pi}{2}$ | rhombohedral (R); |
| $\left\{a, b, c, \frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}\right\}$ | $a \neq b \neq c$ | orthorhombic (o); |
| $\left\{a, a, c, \frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}\right\}$ | $a = b \neq c$ | tetragonal (t); |
| $\left\{a, a, a, \frac{\pi}{2}, \frac{\pi}{2}, \frac{\pi}{2}\right\}$ | $a = b = c$ | cubic (c). |

$$\mathbf{A} = \left(0, \frac{1}{2}, \frac{1}{2}\right);$$

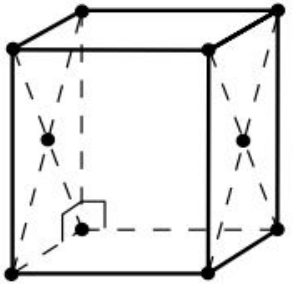
$$\mathbf{B} = \left(\frac{1}{2}, 0, \frac{1}{2}\right);$$

$$\mathbf{C} = \left(\frac{1}{2}, \frac{1}{2}, 0\right);$$

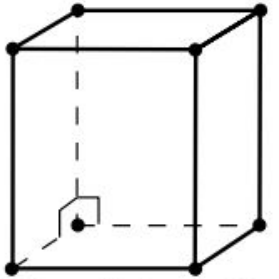
$$\mathbf{I} = \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right).$$



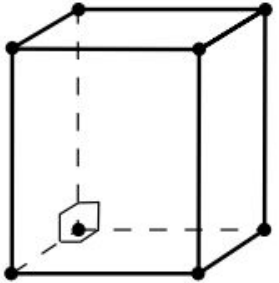
Triclinic (aP)



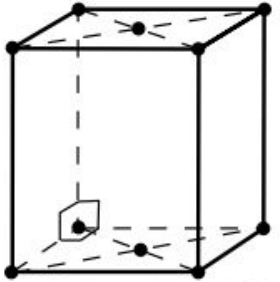
Monoclinic (mC)



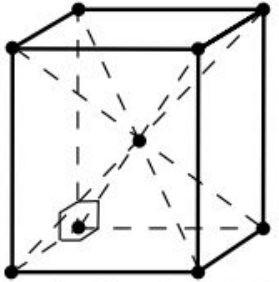
Monoclinic (mP)



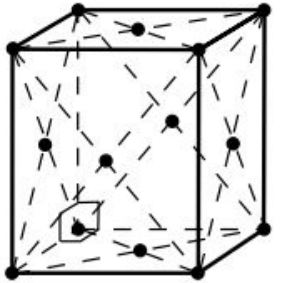
Orthorhombic (oP)



Orthorhombic (oC)



Orthorhombic (oI)



Orthorhombic (oF)

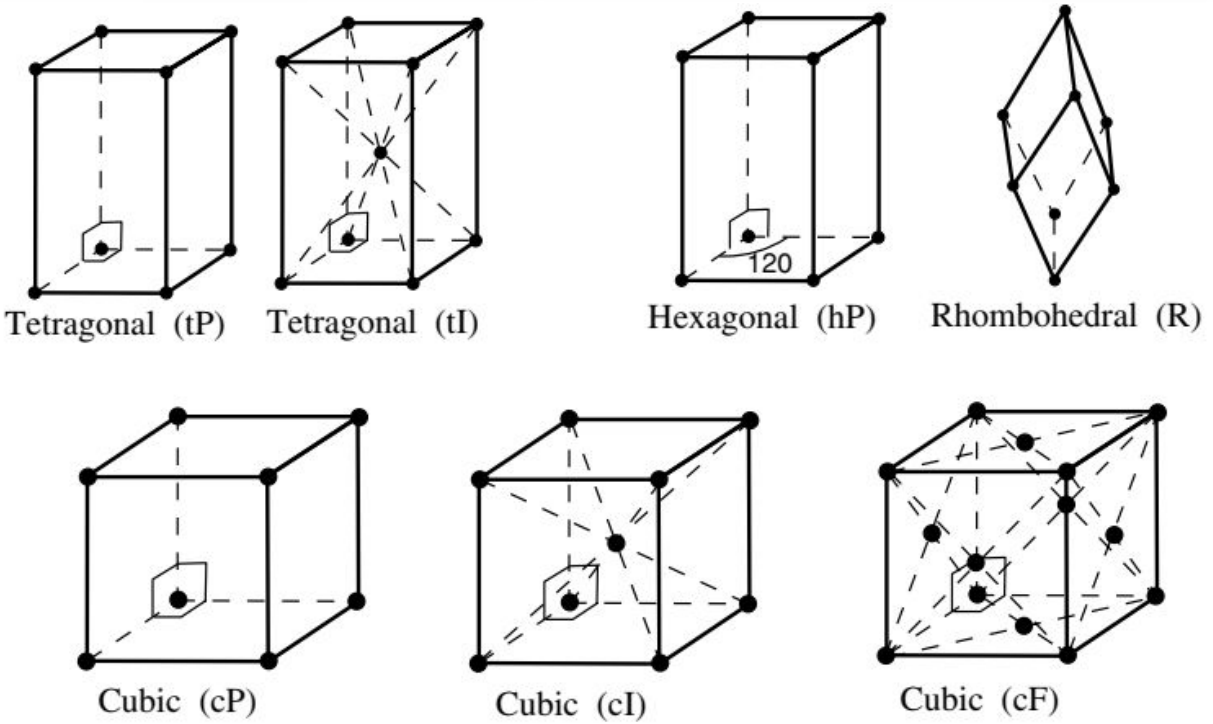
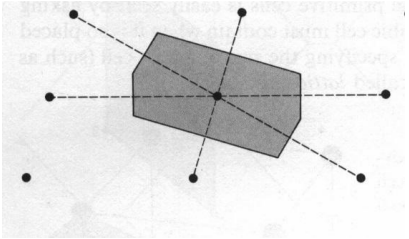



Fig. 1.2. The 14 Bravais lattices and their centering symbols.

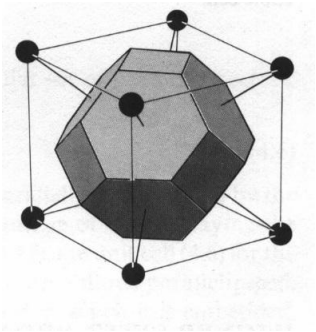
# Célula Primitiva de Wigner-Seitz



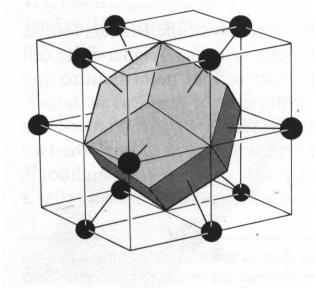
- Célula primitiva de Wigner-Seitz (W-S)
  - Respeita a simetria da rede de Bravais.
  - Contém um ponto de rede.

    (não temos que fazer uma escolha específica de vetores primitivos, então é tão simétrica quanto a rede de Bravais)
- Construção da célula W-S:
  1) Considere um dado ponto da rede.
  2) Trace retas partindo desse ponto de rede até seus vizinhos.
  3) Trace planos perpendiculares a essas retas que passam a meia distância entre os pontos (bissectam as retas).
  4) A célula é o menor volume fechado definido por esses planos.

# Célula Primitiva de Wigner-Seitz



Célula W-S para BCC (octaedro truncado)
Faces hexagonais bissectam as diagonais
Faces quadradas bissectam as retas que unem os pontos centrais de duas células adjacentes



Célula W-S para FCC (dodecaedro rômbico)
Faces congruentes (12) bissectam as retas que unem os pontos em mais de uma célula

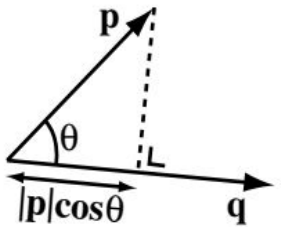
The position of an atom inside the unit cell is described by the position vector $\mathbf{r}$:

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} = \sum_{i=1}^{3} r_i \mathbf{a}_i = r_i \mathbf{a}_i ,$$

where we have again made use of the summation convention. The numbers $(x, y, z)$ are real numbers between 0 and 1, and are known as *fractional coordinates*.

$$D = \sqrt{(p_1 - q_1)^2 + (p_2 - q_2)^2 + (p_3 - q_3)^2}$$

$$\boxed{\mathbf{p} \cdot \mathbf{q} \equiv |\mathbf{p}||\mathbf{q}| \cos\theta.}$$




$$\mathbf{p} \cdot \mathbf{p} = |\mathbf{p}|^2,$$

$$|\mathbf{p}| = \sqrt{\mathbf{p} \cdot \mathbf{p}}.$$

$$|\mathbf{p}| = \sqrt{p_i \mathbf{a}_i \cdot p_j \mathbf{a}_j} = \sqrt{p_i (\mathbf{a}_i \cdot \mathbf{a}_j) p_j} \qquad \left( = \sqrt{\sum_{i=1}^{3} \sum_{j=1}^{3} p_i (\mathbf{a}_i \cdot \mathbf{a}_j) p_j} \right)$$

$$g_{ij} \equiv \mathbf{a}_i \cdot \mathbf{a}_j = |\mathbf{a}_i||\mathbf{a}_j| \cos\theta_{ij}$$

$$g_{ij} = \begin{bmatrix} \mathbf{a}\cdot\mathbf{a} & \mathbf{a}\cdot\mathbf{b} & \mathbf{a}\cdot\mathbf{c} \\ \mathbf{b}\cdot\mathbf{a} & \mathbf{b}\cdot\mathbf{b} & \mathbf{b}\cdot\mathbf{c} \\ \mathbf{c}\cdot\mathbf{a} & \mathbf{c}\cdot\mathbf{b} & \mathbf{c}\cdot\mathbf{c} \end{bmatrix} = \begin{bmatrix} a^2 & ab\cos\gamma & ac\cos\beta \\ ab\cos\gamma & b^2 & bc\cos\alpha \\ ac\cos\beta & bc\cos\alpha & c^2 \end{bmatrix}$$

The matrix $g_{ij}$ is *symmetric*[‡] since $g_{ij} = g_{ji}$

$$g_{ij} = \begin{bmatrix} \mathbf{e}_1\cdot\mathbf{e}_1 & \mathbf{e}_1\cdot\mathbf{e}_2 & \mathbf{e}_1\cdot\mathbf{e}_3 \\ \mathbf{e}_2\cdot\mathbf{e}_1 & \mathbf{e}_2\cdot\mathbf{e}_2 & \mathbf{e}_2\cdot\mathbf{e}_3 \\ \mathbf{e}_3\cdot\mathbf{e}_1 & \mathbf{e}_3\cdot\mathbf{e}_2 & \mathbf{e}_3\cdot\mathbf{e}_3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \equiv \delta_{ij}$$

A quick inspection of the orientation of the vector $\mathbf{n} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c}$

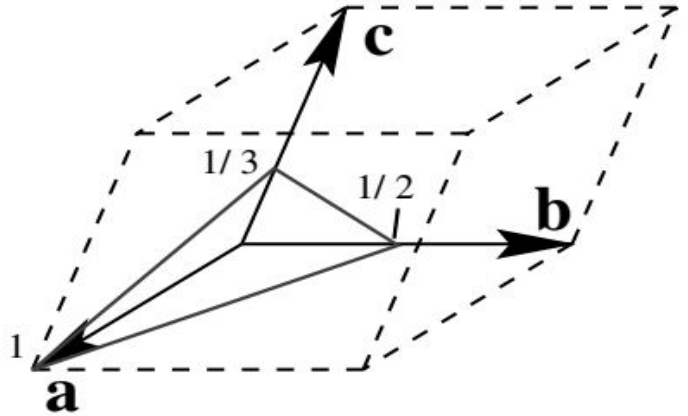



Illustration of the determination of the Miller indices of a plane $(hkl)$

The Miller indices of a plane in an arbitrary crystal system are obtained in the following way.

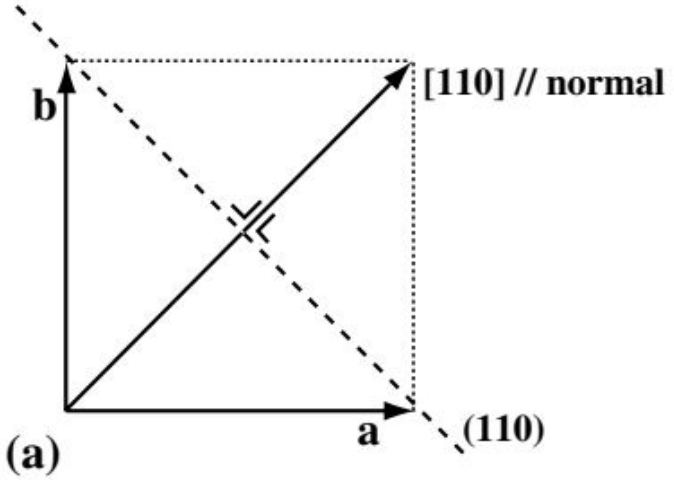
(i) If the plane goes through the origin, then displace it so that it no longer contains the origin.

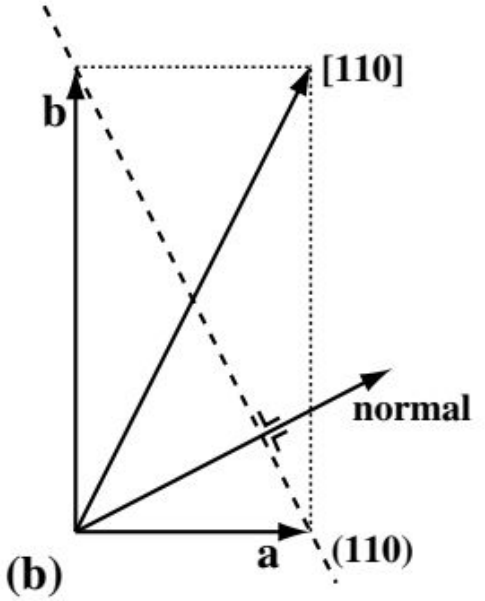
(ii) Determine the intercepts of the plane with the three basis vectors. Call those intercepts $s_1$, $s_2$, and $s_3$. The intercepts must be measured in units of the basis vector length. For the plane shown in Fig. 1.3, these values are $s_1 = 1$, $s_2 = \frac{1}{2}$, and $s_3 = \frac{1}{3}$. If a plane is parallel to one or more of the basis vectors, then the corresponding intercept value(s) must be taken as $\infty$.

(iii) Invert all three intercepts. For the plane in the figure we find $\frac{1}{s_1} = 1$, $\frac{1}{s_2} = 2$, and $\frac{1}{s_3} = 3$. If one of the intercepts is $\infty$, then the corresponding number is zero.

(iv) Reduce the three numbers to the smallest possible integers (relative primes). (This is not necessary for the example above.)

(v) Write the three numbers surrounded by round brackets, i.e. (123). This triplet of numbers forms the *Miller indices* of the plane.


b
[110] // normal
a
(110)
(a)


b
[110]
normal
a
(110)
(b)

The reciprocal basis vectors can be derived from the following definition:

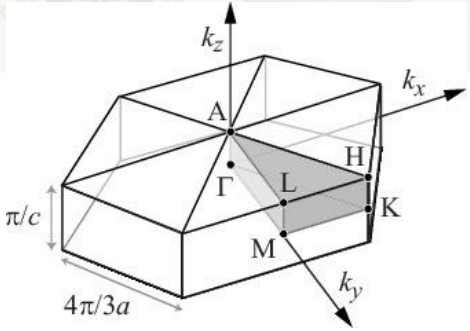
$$\boxed{\mathbf{a}_i \cdot \mathbf{a}_j^* \equiv \delta_{ij},}$$

$$\mathbf{a}^* = K(\mathbf{b} \times \mathbf{c})$$

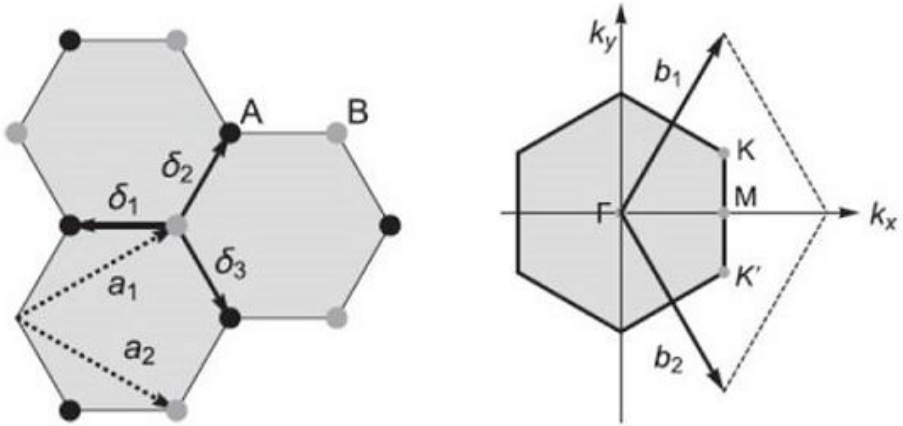
$$K = \frac{1}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \equiv \frac{1}{\Omega}$$

$$\mathbf{a} \cdot \mathbf{a}^* = K\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = 1$$

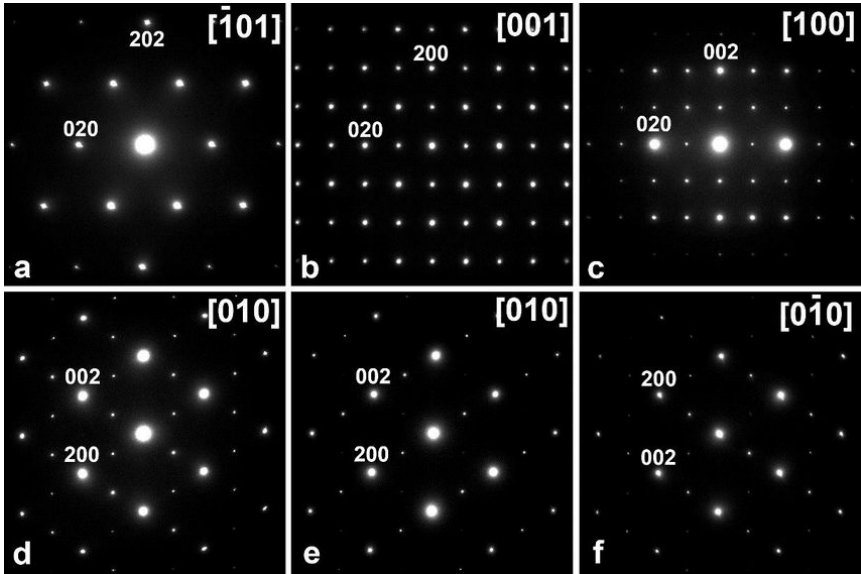
## ZnO




## Graphene




## MnB3



We define the *reciprocal lattice* $\mathcal{T}^*$ as the set of end-points of the vectors of the type

$$\mathbf{g} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* = \sum_{i=1}^{3} g_i \mathbf{a}_i^* = g_i \mathbf{a}_i^*,$$

where $(h, k, l)$ are integer triplets. This new lattice is also known as the *dual lattice*, but in the diffraction world we prefer the name *reciprocal lattice*. We will now investigate the relation between the reciprocal lattice vectors $\mathbf{g}$ and the planes with Miller indices $(hkl)$.

We will look for all the direct space vectors $\mathbf{r}$ with components $r_i = (x, y, z)$ that are perpendicular to the vector $\mathbf{g}$. We already know that two vectors are perpendicular to each other if their dot product vanishes. In this case we find:

$$0 = \mathbf{r} \cdot \mathbf{g} = (r_i \mathbf{a}_i) \cdot \left(g_j \mathbf{a}_j^*\right) = r_i \left(\mathbf{a}_i \cdot \mathbf{a}_j^*\right) g_j .$$

$$\mathbf{r} \cdot \mathbf{g} = r_i \delta_{ij} g_j = r_i g_i = r_1 g_1 + r_2 g_2 + r_3 g_3 = hx + ky + lz = 0$$

$$\frac{x}{s_1} + \frac{y}{s_2} + \frac{z}{s_3} = 1$$

The reciprocal lattice vector $\mathbf{g}$, with components $(h, k, l)$, is perpendicular to the plane with Miller indices $(hkl)$.

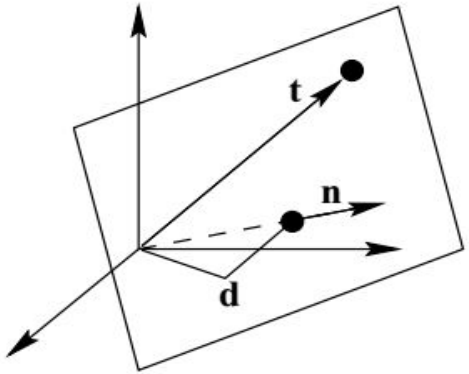
For this reason, a reciprocal lattice vector is often denoted with the Miller indices as subscripts, e.g. $\mathbf{g}_{hkl}$.

Since the vector $\mathbf{g} = g_i \mathbf{a}_i^*$ is perpendicular to the plane with Miller indices $g_i = (hkl)$, the unit normal to this plane is given by

$$\mathbf{n} = \frac{\mathbf{g}_{hkl}}{|\mathbf{g}_{hkl}|}.$$

The length of a reciprocal lattice vector is equal to the inverse of the spacing between the corresponding lattice planes.

$$\mathbf{t} \cdot \mathbf{n} = \mathbf{t} \cdot \frac{\mathbf{g}_{hkl}}{|\mathbf{g}_{hkl}|} \equiv d_{hkl}$$




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

We can arbitrarily select $\mathbf{t} = \frac{\mathbf{a}}{h}$, which leads to

$$\mathbf{t} \cdot \mathbf{g}_{hkl} = \frac{\mathbf{a}}{h} \cdot \left(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\right) = \frac{\mathbf{a}}{h} \cdot h\mathbf{a}^* = 1 = d_{hkl}|\mathbf{g}_{hkl}|$$

$$\frac{1}{d_{hkl}} = |\mathbf{g}| = \sqrt{\mathbf{g}\cdot\mathbf{g}} = \sqrt{\left(g_i\mathbf{a}_i^*\right)\cdot\left(g_j\mathbf{a}_j^*\right)} = \sqrt{g_i\left(\mathbf{a}_i^*\cdot\mathbf{a}_j^*\right)g_j}$$

$$\boxed{g_{ij}^* \equiv \mathbf{a}_i^*\cdot\mathbf{a}_j^*.}$$

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

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

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

$$\left.\begin{aligned} p_i \mathbf{a}_i \cdot \mathbf{a}_m &= p_j^* \mathbf{a}_j^* \cdot \mathbf{a}_m, \\ p_i g_{im} &= p_j^* \delta_{jm} = p_m^*, \end{aligned}\right\}$$

or

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

It is easily shown that the inverse relation is given by

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

If we replace $p_i$ by $p^*_m g^*_{mi}$, then we have

$$\mathbf{p} = p^*_m g^*_{mi} \mathbf{a}_i = p^*_m \mathbf{a}^*_m,$$

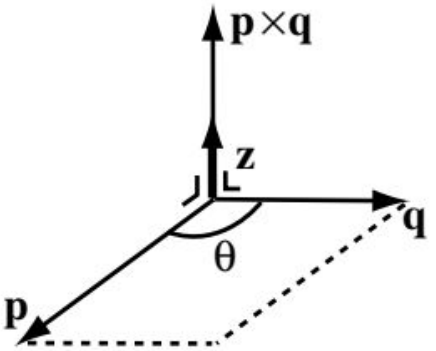
from which we find

$$\mathbf{a}^*_m = g^*_{mi} \mathbf{a}_i,$$

and the inverse relation

$$\mathbf{a}_m = g_{mi} \mathbf{a}^*_i.$$

$$\mathbf{p} \times \mathbf{q} \equiv \sin\theta\, |\mathbf{p}|\, |\mathbf{q}|\, \mathbf{z},$$

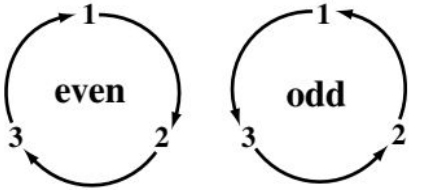



$$\begin{aligned}\mathbf{p} \times \mathbf{q} &= (p_1q_2 - p_2q_1)\,\mathbf{a} \times \mathbf{b} + (p_2q_3 - p_3q_2)\,\mathbf{b} \times \mathbf{c} + (p_3q_1 - p_1q_3)\,\mathbf{c} \times \mathbf{a} \\ &= \Omega[(p_2q_3 - p_3q_2)\,\mathbf{a}^* + (p_3q_1 - p_1q_3)\,\mathbf{b}^* + (p_1q_2 - p_2q_1)\,\mathbf{c}^*],\end{aligned}$$

$$\mathbf{p} \times \mathbf{q} = (p_2 q_3 - p_3 q_2)\,\mathbf{e}_1 + (p_3 q_1 - p_1 q_3)\,\mathbf{e}_2 + (p_1 q_2 - p_2 q_1)\,\mathbf{e}_3$$

$$\boxed{\mathbf{p} \times \mathbf{q} = \Omega e_{ijk} p_i q_j \mathbf{a}_k^*.}$$

$$e_{ijk} = \begin{cases} +1 & \text{even permutations of 123,} \\ -1 & \text{odd permutations of 123,} \\ 0 & \text{all other cases.} \end{cases}$$




$$\mathbf{p} \times \mathbf{q} = \Omega \begin{vmatrix} \mathbf{a}_1^* & \mathbf{a}_2^* & \mathbf{a}_3^* \\ p_1 & p_2 & p_3 \\ q_1 & q_2 & q_3 \end{vmatrix} \left( = \begin{vmatrix} \mathbf{e}_1 & \mathbf{e}_2 & \mathbf{e}_3 \\ p_1 & p_2 & p_3 \\ q_1 & q_2 & q_3 \end{vmatrix} \text{ Cartesian} \right).$$

$$\mathbf{g}_1 \times \mathbf{g}_2 = \Omega^* e_{ijk} \mathbf{g}_{1,i} \mathbf{g}_{2,j} g_{km} \mathbf{a}_m^* = \Omega^* e_{ijk} \mathbf{g}_{1,i} \mathbf{g}_{2,j} \mathbf{a}_k .$$

Explicitly working out the summations over $i$, $j$, and $k$ we find

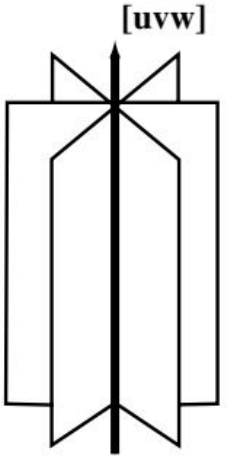
$$\mathbf{g}_1 \times \mathbf{g}_2 \parallel (k_1 l_2 - k_2 l_1)\, \mathbf{a}_1 + (l_1 h_2 - l_2 h_1)\, \mathbf{a}_2 + (h_1 k_2 - h_2 k_1)\, \mathbf{a}_3$$

$$\begin{array}{cccccc} \not{h}_1 & k_1 & l_1 & h_1 & k_1 & \not{l}_1 \\ \not{h}_2 & k_2 & l_2 & h_2 & k_2 & \not{l}_2 . \end{array}$$

Then compute the three $2 \times 2$ determinants formed by the eight remaining numbers above, as in

$$\begin{array}{ccccccc} k_1 & & l_1 & & h_1 & & k_1 \\ & \times & & \times & & \times & \\ k_2 & & l_2 & & h_2 & & k_2 \end{array} .$$

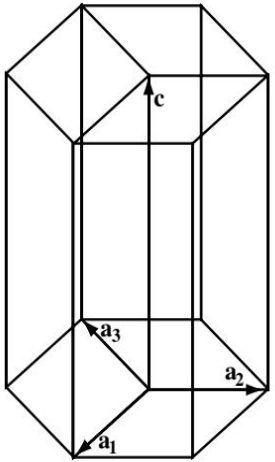
$$\mathbf{g}_{(hkl)} \cdot \mathbf{t}_{[uvw]} = g_i t_j \mathbf{a}_i^* \cdot \mathbf{a}_j = g_i t_j \delta_{ij} = g_i t_i = 0,$$




or in explicit component notation:

$$\boxed{hu + kv + lw = 0.} \tag{1.30}$$

This equation is known as the *zone equation* and it is valid for all crystal systems.




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

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

$$\left.\begin{aligned} u' &= u - t = 2u + v; \\ v' &= v - t = 2v + u; \\ w' &= w. \end{aligned}\right\}$$

$$\mathbf{A}_1^* = \frac{2}{3a^2}\mathbf{a}_1;$$

$$\mathbf{A}_2^* = \frac{2}{3a^2}\mathbf{a}_2;$$

$$\mathbf{A}_3^* = \frac{2}{3a^2}\mathbf{a}_3;$$

$$\mathbf{C}^* = \frac{\mathbf{c}}{c^2}.$$

$$\mathbf{g}_{hkl} = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{c}^* = h\mathbf{A}_1^* + k\mathbf{A}_2^* + i\mathbf{A}_3^* + l\mathbf{C}^* = \mathbf{g}_{hkil}$$

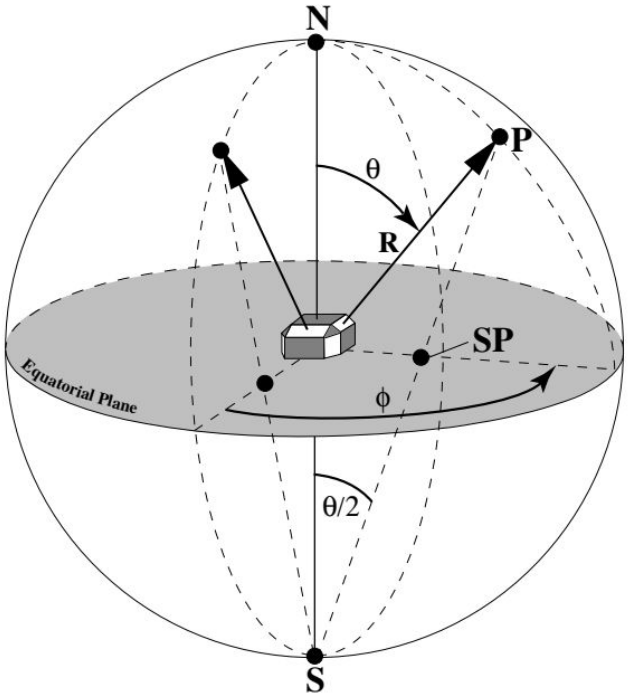



Fig. 1.9. Stereographic projection of the normals on crystal faces.

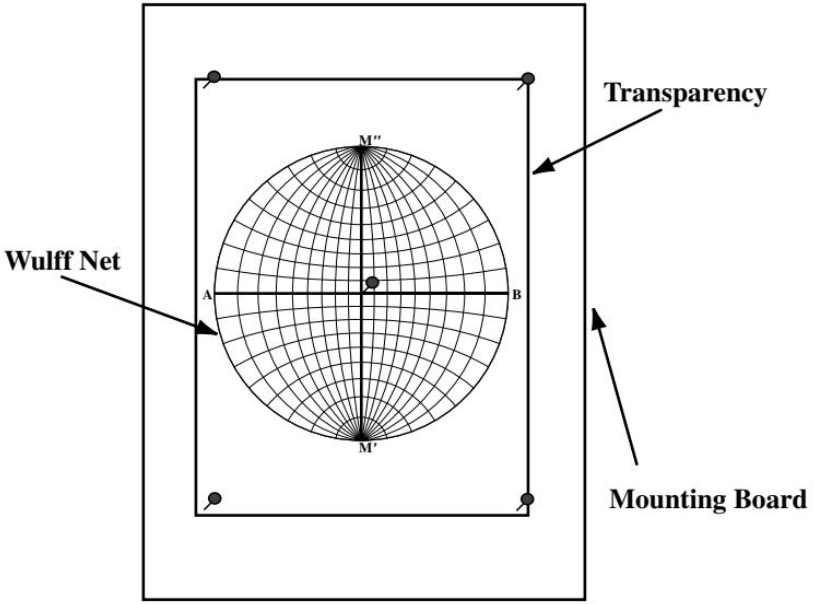
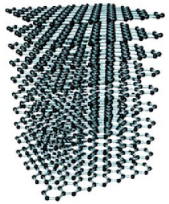
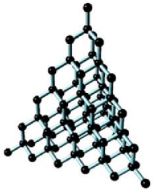



Fig. 1.11. Illustration of the manual use of a Wulff net for stereographic projections.

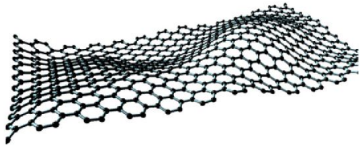
# Redes Cristalinas



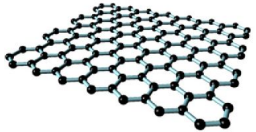
(a) Graphite
(3D)



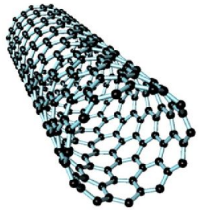
(b) Diamond
(3D)



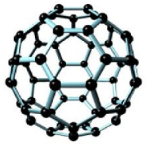
(c) Nanoribbon
(3D)



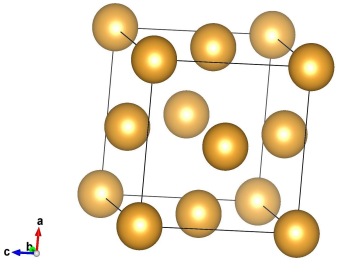
(d) Graphene
(2D)

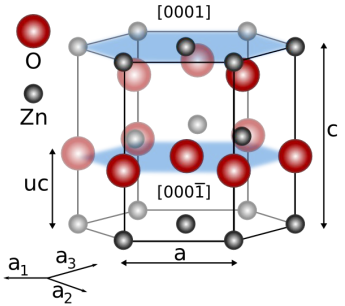


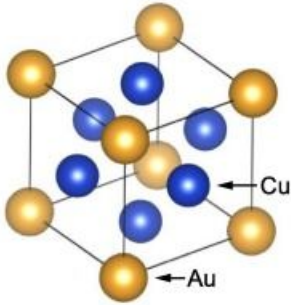
(e) Carbon Nanotube
(1D)

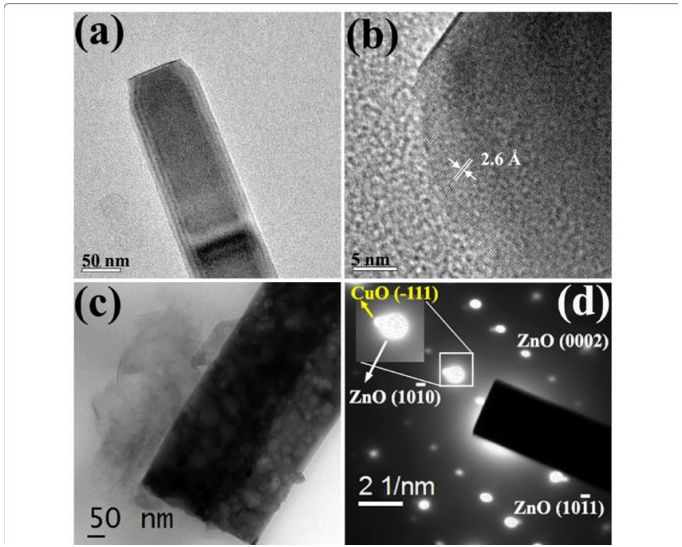


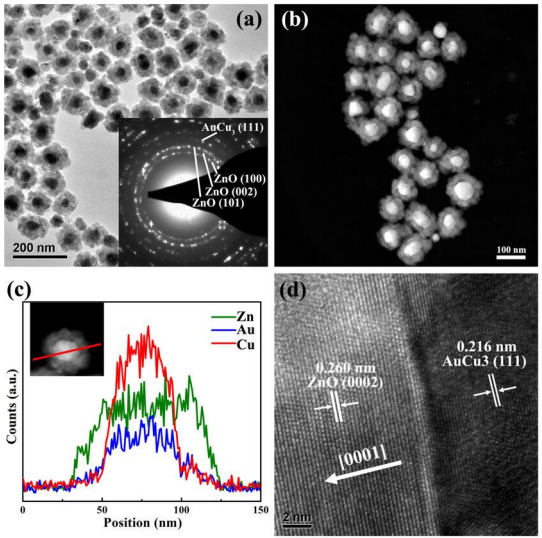
(f) Fullerene
(1D)

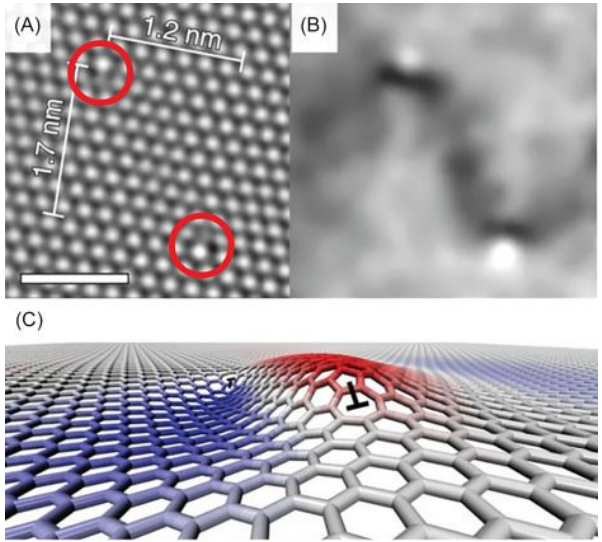


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### *1.6.1 Symmetry operators*

We distinguish between two basic kinds of symmetry operations: those that can be physically realized (rotations and translations), also known as operations of the first kind, or *proper operations*, and those that change the *handedness* of an object (reflection and inversion), operations of the second kind. All symmetry operations are represented by unique graphical symbols.

*Operations of the first kind*

(i) A pure rotation is characterized by a rotation axis $[uvw]$ and a rotation angle $\alpha = 2\pi/n$. The integer $n$ is the *order* of the rotation and we say that a rotation is $n$-fold if its angle is given by $2\pi/n$. A pure rotation of order $n$ is denoted by the symbol **n**. This is the so-called International or Hermann–Mauguin notation.[†] In drawings an $n$-fold rotation axis is represented by a filled regular polygon with $n$ sides. A six-fold rotation axis perpendicular to the drawing plane is then indicated by the ⬢ symbol, a four-fold axis by ◆, a three-fold axis by ▲, and a two-fold axis by ⬮.

(ii) A pure translation is characterized by a translation vector **t**. We have already discussed translations earlier in this chapter. In drawings, translation vectors are indicated by arrowed lines.

## *Operations of the second kind*

(i) A *pure reflection* is characterized by a plane $(hkl)$, and the International symbol for a mirror plane is **m**. The Schœnflies symbol is the Greek letter $\sigma$. In a drawing a mirror plane is always indicated by a thick solid line, ——— .

(ii) An *inversion* is a point symmetry operation that takes all the points $\mathbf{r}$ of an object and projects them onto $-\mathbf{r}$. The operation is usually denoted by $\bar{\mathbf{1}}$ or sometimes by $i$. In drawings the inversion center is denoted by the symbol $\circ$ (i.e. a small open circle).

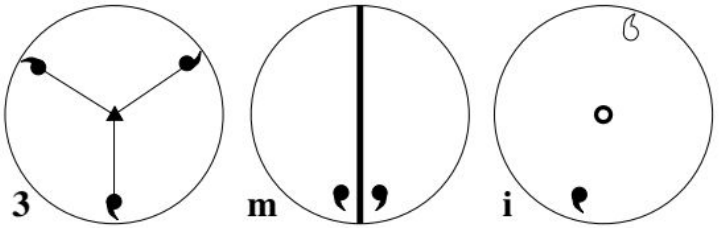



Fig. 1.13. Stereographic representation of a three-fold rotation, a mirror plane perpendicular to the projection plane, and an inversion.

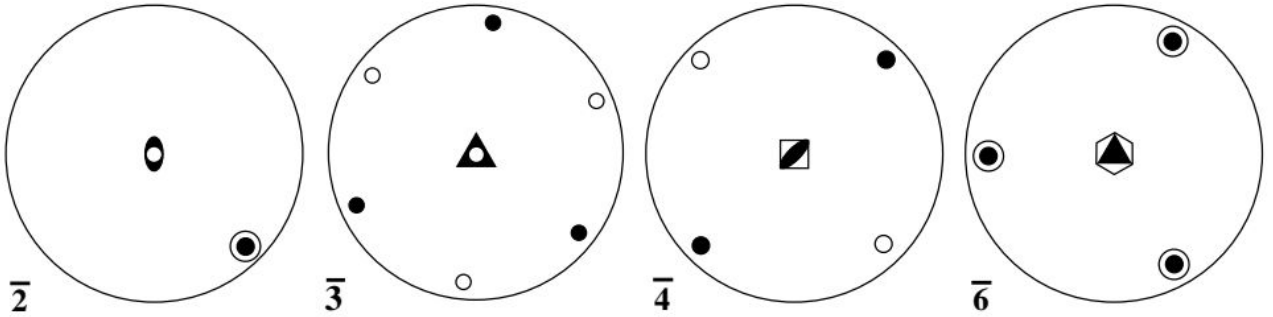



Fig. 1.14. Stereographic representation of the crystallographic rotoinversions.

The basic symmetry operations of the first and second kind can be combined with each other to create new symmetry operations. There are three combinations of interest to crystallography:

- combination of rotations with the inversion center;
- combination of rotations with translations;
- combination of mirrors with translations.

The combination of a rotation axis with an inversion center located somewhere on that axis is called a *rotoinversion operation*. The rotoinversion rotates a point over an angle $2\pi/n$ **and** inverts the resulting point through the inversion center. A rotoinversion of order one is equivalent to the inversion operation $i$. Rotoinversions are represented by the symbol $\bar{\mathbf{n}}$ and the crystallographic rotoinversions are shown in the stereographic projections of Fig. 1.14. They are represented by special symbols: ⧫ for $\bar{\mathbf{2}}$, ▲ for $\bar{\mathbf{3}}$, ◆ for $\bar{\mathbf{4}}$, and ⬢ for $\bar{\mathbf{6}}$.

A *screw axis* $\mathbf{n_m}$ consists of a counterclockwise rotation through $2\pi/n$ followed by a translation $\mathbf{T} = \frac{m}{n}\mathbf{t}_{[uvw]}$ in the positive direction $[uvw]$ along the screw axis. The vector $\mathbf{T}$ is known as the *pitch* of the screw axis. Screw axes of the type $\mathbf{n_m}$ and $\mathbf{n_{n-m}}$ are mirror images of each other. A screw axis is called *right-handed* if $m < n/2$, *left-handed* if $m > n/2$, and *without hand* if $m = 0$ or $m = n/2$. Screw axes related to each other by a mirror operation are called *enantiomorphous*.

The crystallographic screw axes are (with their official graphical symbols): $2_1$  , $3_1$  , $3_2$  , $4_1$  , $4_2$  , $4_3$  , $6_1$  , $6_2$  , $6_3$  , $6_4$  , and $6_5$  . All screw axes are shown in Fig. 1.15: the number next to each circle refers to the height of the circle above the plane of the drawing. The axes are all perpendicular to the drawing.

A symmetry operator $\mathcal{O}$ operating on a material point $\mathbf{r}$ transforms its coordinates into a new vector $\mathbf{r}'$ with components $(x_1', x_2', x_3')$ as follows:

$$\mathbf{r}' = \mathcal{O}[\mathbf{r}]. \tag{1.36}$$

$$x_i' = D_{ij}x_j + u_i,$$

$$\mathbf{r}' = \mathbf{D}\mathbf{r} + \mathbf{t} = (\mathbf{D}|\mathbf{t})[\mathbf{r}\,] = \mathcal{O}[\mathbf{r}\,]$$

The matrix $\mathbf{D}$ describes the *point symmetry transformation* and the vector $\mathbf{t}$ describes the translational component of the operator $\mathcal{O}$. In the crystallographic literature, the point symmetry part is usually called the *linear part* and the whole operator is called a *motion*. The compact notation $(\mathbf{D}|\mathbf{t})$ is called the *Seitz symbol*.

Table 1.4. *Allowed angles between rotation axes of orders A, B, and C, compatible with the Bravais lattices.*

| $A$ | $B$ | $C$ | $B\hat{C}$ | $A\hat{C}$ | $A\hat{B}$ |
|---|---|---|---|---|---|
| 2 | 2 | 2 | 90° | 90° | 90° |
| 2 | 2 | 3 | 90° | 90° | 60° |
| 2 | 2 | 4 | 90° | 90° | 45° |
| 2 | 2 | 6 | 90° | 90° | 30° |
| 2 | 3 | 3 | 70°32′ | 54°44′ | 54°44′ |
| 2 | 3 | 4 | 54°44′ | 45° | 35°16′ |

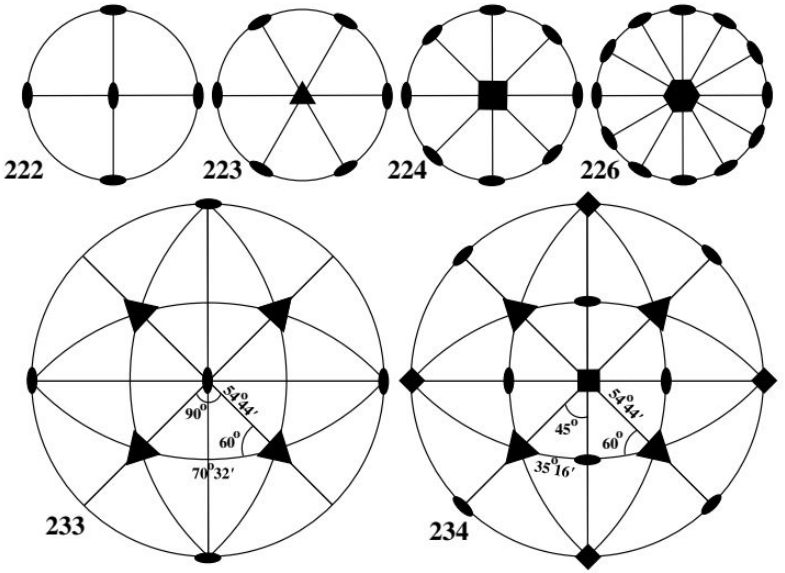



Fig. 1.18. Stereographic projections of the six crystallographically allowed combinations of rotational axes.

These 32 combinations are known as the 32 *point groups*.

Table 1.5. ***International***–[*Schœnflies*] *notation, group order N and crystal system S (a, m, h, R, o, t or c) for the 32 crystallographic point groups.*

| Point group | $N$ | $S$ | Point group | $N$ | $S$ |
|---|---|---|---|---|---|
| **1**–[$C_1$] | 1 | a | $\bar{\mathbf{3}}$–[$S_6$] | 6 | R |
| $\bar{\mathbf{1}}$–[$C_i$] | 2 | a | **32**–[$D_3$] | 6 | R |
| **2**–[$C_2$] | 2 | m | **3m**–[$C_{3v}$] | 6 | R |
| **m**–[$C_s$] | 2 | m | $\bar{\mathbf{3}}$**m**–[$D_{3d}$] | 12 | R |
| **2/m**–[$C_{2h}$] | 4 | m | **6**–[$C_6$] | 6 | h |
| **222**–[$D_2$] | 4 | o | $\bar{\mathbf{6}}$–[$C_{3h}$] | 6 | h |
| **mm2**–[$C_{2v}$] | 4 | o | **6/m**–[$C_{6h}$] | 12 | h |
| **mmm**–[$D_{2h}$] | 8 | o | **622**–[$D_6$] | 12 | h |
| **4**–[$C_4$] | 4 | t | **6mm**–[$C_{6v}$] | 12 | h |
| $\bar{\mathbf{4}}$–[$S_4$] | 4 | t | $\bar{\mathbf{6}}$**m2**–[$D_{3h}$] | 12 | h |
| **4/m**–[$C_{4h}$] | 8 | t | **6/mmm**–[$D_{6h}$] | 24 | h |
| **422**–[$D_4$] | 8 | t | **23**–[$T$] | 12 | c |
| **4mm**–[$C_{4v}$] | 8 | t | **m3**–[$T_h$] | 24 | c |
| $\bar{\mathbf{4}}$**2m**–[$D_{2d}$] | 8 | t | **432**–[$O$] | 24 | c |
| **4/mmm**–[$D_{4h}$] | 16 | t | $\bar{\mathbf{4}}$**3m**–[$T_d$] | 24 | c |
| **3**–[$C_3$] | 3 | R | **m**$\bar{\mathbf{3}}$**m**–[$O_h$] | 48 | c |

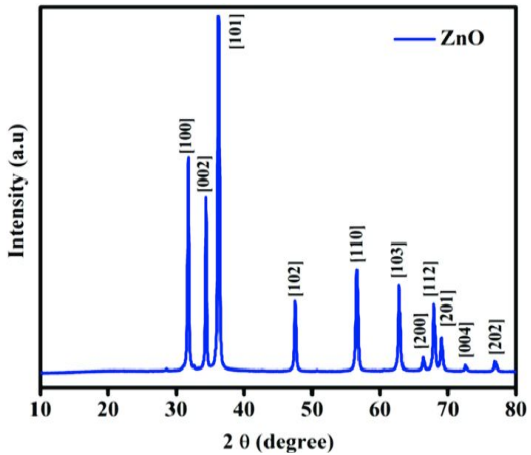
**CuAu3** **m$\bar{3}$m**

**YIn3**

**GIn3**

## Revisar em casa para material cristalino ZnO, YIn3, GdIn3

1-Parâmetros de rede
2-Características da rede recíproca
3-Grupos de simetria

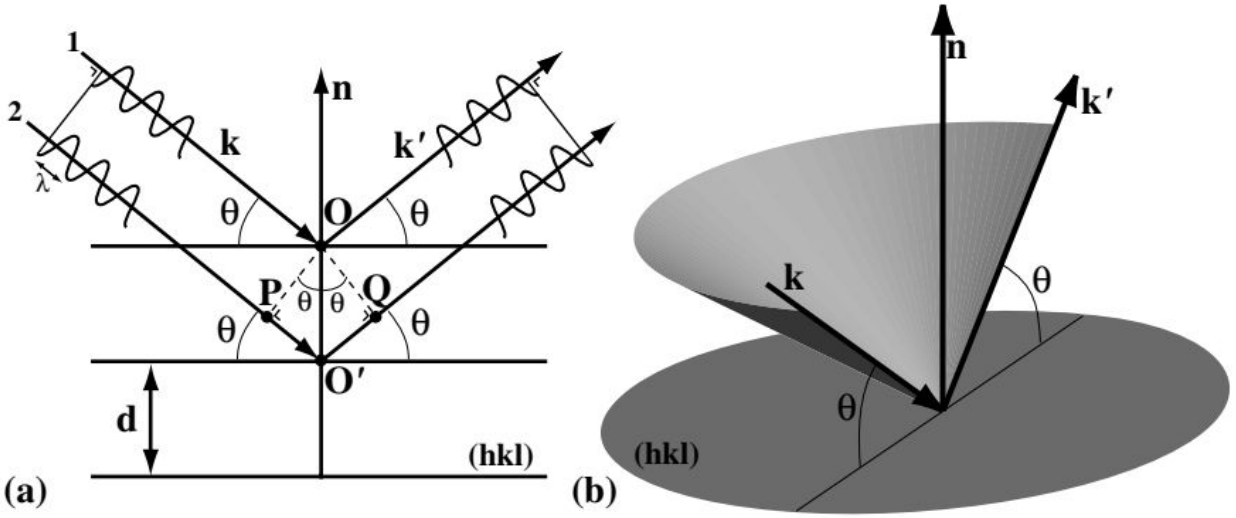



ZnO apresenta estrutura cristalina hexagonal wurtzita, que possui uma célula unitária tetraédrica com parâmetros de rede, a = 3.250 Å e c = 5.207 Å

The Bragg equation in direct space

$$\Delta = PO' + O'Q,$$
$$= d_{hkl}\sin\theta + d_{hkl}\sin\theta,$$
$$= 2d_{hkl}\sin\theta.$$

$$2\frac{d_{hkl}}{n}\sin\theta = \lambda.$$




We recall from the discussion of Miller indices in the previous chapter that the planes with Miller indices $(nh\ nk\ nl)$ are parallel to the planes $(hkl)$, but with an interplanar spacing equal to

$$d_{nh\,nk\,nl} = \frac{d_{hkl}}{n}.$$

$$2d_{hkl} \sin\theta = \lambda.$$

$$\mathbf{k}' = \mathbf{k} + \mathbf{g}.$$

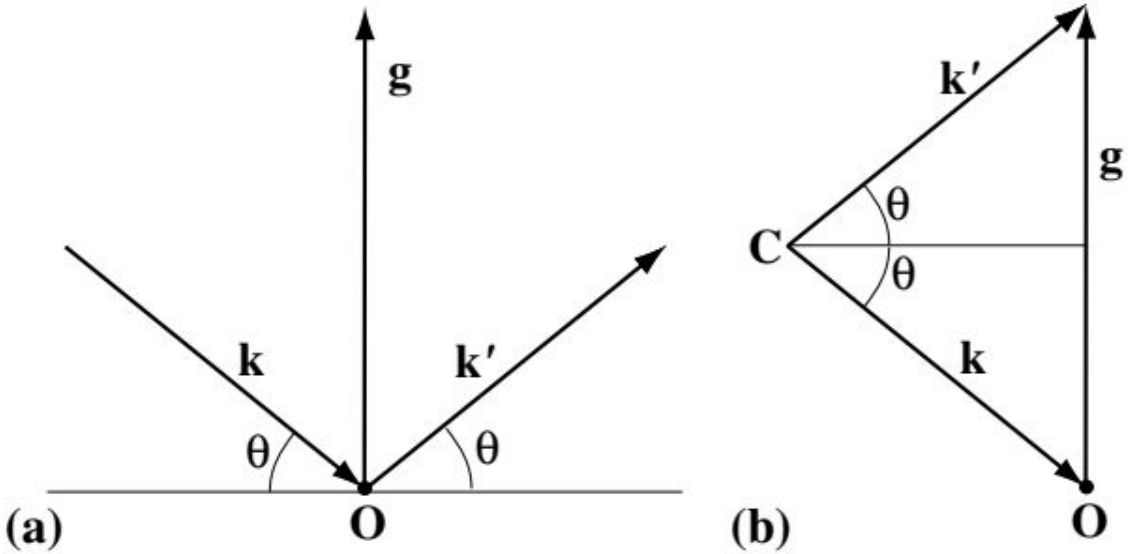



Fig. 2.3. (a) Geometrical construction leading to the reciprocal space Bragg equation; (b) the diffracted wave vector is translated to complete the vector sum $\mathbf{k}' = \mathbf{k} + \mathbf{g}$.

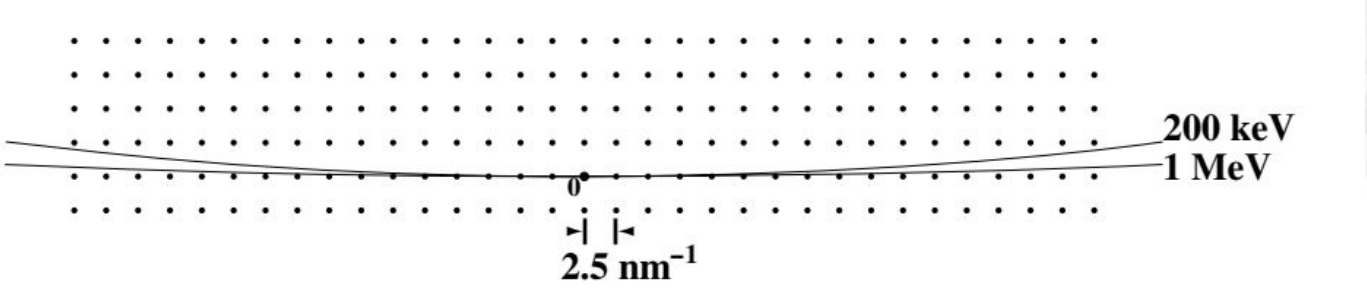



Fig. 2.7. Ewald sphere drawn to scale for the reciprocal lattice of a square crystal with lattice parameter 0.4 nm, and a 200 keV and 1 MeV incident electron beam.

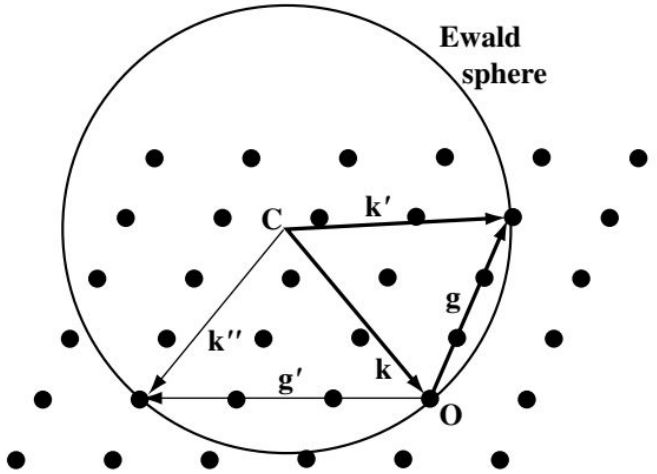



Fig. 2.4. Ewald sphere construction.

$$\mathcal{T}(\mathbf{r}) = \sum_{u,v,w=-\infty}^{+\infty} \delta(\mathbf{r} - \mathbf{t}_{uvw}).$$

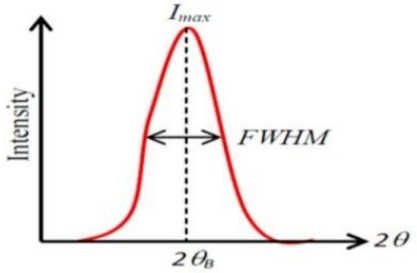
$$V_{\text{cell}}(\mathbf{r}) = \sum_{j=1}^{N} V_j^a(\mathbf{r} - \mathbf{r}_j).$$

$$V(\mathbf{r}) = \sum_{\mathbf{g}} V_{\mathbf{g}} \mathrm{e}^{2\pi \mathrm{i}\mathbf{g}\cdot\mathbf{r}}$$

$$V(\mathbf{r}) = V_{cell}(\mathbf{r}) \otimes \mathcal{T}(\mathbf{r}).$$

# *Finite crystal size effects*

$$\beta = \frac{kD}{\lambda cos\theta},$$




*3.2.2 Williamson–Hall method*

The Williamson–Hall method is a simple visualization of order dependence peak broadening. In this method, it is assumed that the size and strain contribution to the line broadening are mutually independent of each other and closely approximated by Cauchy's function and corresponding integral breadths are linearly additive:

$$\beta_{hkl} = \beta_D + \beta_S \tag{7}$$

Putting the value of $\beta_D$ and $\beta_S$ from Eq. (3) and (5), we get

$$\beta_{hkl} = \frac{K\lambda}{D\cos\theta} + 4\epsilon\tan\theta \tag{8}$$

By rearranging equation (8)

$$\beta_{hkl}\cos\theta = \frac{K\lambda}{D} + 4\epsilon\sin\theta \tag{9}$$

CAPES

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