

Cristalografía y Difracción de Rayos X

Dr. Ricardo Faccio

Cryssmat-Lab.

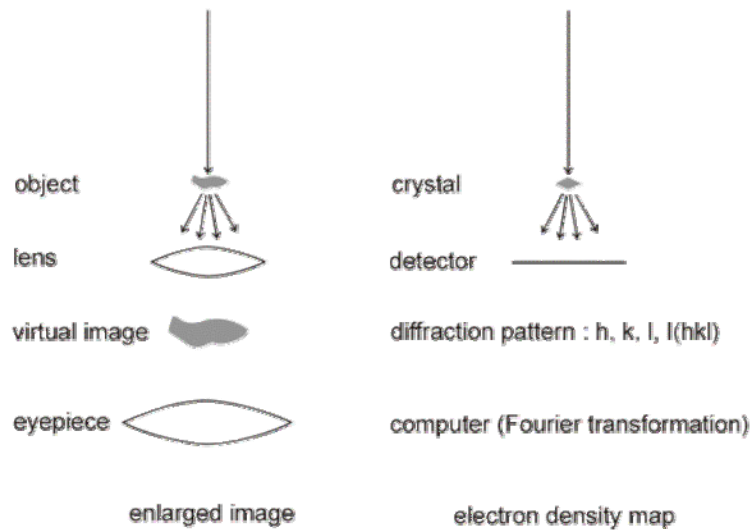
Laboratorio de Cristalografía, Estado Sólido y Materiales.

DETEMA - Facultad de Química

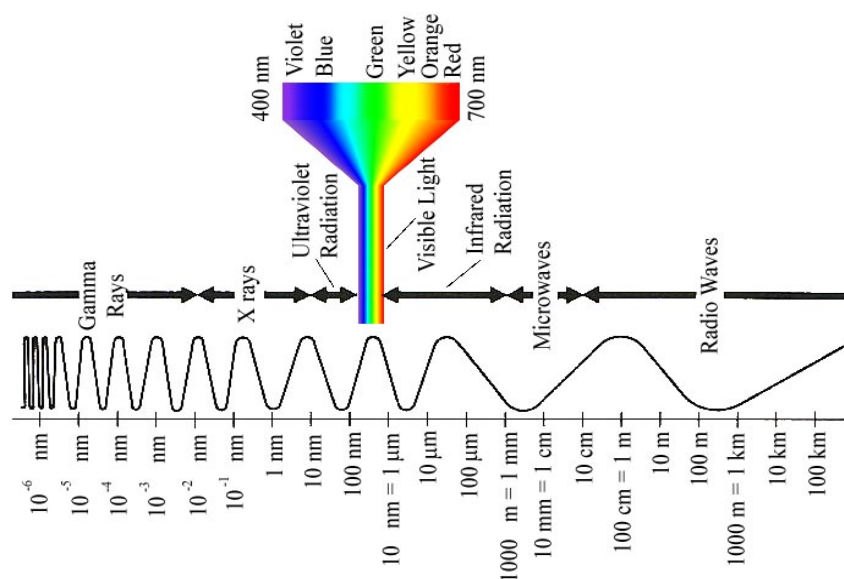
<http://cryssmat.fq.edu.uy/ricardo/drx.pdf>

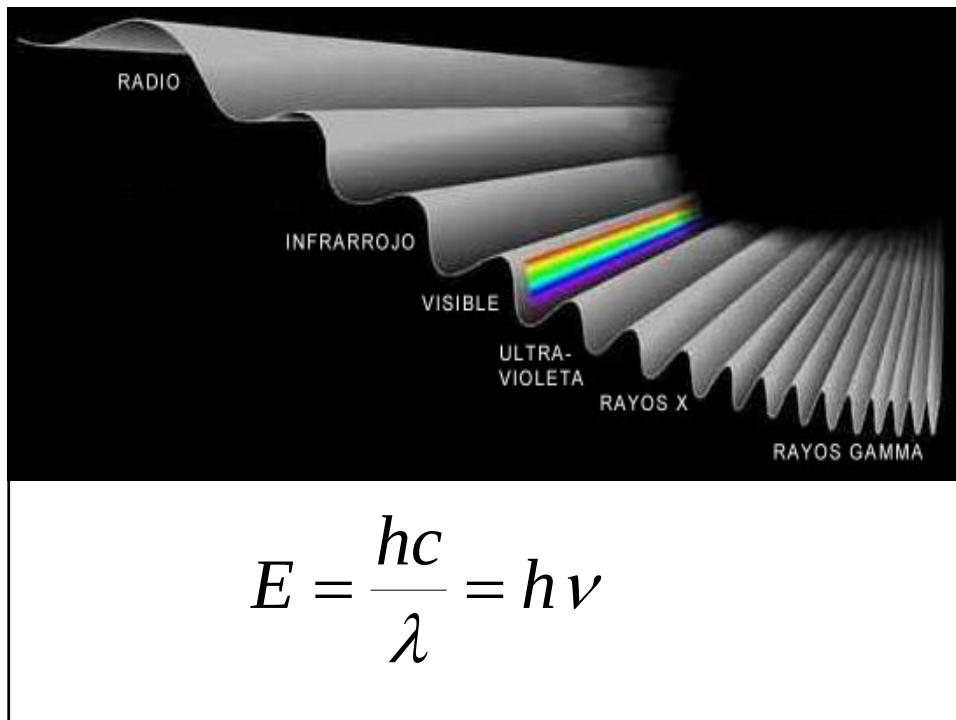
Mail: rfaccio@fq.edu.uy

¿Por qué Rayos X?

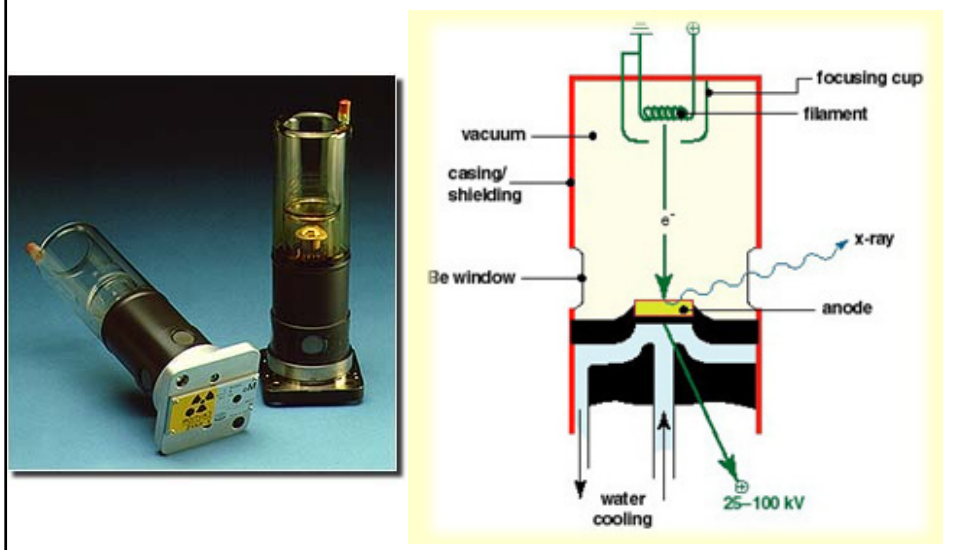


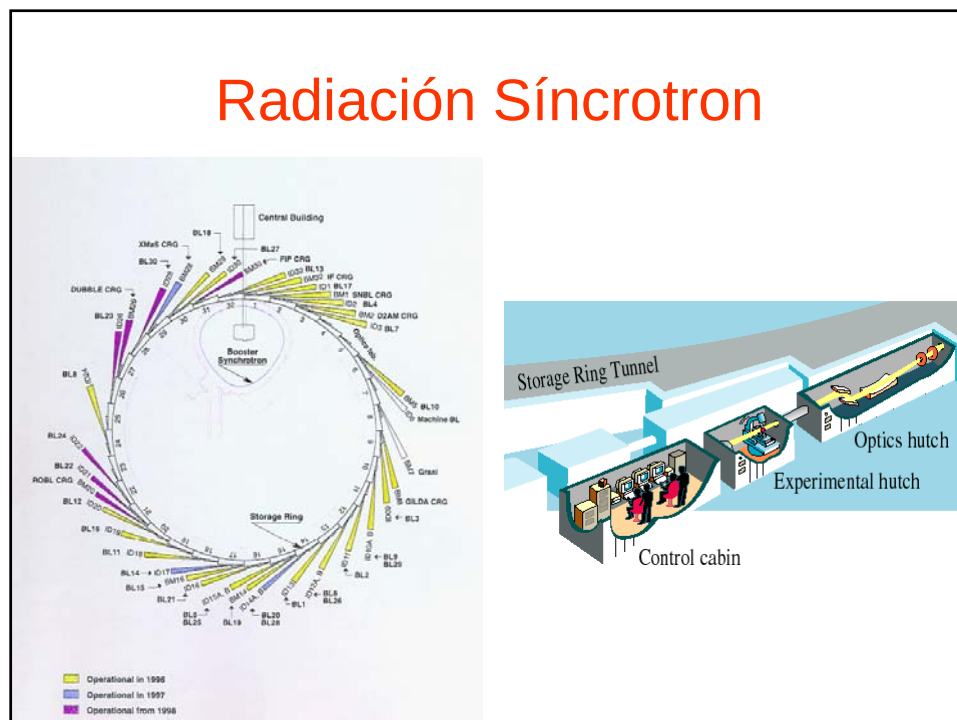
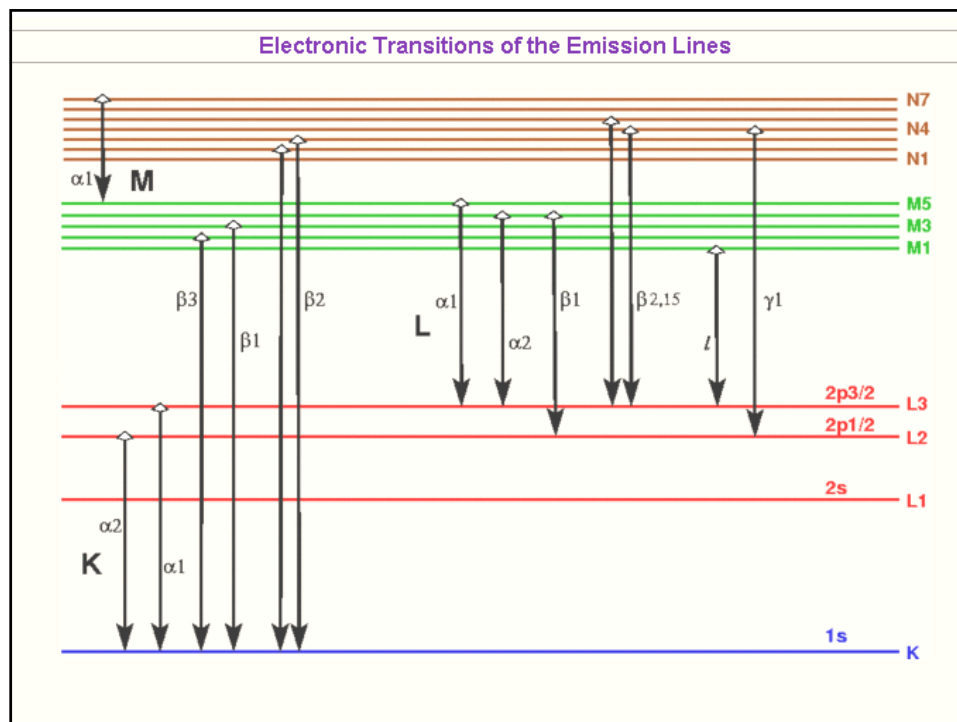
Rayos X





Generación de Rayos X

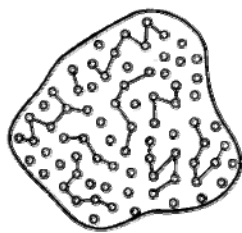




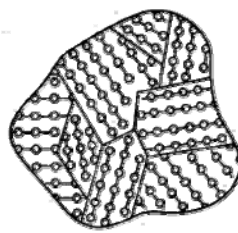
Materia Cristalina

Materiales Cristalinos:

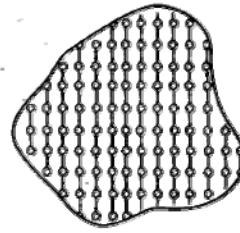
Aquellos materiales sólidos cuyos elementos constitutivos se repiten de manera ordenada y cuya distribución en el espacio muestra ciertas relaciones de simetría.



(a) Amorphous
No recognizable
long-range order

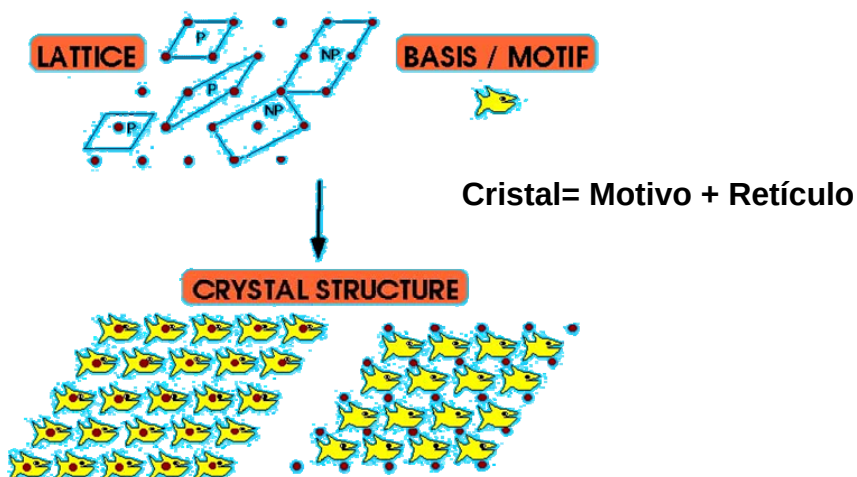


(b) Polycrystalline
Completely ordered
in segments

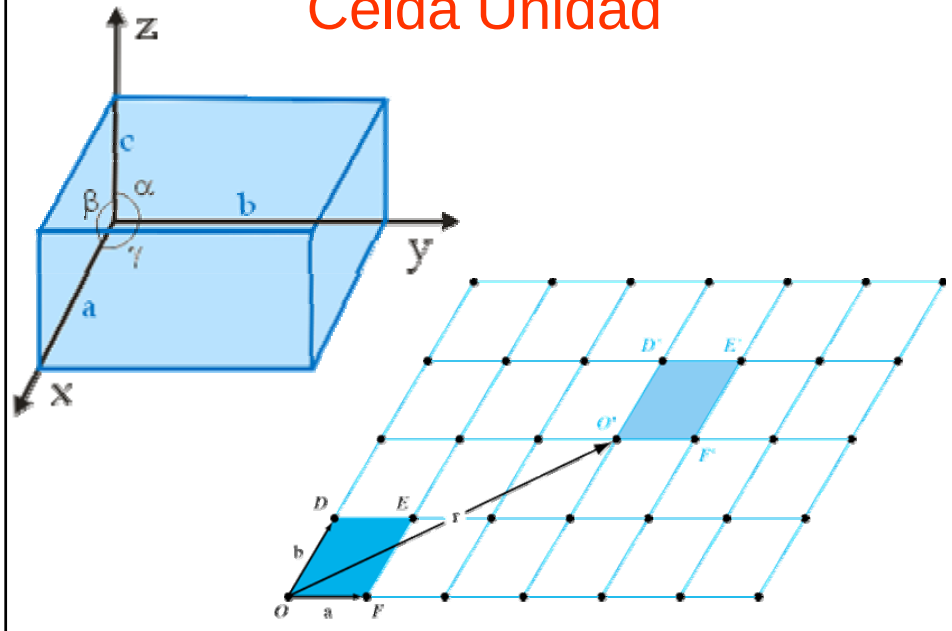


(c) Crystalline
Entire solid is made up of
atoms in an orderly array

Materia Cristalina



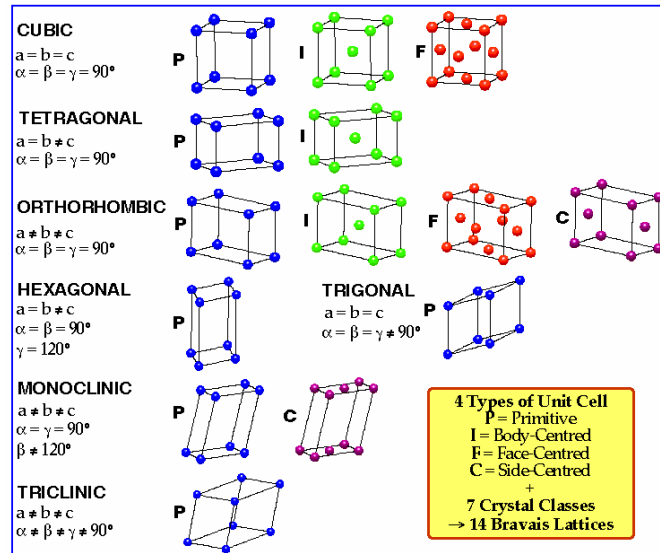
Celda Unidad



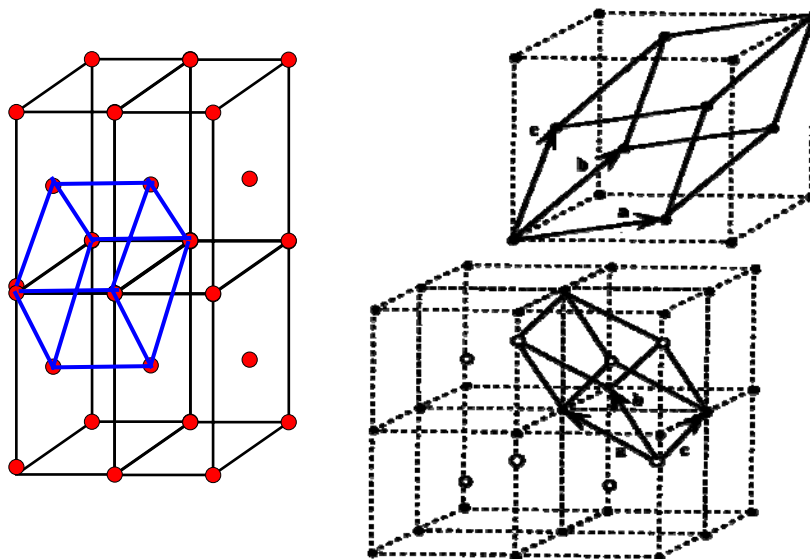
Vectores Traslación



Sistemas Cristalinos y Retículos de Bravais



Celdas Primitivas y No Primitivas

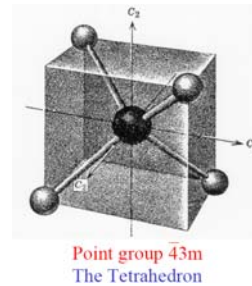
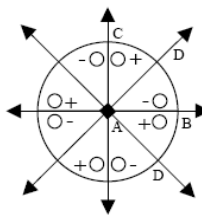
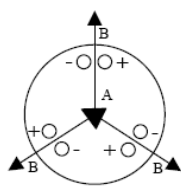
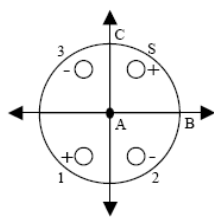


Simetría y Grupos Puntuales

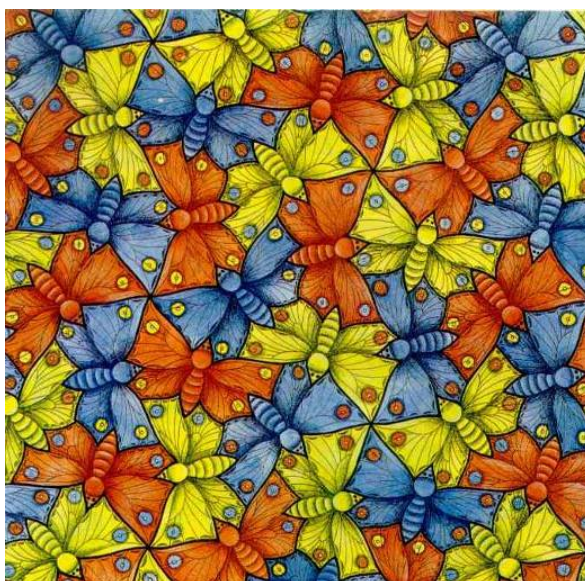
Existen 32 grupos puntuales:

Resultan de combinar distintas operaciones de simetría:

- Sin traslación
- Generando un número finito de elementos



Grupos Espaciales

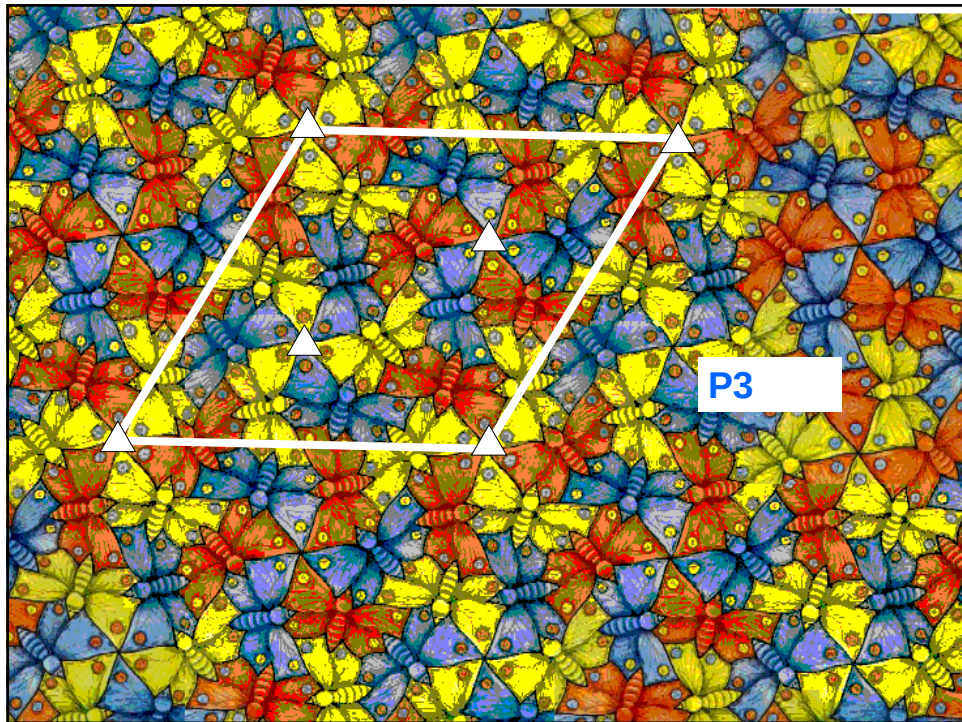


Si combinamos:

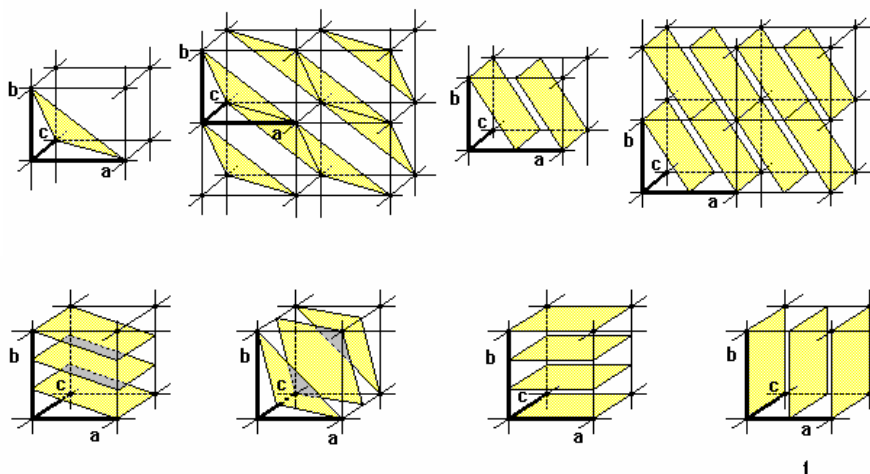
32 grupos puntuales

14 Retículos de Bravais

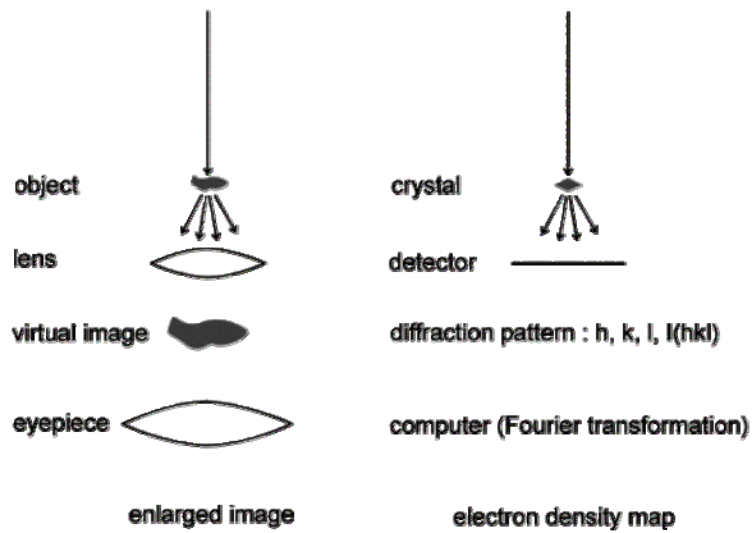
230 Grupos Espaciales



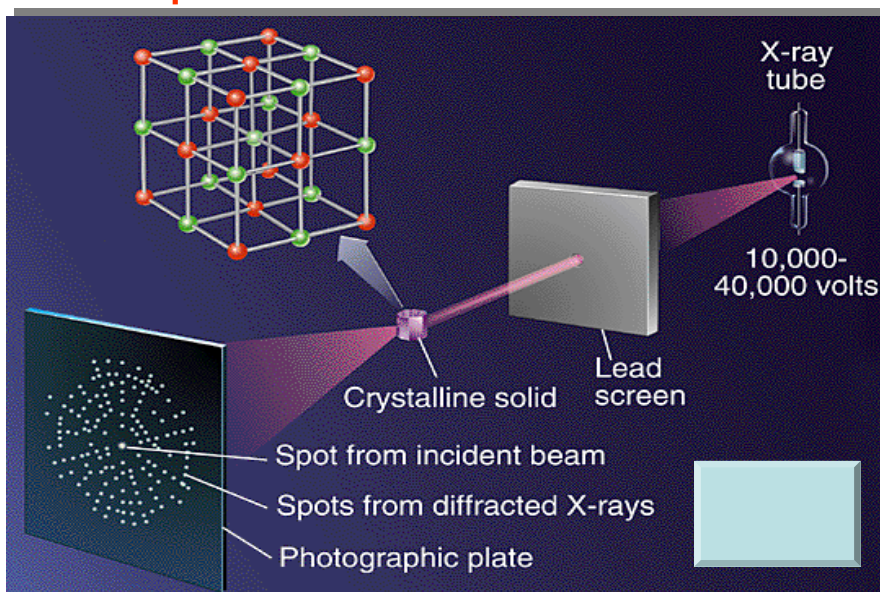
Indices de Miller (hkl)



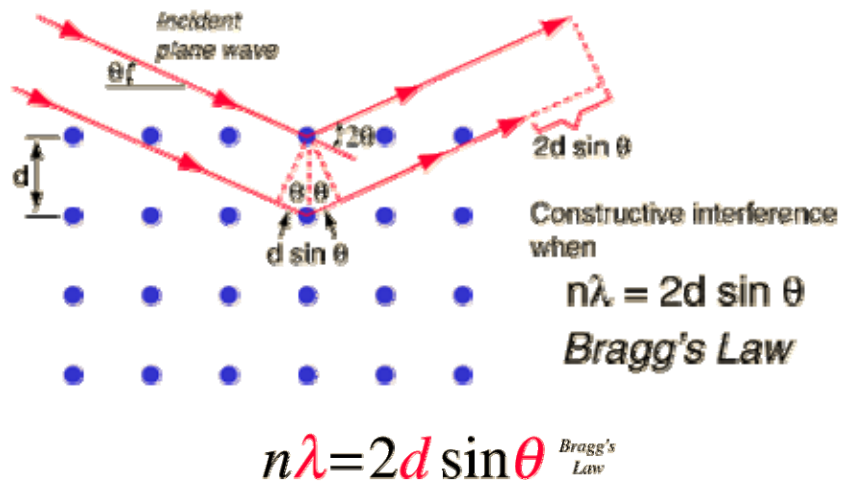
Microscopía vs. Rayos X



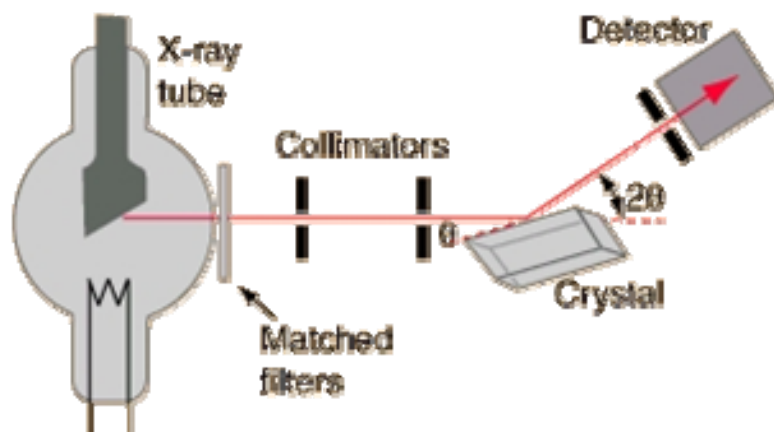
Experimento de Difracción



Difracción de Rayos X (I)



Experimento de Difracción

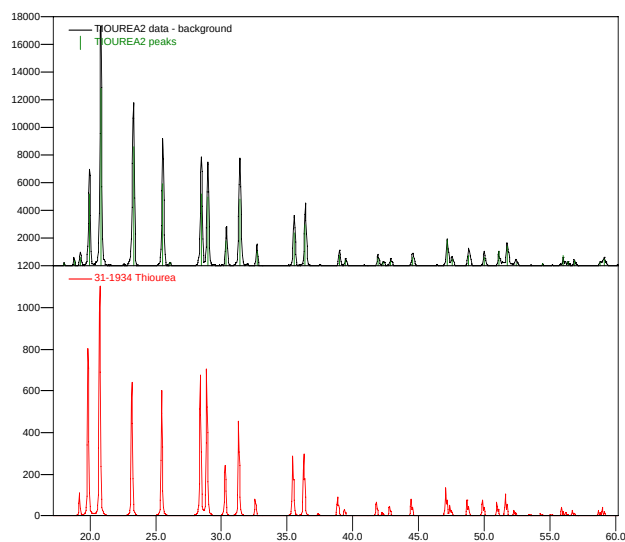


Experimento de Difracción

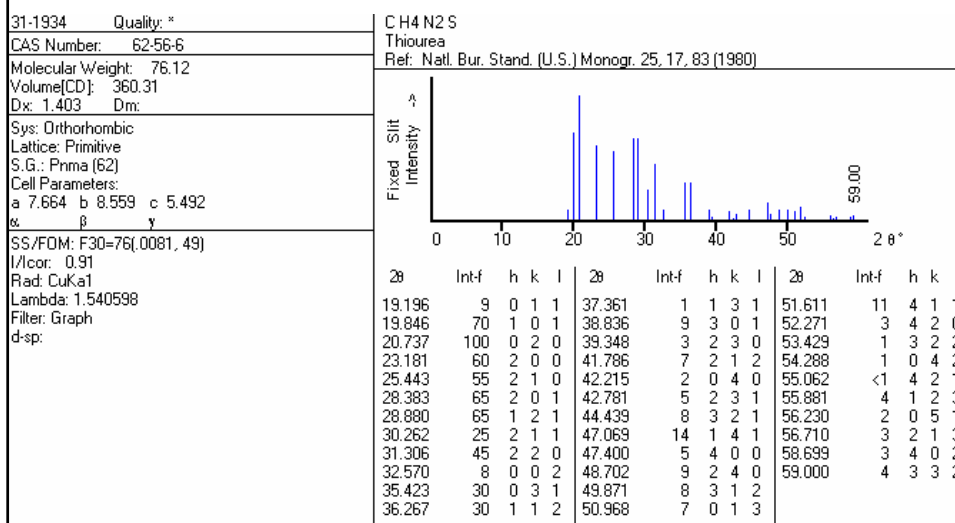




Difracción de Rayos X (I)



Difracción de Rayos X (I)

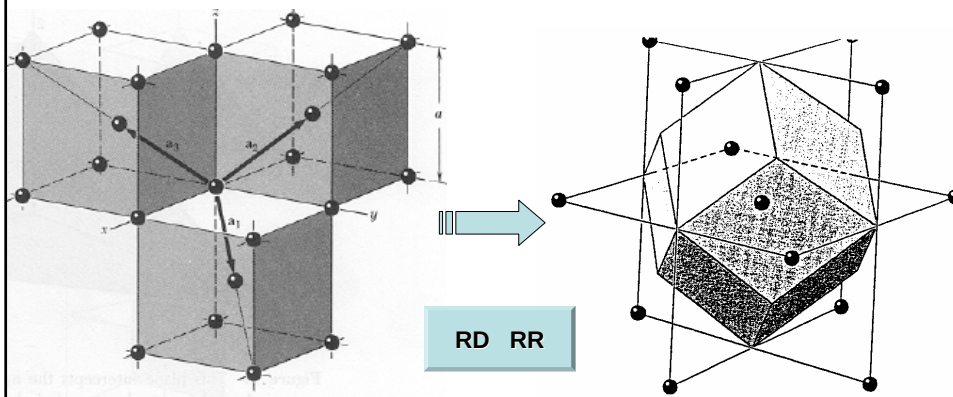


Retículo Recíproco

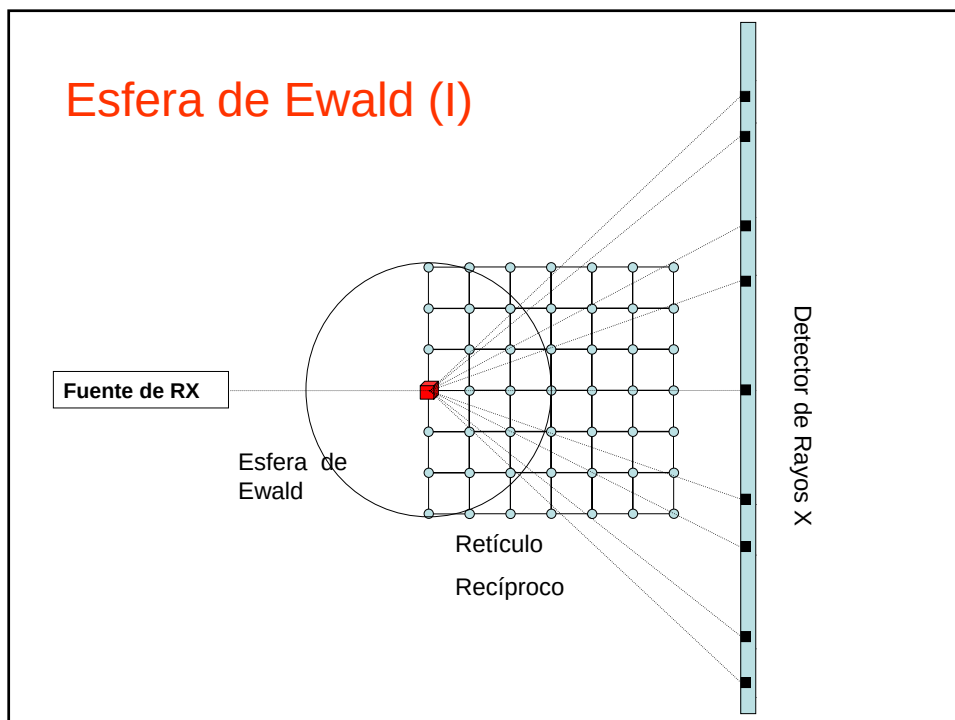
$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$

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

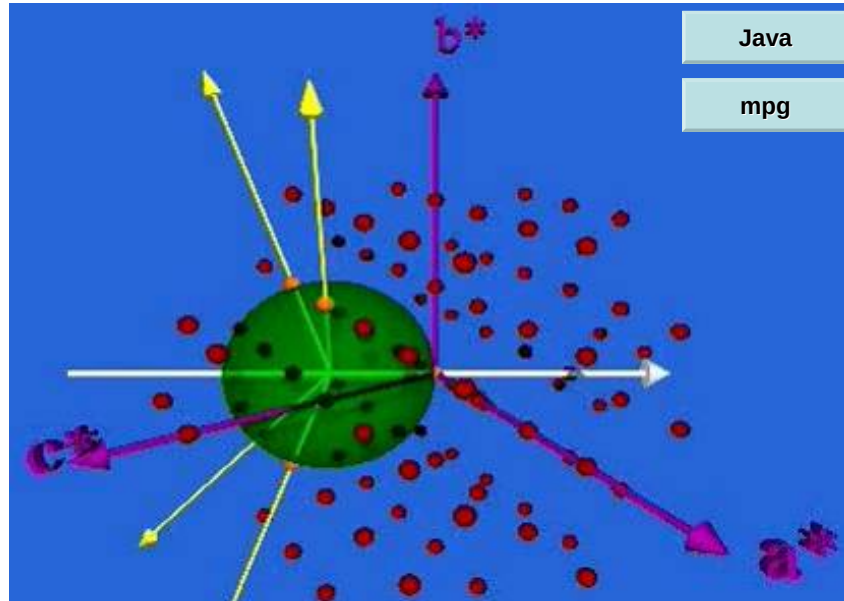
$$\vec{c}^* = \frac{\vec{a} \times \vec{b}}{\vec{a} \cdot (\vec{b} \times \vec{c})}$$



Esfera de Ewald (I)



Esfera de Ewald



Número de Intensidades

Las posiciones de los picos de difracción depende únicamente de la celda unidad.

Entonces la cantidad máxima de picos a medir será función del tamaño de la celda unidad y de la longitud de onda utilizada en el experimento.

$$N = \frac{32\pi}{3} \left(\frac{Vol.}{\lambda^3} \right) \approx 33.5 \left(\frac{Vol.}{\lambda^3} \right) \quad \begin{array}{l} \lambda_{Cu} = 1.5418 \text{ \AA} \\ \lambda_{Mo} = 0.7107 \text{ \AA} \end{array}$$

$$V = 400 \text{ \AA}^3 \Rightarrow N_{Cu} \approx 3657 \quad N_{Mo} \approx 37340$$

$$V = 125000 \text{ \AA}^3 \Rightarrow N_{Cu} \approx 2E6 \quad N_{Mo} \approx 1E7$$

Difracción de Rayos X (II)

- Factor de Estructura atómico

$$f(\theta) = \iiint_{\text{volumen}} \rho(\vec{r}) e^{i 2\pi(\vec{r} \cdot \vec{S})} dV$$

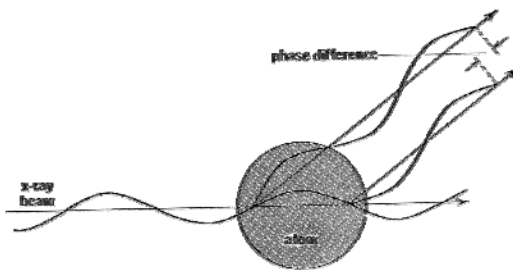
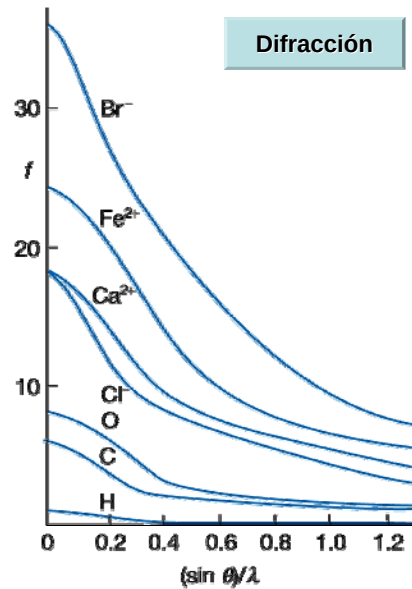


FIG. 32.



Difracción de Rayos X (II)

- Factor de Estructura

$$F_{hkl} = \iiint_{\text{celda unidad}} \rho(\vec{r}) e^{i 2\pi(\vec{r} \cdot \vec{S})} dV$$

$$2\pi\vec{r} \cdot \vec{S} = 2\pi(xh + yk + zl)$$

$$F_{hkl} = \iiint_{\text{celda unidad}} \rho(x, y, z) e^{i 2\pi(xh + yk + zl)} dV$$

$$\rho(x, y, z) = \frac{1}{V} \sum_{hkl} F_{hkl} e^{-i 2\pi(xh + yk + zl)}$$

Difracción de Rayos X (II)

- Factor de Estructura

Difracción II

$$F_{hkl} = \iiint_{\text{celda unidad}} \rho(x,y,z) e^{i 2\pi(xh+yk+zl)} dv$$

$$F_{hkl} = \sum_j f_j(\theta) e^{i 2\pi(xh+yk+zl)}$$

$$F_{hkl} = |F_{hkl}| e^{i\phi_{hkl}}$$



$$I_{hkl} = k \langle E^2 \rangle$$

$$I_{hkl} = k \langle F_{hkl}^2 \rangle$$

$$\rho(x,y,z) = \frac{1}{V} \sum_{hkl} |F_{hkl}| e^{i\phi_{hkl}} e^{-i 2\pi(xh+yk+zl)}$$

Difracción de Rayos X (II)

- Resumen

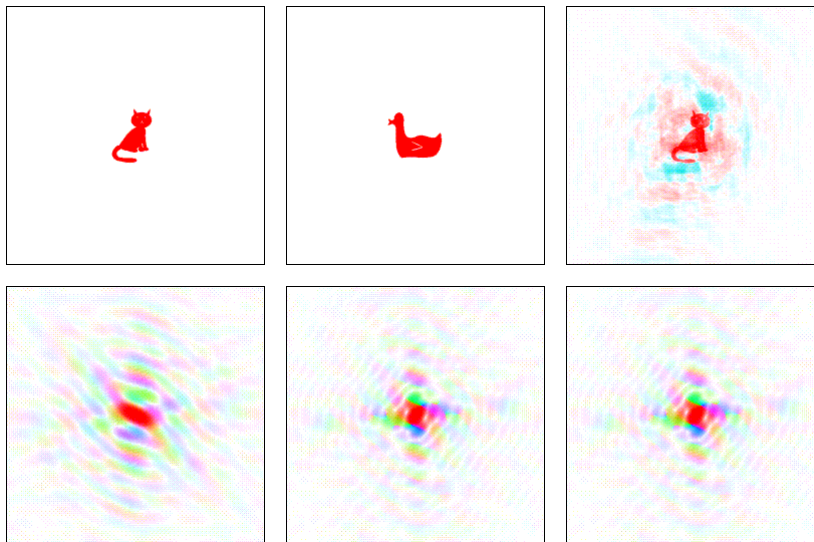
- Conociendo $\rho(\vec{r})$ podemos obtener el patrón de Difracción

- Solo con I_{hkl} no podemos obtener directamente $\rho(\vec{r})$

$$\rho(x,y,z) = \frac{1}{V} \sum_{hkl} |F_{hkl}| e^{i\phi_{hkl}} e^{-i 2\pi(xh+yk+zl)}$$

Problema de las Fases

Importancia de las Fases



Importancia de las Fases



Métodos de Resolución Estructural

$$\rho(x,y,z) = \frac{1}{V} \sum_{hkl} \boxed{F_{hkl}} e^{i\phi_{hkl}} e^{-i 2\pi(xh+yk+zl)}$$

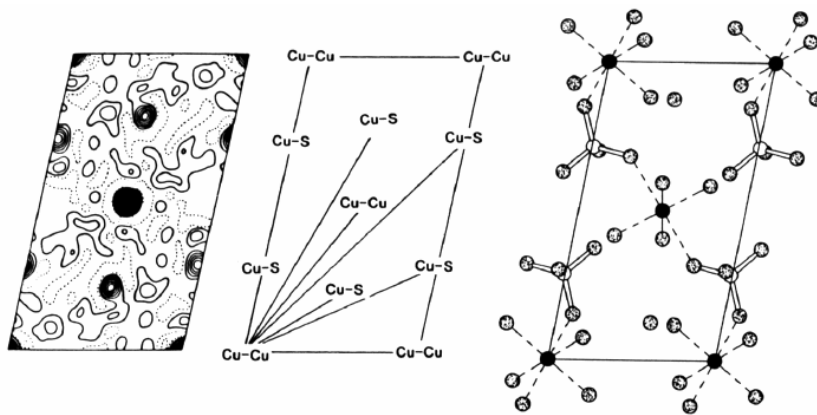
 Procede de las intensidades $|F_{hkl}| \propto \sqrt{I_{hkl}}$

 Hay que asignar estos valores

- MÉTODOS DIRECTOS
- PATTERSON (ÁTOMO PESADO)

$$P(u,v,w) = \sum_{hkl} |F_{hkl}|^2 e^{-i 2\pi(uh+vk+wl)}$$

Ej. Funciones de Patterson



Patterson
map

Cu-Cu and
Cu-S vectors

Crystal
structure