Conceptos básicos de Cristalografía y métodos de análisis

Fernando Aguado Menéndez
Grupo de Altas Presiones y Espectroscopía
Departamento de Ciencias de la Tierra y Física de la Materia Condensada
Universidad de Cantabria

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- Introducción. ¿Qué es la cristalografía?
- Un poco de historia
- Conceptos básicos
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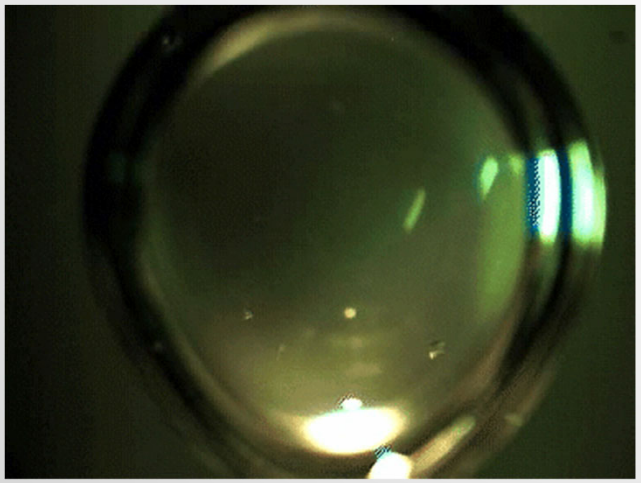
Definición de Cristalografía

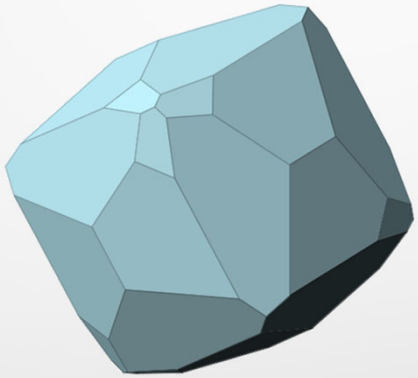
cristalografía

Del gr. κρύσταλλος *krýstallos* 'cristal' y *-grafía.*

1. f. Geol. Descripción de las formas que toman los cuerpos al cristalizar.

Diccionario RAE

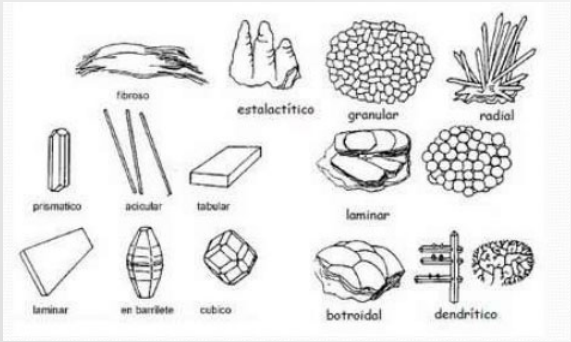




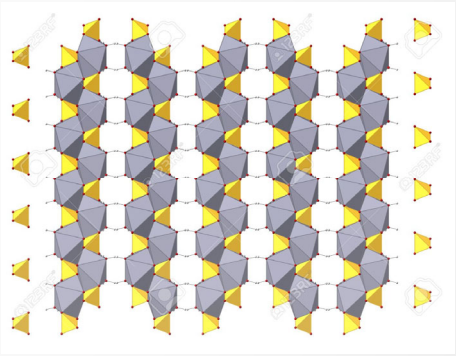
Hábitos cristalinos:
(Formas y caras)

Definición de Cristalografía

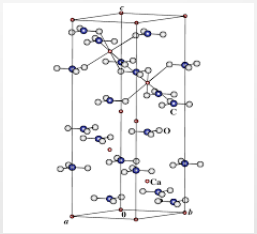
Hábitos cristalinos. Estructura atómica vs. Condiciones

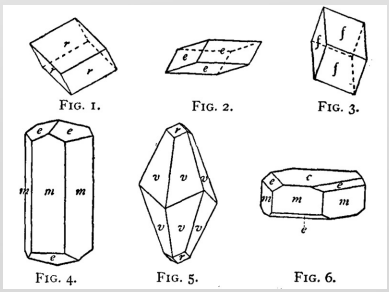



Yeso



¿?





Definición de Cristalografía

cristalografía

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Diccionario RAE

Crystallography, branch of science that deals with **discerning the arrangement and bonding of atoms in crystalline solids** and with the geometric structure of crystal lattices. Classically, the optical properties of crystals were of value in mineralogy and chemistry for the identification of substances. **Modern crystallography is largely based on the analysis of the diffraction of X-rays by crystals acting as optical gratings**. Using X-ray crystallography, chemists are able to determine the internal structures and bonding arrangements of minerals and molecules, **including the structures of large complex molecules, such as proteins and DNA**.

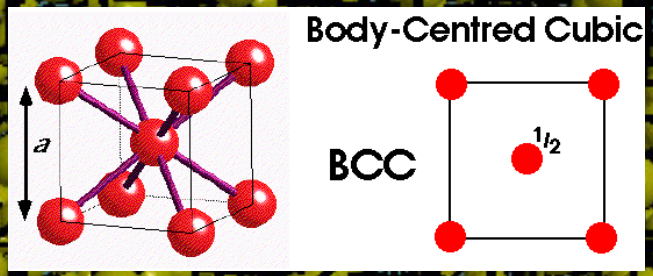
Encyclopedia Britannica

Definición de Cristalografía: Cristal

"… A **Crystal** consists of atoms arranged in a pattern that repeats periodically
in three dimensions…."

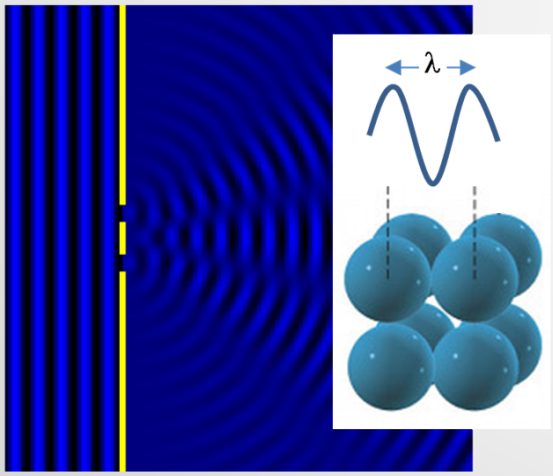
C.S. Barret, Structure of Metals. McGraw-Hill (1952)

Orden regular a largo alcance
Simetría traslacional

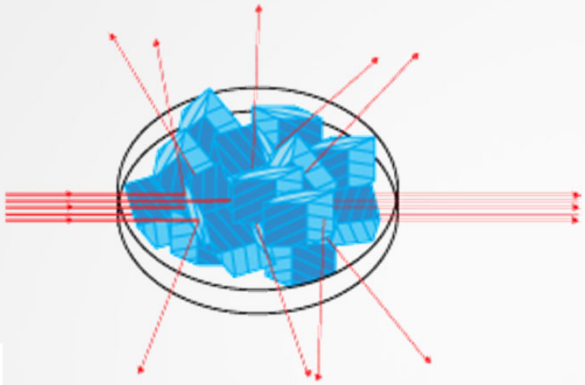


Hierro
$[Fe]^{bb}$

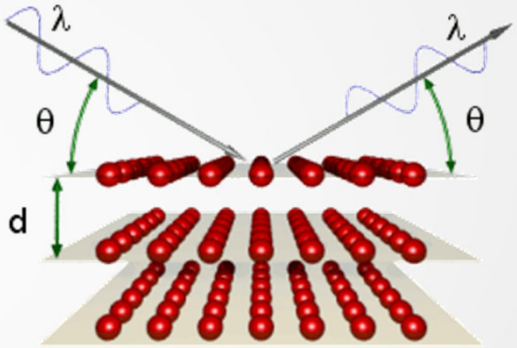
Difracción de rayos X : Proceso de interacción LUZ- MATERIA



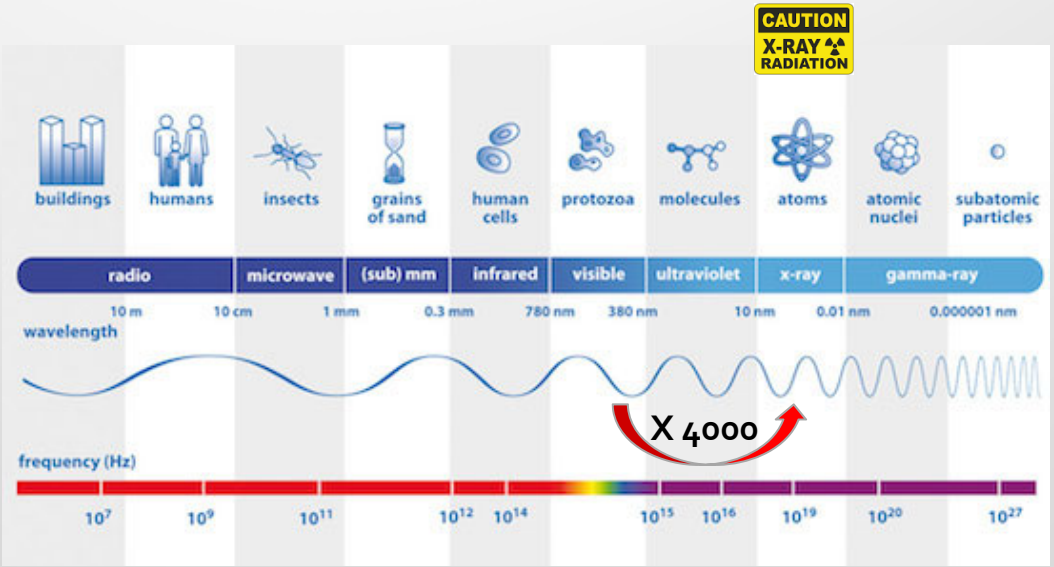
Difracción de la luz



Difracción en un sólido



Difracción de RX por un planos cristalinos



Definición de Cristalografia: Cristal

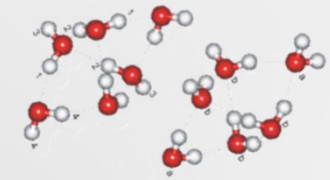
"… A **Crystal** consists of atoms arranged in a pattern that repeats periodically
in three dimensions…."

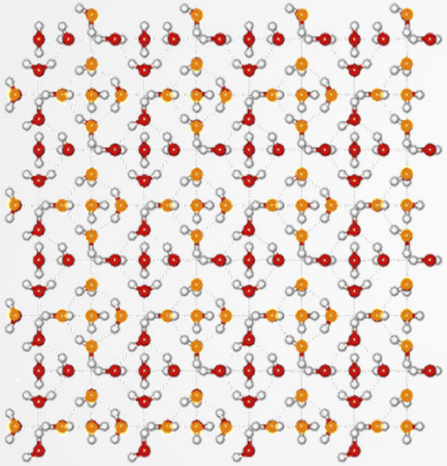
C.S. Barret, Structure of Metals. McGraw-Hill (1952)

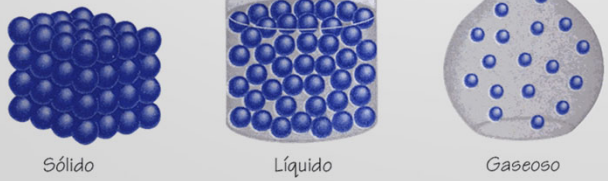
Crystal A material is a crystal if it has essentially **a sharp diffraction pattern**. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp **Bragg peaks**, besides the always present diffuse scattering.

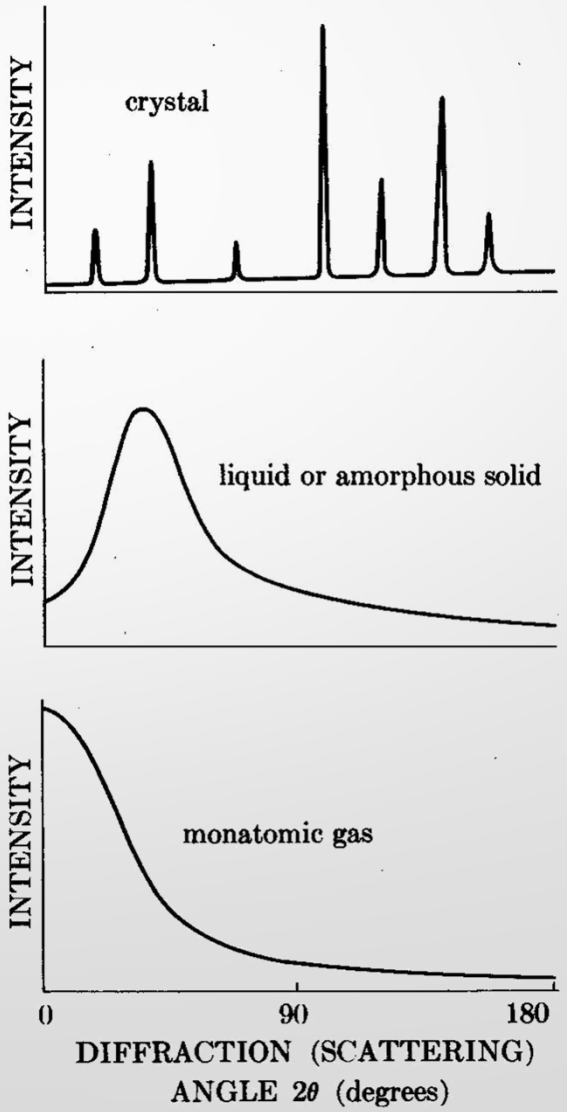
IUCR Online dictionary

Definición de Cristalografía. Sólido Cristalino



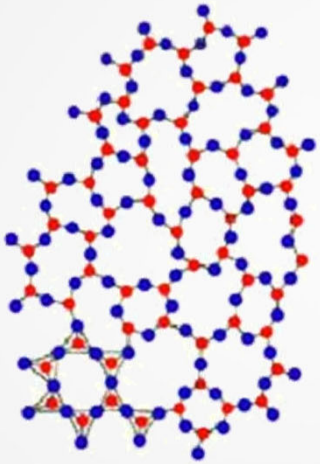


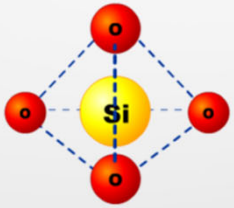


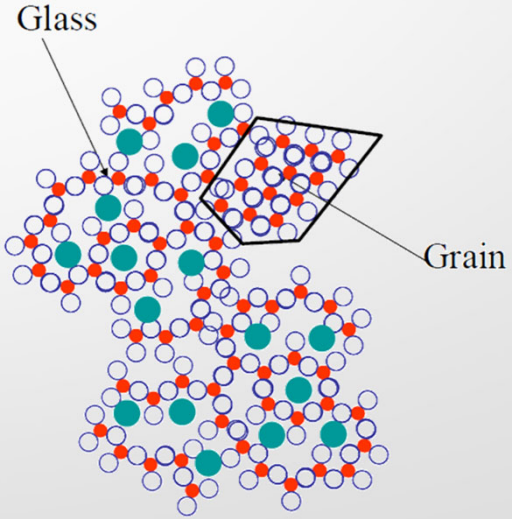


Definición de Cristalografía: Cristal

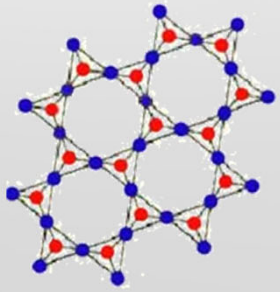
Amorphous SiO_2 (Glass)

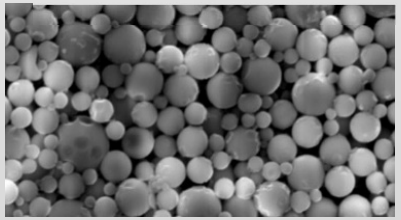


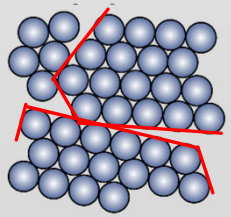




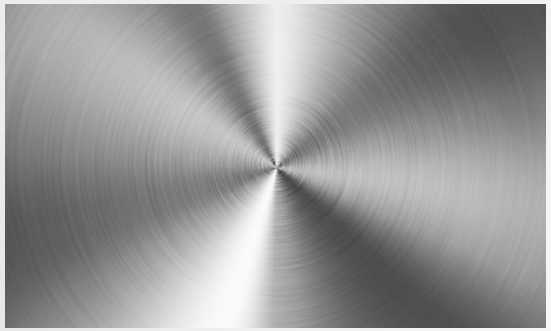
Crystalline SiO_2 (Quartz)



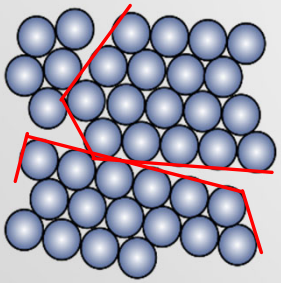


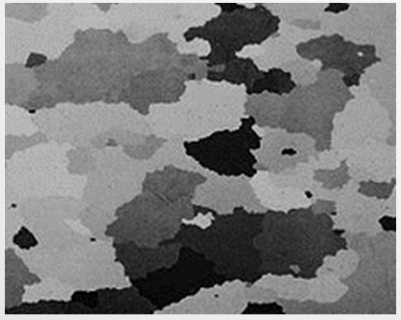


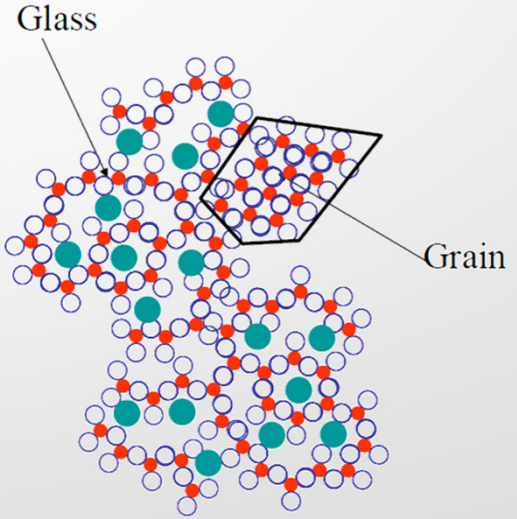
Definición de Cristalografía: Cristal

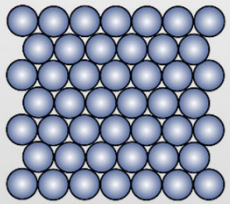


Policristal

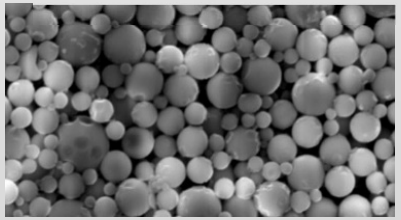


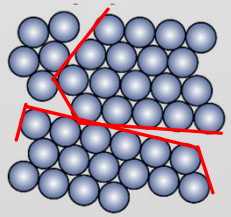






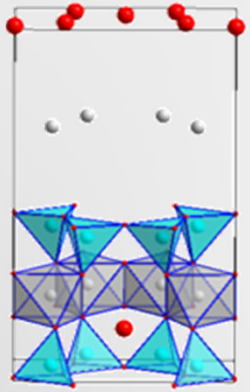
Monocristal

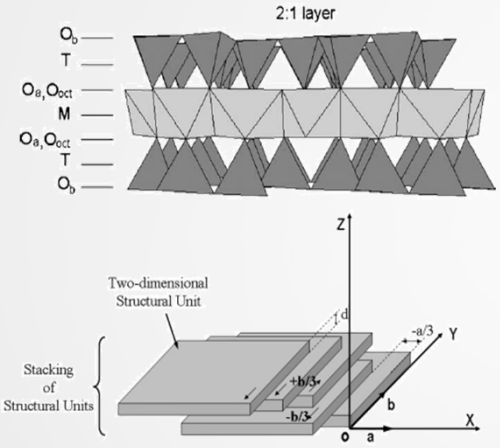


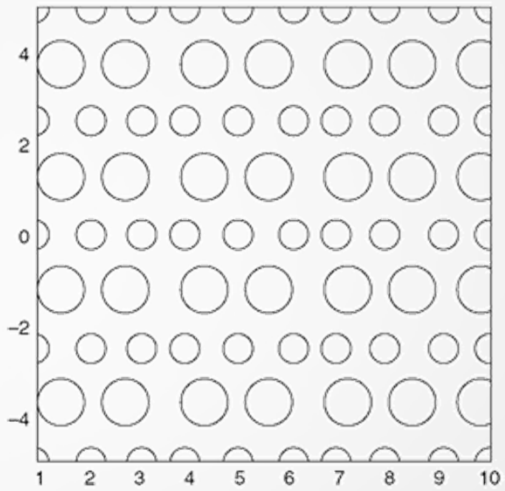


Definición de Cristalografía: Cristal

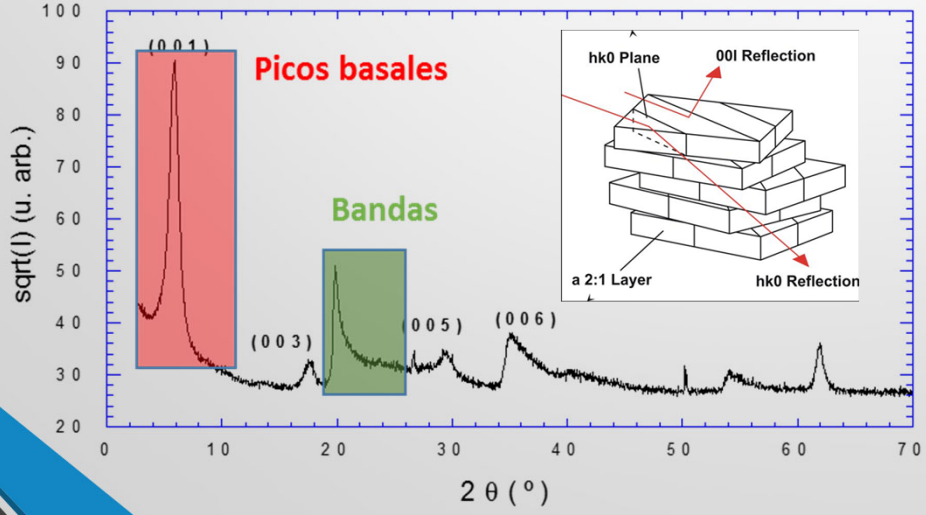
Arcillas: Sistemas "desordenados"

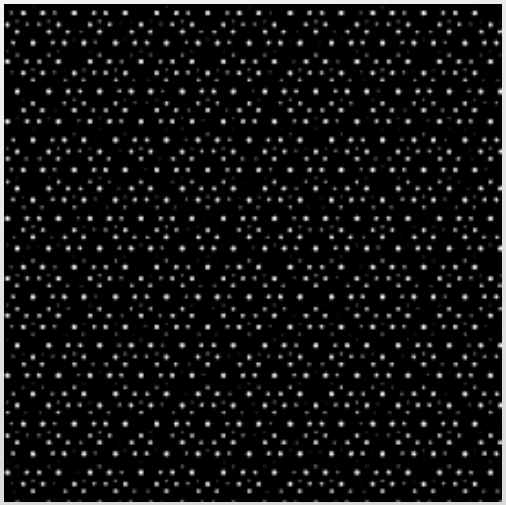






Estructura inconmensurable

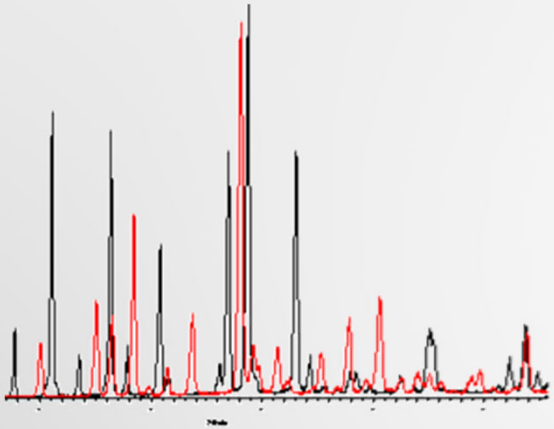


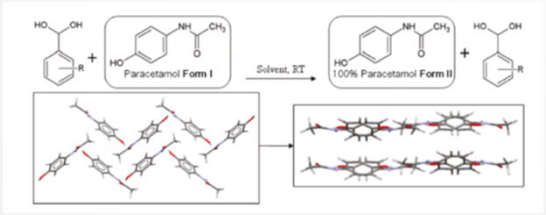


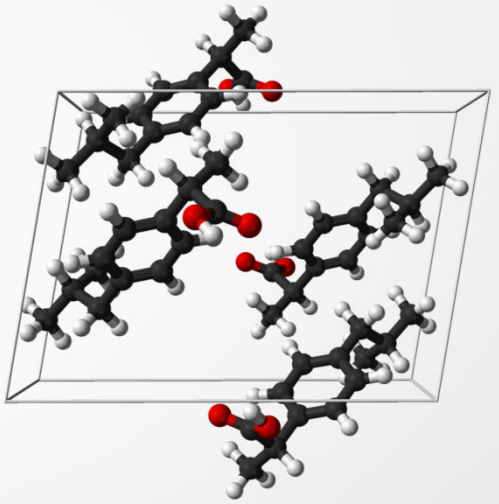
Cuasicristales

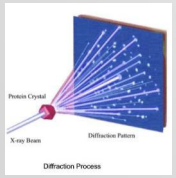
Definición de Cristalografía: Cristal

Acetaminophen (Paracetamol)

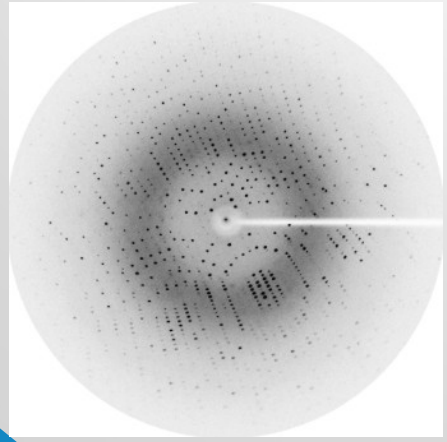


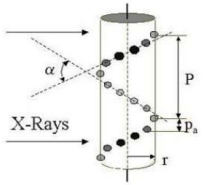


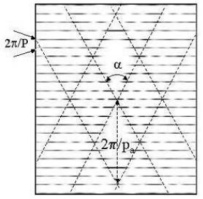




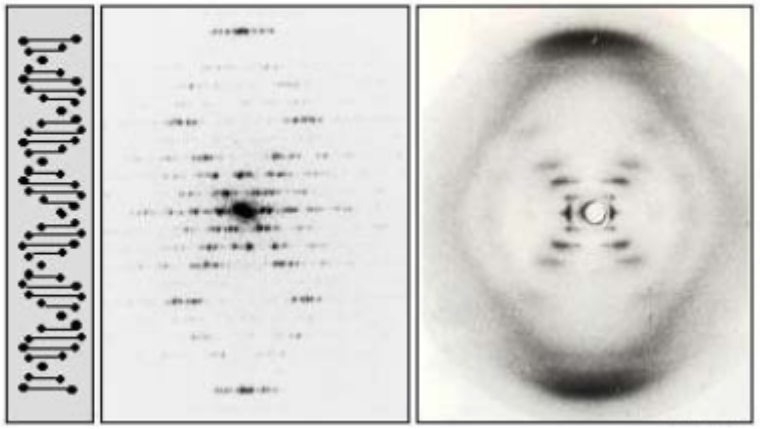
Proteina AtHAL3







B-DNA

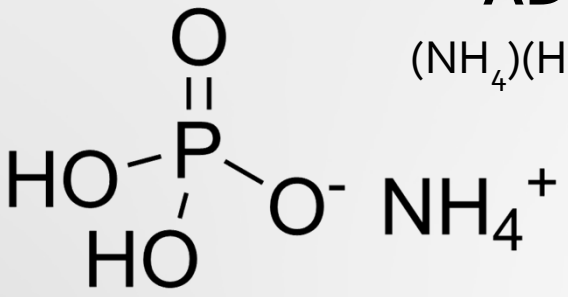


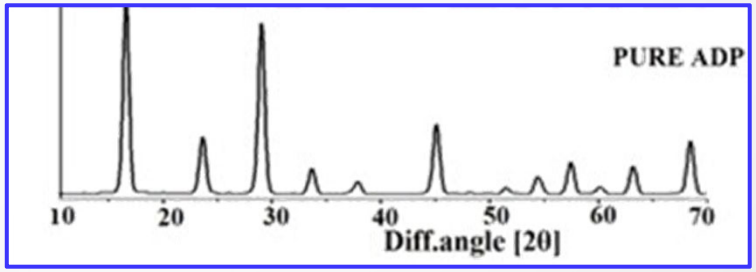
Definición de Cristalografía: Cristal

ADP

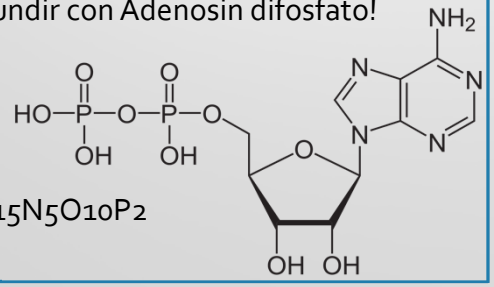
$(NH_4)(H_2PO_4)$

Fosfato monoamónico
dihidrógeno fosfato de amonio

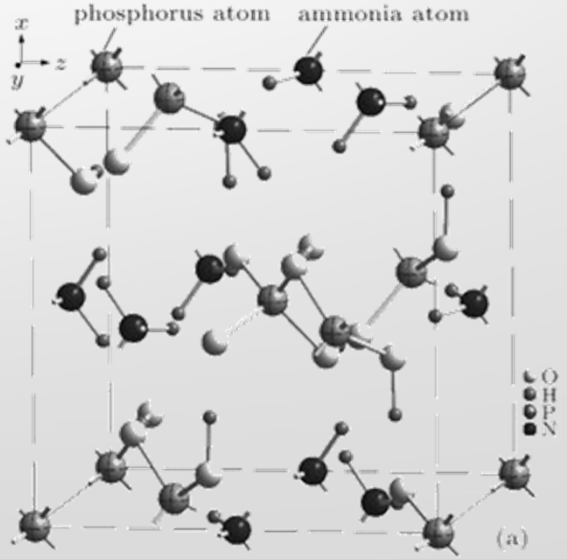




No confundir con Adenosin difosfato!



$C_{10}H_{15}N_5O_{10}P_2$



*¿Por qué la **Cristalografía**?*

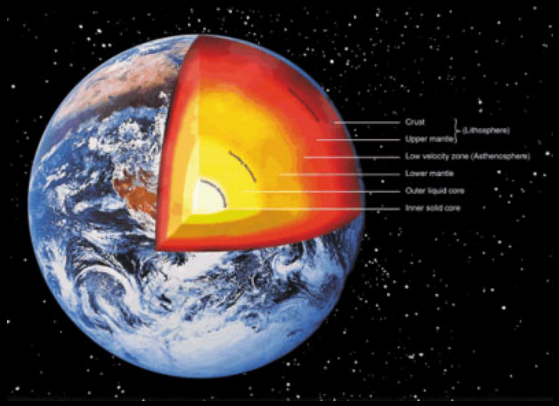
Structural characterization

Why do we need to determine crystal structures ?

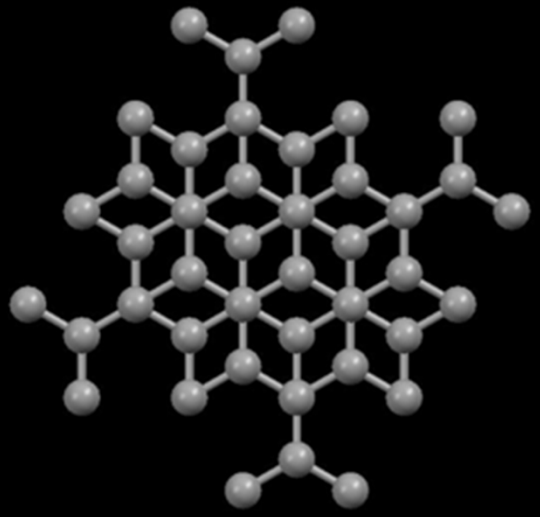
- To **categorize** unknown **compounds**
- To **rationalize structures** / Understanding of bases
- To **establish correlations** between structure and properties

Formas alotrópicas del Carbono. Relación estructura-propiedades

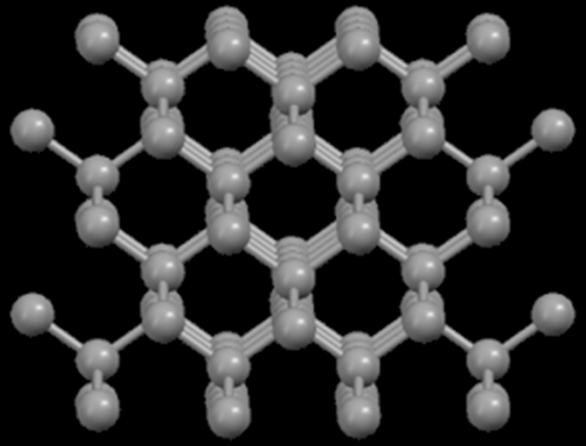
Grafito



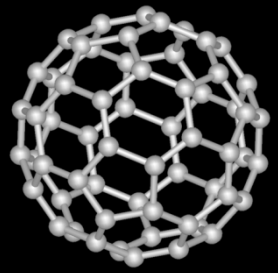
Diamante



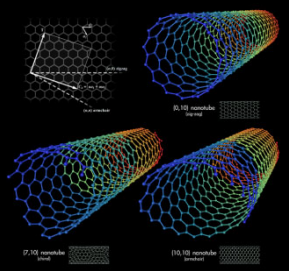
Alta Presión
Alta Temperatura



Fulerenos



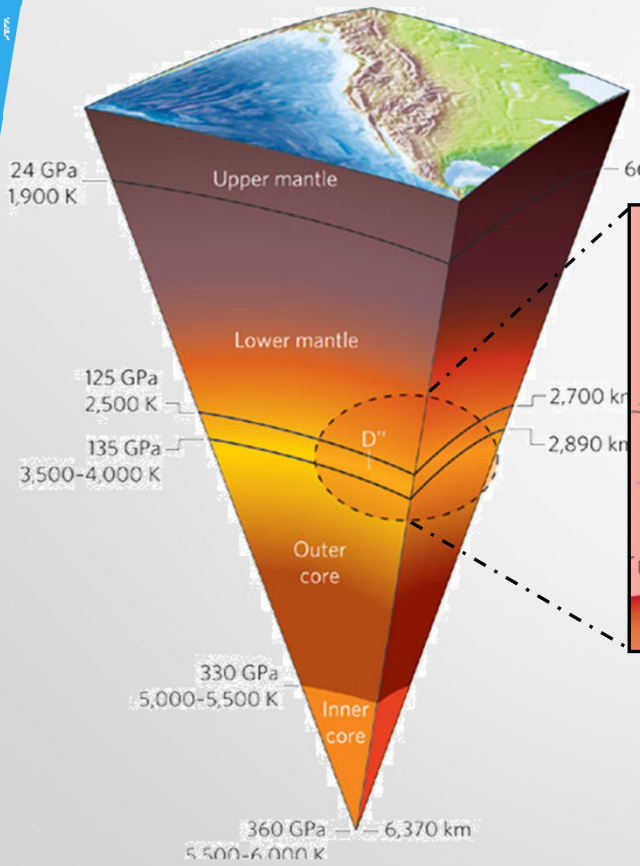
Nanotubos

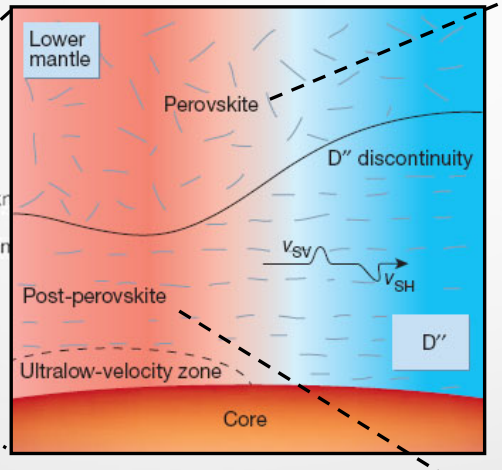


Structure Hexagonal
Space Group $P6_3mc$ (No. 186)
a= 2.4700 Å, b=2.4700 Å, c=6.7900 Å
$\alpha=\beta=90.00$, $\gamma=120.00$
Z=4

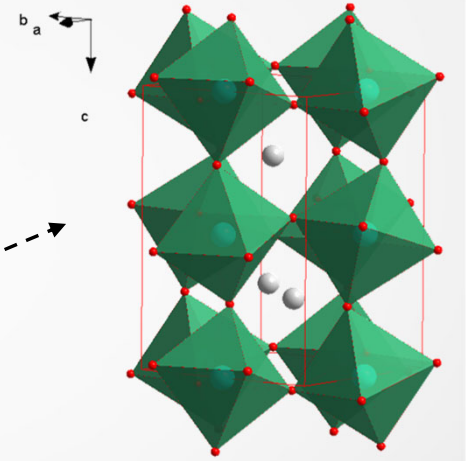
Structure Cubic
Space Group $Fd\text{-}3m$ (No. 227)
a=3.5668 Å
Z=8

Transición de fase Perovskita-Postperovskita

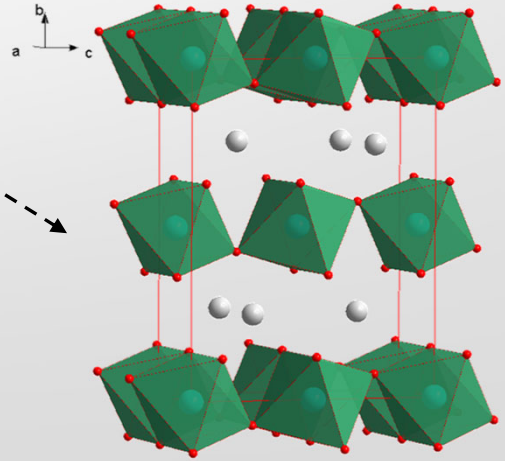




- $(Fe,Mg)SiO_3$
- $(Mg,Fe)O$
- $CaSiO_3$-pv



~120 GPa ↓ **~1-1.5% Vol. ↓**

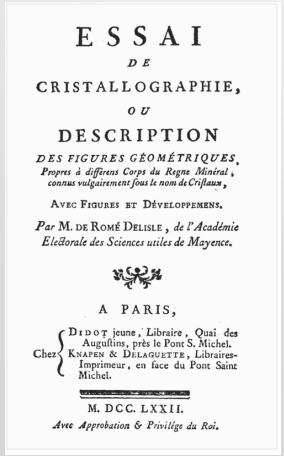


- $(Mg,Fe)SiO_3$
- $CaBO_3$ (B:Ir, Pt, Ru)
- $MgGeO_3$, $MnGeO_3$
- $NaMgF_3$
- A_2X_3 (A: Al, Mn…)

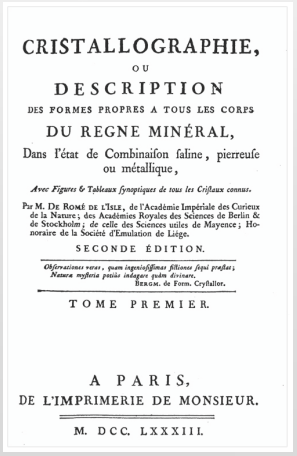
"Prehistoria": de Teofrasto a Schoenflies

Jean Baptiste Louis Romé de l'Isle (1736 – 1790)

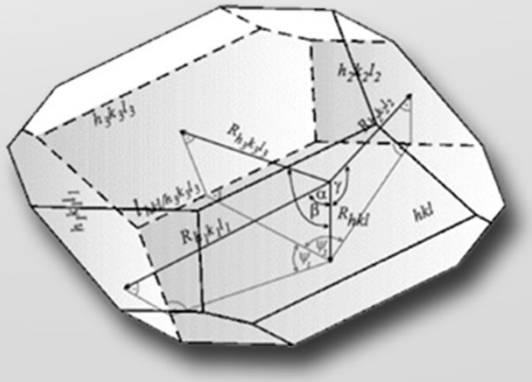
- "La idea de los gérmenes no se puede utilizar para explicar la formación de cristales. Es necesario suponer que las moléculas integrantes, tiene una figura constante determinada…"
- Los cristales de la misma naturaleza química derivan todos de una **forma primitiva común**.
- Basándose en los trabajos previos de Nicolás Steno (1638-1686) elaboró su ***Ley de la Constancia de Ángulos Interfaciales***.



ESSAI
DE
CRISTALLOGRAPHIE,
OU
DESCRIPTION
DES FIGURES GÉOMÉTRIQUES,
Propres à différens Corps du Regne Minéral,
connus vulgairement sous le nom de Cristaux,
AVEC FIGURES ET DÉVELOPPEMENS.
Par M. DE ROMÉ DELISLE, de l'Académie
Electorale des Sciences utiles de Mayence.
A PARIS,
Chez DIDOT jeune, Libraire, Quai des Augustins, près le Pont S. Michel.
KNAPEN & DELAGUETTE, Libraires-Imprimeur, en face du Pont Saint Michel.
M. DCC. LXXII.
Avec Approbation & Privilège du Roi.



CRISTALLOGRAPHIE,
OU
DESCRIPTION
DES FORMES PROPRES A TOUS LES CORPS
DU REGNE MINÉRAL,
Dans l'état de Combinaison saline, pierreuse ou métallique,
Avec Figures & Tableaux synoptiques de tous les Cristaux connus.
Par M. DE ROMÉ DE L'ISLE, de l'Académie Impériale des Curieux de la Nature; des Académies Royales des Sciences de Berlin & de Stockholm; de celle des Sciences utiles de Mayence; Honoraire de la Société d'Emulation de Liége.
SECONDE ÉDITION.
Observationes veræ, quam ingeniosissimas fictiones sæpè præstat; Naturæ mysteria penitùs indagare quàm divinare.
BERGM. de Form. Crystallor.
TOME PREMIER.
A PARIS,
DE L'IMPRIMERIE DE MONSIEUR.
M. DCC. LXXXIII.

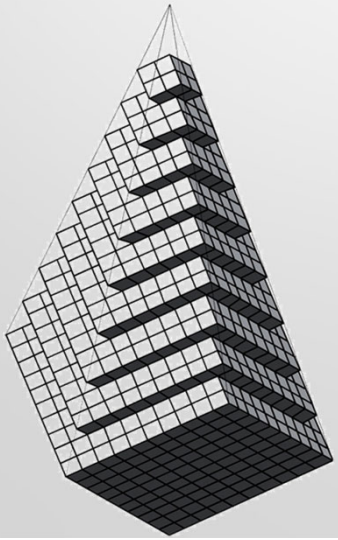


"Prehistoria": de Teofrasto a Schoenflies

René Just Haüy (1743-1822)

- Previa caracterización de cristales solamente morfológica- Nueva interpretación.
- Descubre que los cristales se fracturan a lo largo de los ejes cristalográficos únicamente.
- Dedujo que los cristales deben ser periódicos y construidos por apilamientos de poliedros: los "moléculas integrantes".


ESSAI
D'UNE THÉORIE
SUR LA STRUCTURE
DES CRYSTAUX,
APPLIQUÉE



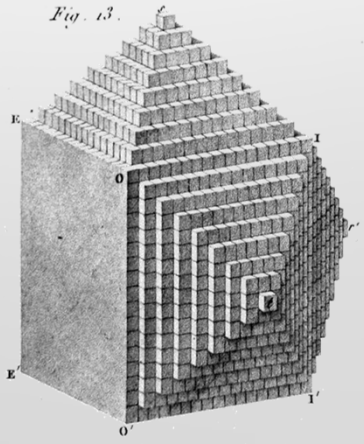


Fig. 13.

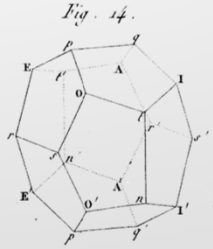


Fig. 14.

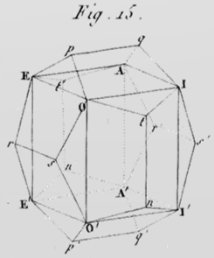


Fig. 15.

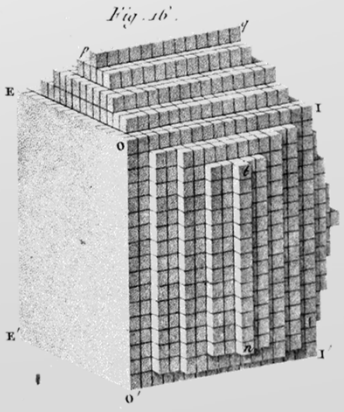
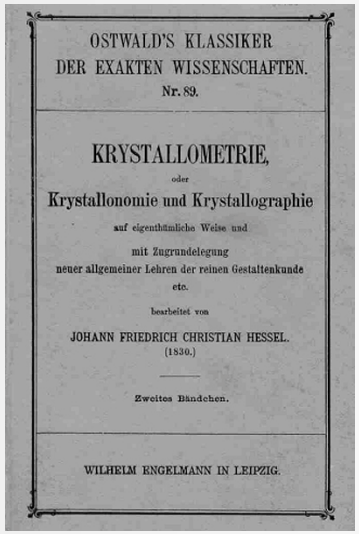
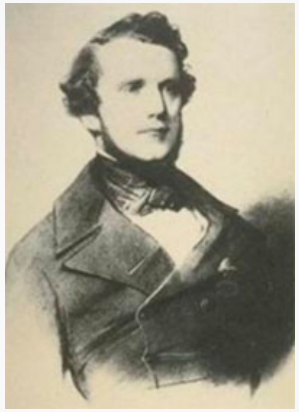


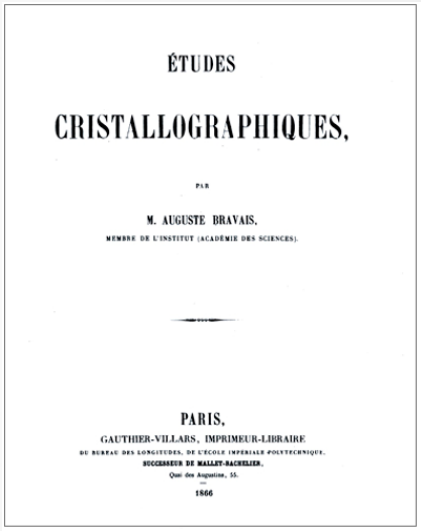
Fig. 16.

"Prehistoria": de Teofrasto a Schoenflies

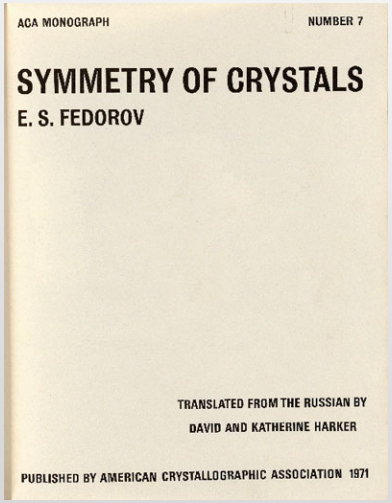


[Johann Friedrich Christian Hessel (1796-1872)]

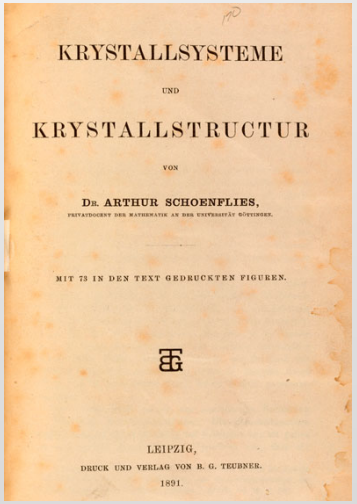




[August Bravais (1811-1863)]

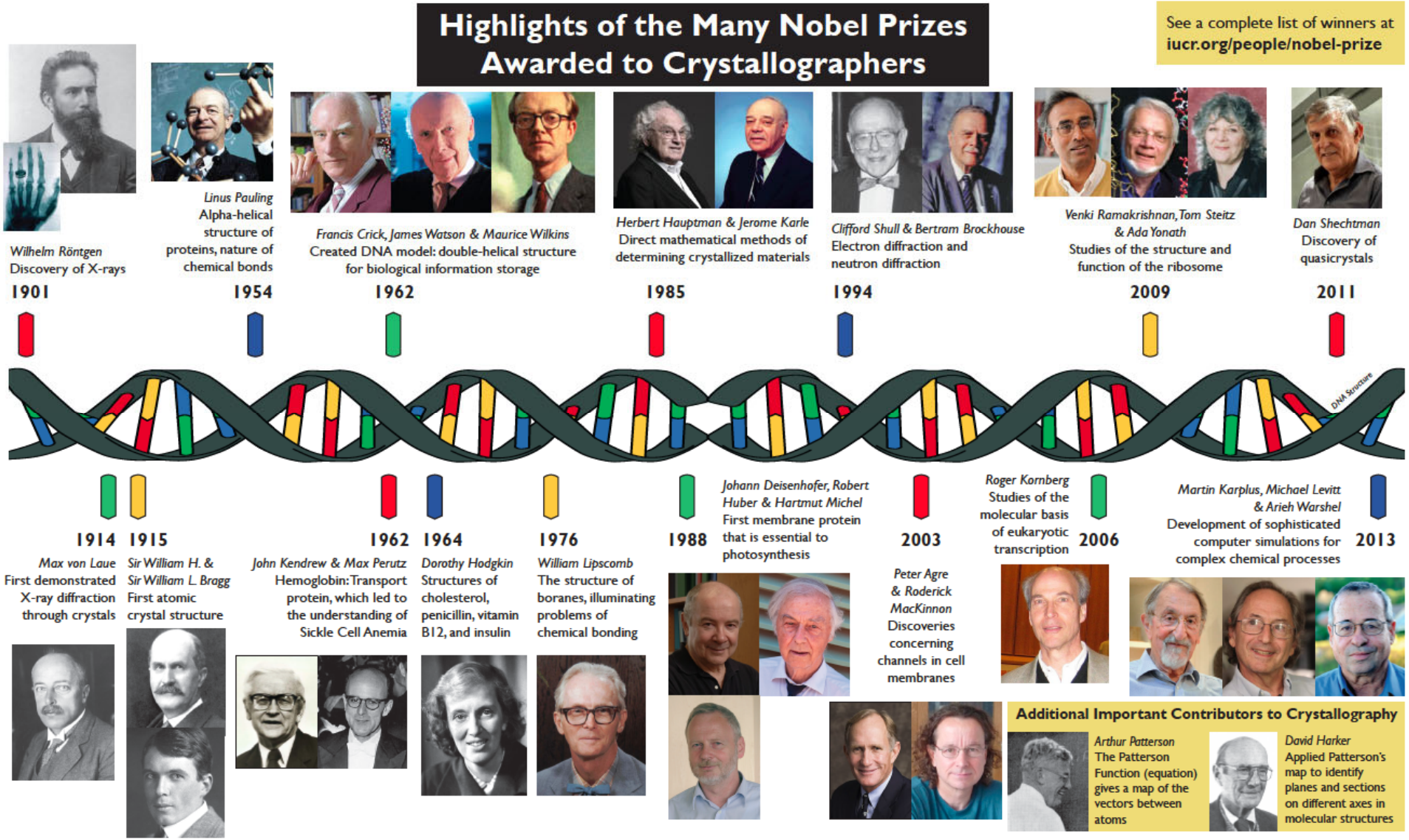


[Evgraf S. Fedorov (1853-1919)]

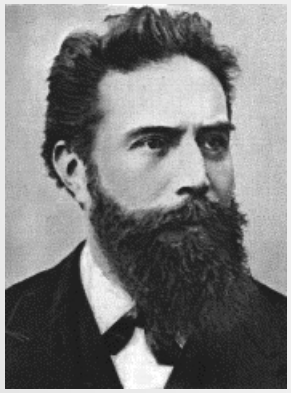


[Arthur Schoenflies (1853-1928)]

Cristalografía moderna: de los Bragg a Shechtman



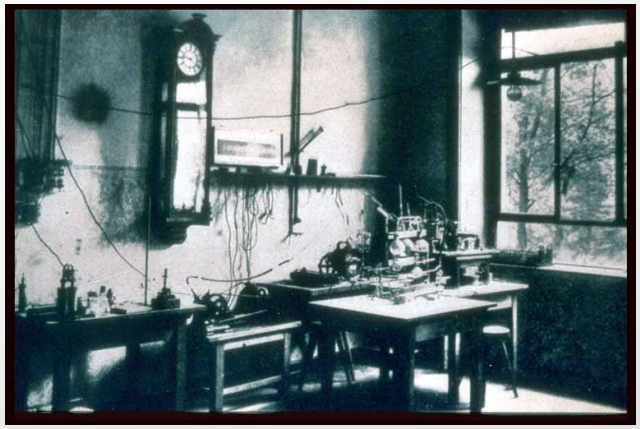
Cristalografía moderna: de los Bragg a Shechtman



Wilhem C. Röntgen

Premio Nobel, ***1901*** *"in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him"*

Professor Röntgen at work.



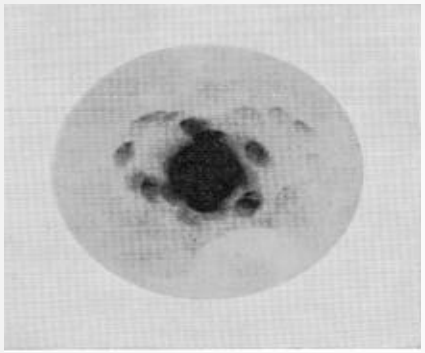
Laboratorio de Roentgen en Wurzburg

Tubo de rayos X utilizado por Roentgen

Cristalografía moderna: de los Bragg a Shechtman

Max von Laue

Premio Nobel, 1914 "for his discovery of the diffraction of X-rays by crystals".



Primera imagen de difracción por un cristal

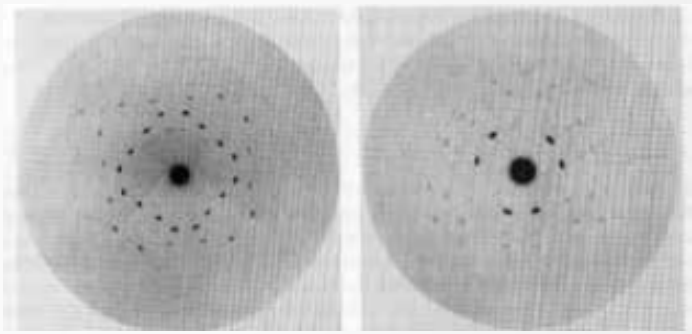
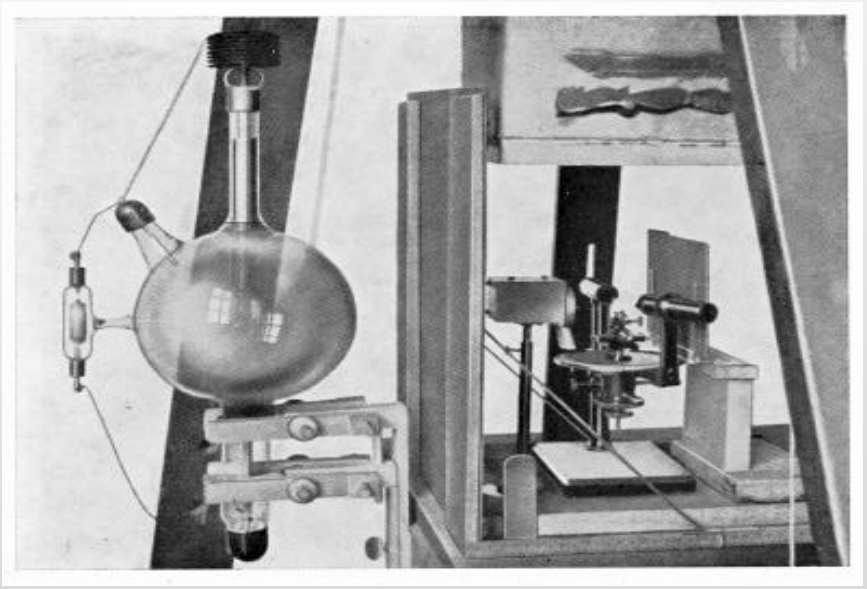


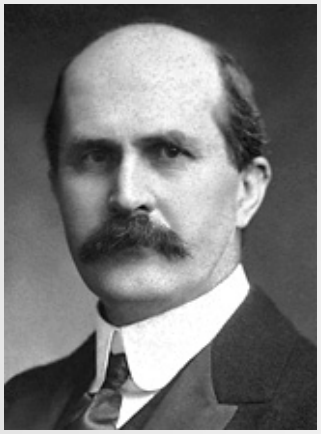
Imagen de difracción de cristales de Zinc blenda (ZnS)

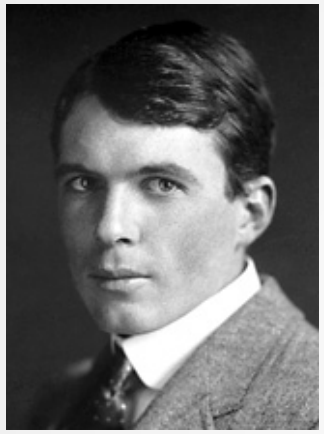
Paul P. Ewald



Dispositivo experimental utilizado por Friedrich y Knipping, asistentes de Laue

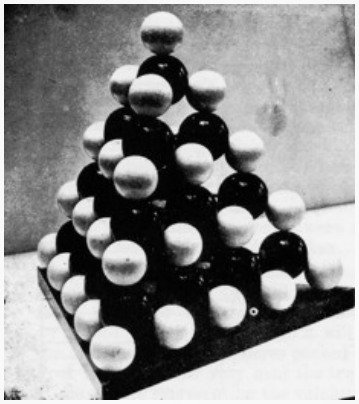
Cristalografía moderna: de los Bragg a Shechtman

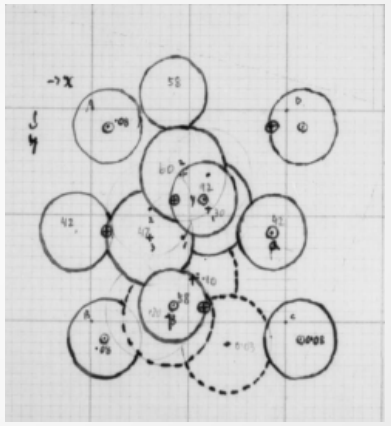




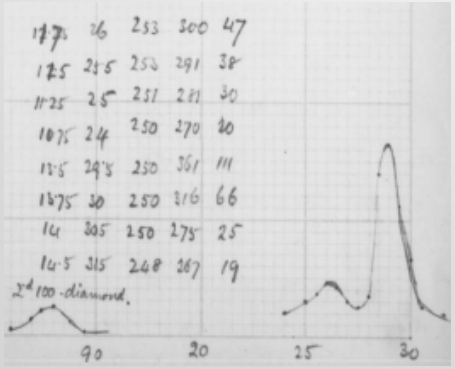
William Henry Bragg

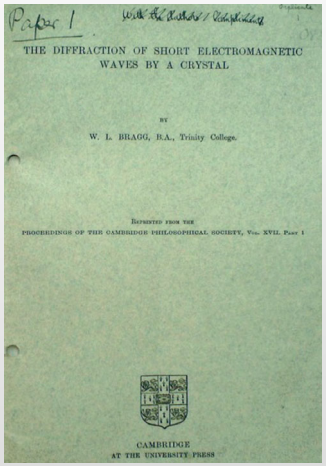
William Lawrence Bragg





Premio Nobel, 1915 "for their services in the analysis of crystal structure by means of X-rays".




Paper I.

THE DIFFRACTION OF SHORT ELECTROMAGNETIC WAVES BY A CRYSTAL

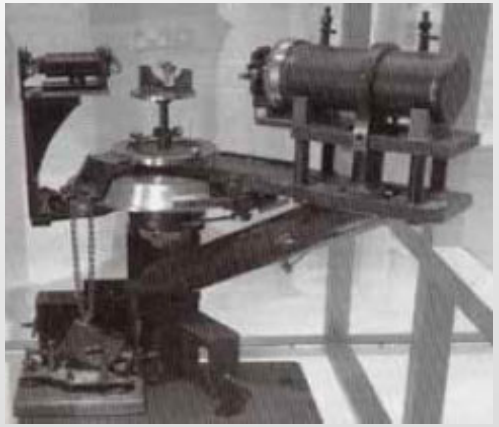
BY

W. L. BRAGG, B.A., Trinity College.

REPRINTED FROM THE PROCEEDINGS OF THE CAMBRIDGE PHILOSOPHICAL SOCIETY, VOL. XVII, PART I

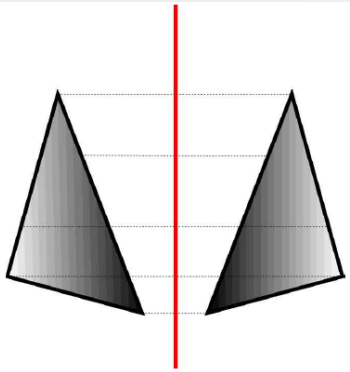
CAMBRIDGE
AT THE UNIVERSITY PRESS

$$n\lambda = 2d \sin \vartheta$$

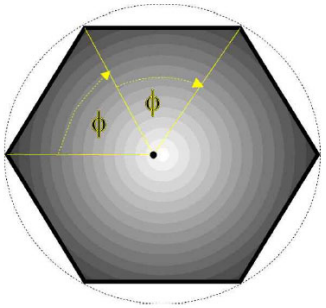


Espectrómetro de ionización de Rayos X, antecesor de los difractómetros modernos

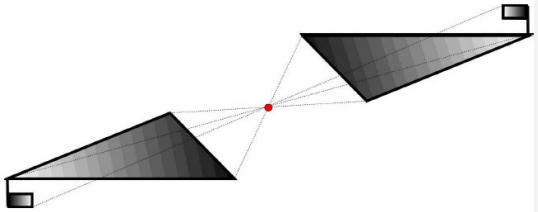
SIMETRÍA : Elementos básicos



Planos especulares

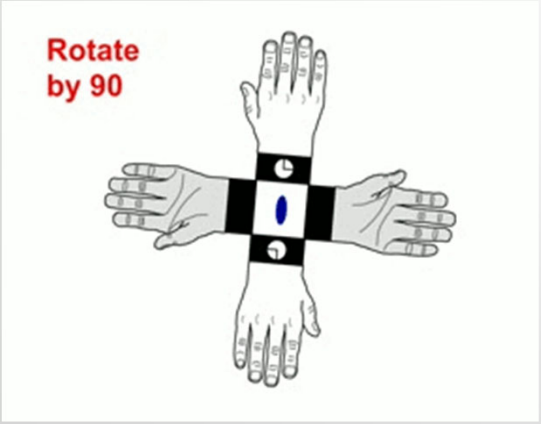


Ejes de rotación

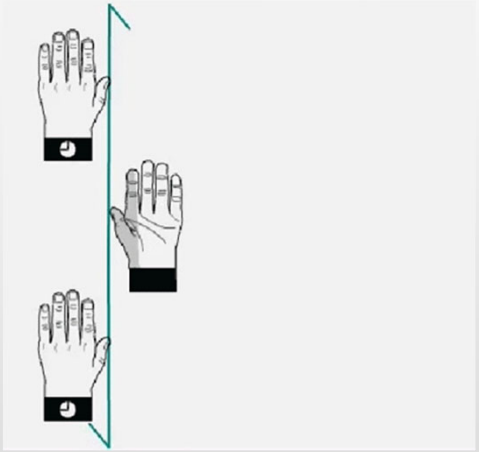


Centro de Inversión

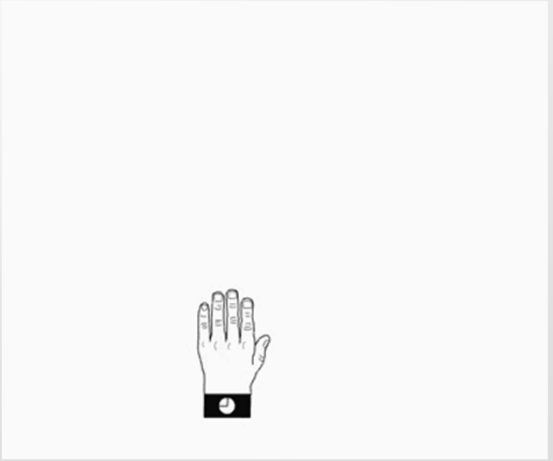
Elementos de simetría puntual



Rotación impropia



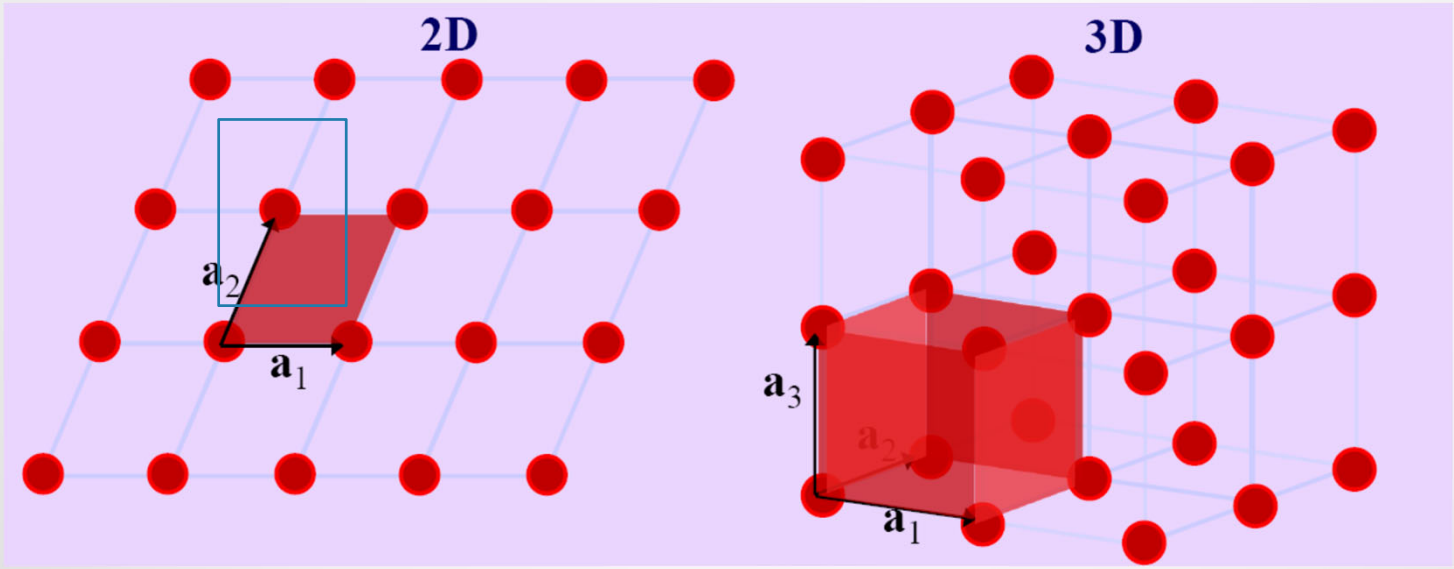
Eje helicoidal (02)



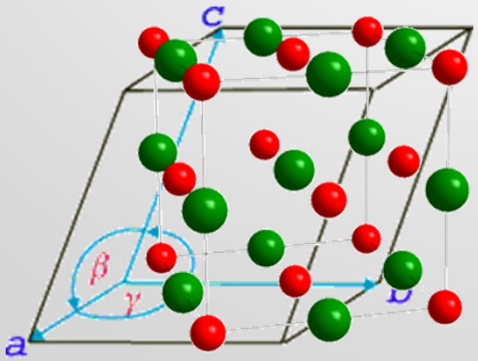
Plano de deslizamiento

Elementos de simetría espacial

Concepto de Celda Unidad. Celda asímetrica



Simetría traslacional



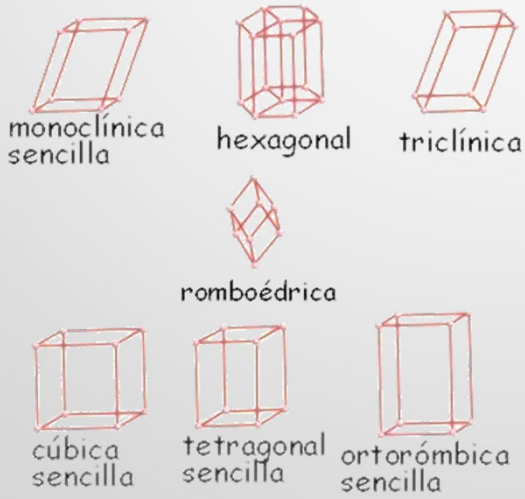
Descripción de la celda unidad:

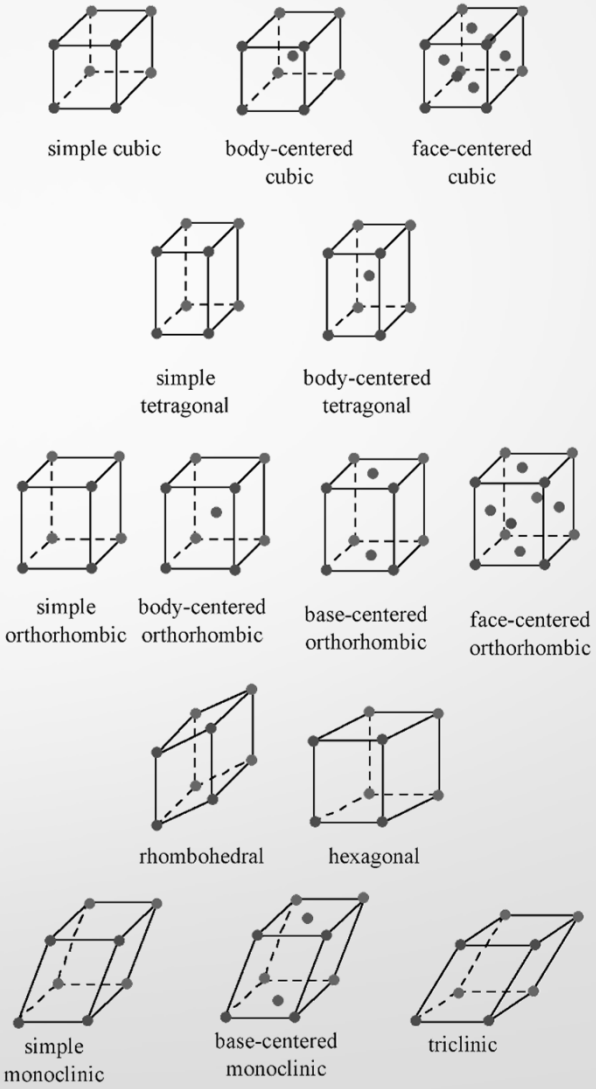
- Dimensiones (a,b,c,α,β,γ)
- Motivo: Atómos y coordenadas
- Factores de vibración
- Ocupación

Generación de la celda unidad a partir de las operaciones de simetría

SIMETRÍA : Elementos básicos

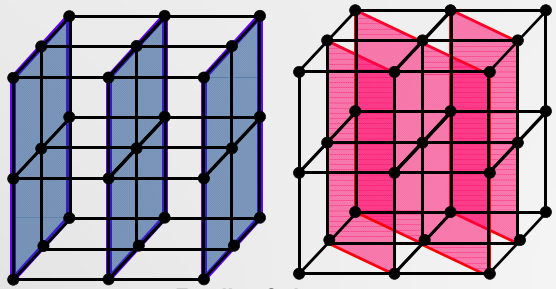
System	Defining symmetry	Unit cell geometry
Triclinic	Only translational	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$
Monoclinic	One diad parallel to [010] or/and one mirror plane perpendicular to [010]	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta > 90°$
Orthorhombic	Each axis should be parallel to a diad or/and perpendicular to a mirror plane	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$
Trigonal	One triad parallel to [001]	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$
Hexagonal	One hexad parallel to [001]	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$
Tetragonal	One tetrad parallel to [001]	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$
Cubic	Four triads parallel to <111>	$a = b = c$; $\alpha = \beta = \gamma = 90°$





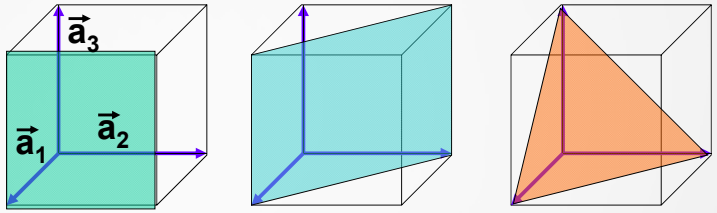
7 sistemas cristalinos, **14** redes de Bravais
32 clases cristalinas, **230** grupos de espacio

Planos cristalinos. Índices de Miller



Family of planes

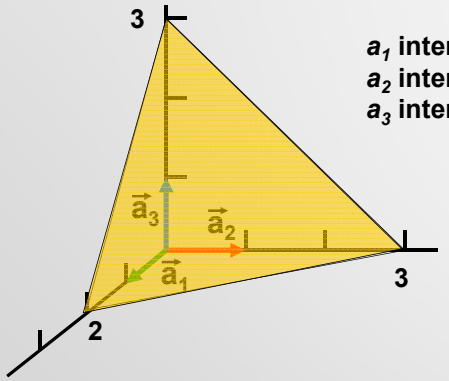
Crystal planes in cubic lattices



(100) $d_{hkl} = a$

(110) $d_{hkl} = a/\sqrt{2}$

(111) $d_{hkl} = a/\sqrt{3}$

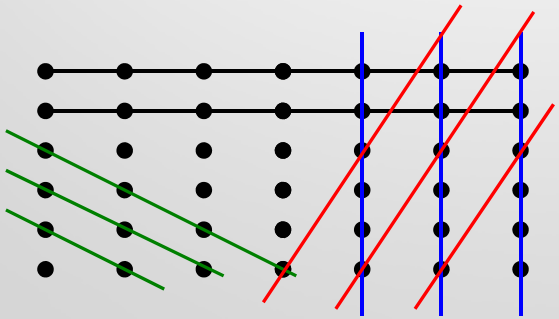


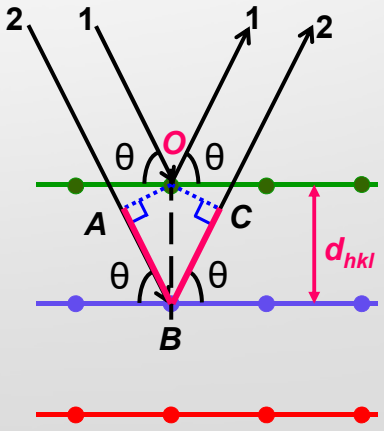
Reciprocal

a_1 intercept is 2 ⟶ 1/2
a_2 intercept is 3 ⟶ 1/3
a_3 intercept is 3 ⟶ 1/3

Hence Miller indices are 3,2,2 and are depicted by

(*hkl*) = (322)





Rays 1 and 2 interfere constructively if Total Path Difference is integral multiple of the wavelength, λ

Total p.d. = *AB + BC*

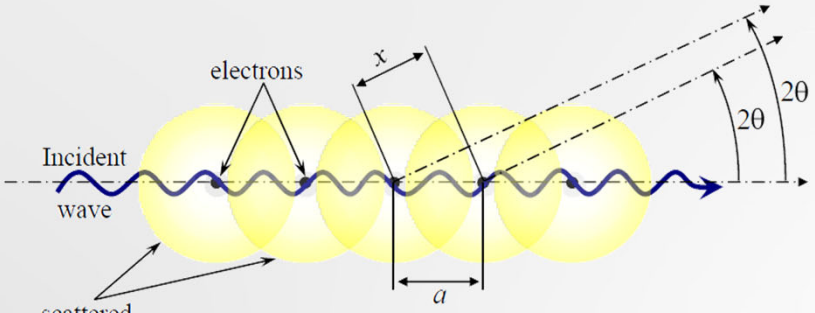
ΔOAB and ΔOCB are equivalent.

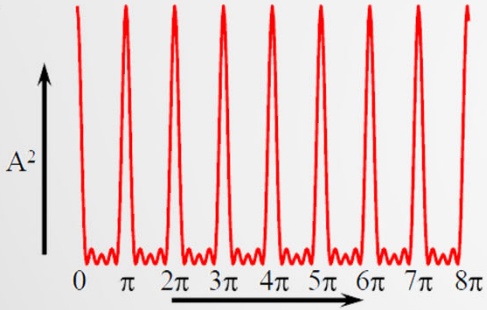
$\therefore AB=BC=d_{hkl}\sin\theta$

Diffraction condition is:

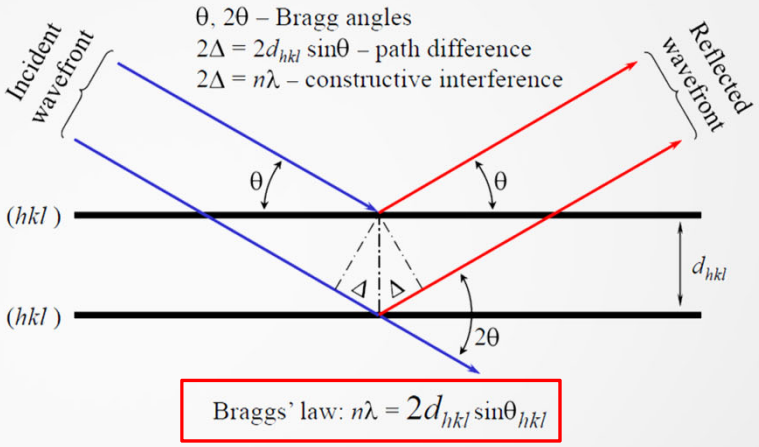
$2\, d_{hkl} \sin\theta = n\,\lambda$

Fundamentos de difracción





$$\varphi = 2\pi\frac{a-x}{\lambda} = 2\pi\frac{a(1-\cos 2\theta)}{\lambda} = 4\pi\frac{a\sin^2\theta}{\lambda}$$



LEY DE BRAGG

Relación entre la distancia interplanar, la longitud de onda de los RX y el ángulo de difracción en el que se observa la condición de máximo para la interferencia (constructiva).

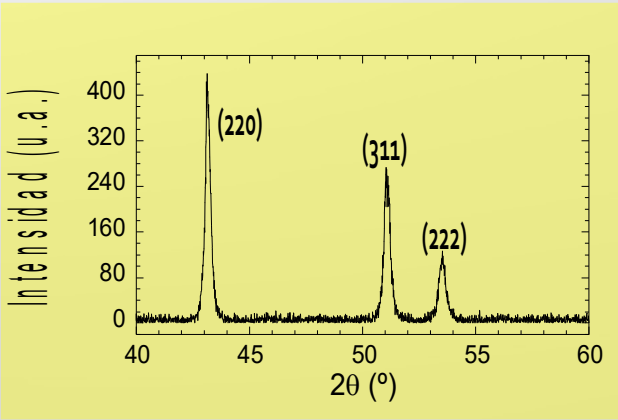
Intensidad de difracción

$$I(\varphi) \propto f^2(\varphi)\frac{\sin^2 N\varphi}{\sin^2\varphi}$$

Factor de *Scattering* atómico

Factor de *Estructura*

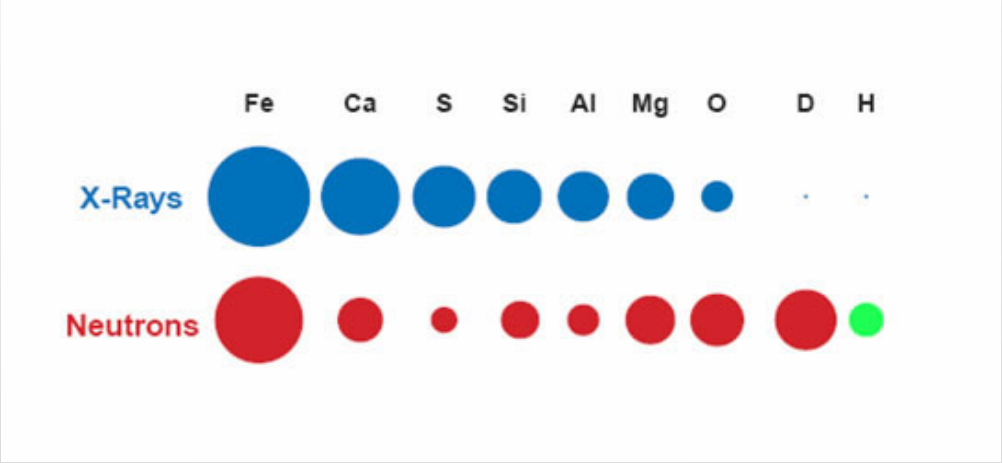
$$I(hkl) \propto F^2(hkl)\frac{\sin^2 U_1 h\pi}{\sin^2 h\pi}\frac{\sin^2 U_2 k\pi}{\sin^2 k\pi}\frac{\sin^2 U_3 l\pi}{\sin^2 l\pi}$$



Difracción. Técnicas experimentales

Técnicas de difracción convencionales para el análisis estructural

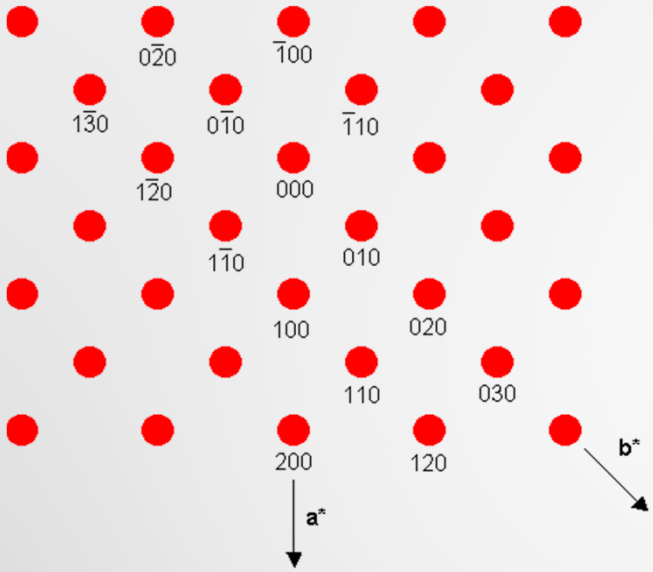
- **Polvo** (muestras policristalinas)
  - Difracción de neutrones (NPD)
  - Difracción de rayos X (XRD)
  - Difracción de electrones (ED)
- **Monocristal** (Todas las fuentes)

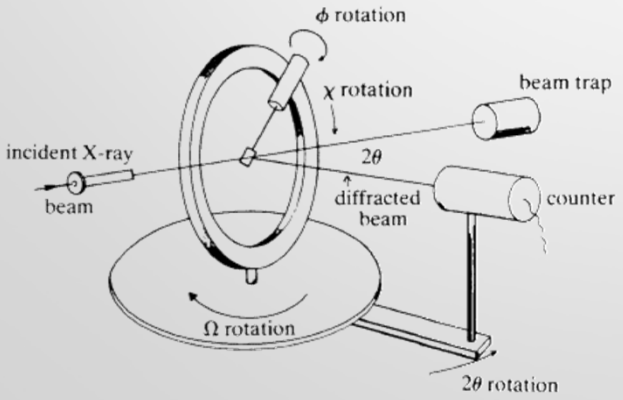


Difracción. Técnicas experimentales

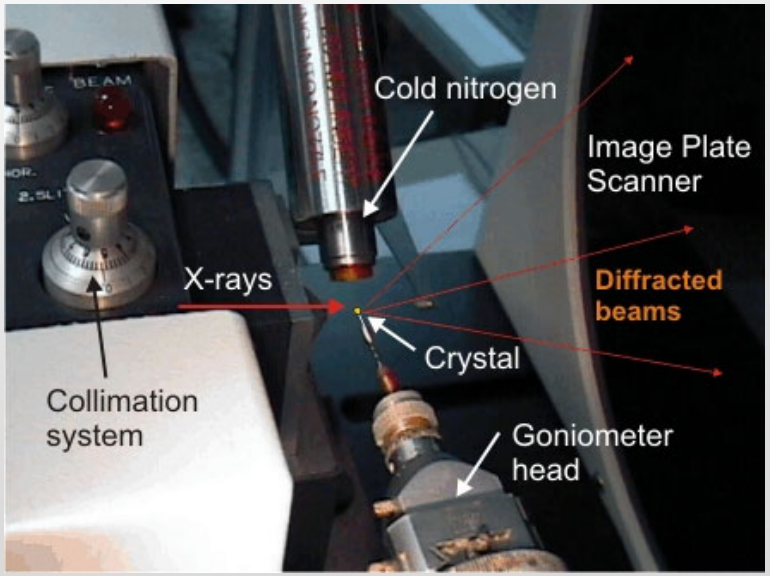
	Rayos x Laboratorio	Rayos x Sincrotrón	Neutrones
Intensidad		✓	
Resolución	✓	✓	
Problemas Absorción	↓ λ / reflexión	↓ λ / reflexión	✓
Discrim. átomos			✓
Atomos ligeros			✓
Muestras pequeñas	✓	✓	
Disponibilidad	✓✓✓		

Difracción de rayos X en monocristal

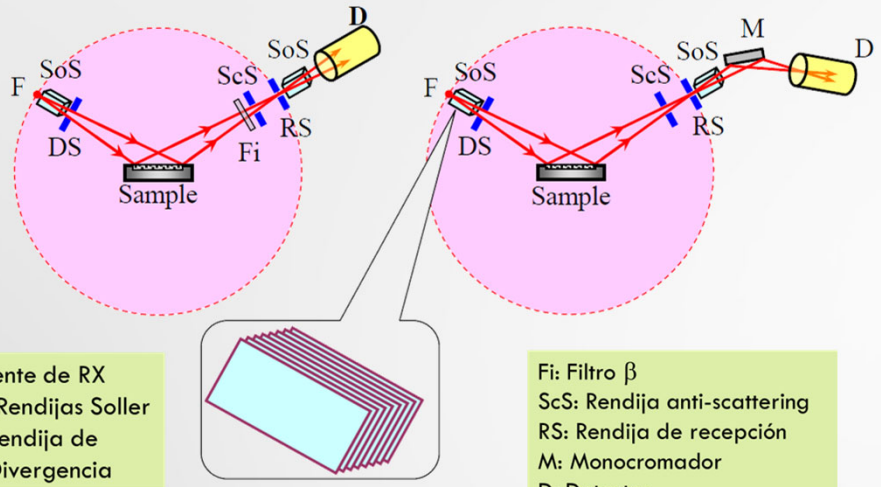




Esquema de un difractómetro de 4 círculos

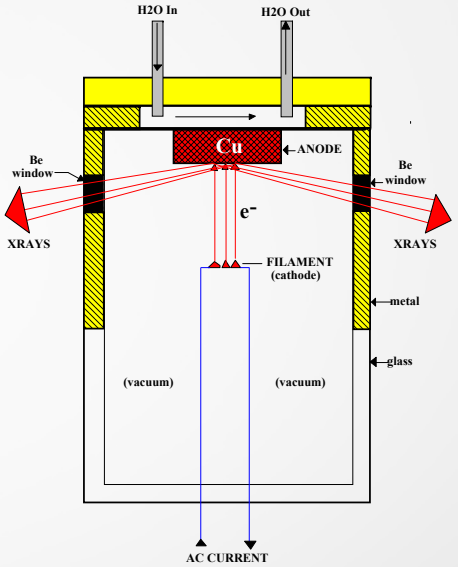


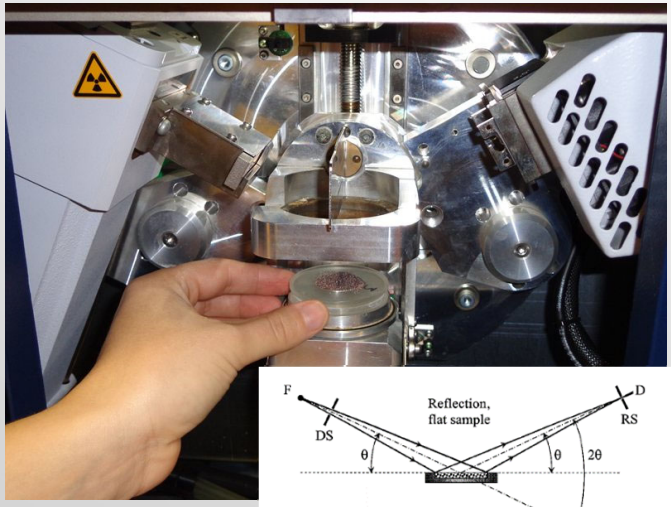
Difracción de rayos X en polvo

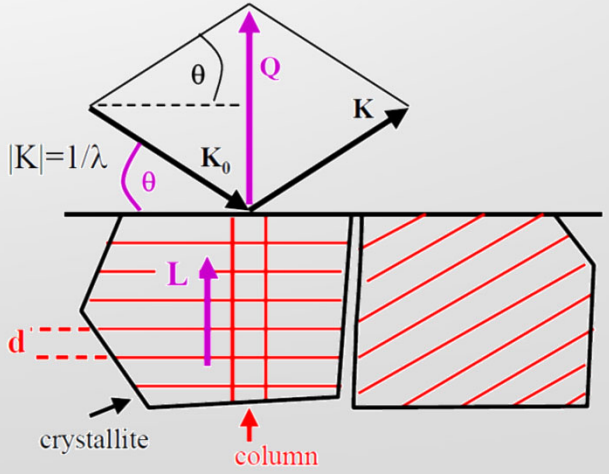


F: Fuente de RX
SoS: Rendijas Soller
DS: Rendija de Divergencia

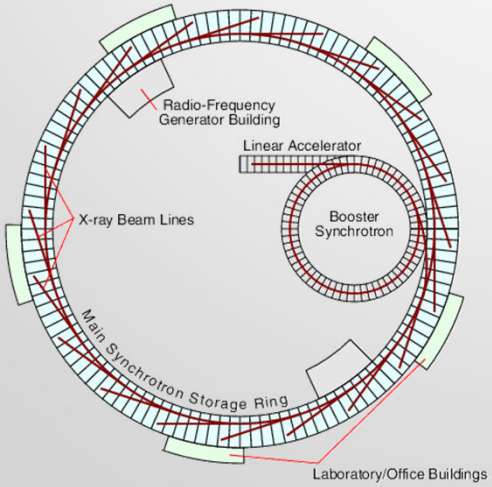
Fi: Filtro β
ScS: Rendija anti-scattering
RS: Rendija de recepción
M: Monocromador
D: Detector







Radiación sincrotrón

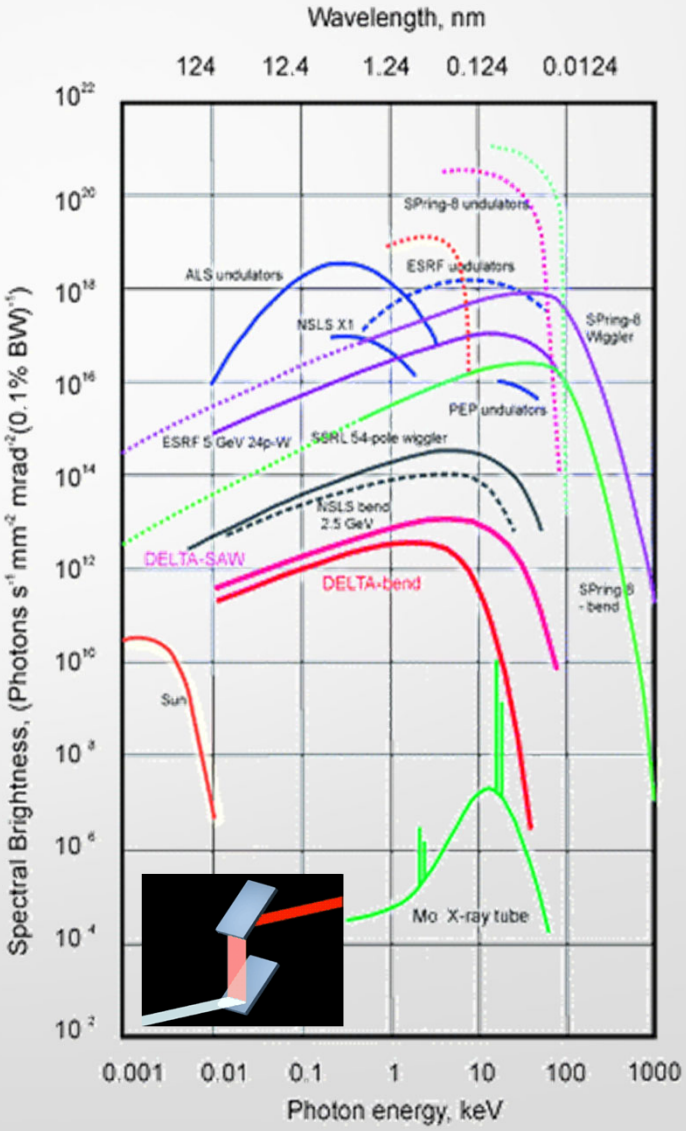


ALBA

ESRF

diamond

SOLEIL
SYNCHROTRON



Difracción de RX en polvo