Advanced Characterization Methods II : Introduction

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ESRF and ILL
Grenoble

MET
Univ. Lille

IR spectrometer
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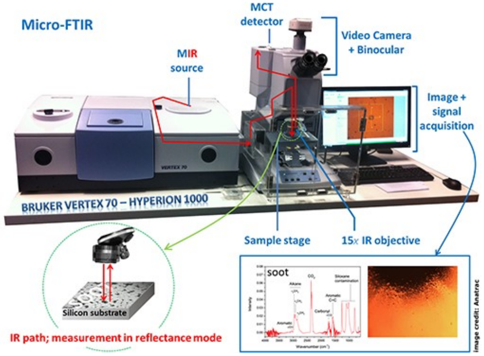

Outline

- Introduction/ diffraction
  - Course: 4h
  - Practicals: 6h
  - Who: Sébastien Merkel
- Electron microscopy
  - Course: 10h
  - Practicals: 10h
  - Who: Damien Jacob

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1- Introduction

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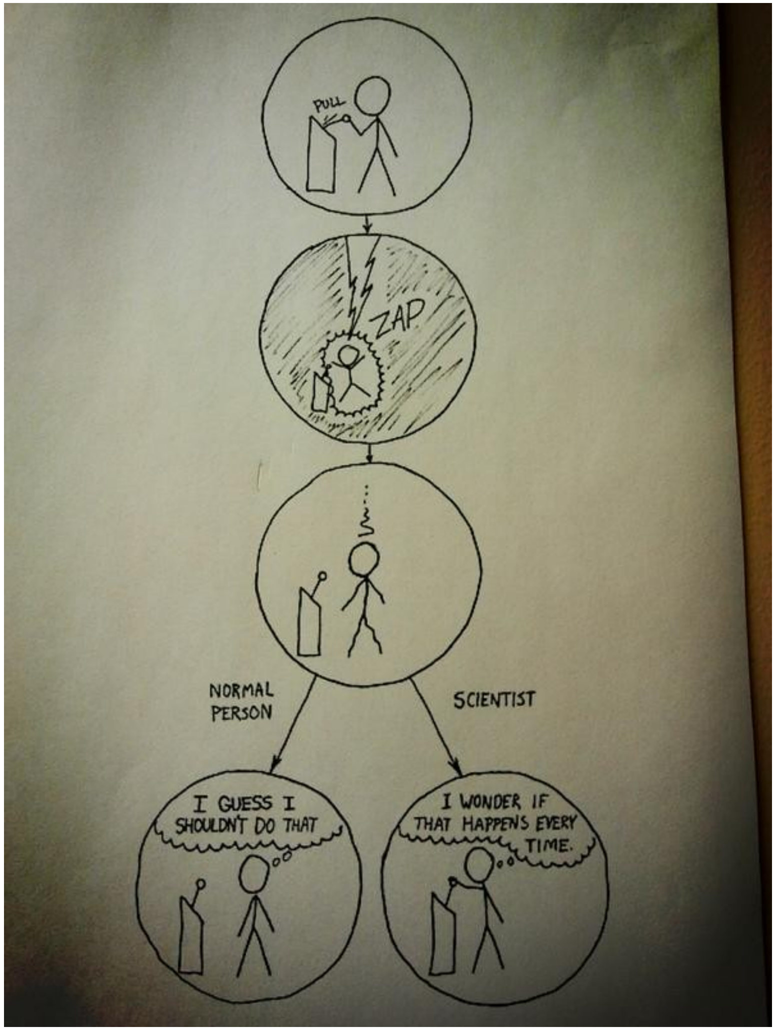
Why would run experiments?

Scientific reasons

- Curiosity
- Measure physical properties
- Test hypotheses from theory
- Test model predictions
- Ex-nihilo discoveries

Things I should not say...

- To play with nice equipment
- Because I like it
- Because experimental campaigns are exciting



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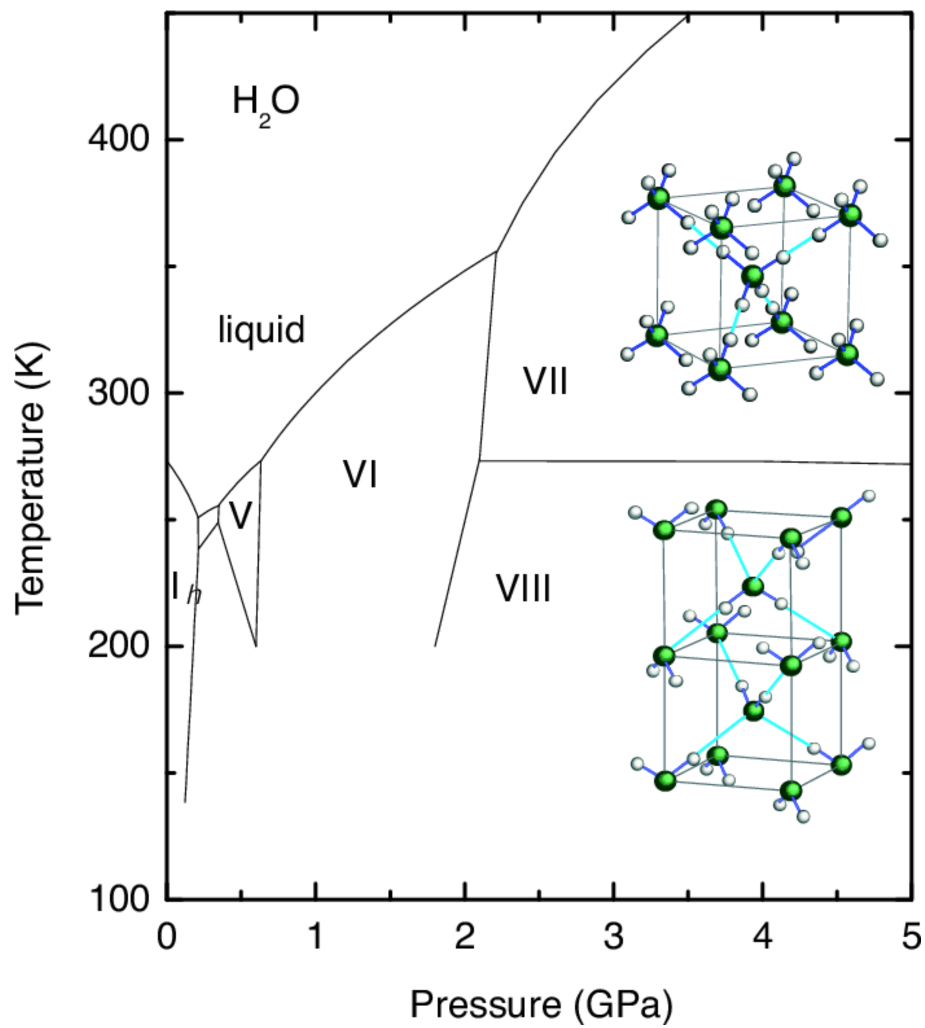
Physical properties measurement

Materials science relies on the measurement of multiple physical properties

- Melting temperature
- Phase diagrams
- Crystallographic structure
- Elastic moduli
- Flow laws
- Type of defects
- etc

Those properties can not be guessed. They must be characterized and measured.



H_2O phase diagram
Klotz et al Europhys. Lett. (2005)

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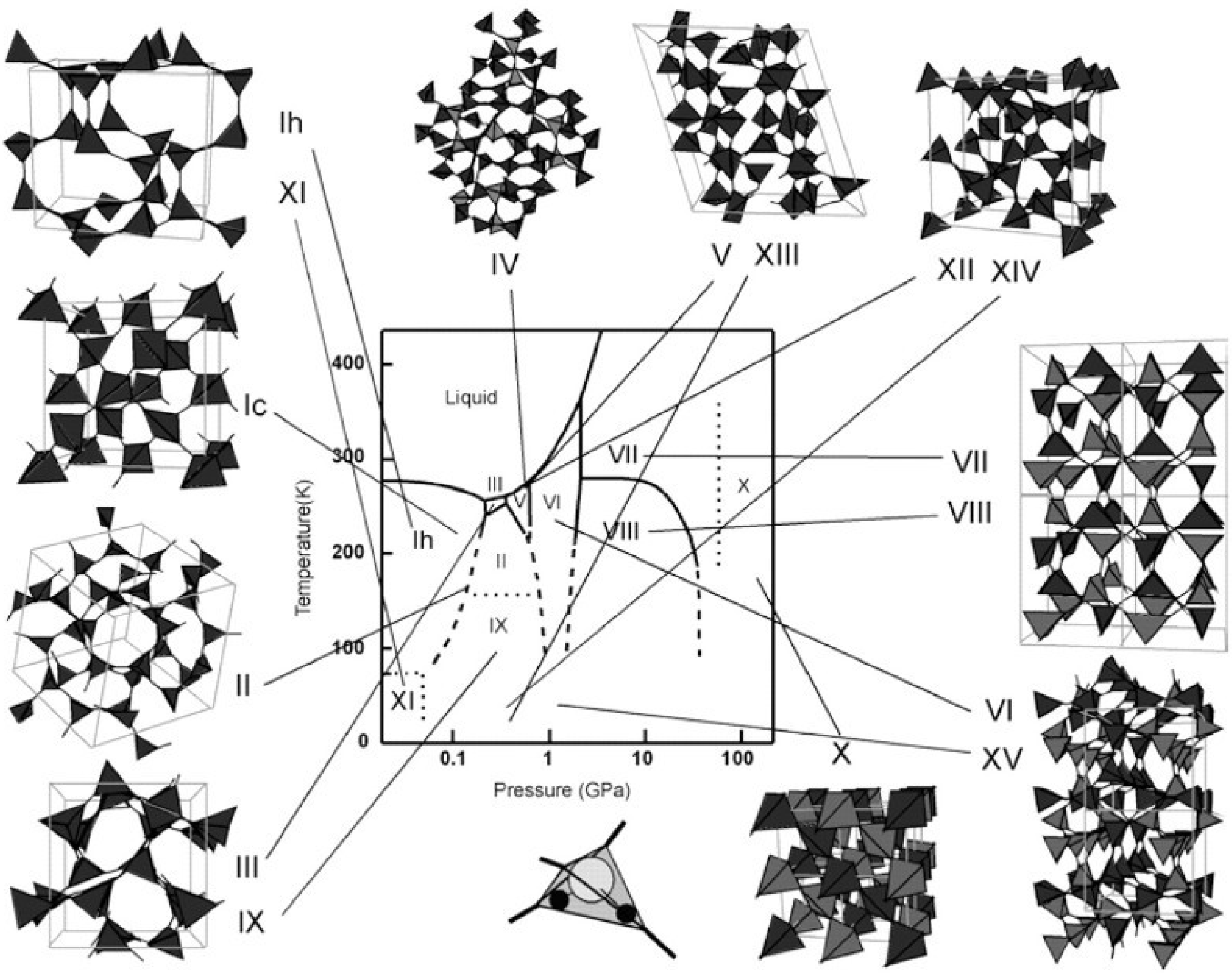
Physical properties measurement



H$_2$O phase diagram
Umemoto Rev. Miner. Geochem. (2015)

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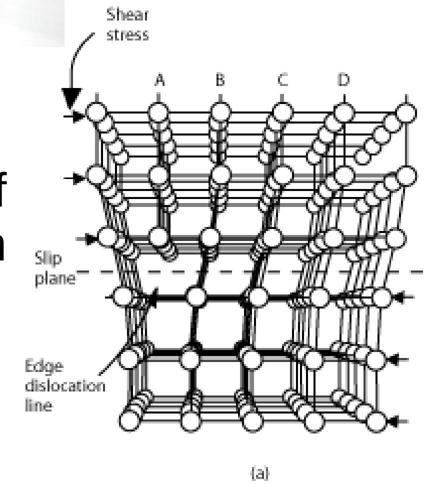
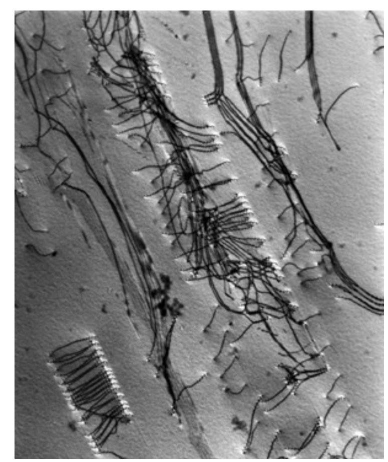
Test hypotheses from theory

- Observation of a physical phenomenon
  - ex. : you can form a metal
- Interpretation with available tools
  - ex. : crystallography
- Problem with theory
  - ex. : you need to break too many bonds
- New hypothesis
  - ex : defect called dislocations
- Validation experiment
  - ex : observation of dislocations in the electron microscope

Forming of metals

Concept of dislocation





Observation of dislocations in electron microscopy

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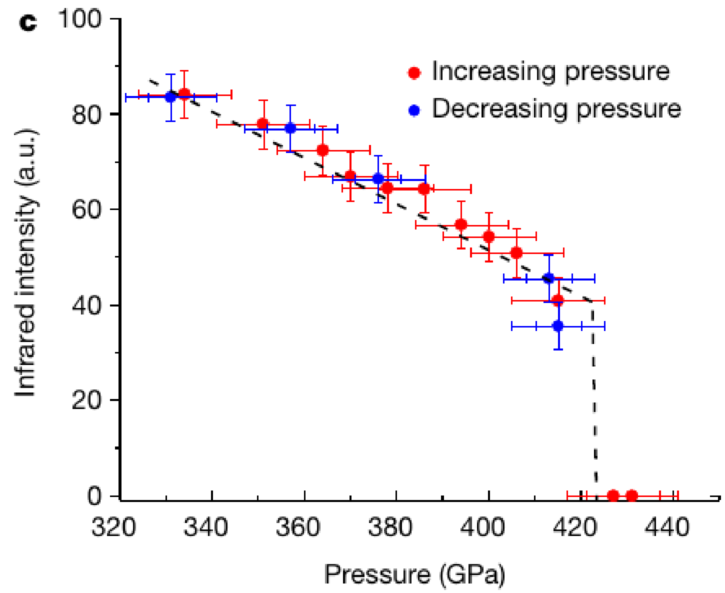
Test model predictions

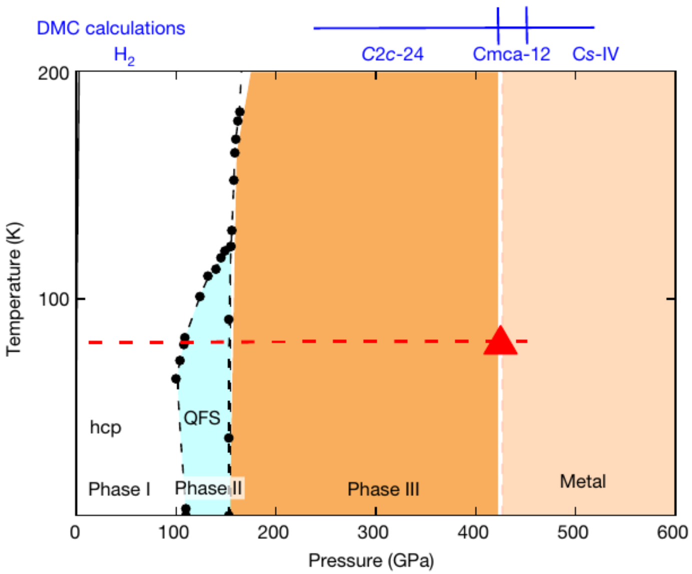
Theoretical prediction

- Hydrogen under pressure: atoms get closer, gap should close, metallic state at ~25 GPa (Wigner and Huntington, 1935)
- Quantum calculation (Tse and Kung, 1995 for instance): gap closure at 160 GPa

Test expérimental de la prédiction théorique

- Loubeyre et al, Nature, 2020
  - infra-red spectroscopy, drop in transmitted intensity and 425 GPa
  - Probably metallic state above 425 GPa





Conclusion

- Band gap does decrease with hydrostatic pressure
- Predictions of the pressure values were incorrect → needed improvement in quantum mechanics calculations

Note : 100 GPa = 1 million atmospheres

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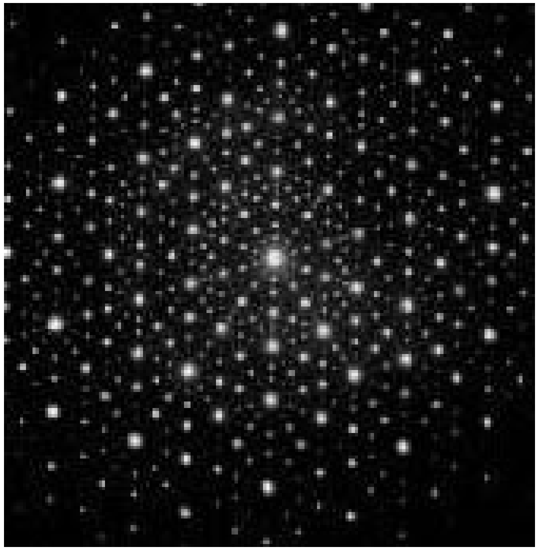
Quasi-crystal
diffraction pattern

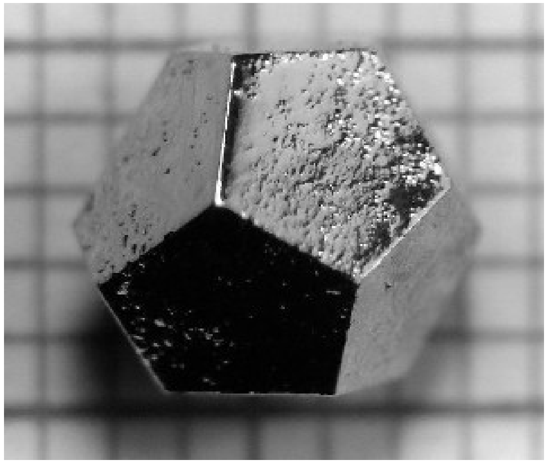


Discoveries of unexpected effect, properties, or de structures

Ex : quasi-crystals

- Mathematical demonstration (based on hypotheses regarding the arrangement of shapes in space): crystals should show 2-fold, 3-fold, 4-fold or 6-fold rotation axes
- 1982: observation of diffraction patterns with 5-fold rotation axes (Dan Shechtman)
- Quasi-crystal : non-periodic arrangement of atoms, but with a discrete diffraction signal
- 1992: change of definition of « crystal » at the International Union of Crystallography
- 2011: Nobel prize

Look at interview on
https://www.youtube.com/watch?v=EZRTzOMHQ4s
(especially at 6:10 – 9:00)



Quasicristal
Ho-Mg-Zn

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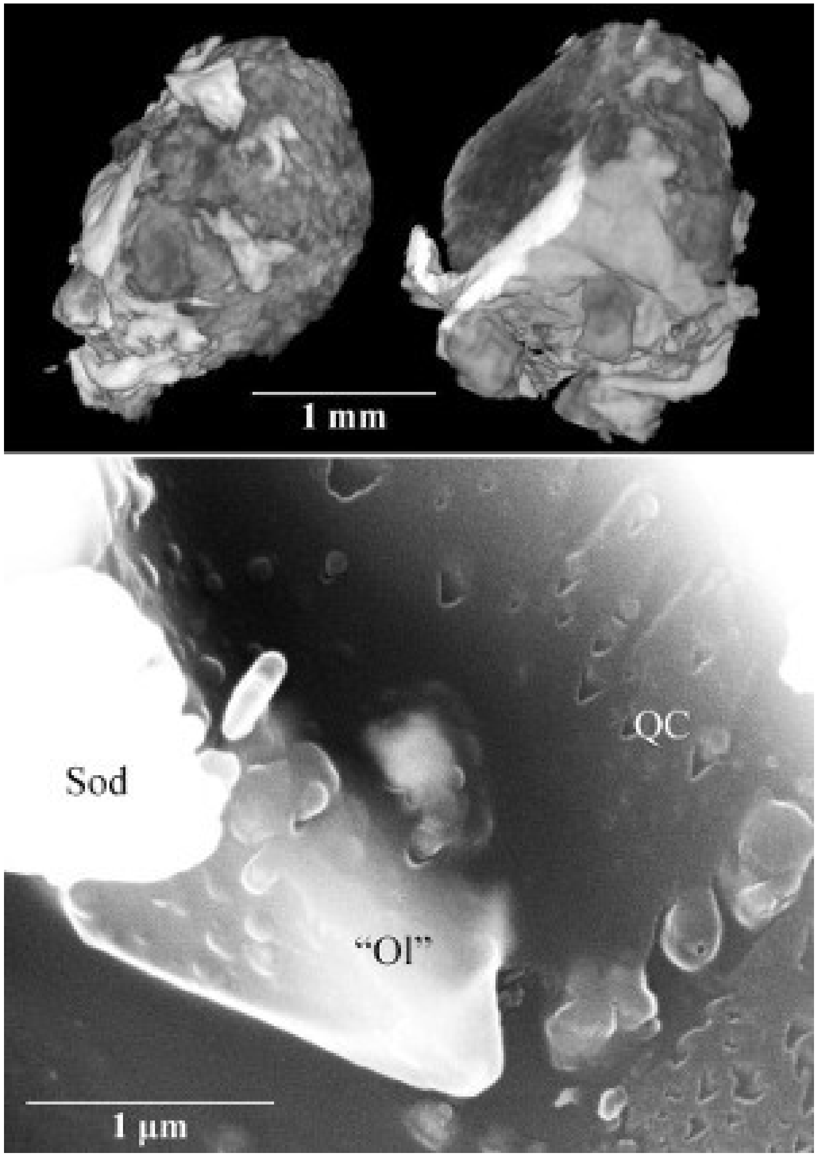
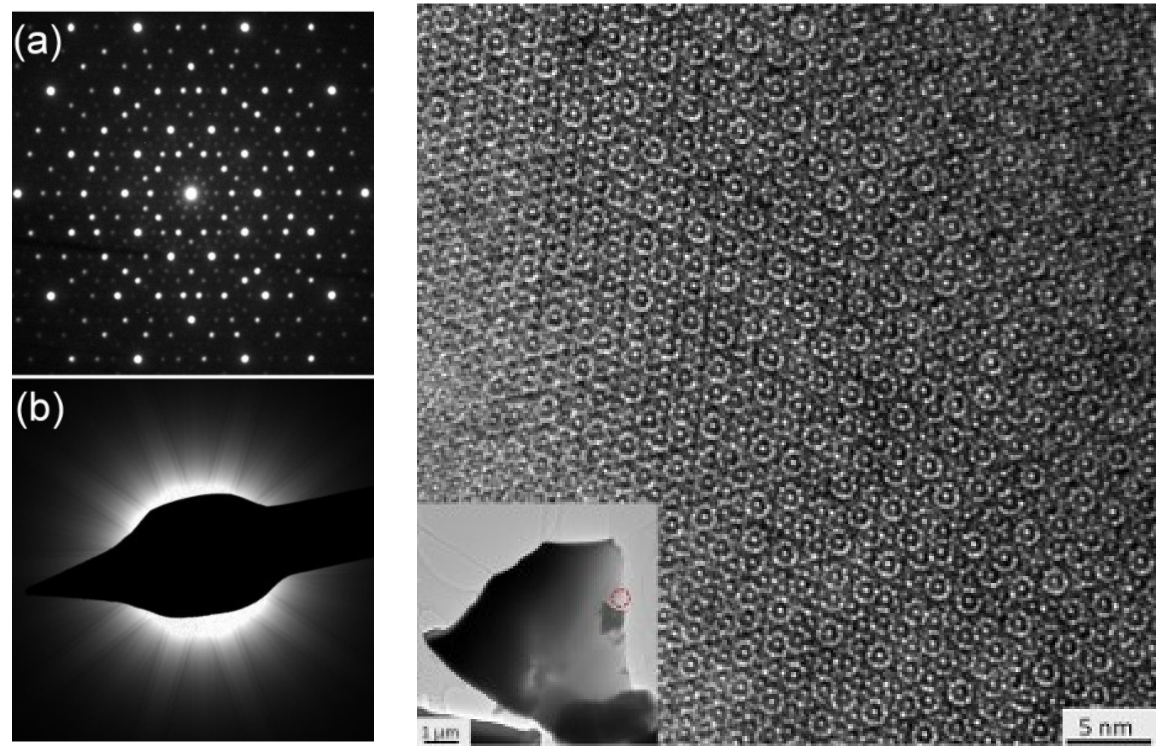
Ex-nihilo discoveries





An example of a natural quasi-crystal
$Al_{71}Ni_{24}Fe_5$ Khatyrka meteorite

Bindi et al, Sci Rep. 2015; 5: 9111

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2- Classes of experiments

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Structural characterization experiments

"Classical" experiments in structural characterization

- Diffraction (X-rays, neutrons, electrons)
  interaction between an incoming wave and an obstacle
  - Atomic arrangement
  - Microstructures
  - Defects
  - Etc
- Spectroscopy
  interaction between matter and radiation as a function of energy (or wavelength, frequency, etc)
  - Chemical composition
  - Atomic liaisons
  - Vibration modes
  - Etc
- Imaging
  - Microstructures
  - Chemical analysis
  - Defects, atomic arrangements
  - Etc

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2.1- Classes of experiments
Spectroscopy

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Types of spectroscopy

Domaine de longueur d'onde	Longueur d'onde	Type de spectroscopie	Commentaires
Radiofréquence	> 100 µm	Spectroscopie de résonance magnétique nucléaire	Liaison chimique, conformation moléculaire, distances interatomiques
		Résonance paramagnétique électronique	entités paramagnétiques (radicaux, espèces transitoires...)
		Résonance ferromagnétique	aimantation matériaux ferromagnétiques
Micro-ondes	> 30 µm	Spectroscopie rotationnelle	structure petites molécules (eau,ozone, chlorure d'hydrogène gazeux...) avec une haute précision
Infrarouge	de 1 à une vingtaine de µm	Spectroscopie infrarouge	groupements fonctionnels d'une molécule organique, liaisons chimiques, structure de la molécule
		Spectroscopie proche infrarouge	
		Spectroscopie vibrationnelle	
visible et ultraviolet	×10^2 nm	Spectroscopie ultraviolet-visible	quantification composés organiques conjugués et métaux de transition
		Spectrophotométrie	
		Spectroscopie Raman	fréquences des modes de vibration du cristal/de la molécule, énergie des ondes de spin
		Spectroscopie de fluorescence	molécules fluorescentes, environnement local de la molécule (conformation et interactions)
		Spectroscopie de corrélation de fluorescence	
		Spectroscopie Brillouin	constantes élastiques et caractéristiques magnétiques d'un matériau (aimantation, échange...)
rayons X	< 100 nm	Spectrométrie d'absorption des rayons X (EXAFS et XANES)	EXAFS: environnement local d'un atome, distances avec les plus proches voisins XANES: état d'oxydation , coordinence
		Spectrométrie photoélectronique X (XPS)	XPS: composition chimique à la surface d'un matériau (état d'oxydation , quantification d'éléments...)
		Spectrométrie de fluorescence X classique et en réflexion totale	quantification d'éléments chimiques
		Microsonde de Castaing	quantification d'éléments chimiques (analyse locale de l'ordre de 1 µm³)
rayons gamma	0.01 nm	Spectrométrie gamma	éléments radioactifs
		Spectroscopie Mössbauer	état d'oxydation, ordre magnétique

Tableau wikipedia, not translated in English as of Oct 2022!

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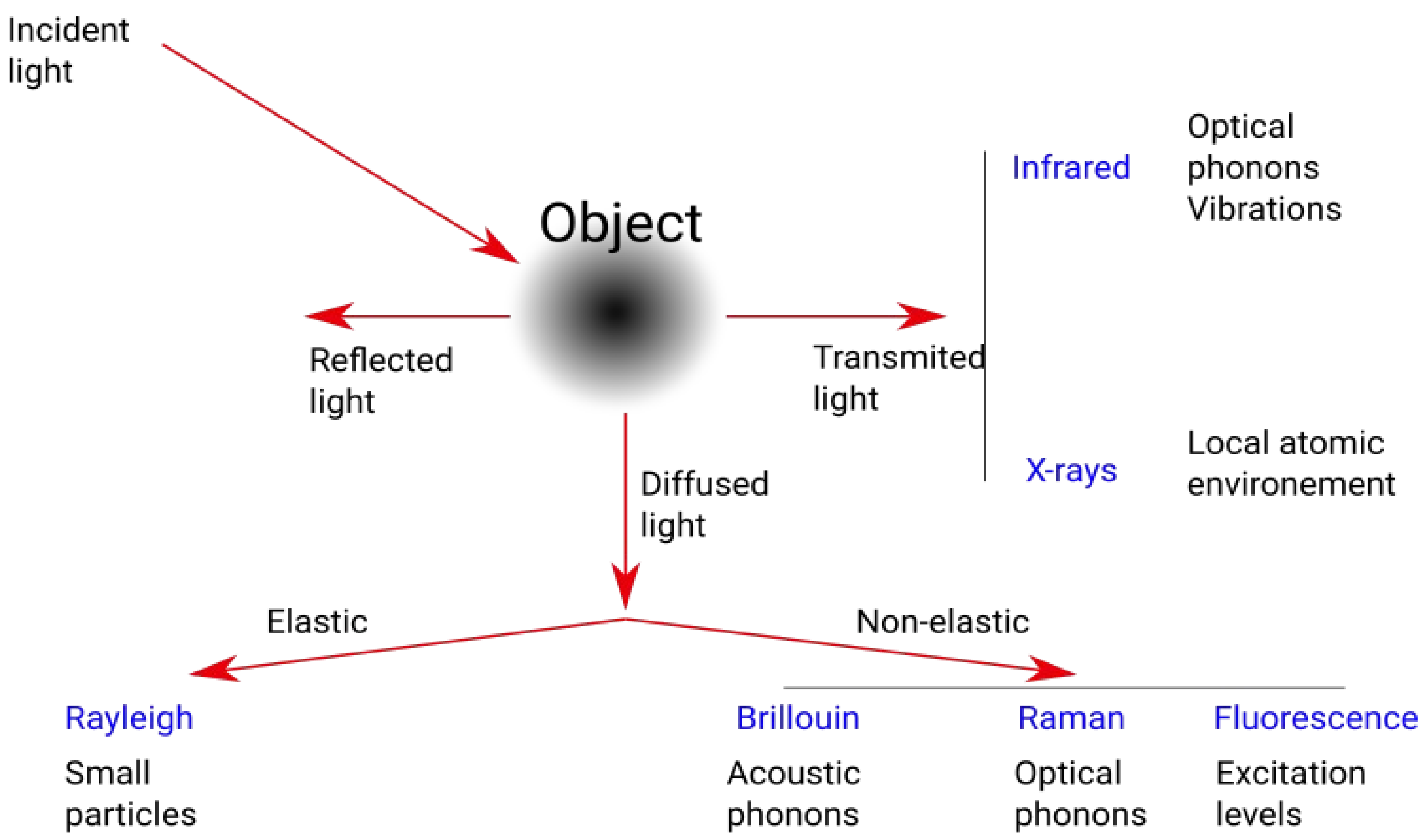
Spectroscopy examples



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Example: infrared and Raman spectroscopy

Principles of infrared and Raman spectroscopy

- Energy exchange between incoming light and vibrations and rotations in a material

Raman sources: visible light

Infrared sources: infrared light

Vibration mode: depends on the crystal structure, the molecule, etc

Some are active (visible) in Raman spectroscopy, others in infra-red

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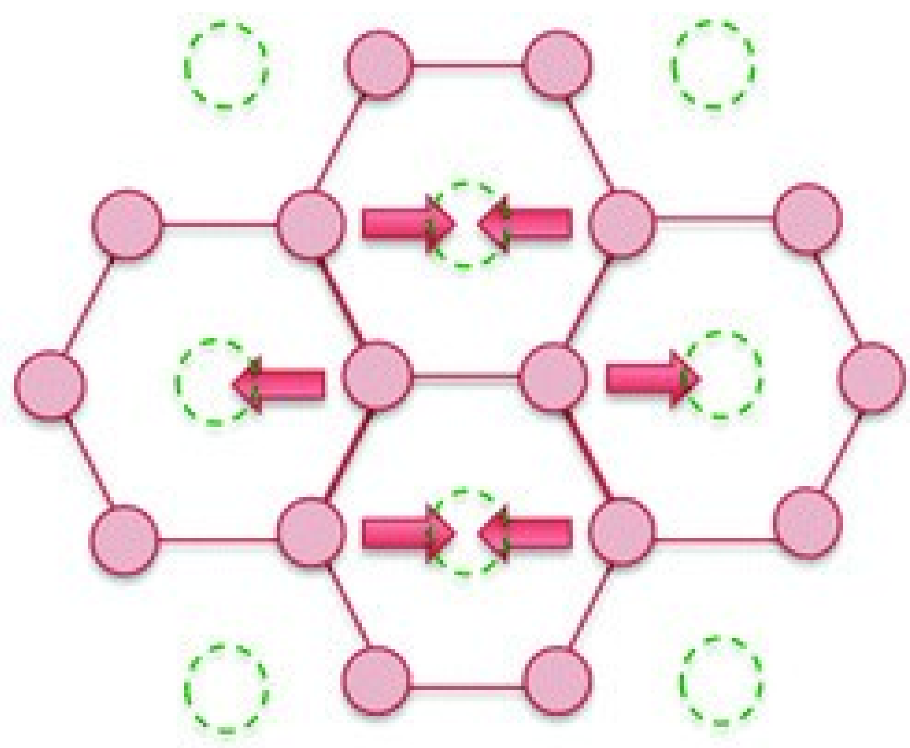
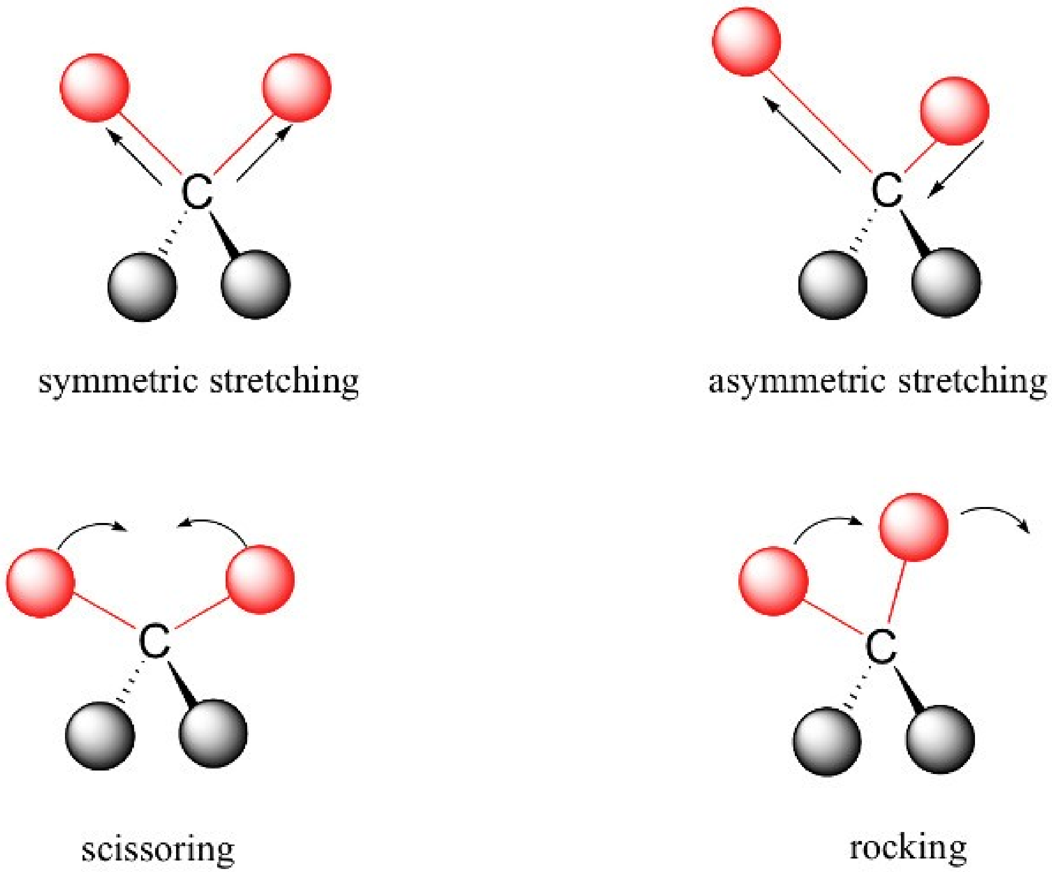
E_{2g} modes for boron atoms in MgB_2
Alarco et al, Phys. Chem. Chem. Phys., 2014





Mode examples in molecules
Source : UC Davis ChemWiki

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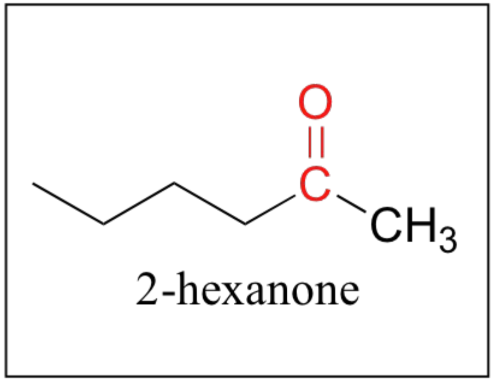
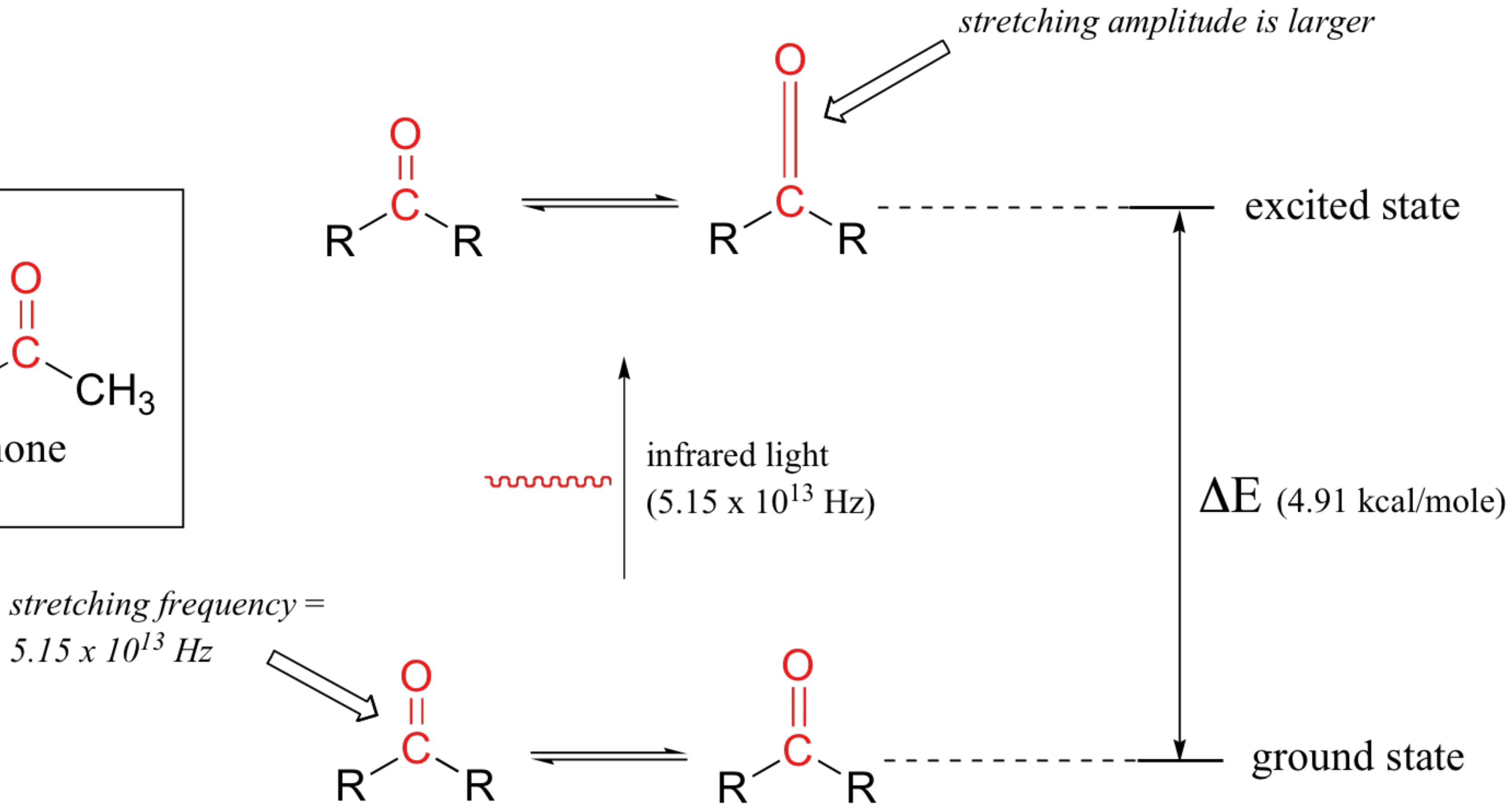
Example in infrared spectroscopy





Source : UC Davis ChemWiki

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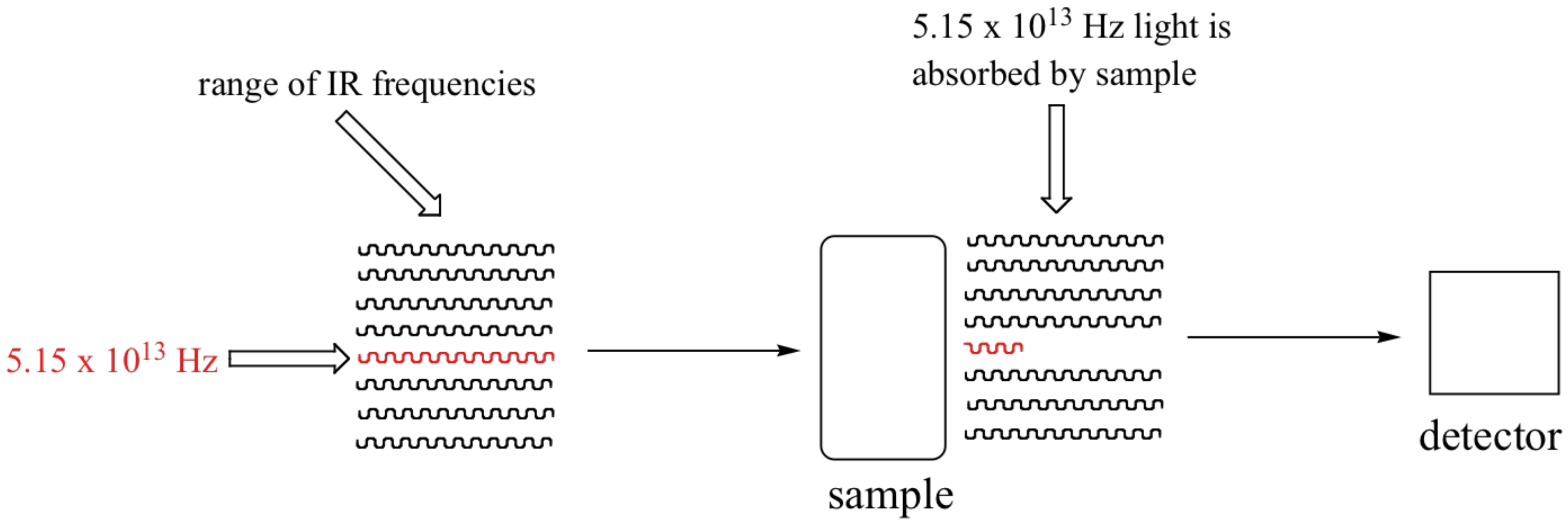
Principles of infrared spectroscopy



Source : UC Davis ChemWiki

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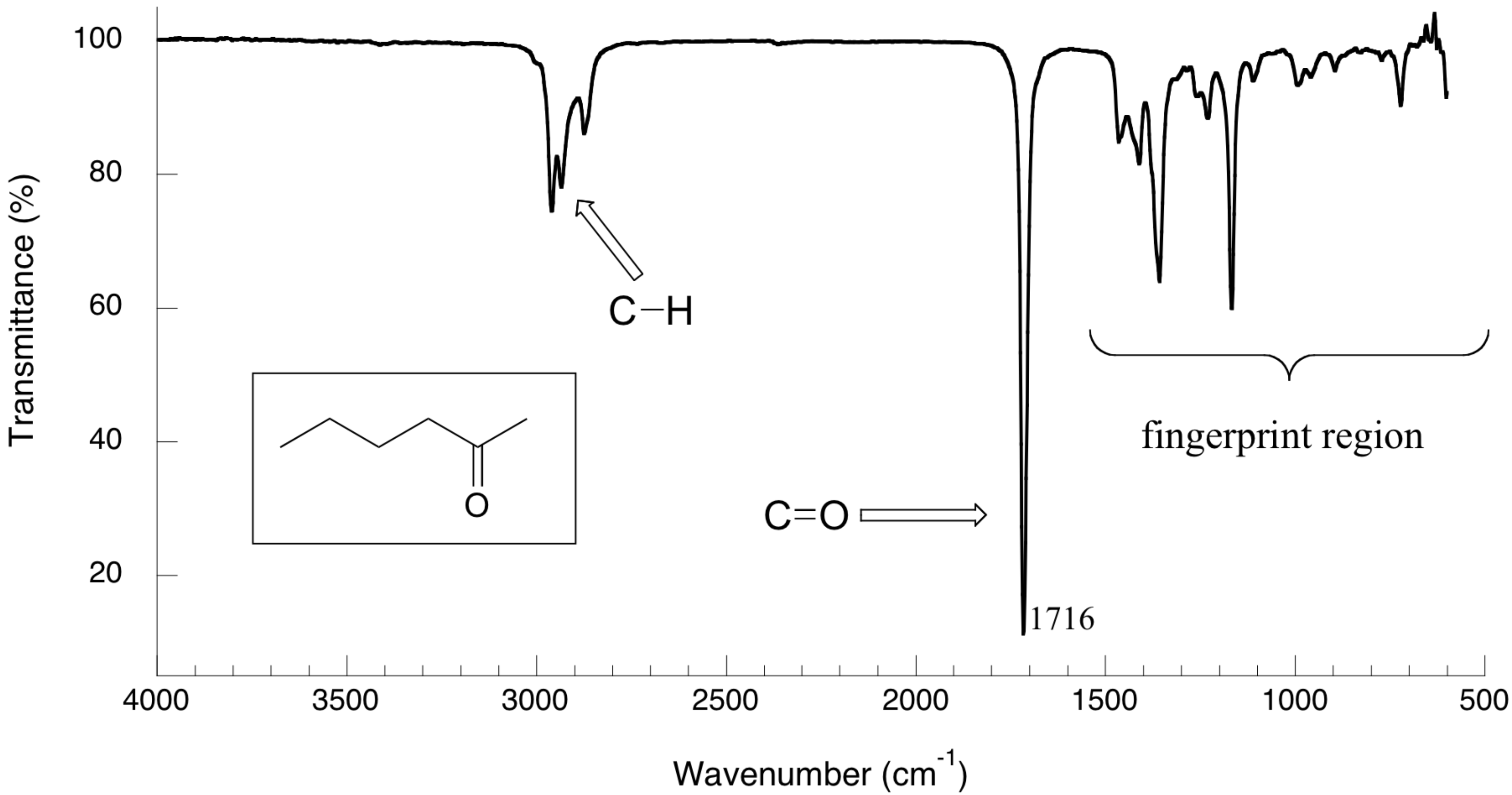
Sample infrared spectrum



Source : UC Davis ChemWiki

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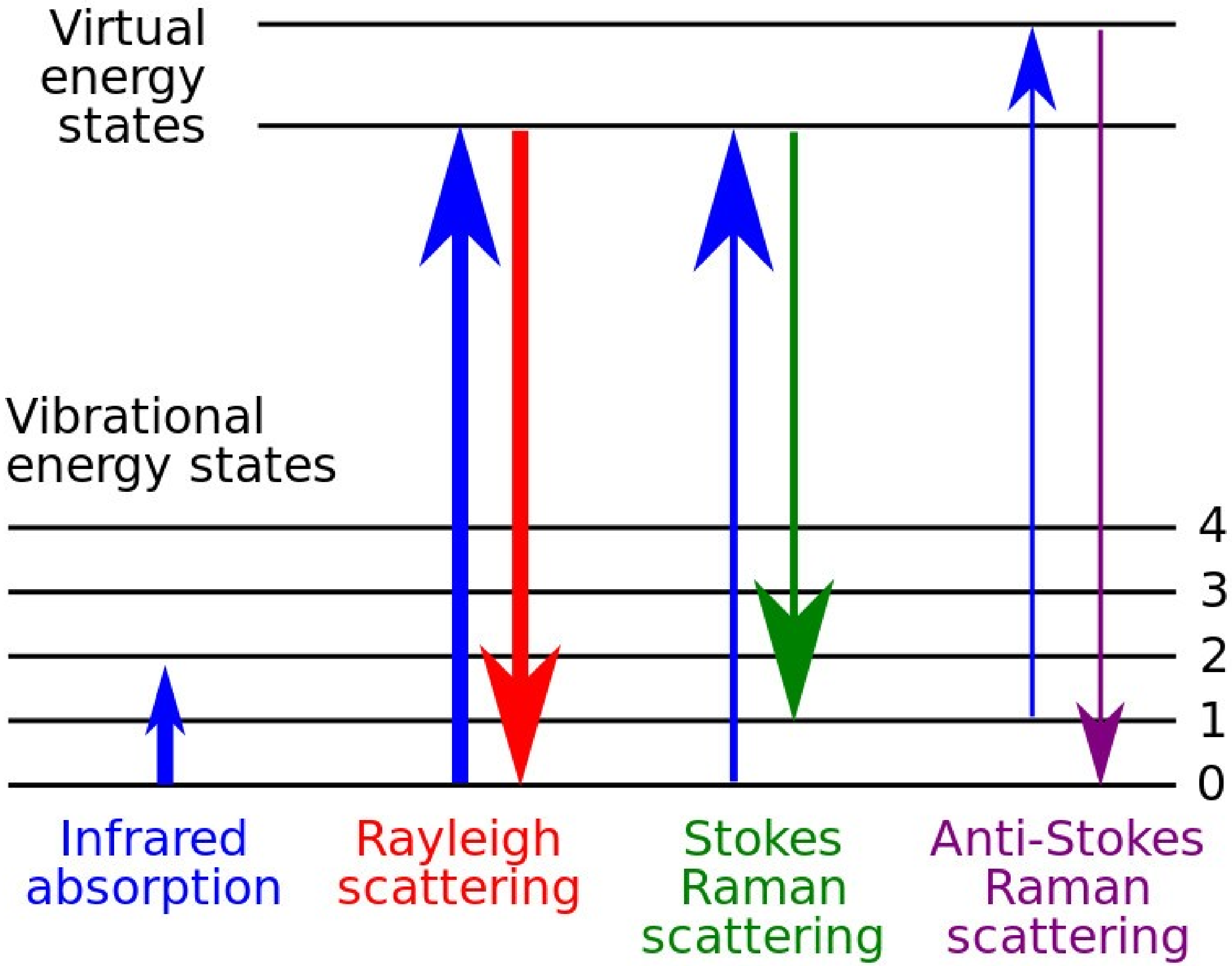
Principles of Raman spectroscopy



Source : Wikipedia

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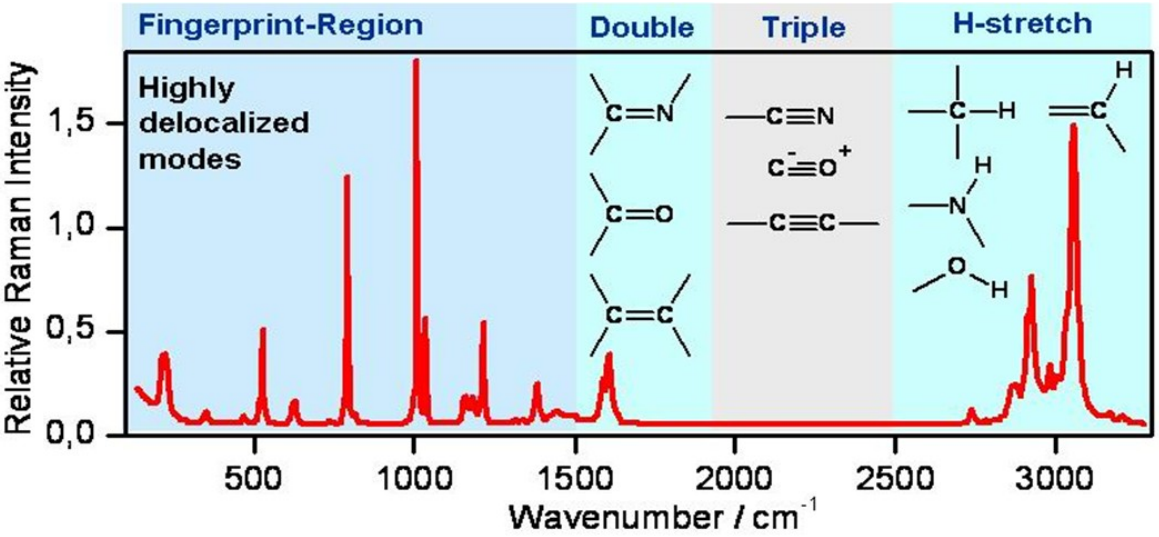

Stokes modes intensity vs. energy

Plotted in cm^{-1}, relative to the Rayleigh diffusion line

Ex :

- laser at 532.0 nm: $E_0 = 3.733 \times 10^{-19}$ J
- mode at 3000 cm^{-1}
  - $\Delta E = 5.9 \times 10^{-20}$ J
  - Stokes mode at E-ΔE : 631 nm
- mode at 100 cm^{-1} : 536.4 nm

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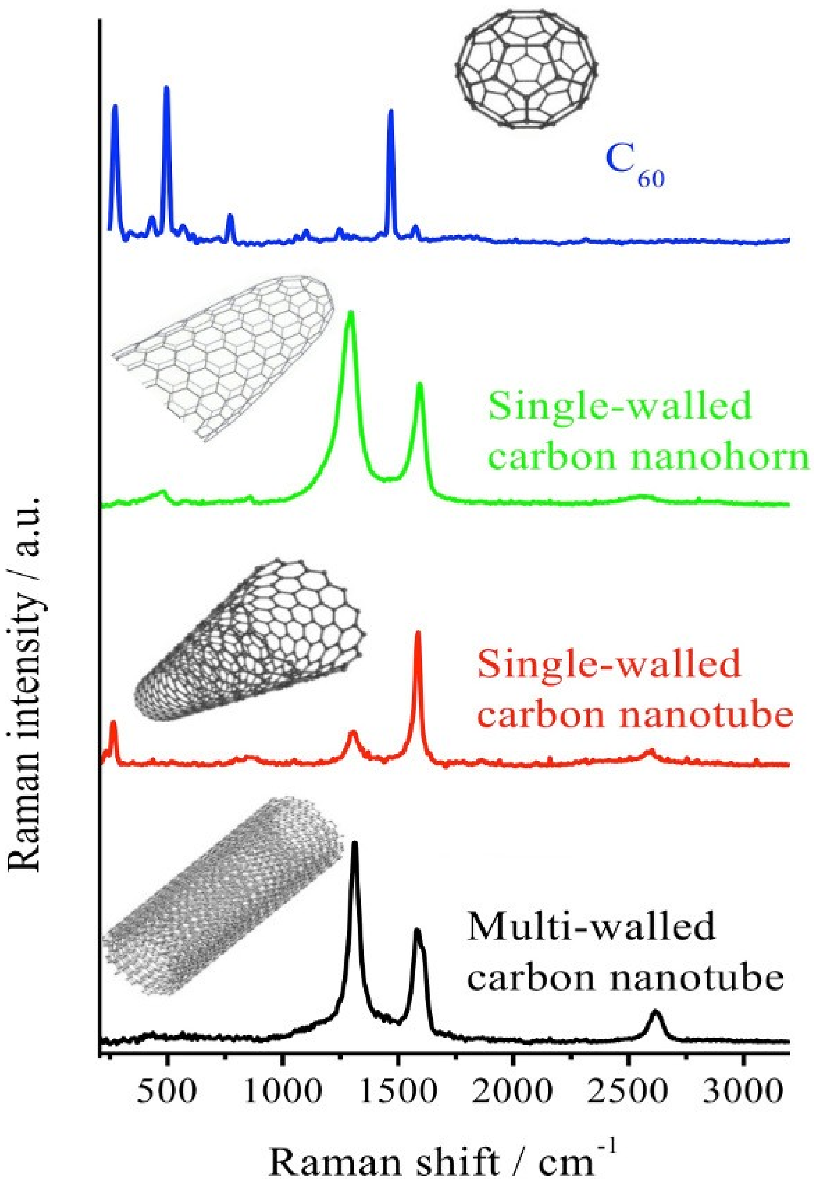
Applications of IR and Raman spectroscopies

- Phase identification
  - Fingerprint modes given by crystal structure
- Local stress analysis
  - ex : nanotubes, quartz, etc
- Phase transformation monitoring
  - solid-liquid, crystal-glass, polymorphism, etc
- Can be used in complex environments
  - pressure, temperature, space robots, etc
- Measurement of water content
  - O-H vibrations
  - glasses, minerals, liquid phases,
- Etc



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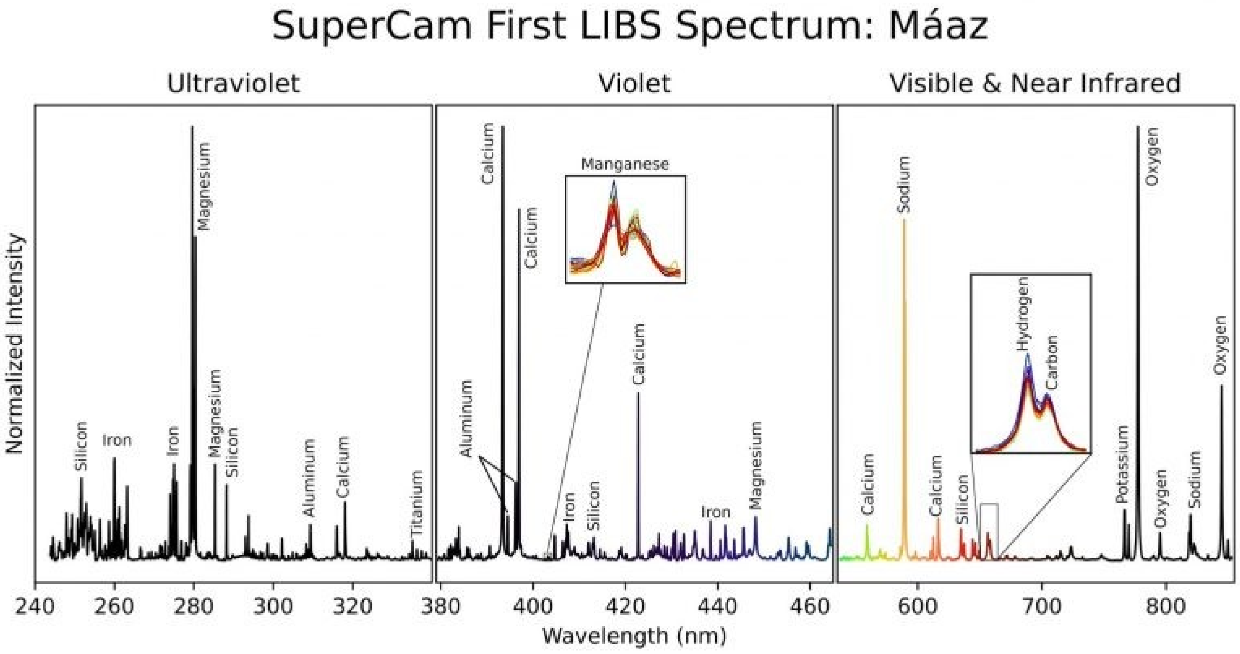
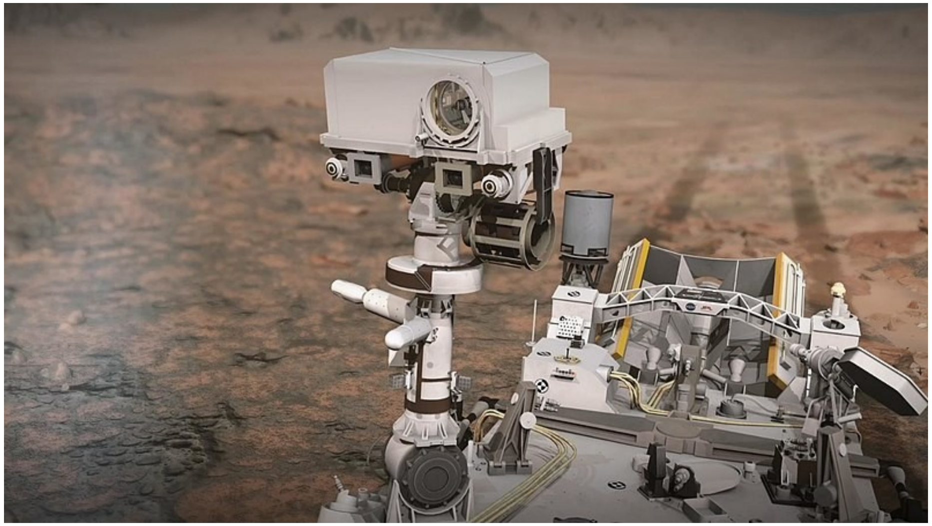
Applications of laser-based spectroscopies



LIBS Spectrum from SuperCam on Perseverance showing the composition of the Máaz rock target.



Supercam on Perserverance (artist rendering)

Raman spectroscopy, time-resolved fluorescence (TRF) spectroscopy, and Visible and InfraRed (VISIR) reflectance spectroscopy

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2.2- Classes of experiments
Diffractions

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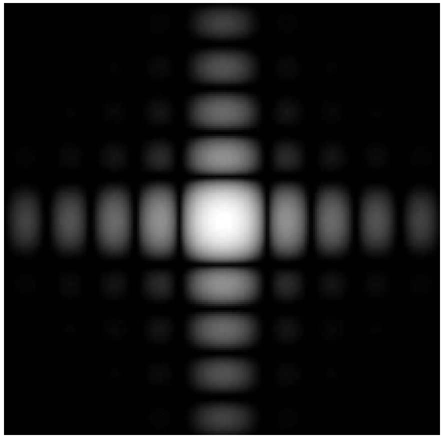
Diffraction

- Interaction between a wave and an obstacle
- Results of interference between scattered waves

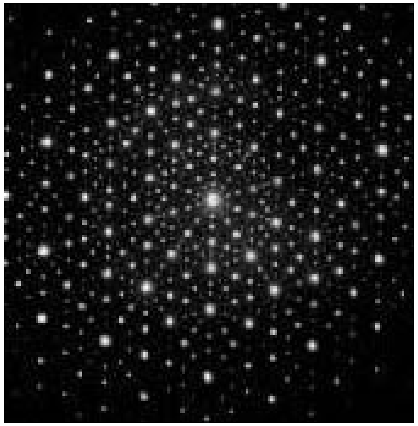
Application examples

- Optics
  - Diffraction by slits, holes, etc
  - Diffraction gratings
- Acoustics
  - Sound propagation in complex shapes
- Crystallography
  - X-ray, neutron, or electron diffraction



Diffraction of light
through a square hole
Source : wikipédia

Electron diffraction
quasi-crystal



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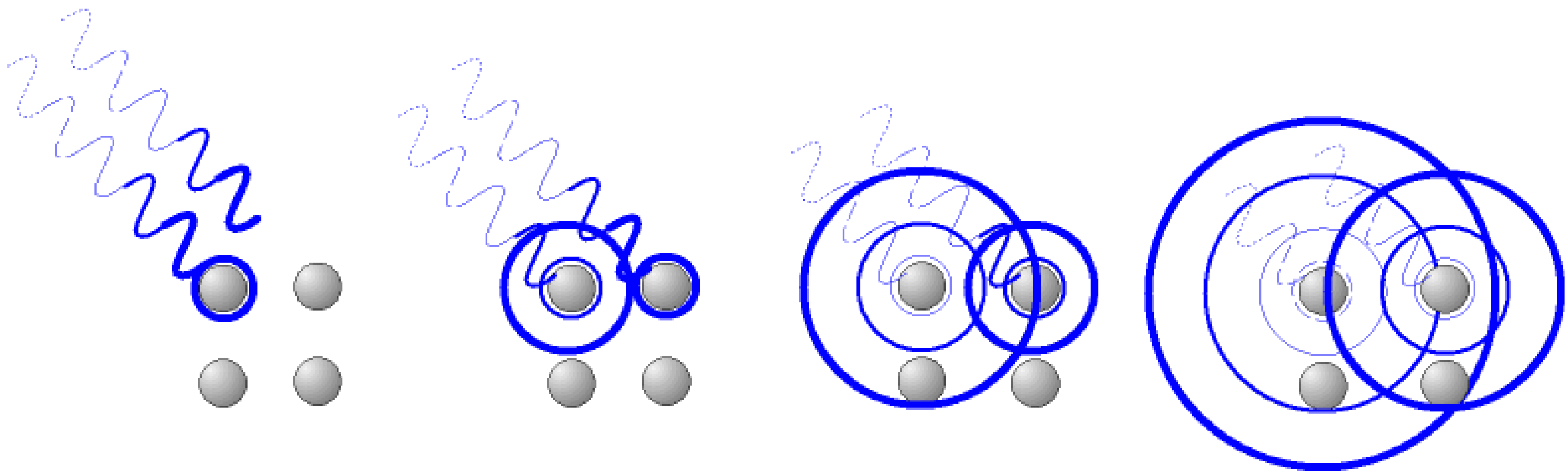
Crystal-radiation interaction



- Incoming radiation → excitation of an atom
- Rayleigh diffusion
  - Same energy than incoming radiation, in all directions
- Path differences between diffusion from each atom → wave displacement between scattered waves
- Periodic arrangement of atoms +
  wavelength ~ distance between atoms
  - Formation of constructive interference → diffraction

Image wikipedia

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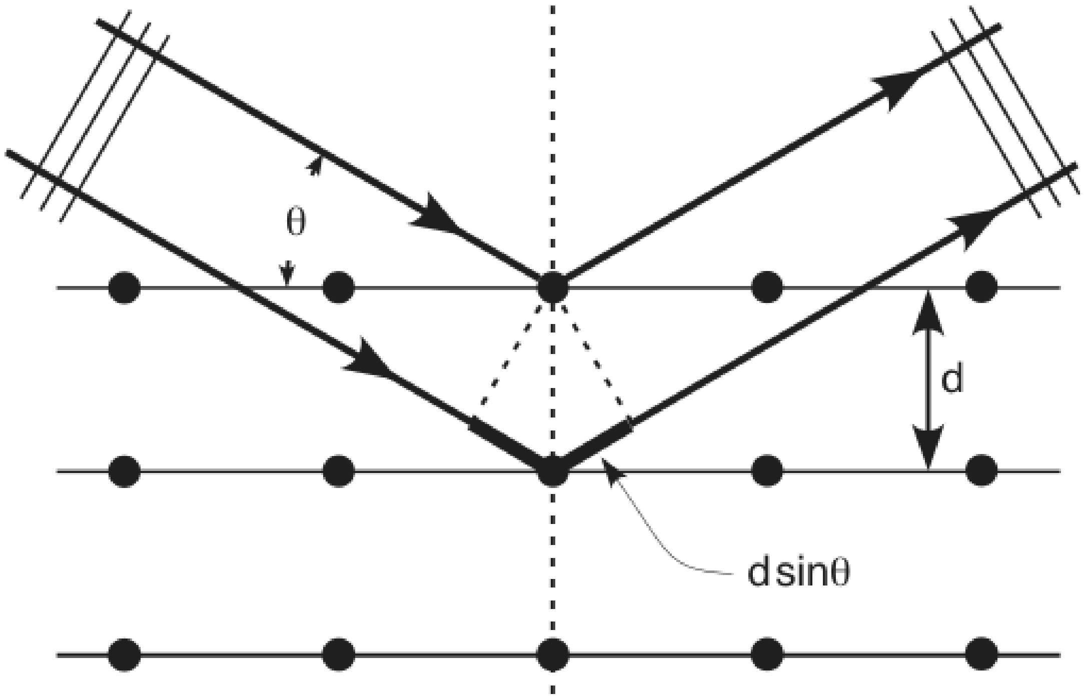
Geometrical interpretation: Bragg's law

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



λ : incident wavelength

d_{hkl} : distance between 2 crystal plane families

θ : Bragg angle

n : order of diffraction (integer)

2 d sin θ = path difference between 2 scattered waves

Attention: crystallographic planes do not exist
Wave are scattered by the atoms, not planes

Image wikipedia

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Diffraction families for crystallography

X-rays

- Incident radiation: electromagnetic waves
- Displacement of electrons around the atom
- X-ray diffraction → image of electron density in a crystal
- 0,1 Å < λ < 2 Å – 6 keV < E < 120 keV (usually)

Neutrons

- Incident radiation: neutrons
- Interaction with the atom nucleus, not the electrons
- 1 Å < λ < 1 µm – 1 MeV < E < 12 keV

Electrons

- Incident radiation: electrons
- interaction: Coulomb forces
- Effect of charged nuclei AND of electrons
- E ~ 10 keV (SEM) E ~ 100 keV (TEM)

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Sources

Important constrain: source of the incoming radiation!

X-rays

- Laboratory diffractometer: ~ 10^5 - 10^6 €
- Synchrotron : ~ 5 x 10^8 € (SOLEIL)
- Free electron lasers: 10^9 € (EuXFEL)

Neutrons

- Nuclear reactor : 5 x 10^8 € (maybe)
- Spallation source : 2 x 10^9 € (ESS)

Electrons

- Scanning electron microscope (SEM) : ~ 10^5 €
- Transmission electron microscope (TEM) : ~ 10^6 €

Usually

- Diffractometer and SEM : common in laboratories and private companies
- TEM : public laboratories and very large corporations (EDF)
- Everything else: national or international consortia

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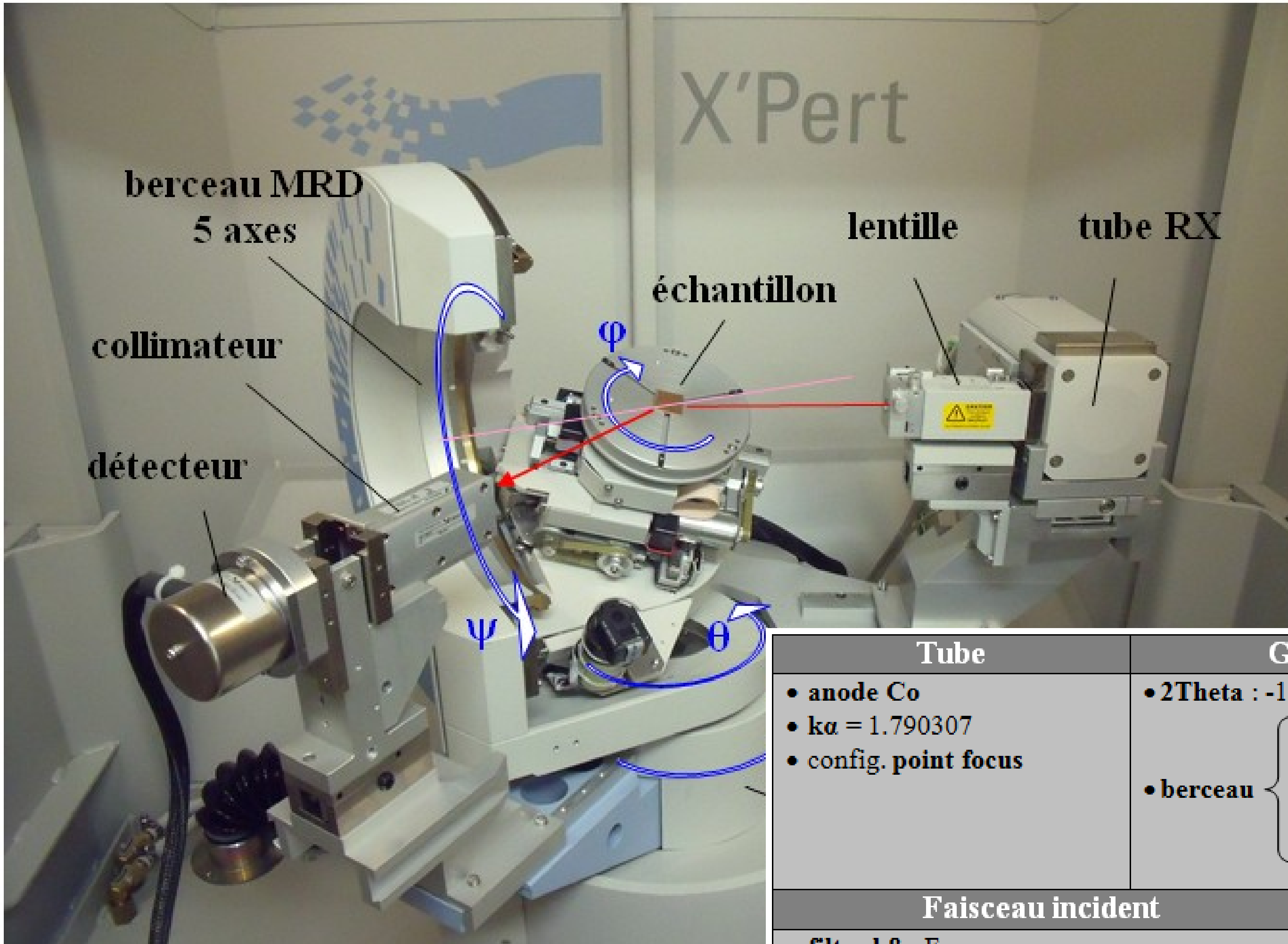
Laboratory diffractometer



X-ray tube:

- Electrons bombarded on a target,
- bremsstrahlung effect, bremsen → to brake, Strahlung → radiation,
- X-rays

Tube	Gonio	Echantillon
• **anode Co** • **kα** = 1.790307 • config. **point focus**	• **2Theta** : -10°<160° • **berceau** { **Psi** : ±90° **Phi** : ±360° **X** : ±50mm **Y** : ±50mm **Z** : 10mm }	• **maxi** 100x100mm • **épaisseur** <24mm • **poids** <500g

Faisceau incident	Faisceau diffracté
• **filtre kβ** : Fe • **lentille poly-capillaires** : Ø8mm • **fentes croisées** : 0<10mm	• **collimateur à lames parallèles** • **fente de soller** 0.27° • **détecteur**

Image : laboratoire MSSMat, Centrale-Supelec

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X-rays : synchrotron

Principe :
- electrons rotating at high speeds
- Radial acceleration
- Scattering of X-rays

SOLEIL synchrotron
Outside Paris

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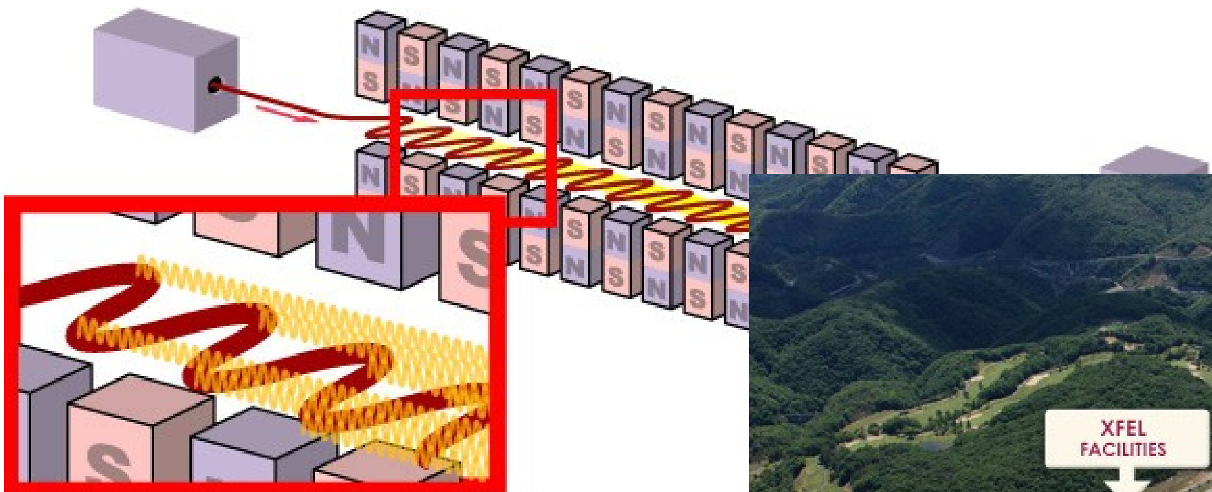
X-rays : free electron lasers

Principe :
- Accelerated electron through oscillator
- Synchrotron radiation
- Interaction between electron and radiation
- Laser effect
- XFEL : FEL optimized to produce X-rays



Sacla XFEL and Spring-8 Synchrotron
Japan

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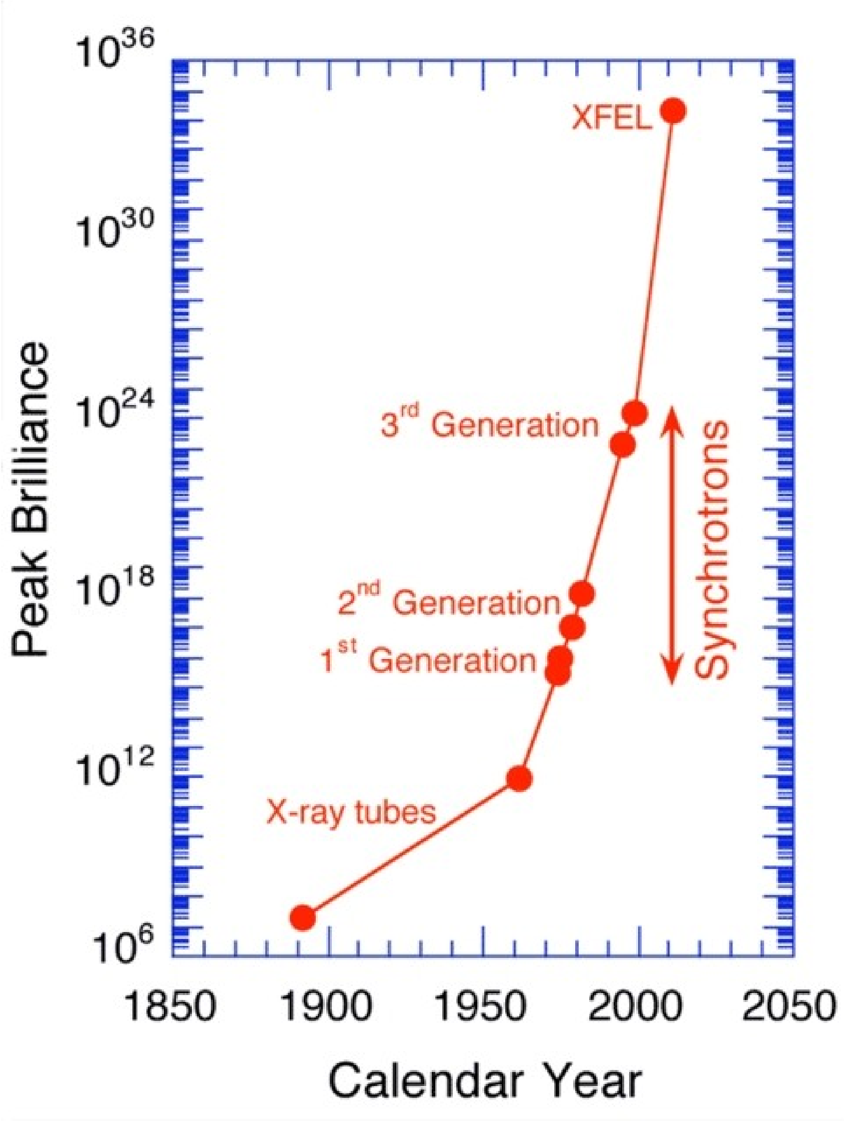
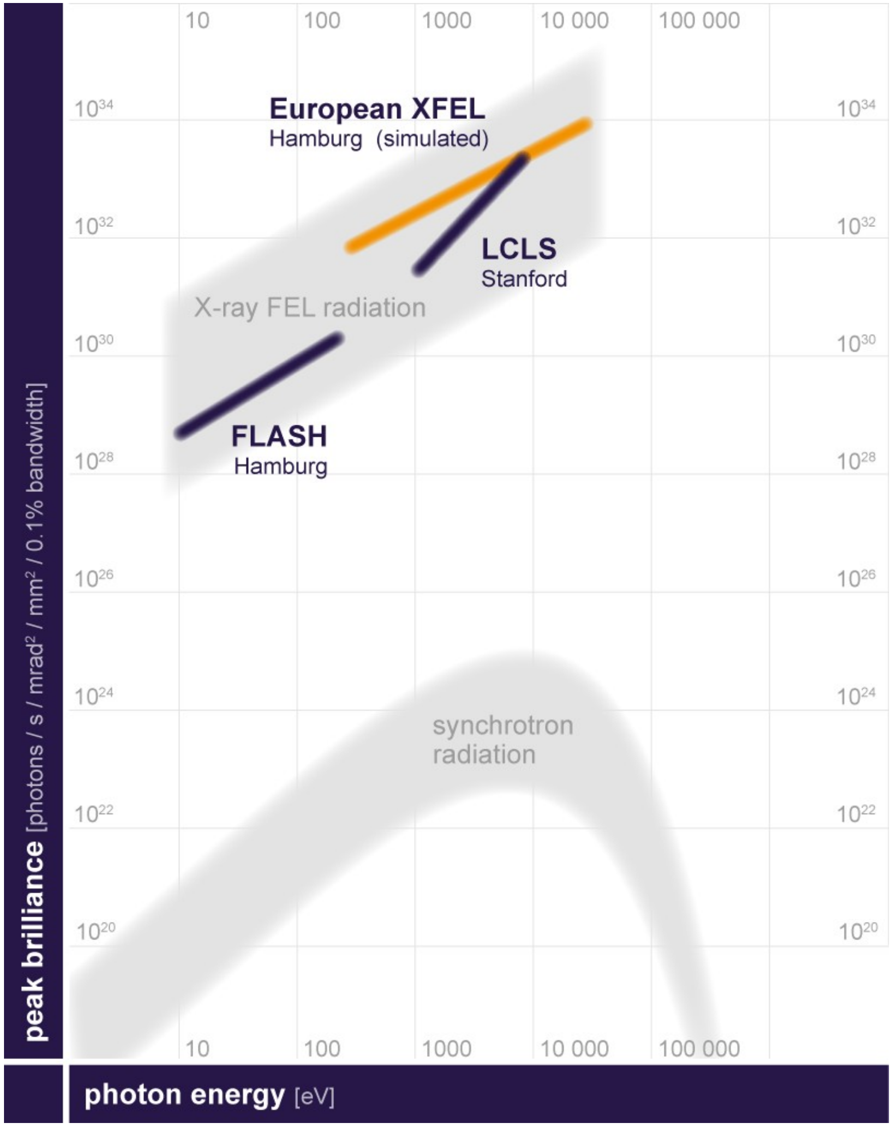
Brillance (~photons flux/s)





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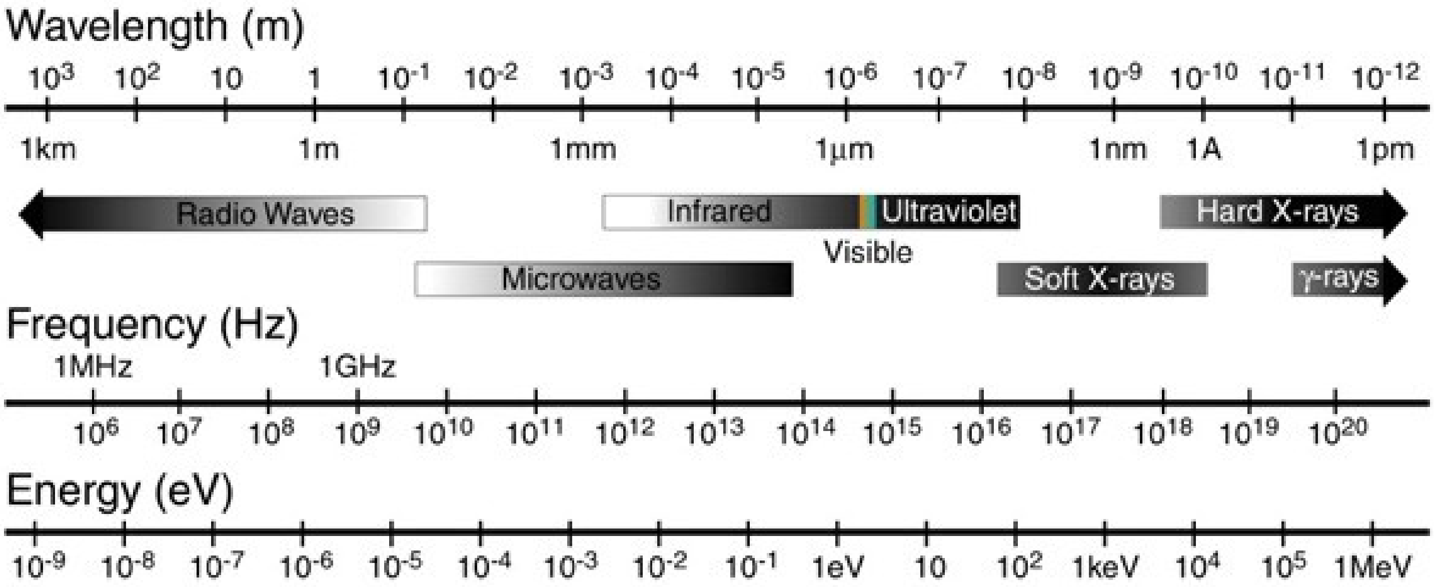
X-ray sources parameters



Energy / wavelength

- ~100 eV to 100 keV (12 nm to 0.012 nm)
- 100 eV – 1 keV : soft X-rays
- 1 keV – 1 MeV : hard X-rays

Pulses structure

- tubes : continuous emission
- Synchrotons : ~ ps at ~ 100 MHz
- EuXEL : ~ 50 ps à ~ 100 Hz to 4 MHz

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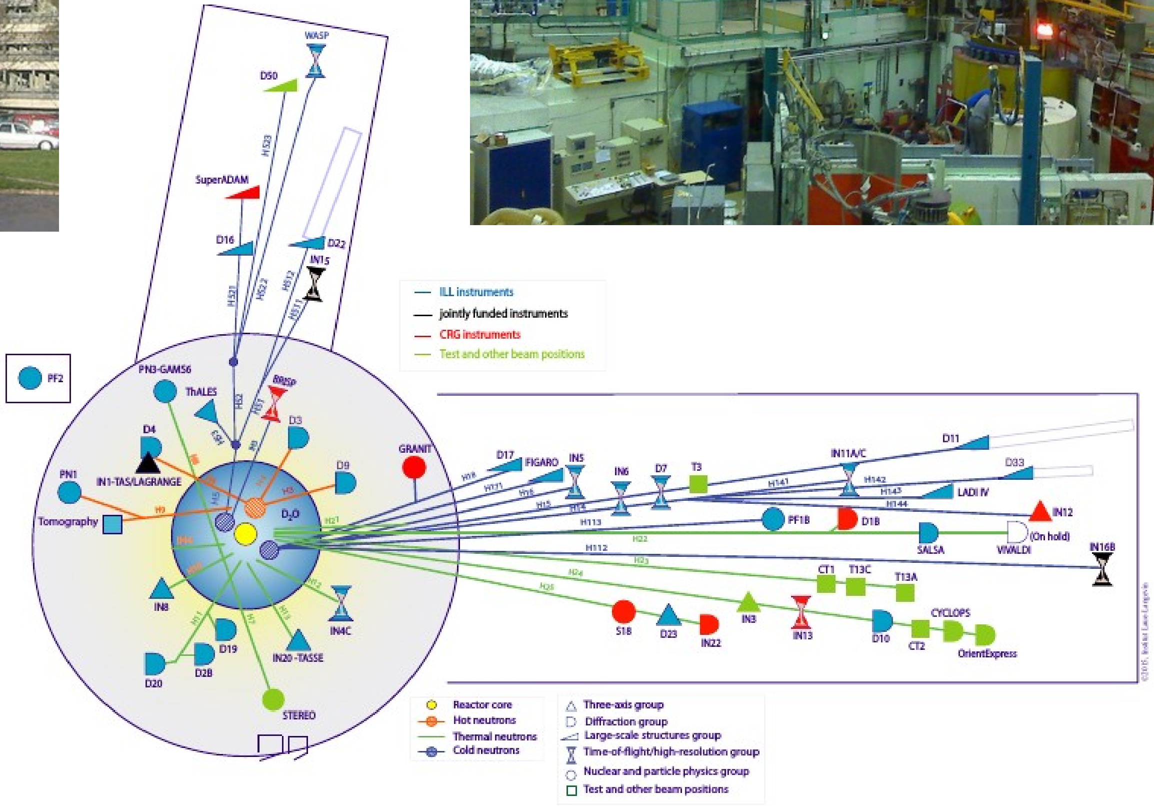
Neutrons : ILL reactor in Grenoble

ILL Grenoble



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Electrons : electron microscope

One SEM at the Chevreul institute

TEM at the Chevreul Institute

SEM : scanning electron microscope
TEM : transmission electron microscope

Cf : Damien Jacob

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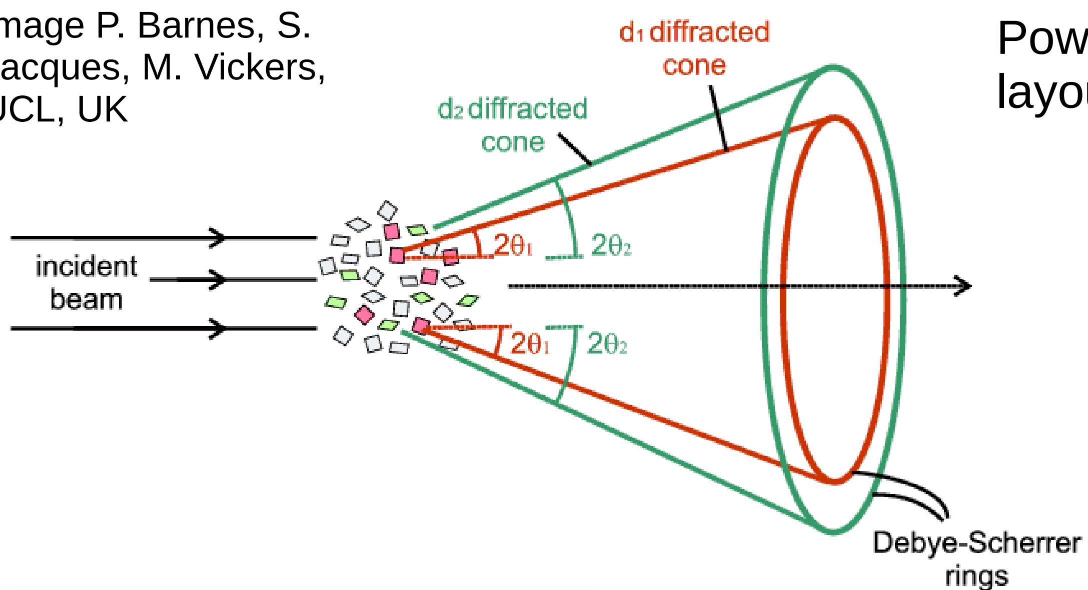
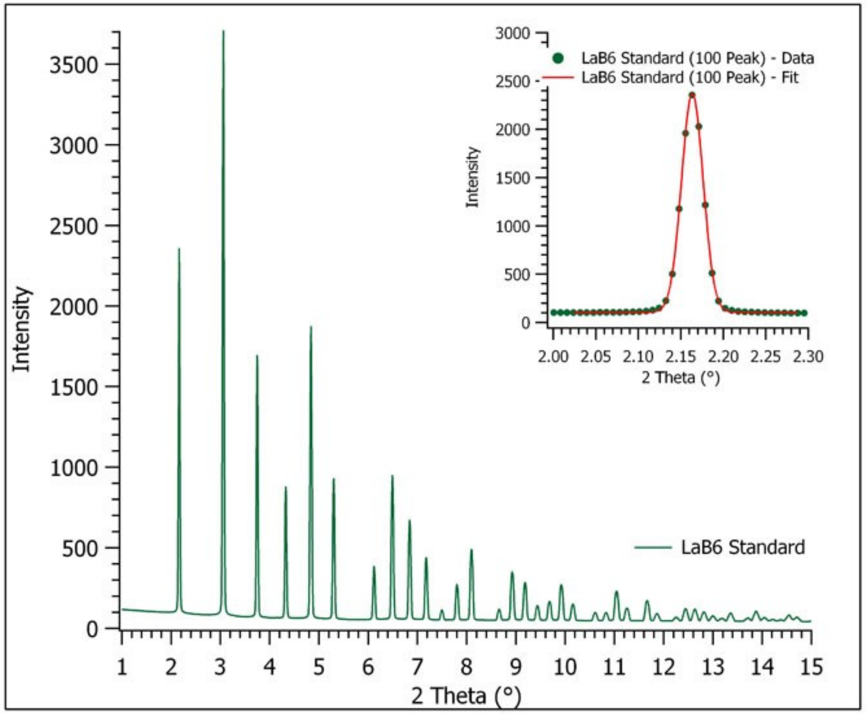
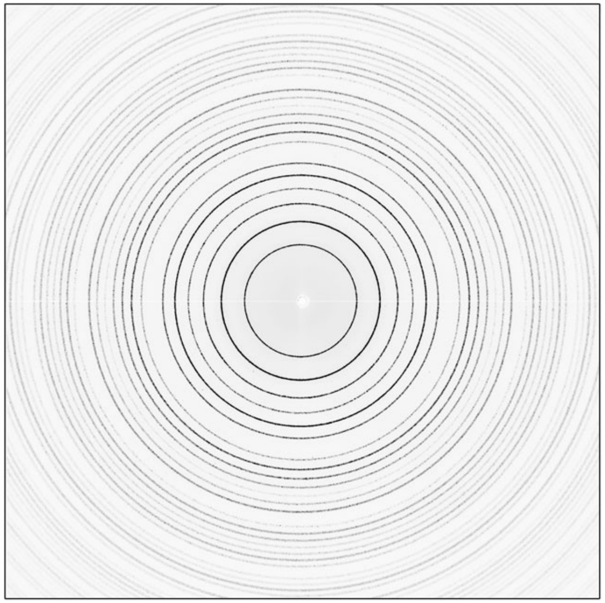
Image P. Barnes, S. Jacques, M. Vickers, UCL, UK



Powder X-ray diffraction layout

Integrated diffraction pattern LaB_6





Diffraction image for LaB_6

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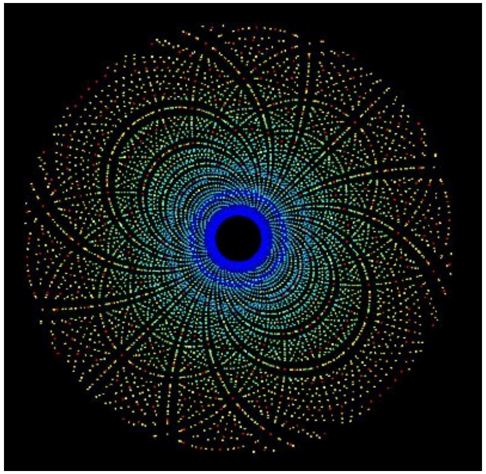
Applications of diffraction in materials science

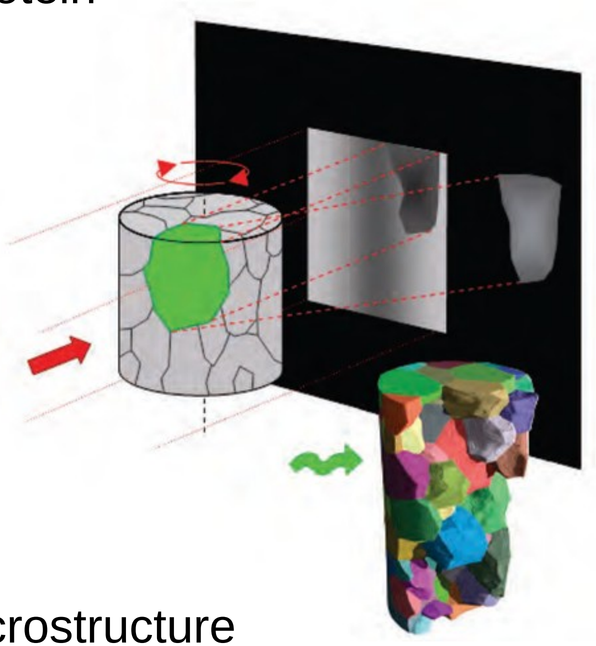
- identification of crystalline structures
- Phase diagrams
- Real-time reaction monitoring
- Stress analysis
- Microstructural analysis
- Grain sizes analysis
- Defects (dislocations)
- …

Diffraction is also at the core of other techniques

- Transmission electron microscopy
- Diffraction contrast tomography (DCT)
- ...



Laue diffraction on a protein



Microstructure reconstruction with DCT

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2.3- Classes of experiments
Imaging

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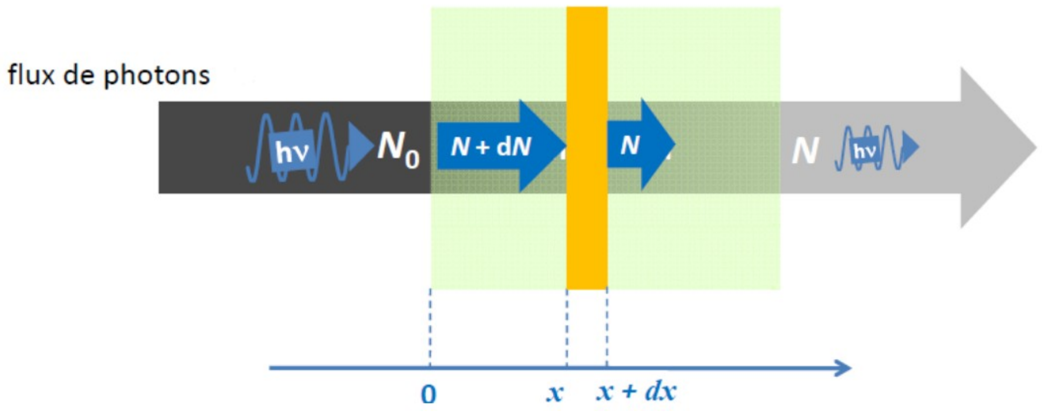
Typically: measurement of X-ray absorption by matter



$$N = N_0\, e^{-\mu x}$$

N : number or flux of photons

x : sample thickness

μ : linear attenuation coefficient

ordre de grandeur *CDA*: CDA = couche de demi-atténuation

	30 keV	100 keV	500 keV
air	25 m	35 m	60 m
eau *(liquide)*	2 cm	4 cm	7 cm
béton	3 mm	2 cm	4 cm
plomb	0,02 mm	0,1 mm	4 mm

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3D reconstruction d'images 3D from multiple 2D absorption images

- X-ray radiography
- Electron microscopy

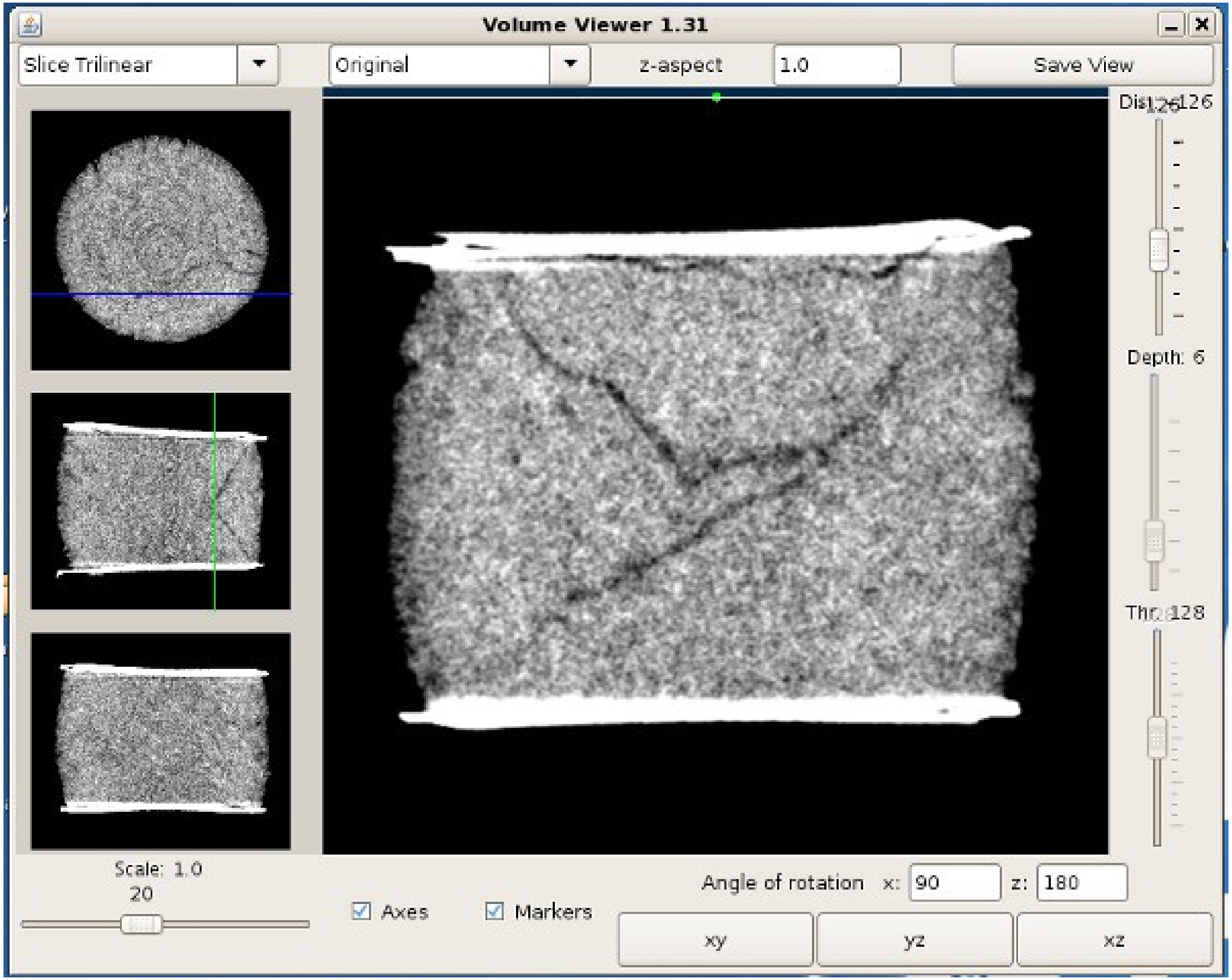

Image N. Hilairet (Lille), F. Brunet (Grenoble)

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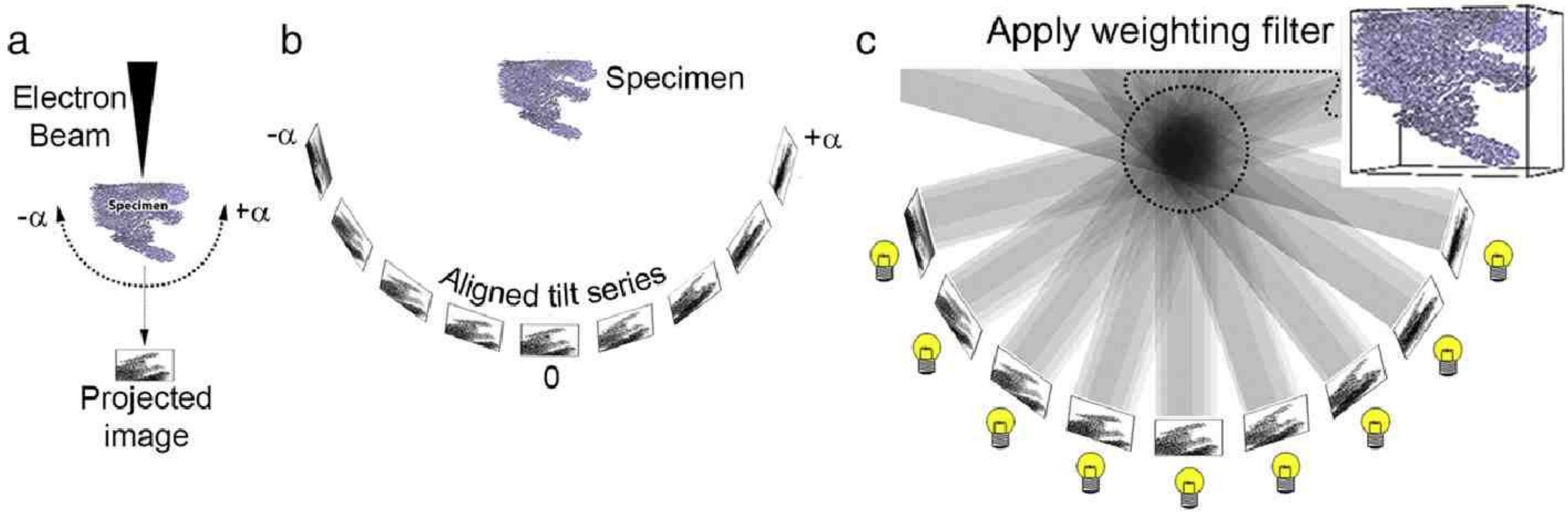

Tomography in the TEM

Liu et al. (Mater. Charact., 2014) : Weighted back projection electron tomography technique.

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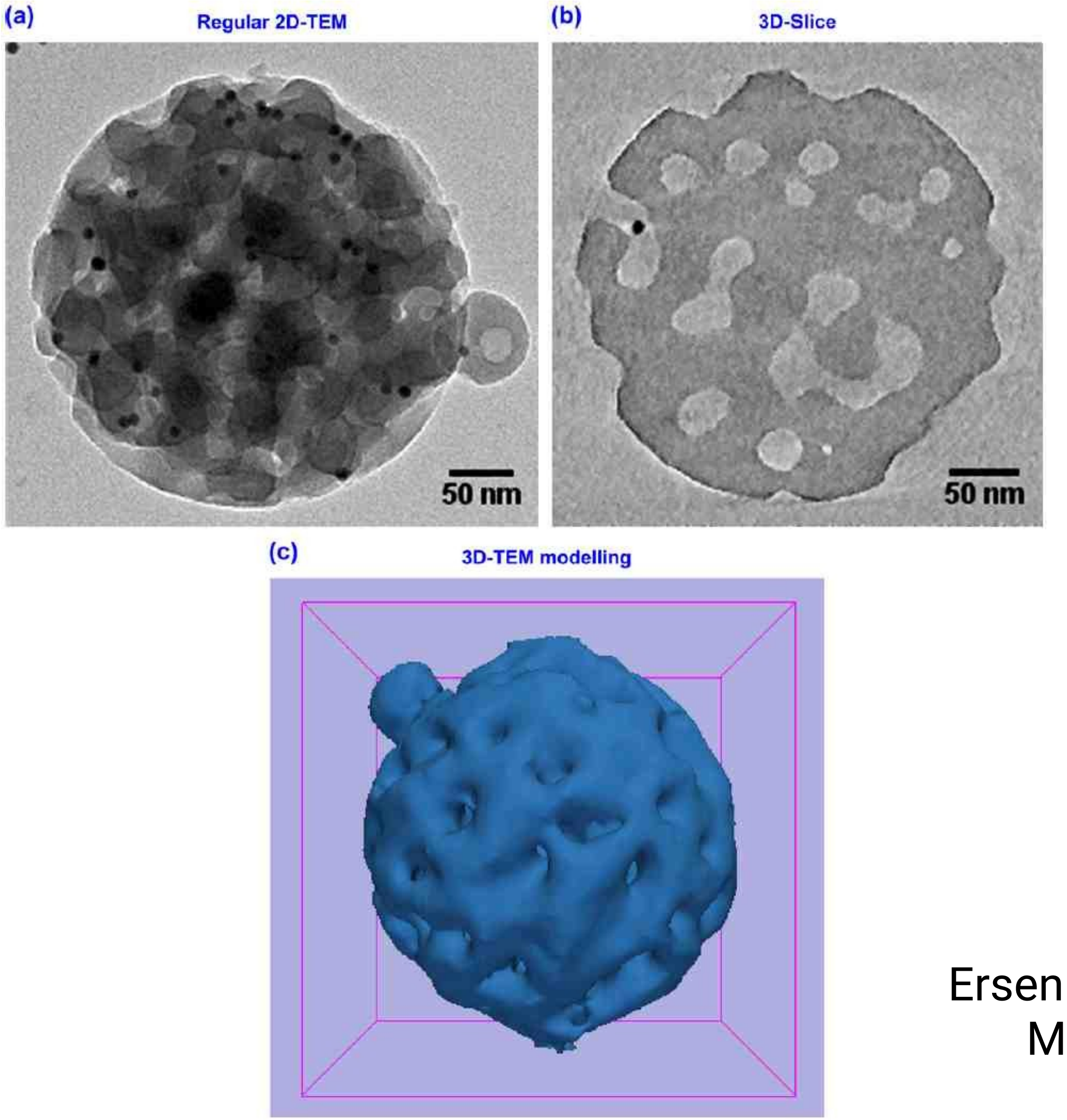
TEM tomography



Ersen et al. (Solid State Sci., 2007)
Macroporous zeolite obtained
by TEM tomography.

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Scanning electron microscope

Topographic, morphological, microstructural, chemical and crystallographic (from nm to µm)

Principle : electrons gun, interactions e-/ surface

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Chevreul Institute

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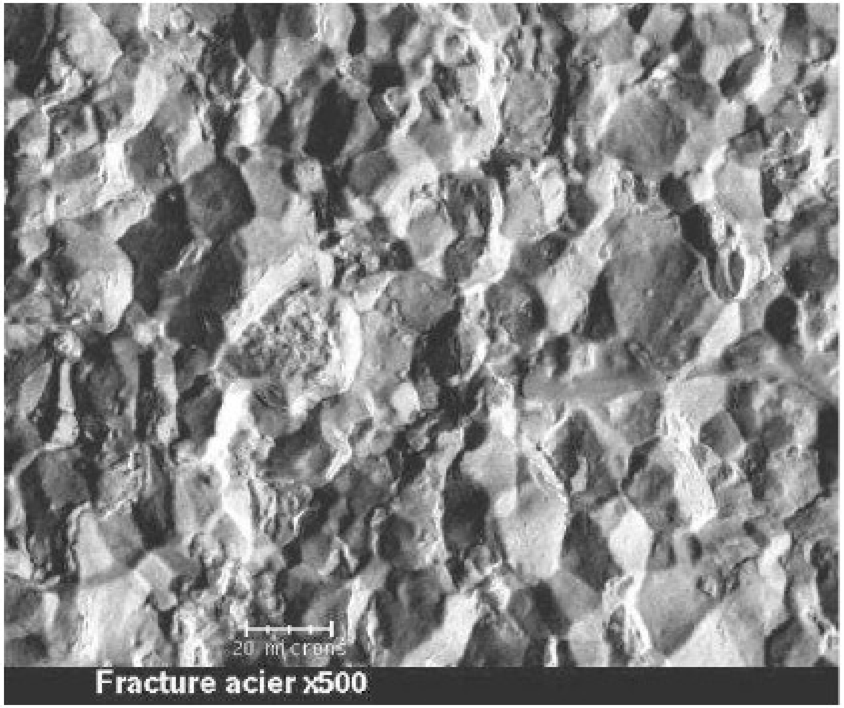
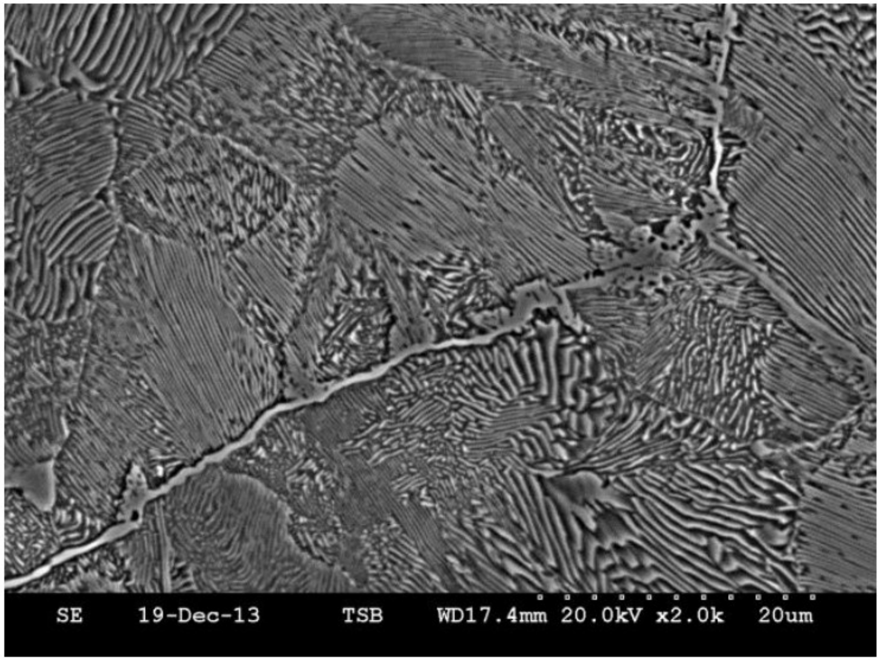
SEM: surfaces imaging



Contraste topographique: rupture fragile d'un acier

Backscattered electron SEM images



Acier duplex après attaque chimique au nital

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2.4- Classes of experiments
Coupled techniqes

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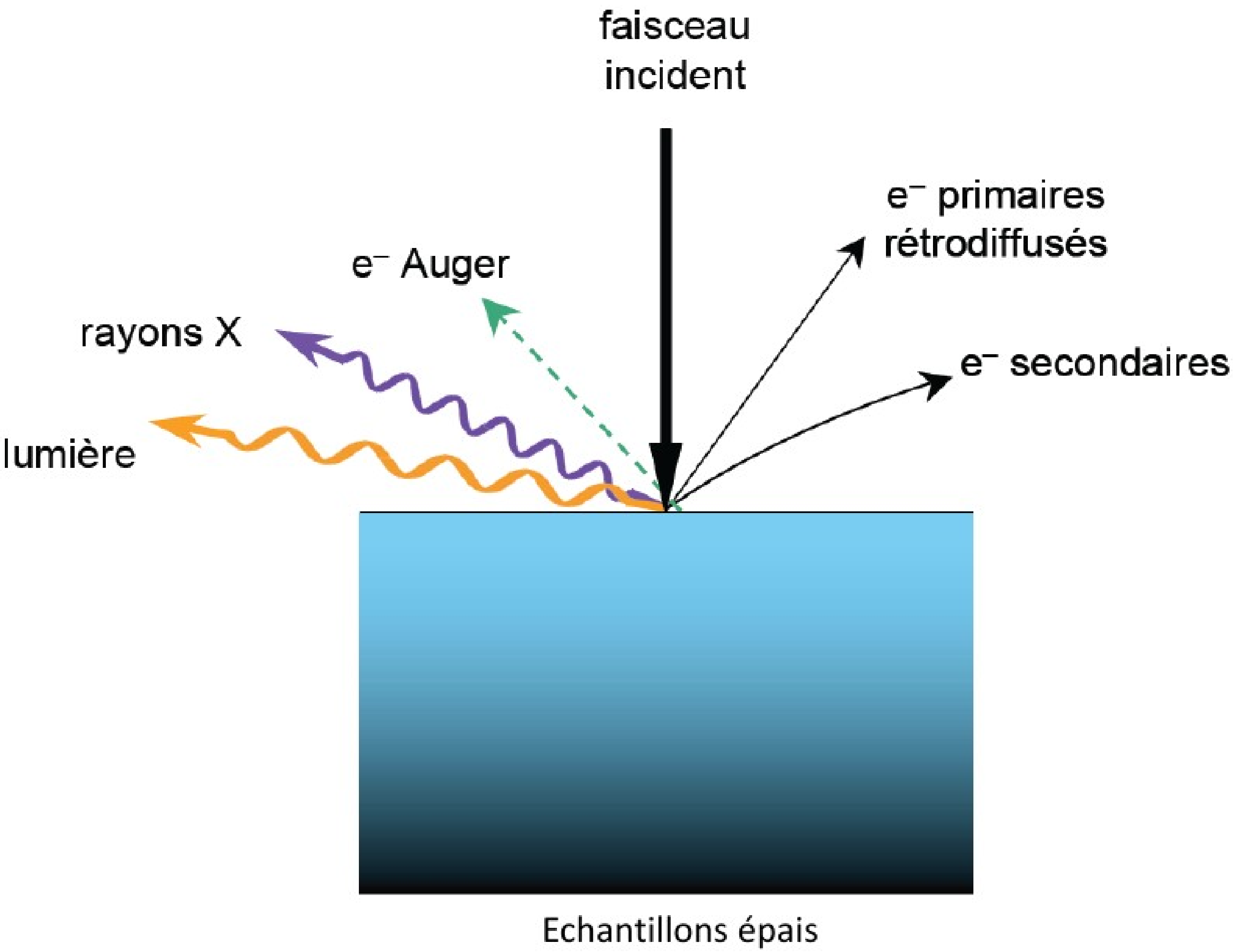
Electron matter interactions in the SEM



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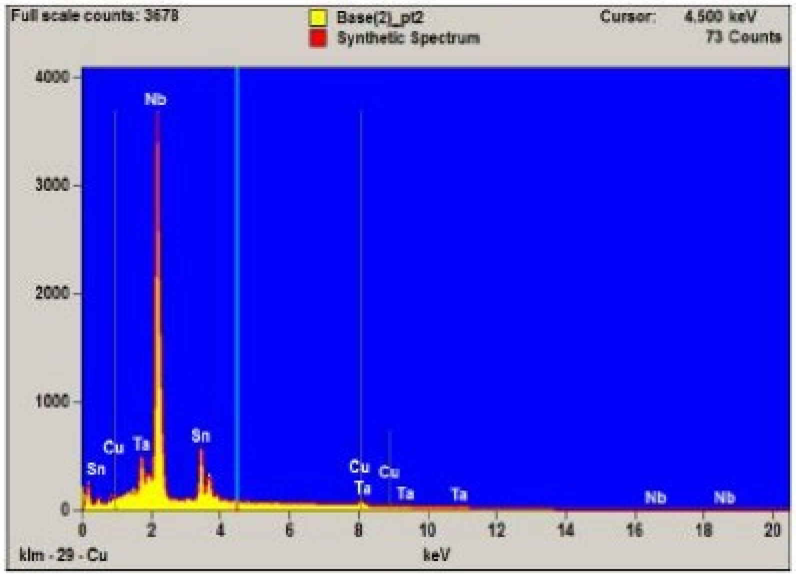
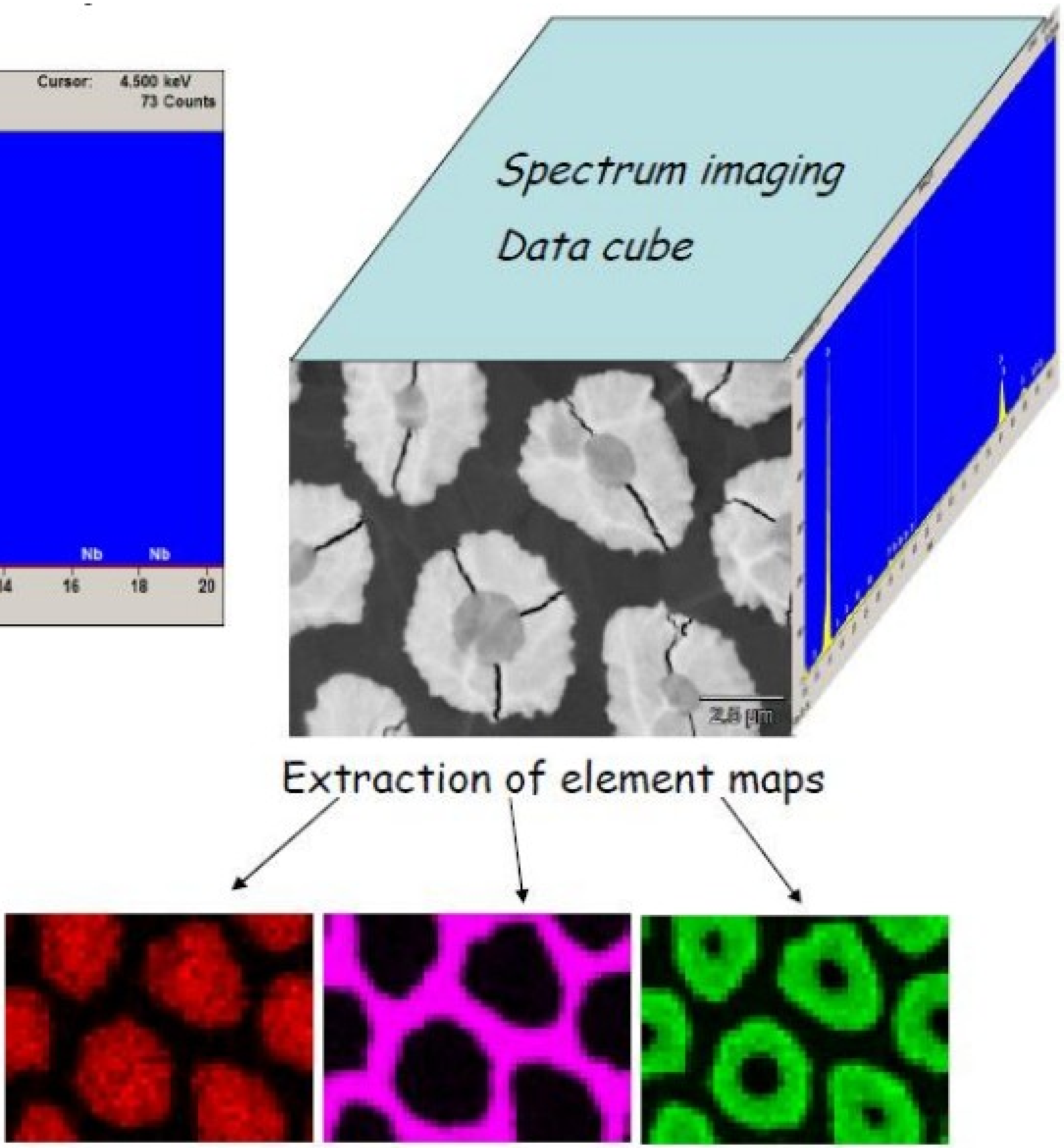


Synthesized spectrum



SEM element mapping

- At each point: fluorescence spectrum
- Reconstitution of the image

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Microstructures : EBSD

EBSD : Electron BackScattered Diffraction

Scanning Electron Microscope

Surface analysis

Main idea:

- Move across the sample, point by point
- At each point: reconstruct grain orientation below the electron beam
- Grain or phase = region in space with the same crystallographic structure and orientation
- Rebuild a sample map based on the above.

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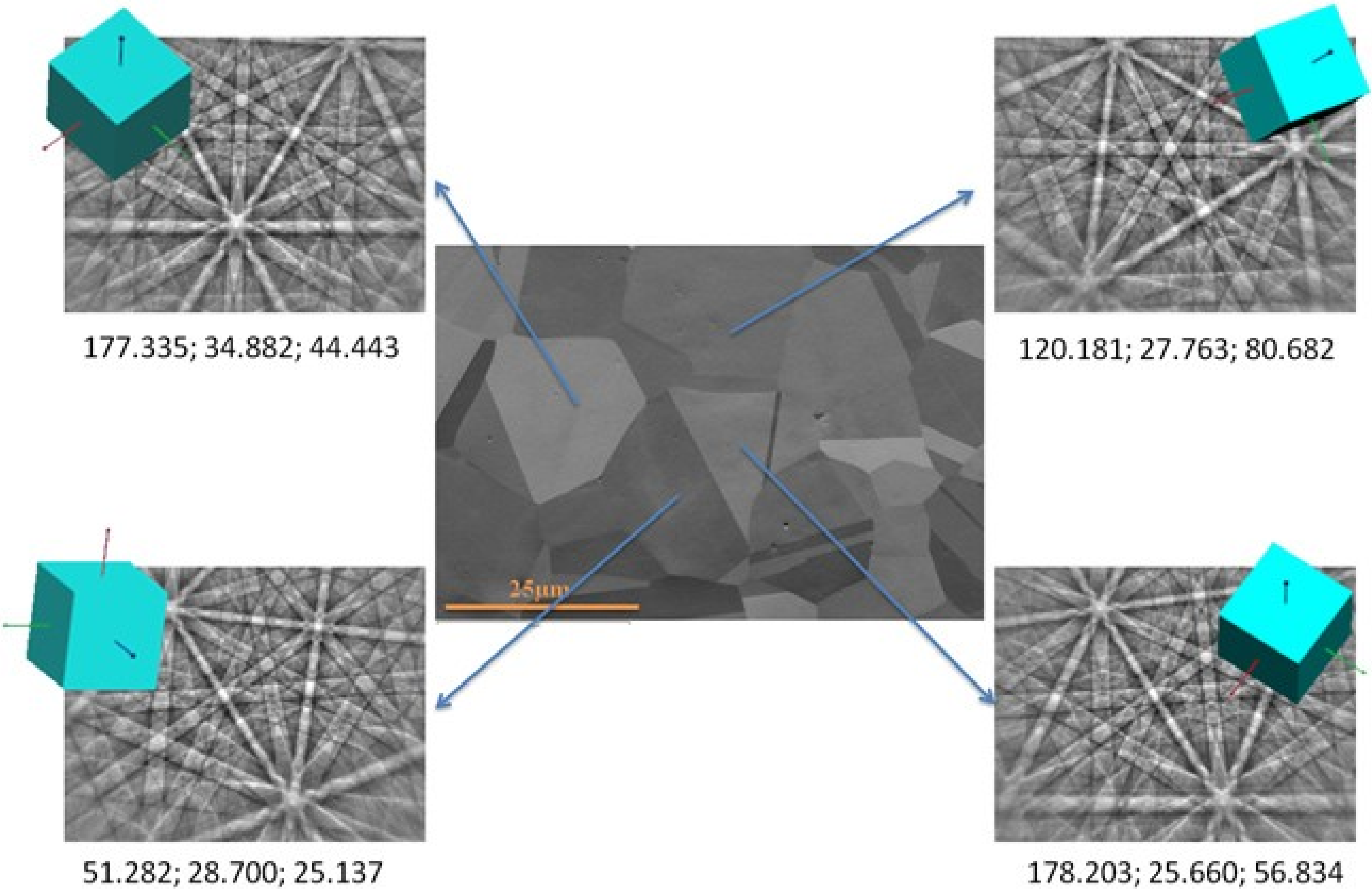
EBSD: example



Images Oxford Instruments

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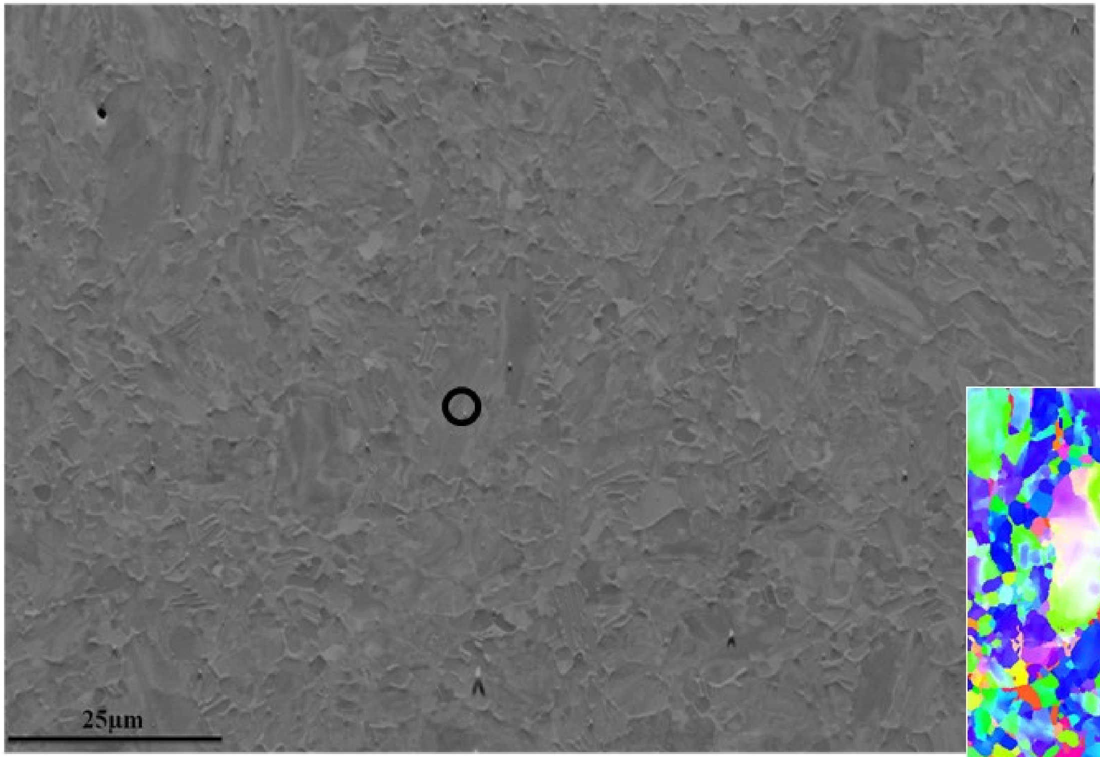
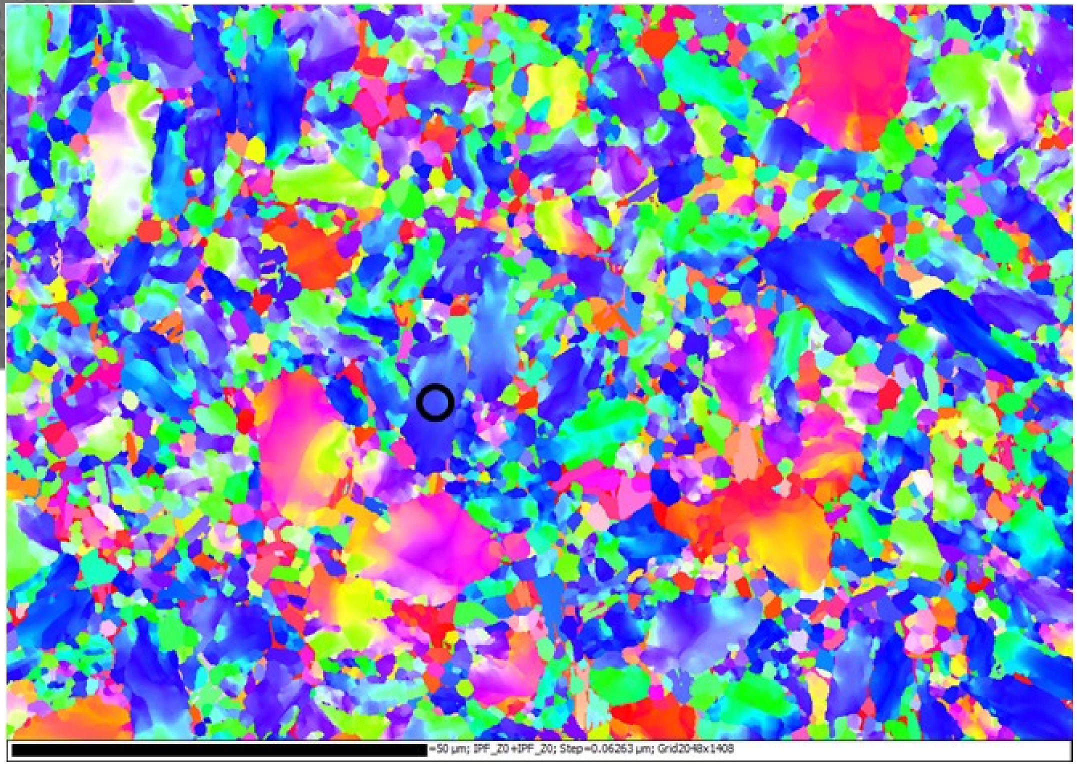
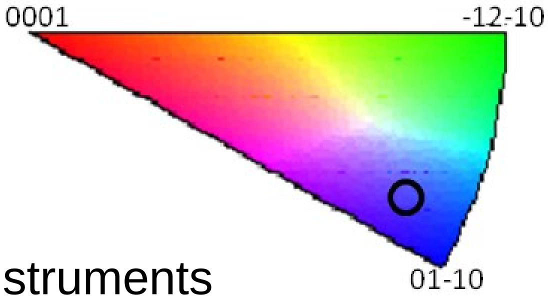


SEM image of a titanium alloy

EBSD map of the same area





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Transmission Electron Microscope (TEM)

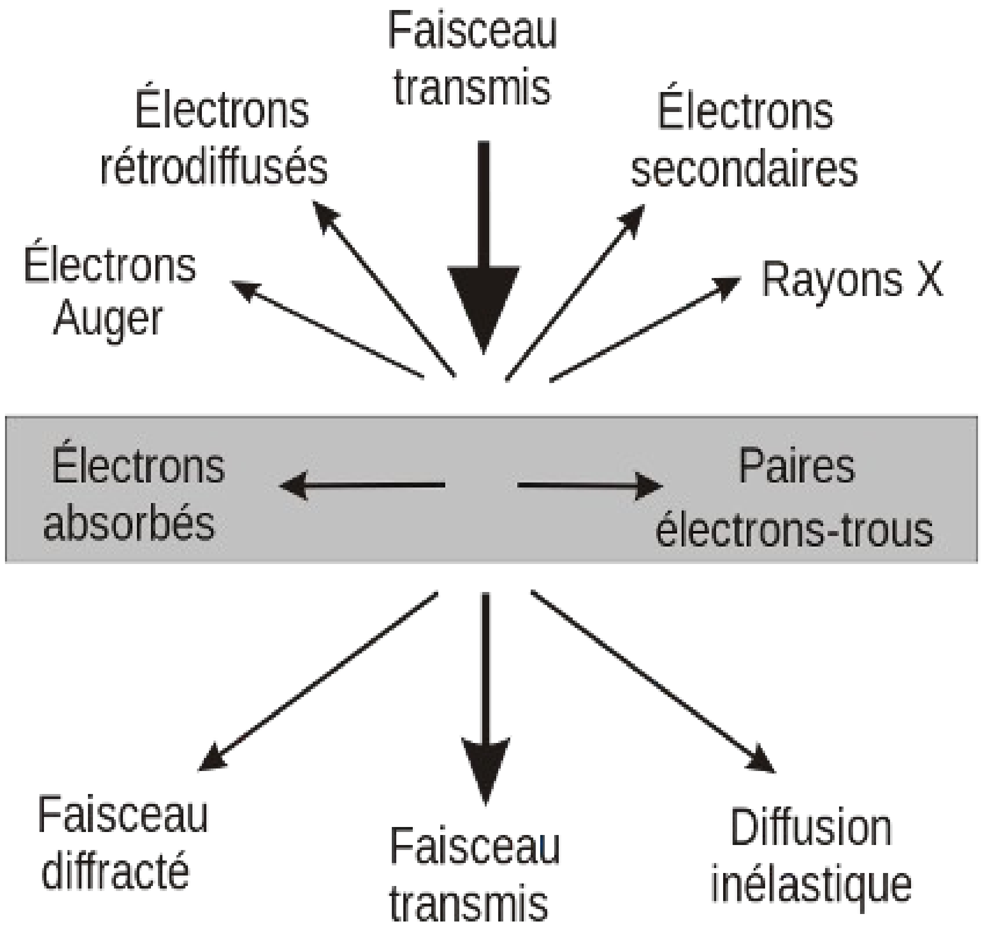
Classes of Damien Jacob

Simple description

- Relies on electron diffraction
- Beam transmitted across a very thin sample

Images based on

- Transmitted intensity (bright field)
- Diffraction (dark field)
- X-ray dispersion (map of chemical elements)
- ...



Electrons-matter interaction in a TEM
Image wikipédia

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TEM at the electron microscopy center

- Tecnai G2-20 twin, delivered in 2004 ?
- META FEI Titan3 Themis 300, delivered in 2016

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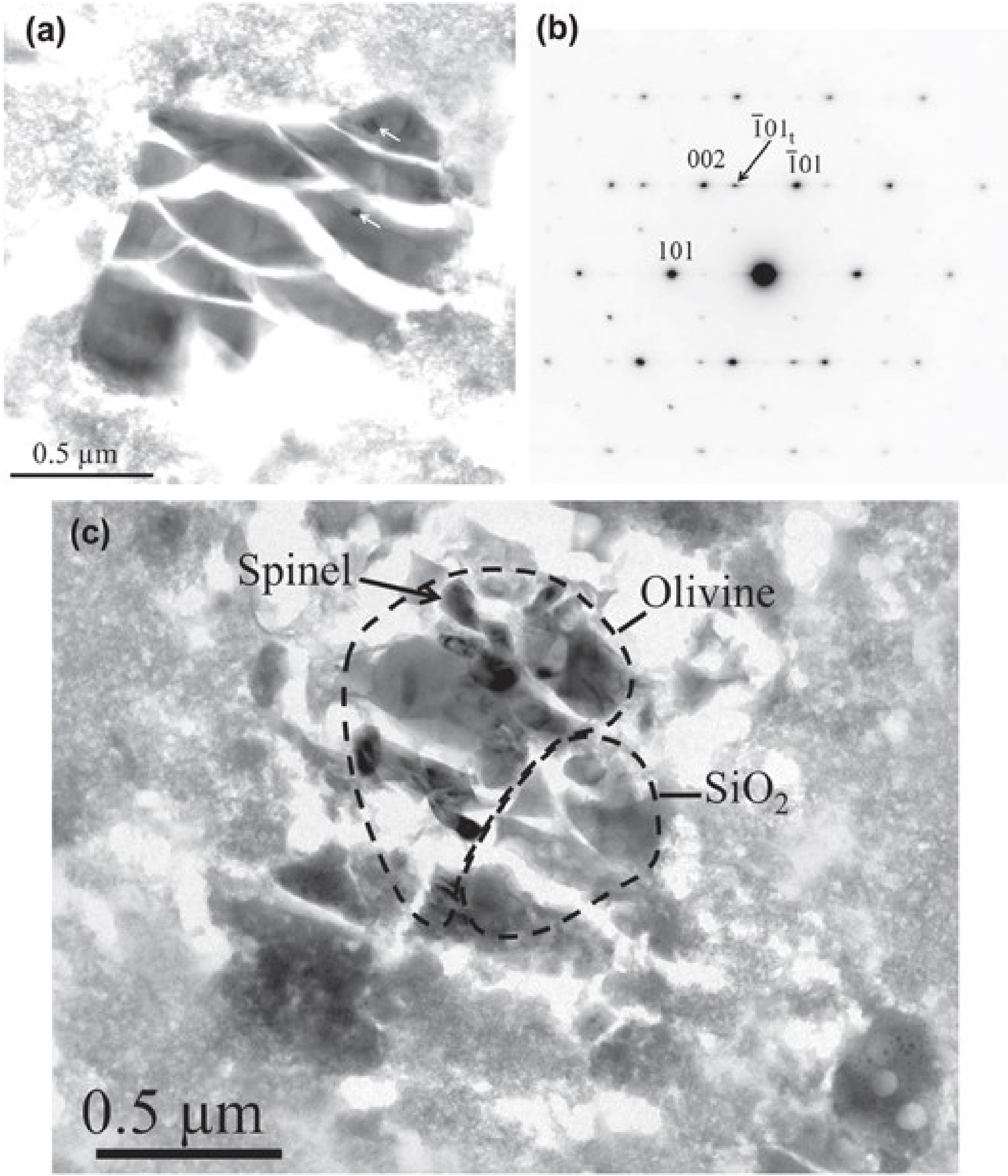
TEM: illustration



a) Cristobaltite in a gel matrix

b) Corresponding diffraction pattern

c) Olivine/ cristobaltite aggregate

Figure from Roskosz and Leroux, Astrophysical Journal, 2015

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3- Large scale facilities

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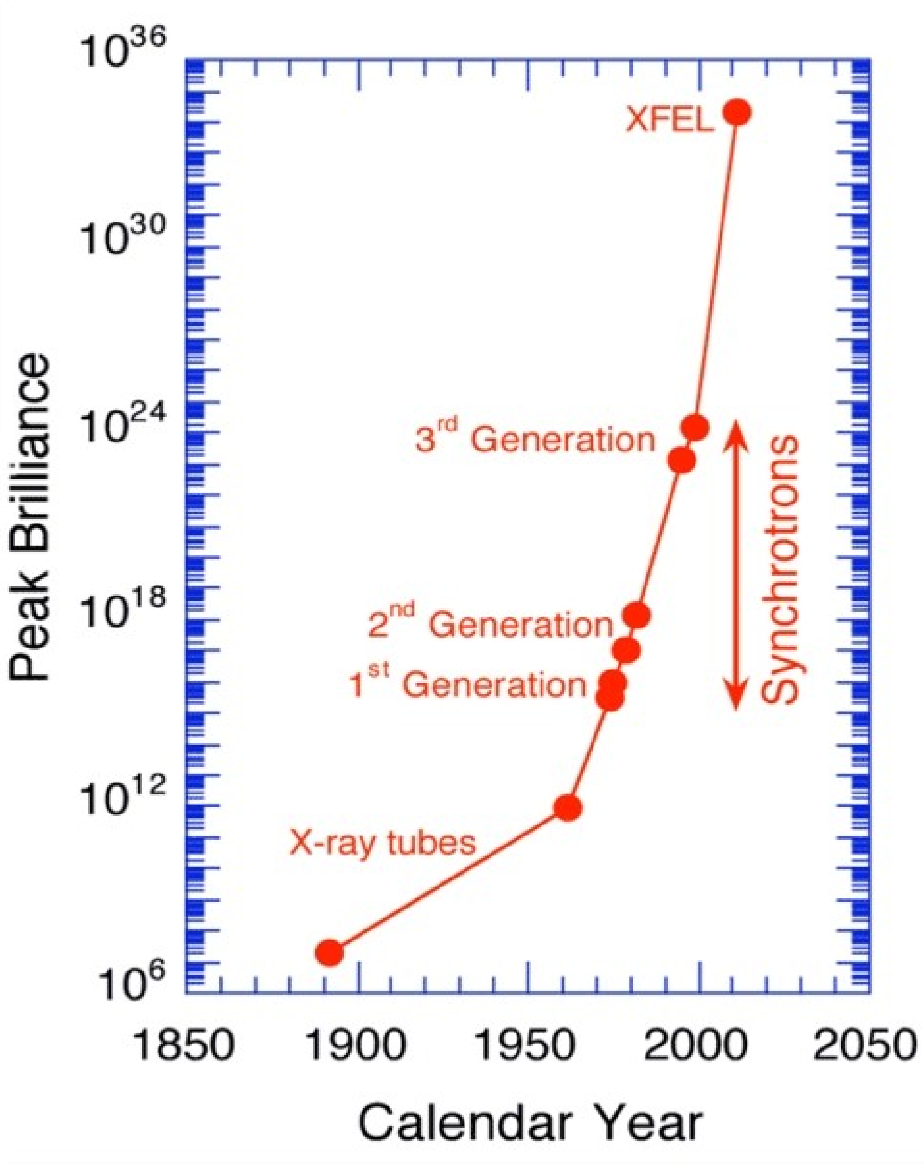
Large scale facilities

For the last ~30 years, we have been building “large scale facilities”

- Expensive instrument with a large user base
- Typically, 1 per country or continent
- Access to the machine based on a proposal system

Example : synchrotron

- Synchrotron: high intensity light source
- Flux 10^{10} larger than on a lab machine



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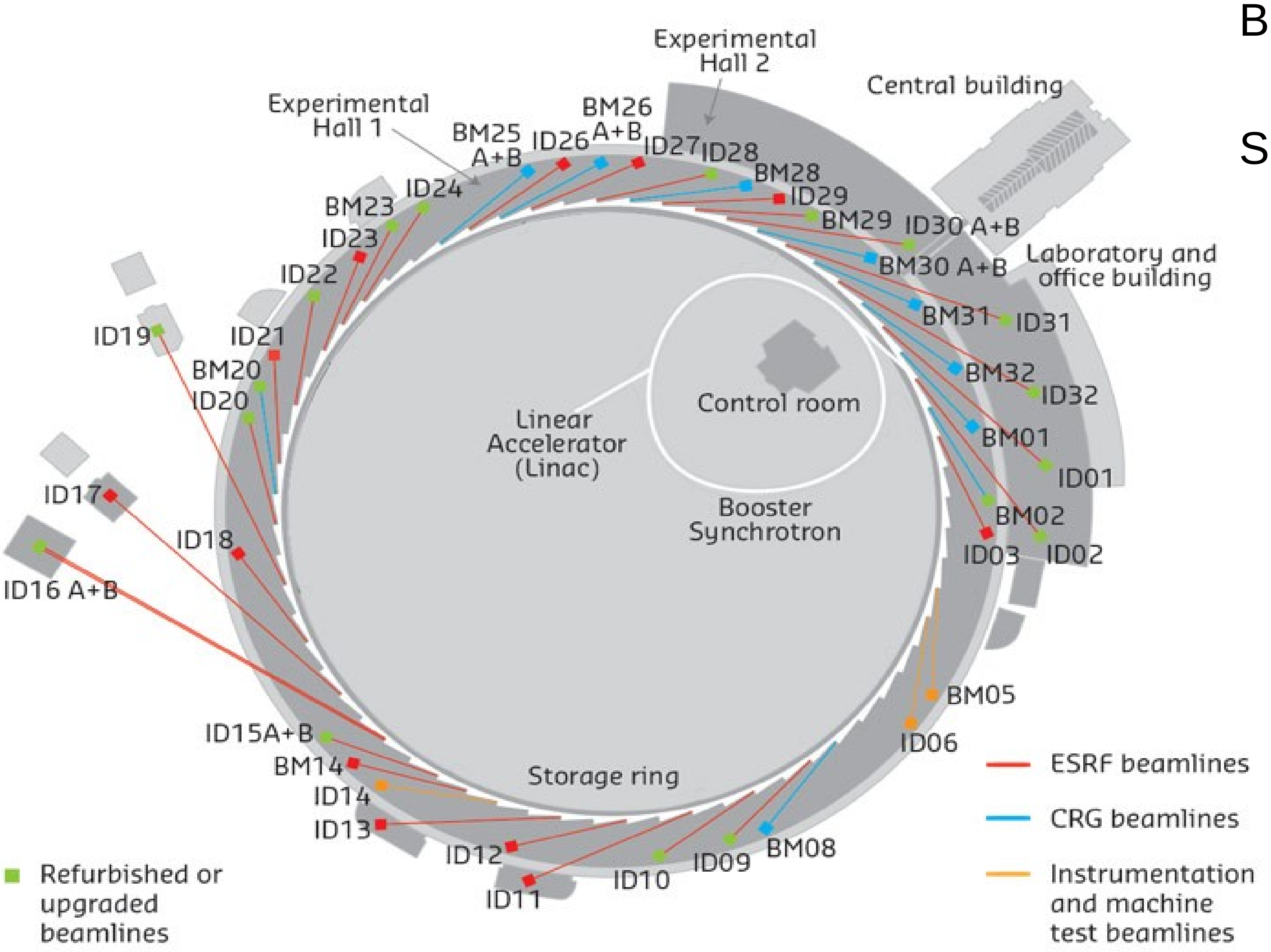
European Synchrotron Radiation Facility



Beamline map (Grenoble)

Some numbers

- E = 6 GeV
- 24 hours / day
- 6 or 7 days / week
- ~9 month / year
- 21 partner countries
- 6500 scientists visiting / yeat
- 2000 publications / year
- 100 M€ / year

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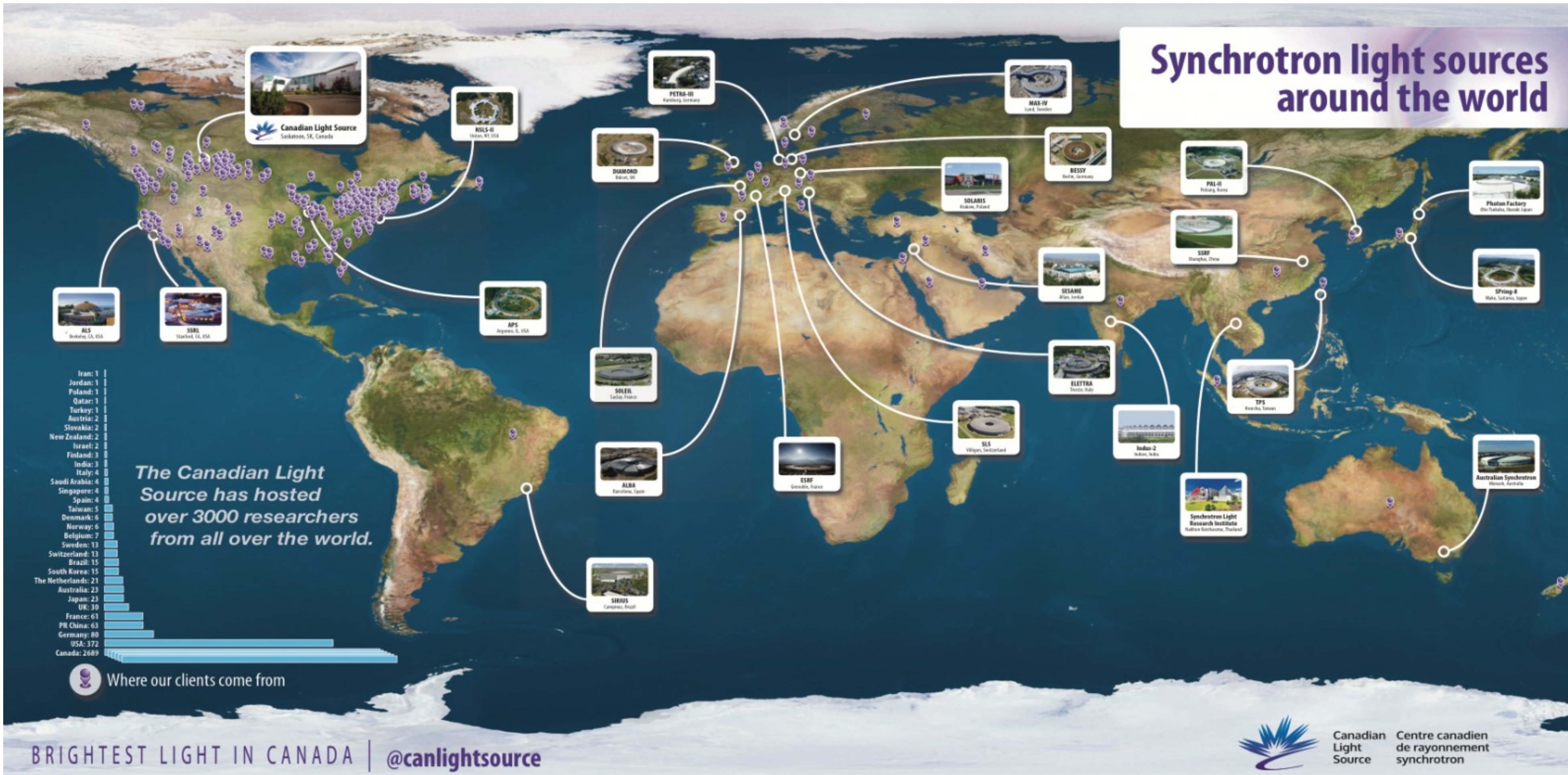
Synchrotron light sources in the world



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