

Structural Analysis

Part III - X-ray tools

Session 2:
X-ray scattering and diffraction

Discovery of X-rays triggered many technological and scientific developments

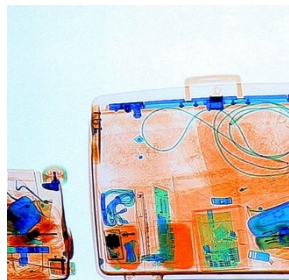
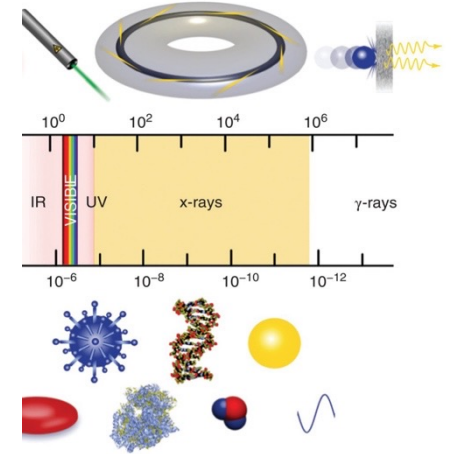
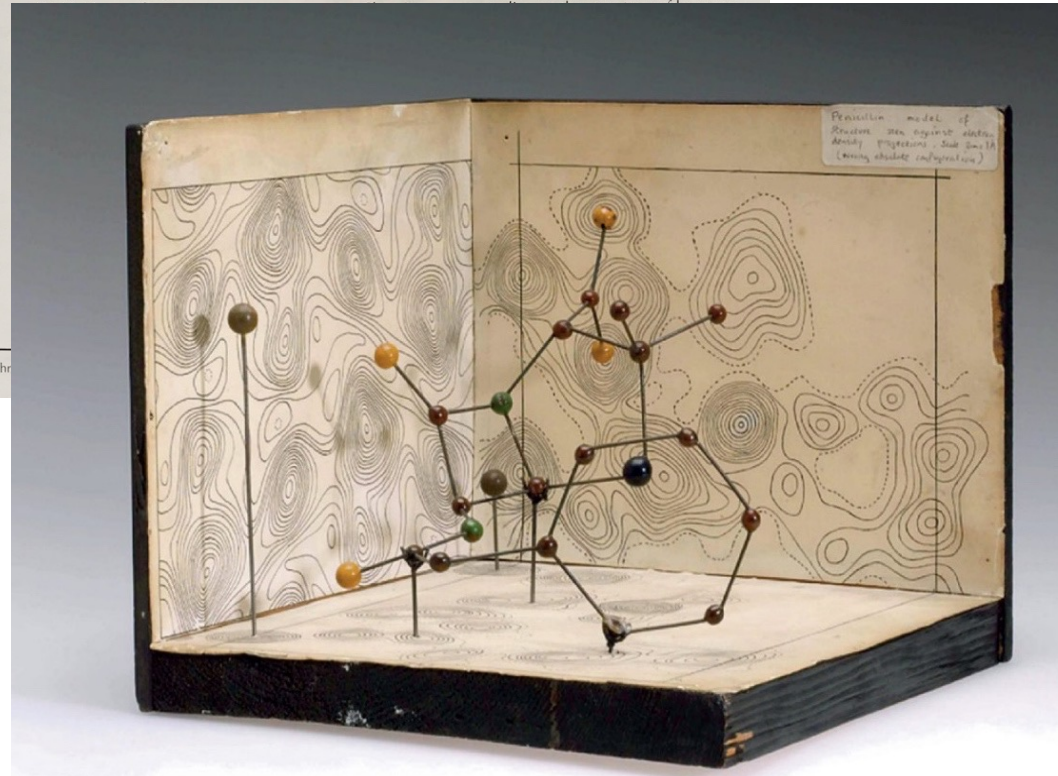


Table 1.1 Nobel Prizes awarded in the field of x-ray research.

Year	Recipient(s)	Research discipline
1901	W. C. Röntgen	Physics; discovery of x-rays
1914	M. von Laue	Physics; x-ray diffraction from crystals
1915	W. H. Bragg and W. L. Bragg	Physics; crystal structure derived from x-ray diffraction
1917	C. G. Barkla	Physics; characteristic radiation of elements
1924	K. M. G. Siegbahn	Physics; x-ray spectroscopy
1927	A. H. Compton	Physics; scattering of x-rays by electrons
1936	P. Debye	Chemistry; diffraction of x-rays and electrons in gases
1946	H. J. Muller	Medicine; discovery of x-ray-induced mutations
1962	M. Perutz and J. Kendrew	Chemistry; structures of myoglobin and haemoglobin
1962	J. Watson, M. Wilkins, and F. Crick	Medicine; structure of DNA
1964	D. Crowfoot-Hodgkin	Chemistry; structure of penicillin
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1979		
1981		
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1988		
1997		
2003		
2006		
2009		
2012		
2018		

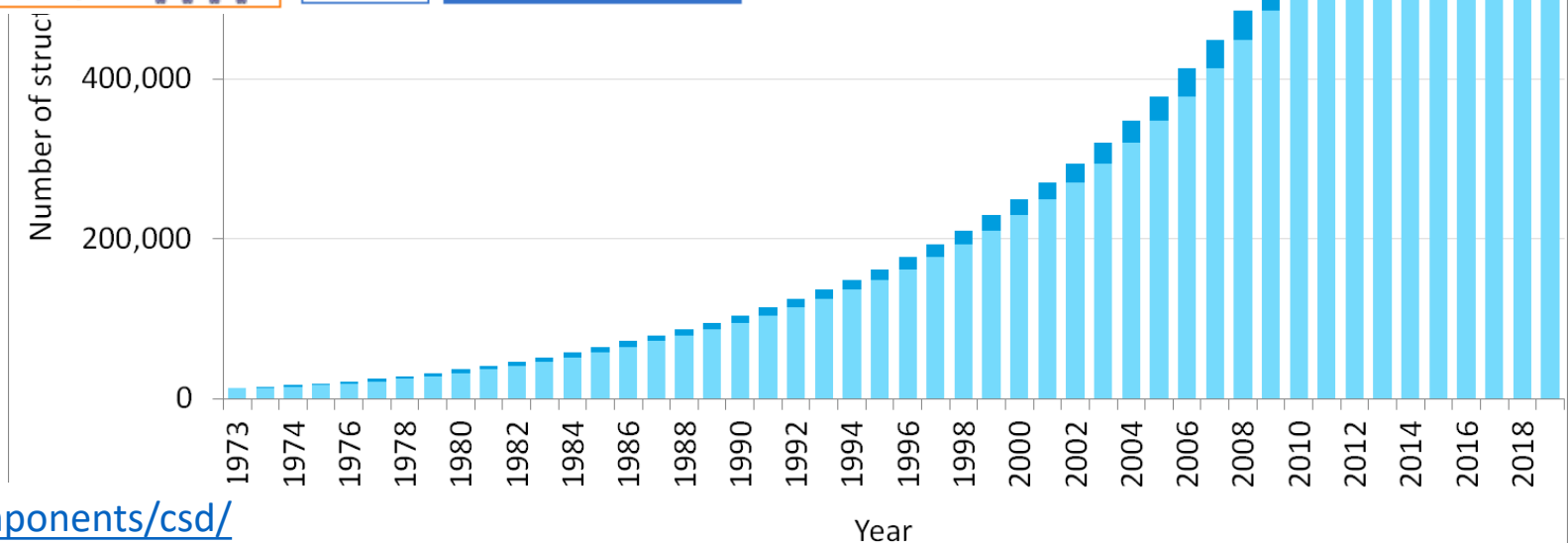
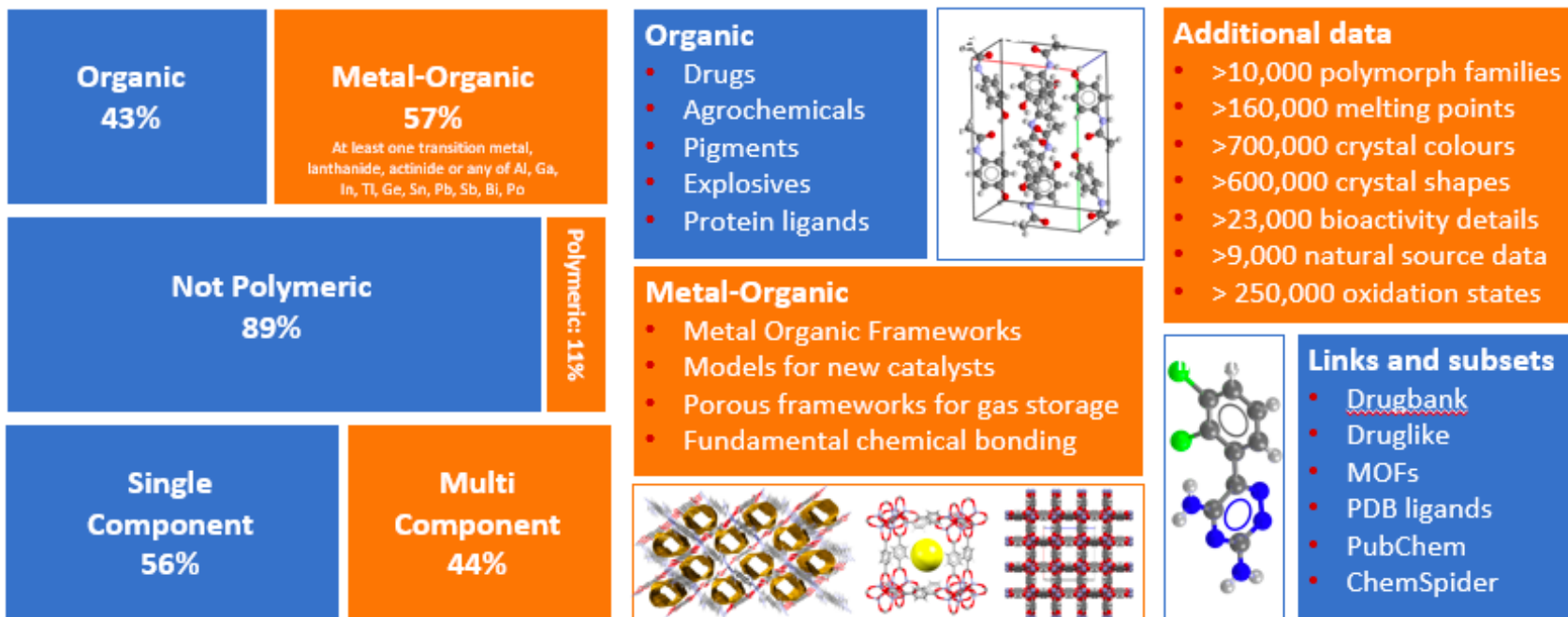
¹Work using synchrotron



Why care about x-ray diffraction of crystals?

Why should we care about x-rays, crystals, lattices, etc?

Source:
The Cambridge Structural Database (CSD)



Example: Diamondoids – Diamond Molecules

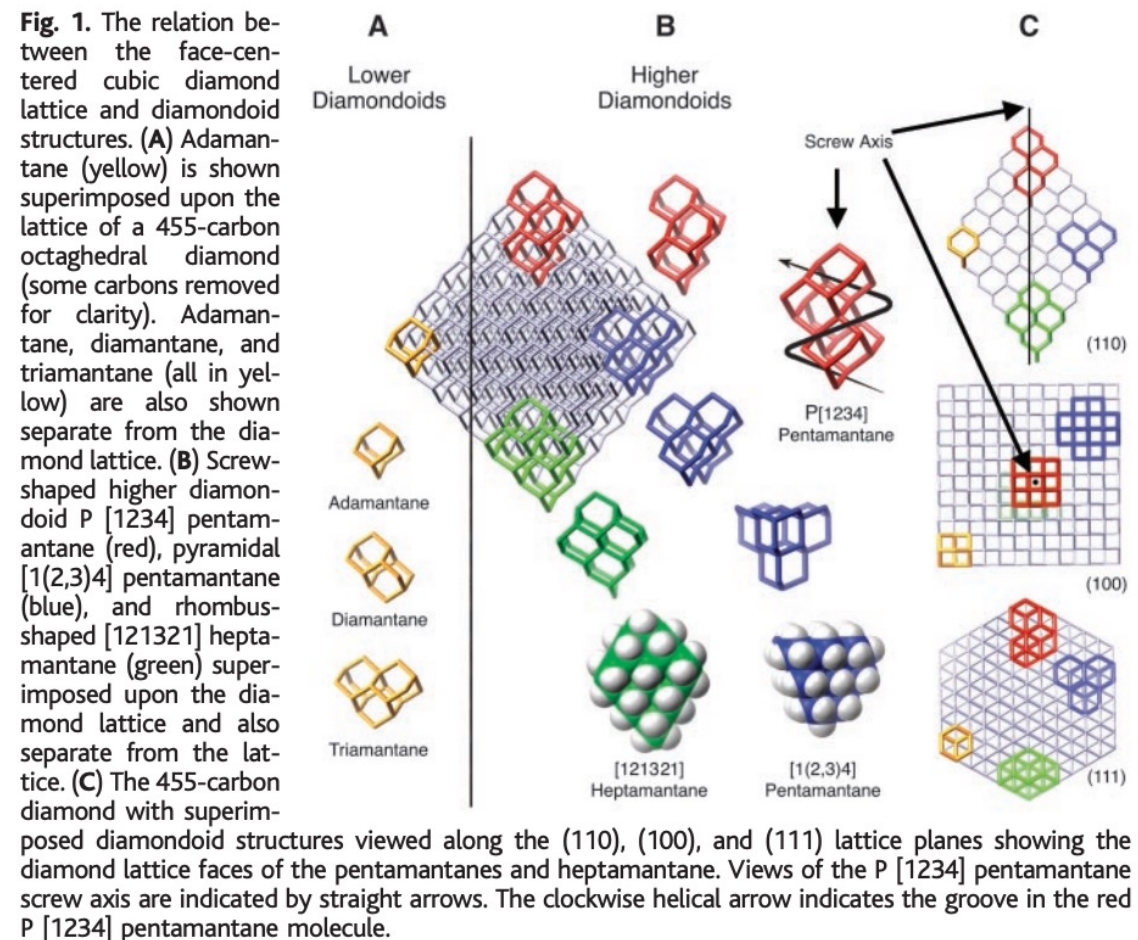
REPORT

Isolation and Structure of Higher Diamondoids, Nanometer-Sized Diamond Molecules

J. E. Dahl, S. G. Liu, R. M. K. Carlson*

+ See all authors and affiliations

Science 03 Jan 2003:
Vol. 299, Issue 5603, pp. 96-99
DOI: 10.1126/science.1078239



Supplemental Material: Crystallization for XRD

Crystallization

We crystallized specific higher diamondoids from Hypercarb HPLC fractions by preparing super-saturated solutions in acetone. Crystallization vials (standard GC-MS autosampler vials) were sealed for approximately one to two weeks after which a small hole was made in the caps and the solvent allowed to evaporate. The crystals were harvested and submitted for structural determination by X-ray crystallography. Fig. S1

2

shows [1(2,3)4] pentamantane (structure 7 in Fig. 3 in the paper) grown using this method.



Fig. S1. Photomicrographs of [1(2,3)4] pentamantane crystals used for X-ray crystallography. Field of view, approx. 3.5 mm. Photograph, Marilyn Olmstead, U. C. Davis.

Cambridge Structural Database entry



CSD Entry: GUTDAA

Licensed to: Paul Scherrer Institute (PSI)

Sign In

Simple Search Structure Search Unit Cell Search Formula Search

Your query was: Compound name: pentamantane and the search returned 6 records.

Back to Search List

Modify Search

New Search

Results

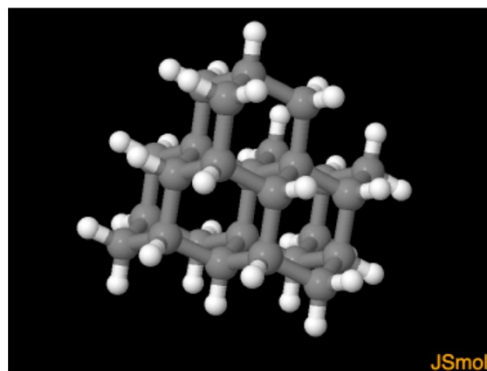
☒	Database Identifier	Deposition Number
☒	GUTDAA	198851

Download ▾

GUTDAA : (12/3/4)Pentamantane

Space Group: $P 2_1/n$ (14), Cell: a 7.7105(9)Å b 27.040(3)Å c 8.9375(10)Å, α 90° β 115.121(4)° γ 90°

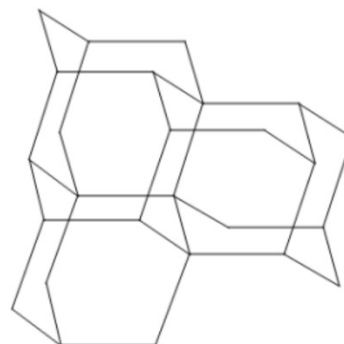
3D viewer



H Disorder Menu Open ▾

Style: Ball and Stick ▾ Labels: No Labels ▾ Packing: None ▾ Measure: None ▾

Chemical diagram



View group symbols key

Additional details

Deposition Number	198851
Data Citation	J.E.Dahl, S.G.Liu, R.M.K.Carlson CCDC 198851: Experimental Crystal Structure Determination, 2003, DOI: 10.5517/cc6nxx9
Deposited on	29/11/2002

Associated publications



J.E.Dahl, S.G.Liu, R.M.K.Carlson, *Science*, 2003, 299, 96, DOI: 10.1126/science.1078239

Chemical details

Formula $C_{26}H_{32}$

Crystal details

Space group	$P 2_1/n$ (14)
Unit cell	a 7.7105(9)Å b 27.040(3)Å c 8.9375(10)Å α 90° β 115.121(4)° γ 90°
Cell volume	1687.14
Reduced cell	a 7.711Å b 8.938Å c 27.040Å α 90.000° β 90.000° γ 115.121°
Z, Z'	4, 1
Habit	needle
Colour	colorless

Experimental details

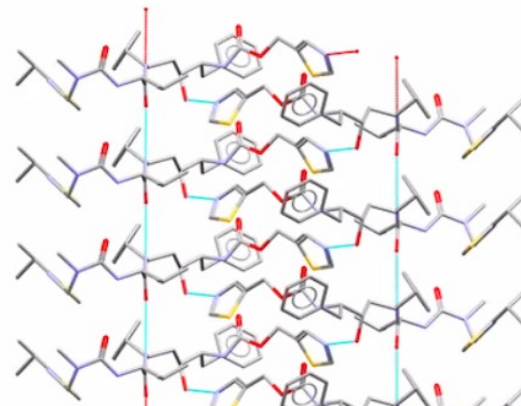
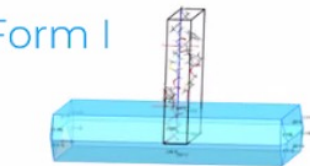
R-factor (%)	5.23
Temperature (K)	90
Density (CCDC)	1.356
Radiation probe	x-ray
Experiment type	single crystal

A real world example: Crystal structure of the Novir Drug

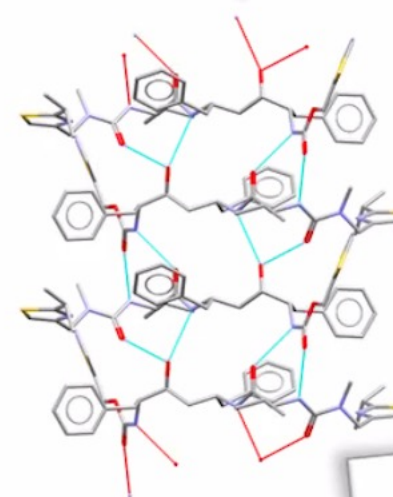
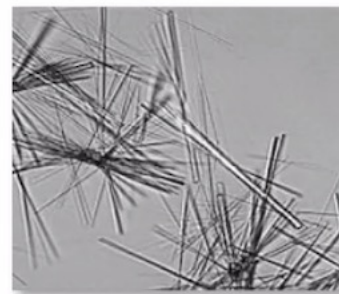
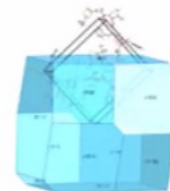
Crystalline structure of (drug) compounds determines

- Melting properties
- Hygroscopicity
- Hydrate formation
- Soluablility
- And other properites

Form I



Form II



A real world example: Crystal structure of the Novir Drug

Science news:

> [Pharm Res.](#) 2001 Jun;18(6):859-66. doi: 10.1023/a:1011052932607.

Ritonavir: an extraordinary example of conformational polymorphism

J Bauer ¹, S Spanton, R Henry, J Quick, W Dziki, W Porter, J Morris

Affiliations + expand

PMID: 11474792 DOI: [10.1023/a:1011052932607](https://doi.org/10.1023/a:1011052932607)

Abstract

Purpose: In the summer of 1998, Norvir semi-solid capsules supplies were threatened as a result of a new much less soluble crystal form of ritonavir. This report provides characterization of the two polymorphs and the structures and hydrogen bonding network for each form.

Methods: Ritonavir polymorphism was investigated using solid state spectroscopy and microscopy techniques including solid state NMR, Near Infrared Spectroscopy, powder X-ray Diffraction and Single crystal X-ray. A sensitive seed detection test was developed.

Results: Ritonavir polymorphs were thoroughly characterized and the structures determined. An unusual conformation was found for form II that results in a strong hydrogen bonding network. A possible mechanism for heterogeneous nucleation of form II was investigated.

Conclusions: Ritonavir was found to exhibit conformational polymorphism with two unique crystal lattices having significantly different solubility properties. Although the polymorph (form II) corresponding to the "cis" conformation is a more stable packing arrangement, nucleation, even in the presence of form II seeds, is energetically unfavored except in highly supersaturated solutions. The coincidence of a highly supersaturated solution and a probable heterogeneous nucleation by a degradation product resulted in the sudden appearance of the more stable form II polymorph.

Similar articles

Business news:



Abbott Reports Production Problems For Norvir

27-07-1998

Abbott Laboratories has reported that it is having difficulties maintaining production of its HIV protease inhibitor Norvir (ritonavir). The problems are related to its capsule formulation of the antiretroviral.

"We have encountered an undesired formation of a Norvir crystalline structure that affects how the capsule form of Norvir dissolves," commented Arthur Higgins, senior vice president for pharmaceutical operations at Abbott. Although the problem has been identified, to date the company has been unable to come up with a solution.

Abbott stressed that capsules already in circulation are not affected, but there will be shortages and an interruption in supply of the product. Given the seriousness of interrupting treatment in highly-active antiretroviral therapy (which could be associated with the development of resistance and ultimately treatment failure), Abbott is planning to manufacture Norvir in a substitute oral solution so that patients on the drug can maintain their supply. It is estimated that 60,000-70,000 people with HIV are taking the drug.

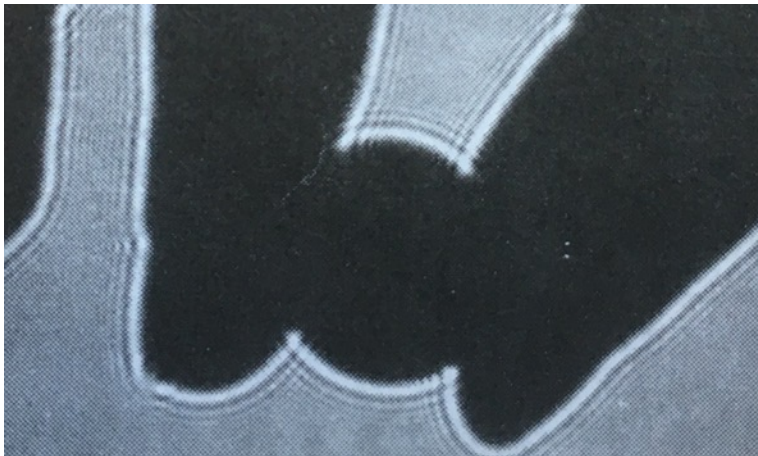
Effect On Full-Year Sales? Abbott had been projecting sales of around \$250 million for Norvir in 1998, and as yet it is unclear whether the supply problems will impact this figure. Sales of the drug last year were around \$170 million, less than the performance seen with the other protease inhibitors in 1997. Datamonitor says that Merck & Co's Crixivan (indinavir) had sales of \$240 million last year, while Agouron's Viracept (nelfinavir) made around \$190 million last year, and Roche's Invirase (saquinavir) made over \$200 million.

Analyst Hemant Shah of HKS & Co told Reuters that the other protease inhibitors would definitely gain market share at the expense of Norvir, adding that the impact on Abbott's bottom line will depend greatly on the duration of the problem.

Some very basics about diffraction and scattering

Diffraction, a short review

- Should be familiar concept
- A wave encountering an object changes its wavefront. Note that this can also be a density change (later more)
- Fundamental properties of all waves with relevant effects from electron microscopy to shaping coastal landscapes
- In optics most commonly known for limiting resolution in optical setups (microscopes)
- But there is much more!

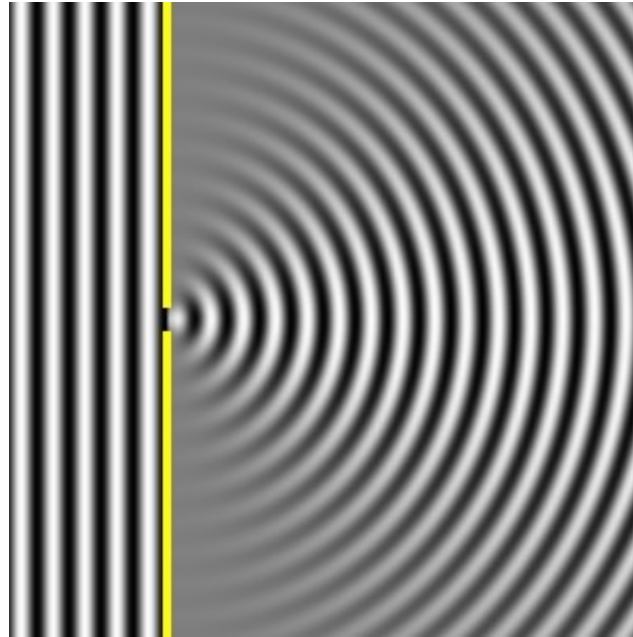


<https://physicsforme.com/2012/01/04/teaching-waves-with-google-earth/>



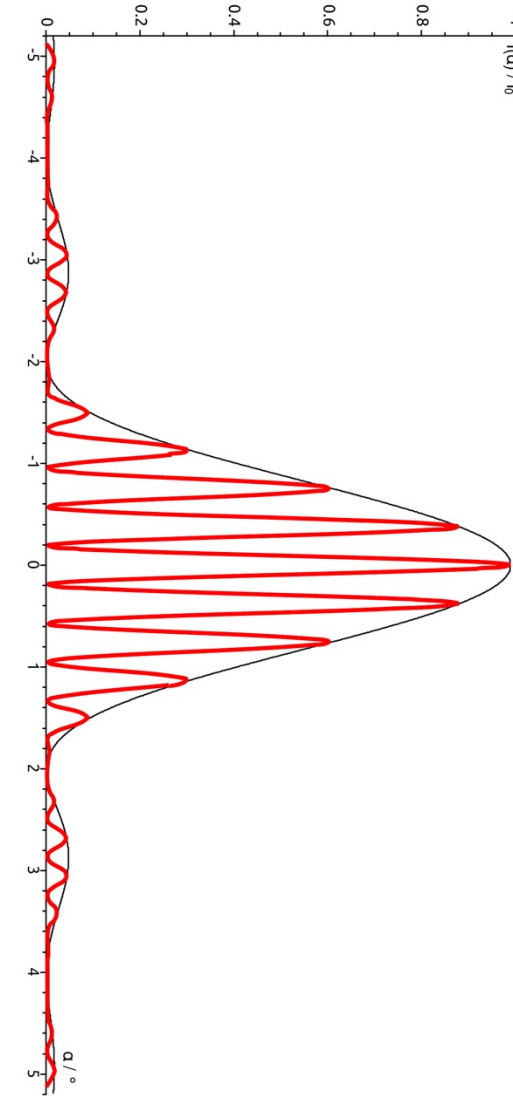
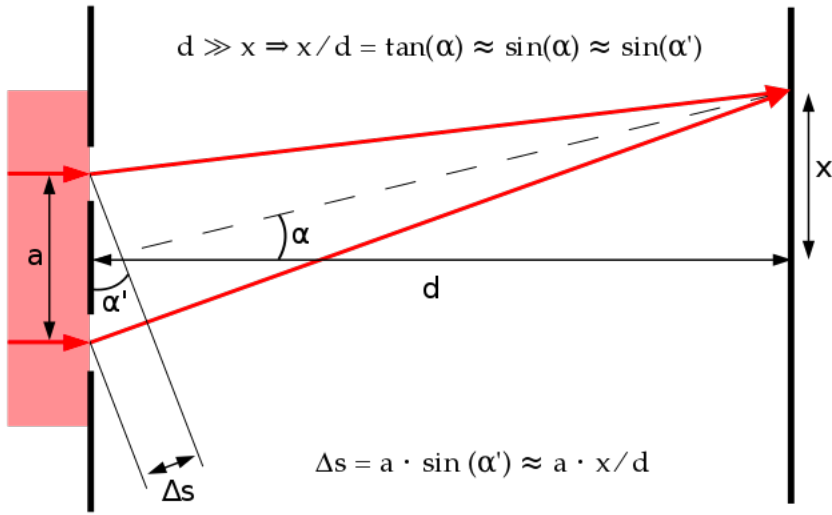
The Huygens-Fresnel Principle

- Hugen: every point a wave (a luminous disturbance) reaches becomes a source of a spherical wave; the sum of these secondary waves determines the form of the wave at any subsequent time.
- Huygens-Fresnel: every unobstructed point of a wavefront serves as a source of spherical secondary wavelets. The amplitude of the wave beyond is the superposition of all these wavelets. (includes amplitude and relative phase)

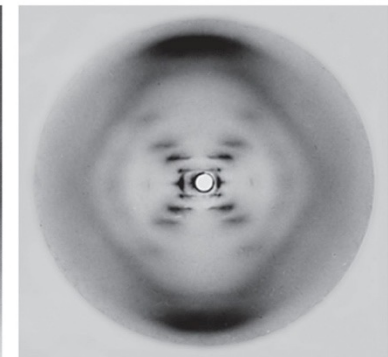
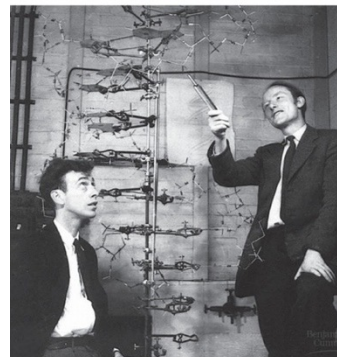
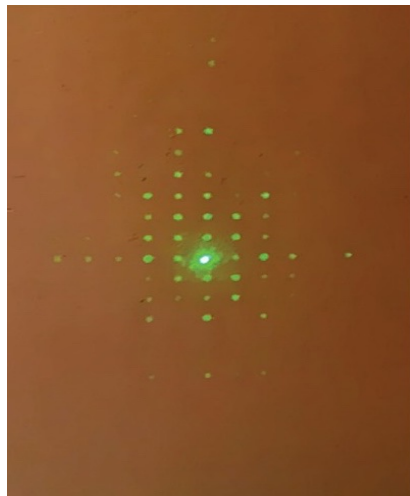
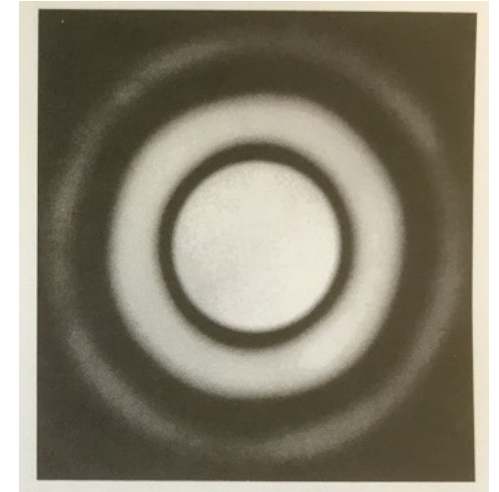
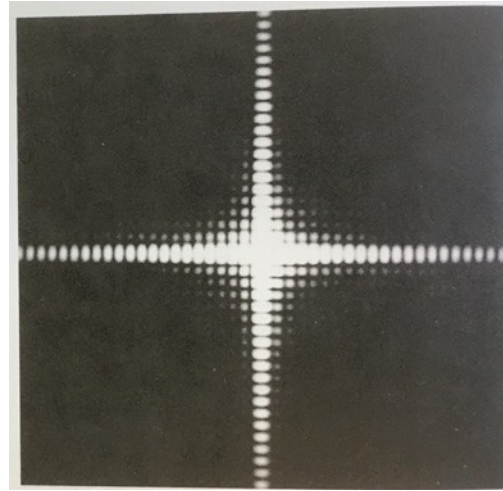
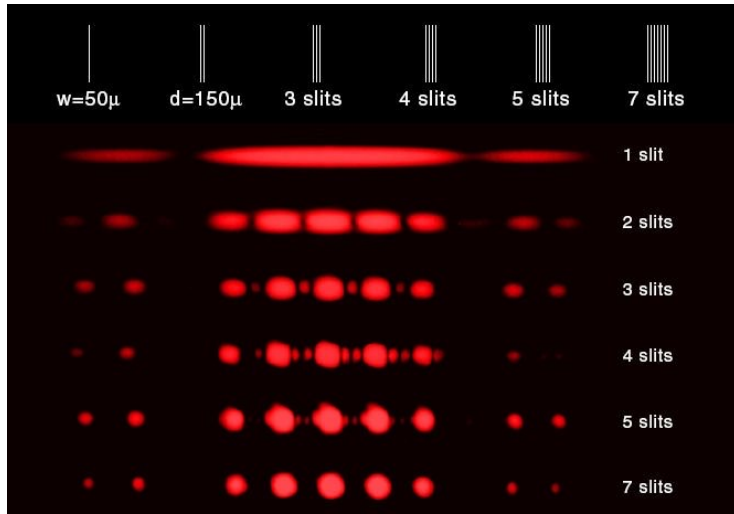


Diffraction from a single slit

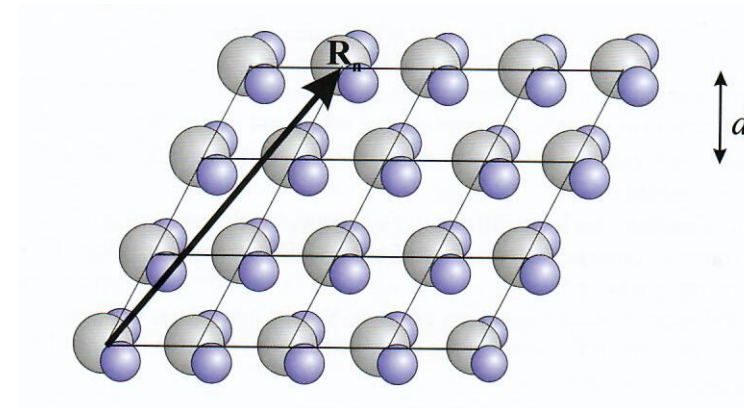
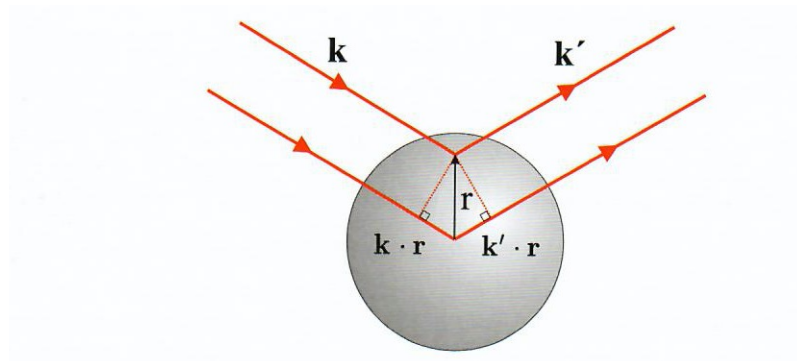
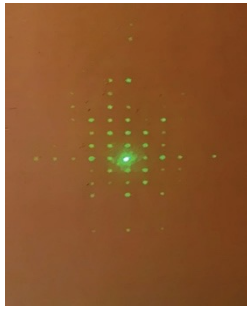
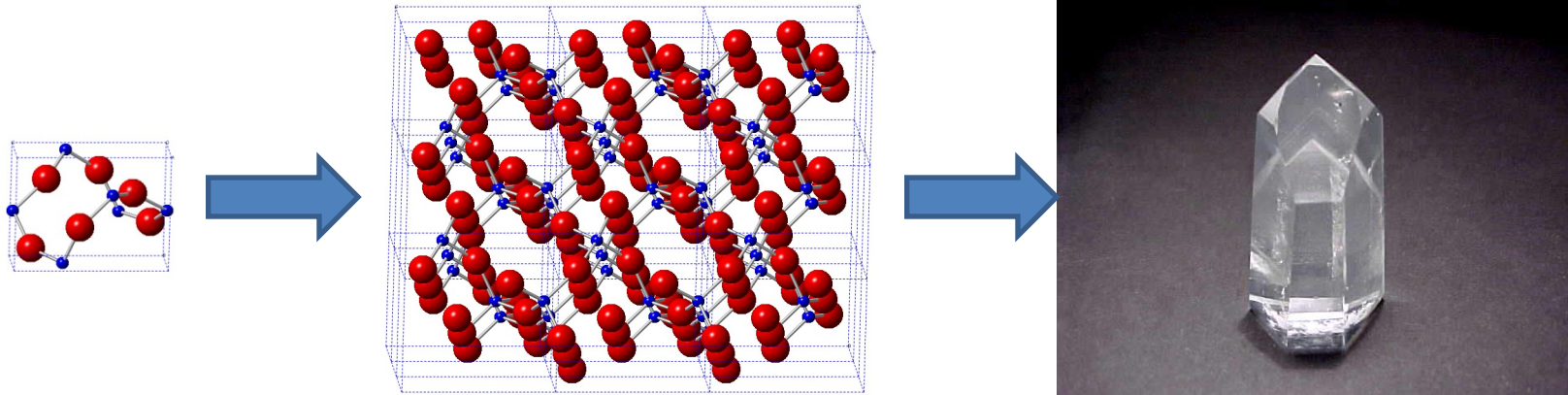
The double slit



Diffraction examples



Crystalline materials are characterized by the long-range order



Bragg scattering

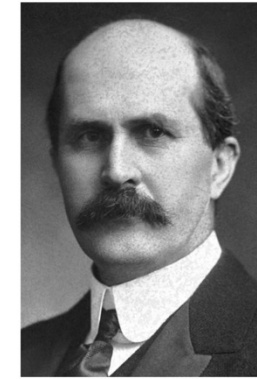
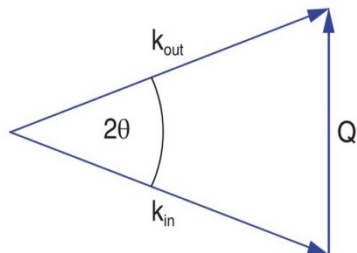
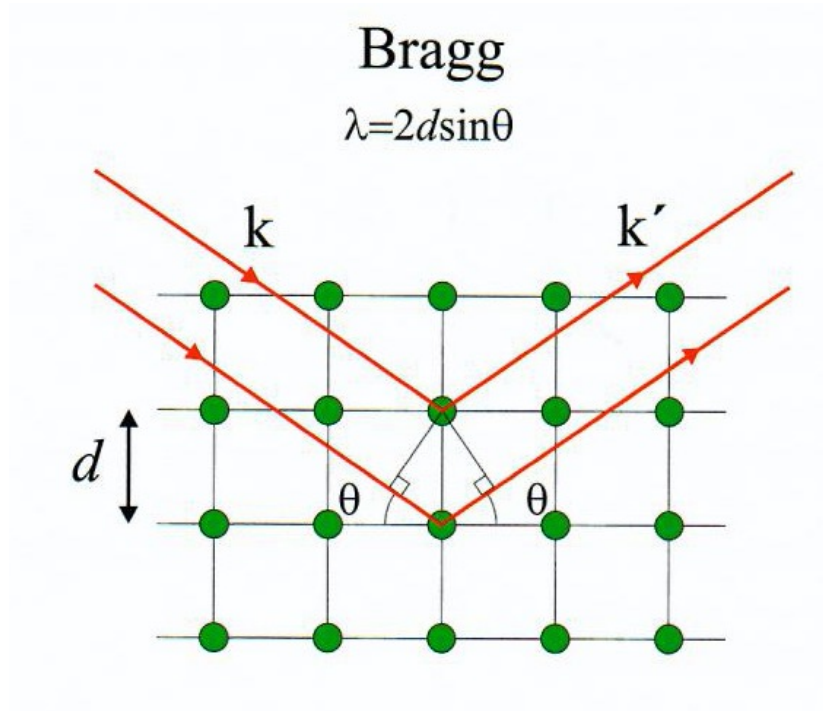


Photo from the Nobel Foundation archive.

Sir William Henry Bragg

Prize share: 1/2

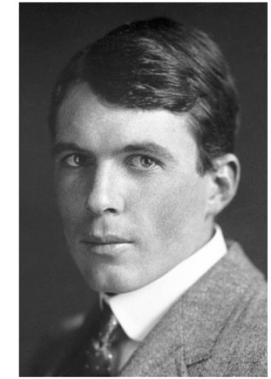
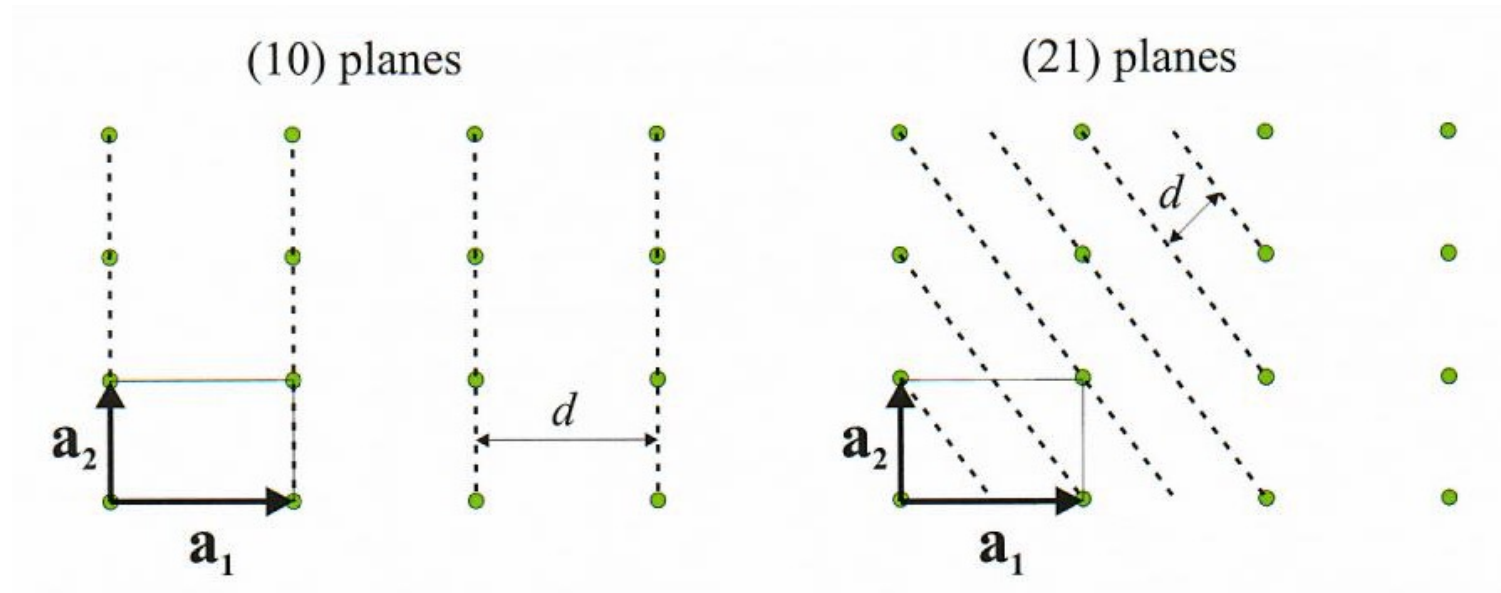
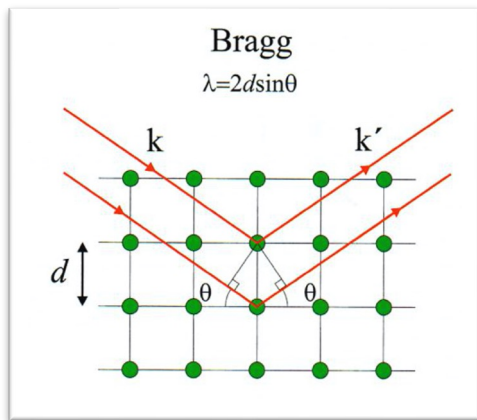


Photo from the Nobel Foundation archive.

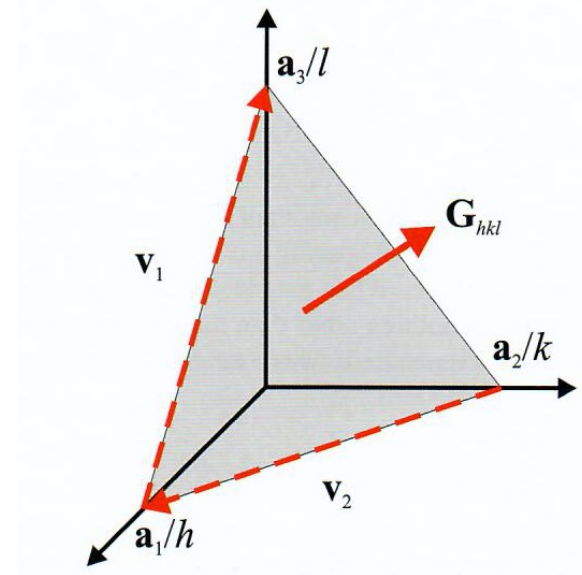
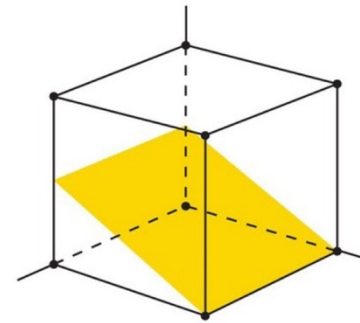
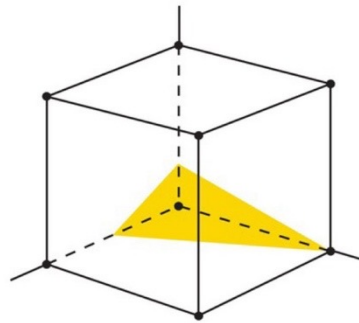
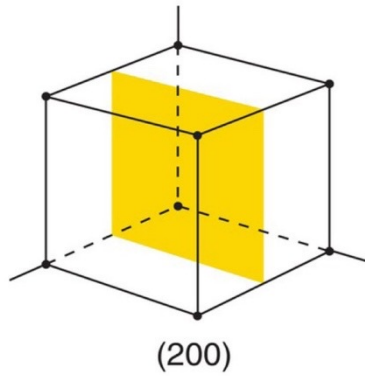
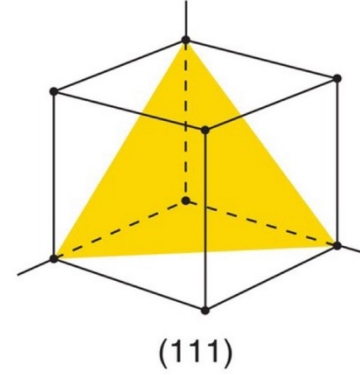
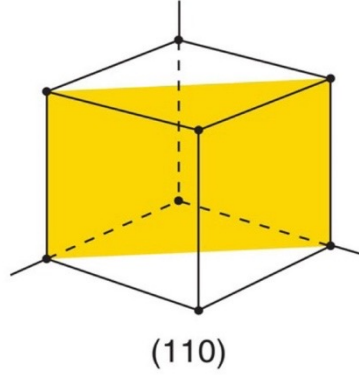
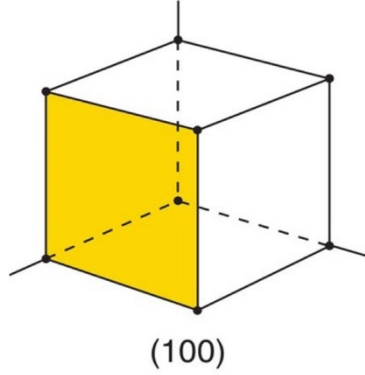
William Lawrence Bragg

Prize share: 1/2

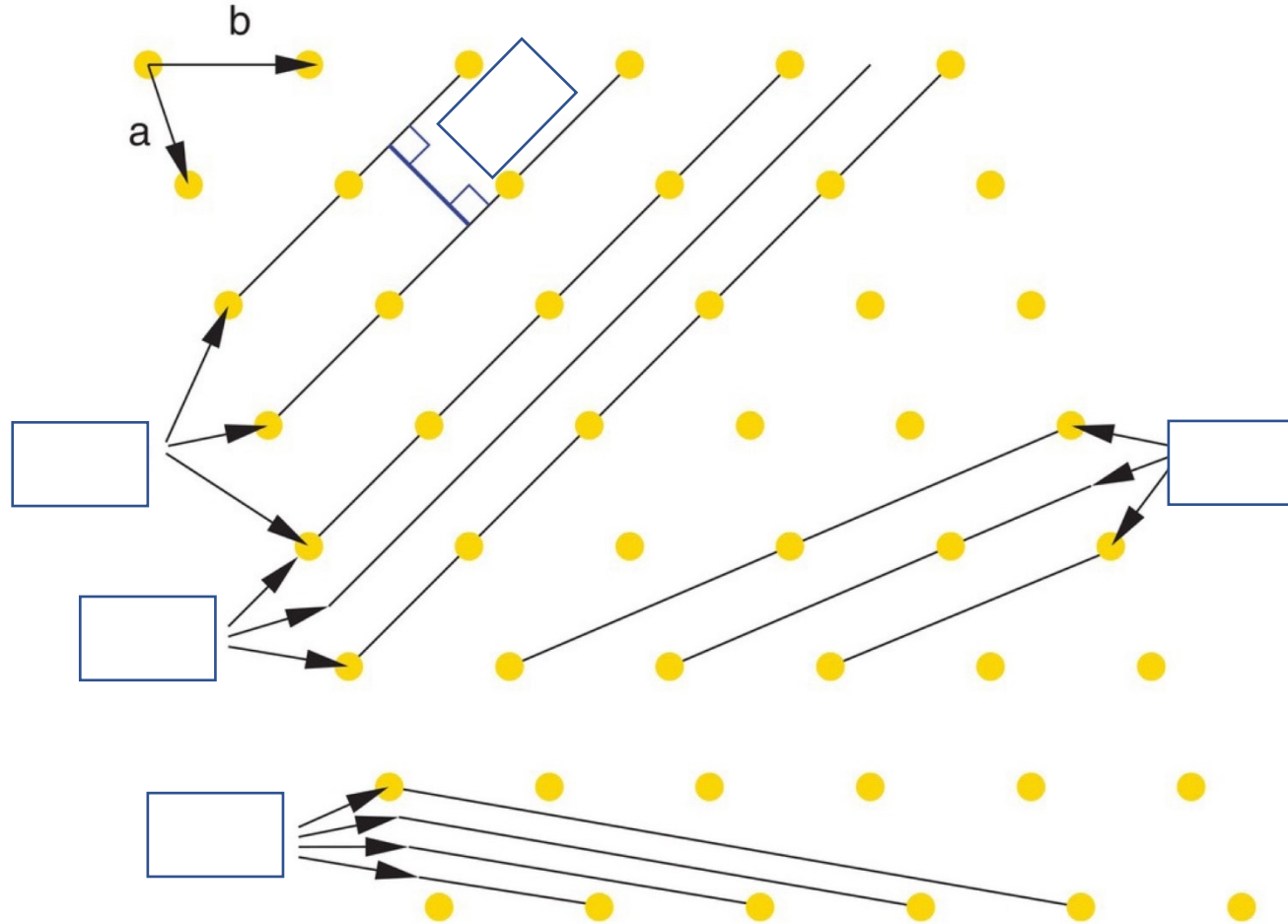
Lattice planes



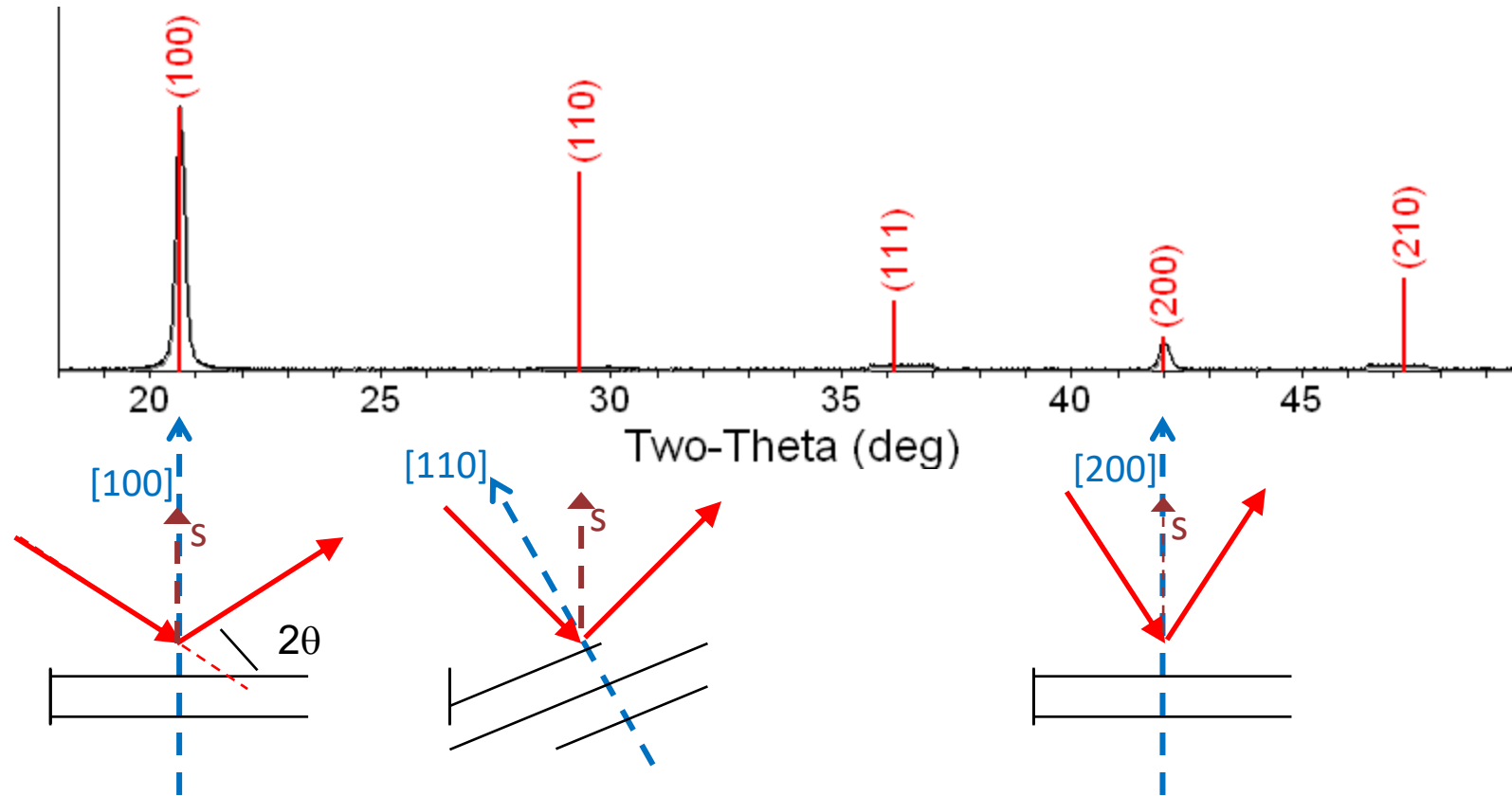
Miller indices



Exercise: Identify lattice planes

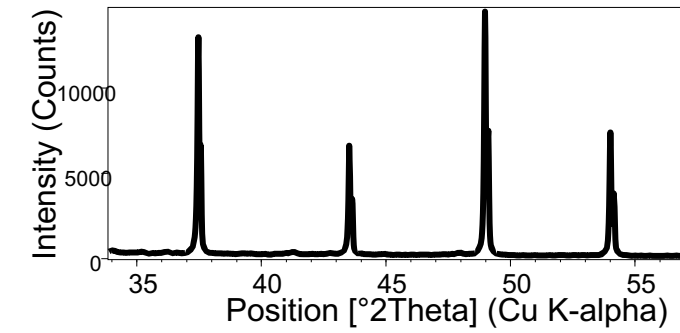
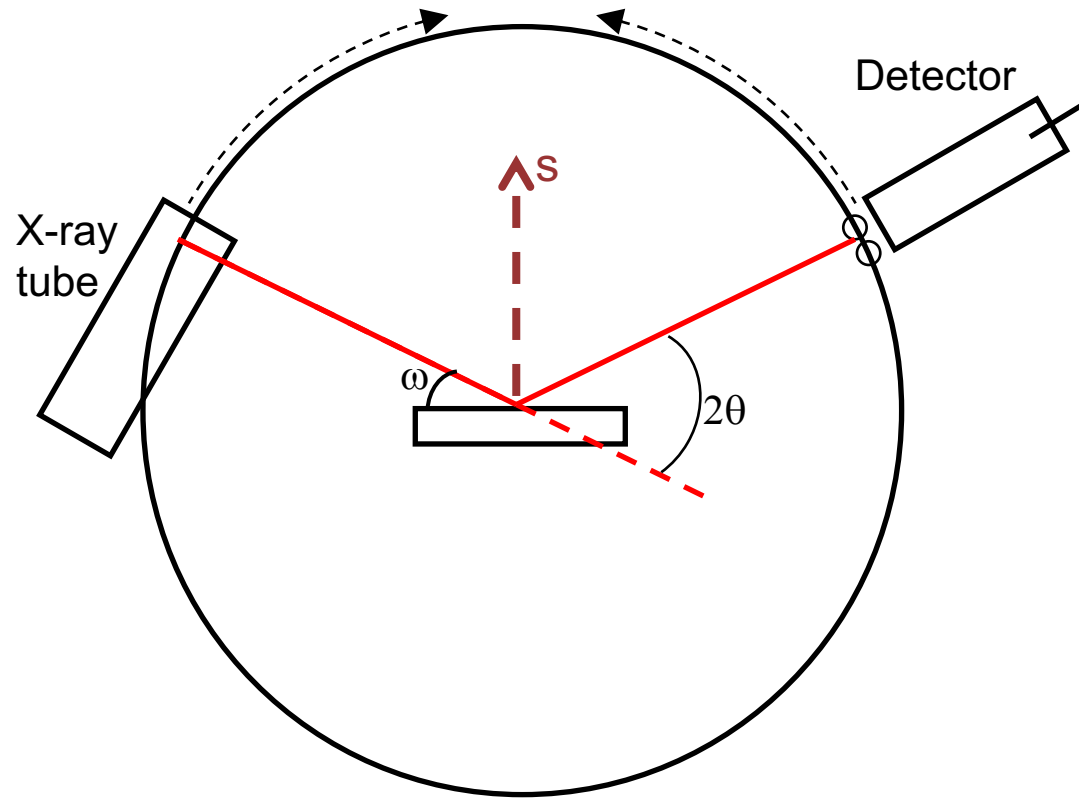


A single crystal (typically) produces one family of Bragg peaks for fixed geometry and λ

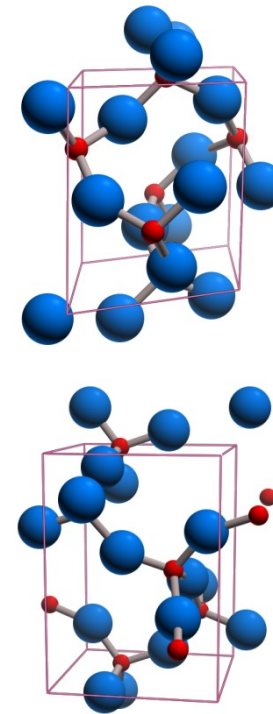
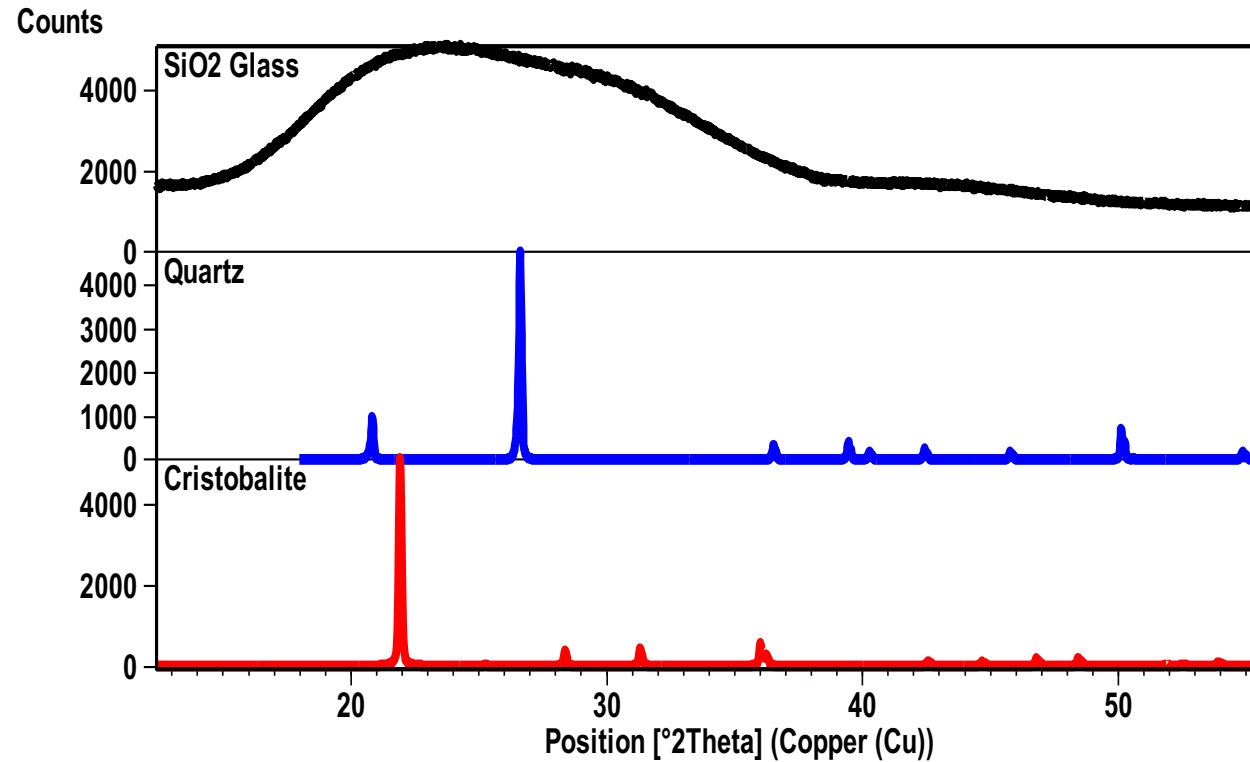


Diffraction examples

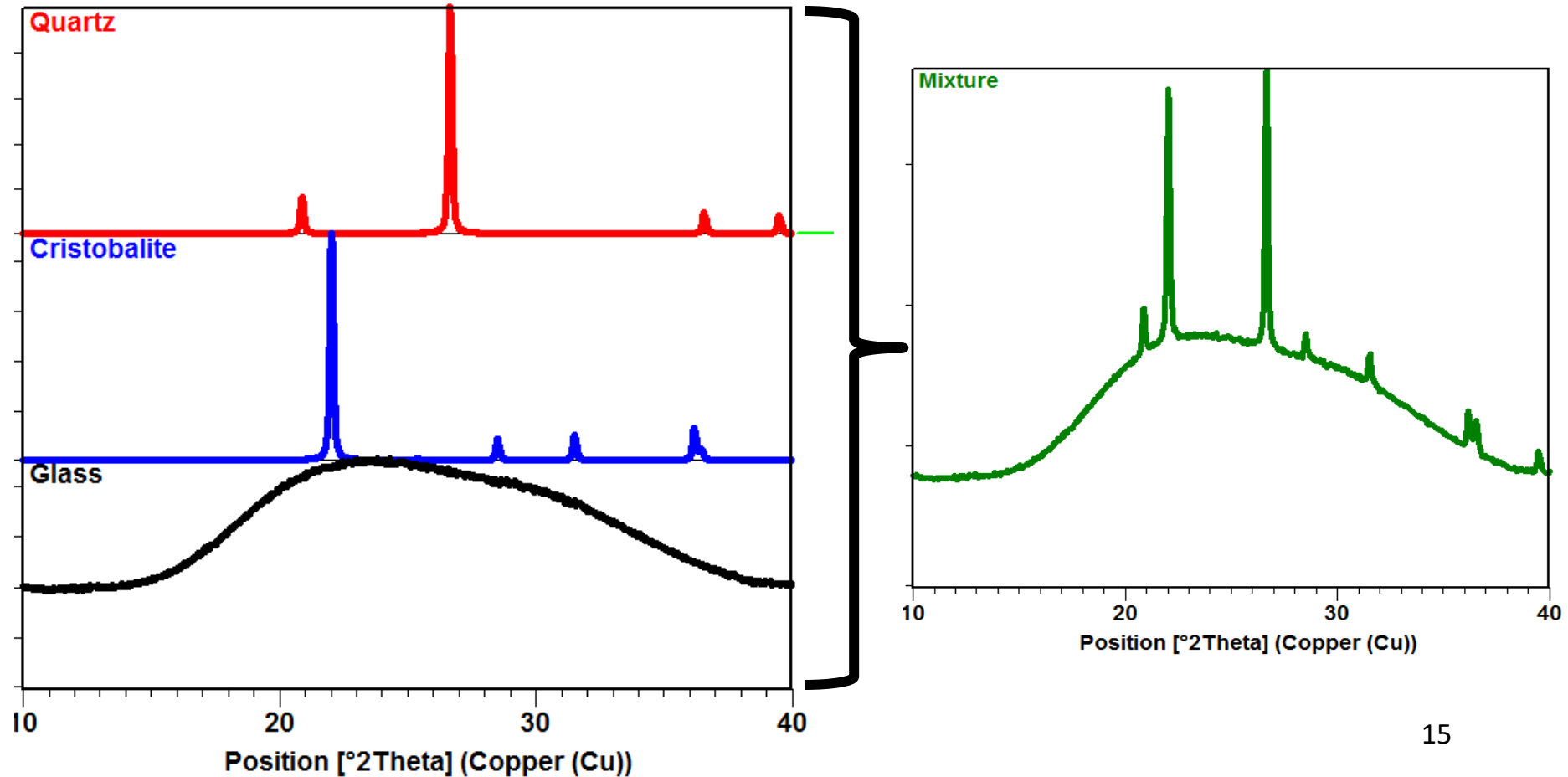
Diffraction experiment - example



Characteristic signals from different – chemically identical – samples

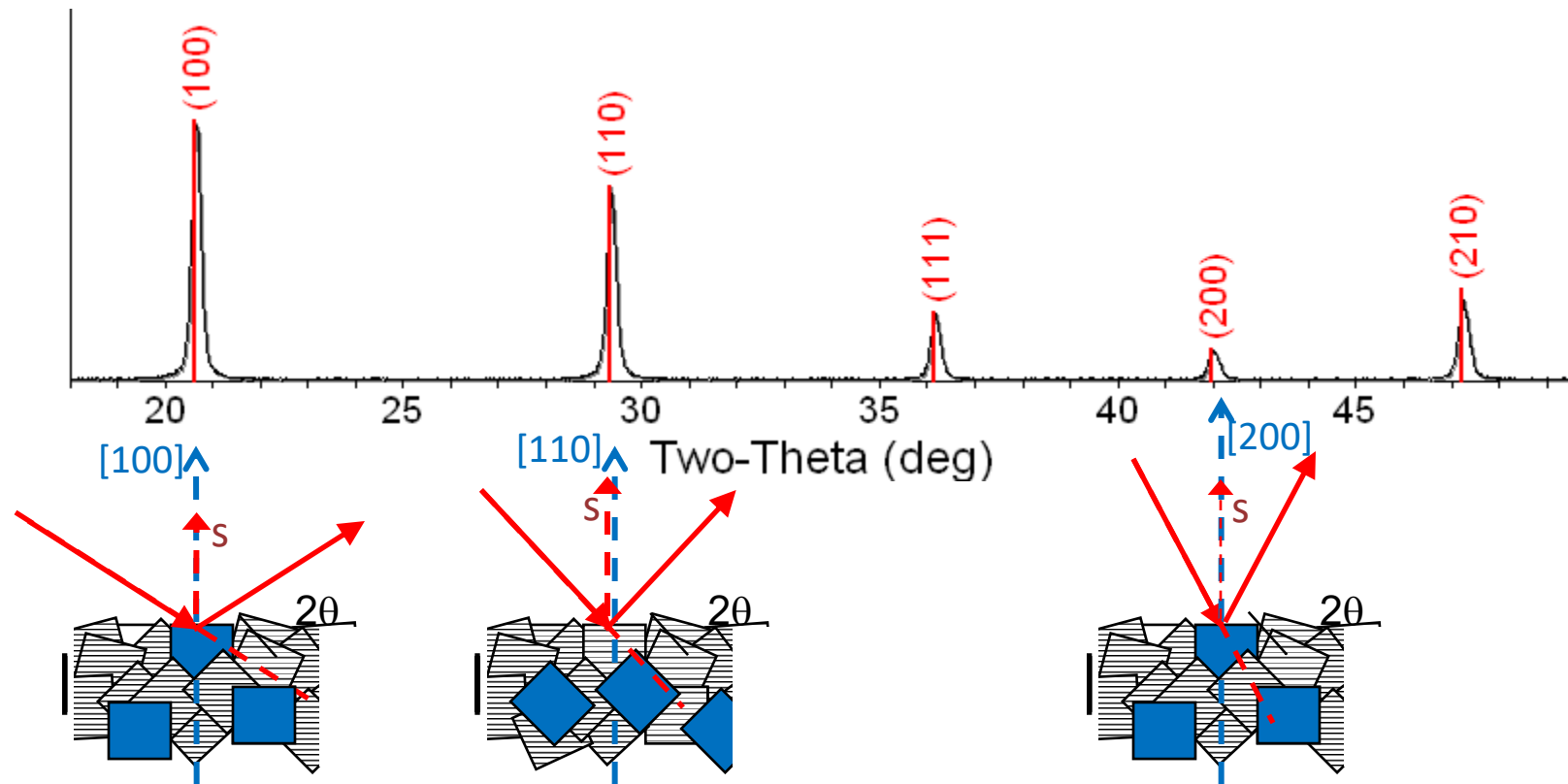


The diffraction pattern of a mixture is a simple sum from each component phase

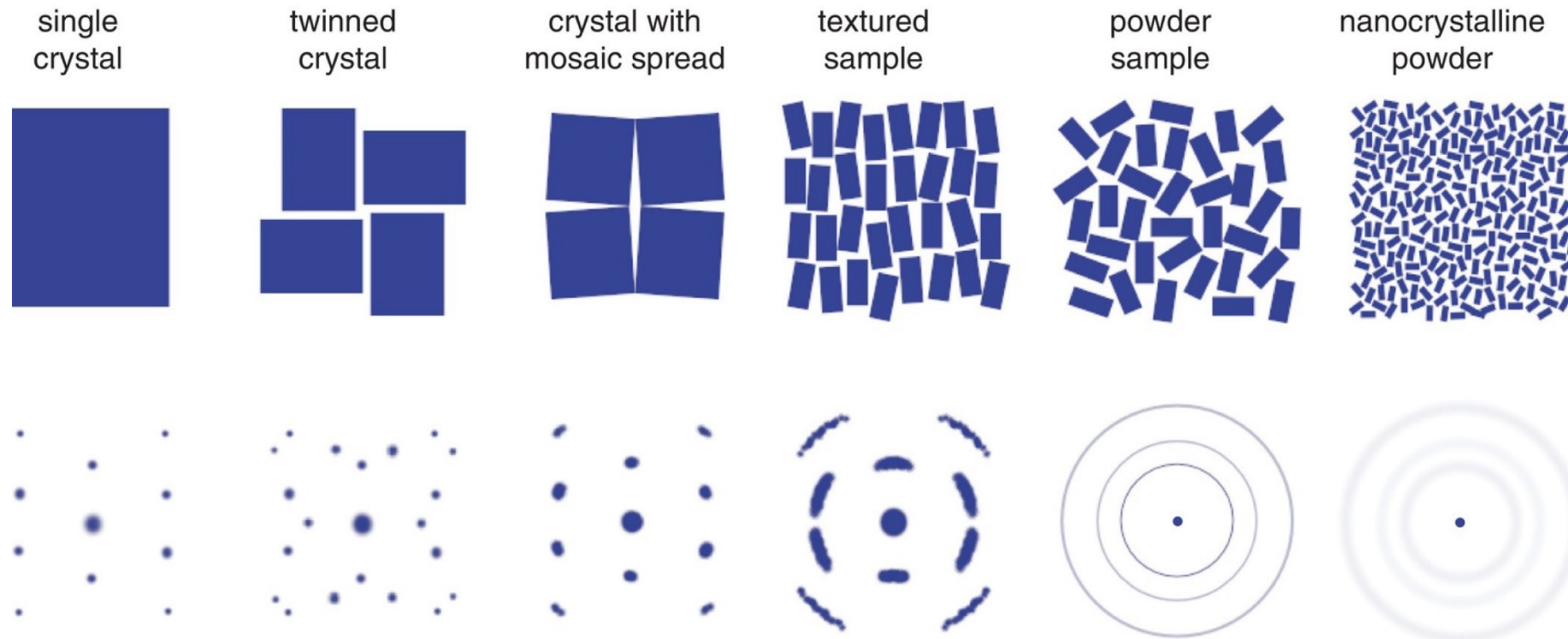


Powder diffraction

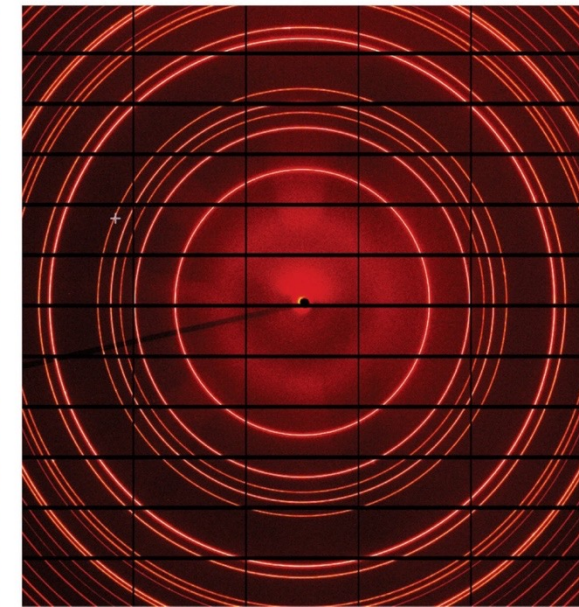
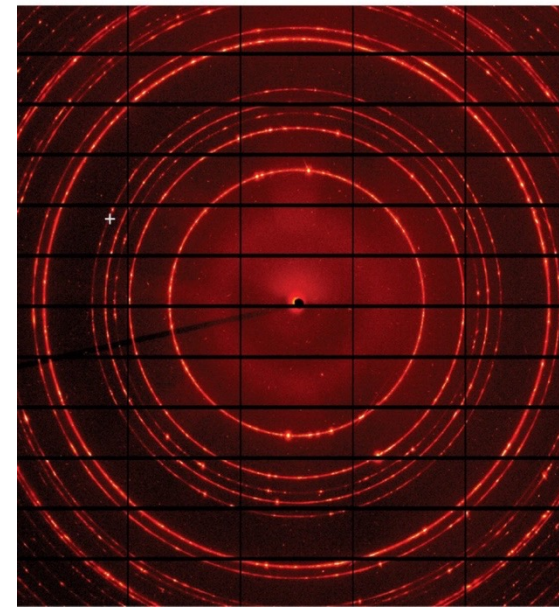
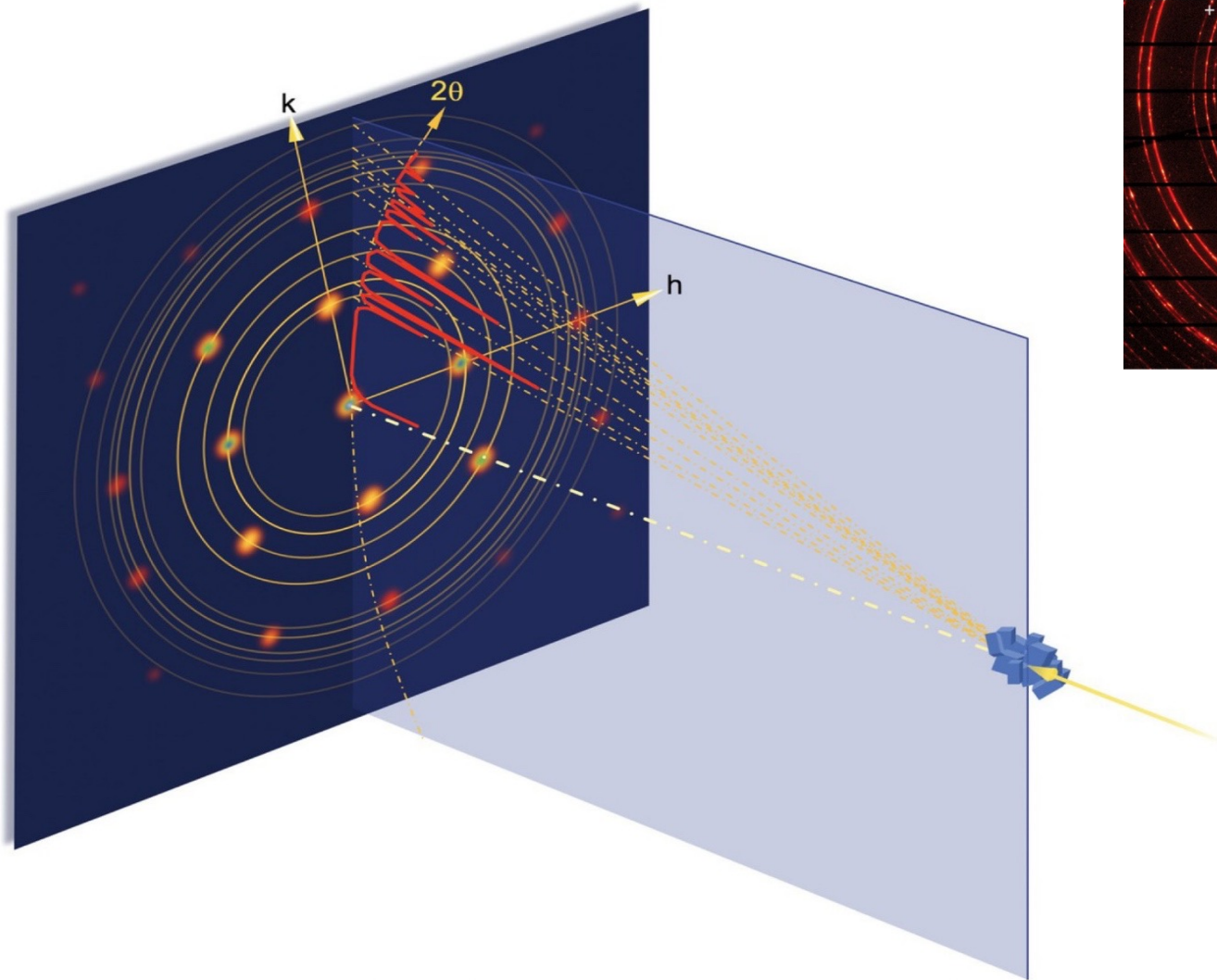
Diffraction of a polycrystalline sample



Diffraction signal of different sample types



Powder diffraction experiments



Powder diffraction geometry

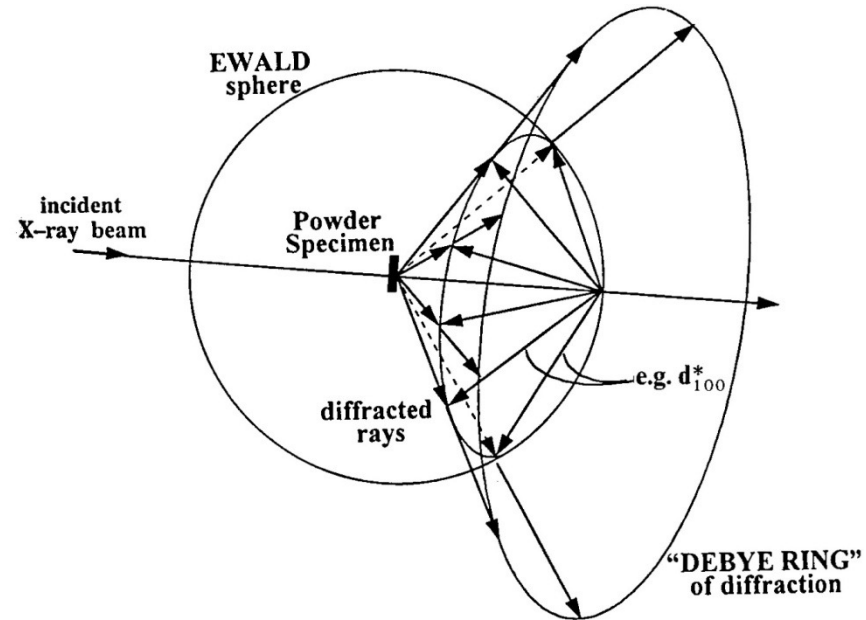
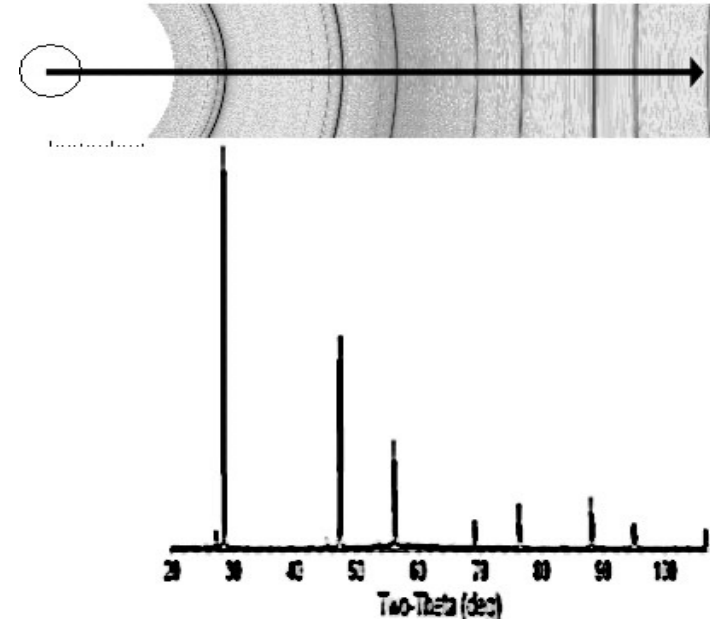
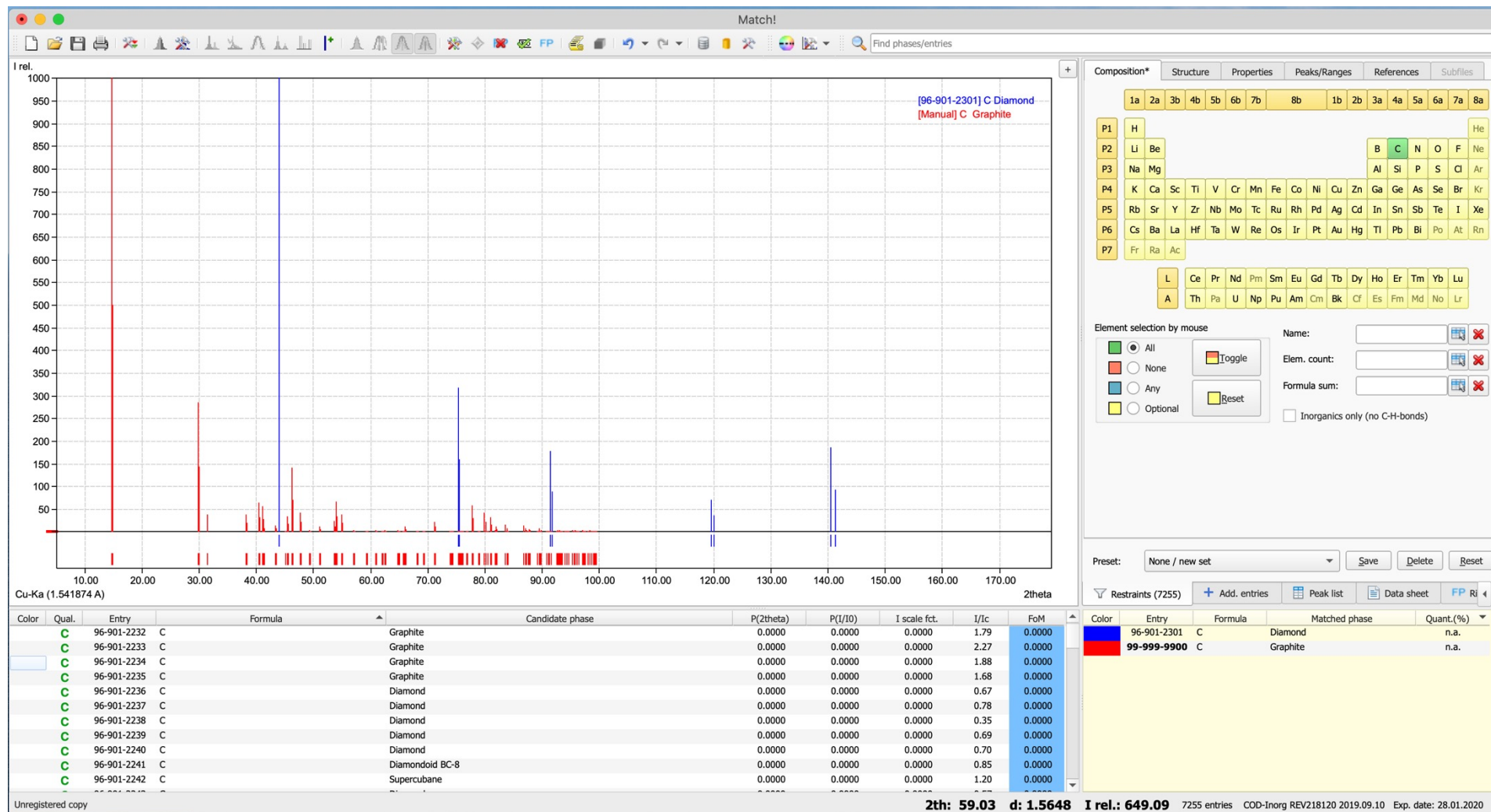


Figure 3.9. The intersection of d_{100}^* vectors from a powder with the Ewald sphere.

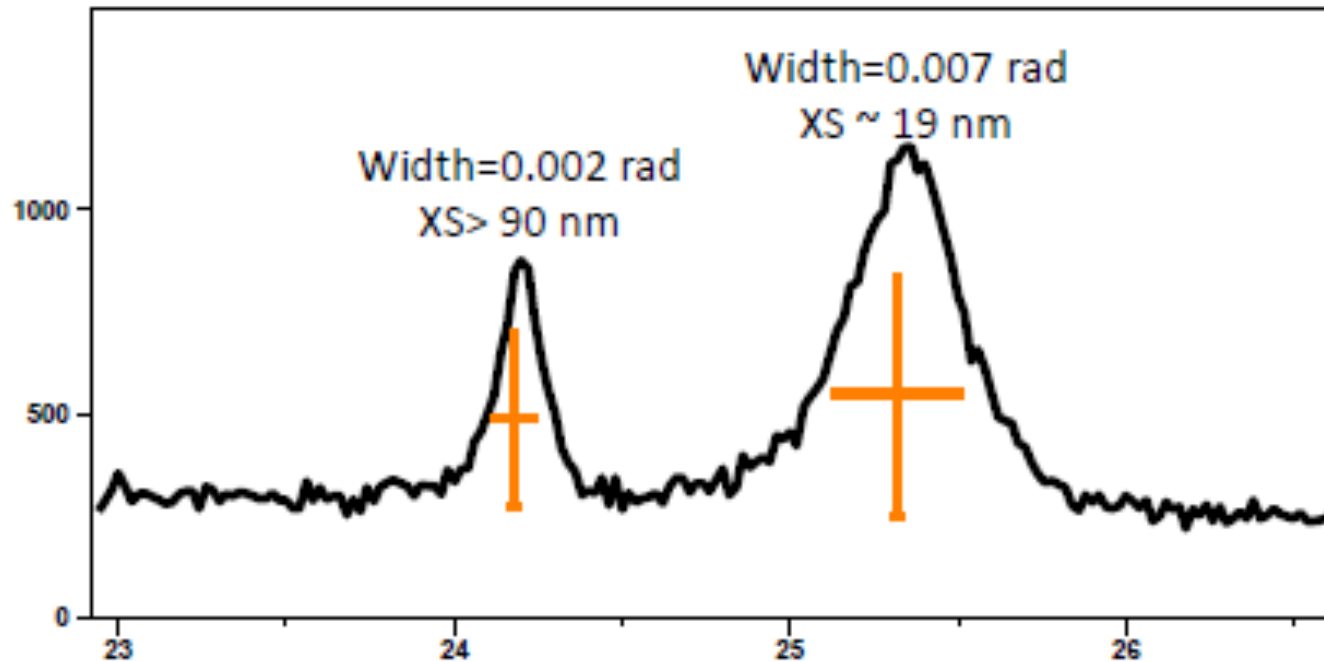


Powder diffraction data bases for elemental analysis

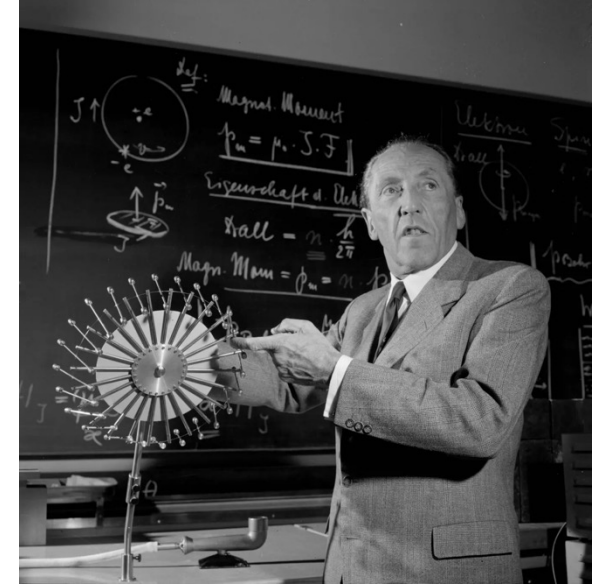


Debye-Scherrer Formula

The diffraction peak width may contain microstructural information



$$\text{Size} = \frac{K\lambda}{\text{Width} \cdot \cos \theta}$$



Paul Scherrer
Swiss Physicist (1890-1969)

Exercise: Colloidal nanoparticles

The diffraction experiments were carried out with a Stoe STADI-P X-ray powder diffractometer at University College London with a Ge(111) monochromator before the sample. A Cu $K\alpha_1$ X-ray beam of wavelength 0.154056 nm was used. The samples were measured in 0.35 mm diameter glass capillaries at room temperature. Capillary diameters were checked to be equal with a micrometer. The diffraction patterns were collected using a position-sensitive

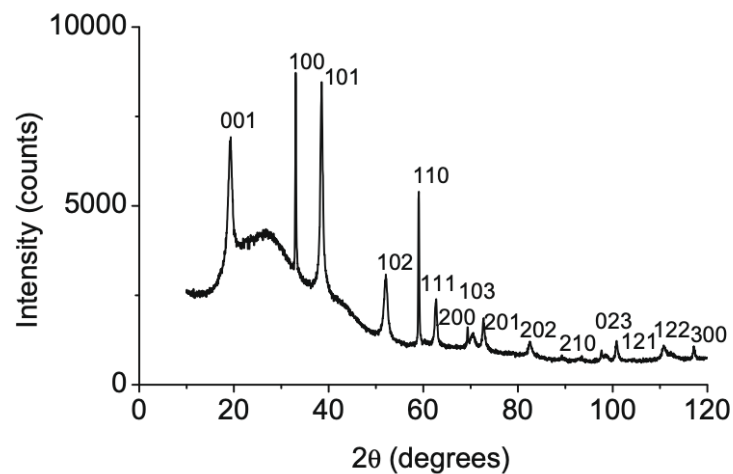


Fig. 1. X-ray diffraction pattern from $\text{Ni}(\text{OH})_2$ dispersion ($c = 4.610(3) \text{ \AA}$) with diffraction peaks labeled with hkl indices

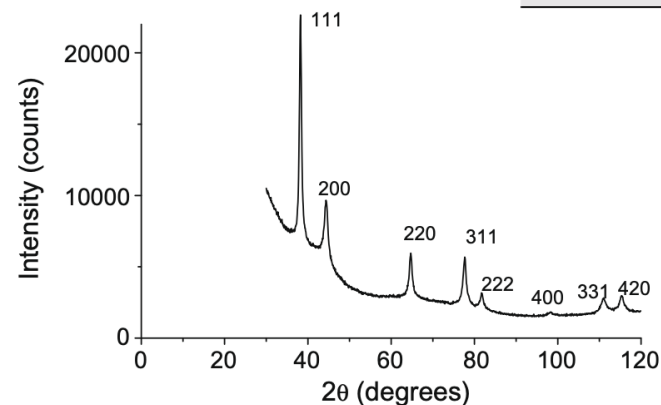


Fig. 2. X-ray diffraction patterns from dispersed Au particles ($a = 4.067(3) \text{ \AA}$) with diffraction peaks are labeled with hkl indices.



Use of wide-angle X-ray diffraction to measure shape and size of dispersed colloidal particles

S. Junaid S. Qazi^{a,*}, Adrian R. Rennie^a, Jeremy K. Cockcroft^b, Martin Vickers^b

^a Materials Physics, Uppsala University, Ångströmlaboratoriet, Box 530, 75121 Uppsala, Sweden

^b Applied Crystallography Group, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Table 1

Results from the pseudo-Voigt function fit to the $\text{Ni}(\text{OH})_2$ sample. 2θ is the peak position for the Cu $K\alpha_1$ radiation wavelength (0.154056 nm).

hkl	Bragg angle 2θ (°)	Peak width ' β ' (°)	Instrument resolution (°)	Corrected β (°)
001	19.25	1.140	0.121	1.02
100	33.06	0.197	0.115	0.08
101	38.52	0.593	0.114	0.48
102	52.06	0.876	0.117	0.76
110	59.05	0.248	0.120	0.13
111	62.67	0.550	0.122	0.43

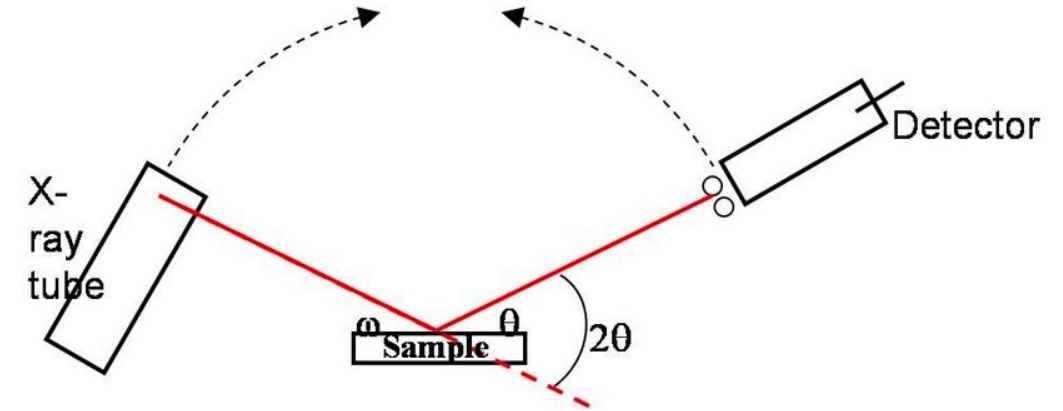
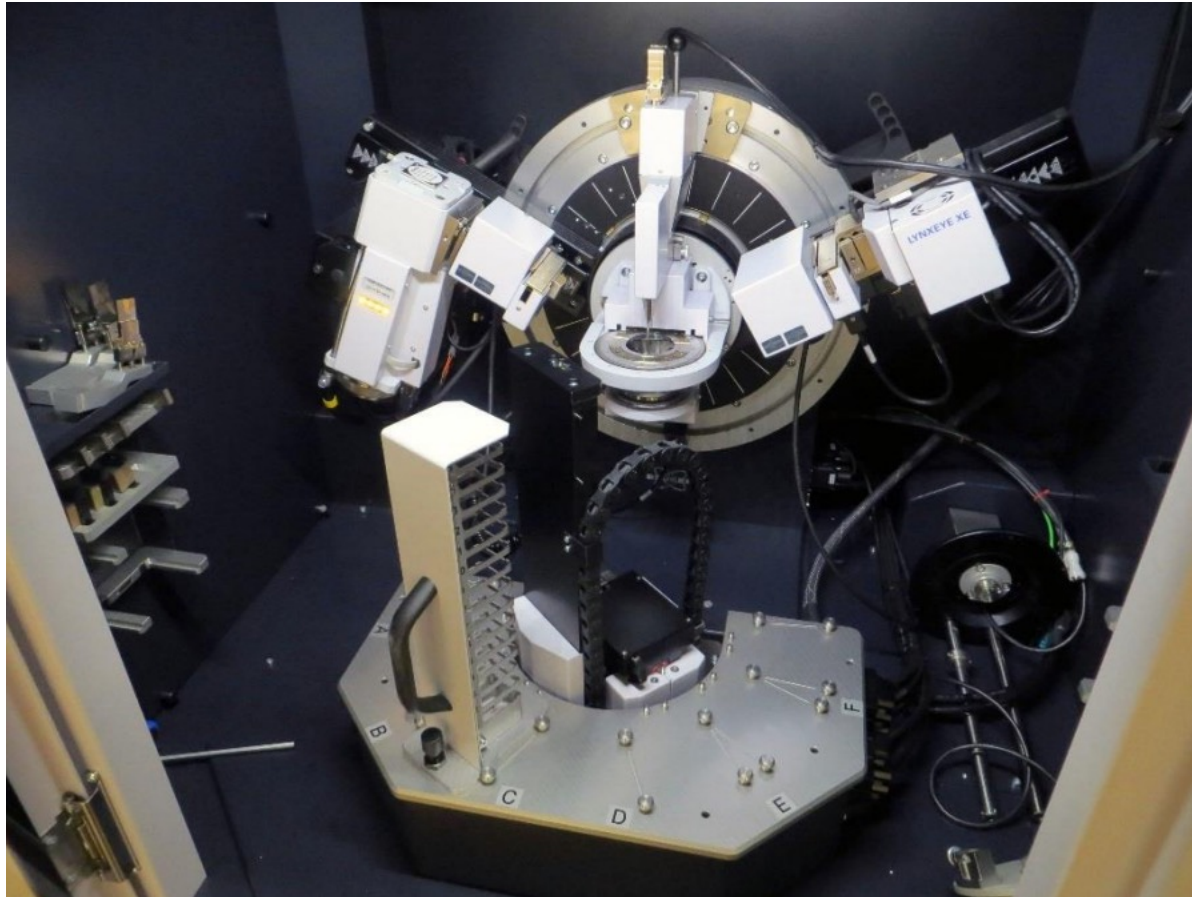
Table 2

Results from the pseudo-Voigt fit to the Au particles. 2θ is the peak position for the Cu $K\alpha_1$ radiation wavelength (0.154056 nm).

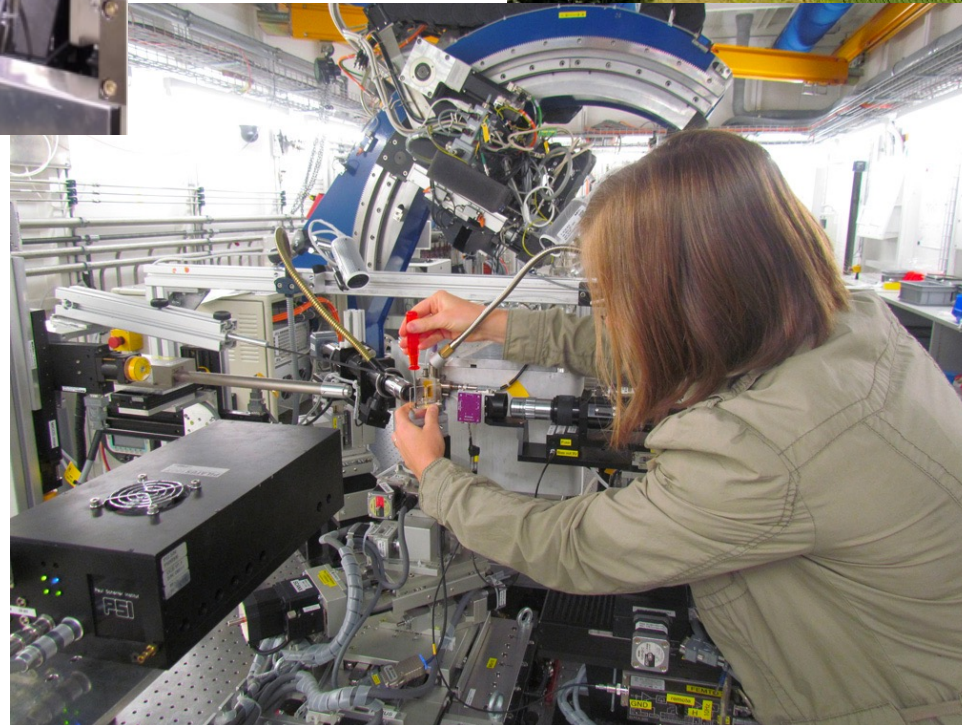
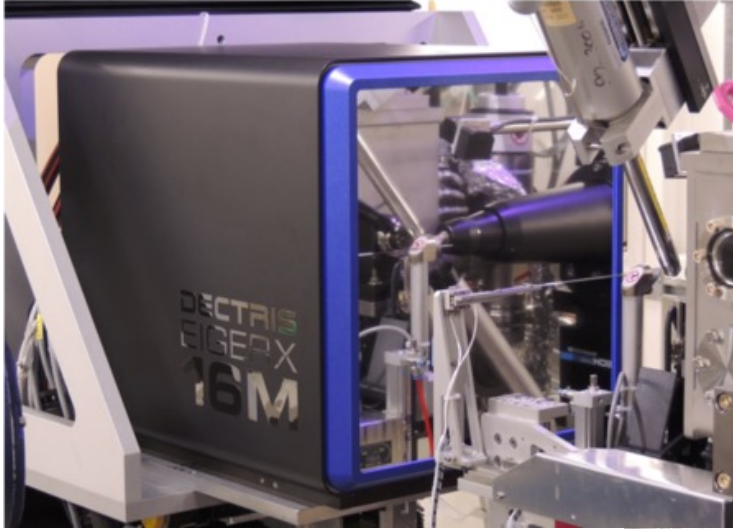
hkl	Bragg angle 2θ (°)	Peak width ' β ' (°)	Instrument resolution (°)	Corrected β (°)
111	38.21	0.580	0.114	0.47
200	44.34	0.822	0.115	0.71
220	64.69	0.810	0.123	0.68
311	77.63	0.905	0.135	0.77
420	115.34	1.194	0.119	1.07

A few examples and case studies

Example: EPFL XRD instrument



Example Synchrotron Source



Example: In-operando battery research

In Operando X-ray Diffraction and Transmission X-ray Microscopy of Lithium Sulfur Batteries

Johanna Nelson,^{†,‡,⊥} Sumohan Misra,^{†,⊥} Yuan Yang,^{§,⊥} Ariel Jackson,[§] Yijin Liu,[†] Hailiang Wang,^{||} Hongjie Dai,^{||} Joy C. Andrews,[†] Yi Cui,^{*,‡,§} and Michael F. Toney^{*,†,‡}

[†]Stanford Synchrotron Radiation Lightsource, and [‡]Stanford Institute for Materials and Energy Science, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States

[§]Department of Materials Science and Engineering, and ^{||}Department of Chemistry, Stanford University, Stanford, California 94305, United States

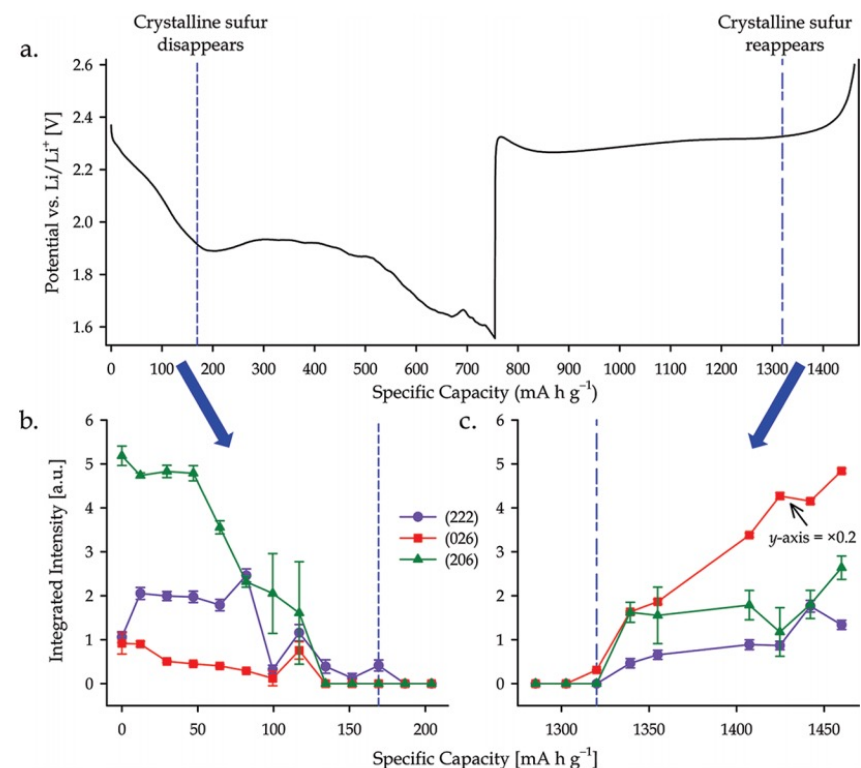


Figure 3. Integrated diffraction intensities of sulfur peaks for a Li–S cell cycled at $C/8$ and with a cathode prepared as a sulfur/Super P composite: (a) electrochemical plot showing the first cycle of the Li–S cell; (b and c) integrated intensity plots for (222), (026), and (206) Bragg peaks, which show the disappearance of crystalline sulfur by the end of the first discharge plateau and its reappearance by the end of the charge cycle. The blue arrows indicate the specific capacity regions over which the integrated intensities are plotted. The dashed lines emphasize where sulfur peaks disappear and reappear. The total discharge capacity is 755 mA h g⁻¹, and the total charge capacity is 707 mA h g⁻¹. Error bars on the integrated intensities were determined using Levenberg–Marquardt minimization.

Example: In operando – laser printing PSI

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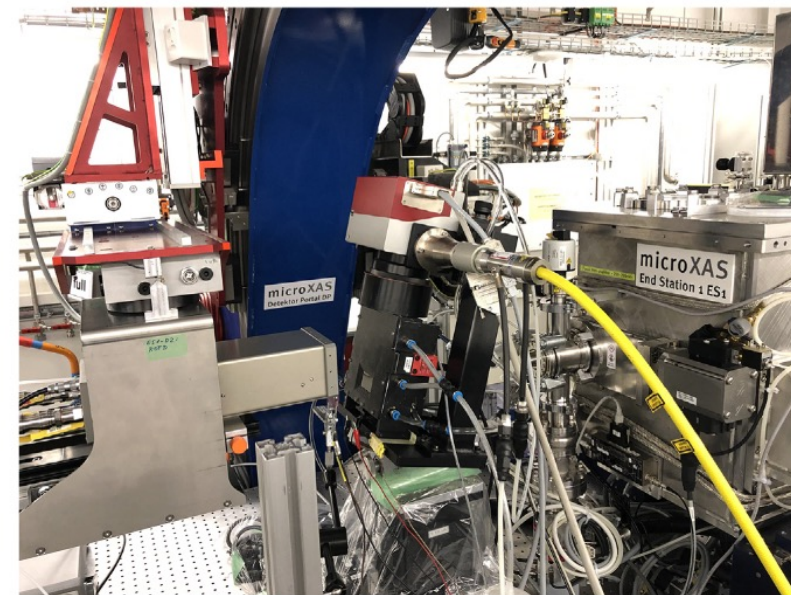
RESEARCH



Operando X-ray diffraction during laser 3D printing

RESEARCH

Samy Hocine^{1,2}, Helena Van Swygenhoven^{1,2,*}, Steven Van Petegem¹,
Cynthia Sin Ting Chang¹, Tuerdi Maimaitiyili¹, Gemma Tinti³,
Dario Ferreira Sanchez⁴, Daniel Grolimund⁴, Nicola Casati⁵



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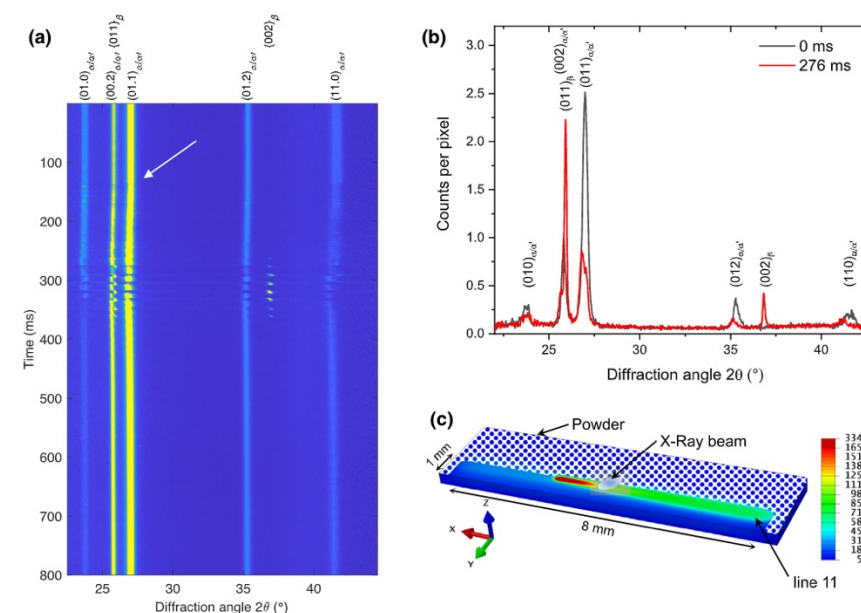


FIGURE 3

(a) Phase evolution during printing of a single layer, shown as an intensity vs. diffraction angle and time by stacking 16,000 individual diffraction patterns. The white arrow indicates the start of the printing process, (b) diffraction patterns recorded prior to printing and during printing of the 11th line at $t = 276$ ms, (c) schematic representation of the relative position of laser, X-ray beam and HAZ at $t = 276$ ms. (Temperature scale in degree Celsius).

Outlook

Diffraction as Fourier Transform

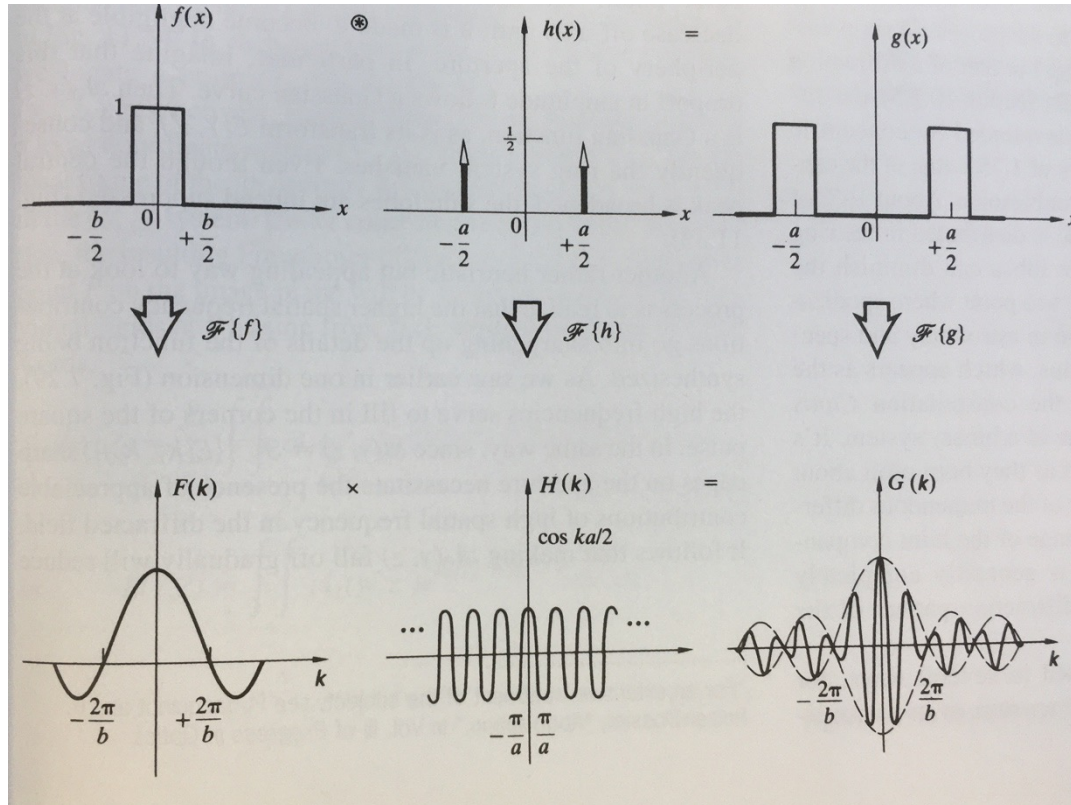
Reciprocal Lattice

Bragg and Laue Diffraction

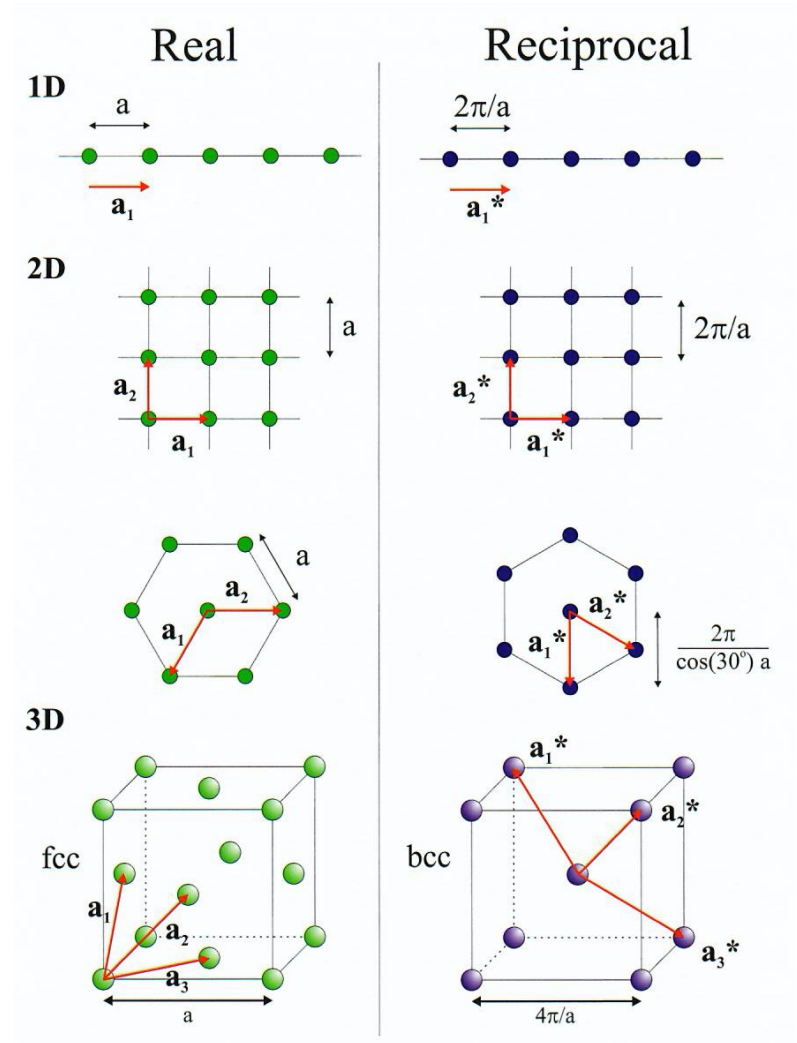
Structure Factor

Detailed Electronic Structure Maps

Diffraction as Fourier transform:

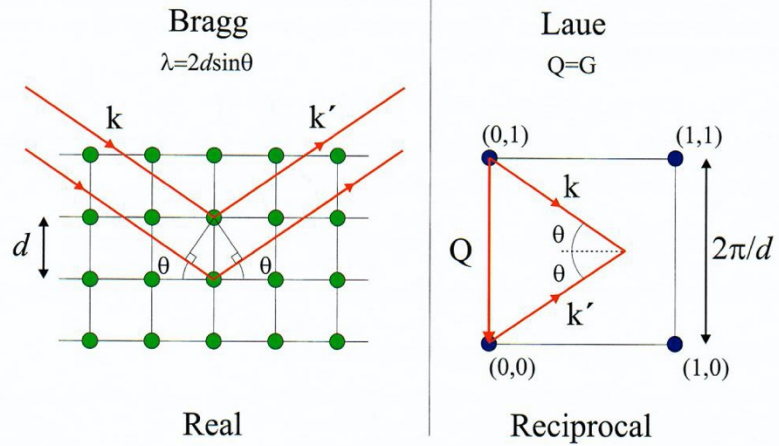


For each lattice a reciprocal lattice can be defined



Bragg and Laue conditions

(a) Equivalence of Bragg and Laue



(b) Miller indices and reciprocal lattice vectors

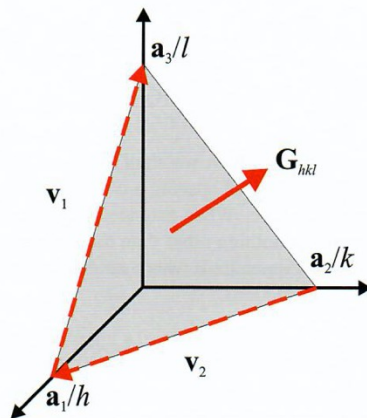
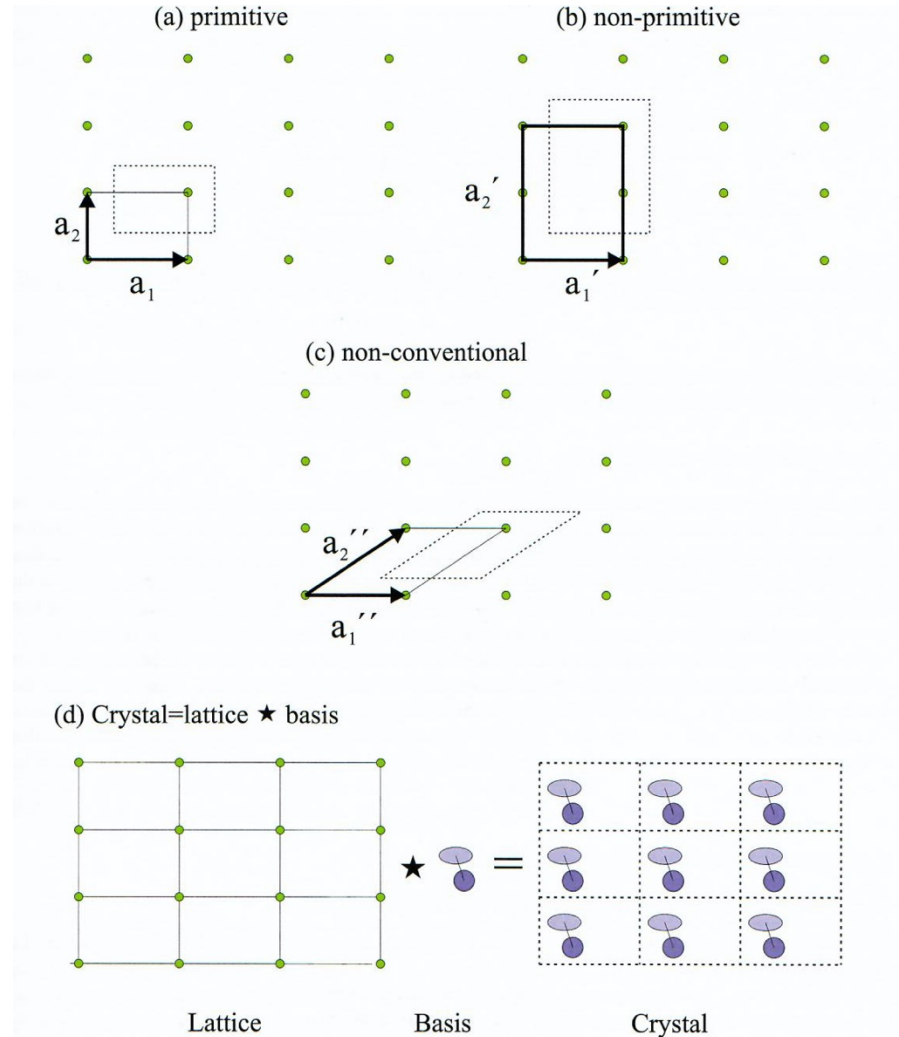


Photo from the Nobel Foundation archive.

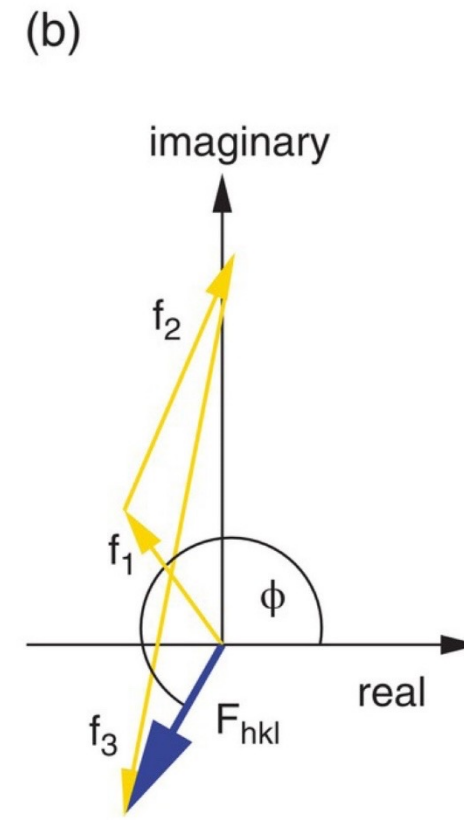
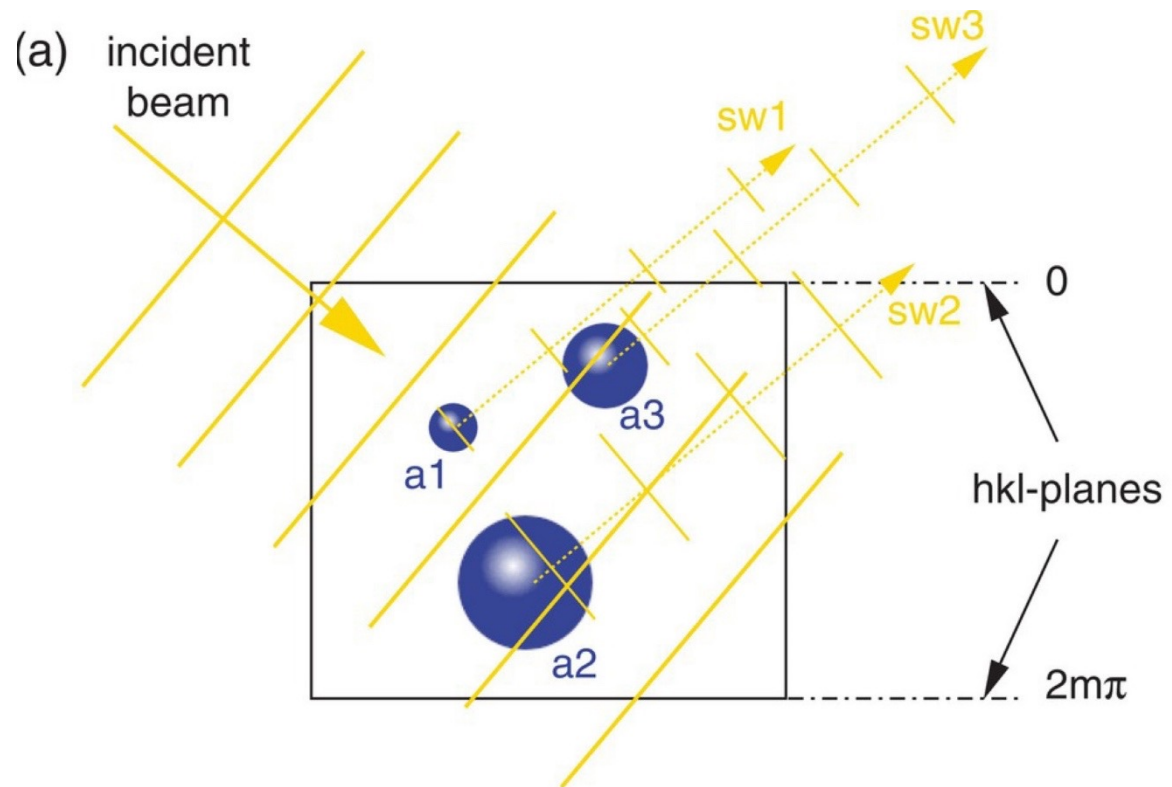
Max von Laue

Prize share: 1/1

A crystal is defined by its lattice and basis



The structure factor



The end