An historical overview of X-ray crystallography

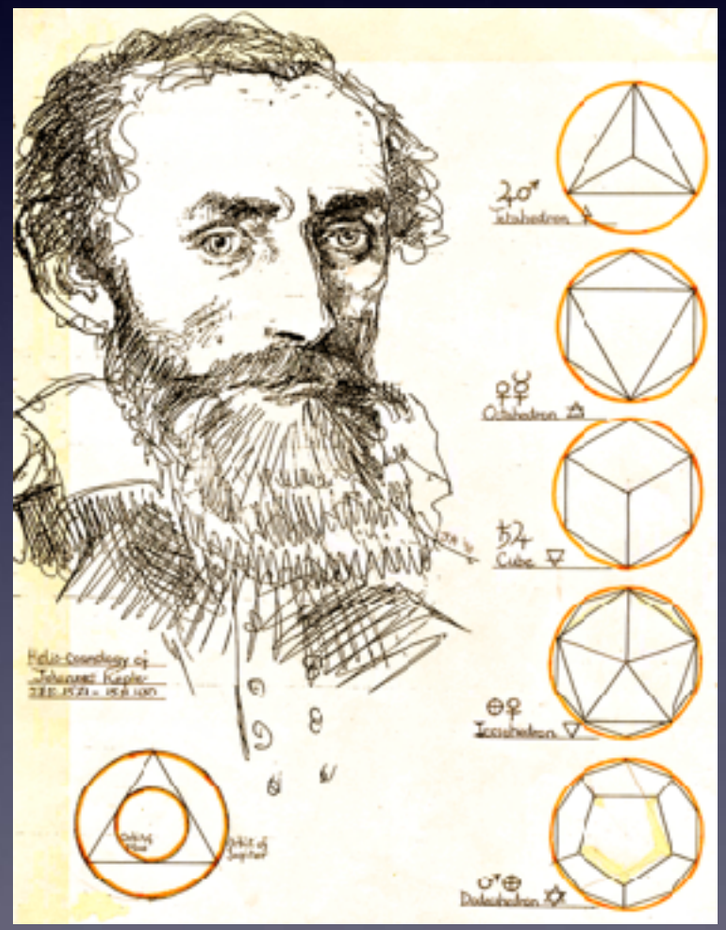
José António Paixão

CFisUC
University of Coimbra

Crystallography

Robert Hooke
(1635-1703)

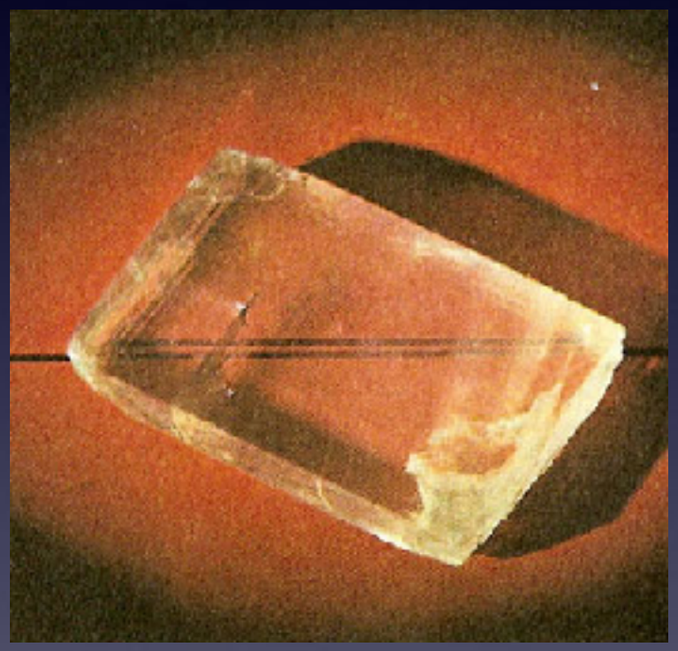
René Descartes
(1596-1650)

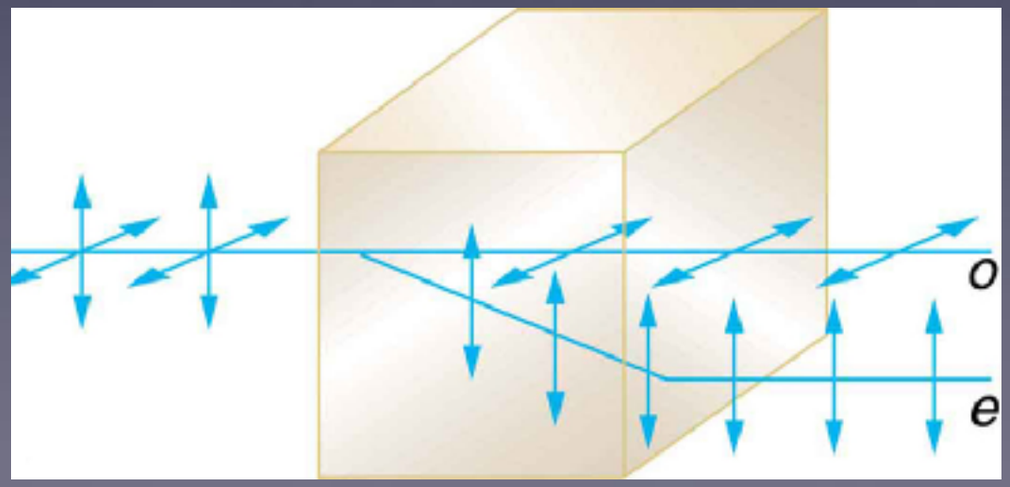


Johannes Kepler
(1571-1630)

Crystals and the atomic theory

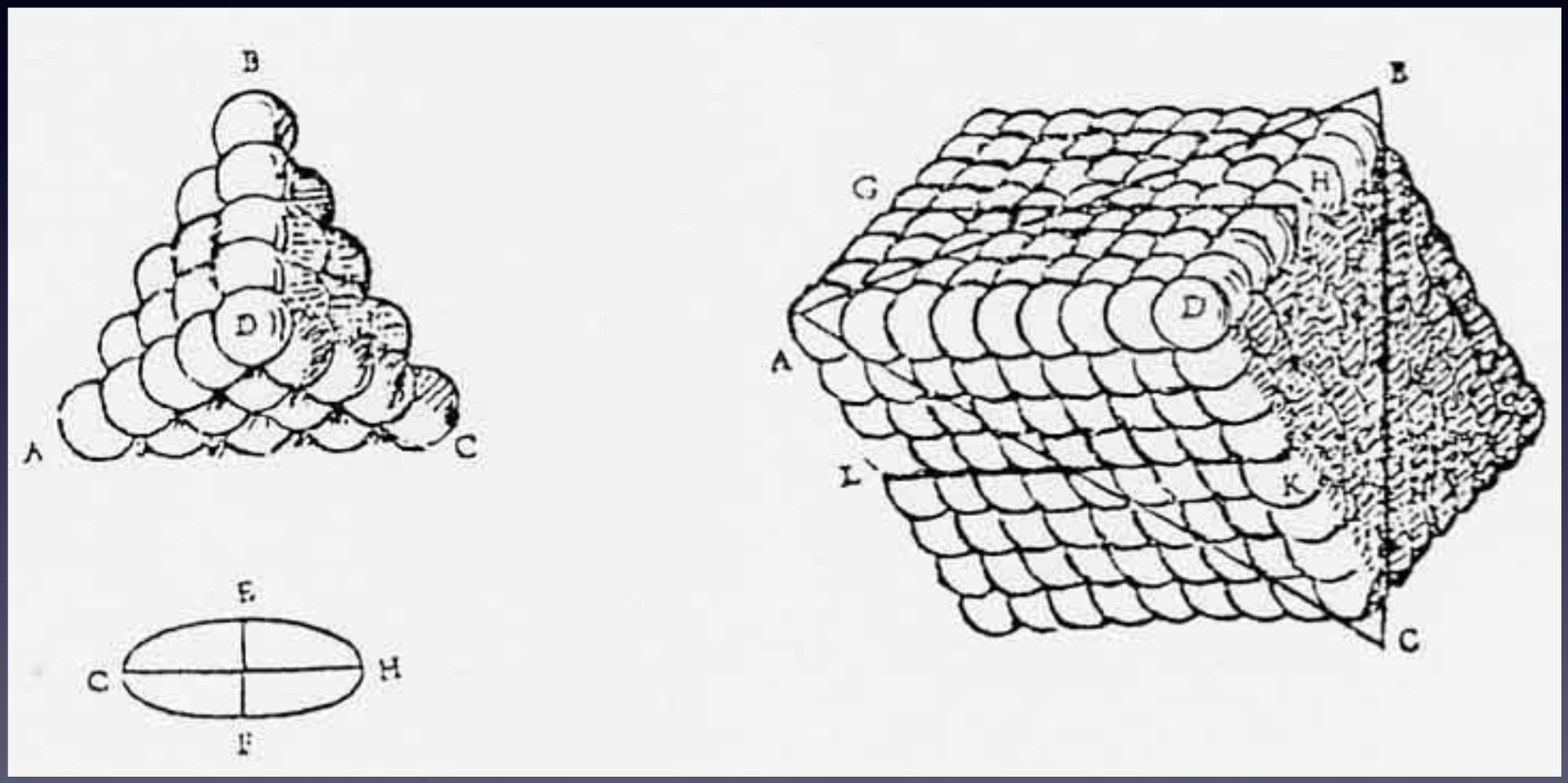
Light birefringence of Iceland spar (calcite)



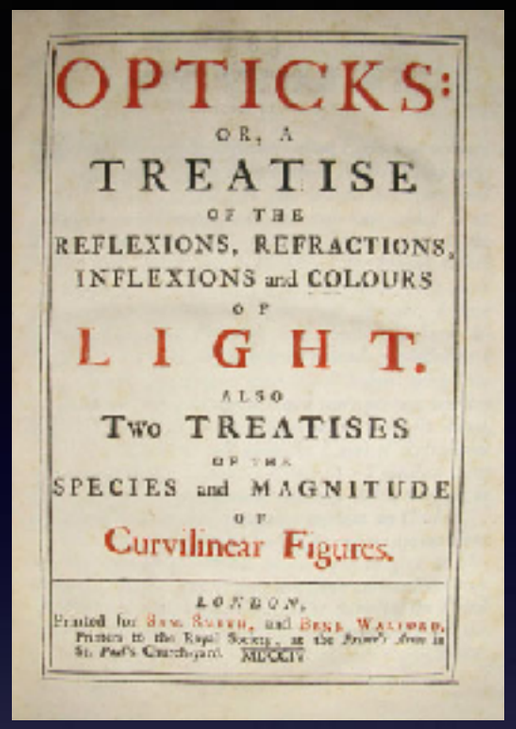


Christiaan Huygens
(1629-1695)

Crystals and the atomic theory



Christiaan Huygens: *Traité de la lumière* (1690)


OPTICKS:
OR, A
TREATISE
OF THE
REFLEXIONS, REFRACTIONS,
INFLEXIONS and COLOURS
OF
LIGHT.
ALSO
Two TREATISES
OF THE
SPECIES and MAGNITUDE
OF
Curvilinear Figures.
LONDON,
Printed for SAM. SMITH, and BENJ. WALFORD,
Printers to the Royal Society, at the Prince's Arms in
St. Paul's Churchyard. MDCCIV.

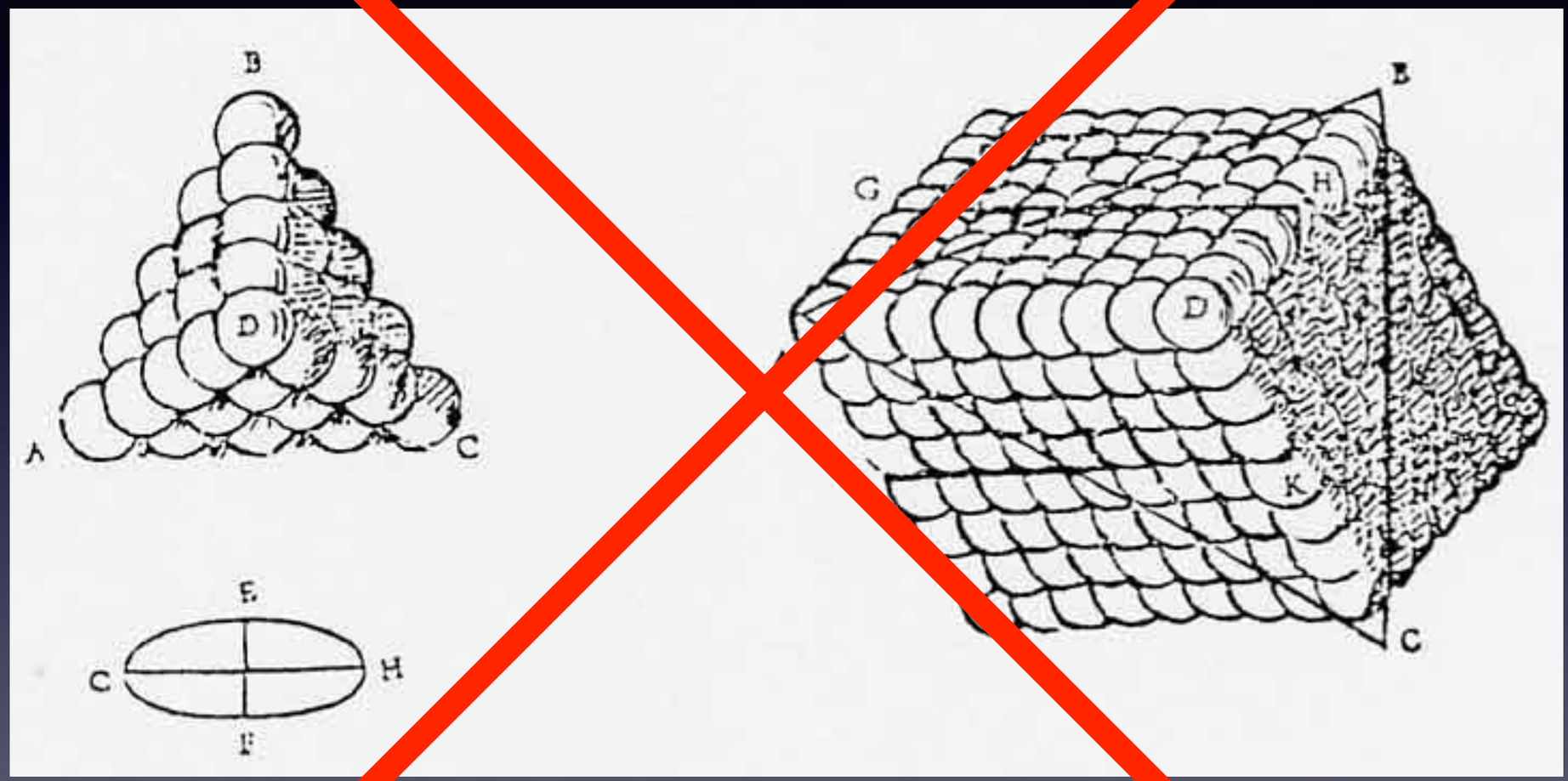
(1704)


TRAITE
DE LA LVMIERE.
Où sont expliquées
Les causes de ce qui luy arrive
Dans la REFLEXION, & dans la
REFRACTION.
Et particulierement
Dans l'etrange REFRACTION
DV CRISTAL D'ISLANDE,
Par C. H. D. Z.
Avec un Discours de la Cause
DE LA PESANTEVR.
A LEYDE,
Chez PIERRE VANDER AA, Marchand Libraire.
M D C X C.

(1690)

LIGHT IS
A PARTICLE!!!

LIGHT IS NOT
A PARTICLE!!!


B
D
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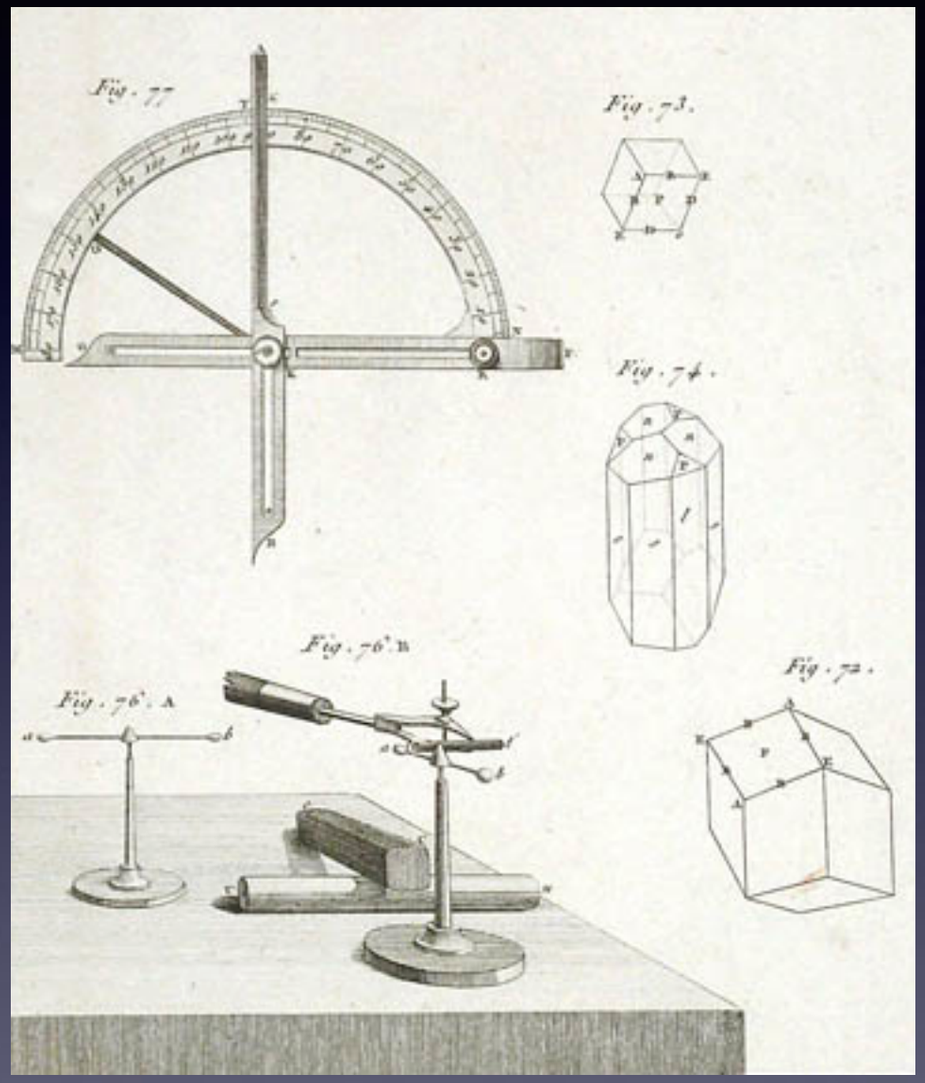
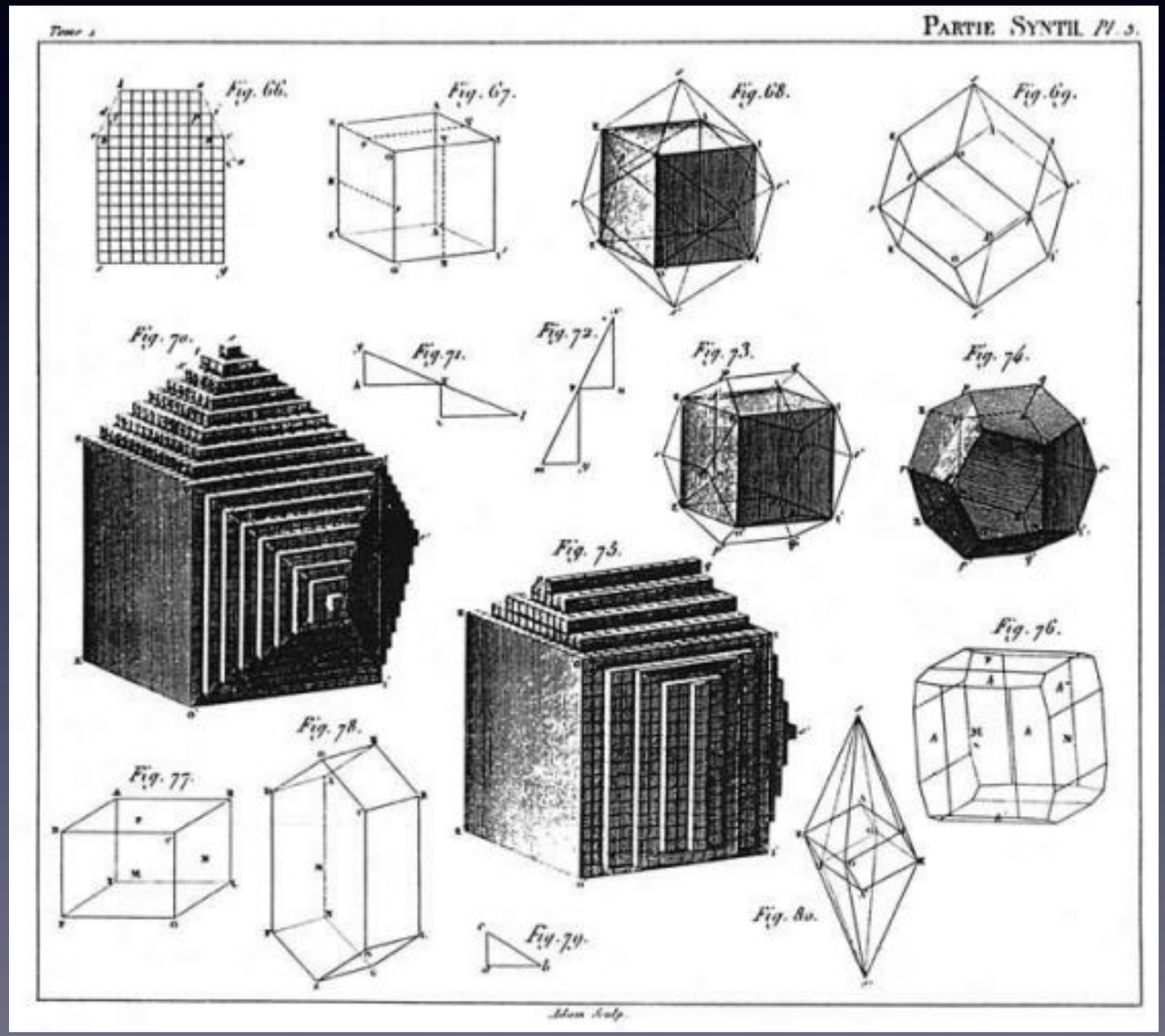
C

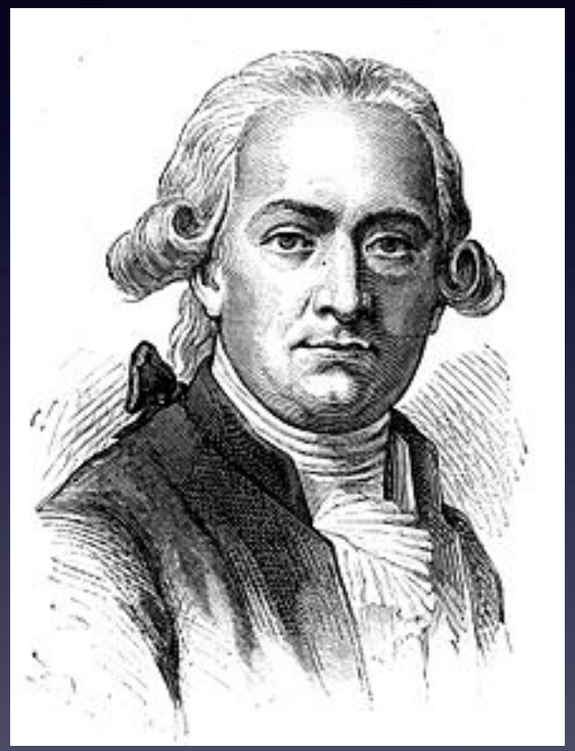
Crystallography
(as a descriptive science)

The work of René Haüy

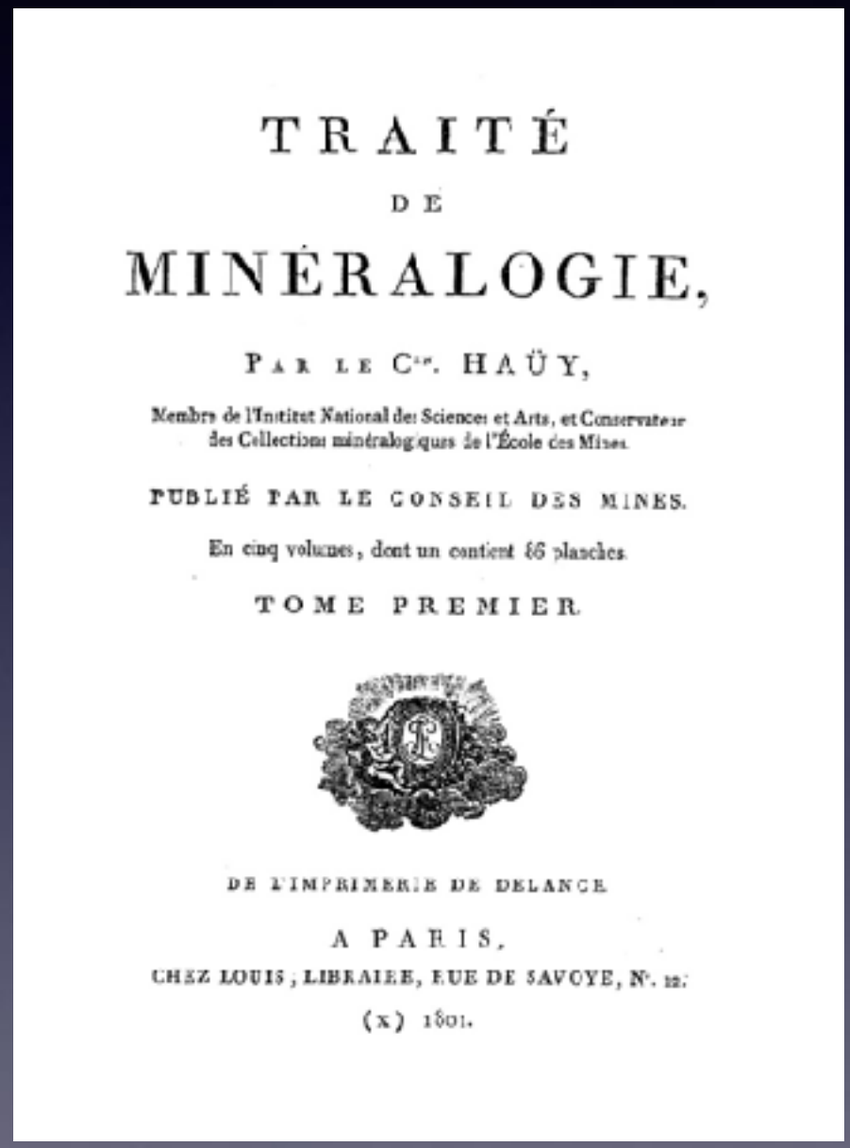




The “integrant molecule” of Haüy



Réne Just Haüy
(1743-1822)



TRAITÉ
DE
MINÉRALOGIE,

PAR LE Cᵉᵛ. HAÜY,

Membre de l'Institut National des Sciences et Arts, et Conservateur des Collections minéralogiques de l'École des Mines.

PUBLIÉ PAR LE CONSEIL DES MINES.

En cinq volumes, dont un contient 86 planches.

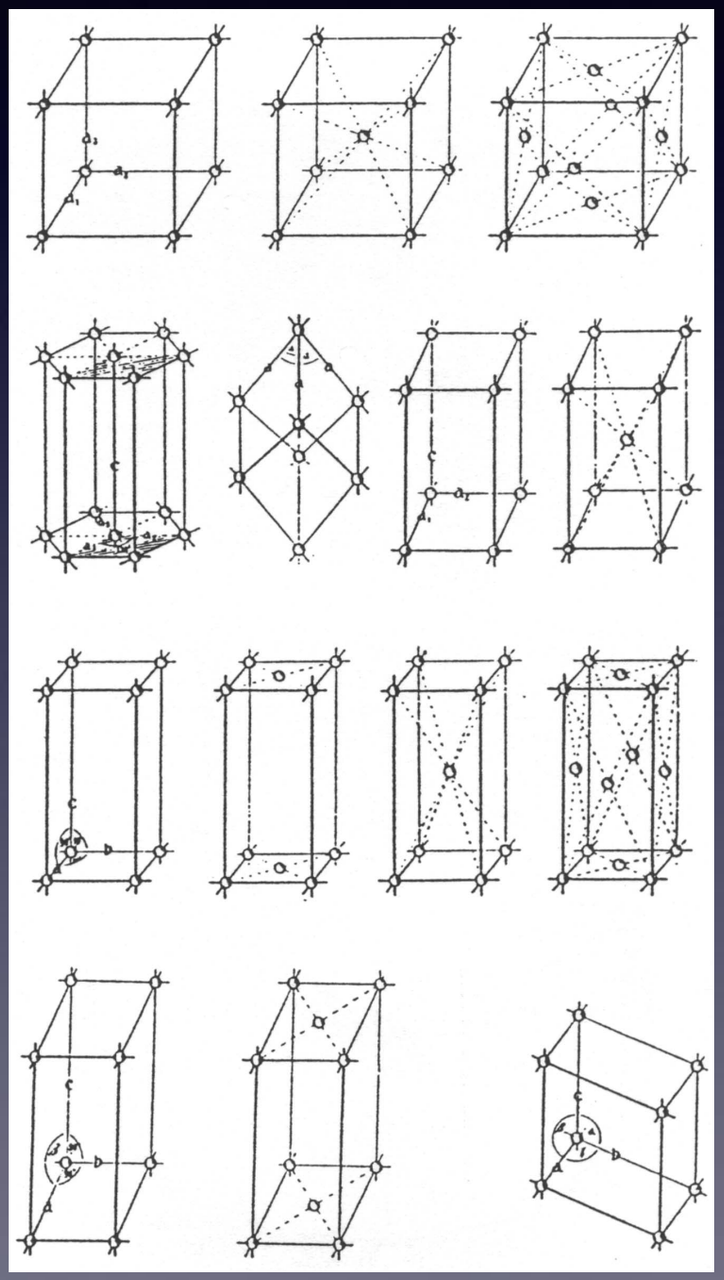
TOME PREMIER.

DE L'IMPRIMERIE DE DELANCE.

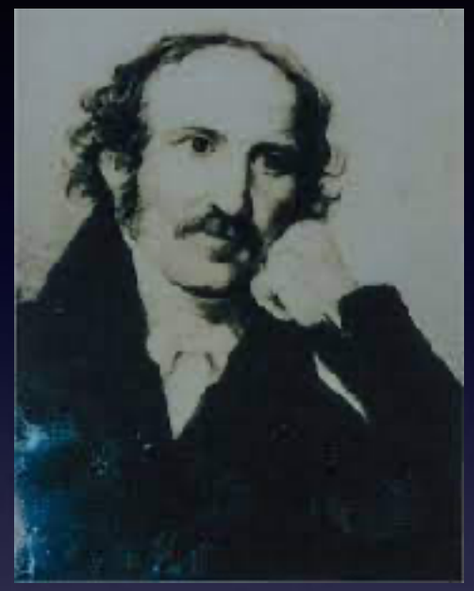
A PARIS,
CHEZ LOUIS, LIBRAIRE, RUE DE SAVOYE, N°. 12.
(X) 1801.

The French and German Schools

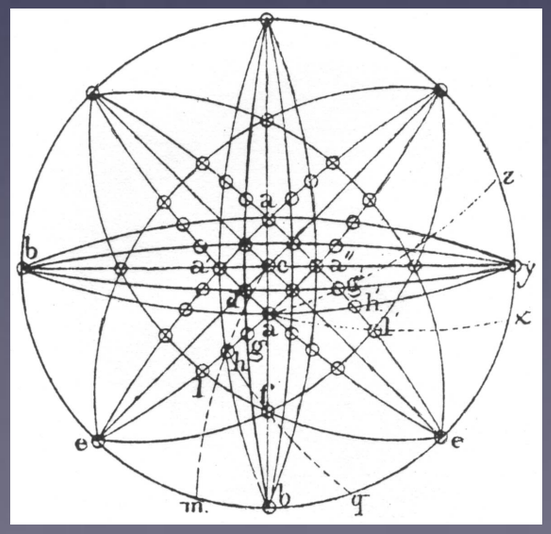
August Bravais
(1811-1863)



The 14 Bravais lattices



Franz Neumann
(1798-1895)

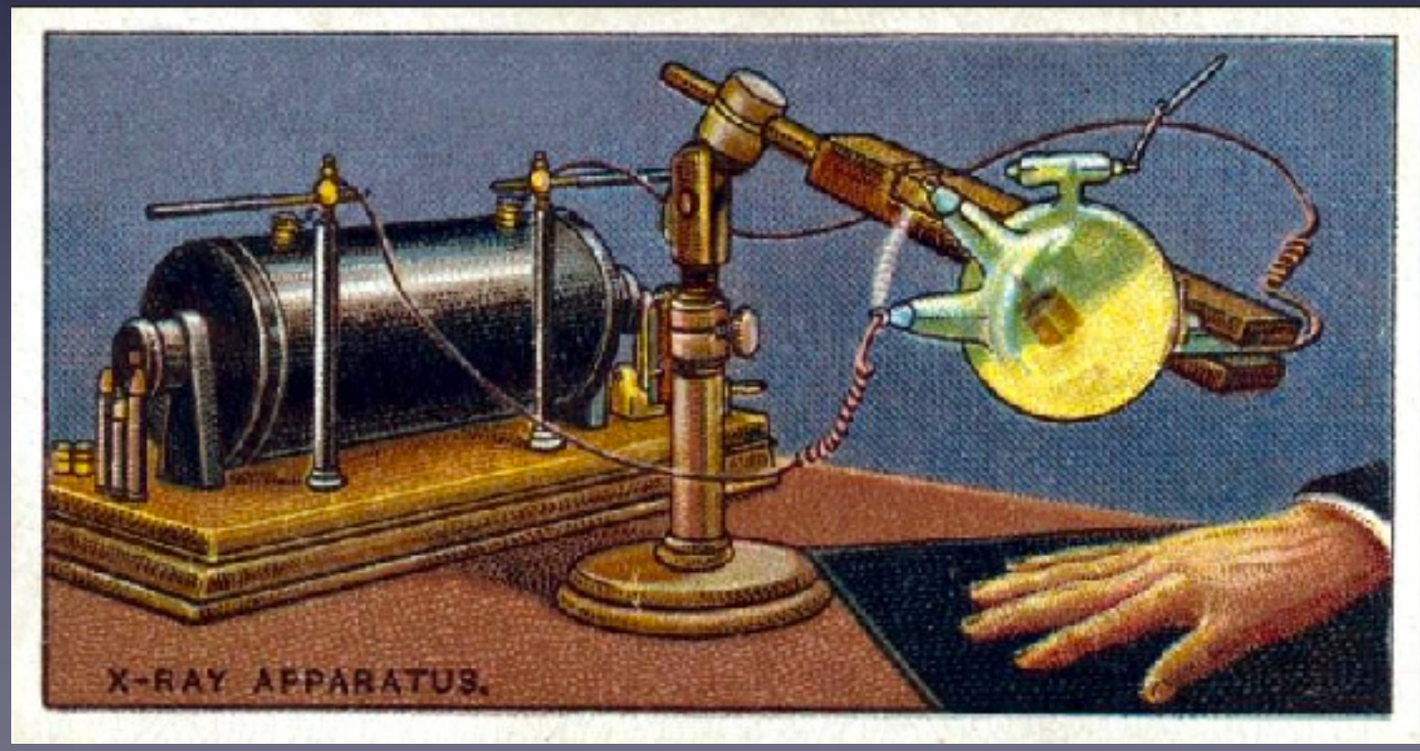


X-Rays

The discovery of X-rays

Wilhelm Conrad Röntgen
(1845-1923)

Hand radiography
(1895)



What are X-rays?

- A new controversy…
- Particles … or short wavelength electromagnetic waves?

Particles

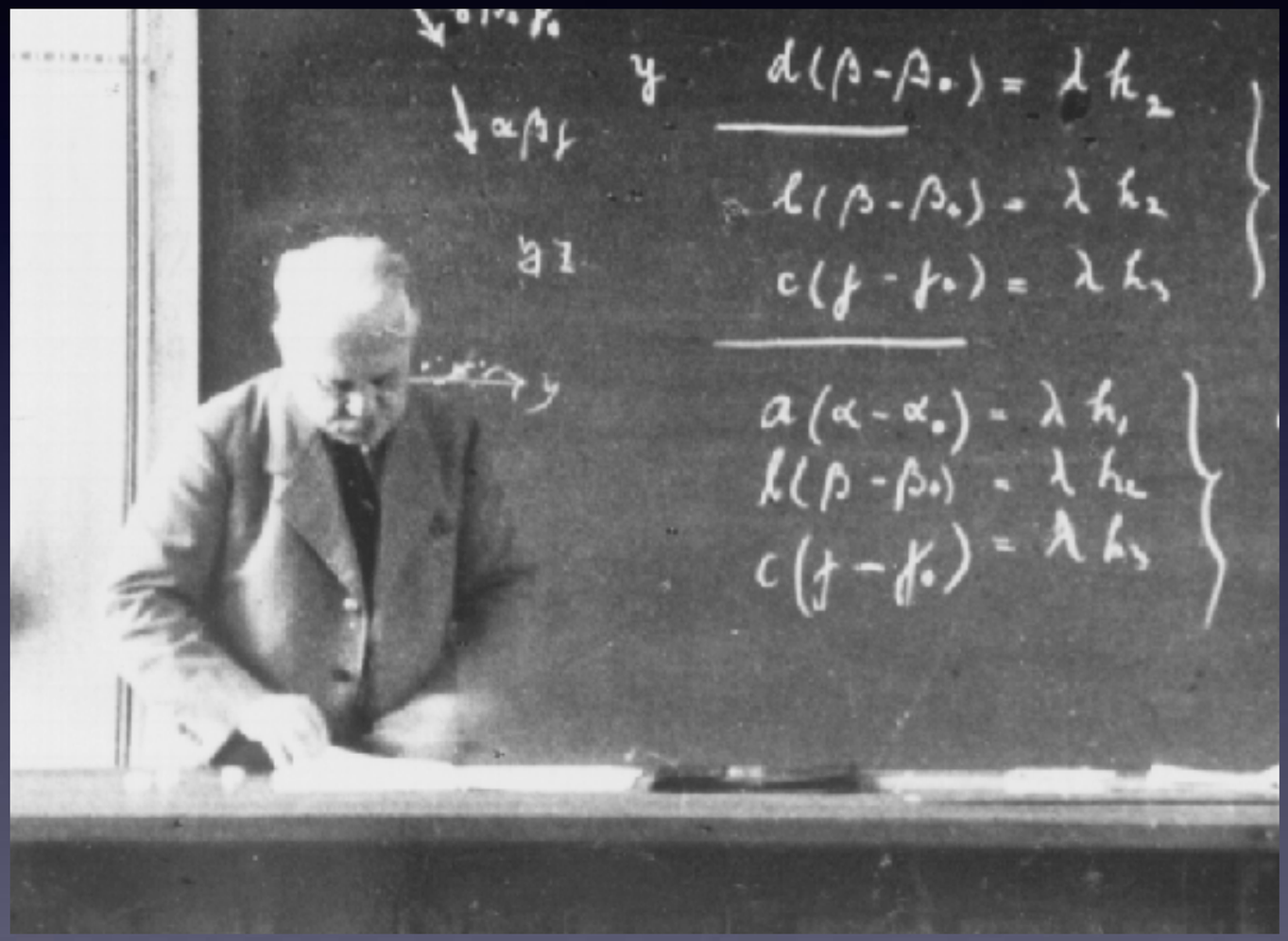
Waves

What are X-Rays?

- Particles: ionising effect, no diffraction by slits, no refraction (Röntgen)
- (Transverse) Waves: X-Ray polarisation (Barkla, 1905)

Charles G. Barkla
(1877-1944)

Sommerfeld's Theoretical Physics Institute in Munich

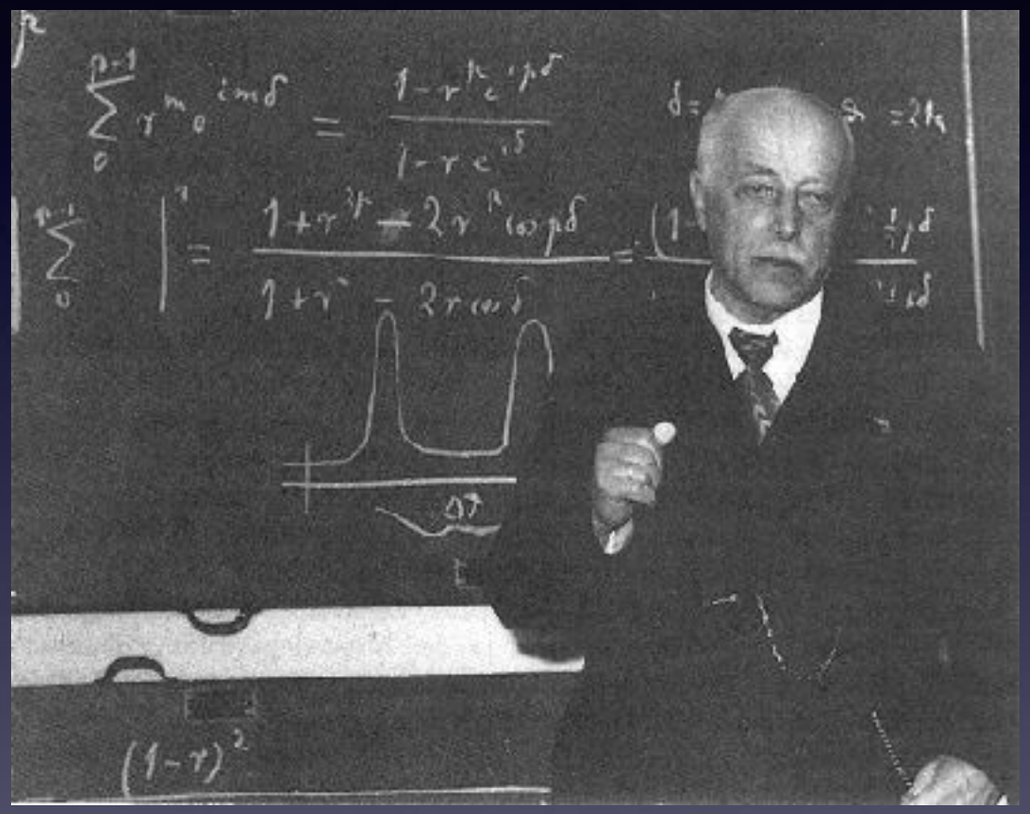


Arnold Sommerfeld
(1868-1951)

Max von Laue
(1879-1960)

Peter Ewald
(1888-1985)

The discovery of X-ray diffraction



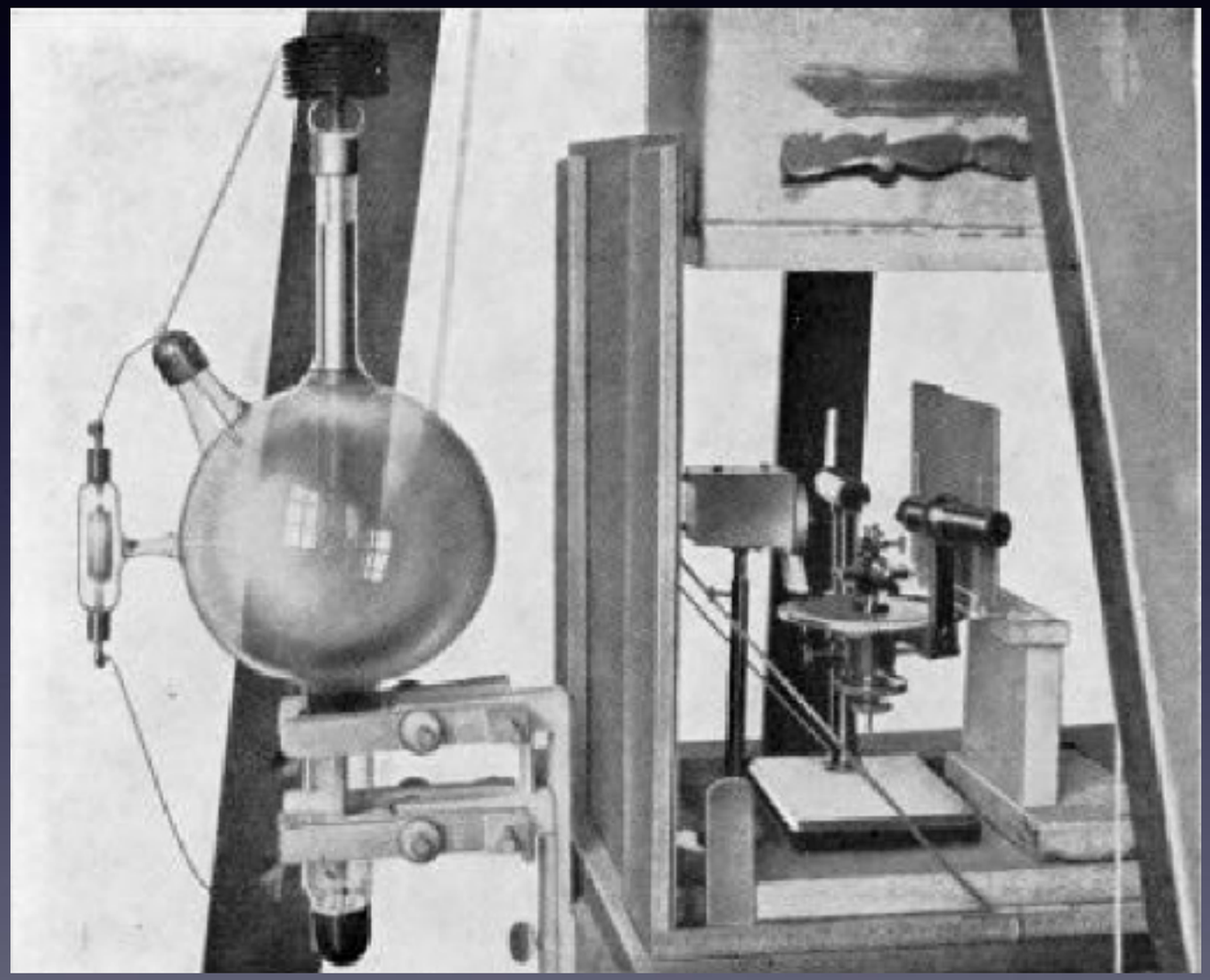
I am a theoretician, find me an assistant to do the experiment!

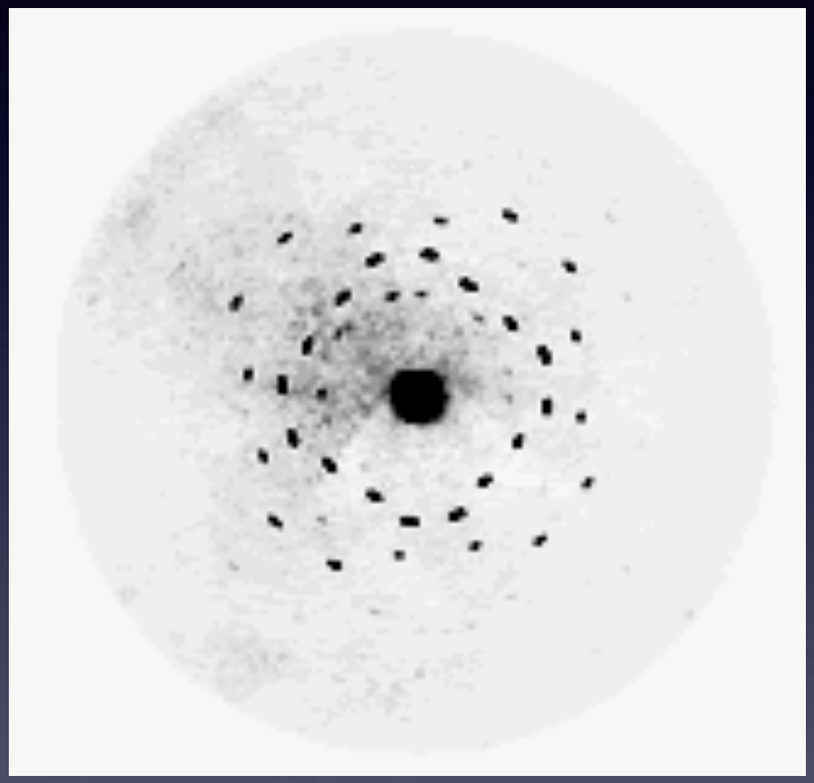
$$\lambda_{\mathrm{XR}} \sim 10^{-8}\ \mathrm{cm}$$

$$d \sim 10^{-8}\ \mathrm{cm}$$

Would crystals diffract X-rays?

Friedrich & Knipping experiment

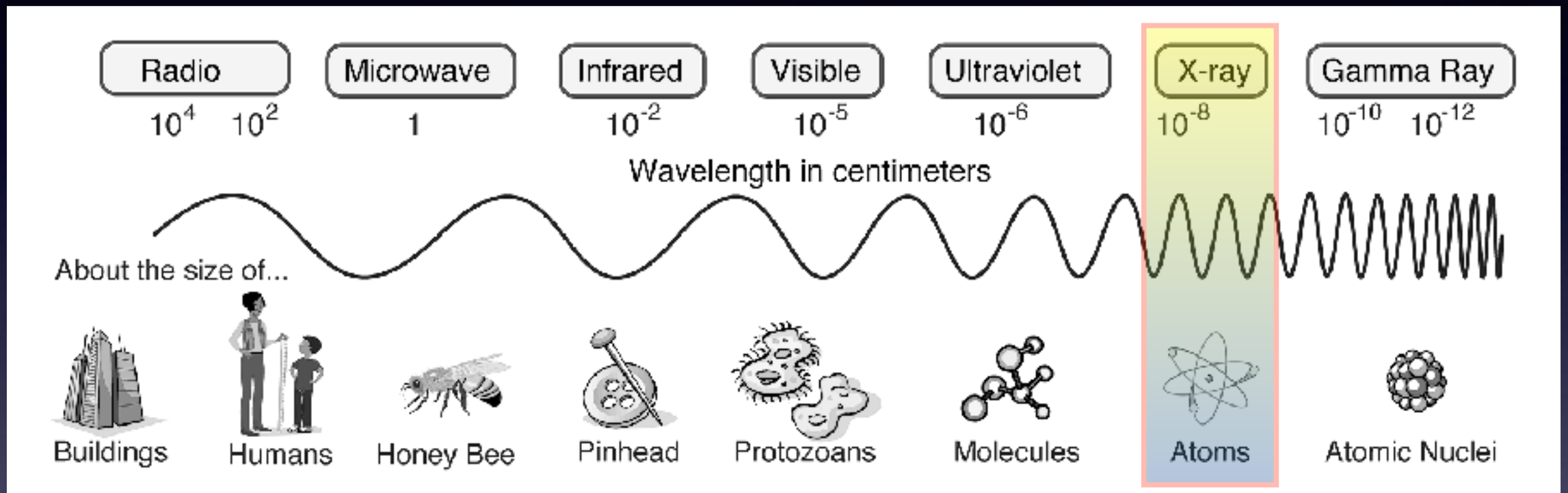




ZnS
(1912)

X-rays are indeed waves!

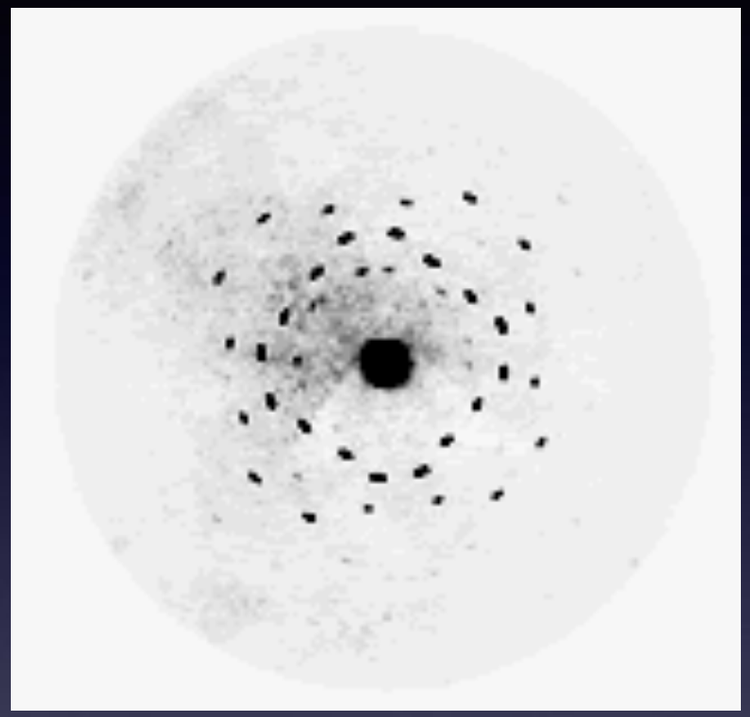
X-Rays



$$\lambda \sim 10^{-8}\ \mathrm{cm} = 10^{-10}\ \mathrm{m} = 1\ \text{Å}$$

$$E = h\nu = hc/\lambda \qquad E[\mathrm{keV}] = 12.40/\lambda[\text{Å}]$$

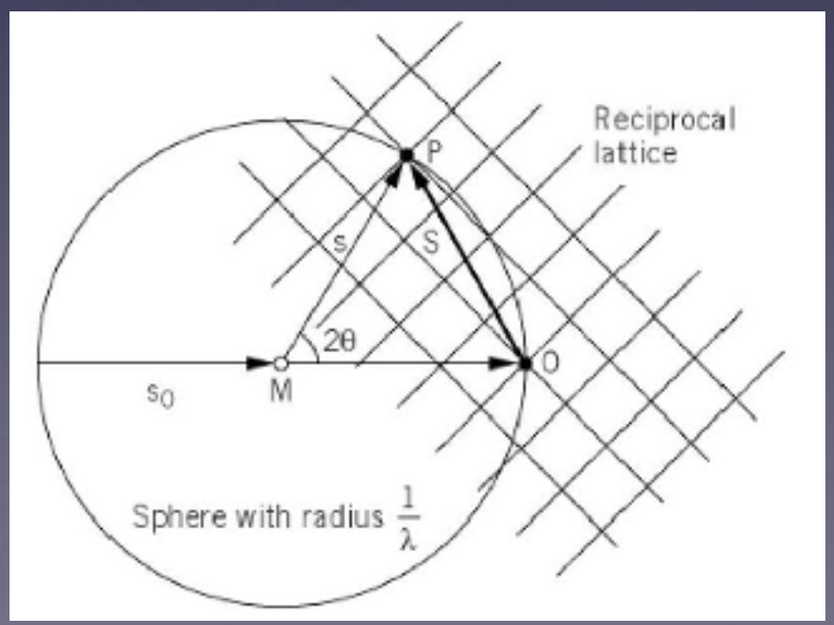
Laue/Ewald equations



$$\vec{a} \cdot (\hat{s} - \hat{s}_0) = h\lambda$$

$$\vec{b} \cdot (\hat{s} - \hat{s}_0) = k\lambda$$

$$\vec{c} \cdot (\hat{s} - \hat{s}_0) = l\lambda$$

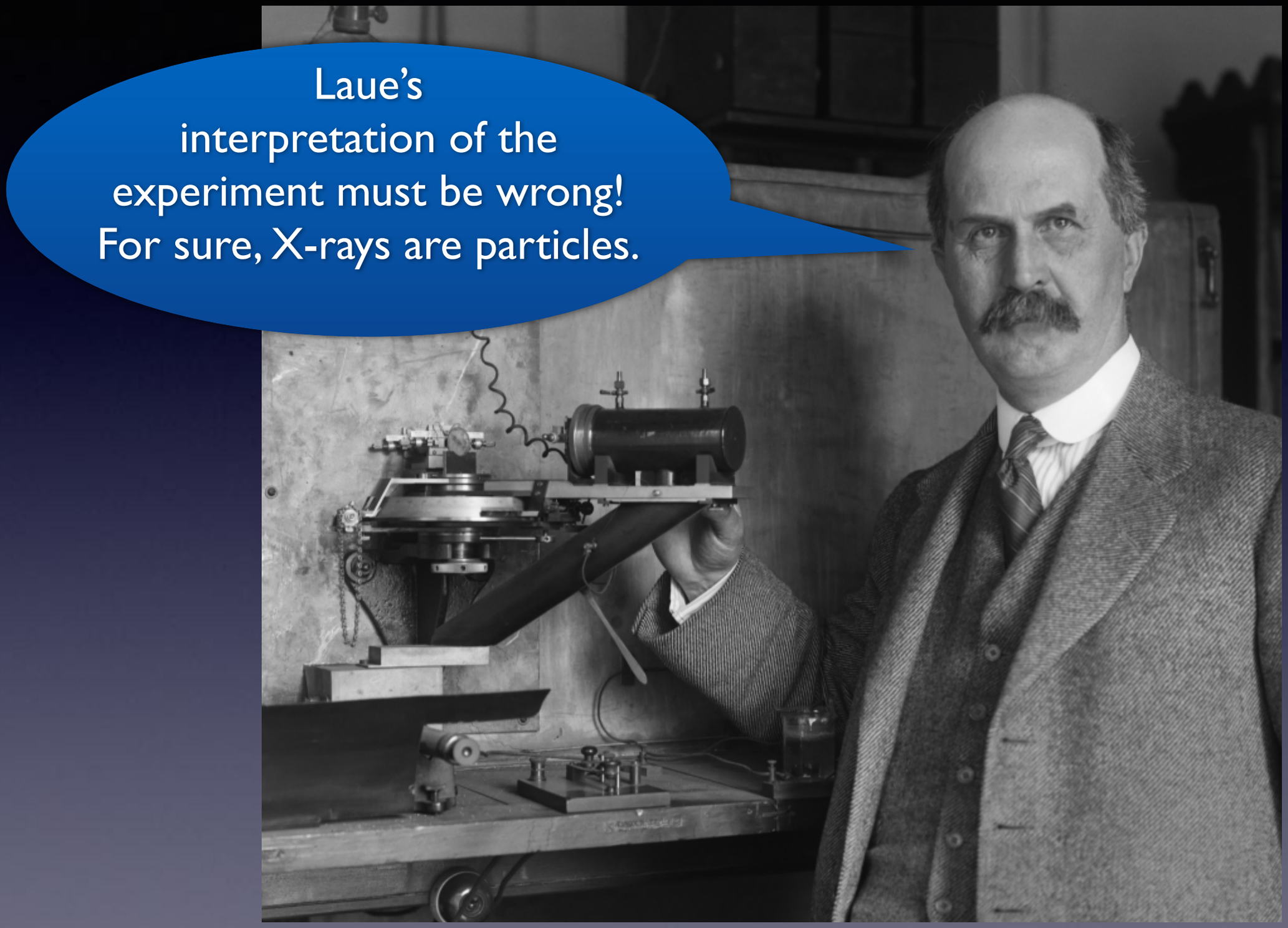


$$\frac{\hat{s} - \hat{s}_0}{\lambda} = \vec{R}^{\star}_{hkl}$$

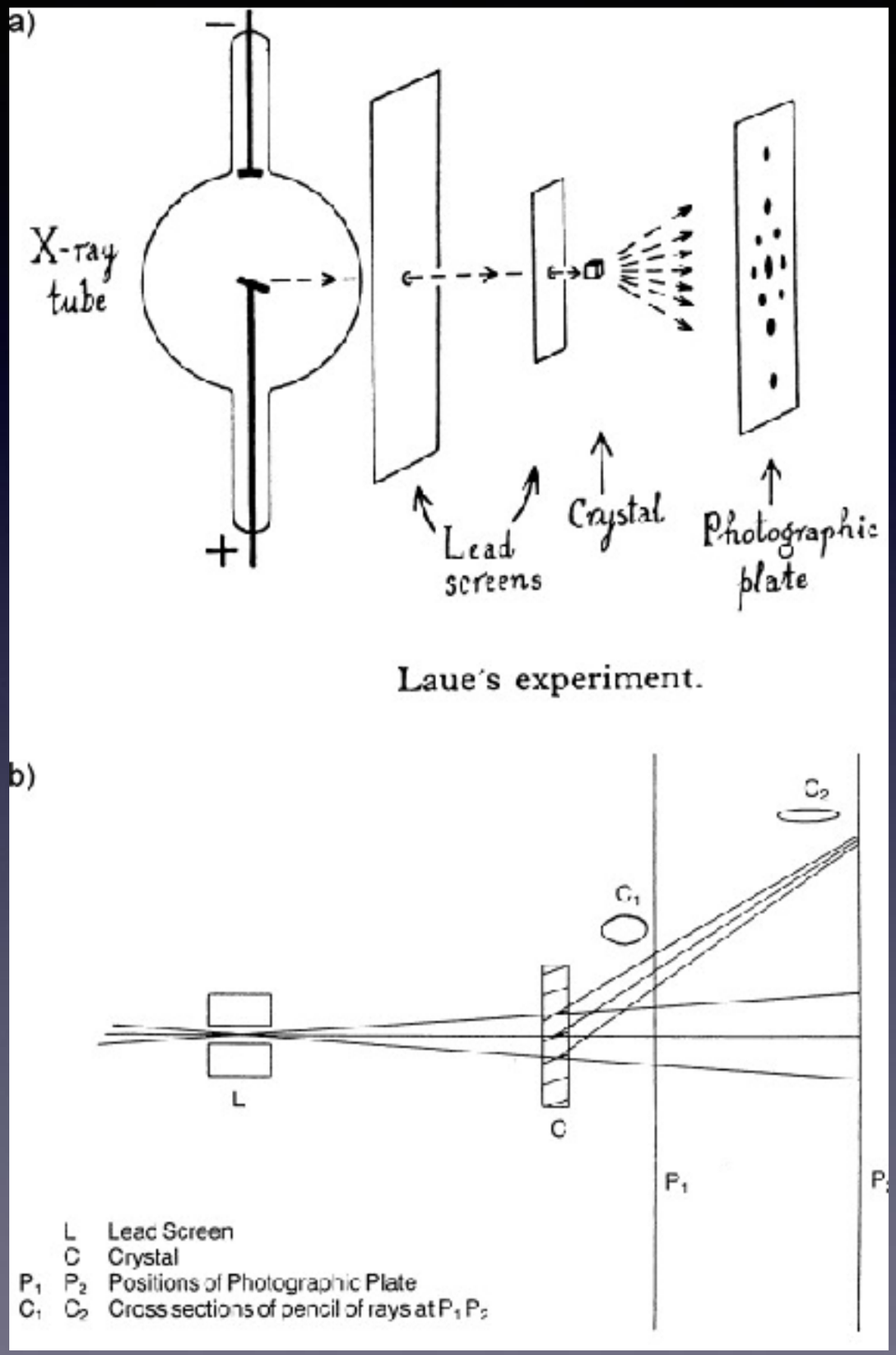
$$\vec{R}^{\star}_{hkl} = h\vec{a}^{\star} + k\vec{b}^{\star} + l\vec{c}^{\star}$$

$$\vec{a}^{\star} \cdot \vec{a} = 1; \vec{a}^{\star} \cdot \vec{b} = 1; \vec{a}^{\star} \cdot \vec{c} = 0$$

The news arrive at England…



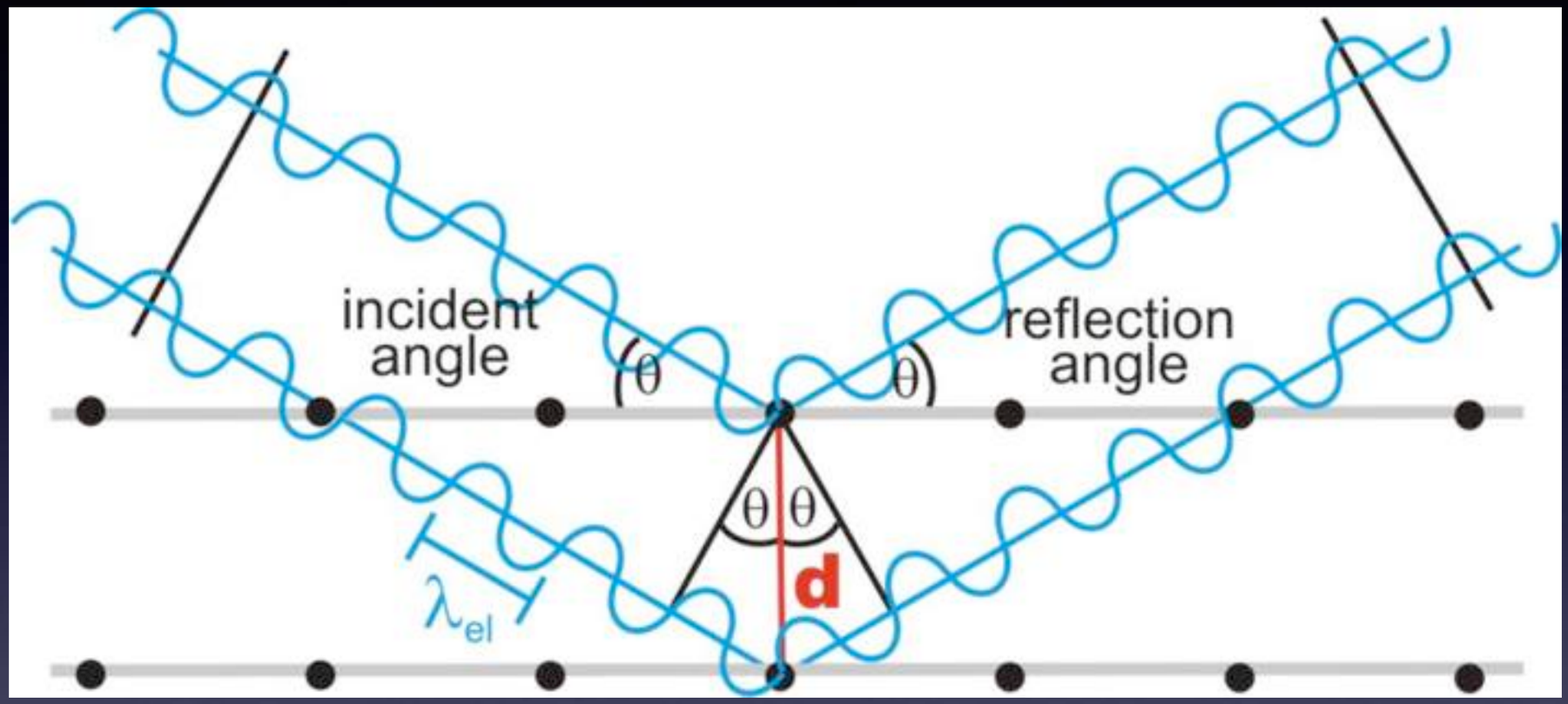
William Henry Bragg (Leeds Physics Laboratory)

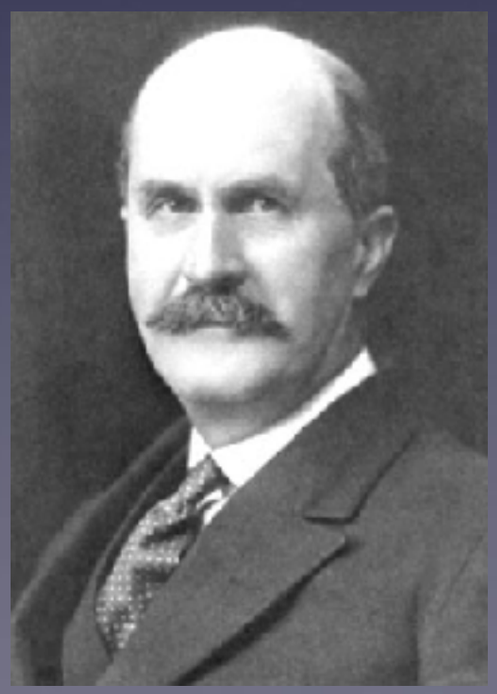


Sorry, Dad. Laue is right.
But I have come out with a simpler explanation.

William Laurence Bragg (Cambridge)

Bragg's law

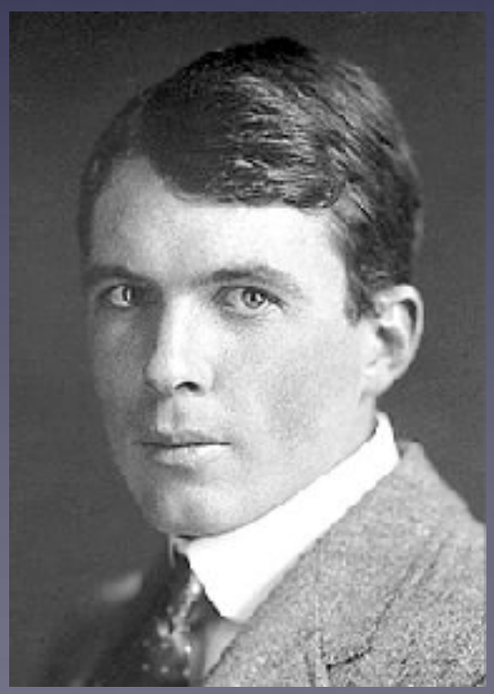




W. H. Bragg
(1862-1942)

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

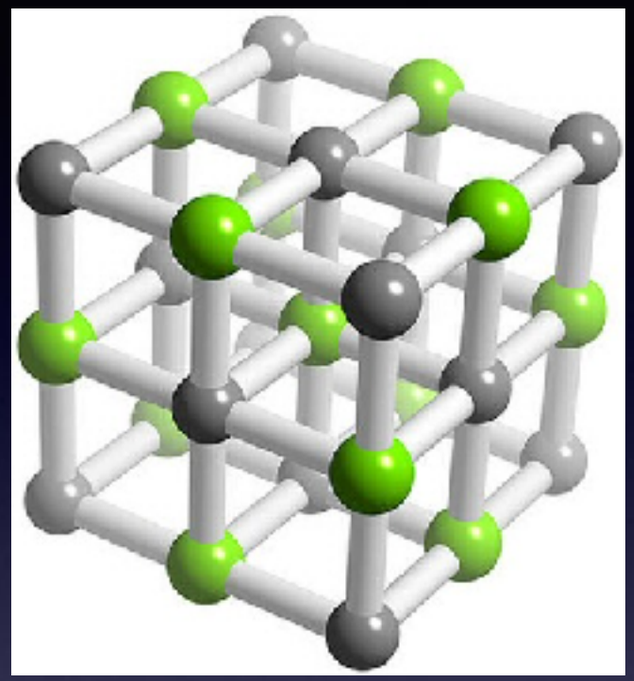
W. L. Bragg
(1890-1971)



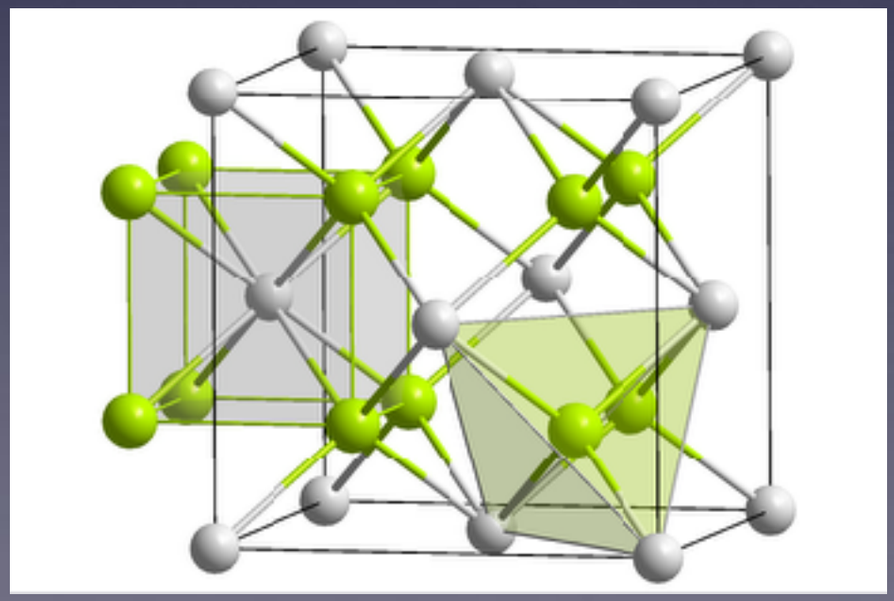
The pioneer work of the Bragg

1913-1914

Ist measurement of X-rays wavelength



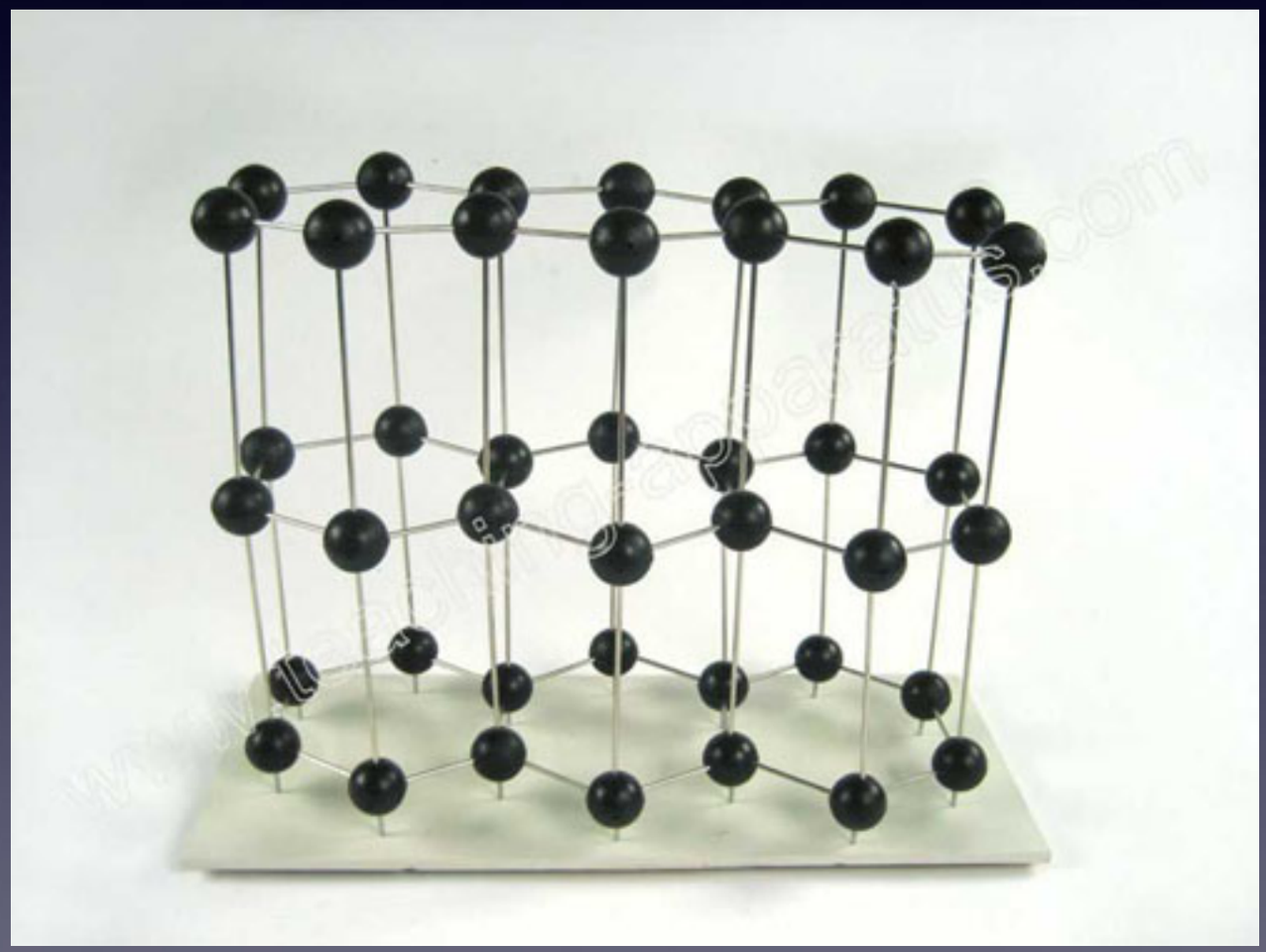
Alkali halides



ZnS

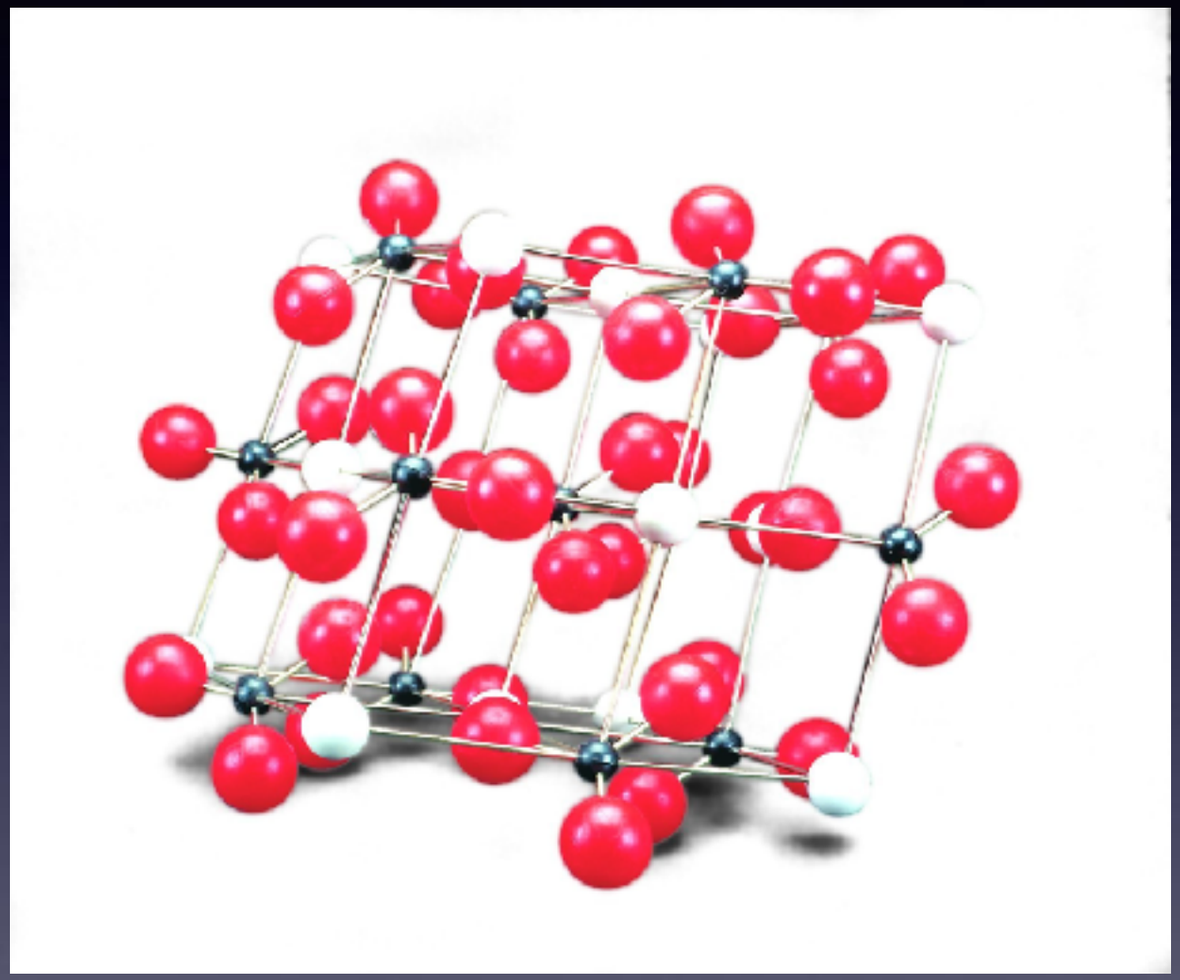
Diamond & Graphite

Diamond
(W.H. Bragg, W.L. Bragg, 1914)

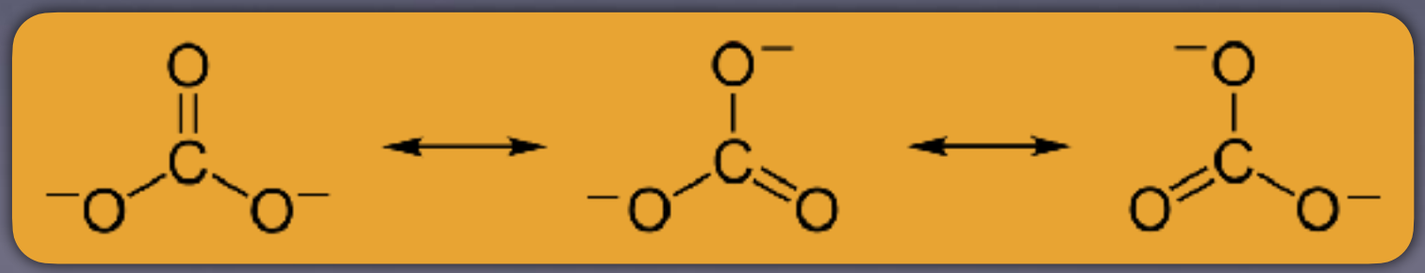


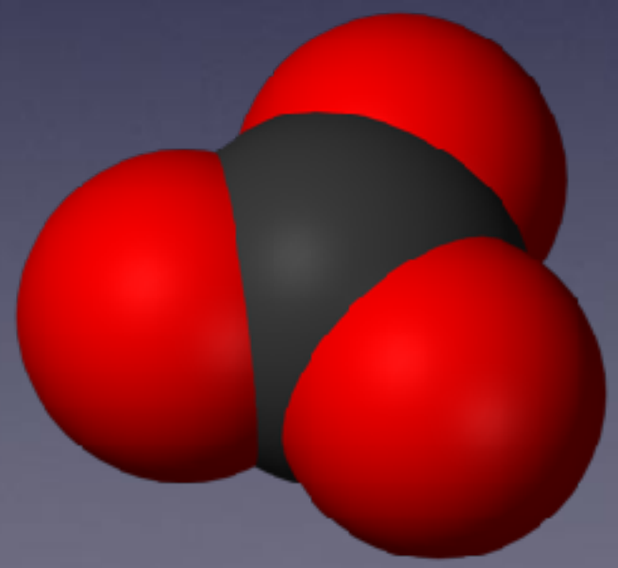
Graphite
(D. Bernal, 1924)

Structures with a free parameter

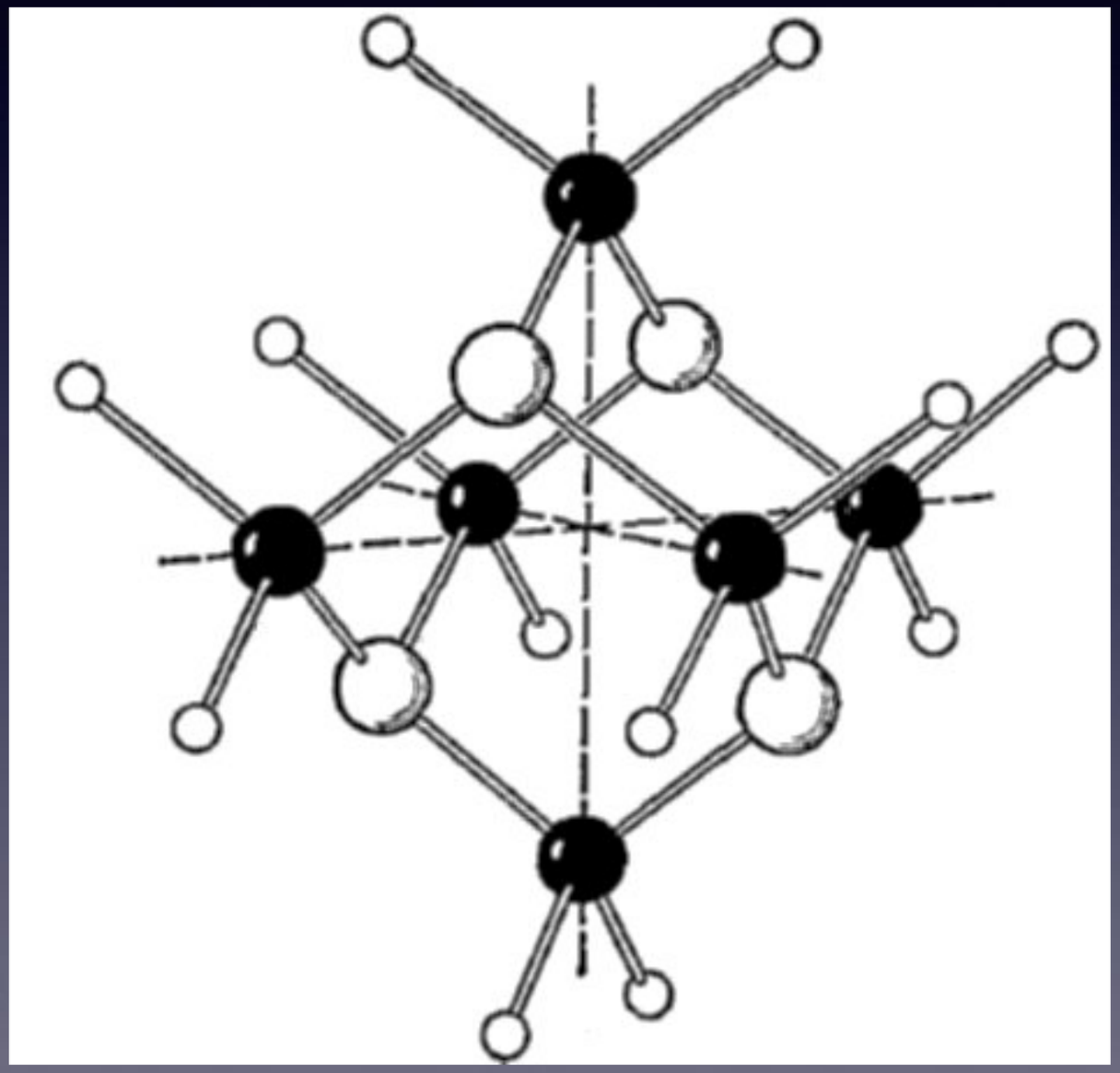


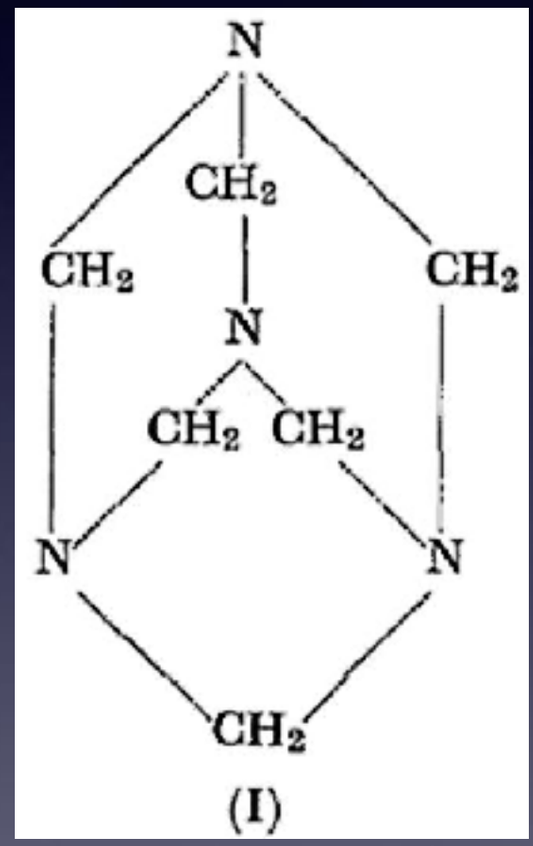
$CaCO_3$





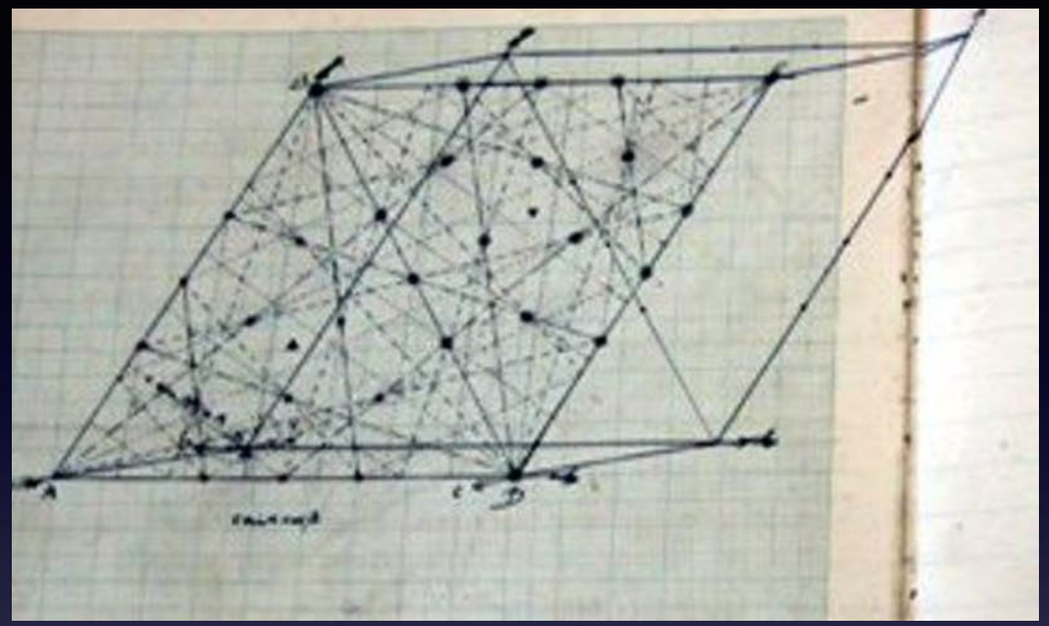
The first organic crystal structure





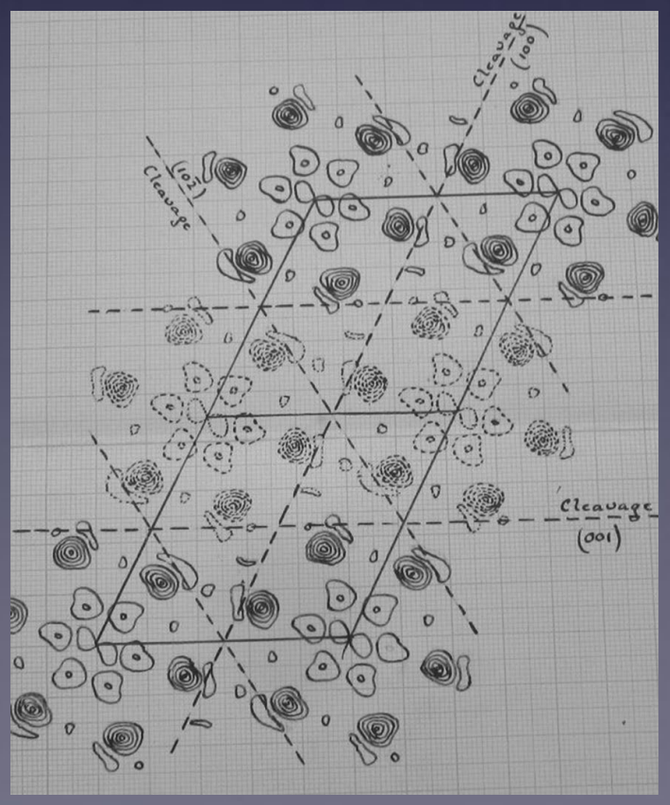
Hexamethyilene tetramine
(Dickinson & Raymond, 1923)

Benzene derivatives



Hexamethylbenzene (1928)

Kathleen Lonsdale
(1903-1971)



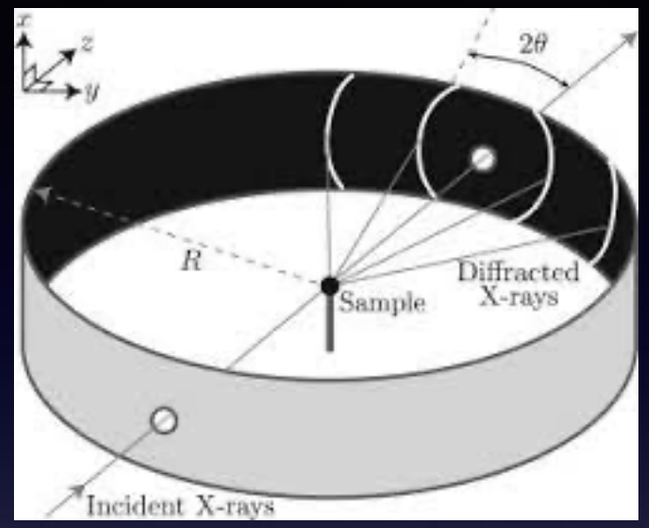
Hexachlorobenzene (1931)

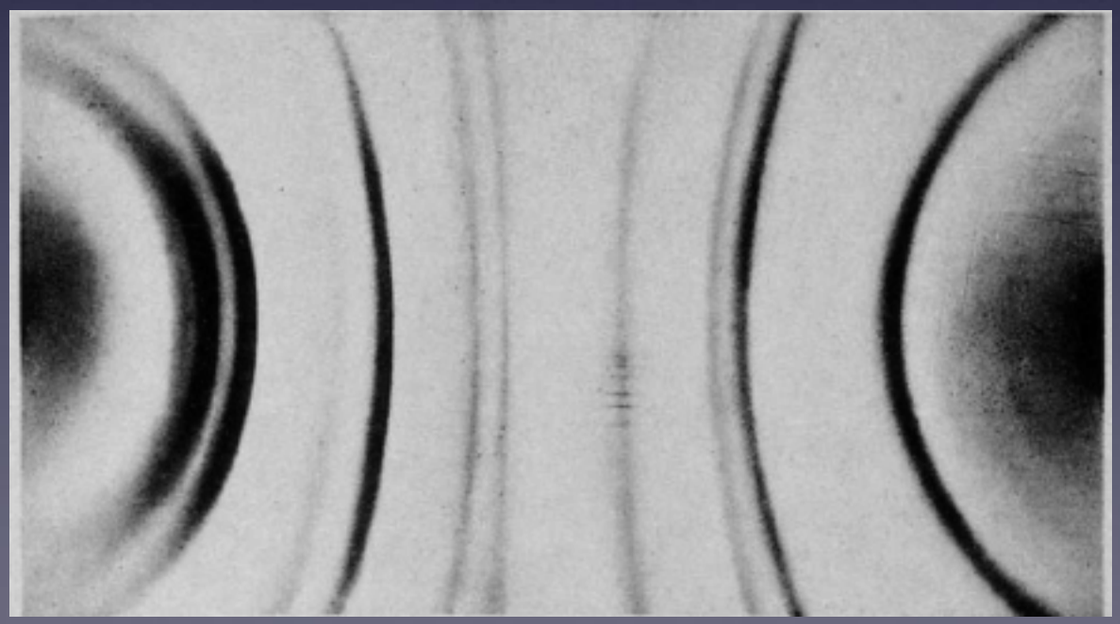
The powder method

Peter Deye
(1888-1966)

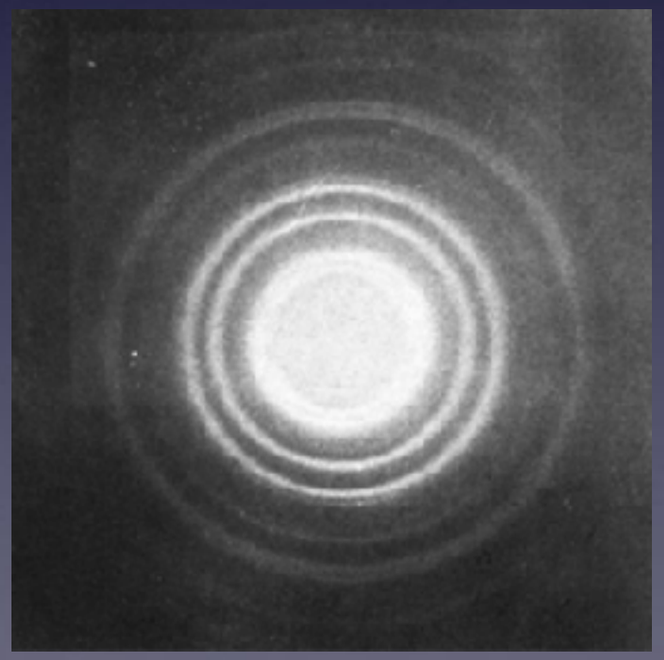
Paul Scherrer
(1890-1969)

Albert Hull
(1880-1966)





LiF
(P. Debye, P. Scherrer, 1916)

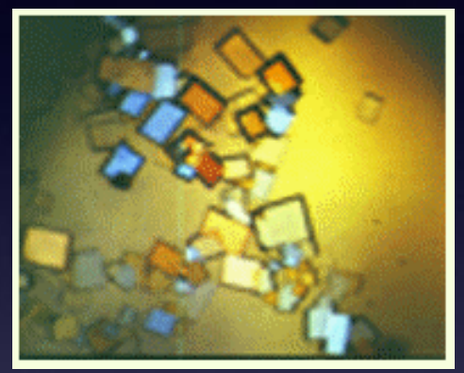


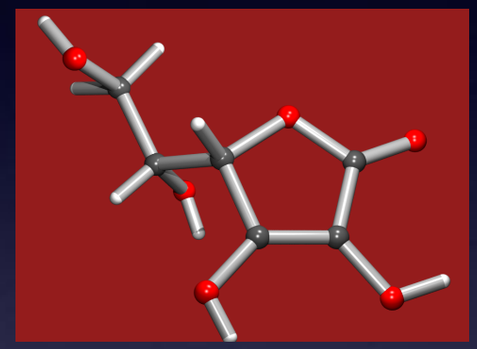
Aluminium
(A.W. Hull, 1917)

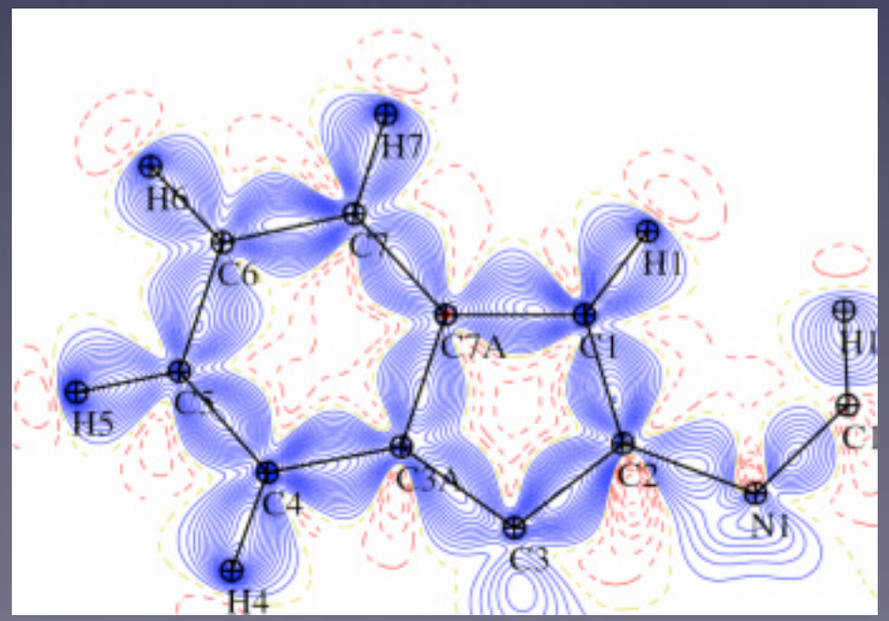
The first structure of a solidified gas

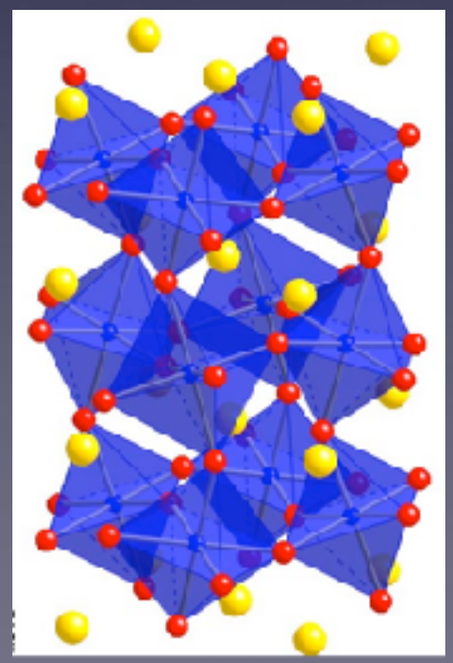
Debye-Scherrer diffraction pattern of solid α-nitrogen at the boiling point of liquid hydrogen (21 K), recorded by L. Vegard in 1929

X-ray crystallography

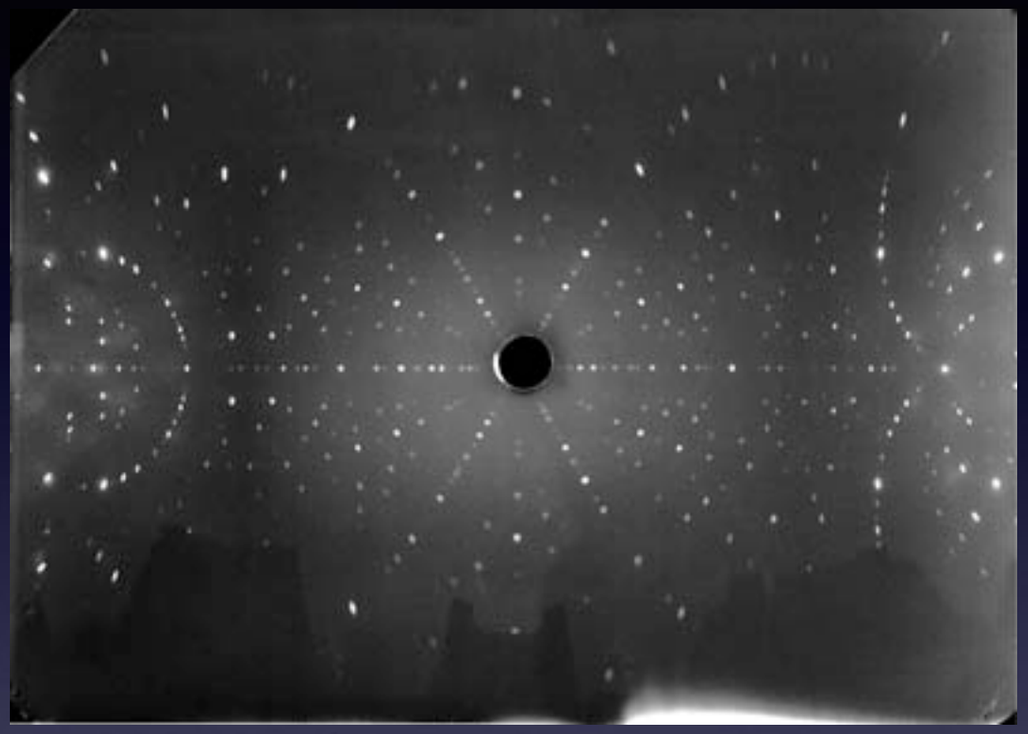


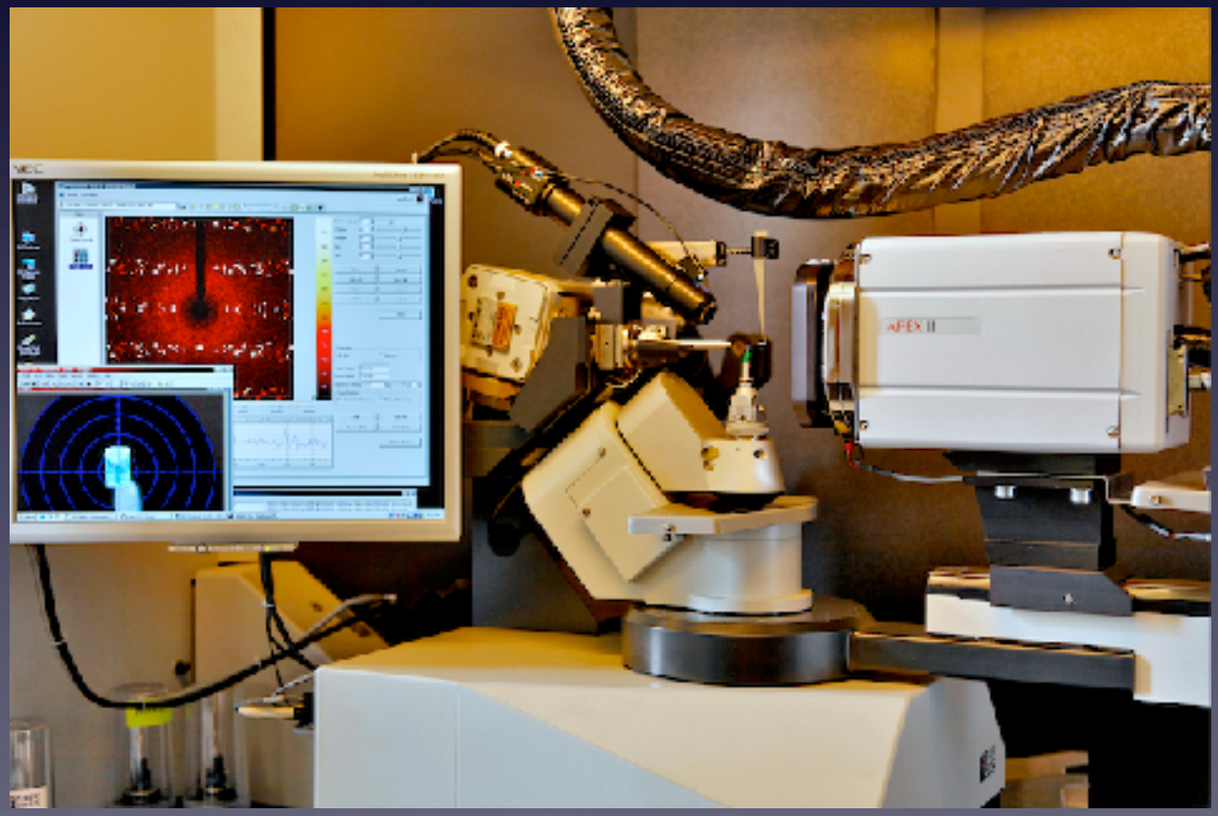


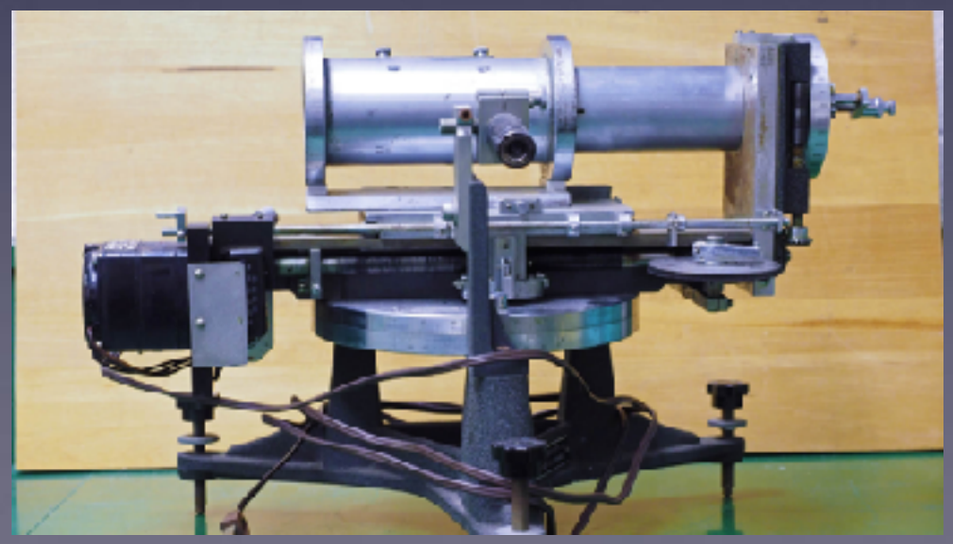




X-Ray Diffraction







X-Ray Diffraction

- The positions of the diffracted beams are determined by the unit cell (Bragg's law)
- The intensity of the diffracted beams are given by the square modulus of the Fourier transform of the electron density:

$$I_{hkl} = |\mathrm{FT}(\rho(\vec{r}))|^2$$

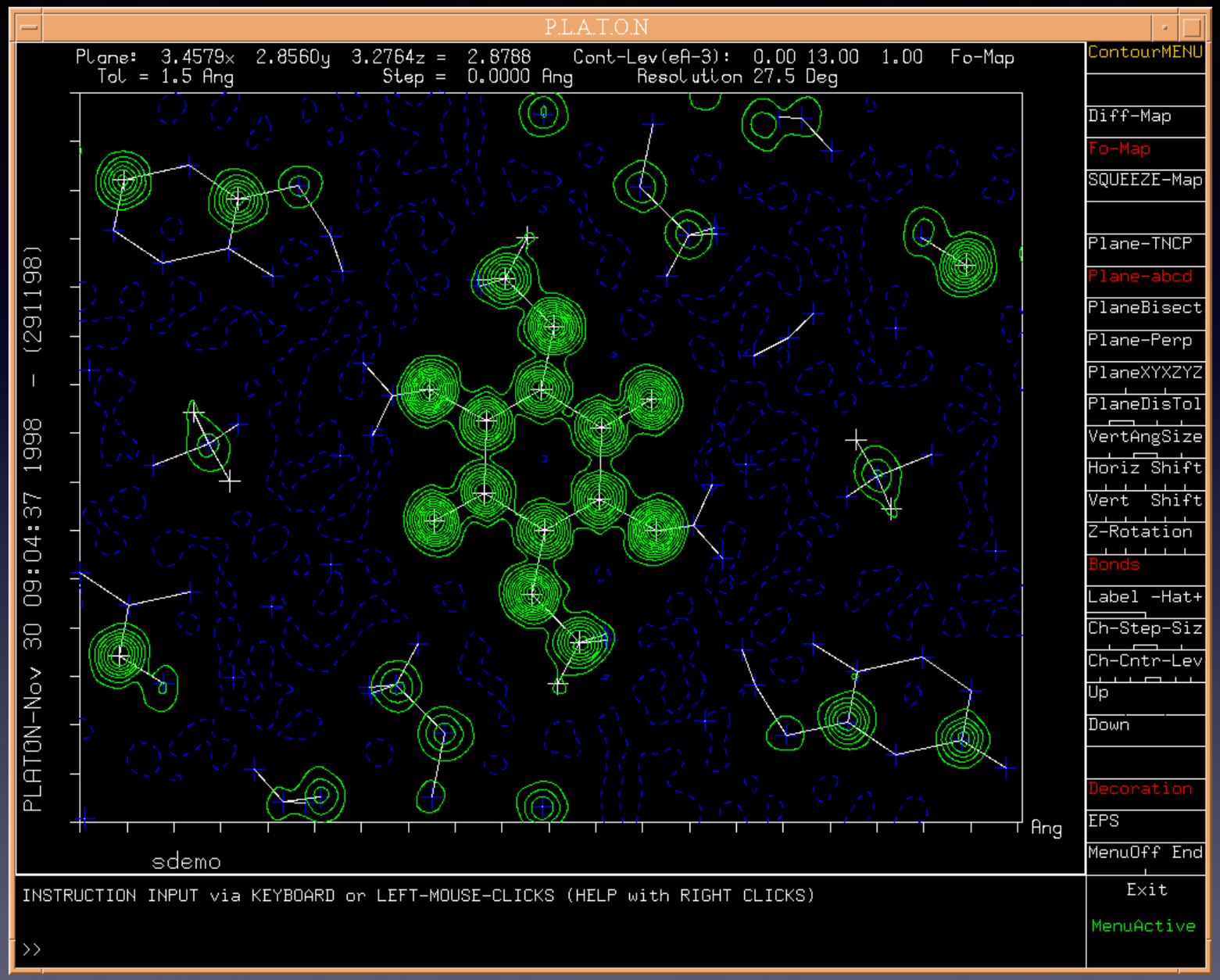
Structure Determination

$$I(h,k,l) \rightarrow |F(h,k,l)|^2$$

$$F(h,k,l) = \mathrm{FT}(\rho(\vec{r}))$$

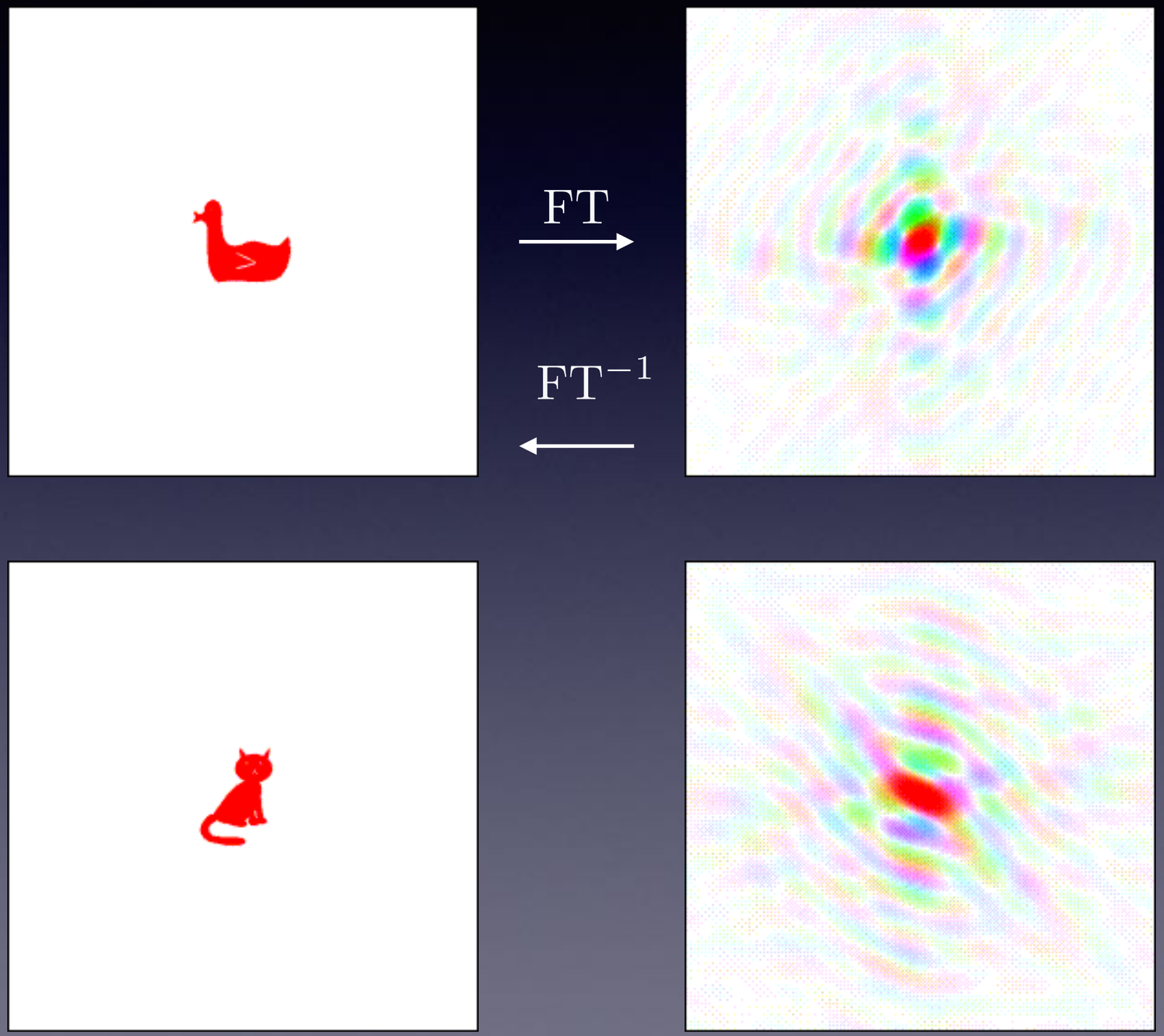
$$F(h,k,l) = |F(h,k,l)|\, e^{(\imath\phi)}$$

$$\rho(\vec{r}) = \frac{1}{V}\sum_{hkl} F(h,k,l) e^{-2\pi\imath(hx+ky+lz)}$$



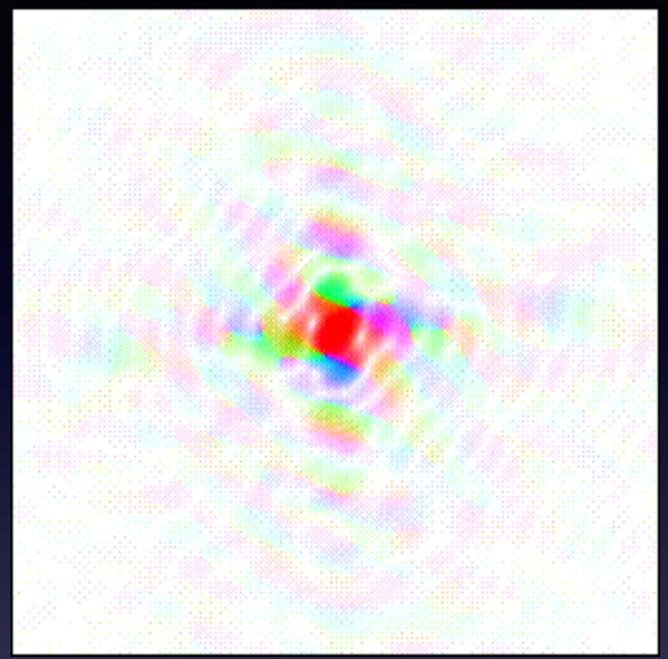
Fourier synthesis of electron density

The phase problem



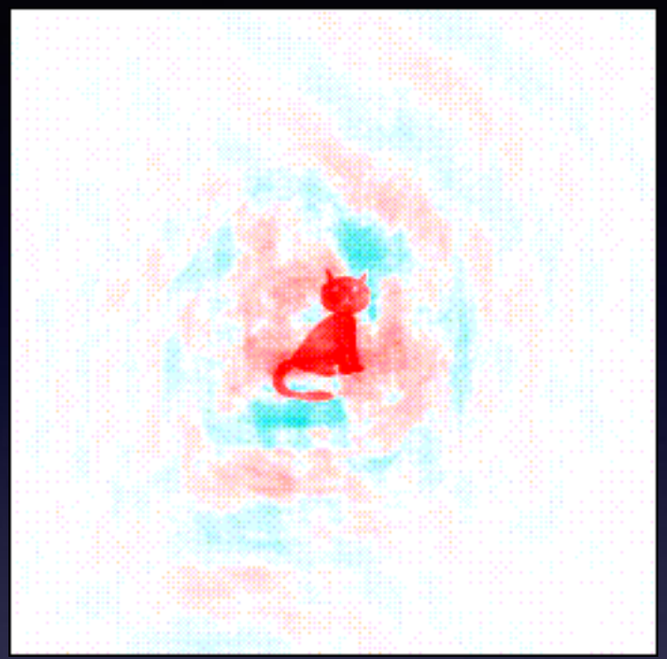
Kevin Cowtan: http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html

The phase problem

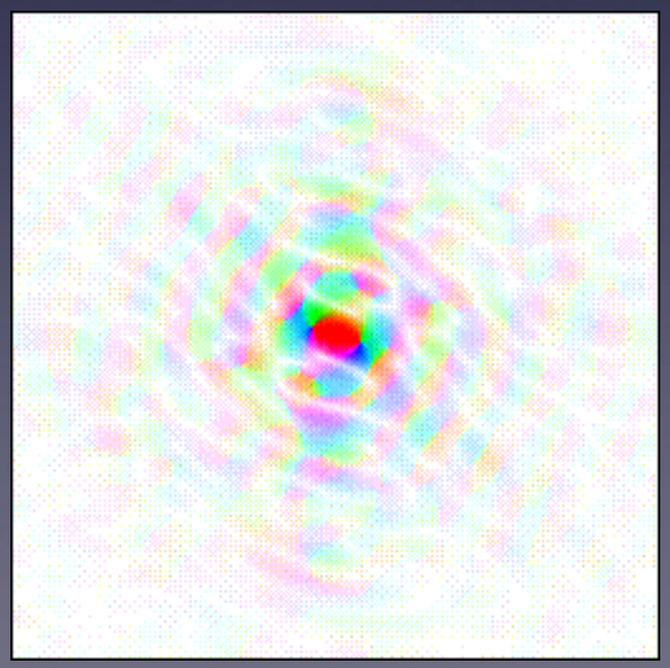


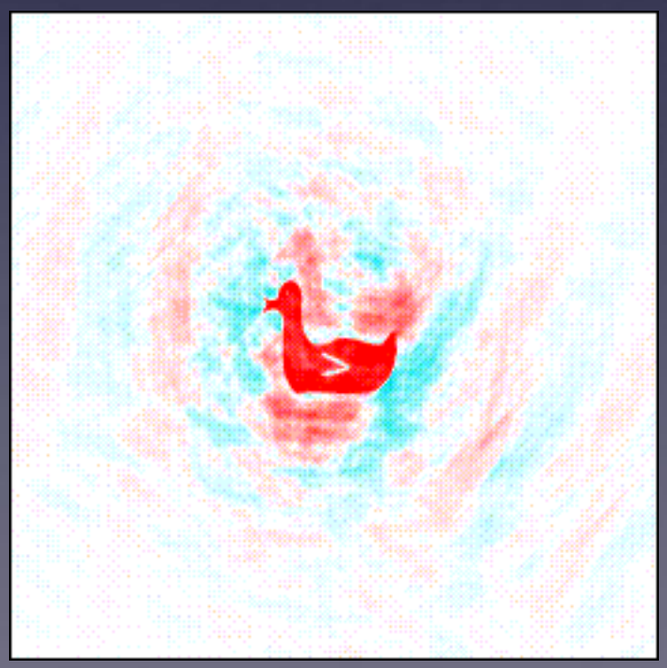
FT

FT^{-1}



Cat phases
+
Duck amplitudes





Cat amplitudes
+
Duck phases

Dealing with the phase problem

- Trial and error
- Heavy atom
- Isomorphous substitution
- Patterson synthesis
- Anomalous dispersion
- Direct methods

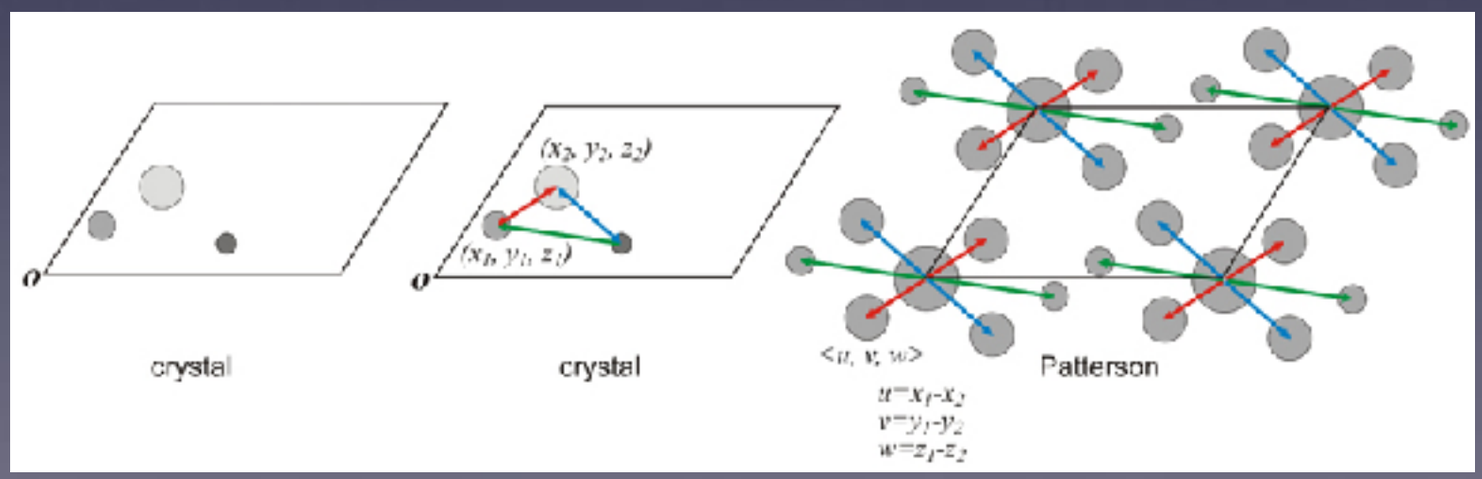
The Patterson function

A. L. Patterson
(1868-1951)

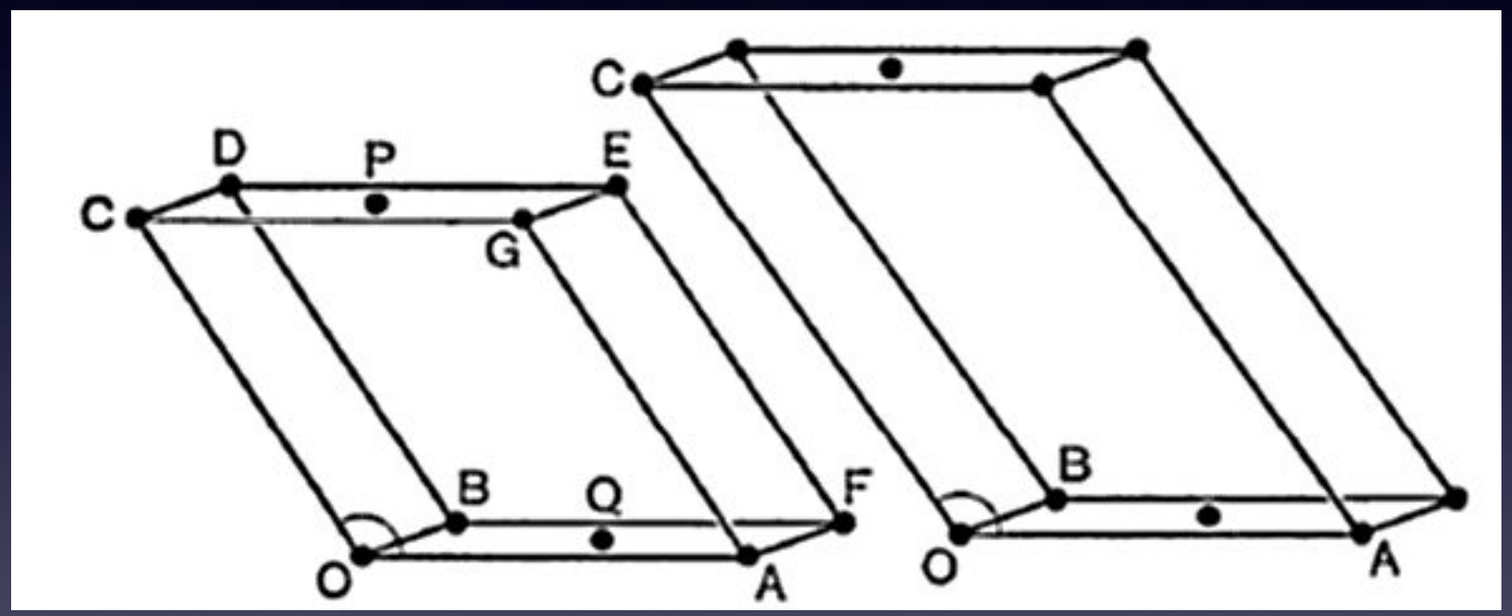
$$P(u,v,w) = \frac{1}{V}\sum_{hkl}|F_{hkl}|^2 e^{-2\pi\imath(hu+kv+lw)}$$

A. L. Patterson
(1934)

$$P(\vec{u}) = \int \rho(\vec{r})\rho(\vec{r}+\vec{u})\,d^3\vec{r}$$

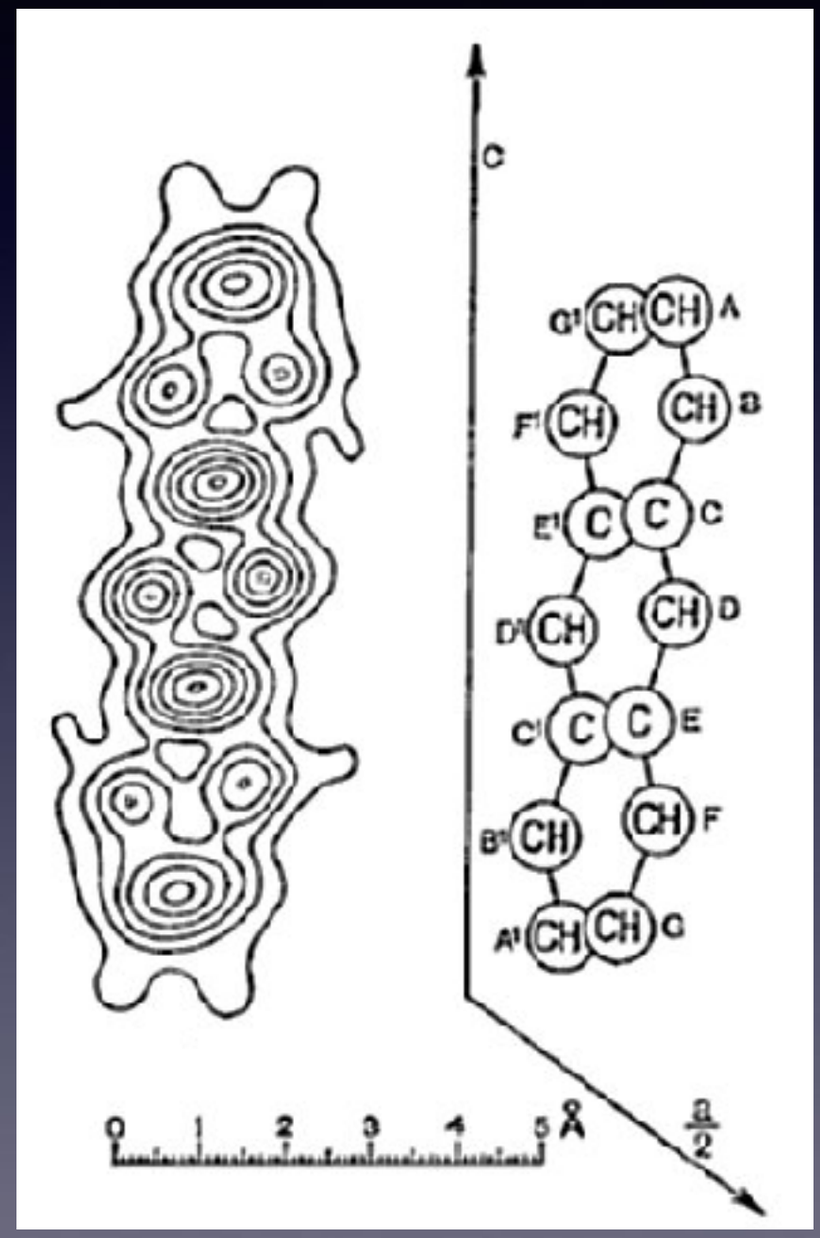


Aromatic compounds



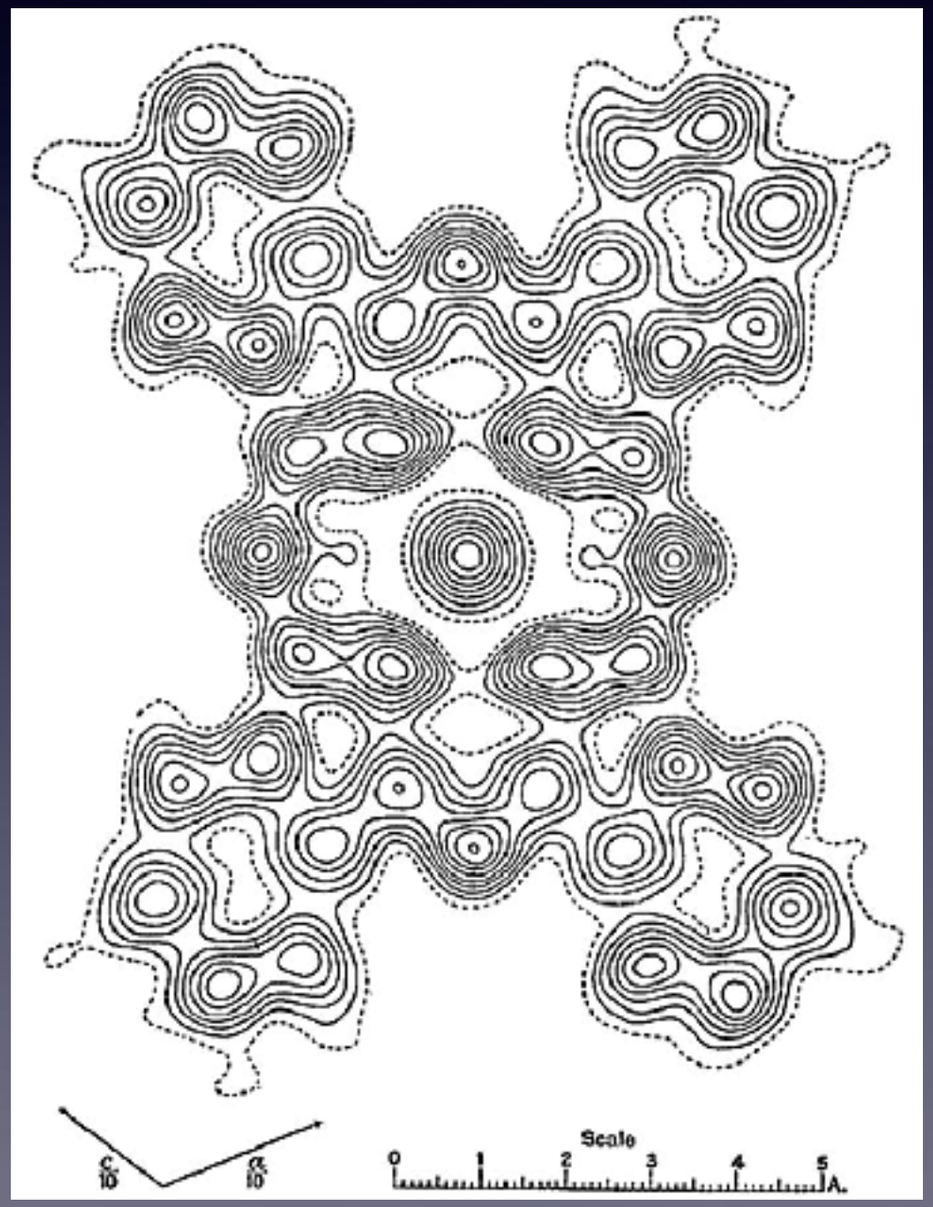
Naphthalene Anthracene

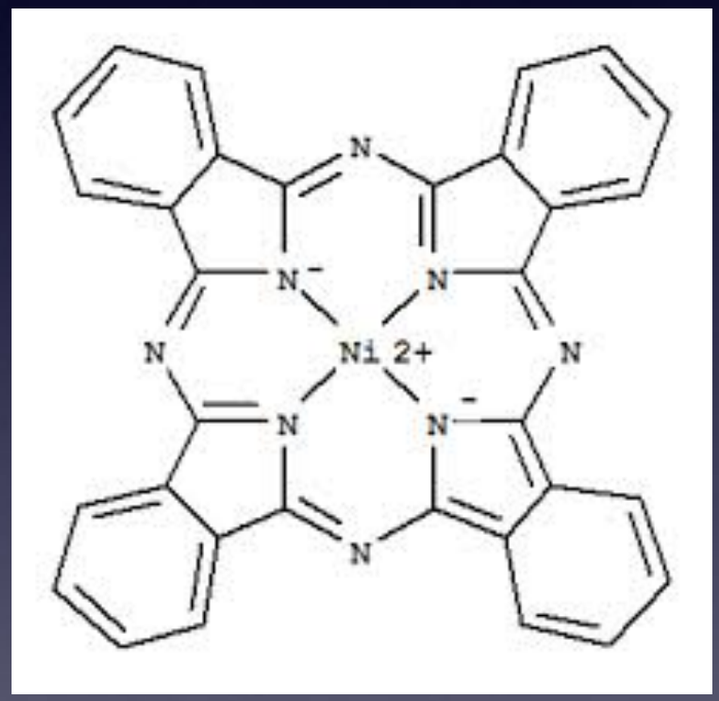
W.H. Bragg
(1922)



J.M. Robertson
(1933)

Coordination compounds

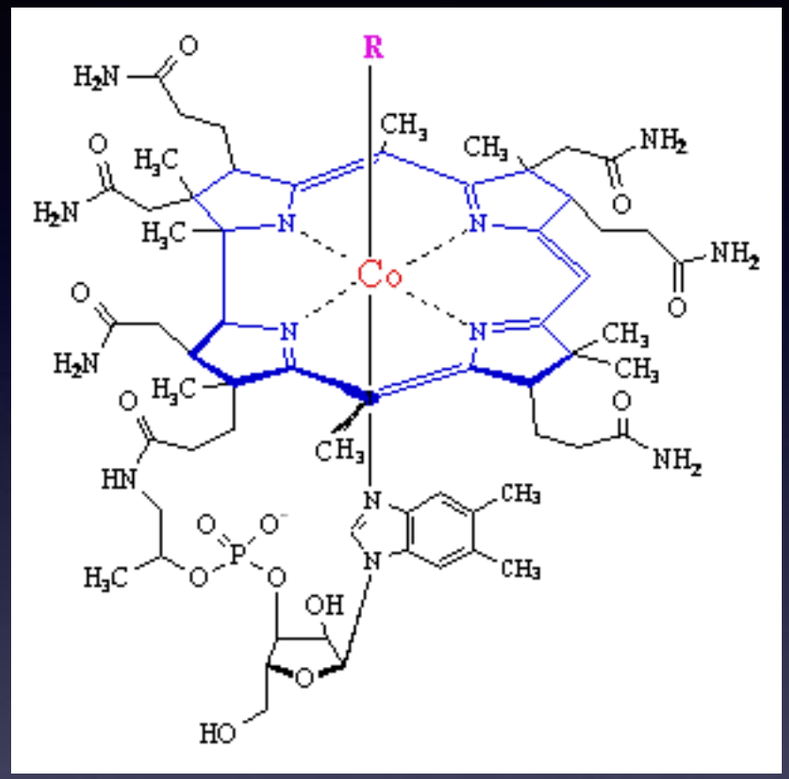




Ni-phtalocyanine
(Robertson & Woodward, 1937)

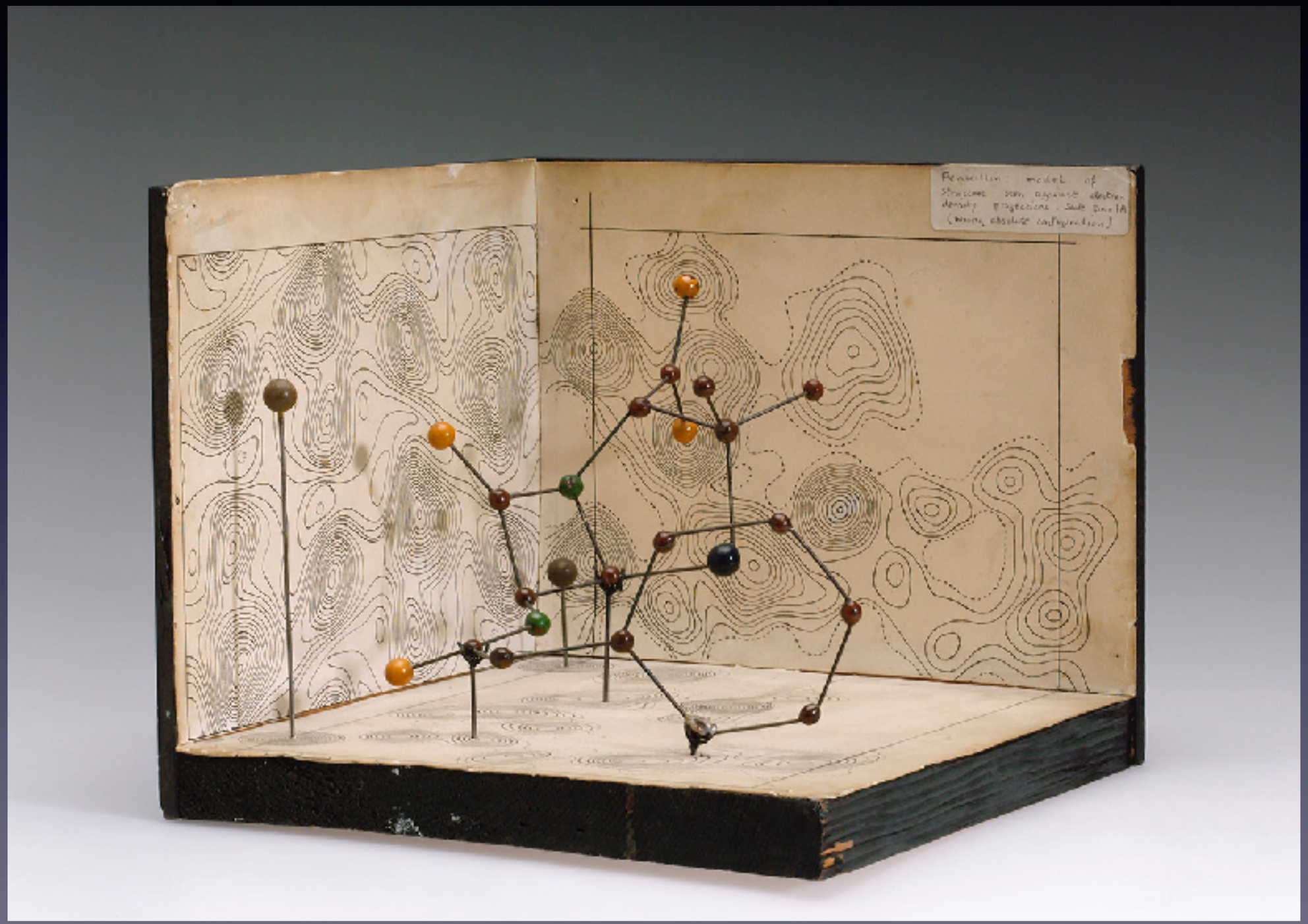
The “big” organic molecules

Dorothy Crowfoot Hodgkin
(1910-1994)



Vitamin B12

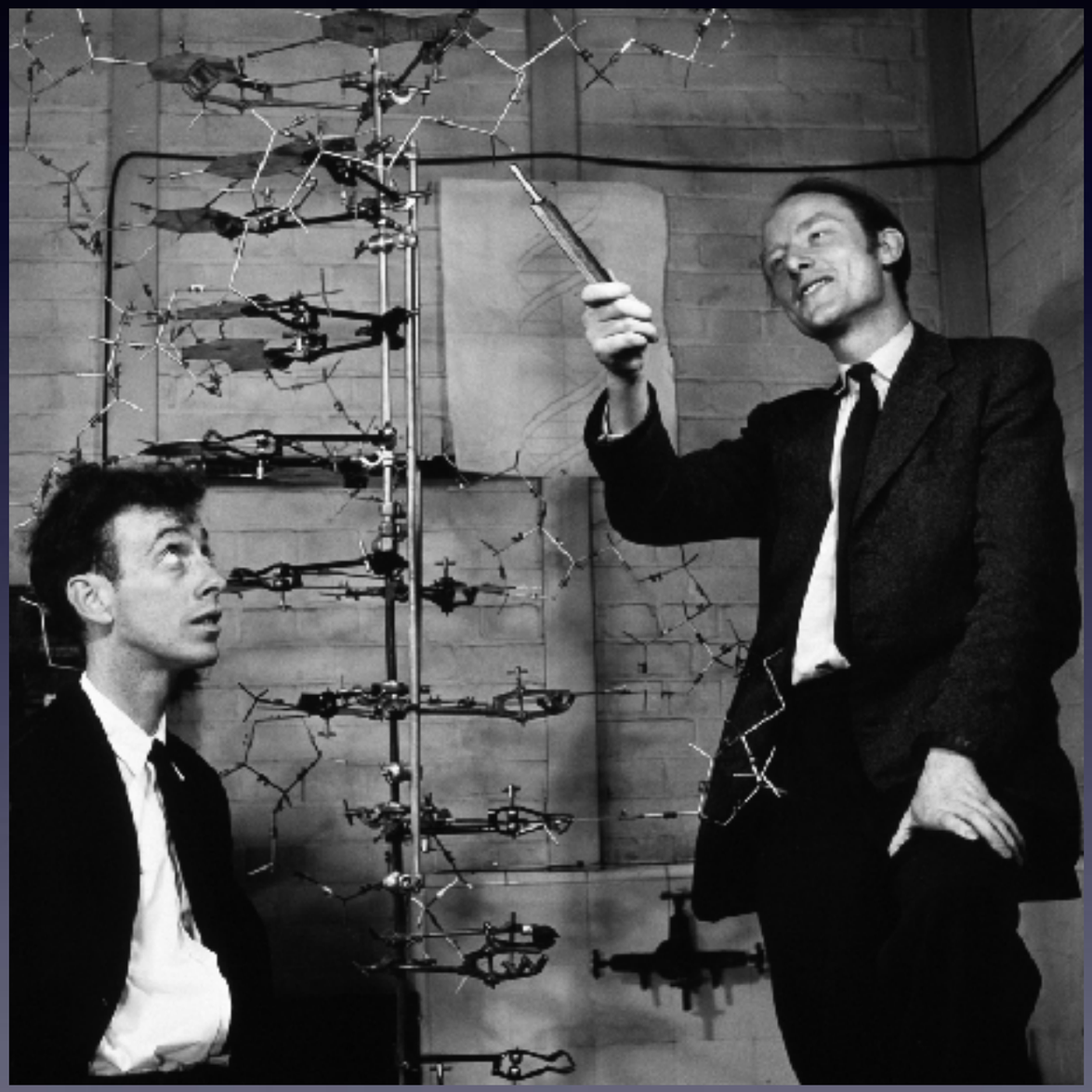
The structure of insulin



(1945)

The structure of DNA

(1953)



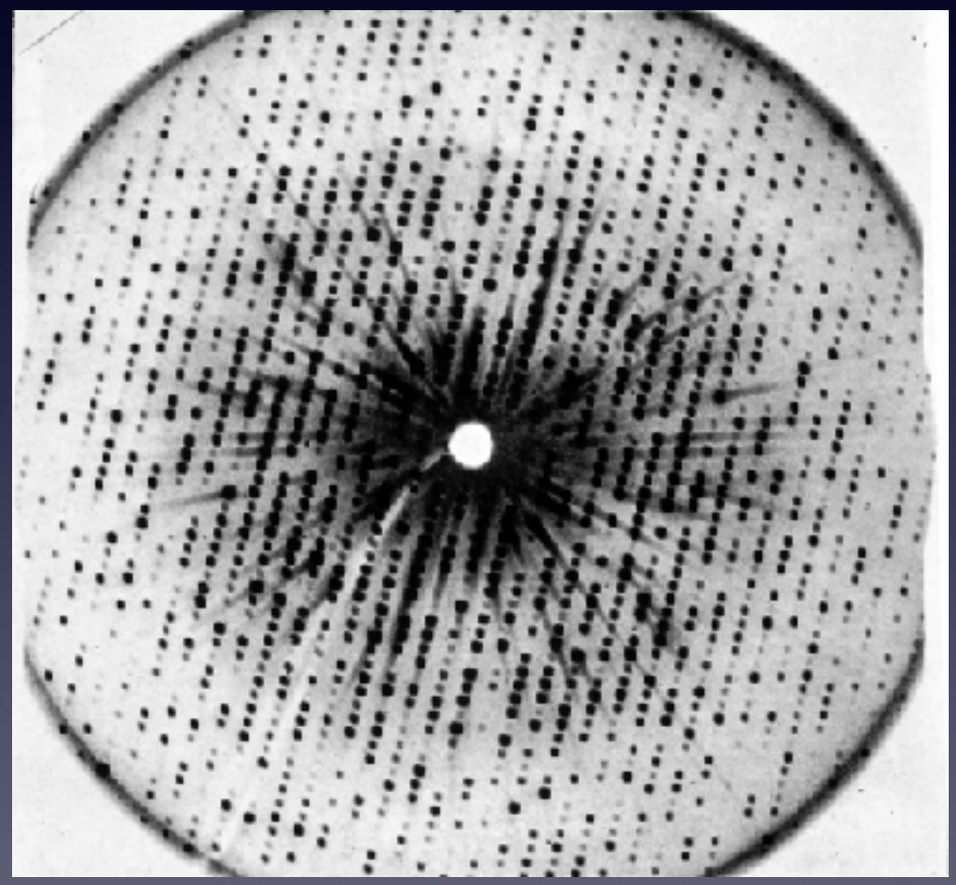
James Watson
(1928-)

Francis Crick
(1916-2004)

Rosalind Fanklin
(1920-1958)

Structures of haemoglobin/ myoglobin

Max Perutz
(1914-2002)

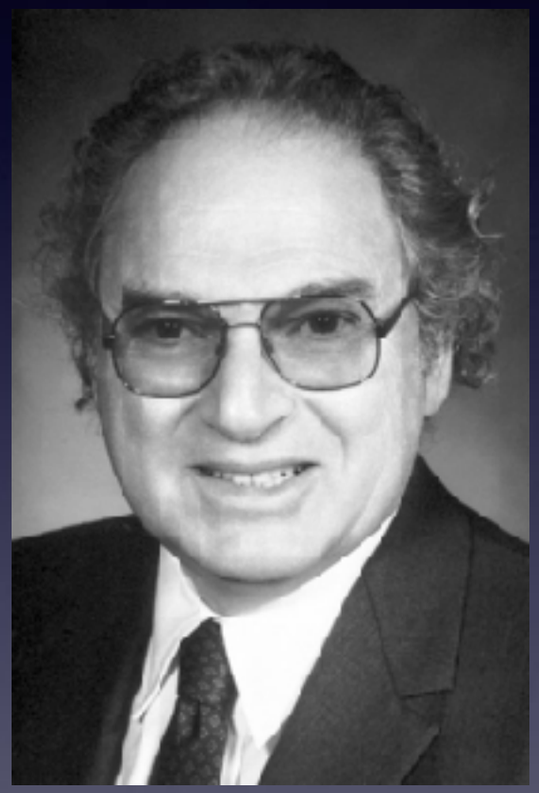


John Kendrew
(1917-1997)

Direct Methods

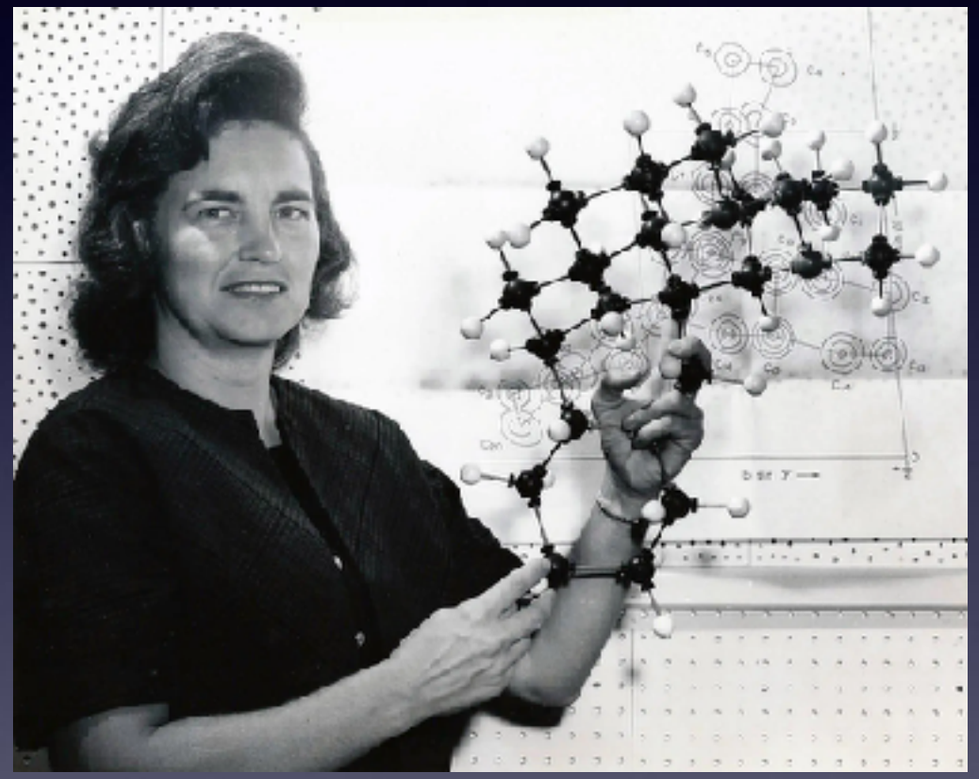
- The nature of the diffracting object (electron density) imposes certain restrictions and relation between the phases of the structure factors
- These may be used to retrieve all the phases by an inference/statistical procedure

Direct methods



Herbert Hauptman
(1917-2011)

Jerome Karle
(1918-2013)



Isabella Karle
(1921-2017)

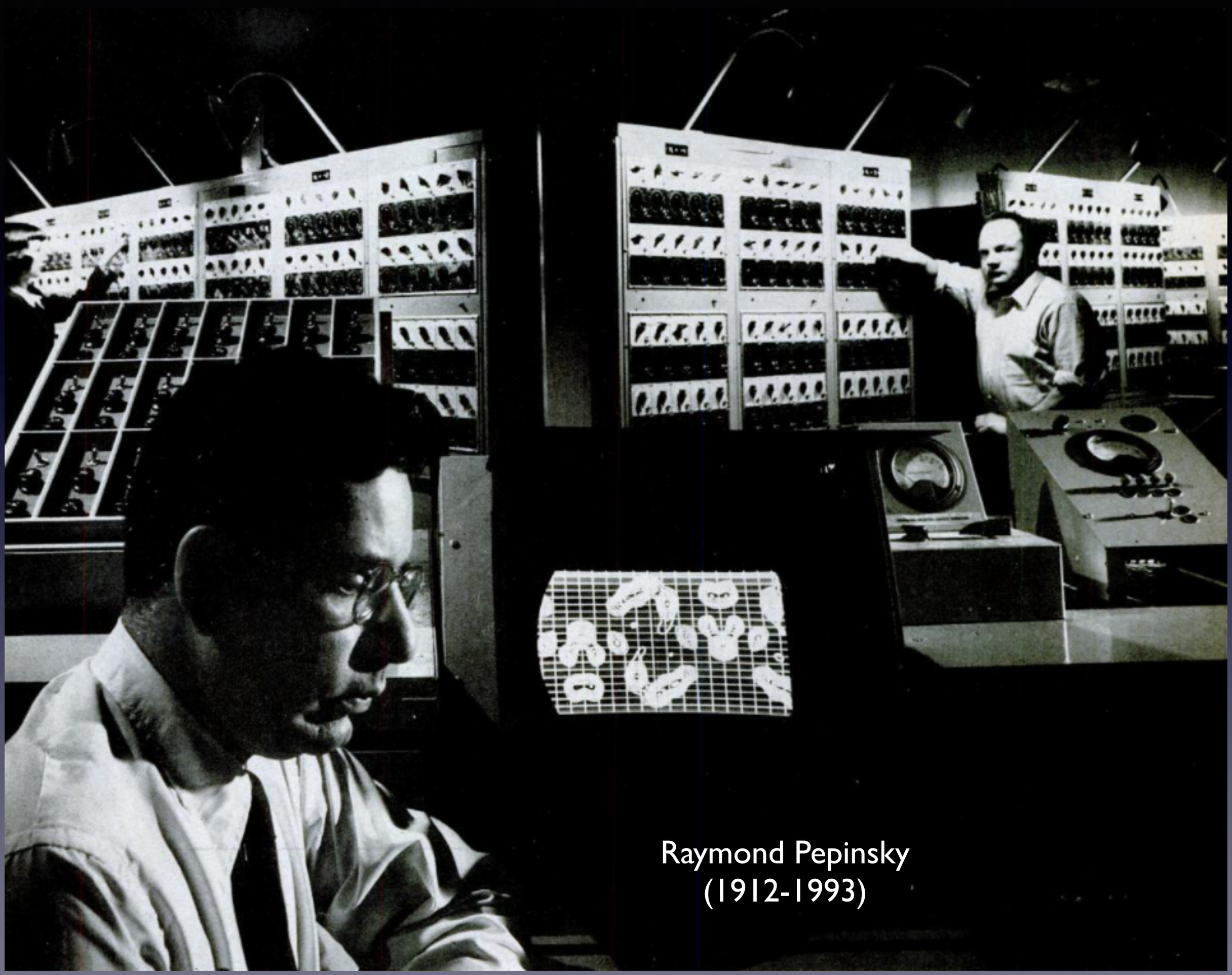
The computing problem

(Women) Computers

Beevers-Lipson strips

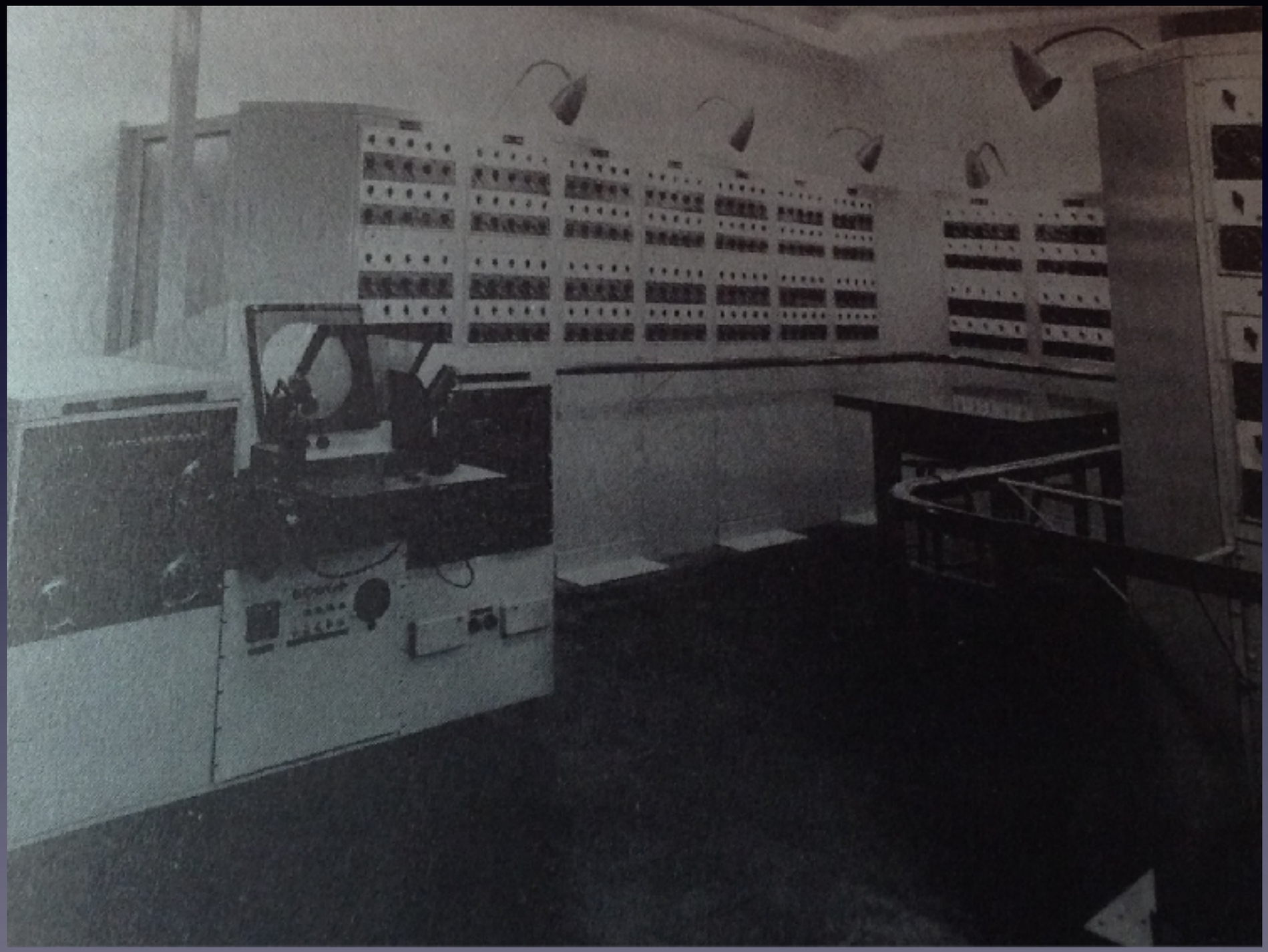
Hand computation of Fourier synthesis was a bottleneck

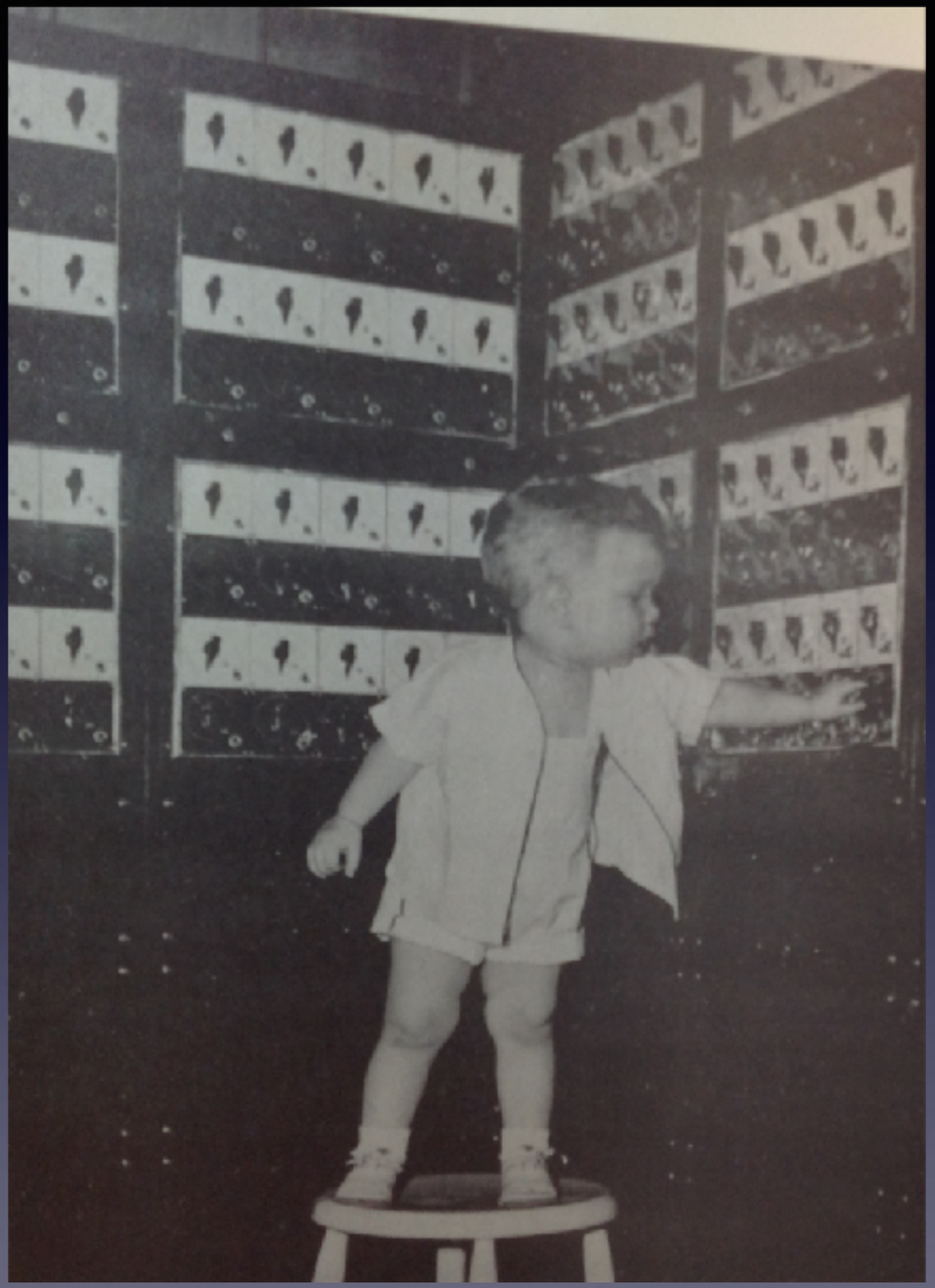
The Analogue Computer



Raymond Pepinsky
(1912-1993)

X-RAC

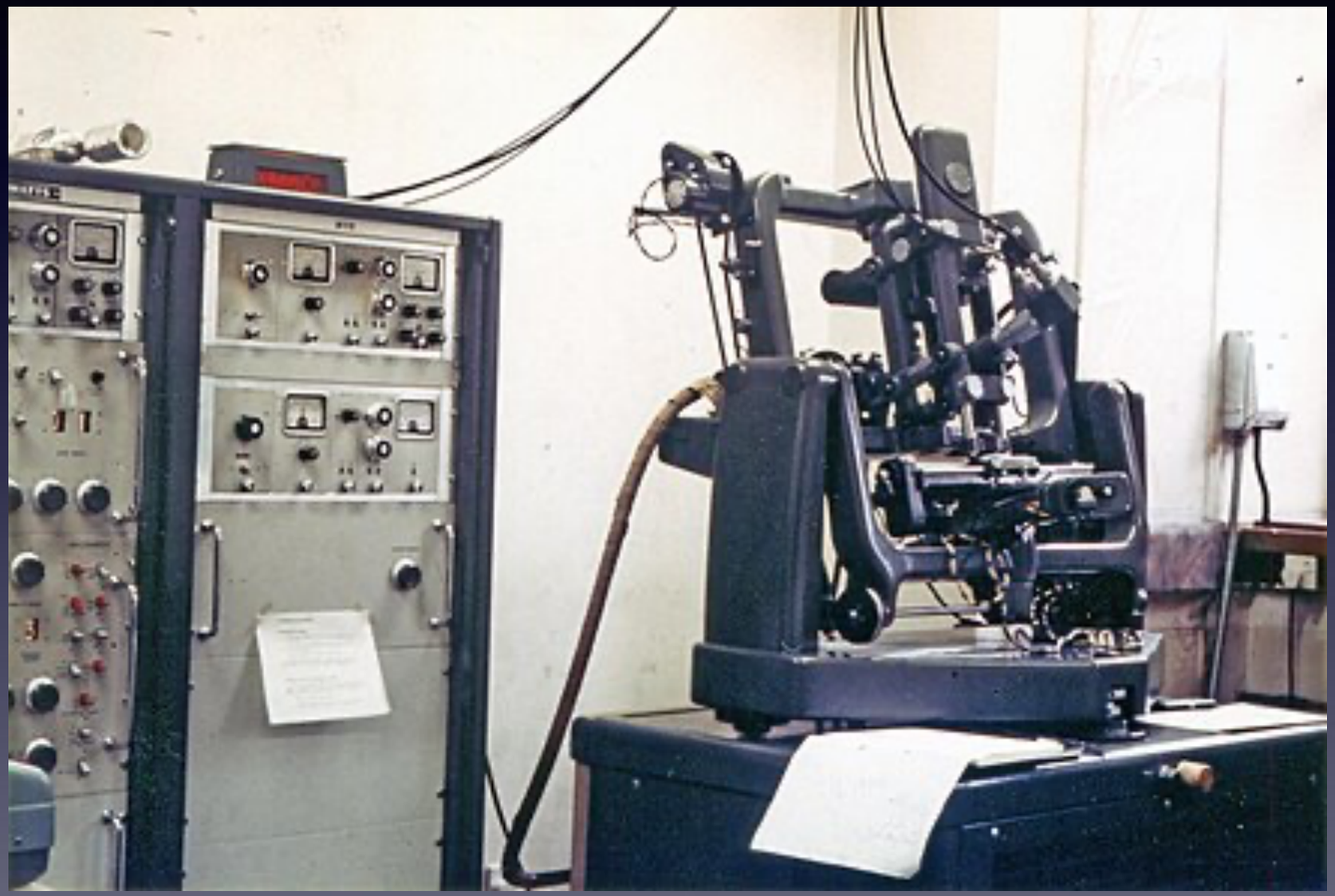




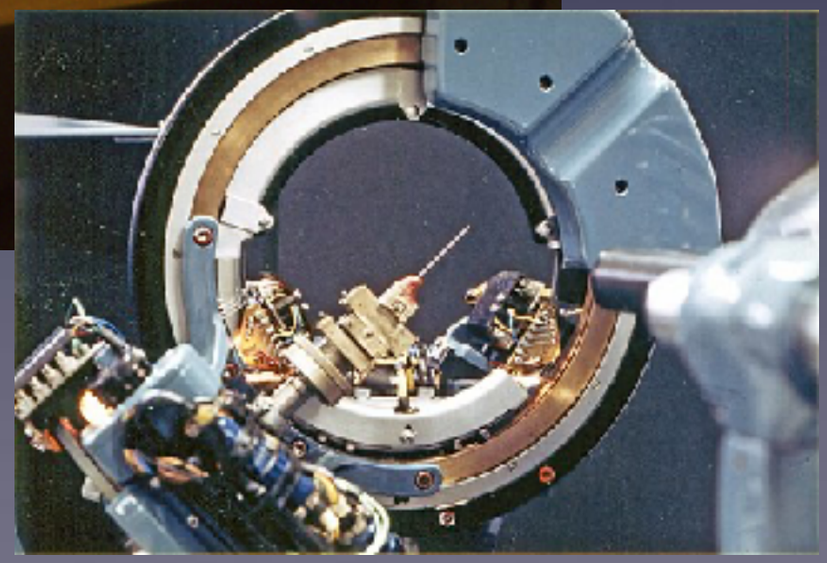
Fourier synthesis became a child's play!

The Digital Computer and the Automation Era

Hilger & Watts diffractometer



Y190 linear diffractometer (~1955)



Y290 4-circle diffractometer (1966)

Enraf-Nonius κ-geometry diffractometer

Minicomputer (PDP-11) controlled (1981)

Crystallography & Computing

Crystallography & Computing

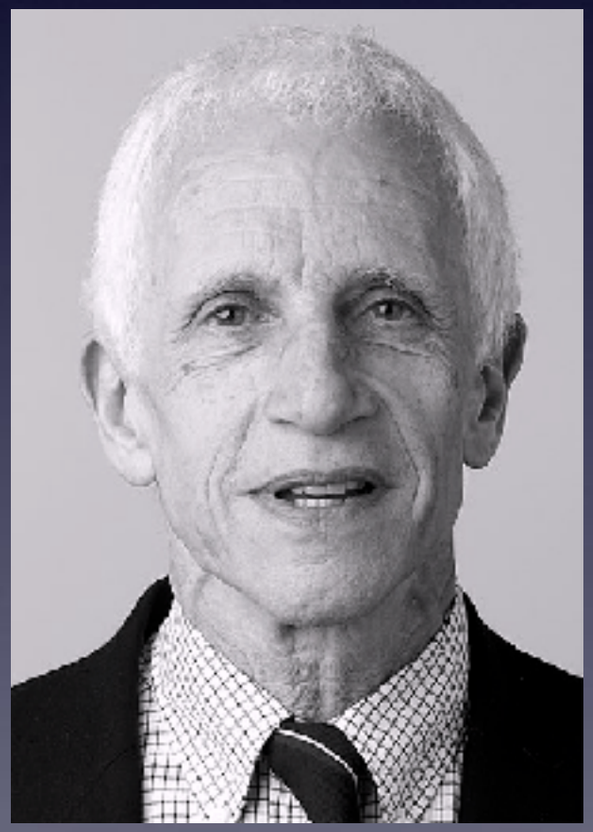
David Sayre
(1924-2012)

- ORFLS
- ORTEP
- MULTAN
- DBWS
- SHELX
- (…)

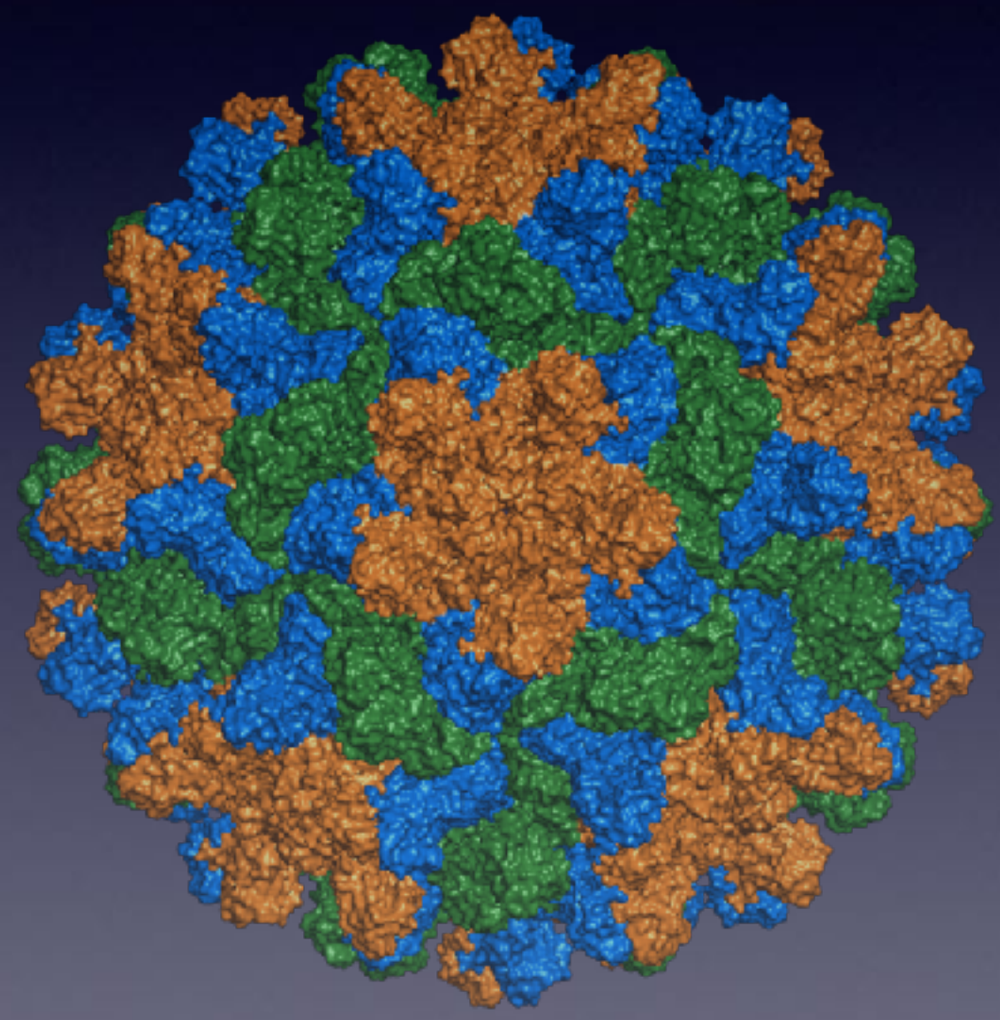
Team FORTRAN compiler

Virus crystallography

Tomato stunt bush virus



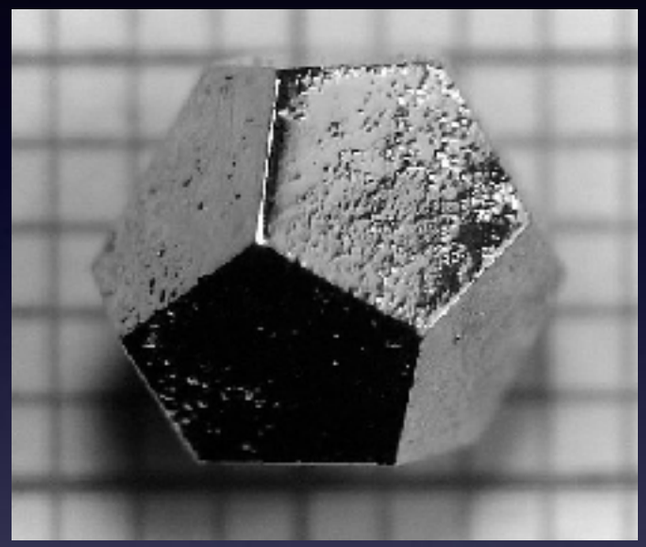
Stephen Harisson
(1941-)



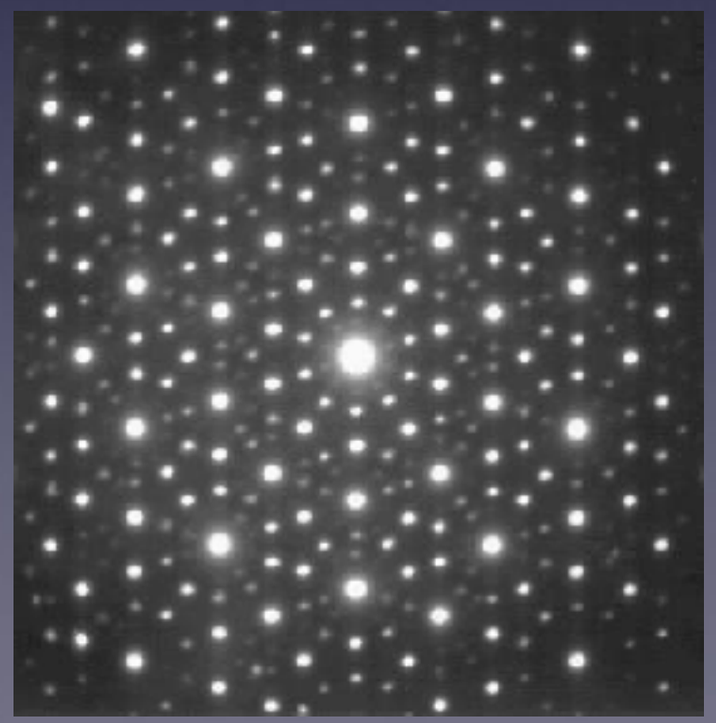
(1978)

Quasicrystals

Dan Shechtman
(1941-)

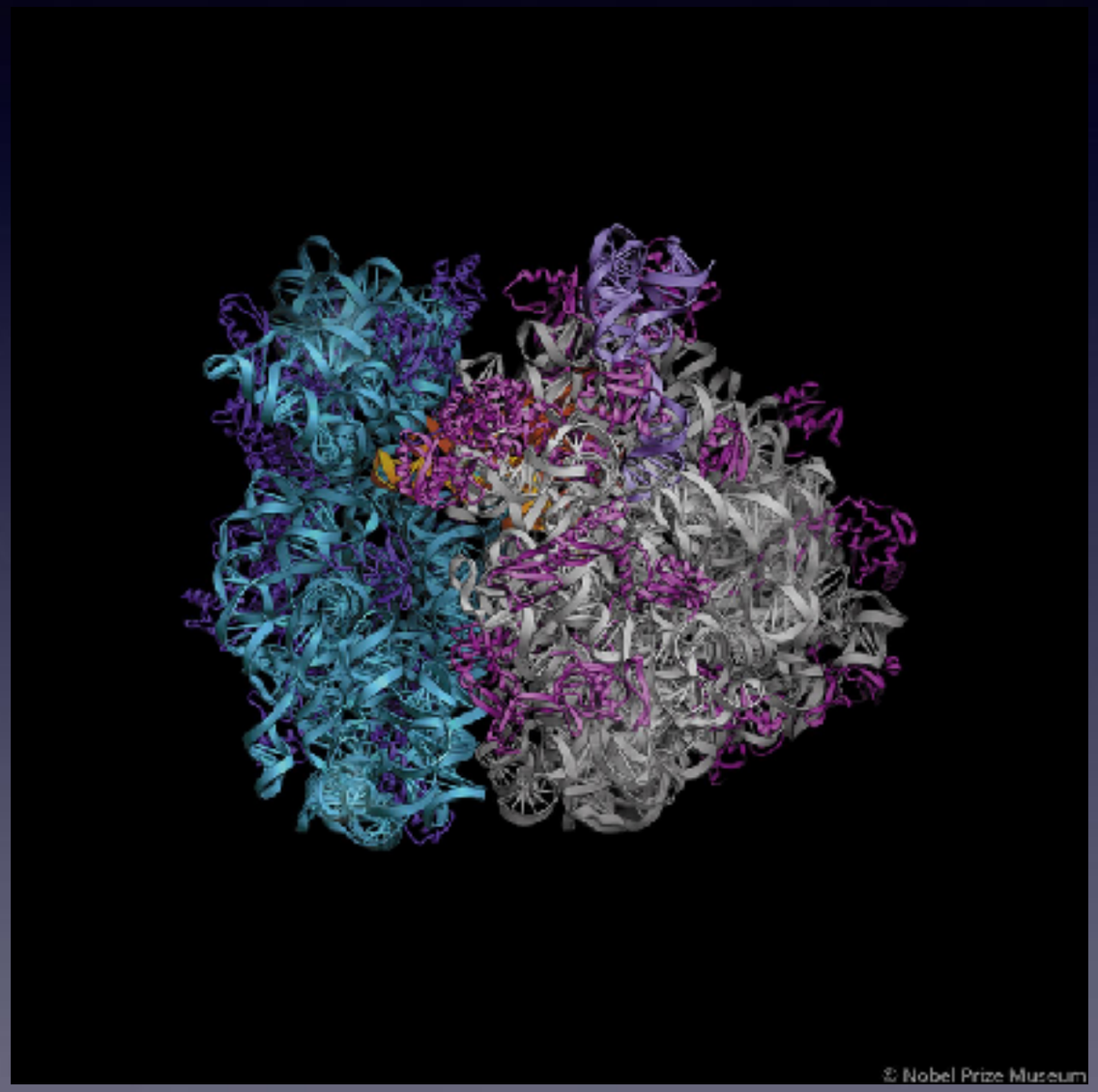


(1984)



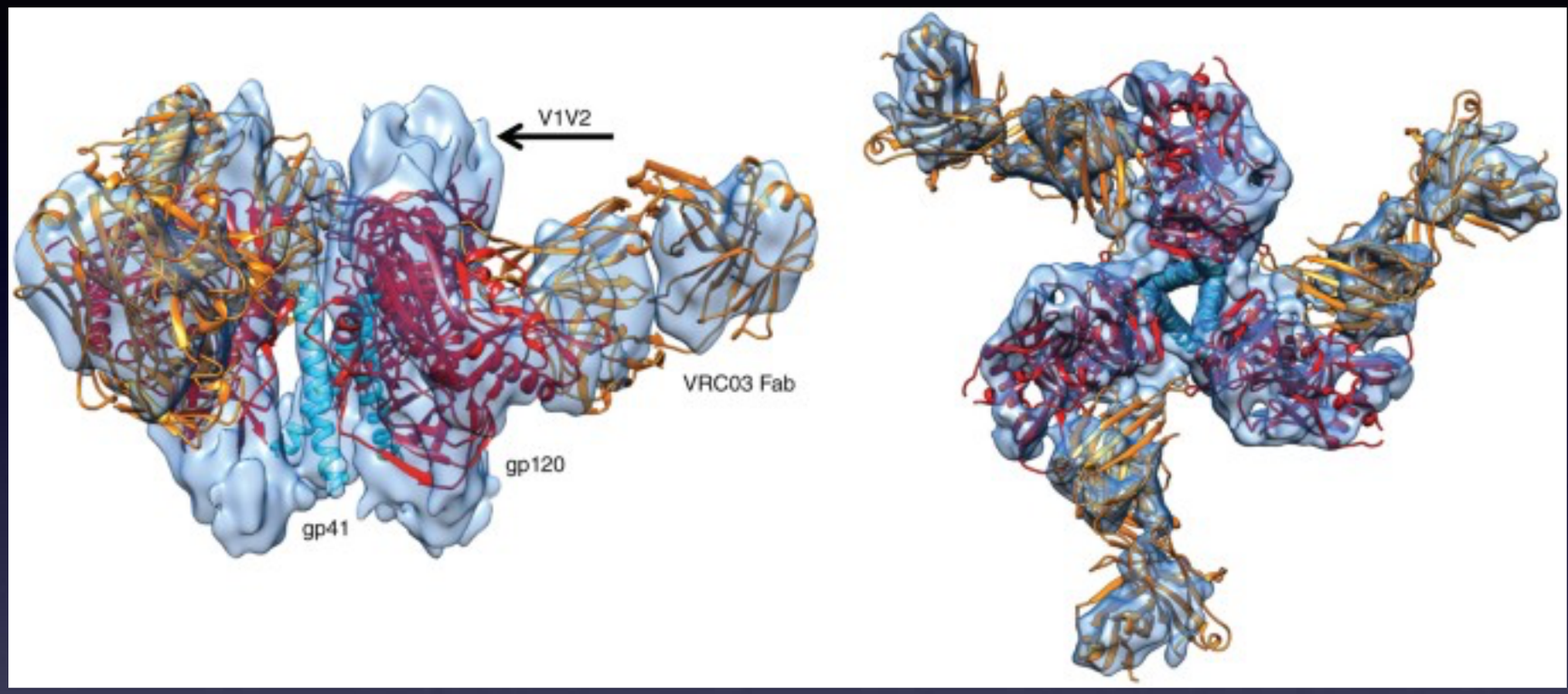
Structure of ribosome

Ada Yonath
(1939-)



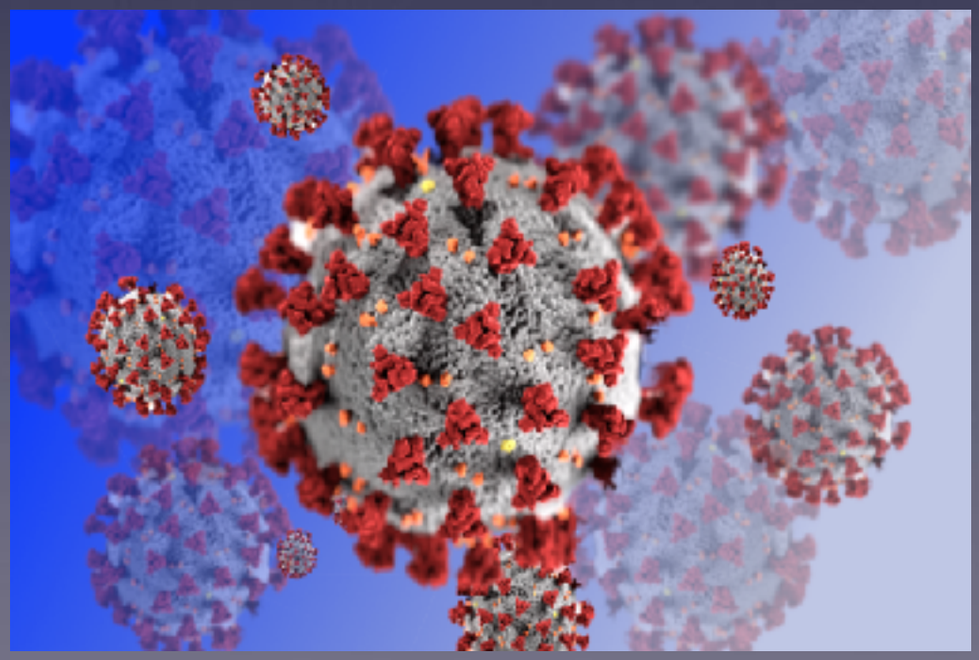
(2000)

HIV Trimer



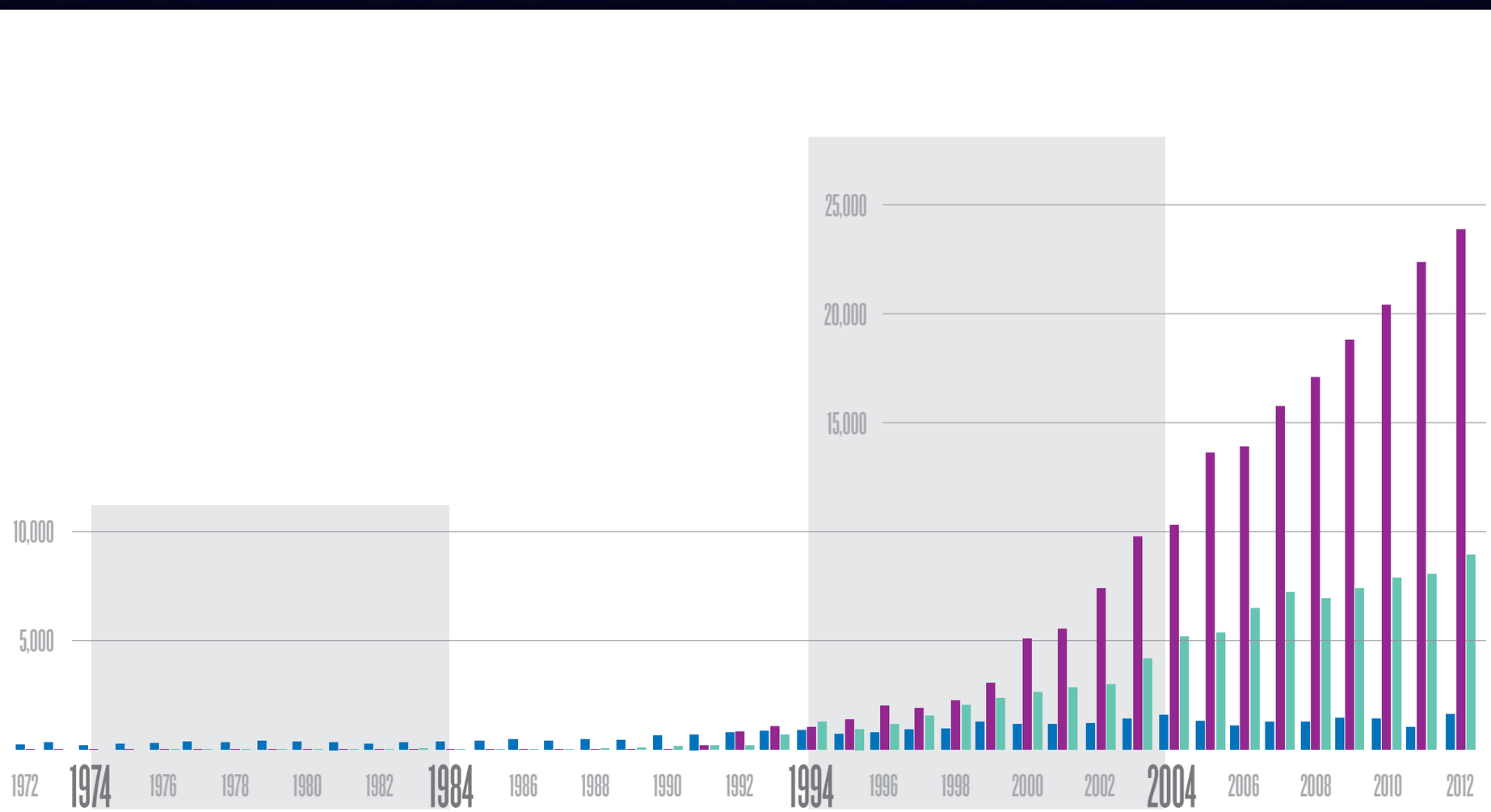
(2013)

(2020)

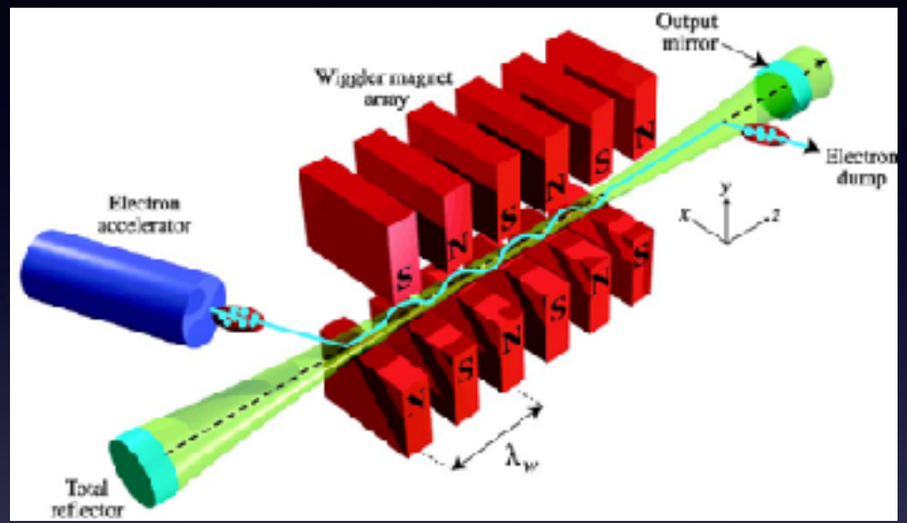


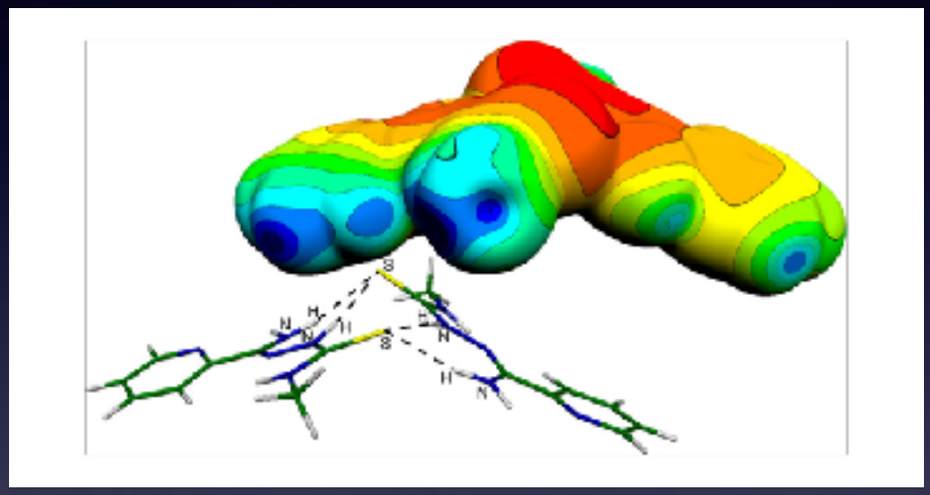
SARS-COV-2

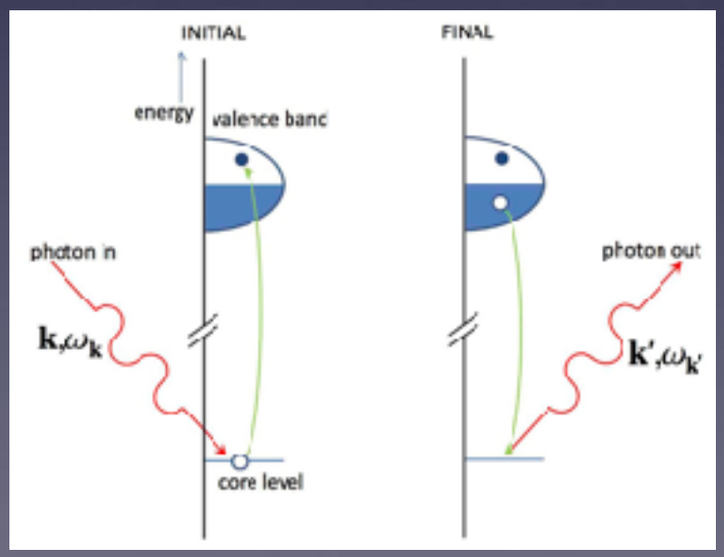
The growing success of X-ray crystallography



The future


Output mirror
Wiggler magnet array
Electron dump
Electron accelerator
Total reflector
λ_w




INITIAL
FINAL
energy
valence banc
photon in
photon out
$\mathbf{k},\omega_{\mathbf{k}}$
$\mathbf{k}',\omega_{\mathbf{k}'}$
core level