X-ray crystallography tutorial

CCDM
Mike Zdilla
Temple Chemistry

Nobel Prize winners associated with crystallography

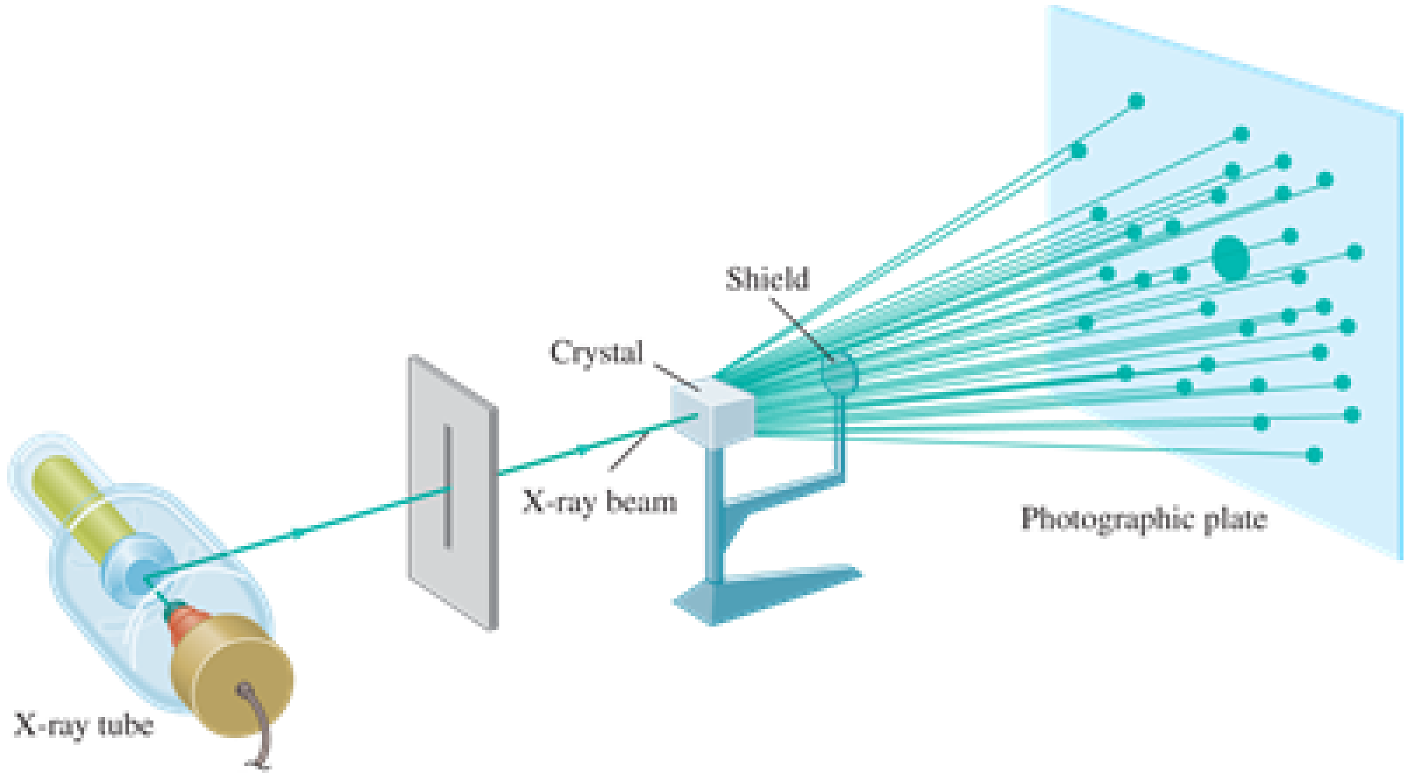
2013 Chemistry
M. Karplus, M. Levitt and A. Warshel
For the development of multiscale models for complex chemical systems
2012 Chemistry
R. J. Lefkowitz and B. K. Kobilka
For studies of G-protein-coupled receptors
2011 Chemistry
D. Shechtman
For the discovery of quasicrystals **2010 Physics**
A. Geim and K. Novoselov
For groundbreaking experiments regarding the two-dimensional material graphene
2009 Chemistry
V. Ramakrishnan, T. A. Steitz and A. E. Yonath
Studies of the structure and function of the ribosome **2006 Chemistry**
R. D. Kornberg
Studies of the molecular basis of eukaryotic transcription
2003 Chemistry
R. MacKinnon
Potassium channels
1997 Chemistry
P. D. Boyer, J. E. Walker and J. C. Skou
Elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP) and discovery of an ion-transporting enzyme
1996 Chemistry
R.Curl, H. Kroto and R. Smalley
Discovery of the fullerene form of carbon
1994 Physics
C. Shull and N. Brockhouse
Neutron diffraction
1992 Physics
G. Charpak
Discovery of the multi wire proportional chamber
1991 Physics
P.-G. de Gennes
Methods of discovering order in simple systems can be applied to polymers and liquid crystals
1988 Chemistry
J. Deisenhofer, R. Huber and H. Michel
For the determination of the three-dimensional structure of a photosynthetic reaction centre
1985 Chemistry
H. Hauptman and J. Karle
Development of direct methods for the determination of crystal structures
1982 Chemistry
A. Klug
Development of crystallographic electron microscopy and discovery of the structure of biologically important nucleic acid-protein complexes

1976 Chemistry
W. N. Lipscomb
Structure of boranes
1972 Chemistry
C. B. Anfinsen
Folding of protein chains
1964 Chemistry
D. Hodgkin
Structure of many biochemical substances including Vitamin B12
1962 Physiology or Medicine
F. Crick, J. Watson and M. Wilkins
The helical structure of DNA
1962 Chemistry
J. C. Kendrew and M. Perutz
For their studies of the structures of globular proteins
1954 Chemistry
L. C. Pauling
For his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances
1946 Chemistry
J. B. Sumner
For his discovery that enzymes can be crystallised
1937 Physics
C. J. Davisson and G. Thompson
Diffraction of electrons by crystals
1936 Chemistry
P. J. W. Debye
For his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases
1929 Physics
L.-V. de Broglie
The wave nature of the electron
1917 Physics
C. G. Barkla
Discovery of the characteristic Röntgen radiation of the elements **1915 Physics**
W. H. Bragg and W. L. Bragg
Use of X-rays to determine crystal structure
1914 Physics
M. Von Laue
Diffraction of X-rays by crystals
1901 Physics
W. C. Röntgen
Discovery of X-rays

Source: International Union of Crystallography
(http://www.iucr.org/people/nobel-prize)

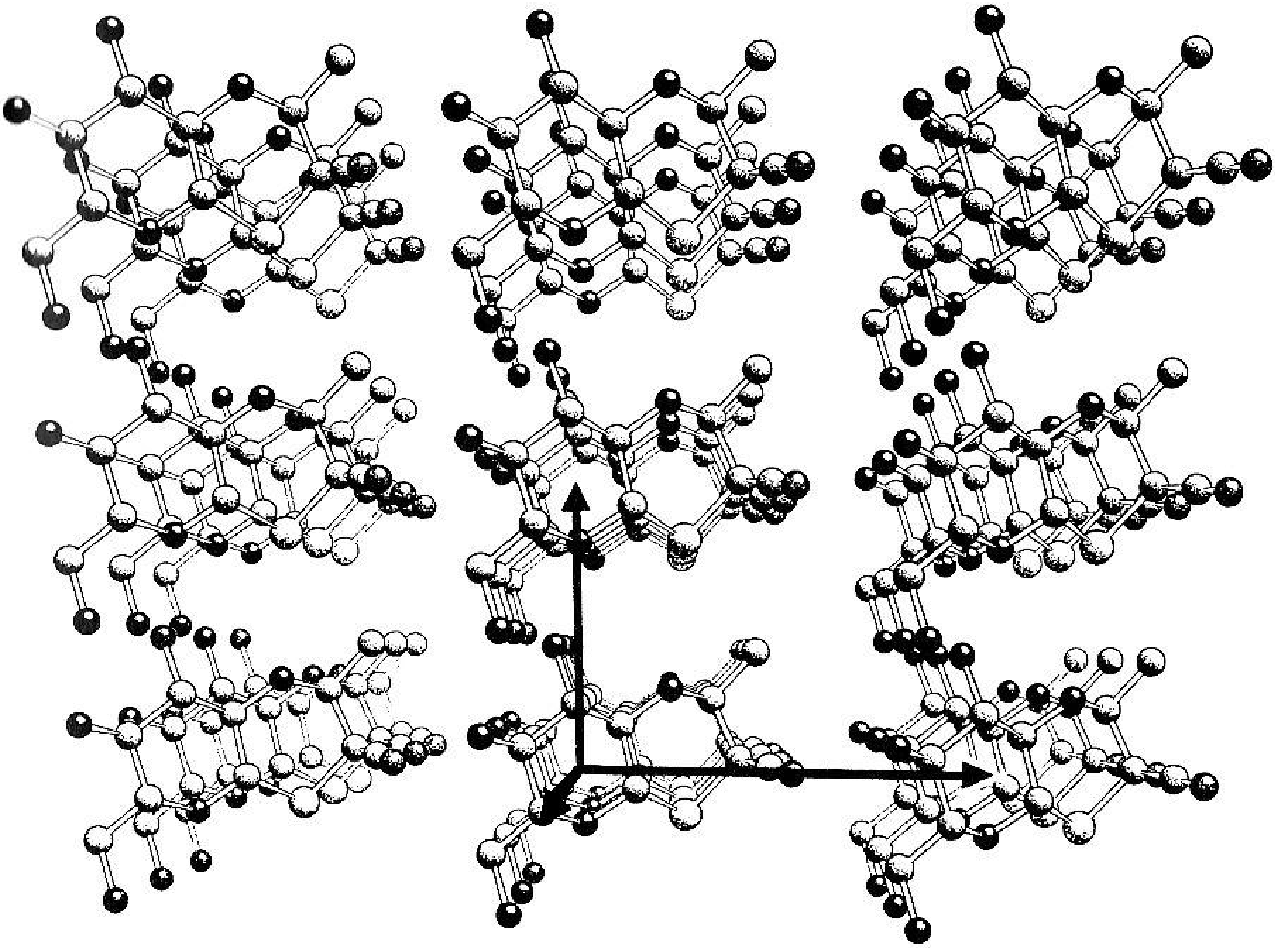
X-ray diffraction on crystals

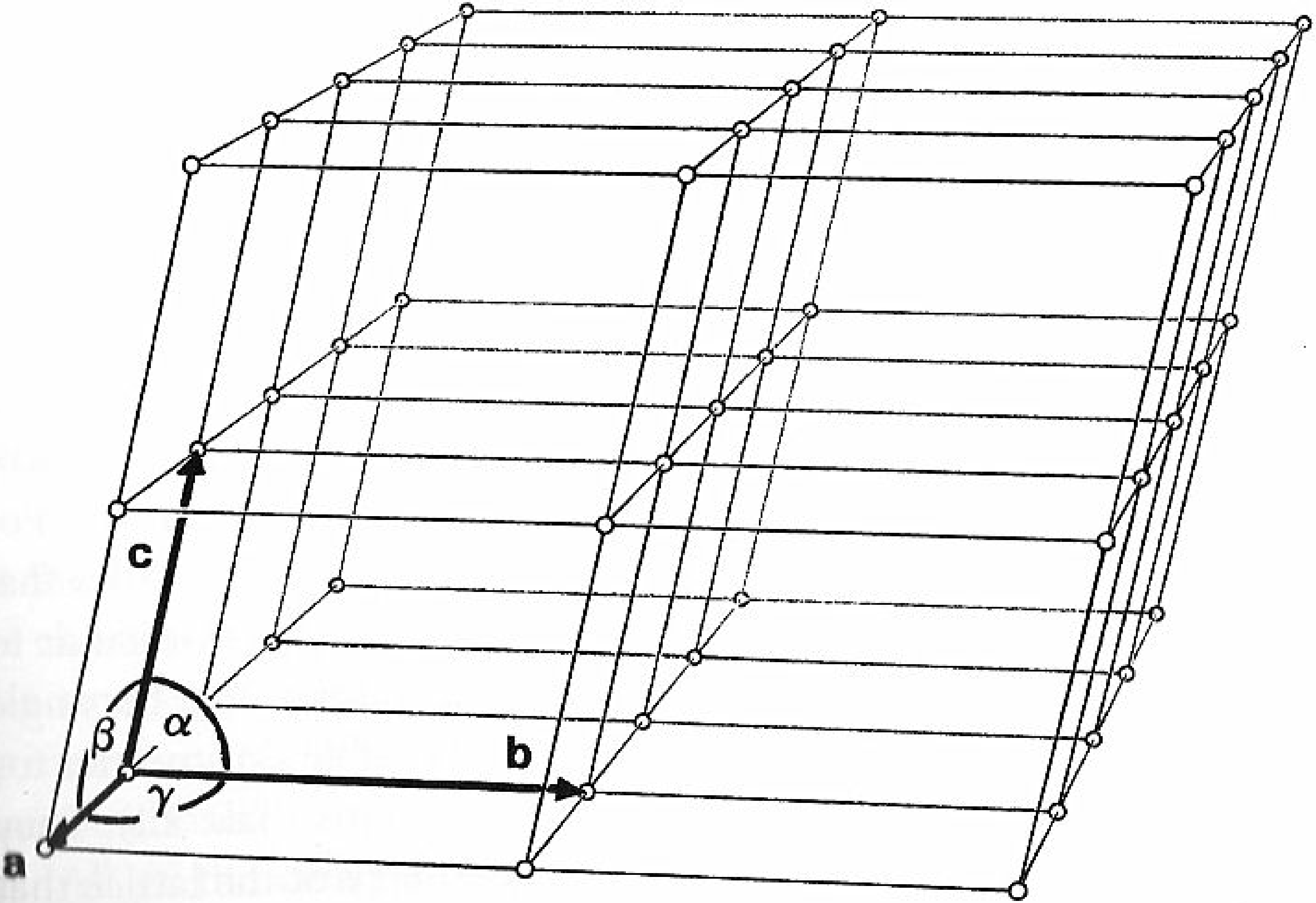
- A monochromatized beam of X-rays diffracts off of atoms in a crystal, giving new diffracted beams



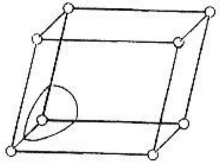
Diffraction experiments

- X-ray
  - Single-crystal
  - powder
- Electron
- Neutron



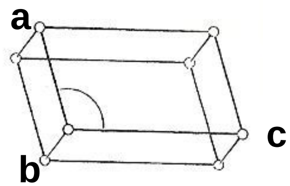

c
α
β
b
γ
a

Bravais Lattices



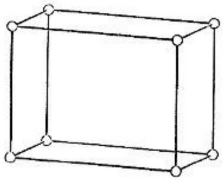
aP

triclinic



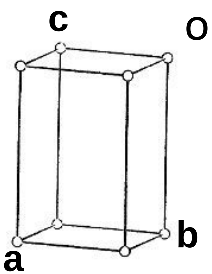
mP

monoclinic



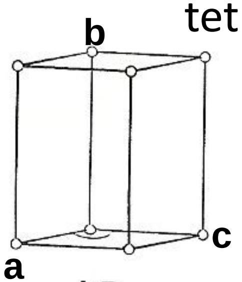
oP

orthorhombic



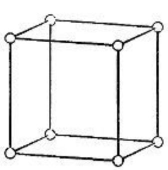
tP

tetragonal



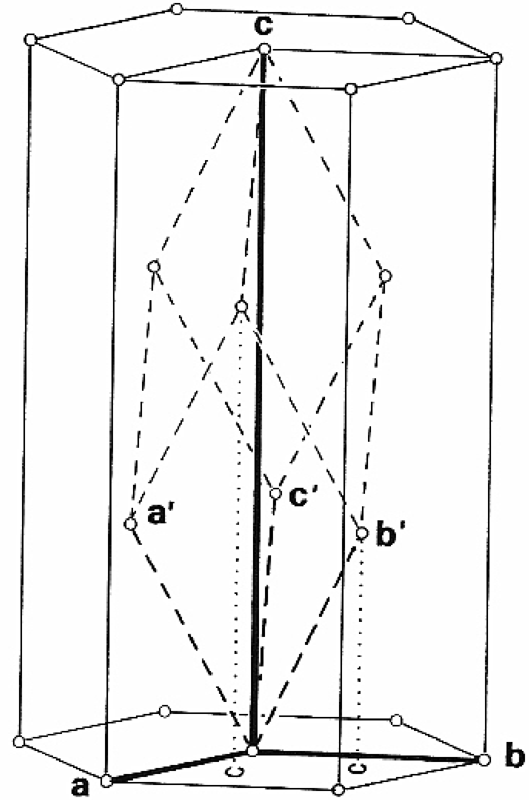
hP

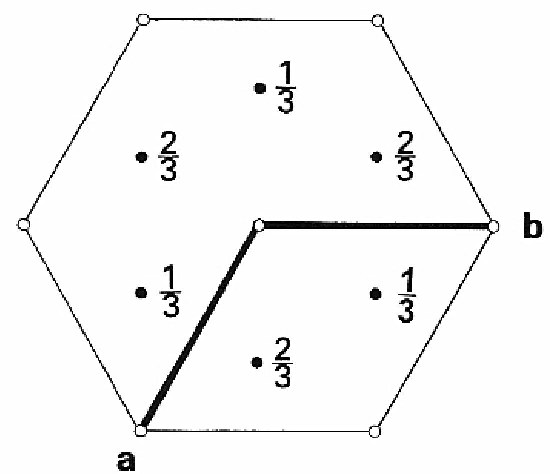
Trigonal/hexagonal



cP

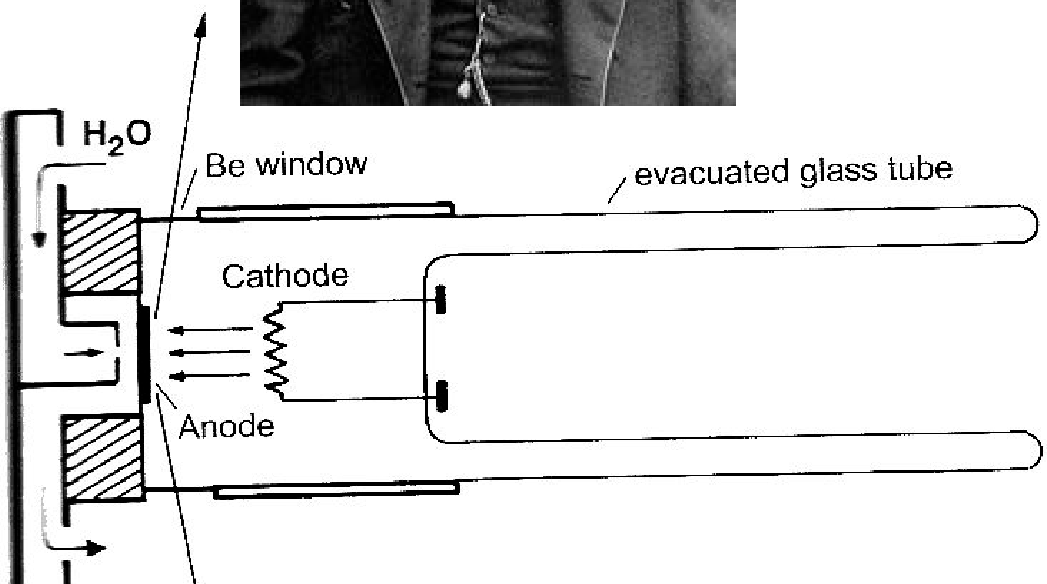
cubic



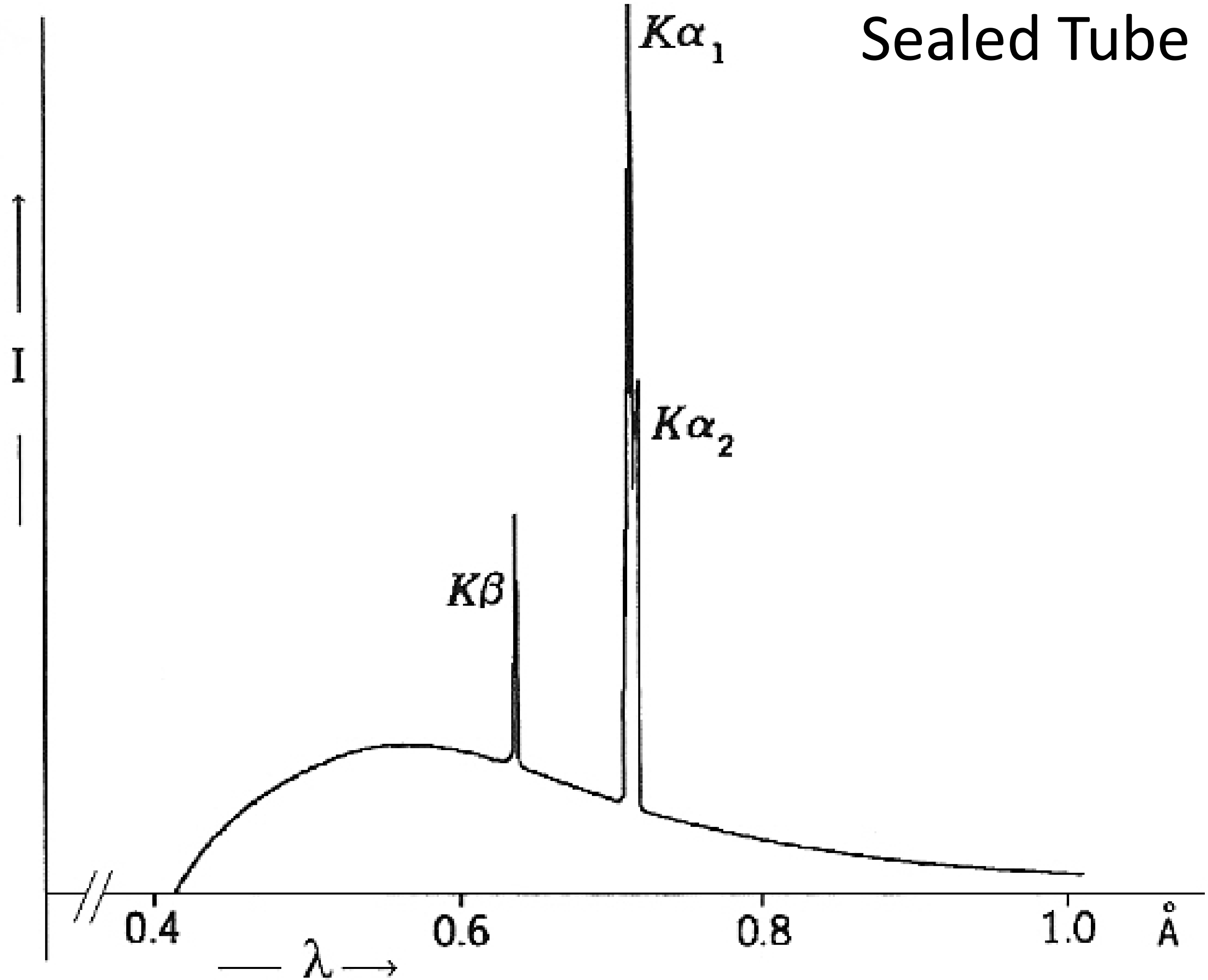


Wilhelm Röntgen

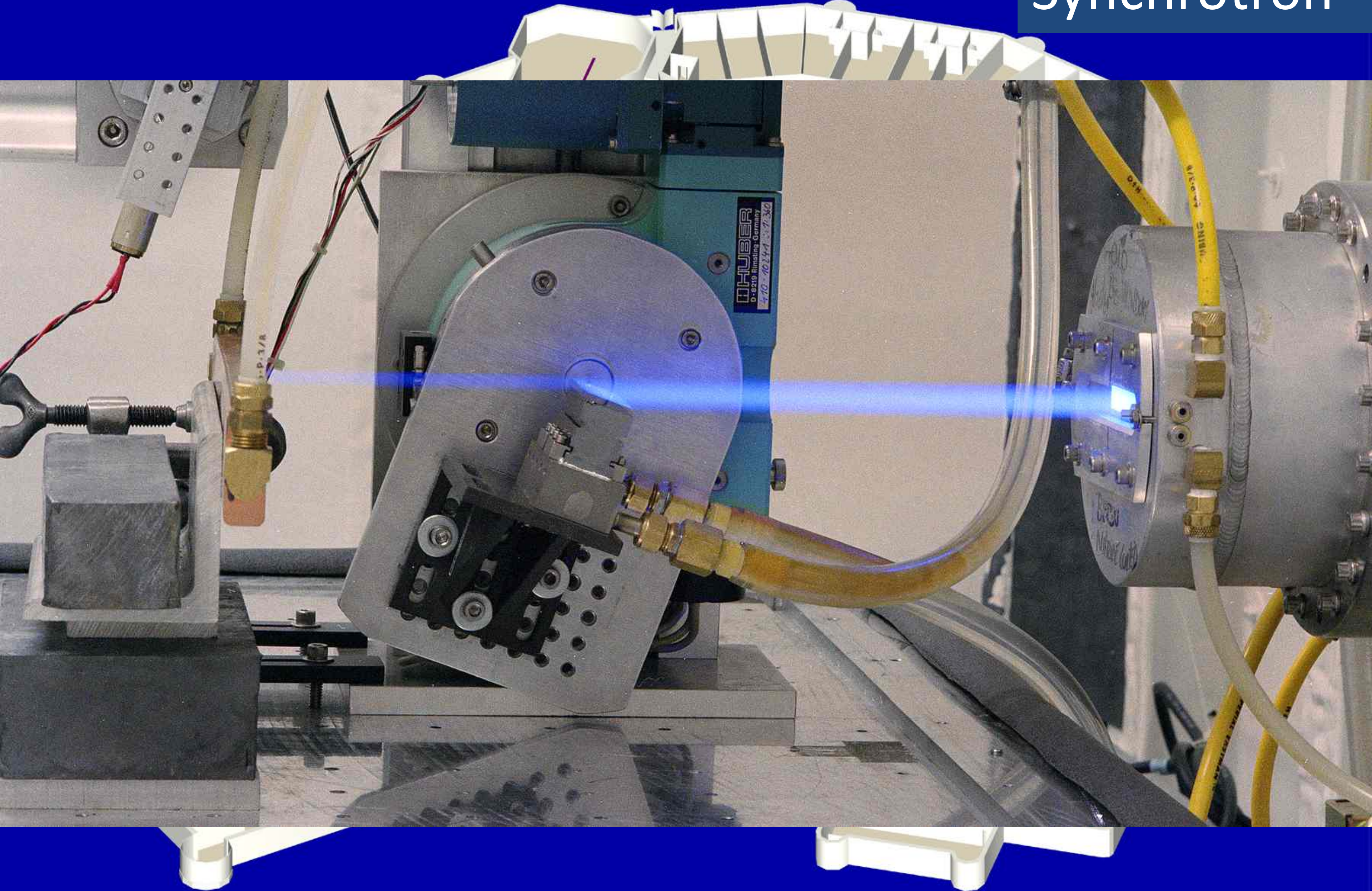
Discoverer of X-rays



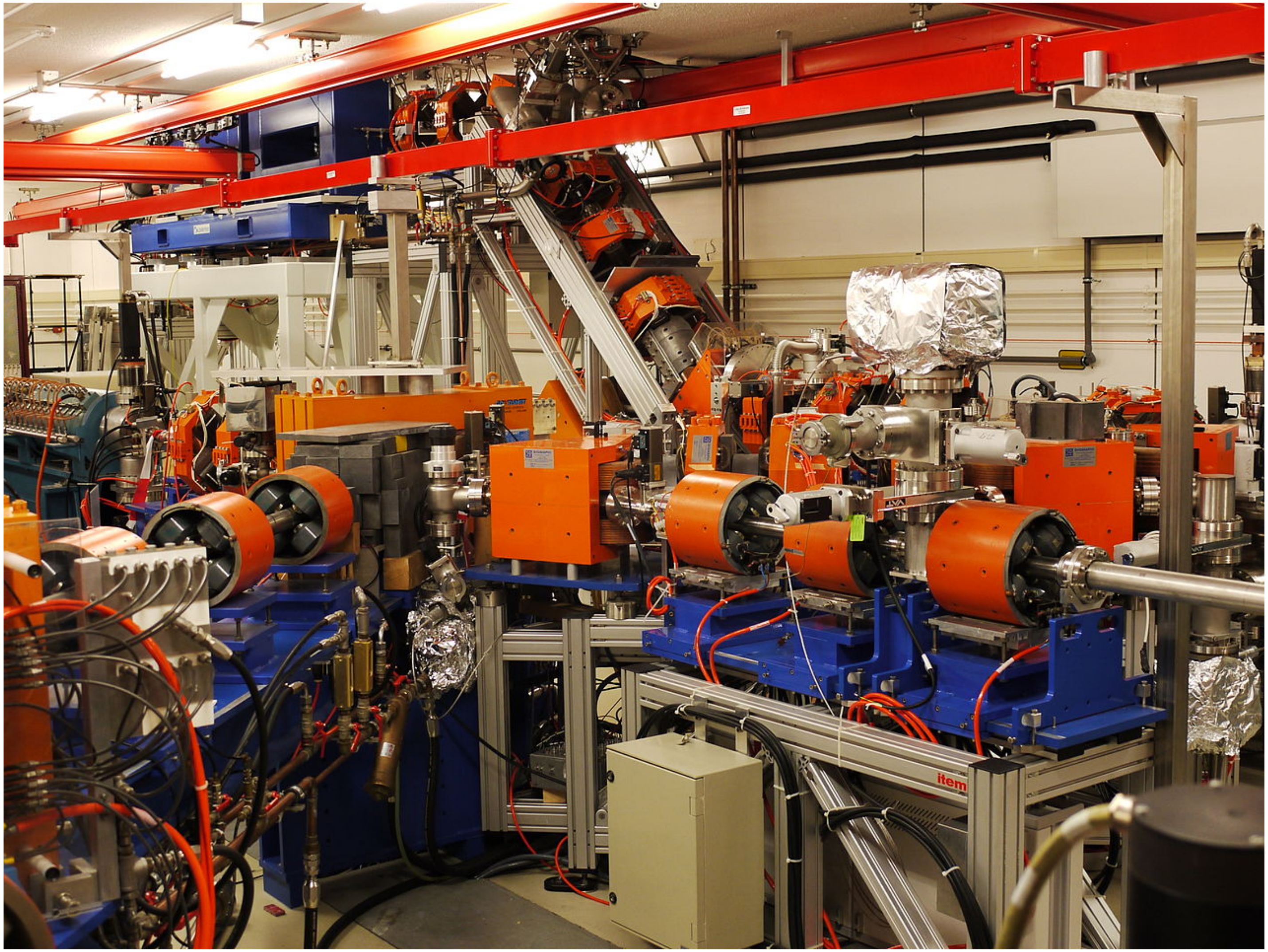
Sealed Tube



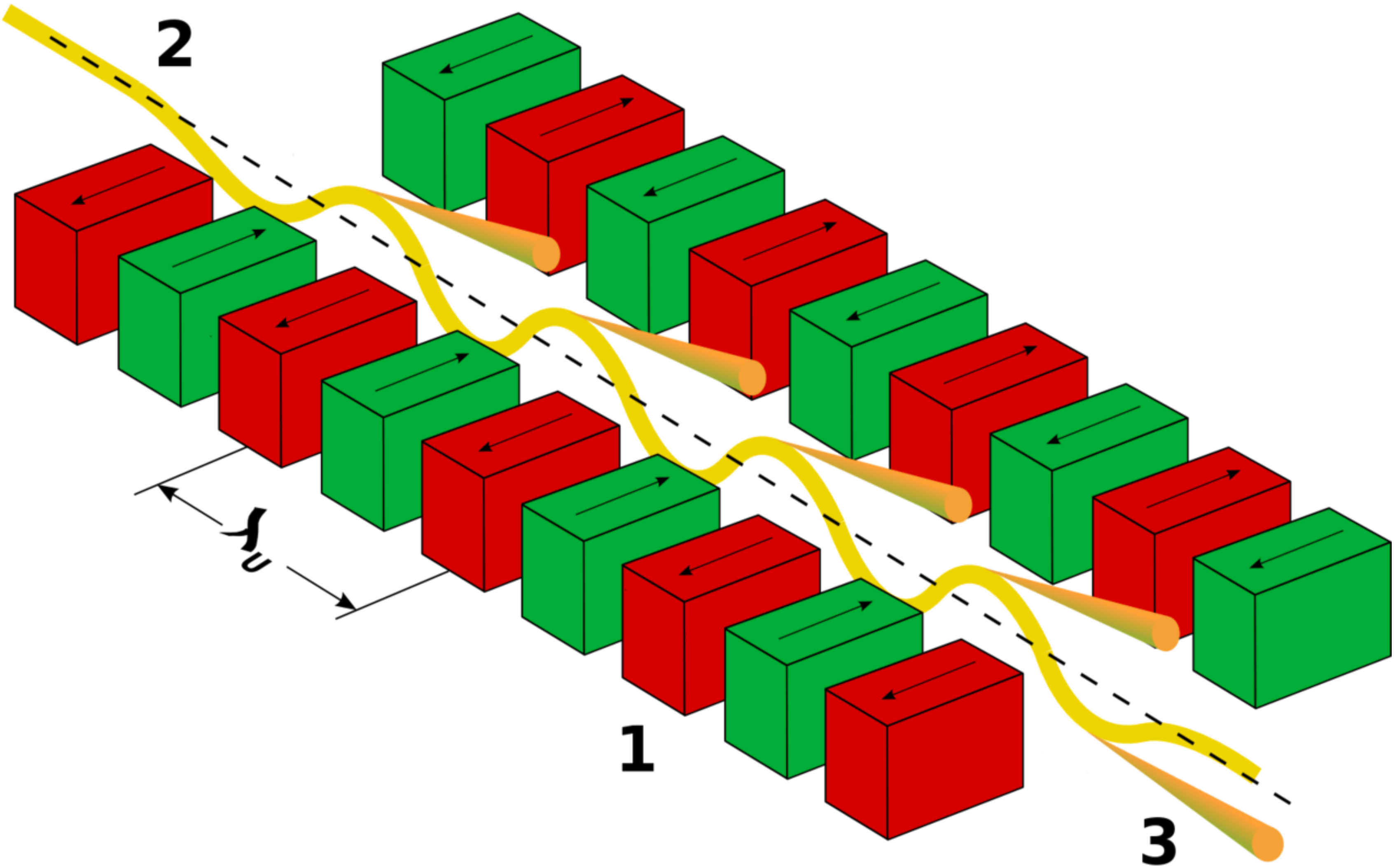
Synchrotron



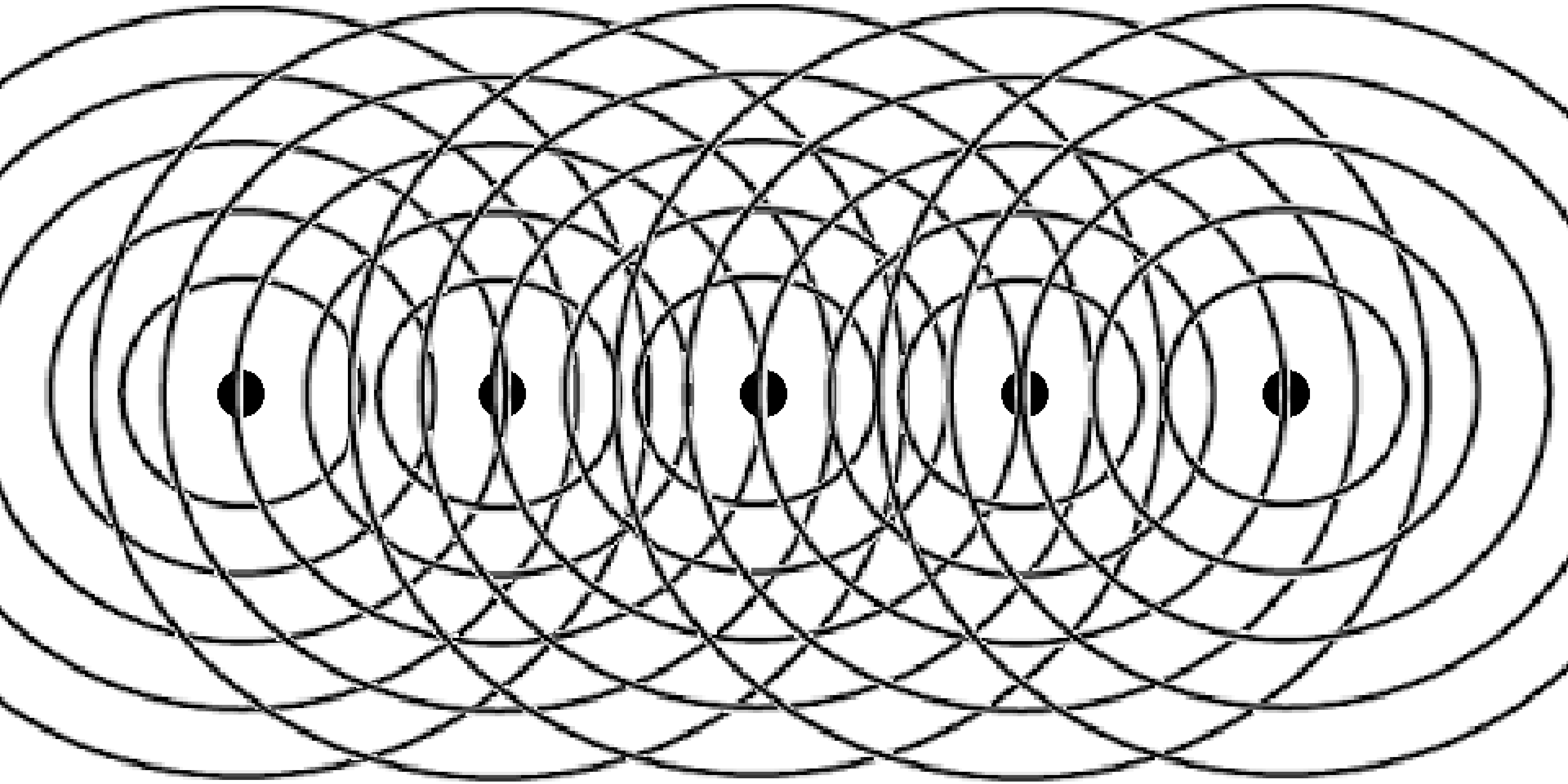
X-ray Free Electron Laser (XFEL)



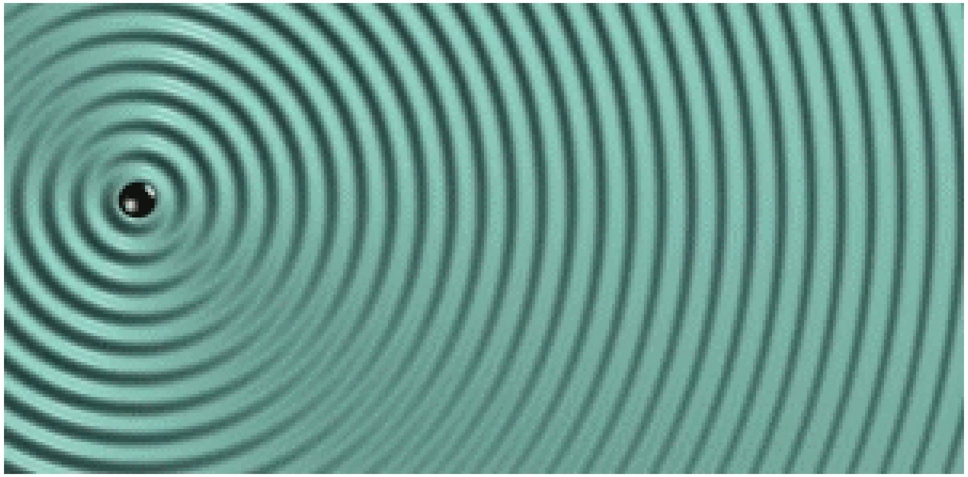
Electrons Oscilate as they travel through alternating magnetic fields.

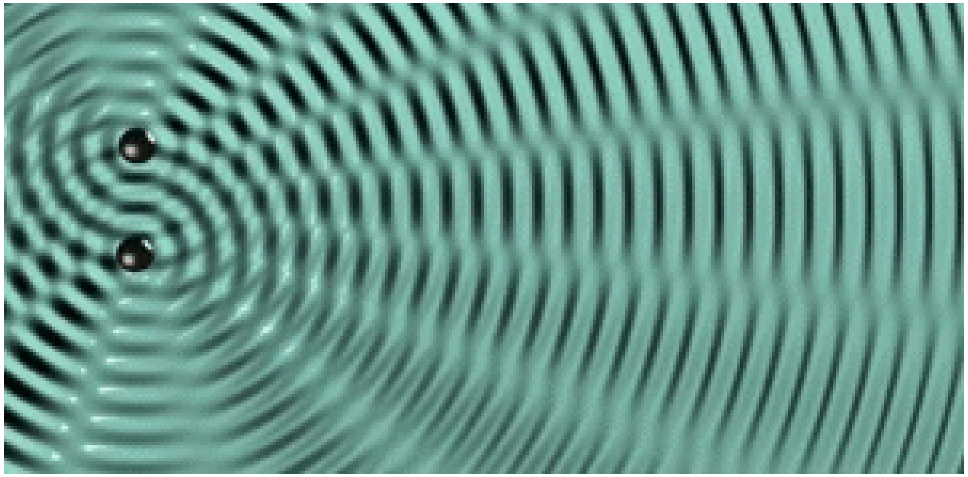


Scattering

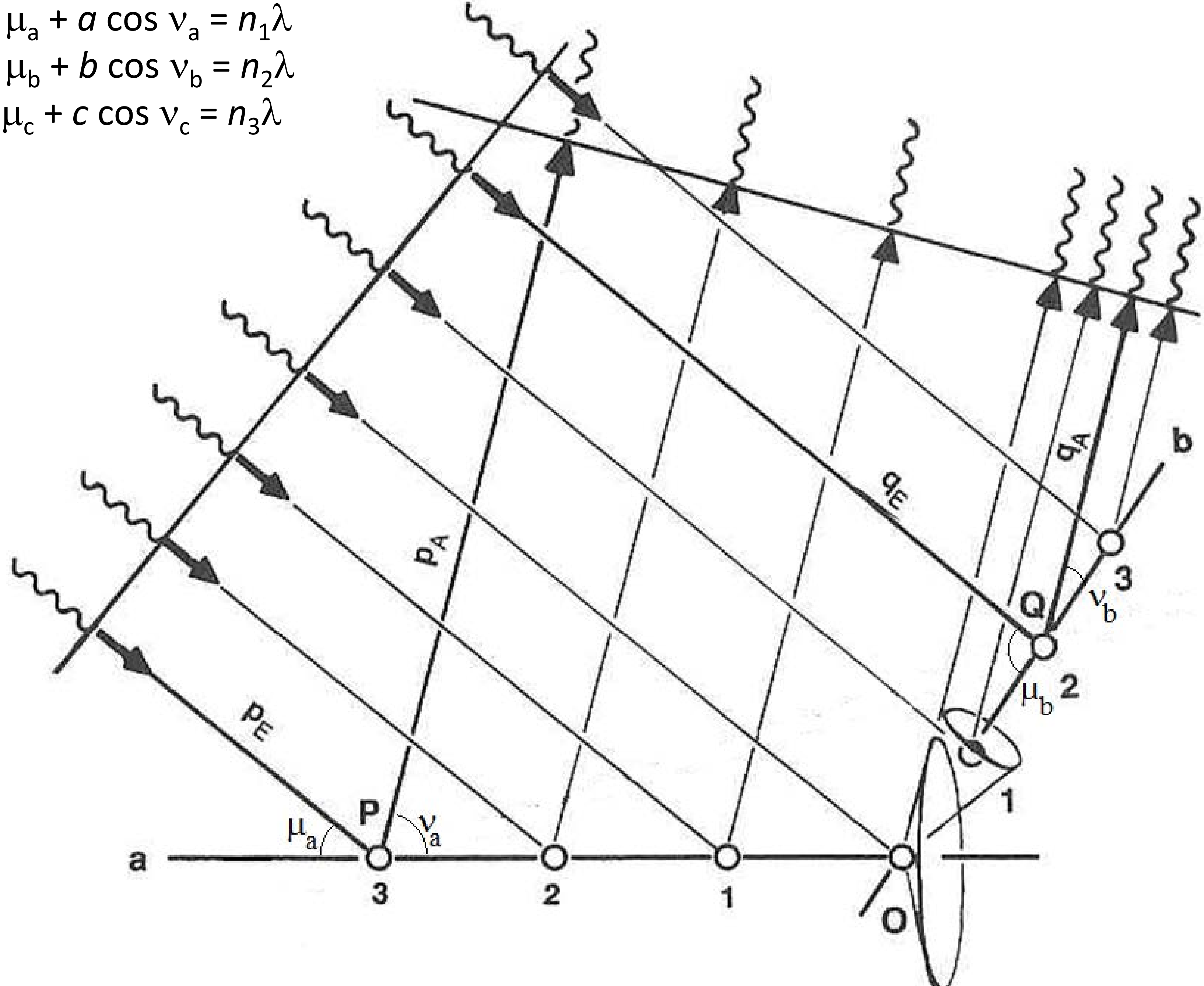


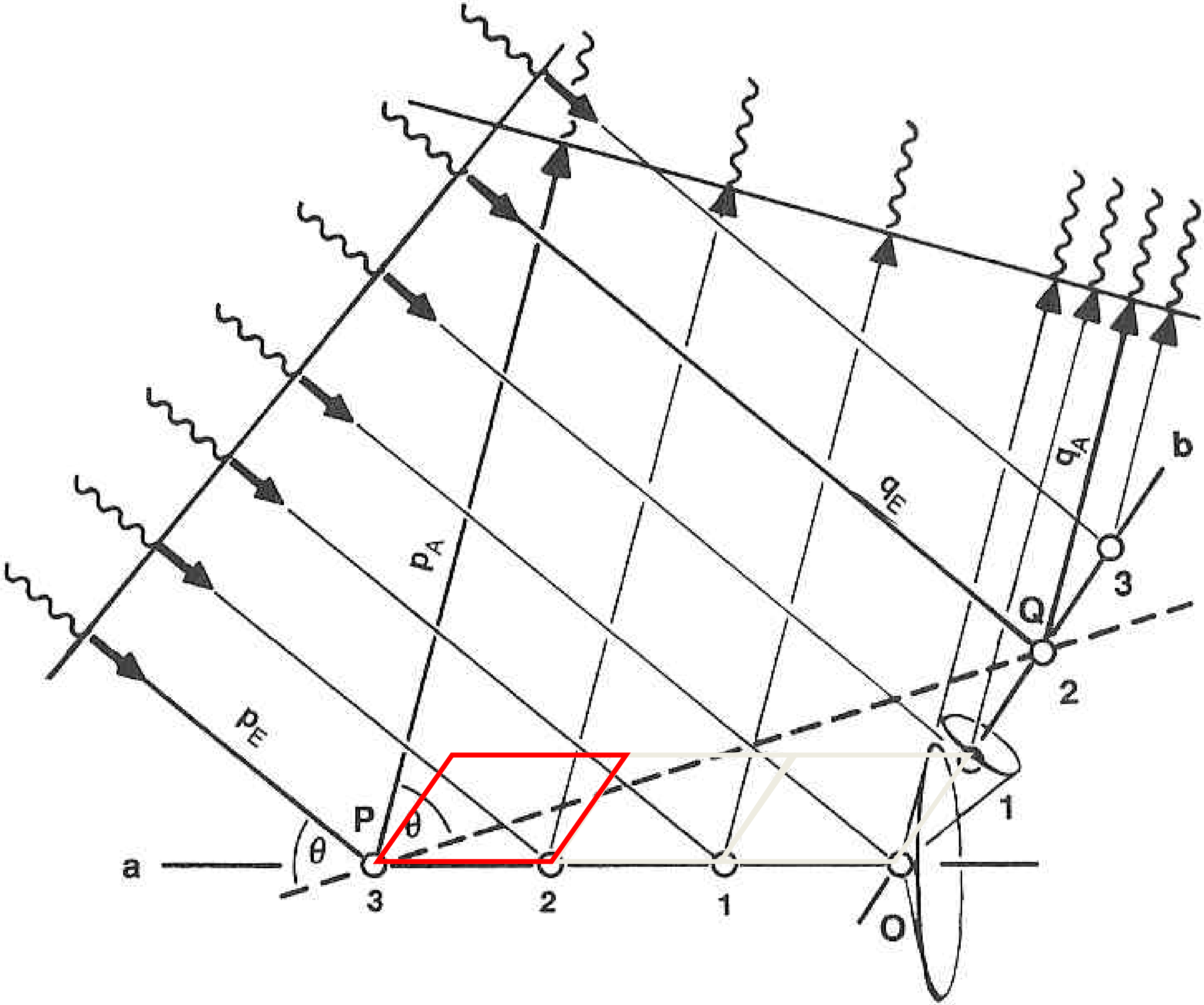
Single vs. Multi-atom scattering





$a \cos \mu_a + a \cos \nu_a = n_1\lambda$
$b \cos \mu_b + b \cos \nu_b = n_2\lambda$
$c \cos \mu_c + c \cos \nu_c = n_3\lambda$



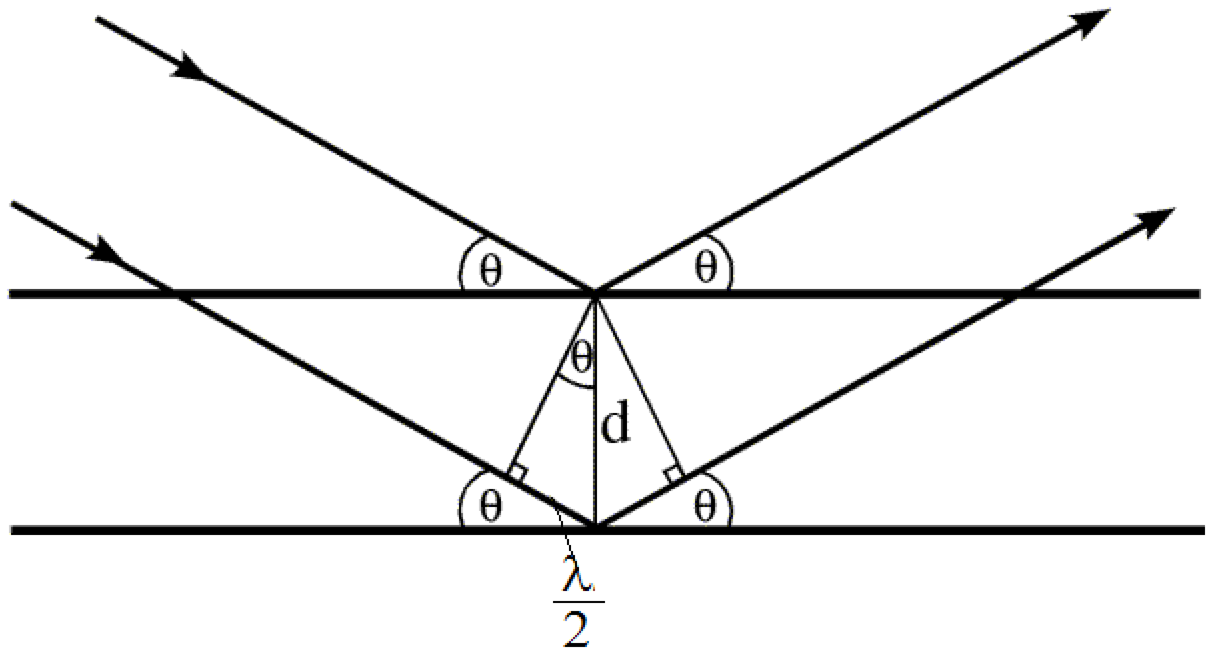


p_A
p_E
q_E
q_A
P
Q
O
a
b
θ
θ
3
2
1
1
2
3

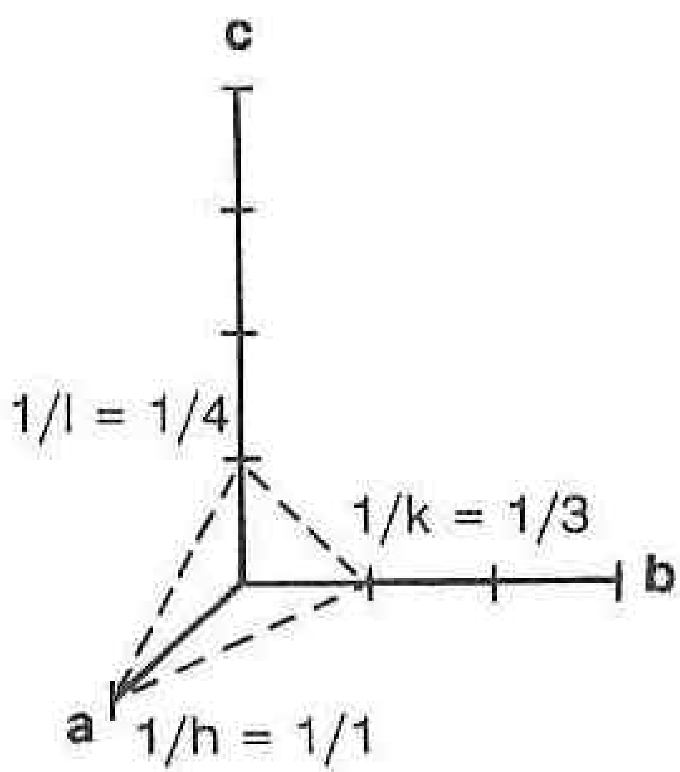
Bragg equation

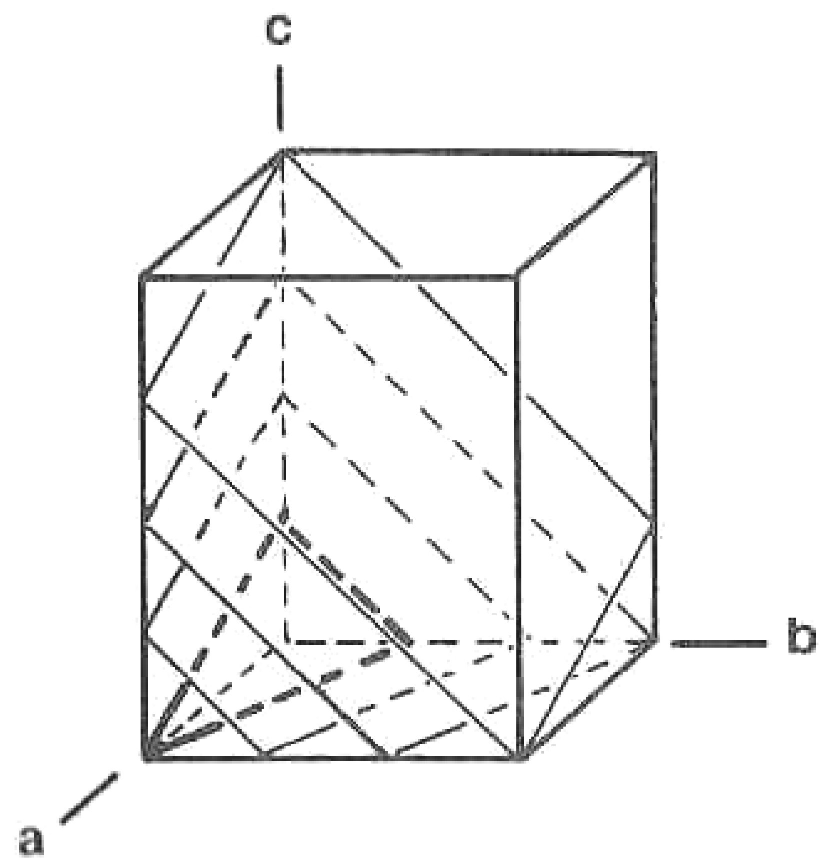
$\sin\theta = n\lambda/2d$

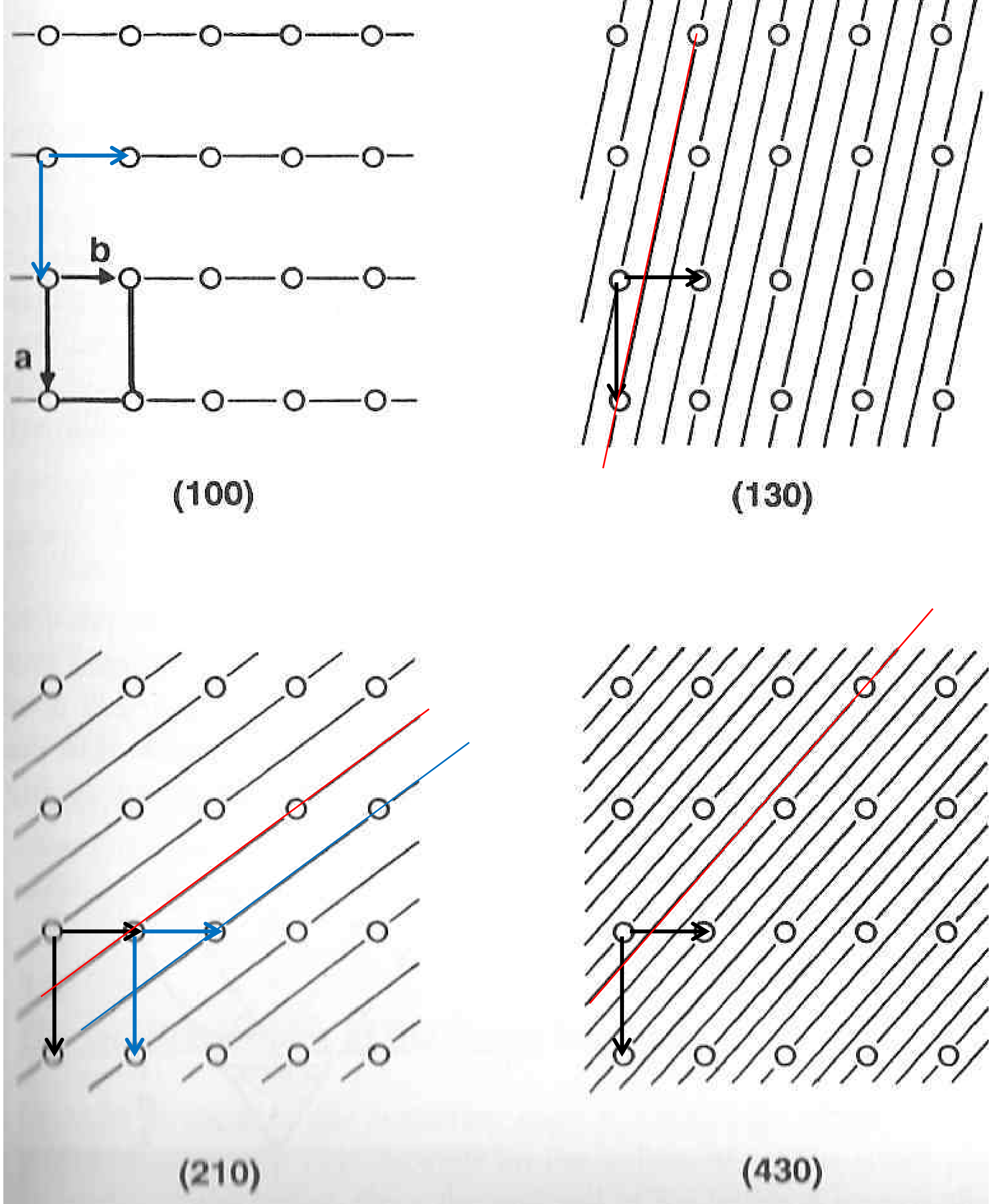
$2d\sin\theta = n\lambda$



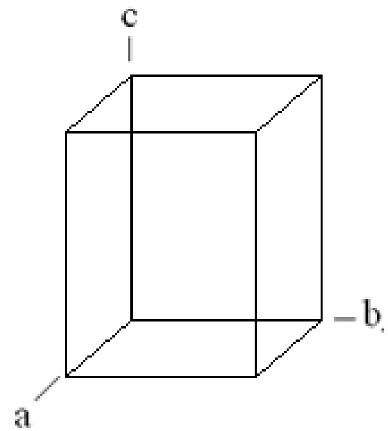
hkl = 134

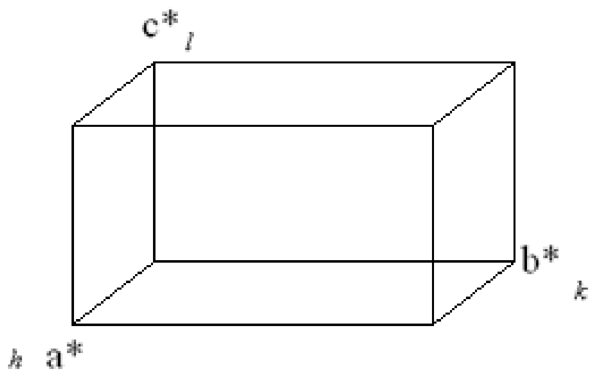





b
a
(100)
(130)
(210)
(430)

Reciprocal Lattice

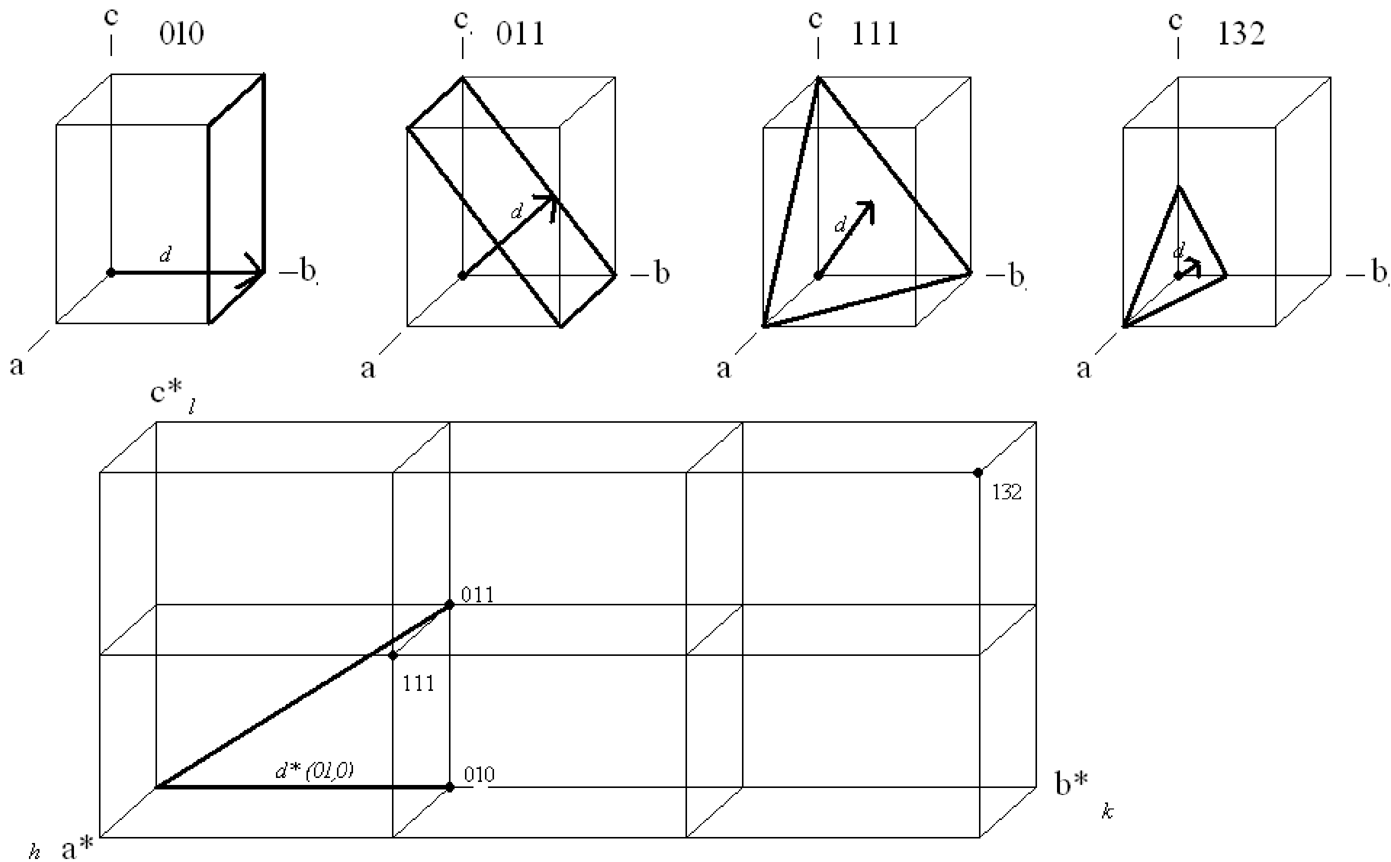




$$a^* = \frac{\mathbf{b} \times \mathbf{c}}{V} \quad b^* = \frac{\mathbf{a} \times \mathbf{c}}{V} \quad c^* = \frac{\mathbf{a} \times \mathbf{b}}{V}$$

$a^* = 1/a$, $b^* = 1/b$, $c^* = 1/c$

Reciprocal Lattice

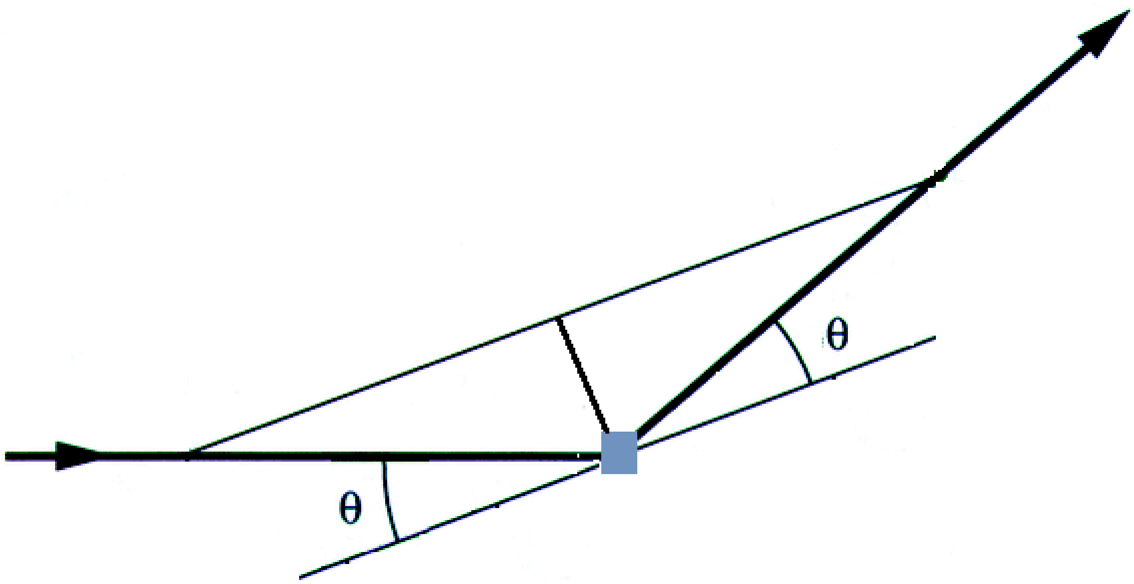


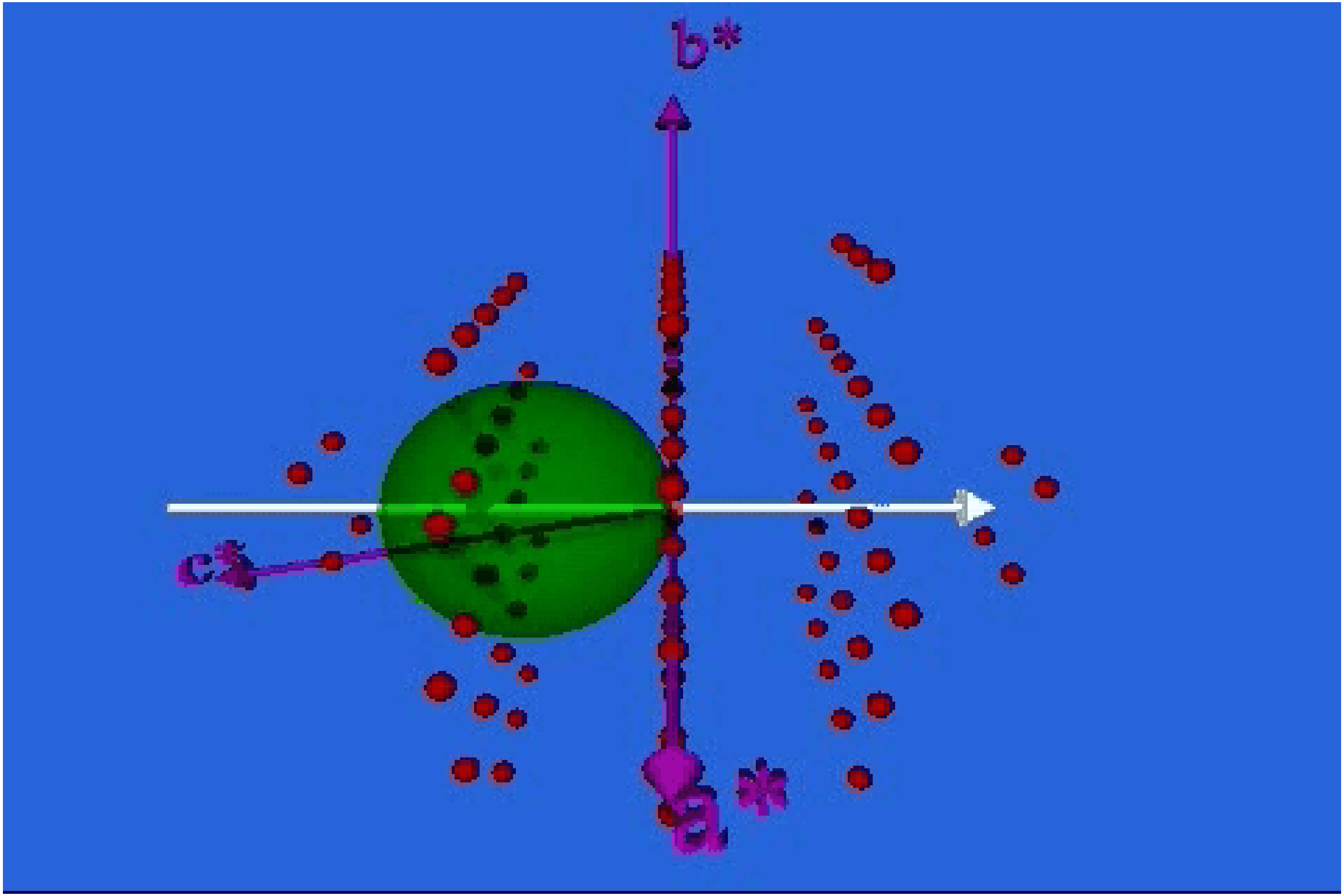
- d* = 1/d, a* = 1/a, b* = 1/b, c* = 1/c
- $d^{*2} = h^2a^{*2} + k^2b^{*2} + l^{*2}c^2$
- $r^2 \quad = x^2 \quad + \; y^2 \quad + z^2$

Ewald Sphere and the Reciprocal Lattice

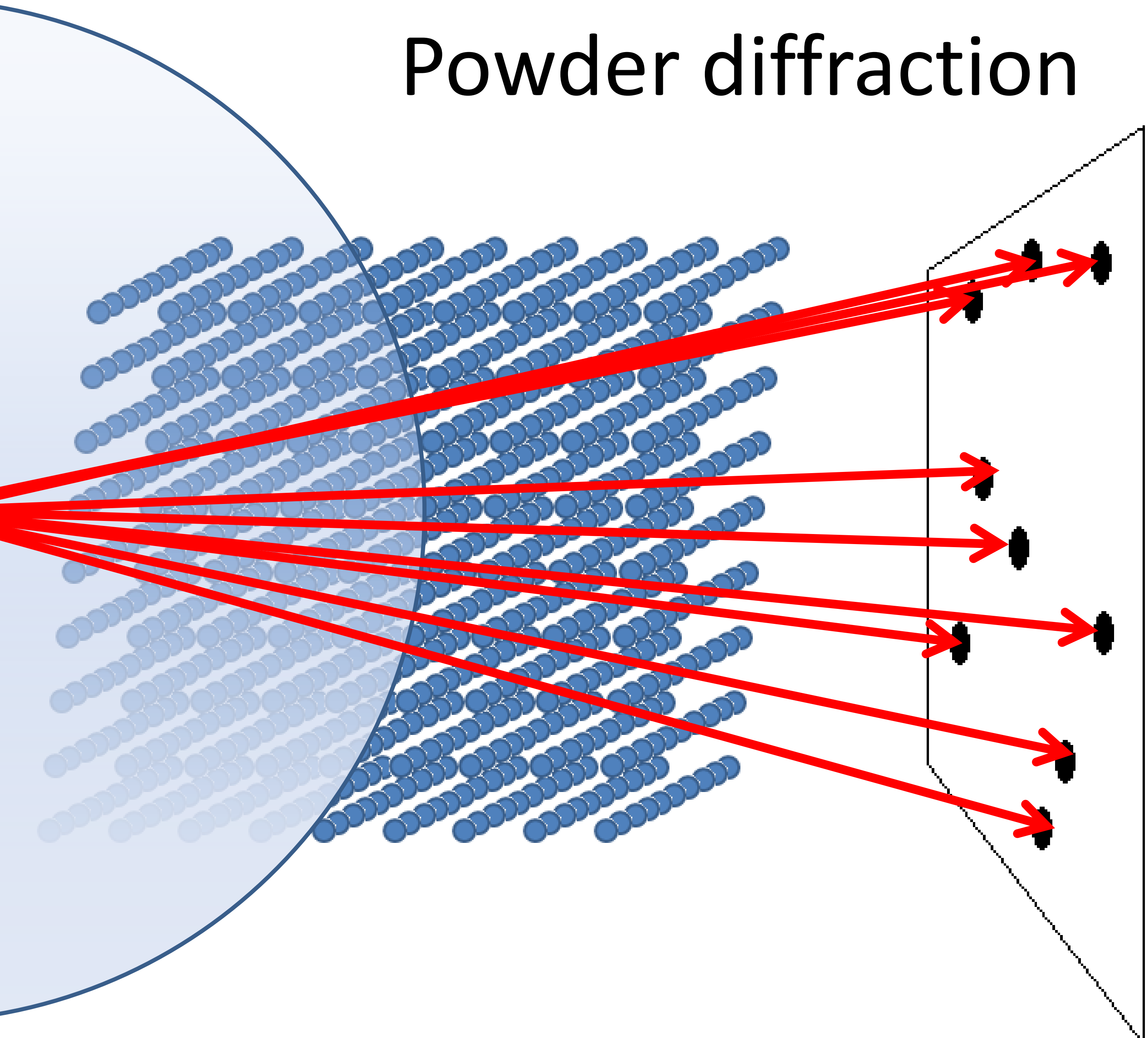
$\sin\theta = \lambda/2d$

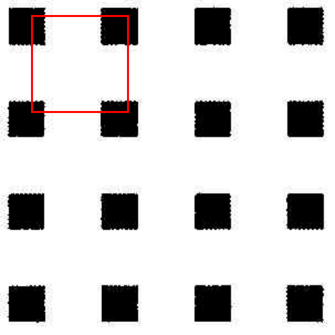
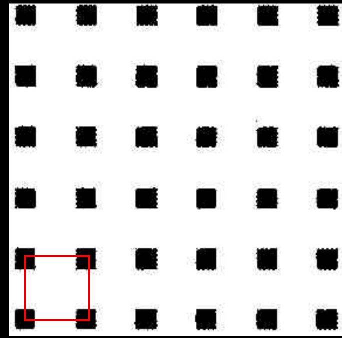
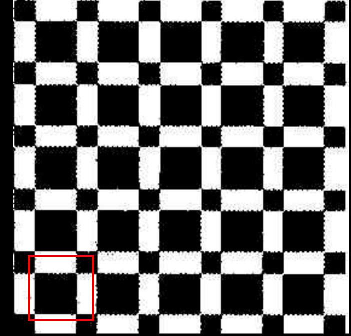
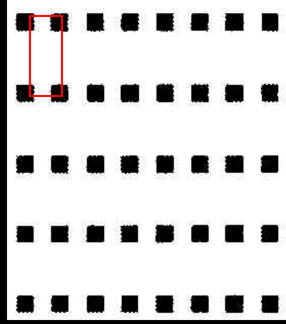
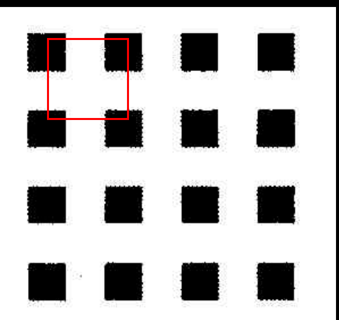
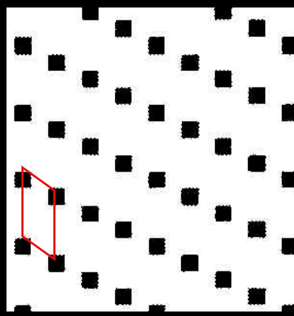
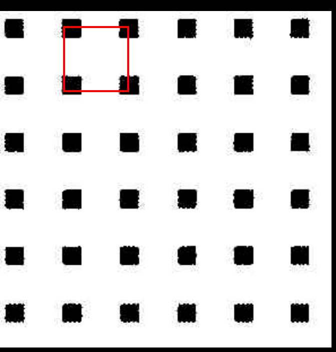
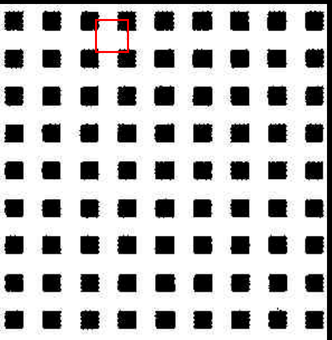
$2d\sin\theta = \lambda$



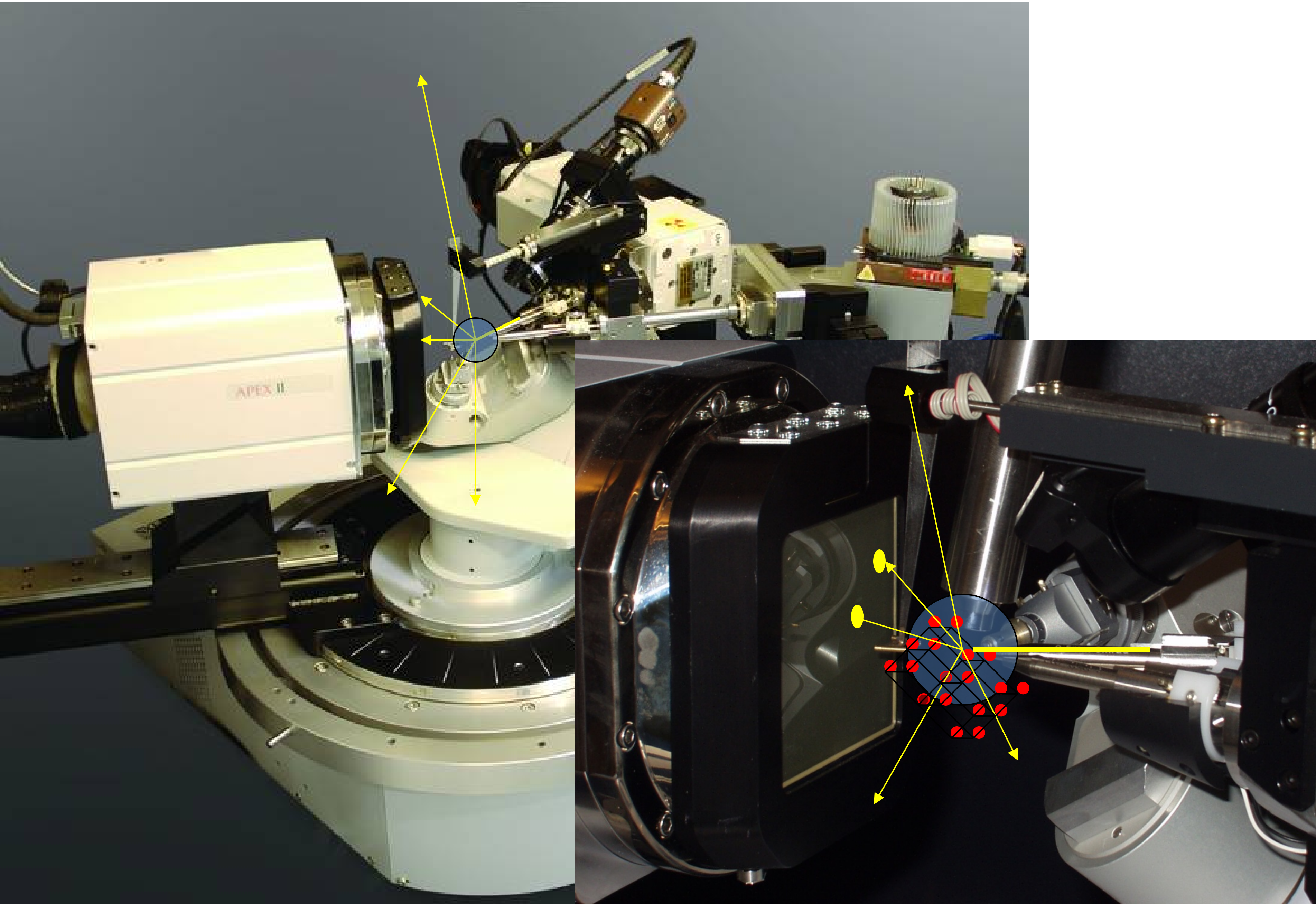

b*
c*
a*

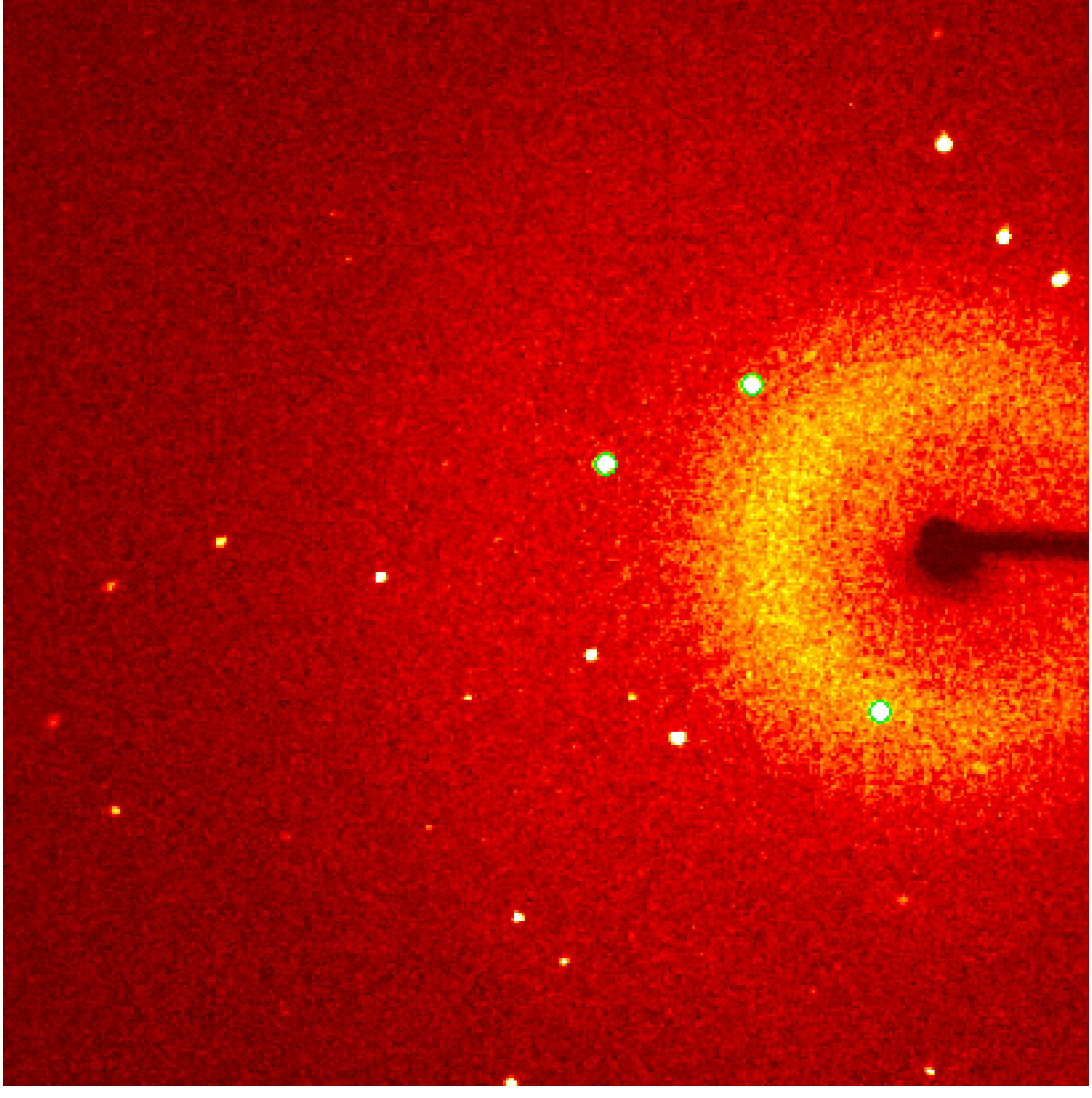
Powder diffraction



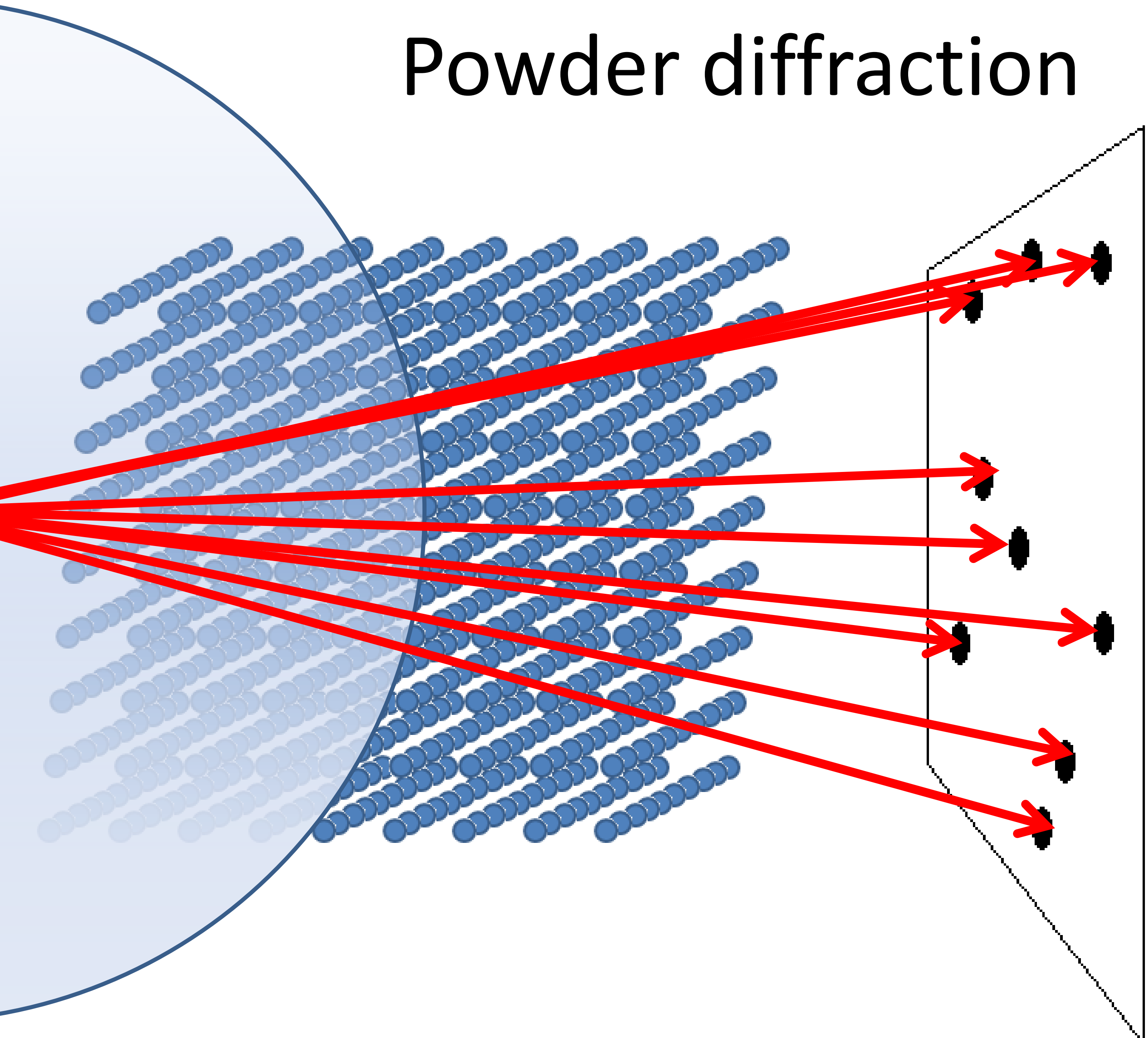









Movable CCD Detector

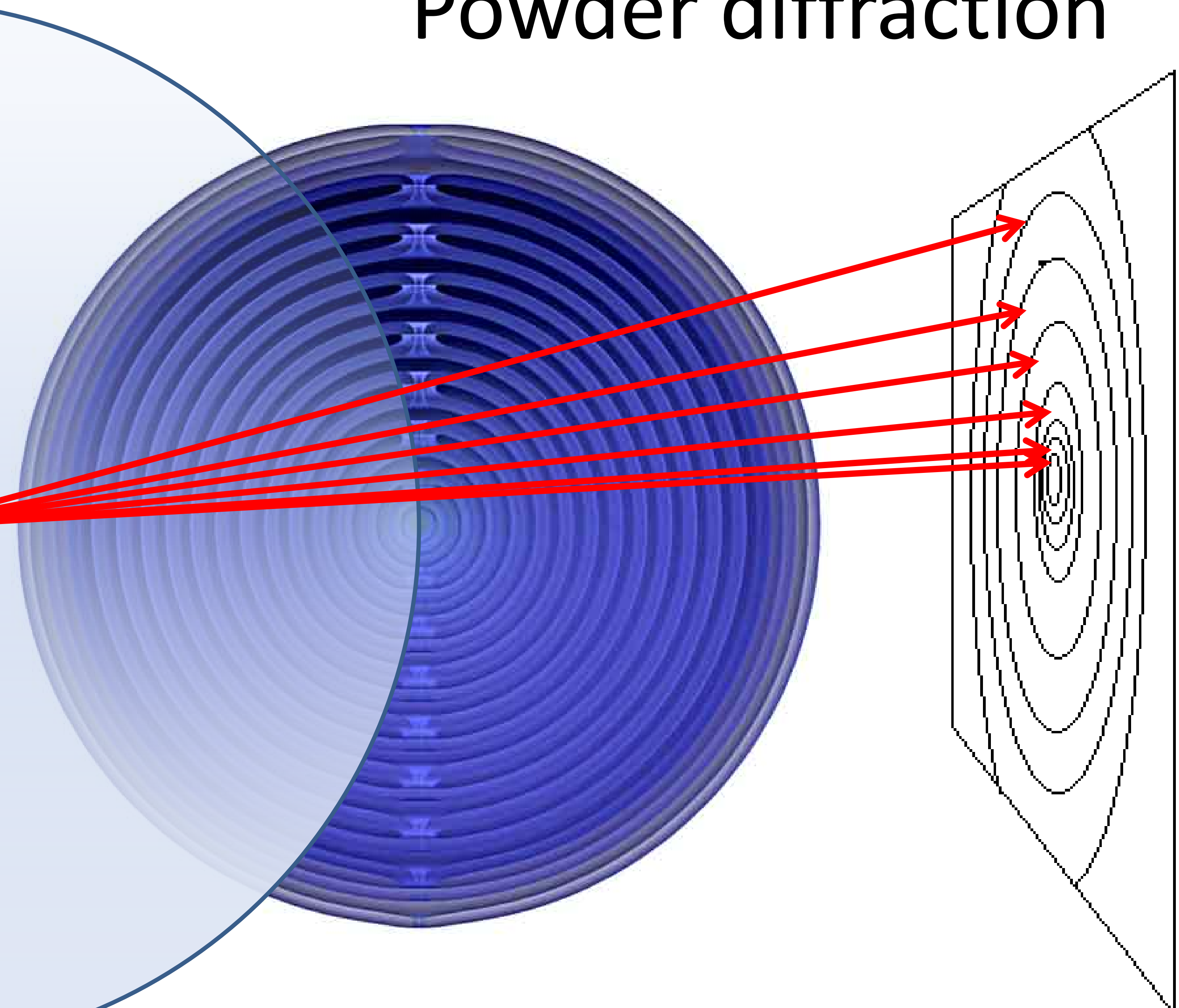




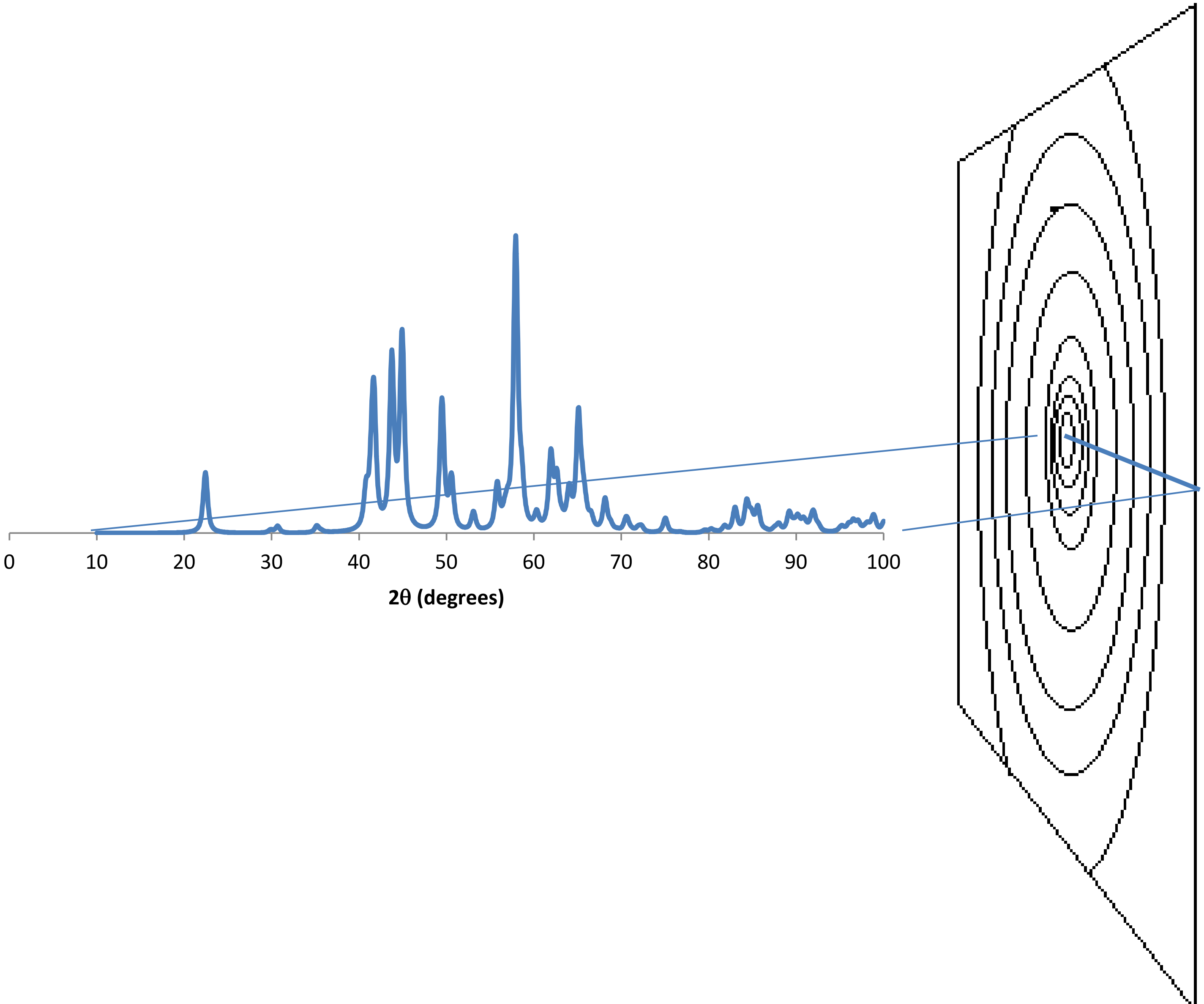
Powder diffraction



Powder diffraction



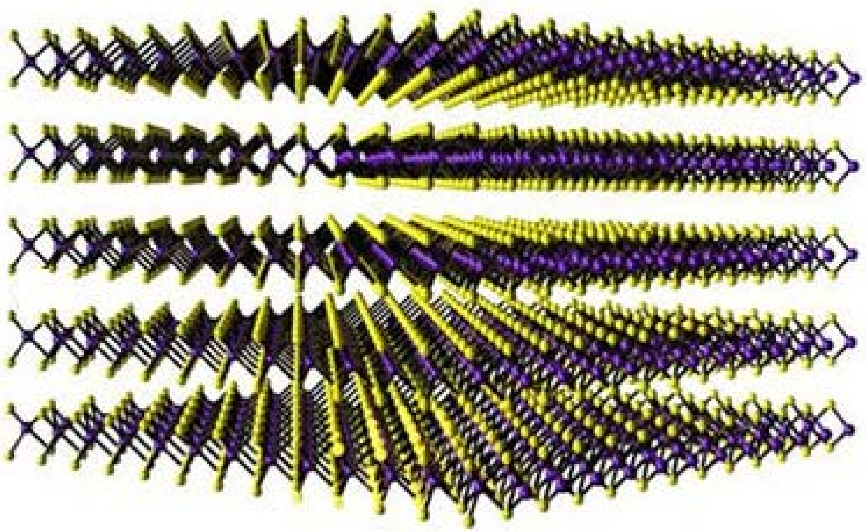
Powder diffraction



Solving the crystal structure:

- Relationship between the intensity weighted reciprocal lattice and the atomistic structure is a fourier transform

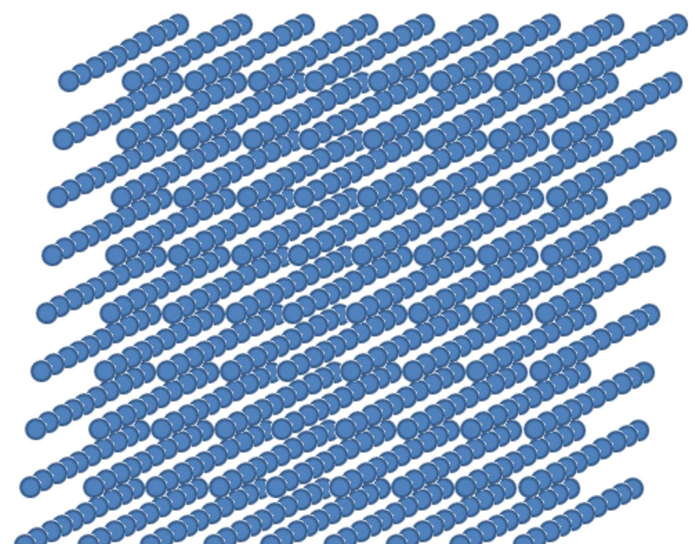
$$F_{hkl} = \sum f_i \, e^{i2\pi(hxi + kyi + lzi)}$$



X, Y, Z

FT

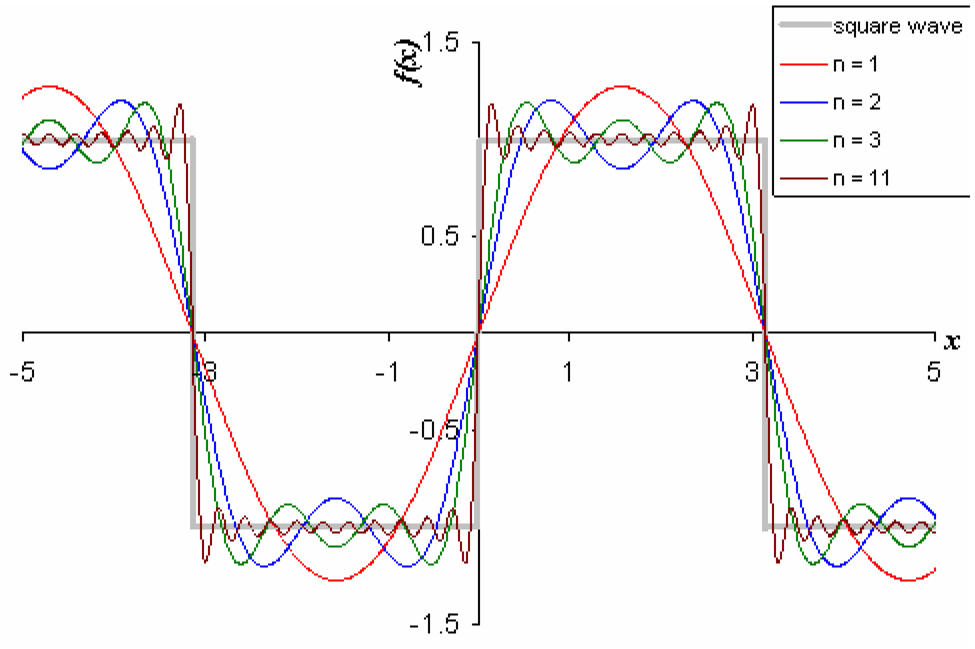
FS???

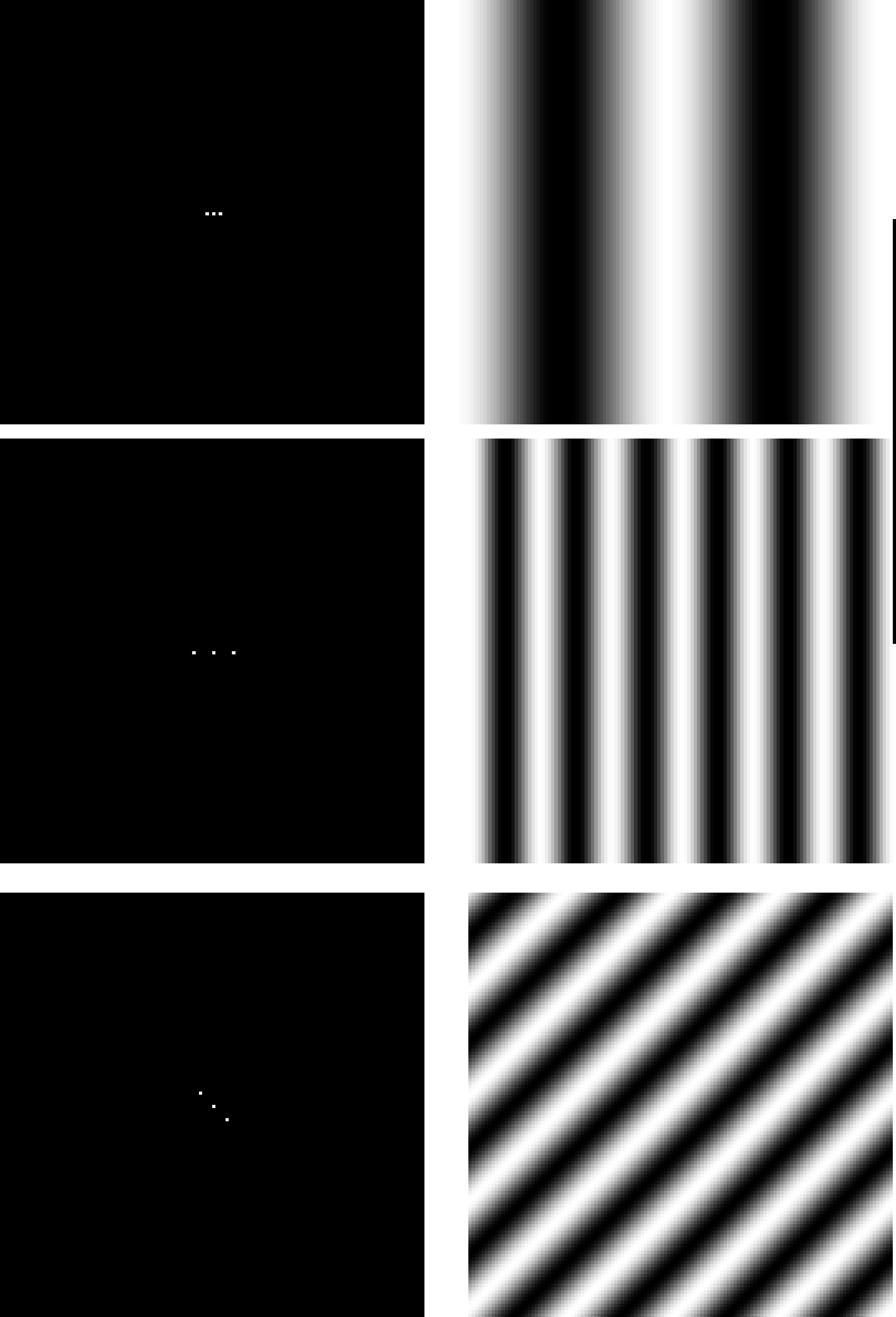


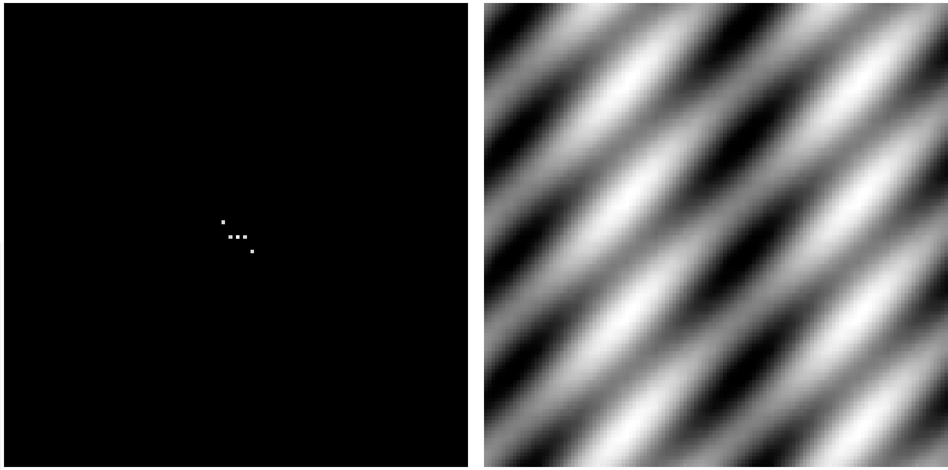
F_{hkl}

Fourier synthesis

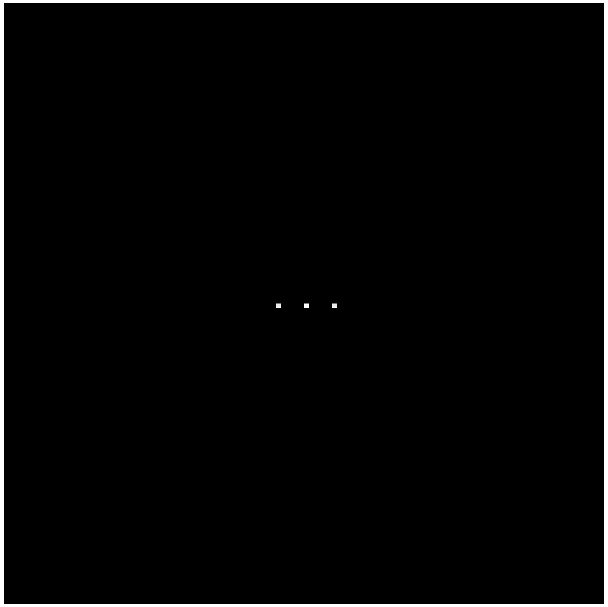
- You can construct any periodic function by the addition of sin waves, properly weighted, and properly phased.

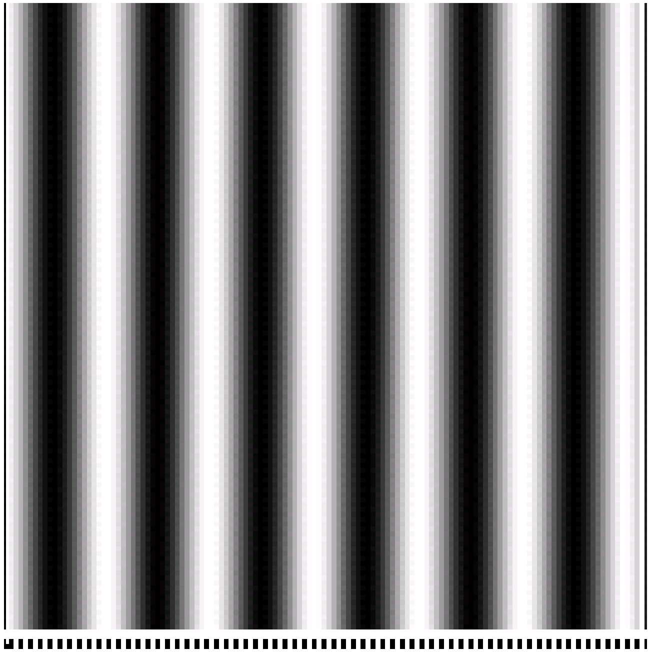


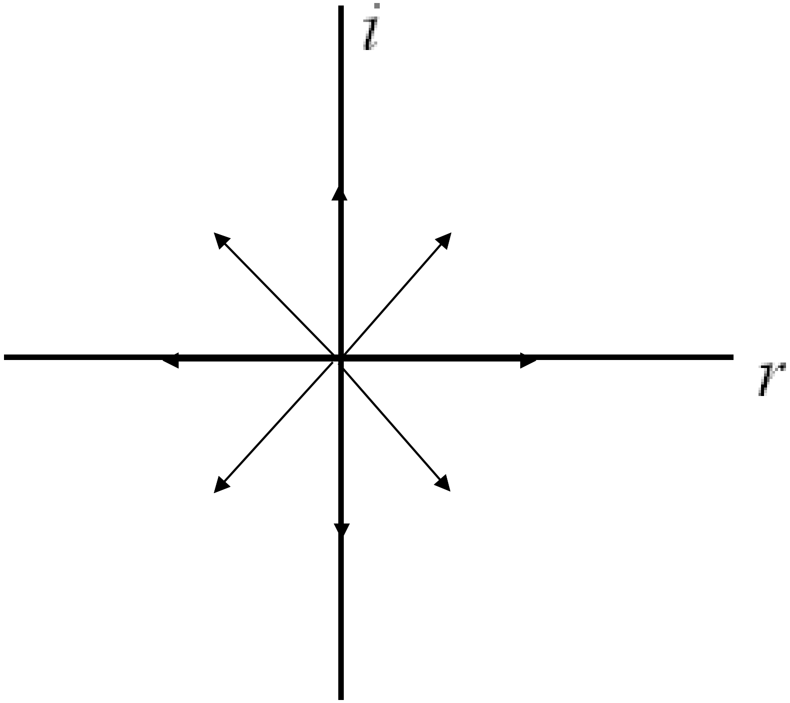




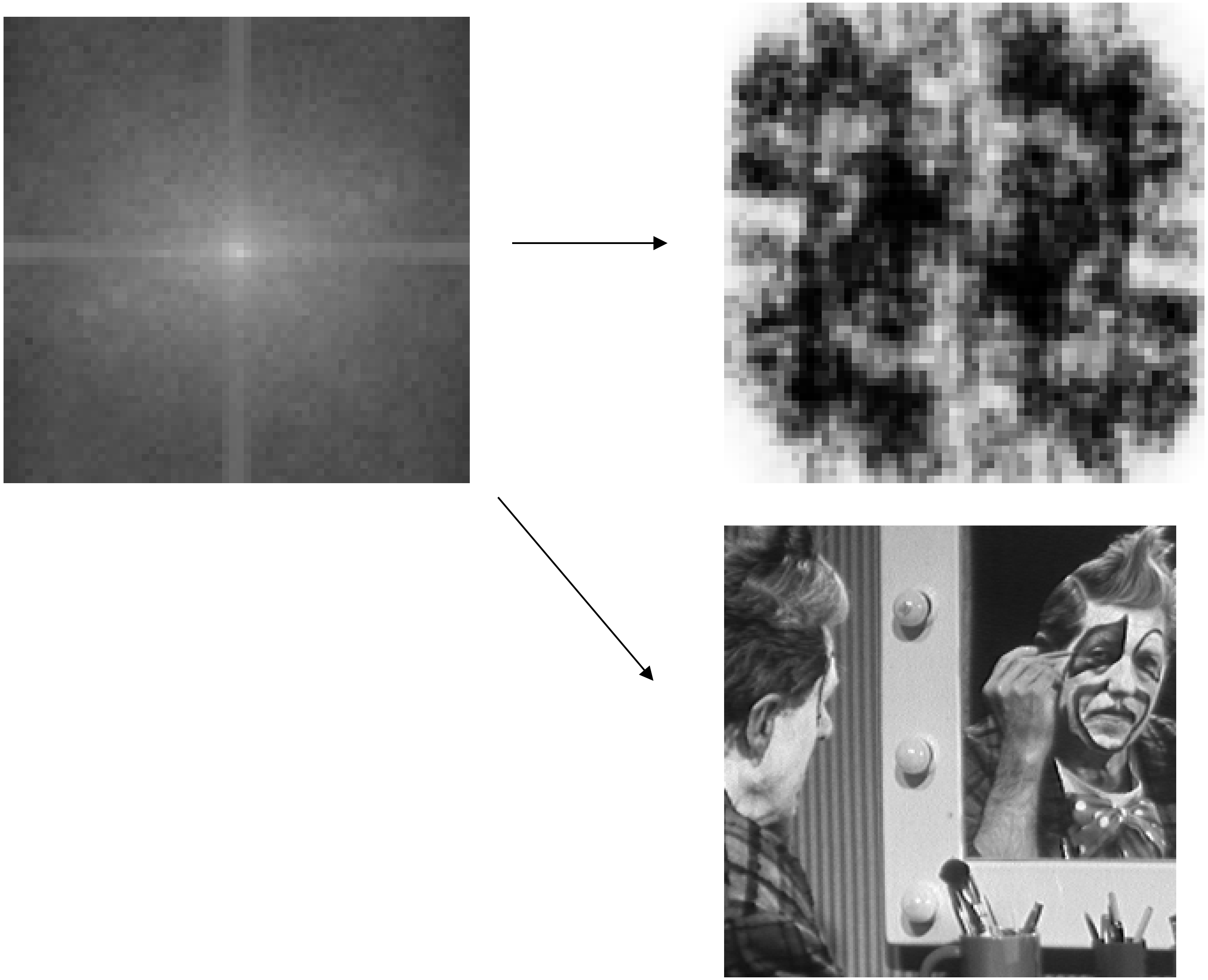
http://cns-alumni.bu.edu/~slehar/fourier/fourier.html



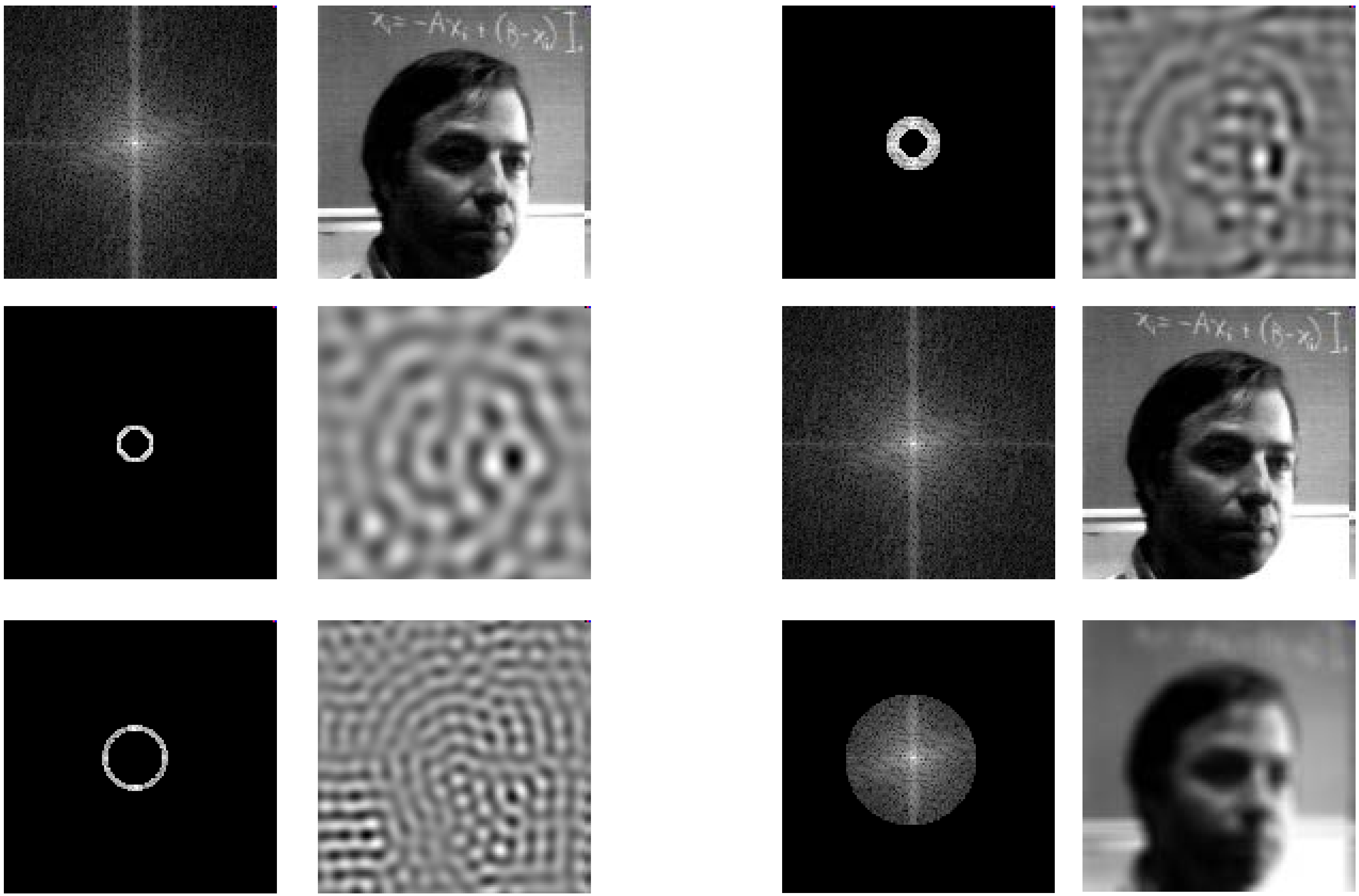



i
r

http://homepages.inf.ed.ac.uk/rbf/HIPR2/fourier.htm



Fourier synthesis of “this guy”



http://cns-alumni.bu.edu/~slehar/fourier/fourier.html

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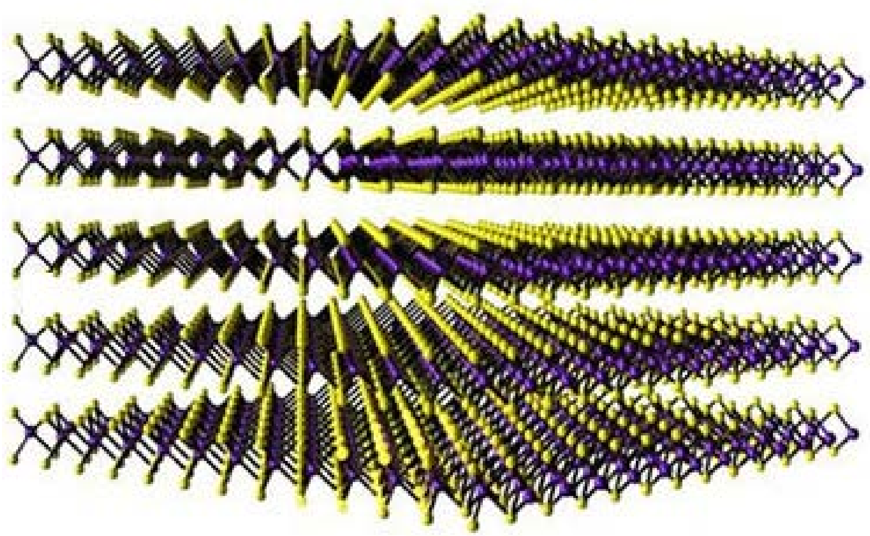
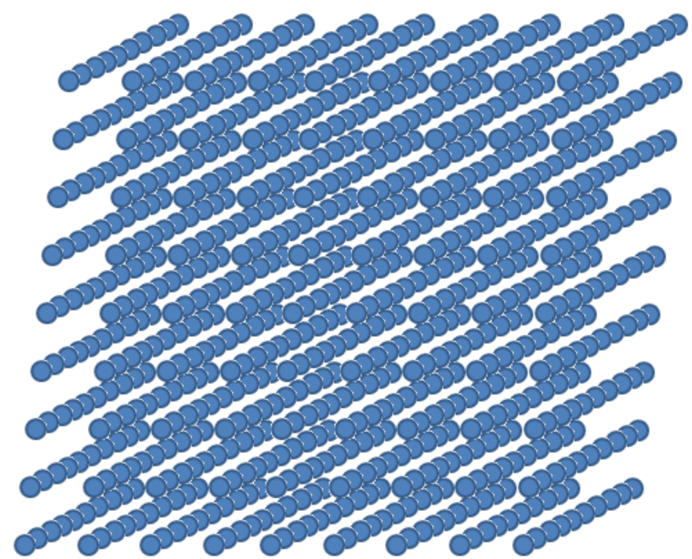


X, Y, Z

FT →

← FS???



F_{hkl}

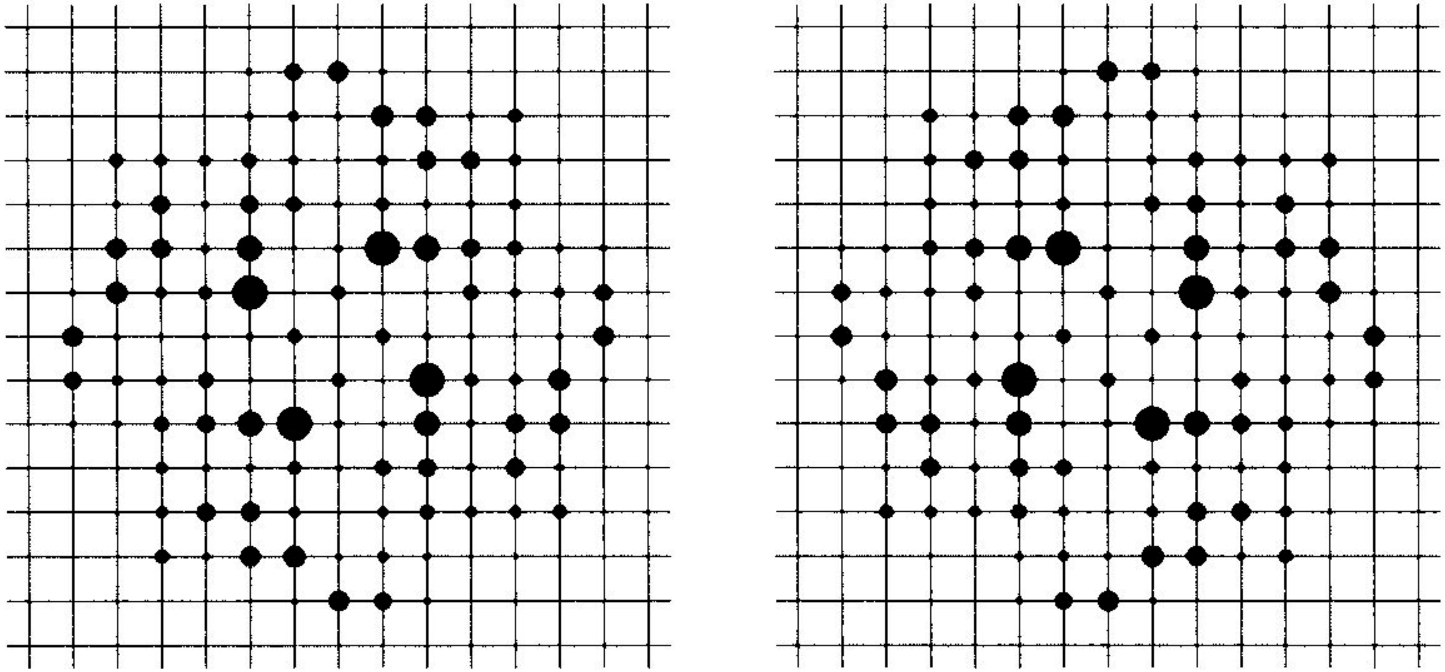
How to solve the structure:

- Patterson/heavy atom methods:
  - A FS with all phases = 0 gives information from which the heavy atoms alone can be located.
  - Phases approximated from heavy atom locations
  - SF with approximated phases gives remaining atoms
  - Least squares refinement of atomic positions against diffraction data.
- Direct methods
  - Karle and Hauptman, Nobel Prize, 1985
  - Rigorous mathematical relationships between spot intensities and phases.
  - Computationally intensive

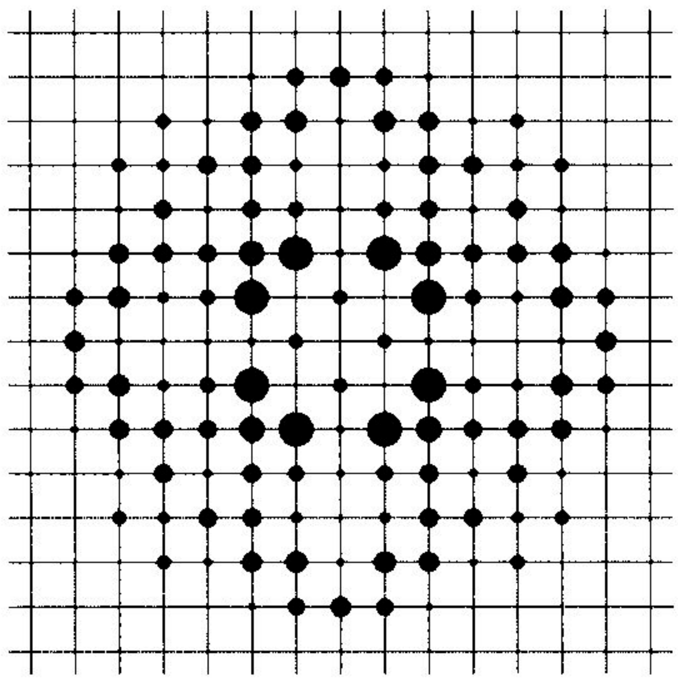
Recent and Current Frontiers in Crystallography

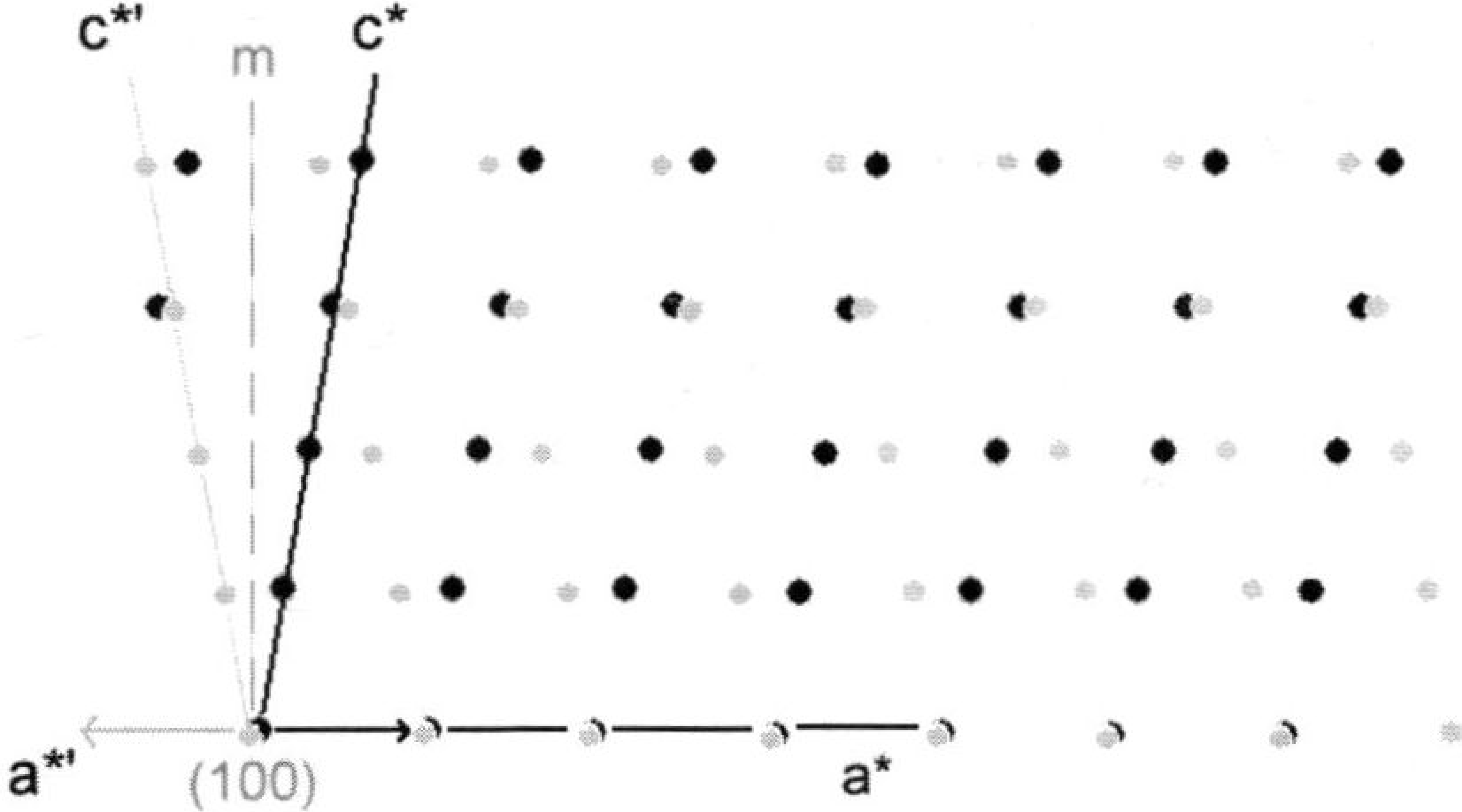
- Twinning
  - Prevents the direct obtainment of the intensity weighted reciprocal lattice.

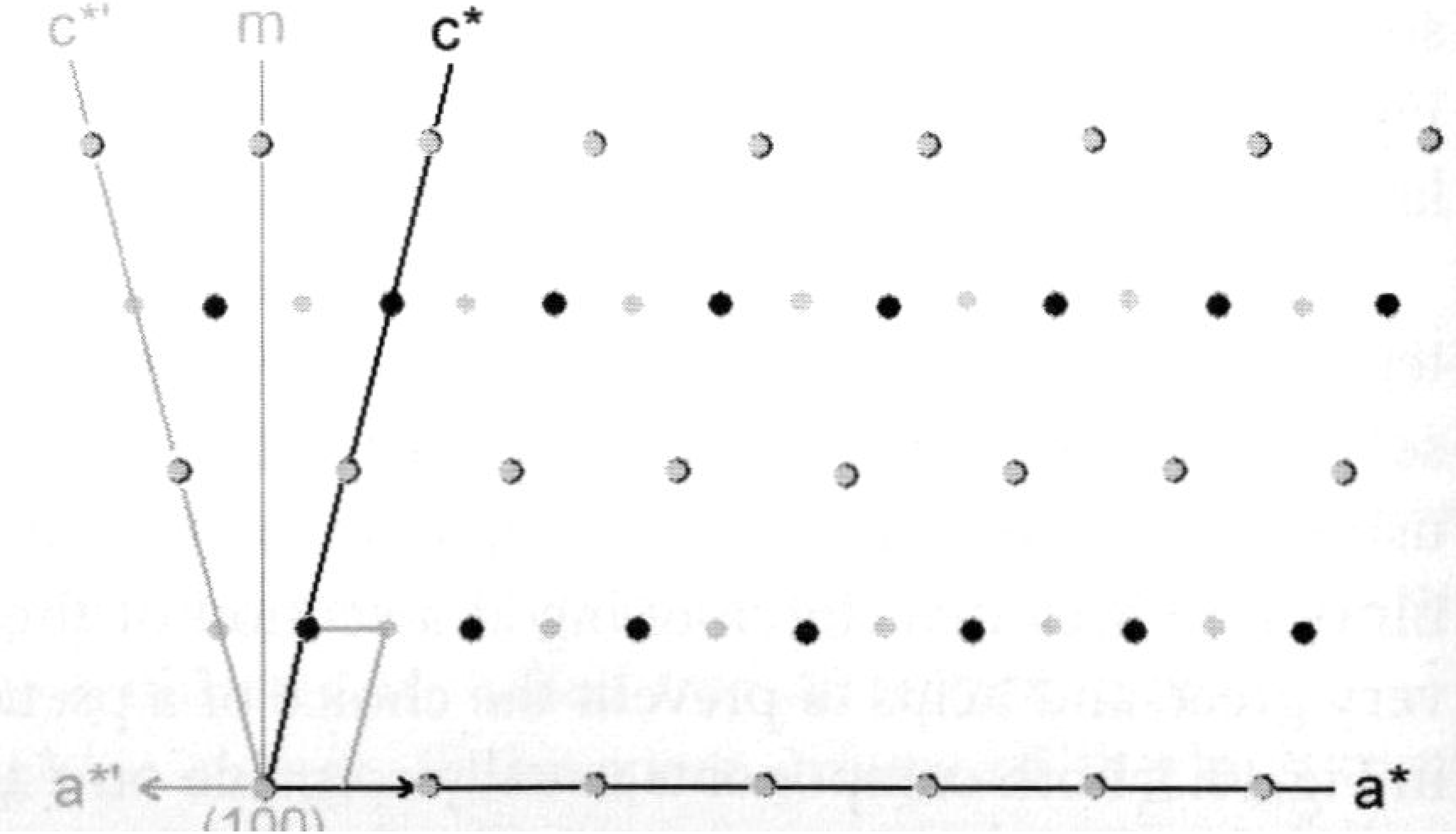
4/m



4/mmm

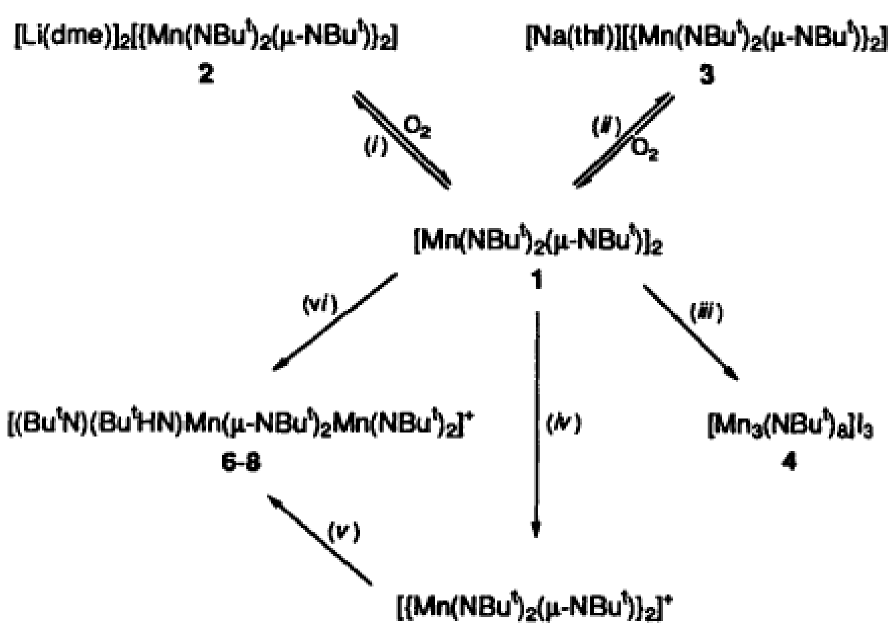


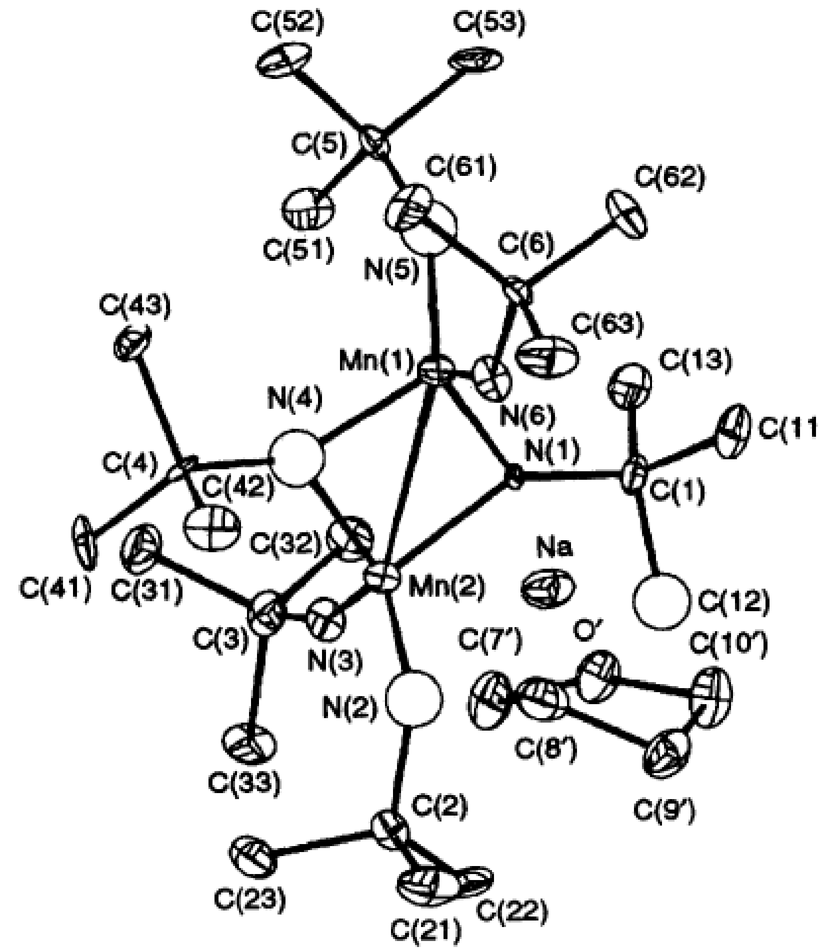

c*'
m
c*
a*'
(100)
a*


c*'
m
c*
a*'
a*

Anionic and Cationic Bi- and Tri-nuclear *tert*-Butylimido Complexes of Manganese-(V) and -(VI)†

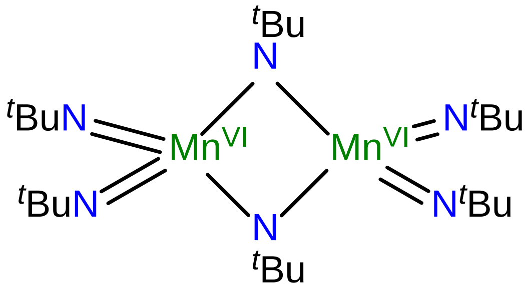
Andreas A. Danopoulos,[a] Geoffrey Wilkinson,*[,a] Tracy K. N. Sweet[b] and Michael B. Hursthouse*[,b]
[a] *Johnson Matthey Laboratory, Chemistry Department, Imperial College, London SW7 2AY, UK*
[b] *Department of Chemistry, University of Wales Cardiff, PO Box 912, Cardiff CF1 3TB, UK*



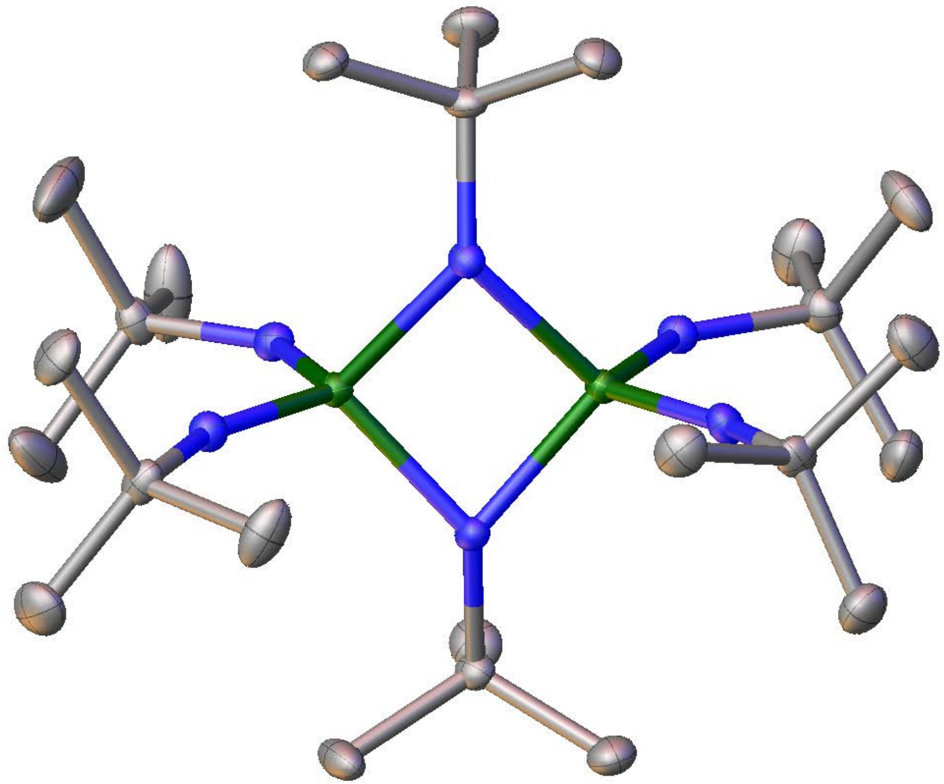


Danopoulos et. al. *J. Chem. Soc. Dalton Trans.* **1995**, 937-950

Structure solution of a Mn(VI) dimer indexed using CELL_NOW (George Sheldrick)

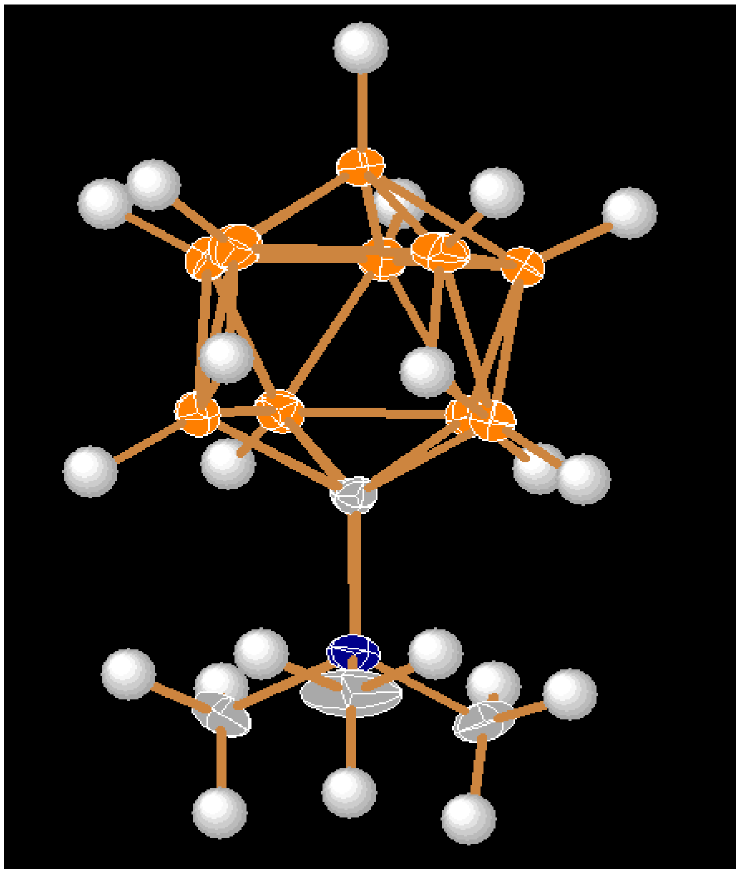


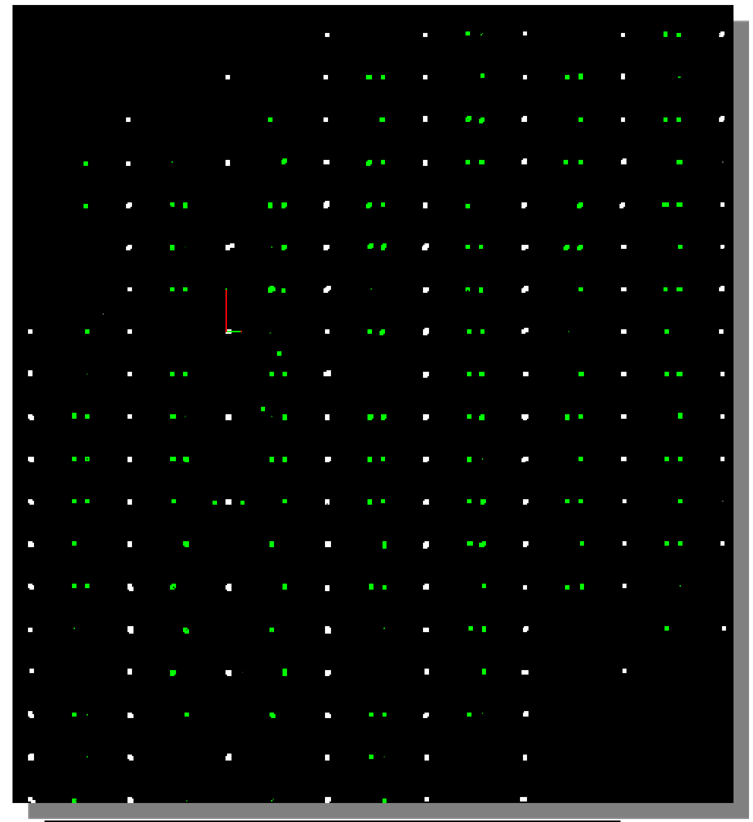
$[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$
1

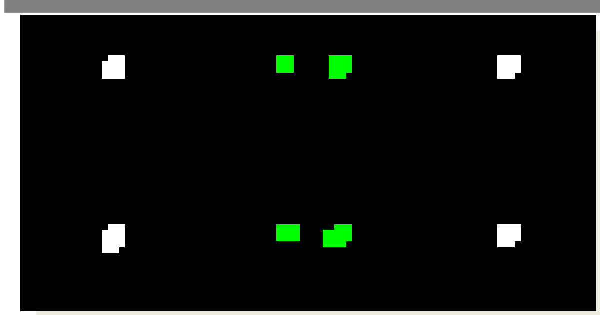


2.5% *R*1(obs)

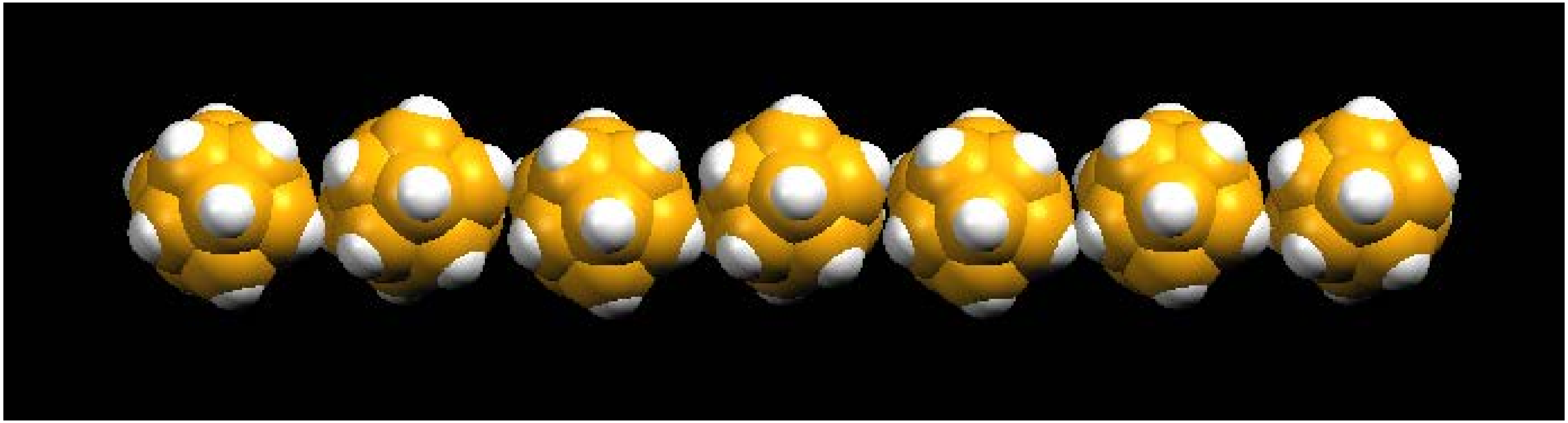
Modulated Carborane (Chuck Campana)

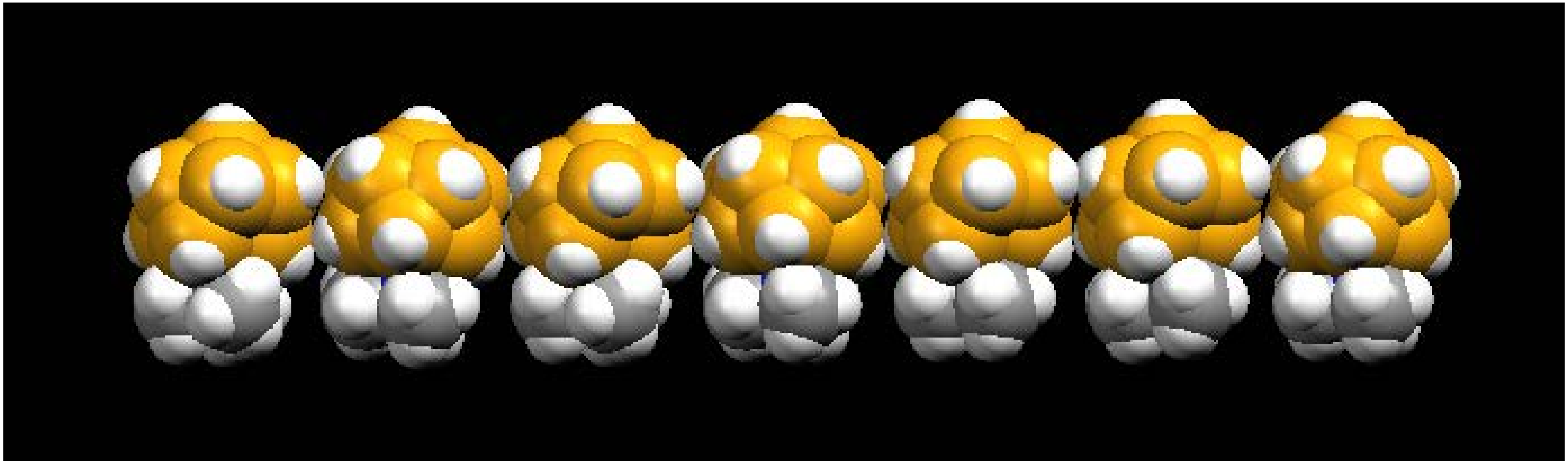




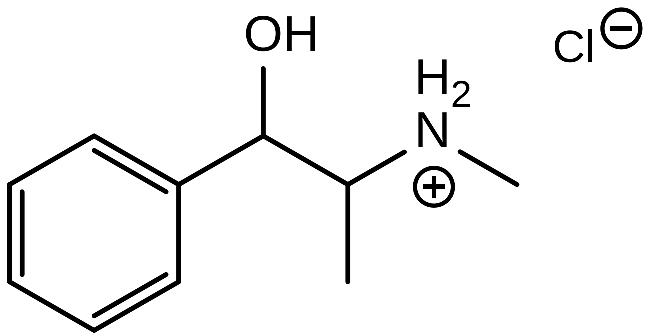


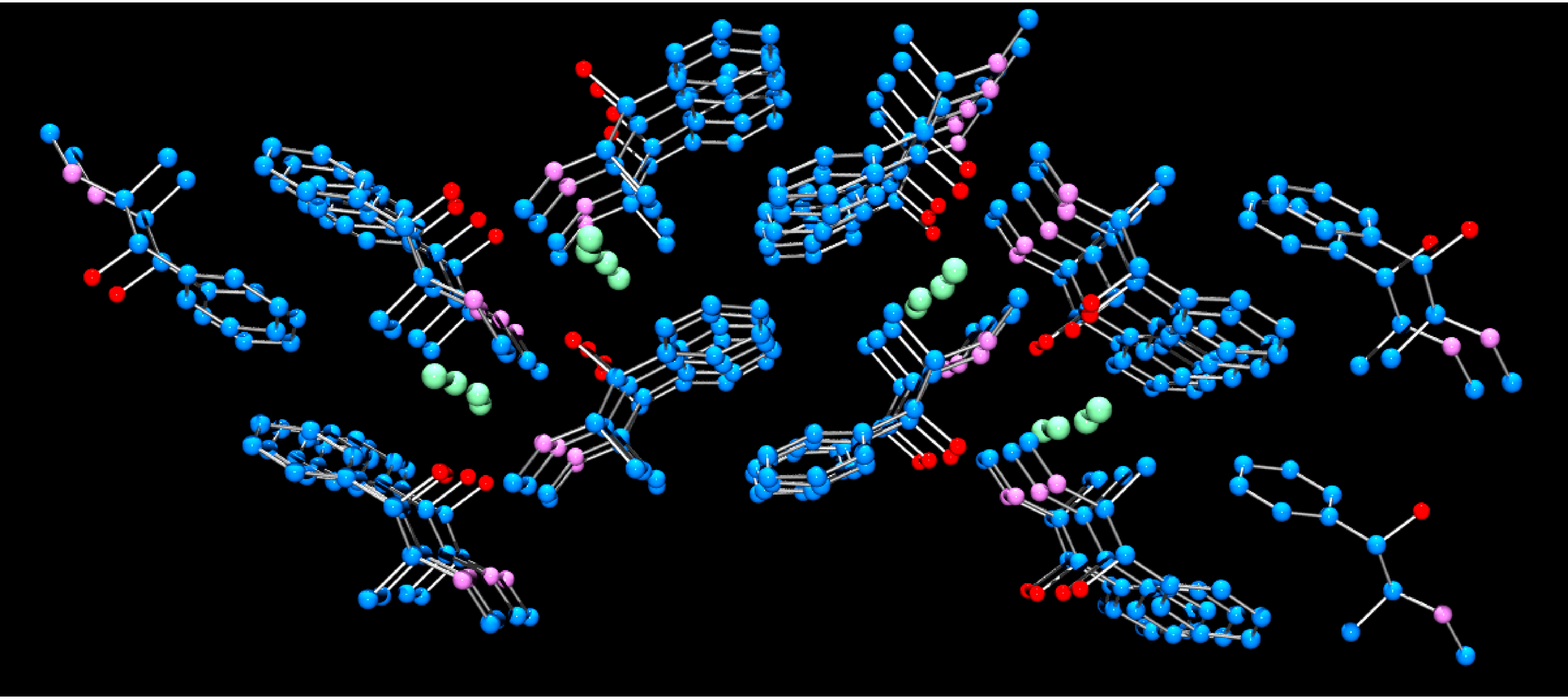
Supercell of Commensurate Modulated structure



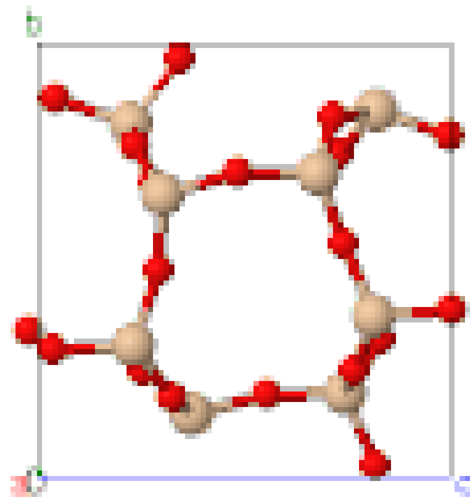


Ephedrine · HCl





Incommensurate modulated structures: Tridymite, high-temperature SiO_2



Acta Cryst. B. **2009**, *65*, 543-550.

http://publcif.iucr.org/cifmoldb/gui/cifjmol.php?cifid=ck5037

Quasicrystals

Angew. Chem. Int. Ed. 2011, 50, 10775 – 10778

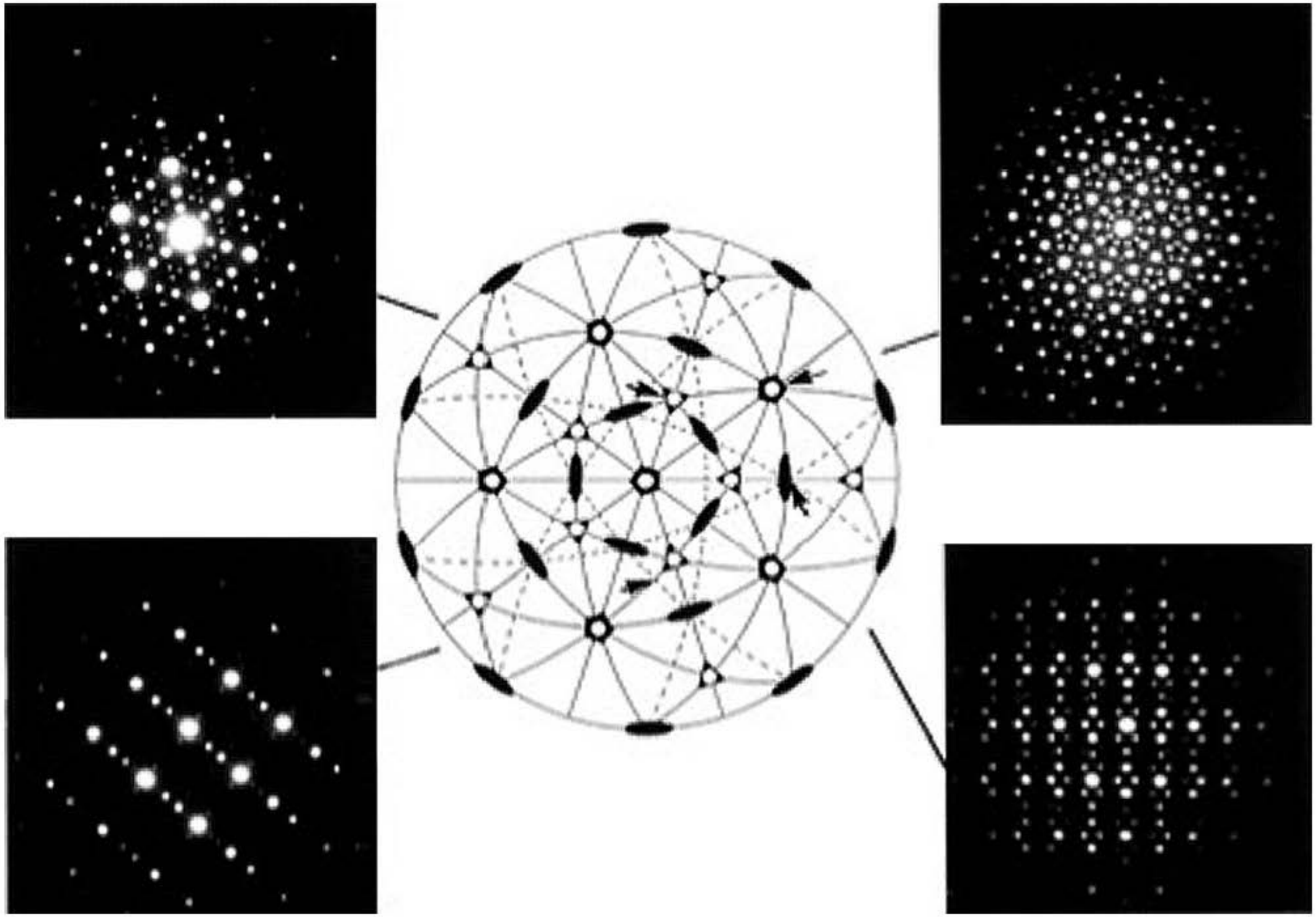
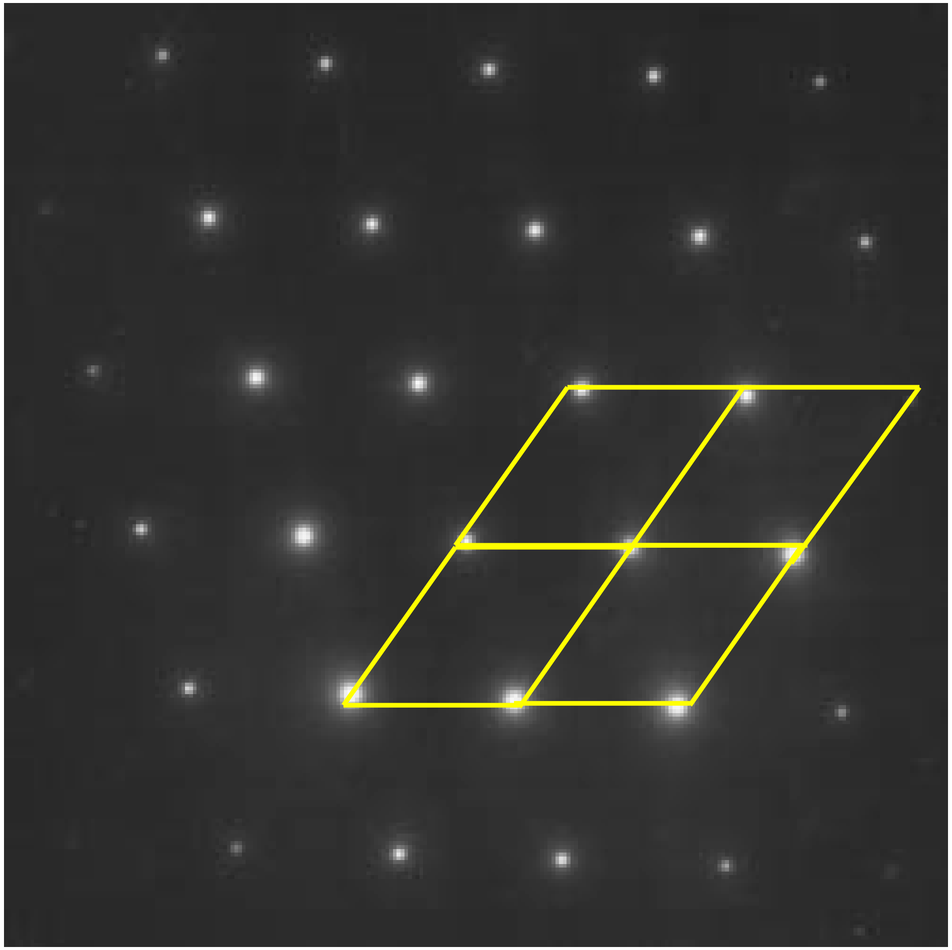
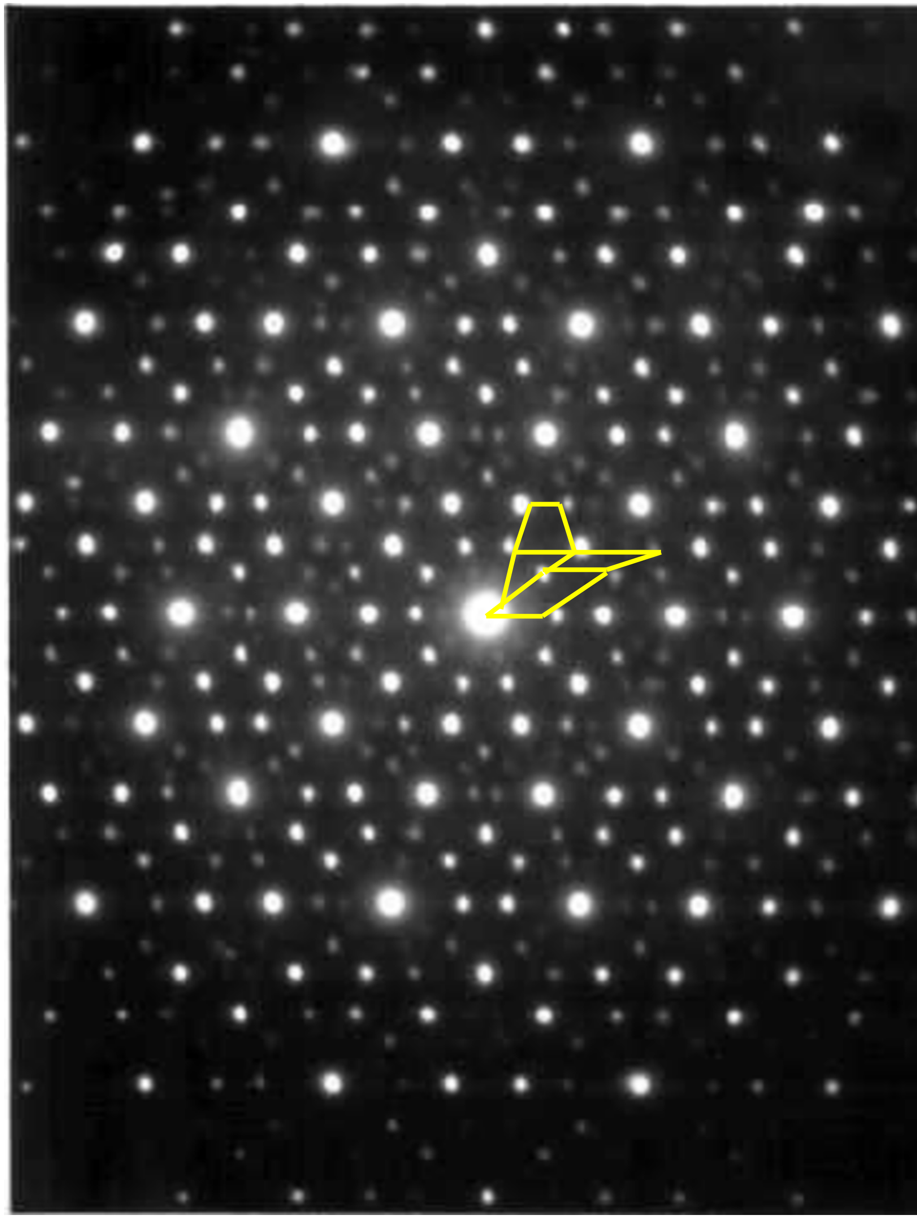
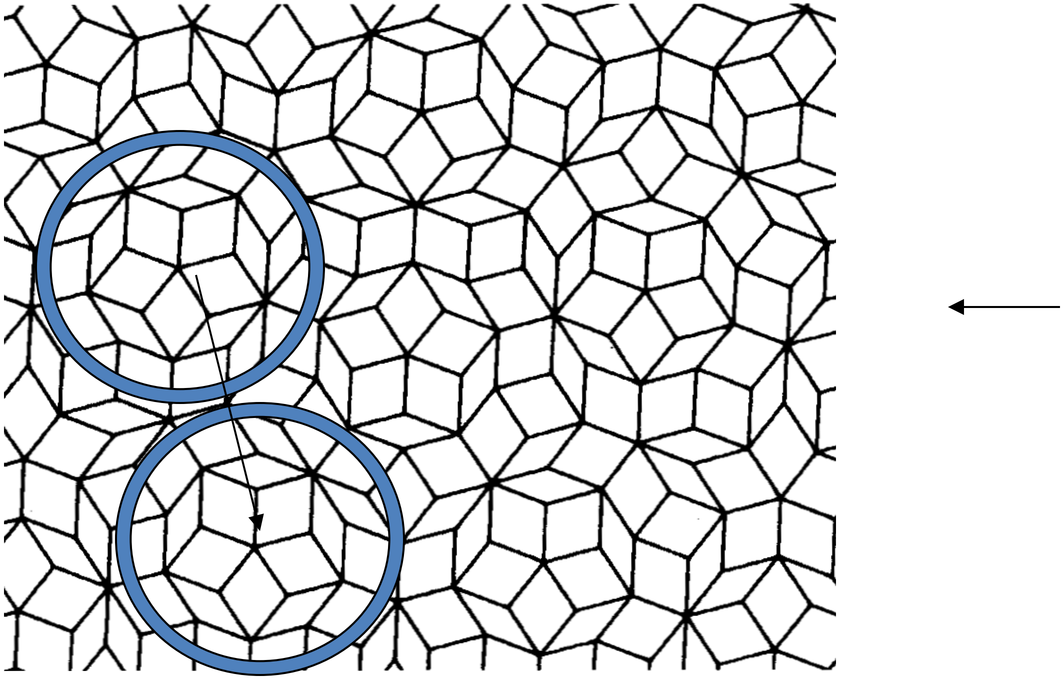


Figure 1. Electron diffraction patterns of the Al-Mn quasicrystal taken along different symmetry directions indicating icosahedral diffraction symmetry. Reprinted from Ref. [1].





Penrose tiling: A 2-D incommensurate modulated structure (quasicrystal)



Roger Penrose
British Mathematician

Nobel Prize – 2011
Dan Shechtman
Technion - Israel Institute of Technology, Haifa, Israel