THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

2014 international year of crystallography

United Nations Educational, Scientific and Cultural Organization

International Union of Crystallography

"Crystallography"

Speaker: Colin Kennard

18h July 2014

For educations purposes

The Courier Mail

IN 1914, **Max von Laue** won the Nobel Prize in Physics for discovering that crystals could diffract X-rays, a finding that helped revolutionise our ability to visualize matter at the atomic scale.

In honour of this centennial, the United Nations Educational, Scientific & Cultural Organization (UNESCO) has declared 2014 the International Year of Crystallography.

The major objectives of the IYCr2014 are:

- to increase public awareness of the science of crystallography and how it underpins most technological developments in our modern society
- to inspire young people through public exhibitions, conferences and hands-on demonstrations in schools
- to foster international collaboration between scientists worldwide
- to promote education and research in crystallography and its links to other sciences

The International Union of Crystallography counts 48 Nobel Prizes that can in some way be attributed to the

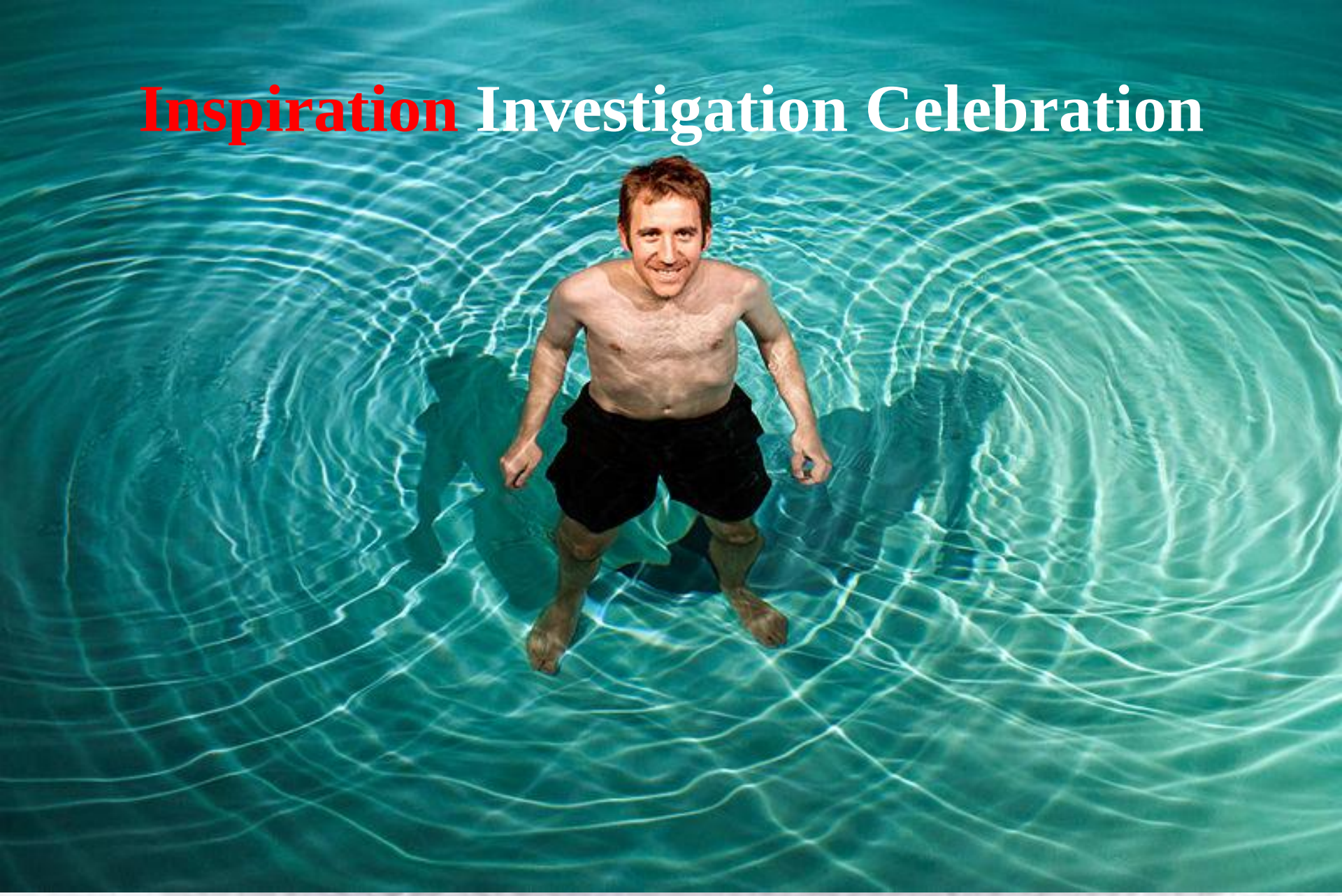
28

$1 face value
$12.27 cost

2014 marks the International Year of Crystallography, commemorating the centennial of X-ray crystallography and the Nobel Prizes to Max von Laue (1914) and father and son duo, Sir William Henry Bragg and Australian Sir William Lawrence Bragg (1915).

This coin is a tribute to all who dare to dream and enquire, and all who are in the pursuit of living in a world where anything is possible.

Inspiration Investigation Celebration



http://en.wikipedia.org/wiki/Interference_pattern_(disambiguation)#mediaviewer/File:Swimming_Pool_Interferometry.jpg

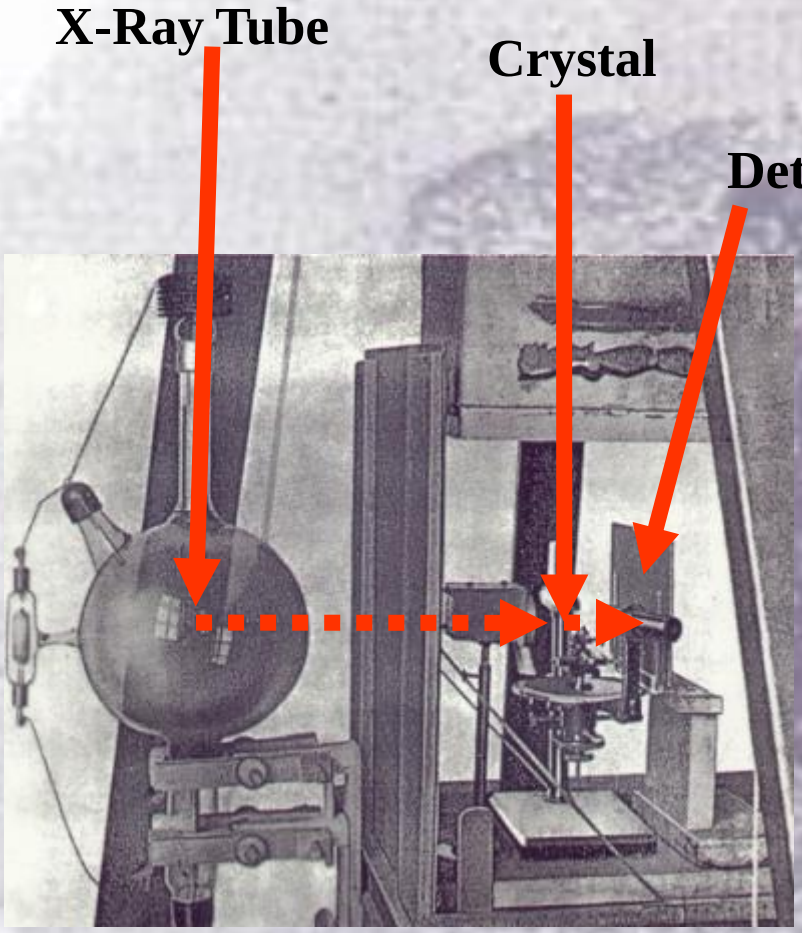
Inspiration

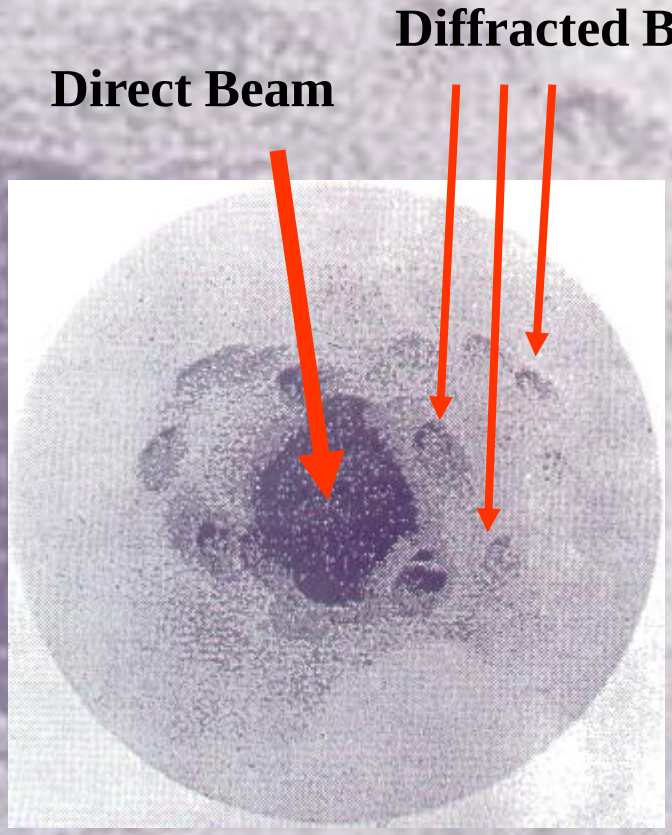
Log onto this

http://ezeducationorama.com/ezMedia/physics/waves/interference/twoSource/twoSource1/twoSource1.php?color=black&backgroundColor=aqua

http://zonalandeducation.com/mstm/physics/waves/interference/twoSource/TwoSourceInterference1.html

Inspiration Investigation Celebration





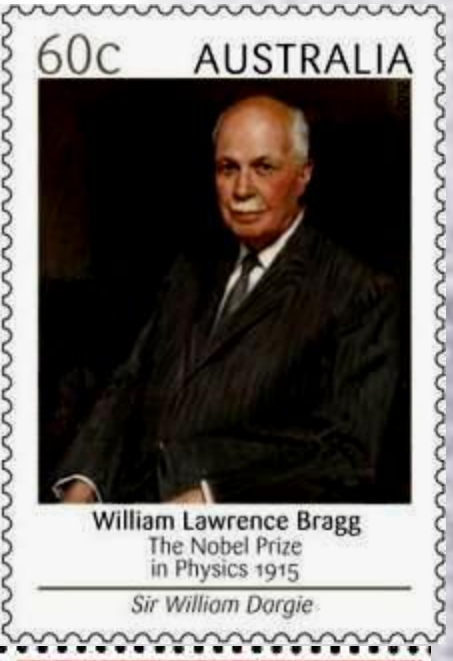
Famous von Laue, Friedrich & Knipping 1912's

X-ray Diffraction Apparatus and photograph

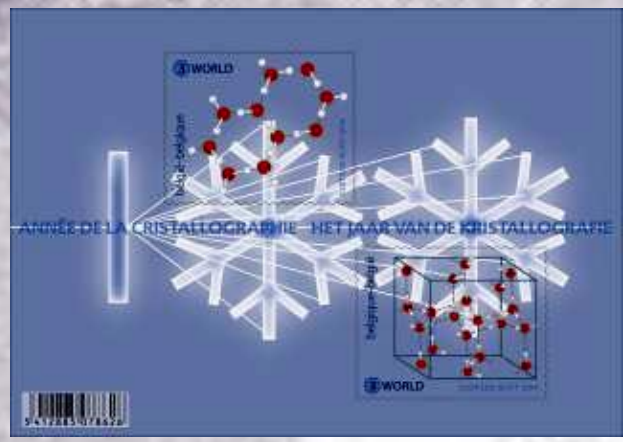
P.P. Ewald, "Fifty Years of X-ray Diffraction", IUCr, 1962

Inspiration Investigation Celebration

Current Crystallographic Stamps



http://www.iycr2014.org/events/postage_stamps



Belgium

The State of Crystallography in 1906

AN INTRODUCTION TO

CHEMICAL CRYSTALLOGRAPHY

PUBLIC LIBRARY QUEENSLAND 648

P. GROTH

PROFESSOR OF MINERALOGY AND CRYSTALLOGRAPHY IN THE UNIVERSITY OF MUNICH

AUTHORISED TRANSLATION

BY

HUGH MARSHALL, D.Sc., F.R.S.

LECTURER ON CHEMISTRY AND ON MINERALOGY AND CRYSTALLOGRAPHY IN THE UNIVERSITY OF EDINBURGH

GOVT. CHEMICAL LABORATORY. BRISBANE.

LONDON

GURNEY & JACKSON

1906

PREFACE

In this short treatise on general chemical crystallography the attempt has been made to present the hitherto recognised relations between the properties of crystallised subtances and their chemical constitution on the basis of a definite view regarding the structure of crystals. In doing so, a knowledge of the crystallographical laws is assumed, to an extent corresponding to the elementary treatment of them as contained in my text book.

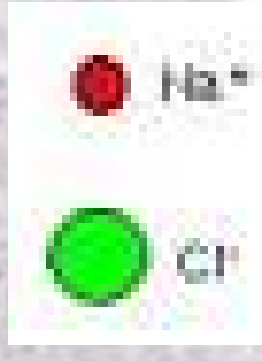
Crystals

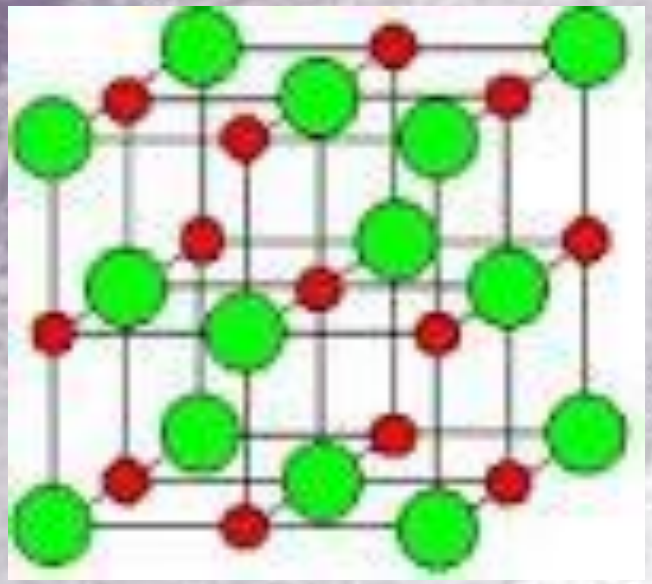
- **This is the crystal cave of giants found in the Naica Mine, Chihuahua, Mexico**
- **Large selenite crystals (1.2 m in diameter and 15 m long)**

http://www.thatcrystalsite.com/caves.php

Table Salt (NaCl)

Dissolve ordinary table salt from water, and evaporate the water in the sun





Actual Structure determined by W.H. and W.L. Bragg on 30th July 1913

http://www.google.com.au/search?client=safari&rls=en&q=structure+of+sodium+chloride&ie=UTF-8&oe=UTF-8&gfe_rd=cr&ei=ngmyU5K3DcGN8QeHnYDYAg

P.P.Ewald, “Fifty Years of X-ray Diffraction”, IUCR, 1962

Inspiration

Max Theodor Felix von Laue (9 October 1879 – 24 April 1960)

- **German physicist who won the Nobel Prize in Physics in 1914 for his discovery of the diffraction of X-rays by crystals**

http://en.wikipedia.org/wiki/Max_von_Laue

Max von Laue

- Laue completed his Degree in 1906 under Arnold Sommerfeld at LMU, Munich

LMU LUDWIG-MAXIMILIANS-UNIVERSITÄT MÜNCHEN

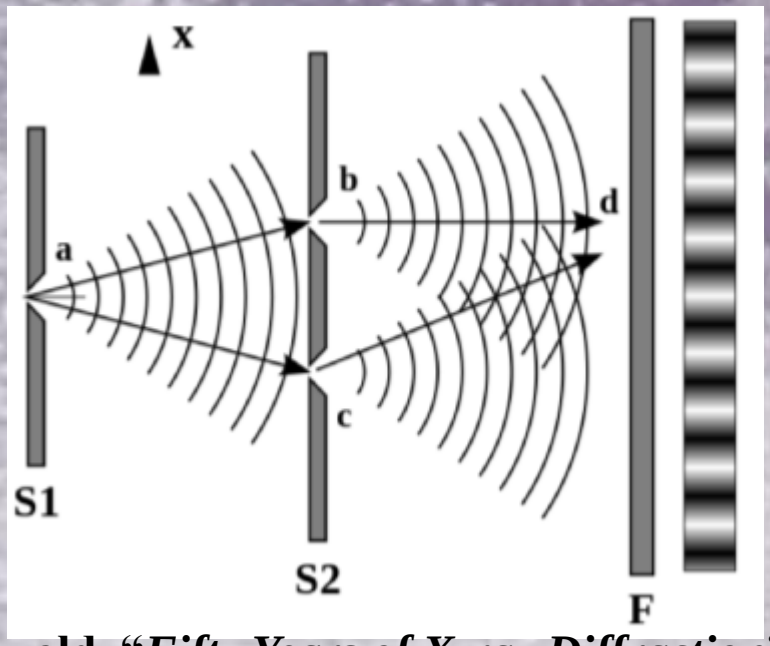
- In 1906-09, became an assistant to Planck and met Albert Einstein for the first time and were friends
- From 1909 to 1912, Laue was a *Privatdozent* at the Institute for Theoretical Physics, under Arnold Sommerfeld, at LMU
- Sommerfeld graduate student P.P. Ewald met Laue in Englische Garten, Munich to discuss his thesis

Englische Garten

http://en.wikipedia.org/wiki/Max_von_Laue

- **Laue had no knowledge of Ewald's work which was to find optical properties of an anisotropic dipoles; "*Could one explain the double refraction of crystals by the regular arrangements of the isotropic resonators*"**
- **Ewald thought that crystals had internal regularity which seemed new to Laue and said that the repeating distance was very small compared to wavelength of visible light (DVD)**

Inspiration



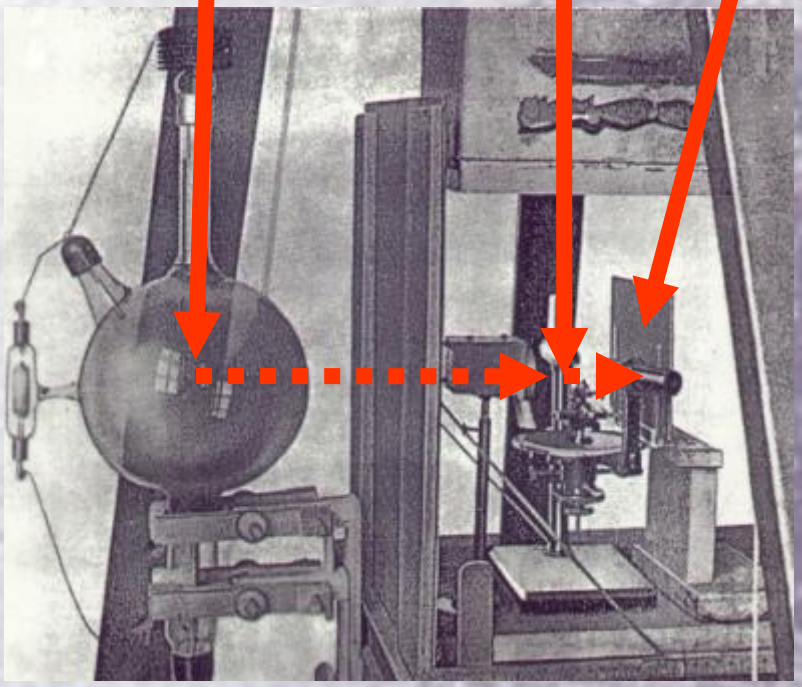
Interference Experiment

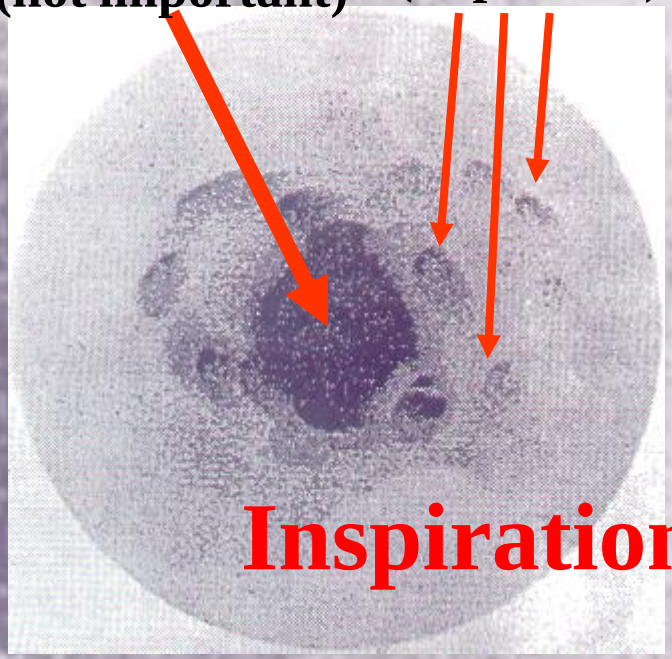
P.P. **Ewald, "*Fifty Years of X-ray Diffraction*", IUCr, 1962**

http://en.wikipedia.org/wiki/File:Ebohr1_IP.svg

- **He reported that Laue was listening in a slightly distracted way and Laue failed to discuss his thesis**
- **He submitted his thesis on 16 February 1912**
- **In June 1912, he heard of a report on Laue-Friedrich-Knipping's successful experiments given to Physical Society of Gottingen**

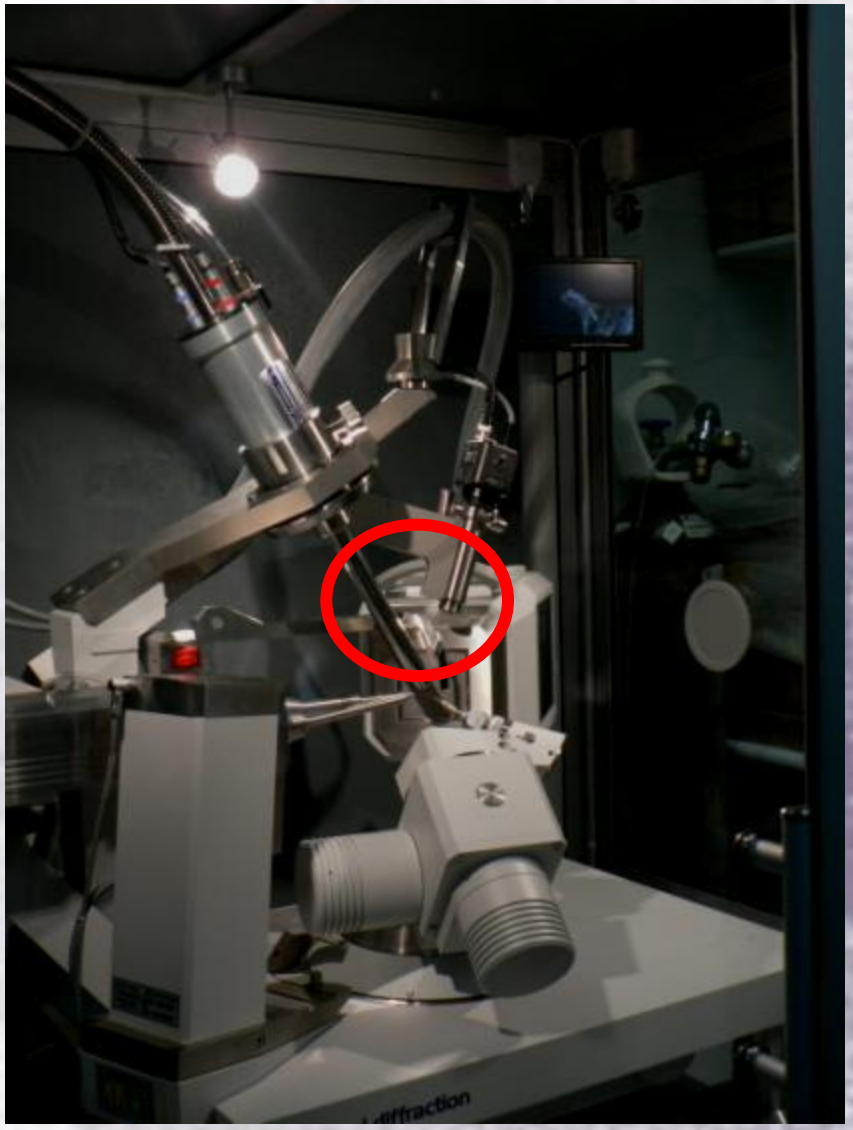
P.P. Ewald, "Fifty Years of X-ray Diffraction", IUCr, 1962



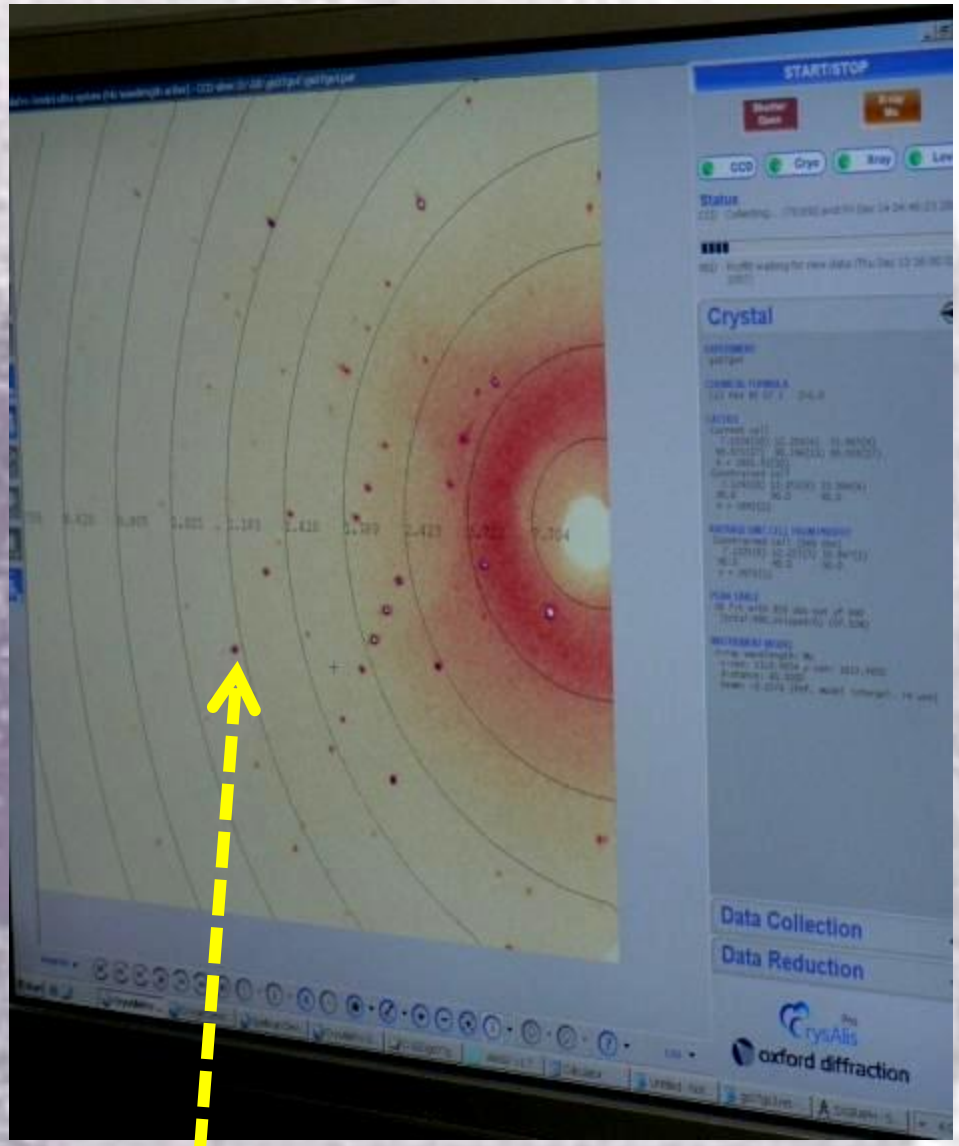


Famous von Laue, Friedrich & Knipping 1912's X-ray Diffraction Apparatus and photograph

P.P. Ewald, "Fifty Years of X-ray Diffraction", IUCr, 1962

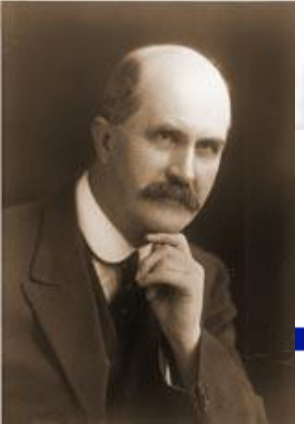


Automatic X-ray Diffractometer



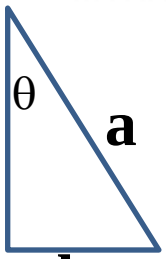
Diffraction Pattern (QUT)

Each spot samples the crystal for a particular *hkl*

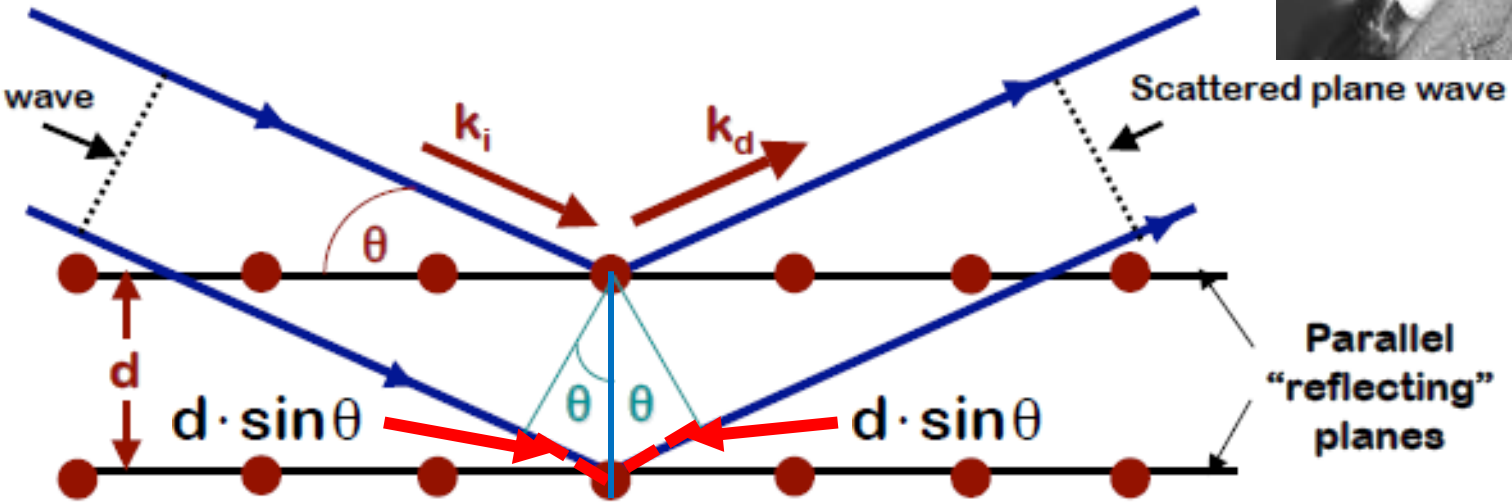


Father and Son: WH and WL Bragg

Bragg's Law



$\sin\theta = b/a$

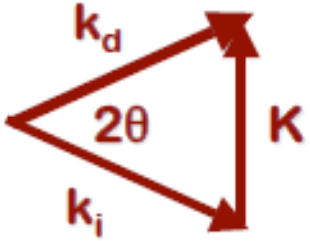


k's - wave vectors

θ= theta; λ= lamda

n = integer

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



$$\vec{k}_d - \vec{k}_i = \vec{K}$$

$$|\vec{K}| = \frac{2\sin\theta}{\lambda} = \frac{n}{d}$$

$$\vec{K} = \vec{g}$$

$$|\vec{K}| \propto \frac{1}{\lambda} \quad \& \quad |\vec{K}| \propto \frac{1}{d}$$

http://nanohub.org/resources/4111/download/2008.02.20-mse640-l4.pdf

Real => Reciprocal

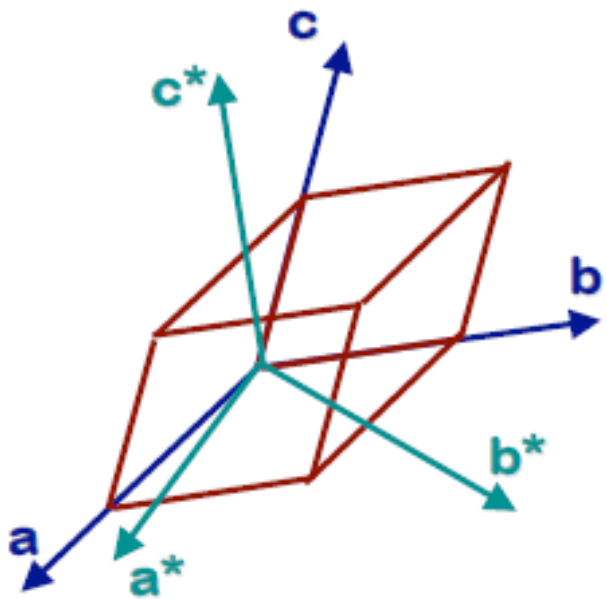
The relationship between real and reciprocal determined by:

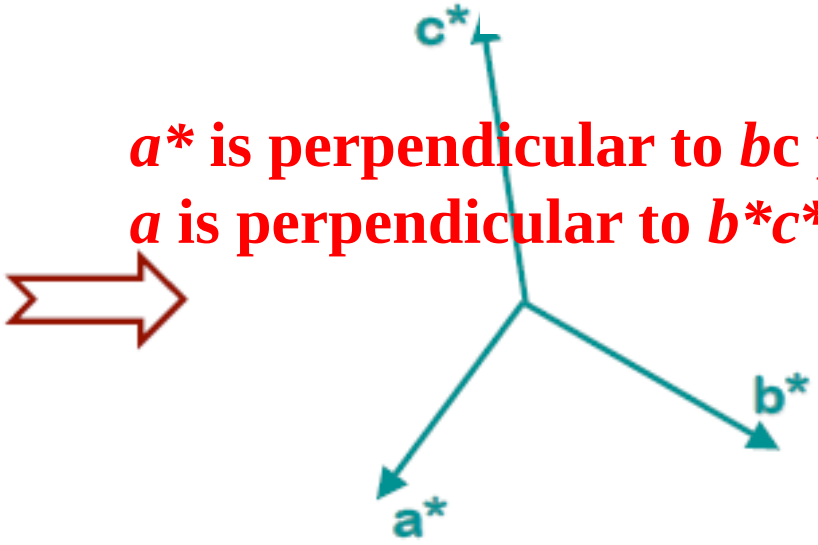
$$\vec{a}^* \cdot \vec{a} = 1 \quad \vec{a}^* \cdot \vec{b} = 0 \quad \vec{a}^* \cdot \vec{c} = 0$$

$$\vec{b}^* \cdot \vec{a} = 0 \quad \vec{b}^* \cdot \vec{b} = 1 \quad \vec{b}^* \cdot \vec{c} = 0$$

$$\vec{c}^* \cdot \vec{a} = 0 \quad \vec{c}^* \cdot \vec{b} = 0 \quad \vec{c}^* \cdot \vec{c} = 1$$

$\vec{a}^*$, $\vec{a}$ are vectors



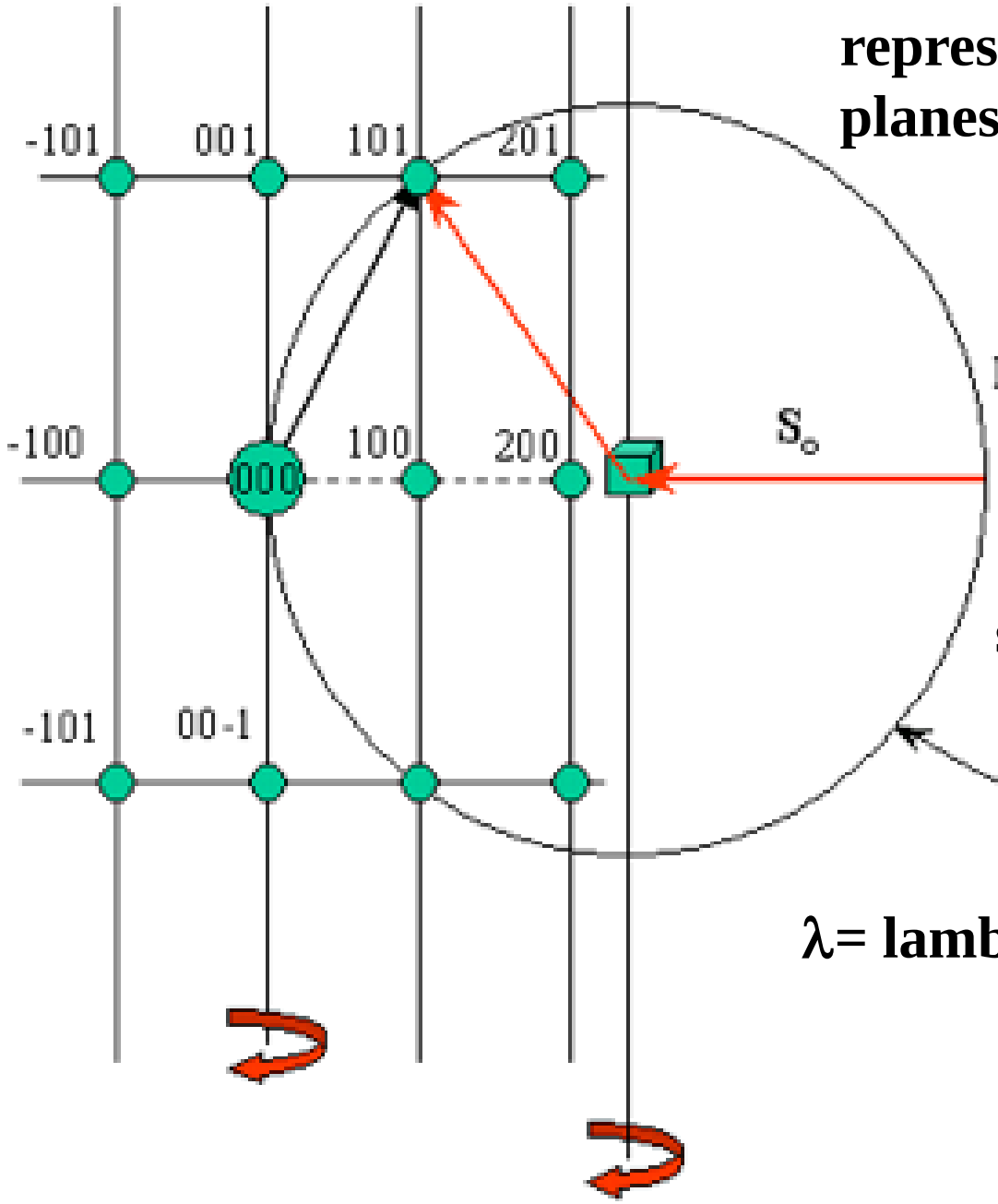


a is perpendicular to **b**c plane*

a** is perpendicular to **bc* plane*

a* only parallel to a if a, b and c are mutually orthogonal

Each reciprocal lattice point represents a series of real planes through the crystal

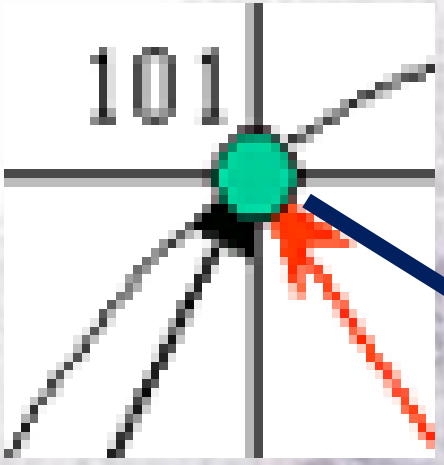


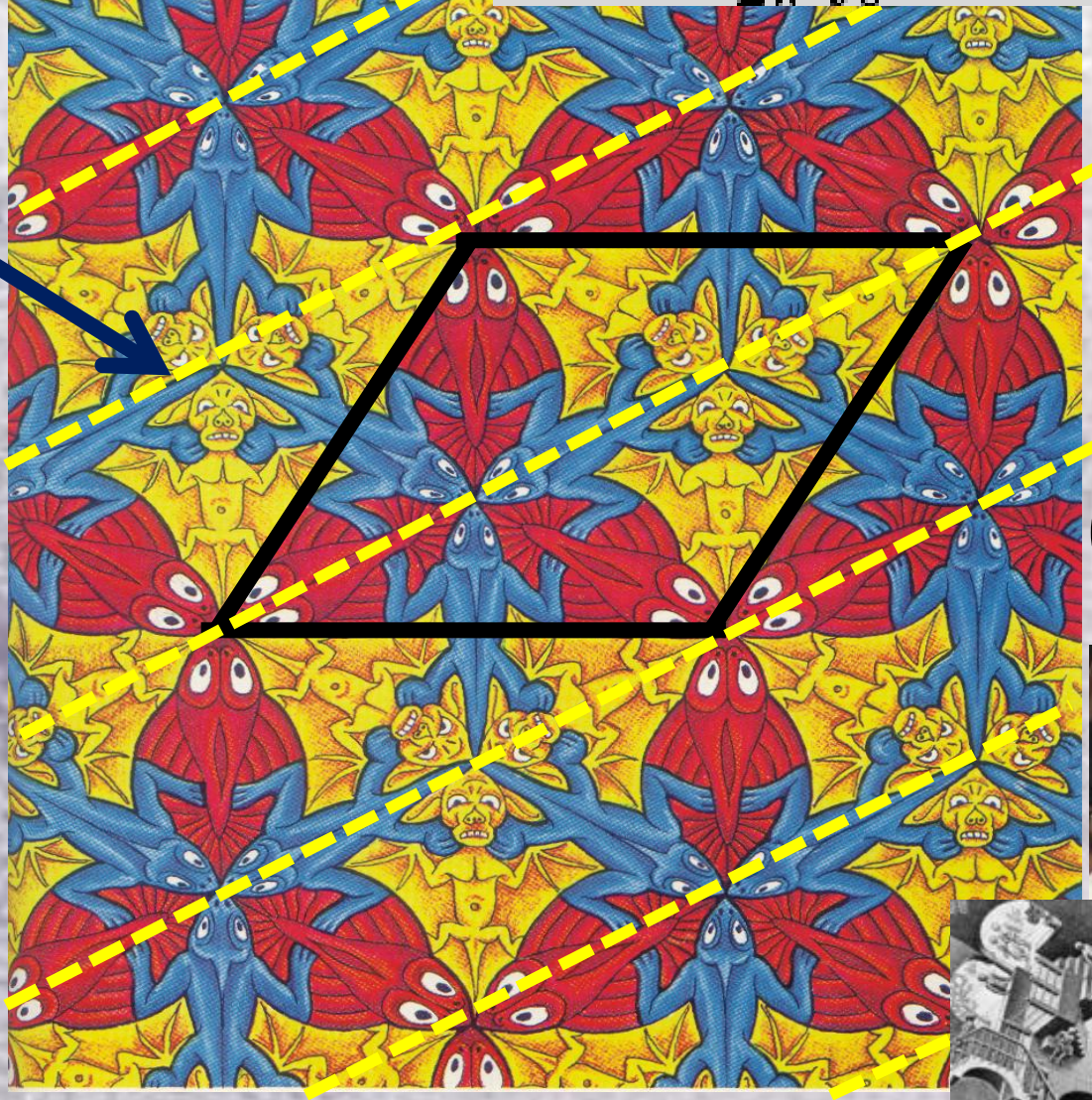
Any position on the circumference is a solution of the Bragg equation

λ= lambda

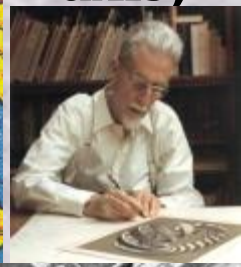
Calculation

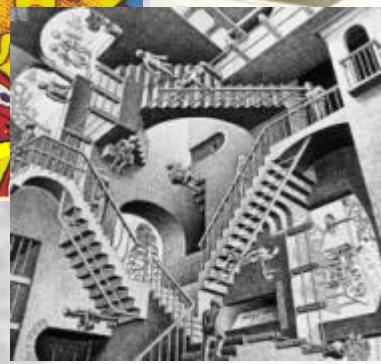
$$F(n) = \frac{1}{2\pi}\int_0^{2\pi} f(x)e^{-inx}\,dx$$





This is a Crystal **Unit Cell** (down b axis)





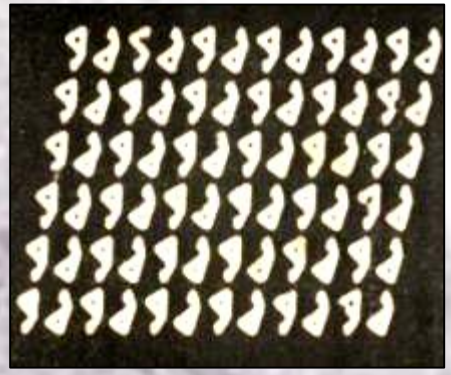
- A reciprocal lattice point [101] represents a series of planes through the unit cell

- Represented by this diffraction spot

Escher Pattern

Plate 9 (p3m1) from p.22, C.H. MacGillavry, "Symmetry Aspects of M.C. Escher's Periodic Drawings", IUCR, Utrecht, 1965.

Simulation

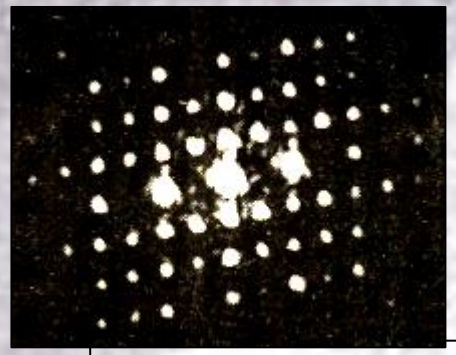


Focussed Laser → Periodic Pattern in Crystal → Image of Pattern Crystal Structure

Structure Determination

Unfocussed Laser → Periodic Pattern in Crystal → Interference Pattern

A mathematical solution gives the original structure



X-ray → Crystal → Detector

Mathematician: Joseph Fourier 1768-1830

- **1798, with Napoléon Bonaparte on his Egyptian expedition and made Governor of Lower Egypt**
- **1822, Published his Théorie analytique de la chaleur, that flow of heat between two adjacent molecules is proportional to the extremely small difference of their temperatures with claims that any function of a variable, whether continuous or discontinuous, can be expanded in a series of sines of multiples of the variable**
- **Sines and cosines are continuous series functions and are also found in Trigonometry**

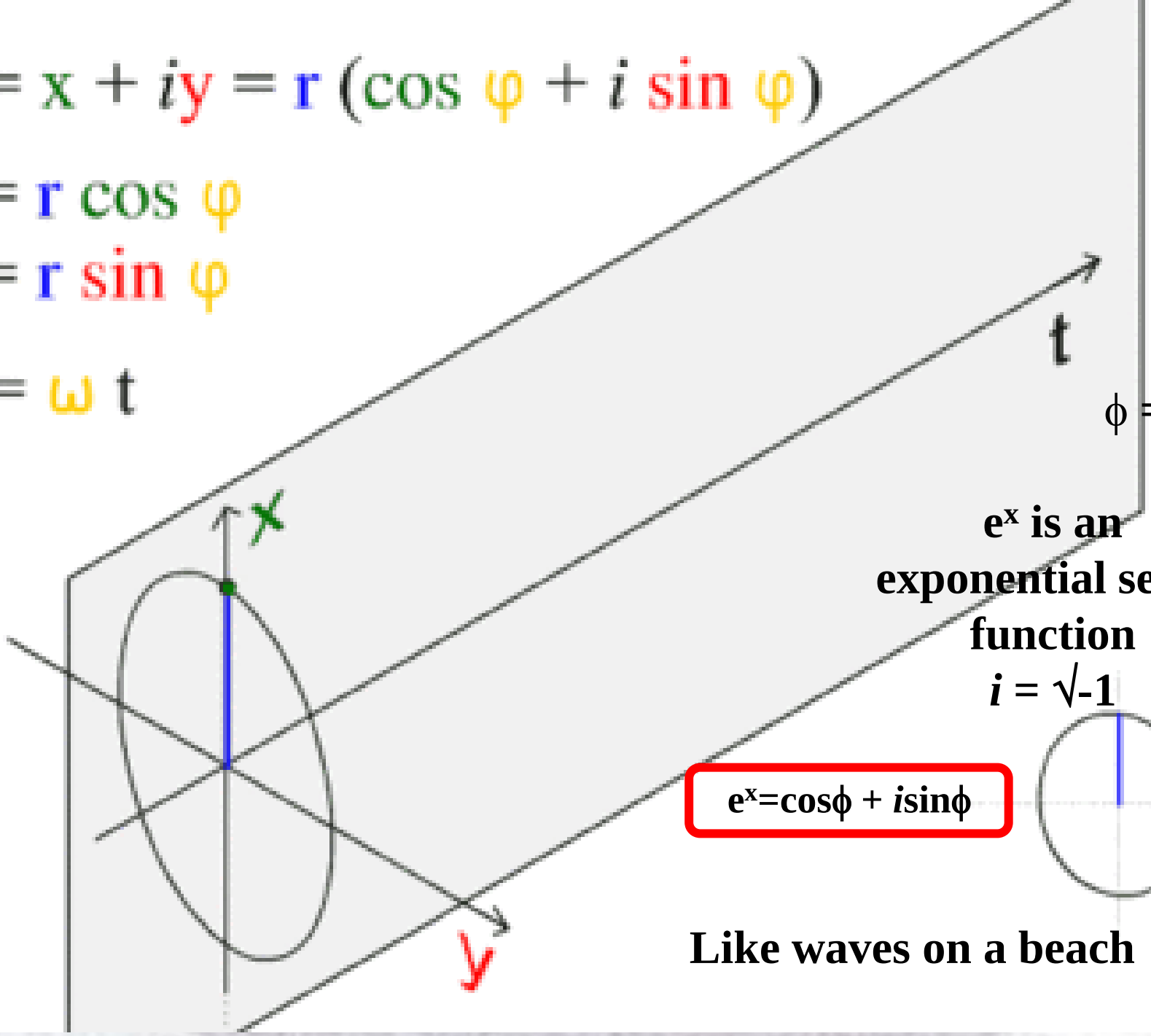
http://en.wikipedia.org/wiki/Joseph_Fourier

$$z = x + iy = r\,(\cos\varphi + i\sin\varphi)$$

$$x = r\cos\varphi$$

$$y = r\sin\varphi$$

$$\varphi = \omega t$$



ϕ = phi

e^x is an exponential series function

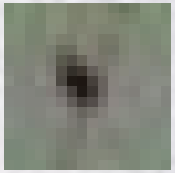
$i = \sqrt{-1}$

$e^x = \cos\phi + i\sin\phi$

Like waves on a beach

Fourier series

- **Suppose that *F(n)* is a regular function repeating every 360°, and can be represented by a combination of sine and cosine functions**
- **Fourier series refers to the infinite series given by:**



$$F(n) = \frac{1}{2\pi}\int_0^{2\pi} f(x)e^{-inx}\,dx$$

for all integers n

n* refers to Miller Index of plane *hkl

- **Fourier series of *F*(n) or *F(hkl)* is given by:**

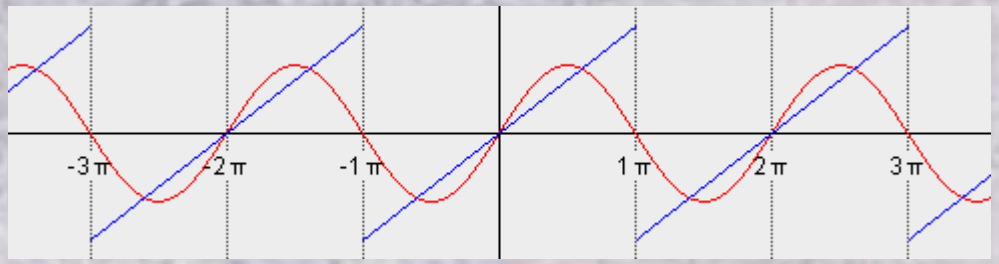
Need to know phase of *F(n)* or where that wave was

$$\rho(xyz) = \frac{1}{V}\sum_h\sum_k\sum_l \underbrace{|F(hkl)|}_{\text{Amplitudes}} \cos 2\pi(hx+ky+lz-\underbrace{\phi(hkl)}_{\text{Phases}})$$

ρ = rho; $\int_0^{2\pi}$ = integral; π = pi ; Σ = sigma

Problem in Crystallography is finding the PHASE

Electron Density or where the atoms are

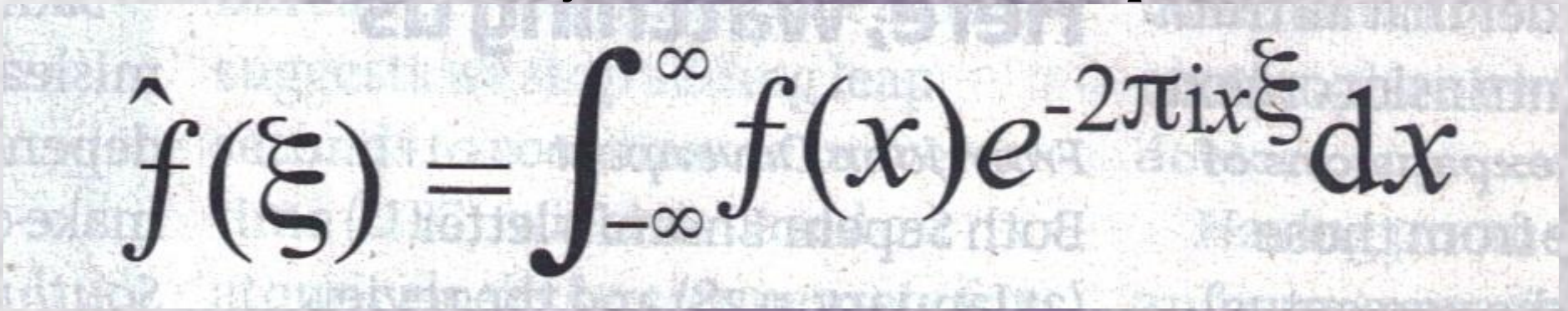


ρ(xyz) will give atomic positions

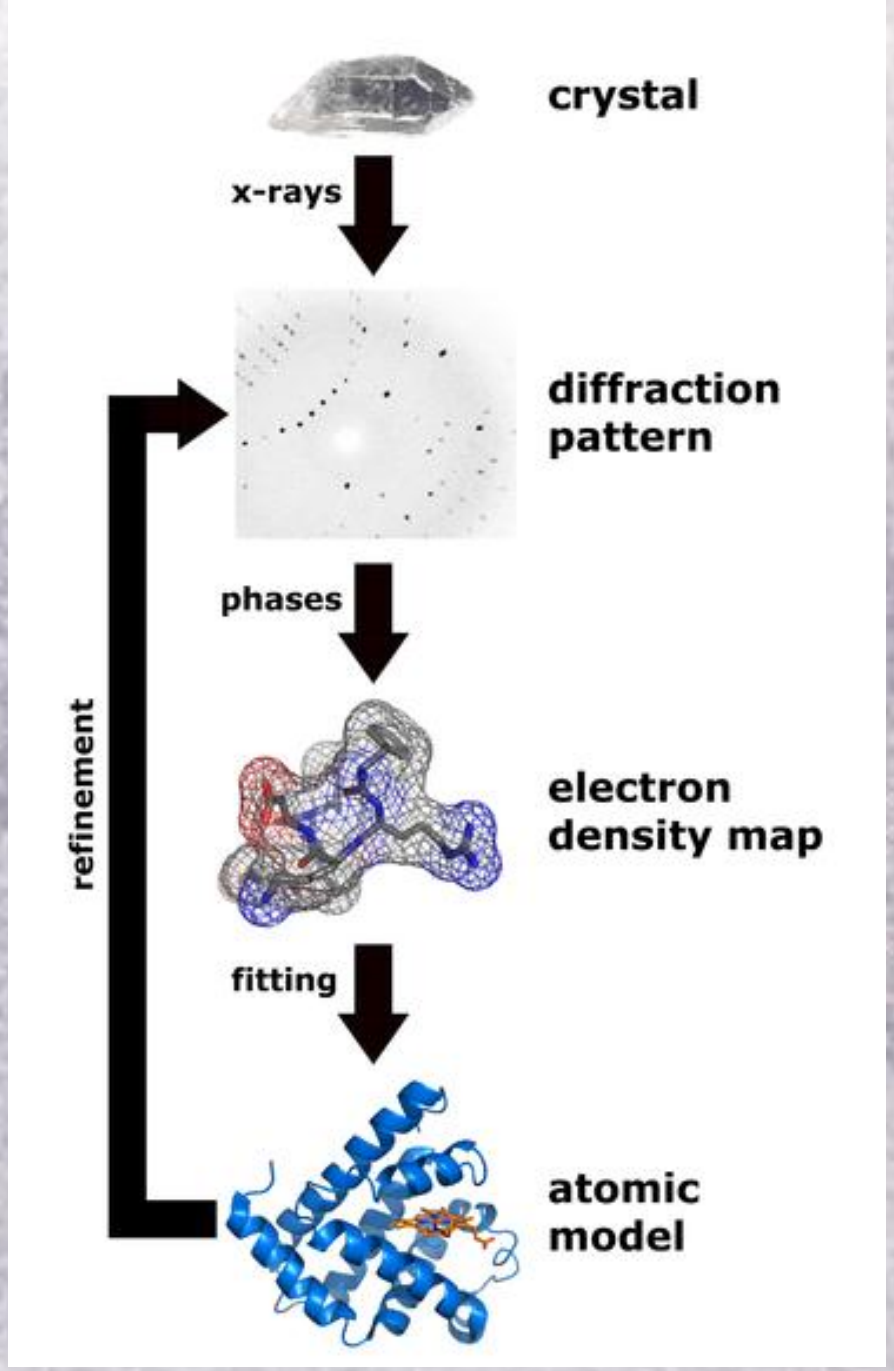
New Scientist 11 February 2012 cover says that

Seven Equations that Changed the World

The Fourier Synthesis is one of these equations

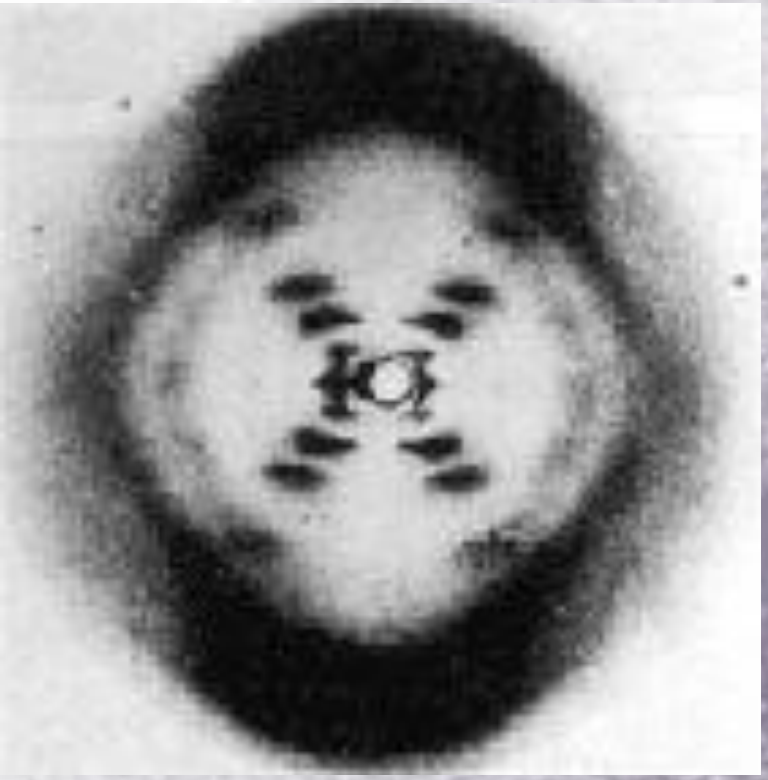


ξ= Xi



http://en.wikipedia.org/wiki/File:X_ray_diffraction.png

Celebration



Rosalind Franklin's Famous X-ray photograph

- **As Brenda Maddox who wrote *Rosalind Franklin: The Dark Lady of DNA* told Howard Berkes for *All Things Considered* of National Public Radio, USA, 6th October 2002, "*it was Franklin's photograph of the DNA molecule that sparked a scientific revolution*"**

http://en.wikipedia.org/wiki/Rosalind_Franklin_University_of_Medicine_and_Science

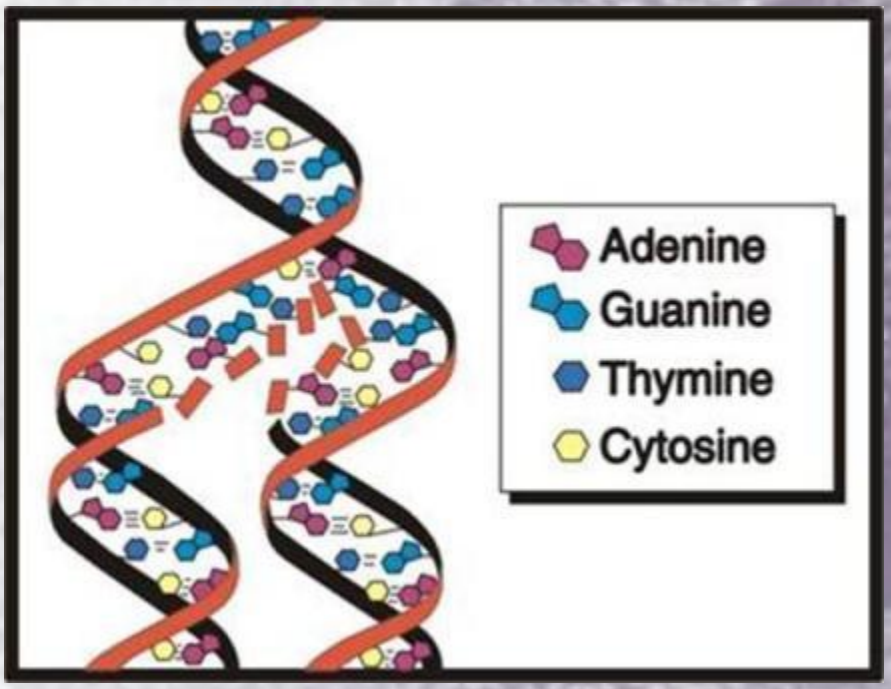
Watson and Crick Nobel Prize 1962

James Watson and Francis Crick with their DNA model at the Cavendish Laboratories in 1953. Photograph copyright A. Barrington Brown. To request permission to use this photo, please visit the Science Photo Library Web site at www.photoresearchers.com.

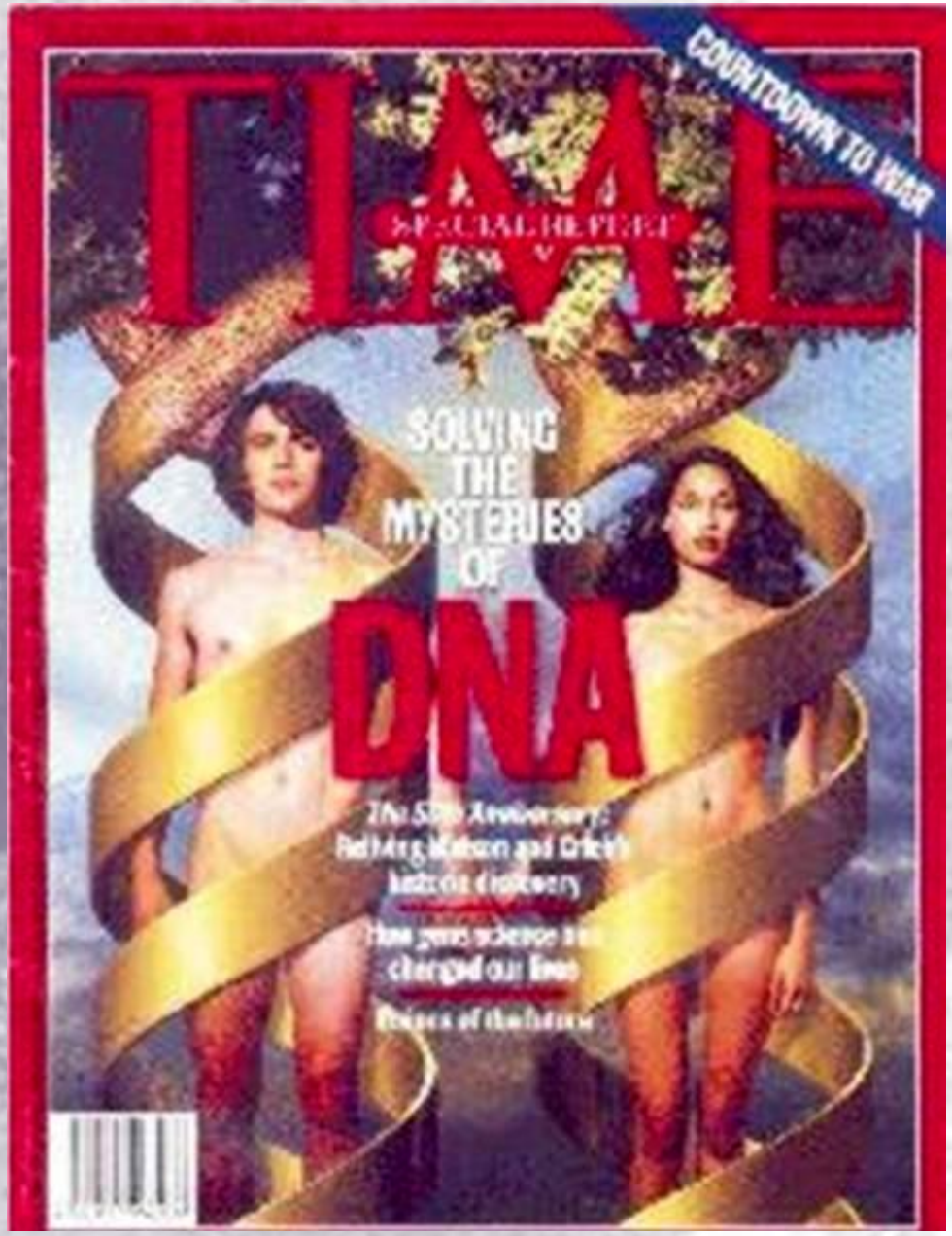
Current State of Model at Science Museum, South Kensington July 2011

http://www.chemheritage.org/discover/chemistry-in-history/themes/biomolecules/dna/watson-crick-wilkins-franklin.aspx

The 50th anniversary of the discovery of the structure of DNA (2003)

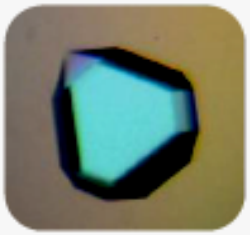


Compounds are nucleobases found in DNA



Celebration

Insulin



Nobel Prize 1964

Work of Dorothy Hodgkin

http://crystallographypatras.files.wordpress.com/2013/07/the-use-of-x-ray-based-methods-for-the-structural-understanding-of-insulin.pdf

Celebration

Prof. Peter Colman, CSIRO, Australia, with a 3D model of the influenza surface protein neuraminidase

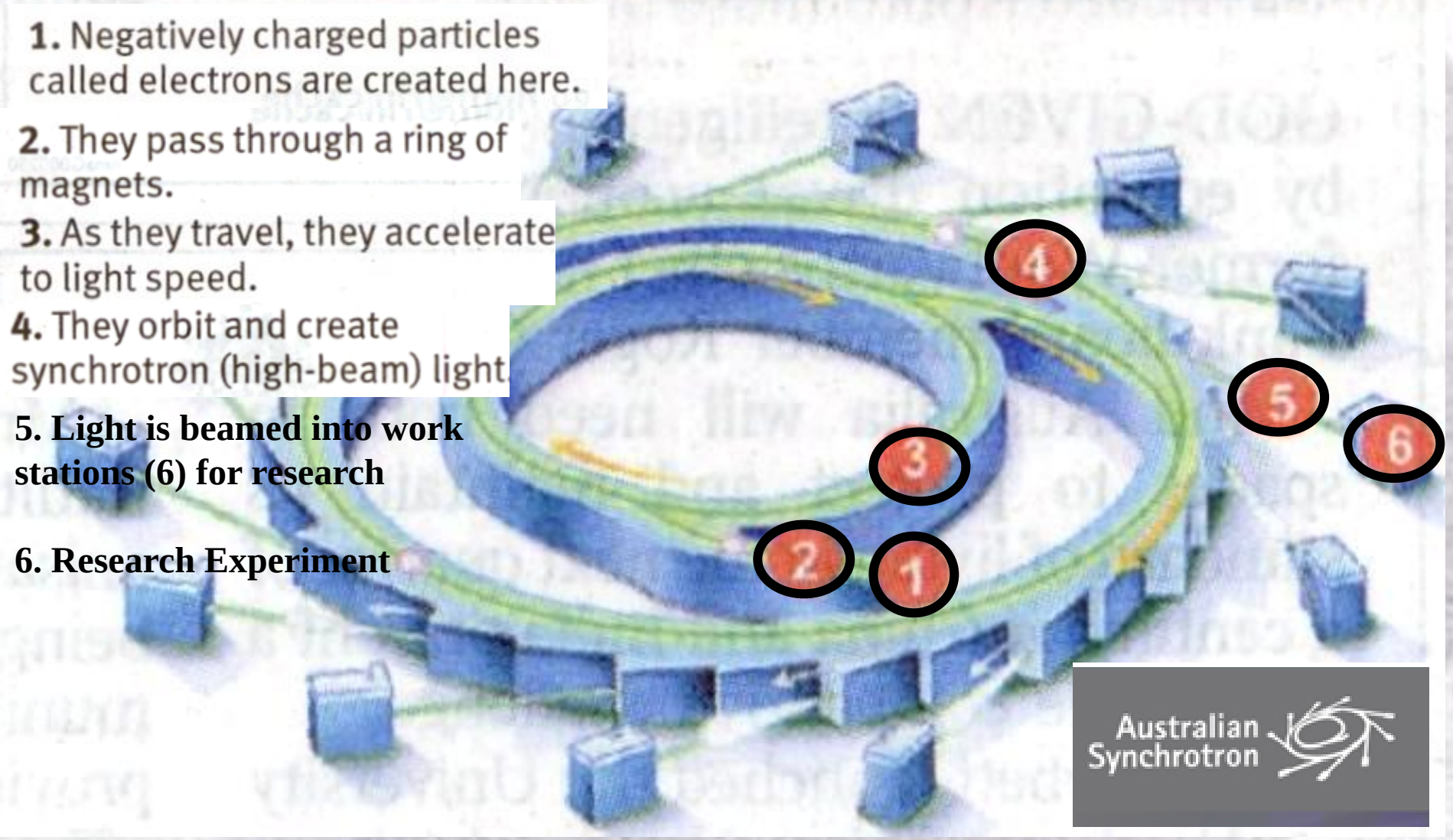
RELENZA is packaged in medicine disks called ROTADISKS® and is inhaled by mouth using a delivery device called a DISKHALER®.

- **Works by binding to the active site of the neuraminidase protein, rendering the influenza virus unable to escape its host cell and infect others**

http://en.wikipedia.org/wiki/Zanamivir

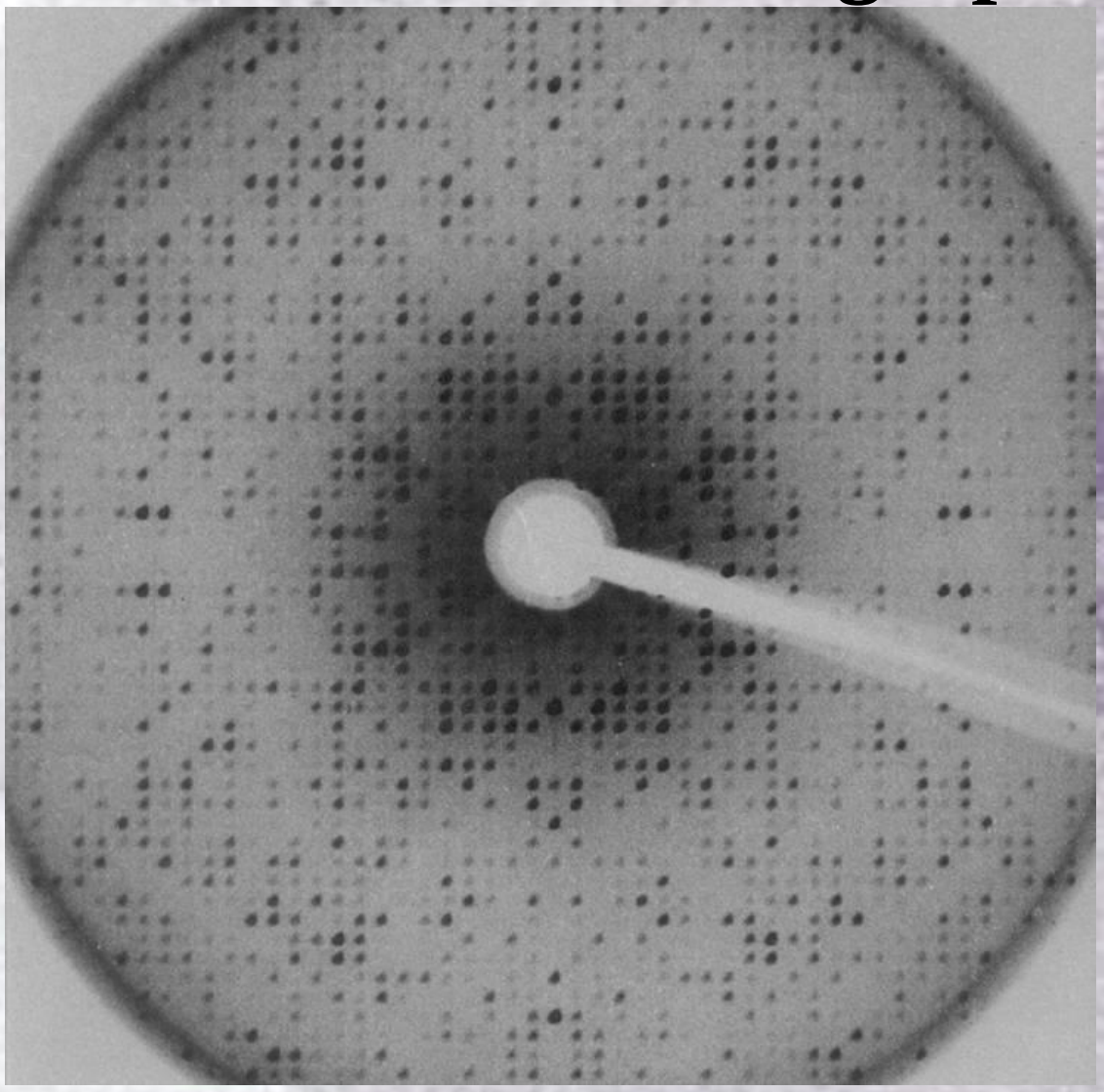
Australian Synchrotron, Monash University

CHARGE OF THE LIGHT BRIGADE



Australian 1st August 2007
p.21

Typical Protein X-ray Diffraction Photograph



Australian Synchrotron

- **Santosh Panjikar (AS, Monash) and Nausad Shaikh (IMB, UQ)) put the AutoRickshaw decision-making system to the test on November 2011, solving a protein structure in just 18 minutes**

http://www.embl-hamburg.de/Auto-Rickshaw/

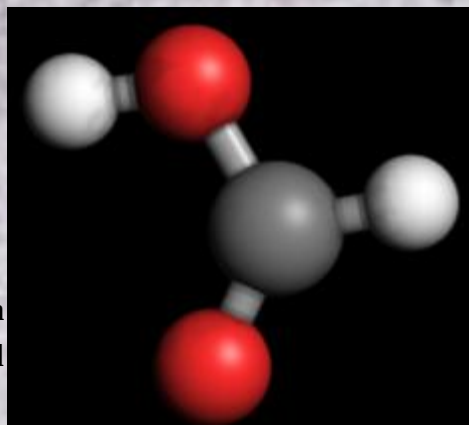
My Experience

- I was a practising Chemical Crystallographer, determining the structure of molecules (597) from 1958-1999
- When I started in 1958, my Supervisor suggested I used the old methods, such as a Madas Calculator and Beer-Lipson Strips to calculate structures using the following formula

$$\rho(xyz) = \frac{1}{V}\sum_h\sum_k\sum_l |F(hkl)| \cos 2\pi(hx + ky + lz - \phi(hkl))$$

Amplitudes — Phases

- I solved a 4 atom problem in a year (1958)
- The following year, 1959, I graduated to UTECOM computer
- I collected data on X-ray film; material not available today



http://www.xnumber.com/xnumber/madas.htm
www.xtal.iqfr.csic.es/Cristalografia/parte_09-en.html
http://www.flickr.com/photos/drsamc/5459247665/lightbox/

"The Crystal Structure of Anhydrous Copper(I1) Formate" by G. A. Barclay and C. H. L. Kennard, *J.Chem.Soc.*, 3289-3294,(1961)

"*Structure factors and Fourier syntheses were calculated on UTECOM, a Deuce digital computer, with programmes written by Dr. J. S. Rollett*"

Next slide: Comparison between Utecom and Home Desktop Pentium 4 PC October 2003

http://users.tpg.com.au/eedeuce/intro.htm

http://kartikcomputers.com/pdimg/Pentium4.jpg

http://pubs.rsc.org.ezproxy.library.uq.edu.au/en/content/articlepdf/1961/jr/jr9610003289?page=search

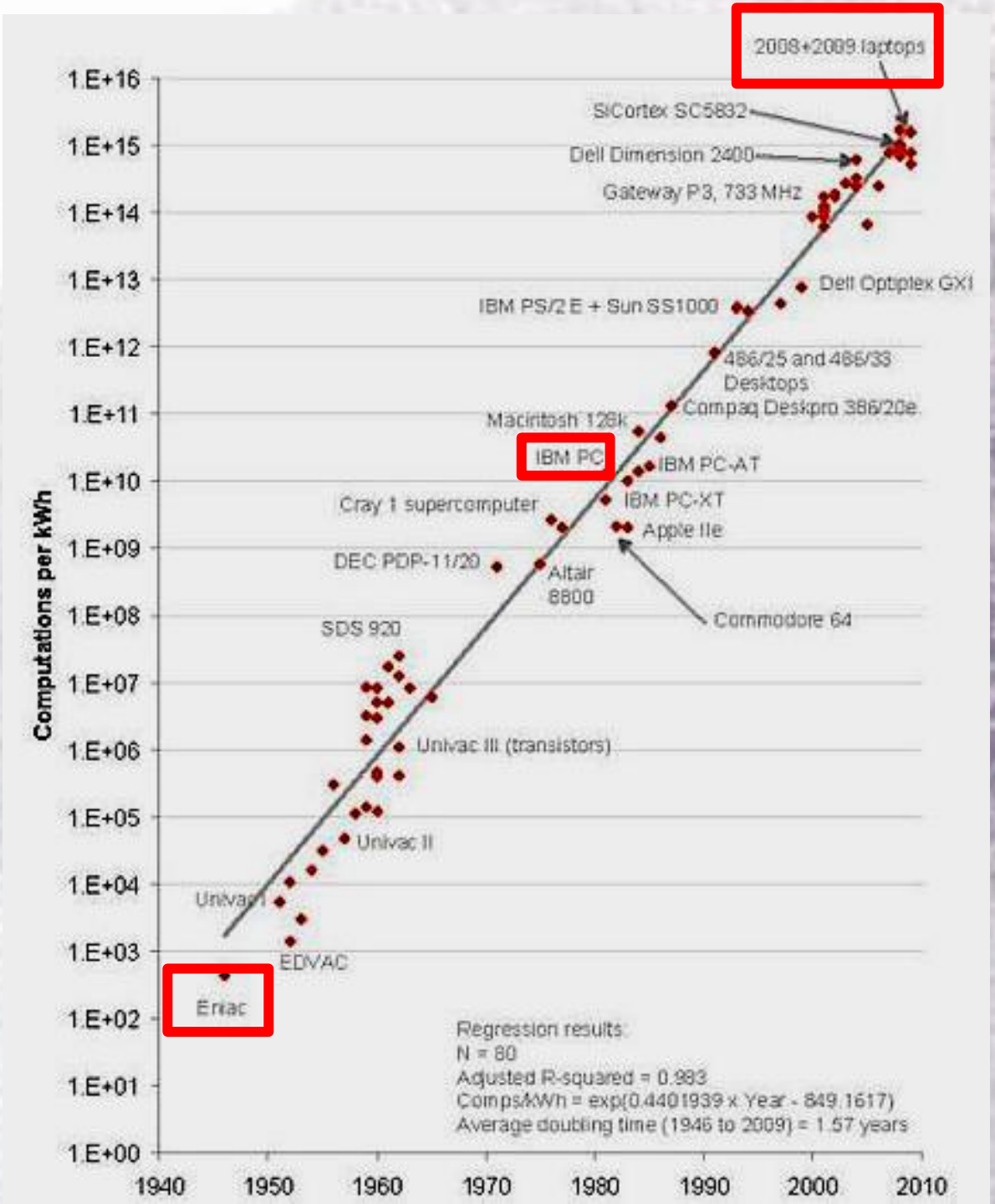
http://www.google.com.au/imgres?imgurl=http://www.members.optu

Published on 01 January 1961 on http://pubs.rsc.org |i:10.1039/JR9610003289.

snet.com.au/deucepix/raegertndaisy.jpg&imgrefurl=http://www.members.optusnet.com.au/deucepix/photoindex.htm&h=604&w=800&sz=60&tbnid=htukvJXhKFue3M:&tbnh=90&tbnw=119&prev=/search%3Fq%3Ddeuce%2Bmachine%2Bphoto%26tbm%3Disch%26tbo%3Du&zoom=1&q=deuce+machine+photo&docid=5nJH0iPzrawu_M&sa=X&ei=2XvVTq-2EK2imQXzs61q&ved=0CCMQ9QEwAA&dur=205

1 m = 1000 mm	Pentium 4 PC	UTECOM
	Pentium 4 Desktop PC	Deuce-Floor mounted computer
Active elements	42,000,000 Transistors	1,450 Thermionic Valves
Clock rate	500 MHZ System bus	1 MHZ
Additions per second	600,000,000	30,300
Mode	Parallel	Serial
Memory	256 MB Semiconductor	1.6 KB Acoustic - Mercury
Backing Store	40 GB Magnetic Hard Disk	32 KB Magnetic Drum
-- Rotation Speed	7200 Revs Per Minute	6510 Revs Per Minute
Monitor	17 inch Colour CRT	2 X 6 inch monochrome CRT
Input - Manual	110 key QWERTY keyboard	32 Input Dynamisiser toggles
-- Automatic	48 X - CD /RW	200 CPM Hollerith Card Reader
-- Transfer rate	7.2 MB per second	1,400 9 digit decimal numbers per minute
Output	Inkjet colour printer	100 CPM Hollerith Card Punch.
-- Transfer rate	10 pages per minute	700 9 digit numbers per minute
Operating System	Windows XP Home	NONE
Software	Word, MS Works etc	User contributed subroutine
Dimensions	-l 406mm –w 177mm –h 330mm	- l 4267mm –w 1371mm –h 2108mm
Weight	---- 31.75 Kg	--- 1193.85 Kg
-- Power Consumption	300 Watts	9,000 Watts
-- Power Requirements	240 Volts 1 phase 50 Hertz AC	440 Volts 3 phase 50 Hertz AC
-- Ventilation Requirements	20 cu. ft. per min. (Internal fan)	2000 cu. ft. per min. (External fan)
-- Space Required	4 sq. ft. desk area	92 sq. ft. floor area
Price	600 UK Pounds	50,000 UK Pounds
Total Sales	1,000,000,000 (PCs April 2000)	33 - From 1955 to 1964

http://users.tpg.com.au/eedeuce/intro.htm



Improvements with Computers

Koomey's law

- **Number of computations per joule of energy dissipated has been doubling approximately every 1.57 years**

http://en.wikipedia.org/wiki/Koomey's_law

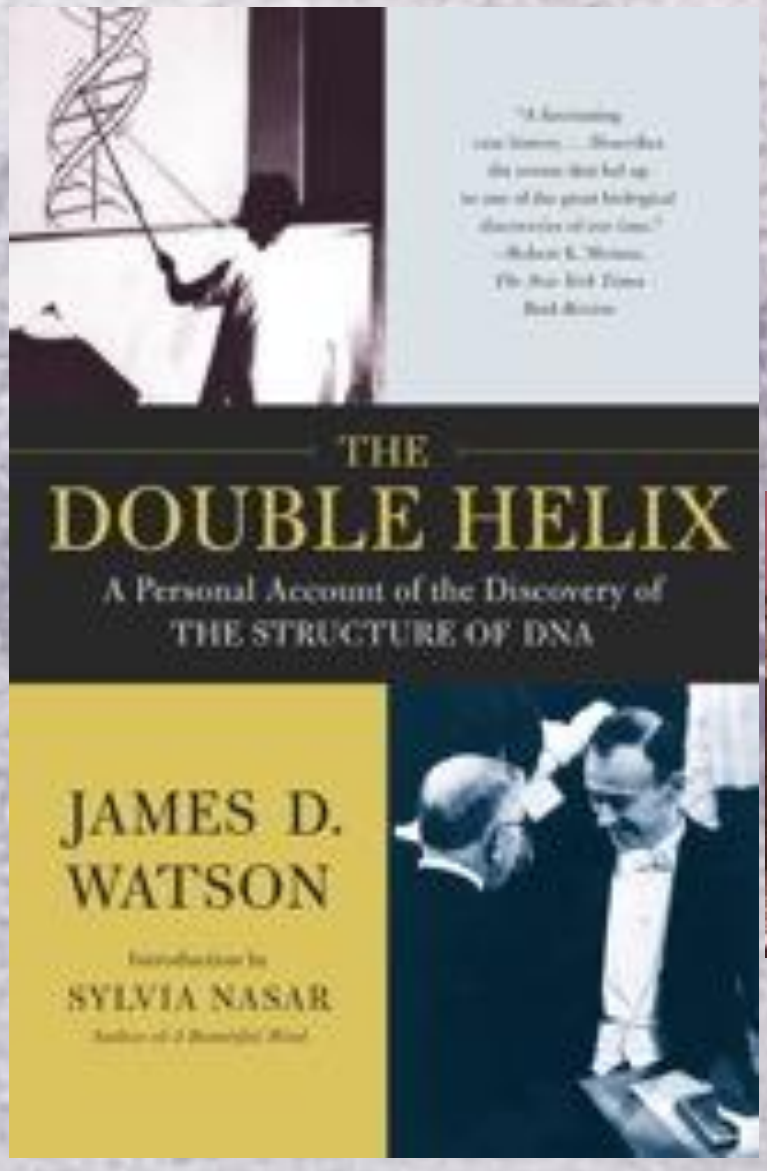
The Future

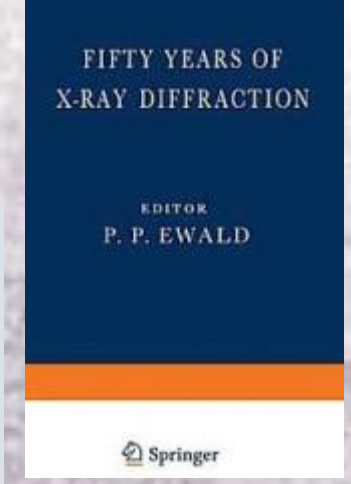
- **Designed to automatically produce publication quality structures for researchers who have no special training in chemical crystallography**

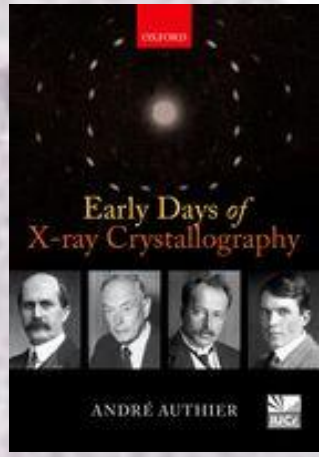
New Scientist

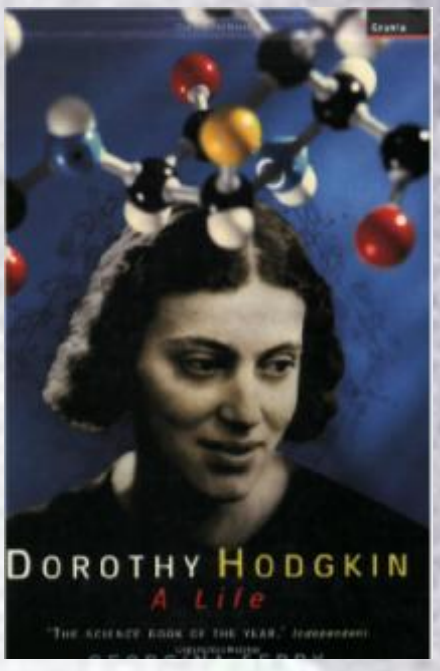
http://www.rigaku.com/products/smc/xtalabmini

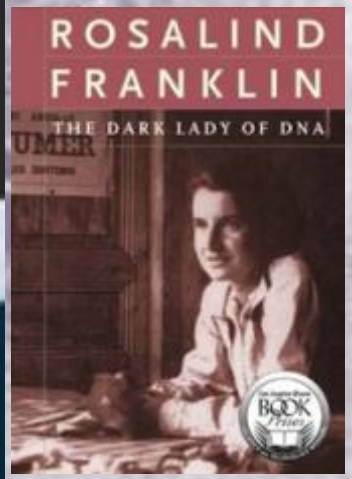
Interesting Books

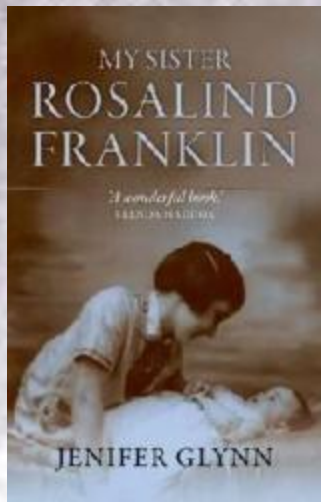




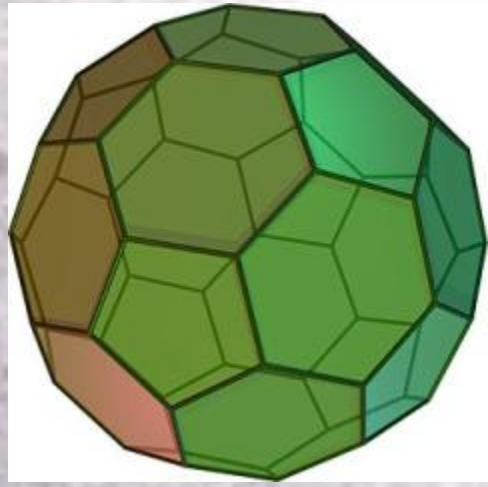


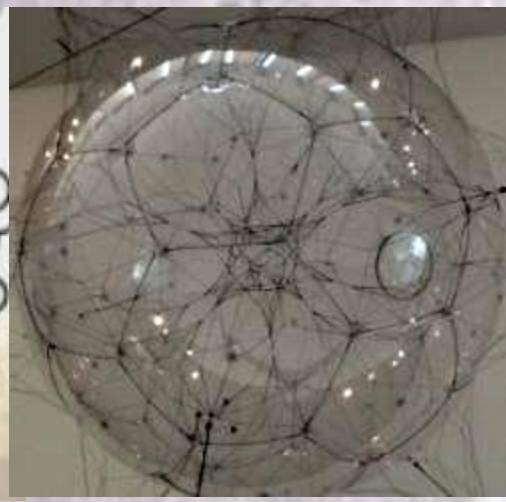






Art and Science





Sculpture by Donna Marius

Sculpture by Tomas Saraceno Harvest Exhibition GOMA

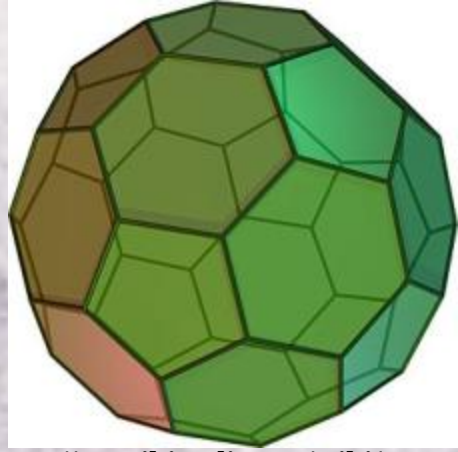
http://journeyjottings.com/blog/2011/03/street-sculptures-in-brisbane/

Art and Science

Icosahedron

There is a pentangular cap around every point

β-Rhombohedral Boron



http://en.wikipedia.org/wiki/Truncated_icosahedron

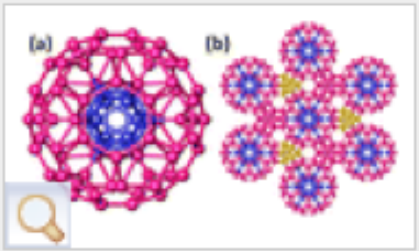
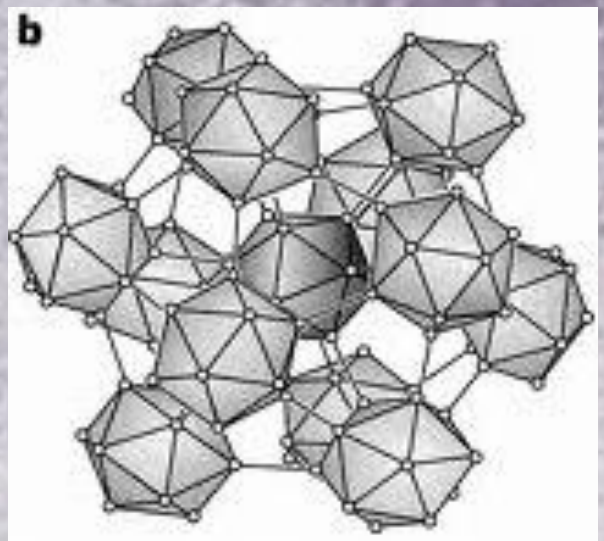


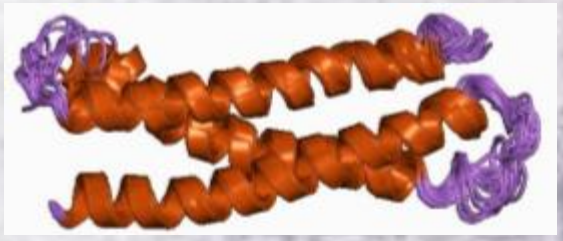
Figure 2. The crystal structure of β-rhombohedral boron in terms of B_{84} and B_{10} units. (a) B_{84} consists of a central B_{12} icosahedron (blue) surrounded by 12 half icosahedra (pink). (b) B_{84} units in adjacent rhombohedral unit cells connected via B_{10} cluster units (gold). This view is from the *c*-axis (perpendicular to the page). These layered structures stick to each other along this axis, and interstitial boron atoms (not drawn) lie between B_{10} clusters connecting the layers.

T. Ogitsu, E. Schwegler, and G. Galli, *Chem. Rev.*, 2013, *113* (5), pp 3425–3449



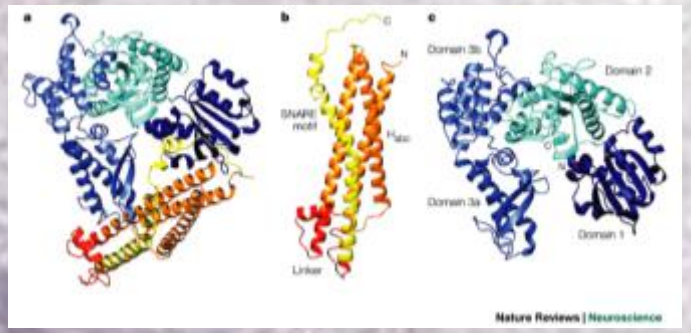
R.E.Hughes,C.H.L.Kennard,D.B.Sullenger,H.A.Weakliem, D.E.Sands and J.L.Hoard, "The Structure of β-Rhombohedral Boron", *J.Amer.Chem.Soc.*, 85, 361 (1962)

Topics covered by Professor Fred Meunier workshop 2 on "Crystals in the Brain"



Syntaxin

http://en.wikipedia.org/wiki/Syntaxin

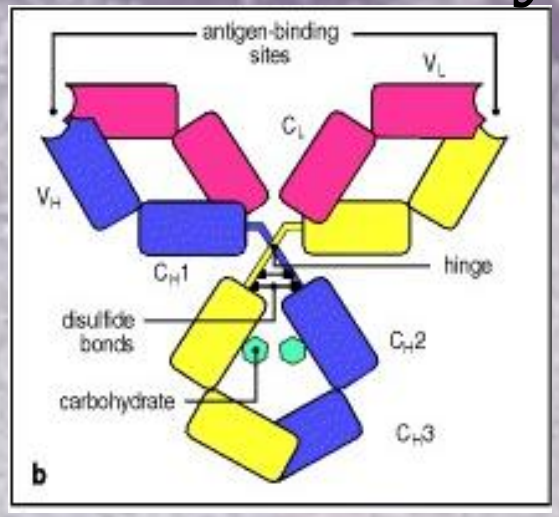


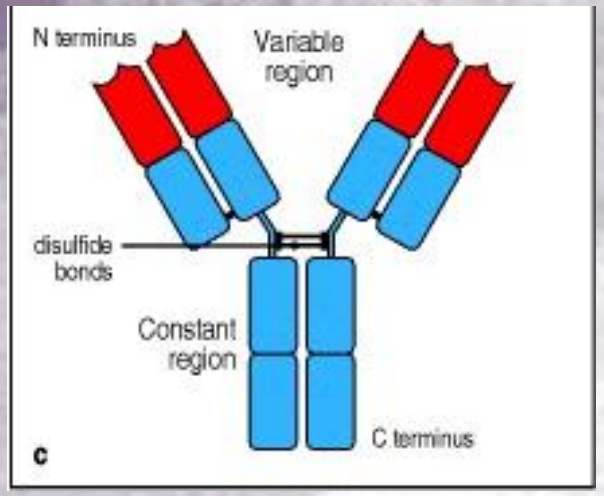
Munc18

http://www.nature.com/nrn/journal/v3/n8/images/nrn898-f4.gif

Shannon Best in workshop 6 on "Crystallography and the immune response to infection"

Structure of an antibody molecule



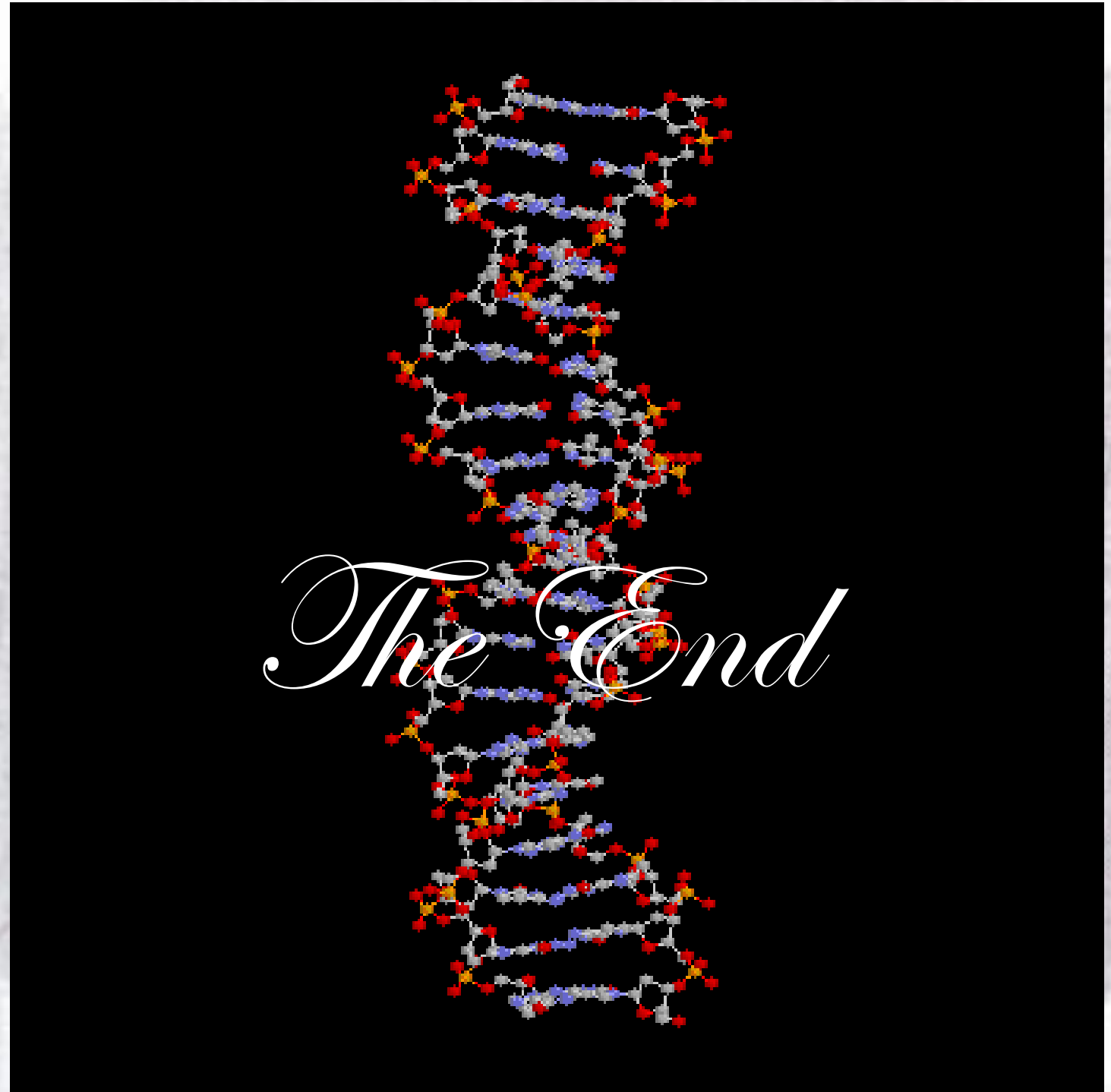


http://www.ncbi.nlm.nih.gov/books/NBK27144/

Advertisement from the sponsor
The International Union of Crystallography

Log onto this

http://www.youtube.com/watch?feature=player_embedded&v=uqQlwYv8VQI


The End