History of X-ray Crystallography and Early Indian Contributions

Talk delivered at the

University of Hyderabad
8-September-2014

Shekhar C. Mande
National Centre for Cell Science
Pune
Dazzling History

Over the past century, x-ray crystallography has transformed scientists' understanding of the structure and behavior of materials.

1913
Braggs determine crystal structure of diamond.

1916
Powder diffraction analysis makes it possible to study small crystals.

1924
John Desmond Bernal determines structure of graphite.

1937
James Sumner demonstrates that any protein can be crystallized.

1945 1964 Chemistry
Dorothy Hodgkin and colleagues determine structure of penicillin, the first complex molecule solved by x-rays.

1946 1994 Physics
First neutron diffraction experiments; the technique provides 3D structures and other details that x-rays cannot.

1952
Rosalind Franklin uses x-ray diffraction to image DNA and suggests it has a helical structure.

1912 1915 Physics
William Henry Bragg and his son William Lawrence Bragg publish Bragg's law, the key to using diffraction to infer crystal structure.
**Tomato bushy stunt virus**

First atomic-scale image of a complete virus; in this case, a plant virus. It revealed structural rules that were found to hold true in human pathogens a few years later.

**Ribosome**

The molecular machine that assembles proteins from instructions encoded in DNA.

**HIV trimer**

An X-ray crystallographic image of the hook that HIV uses to bind to human cells helped to resolve a debate about what this important protein looks like.

**Quasicrystals**

The first crystals were identified with atomic arrangements that do not repeat exactly, defying general wisdom about crystals.

**X-ray free-electron laser**

The Linac Coherent Light Source at the SLAC National Accelerator Laboratory in Menlo Park, California, went into operation, opening up a new world of imaging possibilities (see page 604).
Follow the IYCr2014 activities on Facebook

create your own exhibition
with ready-to-print panels available in different languages

Follow this link for Press and Media resources on IYCr2014.

Latest news

Australian commemorative coin

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June 10 http://t.co/02fOOGetc
RT @ccopalographer: Simon Coles asking an important question. I hope we do. #bca2014 http://t.co/7xCohnJMgg

#MalaysiaCelebrates1IYCr2014attheUniversityofI

Shekhar C. Mande

NCCS, Pune
Discovery of X-rays, 8-Nov-1895

X-rays discovered while studying effect of electric current through gas of extremely low pressure

Building up on the work of Lenard, Perrin and J J Thomson

Recent photograph

Before March 16, 1945

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Röentgen and possibility of discovering diffraction, 1897

*From W. C. Röntgen's Third Communication, March 1897:*

'The experiments on the permeability (for X-rays) of plates of constant thickness cut from the same crystal in different orientations, which were mentioned in my first Communication, have been continued. Plates were cut from calcite, quarz, turmaline, beryl, aragonite, apatite and barytes. Again no influence of the orientation on the transparency could be found.

'Ever since I began working on X-rays, I have repeatedly sought to obtain diffraction with these rays; several times, using narrow slits, I observed phenomena which looked very much like diffraction. But in each case a change of experimental conditions, undertaken for testing the correctness of the explanation, failed to confirm it, and in many cases I was able directly to show that the phenomena had arisen in an entirely different way than by diffraction. I have not succeeded to register a single experiment from which I could gain the conviction of the existence of diffraction of X-rays with a certainty which satisfies me.'
**Principle of X-ray generation**

Kaye, Sommerfield, 1909, “Bremsstrahl”

Barkla for characteristic X-rays (called the K-series and the L-series)

X-rays are produced when accelerated electrons collide the target

Loss of kinetic energy of electrons due to impact is manifested as X-rays

Continuous spectrum arises due to deceleration of electrons within the target

Characteristic spectrum arises due to inner shell electronic transitions

Moseley’s contributions

Shekhar C. Mande
WH Bragg interpreted ionization of gases as transfer of energy by photoelectric effect (unaware of Einstein’s work of 1905). X-rays are a stream of particles of neutral charge, or doublets of ± charged.

Open arguments with Barkla (upon discovery of polarization of X-rays in 1905) on the wave or corpuscular nature.

19 Nov 1908 Nature: As there are few opportunities in Australia for an investigator to place his views quickly before a scientific public, we print the above letter, but with it the correspondence must cease. The subject is more suitable for discussion in special journals devoted to physics than in our columns.

Diffraction by a slit:

Röentgen reported unsuccessful attempts, 1897
Sommerfield, fuzziness of fringes due to “diffraction” by a slit caused by considerable spectral range of X-rays.
The first photographs, June 1912

Conceptualized possibly during a walk with PP Ewald, January 1912

(1) According to Laue, the diffraction in a grating with regularities in three dimensions is most complicated and there is in such a grating a very little chance that a maximum may occur.

(2) The deviated spots seem to be much more distinct than should expected when the points were due to diffraction. It is also very difficult to understand how the scattered points can smaller than the middle point due to the primary rays.

(3) It is not easily understood how by diffraction a heterogenous beam can give such sharp maxima- and sharp maxima only. If the scattered rays are all due to diffraction, it must be from some homogenous group of rays which are mixed up with the primary one.

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John Jenkin, William and Lawrence Bragg, Father and Son, The most extraordinary collaboration in Science, Oxford University Press
The Diffraction of Short Electromagnetic Waves by a Crystal.
By W. L. Bragg, B.A., Trinity College. (Communicated by Professor Sir J. J. Thomson.)

[Read 11 November 1912.]

[Plate II.]

Herren Friedrich, Knipping, and Laue have lately published a paper entitled ‘Interference Phenomena with Röntgen Rays*, the experiments which form the subject of the paper being carried out in the following way. A very narrow pencil of rays from an

strength of a pulse reflected from a single plane will depend on the number of atoms in that plane which conspire in reflecting the beam. When two sets of planes are compared which produce trains of equal wave-length it is to be expected that if in one set of planes twice as many atoms reflect the beam as in the other set, the corresponding spot will be more intense. In what follows
Bragg’s law

\[ 2dsin\theta = n\lambda \]
Zinc Blende crystals are face centered cubic!

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Structure of NaCl

On Pope’s suggestions, Bragg took X-ray photographs of NaCl and reported its structure in June 1913.
The properties of the metals must depend, in the first place, on the properties of the individual atoms, and, in the second place, on the atomic arrangement, which is in effect the state of crystallization - William Henry Bragg (1925) "Concerning the Nature of Things"
Allotropes of Carbon:

Diamond and Graphite
Nobel Prizes of Discovery of X-ray Diffraction

Controversy on Penicillin Structure, 1944

Dorothy Crowfoot Hodgkin

As she later wrote: "I remember sitting on the steps of the Royal Society ... talking to Bernal and I was telling him that we had solved the structure of penicillin. He said 'you will get the Nobel prize for this.' I said 'I would far rather be elected a Fellow of the Royal Society' and he said 'that's more difficult'."

John Cornforth

"If that's the formula of penicillin, I'll give up chemistry and grow mushrooms." Hodgkin was correct, but Cornforth did not become a mushroom farmer.

Shekhar C. Mande

NCCS, Pune
Polypeptide Chain Configurations in Crystalline Proteins

Lawrence Bragg, J. C. Kendrew and M. F. Perutz

Missed the necessity of planar peptide bond unaware of resonance of the peptide group

Bragg to Perutz: I wish I had made you angry earlier!
Pauling’s series of 7 papers in PNAS, 1951

We assume that, because of the resonance of the double bond between the carbon-oxygen and carbon-nitrogen positions, the configuration of each residue is planar.

Dimensions of the polypeptide chain.

Pauling L et al. PNAS 1951;37:205-211
Pauling’s series of 7 papers in PNAS, 1951

CONFIGURATIONS OF POLYPEPTIDE CHAINS WITH FAVORED ORIENTATIONS AROUND SINGLE BONDS: TWO NEW PLEATED SHEETS

By Linus Pauling and Robert B. Corey

Gates and Crellin Laboratories of Chemistry, *California Institute of Technology, Pasadena, California

Communicated September 4, 1951

FIGURE 7
Drawing representing the parallel-chain pleated sheet structure.

FIGURE 8
Drawing representing the anti-parallel-chain pleated sheet structure.
Structural Models of Collagen
THE STRUCTURE OF FIBROUS PROTEINS OF THE COLLAGEN-GELATIN GROUP

BY Linus Pauling and Robert B. Corey

Gates and Crellin Laboratories of Chemistry, * California Institute of Technology, Pasadena, California

Communicated March 31, 1951
Madras model of Collagen & Ramachandran Map
“She is trying to get real Laue aufnahmen”
The Structure of the Benzene Ring in C$_6$(CH$_3$)$_6$.

By Kathleen Lonsdale, D.Sc. (London), Amy Lady Tate Scholar.

(Communicated by R. Whiddington, F.R.S.—Received January 25, 1929.)

Since benzene itself is not crystalline at ordinary temperatures the study of the benzene nucleus or ring has had to be referred to certain of its derivatives. The most hopeful line of attack appeared to be in the direction of the fully substituted derivatives, such as C$_6$Cl$_6$, or else by way of compounds such as naphthalene and anthracene which contain more than one ring. The results
An X-Ray Investigation of the Structure of Naphthalene and Anthracene

J. Monteath Robertson


The close relations between many of the dimensions of the crystal units of naphthalene and anthracene and those of the hydrocarbon C_{29}H_{60} are quite remarkable when we consider how different the substances are in their crystalline form and chemical constitution. These relations seem to afford strong evidence that the tetrahedral properties of the carbon atom are maintained in aromatic structures.
Atomic Physics and Related Subjects.: Communications to Nature.: Structure of Naphthalene and Anthracene

KEDAVESWAR BANERJEE

IN a paper published in the Proceedings of the Royal Society (vol. A, 125, p. 542 1929) on the structure of naphthalene and anthracene, J. M. Robertson comes to the conclusion that "the scattering centres lie nearer the ac planes than the bc planes, but no simple structure with a plane of symmetry parallel to the ac plane is possible", and that the scattering centres lie along a chain structure similar to hydrocarbons. On the other hand, the structure of hexa-methylbenzene as determined by K. Lonsdale (Proc. Roy. Soc., vol. 123, p. 537; 1929) suggests that the benzene rings in aromatic compounds should in all probability be plane structure. This has further support from the plane hexagonal structure of graphite (Ott, Ann. d. Phys., vol. 85, p. 81; 1928). As regards whether the scattering centres are nearer the ac plane or the bc plane, the optical and magnetic anisotropies which have been measured by S. Bhaga-vantam (Proc. Roy. Soc., vol. A, 124, p. 545; 1929) require that the carbon atoms should lie nearer the bc plane than the ac plane. The structure proposed by Robertson, however, does not explain the intensities of reflection from many of the crystal planes, which he supposes are due to small glancing angles for those particular reflections. But on evaluating the angle factors for the intensities it is seen that such large discrepancies cannot be explained in that manner.

This precedes Huckel’s rules (1931) on separation of sigma and pi orbitals

Shekhar C. Mande  
NCCS, Pune
Research Article

Nature 125, 456-457 (22 March 1930) | doi:10.1038/125456b0

Atomic Physics and Related Subjects.: Communications to Nature.: Structure of Naphthalene and Anthracene

J. M. ROBERTSON

I BELIEVE Dr. Banerjee’s structure to be essentially correct. It has been clear to me for some time that the last two sections of my paper to which Dr. Banerjee refers must be amended as regards the distribution of the scattering centres in the $a$ and $b$ directions. During last summer, Sir William Bragg made ‘absolute’ measurements of the intensities of the reflections from a number of anthracene planes. These measurements were expressed as ratios between the structure factors actually found, and the structure factor to be expected if all the atoms were in the reflecting planes. It was intended that these results and deductions therefrom should be incorporated with my paper, the publication of which was to be delayed for the purpose: unfortunately, owing to my absence from England, there was some confusion during the revision of the proofs and this was not done. Sir William Bragg’s figures lead to a structure resembling Dr. Banerjee’s so closely that it is interesting to give the following quotation from a letter which he wrote to me. It is in the form of notes upon a table of structure factors:
Determinations of the Signs of the Fourier Terms in Complete Crystal Structure Analysis

K. Banerjee

Proc. R. Soc. Lond. A 1933 141, 188-193
doi: 10.1098/rspa.1933.0111
Determination of the Absolute Configuration of Optically Active Compounds by Means of X-Rays

, PROF. J. M. BIJVOET, A. F. PEERDEMAN & A. J. van BOMMEL

1. van 't Hoff Laboratory, University of Utrecht
THE USE OF ANOMALOUS SCATTERING FOR THE DETERMINATION OF CRYSTAL STRUCTURES—KMnO₄

BY S. RAMASESHAN, F.A.Sc., K. VENKATESAN AND N. V. MANI

(Department of Physics, Indian Institute of Science, Bangalore-3)

Received May 10, 1957

\[ \Delta f' \text{ and } \Delta f'' \text{ for manganese for CuKα, CoKα and FeKα} \]
\[ f_0 \text{ for Mn is 25. The K-absorption edge of Mn} \ldots \text{1.895 Å} \]

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S. Ramaseshan speaking as Vice-President of the International Union of Crystallography at the Hamburg Congress in 1984.
PHYSICS

An Apparent Paradox in Crystal Structure Analysis

A commonly used test for the correctness of a crystal structure deduced from X-ray diffraction data is to perform a Fourier synthesis using the observed structure amplitudes (|F_o|) and the calculated phases (\(\alpha_c\)) in the Fourier coefficients (namely |F_o| \exp{i\alpha_c}) and to verify that this diagram gives peaks of the right magnitudes at the assumed positions of atoms and none elsewhere. It was thought worthwhile while examining what would happen if the amplitudes and the phases that are fed in belong to different structures. The tests that were carried out are briefly described here, together with an explanation of the results observed and their relation to the methods of structure analysis.

Utility of structures in understanding complexity of Nature
Sickle Cell Anemia caused by One Mutation

• Sickle cell anemia is caused by a point mutation in hemoglobin b chain (a is unaffected)

  val-his-leu-thr-pro-glul-glutamic acid side chain
  val-his-leu-thr-pro-val-glul valine side chain

• Only one amino acid is change in the entire sequence of the protein

  glutamic acid side chain -CH₂-CH₂-COO⁻ acidic side chain
  valine side chain -CH-(CH₃)₂ nonpolar side chain

• The hemoglobin molecule folds up and functions (binds oxygen)

• The mutation caused the protein to clump up in the cells

• The clumping up distorts the cell shape and makes them architecturally weaker
The surface of the protein has side chains sticking out.

Polar and charged side chains help the protein stay dissolved in water.

The glutamic acid to valine mutation is a surface mutation.
Crystal structure of Zanamivir: neuraminidase structure
Future Challenges

- Addressing fundamental problems in biology through understanding structures of many more molecules
- Understanding structure and assembly of large molecular complexes
- Ability to design compounds complementary to defined targets
- Ability to design potential vaccines
- Evolution of molecules that clean up the environment
Thank you!