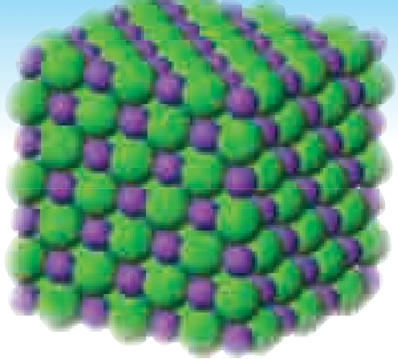

IYCr2014

The year 2014 was designated as the International Year of Crystallography. It commemorates not only the centennial of X-ray diffraction but also the 400th anniversary of Kepler's observation in 1611 of the symmetrical form of ice crystals, which began the wider study of the role of symmetry in matter.

CRYSTALS are pleasing to the eye. Their beautiful shapes and symmetries have always evoked a sense of amazement and wonder since antiquity. Crystalline materials are all around us and find applications in almost all walks of life.

More than 90% of the naturally occurring solids are crystalline. Minerals, rocks, sand, snowflakes, ice, clay, gems, jewels, metals, carbon, and salts all have crystalline structures. This is because regular arrangements of atoms results in lowest energy and hence greatest stabilization.

The Pulpí geode in Almería in southern Spain and crystal caves in Naica, Mexico (where selenite single crystals in excess of 10 m are found) are magnificent examples of the aesthetics of the natural crystalline world. Many living organisms also produce crystals, for example, calcite in the case of most molluscs.

Majority of today's artificially prepared materials used for technology are also crystalline. They include semiconductors, superconductors, light alloys, non-linear optical elements, catalysts, quasicrystals, liquid crystals, fullerenes and graphene.

X-ray crystallography has decoded the invisible structural world of these myriad crystals, further widening the applications to which crystals can be put. The design and synthesis of molecular solid-state structures with desired properties based on an understanding and exploitation of intermolecular interactions has come to be known as Crystal Engineering. Polymorphism, a phenomenon wherein the same chemical compound exists in different crystal forms is one of the most exciting branches of crystal engineering.

Early Research

The word crystal is believed to have originated two thousand years ago when the Greeks described the quartz crystals by the word krystallos, meaning ice due to their resemblance to frozen water. However, for scientists the aesthetics of the crystalline world has been more of a motivation for understanding the crystal structure and its various manifestations. However, the first scientific investigation into the regularity and symmetry of crystals began only in the 17th century.

In 1611, Johannes Kepler proposed that the hexagonal symmetry of snowflake crystals was due to a regular packing of spherical water particles. In 1669, Nicolaus Steno, the Danish geologist, observed in his book "De solido intra solidum naturaliter contento" that the angles between corresponding faces on crystals are the same for all specimens of the same mineral, which came to be known as Steno's law.

René-Just Haüy (1743–1822), the French mineralogist, contributed to this understanding further by proposing the concept of unit cell as a basic building block of a crystal. His interest in crystal structure was triggered when he accidently dropped a calcite crystal while viewing minerals collected by his friend and observed that it shattered along straight planes.

In 1803, John Dalton proposed atoms as basic constituents of matter. Gradually it led to a deeper understanding of how atoms bond together in different ways to form different molecules and solids. Orderly arranged atoms, physics told us, is a reason behind the beauty and symmetry of crystals.

We can consider atoms as points and imagine points arranged in space in an orderly manner. Such an array in which each point has surroundings exactly identical to the surrounding of any other point in that array is called a lattice. In such

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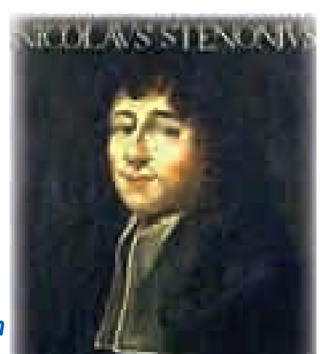


Nicolaus Steno

René-Just Haüy

the Story of Crystals

SANJAY D. JAIN
and
VILAS B. SAPRE

Hundred years after the development of X-ray crystallography, it still continues to be the leading technique for studying the atomic structure and related properties of materials.

a lattice if we attach an atom or a group of atoms, called the basis, then a crystal is formed. The smallest building block of a crystal so formed is then understood as the unit cell of that crystal. Just as a wall is built by systematic repetition of bricks, a crystal can be looked upon as a systematic repetition of unit cells in three dimensions.

In 1845, Auguste Bravais, a French physicist, showed that there can be only 14 such unique lattices, which are named after him as Bravais lattices, i.e., any crystal in nature can be understood in terms of only these 14 lattices. All crystalline materials recognized until now (excluding quasicrystals) fit in one of these arrangements. Bravais published a memoire about Crystallography in 1847.

Bravais lattices can be categorized into seven 'crystal systems', depending on the relations between distances between points in the unit cell, i.e., edges of the unit cell and between the angles between these edges – called the lattice parameters. Cube is the simplest and the most symmetric system for which all the edges of the unit cell are equal and are mutually perpendicular. Triclinic system is the least symmetric and most complicated as all the edges of the unit cell are unequal and also the angles between them are unequal.

In 1839, William Miller, an English physicist, published a *Treatise on Crystallography* in which he described the method of designating the directions and planes in a crystal using numbers called the Miller indices. These indices are widely used even today for specifying crystal planes.

Diffraction – A Key Concept

In the nineteenth century, optical microscopes were discovered and there were many attempts to understand the cause of symmetry in crystals using them. Metals were etched and examined under microscopes to reveal their microstructural features. However, all these investigations could not reveal anything smaller than the wavelength of light (4000-7000 Å). The reason behind this was understood on the basis of the phenomenon of diffraction.

The word diffraction was coined by the Italian physicist, Francesco Grimaldi in 1665 from the Latin word that meant breaking into pieces (referring to light breaking up in different directions). It has to do with bending of light and blurring of images. It was found that not just the light wave but any wave can be diffracted provided its wavelength is of the order of the size of the obstacle which diffracts that wave. Thus, sound waves, due to their large wavelengths – of the order of meters – get diffracted easily by everyday objects. This makes sound heard across close rooms. Light, on the other hand, is more difficult to bend due to its small wavelength.

Light is found to be diffracted by obstacles like thin slits and sharp edges. When a light wave encounters such an obstacle, the secondary waves interfere to produce regions of maximum and minimum intensity, called the diffraction pattern. Coloured rings around a street light in frosty weather and the pattern seen when a distant source of light is seen through a crack between two fingers are examples of diffraction pattern.

Special devices called gratings (an arrangement formed by ruling a large number of lines on a small glass plate so that the separation between adjacent lines is of the order of wavelength of light) were developed by David Rittenhouse in 1787, Joseph von Fraunhofer in 1821 and Rowland in 1882 to study the diffraction of light in a laboratory.

An interesting development took place on 8th November 1895, when W. C.

Auguste Bravais

W. C. Röntgen

W. C. Röntgen, the German physics professor, discovered accidently a new type of radiation which he named 'X-rays', due to its unknown nature and conspicuous properties. He found that X-rays travel in straight lines like visible light

Röntgen, the German physics professor, discovered accidently a new type of radiation which he named 'X-rays', due to its unknown nature and conspicuous properties. He found that X-rays travel in straight lines like visible light but do not show other properties of light such as reflection, refraction, diffraction or polarization.

Rontgen was awarded the first Nobel Prize in Physics for this work in 1901. He was also appointed to the chair of experimental physics at Munich University in 1900. The theoretical physics group at this University was headed by A. Sommerfeld.

Diffraction patterns produced by various obstacles were found to contain the knowledge of both the diffracting obstacle and the diffracted wave. Thus diffraction emerged as a key concept that promised to bring to fore connections between two lengths in nature: the length of the probing wave and the length (size) of the probed obstacle. We see next how this concept united X-rays with crystals.

Birth of X-ray Crystallography

In 1909, Max von Laue, who graduated from the University of Berlin where he worked with Max Planck, joined Sommerfeld's group. He had developed expertise in optics and contributed a chapter on wave optics for the Encyclopedia of the Mathematical Sciences, edited by Sommerfeld. He used optical diffraction gratings extensively and got motivated to use gratings for the study of X-rays. However, the X-rays would just pass through the slits of the grating without any diffraction.

A breakthrough occurred in 1912 when Laue got a brilliant idea during discussions with Paul Ewald, a graduate student of Sommerfeld, in the English garden in Munich. Ewald had proposed a resonator model of crystal lattice in his thesis but could not validate it using visible light due to its large wavelength. When Ewald informed Laue that the distance between the resonators, i.e., the atoms in the lattice assumed by him, was about thousandth of a wavelength of light, Laue got an exciting idea. Why not use X-rays, which have wavelength of the same order (he knew this from his experimental work in Roentgen's laboratory), as a natural grating to probe crystals?

Laue's contribution marks the birth of X-ray Crystallography. He was awarded the Nobel Prize in Physics in 1914 for this pioneering contribution.

Max von Laue

He pursued the idea further by exposing a copper sulphate crystal to X-rays and recording its diffraction pattern. The pattern (called Laue pattern) showed a large number of spots (called Laue spots) arranged in systematic circles. Laue extended his knowledge of the diffraction of light by a grating to the problem of diffraction of X-rays by a crystal and to fit his experimental results in the necessary theoretical framework. His work got published in the proceedings of the Bavarian Academy of Science.

When Einstein, who was born in the same year (1879) as Laue and became his lifelong friend, learnt about this work, he immediately sent Laue a postcard on 10th June 1912 saying, "I congratulate you warmly on your wonderful success. Your experiment is among the finest that physics has ever seen." Laue's contribution marks the birth of X-ray Crystallography. He was awarded the Nobel Prize in Physics in 1914 for this pioneering contribution.

In 1912, the knowledge of crystals got another boost when the father and son team of William Henry Bragg and William Lawrence Bragg pioneered this research further. Henry learnt about Laue's experiment in Leeds through a letter sent by Lars Vegard on 26th June 2012. He designed a spectrograph in which X-rays were incident on the crystal to be probed and the intensities of diffracted beam were measured as a function of the angle through which the X-ray beam got diffracted. When X-rays were incident on crystals at specific angles, intense peaks of diffracted radiation were observed at certain specific wavelengths.

Henry discussed it with Lawrence, who brooded over it and offered a convincing explanation to the Cambridge Philosophical Society on 11th November 1912. He modeled crystals as sets of

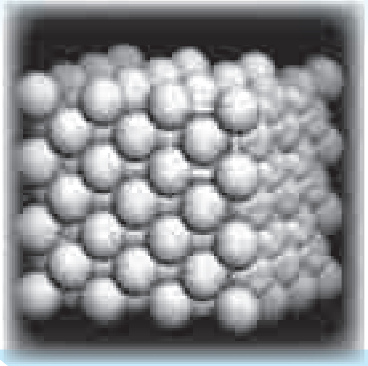
William Henry Bragg and William Lawrence Bragg

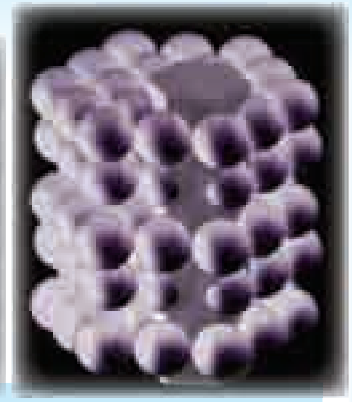
Anecdotes from the Lives of the Braggs

- W. H. Bragg was the first to use X-rays for radiography in Australia. He used it to examine the injured elbow of Lawrence, when he fell from his tricycle at the age of 5.
- W. L. Bragg was Director of the Cavendish Laboratory in 1953 when he played a part in the discovery of the structure of DNA by providing support to Francis Crick and James Watson. He delivered a talk about it at Guys Hospital Medical School in London on 14th May 1953. This was reported the very next day by Ritchie Calder in *The News Chronicle* of London, through an article, "Why You Are You. Nearer Secret of Life."
- W. L. Bragg believed that the field of crystallography was particularly welcoming to women because the crystal structures resembled objects like textiles, curtains, wallpapers, mosaics, and roses. In 1951, the Fes4val Pa: ern Group at the Fes4val of Britain hosted a collabora4ve group of tex4le manufacturers and experienced crystallographers to design lace and prints based on the X-ray crystallography of insulin, china clay, and hemoglobin. In 2008, the Wellcome Collection in London curated an exhibition on the Fes4val Pa: ern Group called "From Atom to Pa: erns."
- During 1912-14, the father and the son worked together. From 1914, both contributed to the war effort. W. H. Bragg worked on submarine detection and W. L. Bragg on sound ranging methods for loca4ng enemy guns. On 2 September 1915, Lawrence's brother was killed in the war and a few days later he received the news that he had been awarded the Nobel Prize. Both, along with other prize winners from 1915-1919, were invited to Stockholm in May 1920. But the pain of the war had destroyed the joy of the award and both refused to deliver a Nobel lecture. Though W. H. Bragg never delivered a Nobel lecture, Lawrence did it in 1922.

The structure of graphite was revealed as atoms arranged in stacked sheets such that within the sheet, atoms are held together by strong covalent bonds but sheets themselves are held together by weak van der Waals bonds. These revelations helped to understand why diamond is strong in all directions whereas graphite is soft and easy to cleave though both are pure carbon.

Graphene was discovered in 2004 by Andre Geim and Konstantin Novoselov of University of Manchester for which they were awarded the Nobel Prize in physics in 2010. Graphene is about one atom thick lattice of graphite


FCC structure


HCP structure

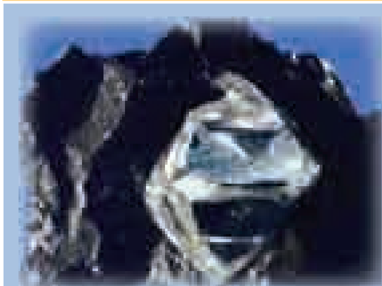
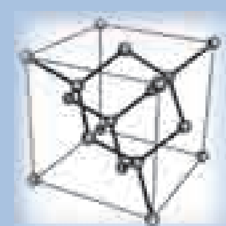
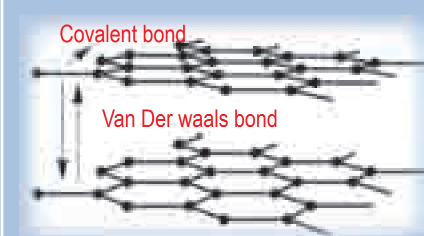
parallel atomic planes that diffract X-rays at different angles and derived a law, $2d \sin\theta = n\lambda$, which connects these angles, θ (called the Bragg angle), with the wavelength of X-rays, λ; the spacing, d between the planes responsible for diffraction; and the order of diffraction, n. Bragg's law became the foundation of X-ray crystallography.

Bragg's law provided a powerful new tool for studying crystals using X-ray diffraction. W. H. Bragg and W. L. Bragg were awarded the Nobel Prize in physics in 1915 for their discovery. So far, they are the only father-son team to jointly receive this honour. W. L. Bragg was 25 years old then, making him the first Australian and the youngest Nobel laureate so far.

The United Nations declared 2014 as the "International Year of Crystallograph" to celebrate the completion of 100 years of these groundbreaking discoveries. This decision was announced by the International Union of Crystallography on 4th July 2012.

Our knowledge about the crystal world owes a lot to the pioneering work of the Braggs father and son team. It is worthwhile to know more about them (see box).

Table 1:
STRUCTURES OF DIAMOND AND GRAPHITE AS REVEALED BY X-RAY CRYSTALLOGRAPHY

Natural Crystal	Structure revealed by X-ray crystallography
 Diamond	
 Graphite	

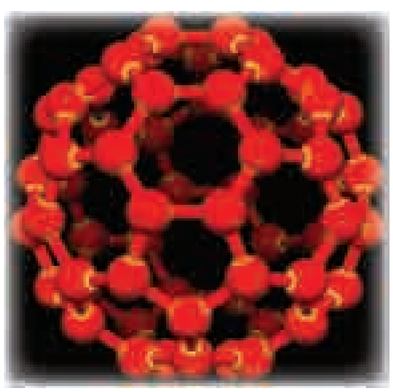
Understanding the Crystal Structure

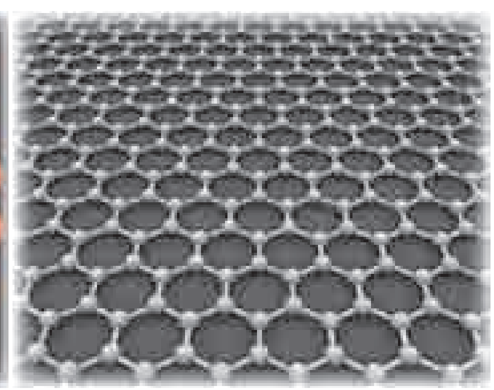
The pioneering work of Laue and Bragg led to the evolution of the following simple recipe to 'see' the inner structure of crystals using X-rays:

1. Expose the crystal, whose structure is to be determined, to X-rays.

2. Record the diffraction pattern and find the angles and intensities of the diffracted X-rays.

3. Using mathematical methods and other known data for the crystal, convert these two-dimensional images into a three-dimensional model of the density


C_{60}: Buckminsterfullerene


Graphene

Crystallographic image of a snowflake
(Courtesy: International Union of Crystallography)

of electrons within the crystal and then determine the mean positions of the atoms in the crystal and other related information.

The first structure, determined in this manner, was that of table salt in 1914. In the same year, the structure of diamond was deciphered as the tetrahedral arrangement of carbon atoms held together by strong covalent bonds (Table 1) that were estimated to be 1.52 Å long. Two years later, the structure of graphite was revealed as atoms arranged in stacked sheets such that within the sheet, atoms are held together by strong covalent bonds but sheets themselves

CRYSTALS AROUND US

- Crystals such as Rochelle salt develop an electrical voltage across its two faces if the faces perpendicular to these faces are squeezed (piezoelectric effect). Inversely, alterna4ng voltage applied to the two faces of such a crystal results in alternate contraction and expansion of the perpendicular faces producing ultrasonic waves. Piezoelectric crystals are used in radio transmitters and 4mepieces.
- Crystals such as Nicol prism have the ability to bend light into its component colors and are used in crystal polarimetry, a technique by which light is polarized. Polarimetry has extensive applica4ons in optics.
- Crystalline silicon is used in solar photovoltaic panels to convert sunlight into electricity. Research into the crystalline aspects of semiconductors is thus significant to the future of solar energy.
- Zeolites, highly porous crystalline materials, are used in petroleum refinement to obtain be: er and cleaner fuel.
- The ability of fullerene molecules to trap different atoms and molecules has led to several applica4ons in the medical field, e.g., a radio isotope encapsulated $C6_0$ has successful applica4on in cancer therapy. Fullerenes can also improve an4wear, an4seize and an4fric4on properties of lubrica4ng oils.
- Graphene has many poten4al industrial applica4ons due to its remarkable strength, very low weight, and high electrical and thermal conductivity. For example, graphene is a promising candidate for bio-electric sensory devices, which find wide usage in LCD touch screens.
- Single crystals of calcite located in the inner ear control our equilibrium. Research into the crystalline properties of such materials is useful in the development of biocompa4ble materials.
- The study of the mineral composi4on of planets using X-ray crystallography can provide vital clues to probe into the deeper secrets of these planets. On 17th October 2012, the Curiosity rover on planet Mars performed the first X-ray diffraction analysis of the Martian soil, which revealed the presence of minerals such as feldspar, pyroxenes and olivine.
- The spa4al arrangement of atoms and molecules in drugs can be visualized using crystallographic techniques helping us to understand how drugs work and how they can be improved.
- Materials used in precious works of art can be iden4fied using crystallographic techniques helping us to understand the reactions that cause these materials to age. The crystalline pa: erns also inspire new decora4ve designs in art.

Dorothy Hodgkin and the models of penicillin structure determined by her using X-ray crystallography

are held together by weak van der Waals bonds. These revelations helped to understand why diamond is strong in all directions whereas graphite is soft and easy to cleave though both are pure carbon.

In this way, X-ray crystallography brought forth the atomic order of several solids. Most metals were discovered to crystallize in face-centered cubic (e.g., aluminium, copper, gold, iridium, lead, nickel, platinum, silver, etc.) and hexagonal close packed (e.g., beryllium, cadmium, magnesium, titanium, zinc, zirconium, etc.) structures due to the maximum packing of atoms (74 %) achievable with these structures.

In addition to diamond and graphite, two more allotropic forms of carbon, viz., fullerenes and graphene, were discovered in later years. The first fullerene molecule was discovered in 1985 at Rice University by Robert Curl and Richard Smalley along with Harold Kroto of University of Sussex for which they received the Nobel Prize in Chemistry in 1996. It was named C_{60}: Buckminsterfullerene after Buckminster Fuller who created the famous geodesic dome structures, the architecture of which the molecule resembles.

Graphene was discovered in 2004 by Andre Geim and Konstantin Novoselov of University of Manchester for which they were awarded the Nobel Prize in physics in 2010. Graphene is about one atom thick lattice of graphite, which comprises of carbon atoms that form hexagonal rings. Graphene is the thinnest and the strongest material known to us.

World of Crystals

After the initial understanding of simple structures scientists were now keen to know about more complicated structures. The fields of mineralogy and metallurgy were the first to be benefited through determination of structure of garnet in 1924 and that of the silicates in 1920s. Determination of the structure of hexamethylbenzene by Lonsdale in 1928 established the hexagonal symmetry of benzene.

The first atomic structure of protein was determined by John Kendrew, an English biochemist, who shared the Nobel Prize in Chemistry with Max Perutz in 1962.

Dorothy Hodgkin, a British Chemist, pioneered the development of protein crystallography and deciphered the structures of cholesterol (1937), penicillin (1946) and vitamin B12 (1956), for which she was awarded the Nobel Prize in Chemistry in 1964. In 1969, she solved the structure of insulin after working for thirty five years.

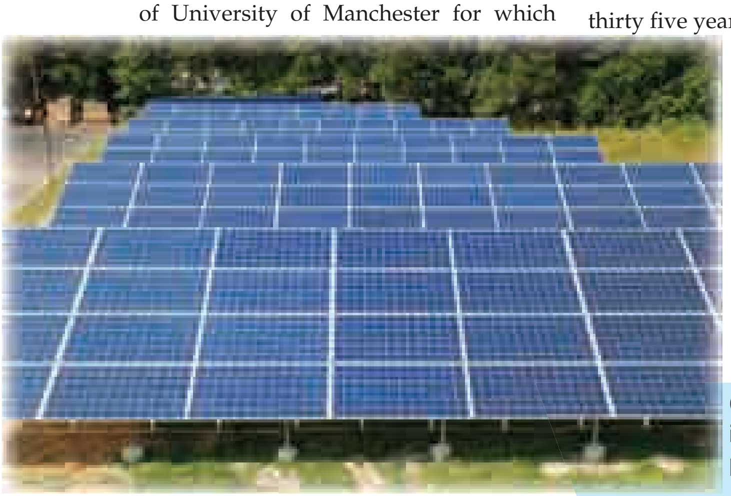
John Kendrew

The first atomic structure of protein was determined by John Kendrew

As mentioned earlier, X-ray crystallography also played an important role in the discovery of the structure of DNA by Crick, Watson and Wilkins in 1953.

X-ray crystallography thus opened the floodgates of knowledge of the world of crystalline materials making it vital to many disciplines such as physics, chemistry, biology, mineralogy, metallurgy, materials science and engineering, geology, medicine and pharmaceutics. Out of the 500,000 structures that have been recorded in the Cambridge Structural Database, over 99% were determined by X-ray diffraction. No wonder, as many as 29 Nobel Prizes have been awarded to the discipline of X-ray crystallography so far.

Hundred years after the development of X-ray crystallography, it still continues to be the leading technique for studying the atomic structure and related properties of materials. And for years to come it is poised to be at the centre of advances in many fields of science.



Crystalline silicon is used in solar photovoltaic panels

Crystal's beautiful shapes and symmetries have always evoked a sense of amazement and wonder since antiquity.

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