COMMENTED CHRONOLOGY OF CRYSTALLOGRAPHY AND STRUCTURAL CHEMISTRY

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Crystal comes from the Greek κρύσταλλος (*krystallos*), that means "ice", from κρύος (*kruos*), "icy cold" or "frost" (VIII BC). The Greeks used the word *krýstallos* with a second meaning that designated "rock crystal", a variety of quartz.

On the occasion of the International Year of Crystallography, and of the centennial of the award of Nobel prizes related with the discovery of X-ray diffraction, the Library of Physics and Chemistry (Biblioteca de Física i Química) of the University of Barcelona organized in 2014 an exhibition on the historical evolution and the bibliographic holdings of these two closely related subjects.

This chronology, far from being comprehensive, provided the conceptual basis for the exhibition, collecting dates, authors and main achievements. This summary is in part based on the following sources (a term in blue contains a link to the cited source):

La Gran Aventura del Cristal. J. L. Amorós, ed. Universidad Complutense de Madrid, 1978.

Historical Atlas of Crystallography, ed. J. Lima-de-Faria, The International Union of Crystallography, Dordrecht-Boston-London: Kluwer Academic Publishers, 1990.

A través del cristal, M. Martínez Ripoll, J. A. Hermoso, A. Albert, eds., Chapter 2: "Una historia con claroscuros plagada de laureados Nobel". M. Martínez Ripoll, Madrid: CSIC, 2014.

Early Days of X-Ray Crystallography. A. Authier. Oxford University Press, 2013.

"2014: Anno della Cristallografia. Quattro secoli di avventura", D. Aquilano. *Emmeciquadro*, nº 52, March 2014, 1-7.

Timelines of Crystallography. Web page of the International Union of Crystallography.

IV century BC - Plato (427-374 BC)

Before the crystal ***- The Platonic solids***

Plato geometrized matter. Mathematics, in particular geometry, are at the basis of every physical phenomenon. He proposed the five regular polyhedra known today as *Platonic solids*: tetrahedron (fire), octahedron (air), icosahedron (water), and cube (earth), to which was later added the dodecahedron to represent the universe.

Carved stone prehistoric polyhedra, Ashmolean Museum, Oxford. Photograph: S. Alvarez

III BC - Theophrastus (372-287 BC)

Before the crystal - ***Description of crystals***

The Greek philosopher, disciple of Aristotle, described the regular shape of crystals in his treatise *De lapidibus* (bilingual edition in English and Greek, 1965).

7 BC - Strabo (ca 64 BC – 24 AD)

Before the crystal - ***Introduction of the term crystal***

Writes *Geographika*, in 17 volumes, in which he describes the ancient world from the Atlantic to the Indus River, mentions the existence of quartz in the Indies and introduces the use of the Greek word ***krystallos*** (crystal).

I AD - Pliny the Elder (23-79)

Before the crystal - ***Crystal morphology, exfoliation***

Great compiler of Roman science in his *Natural History*. Writes on stones and gems. Refers to the morphology of crystals. Does not understand why quartz presents hexagonal faces. Recognizes the regularity of diamond. Talks about exfoliation.

1476 - Albertus Magnus (1193 - 1280)

Before the crystal - ***Mineralogy, mining and metallurgy***

De Mineralibus Libre Quinque, Augsburg: Sigmund Grim[m] and Marx Wirsung, 1519. This book is one of the most important medieval treatises on mining and metallurgy, and contains observations on precious stones and alchemy. The first printed edition appeared in 1476 (Gutenberg introduced printing in Europe in 1450).

1546 - Georg Agricola (1494 – 1555)

Before the crystal - ***Mineralogy, mining and metallurgy***

De Ortu et Causis Subterraneorum [and other works]. Basel: Hieronymus Frobenius and Nikolaus Episcopius, 1546 (in UB, edition of 1558). First modern systematic text on mineralogy. The largest part of this edition of five works of Georg Agricola on mineralogy, geology and mining is a refutation of the ideas of the ancient philosophers, alchemists and astrologers.

1550 - Girolamo Cardanus (1501 – 1576)

Atoms, packing, bonding - ***Crystal shape and spheres packing***

Shape, geometry and crystal structure

Probably the first attempt to explain the shape of crystals as the result of a close packing of spheres. *De Subtilitate*, Nuremberg: John Petreius, 1550.

1597 - Andreas Libavius (1571-1630)

Shape, geometry and crystal structure - ***Geometry of crystals***

First systematic textbook on chemistry, *Alchymia*, Frankfurt: J. Saurius, 1606. Libavius first recognized the geometrical characteristics of crystals, and identified the salts deposited by evaporation of mineral waters from the shapes of the crystals formed.

1600 approx. - Unknown inventor

Instrumentation, diffraction and radiation sources - ***Optical microscope***

It is said that lens manufacturers made the first optical microscopes towards the end of the XVIth century in the Netherlands. Giovanni Faber coined the term *microscope* for Galileo's instrument in 1625, while Galileo called it "occhiolino" or "little eye".

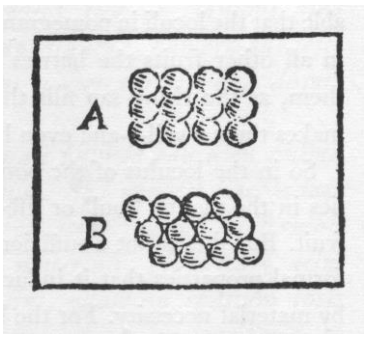
1611 - Johannes Kepler (1571-1630)

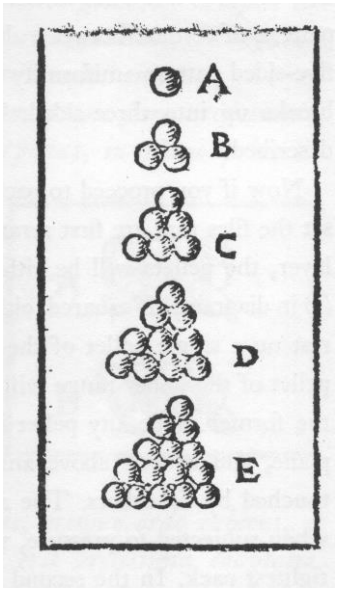
Atoms, packing, bonding ***- Snowflakes***

Shape, geometry and crystal structure

Becomes interested in the hexagonal shapes of the snowflakes, and tries to explain them using geometrical concepts. He makes the observations using a new scientific instrument that Pierre Gassendi (1592-1665) names *engyscope*, the microscope. Kepler's interest in snowflakes could arise from a neoplatonic consideration: How comes the snow crystals are hexagonal when the Platonic ideal for perfection was represented by regular polyhedra of cubic symmetry? *Strena Seu de Nive Sexangula*, Frankfurt: Gottfried Tampach, 1611.

Based on the Greek atomism, Kepler studies the packing of identical spheres in the most compact possible way, in an attempt to explain the hexagonal symmetry of the snow crystals. He arrives at the conclusion that each sphere has six neighbours in the same plane at the same distance, and a total of twelve closest spheres in the upper and lower layers. In this way Kepler formulates the compact packing of spheres.



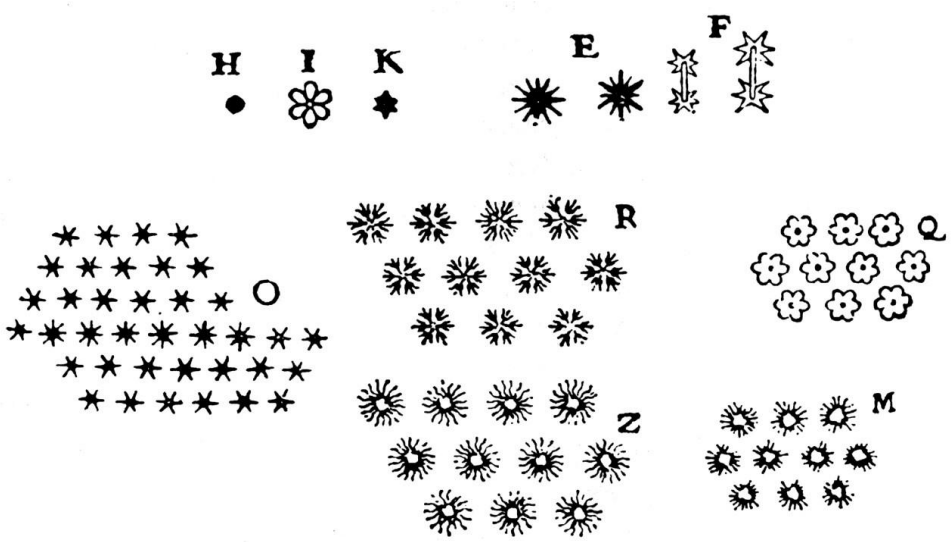


1637 - René Descartes (1596 - 1650)

Atoms, packing, bonding - ***Snowflakes***

Shape, geometry and crystal structure

The French mathematician and philosopher also publishes studies on snowflakes and worries about the regular stacking of the particles that constitute the crystals.

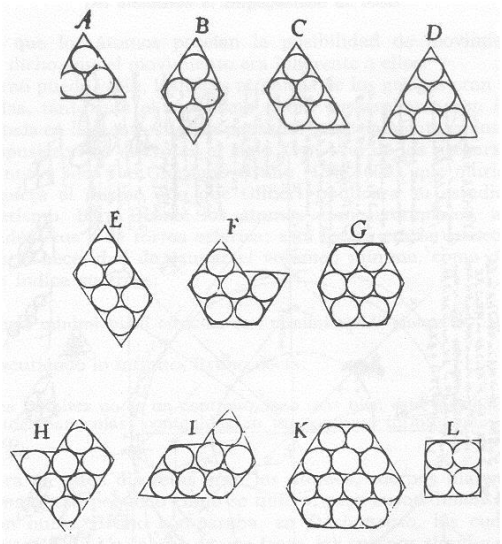


1665 - Robert Hooke (1635-1703)

Atoms, packing, bonding - ***Figures generated by spheres***

Shape, geometry and crystal structure

Hooke, disciple of Robert Boyle (1626-1691), experiments with pellets and concludes that a wide variety of figures can result from a few distributions of particles. He tries to explain the crystal morphology based on the stacking of atoms. In his work *Micrographia* he reports on the regularity of the small quartz crystals observed with the recently invented microscope and proposes that they are formed by spherules.



1669 - Nicolás Stensen or Nicolaus Steno (1638-1686)

Shape, geometry and crystal structure - ***The angles between crystal faces***

Observations on crystal morphology led him to the conclusion that certain angles between faces of crystals of a natural specimen are constant. This is the first quantitative approach in the study of crystals and can be considered as the departing point of crystallography as an independent discipline. *De Solido intra Solidum (On Solids within Solids)*, Florence: Ex Typographia sub Signo Stellae, 1669. Stensen also advances a hypothesis on the growth of crystals from solutions.

1690 - Christiaan Huyghens (1629-1695)

Atoms, packing, bonding - ***Ellipsoidal atoms and exfoliation***

Shape, geometry and crystal structure

Proposes ellipsoidal atoms to explain the exfoliation of calcite.

Light and crystals - ***Light polarization***

Discovers the polarization of light by Iceland spar: *Traité de la Lumière*, Leiden: Pierre van der Aa, 1690.

1723 - Moritz Anton Cappeller (1685-1769)

Shape, geometry and crystal structure - ***First treatise on crystallography***

The Swiss physicist Maurice Capeller (Kappeler, or Moritz Anton Cappeller) publishes *Prodromus Crystallographiae* in Lucern, the first treatise on crystal shapes. The introduction of the term *crystallography* is attributed to Capeller.

1735 - Carl Linnaeus (1707-1778)

Shape, geometry and crystal structure - ***Morphological classification of crystals***

Known for his system of classification of biological species, Linnaeus describes 40 shapes of mineral crystals in *Systema Naturae*.

1772 - Jean Baptiste Romé de l'Isle (1736-1790)

Shape, geometry and crystal structure - ***Conceptual bases of crystallography***

This French crystallographer and mineralogist publishes in 1772 *Essai de cristallographie*, and in 1783 *Cristallographie ou description de formes propres a tous les corps de règne minéral*, two pillars of a new science. In *Christallographie* he includes more than 450 descriptions and drawings of crystals. Delisle (as he is also known) defines the crystal in this way:

> *"Crystals are all the bodies of the mineral kingdom, that have polyhedral and geometrical shape, formed by plane faces that form well defined angles"*

Considers that the shape of a crystal is a consequence of the packing of elemental particles, called *integrant molecules*, with a specific shape, probably polyhedral. Generalizes the law of constancy of angles postulated by Steno for quartz crystals:

"Crystals have a more or less perfect polyhedral or geometrical shape, but its angles present constant values for each species".

In 1773**,** in his work *Description Méthodique d'une collection de Minéraux* presents a classification of his personal collection of minerals and distinguishes seven types of crystal shapes. Distinguishes minerals that had been previously confused, such as ruby and spinel.

1773 - Tobern Bergman (1735-1784)

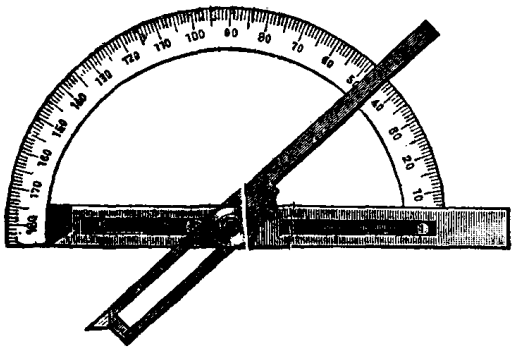
Shape, geometry and crystal structure - ***Classification of minerals***

Chemist and mineralogist, disciple of Linnaeus, described the crystal forms of calcite. Developed also a classification of minerals based on chemical characteristics, with subclasses organized by their external shapes.

1780 - Arnould Carangeot (1742-1806)

Instrumentation, diffraction and radiation sources - ***Contact goniometer***

First instrument that permits the measurement of angles between faces of a crystal and allows for a quantitative geometrical description.



1781 - Réné-Just Haüy (1743-1822)

Symmetry - ***One of the founders of modern crystallography***

In 1781 presents his first work to the Academy of Sciences in Paris, on the structure of garnet, followed by a general theory of the structure of crystals. In 1822 publishes *Traité de Cristallographie*, Paris: Bachelier et Huzard.

Haüy developed a mathematical theory of crystal structure that turned out to be remarkably accurate and gave crystallography a legitimate place among the sciences.

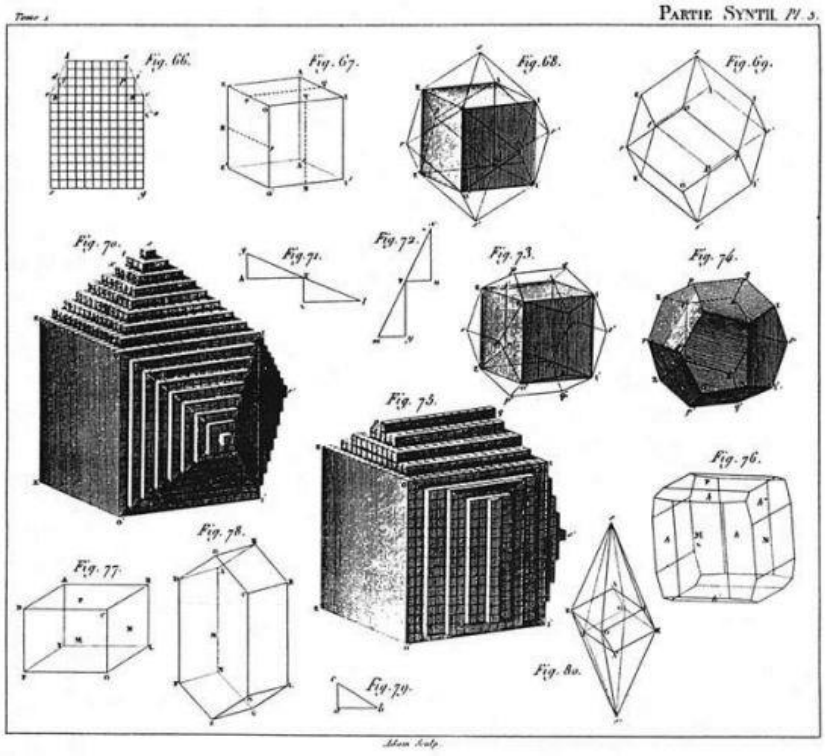
According to the most popular story, Haüy dropped a calcite crystal and, when it broke, he noticed that each small piece had faces similar to those of the larger crystal. Further attempts to cleave the smaller crystals along the same lines as the larger one proved that the interfacial angles (the angles between each set of faces) remained the same no matter how small the crystals were made. Haüy deduced that this was because a "unit cell" (which Haüy called an *integral molecule*) existed that was the same shape as any of the visible crystals and that the crystals were all made up of these invisible unit cells that stacked together to form the larger crystals. He further suggested that the unit cells were made of small cubes that, by stacking in specific arrangements, could be made to form any of

the crystal shapes seen in nature. By changing the manner in which these unit cells were stacked, all the different faces and interfacial angles of the crystals then known (and all known today) could be explained. Although the existence of atoms was still not fully accepted at this time, Haüy's theory demanded some sort of internal structure to crystals that made possible the outward forms we see.

The law of symmetry stands out as one of the foremost contributions by Haüy. It is more an intuition than a true scientific law, but warned crystallographers on the importance of symmetry. This is one of its possible formulations:

> *"A given type of decrement repeats itself on all the parts of the nucleus that are so similar that they can be substituted one for the other, when changing the position of this nucleus with respect to the eye. I call this parts identical."*

According to Haüy, it was enough to determine the primitive shape from the exfoliations and apply different decreases to the edges and vertices of the primitive parallelepiped. In this way, a symbolic terminology could be introduced to unambiguously describe the morphology of a crystal. This proposal is the embryo of the later symbols for faces and edges.



In 1784, in *Théorie sur la Structure des Cristaux*, explored how the edges, angles and faces of a crystal are related by symmetry. *Essai d'une Théorie sur la Structure des Crystaux*, Paris: Chez Gogué & Née de la Rochelle, 1784.

1801 - Réné-Just Haüy (1743-1822)

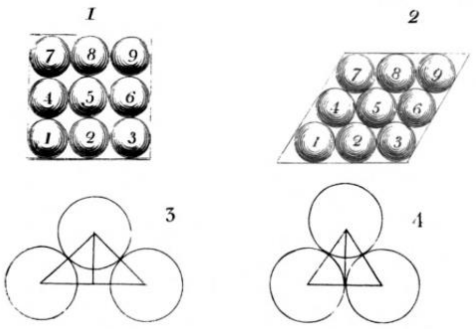
Shape, geometry and crystal structure - ***The unit cell***

In his *Traité de Minéralogie*, published in 1801, Haüy describes how the Law of rational indexes establishes relationships between the orientations of the crystal faces, and explains that crystalline solids are formed by replicas of a unit cell.

1808 - John Dalton (1766-1844)

Atoms, packing, bonding - ***Atomic theory***

The British chemist and physicist develops the atomic theory of matter. In his landmark book *A New System of Chemical Philosophy*, London: R. Bickestraff, the crystals are considered as a periodic coalescence of spherical atoms.

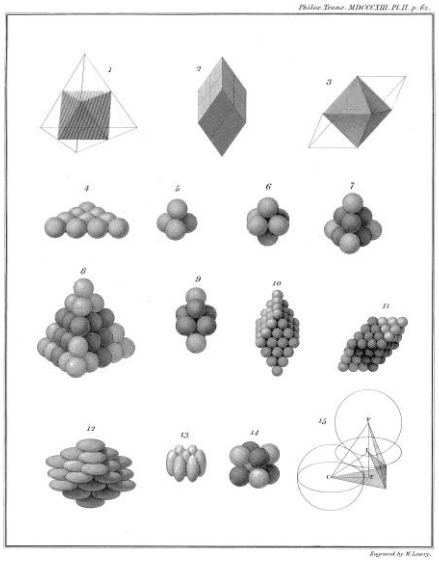


1808 - William Hyde Wollaston (1766-1828)

Instrumentation, diffraction and radiation sources - ***The invention of the reflection goniometer***

Atoms, packing, bonding - ***Spheres packing model***

Disciple of Dalton, Wollaston invents the reflection goniometer, based on the reflection of light by the faces of the crystal, much more precise than the contact goniometer. The new instrument allows measuring the angles between faces in much smaller crystals. He studies the packing of spheres that he considered to be a good model to explain the structure of crystals, even if he did not go beyond the establishment of a hypothesis.



1811 - François Jean Dominique Arago (1786-1853)

Light and crystals - ***Rotation of polarized light by quartz***

Arago observed the rotation of the plane of polarization of light by *rock crystals* (a transparent variety of quartz). He studied polarized light together with Frenkel, invented the first polarizing filter in 1812, and designed the first polarimeter.

1815 - David Brewster (1781-1868)

Light and crystals - ***Optical crystal isotropy and anisotropy***

Symmetry - ***Crystal symmetry and optical properties***

This Scottish physicist classifies crystals according to their optical properties, as *isotropic*, *uniaxial*, or *biaxial*.

Formulates the law of the polarization angle previously suggested by Malus, and names the system of colour rings generated by crystals *figures of light interference*. He observes two cases; in one case the figure consists of a series of concentric circles, crossed by a black line, and in the second case the figure consists of a series of distorted ellipses with two clear centres. The black cross is converted into two hyperboles when the crystal rotates, in contrast with the first case, in which it remains fixed upon rotation. He establishes that the character of the optical properties of a crystal depends on its symmetry.

His observations on a considerable number of crystal species demonstrated that cubic crystals are isotropic, while tetragonal, hexagonal and rhombohedral crystals are uniaxial, and rhombic, monoclinic and triclinic crystals are biaxial. *A Treatise on Optics*, 2ª ed., Philadelphia: Carey, Lea & Blanchard, 1838.

1815 - Jean Baptiste Biot (1884-1826)

Light and crystals - ***Rotatory power of organic compounds***

He observes for the first time that some organic compounds, such as camphor, sugars or tartaric acid also rotate the plane of polarization of the light. In 1818 he established the relationship between the magnitude of the rotation of polarized light, the length of the optical path and the wavelength, and defined the molecular *rotatory power* [α]. He also confirms that some quartz crystals deviate the plane of polarization to the right, while other crystals deviate it to the left: *Ann. Chim. Phys., 2me Sér.*, **9** (4), 372-389 (1818); accessible in digital version.

1815 - Augustin Jean Fresnel (1778-1827)

Instrumentation, diffraction and radiation sources - ***Theory of diffraction of light***

Fresnel extended the wave theory of light to double refraction and diffraction, and established the laws of interference of the rays of polarized light. "Mémoire sur la diffraction de la lumière", *Ann. Chim. Phys.*, **11**, 246-295, 337-378 (1819); available in electronic version.

From experiments on the optics of biaxial crystals he deduces that the refraction index, or equivalently the speed of light, of the ordinary light beam is not constant in these crystals. Explains the double refraction and associated phenomena. Proposes that the optical properties of a crystal can be described by means of a revolution ellipsoid (nowadays termed *optical indicatrix*) for the uniaxial crystals, and by three non-equivalent axes for the biaxial crystals. *Oeuvres completes d'Augustin Fresnel*, Bordeaux: Bergeret, 1995.

1816 - Samuel Christian Weiss (1780-1856)

Shape, geometry and crystal structure - ***Crystal axes***

German geologist and mineralogist, Weiss derives four crystal systems and considers two more derived from them. Introduces a new point of view in the study of crystal morphology as a consequence of the trend that transformed geometry into analytical geometry, based on the works of Descartes, Fermat, de la Hire, Bernouille, and Euler among others. Crystallographic calculations using spherical trigonometry is incorporated to the study of crystals thanks to a close collaboration between crystallographers and mathematicians.

One of the most important contributions from Weiss is the selection of some axes whose direction and magnitude are defined by the inclination of the crystal faces. He calls them crystal axes and labels them *a, b* and *c*, nomenclature that is still in use. Defines a series of crystal systems, based on the existence of different crystal forms that require axes with specific dimensions and direction. Conceives a set of transformations that permit to generate a triclinic prism from a cube.

Establishes the *law of rational intersections* (based on the works of Haüy), and the concept of zone and the *law of zones* rooted in the observation that most of the faces of crystals are parallel to a certain direction.

Weiss provides a method that describes the faces of a crystal in a clear and universal way, using the intersections of the face with the crystal axes. The length of the intersections (parameter) is not constant but depends on the size of the crystal. What are constant for a given face are the relationships between these parameters. Weiss employs this *parametric ratio* as a symbol for the face.

1819 - Eilhard Mitscherlich (1794-1863)

Shape, geometry and crystal structure - ***Polymorphism and isomorphism, a controversy***

Working on phosphates, sulphates and arsenates, shows that different chemical compositions can give raise to the same crystal shape, in contradiction with the proposal of Haüy.

Eilhard Mitscherlich René Just Haüy Jöns Jacob Berzelius

The chemical analysis aragonite, an abundant mineral in Molina d'Aragón, had shown that its composition was the same as that of calcite, or calcium carbonate. The possibility that calcium carbonate could appear as two different mineral species was hard to accept according to Haüy's postulates.

After Mitscherlich it is accepted that the same crystal form may appear in different chemical substances (*isomorphism*) and that the same chemical substance may adopt crystal shapes of different symmetries (*polymorphism*).

"Über die Kristallisation der Salze, in denen das Metall der basis mit zwei Proportionen Sauerstoff verbunden ist", *Abh. K. Akad. Wiss. Berlin*, 427-437 (1819).

1822 - Réné-Just Haüy (1743-1822)
Shape, geometry and crystal structure - - ***Polymorphism and isomorphism, a controversy***

Haüy postulated, "to each specific substance with a well defined chemical composition, capable of existence in a crystalline form, it corresponds a shape that is specific and characteristic of that substance."

1822 - John Herschel (1792-1871)
Symmetry - ***Crystal handedness and optical rotation***
Light and crystals

Proposes a causal relationship between the handedness of quartz crystals (right- or left-handed) and the direction of their optical rotation. "On several remarkable Instances of deviation from Newton's Scale in the Tints developed by Crystals, with one Axis of Double Refraction, on exposure to Polarized Light", *Trans. Cambridge Philos. Soc.*, **1**, 21-53 (1822).

1822 - Friedrich Mohs (1773-1839)
Shape, geometry and crystal structure - ***The seven crystal systems***

German mineralogist, Mohs enumerates the seven crystal systems, or types of polyhedra that can pack regularly filling space.

1830 - Johann Friedrich Christian Hessel (1796-1872**)**
Symmetry - ***Crystal classes***

Develops a method for deducing possible combinations of symmetry elements in crystals, based on Haüy's law of rational indexes, and concludes that there are 32 such combinations which constitute the so called *crystal classes*. *Kristallometrie oder Krystallonomie und Krystallographie*. This result went unnoticed for 60 years and was derived in an independent way by Aksel Gadolin in 1867. *Abhandlung über die Herleitung aller krystallographischer Systeme*.

1833 - Franz Ernst Neumann (1798-1895)
Symmetry - ***Crystal symmetry and physical properties***

Proposes that any symmetry present in a crystal must be reflected also in the symmetry of all its physical properties: "Die thermischen, optischen und krystallographischen Axen des Krystalsystems des Gypses", *Ann. Phys.*, 103, 240-274 (1833).

1839 - Willian H. Miller (1801-1870)
Shape, geometry and crystal structure - ***Indexation of crystal faces***

Introduces a simple notation that relates the faces of a crystal with coordinate axes, the Miller indexes. Mohs, Levy (1825) and Naumann (1826) had previously proposed less practical notations. Miller's indexes are used also to describe lattice planes and, after the discovery of X-ray diffraction, to index diffraction diagrams. W. Miller: *Treatise on Crystallography*, Cambridge: J. and J. J. Deighton, 1839.

1840 - Friedrich Ludwig Hünefeld (1799-1882)

Chemical crystallography - ***First crystallization of a protein***

Describes the first crystallization of a protein that we are aware of, coming from earthworms. In his book *Der Chemismus in der thierischen Organisation*, Hünefeld explains how he obtained lamellar crystals after putting blood of an earthworm between two slides. Felix Hoppe-Seyler introduced the name “haemoglobin” in 1864 to refer to the "colouring substance of blood". The physiologist Claude Bernard proposed its role as an oxygen carrier around 1870. F. L. Hünefeld, *Der Chemismus in der thierischen Organisation* (Chemical Properties in the Animal Organization, p. 160-161), Leipzig: F. A. Brockhaus, 1840.

1849 - Moritz L. Frankenheim (1801-1869)

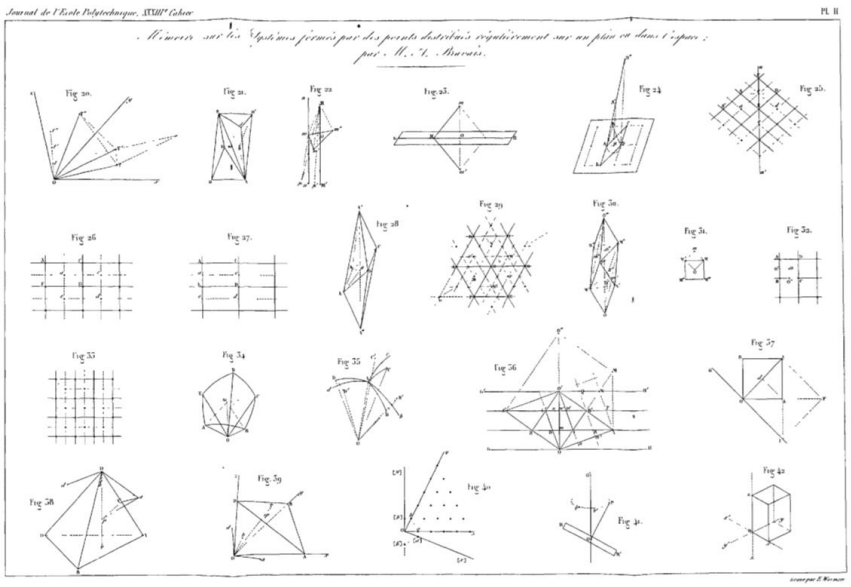
Shape, geometry and crystal structure - ***The Bravais lattices***

In "Crystallonomische Aufsätze" (Essays in crystallography), *Isis*, *19*, 497-515, 542-565 (1826), Frankenheim assigns symmetry elements to the crystal systems defined by Weiss and Mohs, and defines 32 crystallographic point groups (crystal classes), classified in four crystal systems (regular, quaternary, binary and sexenary). From his observations he derives 15 types of crystal lattices.

1850 - Auguste Bravais (1811-1863)

Shape, geometry and crystal structure - ***The Bravais lattices***

Reduces the number of crystal lattices proposed by Frankenheim to 14, known today as *Bravais lattices*. Independently from Hessel, studies the symmetry relationships between polyhedra, based on the symmetric distribution of their vertices. Deduces the relationships between the symmetry elements. Proposes 32 crystal classes.



Precursor of the lattice theory of the crystal, Bravais considers a system of points or *lattice nodes* at regular intervals that he names *rows.* By equidistant and parallel repetition of a row one obtains a *plane*, and by stacking the plains a *lattice* is obtained. The lattice defined in this way is infinite and homogeneous, and the volume of the parallelepiped defined by three non-coplanar translations is constant.

Publishes in 1851 *Études cristallographiques* in which he develops the idea that a crystal is the result of the aggregation of molecules of the same species, kept in their equilibrium positions by the action of attractive and repulsive forces. A. Bravais, *Études Cristallographiques*, Paris: Gauthier-Villars, 1866.

1849 - Thomas Young (1773-1829)

Light and crystals - ***Interference of the wave-light***

He carried out an experiment, making two holes with a pin in a black piece of paper. Looking through the holes at a certain distance from a source of light, he observed a series of rings alternatively bright and dark. With this experiment he discovers the interference of light and interprets it based on the wave hypothesis. See *Miscellaneous works of the late Thomas Young*, vols. 1 and 2, General Books, 2009.

1847 - Louis Pasteur (1822-1895)

Symmetry - ***Dissymmetry and optical resolution of enantiomers***

Discovers one of the most important concepts in crystallography: *dissymmetry. Oeuvres de Pasteur.* "Mèmoire sur la relation qui peut exister entre la forme cristalline et la composition chimique, et sur la cause de la polarisation rotatoire", *C. R. Acad. Sci.* **26**, 535-538 (1848).

Mitscherlich observed that sodium and ammonium tartrate and paratartrate, two seemingly identical substances, presented different optical activity. Pasteur hands out a work on this topic to an elder Biot, to be presented to the Academy of Sciences of Paris. Having read it, Biot invites Pasteur to replicate the experiments at his home. Prepares a solution of paratartrate and lets it crystallize. A few days later selects the two types of hemihedral crystals: right- and left-handed. Biot determines

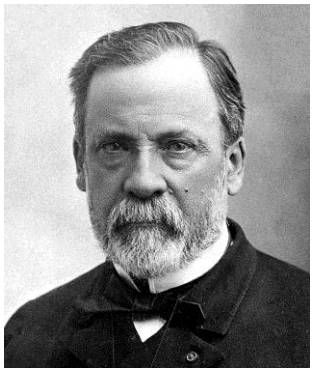
himself the optical activity of the crystals and verifies Pasteur's prediction: the right-handed ones were dextrorotatory and the left-handed ones were levorotatory.

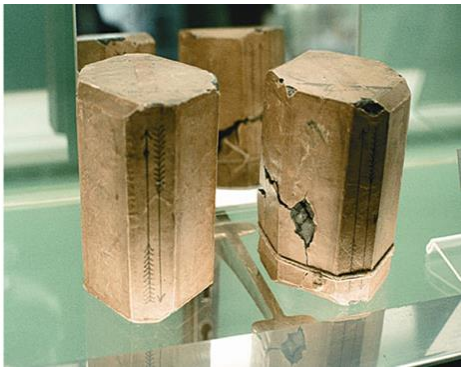
Pasteur demonstrated that all the tartrates that were optically active in solution were hemihedral, and the optically inactive paratartrate was in fact a combination of the same number of molecules of the two identical tartrates, one left-handed, and the other one right-handed, with opposing optical activities that resulted in no net optical activity. He also demonstrated that the crystals of one species were the mirror image of those of the other species:

> *"In the same way that there is a right hand identical but not superimposable to the left hand"*.

Observed that there are two types of optically active substances. In some cases, as in quartz, it is the crystal that is optically active, whereas the SiO_4 structural units are not, and the activity is due to the spatial distribution of the structural units within the crystal. In other substances, as in the salts of tartaric acid, it is the molecular dissymmetry that gives raise to the optical activity.

> *"All the artificial products obtained in the laboratory have a superimposable image. On the contrary, most of the natural organic products, I would say practically all if I refer only to those that play an important role in the phenomena of vegetal and animal life, are dissymmetric, and their mirror images cannot be superimposed."*





1874 - Jacobus Henricus van 't Hoff (1852-1829)
Atoms, packing, bonding - ***Tetrahedral carbon***

Van't Hoff and Le Bel independently propose the tetrahedral shape of the carbon atom in organic molecules. *Voorstel tot uitbreiding der tegenwoordig in de scheikunde gebruikte structuur-formulas in de ruimte* (Proposal to extend to the space the structural formulae currently used in Chemistry) Utrecht, 1874.

***ca.* 1870 - Évariste Galois** (1831-1832), **Camille Jordan** (1838-1922)
Symmetry - ***Group theory***

Group theory was developed by Évariste Galois, who died at the age of 21 in a duel leaving his work unpublished. In the 1870s, Camille Jordan generalized the work of Galois by means of the representation theory, and took care of applying the groups of Galois to crystals, thus introducing the theory of space groups of crystal symmetry. Jordan described up to 16 bidimensional and 174 tridimensional groups of the 230 space groups, unique combinations of the 32 point groups and the 14 Bravais lattices.

1879 - Leonhard Sohncke (1842-1897)

Symmetry - ***Chiral space groups***

Derives the 65 space groups that contain only proper symmetry operation (rotations, translations and roto-translations), i.e., the chiral groups. *Entwickelung einer Theorie der Krystallstruktur*, Leipzig: B. G. Teubner, 1879.

1883 - William Barlow (1845-1934)

Symmetry - ***Space groups***

Derives the 230 space groups independently from Fedorov and Schönflies: "Probable nature of the internal symmetry of crystals", *Nature* (London), **29**, 186-188, 205-207, (1883).

1890 - Evdraph Stepanovitsch Fedorow (1893-1919)

Symmetry - ***Space groups***

Is the first one to describe most of the space groups (228), but published his works in Russian (1885, 1880 and 1890) and they went mostly unnoticed. Only when Schönflies publishes his proposal in 1891, Fedorov submits a summary to a German journal. W. W. Niktin, *La méthode universelle de Fedoroff,* Geneve: Atar, 1914. *La méthode universelle de Fedoroff: Atlas*, 1914.

1891 - Arthur M. Schönflies (1893-1928)

Symmetry - ***Space groups***

Finds 227 space groups independently from Fedorov, to him he recognizes the priority in the discovery. After a mail exchange they jointly establish the 230 space groups. *Krystallsysteme und Krystallstructur*, Leipzig: B. G. Teubner, 1891.

1894 - Pierre Curie (1859-1906)

From networks to space groups

Symmetry - ***Glide planes***

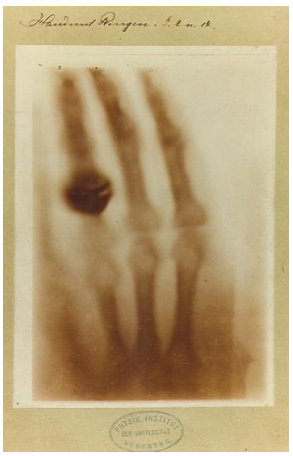
The Curie principle establishes that the symmetry of a cause is transmitted to its effects: *"When some causes produce certain effects, the symmetry elements of the causes must be present in the effects produced".*

This principle would be later formulated in a slightly different way: The effects can have the same symmetry, or a higher one, than the causes, but the latter cannot have a higher symmetry than the effects produced. *Oeuvres de Pierre Curie*, Paris: Gauthier-Villars, 1908.

Curie deduces also new symmetry elements, such as the glide plane, indispensable for the complete deduction of the space symmetry groups.

1895 - Wilhelm Röntgen (1845-1923) 

Instrumentation, diffraction and radiation sources - ***Discovery of X-rays***



At the end of this year Wilhelm Conrad Roentgen, professor at the University of Würzburg, publishes photographs that show the bones of a hand of his wife. He had obtained this image with some new

rays with a high penetrating power, whose nature remained still to be determined. For that reason he proposed to name them “X-rays”. The new radiation came out from the extreme of a “discharge tube” when it was irradiated with cathode rays. For this discovery he received the Nobel Prize of Physics in 1901. "On a New Kind of Rays”, *Science*, *3*, 227-231 (1896).

1905 - Charles Barkla (1877-1944)

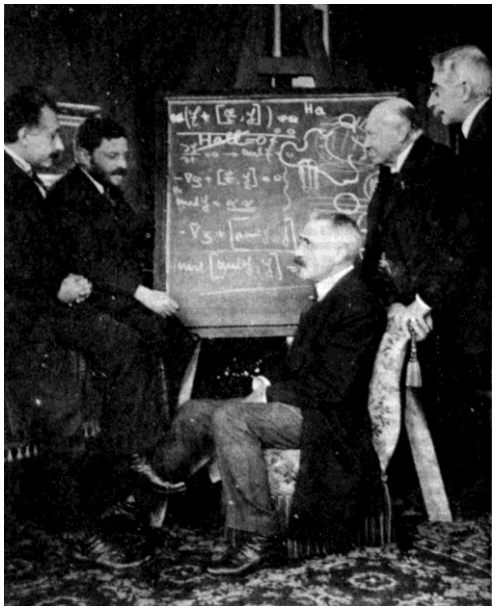
Instrumentation, diffraction and radiation sources - ***Electromagnetic nature of the X-rays***

Barkla reproduces with X-rays the experiments made in 1808 by Étienne-Louis Malus to show the polarization of light, and concludes that the X-rays are transversal electromagnetic waves. He also observes that upon irradiating a substance with X-rays, it emits new characteristic “secondary” X-rays, giving birth to X-ray spectroscopy, a discovery that was recognized with the Nobel Prize of Physics in 1917. C. G. Barkla, "Polarised Röntgen Radiation", *Phil. Trans. Roy. Soc. A*, **204**, 467-479, 1905; C. G. Barkla, "Secondary Röntgen Radiation", *Nature*, **71**, 440.

1905 - Paul Langevin (1872-1946)

Physical crystallography - ***Theory of Magnetism***

Langevin is the first one to propose the theory of diamagnetism. Each ionic species has a specific diamagnetism and, consequently, there is atomic, ionic, molecular and ionic crystal diamagnetism. P. Langevin, "Sur la théorie du magnétisme", *J. Phys. Theor. Appl.*, **4**, 678-693 (1905).



Albert Einstein, Paul Ehrenfest, Paul Langevin, Heike Kamerlingh Onnes
and Pierre Weiss in Kamerlingh Onnes's house in Leiden.

1906 - William Barlow (1845-1934), **William Jackson Pope** (1870-1939), **Paul Heinrich Ritter von Groth** (1843-1927)

Chemical crystallography - ***Chemical composition and crystal shape***

Barlow and Pope develop the principles of packing and show how to deduce the structures of simple compounds: W. Barlow, W. J. Pope, "Development of the Atomic Theory which Correlates Chemical and Crystalline Structure", *J. Chem. Soc., Trans., 89*, 1675-1744 (1906). "The relation between the crystalline form and the chemical constitution of simple inorganic substances", *J. Chem. Soc., Trans.*, **91**, 1150-1214 (1907). "The Relation Between the Crystal Structure and the Chemical Composition, Constitution, and Configuration of Organic Substances", *J. Chem. Soc., Trans., 97*, 2308-2388 (1910).

Paul Heinrich von Groth makes a systematic classification of minerals based on their chemical composition and crystal structure. *Chemische Kristallographie*, 5 Vols., Leipzig: Engelmann, 1906-1919. *Einleitung in die chemische Krystallographie*, Leipzig: Engelmann, 1904. *The Optical Properties of Crystals*, New York: John Wiley, 1910.

1907 - Georges Friedel (1865-1933)

Shape, geometry and crystal structure - ***Experimental evidence for the Bravais law***

The "Friedel law" establishes that the diffraction diagrams reflect 11 different symmetries, which correspond to the centrosymmetric groups. Friedel establishes the first classification of liquid crystals, a mesomorphous state between solid and liquid, with some degree of periodicity. He distinguishes "nematic" or bar-like shapes, "smectic" or layered shapes, and "cholesteric" or shapes derived from cholesterol. Applications of liquid crystals to screens, watches, etc., are highly developed today.

G. Friedel, "Études sur la loi de Bravais", *Bull. Soc. Fr. Mineral.*, **20**, 326-455 (1907). G. Friedel, "Sur les symétries cristallines que peut révéler la diffraction des rayons Röntgen", *C. R. Acad. Sci.*, **157**, 1533-1536 (1913). G. Friedel, "Les états mésomorphes de la matiére", *Ann. Phys. (Paris)*, **18**, 273-474 (1922). G. Friedel, *Leçons de Cristallographie*, Berger Levrault, Paris, 1926.

1908 - Yury Viktorovich Wulff (1863-1925)

Shape, geometry and crystal structure - ***Crystal habit***

Wulff assumes that the rate of growth of a crystal in the direction perpendicular to a face is inversely proportional to its reticular density. Introduces also the "lined sheet of Wulff" in the stereographic projection. G. Wulf, "Zur Theorie der Kristallhabitus", *Z. Kristallogr.* **45**, 433, (1908).

1907 - Vito Volterra (1860-1940)

Cristallophysics - ***Dislocations***

First important work on dislocations. V. Volterra, "Sur l'équilibre des corps élastiques multiplement connexes", *Ann. Ec. Norm. Super. Paris,* **24**, 401-517 (1907).

1909 - Erwin Madelung (1881-1972)

Atoms, packing, bonding - ***Bonding in ionic crystals***

The first models that explain the lattice energy in an ionic crystal are contemporary to the first X-ray diffraction experiments. Madelung formulates the model that represents the success of the electrostatic theory in the solid state, which can be applied to ionic crystals such as the alkaline halides, in which the ions can be considered as point charges. *Die Mathematischen Hilfsmittel des Physikers*, 1936 (3a. ed.). "Das elektrische Feld in Systemen von regelmäßig angeordneten Punktladungen", *Phys. Z.*, **19**, 524-533 (1918). This model was refined in 1918 with the Born-Landé equation, and later with the Born-Mayer equation.

1909 - Hendrik Antoon Lorentz (1853-1928)

Atoms, packing, bonding - ***Metallic bonding***

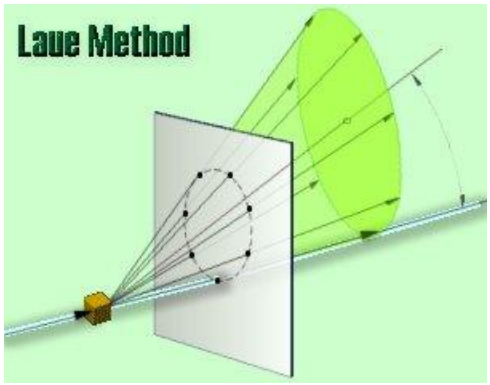
Formulates the electronic theory of matter. Was awarded the Nobel Prize of Physics in 1902. *The Theory of Electrons*, 1952 (English translation of *Resultats et problèmes de la theorie des electrons*, 1909).

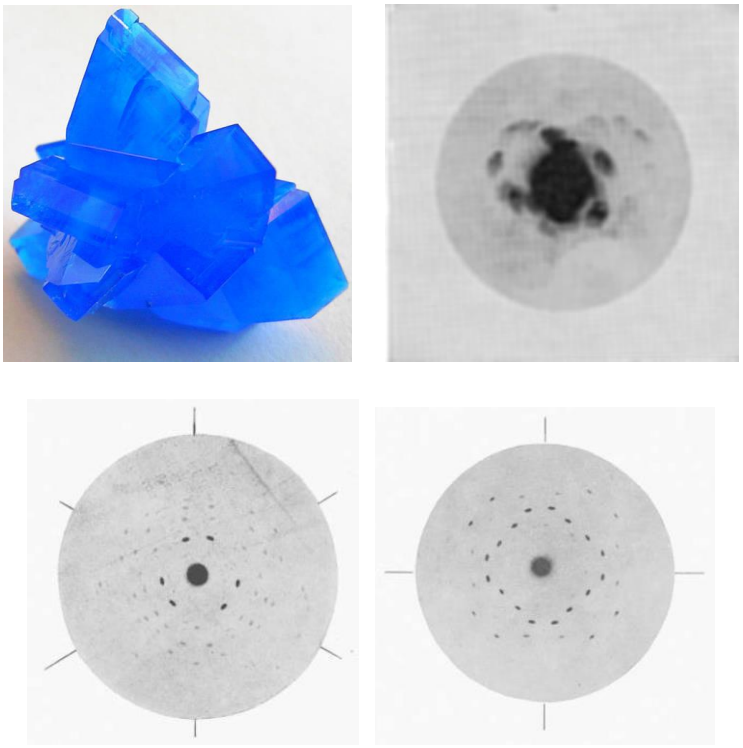
1912 - Max Theodor Felix von Laue (1879-1960)

Instrumentation, diffraction and radiation sources - ***X-ray diffraction***

Laue presents his Ph.D. thesis under the advice of Planck and moves to the Institute of Theoretical Physics of the Munich University, headed by Sommerfeld. There, when the nature of the recently discovered radiation was not yet clear, based on the works of Ewald, and in collaboration with Walter Friedrich and Paul Knipping, observes the effect of the passage of a narrow X-ray beam through a zinc blende crystal, the X-ray diffraction, which proves the electromagnetic character of this radiation and at the same time the lattice structure of the crystal. Laue receives the Nobel Prize of Physics in 1914 for this discovery.

> *"If the wavelength of the X-rays is of the same order of magnitude than the separation between atoms in the crystals, then one should obtain a sort of diffraction when this radiation passes through a crystal."*





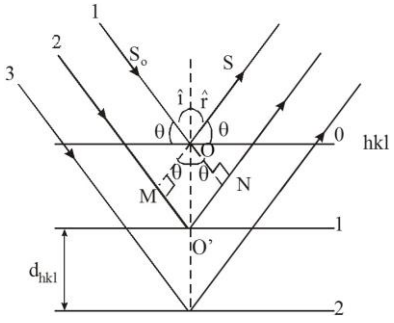
X-ray photographs of the zinc blende taken by Laue along the three- and four-order axes: W. Friedrich, P. Knipping, M. Laue; *Sitz. ber. Bayer. Akademie d. Wiss.*, 303-322, June 8, 1912; reproduced in P. P. Ewald, ed., *50 Years of X-ray Diffraction*, Utrecht: Oosthoek (1962).

Francisco Pardillo, professor at the Universitat de Barcelona, the same year of the discovery of X-ray diffraction by Max Von Laue, writes in *Bol. R. Soc. Esp. Hist. Nat*. **13**, 336-339 (1913): "In the Institute of Theoretical Physics of the Munich University a series of experiments have been carried out at the beginning of this year which are of great importance for crystallography, and which I cannot refrain myself from contributing to disseminate [...]. X-rays can be useful, perhaps, to determine the network of a crystalline substance..." (Salvador Galí, Exposició Centenari del Departament CMDM-UB).

1912 - William Lawrence Bragg (1890-1971)

Instrumentation, diffraction and radiation sources - ***The law of X-ray diffraction***

Establishes the formula that relates the diffraction diagrams with the crystal structure, known as Bragg's law. Reproducing Laue's experiment, deduces that planes of atoms within the crystal reflect X-rays. W. L. Bragg, "The specular reflexion of X-rays", *Nature* (London), **90**, 410 (1912).



1912 - Heinrich Baumhauer (1848-1926)

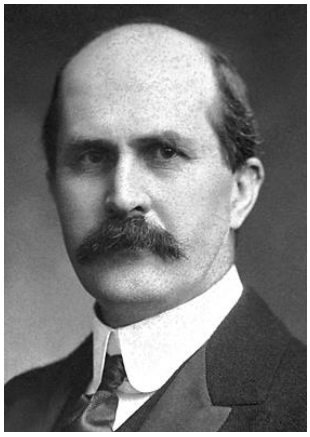
Chemical crystallography - ***Polytipysm***

In his study of the three varieties of silicon carbide, proposes the term “polytypism” to denote the existence of a substance in different but related modifications. It is a particular case of polymorphism, in which two structures differ only in the packing of atom layers. "Über die Kristalle des Carborundums”, *Z. Kristallogr.*, **50**, 33-39 (1912).

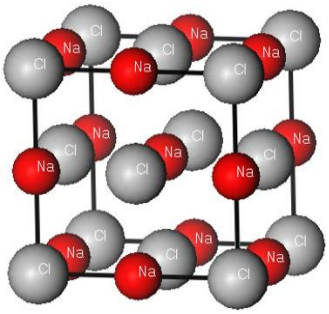
1912 - William Henry Bragg (1862-1942) and **William Lawrence Bragg** (1890 - 1971)

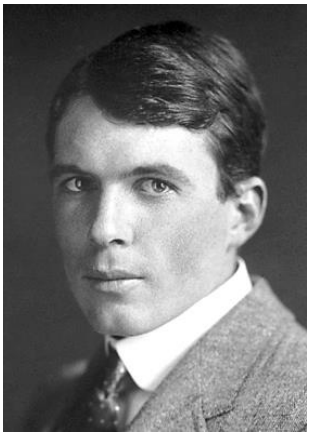
Chemical crystallography - ***Bragg’s law / First crystal structures***

Father and son derive the subjacent atomic structure of crystals from their X-ray diffraction patterns. In their first works they derive the structure of sodium chloride proposed by Pope and determine the structure of diamond. In 1915 they jointly receive the Nobel Prize of Physics. W. H. Bragg, "The reflection of X-rays by crystals. (II)", *Proc. R. Soc. A*, **89**,246–248 (1913); W. L. Bragg, "The Structure of Some Crystals as indicated by Their Diffraction of X-rays", *Proc. R. Soc. A*, **89**, 248-277 (1913), alkaline halides; W. H. Bragg, W. L. Bragg, "The Structure of the Diamond", *Proc. R. Soc. A*, **89**, 277-291 (1913); W. H. Bragg, "The X-ray spectrometer", *Nature*, **94**, 199–200 (1914); W. H. Bragg, W. L. Bragg, *X-rays and Crystal Structure*, London: Bell and Sons, 1916; W. L. Bragg, G. F. Claringbull, *Crystal Structure of Minerals*, London: G. Bell and Sons, 1965; W. L. Bragg, *Atomic Structure of Minerals*, London: Cornell University Press, 1937.

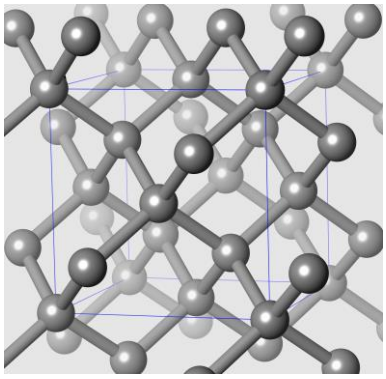


William Henry Bragg





William Lawrence Bragg



Current representation of the diamond structure (left) and atomic model of W. H. Bragg (right, Museum of the Royal Institution, London, photo by A. Authier).

1913 - Henry G. J. Moseley (1887-1915) and **Antonius van der Broek** (1870-1926)

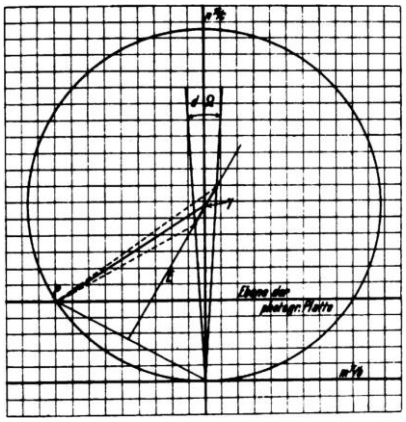
Atoms, packing, bonding - ***X-ray emission and atomic number***

Moseley studies the X-rays emitted by several elements and discovers the law named after him, which relates the wavelength of the emitted radiation to the atomic number proposed by Van der Broek. This milestone discovery consolidates both the periodic system and X-ray spectroscopy. A. Van der Broek, "Intra-atomic charge", *Nature*, **92**, 372–373 (1913). H. G. J. Moseley, "The high-frequency spectra of the elements", *Phil. Mag.*, **26**, 1024 (1913).

1913 - Paul P. Ewald (1888-1985)

Instrumentation, diffraction and radiation sources - ***Reciprocal lattice***

Defines the reciprocal lattice and proposes a geometrical interpretation of Bragg's law. P. P. Ewald, "Zur Theorie der Interferenzen der Röntgenstrahlen in Kristallen", *Phys. Z.,* **14**, 465-472 (1913). P. P. Ewald, "Das "reziproke Gitter" in der Strukturtheorie", *Z. Kristallogr. A*, 56, 129-156 (1921). P. P. Ewald, ed.; *50 Years of X-ray Diffraction*, Utrecht: Oosthoek (1962).



Reciprocal lattice and Ewald construction according to the author (1913).
A. Authier, *Acta Cryst.*, **A68**, 40-56, (2012).

1913 - Georges Friedel (1865-1933)

Chemical crystallography - ***Mesomorphic states***

Liquid crystals and plastic crystals. G. Friedel, "Les états mésomorphes de la matière", *Ann. Phys. (Paris)*, **18**, 273-474 (1922). G. Friedel, *Leçons de Cristallographie*, Paris: Berger Levrault (1926).

1916 - Gilbert Newton Lewis (1875-1946)

Atoms, packing, bonding - ***Covalent bonding through electron pairs***

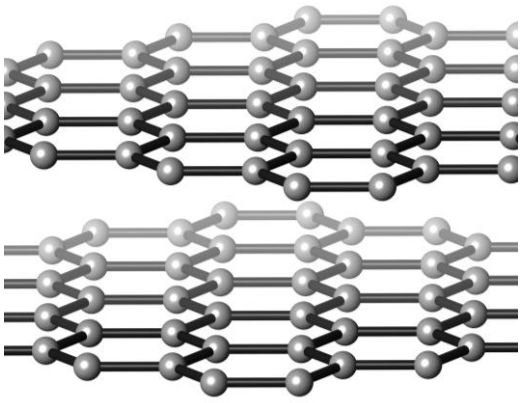
Develops the idea that a covalent bond consists in a shared electron pair. G. N. Lewis, "The atom and the molecule", *J. Am. Chem. Soc.*, **38**, 762-785 (1916); *L'àtom i la molècula*, Barcelona: Societat Catalana de Química, 2004 (translation and introduction by J. Castells).

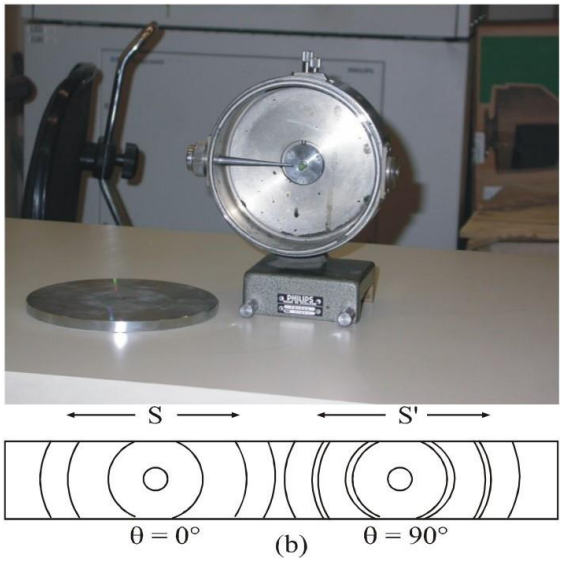
1916 - Peter Debye (1884-1966) and **Paul Scherer** (1890-1969)

Instrumentation, diffraction and radiation sources - ***Powder X-ray diffraction***

Chemical crystallography

These authors show that powdered crystals give a diffraction patter, develop the Debye-Scherrer method to register powder diffraction (*The Collected Papers of Peter J. W. Debye*), and resolve the structure of graphite: "Interferenzen an regellos orientierten Teilchen im Roentgenlicht", *Phys. Z.*, **17**, 277-283, 291-301 (1916). Peter Debye received the Nobel Prize of Chemistry in 1936 for his studies of X-ray and electron diffraction by gases.





1916 – Jan Czochralski (1885-1953)

Crystallophisics - ***Crystal growth from a melt***

Czochralski develops a method for the preparation of single crystals. It is widely applied to the growth of silicon single crystals using a seed crystal deposited in a melt of silicon. It is used by industry to prepare wafers for the manufacture of transistors, electronic circuits and photovoltaic cells. The method employs a crucible that contains a molten semiconductor, with a controlled temperature slightly above the melting point to avoid its solidification. A rod containing a tiny seed crystal of the same semiconductor is introduced in the crucible and slowly rotated. In contact with the seed, the molten semiconductor is deposited on the surface, solidifying with the same crystal lattice and orientation of the seed. The rod is gradually elevated and in its lower extreme a cylindrical single crystal is formed. J. Czochralski; *"Ein neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle", Z. Phys. Chem.*, **92**, 219-221 (1918).

1919 - **Paul Niggli** (1888-1953)

Instrumentation, diffraction and radiation sources - ***Space groups and systematic extinctions***

Although space groups had been described earlier, their information contents have not been used for the study of crystal structures until Niggli, based on graphical and analytical descriptions of the space groups, describes the implications in X-ray diffraction, essentially the systematic extinctions. *Geometrische Kristallographie des Diskontinuums*. Leipzig: Germans Bornträger, 1919. *Handbuch der*

Experimentalphysik, Vol. 7, Part 1, *Kristallographische und structurtheoretische Grundbegriffe*, Leipzig: Akademische Verlagsgesellschaft, 1928.

1920 - Jan Valasek (1926-1968)
Physical crystallography - ***Ferroelectricity***

Based on previous studies of piezoelectricity in the Rochelle's salt, Valasek proposes the same type of behaviour when the electrical polarization is recorded as a function of the strength of an applied electric field, a property that is named *ferroelectricity*, analogous to the magnetic behaviour known as ferromagnetism. The next ferroelectric substance to be discovered was KDP (potassium dihydrogenphosphate). J. Valasek, "Piezoelectric and allied phenomena in Rochelle salt", *Phys. Rev.*, **15**, 537-538 (1920).

1920 - William Lawrence Bragg (1890-1971)
Atoms, packing, bonding - ***The size of the atoms***

Bragg introduces the concept of the covalent radius: "The arrangement of atoms in crystals", *Phil. Mag.*, **40**, 169-189 (1920); electronic version available.

1920 - Alfred Landé (1888-1976)
Atoms, packing, bonding - ***The size of the ions***

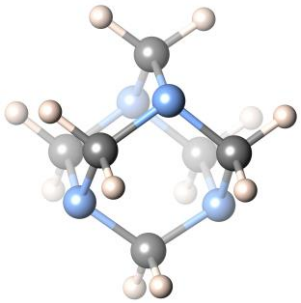
In 1913 his Ph.D. advisor at the Munich University, Arnold Sommerfeld, sent Landé as a Physics assistant with David Hilbert at the University of Göttingen, to replace Paul Peter Ewald, sent also by Sommerfeld in 1912. Landé got also in contact with Max Born. In 1920 he introduces the concept of ionic radii. "Bemerkung über die Grösse der Atome", *Z. Phys.*, **2**, 87-89 (1920).

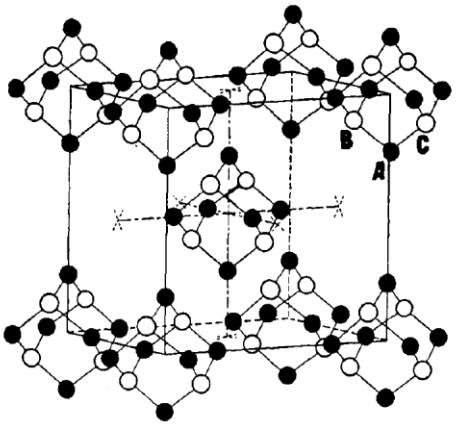
1920 - Evgraf Stepanovich Fedorov (1853-1919)
Chemical crystallography - ***Crystallochemical analysis***

Mathematician, crystallographer and mineralogist, Fedorov published in 1893 his classical paper "The theodolite method in mineralogy and petrology ". In a monumental work published in 1920 Fedorov applies his structural ideas to deduce the lattice parameters of a large number of crystal species from morphological data. E. S. Fedorov; *Das Krystallreich: Tabellen zur Krystallochemischen Analyse*, St. Petesburg: Academy of Sciences, 1920.

1922 - Roscoe G. Dickinson (1894-1945) and **Albert L. Raymond**
Chemical crystallography - ***First 3D molecular structure***

These authors determine the structure of hexamethylenetetraamine, first tridimensional structure of a covalent molecule: "The Crystal Structure of Hexamethylene-Tetramine", *J. Am. Chem. Soc.*, **45,** 22-29 (1922). Presented as a Master Thesis by Raymond at Caltech in 1923.





Other early molecular structures: D-manitol, K. Backer, H. Rose, "Röntgenspektroskopie an organischen Verbindungen", *Z. Phys.* 14, 369 (1923); beryllium acetate and propionate, W. Bragg, T. Morgan, *Proc. R. Soc. London Ser. A*, **104,** 437-451 (1923).

1922 - Ralph W. G. Wyckoff (1897-1994)

Symmetry - ***Space symmetry tables***

In 1919 Wyckoff presented his Ph.D. thesis on the crystallographic resolution of the structures of $NaNO_3$ and $Cs(ICl_2)$. In 1922 he publishes a book that contains tables with the coordinates of the general and special positions allowed by the symmetry elements, which turned out to be the seed of the International X-ray Crystallography Tables, published in 1935. The general and special positions are called now Wyckoff positions as a tribute to him. R. W. G. Wyckoff; *The analytical Expression of the Results of the Theory of Space Groups*, 180 pp., Washington, DC: Carnegie Institute of Washington, 1922.

1922 - Aleksei Vasilevich Shubnikov (1887-1970)

Chemical crystallography - ***Law of chemical crystallography***

A present formulation of Shubnikov's law could be like this: "the numbers of atoms of different species are related to each other as multiplicities of regular point systems, i.e. as the inverse values of corresponding symmetry orders or point group orders". As a corollary of this law he deduced 13 possible chemical formulations for binary compounds and 65 for ternary compounds. "Fundamental law of Crystal chemistry", *Bull. Acad. Sci. USSR*; 515-524 (1922).

1912 - Max Born (1882-1970)

Chemical crystallography - ***Atomic theory of the solid state***

The work of Born represents an inflection point in the theoretical approach to the solid state. He developed the basis of lattice dynamic, applied quantum theory to the vibrations of atoms in the crystal lattice and made contributions to the characteristic frequencies, temperature dependence of the specific heat, thermal expansion and other properties. M. Born, *Atomtheorie des festen Zustandes*, Leipzig: Teubner (1923). M. Born, T. von Karman, "Schwingungen in Raumgittern", *Phys. Z.*, **13**, 297-309 (1912). "A thermo-chemical application of the lattice theory". *Verh. Dtsch. Phys. Ges.,* **21**, 13-24 (1919); M. Born, K. Huang, *Dynamical Theory of Crystal Lattices*, Oxford: Clarendon Press, 1954; E. Madelung, "Molekulare Eigenschwingungen", *Nachr. Ges. Wissen. Göttingen,* 100-106 (1909).

1924 - Karl Weissenberg (1893-1976)

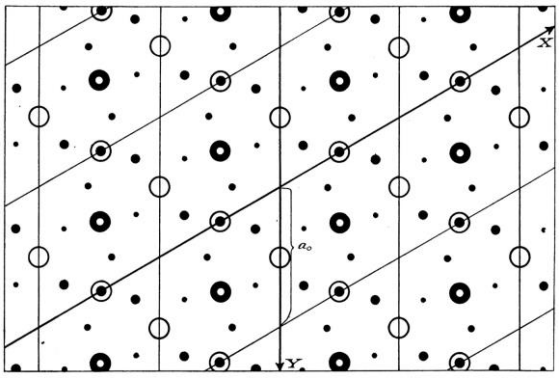
Instrumentation, diffraction and radiation sources - ***Photographs, Weissenberg method***

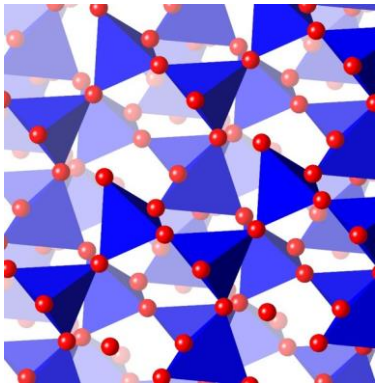
In 1924 Weissenberg, only 12 years after the discovery of X-ray diffraction, established the *Weissenberg method* that has inspired all other methods of single crystal diffraction. It allows us to completely index the diffraction pattern and, measuring the intensity of the diffraction spots, to deduce the atomic positions. K. Weissenberg, "Ein neues Röntgengoniometer", *Z. Phys.*, **23**, 229-238 (1924).

1926 - Ralph W. G. Wyckoff (1897-1994)

Chemical crystallography - ***Structure of β-quartz***

Wyckoff studies for the first time the changes in structure that take place between two polymorphic forms in quartz, from α-quartz to β-quartz at 575° C. "Kriterien für hexagonale Raumgruppen und die Kristallstruktur von β Quarz", *Z. Krist.*, **63**, 507-537 (1926); digital version.





1926 - Yakov (J.) Il'ich Frenkel (1894-1952)

Physical crystallography - ***Vacants and crystal defects***

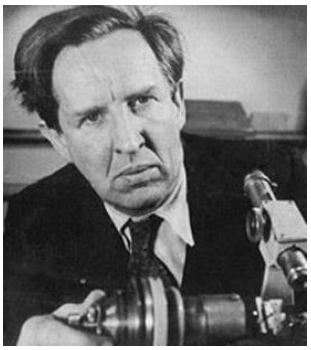
Proposes the concept of "vacant", and contributes to the study of crystal defects and deformations. His theories have been very important for the study of dislocations. "Zur Theorie der Elastizitätsgrenze und der Festigkeit kristallinischer Körper", *Z. Phys.*, **37**, 572-609 (1926).

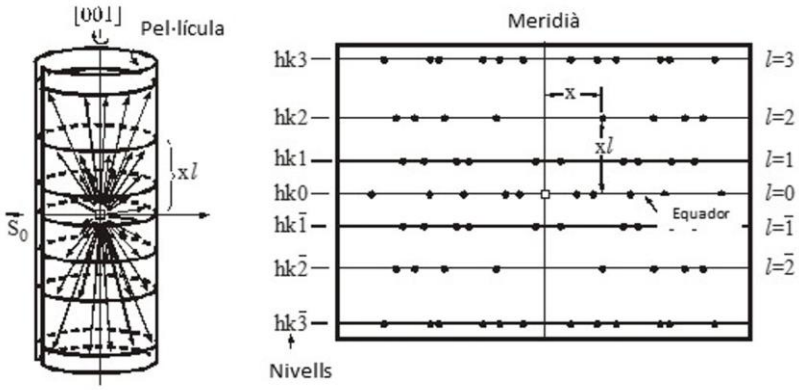
1926 - John Desmond Bernal (1901-1971)

Instrumentation, diffraction and radiation sources -

Reciprocal lattice and oscillating single crystal method

Bernal shows a new direction in the analysis of crystal structures. Provides the basis for future developments, in particular for the moving film methods for single crystal diffractometers. With his work, based on Bravais and Ewald, the reciprocal lattice becomes the core of all the works in X-ray diffraction. J. D. Bernal, "On the interpretation of X-Ray single-crystal rotation photographs", *Proc. R. Soc. London Ser. A*, **113**, 117-160 (1926). J. D. Bernal, D. Crowfoot, X-ray photographs of crystalline pepsin; *Nature (London)*, **133**, 794-795 (1934).





1927 - Clinton Davisson (1881-1958) and **George Paget Thomson** (1892-1975)

Instrumentation, diffraction and radiation sources - ***Electron diffraction by crystals***

These two researchers prove that the crystals also diffract electrons, thus demonstrating the wave nature of the electrons. Both received the Nobel Prize for Physics in 1937. C. Davisson, L. H. Germer, "The Scattering of Electrons by a Single Crystal of Nickel", *Nature*, **119**, 558-560 (1927); G. P. Thomson, A. Reid, "Diffraction of Cathode Rays by a Thin Film", *Nature*, **119**, 890 (1927).

1927 - Victor Moritz Goldschmidt (1888-1947)

Chemical crystallography - ***Crystallochemical rules***

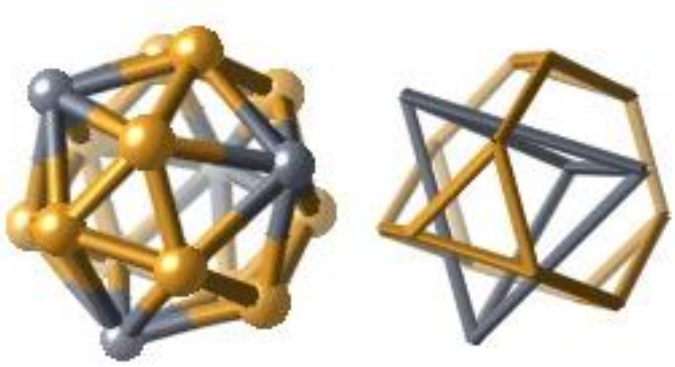
Assuming that in NaCl the ions are in contact, Goldschmidt calculates the radius of the cation from the known radius of the anion. He also proposes that an increase in the coordination number goes along with an increase of the interatomic distance. V. M. Goldschmidt, *Geochemische Verteilungsgesetze der Elemente*, Vol. 8, Untersuchung über Bau und Eigenschaften von Kristallen,

pp. 1-156, Oslo: Norske Videnskaps-Akademi, 1927.

1927 - James Byron Friauf (1896-1972)

Shape, geometry and crystal structure ***- Friauf polyhedra***

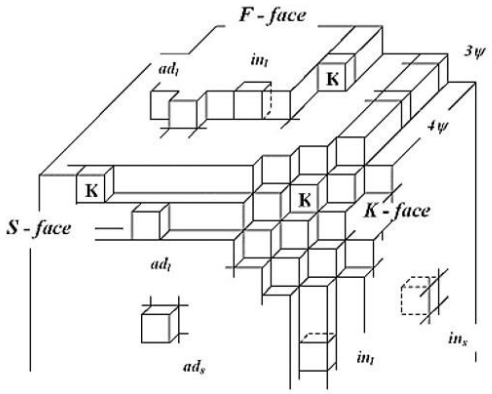
Friauf reports the crystal structures of two intermetallic compounds, Cu_2Mg and $CuAl_2$: "The Crystal Structures of Two Intermetallic Compounds", *J. Am. Chem. Soc.*, **49**, 3107-3114 (1927). A 16 vertex-polyhedron with triangular faces present in those structures is named *Friauf polyhedron*, and is seen to be common in the crystal structure of metal alloys.



1927 - Walther Ludwig Julius Kossel (1888-1956)

Physical crystallography ***- Crystal growth theory***

In 1928 Kossel proposes the kinetic theory of crystal growth, which is later known as the Kossel-Stranski model. W. Kossel, "Zur Theorie des Kristallwachstums", *Nachr. Ges. Wiss. Göttingen Math. Phys.*, 135-143 (1927).



1928 - Ivan Nikolov Stranski (1897-1979)

Physical crystallography ***- Crystal growth theory***

Stranski, in collaboration with Kossel, is considered to be the father of the research in crystal growth. I. N. Stranski, "Crystal Growth", *Z. Phys. Chem.* **136 A**, 259-278 (1928).

1928 - Felix Karl Ludwig Machatschki (1895-1970)

Chemical crystallography ***- Structural classification of silicates***

The development of structural determination allows for the classification of families of compounds, such as silicates. It is recognized that the tetrahedral SiO_4 group can polymerize by sharing vertices. The variety of structures described include dimers, trimers, rings, single and double chains, layers and three-dimensional networks. "Zur Frage der Struktur und Konstitution der Feldspate", *Zentralbl. Mineral. Geol. Paläontol. A*, 97-104, 1928.

1929 - Pierre-Ernest Weiss (1865-1940) and **Robert Forrer**

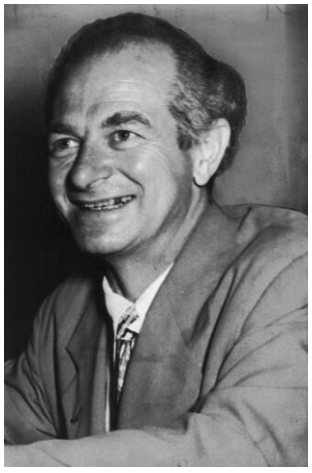
Physical crystallography - ***Experimentation in ferromagnetism***

Weiss and Forrer discover that some mixed oxides present ferromagnetic properties. P. Weiss, R. Forrer, "La saturation absolue des ferromagnétiques et les lois d'approche en fonction du champ et de la temperature", *Ann. Phys. (Paris)*, **12**, 279-372 (1929).

1929 - Linus Carl Pauling (1901-1994)

Chemical crystallography - ***Pauling rules***

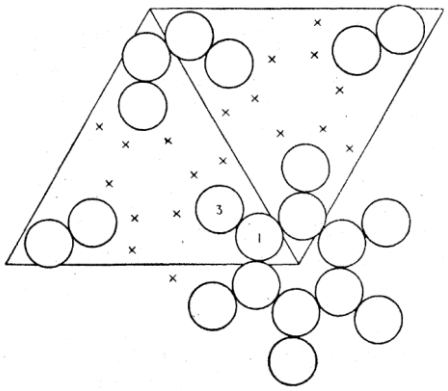
In a paper published in 1927 Pauling employs ionic radii to explain the relative stability of different structures, such as sodium chloride and caesium chloride, for a given compound. This work concludes proposing "Pauling's five rules to predict the structure of ionic solids, still in use today. Pauling received the Nobel Prize for Chemistry in 1954 for his studies on the chemical bond and for the structural elucidation of complex substances. L. Pauling, "The size of ions and the structure of ionic crystals", *J. Am. Chem. Soc.*, **49**, 765-790 (1927). L. Pauling, "The principles determining the structure of complex ionic crystals", *J. Am. Chem. Soc.* **51**, 1010-1026 (1929). L. Pauling, *The Nature of the Chemical Bond*, Ithaca, NY: Cornell University Press, 1939.



1929 - Kathleen Yardley (Lonsdale) (1903-1971)

Chemical crystallography - ***The structure of benzene***

One of the first complete structural determinations of a molecular crystal was that of hexamethylbenzene. This structure demonstrates Kekulé's model of 1865 to be valid: benzene is a cyclic planar hexagonal molecule, with all the C-C bonds of the same. K. Lonsdale, "The structure of the benzene ring", *Nature (London)*, **122**, 810, 1928.



G. Ferry, *Nature*, **505**,609 (2014).

1930 - Léon Brillouin (1890-1970)

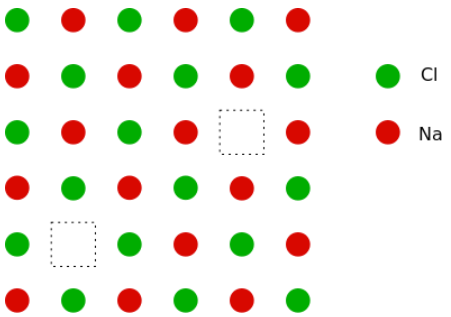
Physical crystallography - ***Zone theory of crystals***

The zone theory is related to the reciprocal lattice. All reciprocal lattice points close to the origin are joined to the origin by straight lines. These lines are bisected perpendicularly by planes and the intersection of these planes forms the first Brillouin zone. Other zones are formed by dealing with the next-nearest-to-the-origin reciprocal points in the same way. The first Brillouin zone is useful for the construction of electronic bands in band theory. L. Brillouin, "Les électrons libres dans les métaux et le role des réflexions de Bragg", *J. Phys. Radium*, **1**, 377-400 (1930). L. Brillouin, *Wave Propagation in Periodic Structures*, New York: McGraw-Hill, 1946.

1930 - Carl Wilhelm Wagner (1901-1977) and **Walter Hermann Schottky** (1886-1976)

Physical crystallography - ***Schottky defects***

Wagner and Schottky propose the first models for the diffusion mechanism in crystalline materials. The first mechanism is *exchange* that implies some motion of the nearest neighbours. The second is the *Frenkel defect*, which implies the motion of an atom to an interstitial position. Finally, the displacement can take place to a pre-existing vacant, termed *Schottky defect*. C. Wagner, W. Schottky, "Theorie der geordneten Mischphasen", *Z. Phys. Chem. B,* **11**, 163-210 (1930).



1931 - Fritz Laves (1906-1978)

Shape, geometry and crystal structure - ***Stability principles***

Deduces the 11 networks that form polygons in the plane that had been proposed by Kepler. F. Laves, "Ebenenteilung und Koordinationszahl", *Z. Kristallogr.*, **78**, 208-241 (1931).

1931 - Wilson A. Bentley (1865 - 1931)

Shape, geometry and crystal structure - ***Again the snowflakes***

Snow Crystals, New York: McGraw-Hill, 1931. First edition of one of the most remarkable books written by an amateur scientist. It provided scientific evidence that "there aren't two equal snowflakes". Wilson Bentley took photographs in his family farm, in Jericho, Vermont and managed to publish them in a book a few days before dying from pneumonia.

1931 - Wolfgang Berg (1908-1984)

Instrumentation, diffraction and radiation sources - ***First experiments on X-ray topography***

X-ray topography is a method based on Bragg diffraction. The topographical images record the intensity profile of a beam of X-rays diffracted by the crystal and represent a bidimensional intensity map. The topographies reveal the irregularities of a non-ideal crystal lattice and are used to monitor the crystal quality and to visualize defects in several crystalline materials. W. Berg, "An X-ray method for study of lattice disturbances of crystals", *Naturwiss.*, **19**, 391-396 (1931).

1933 - Ernst August Friedrich Ruska (1906-1988)

Instrumentation, diffraction and radiation sources - ***Electron microscope***

Ruska postulated that the microscopes that use electrons, with a wavelength 1000 times shorter than the visible light, can provide more detailed images of objects than microscopes that employ visible light, in which the magnification is limited by the wavelength. He obtained the Nobel Prize for Physics in 1986.

1934 - John Desmond Bernal (1901-1971)

Instrumentation, diffraction and radiation sources - ***X-ray diffraction by proteins and viruses***

The results of the determination of crystal structures of complex organic molecules start to appear at the beginning of the decade of 1930. Although protein crystals can in some cases be obtained, they are unstable because of the presence of many crystallization water molecules. In addition, they loose internal order upon dehydration in the air or by the effect of X-rays. Bernal and Crowfoot show that it is necessary to mount the protein crystals with the mother solution to obtain a good diffraction diagram. J. D. Bernal, I. Fankuchen, D. P. Riley, "Structure of the crystals of tomato bushy stunt virus preparation", *Nature*, **142**, 1075 (1938). J. D. Bernal, I. Fankuchen, "X-ray and crystallographic studies of plant virus preparations", *J. Gen. Physiol.*, **25**, 111-65 (1941).

1934 - Arthur Lindo Patterson (1902-1966)

Instrumentation, diffraction and radiation sources - ***Patterson function***

The Patterson function supposed an important step forward toward the resolution of crystal structures. This function allows for the analysis of organic complex structures. Using Fourier theory to analyze the intensities of a diffraction diagram, Patterson derived a tridimensional function, a Fourier series, which employs the squares of the structure factors and does not require information about the phase. A. L. Patterson, "A Fourier series method for the determination of the components of interatomic distances in crystals", *Phys. Rev.* **46**, 372-376 (1934). A. L. Patterson, "A direct method for the determination of the components of interatomic distances in crystals", *Z. Krist.*, **90**, 517-542 (1935). A. L. Patterson, G. Tunell, "A method for the summation of Fourier series used in the X-ray analysis of Crystal structures", *Am. Mineral.*, **27**, 655-679 (1942).

$$P(u,v,w) = \sum_{hkl} |F_{hkl}|^2 \; e^{-2\pi i(hu+kv+lw)}.$$

1934 - Martin Julian Buerger (1903-1986)

Instrumentation, diffraction and radiation sources - ***Interpretation of the X-ray diffraction data***

From 1934 on, most Weissenberg cameras apply the equi-inclination angle method proposed by Buerger that simplifies the full indexing of the diffraction diagrams. M. J. Buerger, "The Weissenberg reciprocal lattice projection and the technique of interpreting Weissenberg photographs", *Z. Krist.*, **88**, 356-380 (1934). M. J. Buerger; *The Precession Method in X-ray Crystallography*, New York: John Wiley, 1964.

1935 - Charles Mauguin (1878-1958) and **Karl Hermann** (1895-1961)

Symmetry - ***Space group symbols***

These authors propose simple symbols for space groups, the Hermann-Mauguin symbols that are still in use today: C. H. Hermann, C. Mauguin; *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Vol. 1, C. H. Hermann, ed., Berlin: Germans Bornträger, 1935.

1936 - Kathleen Yardley (Lonsdale) (1903-1971) and **Kariamanickam Srinivasa Krishnan** (1989-1961)
Physical crystallography - ***Diamagnetic properties of molecular crystals***

Lonsdale and Krishnan measure the diamagnetic properties of a large number of aromatic molecular crystals. From these results they could determine the magnetic susceptibilities of individual aromatic organic molecules. K. Lonsdale, K. S. Krishnan, "Diamagnetic anisotropy of crystals in relation to their molecular structure", *Proc. R. Soc. London*, **156**, 597-613 (1936).

1937 - Hermann Arthur Jahn (1907-1979) and **Edward Teller** (1908-2003)
Chemical crystallography - ***The Jahn-Teller effect***

These authors study the distortions of the coordination polyhedra. The Jahn-Teller effect describes the geometrical distortion of non-linear molecules with a degenerate ground state. It is common in octahedral transition metal complexes, particularly in copper(II) compounds. H. A. Jahn, E. Teller, "Stability of polyatomic molecules in degenerate electronic states. I. Orbital degeneracy", *Proc. R. Soc. London Ser. A*, **161**, 220-235 (1937).

1937 - André Guinier (1911-2000)
Instrumentation, diffraction and radiation source - ***X-ray diffraction method for powders***

Guinier and other authors develop the Debye-Scherrer diffraction method for crystalline powders using monochromatic radiation. A. Guinier, "Rayons-X-dispositif permettant d'obtenir des diagrammes de diffraction de poudres cristallines très intenses avec un rayonement monochromatique", *Compt. R. Acad. Sci.*, **204**, 1115-1116 (1937). A. Guinier, "La diffraction des rayons X aux tres petits angles: application à l'étude de phenoménes ultramicroscòpiques", *Ann. Phys. (Paris)*, **12**, 161-238 (1939).

1937 - Joseph D. H. Donnay (1902-1994) and **David Harke**r (1906-1991)
Chemical crystallography - ***Structure-morphology relationship***

Furthering the work of Bravais, Donnay and Harker show that many anomalies in the relationship between structure and morphology can be solved taking into account that the symmetry elements with a translation component (glide planes and screw axes) reduce the interplanar spacing and the lattice density. They demonstrate that the morphology depends on both the geometry and the space group. J. D. H.Donnay, D. Harker, "A new law of Crystal morphology extending the law of Bravais", *Am. Mineral.*, **22**, 446-467 (1937).

1938 - Powder Diffraction File
Chemical crystallography - ***Compilation of powder diffraction data***

Dow Chemical Company gave access to their data, published initially by Hanawalt, Rinn and Frevel in 1938, reprinted in 3 x 5 inches cards, under the auspices of the American Society for Testing and Materials (ASTM), and which appeared in 1941 as the first data set of the Powder Diffraction File (PDF). J. D. Hanawalt, H. W. Rinn, L. K. Frevel, "Chemical Analysis by X-Ray Diffraction", *Ind. Eng. Chem. Anal.* Ed., **10**, 457-512 (1938).

1939 - Linus Pauling (1901-1994)

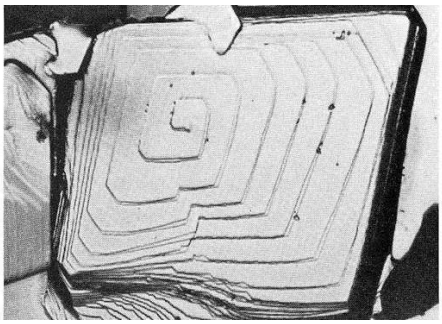
Atoms, packing, bonding - ***The Van der Waals radii***

The publication of Pauling's book exerted a great influence on the ideas of the time about Structural Chemistry, which are also reflected in the X-ray crystallographic studies, specially for the interpretation of intermolecular interactions by comparison of interatomic distances with the Van der Waals radii. *The Nature of the Chemical Bond*, Ithaca, NY: Cornell University Press, 1939.

1939 - Johannes (Jan) Martinus Burgers (1985-1981)

Physical crystallography - ***Helical dislocations***

Burgers introduces a general treatment that encompasses lineal and helical dislocations. J. M. Burgers, "Some considerations on the fields of stress Connected with dislocations in a regular crystal lattice I", *Proc. K. Ned. Akad. Wet.* **42**, 293-325 (1939). J. M. Burgers, "Some considerations on the fields of stress Connected with dislocations in a regular crystal lattice II. Solutions of the equations of elasticity for a non-isotropic substance of regular crystalline symmetry", *Proc. K. Ned. Akad. Wet.* **42**, 378-399 (1939).



D. Aquilano, *J. Cryst. Growth*, 37, 215 (1977).

1939 - Max Volmer (1885-1965)

Physical crystallography - ***Atomic theory of crystal growth***

The works of Volmer constitute the basis for the conceptual development of the crystal growth TLK (Terrace – Ledge – Kink) model. M. Volmer, *Kinetic der Phasenbildung*, Dresden and Leipzig: Steinkopf (1939).

1944 - Gopalasamudram Narayana Ramachandran (1922-2001)

Instrumentation, diffraction and radiation sources - ***X-ray topography***

Ramachandran develops algorithms that extraordinarily increase the quality of the results obtained with X-ray topography and reduce the computational time for the reconstruction of the image. Performs the first experiments with diamond crystals. G. N. Ramachandran, "X-ray topographs of diamond", *Proc. Indian Acad. Sci. Sect. A*, **19**, 280-294 (1944).

1945 - Heinrich Heesch (1906-1995) and **Alexei Vasil'evich Shubnikov** (1945-)

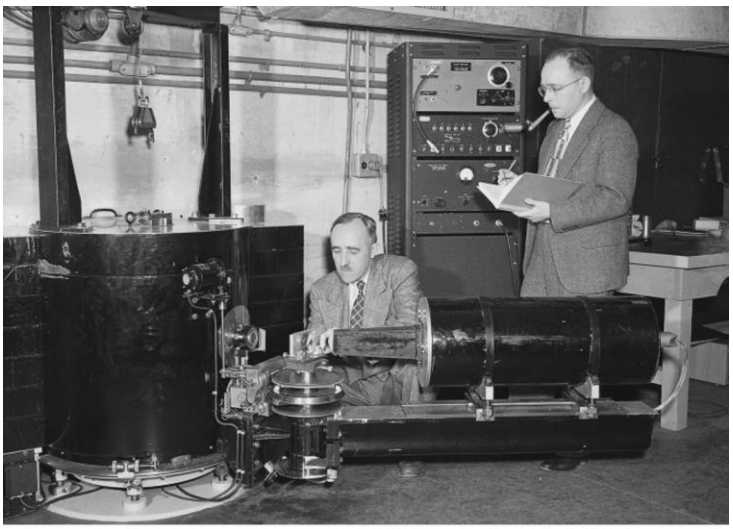
Symmetry - ***Antisymmetry and magnetic groups***

Heesch and Shubnikov introduce antisymmetry in order to consider atoms with spin, giving raise to the 1651 Shubnikov space groups necessary for describing the magnetic structure of crystals formed by atoms or molecules with spin. Antisymmetry (or colour symmetry) is in fact a type of symmetry that consists in repeating the basic components while at the same time inverting some property, for instance the colour from white to black, as did in many of his works the artist Mauritius Escher. A. V. Shubnikov, *Symmetry and Antisymmetry of Finite Figures* (in Russian) Moscow, 1951; translated to English in A. V. Shubnikov, N. V. Below, *Colored Symmetry*, W.T. Holser, ed., Oxford: Pergamon Press, 1964.

1946 - Ernest Omar Wollan (1902-1984) and **Clifford Glenwood Shull** (1915-2001)

Instrumentation, diffraction and radiation sources - ***Neutron diffraction***

Neutrons are added to the waves and particles that can be diffracted thanks to the work of Wollan and Shull. This technique provides information on the position of the atomic nuclei within crystals, while X-ray diffraction locates the electron density. Neutron diffraction is especially useful to determine the position of the hydrogen atoms, although the technique requires a particle accelerator. These two authors were among the first researchers that proposed to use neutrons to investigate the structure of materials. In 1944 they asked the director of the Clinton Laboratories (now Oak Ridge National Laboratory) permission to use the neutrons that came out from the X-10 reactor to study the diffraction of neutrons by single crystals, and installed a spectrometer to make observations on a gypsum crystal. Shull received the Nobel Prize for Physics in 1994, but Wollan had already passed away.



Clifford Shull (right) and Ernest O. Wollan with a neutron double crystal spectrometer at the ORNL X-10 graphite reactor, in 1949.

1946 - Walter Guyton Cady (1874–1974)

Physical crystallography - ***Piezoelectricity***

The vibration of crystals under the influence of an electric field was used by Cady in 1918 to produce a piezoelectric resonator. This device can produce high frequency vibrations that find many applications in quartz watches and in frequency controllers for radio and TV. His book published in 1946 reviews all his work in the field. W. G. Cady, *Piezoelectricity*, New York: McGraw-Hill, 1946.

1947 - Nikolai Vasilyevich Belov (1891-1982)

Atoms, packing, bonding ***- Packing and symmetry groups***

Belov developed the packing theory formulated by Barlow in 1883 for inorganic structures, and by Kitaigorodskii for organic structures. He also works with Shubnikov on colour symmetry. N. V. Belov, *Structures of Ionic Crystals and Metallic Phases* (in Russian), Moscow: Izd-vo An SSSR, 1947. A. V. Shubnikov, N. V. Belov, *Colored Symmetry*, W.T. Holser, ed., Oxford: Pergamon Press (1964).

1947 - General Electric

Instrumentation, diffraction and radiation sources - ***Synchrotron radiation***

First observation of light produced by a synchrotron in Schenectady. F. R. Elder, A. M. Gurewitsch, R. V. Langmuir, H. C. Pollock, "Radiation from Electrons in a Synchrotron", *Phys. Rev.*, **71**, 829-830 (1947).

1948 - Paul Ewald and **Julio Garrido**

Chemical crystallography ***- Birth of the journal Acta Crystallographica***

In 1948 starts the publication of the journal *Acta Crystallographica* by the International Union of Crystallography, established the previous year in the first General Assembly, which chose Sir Lawrence Bragg as President of the Executive Committee and Paul Ewald as the editor of the journal. The subscription price is fixed in $ 10 per volume and the printing is commissioned to *Cambridge University Press*. The first article of the first issue of this journal is written by Julio Garrido, from the Instituto Nacional de Física y Química de Madrid: J. Garrido, "Observations sur la diffusion des rayons X par les cristaux de ClO_3Na", *Acta Crystallogr.*, **1**, 3-5 (1948). In the same issue there is also a recension of the book by Garrido and Orland, *Los rayos X y la estructura fina de los cristales: fundamentos teóricos y métodos prácticos*, Madrid: Dossat (1946).

1948 - Louis Eugène Félix Néel (1904-2000)

Physical crystallography - ***Theory of antiferromagnetism***

Néel develops the theory of antiferromagnetism assuming that there are two interpenetrated sublattices and that the atoms in one sublattice have opposite direction of the magnetic moment than those in the other one. The critical temperature below which all atomic moments are aligned in opposite direction is named “Néel temperature”. L. Néel, "Propriétés magnétiques des ferrites ; ferrimagnétisme et antiferromagnétisme", *Ann. Phys. (Paris)*, **3**, 137-198 (1948).

1949 - Clifford G. Shull (1915-2001) and **James Samuel Smart**

Physical crystallography - ***Magnetic structure***

Shull (Nobel Prize for Physics in 1994) and Smart carry out the first determination of a magnetic structure, that of MnO, by means of neutron diffraction experiments. C. G. Shull, J. S. Smart, "Detection of Antiferromagnetism by Neutron Diffraction", *Phys. Rev.*, **76**, 1256 (1949). I. W. Ruderman, "The Scattering of Slow Neutrons by Paramagnetic Crystals", *Phys. Rev.*, **76**, 1572 (1949).

1949 - Andrew W. Lawson (1861-1952) and **Ting-Yuan Tang**

Instrumentation, diffraction and radiation sources - ***Diamond anvils***

After an unsuccessful attempt to use beryllium cells to carry out high pressure diffraction experiments, Lawson and Tang design a cell with two diamond anvils, transparent to X-rays, that allows them to determine the structure of cerium at high pressure (15 kbar): A. W. Lawson, T.-Y. Tang, "A Diamond Bomb for Obtaining Powder Pictures at High Pressures", *Rev. Sci. Instrum.*, **21**, 815 (1950).

1949 - Tei-ichi Ito (1898-1980)

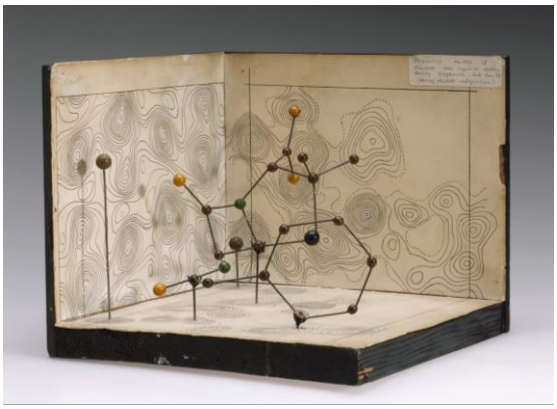
Instrumentation, diffraction and radiation sources - ***Powder diffraction photography indexations***

T. Ito, "A general powder X-ray photography", *Nature (London)*, **164**, 755-756 (1949).

1949 - Dorothy Crowfoot Hodgkin (1910 - 1994)

Chemical crystallography - ***The structure of penicillin***

Dorothy Hodgkin solves the structure of penicillin in 1945, but her work remains unpublished until 1949. She receives the Nobel Prize of Chemistry in 1964 for “her determination, by means of X-ray diffraction of the structures of important biochemical substances”, with specific mention of penicillin and vitamin B_{12}. D. Crowfoot, C. W. Bunn, B. W. Rogers-Low, A. Turner-Jones, "X-ray crystallographic investigation of the structure of penicillin", in H. T. Clarke, J. R. Johnson, R. Robinson, eds.; *The Chemistry of Penicillin*, Princeton University Press, p. 310 (1949). Images: Wikimedia.



1951 - Charles Kittel (1916-)

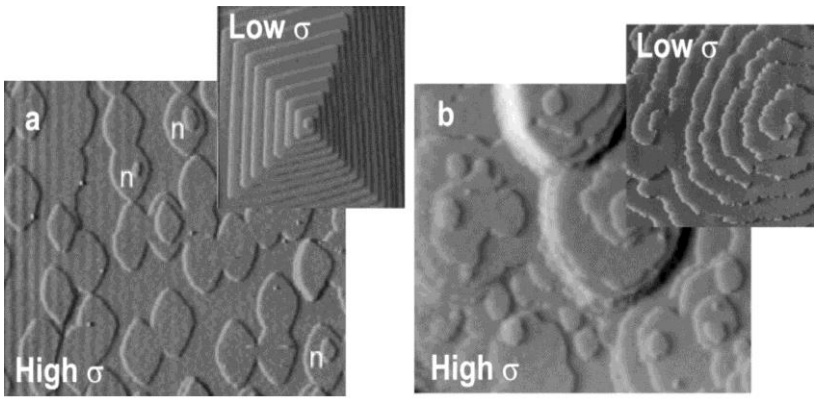
Physical crystallography - ***Antiferroelectricity***

Introduces new concepts in the theory of elasticity. He also works on antiferroelectricity, deducing that it can appear or disappear (most commonly decrease) as a function of temperature, pressure, external electrical fields, growth method and other factors. C. Kittel, "Theory of antifferroelectric crystals", *Phys. Rev.*, **82**, 729-732 (1951). C. Kittel, *Introduction to Solid State Physics*, New York: Wiley, 1966.

1951 - W. R. Burton, Nicolás Cabrera (1913-1989) and **Frederick Charles Frank** (1911-1998)

Physical crystallography - ***Helical dislocations and crystal growth***

The work of Burton, Cabrera and Frank in 1951 is still today a reference for the studies of crystal growth. Contrary to the 2D nucleation that allows the crystal surface to grow only at high supersaturations, one dislocation can explain the crystal growth at very low supersaturations. The theory of Burton, Cabrera and Frank (BCF) has been very important for a variety of applications, since the control of dislocations allows for a control of the degree of perfection and the rate of growth of the crystal faces. W. R. Burton, N. Cabrera, F. C. Frank, "The growth of crystals and the equilibrium structure of their surfaces", *Phil. Trans. R. Soc. London Ser. A*, **243**, 299-358 (1951).



D. Aquilano. Emmerciquadro, nº 52, 2014

1951 - Martin Julian Buerger (1903-1986)

Chemical crystallography - ***Structural classification of polymorphic transitions***

Phase transitions and crystallography are intimately related in the work of Buerger, which takes into account phenomena such as order-disorder (rotational or substitutional), displacive transitions, reconstructive transitions, affected coordination spheres, symmetry relationships between polymorphs, effect of temperature or of the type of bond, and size or perfection of the crystal. M. J. Buerger, "Crystallographic aspects of phase transformations", in *Phase Transformations in solids*, R. Smoluchowski, ed., New York: John Wiley, 1951, pp. 183-211.

1951 - Morris Cohen (1911-2005)

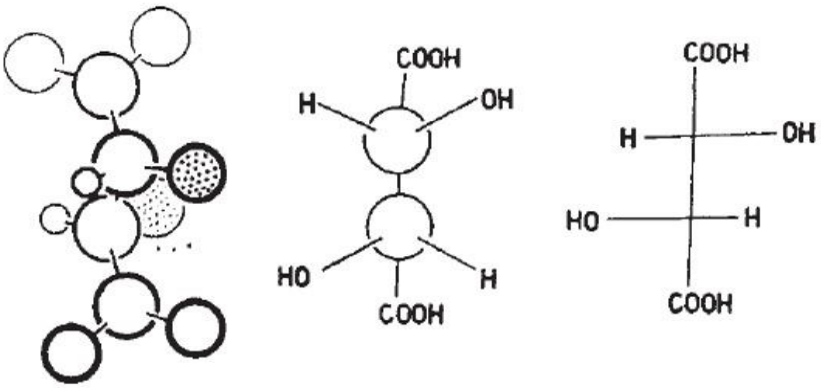
Chemical crystallography - ***Martensitic transitions***

The martensitic transitions are of great importance in the steel industry. While most of the polymorphic transformations take place by nucleation and growth, in the martensitic transformations the mechanism does not imply atomic diffusion, but can be rather considered as a block motion. The alloys with shape memory are also materials with this type of polymorphism. M. Cohen, "The martensite transformation", in *Phase Transformations in solids*, R. Smoluchowski, ed., New York: John Wiley, 1951, pp. 588-660.

1951 - Johannes Martin Bijvoet (1892-1980)

Chemical crystallography - ***Absolute configuration***

Bijvoet determines the absolute configuration of a compound for the first time, taking advantage of the weak effects of the anomalous dispersions. The structure studied is that of the (D)- and (L)-forms of tartrate in its sodium and rubidium salts, and later in the ammonium salt. J. M. Bijvoet, A. F. Peerdeman, A. J. Van Bommel, "Determination of the Absolute Configuration of Optically Active Compounds by Means of X-Rays", *Nature*, **168**, 271 (1951). A. J. van Bommel, J. M. Bijvoet, "The Crystal Structure of Ammonium Hydrogen D-tartrate", *Acta Cryst.*, **11**, 61-70 (1951).

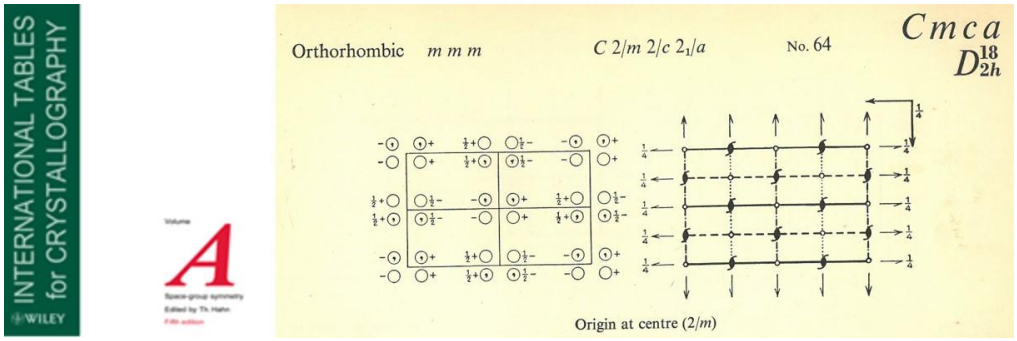


1951 - Linus Pauling (1901-1994)

Chemical crystallography - ***α helix model in proteins***

Pauling becomes one of the pioneers in the interpretation of X-ray diffraction data from proteins. He proposes models based on the first data from α- and β-keratin. He builds an α helix with hydrogen bonds in the helical axis. L. Pauling, R. B. Corey, H. R. Branson, "The structure of proteins: two hydrogen-bonded helical configurations of the polypeptide chain", *Proc. Natl. Acad. Sci. USA*, **37**, 205-211 (1951).

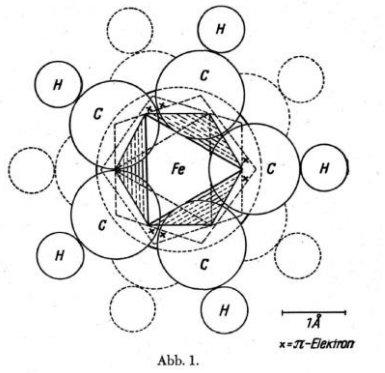
1952 - Norman Fordyce McKerron Henry (1909-1983) and **Kathleen Yardley (Lonsdale)** (1903-1971)
Symmetry - ***International Crystallography Tables***



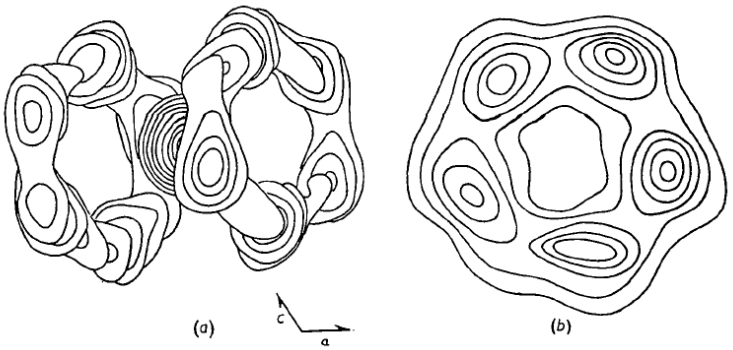
The representation of space groups in a practical way for crystallographers was a challenge since the importance of space groups for structural determination was recognized. Several contributions, together with a graphical representation of the space groups, were presented in the first volume of the *Internationale Tabellen zur Bestimmung von Kristallstrukturen* edited by Hermann in 1935. Henry and Lonsdale edited an English version in 1952, and Theo Hahn was the editor of a new edition published in 1983. C. H. Hermann, ed., *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Vol. 1, Berlin: Germans Bornträger, 1935. J. S. Kasper, K. Lonsdale, J. A. Ibers, W. C. Hamilton, eds., *International Tables for X-ray Crystallography*, Vol. 1. *Symmetry Groups*, Birmingham: Kynoch Press, 1952. T. Hanh, ed., *International Tables for Crystallography*, Vol. A. *Space Group Symmetry*, Dordrecht: D. Reidel, 1983.

1952 - Ernst Otto Fischer (1918-2007)
Chemical crystallography - ***The structure of ferrocene***

Ernst Otto Fischer and Wolfgang Pfab, based on the systematic extinction of the diffraction patterns obtained with a Weissenberg camera, deduced the space group and the unit cell volume calculated from the measured density, deduced also that there are two molecules per unit cell and that, according to the formula $FeC_{10}H_{10}$ the iron atom must be sitting on a symmetry centre. They conclude that the molecule must have a sandwich structure, thus confirming the structure proposed the same year by Wilkinson and Woodward based on a NMR spectrum. Fischer received the Nobel Prize for Chemistry in 1973, shared with Geoffroy Wilkinson for his work in organometallic chemistry.

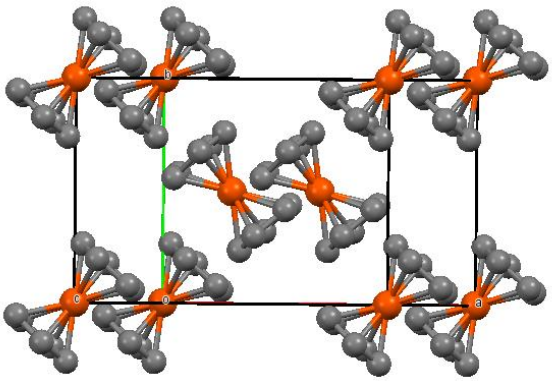


Fischer and Pfab



Orgel and Dunitz

Philip Frank Eiland and Ray Pepinsky independently arrive to the same conclusion two months later. Jack Dunitz and Leslie Orgel made the first complete structural determination of this compound in 1956. Ferrocene is the first sandwich compound known, prepared independently by the groups of Pauson and Miller in 1951, and its structure presents a type of chemical bond unknown so far. E. O Fischer, W. Pfab, "Cyclopentadien-Metallkomplexe, ein neuer Typ metallorganischer Verbindungen", *Z. Naturforsch. B*, **7**, 377-379 (1952); P. F. Eiland, R. Pepinsky, "X-Ray Examination of Iron Biscyclopentadienyl", *J. Am. Chem. Soc.*, **74**, 4971 (1952); J. D. Dunitz, L. E. Orgel, A. Rich, "The Crystal Structure of Ferrocene", Acta Cryst., **9**, 373-375 (1956).



1952 - Cornell University

Instrumentation, diffraction and radiation sources - ***Synchrotron radiation***

Launch of the first synchrotron line at the Newman Laboratory of Cornell University in Ithaca, New York. Hartman, Tomboulian and Corson publish the first studies with synchrotron radiation.

1952 - Frederik William Houlder Zachariasen (1906-1979)

Instrumentation, diffraction and radiation sources - ***Method of the heavy atom***

With the heavy atom method Zachariasen makes an important contribution in a moment in which many crystallographers are trying to solve the phase problem. W. H. Zackariasen, "A new analytical method for solving complex crystal structures", *Acta Cryst.*, **5**, 68-73 (1952).

1952 - David Sayre (1924-2012)

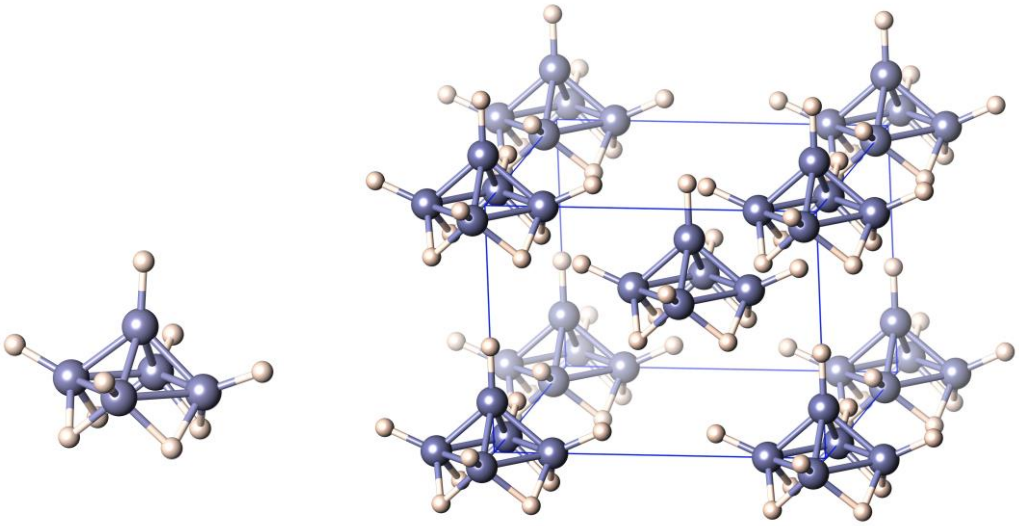
Instrumentation, diffraction and radiation sources - ***Direct methods for the resolution of structures***

Between 1952 and 1962 the number of known crystal structures increases extraordinarily. The direct methods allow for the resolution of structures using the Patterson function that provides the phase information from the measured intensity. Nowadays, with the help of powerful computers, these methods are of common use. D. Sayre, "The squaring method: a new method for phase determination", *Acta Cryst,* **5**, 60-65 (1952).

1952 - William Lipscomb (1919-2011)

Chemical crystallography - ***The structures of boranes***

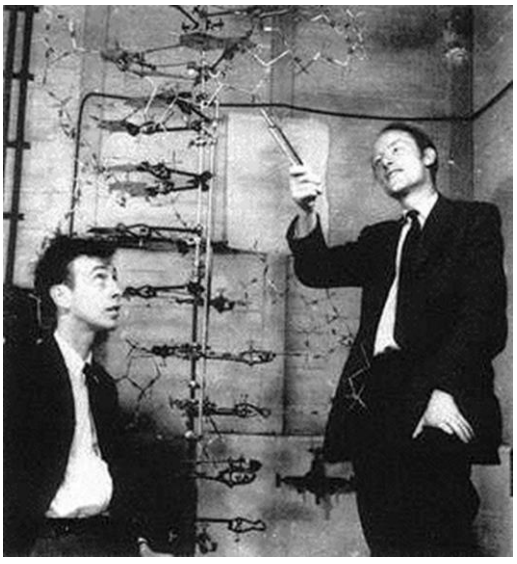
With the structure of pentaborane Lipscomb initiates his structural study of boranes that ended up in him being awarded the Nobel Prize of Chemistry in 1976. J. W. Dulmage, W. N. Lipscomb, "The Crystal and Molecular Structure of Pentaborane", *Acta Cryst.*, **5**, 260 (1952).



1953 - Francis Crick (1916-2004) **, James D. Watson** (1928-) , **Maurice H. F. Wilkins** (1916-2004), **Rosalind E. Franklin** (1920-1958)

Chemical crystallography – ***The structure of DNA***

The X-ray image of DNA obtained by Rosalind Franklin allowed James Watson and Francis Crick to figure out their famous double helix model, although the structure was obtained with atomic resolution only in 1980. Crick and Watson were awarded the Nobel Prize in Physiology and Medicine in 1962 for their discoveries in regard with the molecular structure of nucleic acids and their importance to transmit information in living matter.



J. D. Watson, F. H. C. Crick, "Molecular Structure of Nucleic Acids: A Structure for Deoxyribose Nucleic Acid", *Nature (London)*, **171**, 737-738 (1953). J. D. Watson, *The Double Helix: a personal account of the discovery of the structure of DNA*, London: Penguin Books, 1970.

1953 - Herbert A. Hauptman (1917-2011)

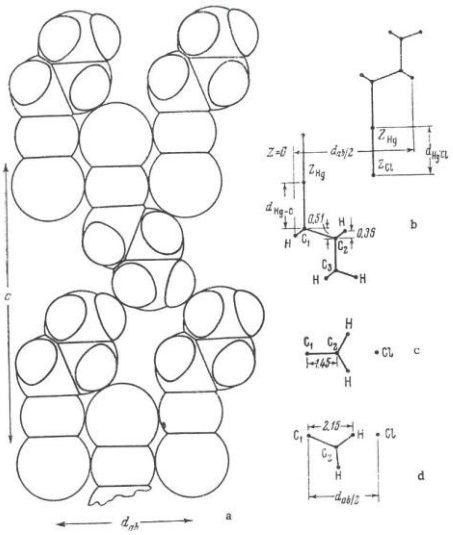
Instrumentation, diffraction and radiation sources - ***Development of direct methods***

Following the proposals of Sayre, Hauptman and Karle statistically analyse the relationships between the signs of the reflections related by symmetry. H. Hauptman, J. Karle, The probability Distribution of the magnitude of a structure factor. II. The noncentrosymmetric Crystal; *Acta Cryst.*, **6**, 136-141 (1953).

1955 - Aleksandr Isaakovich Kitaigorodskii (1914-1985)

Atoms, packing, bonding - ***Packing of molecules and miscibility in the solid state***

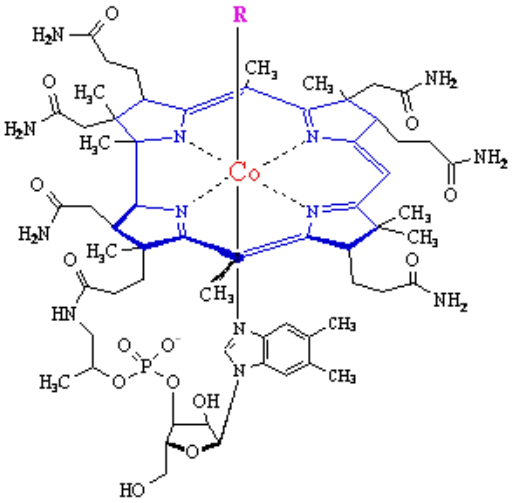
Kitaigorodskii studies the packing of organic molecules in crystals. He shows that if the size of the molecules is defined from the van der Waals radii of their atoms, there is a tendency to form a dense packing leaving as minimum empty space as possible, which he complements with the tendency for the maximum symmetry. He finds that the coordination number of a molecule is usually twelve. Studies many families of organic compounds (hydrocarbons, benzene derivatives, etc.) and makes conceptual contributions to the understanding of miscibility in the solid state between organic compounds, which will become a reference in the future. A. I. Kitaigorodsky, *Organic Chemical Crystallography*, New York: Consultants Bureau, 1961; A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, New York: Academic Press, 1973; A. I. Kitaigorodsky, "General View on Molecular Packing", a *Advances in Structure Research by Diffraction Methods*, R. Brill, R. Mason, eds., Oxford: Pergamon Press, 1970, Vol. 3, 173-247; A. I. Kitaigorodsky, *Mixed Crystals*, Berlin: Springer-Verlag, 1984.

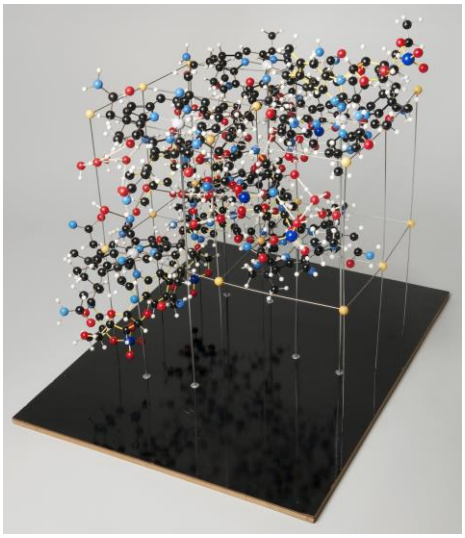


1955 - Dorothy Crowfoot Hodgkin (1910-1994)

Chemical crystallography - ***Crystal structure of vitamin B_{12}***

Vitamin B_{12} was one of the structures of large molecules to be solved using the heavy atom method. The only known data were the elemental composition, that benzimidazole, ribose and phosphate units were present, and that its spectrum was similar, but not identical, to those of porphyrins. D. C. Hodgkin, J. Pickworth, J. H. Robertson, K. N. Trueblood, R. J. Prosen, J. G. White, "The Crystal structure of the hexacarboxylic acid derived from B_{12} and the molecular structure of the vitamin", *Nature (London)*, **176**, 325-328 (1955).





1956 - David Harker (1906-1991)

Instrumentation, diffraction and radiation sources

- ***Phase determination in non-centrosymmetric crystals***

In 1936, barely two years after the first paper of Patterson, Harker pointed that in centrosymmetric crystals there are certain planar sections and certain lines in the geometry of the Patterson function, in which ideally one can also find peaks resulting from pairs of atoms related by symmetry, and known as Harker sections and Harker lines, respectively. The atoms sitting in these sections and lines are easy to locate. In 1956 Harker reported a simple graphical description of the specific problem of non-centrosymmetric crystals, which would be later used for the resolution of protein structures. D. Harker, "The application of the three-dimensional Patterson method and the crystal structures of proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3", *J. Chem. Phys.*, **4**, 381-390 (1936). D. Harker, "The determination of the phases of the structure factors of non-centrosymmetric crystals by the method of double isomorphous replacement", *Acta Cryst.*, **9**, 1-9 (1956).

1957 - John C. Jamieson (1924-1983)

Chemical crystallography

- ***Structures under higher pressure***

Jamieson, a student of Lawson, designs a high pressure cell formed by a single diamond (transparent to X-rays), in which there is a hole that contains the sample, that is suitable for work at pressures of up to 24 kbar: "Introductory Studies of High-Pressure Polymorphism to 24,000 Bars by X-Ray Diffraction with Some Comments on Calcite II", *J. Geol.*, **65**, 334-343 (1957). In that way he shows that potassium iodide changes its sodium chloride structure to a caesium chloride one above 18 kbar.

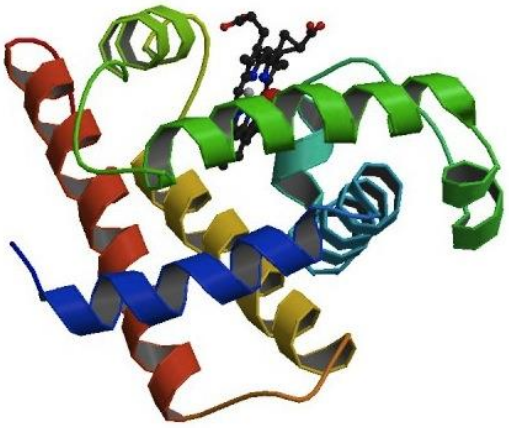
1958 - John Condery Kendrew (1917-1997)  , **Max Ferdinand Perutz** (1914-2002) 

Chemical crystallography - ***First structures of proteins***

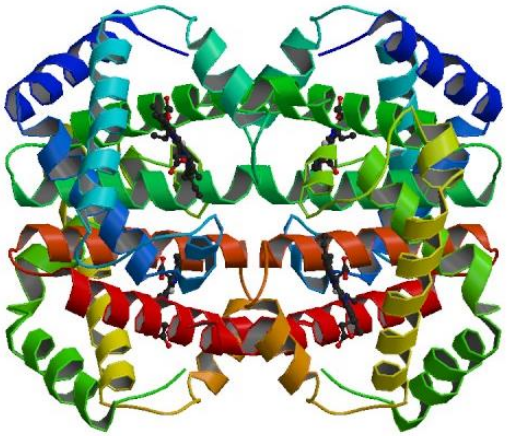
The first structural determination of proteins, myoglobin and haemoglobin, are carried out by Kendrew and Perutz, respectively, and mark the birth of structural molecular biology. Both authors received the Nobel Prize in Chemistry in 1962.

D. W. Green, V. M. Ingram, M. F. Perutz, "The structure of haemoglobin. IV. Sign determination by the isomorphous replacement method", *Proc. R. Soc. London Ser. A*, **225**, 287-307 (1954).

J. C. Kendrew, G. Bodo, H. M. Dintzis, R. G. Parrish, H. Wyckoff, D. C. Phillips, "A three-dimensional model of the myoglobin molecule obtained by X-ray analysis", *Nature*, **181**, 662–666 (1958).
M. F. Perutz, M. G. Rossman A. F. Cullis, H. Muirhead, G. Will, A. C. T. North, "Structure of haemoglobin: a three-dimensional Fourier synthesis at 5.5 Å resolution, obtained by x-ray analysis", *Nature*, **185**, 416–422 (1960).



Myoglobin (Kendrew)



Haemoglobin (Perutz)

1958 - Andrew Richard Lang (1924-2008)

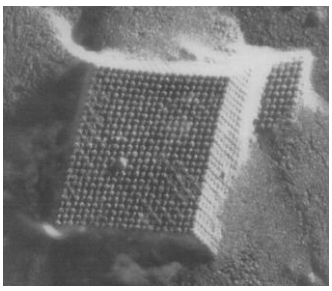
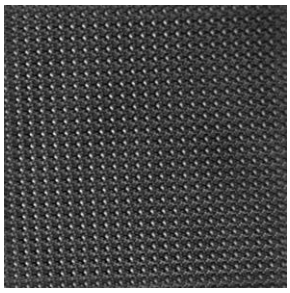
Instrumentation, diffraction and radiation sources – ***Development of X-ray topography***

Lang develops a camera in which the film and the crystal move simultaneously, and in which the use of monochromatic radiation allows to study the distribution of dislocations. A. R. Lang, "Direct observation of individual dislocations by X-ray diffraction", *J. Appl. Phys.*, **29**, 597-598 (1958).

1958 - Ralph W. G. Wyckoff (1897-1994)

Instrumentation, diffraction and radiation sources - ***High-resolution electron microscopy***

In an attempt to obtain an image of the molecular structure of a crystal, electron microscopy was used both as an observation method and as a complement to X-ray diffraction. In one of the first interesting works Wyckoff showed the packing of molecules in micrographies of crystals obtained by high-resolution microscopy (HREM). The paper of Labaw and Wyckoff shows the formation of the faces of a crystal. L. W. Labaw, R. W. G. Wycoff, "The electron microscopy of tobacco necrosis virus crystals", *J. Ultrastruct. Res.*, **2**, 8-15 (1958).

Wyckoff's micrography of the crystal surface of the tobacco necrosis virus (left). HRTEM (high resolution transmission electron microscopy) image of a barium and strontium niobate crystal, with tungsten bronze structure (right), courtesy of Lluís López Conesa, CCIT-UB.

1962 - Nonius

Instrumentation, diffraction and radiation sources ***- First automatic diffractometer***

The resolution of single crystal X-ray structures made a significant step forward with the appearance of the so-called "automatic diffractometers". Apparently, the first company to market those equipments was Nonius in 1962, with its instrument CAD3. Soon other companies would follow, such as Rigaku, Philips, Stoe, Syntex, and Siemens. Those instruments allowed to drastically reduce the time for the data recording and structural resolution.

1964 - Alexey Vasilyevich Shubnikov (1887-1970)

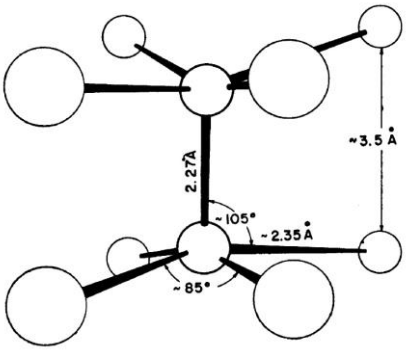
Symmetry - ***Colour Symmetry***

Shubnikov provided a new vision of symmetry by introducing "colour", which plays an important role in the physical properties of crystals, as well as in art. Following his contribution, 46 dichromatic bidimensional and 1651 tridimensional space groups were determined. His contributions apply as well to the study of liquid crystals. He worked also on piezoelectric crystals. A. V. Shubnikov, N. V. Belov, *Colored Symmetry*, W.T. Holser, ed., Oxford: Pergamon Press, 1964.

1964 - F. Albert Cotton (1930-2007)

Atoms, packing, bonding - ***Rhenium-rhenium quadruple bond***

In 1963, Kuznetsov and Koz'min published the structure of a pyridinium salt of an anion that they formulated as $[Re_2Cl_8]^{4-}$, with a short Re-Re distance (2.22 Å). Francis Albert Cotton and co-workers redetermined the structure, proved that the correct formula of the anion was $[Re_2Cl_8]^{2-}$ and proposed a convincing explanation for the metal-metal bond, which could explain both the diamagnetism of the salt and the eclipsed conformation of the anion. As a conclusion, they stated, "This would seem to be the first quadruple bond discovered". V. G. Kuznetsov, P. A. Koz'min, "A study of the structure of (PyH)HReCl$_4$", *Zh. Strukt. Khim.* (*J. Struct. Chem.*) **4**, 55-62 (1963). F. A. Cotton, N F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson, J. S. Wood, "Mononuclear and polynuclear chemistry of rhenium(III): its pronounced homophilicity", *Science*, **145**, 1305–1307 (1964).



Photograph: S. Alvarez

1964 - Gerhard Martin Julius Schmidt (1919-1971)

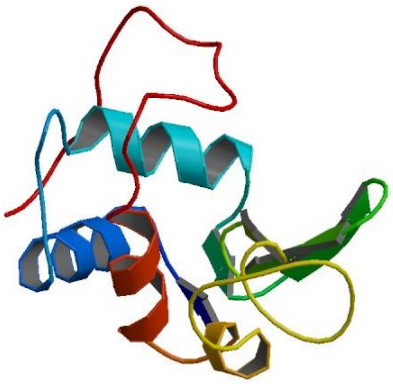
Chemical crystallography - ***Topochemical reactions***

His pioneering studies during the 60s and 70s of the XXth century showed that the products of photoinduced intramolecular reactions in the solid state are topochemically controlled by the relative arrangement of the reacting groups in the crystal. M. D. Cohen, G. M. J. Schmidt, "Topochemistry. Part I. A Survey", *J. Chem. Soc.*, 1996-2000 (1964). Schmidt had introduced crystallography in Israel in the decade of 1950 and was the Director of the Weizmann Institute.

1965 - David Chilton Phillips (1924 - 1999)

Chemical crystallography - ***First structure of an enzyme***

Lysozyme is a small enzyme that cuts the sugar chains in the walls of bacterial cells, and protects our body from infections. Its structure was the first enzyme structure to be known, obtained from hen's egg white, and solved in the laboratory of D. C. Phillips, at the Royal Institution of London. C- C. F. Blake, D. F. Koenig, G. A. Mair, A. C. T. North, D. C. Phillips, V. R. Sarma, "Structure of Hen Egg-White Lysozyme, a Three-Dimensional Fourier Synthesis at 2 Å Resolution", *Nature*, **206,** 757-761 (1965).



1965 - Carroll K. Johnson (1929-)

Chemical crystallography - ***ORTEP program for the representation of structuress***

During the decade of 1960 the computational methods become capable of handling the resolution of more complex crystal structures. One of the programs that deserve to be highlighted is ORTEP,

designed to draw structural models with thermal motion ellipsoids and with stereoscopic visualization. C. K. Johnson, *ORTEP: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*; Report ORNL-3794, Oak Ridge National Laboratory, Tennessee. (1965). M. N. Burnett, C. K. Johnson, ***ORTEP-III: Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations***, 1966.

1965 - Olga Kennard (1924-)

Chemical crystallography - ***Cambridge Structural Database***

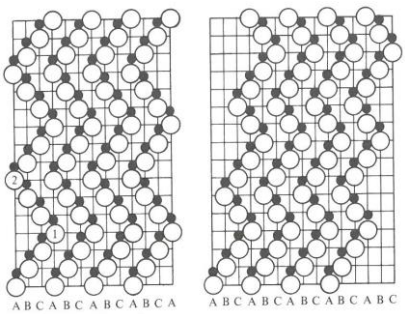
Establishment of the Cambridge Structural Database by the crystallography group of Olga Kennard at the Cambridge University. Olga Kennard was for a long time the Director of the Cambridge Crystallographic Data Centre, in charge of the update and improvement of this database that contains today over 900.000 crystal structures of molecular compounds. The Centre occupies a building made in 1965 by architect Erik Sørensen.

Photograph: S. Alvarez

1966 - Ajit Ram Verma (1921-2009**)** and **Padmanabhan Krishna (**1938**-)**

Chemical crystallography - ***Polymorphism and polytypism***

Polytypism can be considered as a one-dimensional polymorphysm in which the different polytypes of a material differ in the dimensions of the unit cell in one of the three crystallographic directions. Polytypism is frequent in layer structures in which the stacking sequence can vary. P. Krishna, A. R. Verma, "Anomalies in silicon carbide polytypes", *Proc. R- Soc. London Ser. A*. **272**, 490-502 (1963). A. R. Verma, P. Krishna, *Polymorphism and Polytypism in Crystals*, New York: John Wiley, 1966.



1966 - Jerome Karle (1918 - 2013) and **Isabella H. Karle** (1921-)

Instrumentation, diffraction and radiation sources - ***Symbolic addition procedure in direct methods***

The method of symbolic addition developed by the Karles stands out among the direct methods for the resolution of crystal structures. "The symbolic addition procedure for phase determination for cenmtrosymmetric and non centrosymmetric crystals", *Acta Cryst*., **21**, 849-859 (1966).

1967 - Hugo Rietveld (1932-2016)

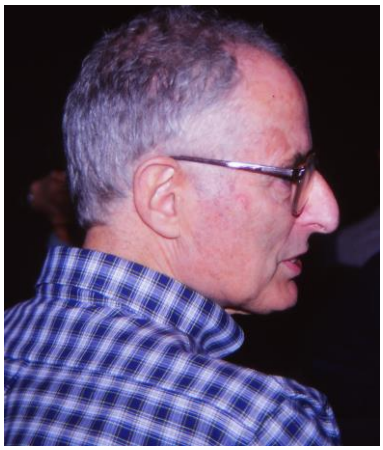
Instrumentation, diffraction and radiation sources - ***Powder diffraction structures***

Rietveld develops a method to refine the structure of a compound by fitting a profile to the powder diffraction pattern. H. M. Rietveld, "A profile refinement method for nuclear and magnetic structures", *J. Appl. Cryst*., **2**, 65–71 (1969).

1967 - Philip Coppens (1930- 2017)

Instrumentation, diffraction and radiation sources – ***Electron density determination***

Coppens develops the methodology for the determination of the electron charge density from high resolution X-ray diffraction data. "Comparative X-Ray and Neutron Diffraction Study of Bonding Effects in s-Triazine", *Science*, **158**, 1577-1579 (1967). P. Coppens, *X-ray Charge Densities and Chemical Bonding*, Oxford*:* Oxford University Press, 1997.



Photograph: S. Alvarez

1969 - Robert Day Shannon (1935-) and **Charles Thompson Prewitt** (1933-)

Atoms, packing, bonding - ***Ionic radii***

Shanon and Prewitt publish tables of ionic radii deduced from resolved crystal structures. They are termed “effective ionic radii”, since they have been determined empirically from average bond distances. R. D. Shannon, C. T. Prewitt, "Effective ionic radii in oxides and fluorides", *Acta Cryst. B*, **25**, 925-946 (1969).

1969 - Olga Kennard (1924-) and **David G. Watson** (1934-)

Chemical crystallography ***– Molecular dimensions***

These two crystallographers compile a wide collection of bond distances. O. Kennard, D. G. Watson, eds. *Molecular Structures and Dimensions*, 15 Vols., Dordrecht: D. Reidel, 1970-1983.

1971 - Brookhaven National Laboratory

Chemical crystallography ***- PDB protein database***

The Protein Data Bank is established at the Brookhaven National Laboratory, Long Island, NY, with only seven structures. Today it holds information on more than 137,000 protein structures.

1973 - Hans-Beat Bürgi (1942-) and **Jack Dunitz** (1923-)

Chemical crystallography ***- Structural correlation and reaction paths***

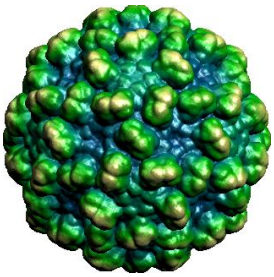
The structures of analogous molecules in a large number of compounds provide a way of "visualizing" reaction paths. H.-B. Bürgi, J. Dunitz, E. Shefter, "Geometrical reaction coordinates. II. Nucleophilic addition to a carbonyl group", *J. Am. Chem. Soc.*, **95**, 5065-5067 (1973). H-B. Bürgi, J. D. Dunitz: *Structure Correlation*, New York: VCH, 1994.

Photograph: S. Alvarez (1999)

1978 - Stephen C. Harrison

Chemical crystallography ***- First structure of a virus with atomic resolution***

The tomato bushy stunt virus (TBSV) was the first crystallized spherical virus: F. C. Bawden, N. W. Pirie, "Crystalline preparations of tomato bushy stunt virus", *Brit. J. Exp. Pathol.*, **19**, 251–263 (1938). Numerous X-ray diffraction studies were carried out on this virus, from the pioneer work of Bernal: J. D. Bernal, I. Fankuchen, D. P. Riley, "Structure of the crystals of tomato bushy stunt virus preparations", *Nature*, **142**, 1075 (1938); J. D. Bernal, I. Fankuchen, "X-ray and crystallographic studies of plant virus preparations", *J. Gen. Physiol.*, **25**, 111-65 (1941). However, it wasn't until 1978 that the structure of this virus could be obtained at atomic resolution: S. C. Harrison, A. J. Olson, C. E. Schutt, F. K. Winkler, G. Bricogne: "Tomato bushy stunt virus at 2.9 Å resolution", *Nature*, **276**, 368-373 (1978).



1978 - Günther Bergerhoff and **I. David Brown**

Chemical crystallography - ***ICSD inorganic structures database***

Bergerhoff and Brown establish the inorganic structures database (ICSD) that is nowadays managed by FIZ Karlsruhe (Leibniz-Institut für Informationsinfrastruktur) and contains information from around 200.000 crystal structures.

1981 - SRS Daresbury

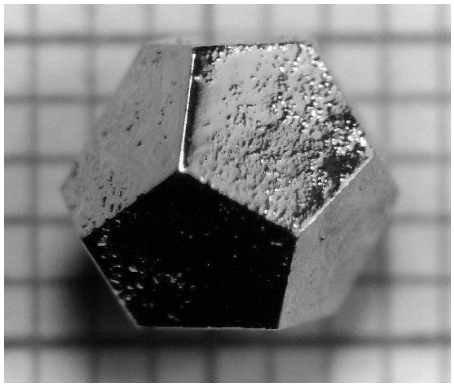
Instrumentation, diffraction and radiation sources - ***Second generation X-ray synchrotron radiation***

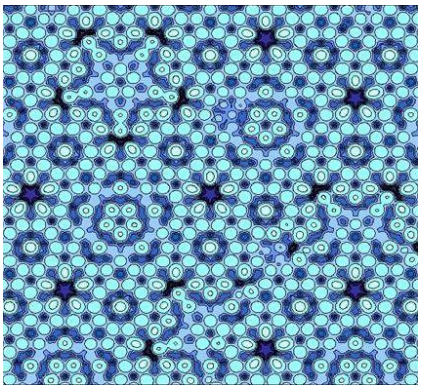
The first synchrotron designed to produce X-rays (second generation synchrotron) starts its operation.

1982 - Dan Schechtman (1941-) 

Chemical crystallography - ***Quasicrystals***

Schetchman discovers quasicrystals of metal alloys, substances that exhibit some properties characteristic of crystals, such as symmetry and structural order, but are aperiodic. These crystals require more than one type of unit cell to fill the space and present 5- and 10-order symmetries, forbidden to conventional crystallography. Schechtman received the Nobel Prize for Chemistry in 2011 for this discovery.





1983 - Howard Flack (1943-2017)

Chemical crystallography - ***Structure of chiral molecules***

Flack proposes a robust method to prove the absolute structure of a chiral compound as a part of the structural refinement process. From the value of the Flack parameter, obtained from X-ray diffraction data, one can know if the structure corresponds to one of the two enantiomers or if it

may be a racemic or a twin crystal. H. D. Flack, "On enantiomorph-polarity estimation", *Acta Cryst. A*, **39**, 876-881 (1983).

1985 - Gerd Binnig (1947-) and **Heinrich Rohrer** (1933-2013)

Instrumentation, diffraction and radiation sources - ***Scanning tunnel microscope (STM)***

The tunnel effect microscope is based on the quantum mechanical tunnel effect, observed as a flux of an electrical current between a sharp tip and a conducting surface under an applied voltage. It allows drawing a tridimensional map of the surface at the atomic scale. G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel, "Surface Studies by Scanning Tunneling Microscopy", *Phys. Rev. Lett.*, **49**, 57-61 (1982); G. Binnig, H. Rohrer, "Scanning tunnelling microscopy", *Helv. Phys. Acta*, **55**, 726-735 (1982). The design of the tunnel effect microscope by Binnig and Rohrer was awarded with the Nobel Prize for Physics in 1986, shared with Ernst Ruska.

1985 - Gerd Binnig (1947-), **Christoph Gerber** (1942-) and **Calvin Quate** (1923-)

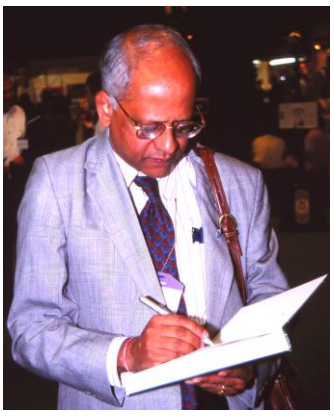
Instrumentation, diffraction and radiation sources - ***Atomic force microscopy (AFM)***

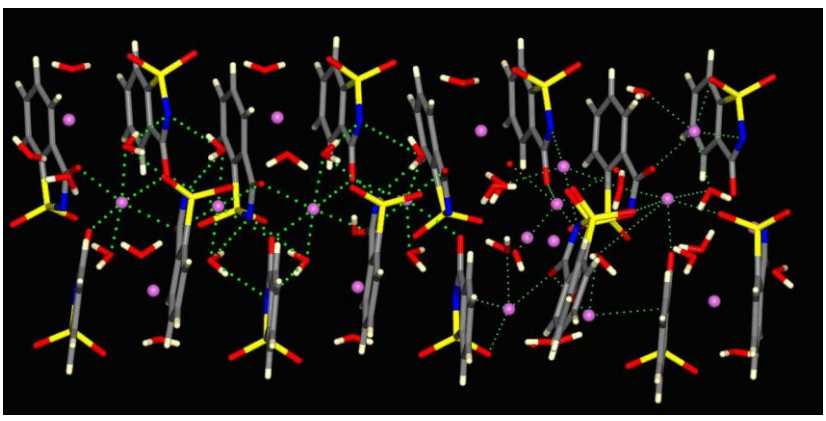
After the invention of the tunnel microscope (STM) Binnig and Gerber worked in California with scientists of Stanford University and IBM in the atomic force microscopy. In this case the force produced by an electric field between the atoms of a tip and those of the surface is measured. The map of the forces produced throughout the surface generates an image of its atomic topography. G. Binnig, C. F. Quate, Ch. Gerber, "Atomic Force Microscope", *Phys. Rev. Lett.*, **56**, 930-933 (1986).

1989 - Gautam Radhakrishna Desiraju (1952-)

Chemical crystallography - ***Crystal engineering***

Desiraju, one of the precursors of Crystal Engineering, develops the concept of "supramolecular synthon", a molecular unit that allows for the build-up of the crystal structure of a molecular solid. He is also co-responsible of the acceptance of the term "weak hydrogen bond" in structural and supramolecular chemistry. He has been president of the International Union of Crystallography between 2011 and 2014. *The Design of Organic* Solids, Elsevier (1989); *The Crystal as a Supramolecular Entity*, Wiley (1996); *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press (1999); Crystal *Design: Structure and Function*, Wiley (2003); G. R. Desiraju, J. J. Vittal, A. Ramanan, *Crystal Engineering: A Textbook*, World Scientific (2011).





Photograph: S. Alvarez

1992 - Helen M. Berman (1943-)

Chemical crystallography - ***Nucleic acid database***

Helen Berman and colleagues at the Rutgers University (New Jersey) establish the Nucleic Acid Database (NDB) as a resource to collect and distribute structural information on nucleic acids.

1992 - 1994 – ESRF

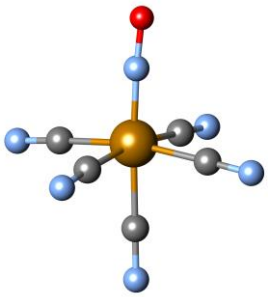
Instrumentation, diffraction and radiation sources ***– Third generation synchrotrons***

First third-generation synchrotron in Grenoble, also known as storage ring, based on undulators. The first beam of electrons is produced in 1992 and 15 radiation lines are available for applications since 1994.

1992 -Theo Woike

Chemical crystallography ***- The structure of an excited state***

First publication of a crystallographic research in which photoinduced steady state methods are applied to the observation of structural changes in sodium nitroprusside using neutron diffraction. M. Rüdlinger, J. Schefer, G. Chevrier, N. Furer, H. U. Güdel, S. Haussühl, G. Heger, P. Schweiss, T. Vogt, T. Woike, H. Zöllner, "Light-induced structural changes in sodium nitroprusside ($Na_{2(}Fe(CN)_5NO)\cdot 2D_2O$) at 80 K", *Z. Phys. B Condens. Matter*, **83**, 125–130 (1991). The interpretation of this process would be later established by Coppens.



1994 -PDB

Chemical crystallography ***– Structural database available through the Internet***

The Protein Data Bank (PDB) establishes a web using the http protocol of the www network and allows for free access to the crystallographic data of more than 130.000 proteins.

1997 - Phillip Coppens (1930-2017)

Instrumentation, diffraction and radiation sources

Chemical crystallography - ***Photocrystallography and photoisomerization***

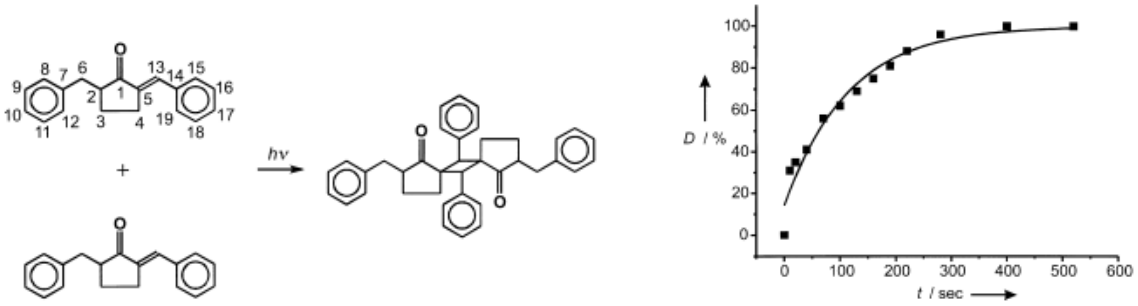
If a photoinduced species has a mean life shorter than a few milliseconds, a stroboscopic experiment can be performed in which a pulsed laser beam is combined with a pulsed X-ray beam to obtain X-ray diffraction data with time resolution. P. Coppens, "Time-resolved diffraction in chemistry and materials science: The developing field of photocrystallography", *Synchr. Rad. News*, **10**, 26 (1997).

Coppens demonstrates also that the process studied initially by Woike is in fact a photoisomerization of the coordination mode of the NO ligand, from N-bonded to O-bonded to iron, not just a simple change in bond distances: M. D. Carducci, M. R. Pressprich, P. Coppens, "Diffraction Studies of Photoexcited Crystals: Metastable Nitrosyl-Linkage Isomers of Sodium Nitroprusside", *J. Am. Chem. Soc.*, **119**, 2669–2678 (1997).

2001 - Ilona Turowska-Tyrk

Chemical crystallography - ***X-ray monitoring of a reaction***

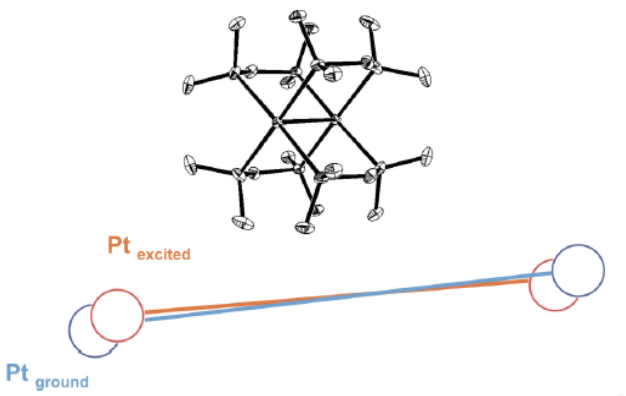
The atomic motions that take place during a photochemical reaction in the crystal phase are monitored for the first time with X-rays, the [2 + 2] photodimerization of 2-benzyl-5-benzylidenecyclopentanone: I. Turowska-Tyrk, "Structural Transformations in a Crystal during the Photochemical Reaction of 2-Benzyl-5-benzylidenecyclopentanone", *Chem. Eur. J.*, **7**, 3401 (2001).



2002 - Phillip Coppens (1930-2017)

Chemical crystallography - ***Time resolved photocrystallography***

First experiment of diffraction by a single crystal in the excited state, carried out by the group of Phillip Coppens at the Brookhaven National Laboratory. The results show that rhodium and platinum compounds of the "paddlewheel" type experience a pronounced shortening of the metal-metal bond in the excited state. In this experiment they synchronize a pulsed laser that generates the excited state and the X-ray pulses obtained from a synchrotron that provide the diffraction data for the structure resolution. The previous photocrystallographic experiments allowed only to observe the molecules before and after the photoreaction, while with the new technique snapshots along the reaction can be seen. C. D. Kim, S. Pillet, G. Wu, W. K. Fullagar, P. Coppens, "Excited-state structure by time-resolved X-ray diffraction", *Acta Crystallogr. A*, **58**, 133 (2002). ICSD 281104-281107



2005 - FLASH

Instrumentation, diffraction and radiation sources - ***Soft X-ray lasers***

The first X-ray free electron laser (XFEL), FLASH, becomes operative. The radiation of these sources is so intense that it destroys molecules and crystals. However, since the X-ray pulses are very short (1 femtosecond, or 10^{-15} seconds) a diffraction pattern can be obtained before the sample is destroyed. These radiation sources will allow us to determine structures of crystals of nanometric dimensions, formed by only a few hundred molecules, which are much easier to obtain and have less deffects than the macroscopic crystals used in conventional X-ray crystallography.

2009 - SLAC

Instrumentation, diffraction and radiation sources - ***Hard X-ray lasers***

The first hard X-rays XFEL starts to operate at SLAC National Accelerator Laboratory, in Silicon Valley. P. Emma and 38 co-authors: "First lasing and operation of an Ångstrom-wavelength free-electron laser", *Nature Photon*, **4**, 641-647 (2010).

2013 - Henry N. Chapman, Christian Betzel, and 47 co-workers

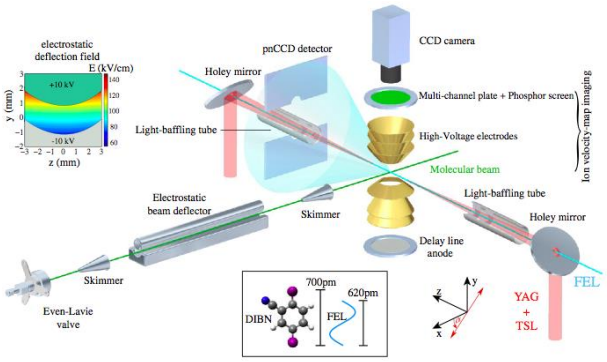
Chemical crystallography - ***First protein structure with XFEL***

Determination of the first structure of a crystal of micrometric dimensions of a protein, cathepsin B (that produces the human sleeping sickness) in a complex with an inactivating peptide, using XFEL radiation: L. Redecke et al., "Natively Inhibited *Trypanosoma brucei* Cathepsin B Structure Determined by Using an X-ray Laser", *Science*, **339**, 227-230 (2013).

2014 - Jochen Küper and 54 co-authors

Instrumentation, diffraction and radiation sources - ***X-ray diffraction by molecules in the gas phase***

Demonstrate that molecules in the gas phase can diffract X-rays, which is a first step toward the structural determination of independent molecules in the gas phase by X-ray diffraction. The authors made a beam of 2,5-diiodobenzonitrile molecules interact with a pulse of an X-ray laser (XFEL), and observed the interference patterns of the rays diffracted by the two iodine atoms. In this way they could determine that these atoms are 800 pm (8.00 Å) apart: J. Küper et al., "X-Ray Diffraction from Isolated and Strongly Aligned Gas-Phase Molecules with a Free-Electron Laser", *Phys. Rev. Lett.* , **112**, 083002 (2014).



TOPICS

Before the crystal

Atoms, packing, bonding

Shape, geometry and crystal structure

Instrumentation, diffraction and radiation sources

Light and crystals

Symmetry

From networks to space groups

Chemical crystallography

Physical crystallography