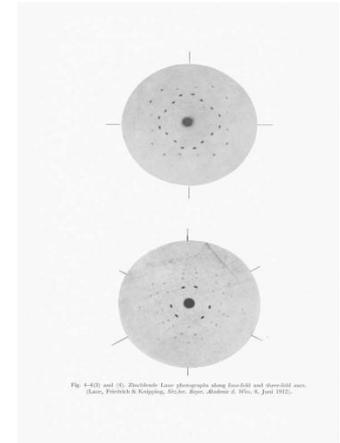
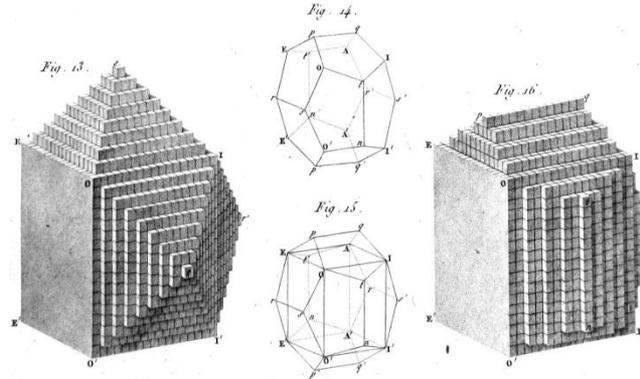
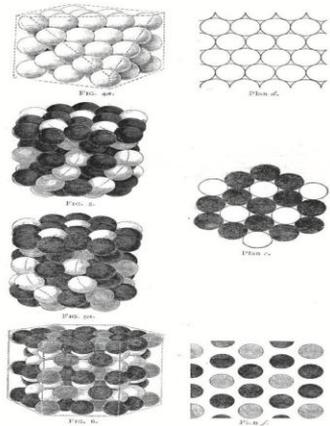
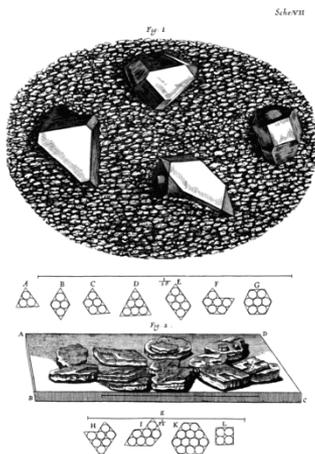


# Seeds to Symmetry to Structure: Crystallography and the Search for Atomic- Molecular Arrangement



Seymour Mauskopf  
Professor Emeritus of History  
Duke University

University of Illinois  
April 30, 2012



<b>CUBIC</b> $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	<b>TETRAPYRAMIDAL</b> $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	<b>ORTHORHOMBIC</b> $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	<b>TRIGONAL</b> $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$
<b>TETAGONAL</b> $a = b \neq c$ $\alpha = \beta = 90^\circ$ $\alpha = \gamma = 90^\circ$	<b>MONOCLINIC</b> $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ $\beta \neq 120^\circ$	<b>TRICLINIC</b> $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	

4 Types of Unit Cell  
P = Primitive  
I = Body-Centred  
F = Face-Centred  
C = Side-Centred

7 Crystal Classes  
→ 14 Bravais Lattices

# Centenary of X-Ray Diffraction

This is the year – indeed the month – that marks the centenary of the first x-ray diffraction photographs taken by **Walter Friedrich** and **Paul Knipping** in Munich under the direction of **Max von Laue**.

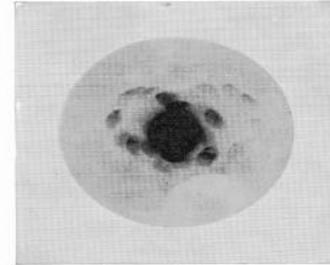


Fig. 4-4(1). Friedrich & Knipping's first successful diffraction photograph.

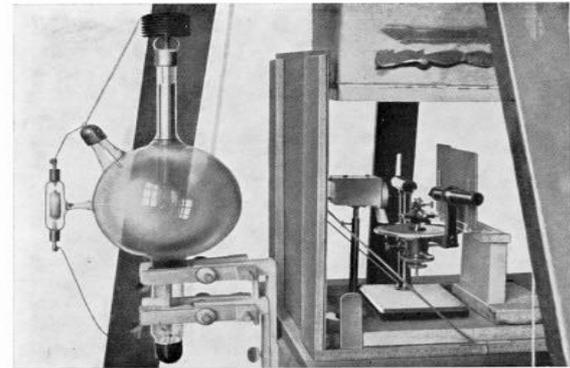


Fig. 4-4(2). Friedrich & Knipping's improved set-up.

# Apologia Pro Oratione Mea

I am **NOT** a crystallographer.

I wrote my dissertation many decades ago on the background to **Louis Pasteur's** first major discovery (the relationship between enantiomorphism in tartrate crystals and optical activity in their solutions).

This was published as ***Crystals and Compounds*** 36 years ago.

Since then, I have done research in very different history of science fields (marginal science and parapsychology, development of explosives & munitions)

# Theme of Talk:

## Interplay of Crystallography & Chemistry

X-ray diffraction photographs have afforded unprecedented opportunity to elucidate spatial arrangements of atoms and molecules.

Celebrating the centenary of the discovery (or invention) of x-ray diffraction, I shall focus on the pre-history of this discovery in the **interplay of crystallography and chemistry to elucidate the invisible spatial arrangements of atoms and molecules.**

# Organization of My Talk

My talk will be focused around **three major moments** in the elucidation of atomic-molecular arrangements.

## **Prehistory: Seeds, Corpuscles, Salts**

- (1) Molecular crystal structure theory through the early 19<sup>th</sup> century (R. J. Haüy's in particular).**
- (2) Interplay with chemistry and optics leading up to the discovery in 1848 by Louis Pasteur of the asymmetrical forms of sodium-ammonium tartrate crystals and their correlation with "optical activity."**

## **Interlude: Separate sequels:**

**Chemistry:** Development of Stereochemistry.

**Crystallography:** Development of Mathematical Structure and Groups.

- (3) The discovery (or invention) of x-ray diffraction photography in 1912 under the direction of Max von Laue and its implementation as a means to ascertaining atomic-molecular arrangement by the Braggs, William Henry and William Lawrence.**

# Prolegomenon: Crystallography: A Scientific Discipline or “Inter-discipline”?

“Although **crystallography is today recognized as a mature science** and crystal-structure analysis is still seen at its core, crystallography must not be reduced to its set of powerful diffraction techniques and methods.

**Crystallography is the interdisciplinary science** that studies condensed matter of any origin from the structural point of view. Despite the fact that **most scientists using crystallographic techniques would not call themselves crystallographers**, **the structural point of view has become crucial in all fields where structure–property or structure–function relationships play a role.”**

Wolfgang W. Schmahl & Walter Steurer, “Laue Centennial” [Introduction], *Acta Crystallographica* (2012) A68 [Laue Centennial], p. 2.

# Crystallography: A Scientific Discipline or “Inter-discipline”?

This quotation, from the Introduction to the Laue Centennial volume of the **Acta Crystallographica** seems to me inadvertently to highlight the “ambiguity” of crystallography as a scientific discipline. Is it a:

**“mature science?”**

**an “interdisciplinary science?”**

or

**a set of techniques used by scientists who “would not call themselves crystallographers”?**

**There are perhaps parallels here between crystallography and statistics.**

# Seeds to Symmetry to Structure

**Prehistory: Seeds, Corpuscles, Salts**

# 16<sup>th</sup>- 17<sup>th</sup> century Seminal Theories of Mineral Formation

**Paracelsus**, **seminal model**: Analogy to fruit-bearing plants:

“Clearly plants develop from seeds within the element earth into the element air, where fruits are born. Earth, then, serves as a matrix for the seed of the plant, providing it with appropriate nourishment. The branches of the plant extend upward into the neighboring element, air.”



David Oldroyd, “Some Neo-Platonic and Stoic Influences on Mineralogy in the Sixteenth and Seventeenth Centuries” (1974) in Allen G. Debus, *Alchemy and Early Modern Chemistry: Papers from Ambix* p. 220 (p. 132 in original).

Philippus Aureolus Theophrastus Bombastus von Hohenheim (aka “PARACELSUS”)

# 16<sup>th</sup>- 17<sup>th</sup> Century Seminal Theories of Mineral Formation

“Similarly, thinks **Paracelsus**, **the matrix element, water, nourishes the seeds of minerals and metals, which grow into mature specimens within the earth. The matrix of minerals, the element water – forms a ‘tree’ within the body of the earth, which deposits its fruits in due season, later to be harvested by man.**”



David Oldroyd, “Some Neo-Platonic and Stoic Influences on Mineralogy in the Sixteenth and Seventeenth Centuries” pp. 222-223 (pp. 134-135 in original).

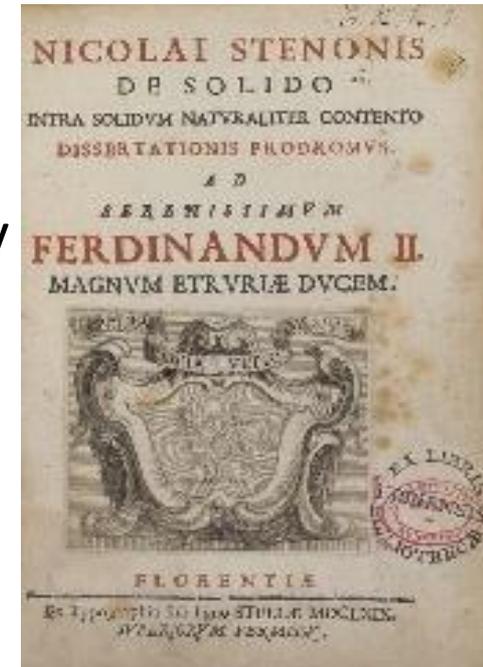
The tree that Larry Principe made out of philosophical mercury and a seed of gold. Credit: Larry Principe

<http://cenblog.org/newscripts/2011/08/reconstructing-alchemical-experiments/S>

# 17<sup>th</sup>-Century Materialistic Explanations for Crystal Formation

“By the latter half of the seventeenth century, modes of explanation alternative to the old ‘idealistic’ concepts were being proposed, and were gradually displacing the earlier explanatory schemes....

In **Steno’s *Prodromus* (1669)**, usually taken to be the herald of the new age for geological sciences, **one finds no attempt to explain mineralogical phenomena in terms of seeds, ferments or spiritual essences.** The accretion of crystalline matter provides the basis of the proposed explanations of crystal formation and an organic origin of mineral crystals is explicitly denied.”



David Oldroyd, “Some Neo-Platonic and Stoic Influences on Mineralogy in the Sixteenth and Seventeenth Centuries,” p. 241 (p. 153 in original).

# 17<sup>th</sup>-Century Corpuscular Explanations of Crystal Structure

Robert Hooke, *Micrographia* (1665)

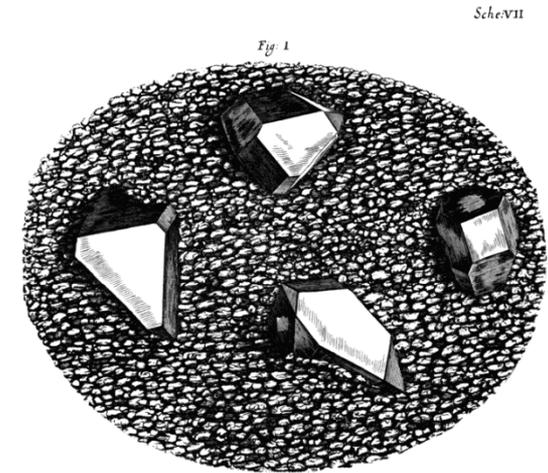
“I could make probable that all these regular Figures that are so conspicuously *various* and *curious*,... arise onely from **three or four several positions of *Globular* particles**, and those the most plain, obvious, and necessary conjunctions of such figur'd particles that are possible....

I could also instance in the figure of *Sea-salt*, and *Sal-gem*, that it is compos'd of a texture of *Globules*, placed in a *cubical* form, as in L.”

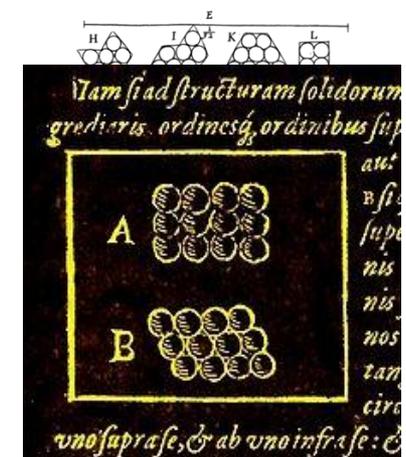
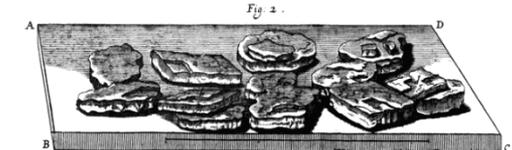
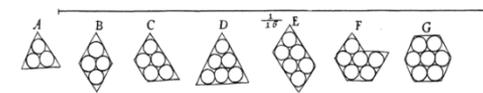
Observ. XIII. *Of the small Diamants, or Sparks in*

Flints. <http://www.gutenberg.org/files/15491/15491-h/15491-h.htm>

J, Kepler, Drawing of a square (Figure A, above) and hexagonal (Figure B, below) packing from Kepler's work, *Stena seu de Niva Sexangula*. Wikipedia, X-ray cristallography. [1611]

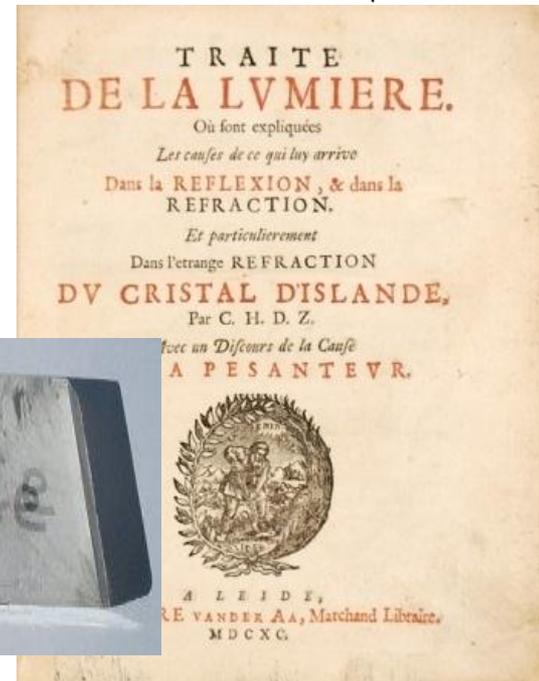
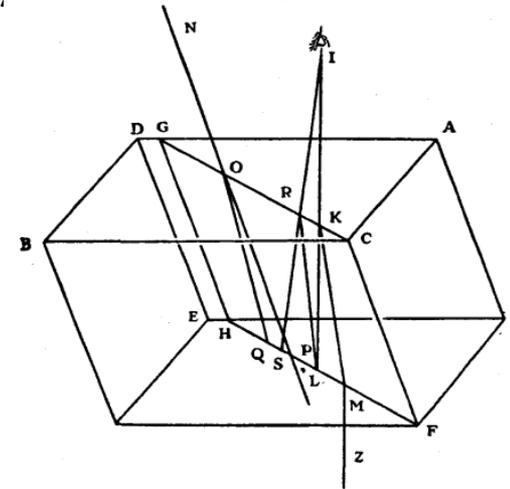


SchevII



# Huyghens, *Traité de la Lumière* (1690), Island Spar Double Refraction

“In all other transparent bodies that we know there is but one sole and simple refraction; **but in this substance there are two different ones.** The effect is that objects seen through it, especially such as are placed right against it, appear double; and that **a ray of sunlight, falling on one of its surfaces, parts itself into two rays and traverses the Crystal thus.**”

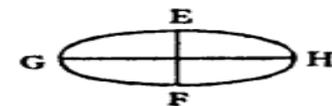
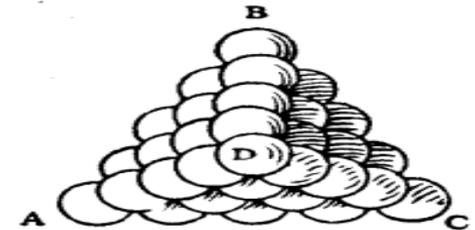
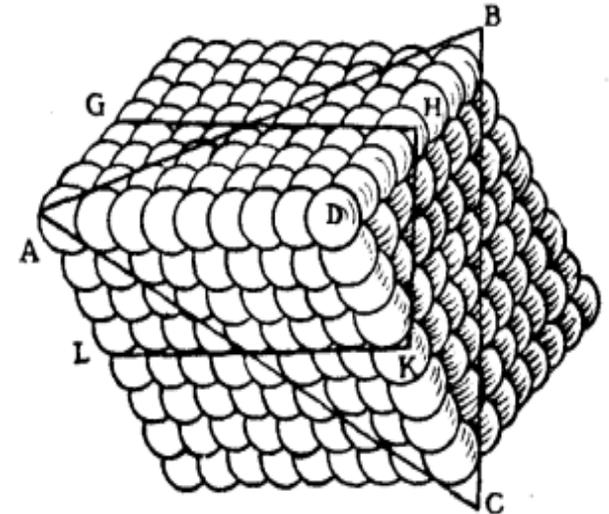


# Huyghens, *Traité de la Lumière* (1690), Island Spar

## Double Refraction, Molecular Model

“It seems that in general that *the regularity that occurs in these productions comes from the arrangement of the small invisible equal particles of which they are composed.*”

And, coming to our Island Crystal, I say that if there were a pyramid such as ABCD, composed of small rounded corpuscles, **not spherical but flattened spheroids**, such as would be made by the rotation of the ellipse GH around its lesser diameter EF...I say that the solid angle of the point D would be equal to the obtuse and equilateral angle of this Crystal.”



# Another Conceptual Tradition: **Salts**

The mechanical models of crystal structure outlined so far ***had little or nothing to do with chemistry***.

However, there was a tradition that linked crystal form to a **“form-giving” saline principle** (Paracelsian and Aristotelian traditions).

By the eighteenth century, **“salt” was being differentiated into different types of salts, the union of acids and bases.**

The correlation between different salts and crystal forms was elaborated by **Carl Linnaeus** and his students.

# Linnaean “saline” crystal morphology

Crystals were generated by the “impregnation” of earths by different salts to produce four types of crystalline stones, each with a distinct crystalline form. All crystalline rocks could be related morphologically (and therefore chemically) to one of these four types.

The four types were **niter**, **muria**, **natrum** and **alum**.



Martin Kaelher & Carl Linnaeus, *De crystallorum generatione* (1747).

Text of this frame taken from Seymour Mauskopf, *Crystals and Compounds* (1976).

# Seeds to Symmetry to Structure

(1)

## Molecular Crystal Structure Theory

## Another Molecular Approach:

### Polyhedral Molecules

The bringing together of chemical composition and crystalline form suggested that the particles that made up the crystal might also be **polyhedra of constant geometrical form for each salt.**

In France, **G.– F. Rouelle** asserted that his microscopic observations of the crystallization of **sel marin (common salt)** indicated that the component particles of this salt might be **cubic** in form.

# Polyhedral *Molecules Integrantes*

This view was spread in the popular *Dictionnaire de chymie* of P.– J. Macquer (1766), as in these two principles on the mechanism of crystallization:

“That, although we do not know the figure of the primitive integrant [compound] molecules of any body, we cannot doubt but that **the primitive integrant molecules of every different body have a constantly uniform and peculiar figure.**

If...they have time and liberty to unite with each other by the sides most disposed to this union, **they will form masses of a figure constantly uniform and similar.**”

Text of this frame taken from Seymour Mauskopf, *Crystals and Compounds* (1976).

# J.—B.—L.— Romé de l'Isle (1736 – 1790): **crystalline molecules**

The ideas of **Linnaeus**, **Rouelle** and **Macquer** were displayed in the first work that attempted to develop geometrical ideas on crystal structure, the ***Essai de cristallographie*** (1772) of **Romé de l'Isle**.

**“Germs being inadmissible for explaining the formation of crystals, it is necessary to suppose that the integrant molecules of bodies have each, according to its own nature, a constant and determinate figure.”**

Romé de l'Isle, *Essai de cristallographie* (1772), p. 10. Text of this frame taken from Seymour Mauskopf, *Crystals and Compounds* (1976).

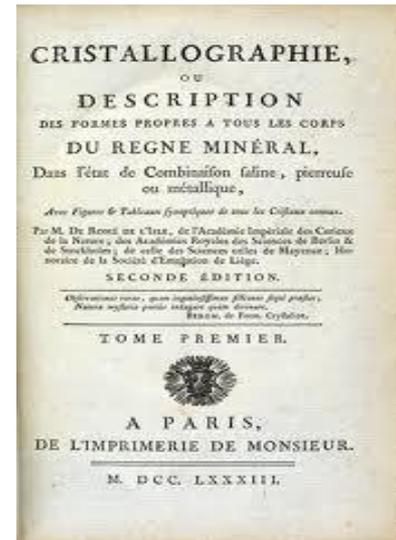
Statue of Romé de l'Isle in town hall of Gray, Haut Saône, his birthplace.



# J.—B.—L.— Romé de l'Isle

Although he did not try to develop this idea into a molecular model of crystal structure as did his rival, Haüy, Romé de l'Isle did postulate in the **Essai** and an expanded **Cristallographie** (1783) that:

- \*\* Crystals of the same (chemical) nature all derived from a common “**primitive form.**”
- \*\* Utilizing the **contact goniometer**, he discovered the **law of constant interfacial angles**: these angles were constant and characteristic for crystals of the same chemical substance.



# Instrumental Technology: Goniometers

**Contact** (A. Carangeot, 1783): To determine the angle between two surfaces, one has to hold the crystal edge at the scissor opening between the limbs of the goniometer. The angle being measured is read from the scale.



**Reflecting** (W.H. Wollaston, 1809): Instead of measuring the angle formed by the meeting of two faces of a crystal directly, it measured the angle formed by the meeting of rays of light reflected from them.



Full circle Carangeot-type contact goniometer – Harvard University.

“Life of Wollaston,” *Littell’s Living Age*, Vol. XI (1846), p. 14.

# Molecular Crystal Structure Theory

The first comprehensive **molecular crystal structure theory** was the creation of the **Abbé René Just Haüy** (1743 – 1822).



**Haüy**, one of the few major scientists to be a catholic priest, [**parallels with Gregor Mendel?**] had received a good scientific education and became interested in natural history (botany --} mineralogy/crystallography.

In 1784, he published his ***Essai d'une théorie sur la structure des cristaux***, based on the unit of the compound **molécule intégrante**, specific in shape and composition for every compound.



# Haüy's Theory: Molecules

## Matter Theory: 2 Stage Molecular Model

**Compound** determinately-shaped polyhedral *molécules intégrantes* built out of

**Elementary** *molécules constituantes* whose shapes are not inferable

## Crystal Structure Theory: 2 Stage

**Core: Primitive form**, constant and common to crystals of same species, revealed by **cleavage**

**Secondary (external) forms**: Derived from primitive form by **decrements (recessions)** in each successive layer of *molécules intégrantes* by **small integer number of molecules**.

# Haüy's Theory: Crystal Structure

Haüy's molecular structural models

*Traité de Minéralogie*

(1801). Fig. 13 & 16:

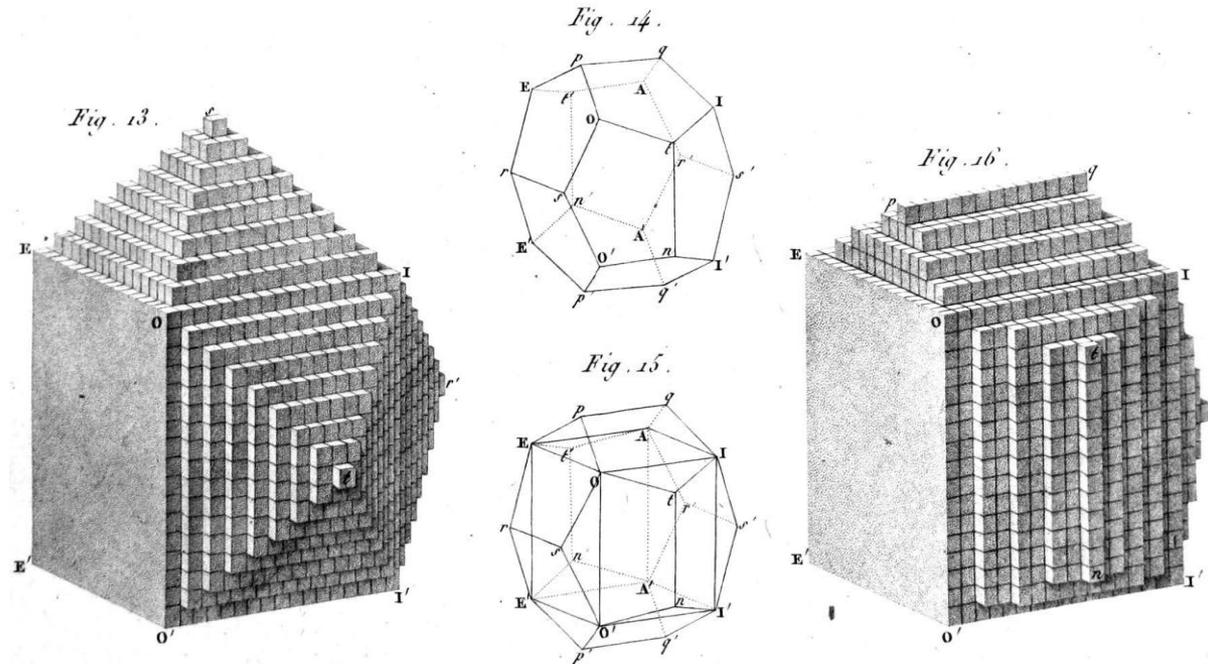
**cubic** *molécules intégrantes*,  
**cubic** *primitive form*

**simple decrement** -----}

rhombo-dodecahedron (Fig. 13)

**complex decrements** -----}

pentagon-dodecahedron (Fig.  
16)



# Haüy and Fixed Mineral Species

Haüy applied his ideas on the nature of the crystallo-chemical molecule to mineral classification.

He believed that there were

***fixed mineral species***, which were embodied in the ***molécule intégrante*** of that mineral, and characterized by:

***fixed form*** and

***constant chemical composition.***

This was a mineralogical equivalent to the contemporary

***Chemical law of definite proportions.***

# Seeds to Symmetry to Structure

(2)

Interplay with Chemistry & Optics

-----} Pasteur's Discovery

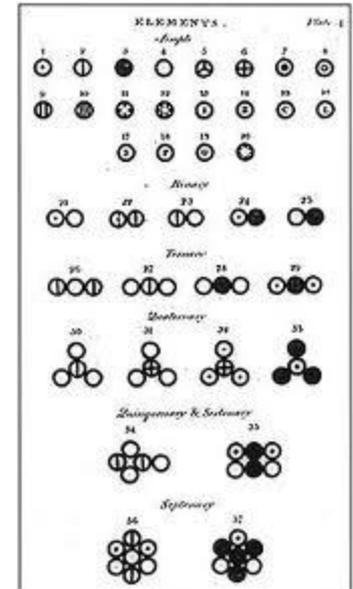
# Haüy and Dalton

It was, of course, **John Dalton** who came to focus on what had Haüy called *molécules constituantes*.

But Dalton was primarily interested in their gravimetric characteristics, not in their geometrical and spatial ones.

Despite his doctrine of fixed mineral species, Haüy was not interested in Daltonian atomism.

**However, Haüy's molecular crystal structure models was combined with the chemical atomic theory (1830s) to produced a view of the chemical molecule as the arrangement of atoms in space.**



# André-Marie Ampère (1814)

A first move towards such a union was made by **Ampère** (paper with Avogadro-Ampère gas law): general model of chemical combination.

**Chemical combination = mutual penetration of molecular polyhedra (of the reactants) to form compound polyhedra molecules (“particules”).**

**All molecules (elementary and compound) were composed of point atoms with Daltonian gravimetric attributes located at the solid angle apices.**

**Simplest molecular polyhedra (of elementary gases) had the forms of five of Haüy’s crystalline primitive forms.**

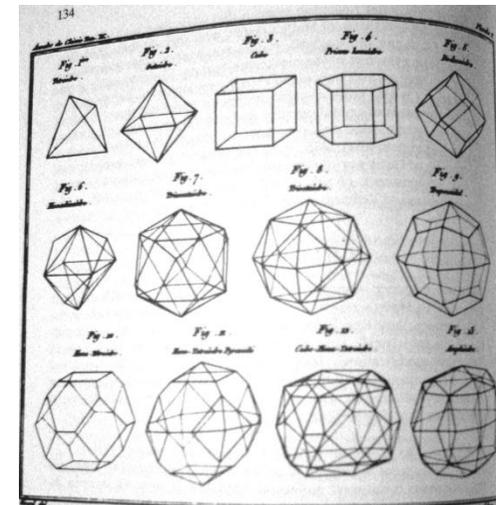


Fig. 2. Ampère's models of molecular polyhedra. From *Annales de Chimie*, Vol. 9 (1814).

nian gravimetric attributes, located at the apices of the solid angles of the polyhedra. (See Figure 2.)  
1. Simplest molecular polyhedra were of the form of five of Haüy's primitive forms of crystals. These posited especially for elementary gaseous molecules.

# French Crystallographical-Chemical Molecular Tradition

Under **the template of Ampère's models**, Haüy's molecular crystal structure models were combined with the chemical atomic theory to produce a view of the chemical molecule as the *polyhedral arrangement of atoms in space*.

*Inspired a French tradition.*

Most notable here were two scientists:

***Gabriel Delafosse***

***Auguste Laurent***

Each had a profound influence on **Louis Pasteur**.

Images: Delafosse, Laurent.

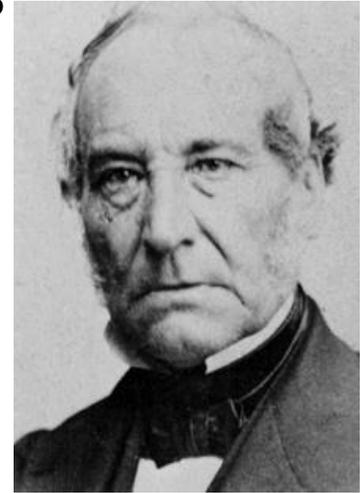


Fig. 7.10. Auguste Laurent  
painting by J. B. L. S.

# Gabriel Delafosse (1796-1878)

**Delafosse**, who had been Haüy's own student, was Pasteur's lecturer in mineralogy. *Pasteur's notes on Delafosse's lectures survive.*

Theoretical program: get at actual shapes of *physical/chemical crystalline polyhedral molecule, comprised of atoms arranged in space.*

Focused on crystals with **hemihedral** characteristics and with certain peculiar physical properties like surface striations, electrical polarity – and optical activity.

**Hemihedral crystals possess incomplete symmetry**; the requirement that any modification of an angle or edge be reproduced on all other symmetrically placed angles and edges, was not fulfilled.

# Delafosse's Molecular Models

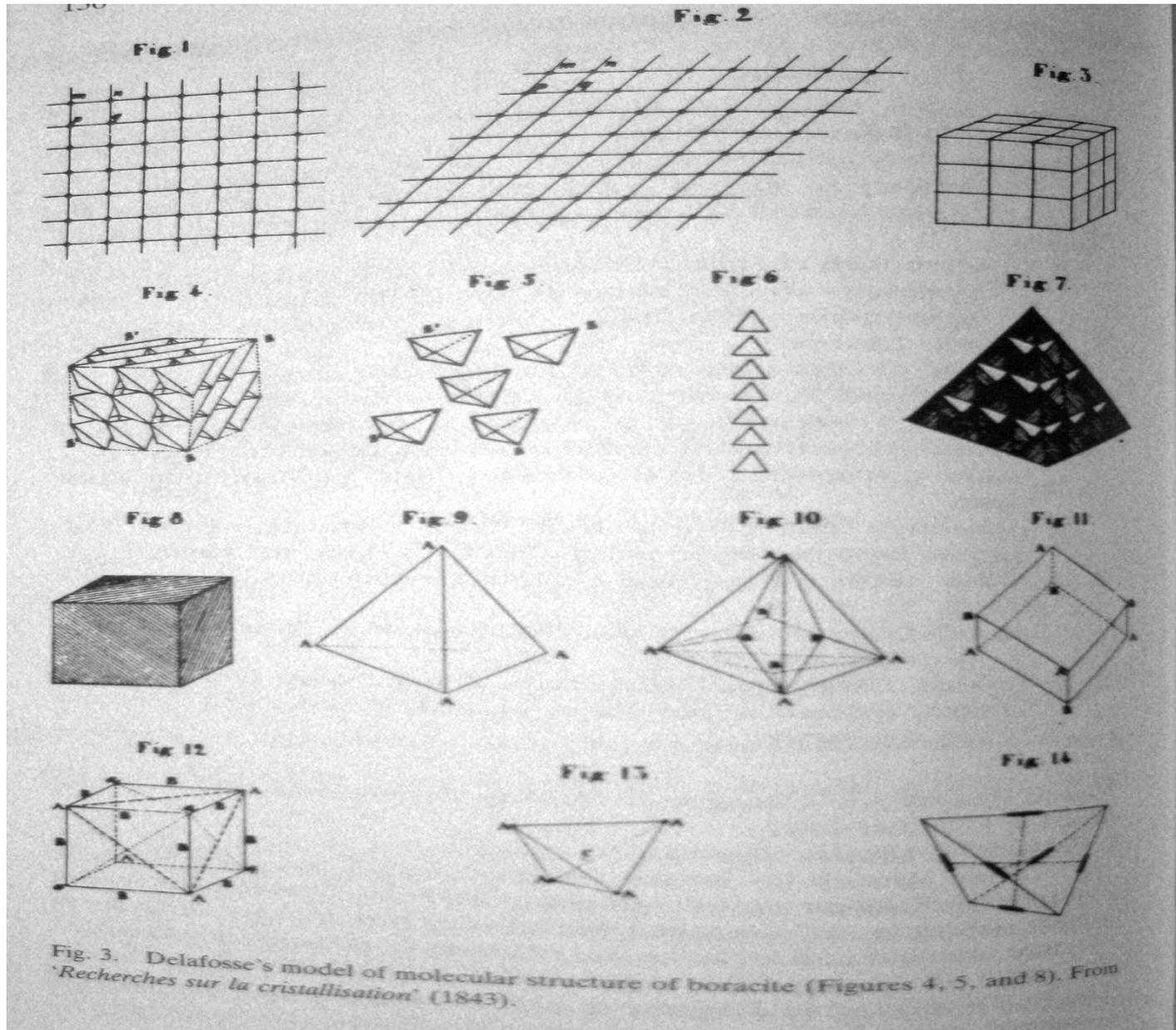


Fig. 3. Delafosse's model of molecular structure of boracite (Figures 4, 5, and 8). From 'Recherches sur la cristallisation' (1843).

# Auguste Laurent (1807-1853)

Even more important was the influence of the chemist, **Auguste Laurent**, on Pasteur.

Like Delafosse, he was profoundly influenced by Haüy's crystallography. He believed that there was an intimate relationship between crystal form and atomic-molecular arrangement within the crystal.

Moreover, he extended, by analogy, Haüy's two-part crystal structure model to the explication of organic chemistry taxonomy. **Laurent believed that chemical properties and relations depended ultimately on atomic-molecular structure.**

# Laurent: Structural Substitution

Taking as his point of departure, organic substitution reactions, he suggested that families of similar chemical substances all shared a common nuclear “radical,” modified among the members of a family (e.g. naphthalene compounds) by substitutions of the hydrogen atoms in the outer layers of the molecule by atoms (or atomic groups) of other elements.

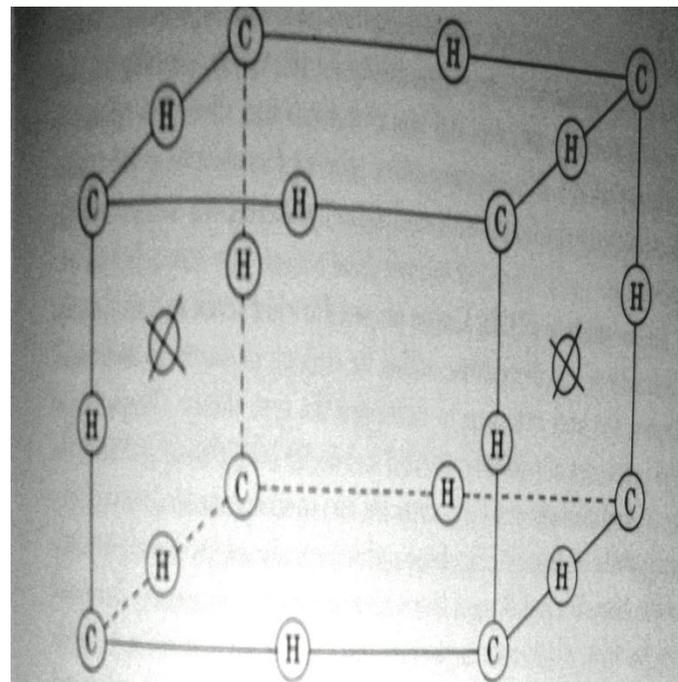


Fig. 7.11. LAURENT'S NUCLEUS THEORY. The rectangular prism represents a nucleus consisting of 8 carbon atoms joined with 12 hydrogen atoms to form a fundamental radical,  $C^8H^{12}$ . The two positions marked with a circle with crossed lines may be occupied by hydrogen, chlorine, or some other element. Substitution at these positions is possible without destroying the fundamental radical, or nucleus.

# Problem Posed to Pasteur

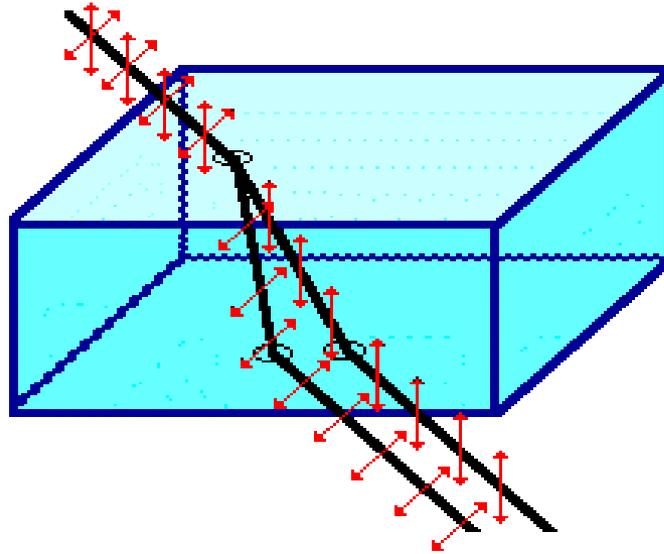
In 1844, **Eilhard Mitscherlich** announced a discovery regarding **the isomer pair, sodium-ammonium tartrate, and sodium-ammonium racemate (or paratartrate)**.

Mitscherlich had found *no differences in crystal forms*, chemical compositions, specific weights, or optical structures of these isomers.

**Yet the tartrate isomer was optically *active*, the racemate *inactive*\***.

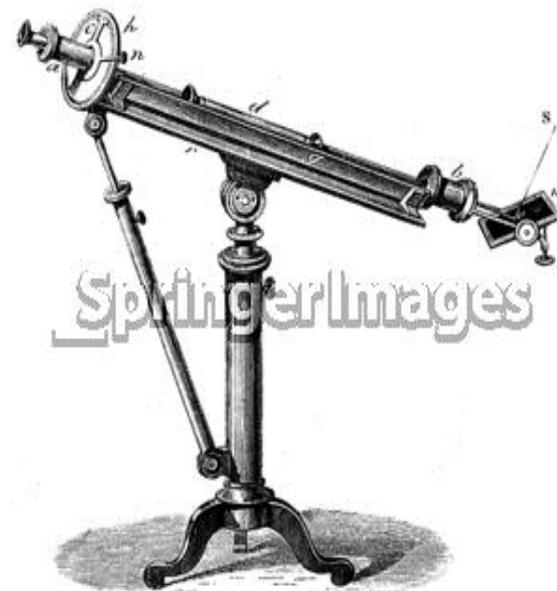
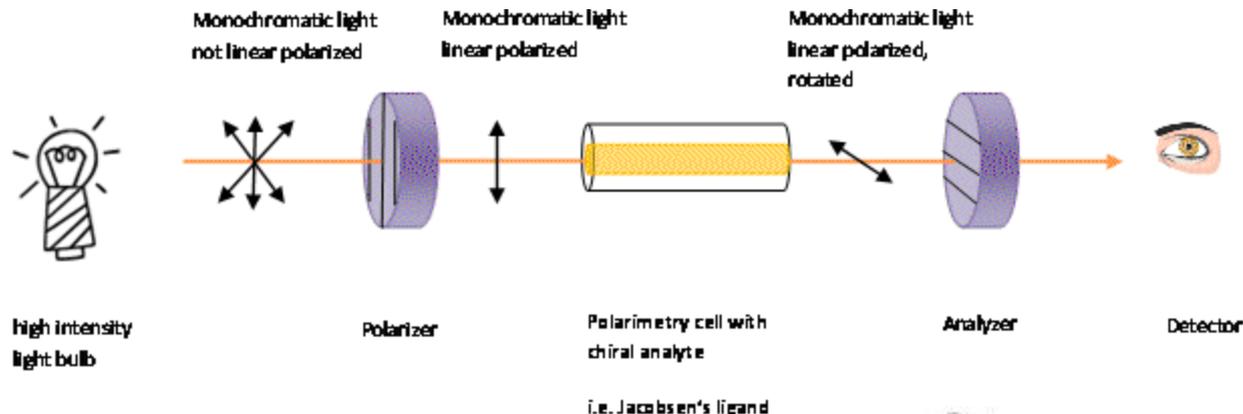
\*optical activity = turning the plane of linearly polarized light as it passes through a solution of the organic salt, discovered by J.-B. Biot .

# Plane Polarization through Double Refracting Crystal



**The two refracted rays passing through the Iceland Spar crystal are polarized with perpendicular orientations.**

# Instrumental Technology: Polarimetry

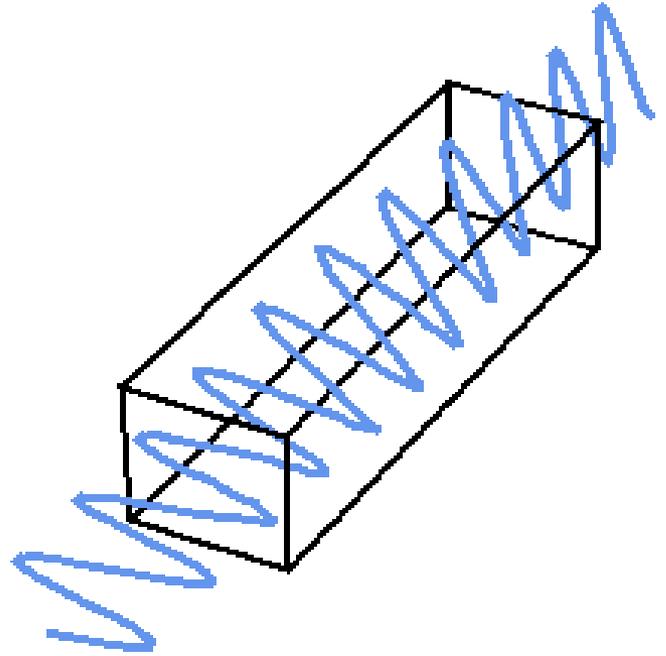


<http://www.chem.ucla.edu/~bacher/General/30BL/tips/Polarimetry.html>

, Biot's polarimeter (from A. Ganot, *Treatise on Experimental and Applied Physics* (1857)).

# Optical Activity

“Optical rotation means the rotation of the plane of polarization of a linearly polarized light beam as it passes through an optically active medium, for instance a solution of chiral molecules.”



# The First Major Discovery of Louis Pasteur, Spring, 1848

In his research, Pasteur discovered that there were *differences in crystal forms*:

- (1) **Sodium-ammonium tartrate** crystals were hemihedral: they had **small asymmetrical-placed facets on some of their edges**, corresponding to the direction of its optical activity.
- (2) **Sodium-ammonium racemate** was composed of **two types of crystals**: some similar to the sodium-ammonium tartrate crystals and **others with the assymetrically-placed facets oriented in the opposite direction to produce mirror-images** of the first kind.
- (3) When the racemate crystals were separated into the two forms, **each was optically active but in opposite directions**. Images: Louis Pasteur, sodium-ammonium tartrate crystals.

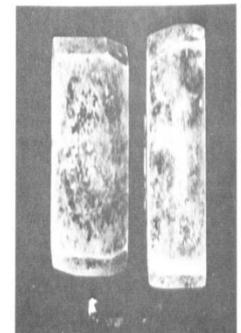
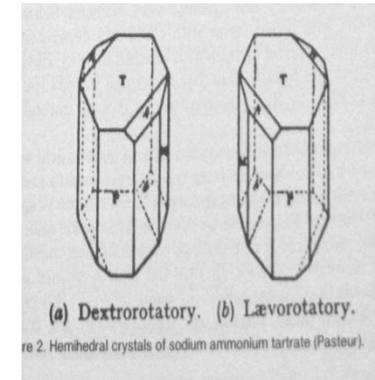
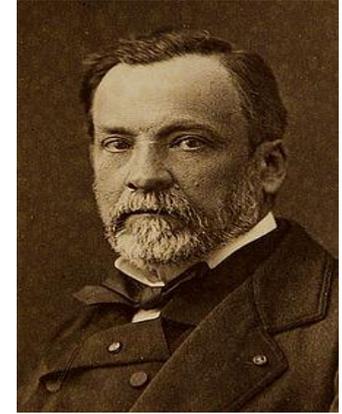


Figure 7. Sodium ammonium tartrate. (left) (-) form, right) (+) form.  
(bottom) racemate (+-) form.

# Pasteur and French Tradition

In his retrospective construction of the path leading to his discovery, Pasteur claimed that he was “guided” **by the “sagacious views” of Delafosse:**

“ With whom hemihedry has always been a law of structure and not an accident of crystallization, **I believed that there might be a relation between the hemihedry of the tartrates and their property of deviating the plane of polarized light.**”

# Pasteur and Laurent at the Time of Discovery

**Laurent** and **Pasteur** interacted directly in the years 1846 - 1848, when Pasteur and Laurent were both in the laboratory of Antoine Jerome Balard at the *École normale*.

**Laurent served, in effect, as Pasteur's mentor.**

**Pasteurs' first molecular speculation was *Laurentian*:**

“All the tartrates are hemihedral. Thus, the molecular group common to all these salts, and which the introduction of water of crystallization and of oxides comes to modify at the extremities, does not receive the same element at each extremity, or, at least, they are distributed in a dissymmetrical manner. On the contrary, the extremities of the prism of the paratartrates are all symmetrical.”

# Later Speculation of Pasteur:

## *Dissymétrie Moléculaire*

“Are the atoms of the right acid [rotating the plane of polarized light to the right] grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron, or disposed according to some particular dissymmetric grouping or other?”

We cannot answer these questions. **But it cannot be doubted that there exists an arrangement of the atoms in a dissymmetric order, having a non-superposable image, and it is no less certain that the atoms of the *levo*-acid realize precisely the inverse dissymmetric grouping to this.”**

# Seeds to Symmetry to Structure

## Interlude: Separate sequels:

**Chemistry:** Development  
of Stereochemistry

**Crystallography:**  
Development of Mathematical  
Structure and Groups

# Chemistry: “The Quiet Revolution” Structural Chemistry

In the two decades after Pasteur’s discovery, **chemistry underwent what Alan Rocke has termed a “quiet revolution”**:

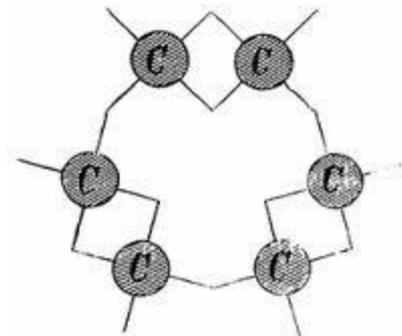
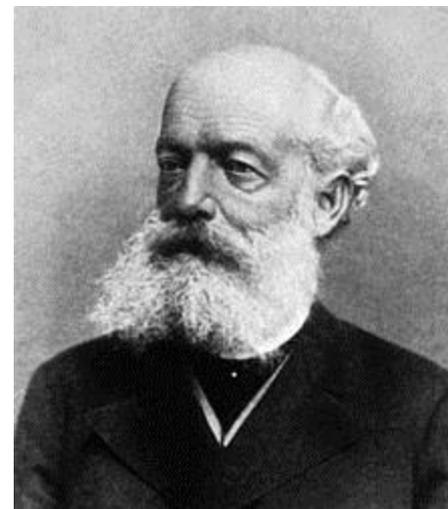
(1) **Atomic weight** clarified (Cannizzaro).

(2) **Idea of “valence”** enunciated.

(3) **Structural ideas** moving beyond Laurent’s program (and separating from crystallography), e.g. **Kekulé & benzene**.

August Kekulé von Stradonitz.

Representation of benzene ring from Lehrbuch der organischen Chemie (1861-1867).



# Chemistry: Van't Hoff, Le Bel & the Tetrahedral Carbon Atom

Pasteur's correlations explored by **Johannes Wislicenus** (1835-1902) [lactic acid], whose quest for **models of "the three-dimensional arrangement of the molecule's atoms in space"** was realized by two scientists in 1874:



**Jacobus Henricus Van't Hoff** and **Joseph-Achilles Le Bel.**



Wislicenus  
Van't Hoff  
Le Bel

# Van't Hoff's Realism

Assumption: the four valences of a carbon atom were satisfied by bonds that were fixed and rigid, directed to the four corners of a tetrahedron.

To deal with **optically active isomers**:

**“In cases where the four affinities of the carbon atom are saturated with four mutually different univalent groups, two and not more than two different tetrahedra can be formed, which are each other's mirror images, but which cannot ever be imagined as covering each other, that is, we are faced with two isomeric structural formulas in space.”**

Van't Hoff's model of the tetrahedral bonding of carbon was intended as a general geometrical structural model for all carbon bonding.

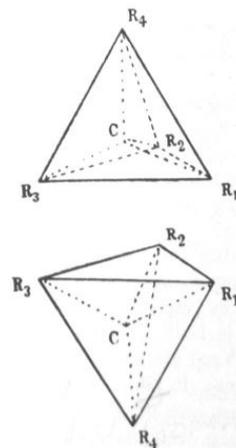


Figure 18. Van't Hoff's illustration of the enantiomers of  $CR_1R_2R_3R_4$ .

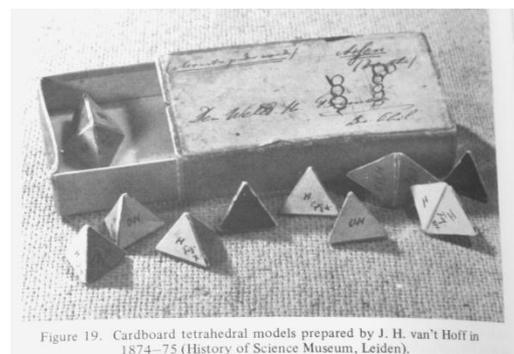


Figure 19. Cardboard tetrahedral models prepared by J. H. van't Hoff in 1874-75 (History of Science Museum, Leiden).

# Crystallography Distances Chemistry

The model of the asymmetrical tetrahedral carbon bonding, stemming from Pasteur's discovery, was **the basis for the development of stereochemistry.**

**But Pasteur's work was the last synthetic union of crystallography and chemistry for about half a century.**

**Crystallography had already been developing in very different directions, and these continued for the rest of the century.**

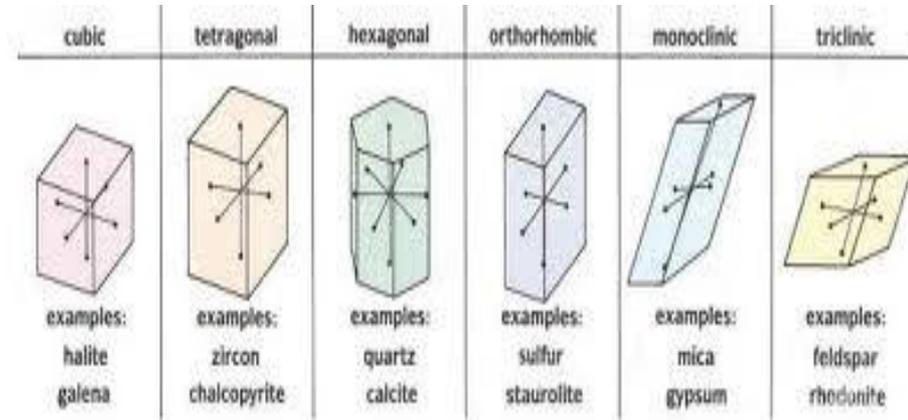
# Crystalline Symmetry & Systems

The over-riding focus in 19<sup>th</sup>-century crystallography: abstract, mathematical considerations of **crystalline symmetry**.

This was initiated early in the 19<sup>th</sup> century in Germany by **Christian Samuel Weiss**, (1780 – 1856) who **abjured molecule models of crystal structure in favor of more dynamical ones, relating to axes of symmetry**.

Influence of German **Naturphilosophie**.

Monoclinic & triclinic systems identified by **Friedrich Mohs**. Subsequently, the hexagonal system was divided into the trigonal and hexagonal, making 7 systems.



# Auguste Bravais (1811 -1863)

Bravais, a graduate of the **École Polytechnique** and a professor of physics, worked out a *mathematical theory of crystal symmetry* based on the concept of the **crystal lattice, of which there were 14.**



# Bravais Lattices

If you have to fill a volume with a structure that's repetitive,  
Just keep your wits about you, you don't need to take a sedative!  
Don't freeze with indecision, there's no need for you to bust a  
seam!

Although the options may seem endless, really there are just  
fourteen!

There's cubic, orthorhombic, monoclinic, and tetragonal,

There's trigonal, triclinic, and then finally hexagonal!

There's only seven families, but kindly set your mind at ease—

'Cause four have sub-varieties, so there's no improprieties!

(Chorus:

'Cause four have sub-varieties, so there's no improprieties.

These seven crystal systems form the fourteen Bravais lattices.

They've hardly anything to do with artichokes or radishes –

They're great for metals, minerals, conductors of the semi-kind –

The Bravais lattices describe all objects that are crystalline!

The cubic is the most important one in my "exparience",

It comes in simple and in face- and body-centered variants.

And next in line's tetragonal, it's not at all diagonal,

Just squished in one dimension, so it's really quite rectangular!

The orthorhombic system has one less degree of symmetry

Because an extra squish ensures that *a not equals b or c*.

If angle gamma isn't square, the side lengths give the "sig-o-nal"

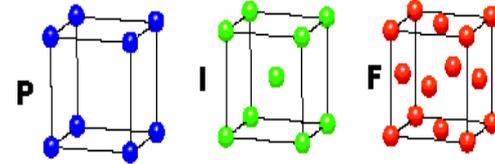
For monoclinic if they're different, or, if equal, trigonal! Bravais

Lattice Song

## CUBIC

$$a = b = c$$

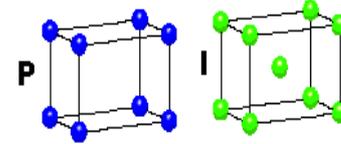
$$\alpha = \beta = \gamma = 90^\circ$$



## TETRAGONAL

$$a = b \neq c$$

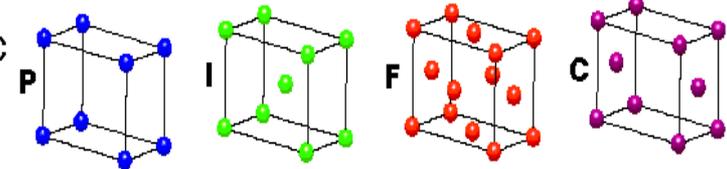
$$\alpha = \beta = \gamma = 90^\circ$$



## ORTHORHOMBIC

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

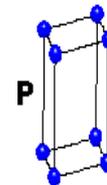


## HEXAGONAL

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ$$

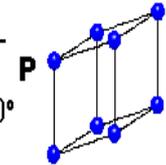
$$\gamma = 120^\circ$$



## TRIGONAL

$$a = b = c$$

$$\alpha = \beta = \gamma \neq 90^\circ$$

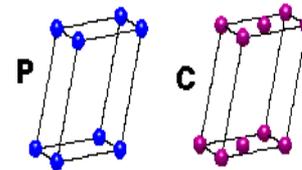


## MONOCLINIC

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ$$

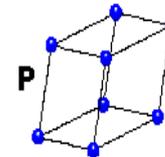
$$\beta \neq 120^\circ$$



## TRICLINIC

$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma \neq 90^\circ$$



4 Types of Unit Cell

P = Primitive

I = Body-Centred

F = Face-Centred

C = Side-Centred

+

7 Crystal Classes

→ 14 Bravais Lattices

# Crystallography After Bravais

During the remainder of the 19<sup>th</sup> century, the basis for modern crystal structure theory was development on the basis of Bravais's formulation of crystal lattices.

**These developments were largely mathematical and had little concern with the actual elucidation of atomic and molecular arrangement.**

There was one exception, **William Barlow**.

# Symmetry Elements and Operations

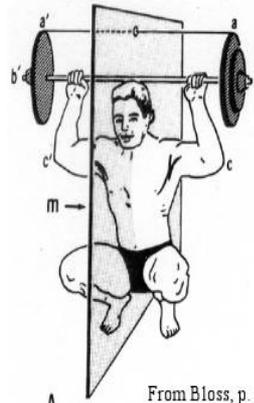
***“Symmetry elements*** define the (conceptual) motion of an object in space the carrying out of which,

the ***symmetry operation***, leads to an arrangement that is indistinguishable from the initial arrangement.”

# Symmetry Operations ---} 32 Point Groups

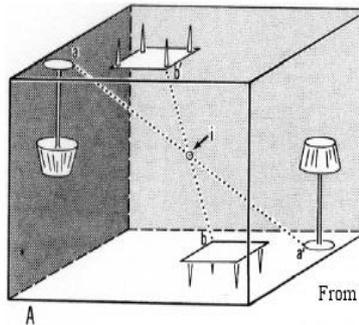
**Rotation,**  
**reflection** and  
**inversion**

operations  
generate a variety  
of unique  
arrangements of  
lattice points (i.e.,  
a shape structure)  
in three  
dimensions.



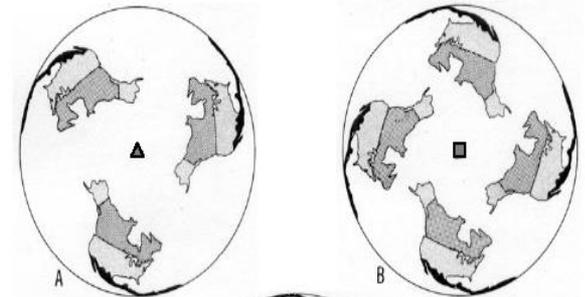
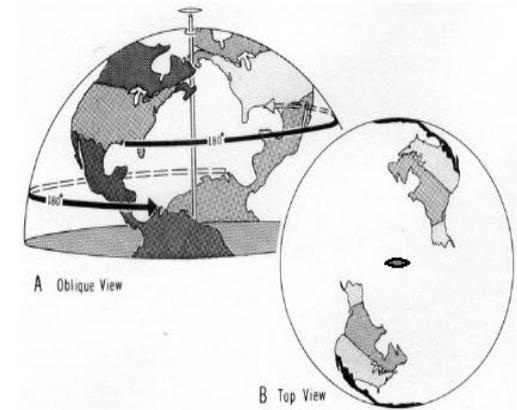
From Bloss, p. 2

2. REFLECTION =  $m$



From Bloss, p. 6

4. INVERSION =  $i$



From Bloss, pp. 4, 5

$$\alpha = 360^\circ/n$$

$n$  = fold of axis = 1, 2, 3, 4 or 6

3. ROTATION

# Symmetry Operations ---} 230 Space Groups

“Translations are used to generate a lattice from that shape structure. The translations include

**a simple linear translation,**

**a linear translation combined with mirror operation (glide plane), or**

**a translation combined with a rotational operation (screw axis).**

A large number of 3-dimensional structures (*the 230 Space Groups*) are generated by these translations acting on the 32 point groups.”“Elementary Crystallography for X-Ray Diffraction,” p. 4. 04 Crystallography-for-XRD.pdf.

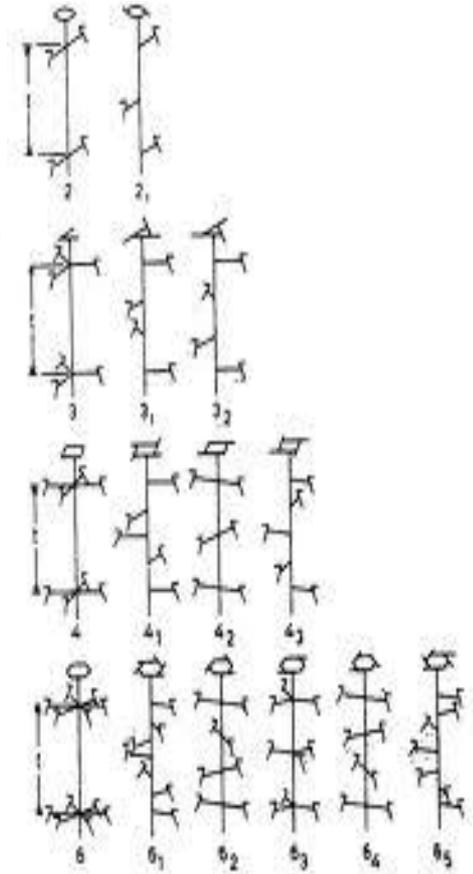


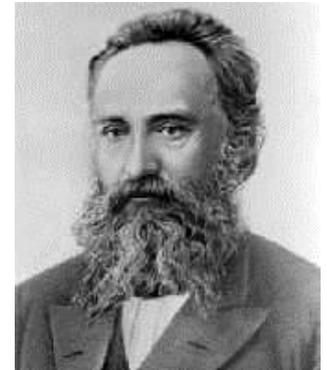
Image: 11 possible screw axes.

# Space groups

The combination of all available symmetry operations (32 point groups), together with translation symmetry, within the all available lattices (14 Bravais lattices) lead to 230 Space Groups that describe the only ways in which identical objects can be arranged in an infinite lattice. The International Tables list those by symbol and number, together with symmetry operators, origins, reflection conditions, and space group projection diagrams.

SpaceGroupslecture2.ppt

Arthur Moritz Schönflies (1853-1928)  
Yevgraf Stepanovich Federov (1853-1919)



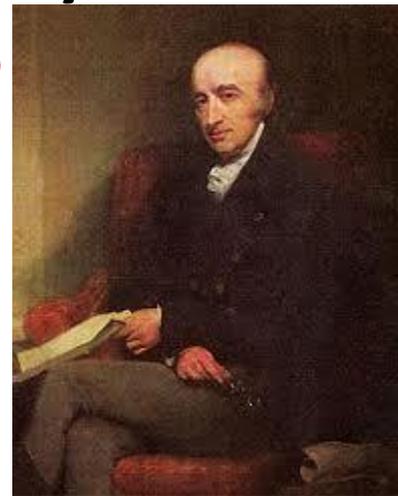
# Other National Traditions of Molecular Crystal

## Structure: **SPHERES & SPHEROIDS**

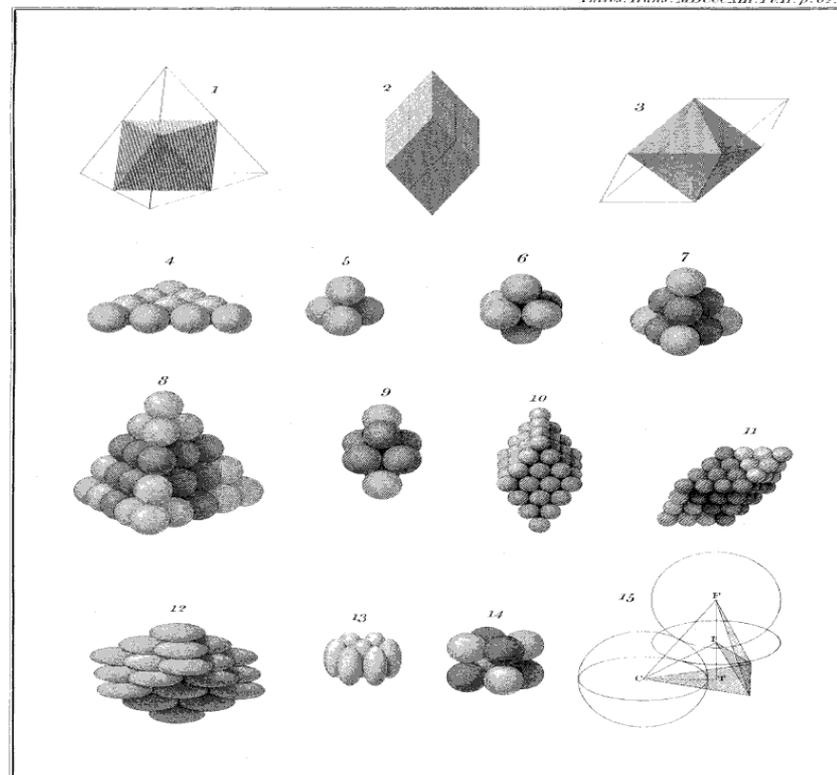
The French Haüyian tradition based on polyhedral molecules wasn't the only one in the early 19<sup>th</sup> century.

The British had a tradition of **spherical/spheroidal molecular structure** dating back to the 17<sup>th</sup> century and espoused in the early 19<sup>th</sup> century most notably by **William Hyde Wollaston**.

Taken up again in the 1880s but English self-taught crystallographer, **William Barlow**



*Philos. Trans. MDCCLXIII. PL. II. p. 62.*



*Engraved by W. Lowry.*

Images, Wollaston (upper right),  
W.H. Wollaston "On the Elementary Particles of Certain Crystals (1813)

# William Barlow (1845-1934)

“Barlow, a privately educated genius, was perhaps one of the last great amateurs in science. It was only when he was in his early thirties, however, after he attained the leisure afforded by an inheritance from his father, that he began to study and work in crystallography. His original view of the nature of crystalline matter united the mathematical system of symmetry, for which he wrote his own final chapter in the 1890’s with an anticipation of the new determinations of atomic structure that were to follow after 1910....



**Barlow’s theories of the properties of crystals were based on the close packing of atoms.”**

**Independently of Schönflies and Federov , Barlow derived the 230 space groups.**

William T. Hosler, “Barlow, William,” *Complete Dictionary of Scientific Biography*. 2008. Encyclopedia.com. 20 May, 2012. <http://www.encyclopedia.com>

# William Barlow, “Probable Nature of the Internal Symmetry of Crystals,” *Nature*, December, 1883

“Some studies pursued by the present writer as to the nature of molecules have **led him to believe that in the atom-groupings which modern chemistry reveals to us the several atoms occupy distinct portions of space and do not lose their individuality. The object of the present paper is to show how far this conclusion is in harmony with, and indeed to some extent explains, the symmetrical forms of crystals,** and the argument may therefore in some sort be considered an extension of the argument for a condition of internal symmetry derived from the phenomenon of cleavage.”

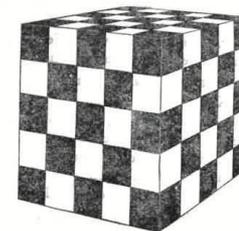


FIG. 1.

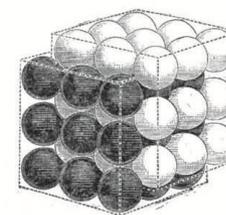
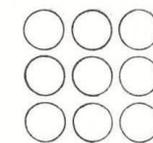


FIG. 2.



Plan  $\alpha$ .

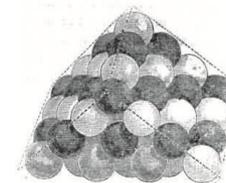
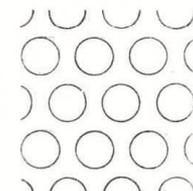


FIG. 3.



Plan  $\beta$ .

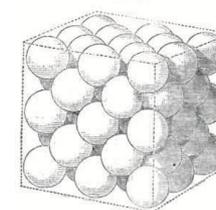
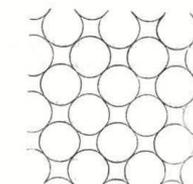


FIG. 4.

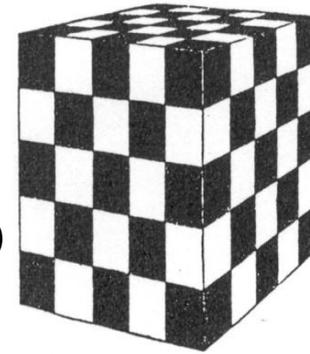


Plan  $\gamma$ .

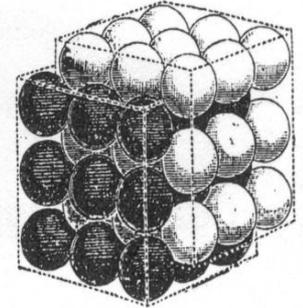
# William Barlow, “Probable Nature of the Internal Symmetry of Crystals,” **CRYSTALLOGRAPHY & CHEMISTRY**

“To proceed then to the facts, we notice first that, as a rule, compounds consisting of an equal number of atoms of two kinds **crystallise in cubes**. The following may be mentioned:-  
- **KCl, KBr** [etc.]....”

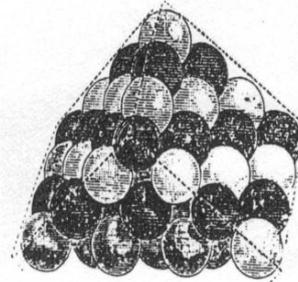
Images from Barlow, 1883, taken from Kubbinga, “Crystallography from Haüy to Laue,” p. 24, fig. 16. “Packing (b) represents the body-centered cubic lattice (an envelope of 8 black atoms surrounds 1 white atom), (c) the normal cubic lattice (envelope 6) and (d) the face-centered cubic lattice.”



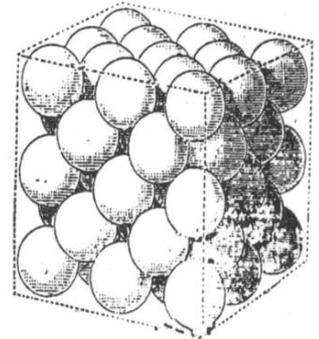
(a)



(b)



(c)



(d)

# Barlow and Cubic Structure of Alkali Halides: **Evaluation**

“In his first paper, **Barlow...recognized that body-centered cubic and simple cubic structures admit packing of spheres of two kinds – but of equal size, and are therefore suited to be structures of the alkali halides.** Not until his definitive paper on structure...(1897) did Barlow explicitly display the variations possible in making the two kinds of spheres of two corresponding sizes....

**This was a correct guess for the structure of alkali halides** *and...this structure was suggested by [W. J.] Pope [Barlow's collaborator] to W. L. Bragg, who, in 1913 confirmed it with the first structure determination by X-ray diffraction.*

William T. Hosler, "Barlow, William,"

# Seeds to Symmetry to Structure

(3)

The centenary event which we are celebrating here: the discovery (or invention) of **x-ray diffraction photography in 1912** under the direction of **Max von Laue** and its implementation as a means to ascertaining atomic-molecular arrangement by the **Braggs, William Henry and William Lawrence.**

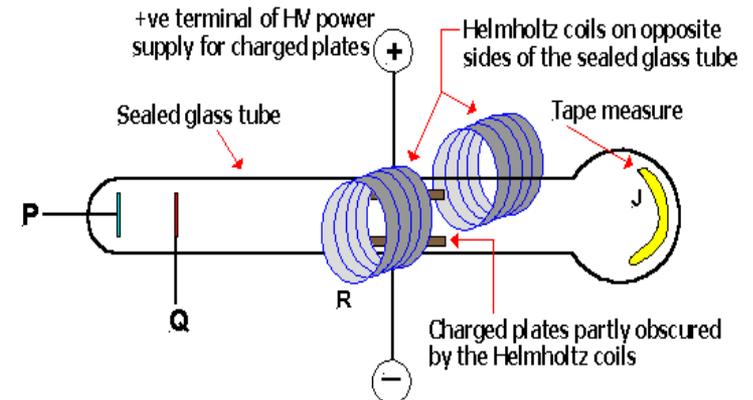
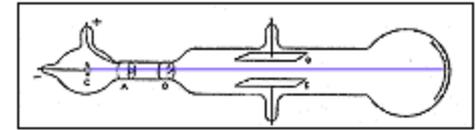
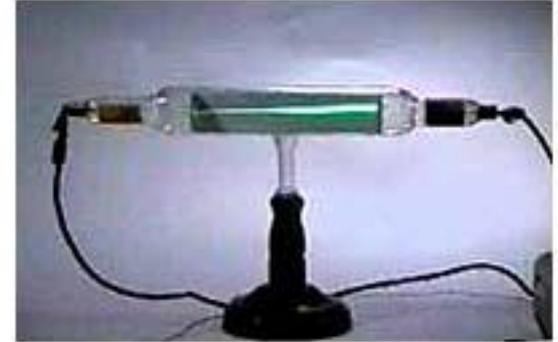
# X-Ray Diffraction: Cathode Rays

**Phenomenon:** When electricity discharged at one end (the cathode), a phosphorescent *glow* produced at other end.

a. It could be interrupted by the interposition of material objects and

It could be deflected by a magnetic field.

Recognized that **some kind of negative electrical discharge being produced; debate as it whether it was wave-like or particulate.**



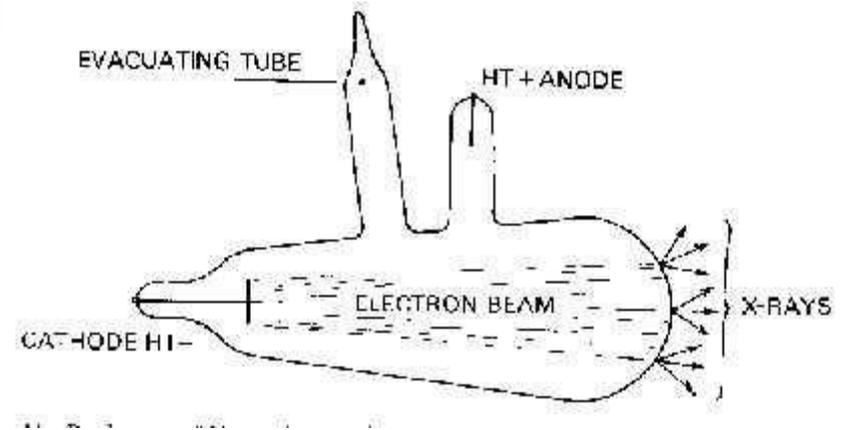
J J Thomson's Cathode Ray Tube for determining  $q/m$  ratio of the electron

# X-Ray Diffraction: Discovery of X-Rays

Nov., 1895: **Wm. Röntgen** discovered that **when certain substances are exposed to the beam of a cathode ray tube, a new kind of penetrating ray capable of fogging photographic plates even when shielded** was emitted -- called it "x-rays". These x-rays also ionized gases through which they passed---

**1<sup>st</sup> Nobel Prize in physics (1901).**

**Wave nature of x-rays (transverse)** established by **Charles Glover Barkla** in 1906 although there continued to be controversy about this.



# X-Ray Diffraction: Ludwig-Maximilians University of Munich Group in 1912

**Röntgen**, director of the physics laboratory.

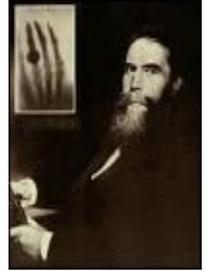
**Arnold Sommerfeld**, Director of the Institute for Theoretical Physics. Experimental work on wave-nature (and wave length) of x-rays.

**Paul von Groth**, professor of mineralogy, world renowned authority on crystallography and mineralogy. Interested in atomic/molecular meaning of crystal structure.

**Paul Peter Ewald**, student of Sommerfeld, working on propagation of x-rays in single crystals.

**Max von Laue**, *Privatdozent* in Sommerfeld's

**Institute**. Photos: Röntgen Sommerfeld, von Groth, Ewald, von Laue.  
Hofgarten café. [http://www.munich-info.de/portrait/p\\_hofgarten\\_en.html](http://www.munich-info.de/portrait/p_hofgarten_en.html)



# X-Ray Diffraction: April, 1912

Max von Laue joined Sommerfeld's group as a private lecturer in 1909, and he was immediately struck by the atmosphere that was "saturated with questions for the nature of X-rays...."

Many institutes in Munich University had mathematical models of these proposed space-lattice structures, mainly thanks to the enthusiastic support of the theory by the crystallographer Paul von Groth, but no one had yet proved that crystals have this structure. von Groth was another frequent participant of the Hofgarten café circle, and thanks to him von Laue quickly learned about crystal optics, and soon became known as a local specialist in the subject.

Parallels here to Bell Labs? [Jon Gertner, *The Idea Factory: Bell Labs and the Great Age of American Innovation*].

# X-Ray Diffraction: April, 1912

One evening in **February 1912**, the physicist **Peter Paul Ewald** sought von Laue's advice about some difficulties he was having with his doctoral thesis on the behaviour of long electromagnetic waves in the **hypothetical space lattices of crystals**. Von Laue couldn't answer Ewald's question, but his mind began to wander.

***Suddenly, a connection clicked in his mind.*** If diffraction and interference occurs when the wavelength of light is a similar size to the width of the slit of an optical grating, and ***if X-rays were indeed waves that have a wavelength at least ten thousand times shorter than visible light, then in theory the spaces between the atoms in a crystal might be just the right size to diffract X-rays.*** If all this were true, von Laue thought, ***a beam of X-rays passing through a crystal will be diffracted, forming a characteristic interference pattern of bright spots on a photographic plate.***

# X-Ray Diffraction: April, 1912

Von Laue designed an experiment in which he placed a copper sulphate crystal between an X-ray tube and a photographic plate. His assistants, **Walther Friedrich** and **Paul Knipping**, carried out the experiment. After a few initial failures, **they met with success on 23 April, 1912.** X-rays passing through the crystal formed the pattern of bright spots that proved the hypothesis was correct.”

[http://www.nobelprize.org/nobel\\_prizes/physics/laureates/1914/perspectives.html](http://www.nobelprize.org/nobel_prizes/physics/laureates/1914/perspectives.html)

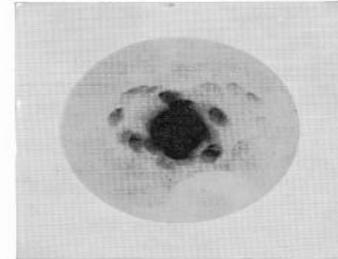


Fig. 4-4(1). Friedrich & Knipping's first successful diffraction photograph.

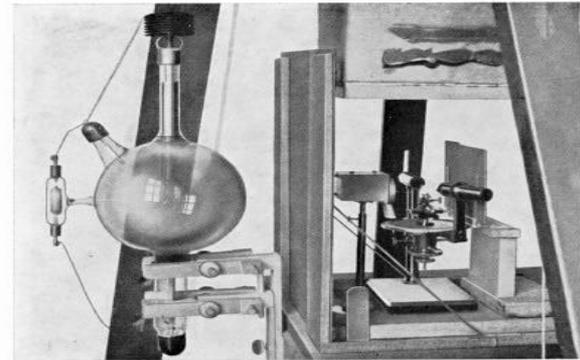
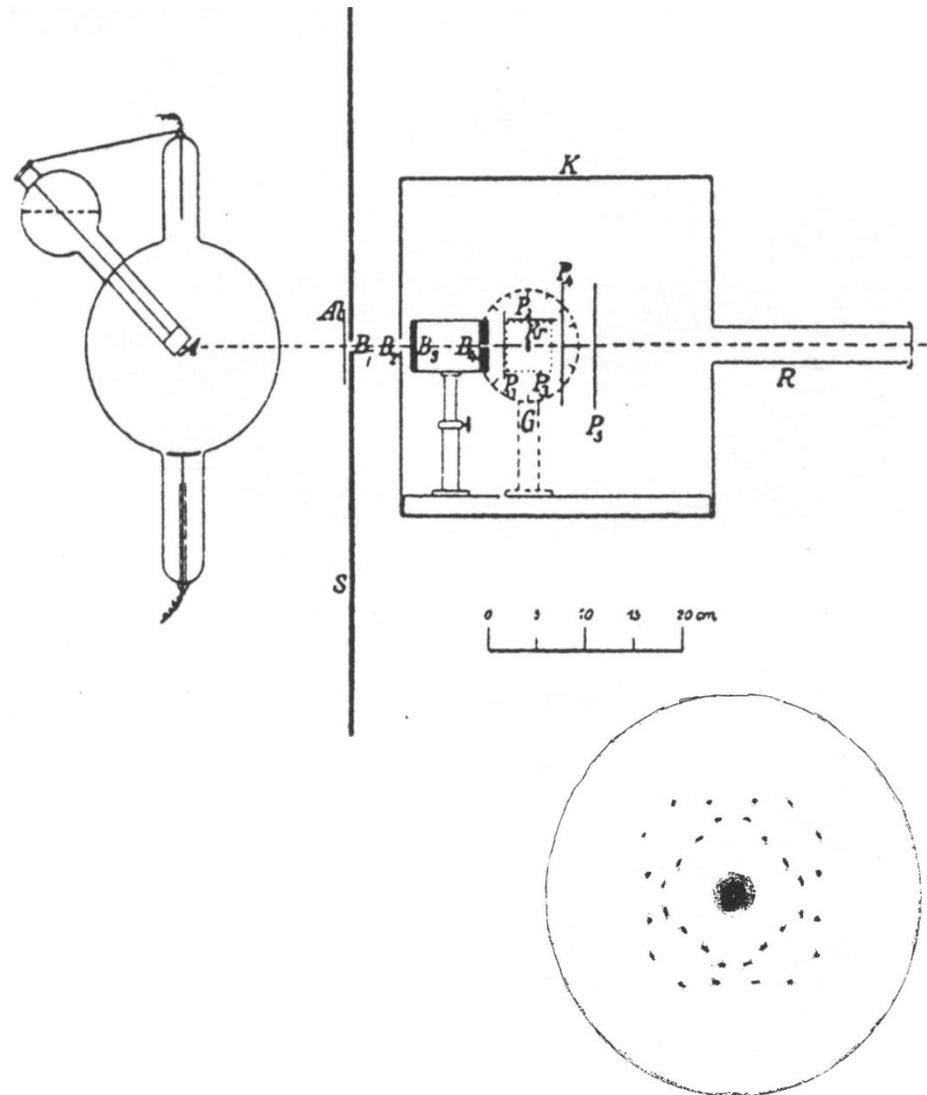


Fig. 4-4(2). Friedrich & Knipping's improved set-up.

# Instrumental Technology: X-Ray Diffraction: Setup of Laue, Friedrich and Knipping

The source of Röntgen's radiation is separated from the crystal under investigation by a lead screen, *S*, pierced at *B1*, and a series of ever-finer lead diaphragms *B2* (in the lead chamber *K*), *B3* and *B4*. Around the crystal *Kr* photographic plates may be placed at various positions *P1*–*5*. The extension *R* is added to trap the straightforwardly passing rays and obviate disturbing secondary rays of the wall. For precision measurements there is a diaphragm *Ab* for the pinhole *B1* in screen *S* (Friedrich et al., 1912). Kubbinga,



# Von Laue --} Braggs

“Regarding the explanation, **Laue** thinks it is due to the diffraction of the röntgen rays by the regular structure of the crystal....**He is, however, at present unable to explain the phenomenon in its detail.’\*** ...

Once back in Cambridge, **Willie** [W. L. Bragg] continued to pour over the Laue results, and **recalled...the crystal structure theories of William Pope and William Barlow**. He became convinced that the effect was optical and... visualized an explanation in terms of the simple reflection of X-rays from the planes of atoms in the crystal.

He thereby devised **Bragg’s Law**.,  $n\lambda=2d\sin\theta$ .”

\*Letter, Lars Vegard – W.H. Bragg, June 26, 1912. John Jenkins, “A Unique Partnership: William and Lawrence Bragg and the 1915 Nobel Prize in Physics,” *Minerva*, 2001, Vol. 39, No. 4, pp. 380-381.

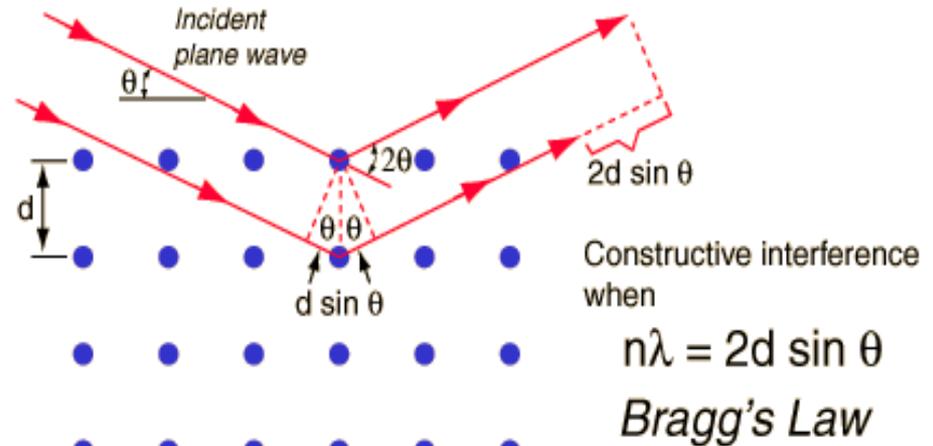
# Bragg's Law

When x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed which correspond to the following conditions:

The angle of incidence = angle of scattering.

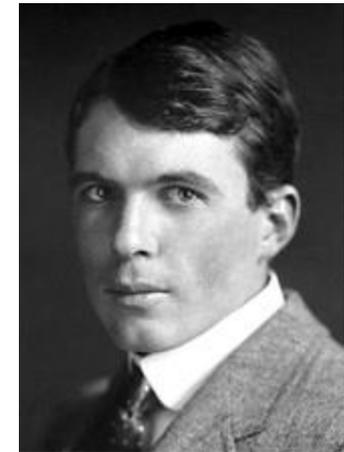
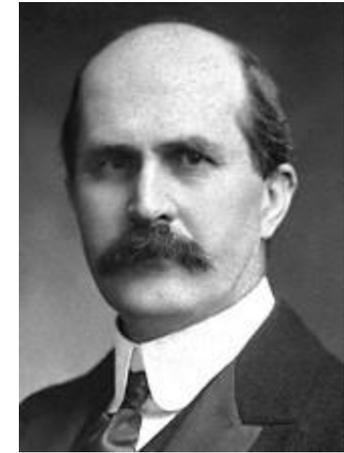
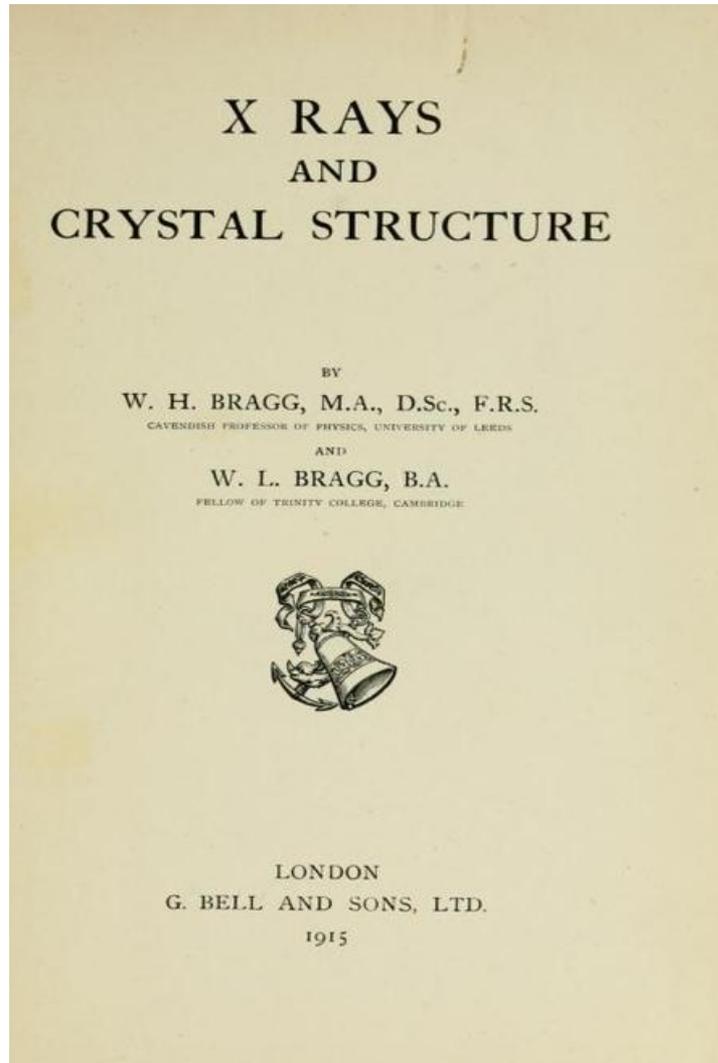
The pathlength difference is equal to an integer number of wavelengths.

The condition for maximum intensity contained in Bragg's law above allow us to calculate details about the crystal structure, or if the crystal structure is known, to determine the wavelength of the x-rays incident upon the crystal.



$$n\lambda = 2d \sin \theta \quad \text{Bragg's Law}$$

# W. H. & W. L. Bragg, *X-Rays and Crystal Structure* (1915)



Photos

Top: William Henry Bragg  
(1862 – 1942);

Bottom William Lawrence  
Bragg  
(1890-1971)

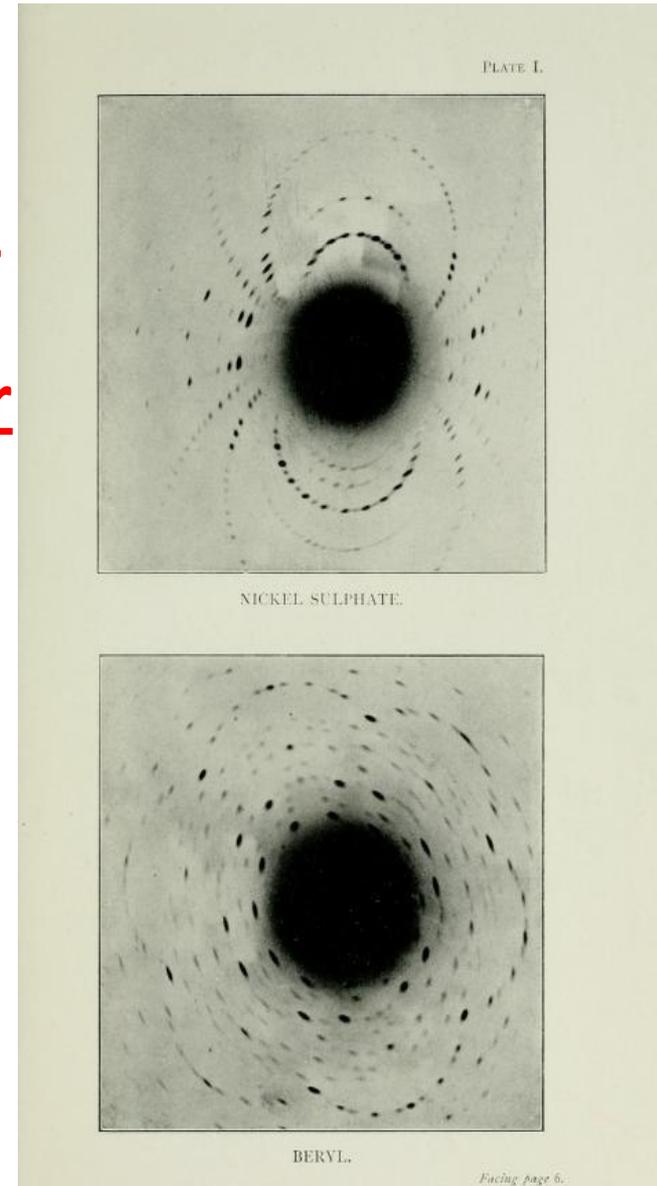
Swedish postage stamp  
with Braggs



# W.H. & W. L. Bragg, X-Rays and Crystal Structure (1915)

Plate I. "It is natural to suppose that the Laue pattern owes its origin to the interference of waves diffracted at a number of centres which are closely connected with the atoms or molecules of which the crystal is built, and are therefore arranged according to the same plan.

**The crystal is, in fact, acting as a diffraction grating."** (pp. 8-9).



# Von Laue's Photograph of Zinc Blende (Sphalerite, ZnS), 1912

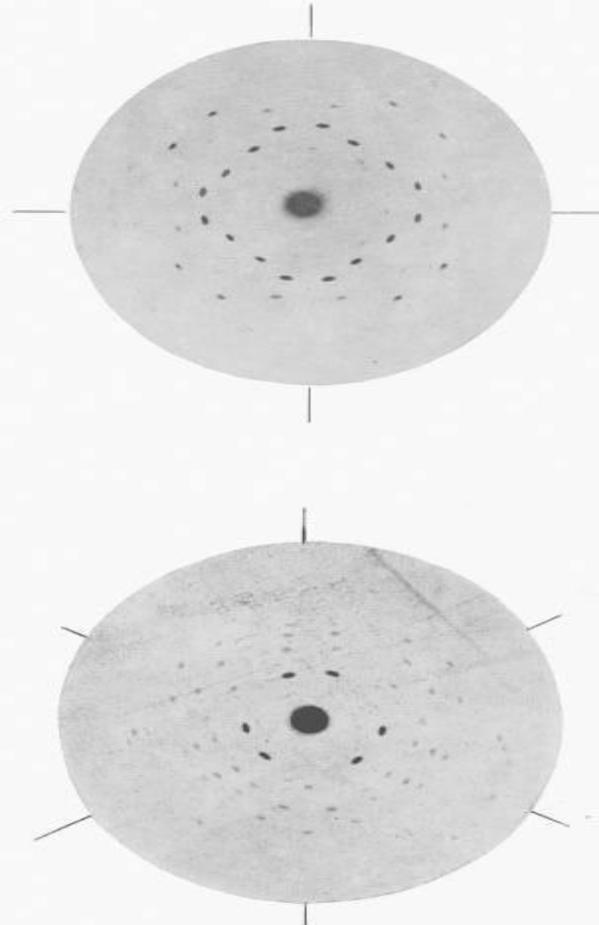


Fig. 4-4(3) and (4). Zinblende Laue photographs along four-fold and three-fold axes.  
(Laue, Friedrich & Knipping, *Sitz.ber. Bayer. Akademie d. Wiss.* 8. Juni 1912).

# Zinc Blende: Von Laue & the Braggs

“The most satisfying result was on von Laue’s photograph of diffraction from zincblende crystals.

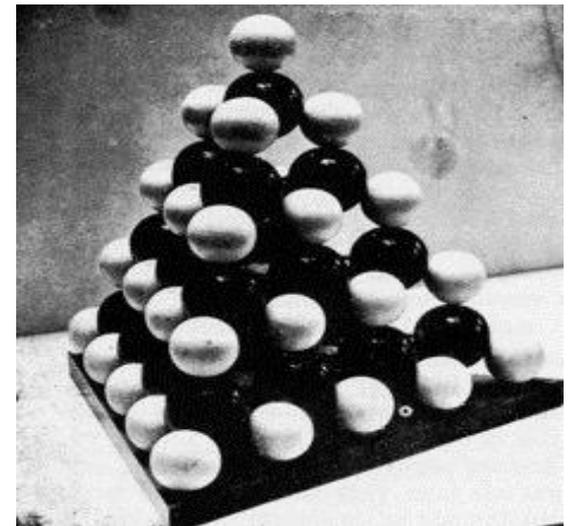
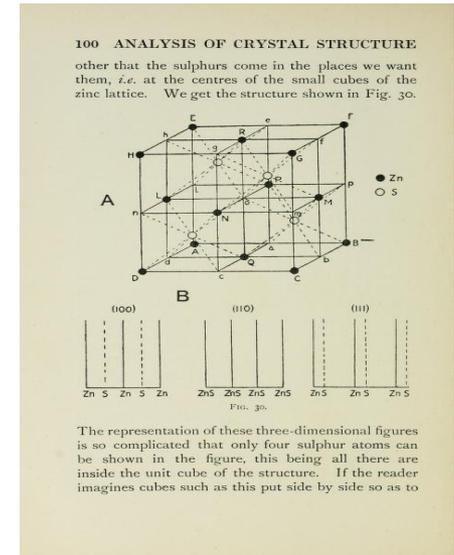
Von Laue had assumed that atoms in zincblende are arranged in a simple cubic lattice, but if this was true Bragg’s law wouldn’t explain the diffraction pattern.

But **if the arrangement of atoms was...arranged in a**

**face centred cubic lattice**, the diffraction pattern was explained perfectly.”

<http://www--outreach.phy.cam.ac.uk/camphy/xraydiffraction>

A model of **Zincblende (ZnS)**, published in the Proceedings of the Royal Institution in 1920.



# Kathleen Lonsdale and Benzene Structure: Structural Chemistry and X-Ray Diffraction

“A number of important deductions can be made even from this approximate result:

- (1) The molecule exists in the crystal as a separate entity.**
- (2) The benzene carbon atoms are arranged in ring formation.**
- (3) The ring is hexagonal or pseudo-hexagonal in shape.** These facts have been believed by chemists for a long time and nearly all the models which have been suggested have conformed to these rules; but so far no aromatic substance except the one under investigation has had a simple enough structure for the positions of the separate atoms to be found without any previous hypotheses as to the shape or size of the molecule. The above reasoning, in fact, supplies a definite proof, from an X-ray point of view, that the chemist's conception of the benzene ring is a true representation of the facts.”



K. Lonsdale, “The Structure of the Benzene Ring in  $C_6(CH_3)_6$ ,” *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, Vol. 123, No. 792 (Apr. 6, 1929), pp. 502-503. Kathleen Lonsdale in 1948