Morphological Crystallography

κρυσταλλος
krystallos "hard ice"
low quartz (α-SiO$_2$)

Crystals

- plane *faces*
- straight line *edges*
- point *vertices*

- constant interfacial angles
- rational intercepts

- 3-D periodic internal lattice

κρυσταλλος
krystallos "hard ice"
low quartz (α-SiO_2)

Large (~400 kg) KDP crystals
KH_2PO_4 , sp. gp. $I\bar{4}2d$
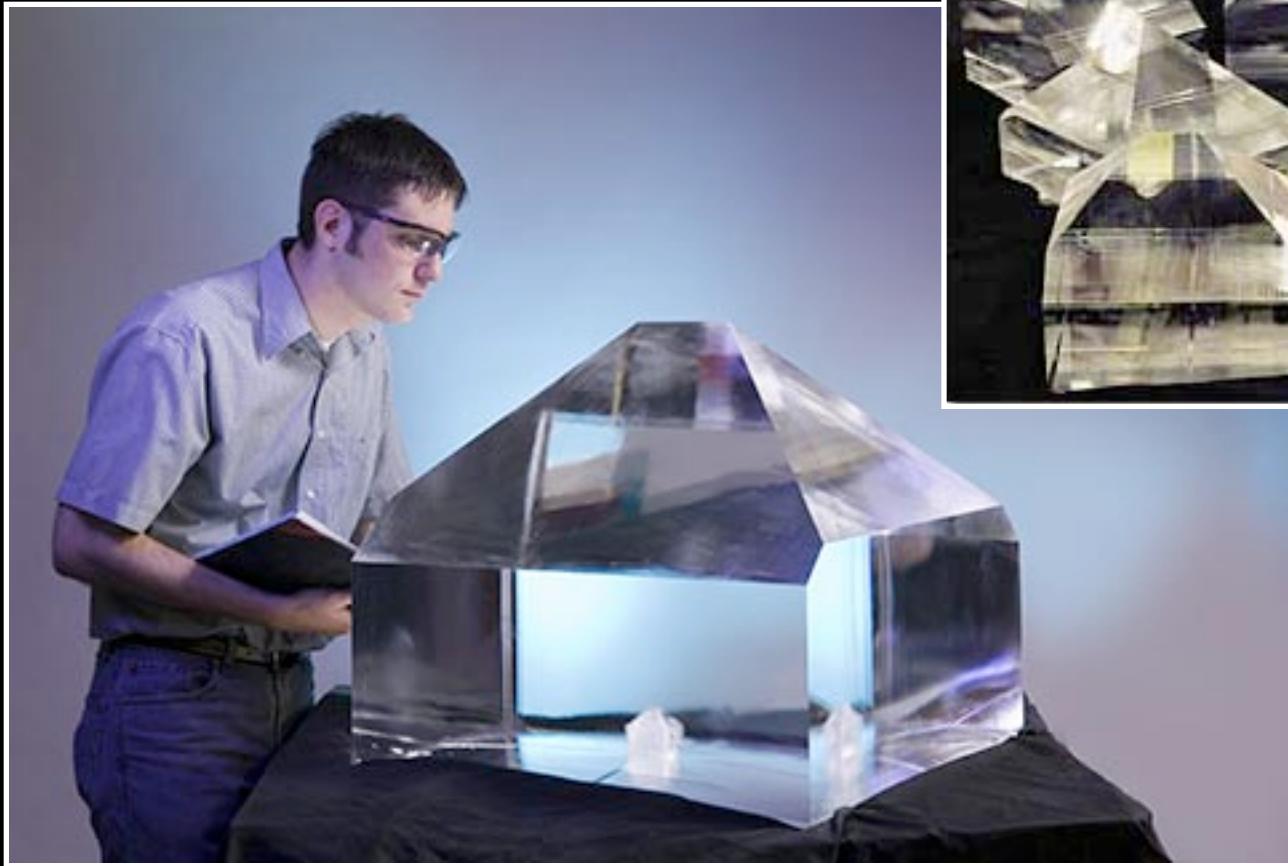
Grown for fabricating frequency converters for high power laser systems for nuclear fusion experiments.

Giant selenite gypsum crystals $CaSO_4 \cdot 2H_2O$
Cueva de los Cristales, Naica mine, Chihuahua, Mexico

Giant crystals grew over many millennia from satd. aq. soln. at const. 58°C temp. in flooded caverns, and were revealed when pumping for mining lowered the water table.

monoclinic point group 2/*m*
space group *A*2/*a*

http://ngm.nationalgeographic.com/2008/11/crystal-giants/shea-text/1

http://ngm.nationalgeographic.com/2008/11/crystal-giants/shea-text/1
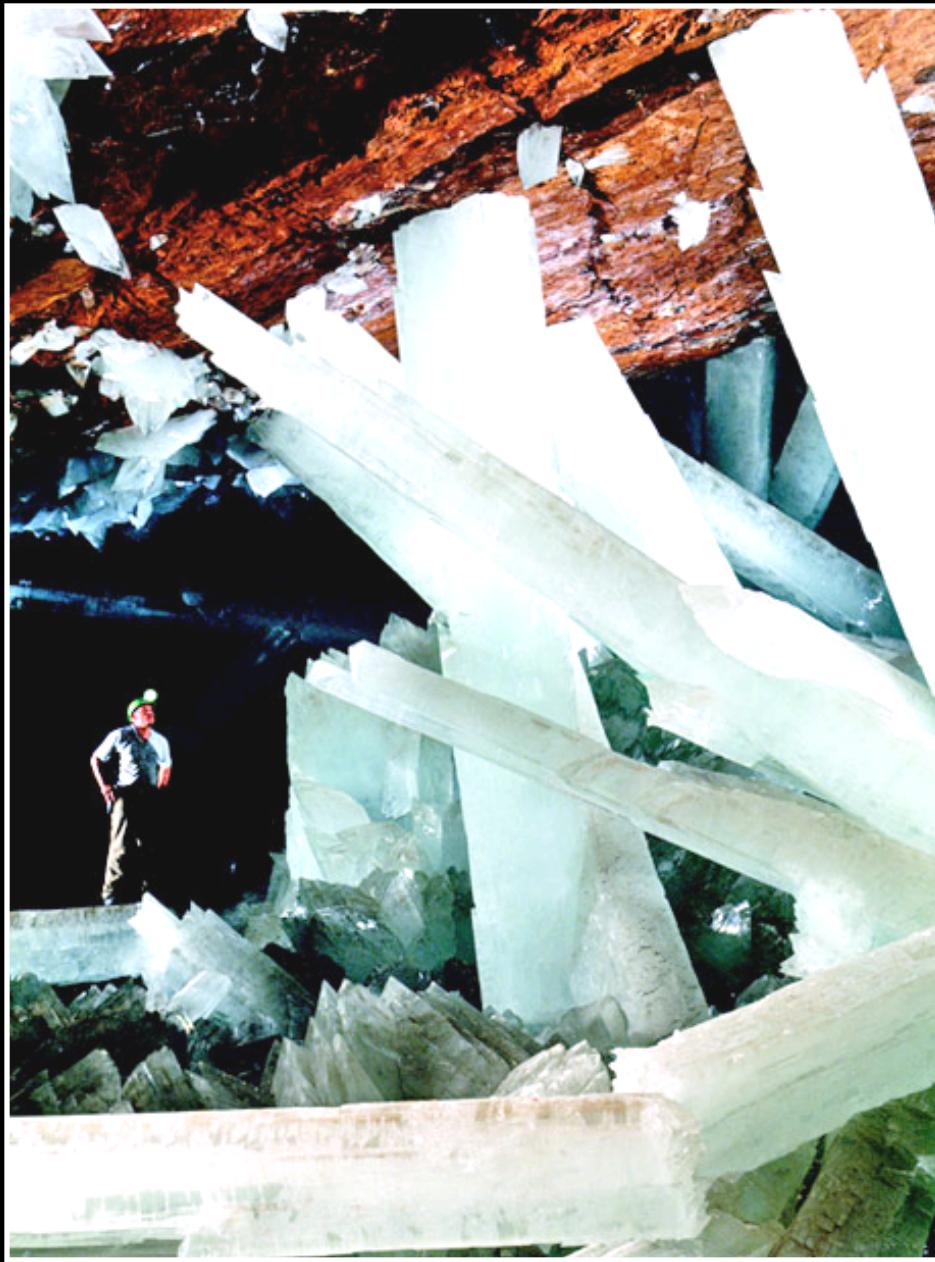
Crystals and Crystallographic Sciences

Crystals
- Ionic
- Covalent
- Metallic
- Molecular
- Macromolecular

Small Unit Cell / Small Molecule → Crystallography
- Solid State Physics
- Structural Chemistry
- Materials Science

Biocrystallography – Structural Molecular Biology
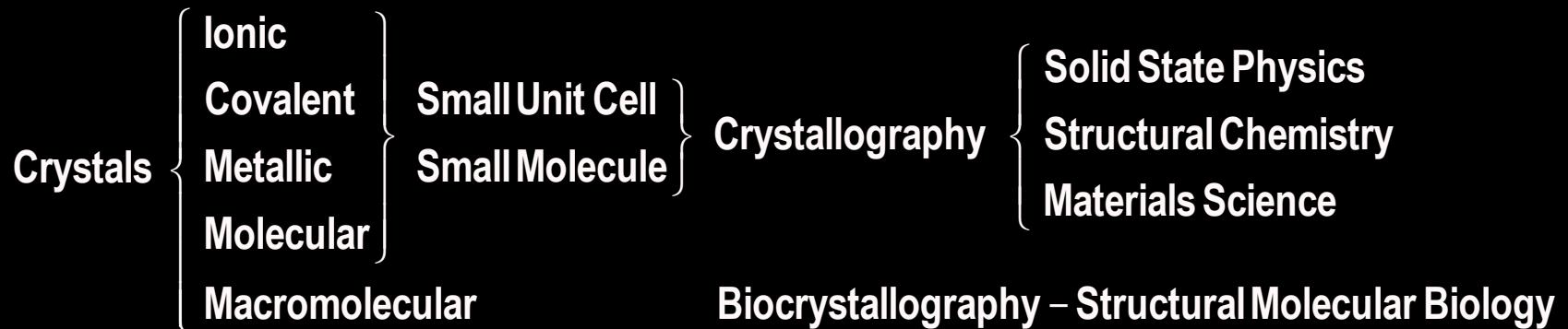
A Chronology of Crystallography

Classical antiquity

      Greco-Roman thinkers – Nature of matter, polyhedral geometry, κρυσταλλος

1611   Johannes Kepler – Hexagonal snow crystals, hcp and ccp spheres

1600s René Descartes, Robert Hooke, Christiaan Huygens –
        Speculations on periodic spheroid packing in crystals

1669   Nicolaus Steno (Niels Stensen),

1688   Domenico Gugliemini, and

1772   Jean-Baptiste Louis Romé de l'Isle – Law of Constant Interfacial Angles

1783   Abbé René-Just Haüy –
        Law of Rational Indices, "*molécules intégrantes*," unit cells

1839   William Hallowes Miller – stereographic projection, Miller indices

1849   Auguste Bravais – Lattice theory

1883   William J. Pope and William Barlow –
        Speculations on atomic and ionic sphere-packing in crystals.

1890   Evgraf Stepanovich Federov,

1892   Arthur Moritz Schoenflies, and

1894   William Barlow (all three independently) – Space group theory

1883   Paul Heinrich Ritter von Groth – Chemical and optical crystallography

1895   Wilhelm Conrad Röntgen – X-rays

1912   Walther Friedrich, Paul Knipping, and Max von Laue – X-ray diffraction

1913   William Henry and William Lawrence Bragg – X-ray crystal structures

The Platonic Solids

Name	Image	Vertices V	Edges E	Faces F	Euler characteristic: V − E + F
Tetrahedron		4	6	4	2
Cube		8	12	6	2
Octahedron		6	12	8	2
Dodecahedron		20	30	12	2
Icosahedron		12	30	20	2
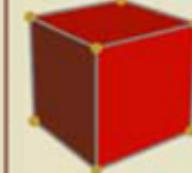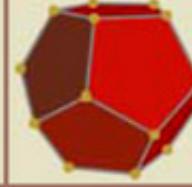
Kepler's Platonic solid model of the solar system from Mysterium Cosmographicum (1596)
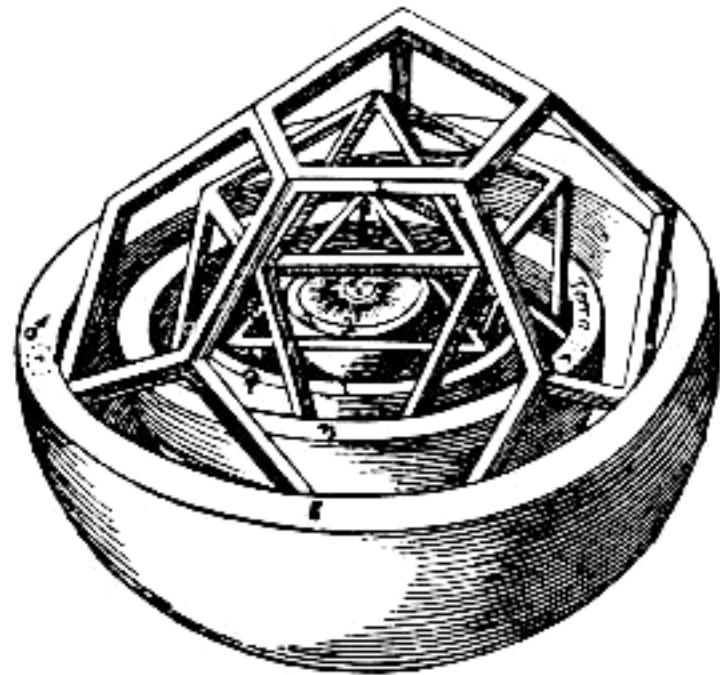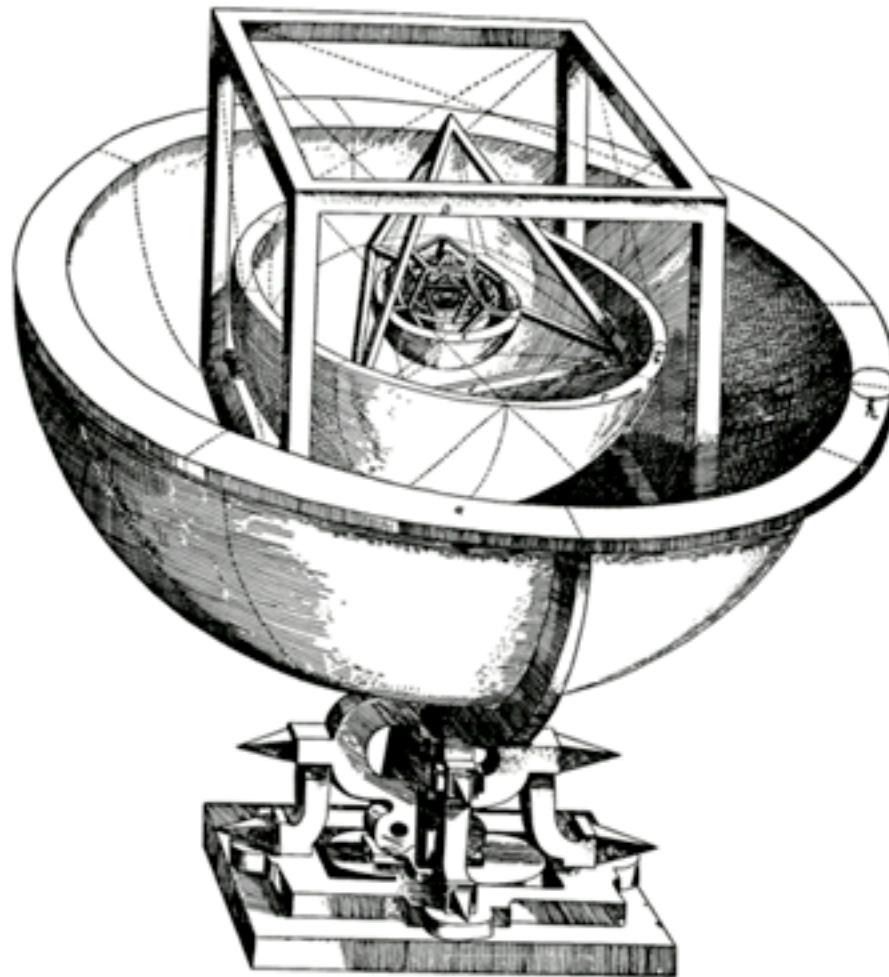
Detailed view of the inner sphere

# Johannes Kepler (1611)
On the Six-Cornered Snowflake

http://quinceandquire.typepad.com/quince_and_quire/2011/01/images-of-snow-crystals.html

How full of the creative genius is the air in which these are generated!
I should hardly admire more if real stars fell and lodged on my coat.
Nature is full of genius, full of the divinity; so that not a snowflake
escapes its fashioning hand.
—Henry David Thoreau (1817–1862)

http://blog.makezine.com/snowflakes.jpg

Johannes Kepler (1611)
On the Six-Cornered Snowflake
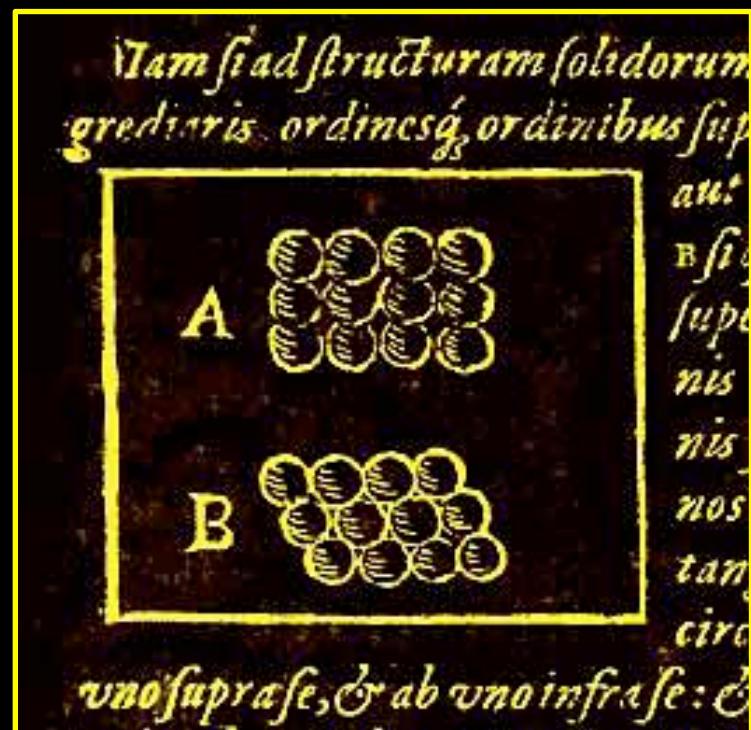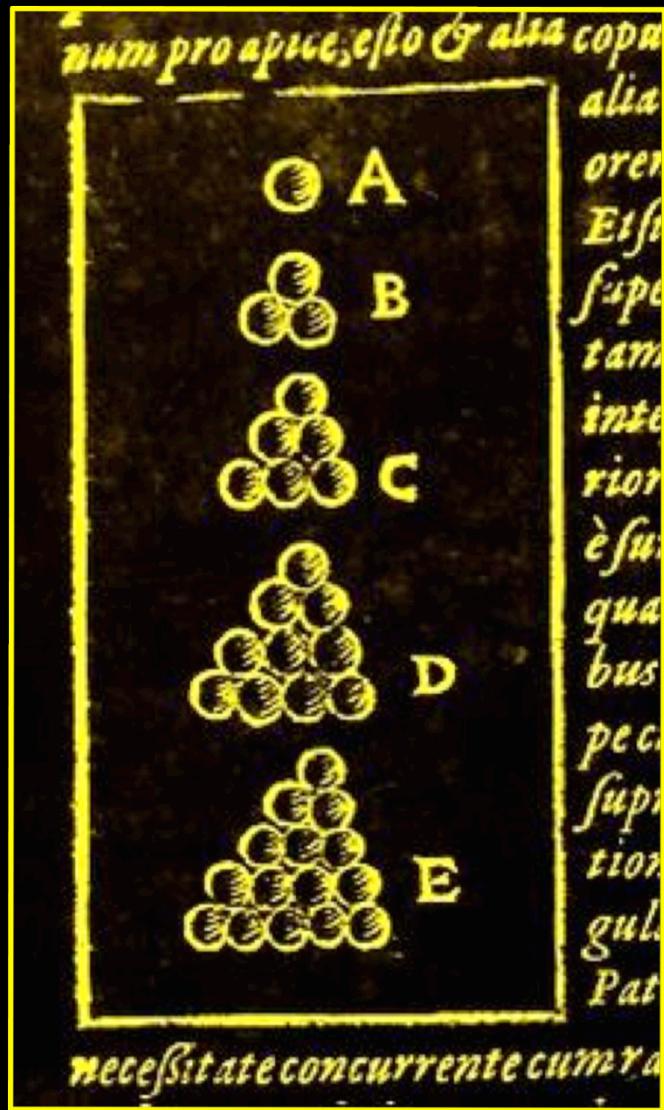
Kepler's conjecture (1611)
hcp and fcc-ccp densest packing of equal spheres

Computational proof by exhaustion (Thomas Hales, 1997)

https://sites.google.com/site/thalespitt/
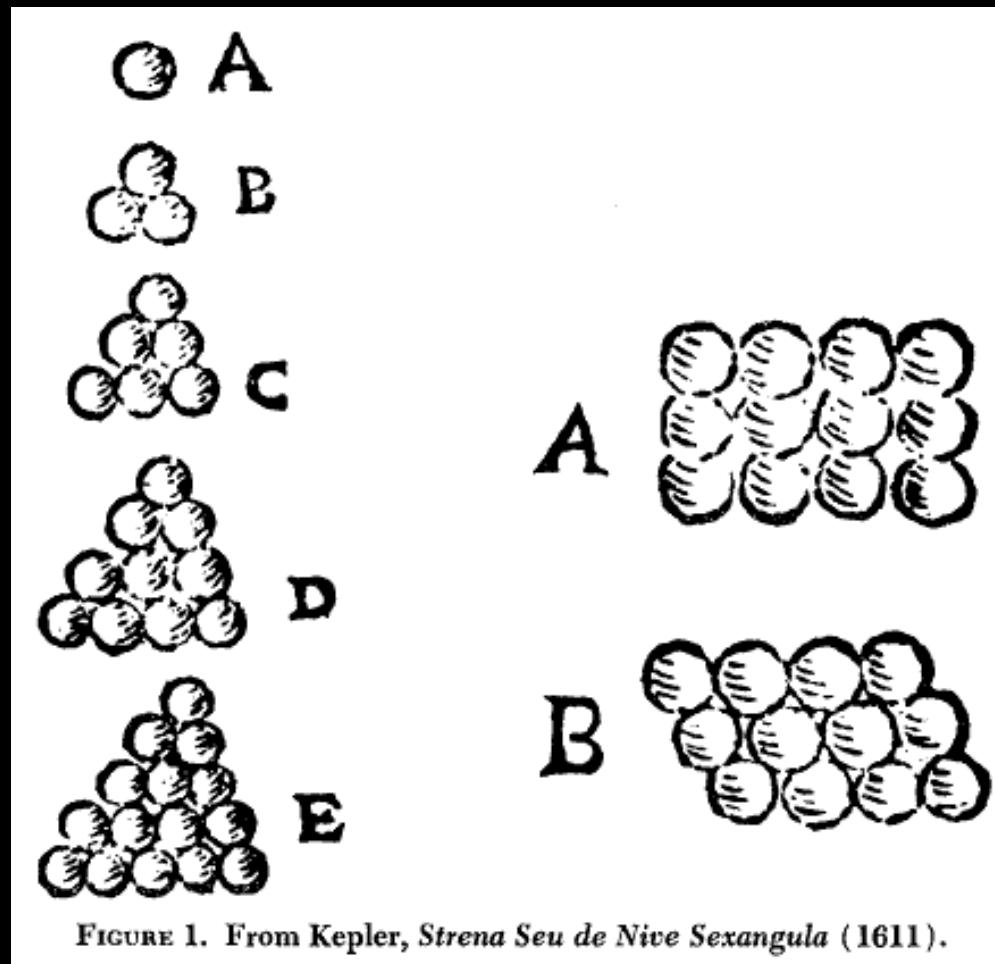
FIGURE 1. From Kepler, *Strena Seu de Nive Sexangula* (1611).

Cecil Schneer (1960). Kepler's New Year's Gift of a Snowflake. *Isis,* 51(4), 531-545.
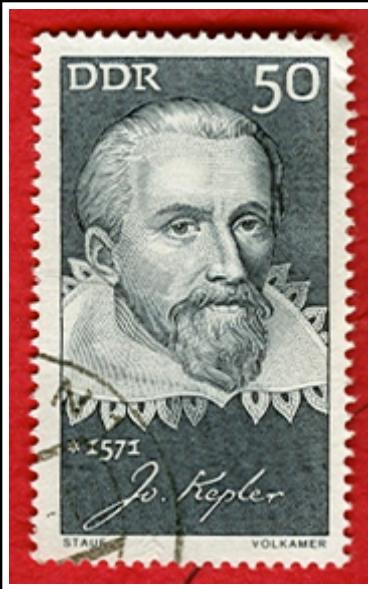
"Each single plant has a single animating principle of its own, since each instance of a plant exists separately, and there is no cause to wonder that each should be equipped with its own peculiar shape. But to imagine an individual soul for each and any starlet of snow is utterly absurd, and therefore the shapes of snowflakes are by no means to be deduced from the operation of soul in the same way as with plants."

Johannes Kepler (1611). *De Nive Sexangula*
(*On the Six-Cornered Snowflake*).

"These were little plates of ice, very flat, very polished, very transparent, about the thickness of a sheet of rather thick paper...but so perfectly formed in hexagons, and of which the six sides were so straight, and the six angles so equal, that it is impossible for men to make anything so exact."

"I only had difficulty to imagine what could have formed and made so exactly symmetrical these six teeth around each grain in the midst of free air and during the agitation of a very strong wind, until I finally considered that this wind had easily been able to carry some of these grains to the bottom or to the top of some cloud, and hold them there, because they were rather small; and that there they were obliged to arrange themselves in such a way that each was surrounded by six others in the same plane, following the ordinary order of nature."

Rene Descartes (1635). Notes.

F.C. Frank (1974). Descartes' Observations on the Amsterdam Snowfalls of 4, 5, 6, and 9 February 1634. *J. Glaciology* **13**, 535.

http://www.its.caltech.edu/~atomic/snowcrystals/earlyobs/earlyobs.htm

Robert Hooke (1635-1703)

In 1665 Robert Hooke published a large volume entitled *Micrographia*, containing sketches of practically everything Hooke could view with the latest invention of the day, the microscope. Included in this volume are many snow crystal drawings, which for the first time revealed the complexity and intricate symmetry of snow crystal structure.

Hexagonal Snow Crystals
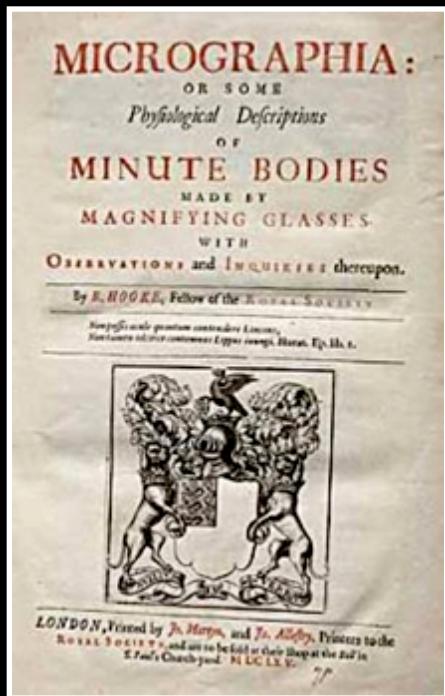
"The First Law of Crystallography"
## Steno's Law of Constant Interfacial Angles (1669)

Niels Stensen
Nicolaus Steno

NICOLAI STENONIS
DE SOLIDO
INTRA SOLIDVM NATVRALITER CONTENTO
DISSERTATIONIS PRODROMVS.
AD
SERENISSIMVM
FERDINANDVM II.
MAGNVM ETRVRIÆ DVCEM.

FLORENTIÆ
Ex Typographia sub signo STELLÆ MDCLXIX.
SVPERIORVM PERMISSV.
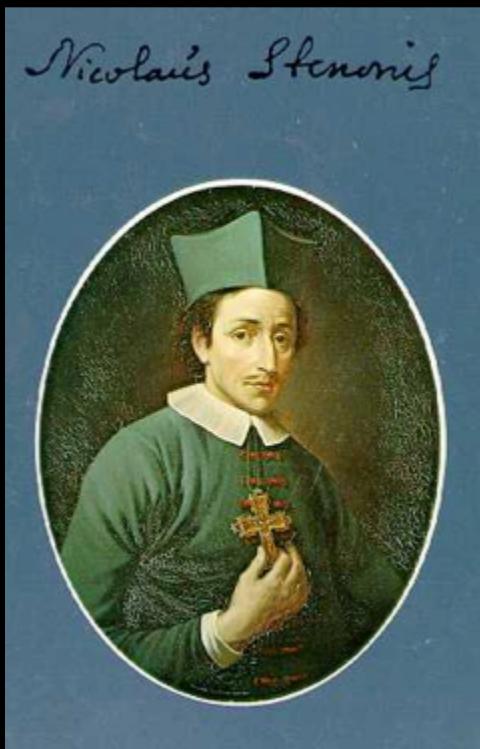
1638-1686

M.DC.LX.IX
1669
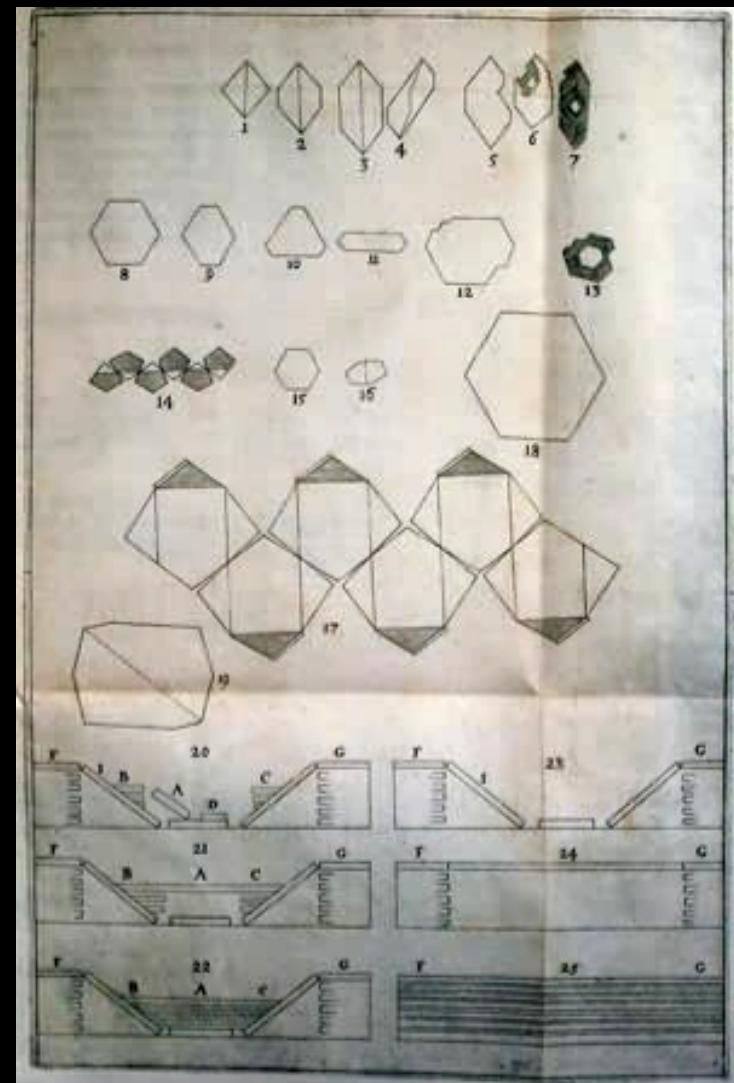
from Steno's notebook

The First Law of Crystallography"
Steno's Law of Constant Interfacial Angles (1669)

The angles between corresponding faces on crystals of any solid chemical or mineral species are constant and are characteristic of the species.

The interfacial angle is measured between face normals.

The law constant of interfacial angles holds for any two crystals a given species, whether they are natural or man-made, regardless of size or provenance.
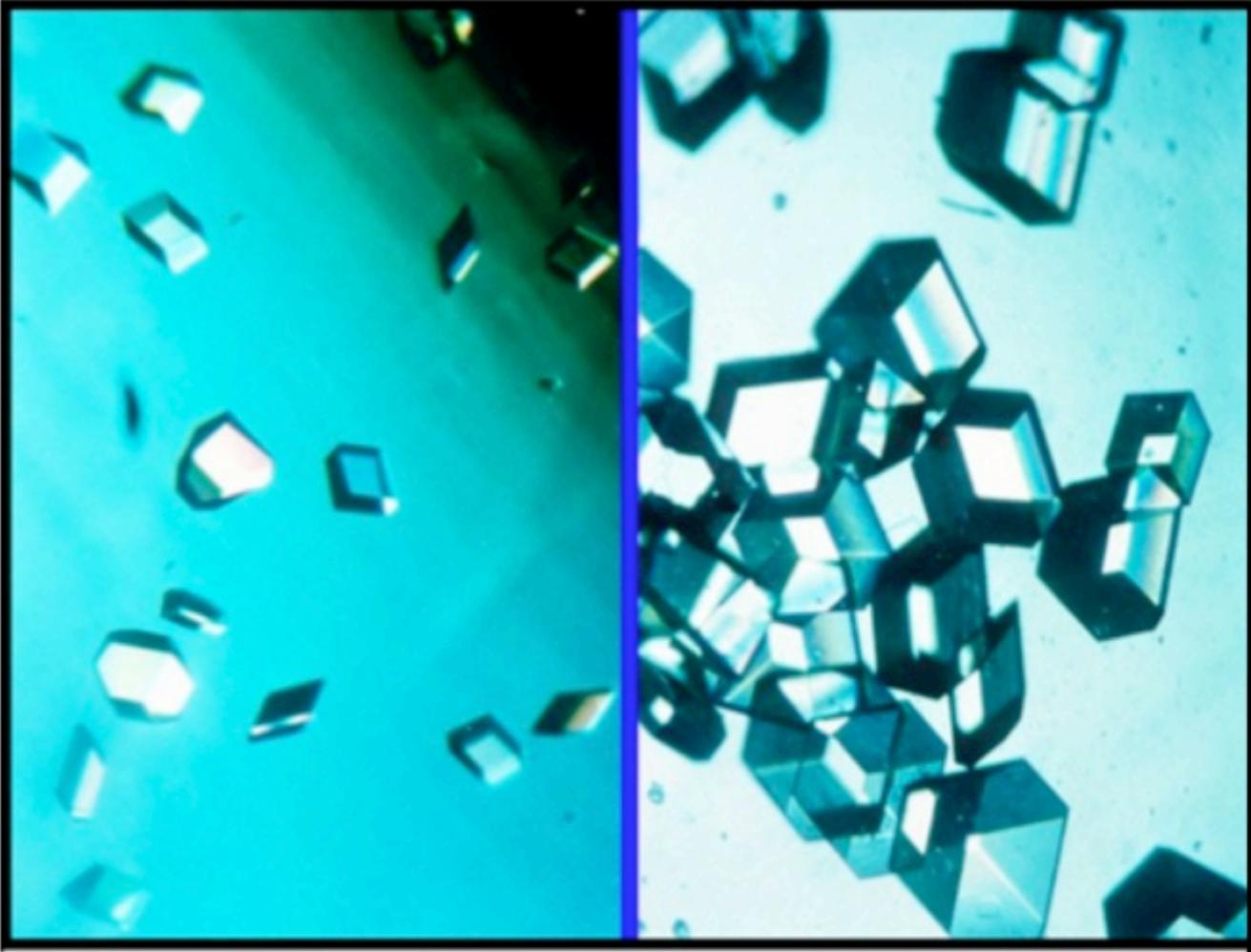
Crystals of T_3R_3 human insulin complexed with *p*-hydroxybenzamide

NASA STS60 (Discovery, 1994): left, 1 G; right, μG. Both photomicrographs at the same magnification.
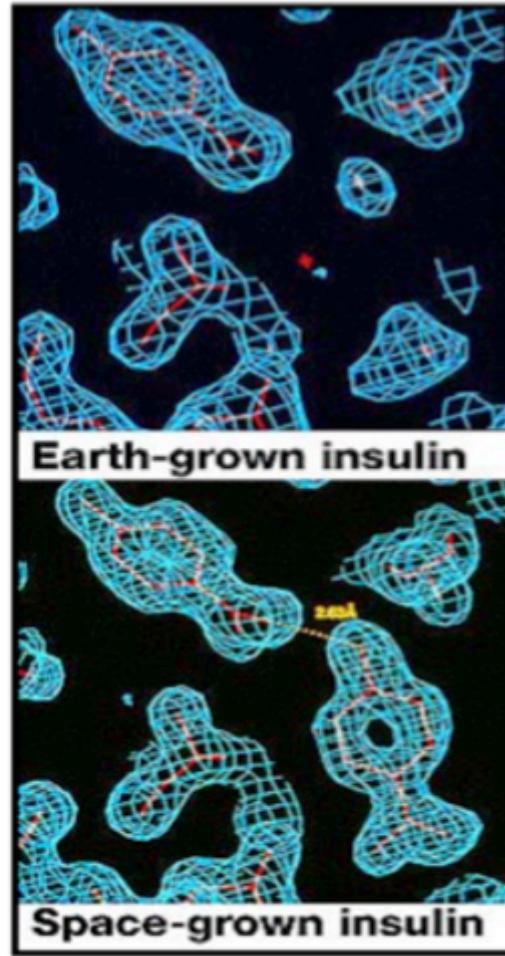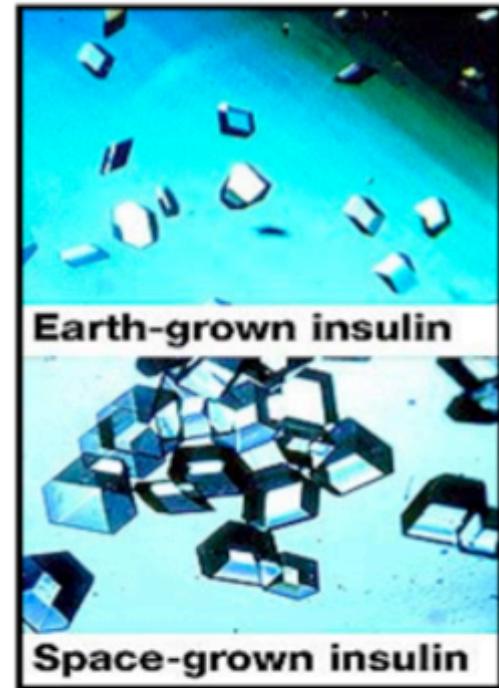
Crystals of T_3R_3 human insulin
complexed with *p*-hydroxybenzamide

NASA STS60 (Discovery, 1994): left, 1 G; right, µG.

Earth grown   (1 G)   1.9 Å resolution;
Space grown (µG STS60)   1.4 Å resolution.

Photomicrographs at the same magnification.

Steno's Law of Constant Interfacial Angles

Niels Stensen
Nicolai Stenonis
Nicholas Steno
1628-1686
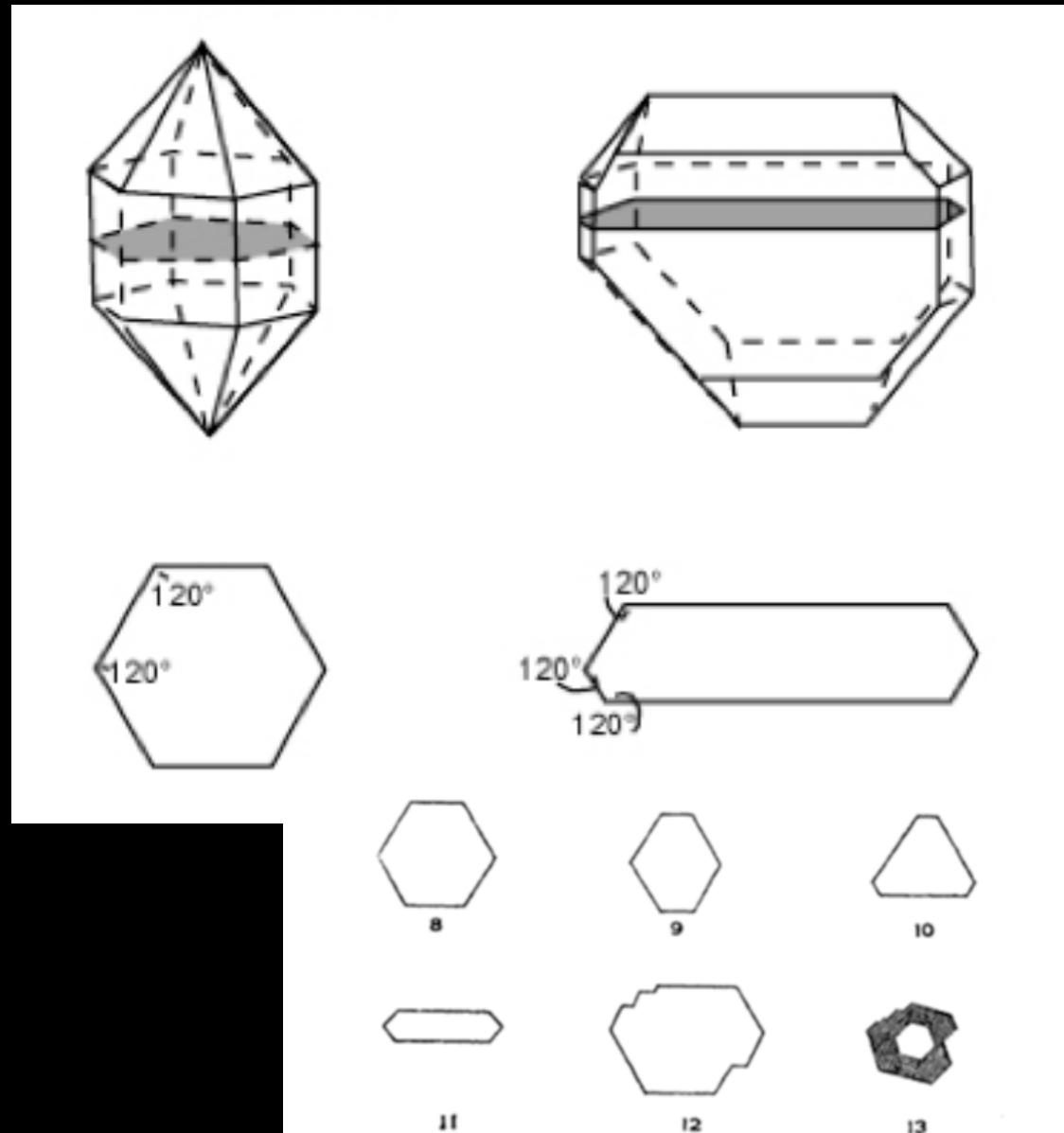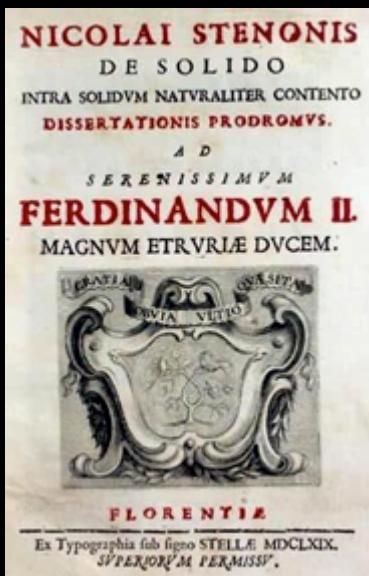
"The first law of crystallography"
The law of constant interfacial angles
[Nicolas Steno (Niels Stensen), 1669; Jean-Baptiste Romé de l'Isle, 1793]
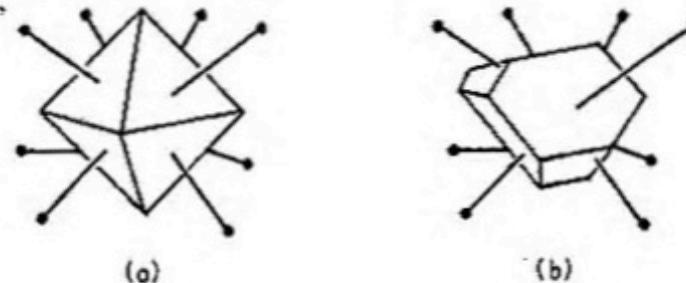

Fig. 2.5(a). Face normals of a regular octahedron.

Fig. 2.5(b). Same face normals as in Fig. 2.5(a) from octahedron of irregular growth.
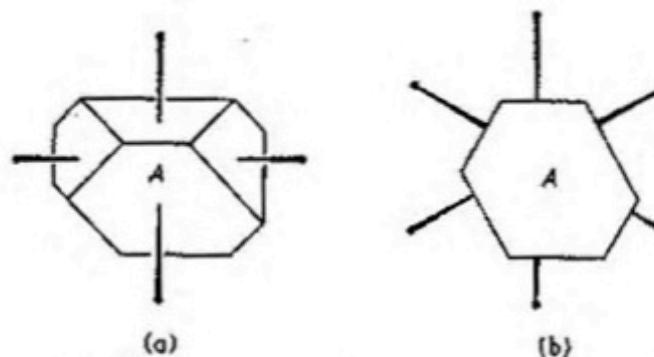
Fig. 2.6. Crystal of Fig. 2.5(b) showing (a) fourfold axis and (b) threefold axis.

S.C. Nyburg (1961). *X-Ray Analysis of Organic Structures*. New York: Academic Press.

Hooke (1665)

Steno (1669)

Fig. 1

A   B   C   D   ⅟₁₆ E   F   G

Fig. 2

A   D

B   C

E

H   I   ⅟₄ K   L
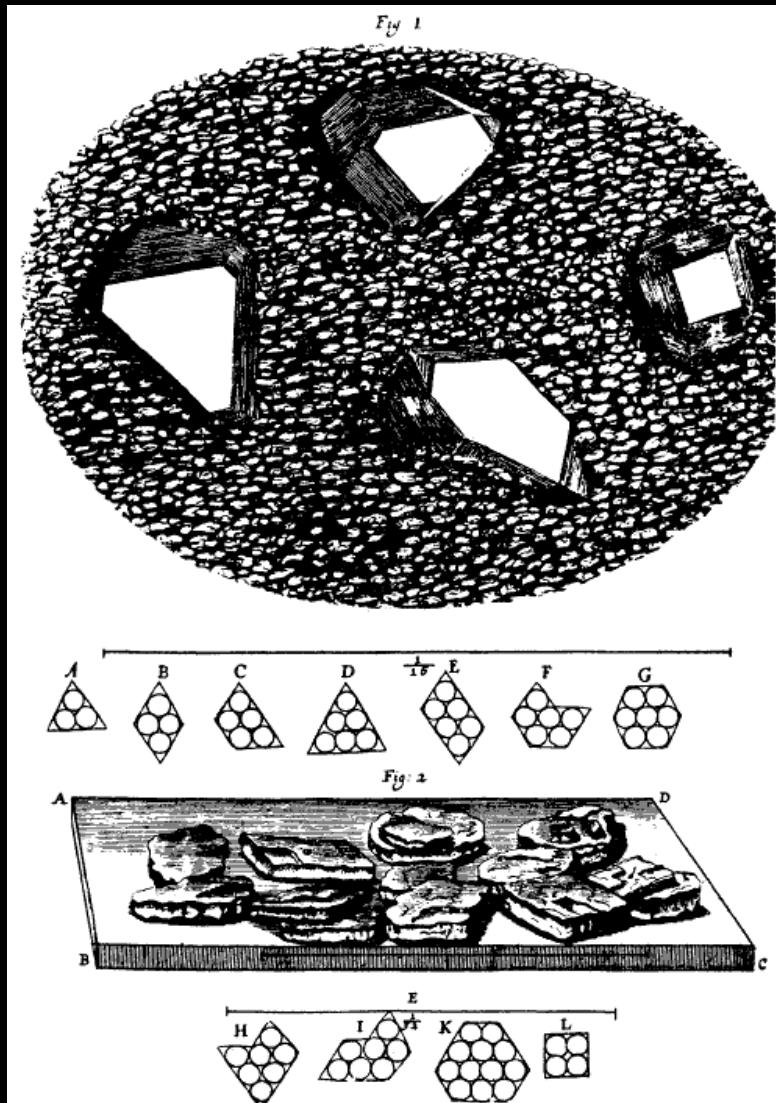
FIGURE 2. From Robert Hooke, *Micrographia* (1665). Hooke's drawings express the two fundamental laws of crystallography: Steno's Law (the constancy of interfacial angles), and Haüy's Law (the law of rational axial intercepts—integral axial ratios).

1   2   3   4

5   6   7

8   9   10

11   12   13
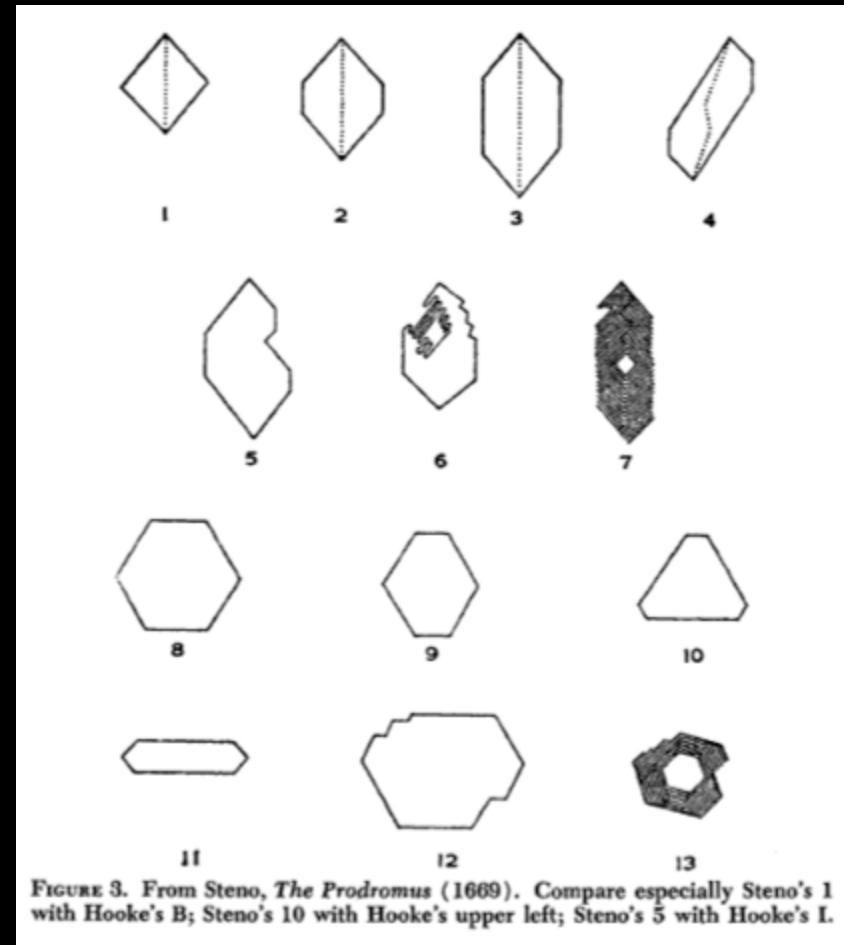
FIGURE 3. From Steno, *The Prodromus* (1669). Compare especially Steno's 1 with Hooke's B; Steno's 10 with Hooke's upper left; Steno's 5 with Hooke's L.

Quartz crystals
(1-7) elevations
(8-13) cross-sections

Cecil Schneer (1960). Kepler's New Year's Gift of a Snowflake. *Isis,* 51(4), 531-545.

Confirmation of Steno's Law of Constant Interfacial Angles

CRISTALLOGRAPHIE,
OU
DESCRIPTION
DES FORMES PROPRES A TOUS LES CORPS
DU REGNE MINÉRAL,
Dans l'état de Combinaison faline, pierreufe
ou métallique,

Avec Figures & Tableaux fynoptiques de tous les Criftaux connus.

Par M. DE ROMÉ DE L'ISLE, de l'Académie Impériale des Curieux de la Nature; des Académies Royales des Sciences de Berlin & de Stockholm; de celle des Sciences utiles de Mayence; Honoraire de la Société d'Emulation de Liège.

SECONDE ÉDITION.

Obfervationes veras, quam ingeniofiffimas fictiones fepi praftat; Natura myfteria potiùs indagare quàm divinare.
BEROM. de Form. Cryftallor.

TOME PREMIER.

A PARIS,
DE L'IMPRIMERIE DE MONSIEUR.

M. DCC. LXXXIII.

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

**Pre-Revolutionary French artillery officer and by avocation a mineralogist**

Confirmed Steno's *Law of Constant Interfacial Angles* with hundreds of mineral crystals.

Essai de Cristallographie (1772)
and
Cristallographie (1783).
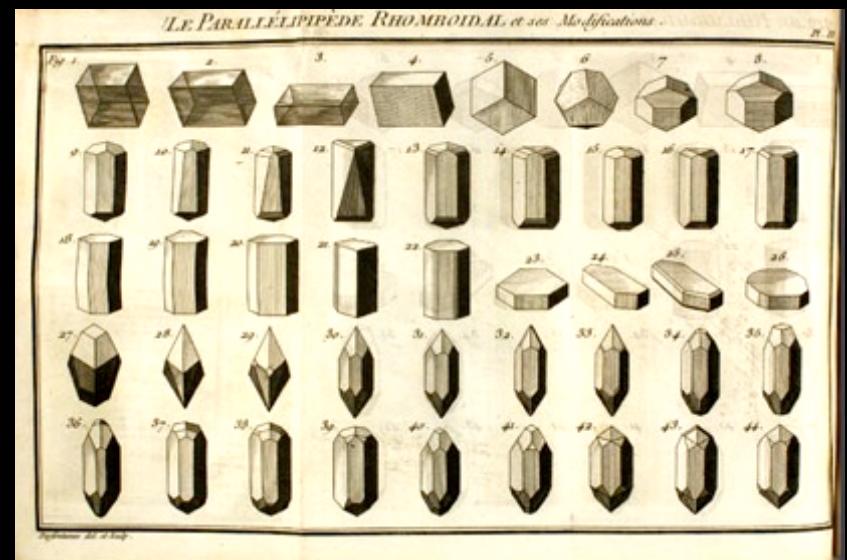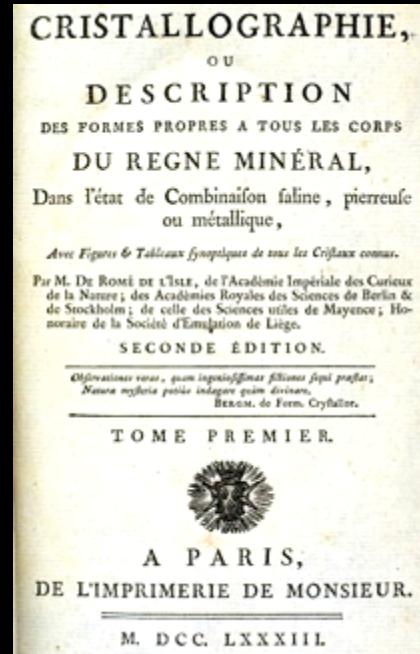
LE PARALLÉLIPIPÈDE RHOMBOIDAL et ses Modifications.

Birefringent Iceland spar (calcite, CaCO$_3$)

120°
↺
→
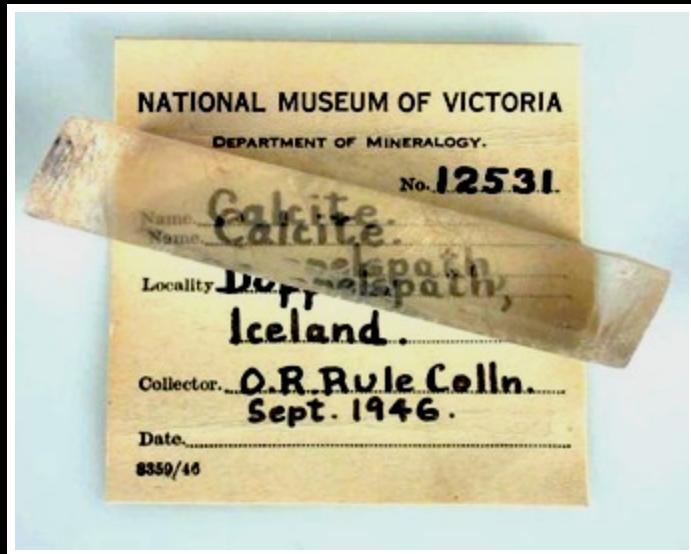
# Huygens' principle and birefringent Iceland spar

Christiaan Huygens (1629-1695)

"Huygens Principle" considers all points on a wavefront to be sources of spherical wavefronts that add up to build the propagating wavefront. Huygens realized that if the velocity of light varied with the direction the spheres would deform to ellipsoids and thus was able to explain the refraction law for crystals such as Iceland Spar.

Huygens (1678). *Traité de la Lumière*.

Christiaan Huygens (1629-1695)
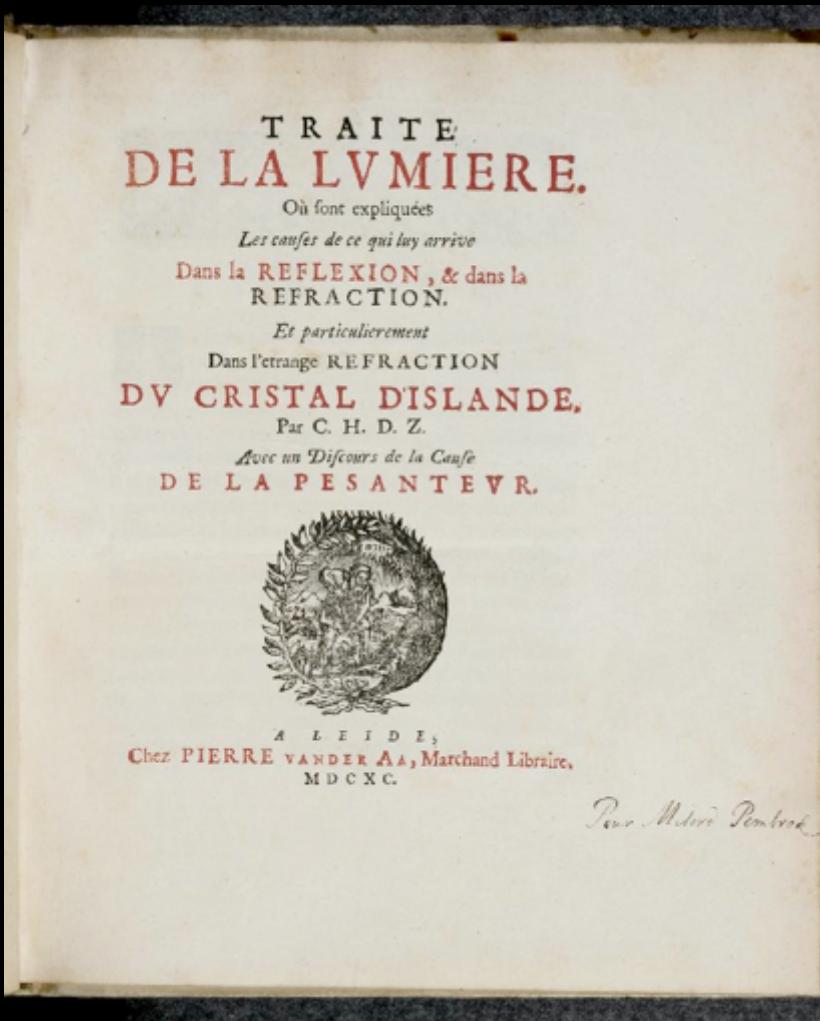
Christiaan HUYGENS. *Traité de la Lumiere.*
Où sont expliquées les causes de ce qui luy arrive dans la reflexion, & dans la refraction.
Et particulierement dans l'etrange refraction du Cristal d'Islande….
Avec un discours de la cause de la pesanteur. MDCXC (1690).

http://www.jonathanahill.com/book.php?book_id=1242

Isaac Newton (1643-1727)

OPTICKS:
OR, A
TREATISE
OF THE
REFLEXIONS, REFRACTIONS,
INFLEXIONS and COLOURS
OF
LIGHT.
ALSO
Two TREATISES
OF THE
SPECIES and MAGNITUDE
OF
Curvilinear Figures.

LONDON,
Printed for SAM. SMITH, and BENJ. WALFORD,
Printers to the Royal Society, at the Prince's Arms in
St. Paul's Church-yard. MDCCIV.

SAACVS NEWTONVS.

MDCCIV (1704)

http://en.wikipedia.org/wiki/Opticks
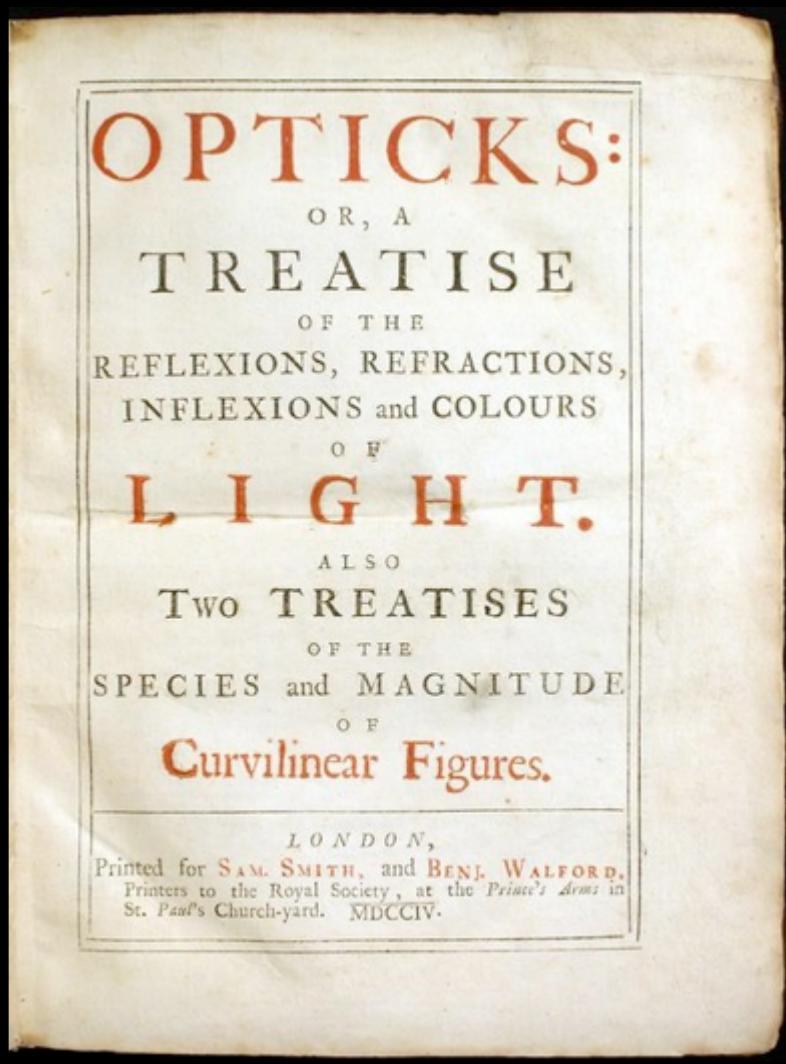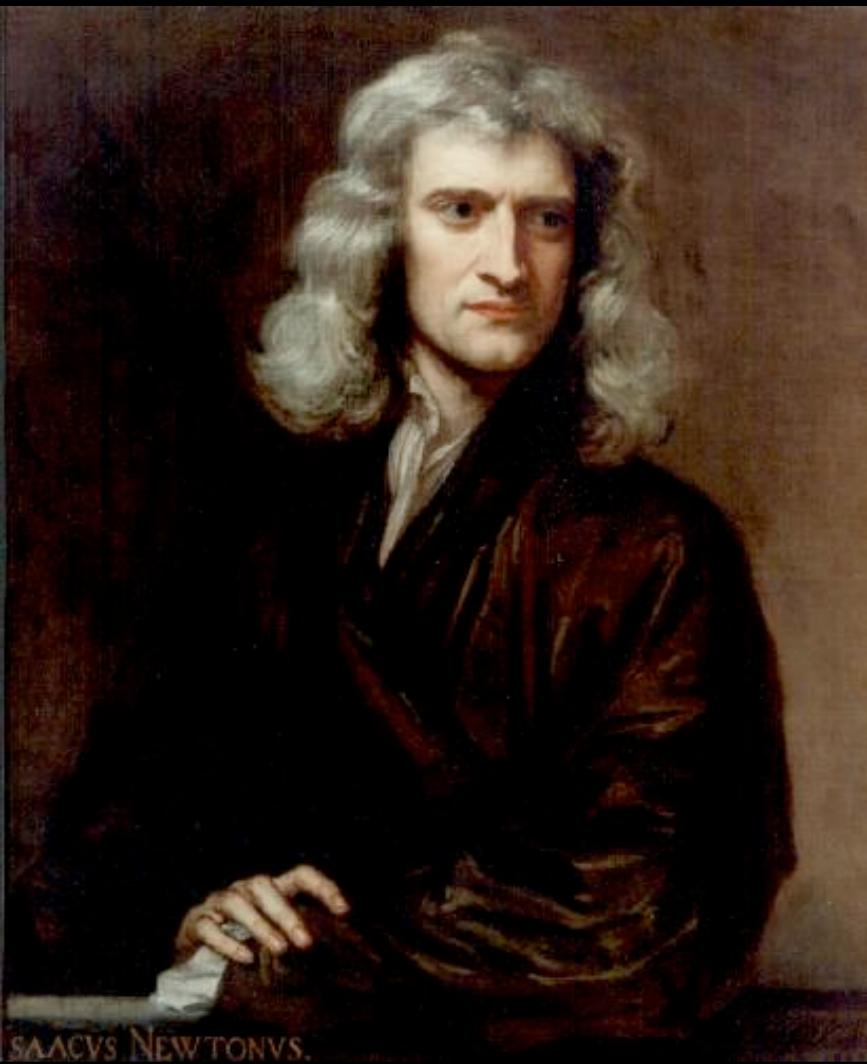
Birefringent Iceland spar (calcite, CaCO$_3$)
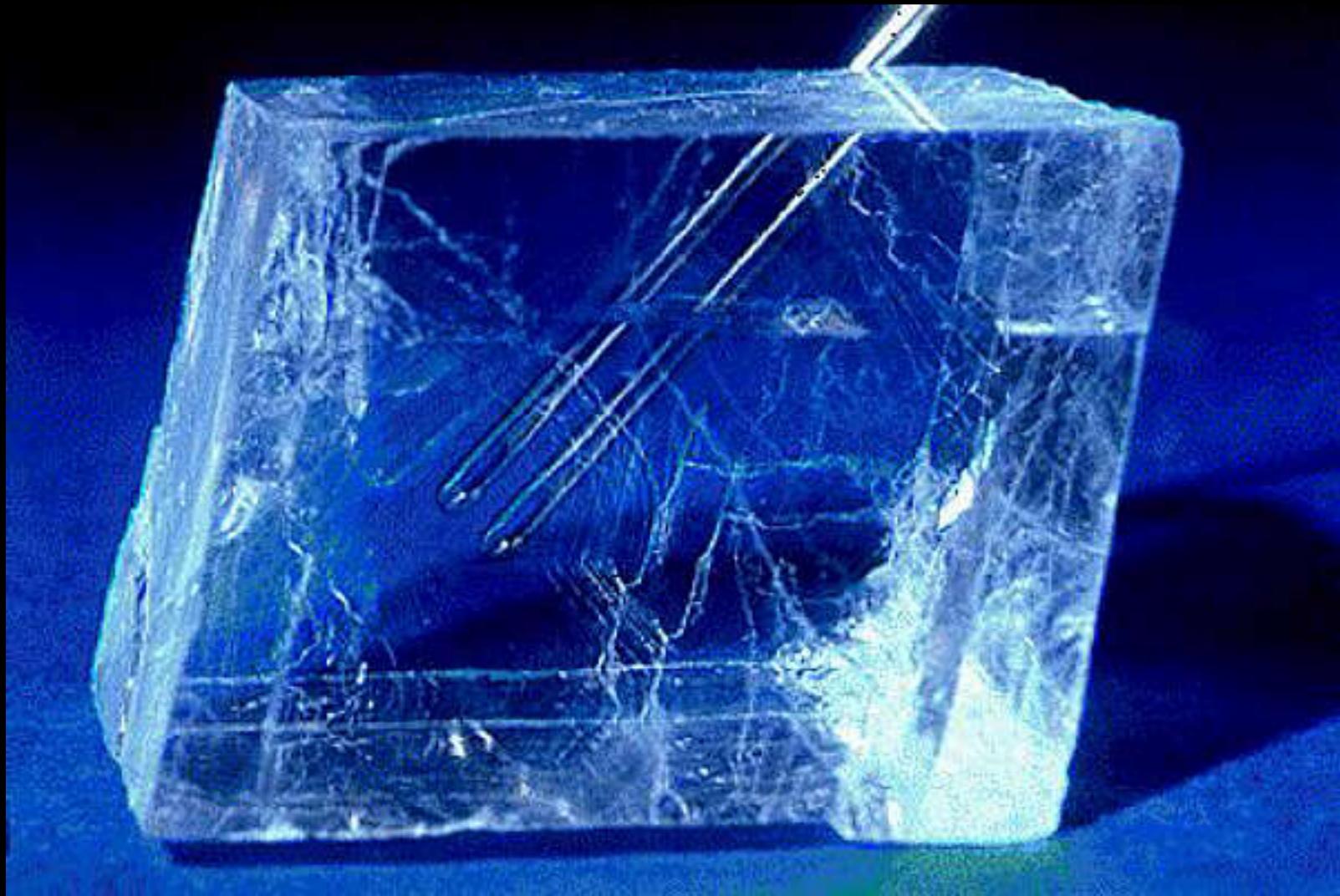
Huygens (1690)
Calcite ($CaCO_3$) cleavage rhombohedron
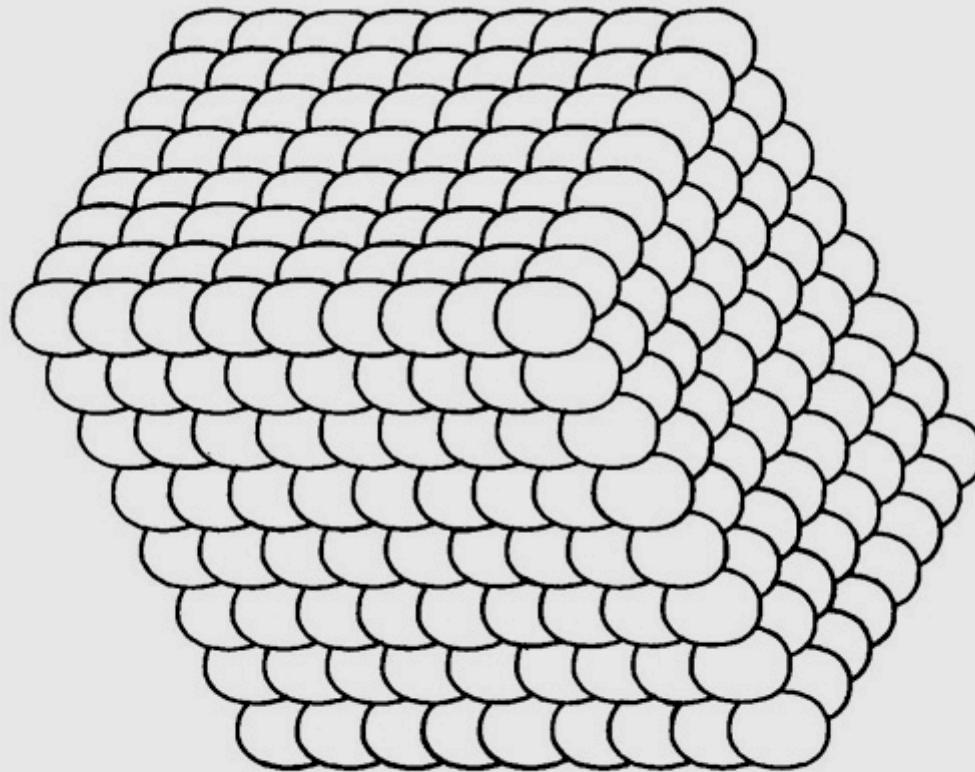
Fig. 1-24.   Fine structure of the calcite cleavage rhombohedron according to Huygens.   (Klug, *Am. Scientist*, 36, 377.)

Hypothetical ellipsoids rather than spheres in order to produce the rhomboid shape.

Huygens' (1690) calcite cleavage hypothesis
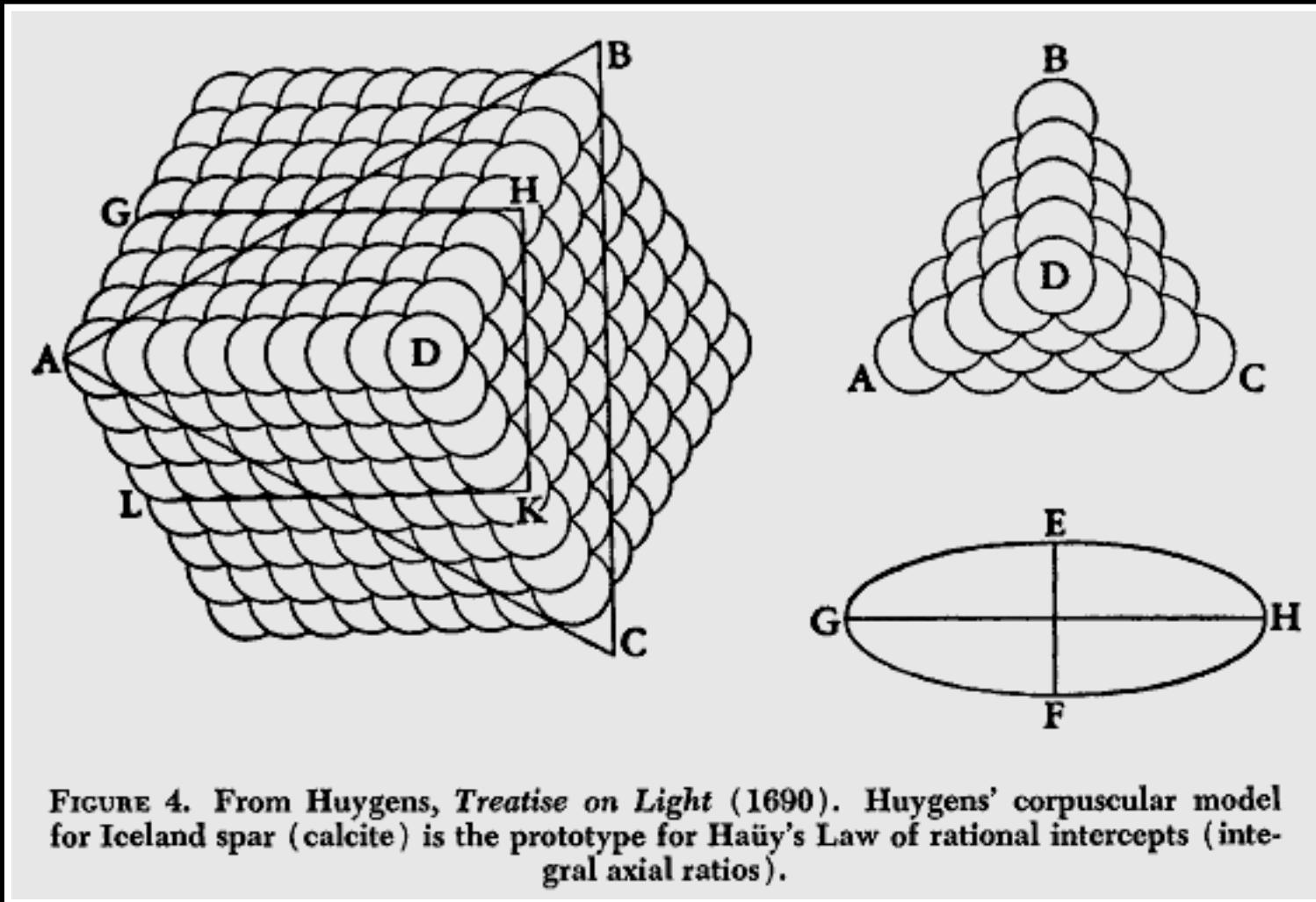
FIGURE 4. From Huygens, *Treatise on Light* (1690). Huygens' corpuscular model for Iceland spar (calcite) is the prototype for Haüy's Law of rational intercepts (integral axial ratios).

Cecil Schneer (1960). Kepler's New Year's Gift of a Snowflake. *Isis,* 51(4), 531-545.

Calcite (CaCO$_3$) birefringence

o-ray ordinary ray
           straight-through
e-ray extra-ordinary ray
           refracted

$\bar{3}1m$

$R\bar{3}c$
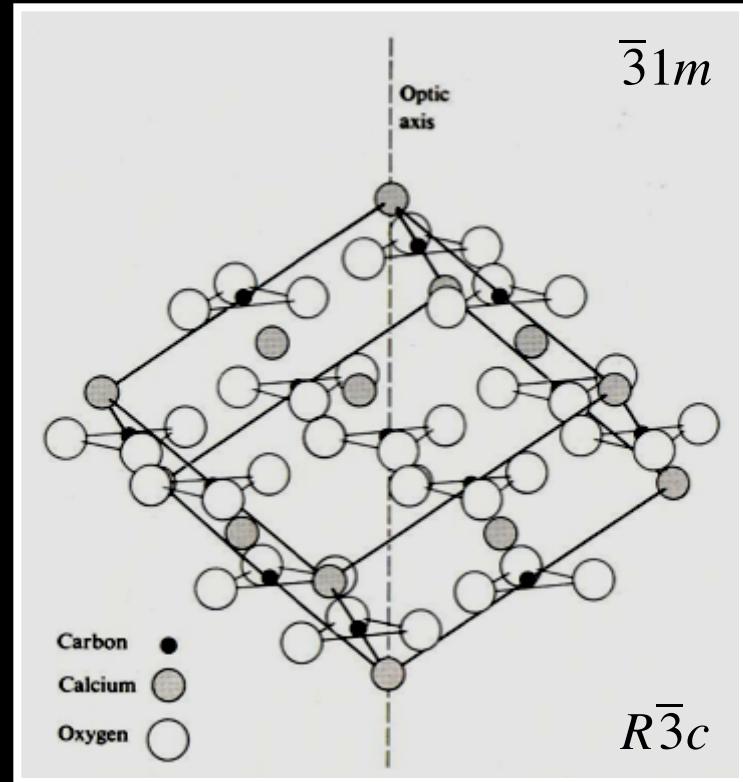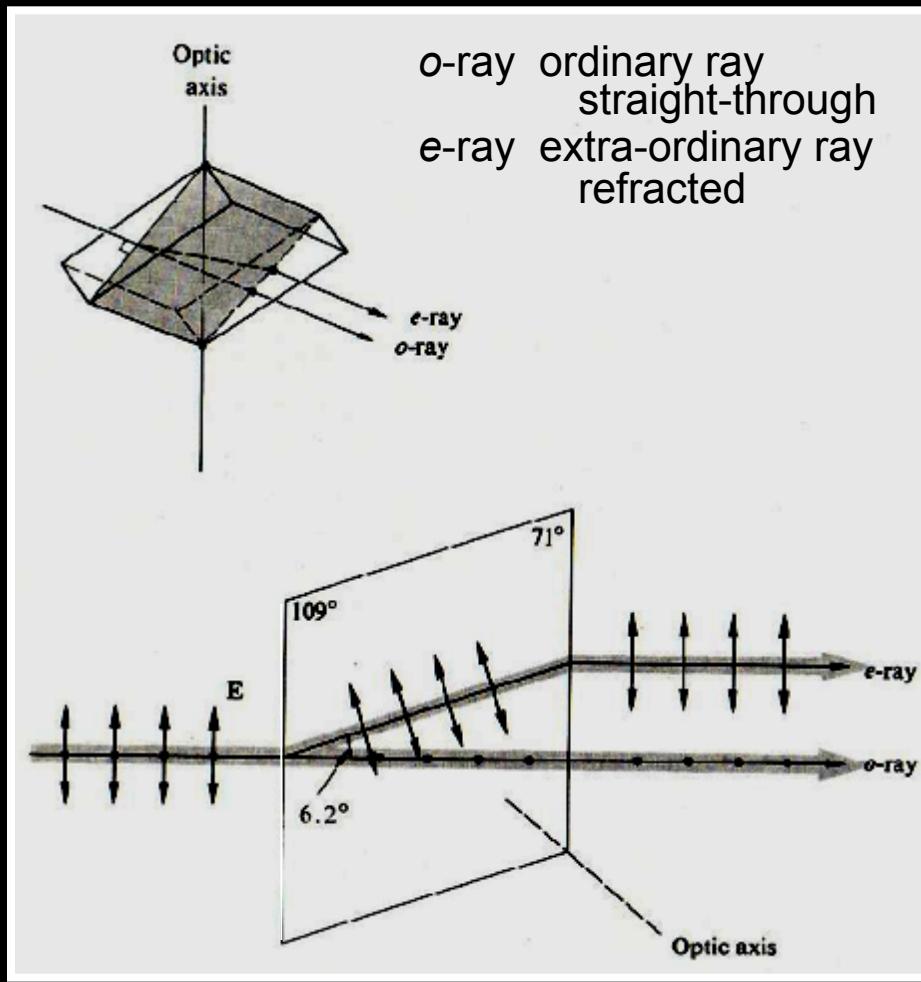
$\{10\bar{1}4\}$ faces

"The Second Law of Crystallography"
Haüy's Law of Rational Intercepts (1784)

According to Haüy, if three non-coplanar edges of a crystal are taken to define the directions of three axes of a coordinate system, then the ratios of the axial intercepts of two crystal faces are always found to be rational fractions. That is, the lengths of the axial intercepts can be expressed as integer multiples of some elementary axial lengths.

**Abbé René-Just Haüy
(1743-1822)
making goniometric
measurements on a
calcite (CaCO$_3$) crystal**

ESSAI
D'UNE THÉORIE
SUR LA STRUCTURE
DES CRYSTAUX,
APPLIQUÉE
A PLUSIEURS GENRES DE SUBSTANCES
CRYSTALLISÉES;

Par M. l'Abbé HAÜY, de l'Académie Royale des Sciences, Professeur d'Humanités dans l'Université de Paris.

A PARIS,
Chez Gogué & Née de la Rochelle, Libraires, Quai des Augustins, près le Pont Saint-Michel.

M. DCC. LXXXIV.
SOUS LE PRIVILÉGE DE L'ACADÉMIE.
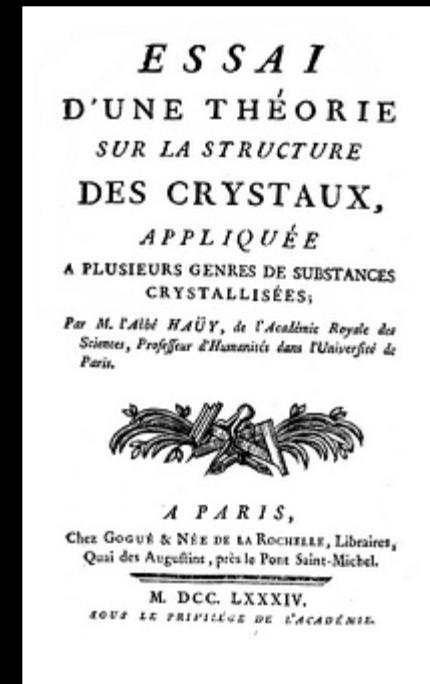
**Monsieur l'Abbé HAÜY
M.DCC.LXXX.IV
1784**

**Abbé René-Just Haüy (1743-1822)
making goniometric measurements on a calcite (CaCO₃) crystal**

ESSAI
D'UNE THÉORIE
SUR LA STRUCTURE
DES CRYSTAUX,
APPLIQUÉE

A PLUSIEURS GENRES DE SUBSTANCES
CRYSTALLISÉES;

Par M. l'Abbé HAÜY, de l'Académie Royale des Sciences, Professeur d'Humanités dans l'Université de Paris.

A PARIS,

Chez GOGUÉ & NÉE DE LA ROCHELLE, Libraires, Quai des Augustins, près le Pont Saint-Michel.

M. DCC. LXXXIV.
SOUS LE PRIVILÉGE DE L'ACADÉMIE.

**Monsieur l'Abbé HAÜY
M.DCC.LXXX.IV
1784**

A collection of crystallographic solids
gifted by l'Abbe René Just Haüy (1743-1822)
to the Galician mathematician José Rodríguez González (1770-1824)

http://www.xtal.iqfr.csic.es/Cristalografia/parte_12_1-en.html

Contact goniometer
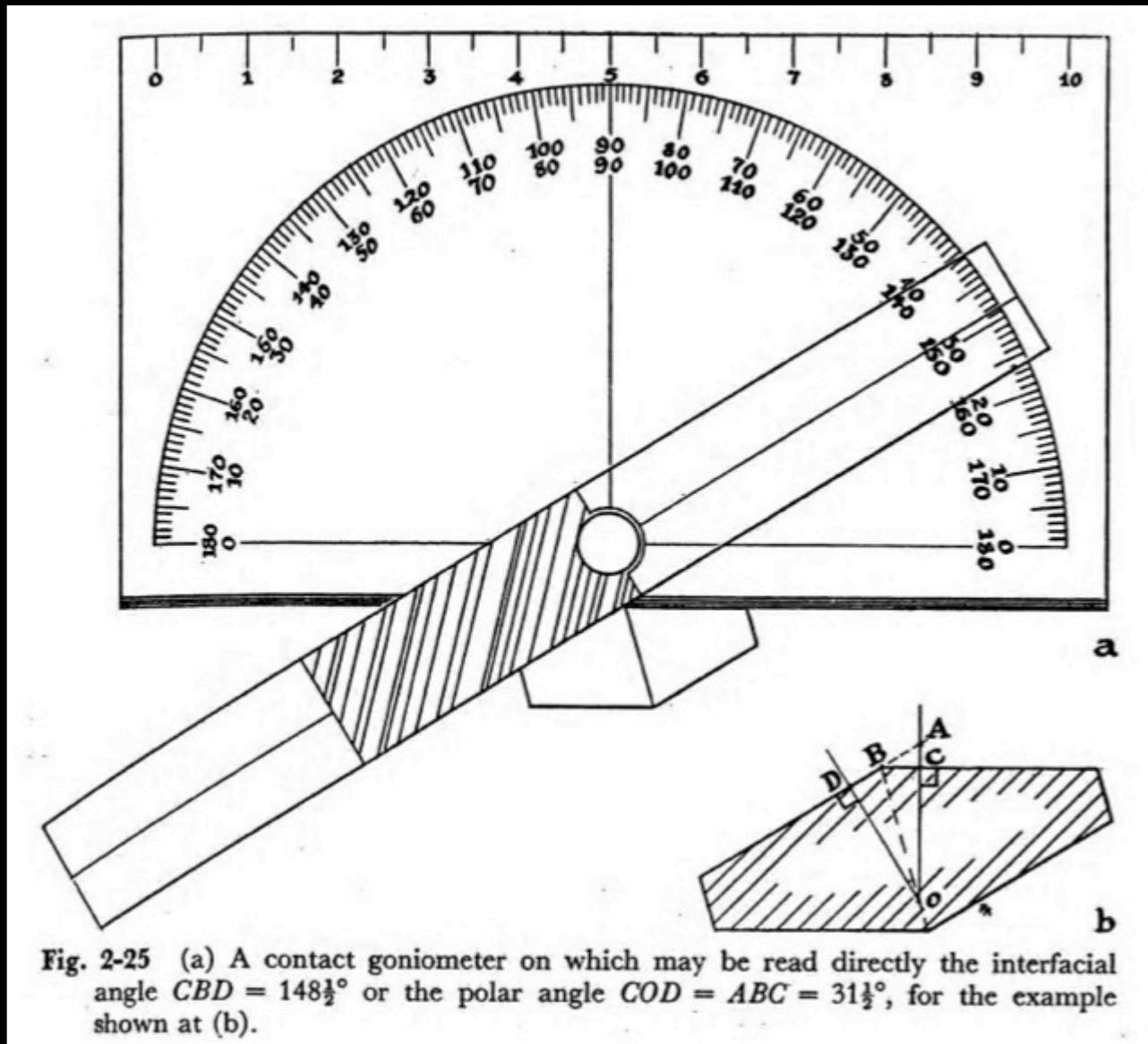
Fig. 2-25 (a) A contact goniometer on which may be read directly the interfacial angle $CBD = 148\frac{1}{2}°$ or the polar angle $COD = ABC = 31\frac{1}{2}°$, for the example shown at (b).

L.G. Berry and Brian Mason (1959). *Mineralogy*. San Francisco: W.H. Freeman & Co.

Haüy (1784)
The law of rational intercepts implies *"molécules intégrantes"* or unit cells.

Abbé René-Just Haüy (1743-1822) making goniometric measurements on a calcite ($CaCO_3$) crystal
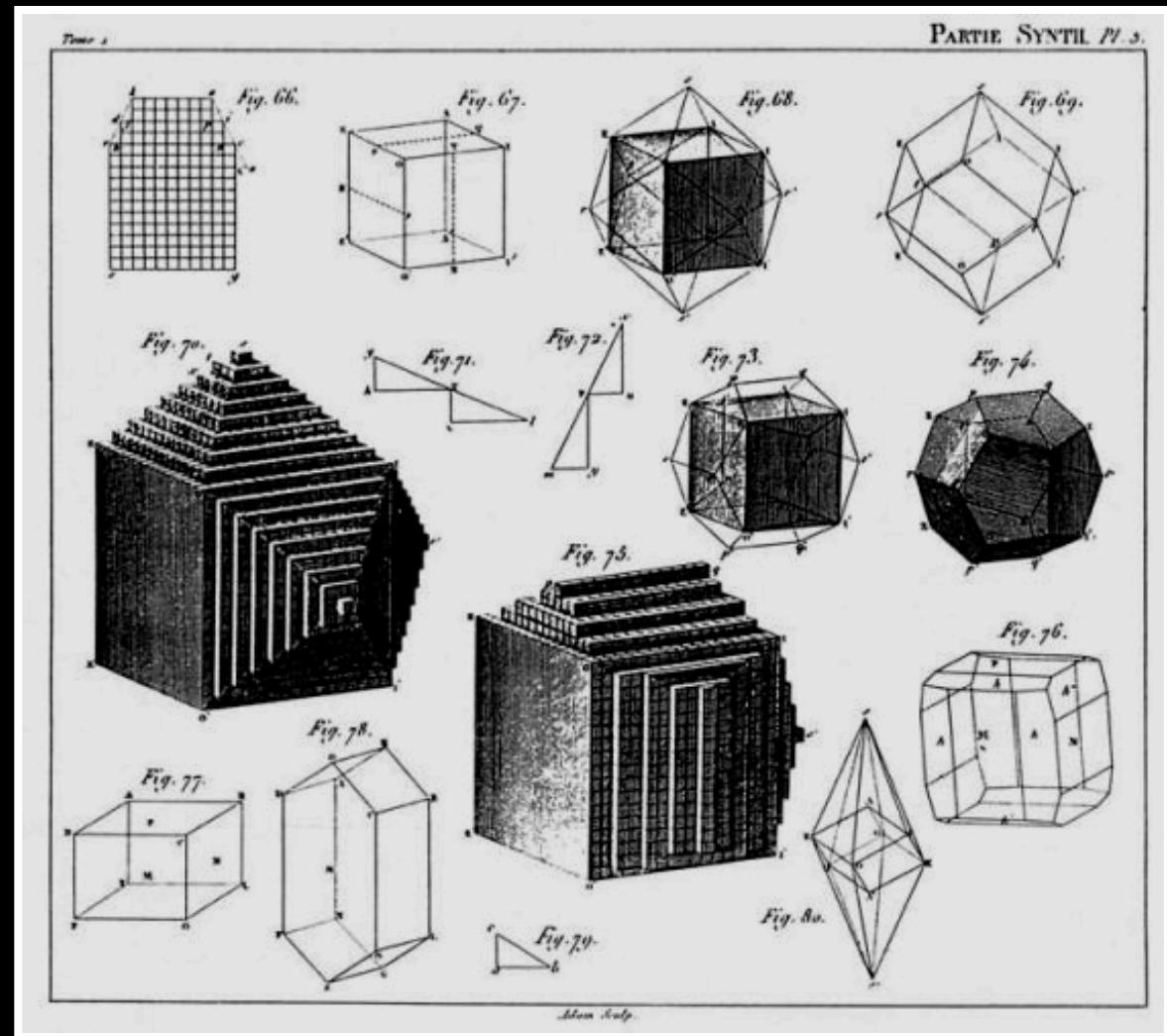
Haüy (1784). *"molécules intégrantes"* or unit cells
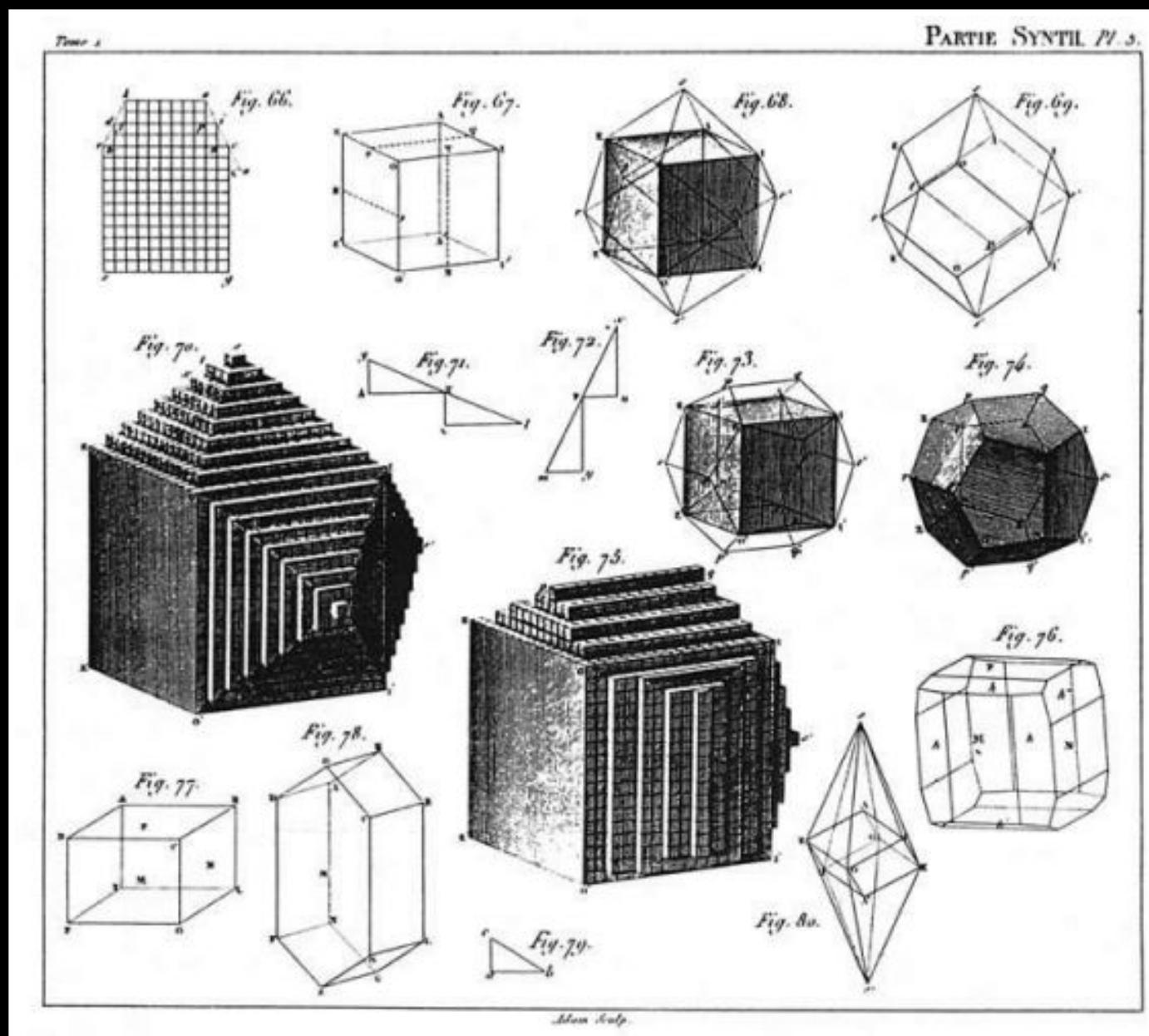
Two of Haüy's 1784 drawings of crystal structure models
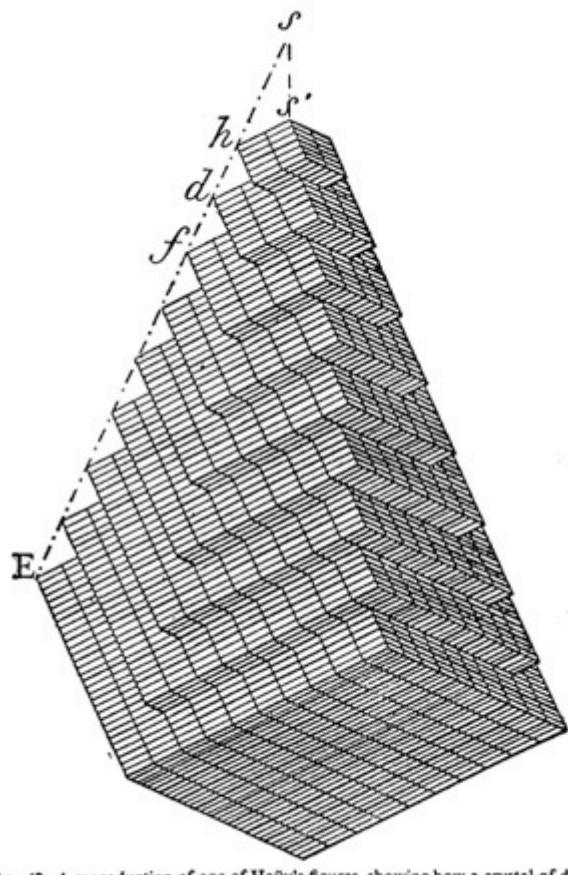
FIG. 49. A reproduction of one of Haüy's figures, showing how a crystal of dog-tooth spar may be considered to be built up from rhombohedral units.
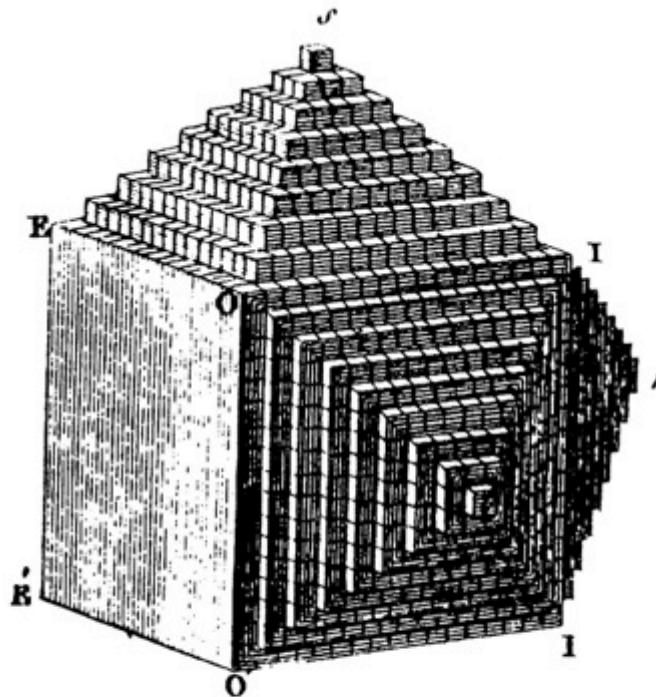
Fig. 17.2.1.1. Model of a crystal structure proposed by René Häuy in *Traite elementaire de Physique*, Vol. 1 [Paris: De L'Imprimerie de Delance et Lesueur, 1803]. This model, proposed in 1784, was the first to connect the external facets of a crystal with an underlying regular arrangement of building blocks.

Development of a trigonal scalenohedron dogtooth spar crystal

Development of a cubic rhombic dodecahedron

Some Haüy constructions of crystal models
(Abbé René-Just Haüy, 1784)
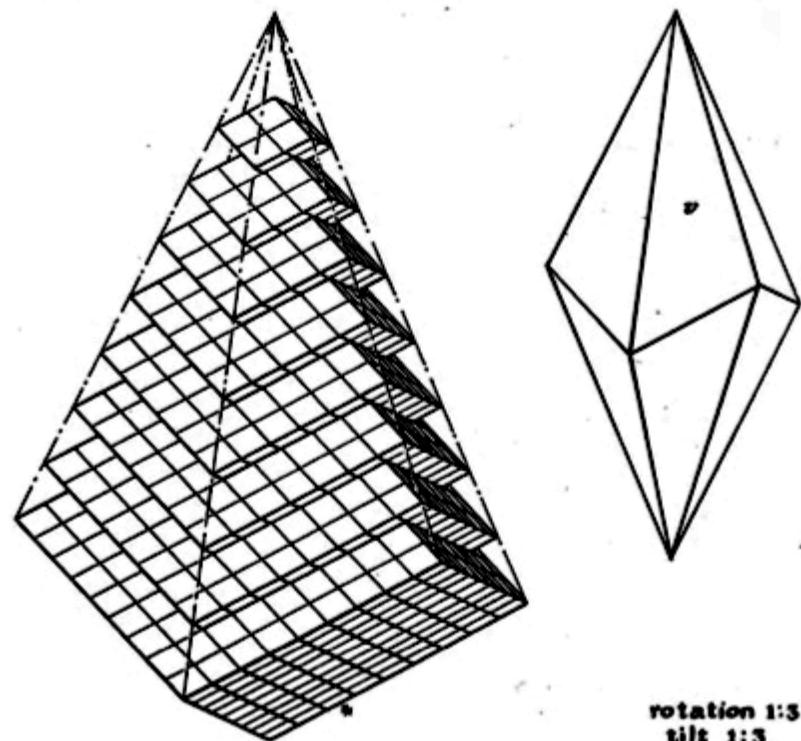
Fig. 2-1 Haüy's conception of structural units, with the shape of the cleavage rhombohedron, building up a crystal of calcite in the form of a scalenohedron v{2131}. [Left-hand drawing after Haüy.]

rotation 1:3
tilt 1:3
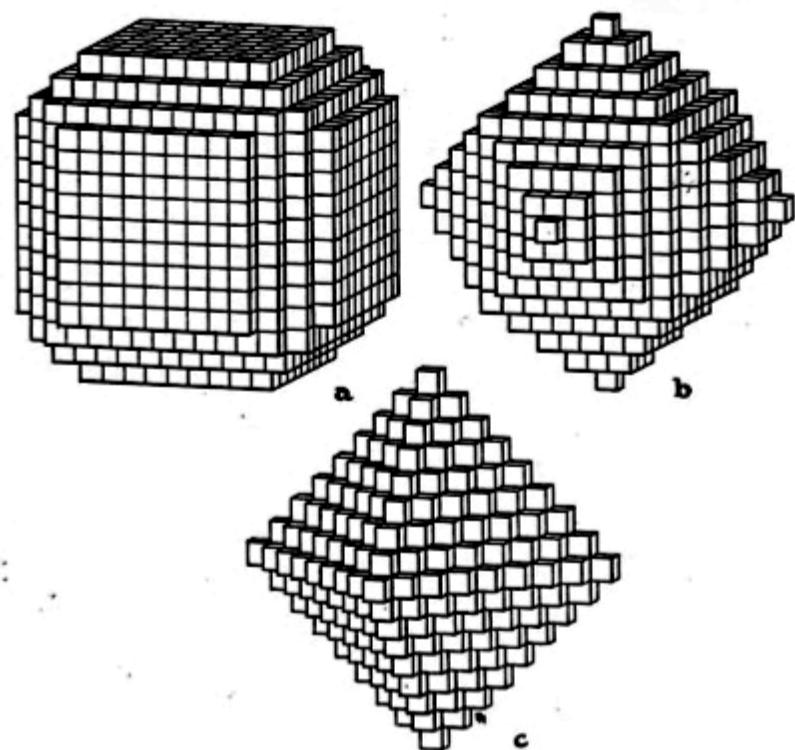
Fig 2-2 Haüy's conception of structural units, with the form of cleavage cubes of galena or halite, building up (a) a cube modified by dodecahedron faces, (b) a dodecahedron, (c) an octahedron.

trigonal calcite
cleavage rhombohedron unit cell

cubic halite
cleavage cube unit cell

L.G. Berry and Brian Mason (1959). *Mineralogy*. San Francisco: W.H. Freeman & Co.

Three of Haüy's 1784 crystal structure models

rhombic dodecahedron
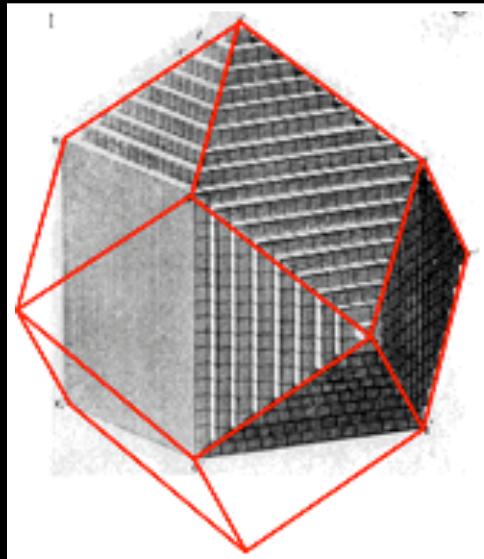
pentagonal dodecahedron
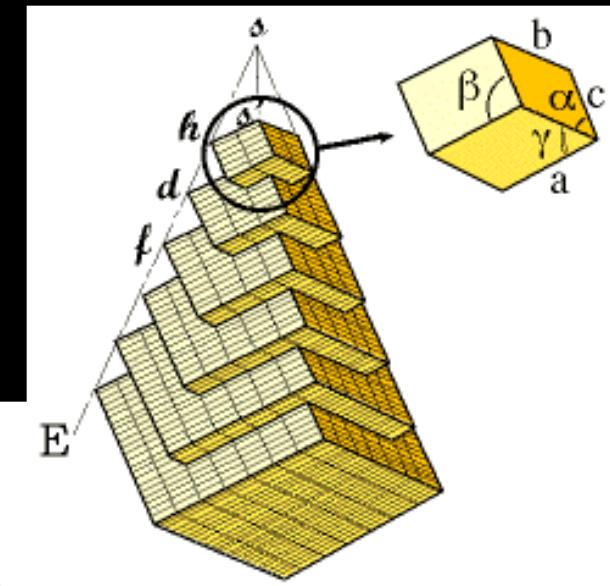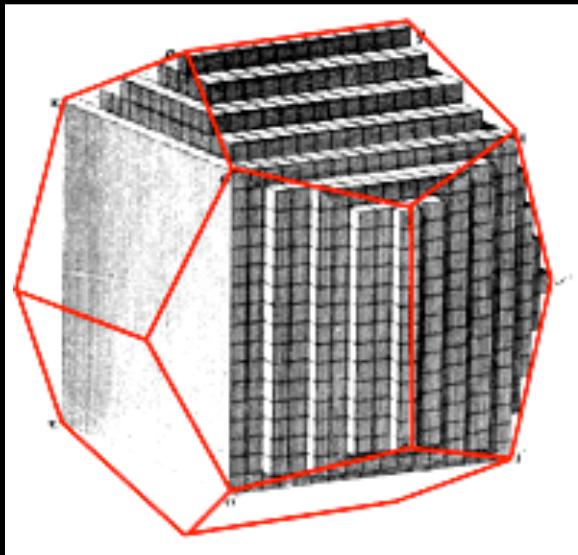
scalenohedron
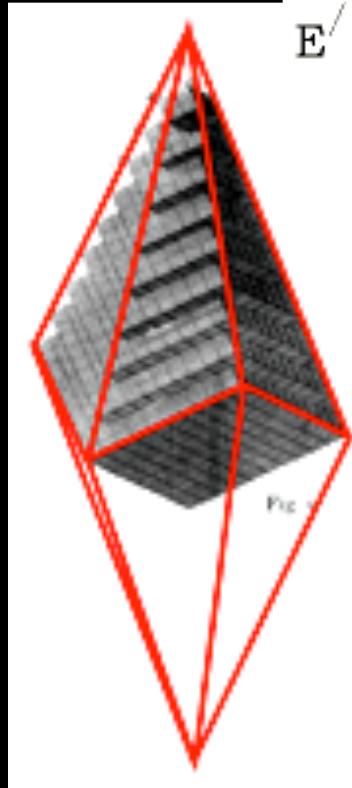
Crystallographic axes and unit cell dimensions
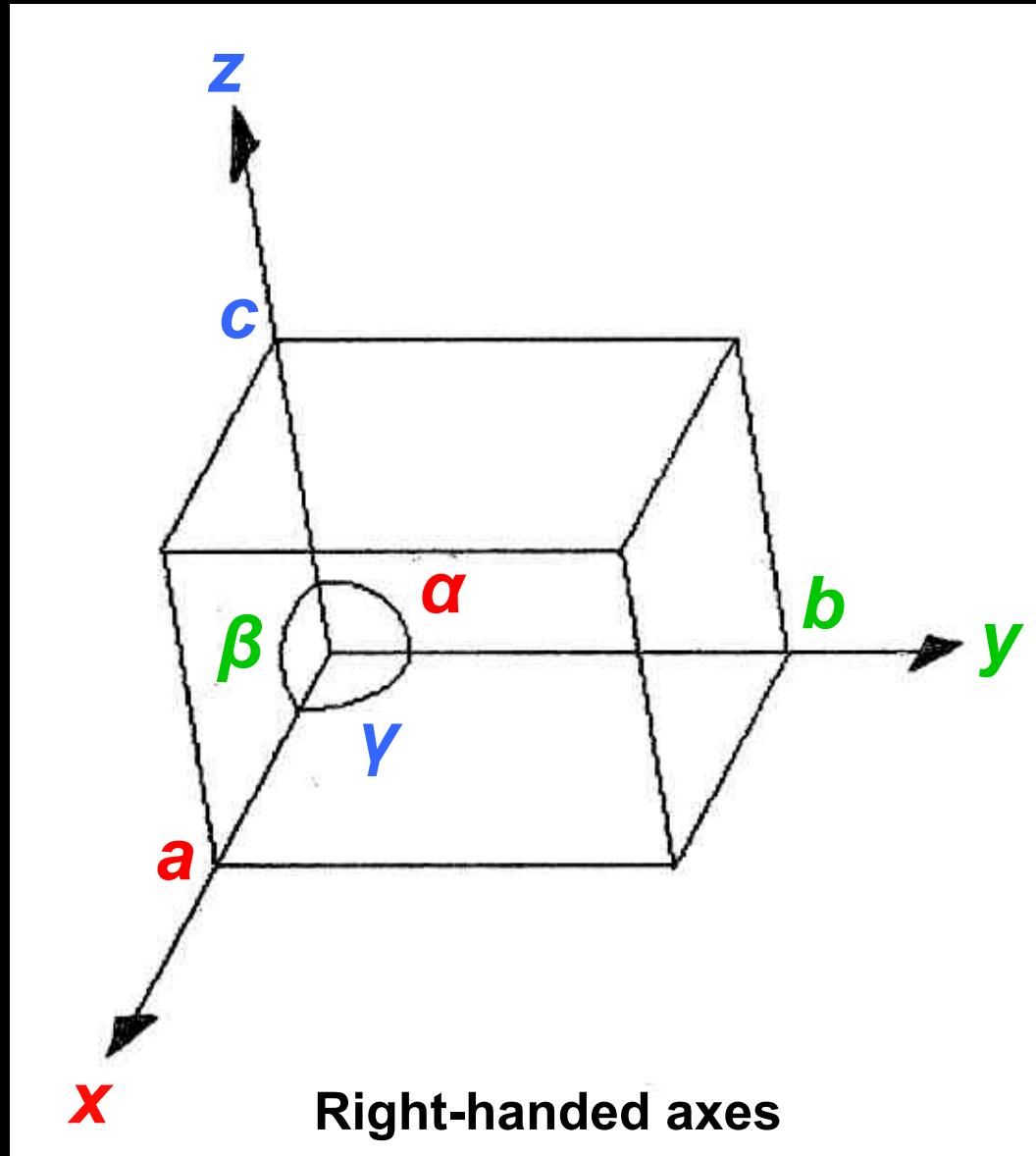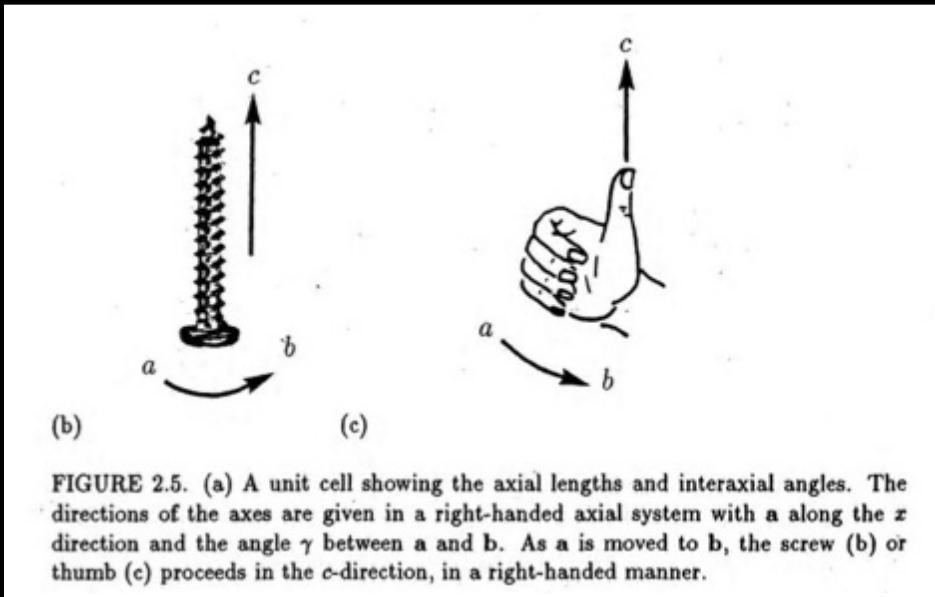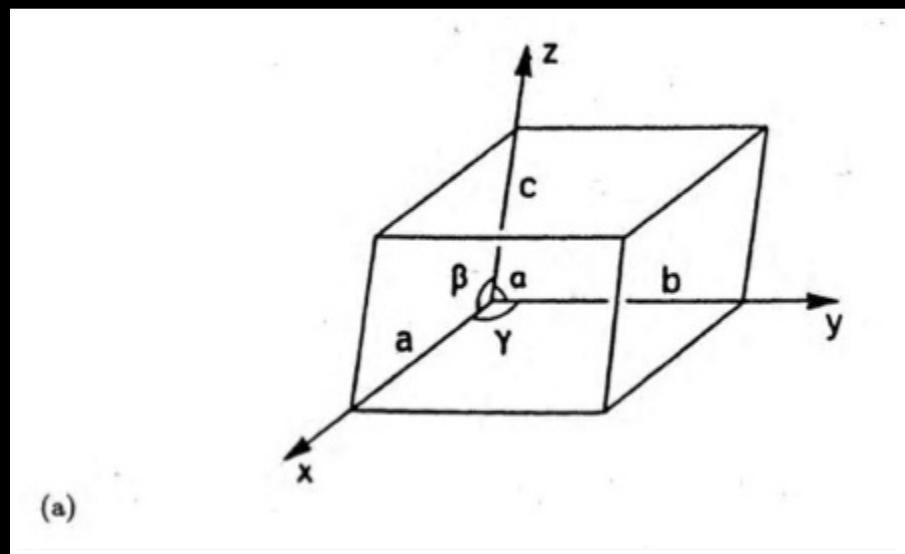
**Right-handed axes**

Crystallographic axes and lattice parameters

FIGURE 2.5. (a) A unit cell showing the axial lengths and interaxial angles. The directions of the axes are given in a right-handed axial system with a along the x direction and the angle γ between a and b. As a is moved to b, the screw (b) or thumb (c) proceeds in the c-direction, in a right-handed manner.

Jenny P. Glusker, with Mitchell Lewis and Miriam Rossi (1994).
Crystal Structure Analysis for Chemists and Biologists. New York: Wiley-VCH, Inc.

The Right-Hand Rule

+Y Axis

+Z Axis

+X Axis

Fingers curl in the direction of a positive, right-handed rotation of the +x axis into the +y axis.

Positive rotation
$\theta > 0$

Thumb points in the direction of the +z axis.
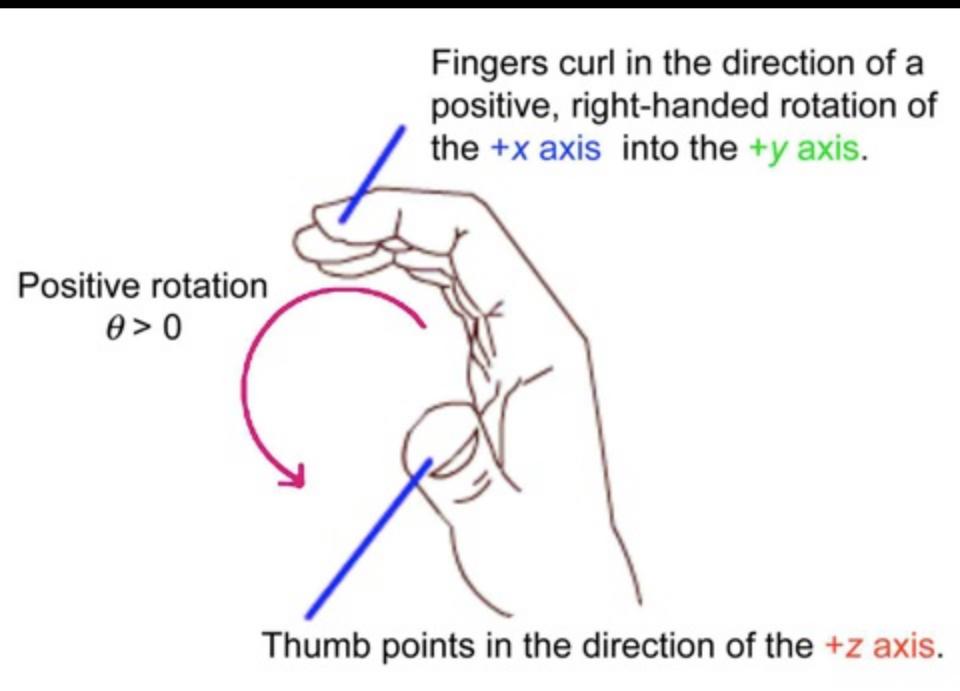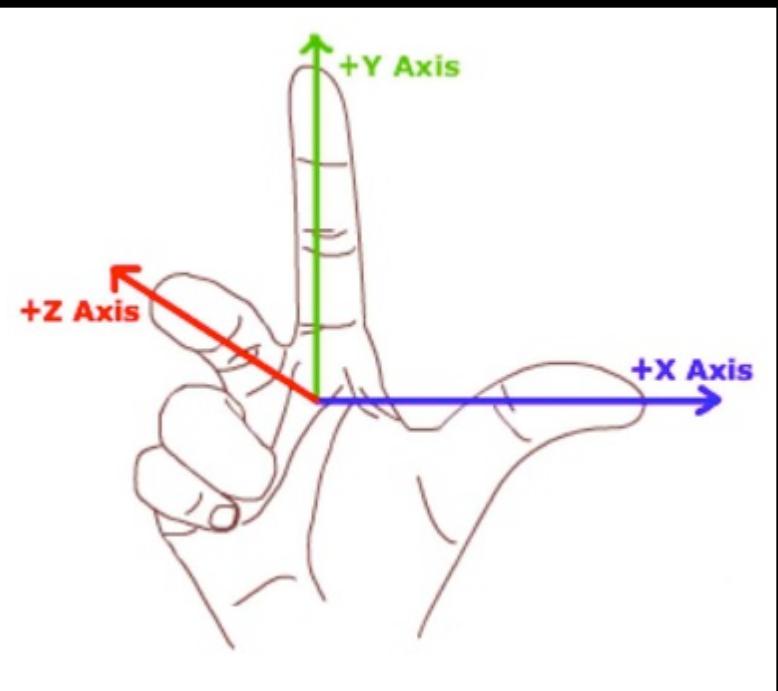
Unit cell and crystal sizes

For a relatively large unit cell with dimensions
$$a \approx b \approx c \approx 100 \text{ Å} = 100 \times 10^{-10} \text{ m},$$
the unit cell volume is
$$V_{\text{cell}} \approx 10^{6} \text{ Å}^{3} = 10^{-24} \text{ m}^{3}.$$

And for a relatively small crystal with dimensions
$$\sim 100 \times 100 \times 100 \text{ μm} = 0.1 \times 0.1 \times 0.1 \text{ mm},$$
the crystal volume is
$$v_{\text{xtal}} \approx 10^{-3} \text{ mm}^{3} = 10^{-12} \text{ m}^{3}.$$

Thus,

$$\frac{v_{\text{xtal}}}{V_{\text{cell}}} \approx 10^{12},$$

so that, even in a small crystal with a large unit cell, there are on the order of a *trillion*, i.e., a *million millions* of unit cells, and some $\left(10^{12}\right)^{1/3} = 10^{4}$ or *ten thousand* unit cells along each crystal edge!

Solvent volume fraction and Matthews coefficient in protein crystals

$$f_{\text{solv}} = \frac{V_{\text{solv}}}{V_{\text{cell}}} = 1 - \frac{V_{\text{prot}}}{V_{\text{cell}}} = 1 - \frac{Z\, M_r\, m_u\, \overline{v}_{\text{prot}}}{10^{-24}\, V_{\text{cell}}} = 1 - 1.23\, \frac{Z\, M_r}{V_{\text{cell}}}$$

V_{cell} unit cell volume (Å^3),

M_r molar mass (Da) of protein in the asymmetric crystal chemical unit,

Z number of asymmetric crystal chemical units per unit cell,

m_u atomic mass constant, $m_u = m\left(^{12}\text{C}\right)/12 = 1.66 \times 10^{-24}\,\text{g Da}^{-1}$, and

$\overline{v}_{\text{prot}}$ partial specific volume of the protein, which is assumed to be the same from one protein to the next, and the same in hydrated crystals as in aqueous solution.

$$\overline{v}_{\text{prot}} = \frac{1}{M_r}\left(\frac{\partial V}{\partial n_{\text{prot}}}\right)_{P,T,n_{\text{solv}}} \approx 0.74 \text{ mm}^3\,\text{mg}^{-1}\,, \qquad \frac{1}{\overline{v}_{\text{prot}}} \approx 1.35 \text{ mg mm}^{-3}$$

The quantity $V_M = V_{\text{cell}}/\left(Z M_r\right)$ is called the Matthews coefficient.

$$1.6 \text{ Å}^3\,\text{Da}^{-1} < V_M < 4.9 \text{ Å}^3\,\text{Da}^{-1}\,, \qquad \langle V_M \rangle \approx 2.2 \text{ Å}^3\,\text{Da}^{-1}$$

$$25\% < f_{\text{solv}} < 75\%\,, \qquad \langle f_{\text{solv}} \rangle \approx 45\%$$

Matthews, B.W. (1968). Solvent Content of Protein Crystals. *J. Mol. Biol.* **33**, 491-497.

Kantardjeff, K., & Rupp, B. (2003). Matthews coefficient probabilities: Improved estimates for unit cell contents of protein, DNA, and protein-nucleic acid crystals. *Protein Science*, **12**, 1865-1871.

http://ruppweb.dyndns.org/mattprob/

Bulk Solvent Correction

Protein crystals average ~50% by volume bulk solvent, much of it liquid-like water.

The protein and bulk solvent regions have

$$\langle \rho_{\text{prot}} \rangle \approx 0.43 \, \text{e} \, \text{Å}^{-3} \qquad \text{and} \qquad 0.33 \, \text{e} \, \text{Å}^{-3} \, < \, \langle \rho_{\text{solv}} \rangle \, < \, 0.41 \, \text{e} \, \text{Å}^{-3}$$

$$\text{pure } H_2O \qquad\qquad 4\text{-M} \left(NH_4 \right)_2 SO_4$$

$$\sim \text{half sat'd}$$

The protein and solvent regions are Babinet-complimentary, opposite-phase scattering masks. Thus,

$$F_{\text{total}} = F_{\text{prot}} + F_{\text{solv}} \ ,$$

$$F_{\text{solv}} \approx -F_{\text{prot}} \, k_{\text{solv}} \exp\left(-2\pi^2 \, \frac{\langle u_{\text{solv}}^2 \rangle}{d_{hkl}^2} \right) ,$$

$$F_{\text{total}} \approx F_{\text{prot}} \left[1 - k_{\text{solv}} \exp\left(-2\pi^2 \frac{\langle u_{\text{solv}}^2 \rangle}{d_{hkl}^2} \right) \right] = F_{\text{prot}} \left\{ 1 - k_{\text{solv}} \exp\left[-B_{\text{solv}} \left(\frac{\sin\theta_{hkl}}{\lambda} \right)^2 \right] \right\} ,$$

where

$$B = 8\pi^2 \langle u^2 \rangle \ .$$

Typical values for the bulk solvent parameters are

$$k_{\text{solv}} \approx \frac{\langle \rho_{\text{solv}} \rangle}{\langle \rho_{\text{prot}} \rangle} \qquad\qquad 2.5 < \langle u_{\text{solv}}^2 \rangle < 5 \, \text{Å}^2$$

$$0.75 < k_{\text{solv}} < 0.95 \qquad\qquad 200 < B_{\text{solv}} < 400 \ \text{Å}^2$$

The seven crystal systems and fourteen Bravais lattices

Auguste Bravais
1811-1863

The Seven Crystal Systems

System	Defining Symmetry	Unit Cell Conditions
Triclinic	1-fold identity or inversion symmetry	none
Monoclinic	one 2-fold rotation or roto-inversion axis	$\alpha = \gamma = 90°$
Orthorhombic	three perpendicular 2-fold rotation or roto-inversion axes	$\alpha = \beta = \gamma = 90°$
Tetragonal	one 4-fold rotation or roto-inversion axis	$a = b$ $\alpha = \beta = \gamma = 90°$
Trigonal	one 3-fold rotation or roto-inversion axis	H: $a = b$ $\alpha = \beta = 90°, \gamma = 120°$ R: $a = b = c$ $\alpha = \beta = \gamma < 90°$
Hexagonal	one 6-fold rotation or roto-inversion axis	$a = b$ $\alpha = \beta = 90°, \gamma = 120°$
Cubic	four intersecting 3-fold axes	$a = b = c$ $\alpha = \beta = \gamma = 90°$

Roto - inversion axes

$$\bar{1} \equiv i$$
$$\bar{2} \equiv m$$
$$\bar{3} \equiv 3 + i$$
$$\bar{4}$$
$$\bar{6} \equiv 3\,/\,m$$

The 14 Bravais lattices
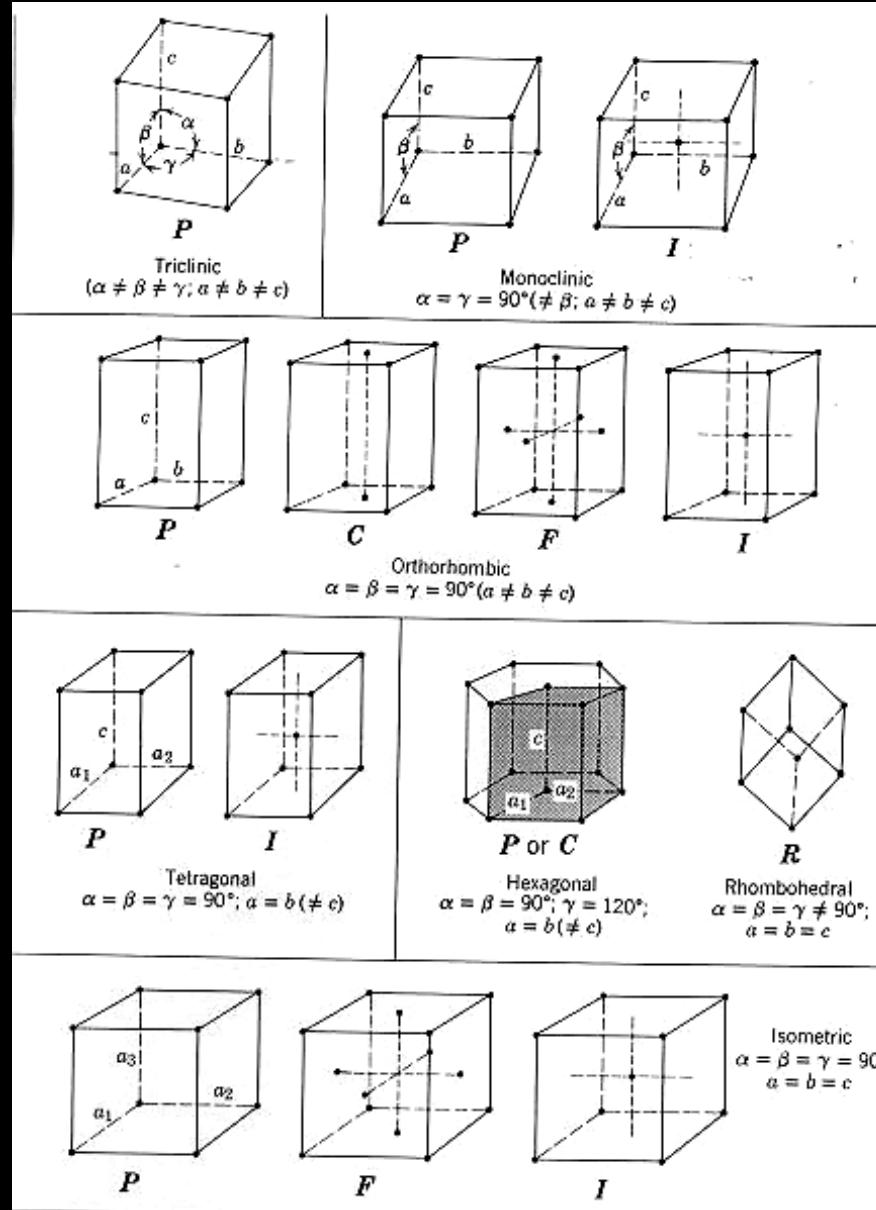
The 14 Bravais lattices

cubic
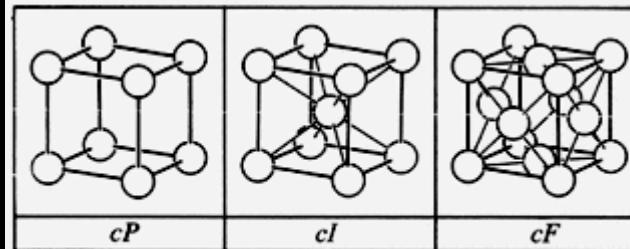
trigonal
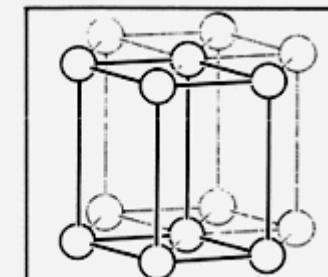
tetragonal
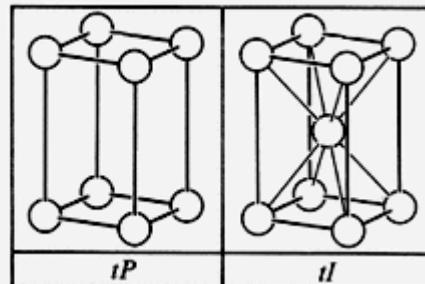
rhombohedral
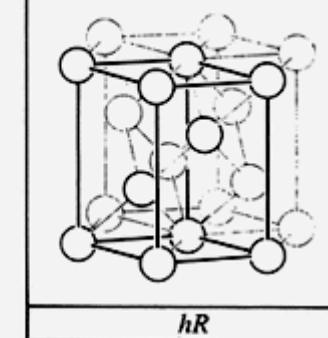
orthorhombic
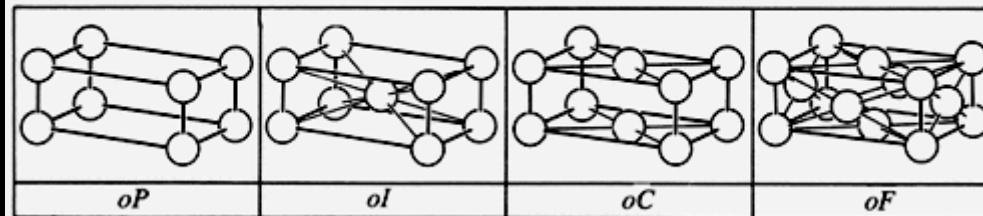
monoclinic

(anorthic) triclinic

International Tables for Crystallography, Vol A.
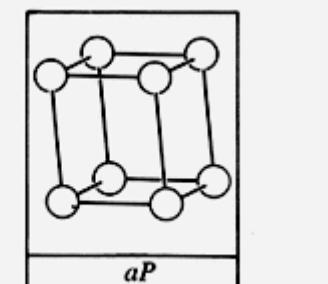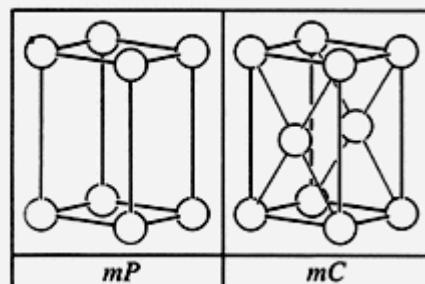
Models of the 14 Bravais lattices
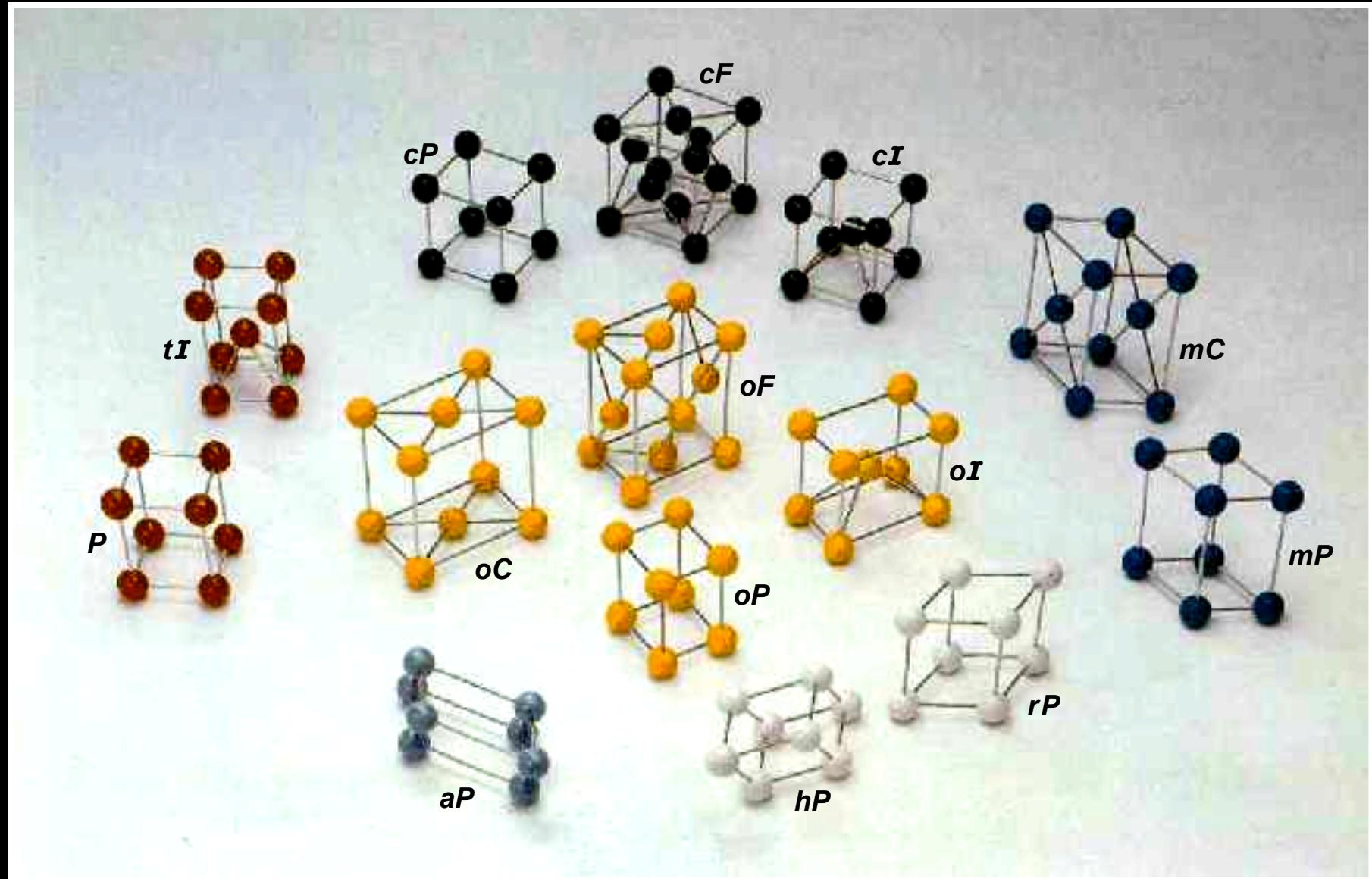
Crystallographic Symmetries Hierarchy

7 crystal systems

14 Bravais lattices

    6 primitive

    8 centered

32 crystallographic point groups

    11 centrosymmetric - Laue groups

    11 noncentrosymmetric, chiral

    10 noncentrosymmetric, polar

230 space groups

    93 centrosymmetric

       24 Patterson space groups

    137 noncentrosymmetric

       65 chiral (enantiomorphic) space groups

       72 polar space groups
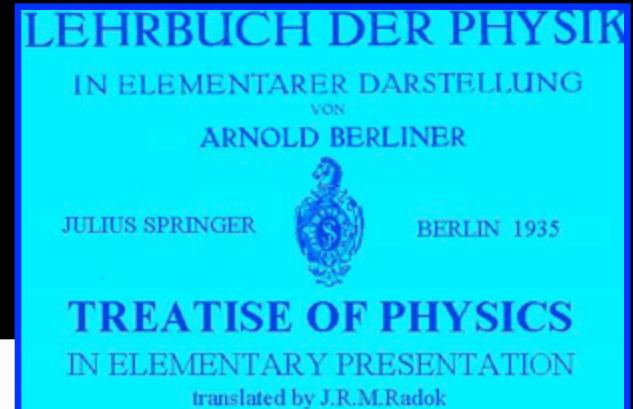
1-, 2-, and 3-D lattices
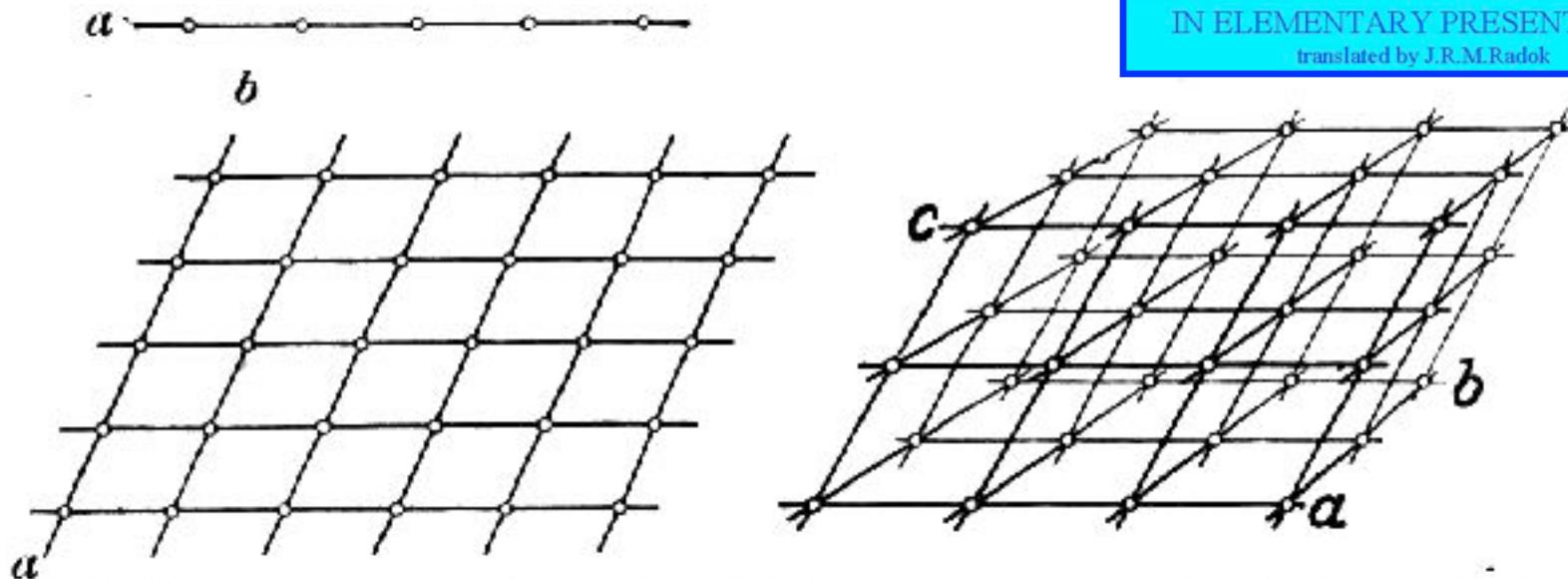
Fig. 154 Arrangement of points and translations a b c in a crystal; In a b the net-, in abc the lattice-arrangement. Points are indicated by circles, translations by lines.

Rainer Radok, 1.10.2001, radok81@bkk2.loxinfo.co.th
28/2 Mu 13 Nongnae 24120, Thailand
038-523492
http://en.wikipedia.org/wiki/Arnold_Berliner
www.austms.org.au/Gazette/2005/Mar05/radok.pdf

http://kr.cs.ait.ac.th/~radok/physics/
http://kr.cs.ait.ac.th/~radok/physics/d2.htm#definite%20direction
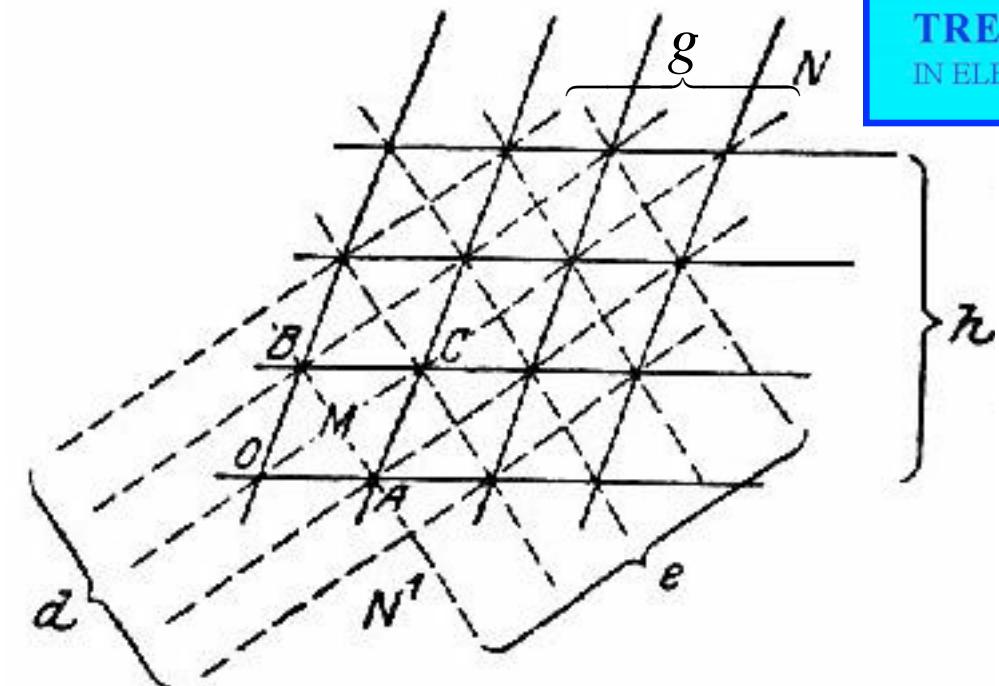
Fig. 155 Positions of the translation nets *N* and *N'* in the point net of a crystal

Fig. 156 Seven crystal systems and the elementary bodies of their translation lattices

Triclinic **Monoclinic** **Rhombic** **Trigonal** **Tetragonal** **Hexagonal** **Cubic**
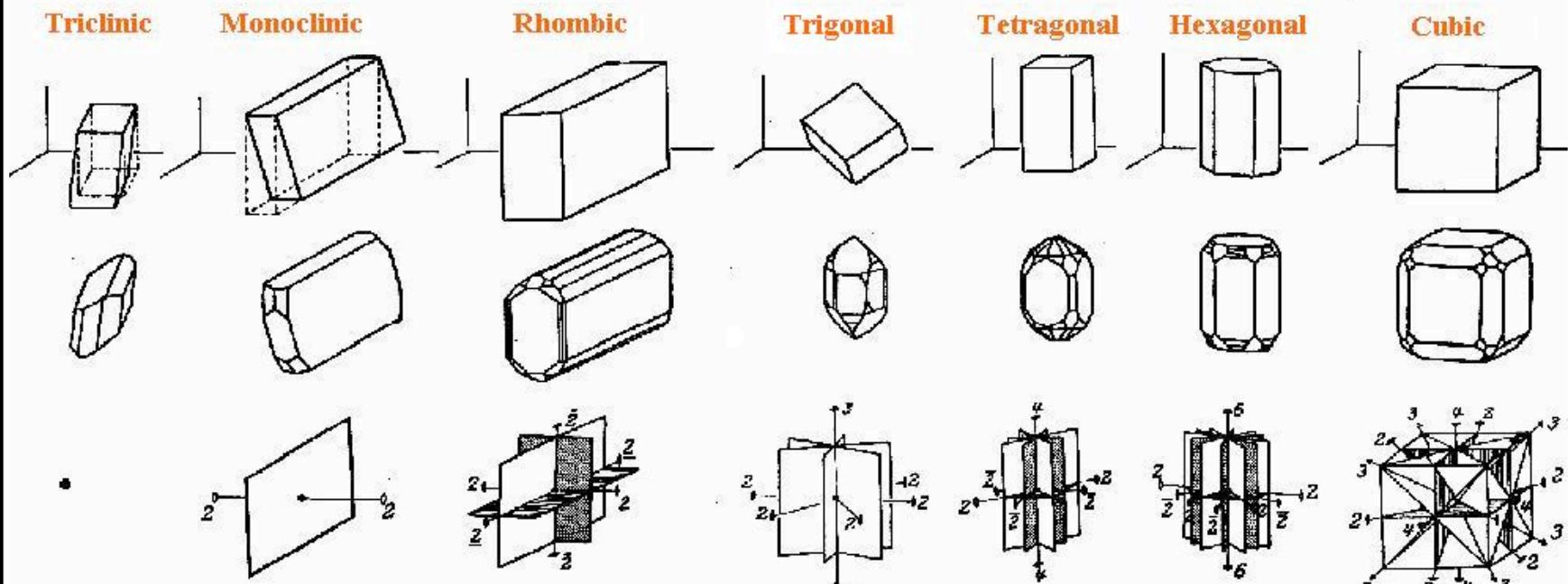
The top row shows the simplest, crystal forms with the least faces which have the full symmetry of the respective crystal systems. The natural forms of the cristals derive from them by addition of other planes the positions of which arise in the simplest manner, for example, diagonal planes.

The second row shows corresponding forms of boundaries of natural crystals.

The third row shows the characteristic symmetry groups in symbolic representation:
the axes of rotation with the numbers 2, 3, 4 and 6 - those which are not equivalent and in pairs are distinguished by 2, 2 and 2;
the planes of reflection in the geometrically standard of a plane - different reflection planes are shaded for the sake of clearness;
the symmetry centre is indicated by a point · .

http://kr.cs.ait.ac.th/~radok/physics/
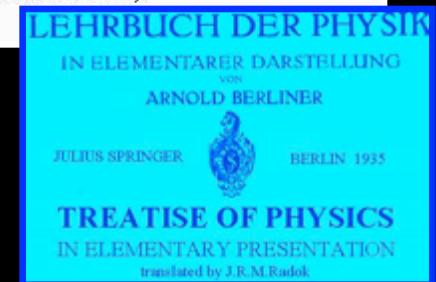
Fig. 156 continued: The elementary bodies of the point- and translation- lattice.

| Triklin	Monoklin	Rhombisch	Trigonal	Tetragonal	Hexagonal	Cubic

Three obliquely angled axes, One translation lattice, (Boric acid, copper sulfate)

Two obliquely angled axes and one on the plane of which perpendicular all unequal, two translation lattices. (Iron sulfate, gypsum, mica, sugar of milk, sugar cane, sulphur, soda, acidity of wine.)

Three unequal, mutually perpendicular axes, 4 translation lattices. (Epsom salt, topaz, sulphur, iodine)

Three equal axes at equal angles, two translation lattices. The lattice derived from the second elementary body is identical to that derived from the hexagonal one. (Antimony, arsenic, ice, graphite, graphite, natron-salpter, quartz, bismuth, cinnabar)

One principal axis and two secondary axes, perpendicular to it and to one another, two (Tin, zircon)

One principal axis and three equal secondary axes, perpendicular to it at angles of 60 degree to each other , one translation lattice (Beryl, zinc)

Three mutually perpendicular equal axes, three translation lattices. (Alum, lead, diamond, iron, gold, copper, platinum, mercury, ammoniac, silver, rock-salt.)

The elementary bodies are the smallest and at the same time simplest (that is, have fewest faces) parallelepipeds of the point lattice, which have still the full symmetry of the crystal systems above. The directions of their edges are chosen as crystallographic axes. If repeated parallel in the three dimensions as in Fig. 154, every elementary body yields the corresponding translation lattice.

http://kr.cs.ait.ac.th/~radok/physics/

LEHRBUCH DER PHYSIK
IN ELEMENTARER DARSTELLUNG
VON
ARNOLD BERLINER

JULIUS SPRINGER   BERLIN 1935

TREATISE OF PHYSICS
IN ELEMENTARY PRESENTATION
translated by J.R.M.Radok
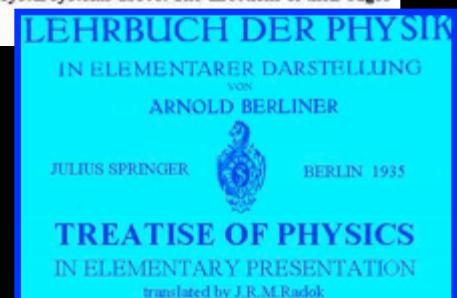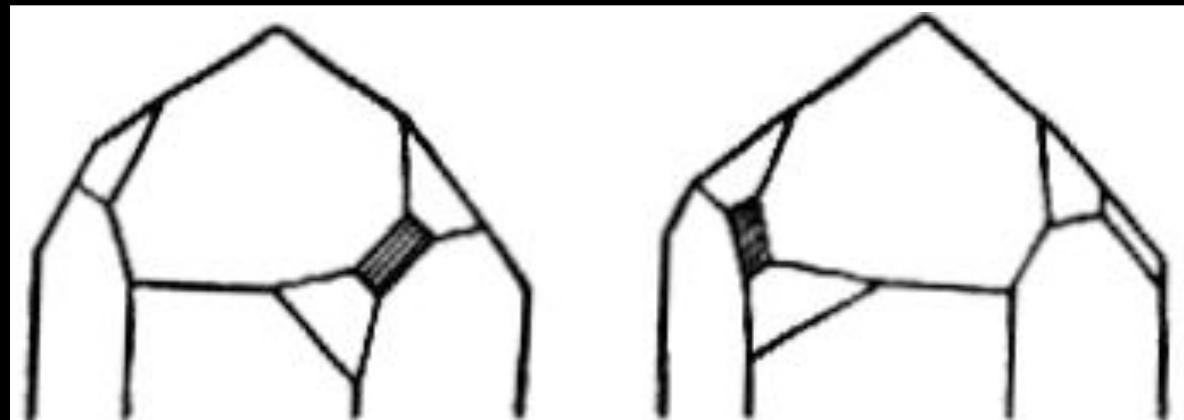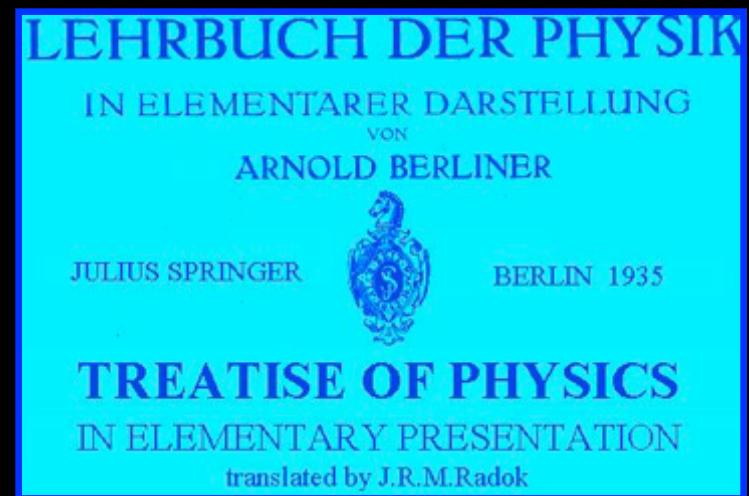
Fig. 152 Enantiomorphous crystals
(ἐν-αντίος = opposite)

http://kr.cs.ait.ac.th/~radok/physics/

Crystallographic point groups of protein homooligomers
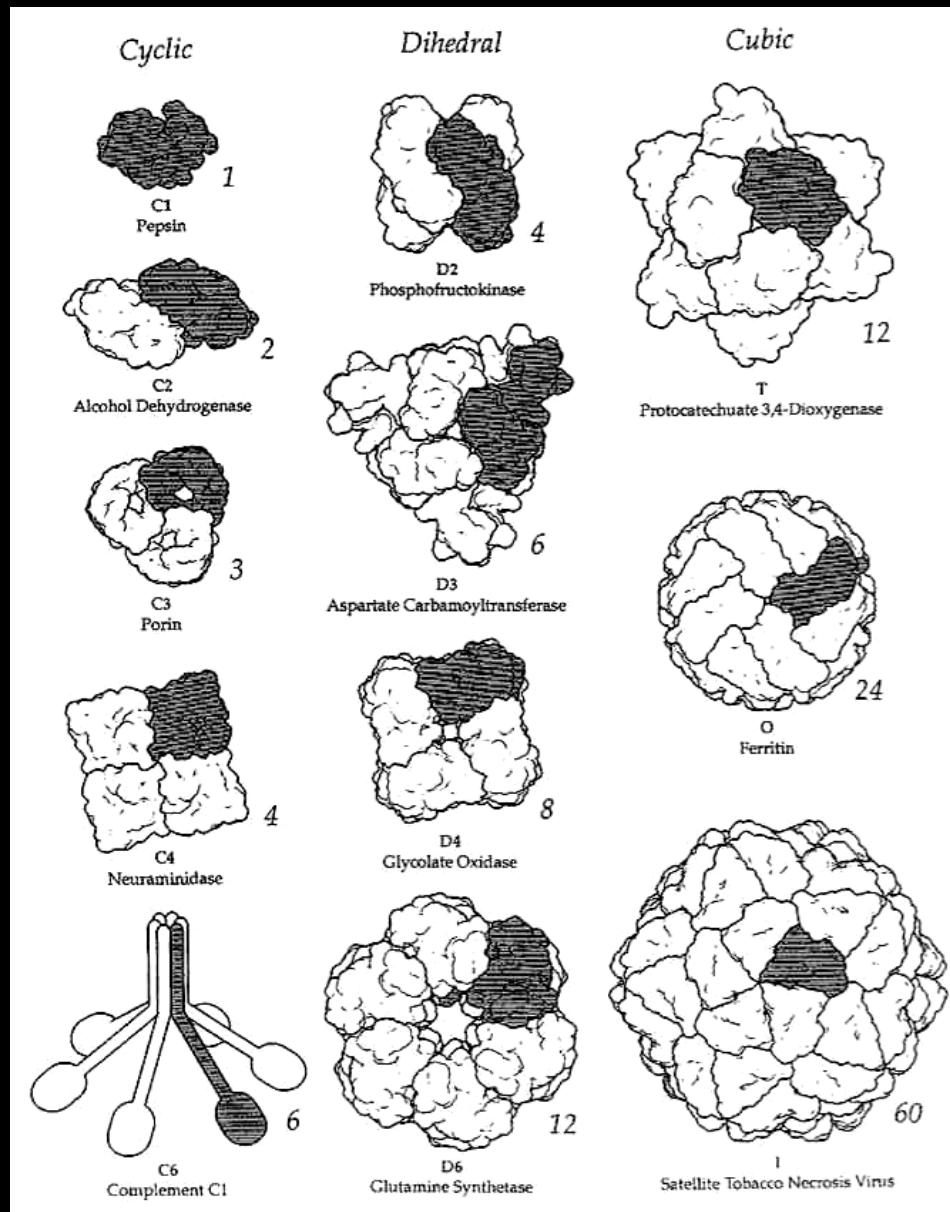
Goodsell & Olsen (2000). *Ann. Rev. Biophys. Biomol. Struct.* **29**, 105.

# Crystal habit is variable, depending on crystal growth conditions, but interfacial angles are constant.

FIG. 8. A rounded crystal of sodium chlorate, on being put into supersaturated solution, develops 110 and 100 faces. The more rapidly growing 110 faces are subsequently eliminated.

FIG. 3. Variation of crystal shape with conditions of growth. Sodium chlorate, $NaClO_3$, grown (a) rapidly and (b) slowly; gypsum, $CaSO_4 . 2H_2O$, grown (c) slowly and (d) rapidly; sodium chloride, NaCl, grown (e) from pure solution and (f) from solution containing 10 per cent. of urea.

Fast growing faces "grow out of the crystal."

C.W. Bunn (1961). *Chemical Crystallography*, **2nd ed. Oxford University Press.**

Some symmetric cubic crystal habits
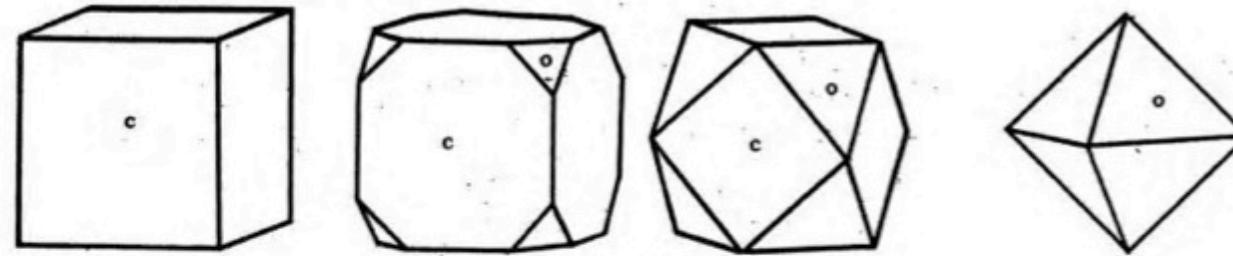
Figure 17: from cube to octahedron (cube face *c*, octahedron face *o*)
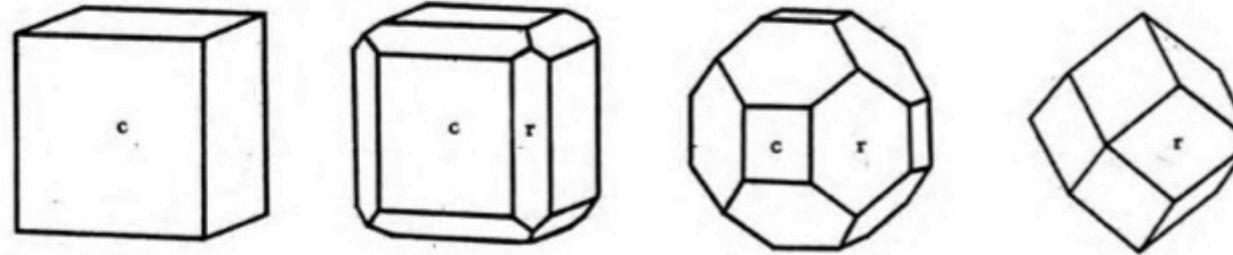
Figure 18: from cube to rhombic dodecahedron (faces *c* and *r* respectively)
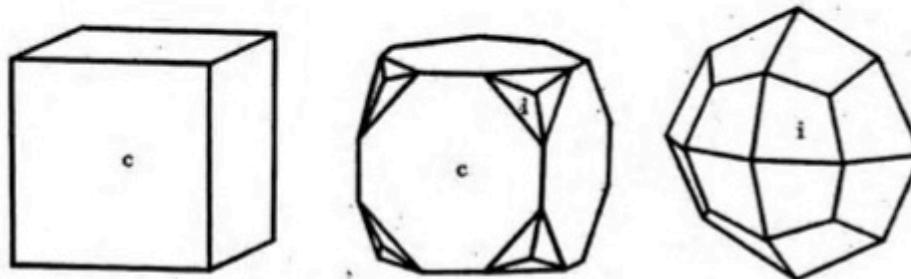
Figure 19: from cube to icositetrahedron (faces *c* and *i* respectively)

# Some additional symmetric cubic crystal habits
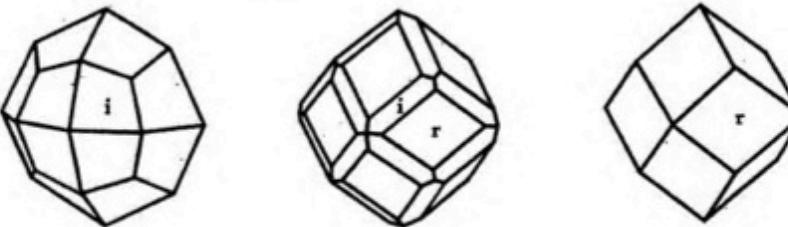
Figure 20: from icositetrahedron to rhombic dodecahedron (faces *i* and *r* respectively)
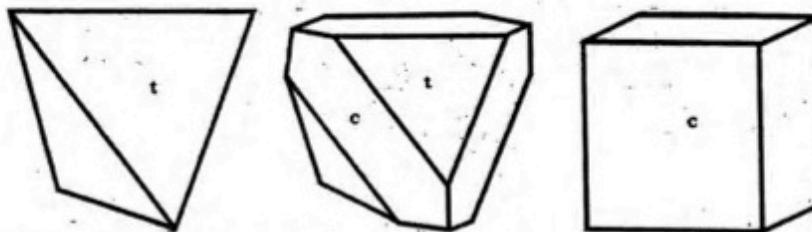
Figure 22: from tetrahedron to cube (faces *t* and *c* respectively)
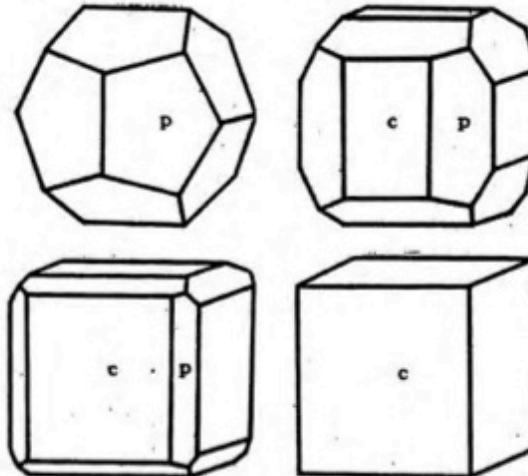
Figure 23: from pentagonal dodecahedron to cube (faces *p* and *c*)

Protein crystals are not perfect inside

Figure 3-11 Atomic force microscope images of crystal growth. (Panel A) The atomic force microscope images of the 001 surface of glucose isomerase show the two most common growth patterns observed in crystal growth: step growth starting from 2-dimensional nucleation islands (A, left image) and a double-spiral growth pattern (A, right image). Panel B shows formation of supercritical 2-dimensional nuclei on the 001 surface of cytomegalovirus (CMV), a member of the herpes virus family. As indicated by the arrows, in this case only two virions (B, left image) suffice to generate a critical nucleus from which new step growth commences (B, right image). Images courtesy of Alexander McPherson and Aaron Greenwood, University of California, Irvine.

Figure 3-12 Growth of a real mosaic crystal. The schematic drawing shows a crystal growing in a solution of protein molecules (blue spheres). Small impurities (red) and some larger detritus (green squares) are also present in the solution. New molecules attach preferentially to steps and edges (red arrows) and we can recognize a growth defect in the form of a hole; impurities are enclosed at the domain boundaries; and a larger piece of detritus is incorporated at a domain boundary. Individual domains can be substantially misaligned, in this case about 6°; such a highly mosaic crystal would not be useful for diffraction experiments.

Phenomena of mosaicity and twinning complicate data collection

http://escher.epfl.ch/eCrystallography/

# Alternative *primitive* unit cells for a given point lattice
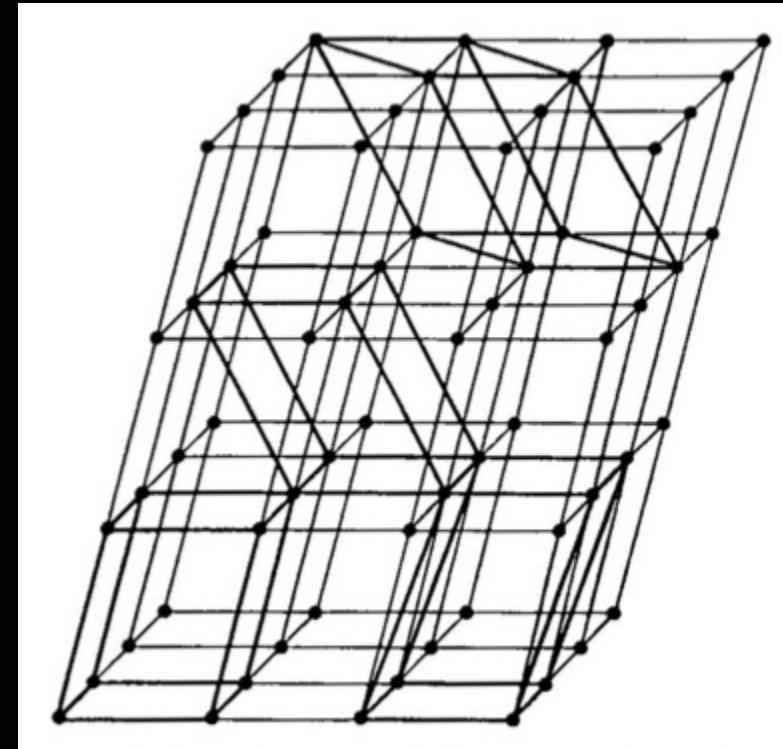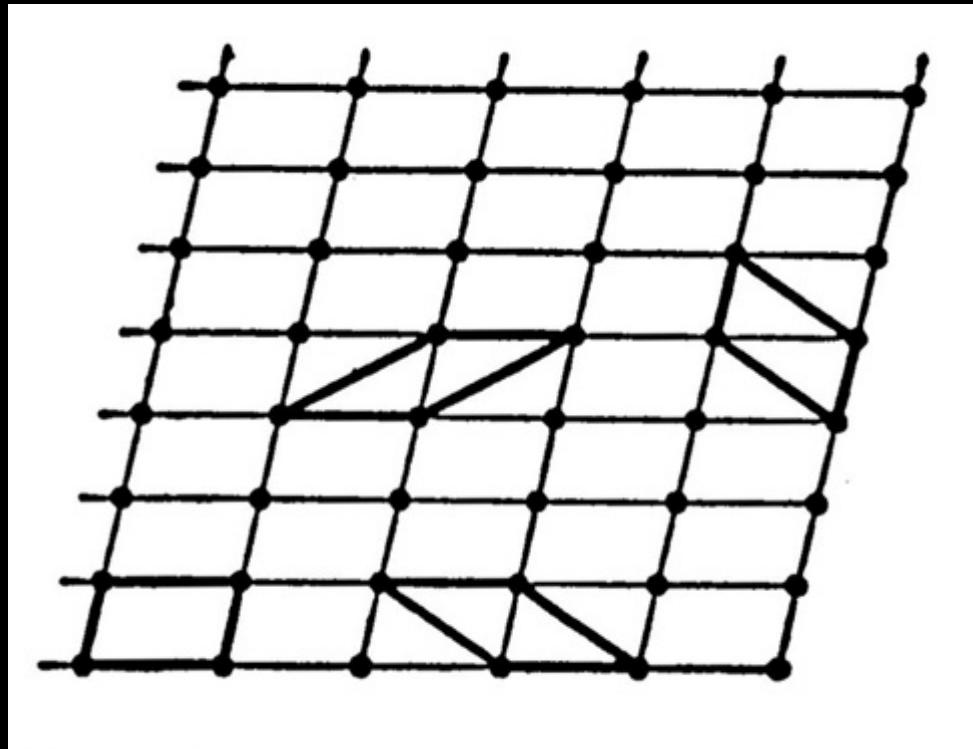
# Alternative primitive unit cells in the same space lattice
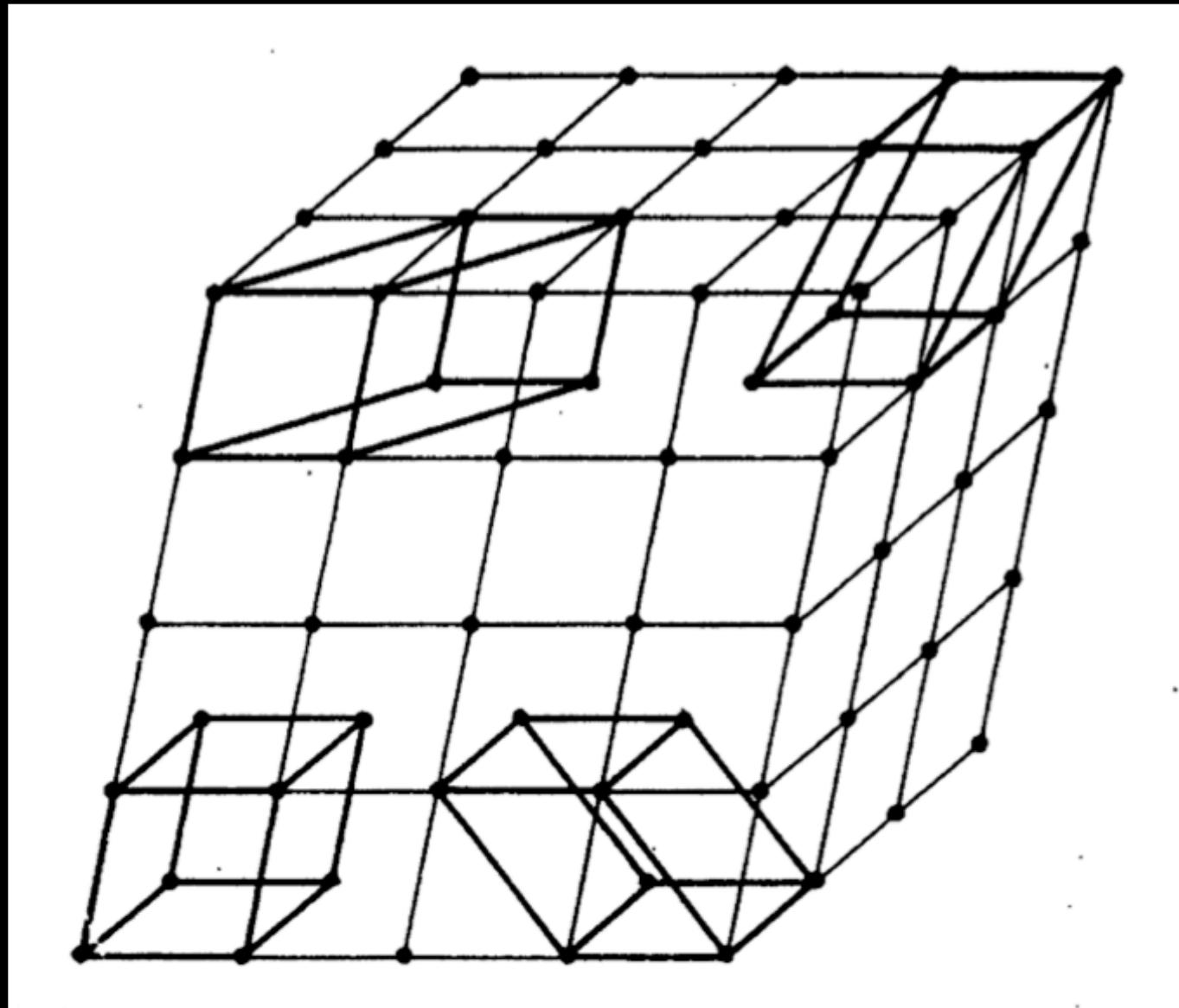
Henry S. Lipson (1970). *Crystals and X-Rays*. London: Wykeham Publications.

Alternative unit cells on a given plain lattice:

one face-centered (D), two side-centered (E,F), and three primitive cells (A,B,C)

http://www.meta-library.net/cqmedia/esch-body.html
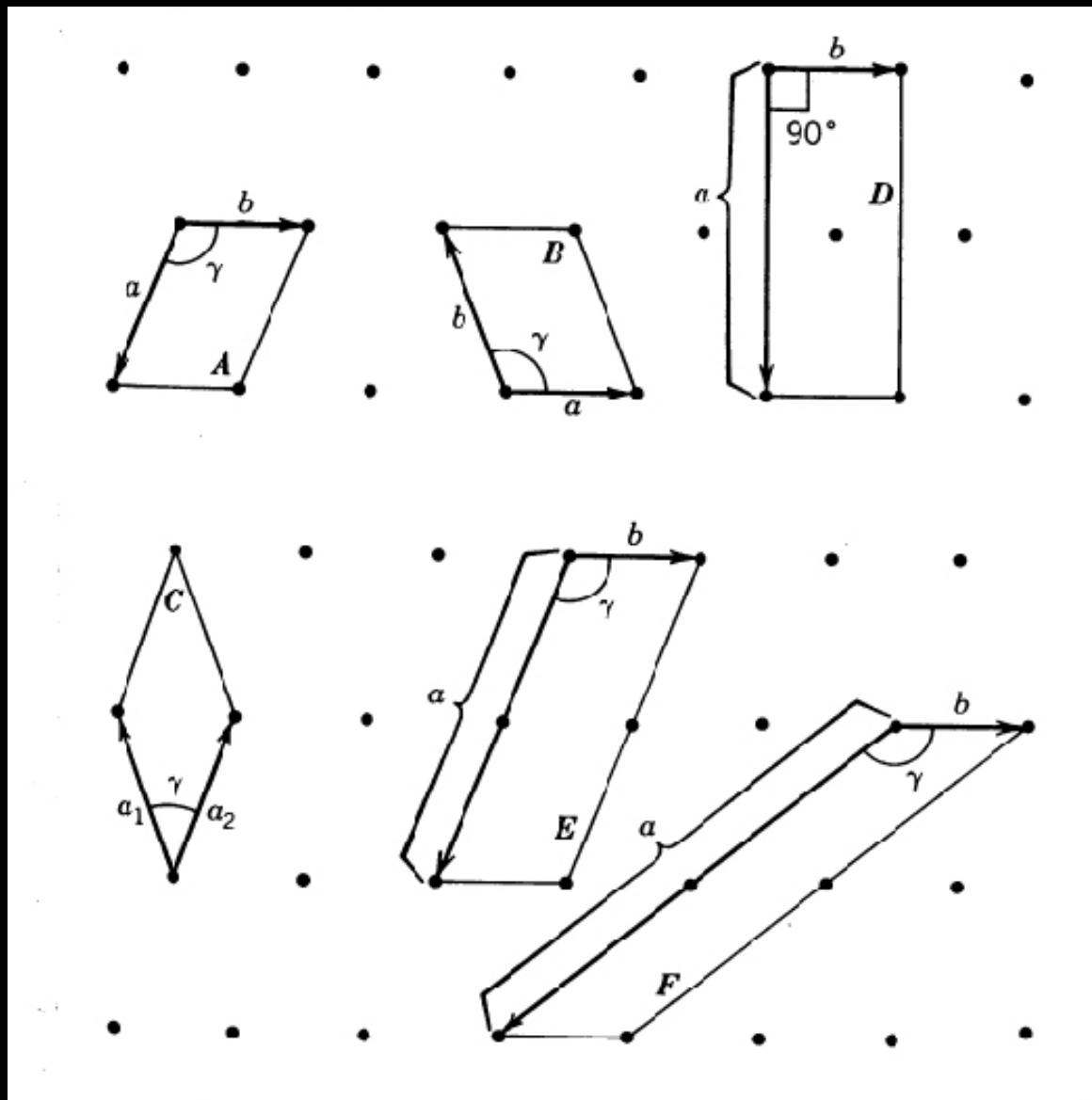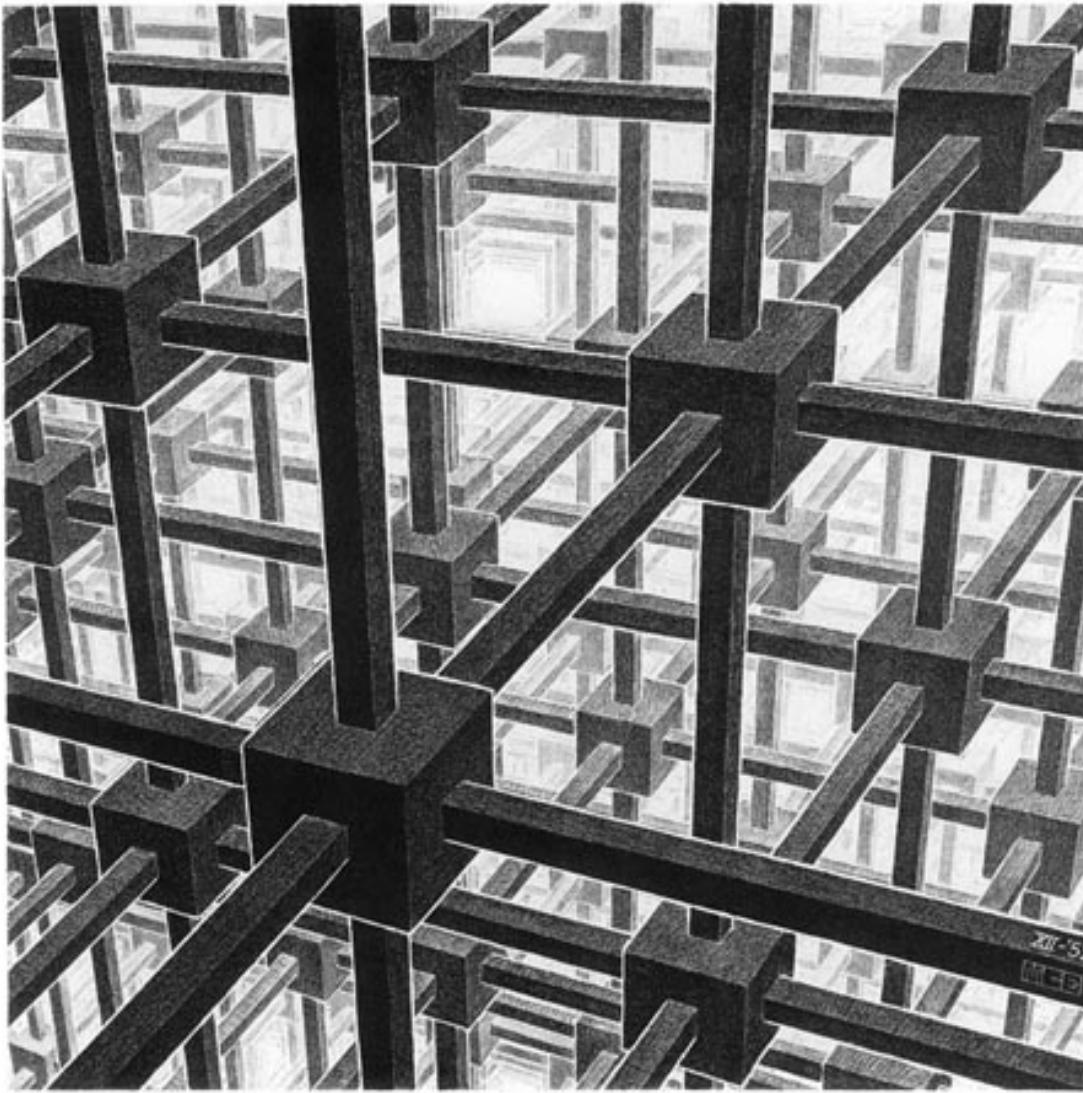
Alternative primitive unit cells in the same space lattice
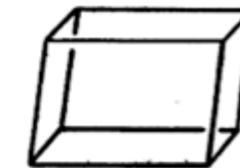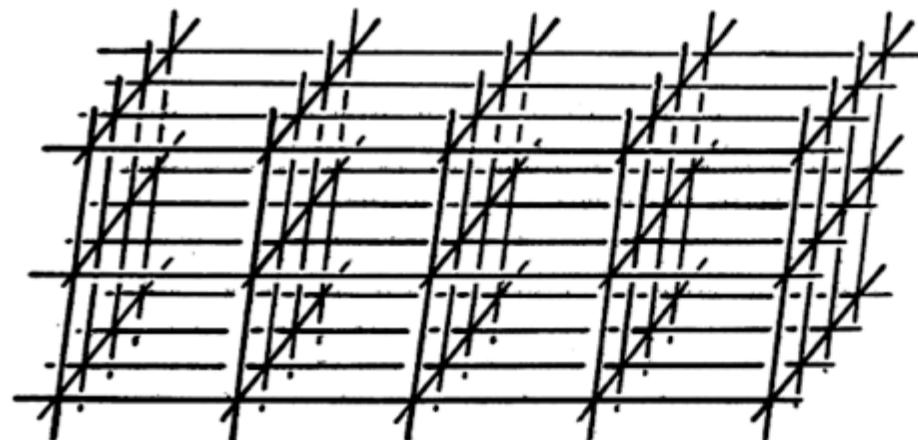
Fig. 2.8. Crystal lattice and one unit cell.
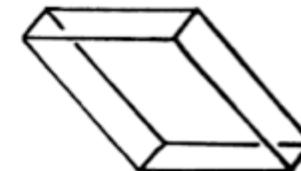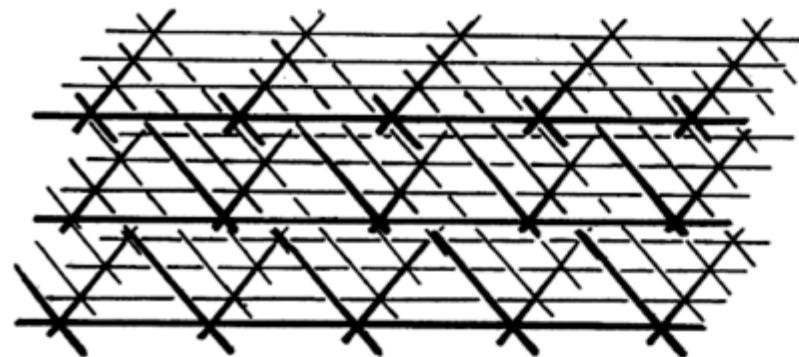
Fig. 2.9. Alternative lattice (and one unit cell) to that in Fig. 2.8.

S.C. Nyburg (1961). *X-Ray Analysis of Organic Structures*. New York: Academic Press.

Primitive and Centered Lattices and Unit Cells

(a) A centered lattice and unit cell have
(b) an equivalent primitive lattice and unit cell

(a)

(b)

S.C. Nyburg (1961). *X-Ray Analysis of Organic Structures*. New York: Academic Press.
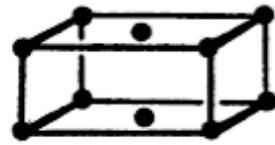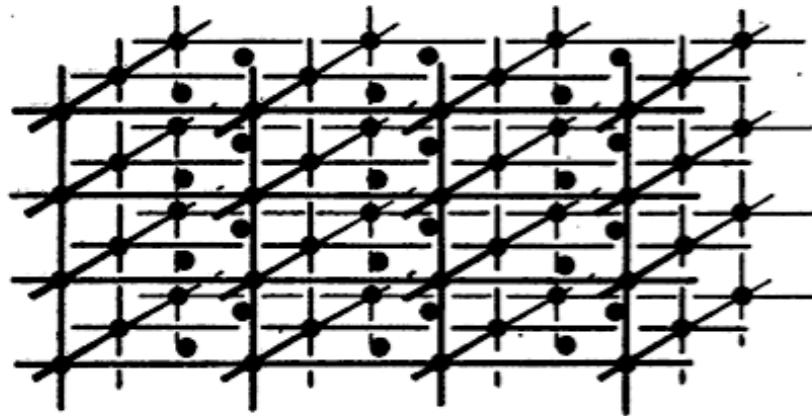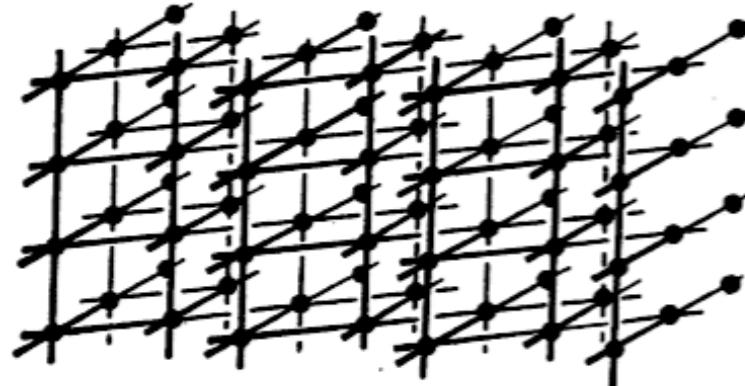
Two different families of lattice planes in the same lattice

S.C. Nyburg (1961). *X-Ray Analysis of Organic Structures*. New York: Academic Press.
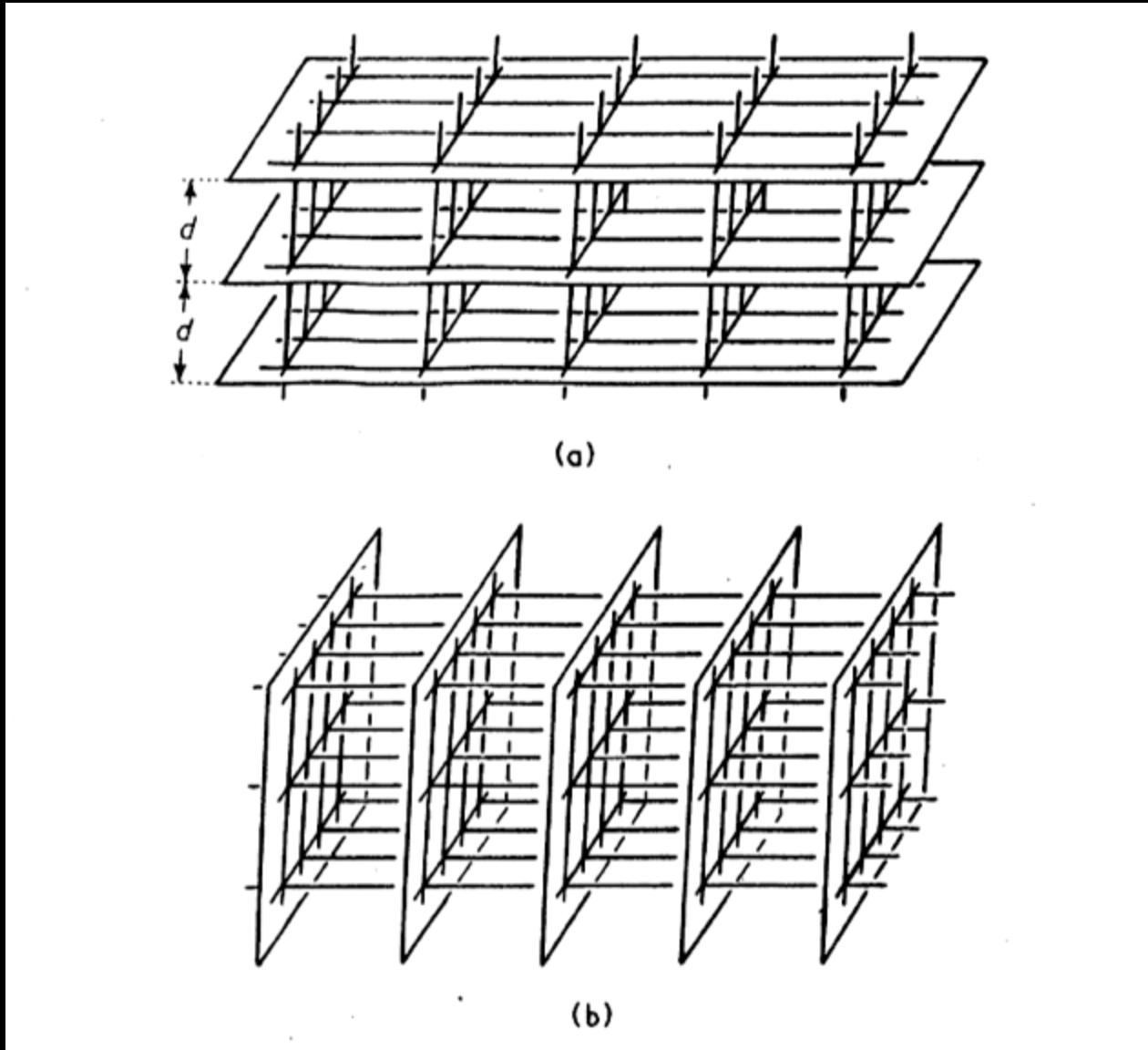
Lattice points, lattice rows, and lattice planes
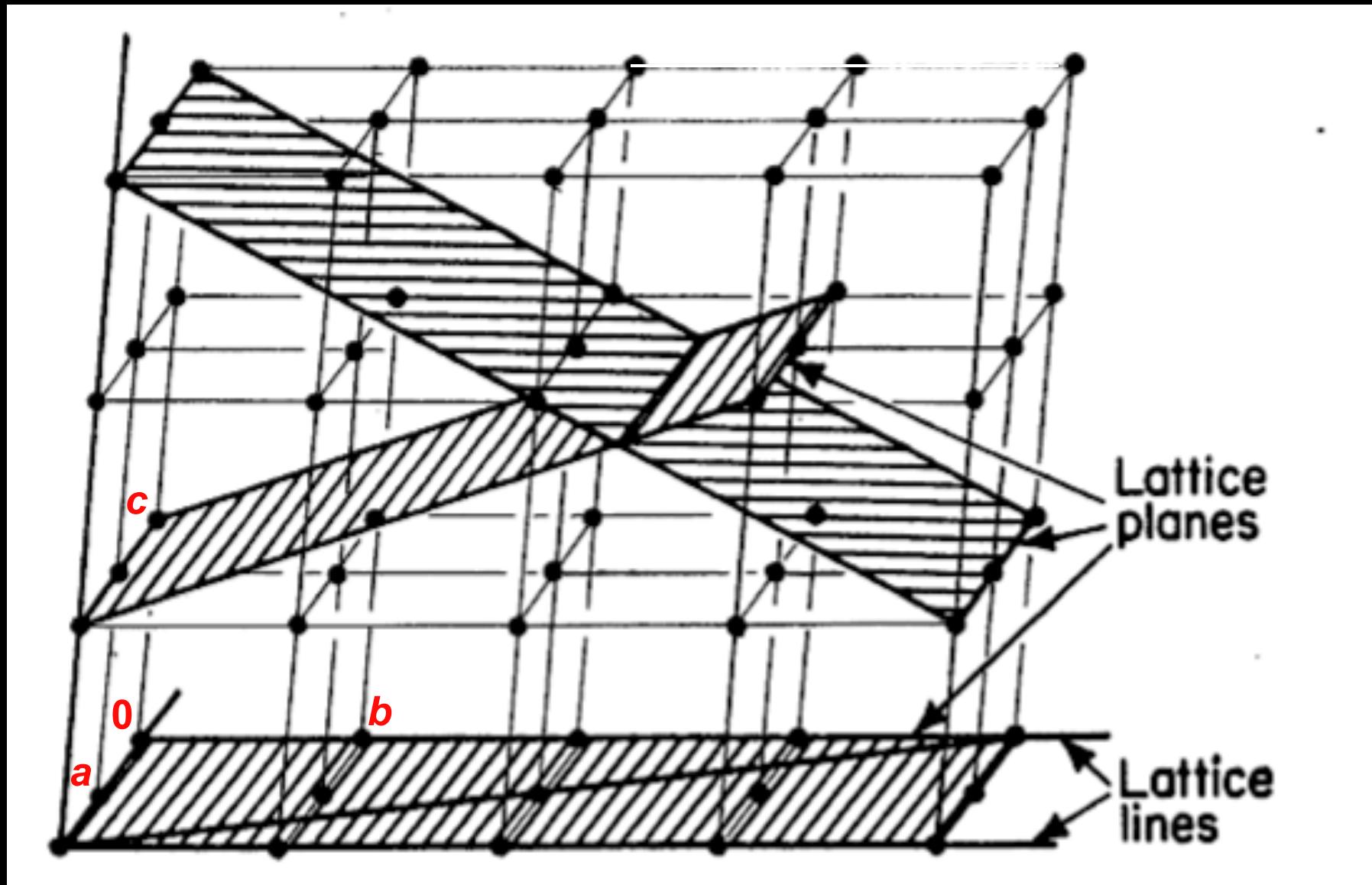
Families of equidistant lattice planes pass through *all* the lattice points.
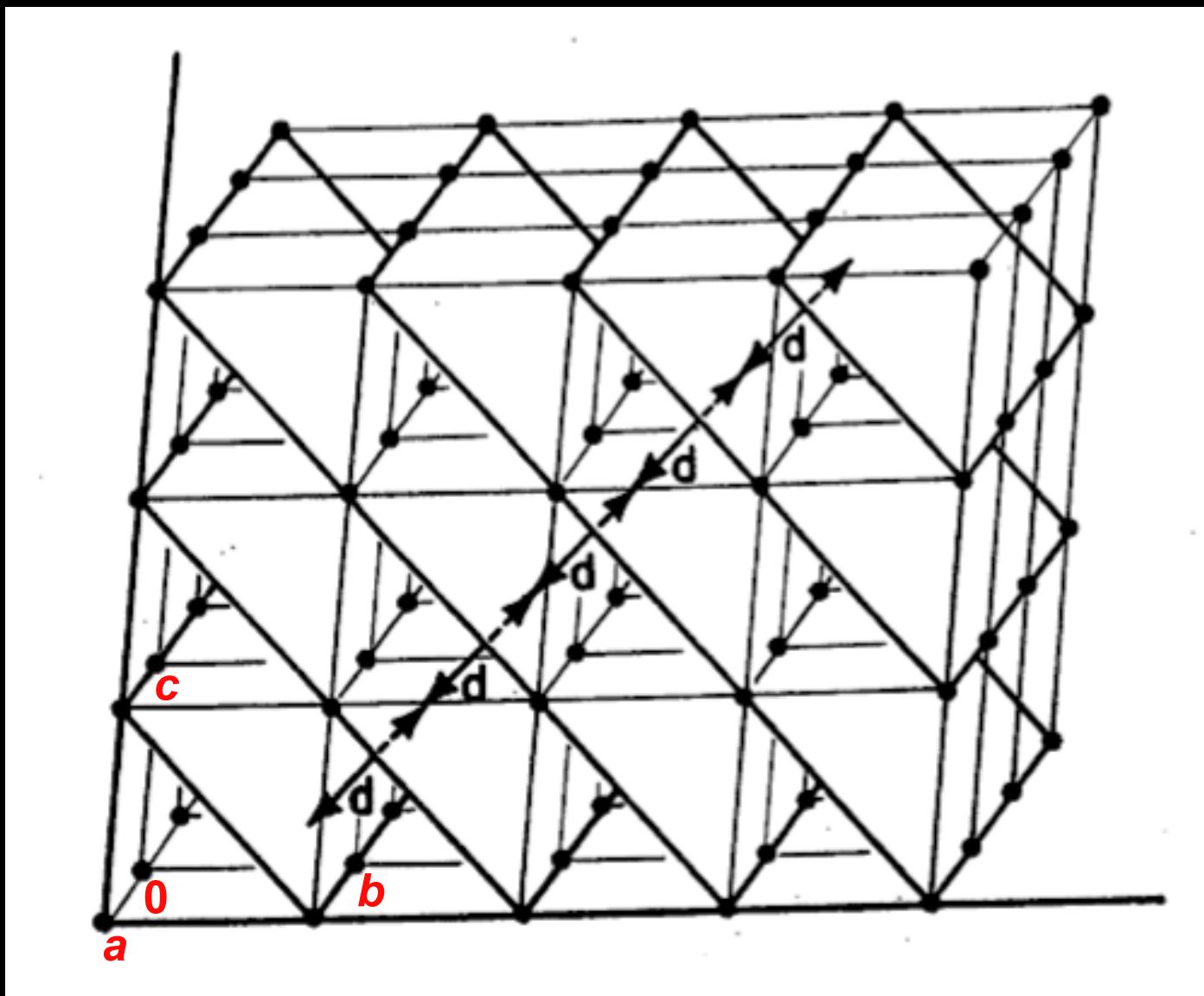
Every family of lattice planes passes through *all* the lattice points.
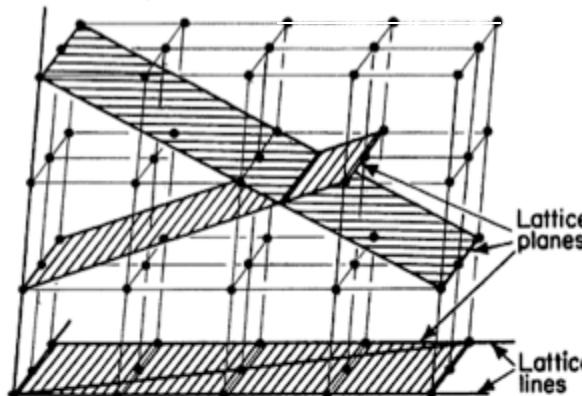
Fig. 3.7. Lattice lines or rows and lattice planes.
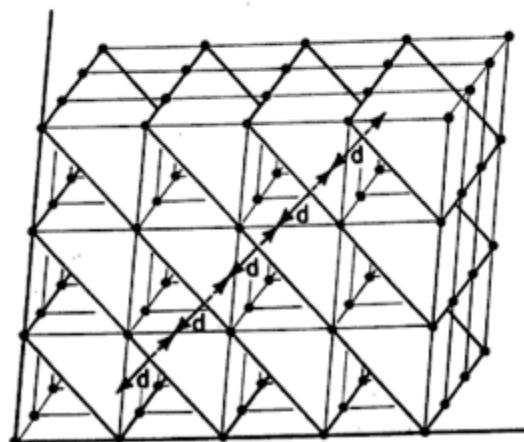
A set of equidistant planes passing through all the lattice points shown in fig. 3.7.

Henry S. Lipson (1970). *Crystals and X-Rays*. London: Wykeham Publications.

Some Cubic Lattice Planes
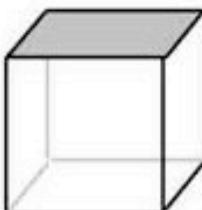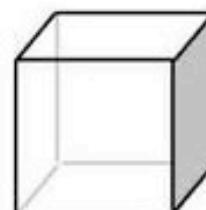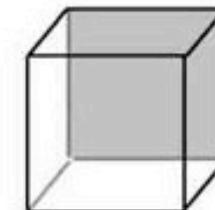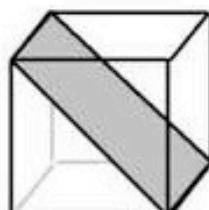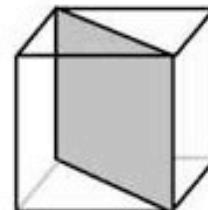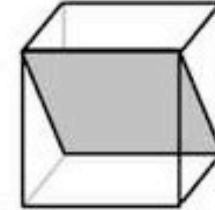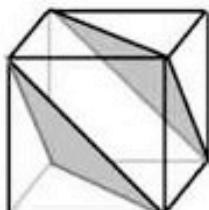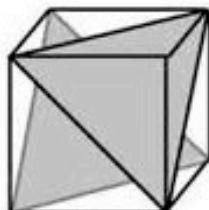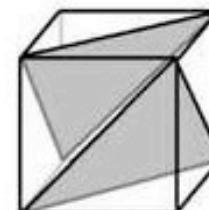
Actual and Virtual Lattice Planes

660   1962 M.F.PERUTZ

h = 1
k = 3
l = 4

h = 1
k = -1
l = 2

h = 1
k = 4
l = -1

h = 0
k = 0
l = 4

co-prime indices have no common factor > 1

h = 2
k = 2
l = 2

h = 0
k = 3
l = 0

composite indices have a common factor > 1

h = 2
k = 0
l = 2

h = 2
k = 0
l = 0

h = 0
k = 1
l = 1

h = 1
k = 0
l = 0
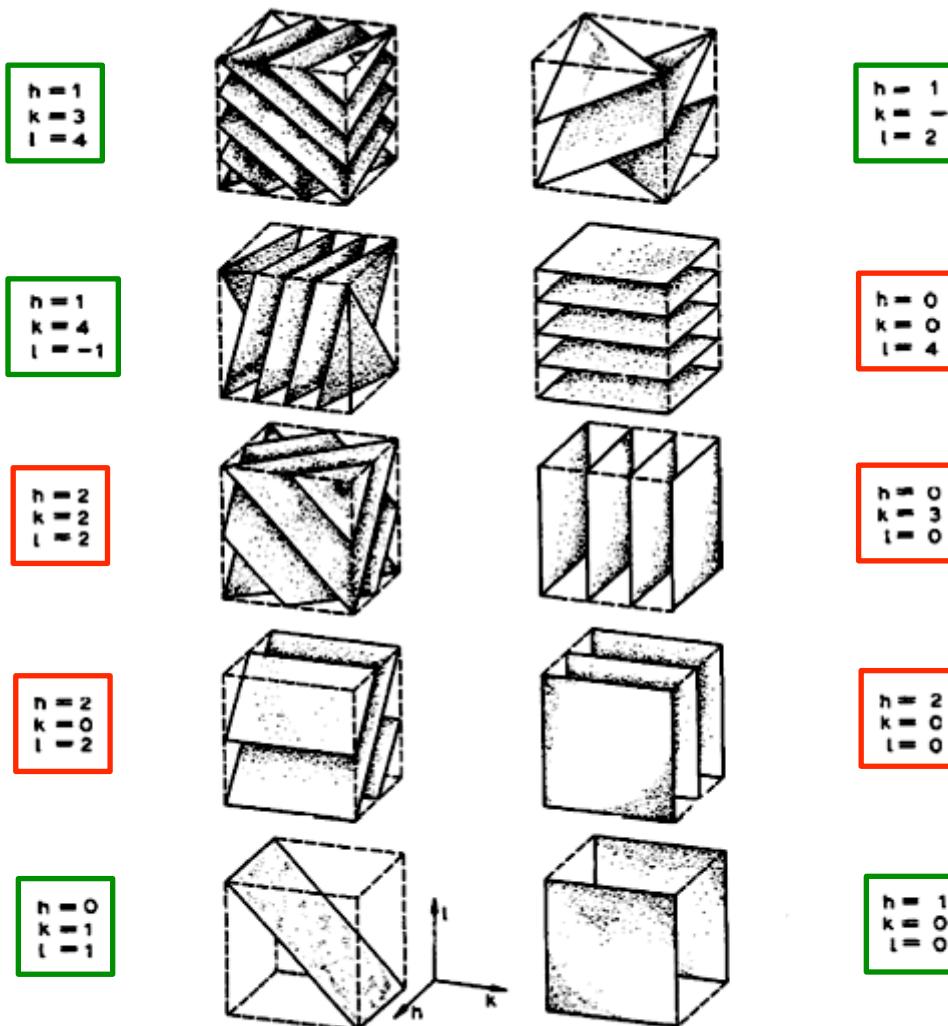
Fig. 7. Set of three-dimensional fringes used to build up image of the electron density. (Reproduced, by permission, from W. de Beauclair, "Verfahren und Geräte zur mehrdimensionualen Fouriersynthese", Akademie-Verlag, Berlin, 1949.)

Max Perutz, Nobel Lecture (1962).

http://www.doitpoms.ac.uk/tlplib/miller_indices/lattice_index.php

Families of equally spaced lattice planes
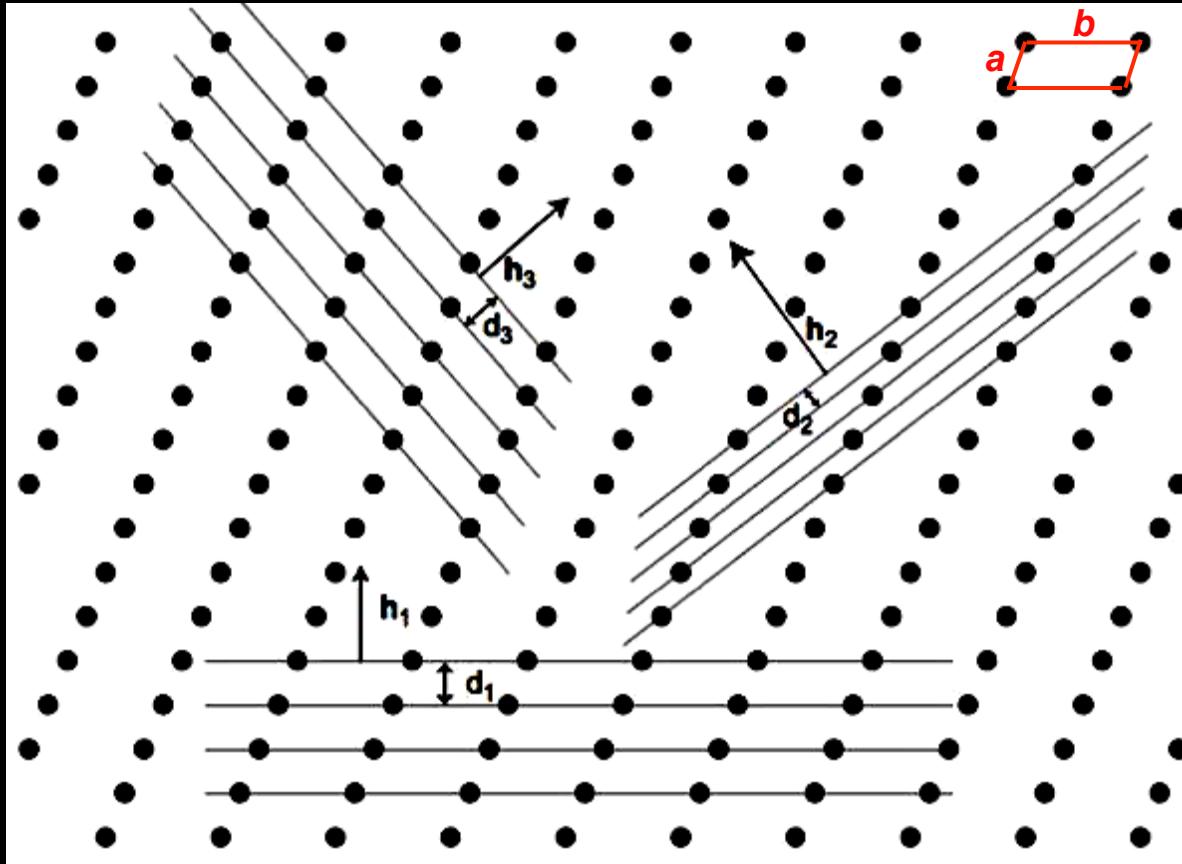
h_1	$h_1 k_1 l_1$	1 0 0
h_2	$h_2 k_2 l_2$	1 3 0
h_3	$h_3 k_3 l_3$	-1 2 0

$$d_1 > d_3 > d_2$$
$$d_{100} > d_{-120} > d_{130}$$

The higher the indices, the smaller the interplanar spacing, and the lower the reticular density.

http://escher.epfl.ch/eCrystallography/print.php
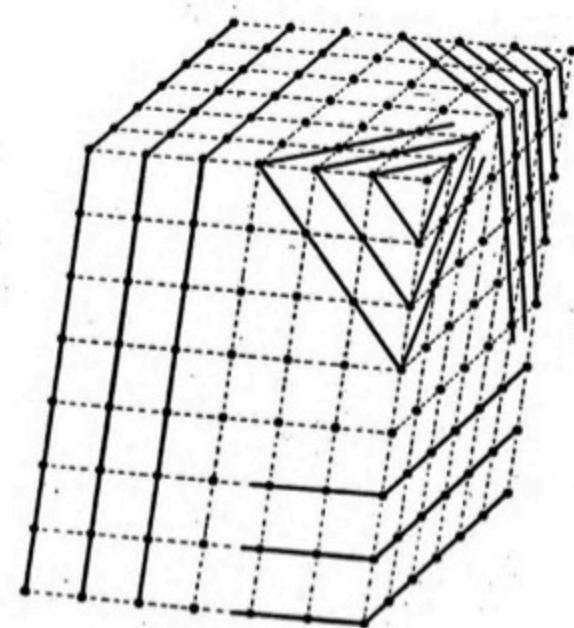
FIG. 7. Dividing a crystal into layers. A few of the simpler ways. (Each dot is a lattice point.)
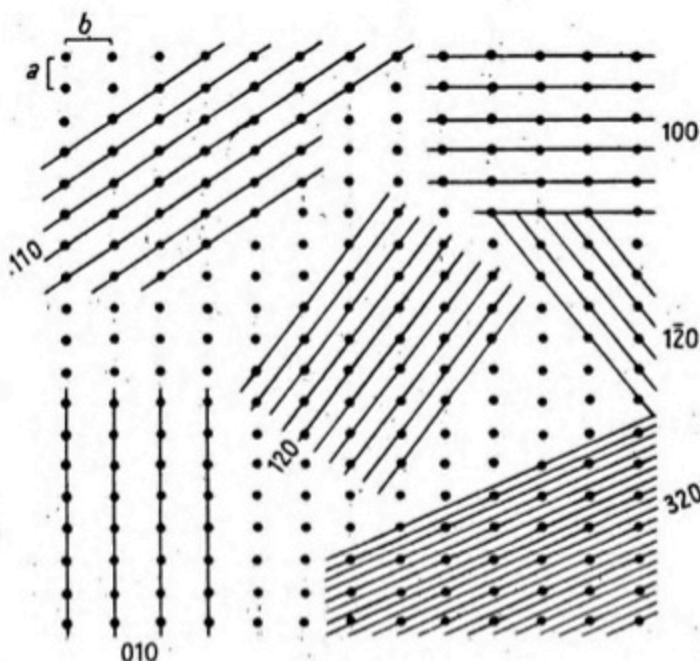
FIG. 9.
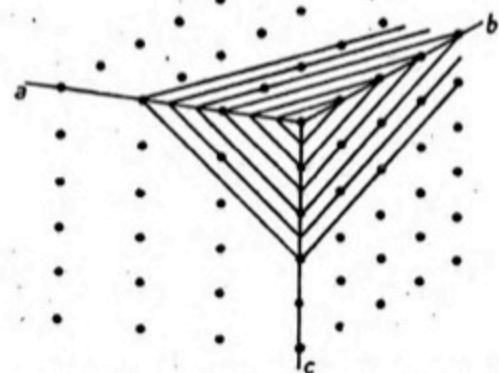
FIG. 10. This set of parallel planes has indices 312.

lattice points
lattice planes
Haüy's Law of Rational Indices (1783)
and
Miller indices (1839)

C.W. Bunn (1961). *Chemical Crystallography*, 2nd ed. Oxford University Press.

Lattice planes define the crystal faces.

possible macroscopic crystal shape depending on the lattice periodicity
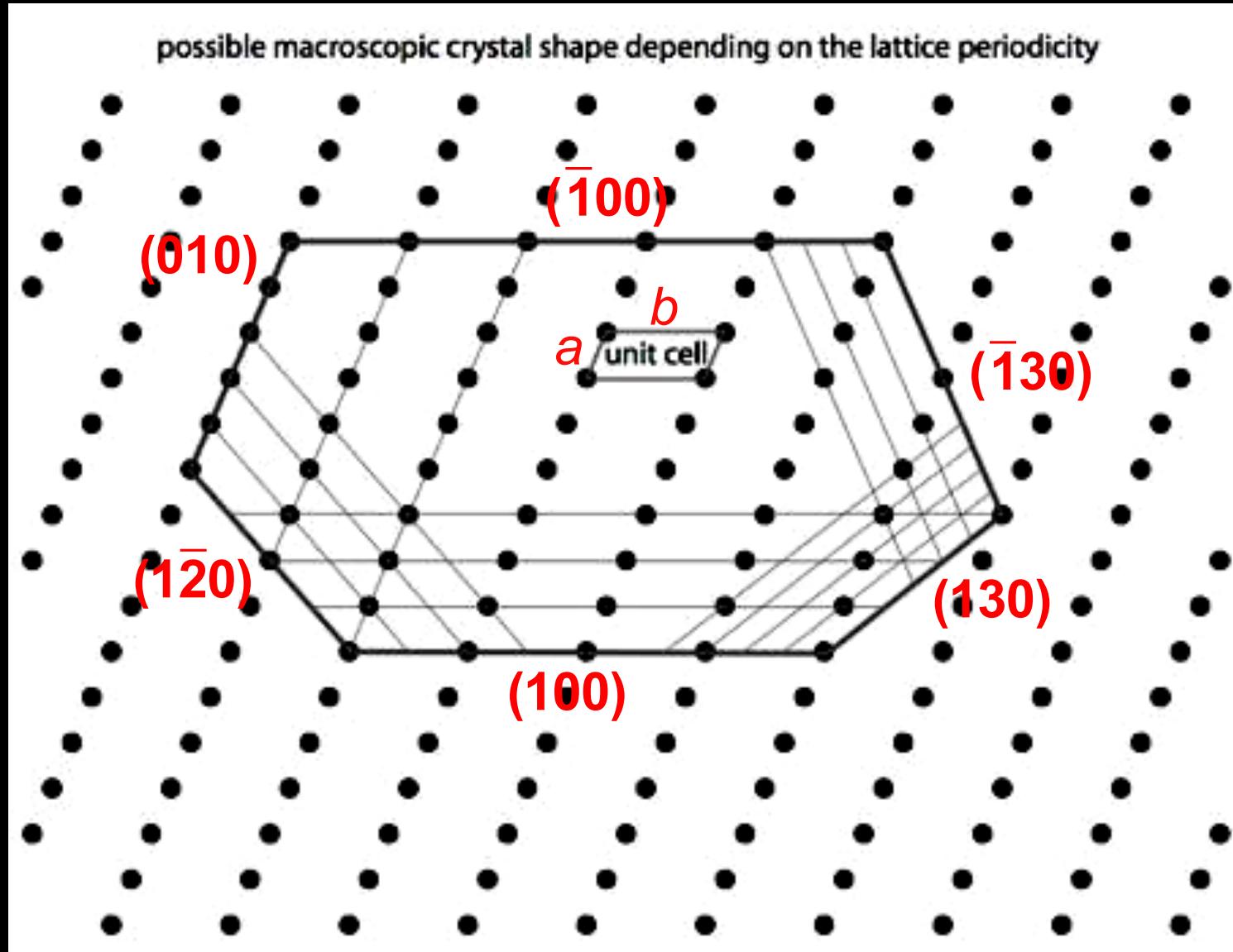
Miller Indices and Reticular Density
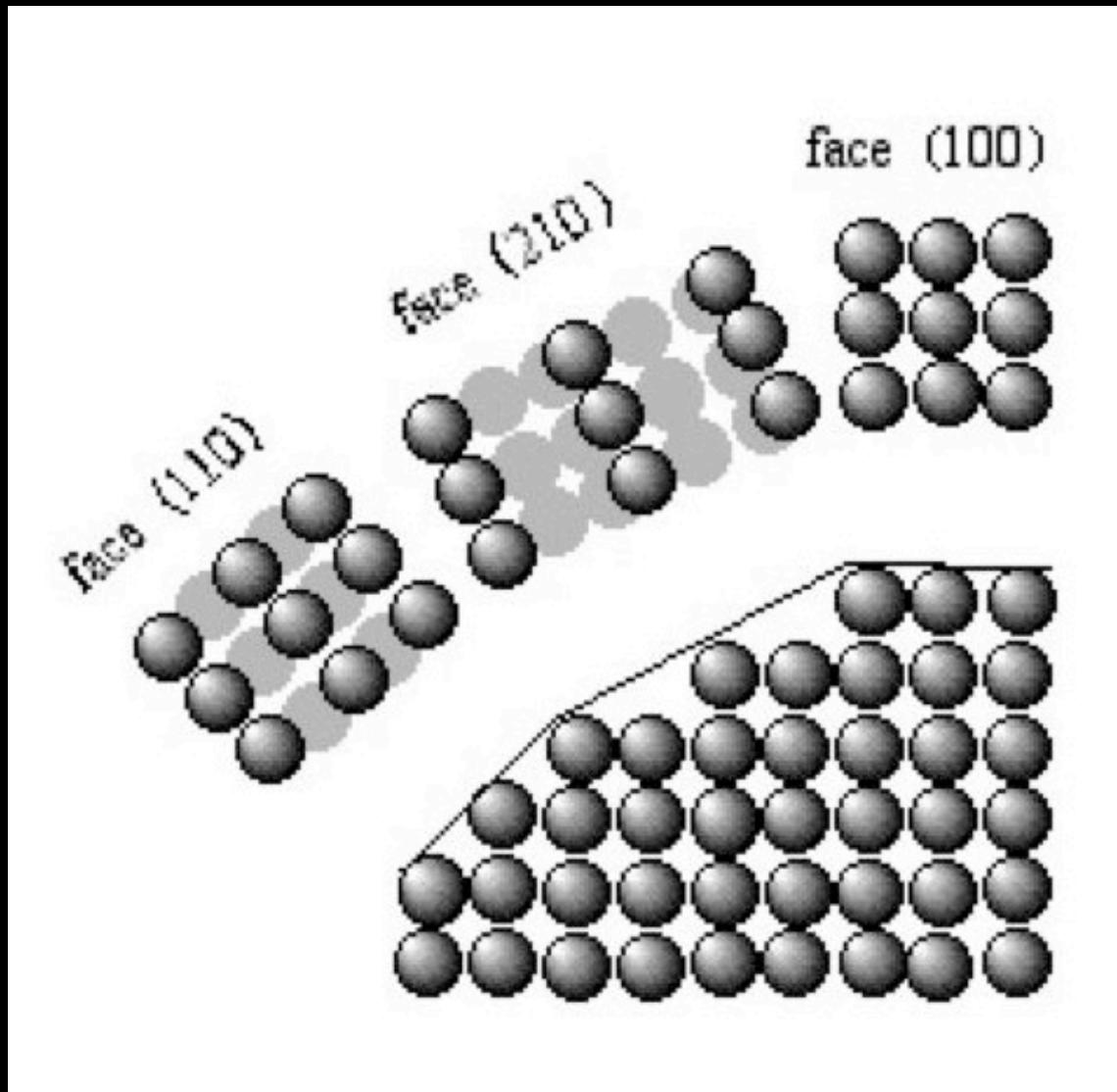
Crystal faces are lattice planes with:
- **small Miller indices,**
- **large interplanar spacing, and**
- **high reticular density.**
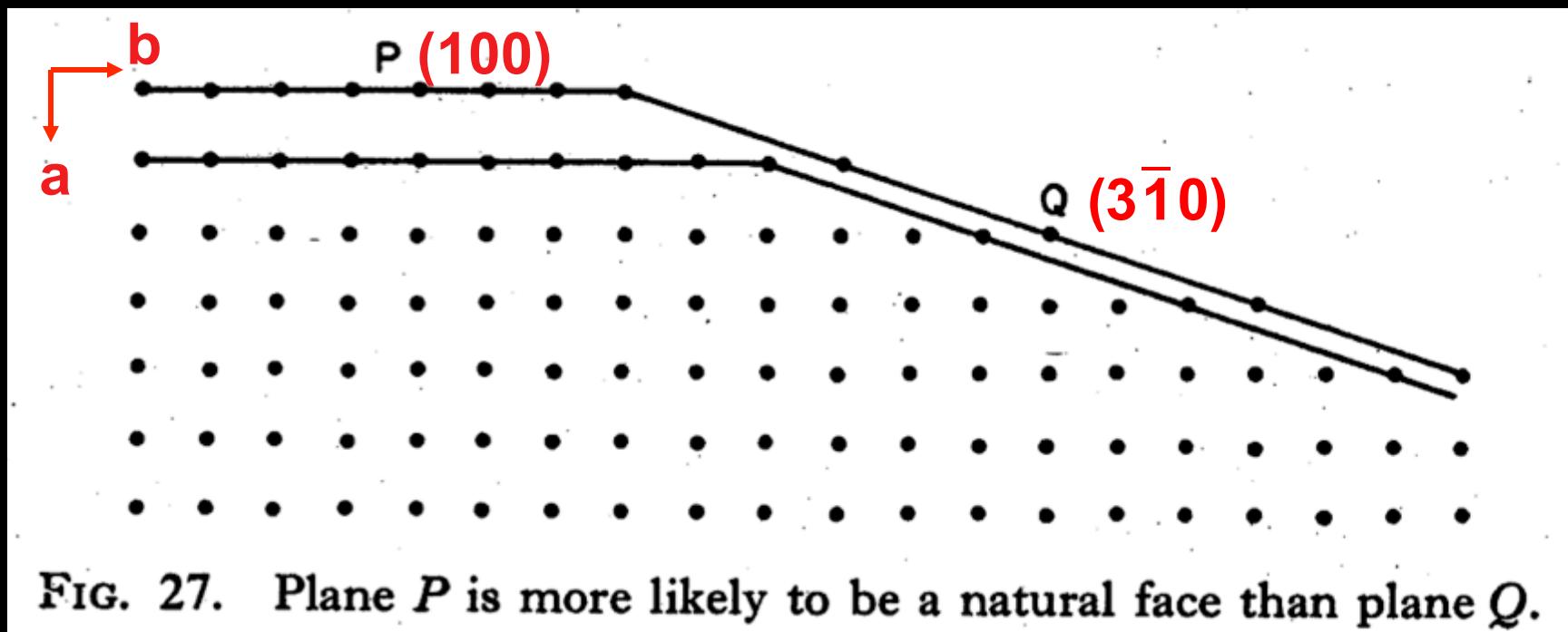
FIG. 27. Plane *P* is more likely to be a natural face than plane *Q*.

Charles W. Bunn (1964). *Crystals: Their Role in Nature and in Science*. New York: Academic Press.

Indexing Lattice Axes [*uvw*] and Lattice Planes (*hkl*)
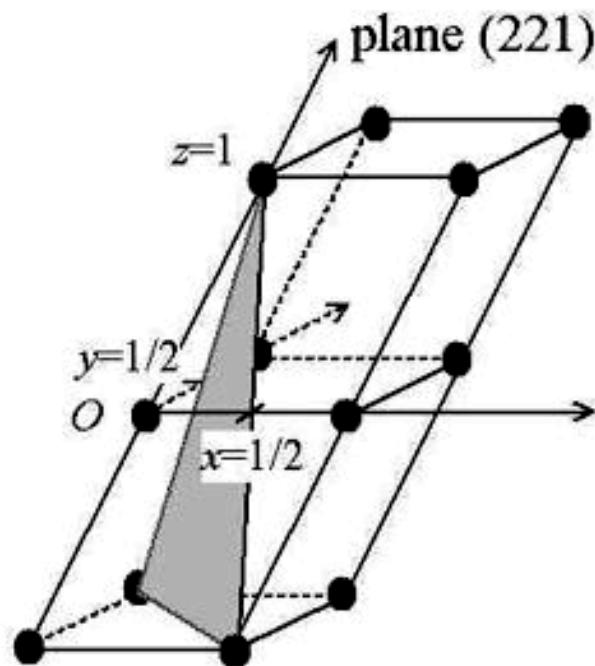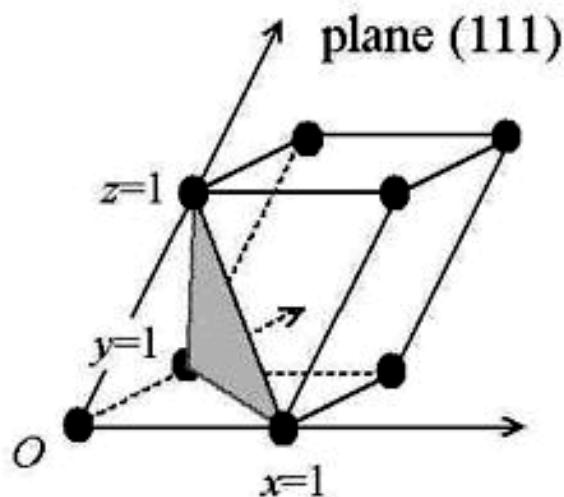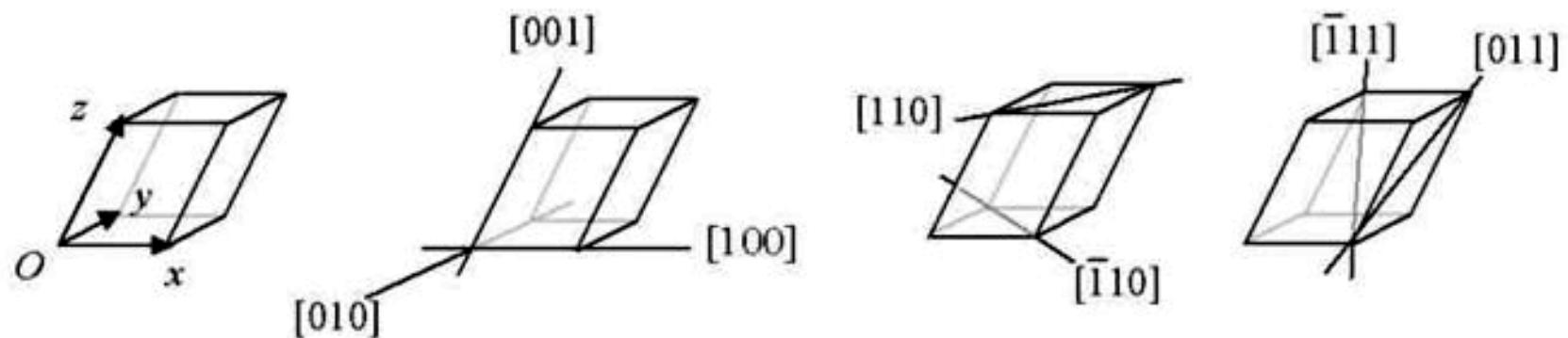
Miller indices of some cubic crystal faces
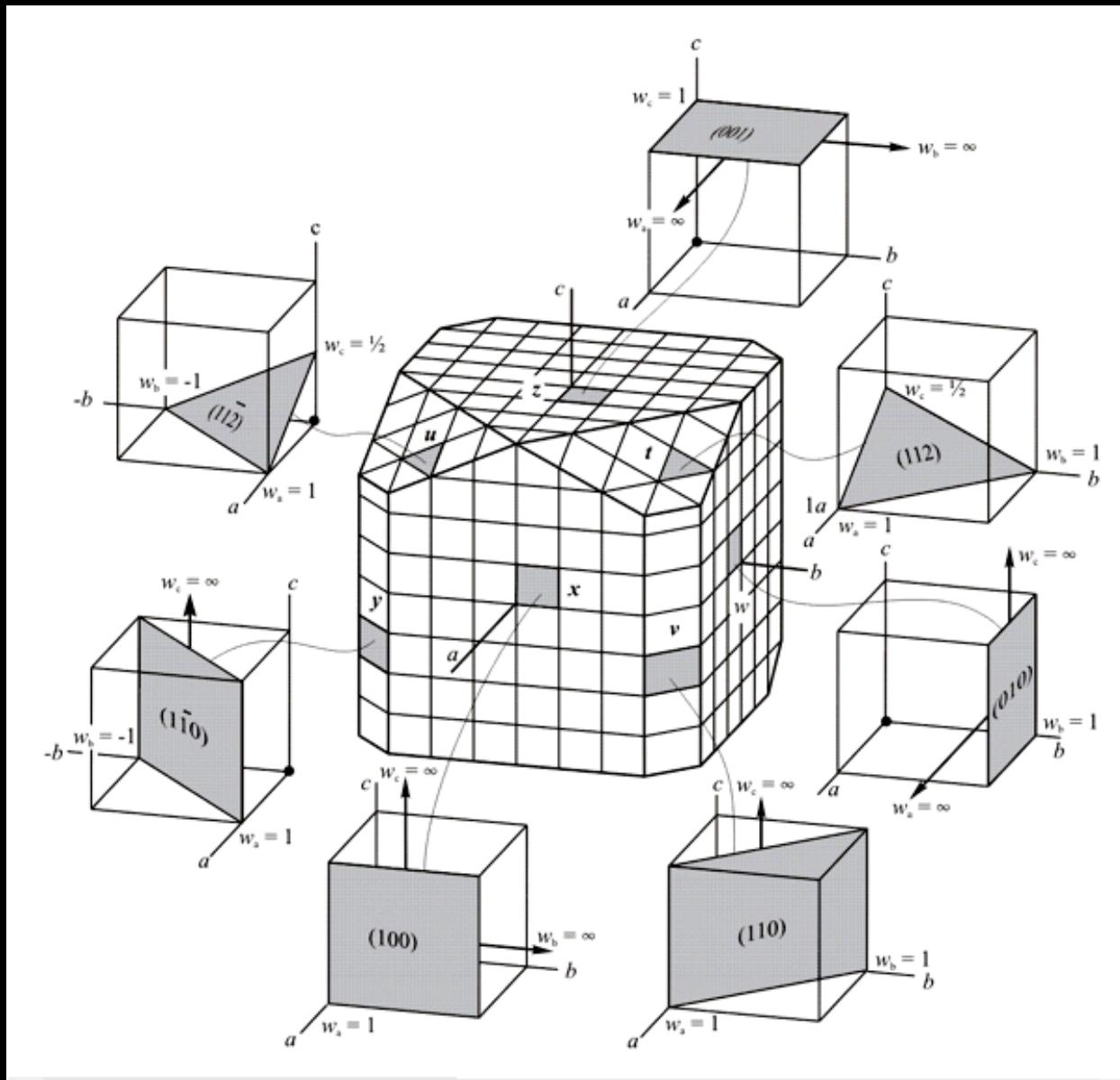
Some faces of a truncated cube
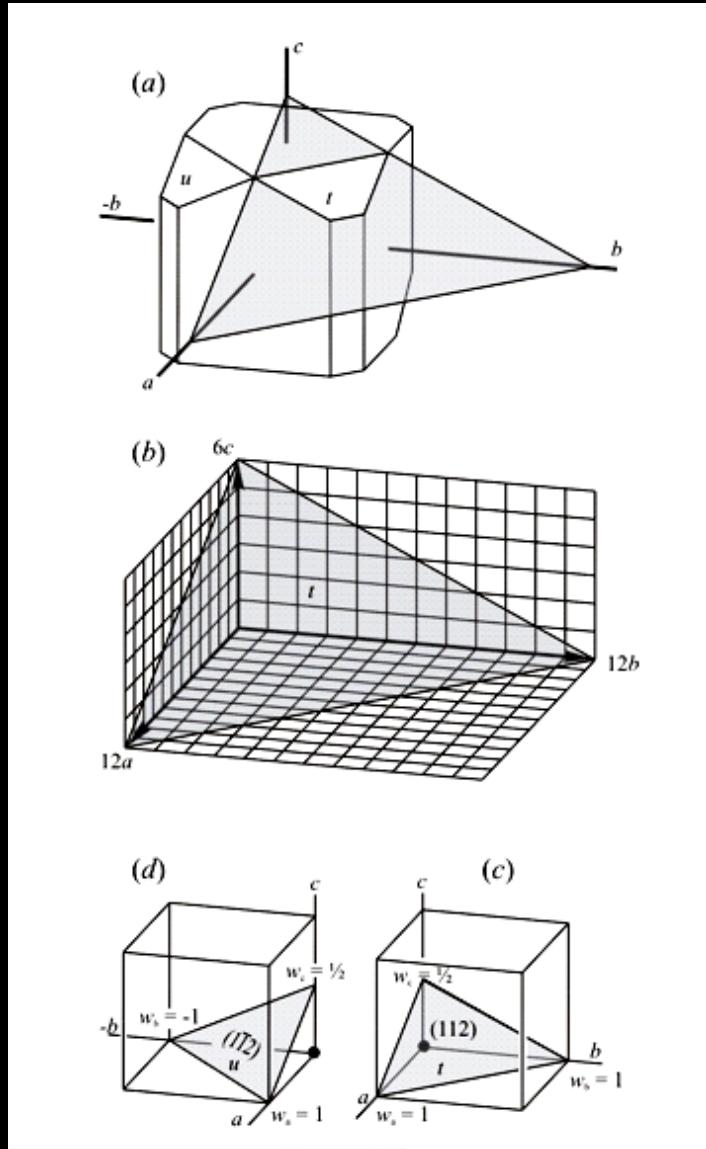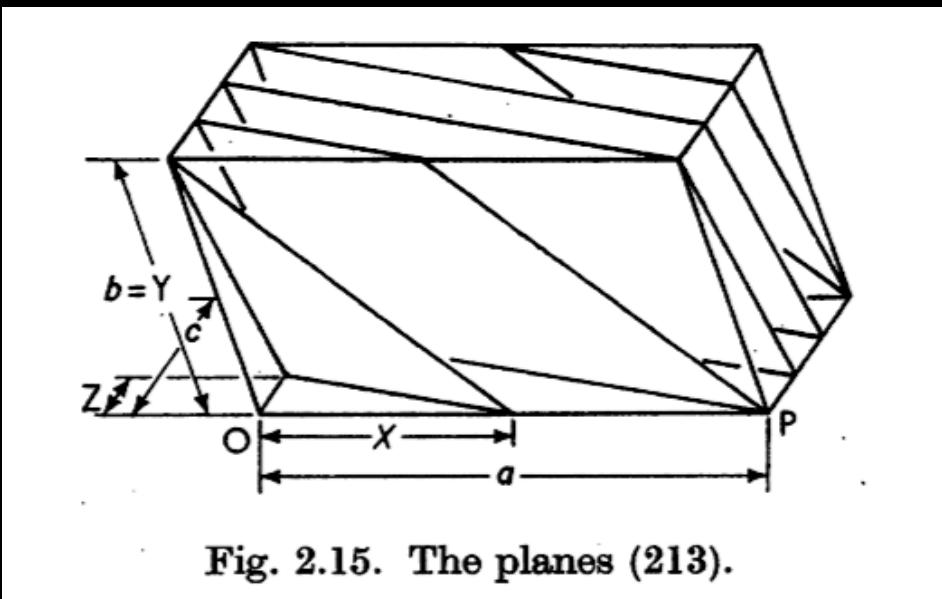
Fig. 2.15. The planes (213).

Fig. 2.16. The planes (2̄13).

S.C. Nyburg (1961). *X-Ray Analysis of Organic Structures*. New York: Academic Press.
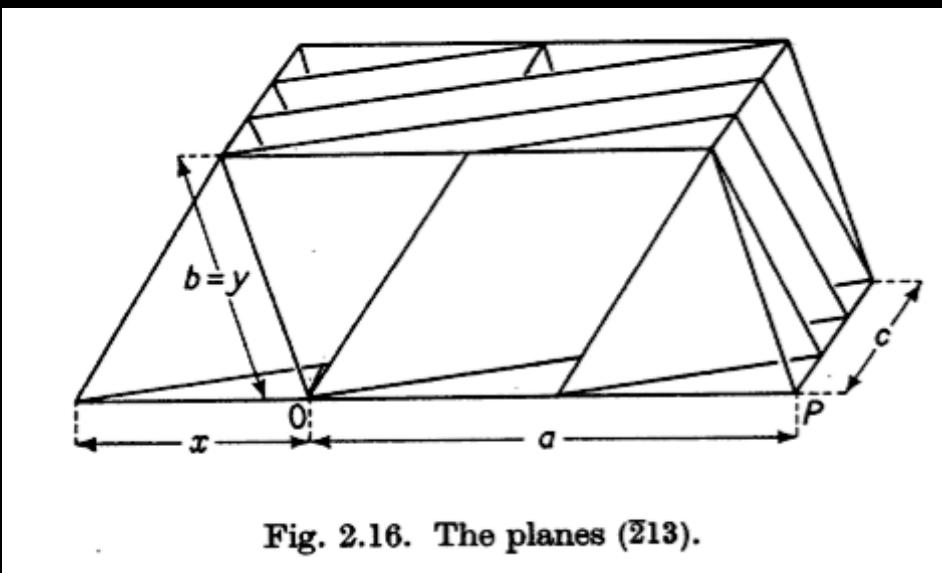
Three-index (*hkl*) Trigonal or Hexagonal Indexing
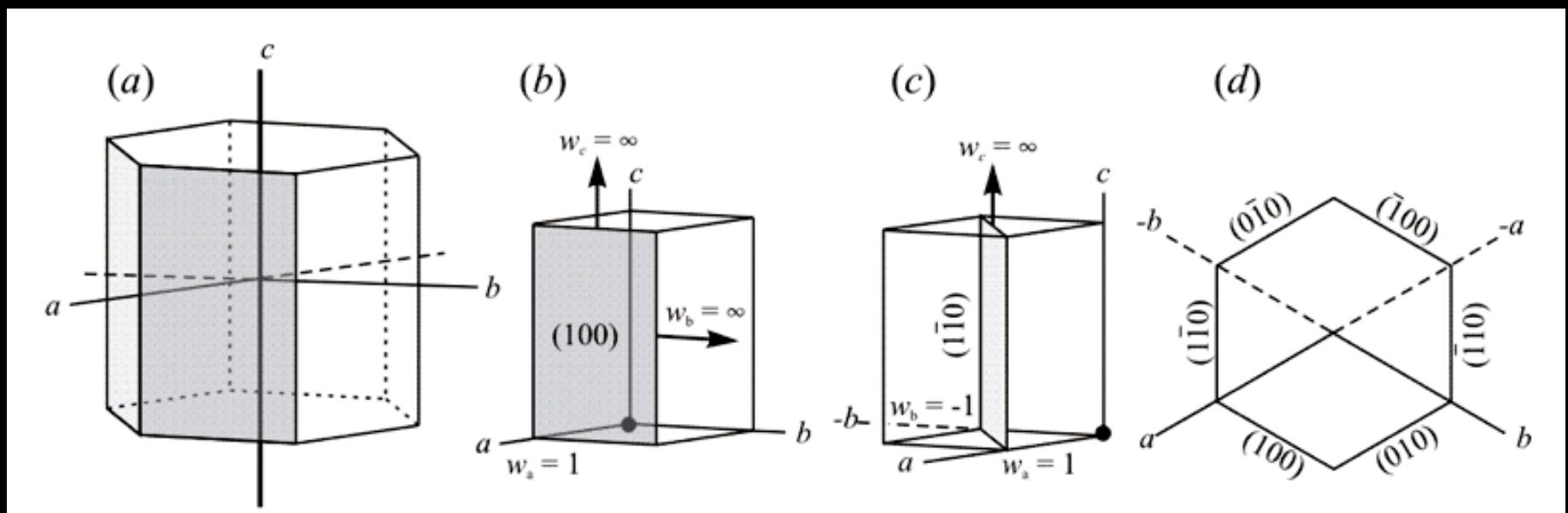
Four-index ($h\,k\,i\,l$) = ($h, k, -h-k, l$) Hexagonal Indexing
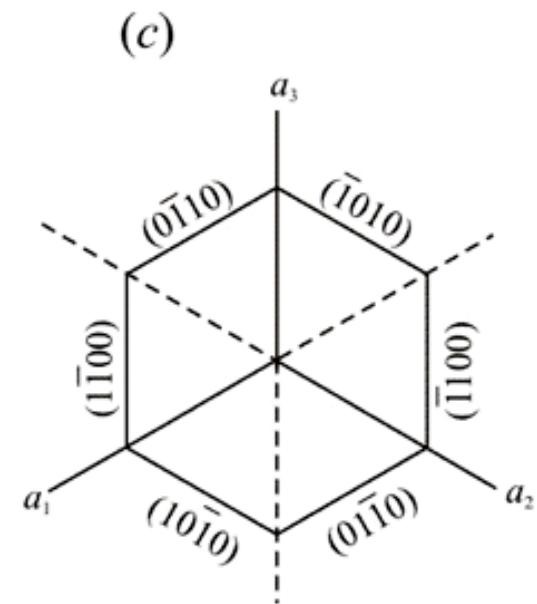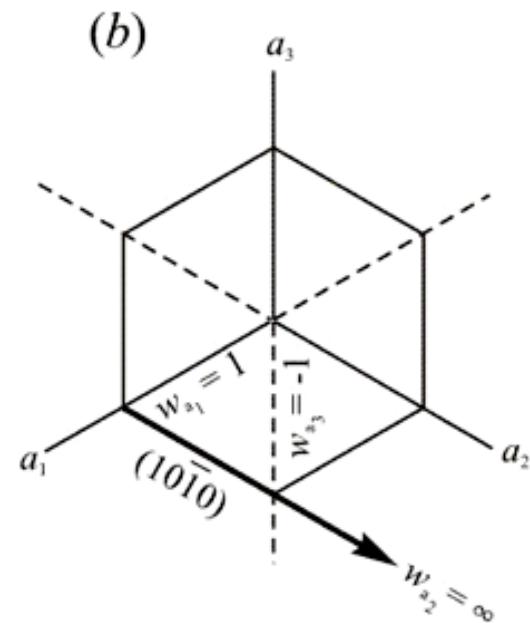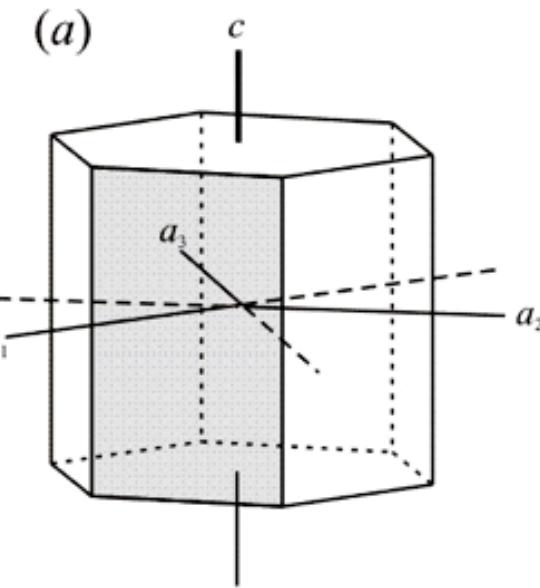
Four-index $(hkil) = (h, k, -h-k, l)$ Hexagonal Indexing
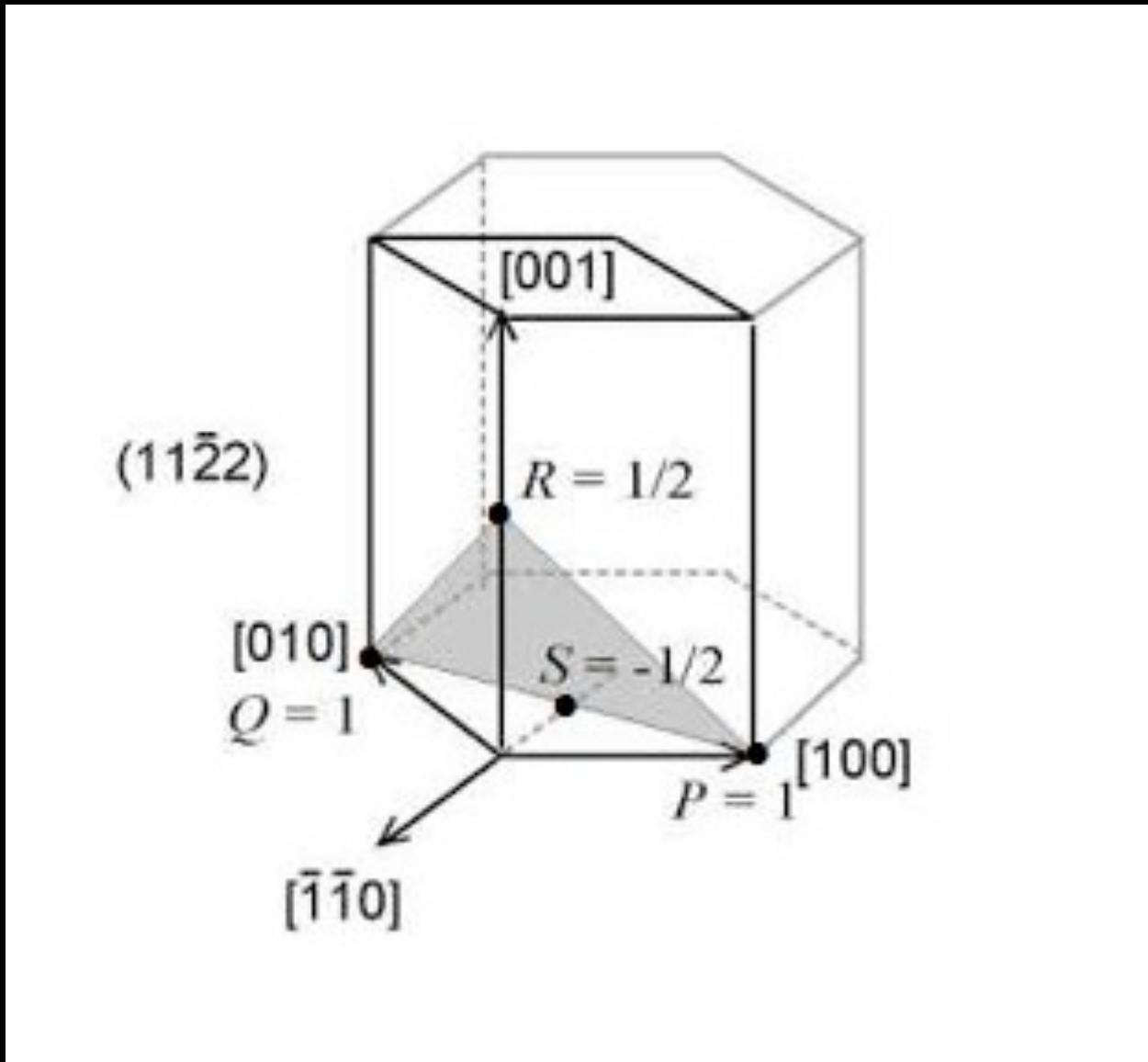
Development of a *zone* of crystal faces {*hkl*} = {*h0l*}
Around a *zone axis* [uvw] = [010]

A (100)
B (010)
C (001)

Q (102)

T (101)
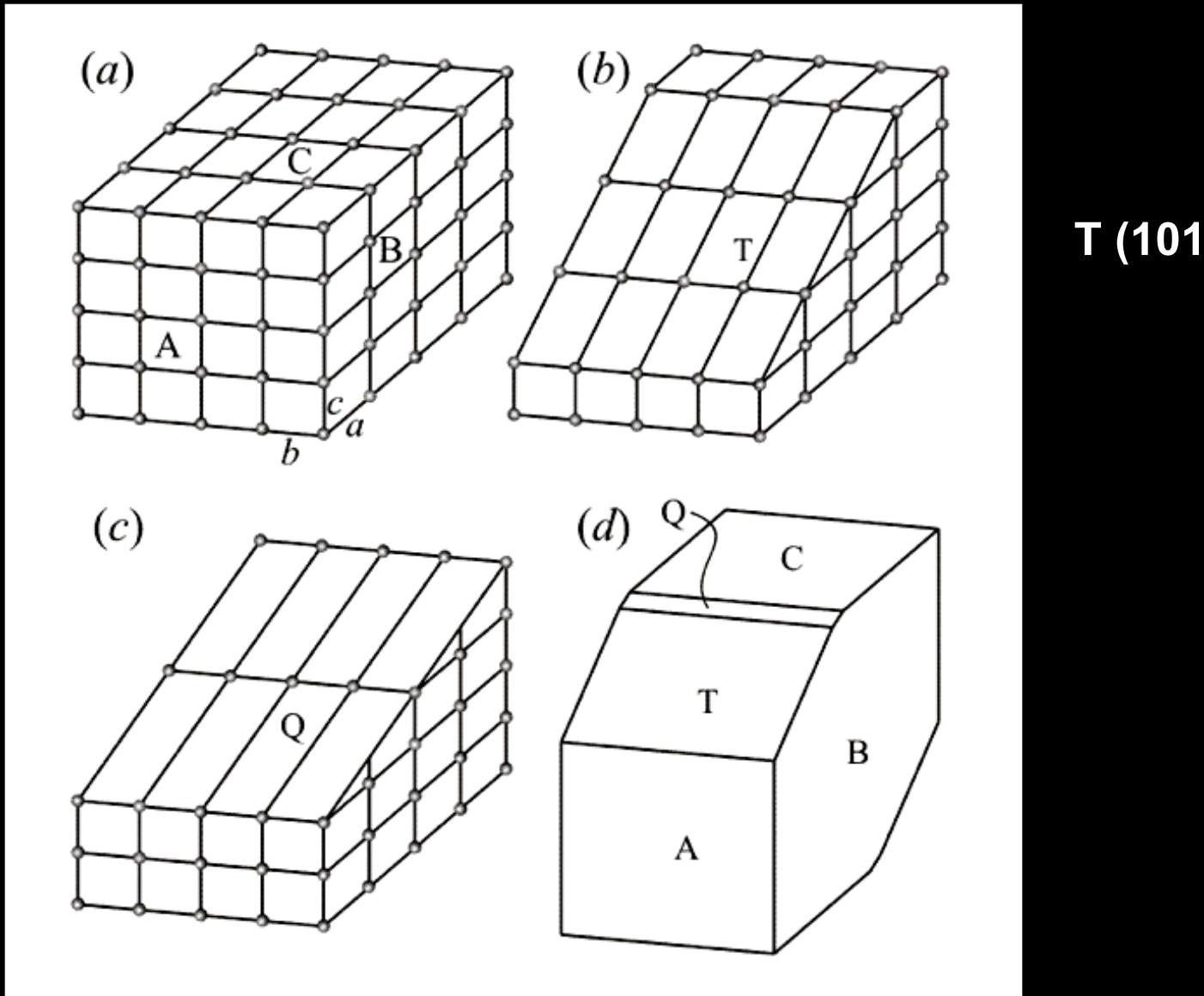
Crystal face development by omitted stacks of unit cells
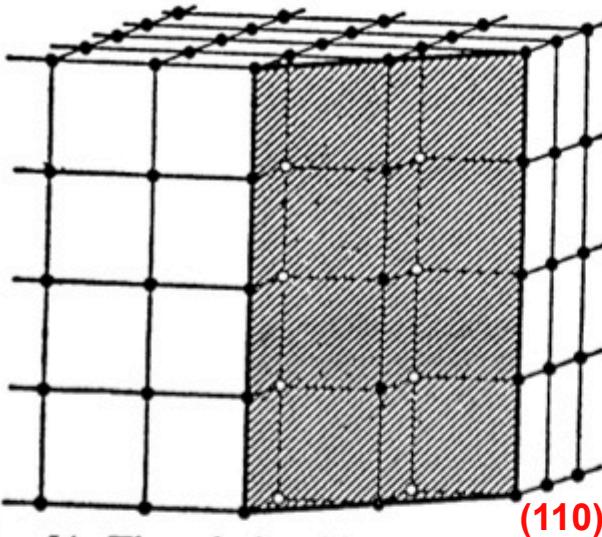
FIG. 54. The relationship of a face of the rhombic dodecahedron (shaded plane) to the structural units.

(110)
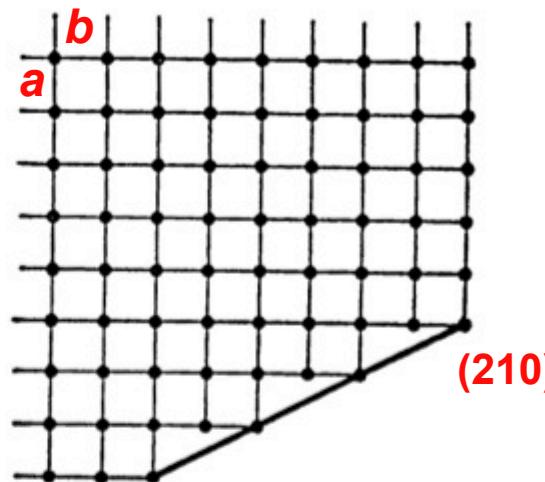
FIG. 55. Plan of the development of a further face modifying a cube edge.

(210)
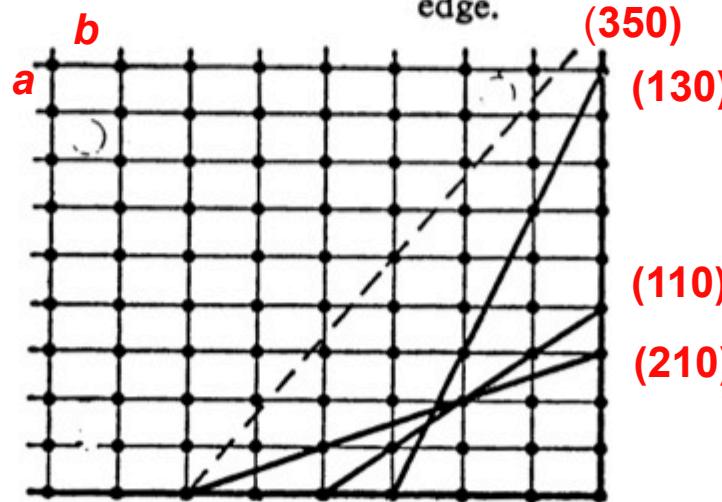
FIG. 56. The slopes of some possible planes in a crystal based on an orthorhombic structural unit.

(350)
(130)
(110)
(210)

Enantiomorphic pairs of low quartz (α-SiO₂) crystals
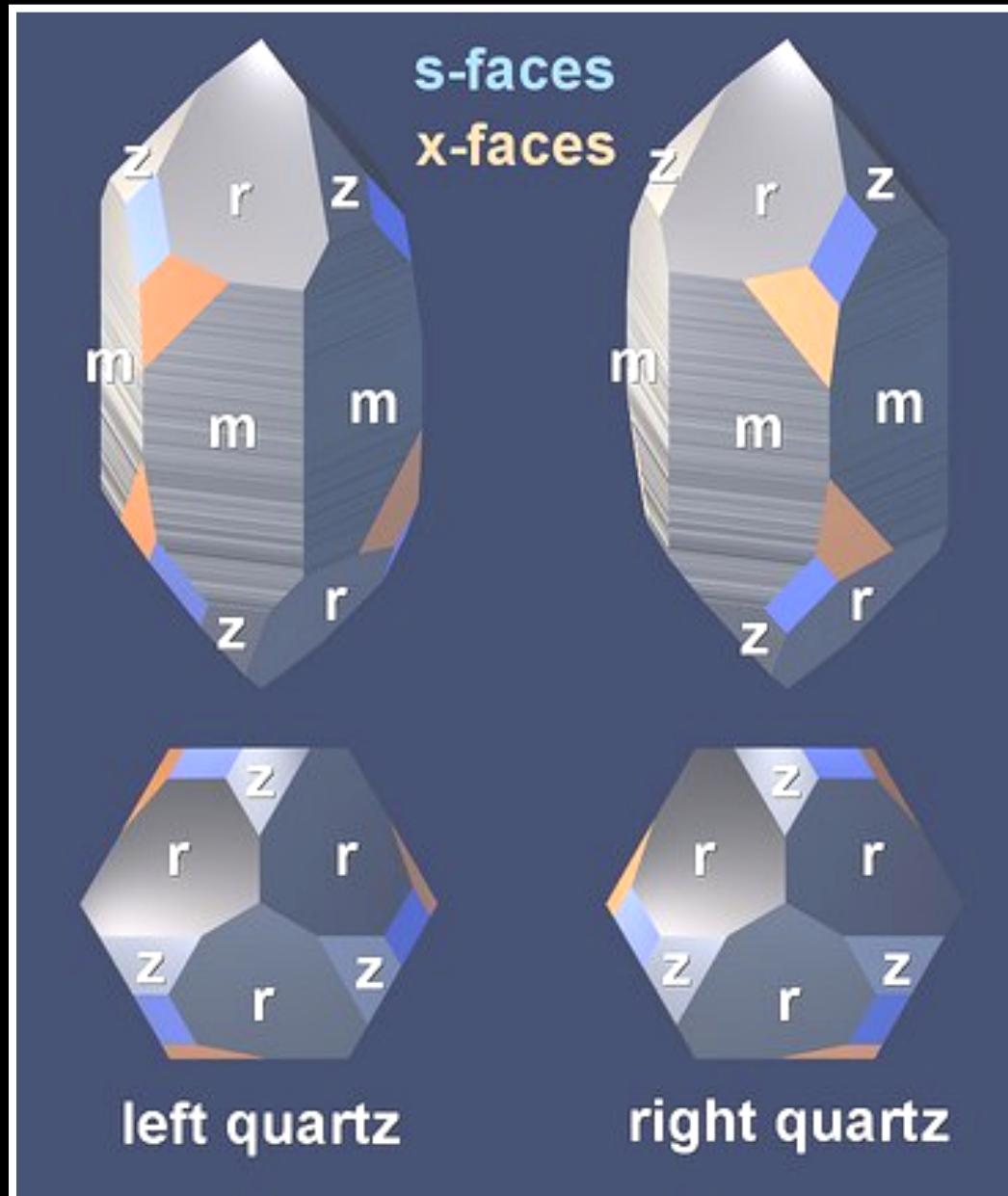
Enantiomorphic low quartz (α-SiO$_2$) crystals

Left crystal   Right crystal
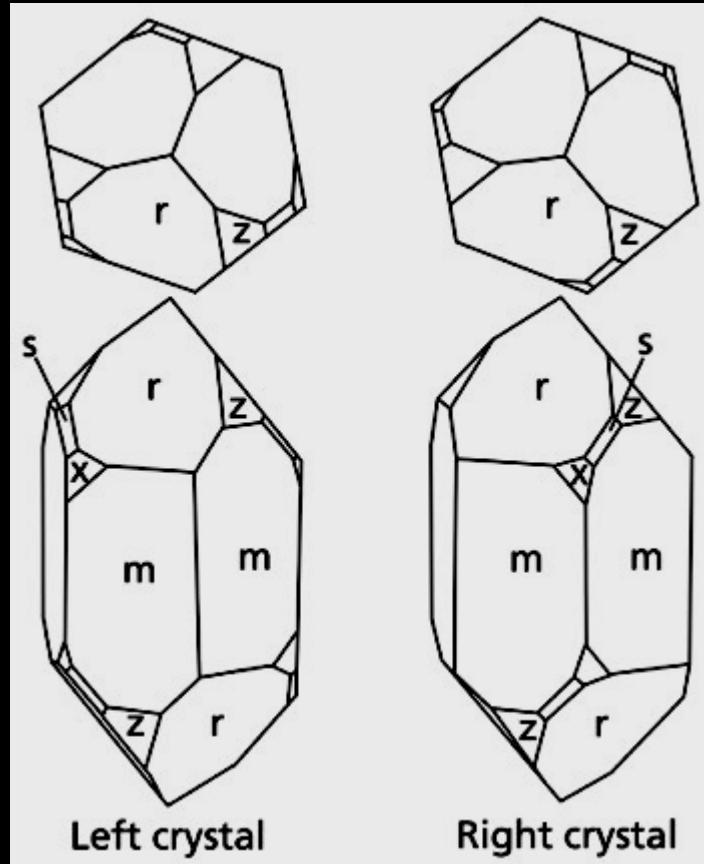
$$m = \{10\bar{1}0\} = (10\bar{1}0), (01\bar{1}0), (\bar{1}100), (\bar{1}010), (0\bar{1}10), (1\bar{1}00)$$

$$r = \{10\bar{1}1\} = (10\bar{1}1), (01\bar{1}1), (\bar{1}101), (\bar{1}01\bar{1}), (0\bar{1}1\bar{1}), (1\bar{1}0\bar{1})$$

$$z = \{01\bar{1}1\} = (01\bar{1}1), (01\bar{1}1), (\bar{1}101), (\bar{1}01\bar{1}), (0\bar{1}1\bar{1}), (1\bar{1}0\bar{1})$$

$$s = \{2\bar{1}\bar{1}1\} \text{ left}, \{11\bar{2}1\} \text{ right}$$

$$x = \{6\bar{1}51\} \text{ left}, \{51\bar{6}1\} \text{ right}$$

An enantiomorphic pair of chiral, hemihedral,
low quartz, α-SiO$_2$, crystals

à la bicapped "Herkimer diamonds"
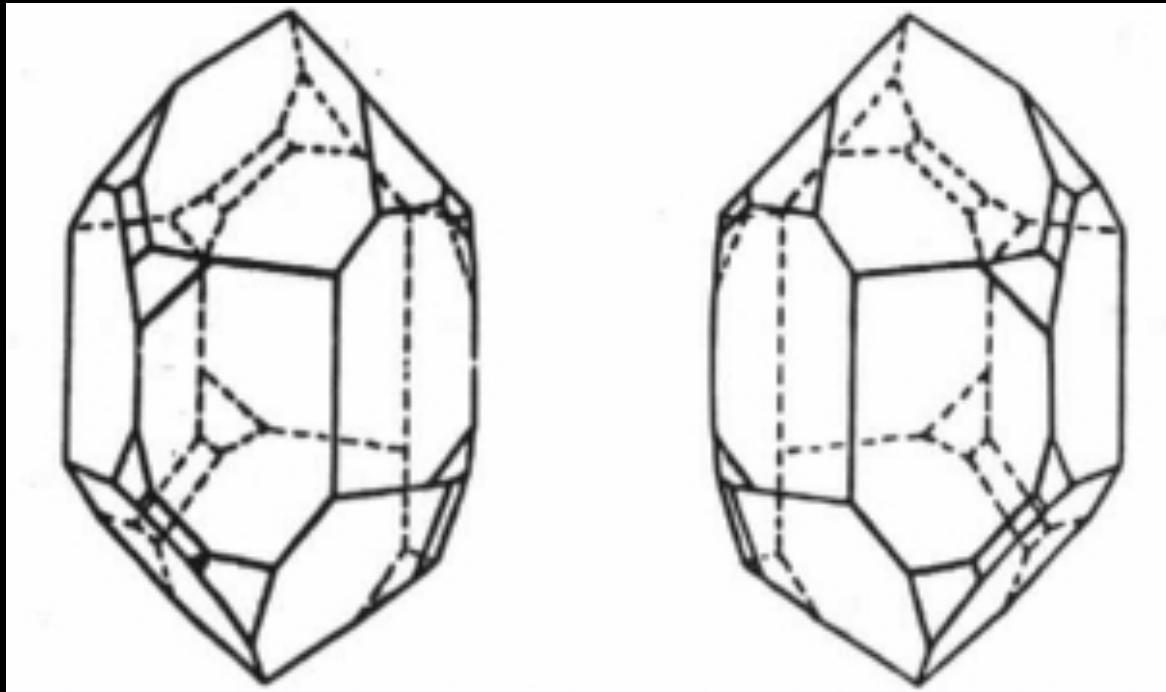
enantiomorph from εναντιος (*enantios*) "opposite" + μορφη (*morphe*) "form"

chiral, chirality from χειρ (*cheir*) "hand"

hemihedral "half the faces" from ημι (*hemi*) "half" + εδρον (*edron*) "seat, base, or face"

http://cabierta.uchile.cl/revista/3/chiral1.jpg

Enantiomorphic pairs of low quartz (α-SiO₂) crystals
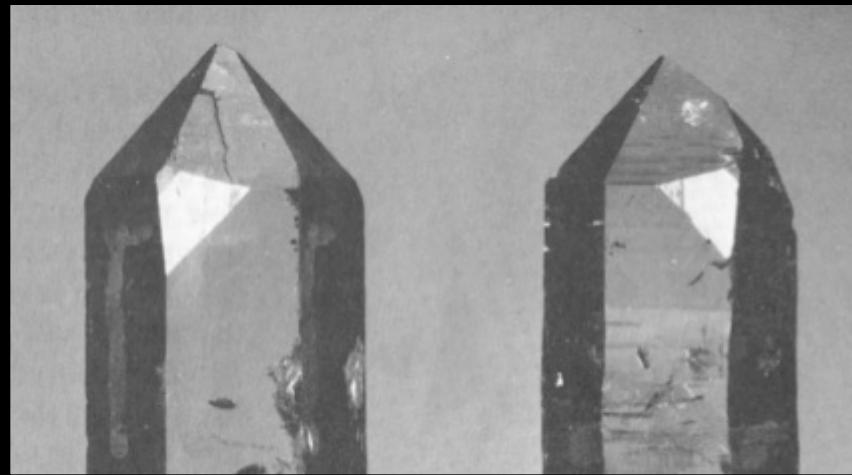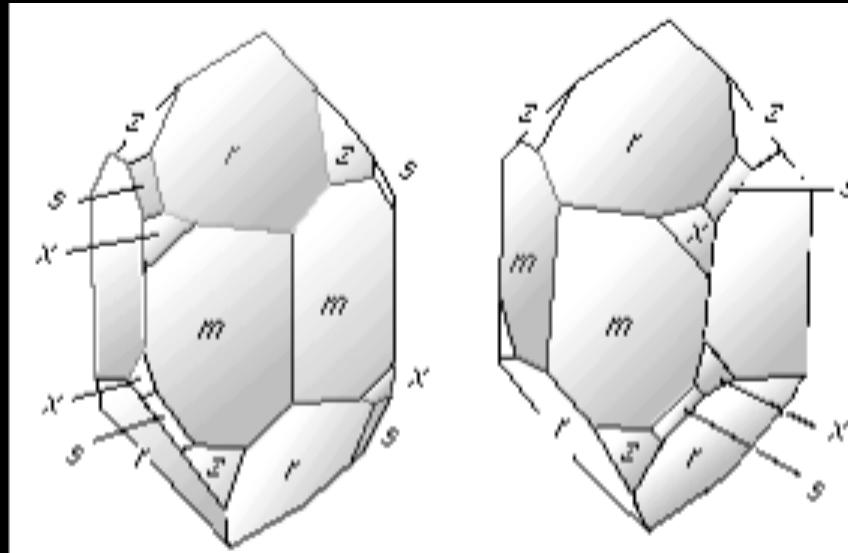
left-handed
dextro-rotatory

right-handed
levo-rotatory

(Photograph from Vladimir Prelog's Chemistry Nobel Lecture in 1975)

Enantiomorphic pair of sodium ammonium tartrate crystals
$Na^+NH_4^+[^{(-)}O_2C-CH(OH)-CH(OH)-CO_2^{(-)}]^{2-}$

à la Louis Pasteur (1849)
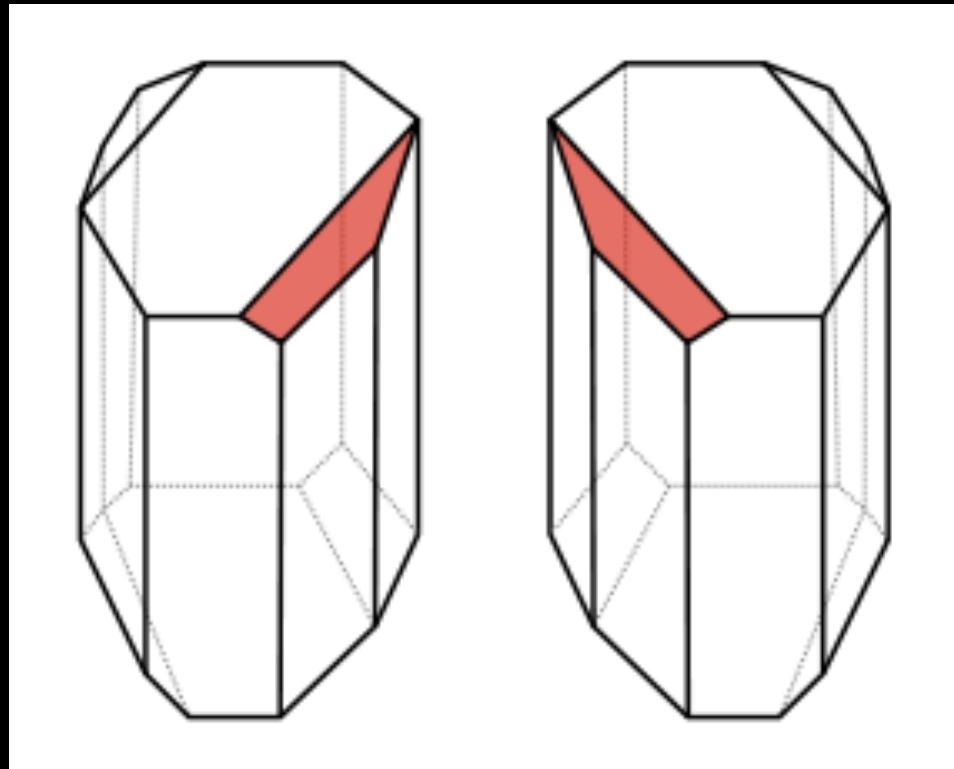
The "cornerstones" of systematic stereochemistry

Charles W. Bunn (1964). *Crystals: Their Role in Nature and in Science*. **New York: Academic Press**

http://en.wikipedia.org/wiki/Louis_Pasteur
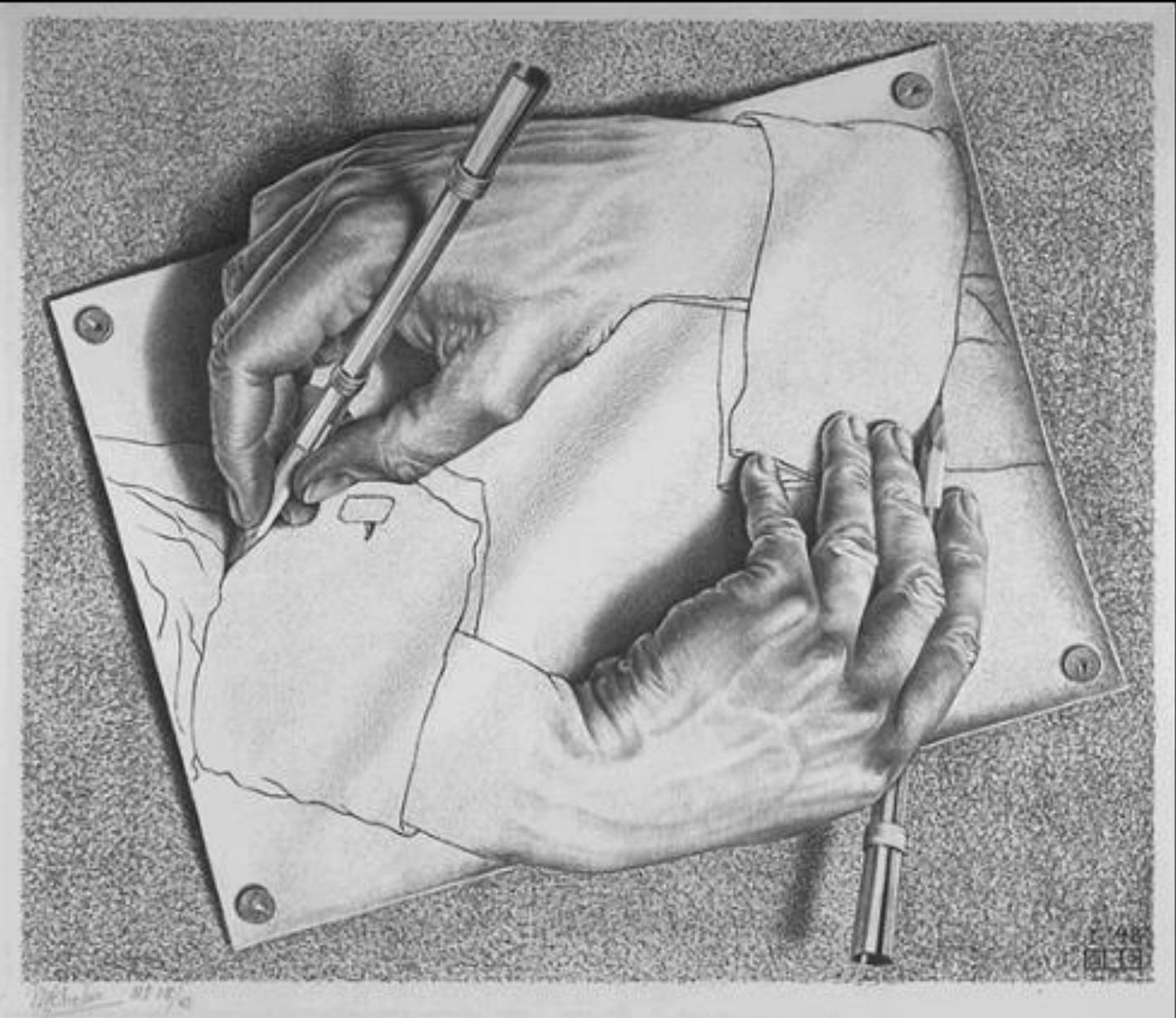
Miller indices (*hkl*) of crystal faces

1. Choose as *crystal axes* three non-coplanar crystal edges or directions. In particular, choose evident symmetry directions.

2. Choose as a *unit plane* or *parametral plane* a crystal face that intersects all three axes.

3. From goniometric measurements of the interfacial angles, deduce the relative lengths *a*, *b*, *c* of the *intercepts* of the parametral plane on the crystal axes, *i.e.*, the *axial* or *parametral ratios* *a* **:** *b* : *c* .

4. Determine the intercepts *pa*, *qb*, *rc* of the crystal faces on the crystal axes, where *p*, *q*, and *r* are small integers or infinity. Thence determine the Miller indices (*hkl*) of the crystal faces as the *smallest co-prime integer values* of the *fractions-cleared reciprocals of the intercept multiples*

$$h \propto \frac{1}{p}, \quad k \propto \frac{1}{q}, \quad l \propto \frac{1}{r}.$$

Different observers might choose different crystal axes and parametral planes and hence determine different internally consistent sets of indices.

Miller indices of crystal faces
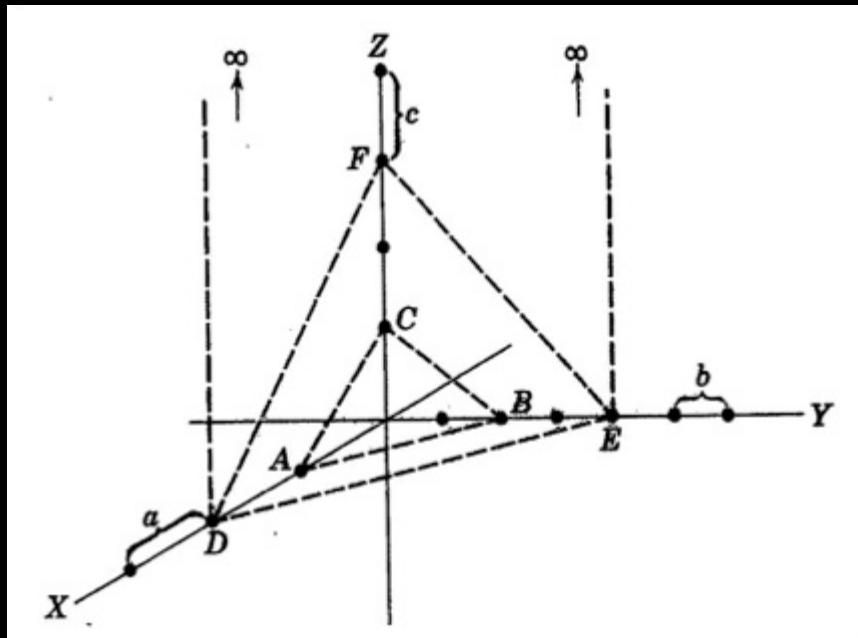
Face	Intercepts	Reciprocals of Intercept Multiples	Cleared of Fractions	Miller Indices (hkl)
ABC	$1a : 2b : 1c$	$\frac{1}{1} \frac{1}{2} \frac{1}{1}$	2 1 2	(212)
DEF	$2a : 4b : 3c$	$\frac{1}{2} \frac{1}{4} \frac{1}{3}$	6 3 4	(634)
$DE\infty$	$2a : 4b : \infty c$	$\frac{1}{2} \frac{1}{4} \frac{1}{\infty}$	2 1 0	(210)

Harold P. Klug and Leroy E. Alexander (1974). *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*. New York: John Wiley.

In Fig. 59, *ABC*, *DBC* and *DBE* represent the slopes of three faces in a crystal the structural unit of which, with edges of lengths
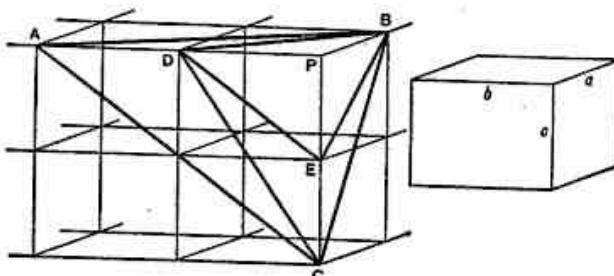
FIG. 59.

a, *b*, *c*, is represented on the right of the figure. Suppose that, for this particular substance, the ratios *a* : *b* : *c* of the actual unit =0·816 : 1 : 0·924. (It is customary to express the ratio *a* : *b* : *c* in the form *a/b* : 1 : *c/b*, reducing *b* to unity.)

The first observer selects the plane *ABC* as parametral plane; he therefore assigns to it the index 111. From its slope in relation to the three axial directions he would determine *axial ratios* of values *BP* : *AP* : *CP*, 0·408 : 1 : 0·924.

The index of the plane *DBC* is $\frac{BP}{BP} \frac{AP}{DP} \frac{CP}{CP}$, i.e. 121.

" " " *DBE* is $\frac{BP}{BP} \frac{AP}{DP} \frac{CP}{EP}$, i.e. 122.

The second observer selects the plane *DBC* as 111, and hence calculates axial ratios *BP* : *DP* : *CP*, 0·816 : 1 : 1·848.

The index of the plane *ABC* is $\frac{BP}{BP} \frac{DP}{AP} \frac{CP}{CP}$, 1½1, i.e. 212.

" " " *DBE* is $\frac{BP}{BP} \frac{DP}{DP} \frac{CP}{EP}$, i.e. 112.

To the third observer, *DBE* seems the best choice as 111. His calculated axial ratios, *BP* : *DP* : *EP* =0·816 : 1 : 0·924, are actually those of the edges *a* : *b* : *c* of the structural unit.

The index of the plane *ABC* is $\frac{BP}{BP} \frac{DP}{AP} \frac{EP}{CP}$, 1½½, i.e. 211.

" " " *DBC* is $\frac{BP}{BP} \frac{DP}{DP} \frac{EP}{CP}$·1½, 1, 221. i.e.

Tabulating these results, we have three correct but different descriptions of the slopes of the three planes present on the crystal:

		Axial ratios	Indices of planes		
			ABC	DBC	DBE
Observer 1	-	0·408 : 1 : 0·924	111	121	122
Observer 2	-	0·816 : 1 : 1·848	212	111	112
Observer 3	-	0·816 : 1 : 0·924	211	221	111

Each description illustrates the rationality (and the simplicity) of the indices, but only when we have advanced so far that we can determine the exact arrangement of the internal structure, and hence the absolute lengths of the edges *a*, *b*, *c* of the unit of structure, could we say that the description given by observer 3 is preferable to those offered by observers 1 and 2.

It is clear, also, that the rationality lies only in the *ratios of intercepts* on corresponding axes, and there is no rational relationship between the intercepts on different axes unless by chance the symmetry of the system permits the choice of a symmetrically-situated plane as parametral plane. Hence the name *Law of Rational Intercepts* sometimes used is particularly misleading; it can be corrected by writing *Law of Rational Ratios of Intercepts*, but as a ratio of intercepts defines an index the correct name of the Law is that which we have used above.

Finally, it must be observed that there is nothing in this discussion which determines the relative dimensions of the whole crystal; we have been concerned only with the slopes of faces, and the habit of the crystal is in no way necessarily related to the units of measurement *a b c* which determine these slopes. All these points will be much clearer when we have been able to practise making accurate drawings of crystals.

"The second law of crystallography"

The Law of Rational Indices
(Haüy, 1784)

The faces of a crystal have indices (*i.e.*, reciprocals of the face intercepts on the crystallographic axes) that stand in the ratio of small whole numbers.

Abbé René-Just Haüy
(1743-1822)
making goniometric
measurements on a
calcite crystal

A well-developed
$(NH_4)_2SO_4$
crystal
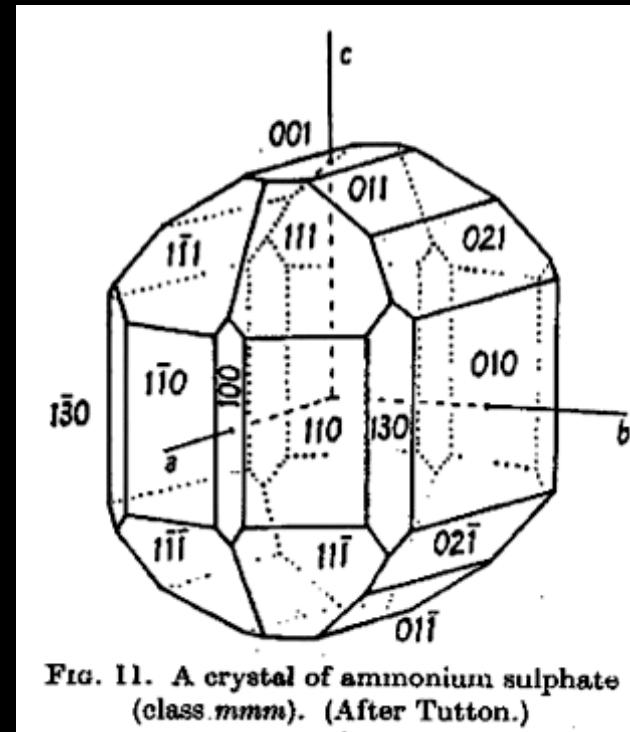
Fig. 11. A crystal of ammonium sulphate (class *mmm*). (After Tutton.)

C.W. Bunn (1961). *Chemical Crystallography*, **2nd ed. Oxford University Press.**

Axial ratios from interfacial angles
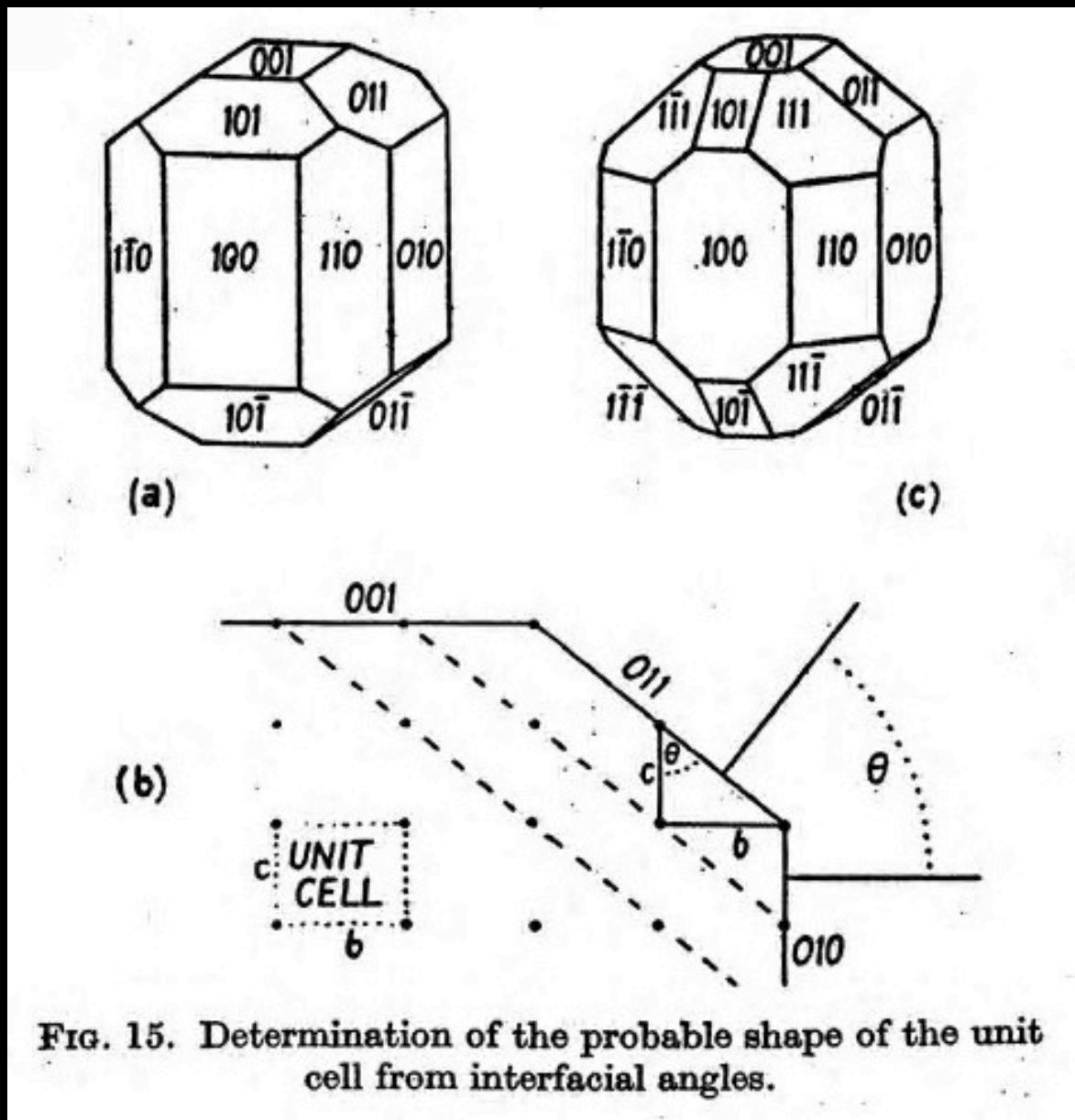
FIG. 15. Determination of the probable shape of the unit cell from interfacial angles.

C.W. Bunn (1961). *Chemical Crystallography*, 2nd ed. Oxford University Press.

Axial ratios from interfacial angles
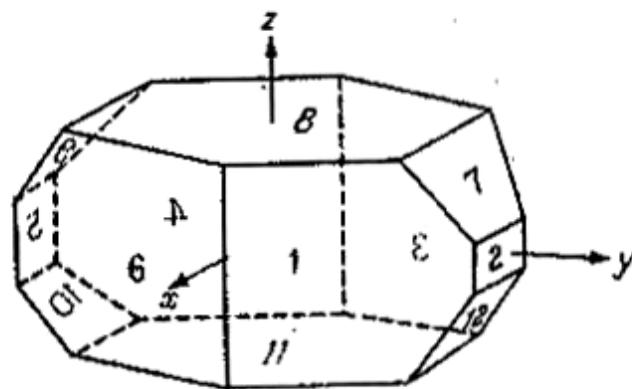
$$\frac{a}{b} = \tan\left(\frac{56°44'}{2}\right) = 0.5399$$
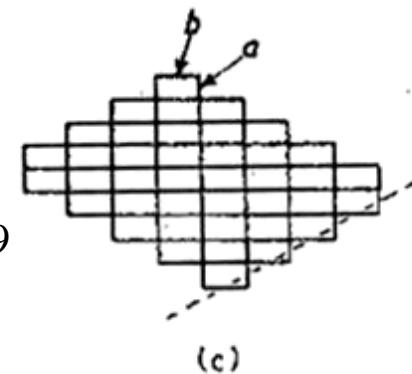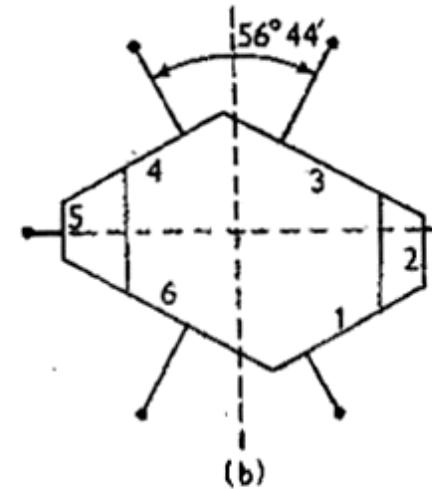
Fig. 2.12(a). Crystal of potassium succinate trihydrate.
Fig. 2.12(b). Crystal of Fig. 2.12(a) seen along z-axis.
Fig. 2.12(c). Simplest axial ratios of unit cell.

Contact goniometer
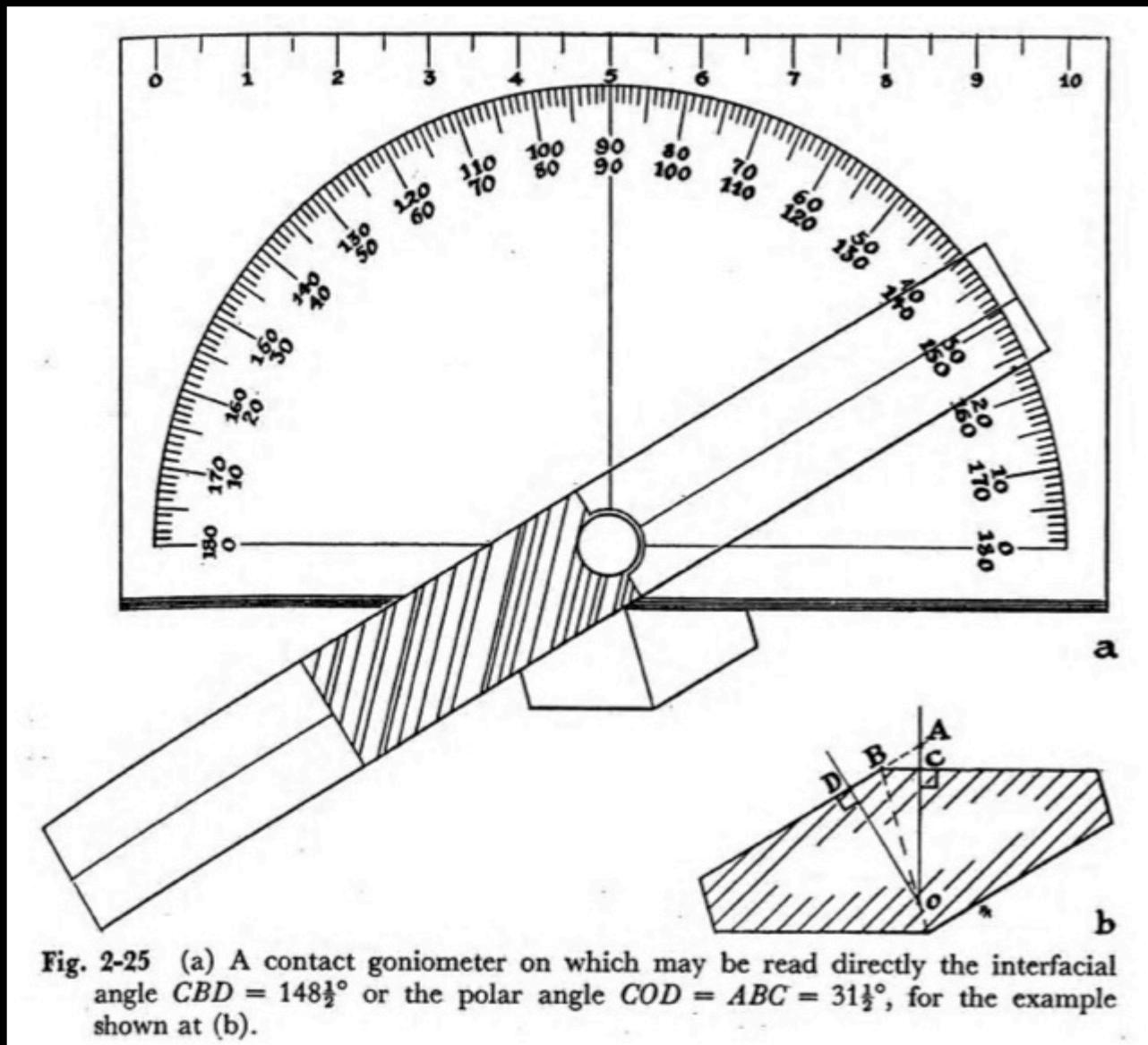
Fig. 2-25 (a) A contact goniometer on which may be read directly the interfacial angle $CBD = 148\frac{1}{2}°$ or the polar angle $COD = ABC = 31\frac{1}{2}°$, for the example shown at (b).

L.G. Berry and Brian Mason (1959). *Mineralogy*. San Francisco: W.H. Freeman & Co.

Optical goniometer

telescope for reading vertical circle

straight slides for locating specimen

curved slides for orienting specimen

telescope collimator

light source

tangent screw

horizontal circle

leveling screw

telescope for reading horizontal circle

eyepiece for examining crystal faces
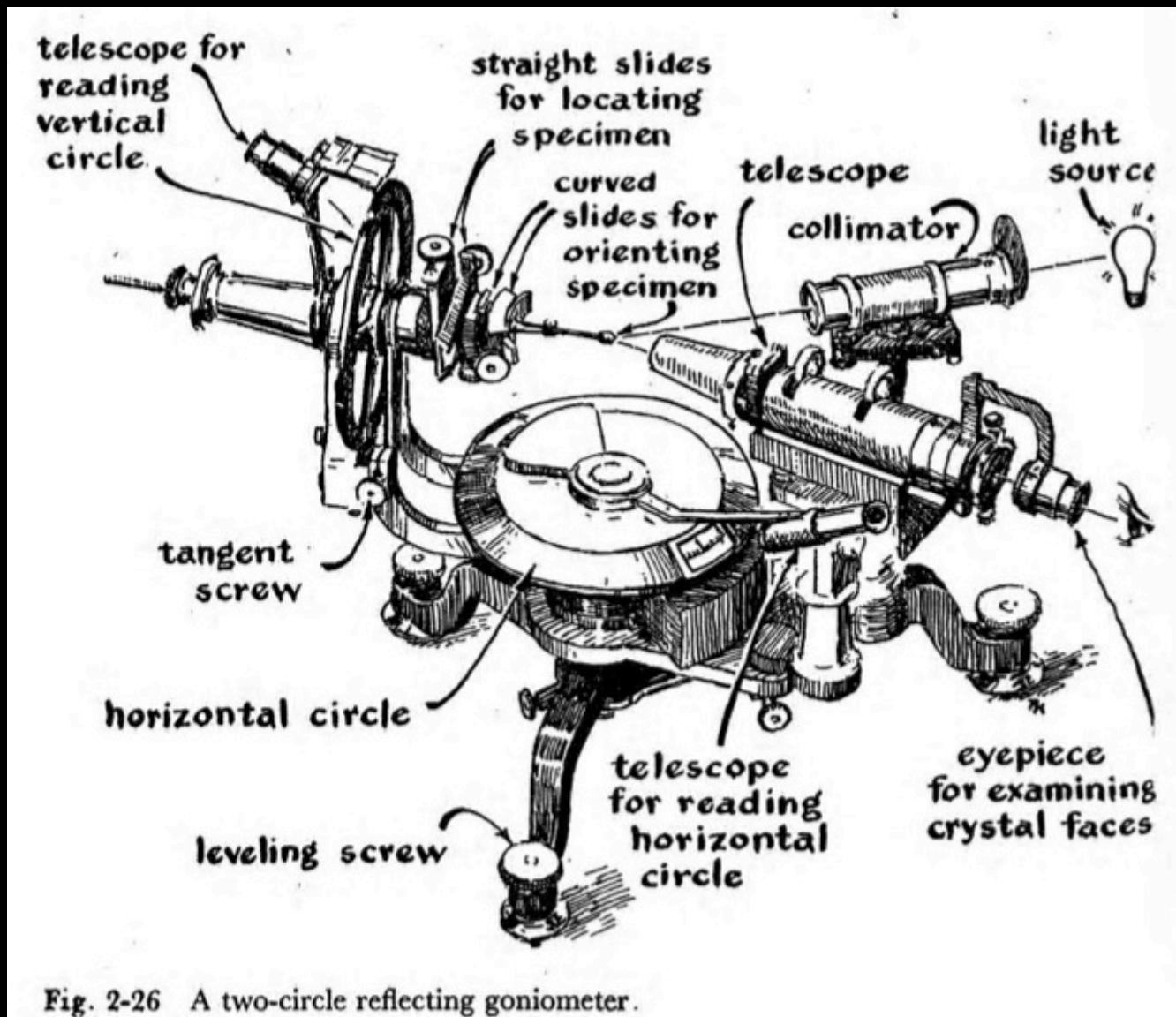
Fig. 2-26 A two-circle reflecting goniometer.

(a)

(b)

(c)
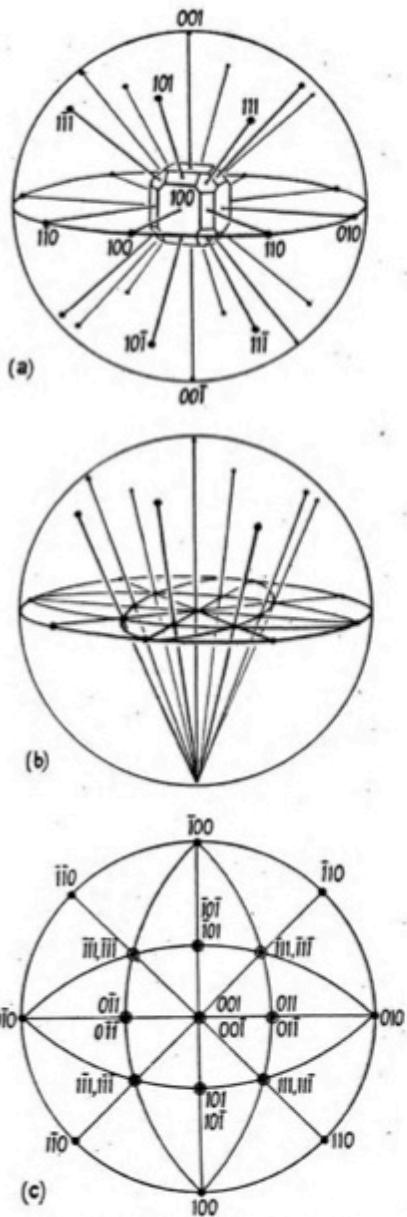
FIG. 14. The stereographic projection.
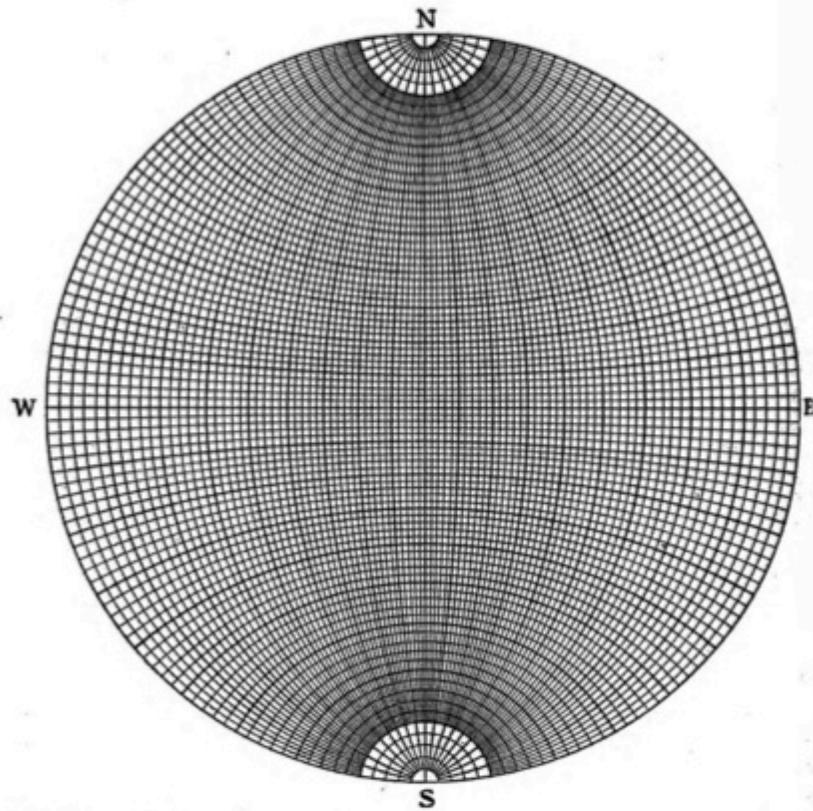
Fig. 2-19 A Wulff net. Stereographically projected great circles appear as lines of equal longitude, and small circles centered about the north and south poles appear as lines of equal latitude at two-degree intervals.

C.W. Bunn (1961). *Chemical Crystallography*, 2nd ed. Oxford University Press.

Paul Heinrich Ritter von Groth
1843-1927

In 1888, Groth was the first to suggest the possibility that spherical atoms reside at equivalent positions of space lattices.

CHEMISCHE

KRYSTALLOGRAPHIE

VON

P. GROTH

ERSTER TEIL

ELEMENTE — ANORGANISCHE VERBINDUNGEN OHNE SALZ-
CHARAKTER — EINFACHE UND COMPLEXE HALOGENIDE,
CYANIDE UND AZIDE DER METALLE, NEBST DEN ZUGE-
HÖRIGEN ALKYLVERBINDUNGEN

MIT 389 TEXTFIGUREN

LEIPZIG

VERLAG VON WILHELM ENGELMANN

1906

NATURAL HISTORY

CHEMISCHE KRYSTALLOGRAPHIE

VON

P. GROTH

Schwefel.

α-Modification (gewöhnlicher rhombischer Schwefel).

Schmelzpunkt 113,0° — 113,5° Muthmann[1]).

Spec. Gew. 2,037 (aus CS_2 kryst.), 2,069 (nat.) Spring[15]),
2,067 » Schrauf[16]),
2,091 » Zehnder[17]).

Rhombisch bipyramidal (natürliche Krystalle sind zuweilen auffallend bi-sphenoïdisch ausgebildet).

$a : b : c = 0,8108 : 1 : 1,9005$ Brežina[18]).

Durch Sublimation gebildete Krystalle sind gewöhnlich sehr flächenreich; hierzu gehören außer den an Vulkanen vorkommenden natürlichen Krystallen die von Ulrich in Rösthaufen der Okerhütte am Harz beobachteten kleinen Krystalle, welche nach Brežina[18]) folgende Formen zeigten (s. Fig. 19): $c\{001\}$, $v\{013\}$, $n\{011\}$, $b\{010\}$, $m\{110\}$, $p\{111\}$, $s\{113\}$, $t\{115\}$, $\omega\{117\}$, $x\{133\}$, $z\{135\}$, $q\{131\}$, $u\{103\}$, $l\{344\}$, $a\{100\}$, $r\{311\}$.

Aus dem Schmelzflusse kann rhombischer Schwefel krystallisieren, wenn jener unter den Umwandlungspunkt (96°) unterkühlt wird. An großen Krystallen des sogenannten Jungfernschwefels, in Rösthaufen entstanden, beobachtete

Fig. 19.

Ulrich[19]) vorherrschend $p\{111\}$, ziemlich groß $n\{011\}$, untergeordnet $s\{113\}$. Auch in anderen Fällen directer Bildung der rhombischen Modification aus dem Schmelzflusse wurden nur flächenarme Krystalle beobachtet, so von Silvestri[20]) die Combination $\{111\}$ $\{011\}$. Künstlich kann man die rhombische Krystallisation in einem unterkühlten Schmelzflusse einleiten durch Berühren mit einem rhombischen Schwefelkrystalle; am leichtesten erhält man sie, wenn man auf einem Objectglase Schwefel theilweise zum Schmelzen bringt, ohne daß er sich in die β-Modification umwandelt, und dann abkühlen läßt, wobei dann die rhombischen Krystalle weiterwachsen (Brauns[4]).

Durch Umwandlung entsteht der rhombische Schwefel als die stabilste Modification aus allen übrigen Modificationen.

Aus Lösungen in Schwefelkohlenstoff, Chloroform, Bromoform u. a. bei gewöhnlicher Temperatur bildet sich $p\{111\}$ (Fig. 20) allein oder wenigstens vorherrschend; bei rascher Krystallisation stabförmige Parallelverwachsungen nach der c-Axe aneinander gereihter Bipyramiden p (Gaubert[21])); bei langsamem Wachstum tritt zu $\{111\}$ häufig hinzu $b\{010\}$, ferner $s\{113\}$, $c\{001\}$, $n\{011\}$ (Fig. 21), aus CS_2 zuweilen auch $m\{110\}$, selten $a\{100\}$. Nach Mitscherlich[10]) erhält man die besten Krystalle, wenn man eine große Quantität Schwefelkohlenstoff darstellt, ca. $^9/_{10}$ davon abdestillirt und den mit Schwefel gesättigten Rest langsam verdunsten läßt. Aus Acetylentetrabromid entstehen nach $c\{001\}$ tafelförmige Krystalle (Gaubert[21]).

Fig. 20.   Fig. 21.

Die aus CS_2 erhaltenen Krystalle wurden von Mitscherlich[22]) und Schrauf[23]) gemessen.

Bei der freiwilligen Zersetzung von Schwefelammoniumlösung bilden sich zuweilen sehr schöne Zwillinge nach $n\{011\}$ oder nach $\{101\}$ in Form langer Prismen, verlängert nach derjenigen Polkante von p, welche durch die Zwillingsebene gerade abgestumpft wird.

Die natürlichen Krystalle, welche teils durch Sublimation, teils durch Zersetzung von H_2S usw. entstanden sind[24]), zeigen außer den bereits angeführten Formen noch: $\{120\}$, $\{130\}$, $\{023\}$, $\{031\}$, $\{101\}$, $\{119\}$, $\{114\}$, $\{337\}$, $\{112\}$, $\{335\}$, $\{553\}$, $\{221\}$, $\{331\}$, $\{551\}$, $\{122\}$, $\{151\}$, $\{315\}$, $\{313\}$. Zwillinge wurden beobachtet nach $\{101\}$, $\{011\}$, $\{110\}$ und $\{111\}$.

11) Tammann, Krystallisieren und Schmelzen, Leipzig 1903, S. 58.
12) Beljankin, Journ. phys. chim. russ. 1901, **33**, 670.
13) Hallopean, Bull. soc. chim. Paris 1899, **21**, 266.
14) Berthier, Traité de essays p. l. voie sèche. Paris 1848, **2**, 89.
15) Spring, Bull. Acad. R. Belg. 1881 (3), **2**, 83. Ber. d. d. chem. Ges. **5**, 854.
16) Schrauf, Zeitschr. f. Krystall. 1887, **12**, 321.
17) Zehnder, Ann. d. Phys. 1904, (4) **15**, 328.
18) Brežina, Sitz.-Ber. Akad. Wien 1869, **60** (I) 539.
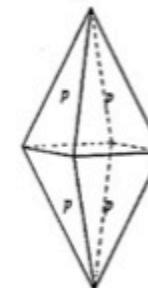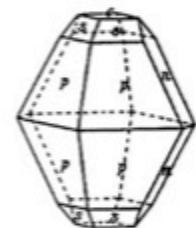
19) Ulrich, Berg- u. hüttenmänn. Zeitung 1854, 97.
20) Silvestri, Gazz. chim. ital. 1873, **3**, 578.
21) Gaubert, Bull. soc. fr. minér. Paris 1905, **28**, 157.
22) Mitscherlich, Abhandl. Berl. Akad. 1822—1823, 43. Ann. chim. phys. 1823, **24**, 264. M.s Werke 189.
23) Schrauf, Sitz.-Ber. Akad. Wien 1860, **41**, 794.
24) Ilosvay, »Über die Bedingungen der Bildung von gediegenem Schwefel«. Földtany Közlöni 1884, **14**, 38, 147; Zeitschr. f. Krystall. **10**, 91.

	Berechnet:	Brežina*):	Mitscherlich:	Schrauf:	Silvestri:
$p:p = (111):(1\bar{1}1) =$	73°26′	—	—	73°32′	73°10′
$p:p = (111):(\bar{1}11) =$	95 0½	—	95° 2′	94 57½	95 0
$p:p = (111):(11\bar{1}) =$	36 40	*36°40′	36 43	36 46	36 14
$n:n = (011):(01\bar{1}) =$	55 30	—	—	55 32	55 25
$v:c = (013):(001) =$	32 21½	*32 25	—	—	—
$w:c = (023):(001) =$	51 43	—	—	—	—
$v:n = (013):(011) =$	29 53½	*29 53½	—	—	—
$n:b = (011):(010) =$	27 45	*27 45	—	—	—
$u:c = (103):(001) =$	38 0	—	—	—	—
$m:m = (110):(1\bar{1}0) =$	78 4	—	—	—	—
$r:a = (311):(100) =$	16 59	16 35	—	—	—
$l:a = (344):(100) =$	50 41½	—	—	—	—
$x:n = (133):(011) =$	19 59½	19 56	—	—	—
$\omega:c = (117):(001) =$	23 19½	23 39	—	—	—
$t:c = (115):(001) =$	31 7	31 5	—	—	—
$s:c = (113):(001) =$	45 10	—	—	—	—
$s:s = (113):(1\bar{1}3) =$	53 3½	—	—	—	—
$s:s = (113):(\bar{1}13) =$	66 50	—	—	—	—
$z:c = (135):(001) =$	50 57½	—	—	—	—
$z:x = (135):(133) =$	13 5½	*13 5½	—	—	—
$x:q = (133):(131) =$	16 44	*16 43½	—	—	—
$q:q = (131):(13\bar{1}) =$	18 25	*18 23	—	—	—

Spaltbarkeit unvollkommen nach $p\{111\}$, $c\{001\}$, $m\{110\}$.

Ebene der opt. Axen $b\{010\}$, c 1. Mittell., Doppelbr. +. Brechungsindices nach Schrauf (Zeitschr. f. Krystall. 1891, 18, 157) bei 20° (bezogen auf den leeren Raum):

Li:	$\alpha = 1,93975$	$\beta = 2,01709$	$\gamma = 2,21578$
Na:	1,95791	2,03770	2,24516
Tl:	1,97638	2,05865	2,27545

$2V = 68°58′ (Na)$, $68°46′ (Tl)$.

Vorstehende Werte, ferner die Ausdehnung durch die Wärme und die Diëlektricitätsconstanten wurden an natürlichen Schwefelkrystallen bestimmt (s. Hintze, Handb. d. Min. 1, 72).

β-Modification (monokliner Schwefel).

Schmelzp. 119,4° — 119,8° (Muthmann[1]).
Spec. Gew. 1,958 (Deville[25]),
       1,915 bei 103° (Zehnder[17]).
Aus Schmelzfluß; meßbare Krystalle nur bei sehr großen Mengen, Mitscherlich[22].

Protein crystals are not perfect inside

Figure 3-11 **Atomic force microscope images of crystal growth.** (Panel A) The atomic force microscope images of the 001 surface of glucose isomerase show the two most common growth patterns observed in crystal growth: step growth starting from 2-dimensional nucleation islands (A, left image) and a double-spiral growth pattern (A, right image). Panel B shows formation of supercritical 2-dimensional nuclei on the 001 surface of cytomegalovirus (CMV), a member of the herpes virus family. As indicated by the arrows, in this case only two virions (B, left image) suffice to generate a critical nucleus from which new step growth commences (B, right image). Images courtesy of Alexander McPherson and Aaron Greenwood, University of California, Irvine.

Figure 3-12 **Growth of a real mosaic crystal.** The schematic drawing shows a crystal growing in a solution of protein molecules (blue spheres). Small impurities (red) and some larger detritus (green squares) are also present in the solution. New molecules attach preferentially to steps and edges (red arrows) and we can recognize a growth defect in the form of a hole; impurities are enclosed at the domain boundaries; and a larger piece of detritus is incorporated at a domain boundary. Individual domains can be substantially misaligned, in this case about 6°; such a highly mosaic crystal would not be useful for diffraction experiments.

**Phenomena of mosaicity and twinning complicate data collection**

http://escher.epfl.ch/rlattice/

*p*1
with
color

*p*3
ignoring
color

p3
with
color

p6
ignoring
color

http://www.mcescher.com/

*p*1

*p*1
square

http://www.meta-library.net/cqmedia/esch-body.html
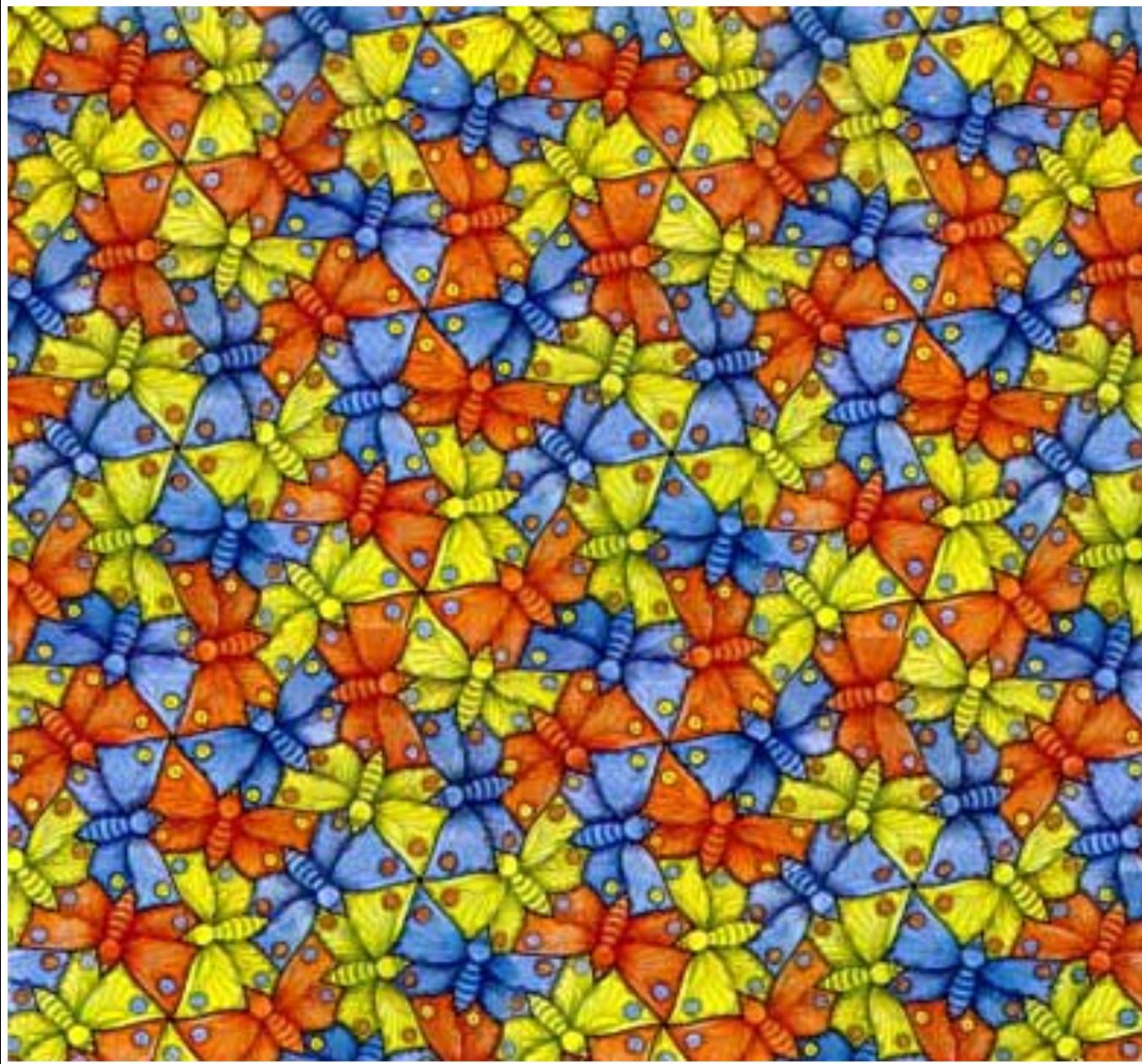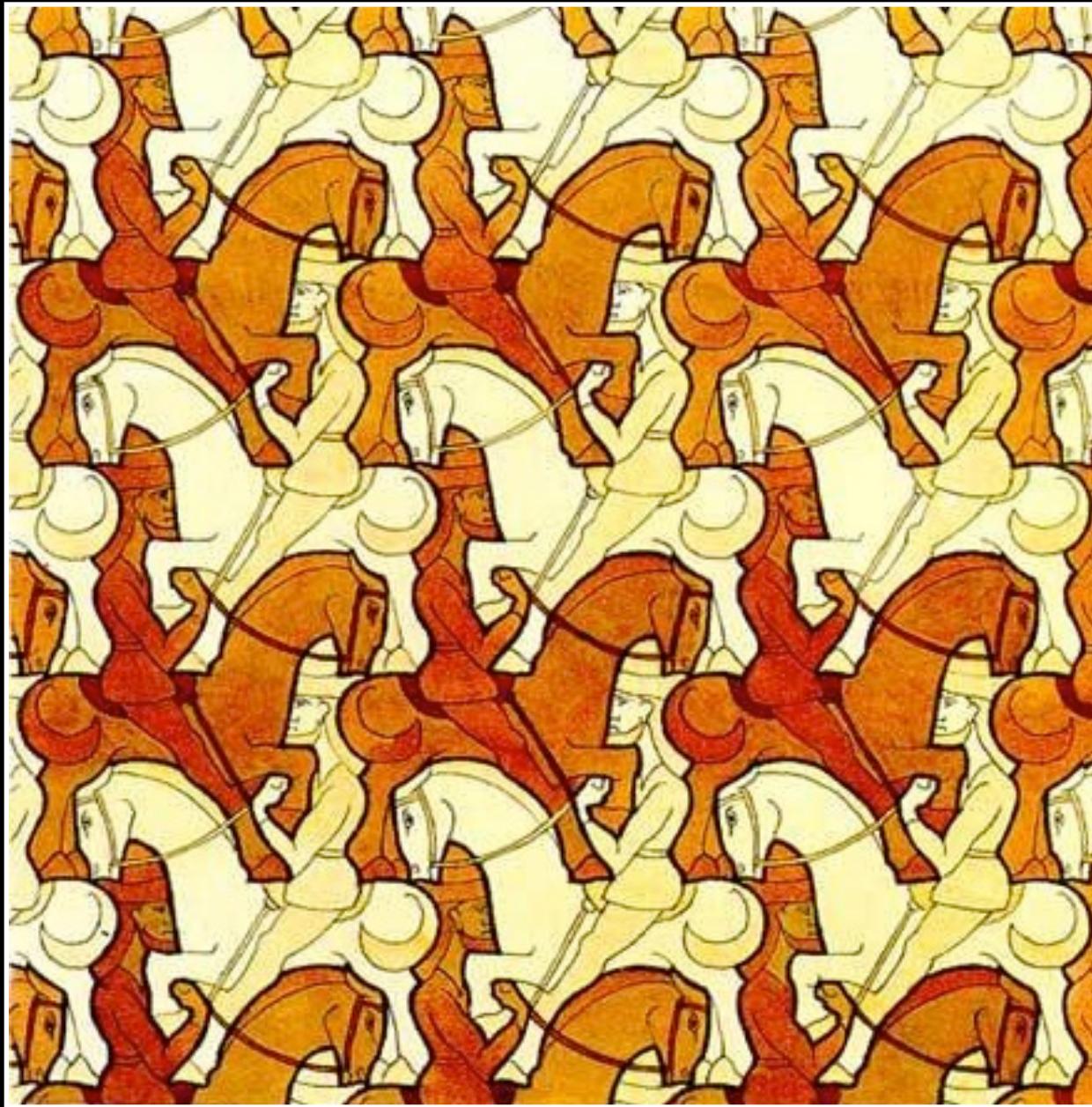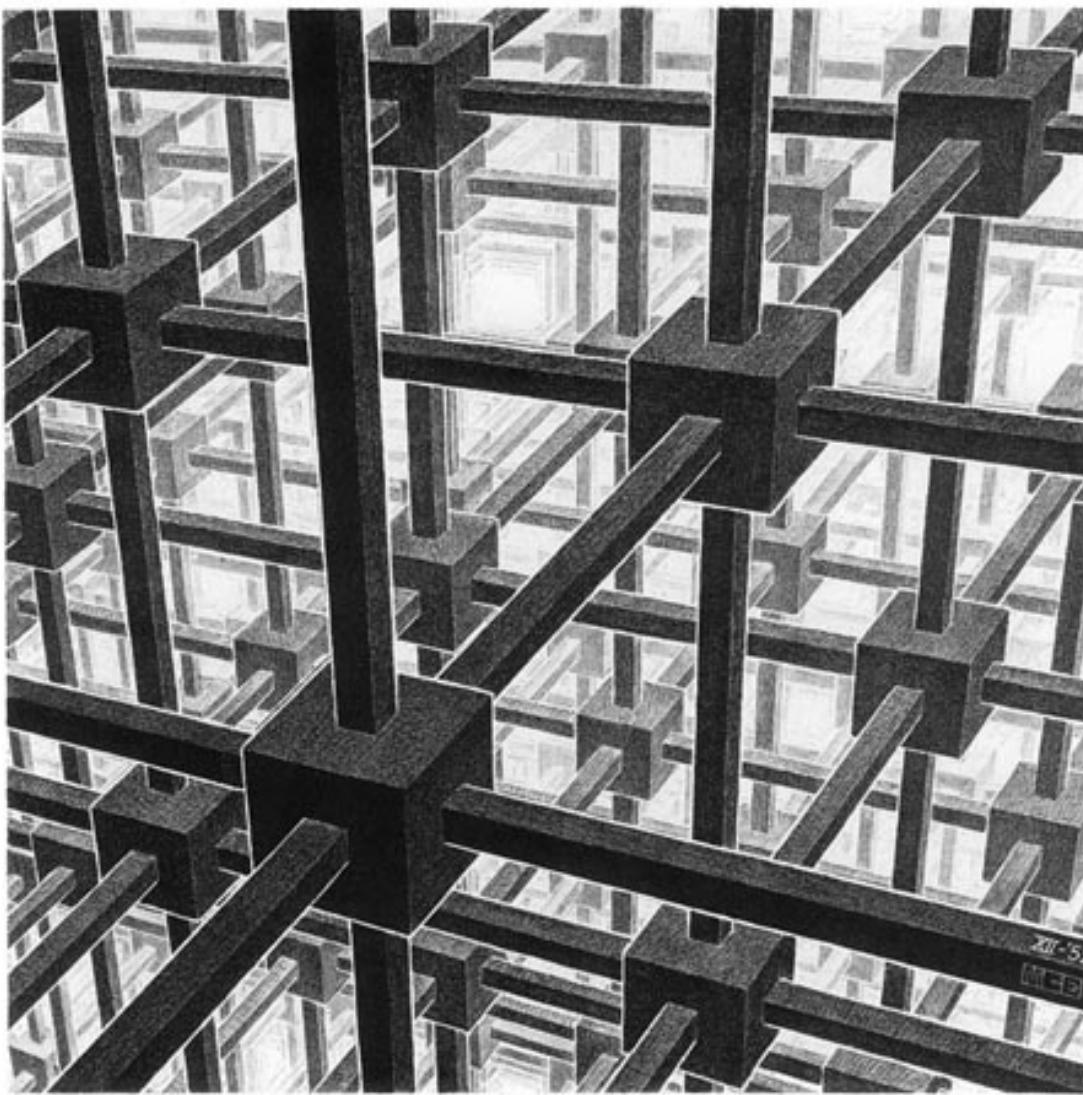
M.C. Escher (1955). Depth

Crystallographic point groups of protein multimers

Goodsell & Olsen (2000). *Ann. Rev. Biophys. Biomol. Struct.* **29**, 105.

λ

$\vec{k}_0 = \dfrac{\hat{s}_0}{\lambda}$

$\Delta\varphi$

$\vec{k} = \dfrac{\hat{s}}{\lambda}$

θ

d_{hkl}

$hkl = 120$

b

a

$\sin\theta_{hkl} = \dfrac{\lambda}{2d_{hkl}}$

(

Alexander McPherson (2003). *Introduction to Macromolecular Crystallography.* **New York: Wiley-Liss.**

$$\vec{k}_0 = \frac{\hat{s}_0}{\lambda}$$

$$\vec{d}^*_{hkl}$$

$$\vec{k} = \frac{\hat{s}}{\lambda}$$

$\phi = 0$

$d/4 \quad \phi = \pi/2$

$d/2 \quad \phi = \pi$

$3d/4 \quad \phi = 3\pi/2$

$d \quad \phi = 2\pi = 0$

$hkl = 120$

Alexander McPherson (2003). *Introduction to Macromolecular Crystallography.* **New York: Wiley-Liss**

$$\vec{k}_0 = \frac{\hat{s}_0}{\lambda}$$

$$\vec{k} = \frac{\hat{s}}{\lambda}$$

φ

θ

d_{hkl}

$hkl = 120$

$$\sin \theta_{hkl} = \frac{\lambda}{2d_{hkl}}$$

$$\vec{k}_0 = \frac{\hat{s}_0}{\lambda}$$

$$\vec{d}^*_{hkl}$$

$hkl = 120$

$$\vec{k} = \frac{\hat{s}}{\lambda}$$

$\phi = 0$
$d/4 \quad \phi = \pi/2$
$d/2 \quad \phi = \pi$
$3d/4 \quad \phi = 3\pi/2$
$d \quad \phi = 2\pi = 0$

Δd_{hkl}	$\Delta \varphi_{hkl}$
0	0
$d/4$	$\pi/2$
$d/2$	π
$3d/4$	$3\pi/2$
d	2π

Alexander McPherson (2003). *Introduction to Macromolecular Crystallography.* **New York: Wiley-Liss**

Bragg reflection from families of parallel *hkl* lattice planes

$$2d_{hkl}\sin\theta = n\lambda \ , \qquad 2\left(\frac{d_{hkl}}{n}\right)\sin\theta = \lambda \ , \qquad 2d_{nh\,nk\,nl}\sin\theta = \lambda$$
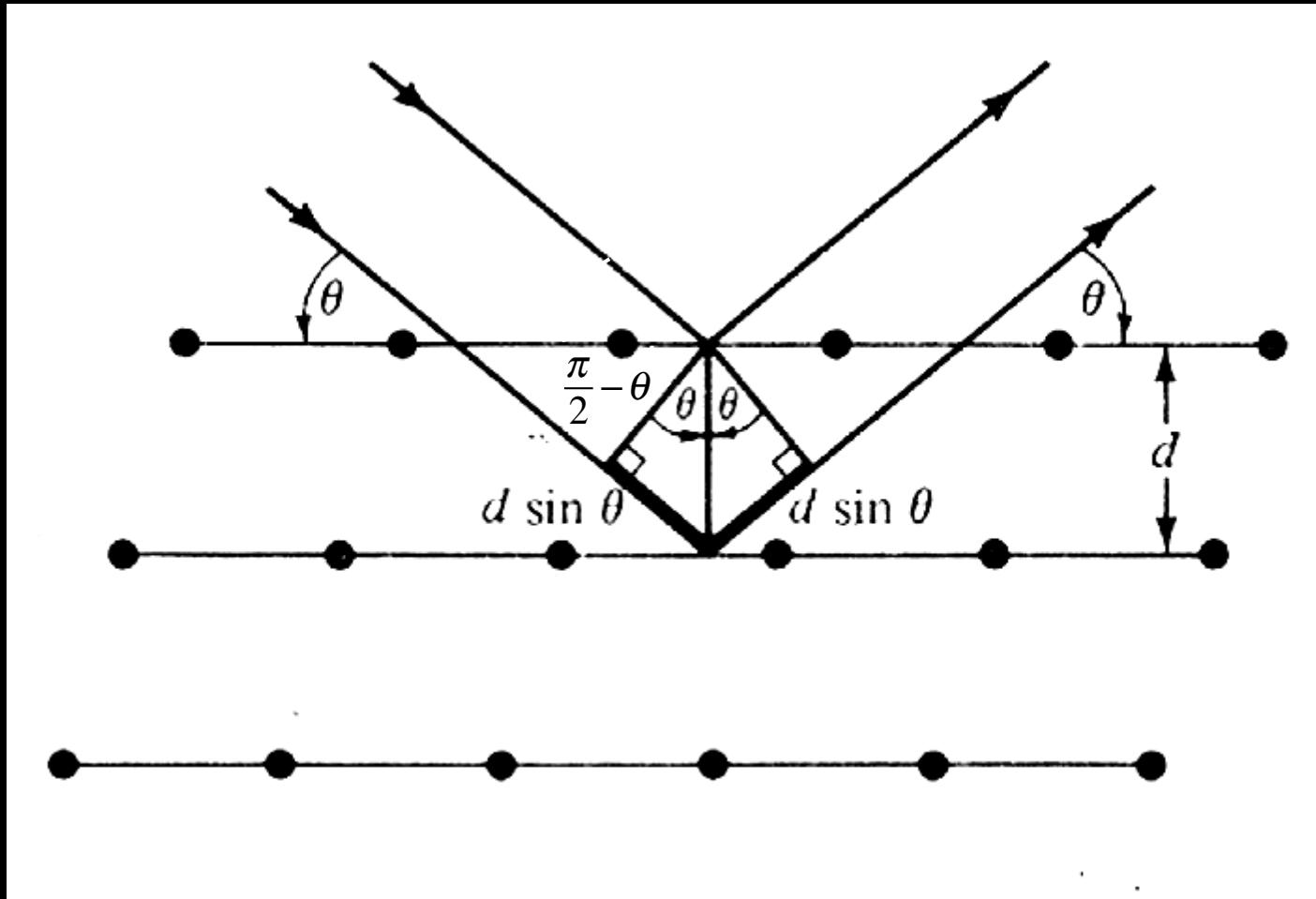
The Ewald construction

θ **Bragg angle**
2θ **Scattering angle**
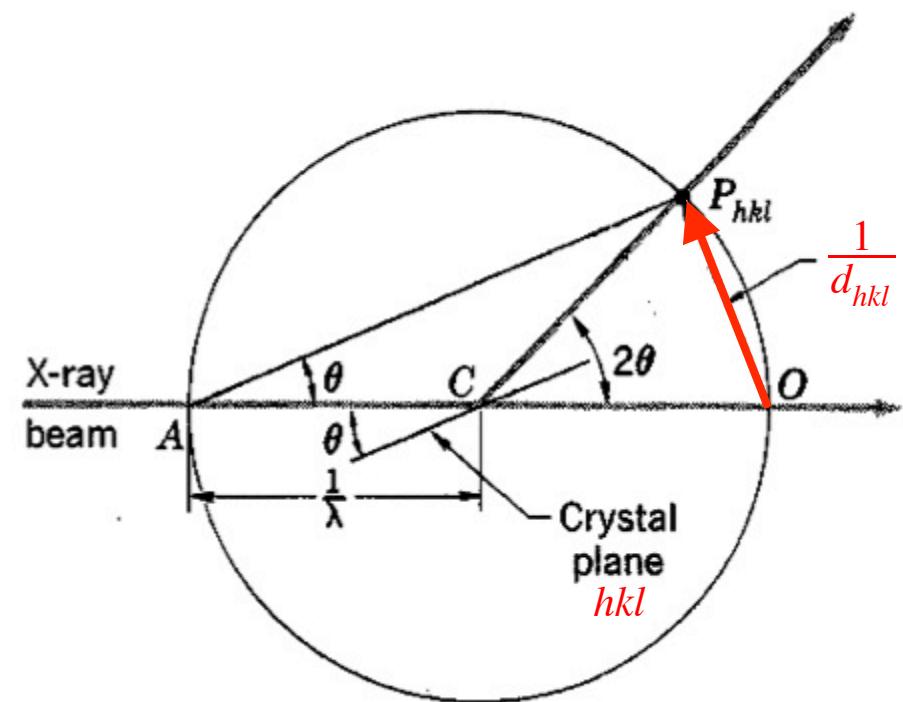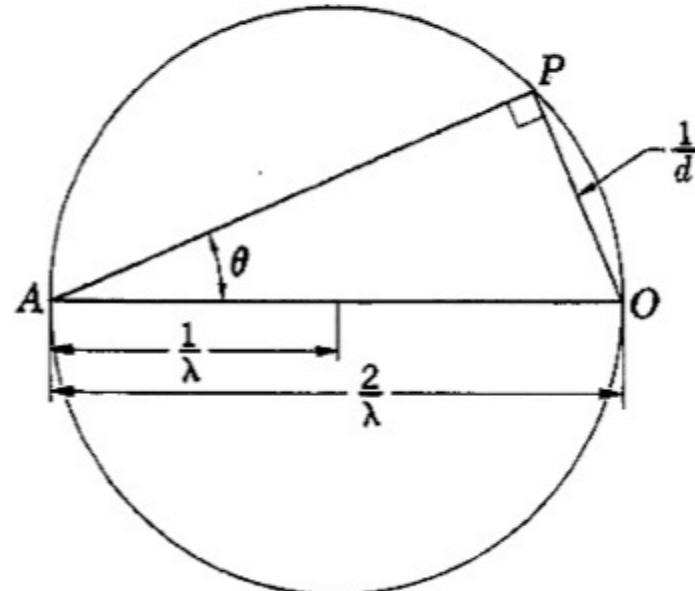
$\begin{cases} \text{Wm. Henry \& Wm. Lawrence Bragg (1913)} & 2d\sin\theta = \lambda \\ \text{Paul Peter Ewald (1913)} & \sin\theta = \dfrac{1}{d}\dfrac{\lambda}{2} = \left(\dfrac{1}{d}\right)\bigg/\left(\dfrac{2}{\lambda}\right) \end{cases}$

Leonid V. Azároff (1968). *Elements of X-ray Crystallography*. **McGraw-Hill Book Co.**

The sum of angles in a plane triangle equals a straight angle.
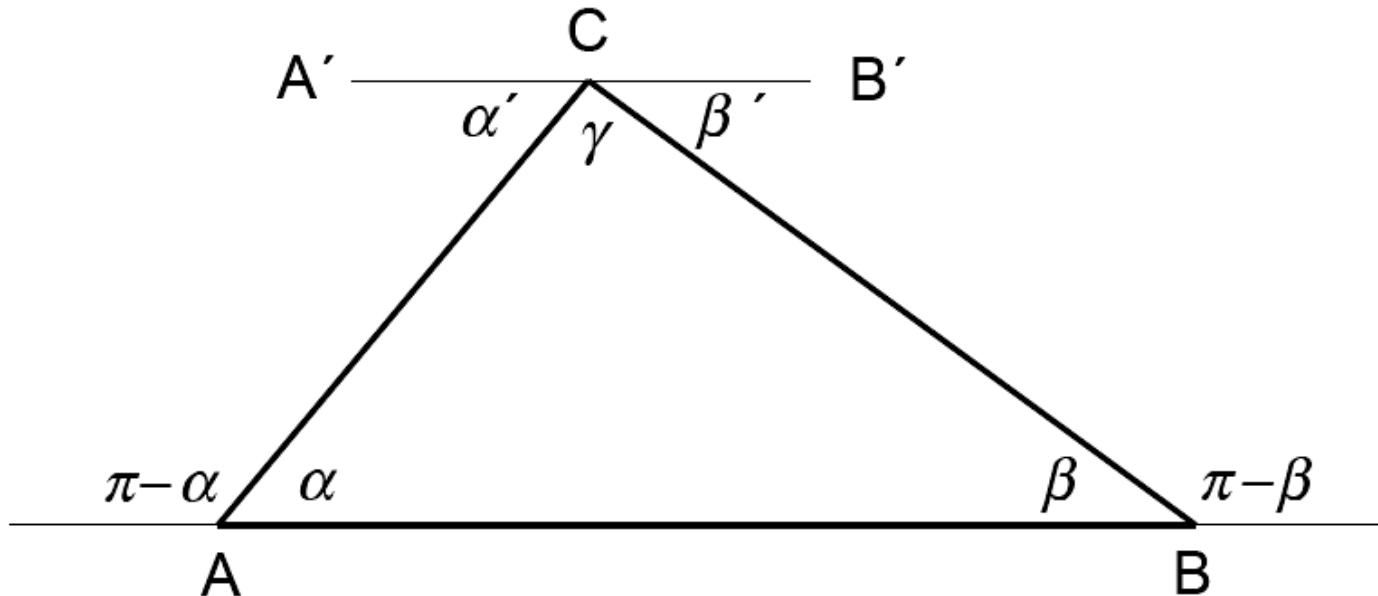
Thales Theorem

**Any angle subtended by the diameter of a circle is a right angle.**

$$\alpha + \beta + (\alpha + \beta) = \pi$$

$$2\alpha + 2\beta = \pi$$

$$\alpha + \beta = \frac{\pi}{2}$$

Crystallographic axes and lattice parameters

FIGURE 2.5. (a) A unit cell showing the axial lengths and interaxial angles. The directions of the axes are given in a right-handed axial system with a along the *x* direction and the angle γ between a and b. As a is moved to b, the screw (b) or thumb (c) proceeds in the *c*-direction, in a right-handed manner.