



nanomat

Nanostructured Materials for Nanotechnology Applications

Materiales Nanoestructurados para Aplicaciones en Nanotecnología

Module 4 -- Characterization I: Physical-Chemical Techniques

X-Ray Diffraction

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Information that can be obtained from diffraction studies (not comprehensive)

Single crystal diffraction:

internal structure of the crystal at atomic resolution -- molecular shape
information about atomic or molecular motion within the crystal
composition

Powder diffraction:

phase identification (qualitative composition analysis)
composition of multi-phase samples (quantitative composition analysis)
phase changes (varying thermodynamic parameters)
degree of crystallinity (*e.g.*, for semicrystalline polymers)
lattice parameters and their changes
strain
particle size
internal structure -- molecular shape

What kind of information can we derive from a diffraction study?



Structure -- the most common use of single-crystal diffraction in research. Structure analysis is broadly classified as "small-molecule structure analysis" or "macromolecular" structure analysis. The latter term is applied to biological macromolecules, mostly proteins. The former term applies to everything else.

Dynamics -- sometimes overlooked, less often reliable, but can be very useful in conjunction with structural information. This is most often a single-crystal diffraction technique.

Composition / phase identification -- more common in powder diffraction, fingerprint techniques, useful in quality control. Compare experimental diffraction with an existing database of diffraction patterns. Applications in chemistry, pharmacology, physics, metallurgy, mineralogy, forensics.



Class (today, 2 hours): Basic principles of diffraction from single crystals and powders.

Lab/demo (4 hours): Powder diffraction, neutron diffraction.

Practical demos on single-crystal and powder diffraction.

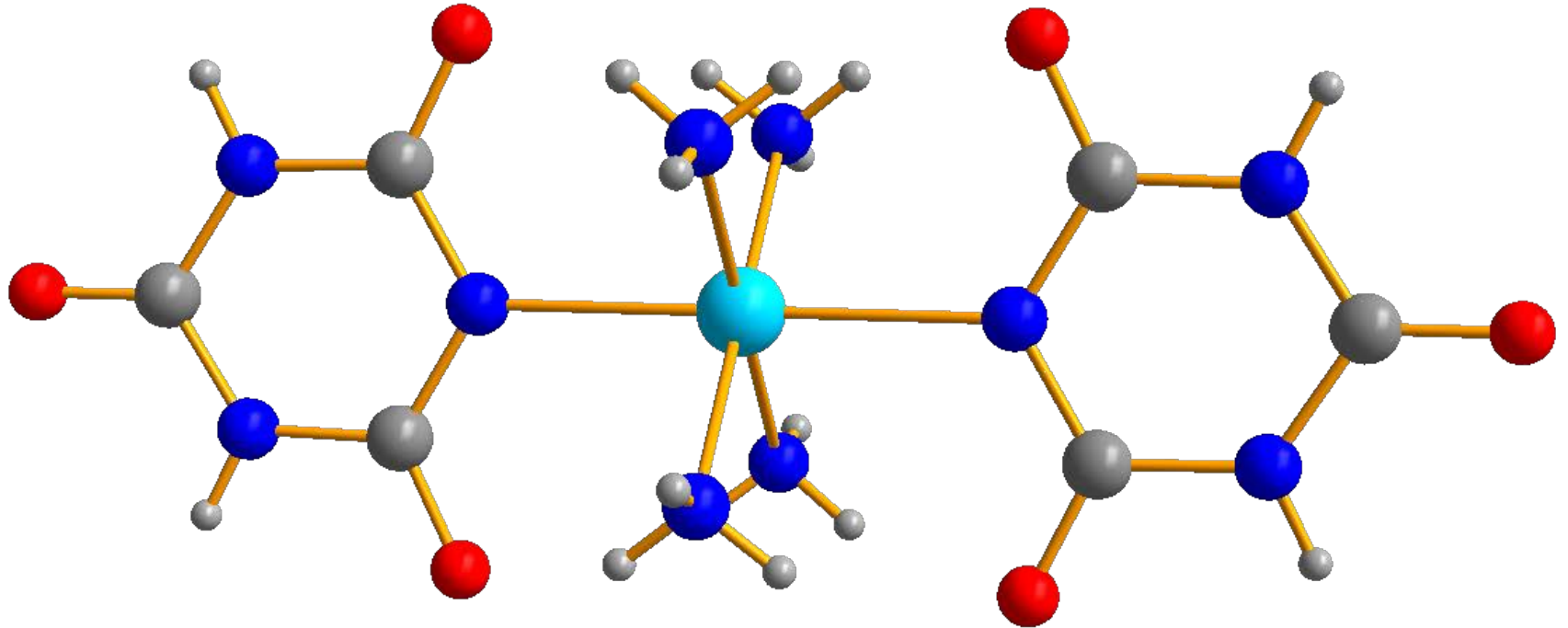
Lab: From 16:00 – 20:00, Friday, 28 February, 2020.

Aula Informatica Mathematics Building

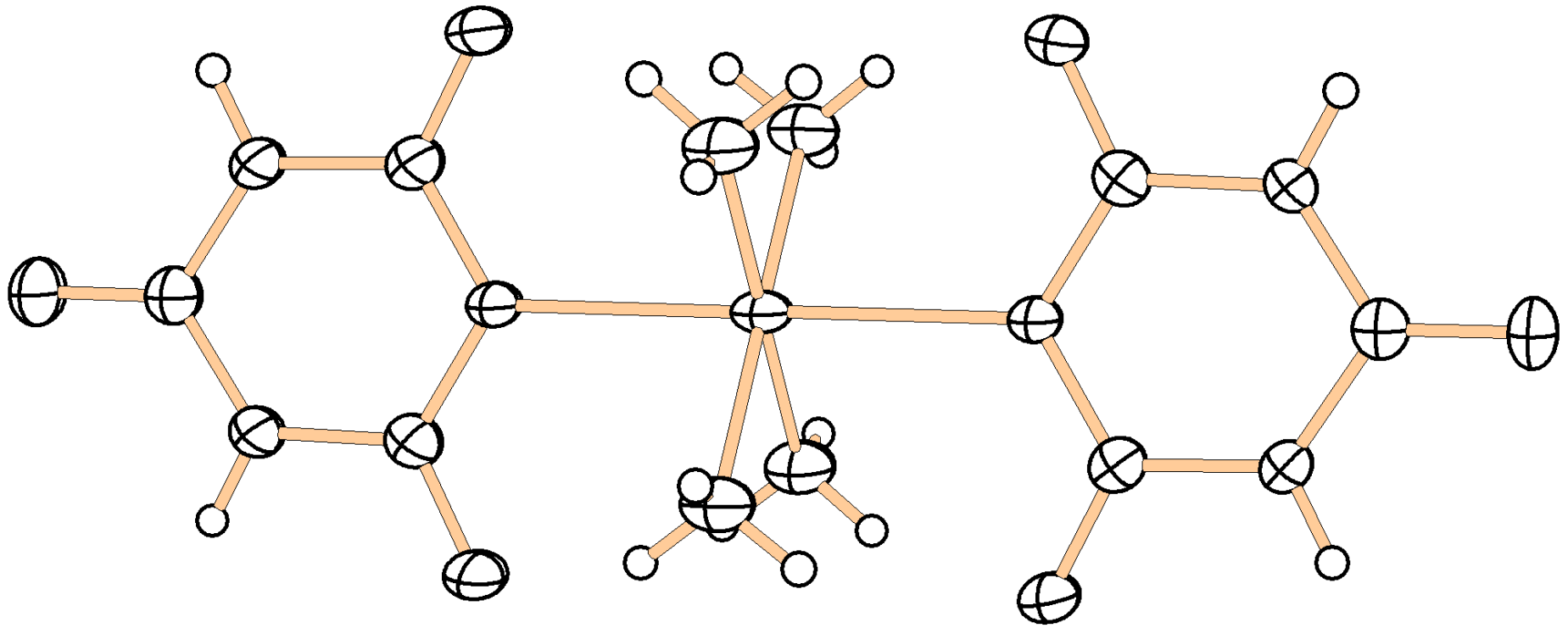
Problems:

Please turn in the problem set by 9 March, 2020.

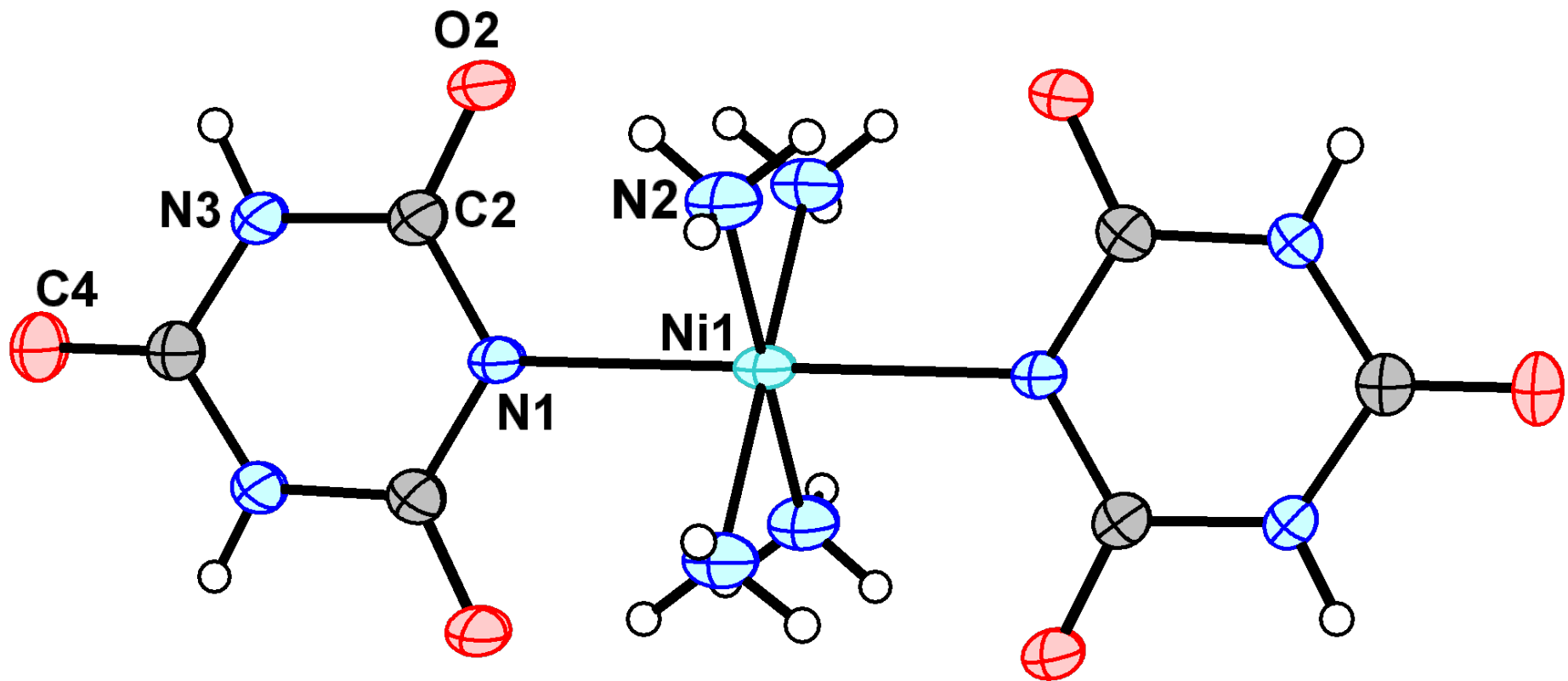
Structural information from single-crystal diffraction analysis -- molecular shape



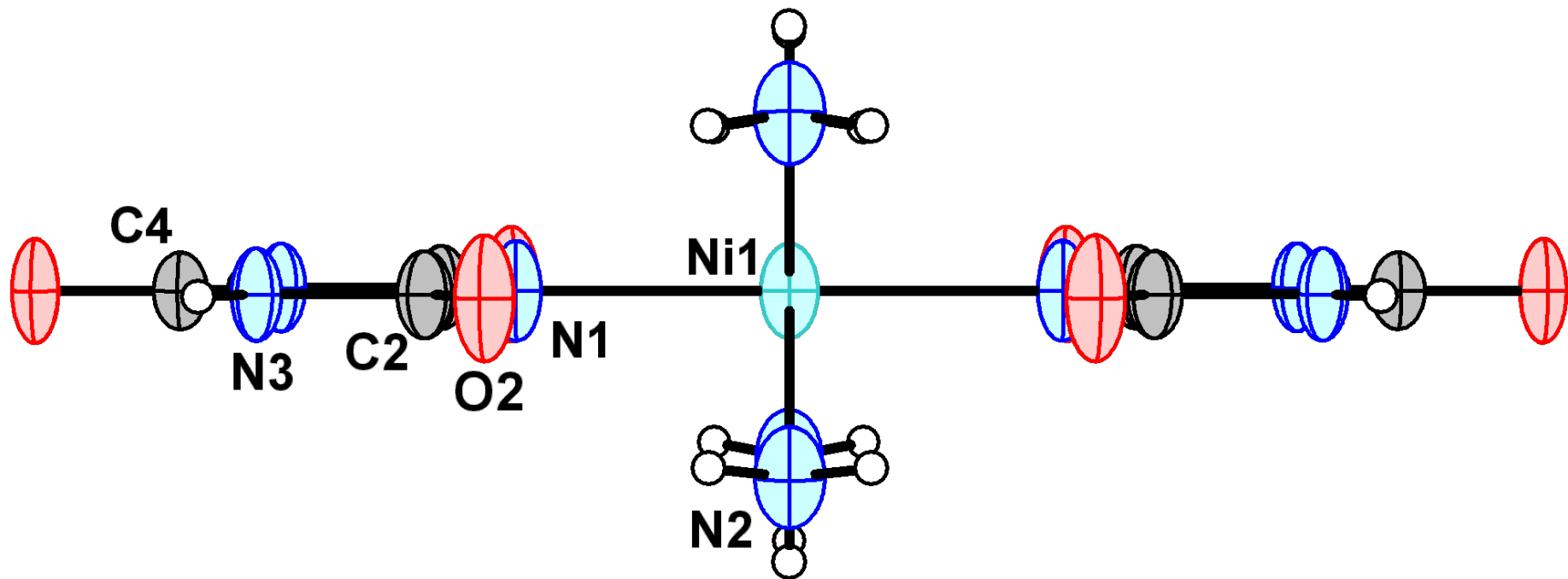
Structural information from single-crystal diffraction analysis -- molecular shape, displacement ellipsoids



Structural information from single-crystal diffraction analysis -- molecular shape, displacement ellipsoids, element types

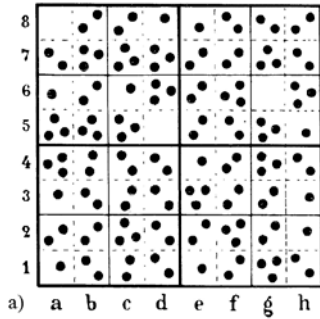


Structural information from single-crystal diffraction analysis -- molecular shape, displacement ellipsoids, element types, nascent phase transition

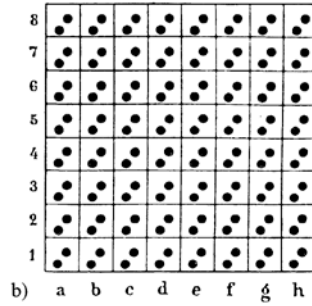


Basic methodology for obtaining this information

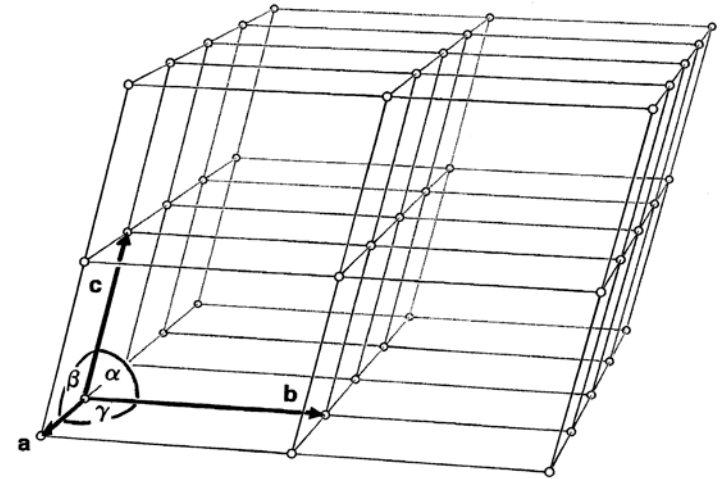
DIFFRACTION -- As used for chemical and materials analysis, requires a periodic structure.(1)



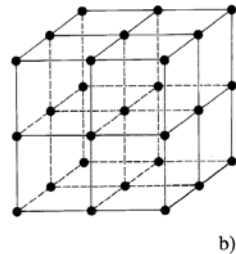
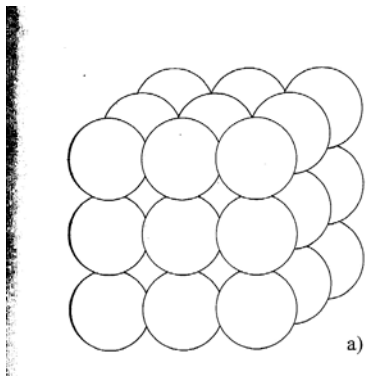
statistically homogeneous
(liquid, gas)



periodically homogeneous
(crystal)



Conventional definition of lattice parameters $a, b, c, \alpha, \beta, \gamma$. Right-handed.



Lattice -- set of "points" equivalent by translation.

Crystallography, 2nd Ed. Walter Borchardt-Ott, tr. Robert O. Gould. Springer, 1995.

Crystal Structure Determination, 2nd Ed. Werner Massa, tr. Robert O. Gould. Springer, 2004.

(1) Extension to sub-periodic structures will be considered at a later point.

In order to understand and to apply diffraction methods, we will need to use some basic crystallographic concepts.

Symmetry

- Crystal systems

- Lattice types

- Point groups and crystal classes

- Space groups

Reference frames

- Direct space or crystal reference frame

- Fractional crystallographic coordinates

- Reciprocal space

Vectors and higher-rank tensors

Transformations

REVIEW -- Crystallographic Concepts



The longstanding concept of a crystal is that of a periodic array of unit cells related to each other by three lattice translations.

There are two conceptual components to the crystal, and from them are derived most of what we need in order to analyze diffraction of radiation by crystals:

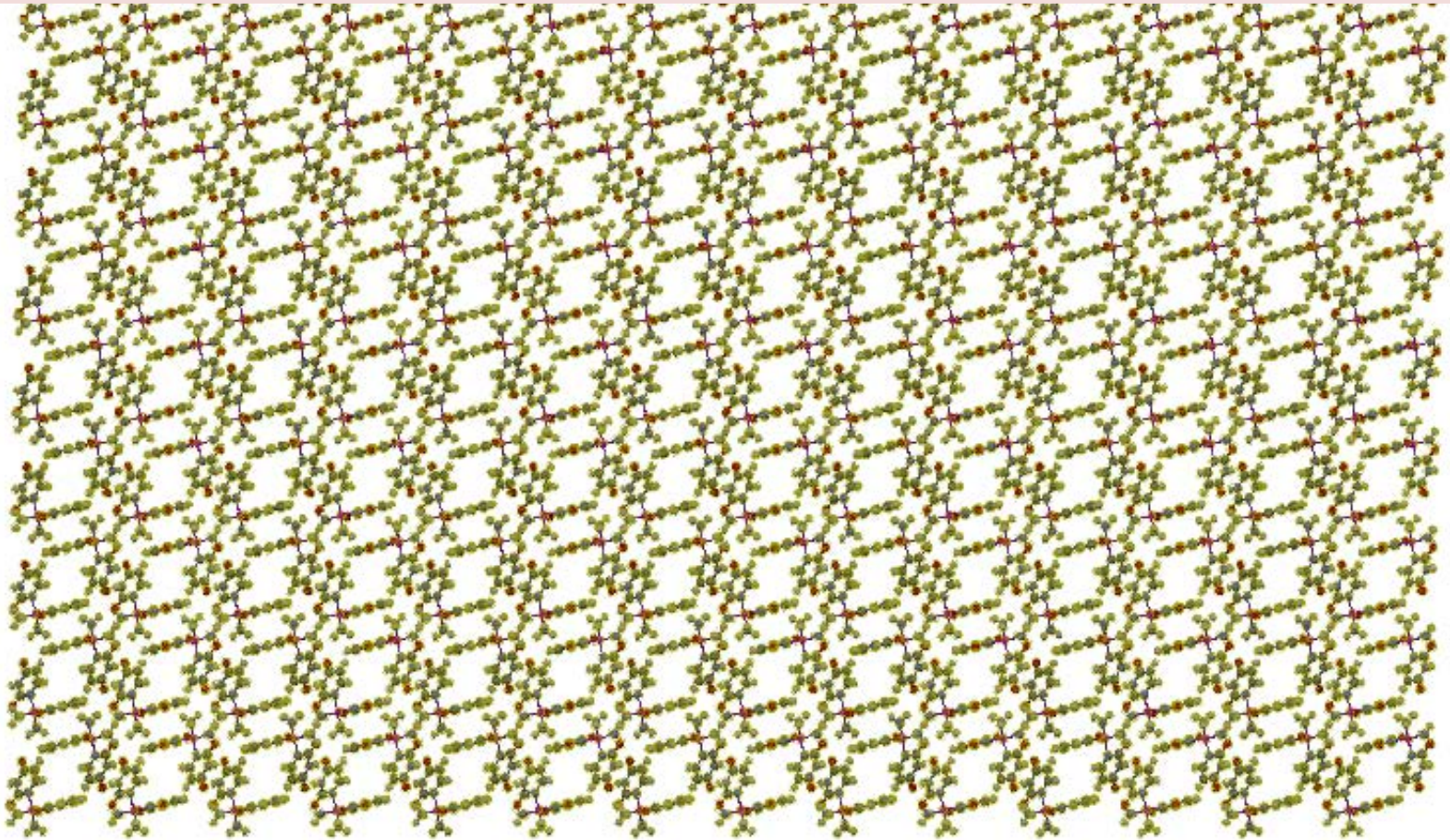
-- The **unit cell**, which is the basic building block of the crystal. It is bounded by a parallelepiped, whose dimensions are the cell constants $a, b, c, \alpha, \beta, \gamma$. Very often the goal of a diffraction analysis is to obtain an accurate description of the contents of one unit cell.

-- The **lattice**, which is the periodicity that relates equivalent points in successive unit cells. Since in the traditional description of a crystal no space is left unfilled, the unit cells are stacked on each other in three dimensions, and the parameters of the lattice are the same as the cell dimensions. The terms "lattice dimensions" and "unit cell dimensions" are usually used interchangeably.

The cell dimensions and the (equivalent) lattice parameters can be given as the six scalar cell constants, or alternatively they can be represented by three vectors **a**, **b**, **c**.

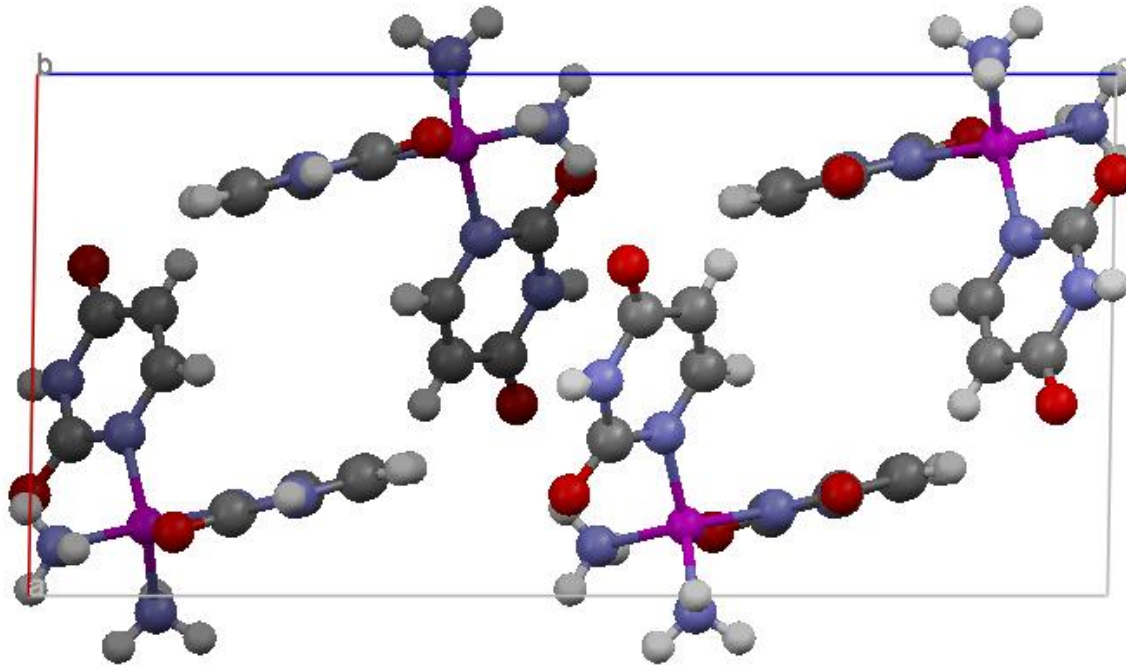
REVIEW -- Crystallographic Concepts

This is a picture of a simple crystal structure. It is clear that in order to understand it we shall have to break its description down into manageable components. Our conceptual division into (1) the contents of one unit cell and (2) the lattice translations that relate successive unit cells, is a useful first step.



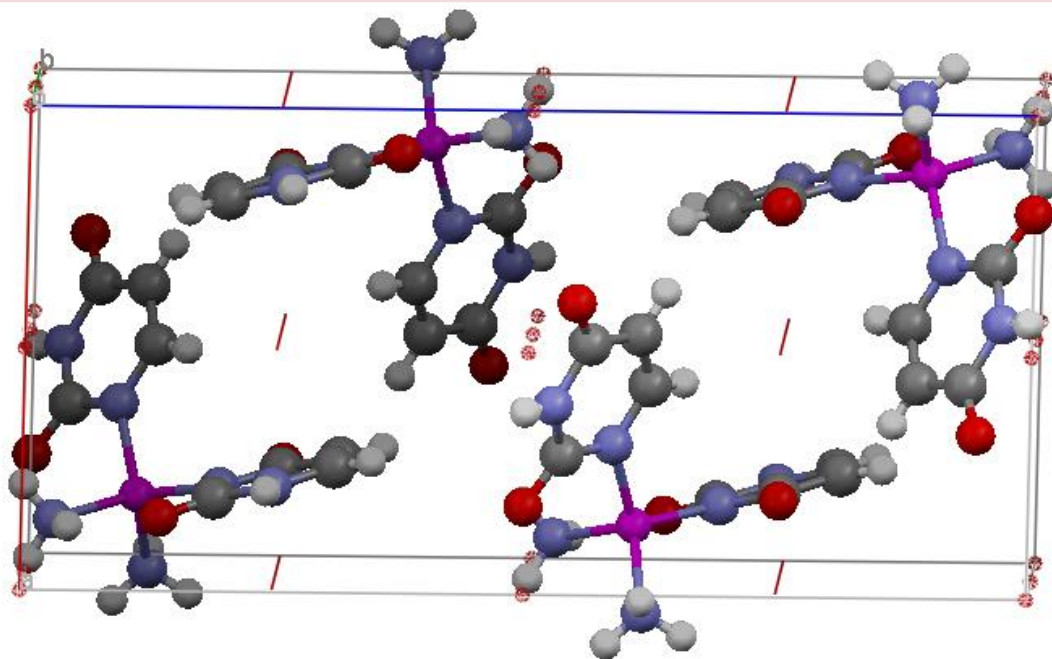
REVIEW -- Crystallographic Concepts

This is the basic pattern -- the unit cell -- that is repeated by translation in three dimensions, in order to form the crystal. The cell is bounded by a parallelepiped that also represents the lattice translations. The contents of the unit cell are four molecules, all chemically identical to each other.



REVIEW -- Crystallographic Concepts

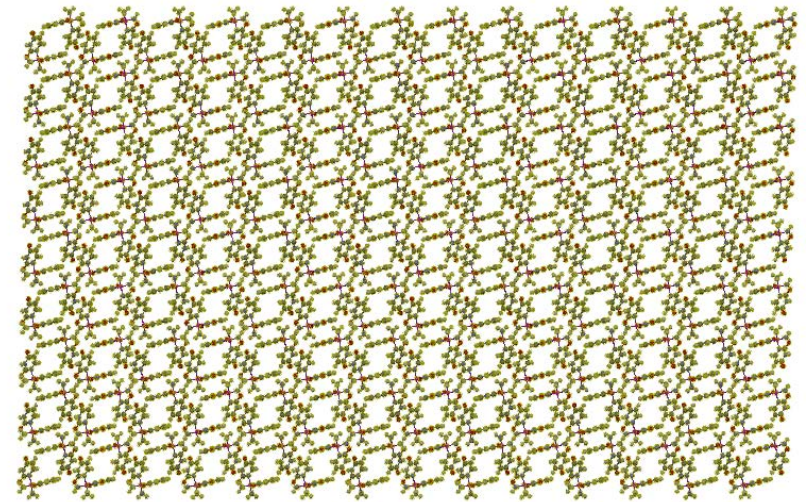
Furthermore, the four molecules in the unit cell are related by symmetry. So our description of the crystal requires (1) the coordinates of all of the atoms of one molecule, (2) the symmetry operations that relate that molecule to the others in the unit cell, and (3) the lattice parameters that relate one unit cell to all the rest.



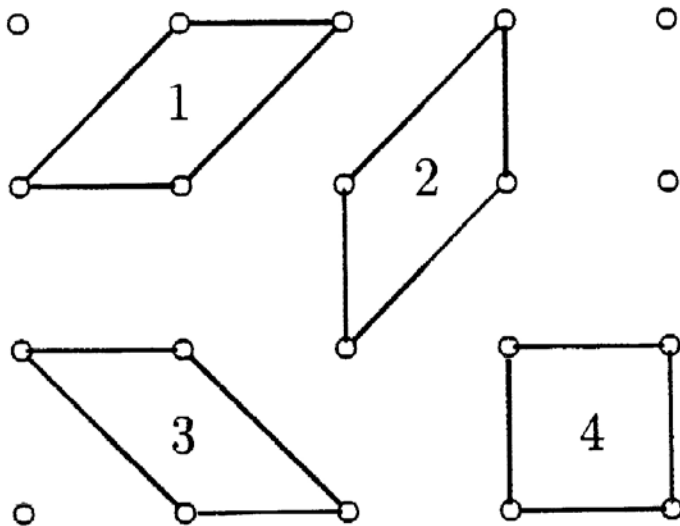
The basic structural unit, or asymmetric unit, does not have to be one molecule. It might be more than one molecule; or if the molecule resides on a point symmetry element, the asymmetric unit can be a fraction of the molecule. The asymmetric unit is the part of the structure that is related by space group symmetry elements to the rest of the contents of one unit cell.

REVIEW -- Crystallographic Concepts. There is more than one way to choose a unit cell for a given crystal.

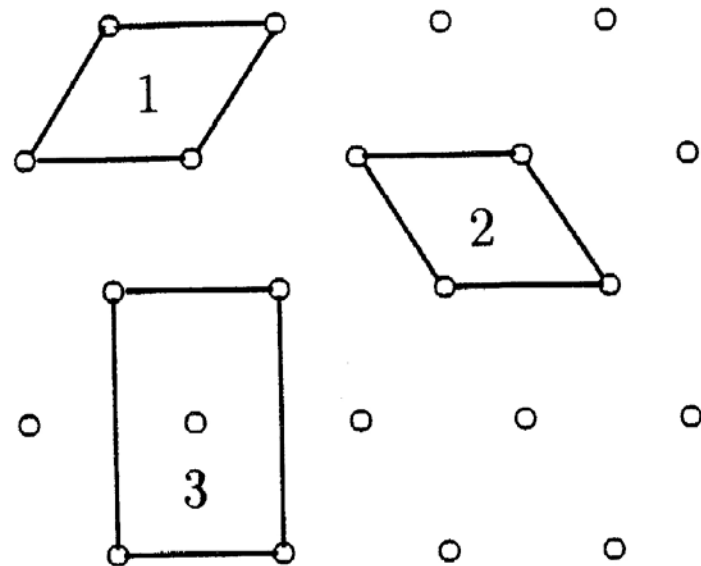
- (a) **Primitive** cell (objective) -- smallest possible volume.
- (b) **Reduced** cell (objective) -- shortest possible axes. This cell is also primitive.
- (c) **Conventional** cell (subjective) -- unit-cell axes aligned with symmetry elements. May be primitive or non-primitive. Corresponds to one of the 14 "**Bravais lattices**."



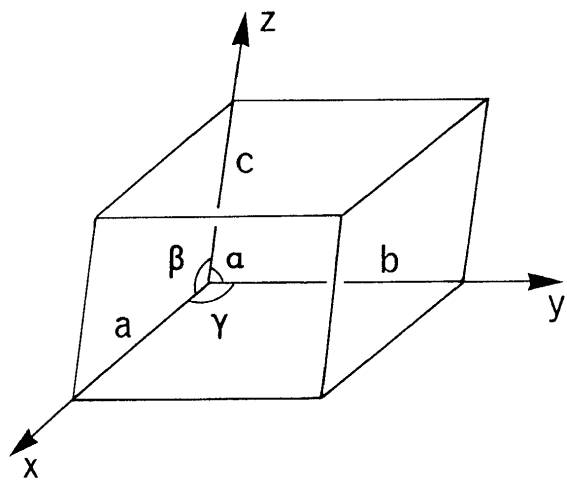
Example 1.



Example 2.



REVIEW -- Crystallographic Concepts. The presence of translational symmetry (in the form of lattice translations) limits the number of rotational symmetries (and their combinations) which can exist in the crystal. Because of this, there are only seven possible symmetry/shape combinations for the unit cell. (But there is no limit on the cell dimensions.) The classification according to the point symmetry of the lattice and the resulting unit-cell shape gives the seven **crystal systems**.(1)



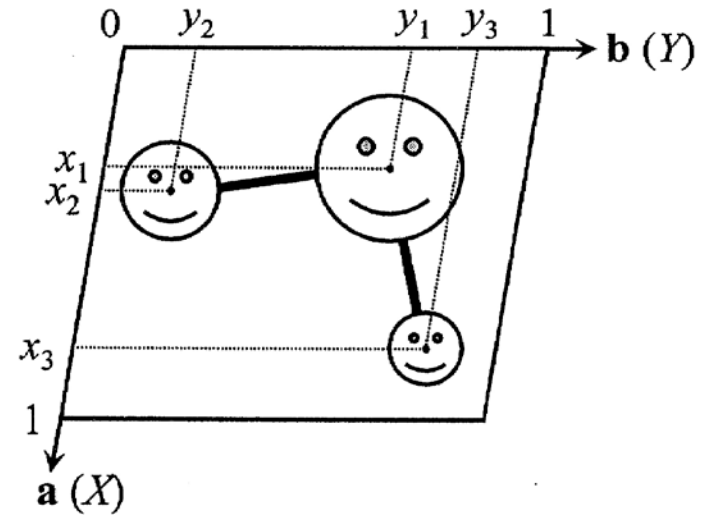
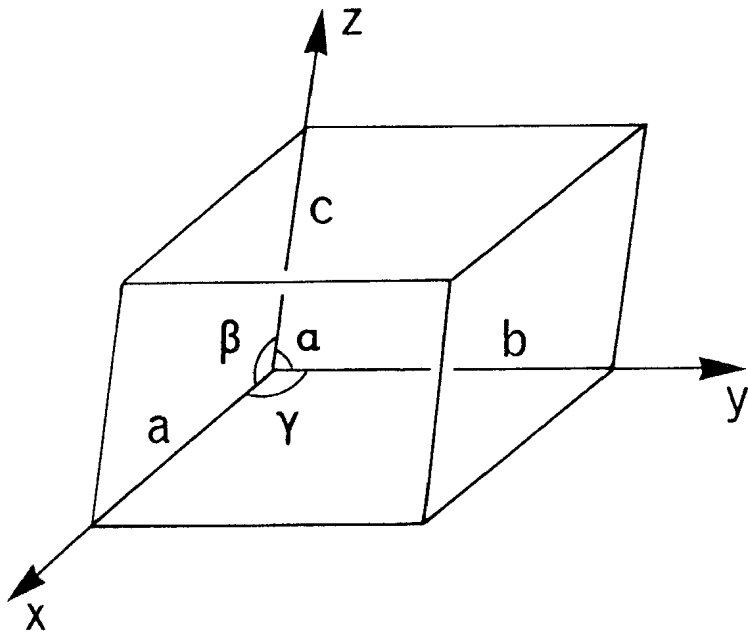
Unit-cell nomenclature.
From *Crystalline Solids*, by
Duncan McKie and
Christine McKie. (Fig. 1.2.)

Restriction in	cell edges	cell angles
triclinic	none	none
monoclinic	none	$\alpha = \gamma = 90^\circ$
orthorhombic	none	$\alpha = \beta = \gamma = 90^\circ$
tetragonal	$a = b$	$\alpha = \beta = \gamma = 90^\circ$
trigonal, hexagonal	$a = b$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

Crystal Structure Determination, 2nd Ed. Werner
Massa, tr. Robert O. Gould. Springer, 2004.

(1) There are alternative classifications of the crystal systems. See, for example, *X-Ray Structure Determination*, G. H. Stout and L. H. Jensen. Some authors define six crystal systems, and others define seven.

Crystal reference frame and fractional crystallographic coordinates



Pecharsky, V. K & Zavalij, P. Y., *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. Springer, 2005. e-ISBN: 0.387-2456-7

The coordinates of any point of interest, usually atomic coordinates, are expressed in terms of a reference system defined by the unit-cell basis vectors **a**, **b**, **c**. The corners of the unit cell have coordinates (0,0,0), (1,0,0), (0,1,0), etc.

Crystallographic Symmetry

Crystallographic symmetry is a full subject in its own right.

In order to be a fluent user of crystallographic symmetry concepts, it is important to know about several diverse topics:

- What symmetry is, in general.
- What symmetry operations can operate on crystalline solids.
- What combinations of symmetry operations are possible in crystalline solids.
- Proper and improper symmetry.
- Point symmetry and translational symmetry.
- "Interactions" among symmetry elements.
- Symmetry groups.
- Graphical symbols used for symmetry elements.
- Textual symbology used for symmetry elements, operators, and coordinates.
- Matrix / vector representation of symmetry operators.
- The *International Tables for Crystallography*. Space group representations.
- How computer programs handle and represent symmetry elements.

- "The Addressable Point"

- The point group table and the isogonality relationships.

Symmetry operations in three-dimensional crystals, and their symbols

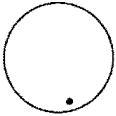
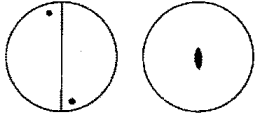
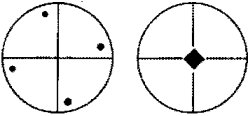
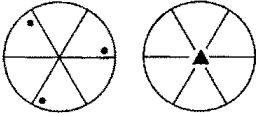
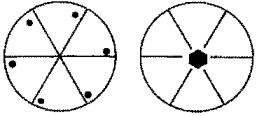
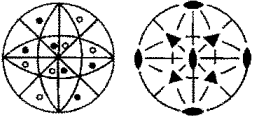
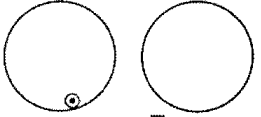
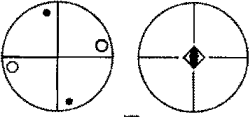
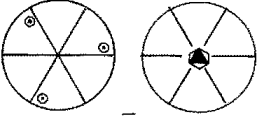
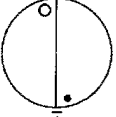
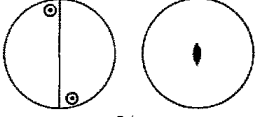
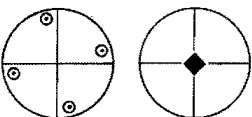
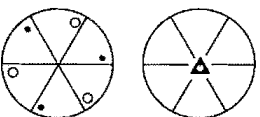
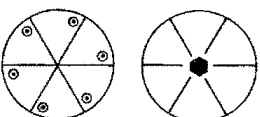
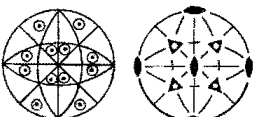
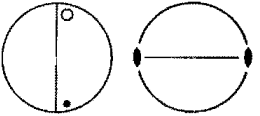
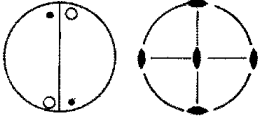
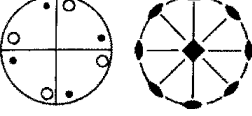
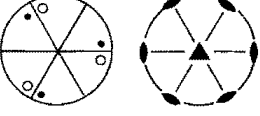
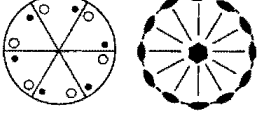
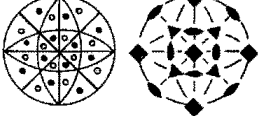
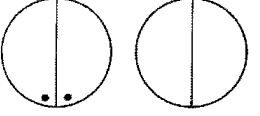
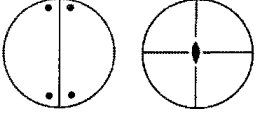
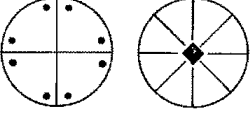
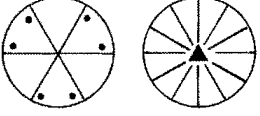
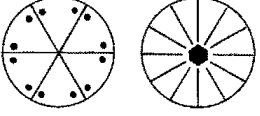
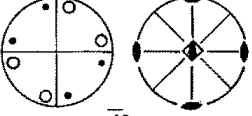
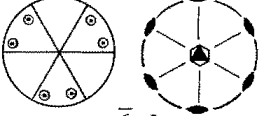
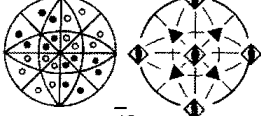

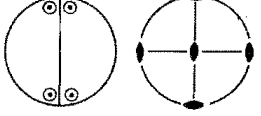

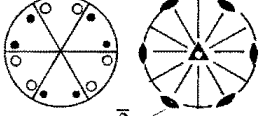
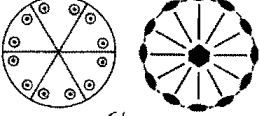
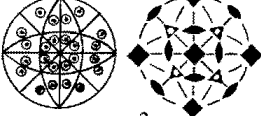


Internal Symmetry of Crystals

Table 2.3. Standard symbols for symmetry elements of space groups

Symmetry element	Symbol	Graphical symbol	
		Normal to projection plane	Parallel to projection plane
Reflection (mirror) plane	m		
Axial glide plane	a, b, c		
Diagonal glide plane	n		
"Diamond" glide plane	d		
Center of inversion	$\bar{1}$		
Rotation axis	2, 3, 4, 6		
Rotatory-inversion axis	$\bar{3}, \bar{4}, \bar{6}$		
Screw axis	2_1 $3_1, 3_2$ $4_1, 4_2, 4_3$ $6_1, 6_2, 6_3, 6_4, 6_5$		



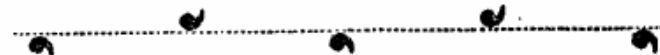
	Triclinic	Monoclinic (1st setting)	Tetragonal	Trigonal	Hexagonal	Cubic	
X	 1	 2	 4	 3	 6	 23	X
\bar{X} (even)	—	 $m(=\bar{2})$	 $\bar{4}$	—	 $\bar{6}$	—	\bar{X} (even)
X (even) plus centre and \bar{X} (odd)	 $\bar{1}$	 $2/m$	 $4/m$	 $\bar{3}$	 $6/m$	 $m\bar{3}$	X (even) plus centre and \bar{X} (odd)
	Monoclinic (2nd setting)	Orthorhombic					
$X2$	 2	 222	 422	 32	 622	 432	$X2$
Xm	 m	 $mm2$	 $4mm$	 $3m$	 $6mm$	—	Xm
$\bar{X}2$ (even) or $\bar{X}m$ (even)	—	—	 $\bar{4}2m$	—	 $\bar{6}m2$	 $\bar{4}3m$	$\bar{X}2$ (even) or $\bar{X}m$ (even)
$X2$ or Xm plus centre and $\bar{X}m$ (odd)	 $2/m$	 mmm	 $4/m\bar{m}m$	 $\bar{3}m$	 $6/m\bar{m}m$	 $m\bar{3}m$	$X2$ or Xm plus centre and $\bar{X}m$ (odd)

Stereograms of poles of general equivalent directions, and symmetry elements of each of the 32 point groups (z-axis normal to the paper in all drawings)

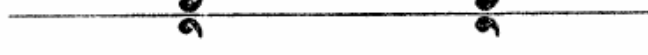
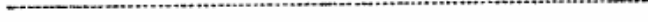
Symmetry elements with translational components -- glide plane



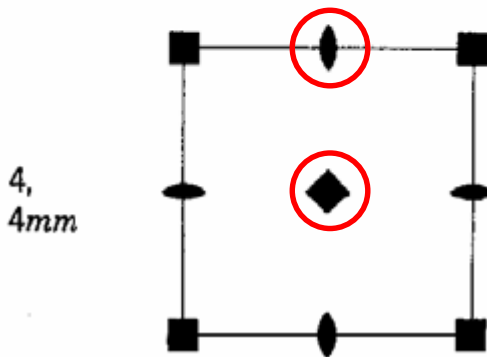
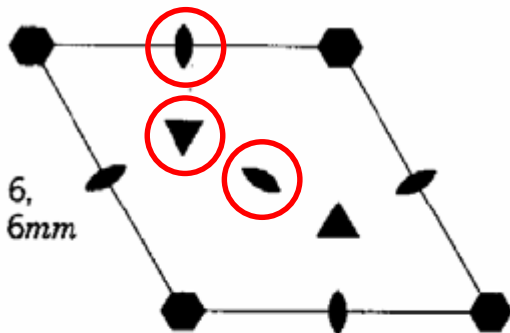
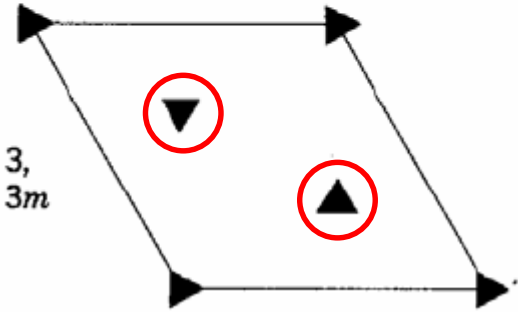
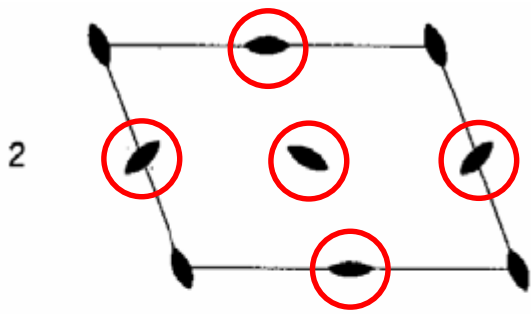
$C_1^I, P1$



$C_1^{II}, P2$



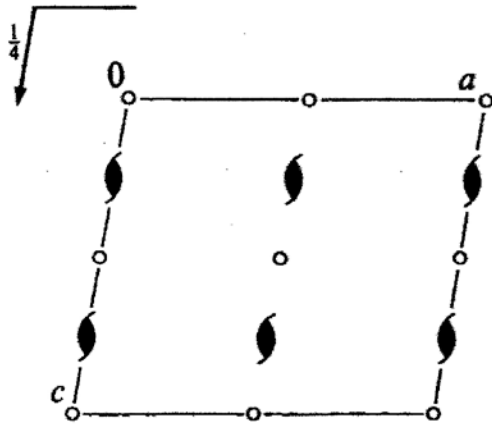
$C_1^{III}, C1$



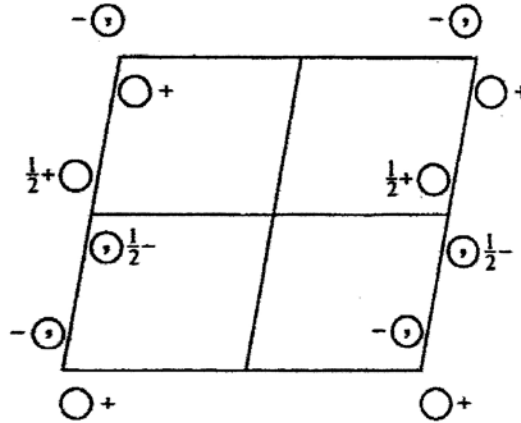
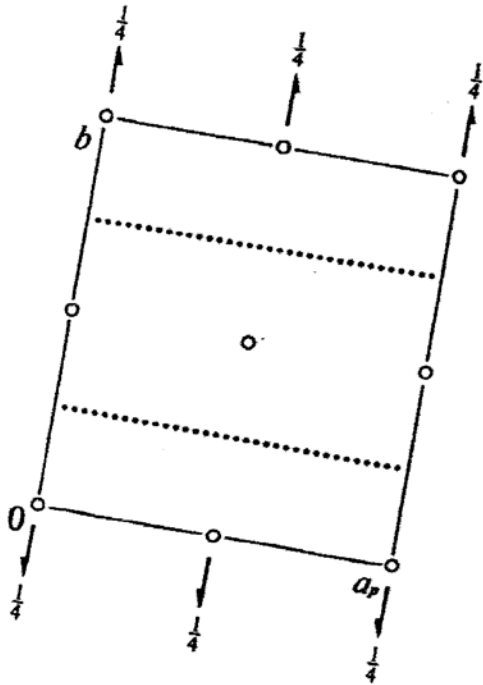
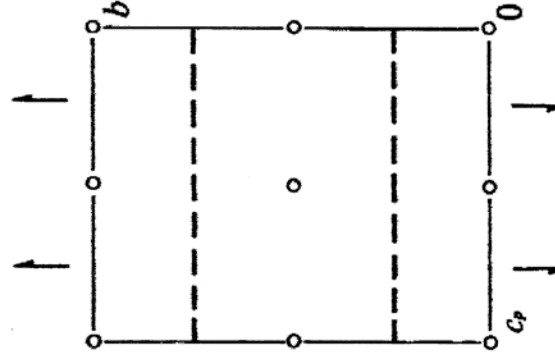
When symmetry elements are present in a crystal, the coexistence of the symmetry elements and the translational symmetry of the lattice requires the existence of additional, interleaved symmetry elements.

Martin J. Buerger, *Elementary Crystallography*.

Space group representations in the *International Tables for Crystallography, Volume A*

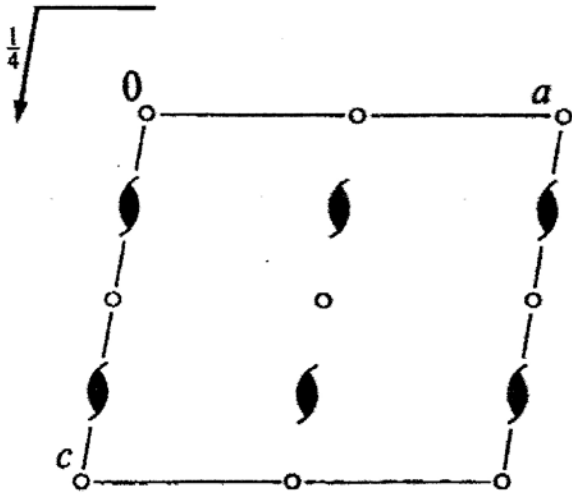


$P2_1/c$



P2₁/c

Symmetry representations: Symbols, operators



operation

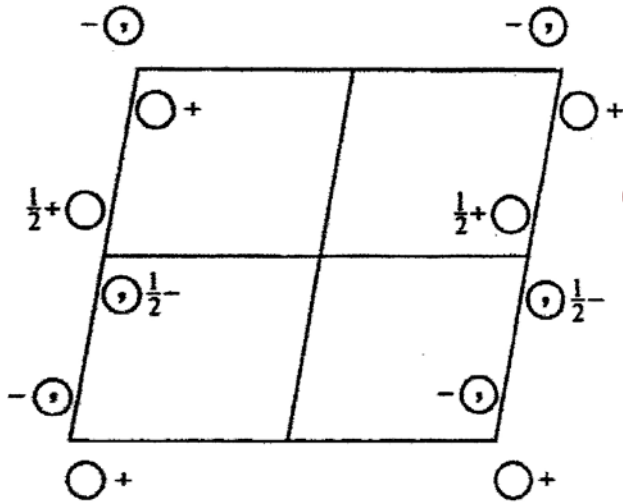
operator: $[R] + \vec{t}$

(1) x, y, z

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

(2) $-x, -y, -z$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$



(3) $-x, 1/2+y, 1/2-z$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 1/2 \\ 1/2 \end{pmatrix}$$

(4) $x, 1/2-y, 1/2+z$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 1/2 \\ 1/2 \end{pmatrix}$$

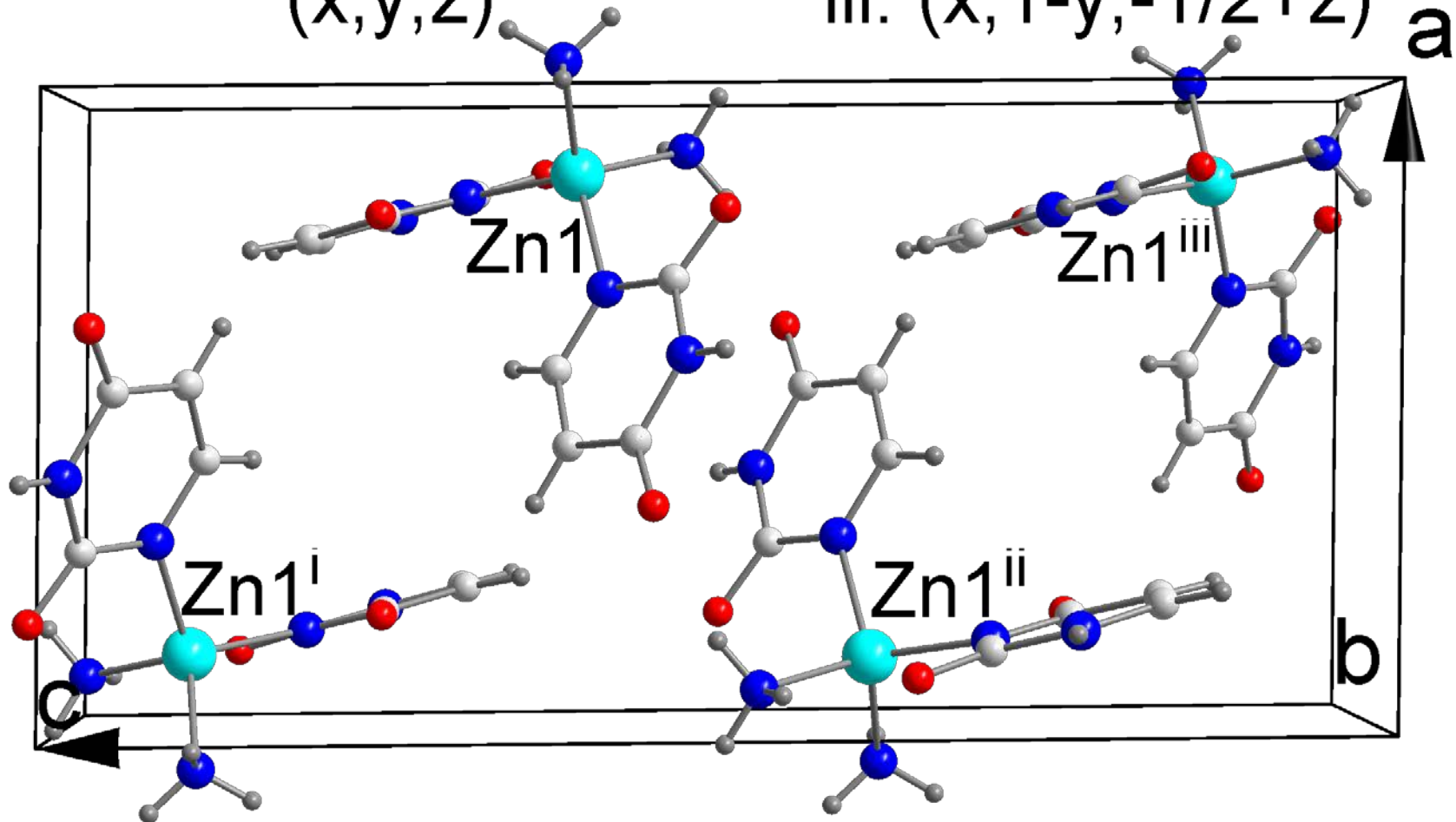
Graphical example of the practical use of symmetry operations.

the atoms list

(x, y, z)

glide plane

iii: $(x, 1-y, -1/2+z)$



i: $(1-x, y, 3/2-z)$

two-fold axis

ii: $(1-x, -y, 1-z)$

inversion center

How to report the formula and number of "molecules" in the unit cell, when describing a crystal structure

(1) Decide on a formula for the **chemical entity** that you want to use as the basic structural unit.

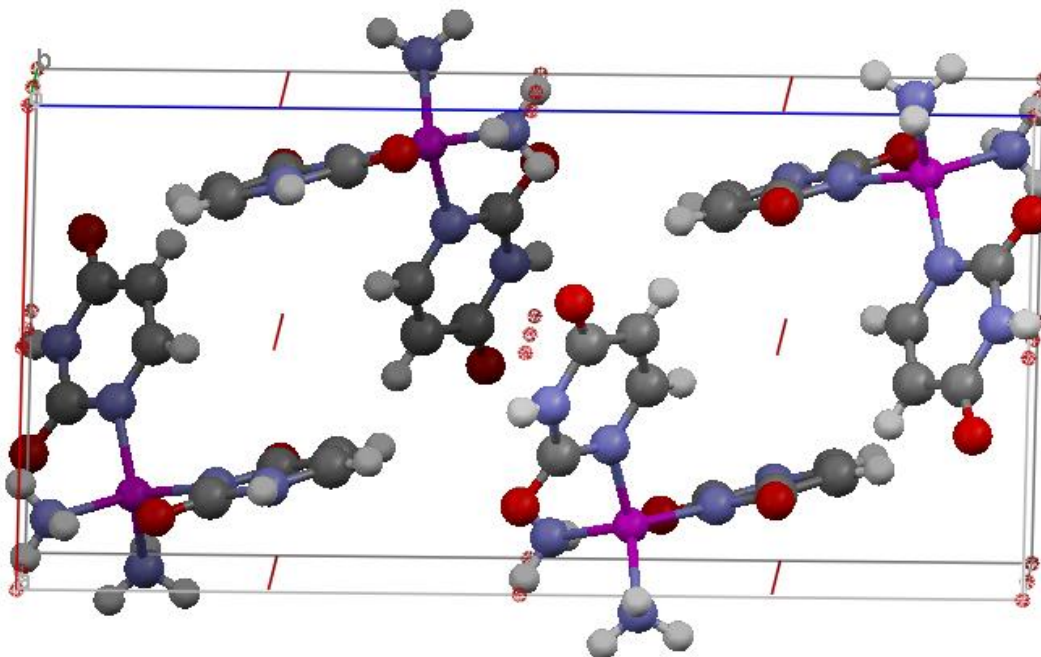
- This could be a single molecule, for a discrete molecular structure.
- It could be a single repeat unit for a polymeric structure.
- It is the responsibility of the person conducting the analysis, to define this structural unit.

(2) Determine the parameter **Z**, which is the number of these chemical units in one crystallographic unit cell.

- The number Z may or may not be the same as the number of symmetry operations in the space group. (The number of symmetry operations in the space group is equal to the number of asymmetric units in one unit cell.)

Reporting the chemical formula and Z. Example 1.

This structure is composed of discrete molecules. There are four molecules in the unit cell. The asymmetric unit consists of one molecule. There are four symmetry operations in the space group, $P2/n$, and thus **four asymmetric units** in one unit cell.



We choose a single molecule as our basic **chemical** unit.

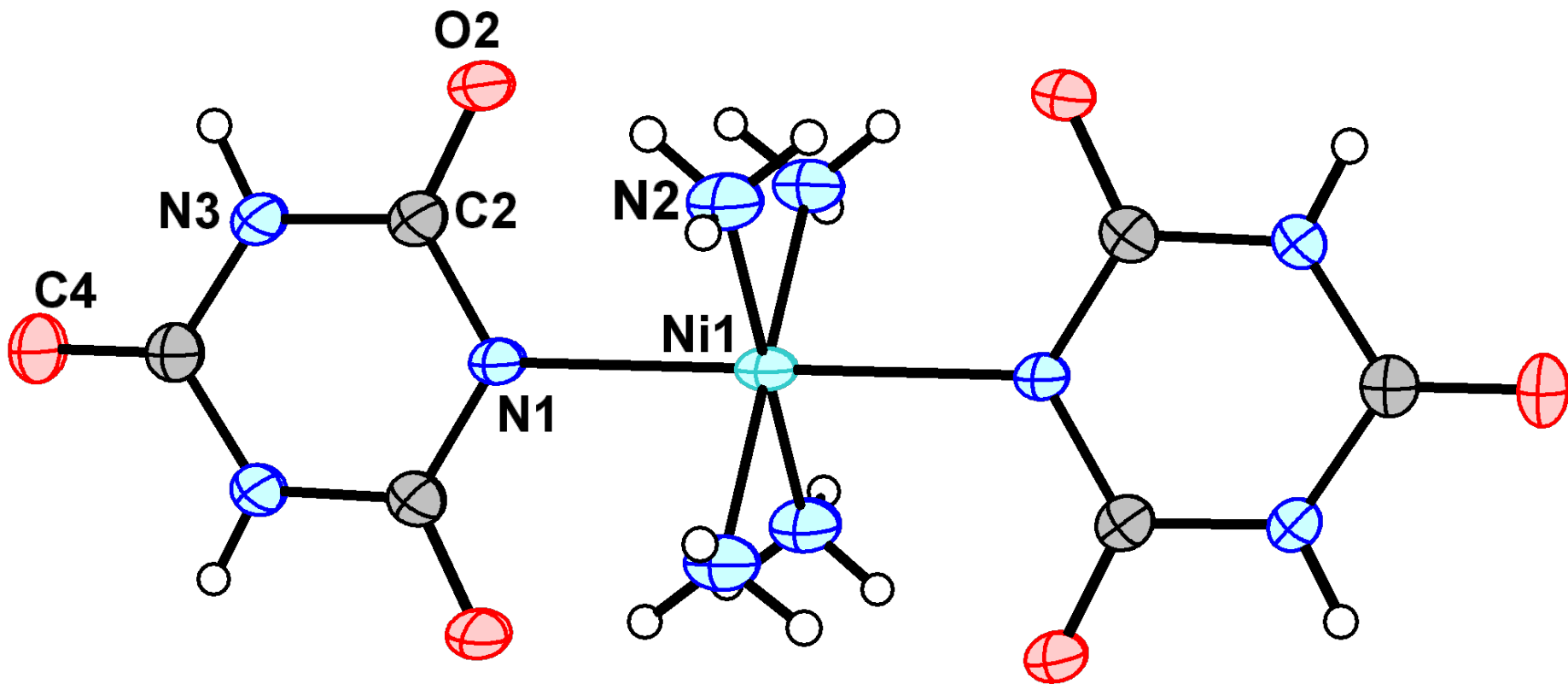
Its formula is $\text{Zn}(\text{uracilate})_2(\text{NH}_3)_2$, or $\text{Zn}(\text{C}_4\text{H}_3\text{N}_2\text{O}_2)_2(\text{NH}_3)_2$, or $\text{C}_8\text{H}_{12}\text{N}_6\text{O}_4\text{Zn}$.

The number of chemical units in one crystallographic unit cell is Z. Here, $Z = 4$.

As per an IUCr recommendation, the elements are listed in this order -- first C, if present, then H, if present, and then the rest of the elements in alphabetical order.

Reporting the chemical formula and Z. Example 2.

This structure is composed of discrete molecules. There are four molecules in the unit cell. The asymmetric unit consists of one-eighth molecule. There are 32 symmetry operations in the space group, *Fmmm*, and thus **32 asymmetric units** in one unit cell.



We choose a single molecule as our basic **chemical** unit.

Its formula is $\text{Ni}(\text{cyanurate})_2(\text{NH}_3)_4$, or $\text{Ni}(\text{C}_3\text{H}_2\text{N}_3\text{O}_3)_2(\text{NH}_3)_4$, or $\text{C}_6\text{H}_{16}\text{N}_{10}\text{NiO}_6$.

The number of chemical units in one crystallographic unit cell is Z. Here, $Z = 4$.

density

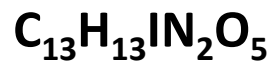
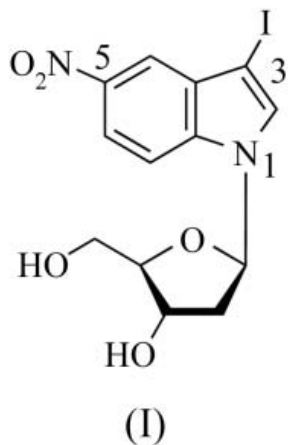
The density of a crystalline solid is calculated this way:

$$\rho(g / cm^3) = \frac{m.w. \cdot Z \cdot 1.6604}{V(\text{\AA}^3)}$$

The origin of the formula is this:

$$\rho(g / cm^3) = \frac{(m.w.)(g / mole) \cdot Z(\text{molecules} / \text{cell}) \cdot (10^{24} \text{\AA}^3 / cm^3)}{V(\text{\AA}^3 / \text{cell}) \cdot (6.023 \times 10^{23} \text{ molecules} / \text{mole})}$$

Typical problems include: (1) calculating the density, given a formula and Z; (2) calculating the formula of one unit cell, given density and V; (3) estimating Z given the unit cell volume and the formula (but without knowing the density). For this, if the crystal contains organic fragments, an initial estimate of 18 \AA^3 per non-H atom is used. (For a pure inorganic, this number will not provide a good estimate.)

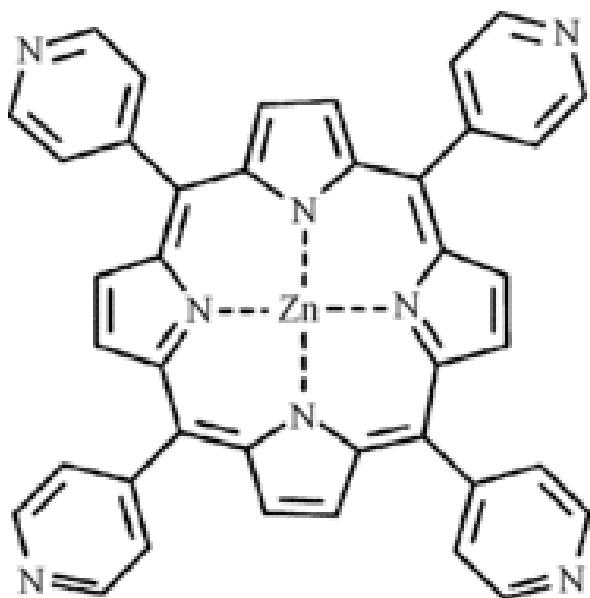


Mr = 404.15

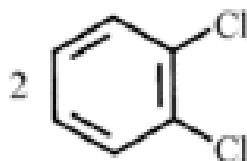
$a = 17.549$ $b = 7.0981$ $c = 10.9242$ \AA $\alpha = \beta = \gamma = 90^\circ$ $V = 1360.8$ \AA^3

How many molecules in the cell? ($Z = 4$)

$$\rho = 1.972 \text{ g}\cdot\text{cm}^{-3}$$



(I)



$$\rho = 1.502 \text{ g}\cdot\text{cm}^{-3}$$

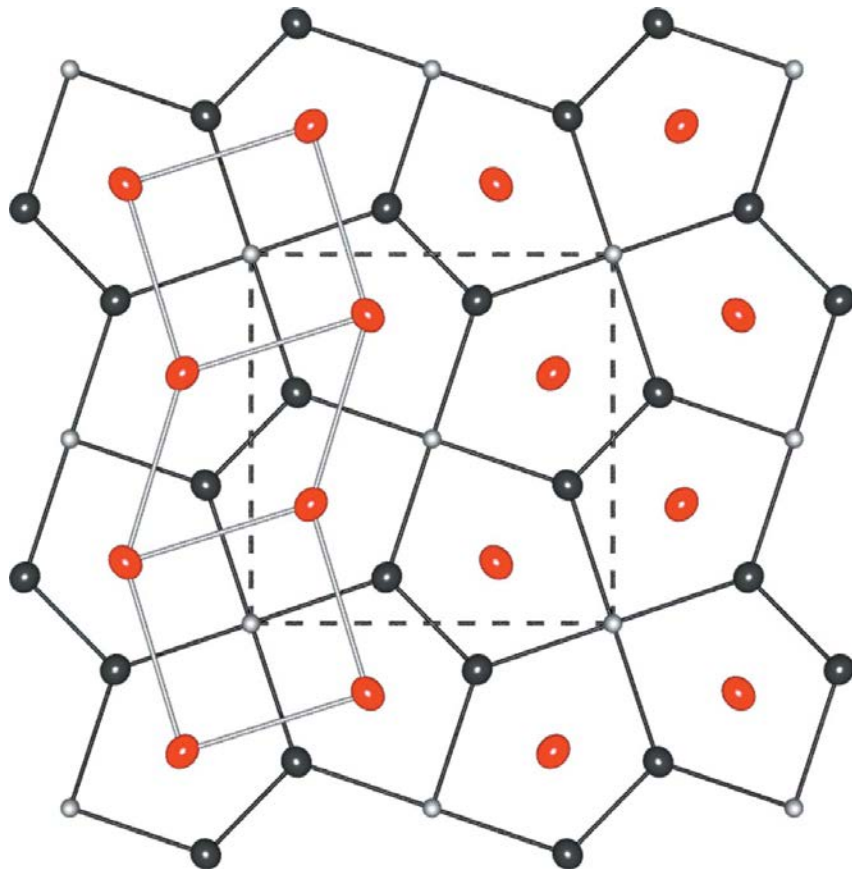


Mr = 976.03

a = 11.0295 b = 13.8207 c = 14.1529 Å

$\alpha = \gamma = 90^\circ$ $\beta = 90.2382$ V = 2157.39 Å³

How many molecules in the cell? (Z = 2)



Sc₂MgGa₂

M_r = 253.67

a = b = 7.1577 c = 3.9166 Å

α = β = γ = 90° V = 200.66 Å³

Mg: white

Ga: black

Sc: red

Z = 2

$\rho = 4.198 \text{ g}\cdot\text{cm}^{-1}$



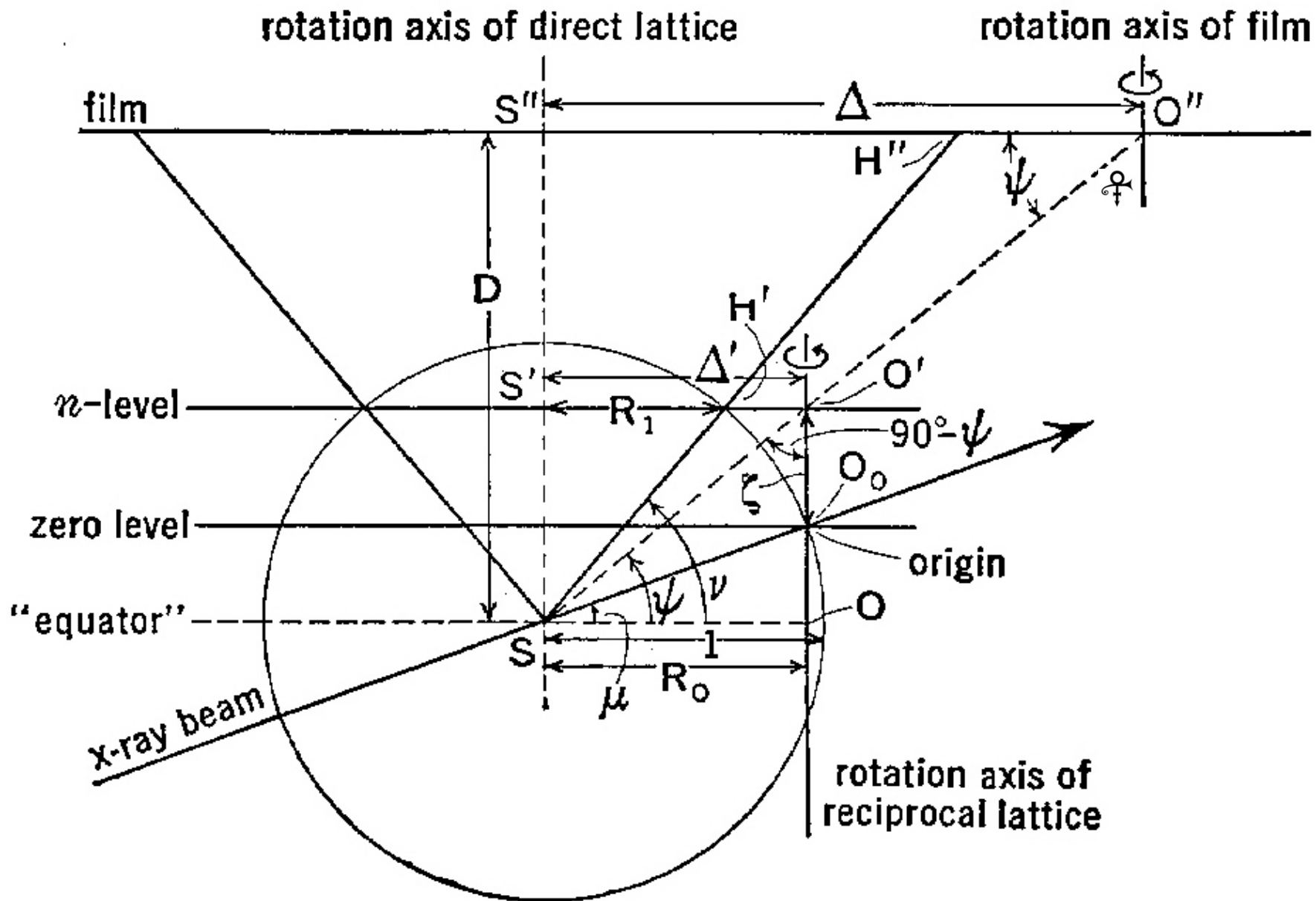
Interpretation of Diffraction – Geometry and Intensity

Diffraction patterns are interpreted with various goals and in different contexts. The methods used to analyze diffraction data depend on the result that is required. For example, for detailed structure analysis of a single crystal, we interpret both the geometry of the diffraction pattern and the diffracted intensities.

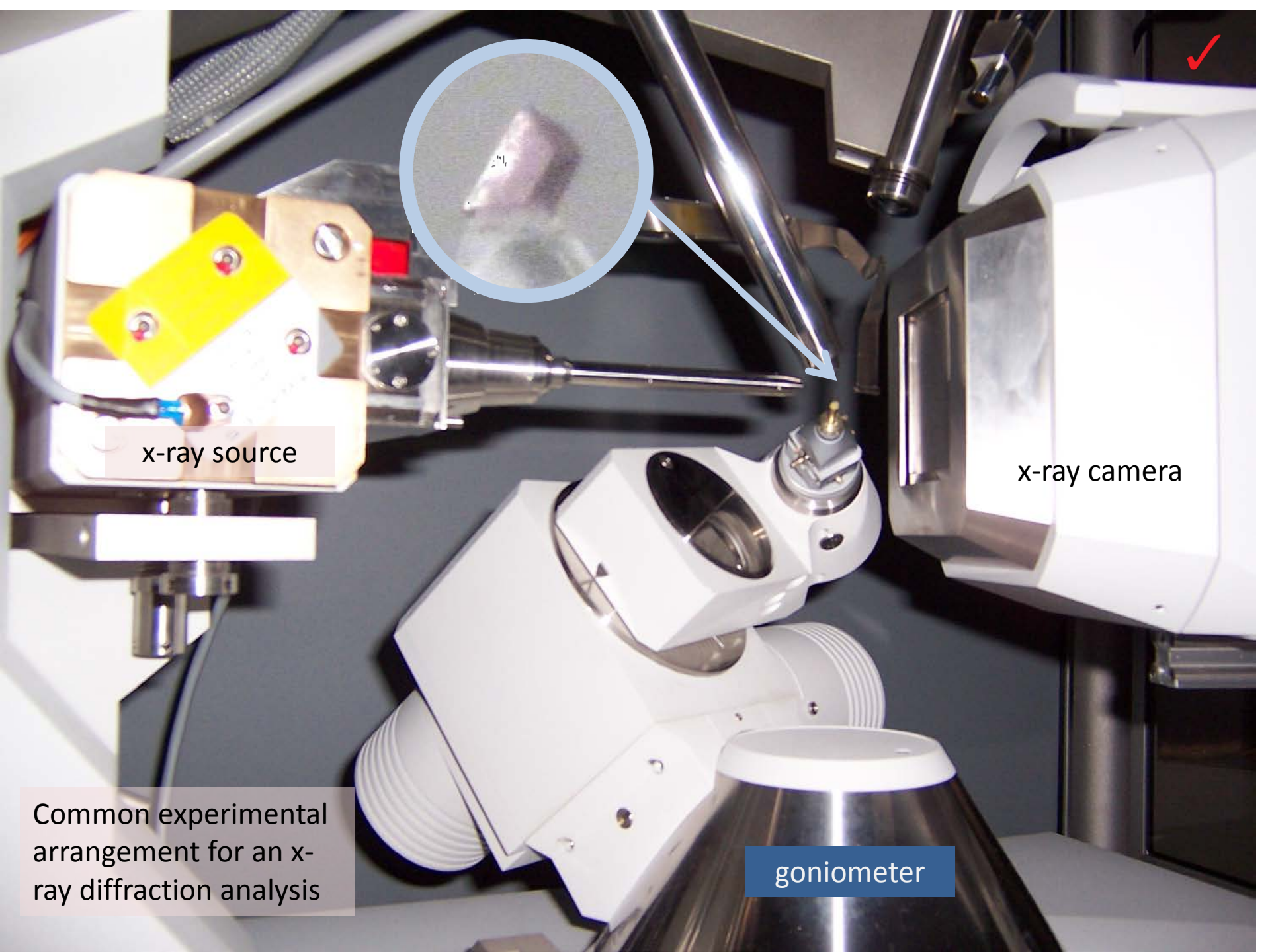
If we need a quantitative description of the phases present in a powder sample, we use partial geometrical information (2θ or scattering angle) and the intensities. We may also refer to a data base of known powder patterns when doing this analysis.

Various conceptual tools are available for understanding the geometries and intensities of diffracted beams. For present purposes we will consider them in two parts:

- For interpreting diffraction geometry, we use the reciprocal lattice.
- For interpreting diffracted intensities, we use Fourier transformation.



There are many ways of interpreting diffraction geometry.
 We shall begin by looking at a single-crystal diffraction experiment.



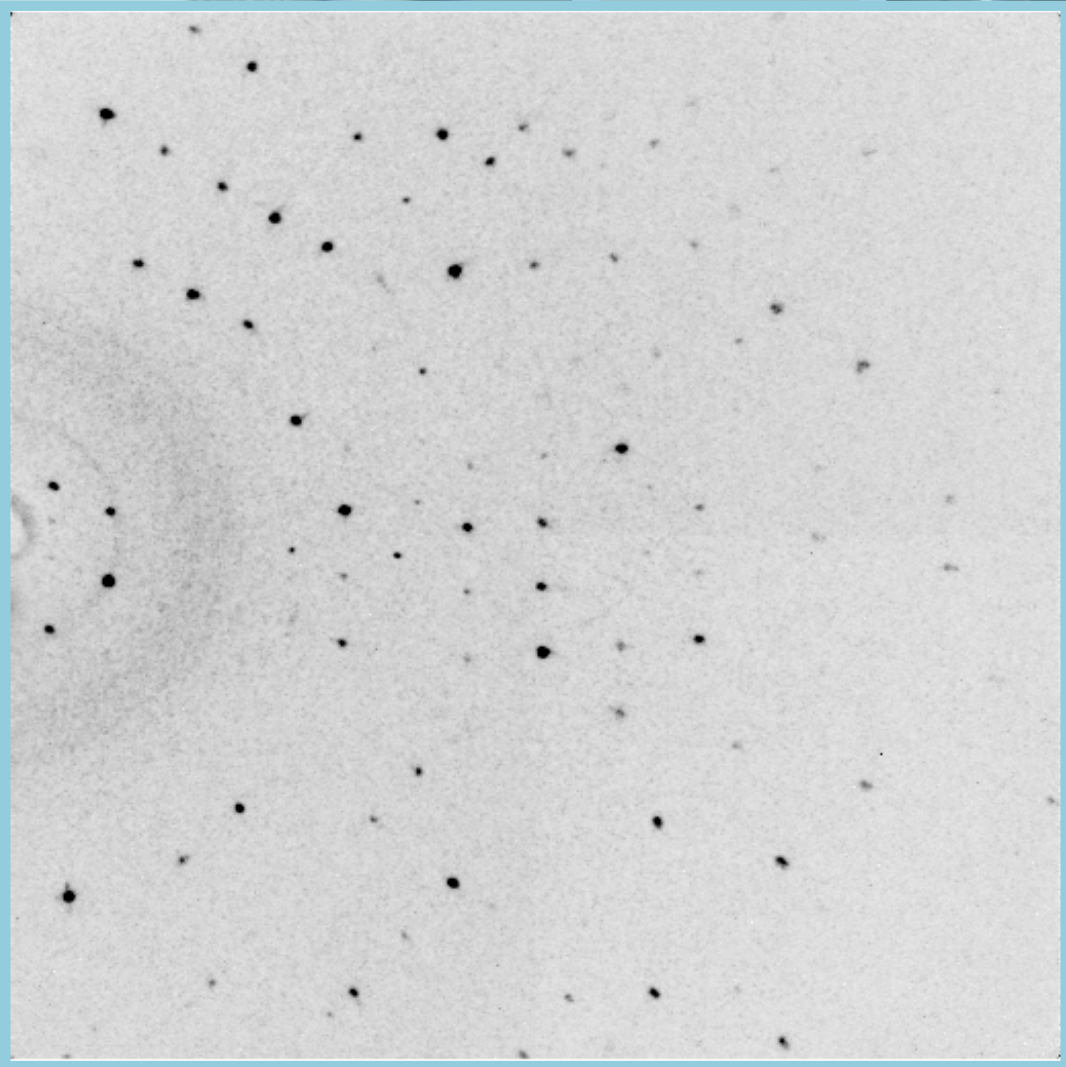
x-ray source

x-ray camera

Common experimental arrangement for an x-ray diffraction analysis

goniometer

Image recorded by the x-ray camera



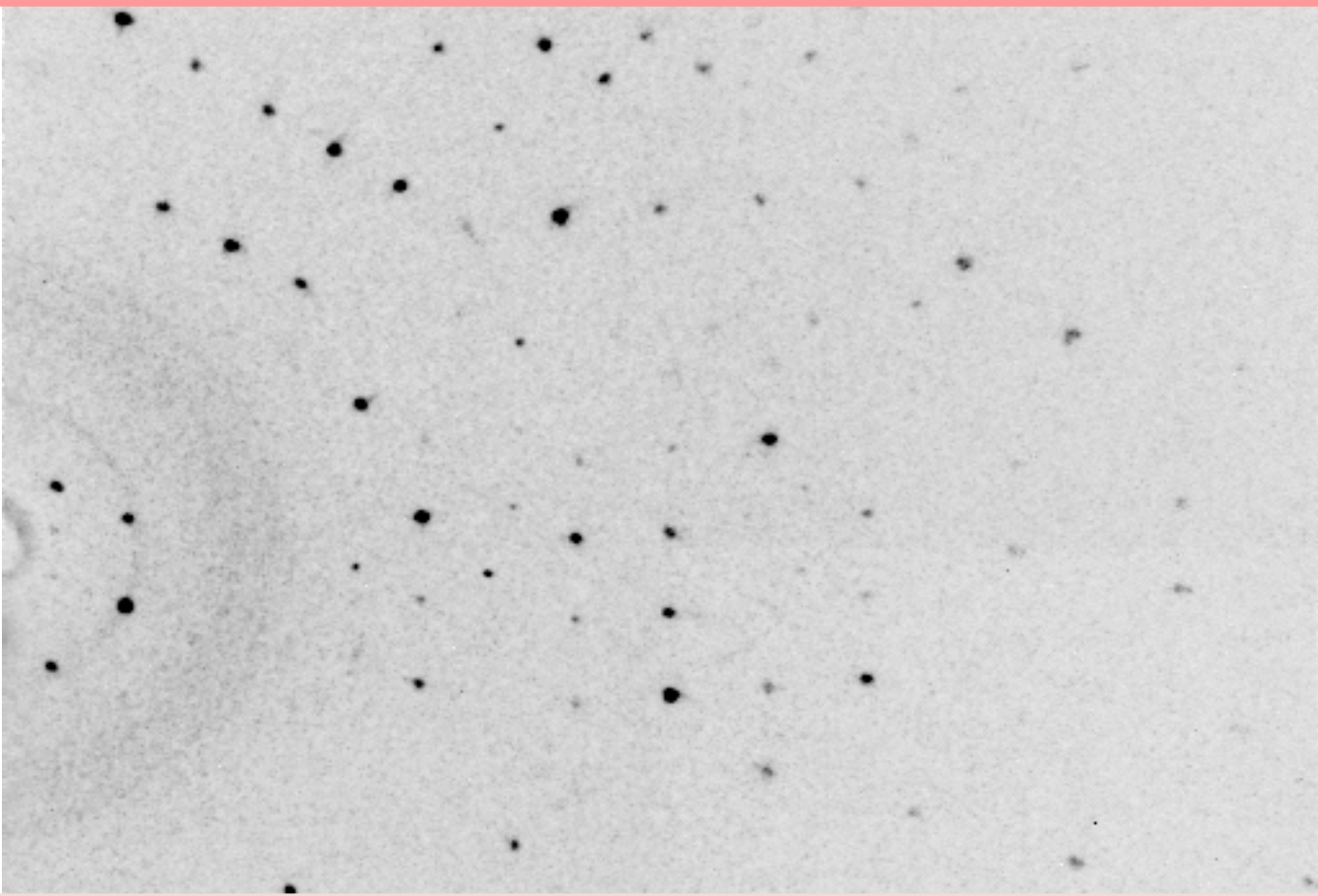
Common experimental arrangement for an x-ray diffraction analysis



x-ray camera

goniometer

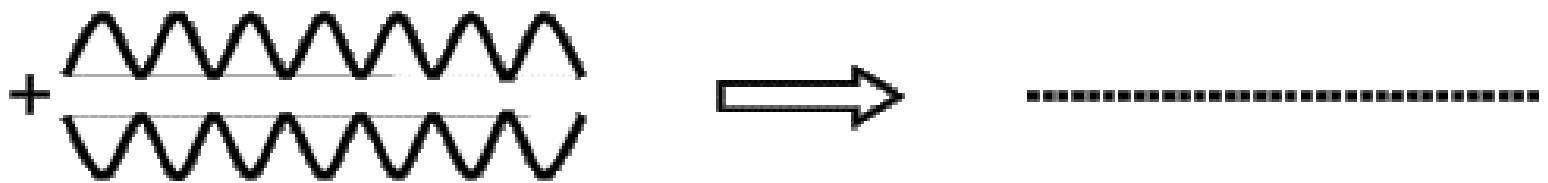
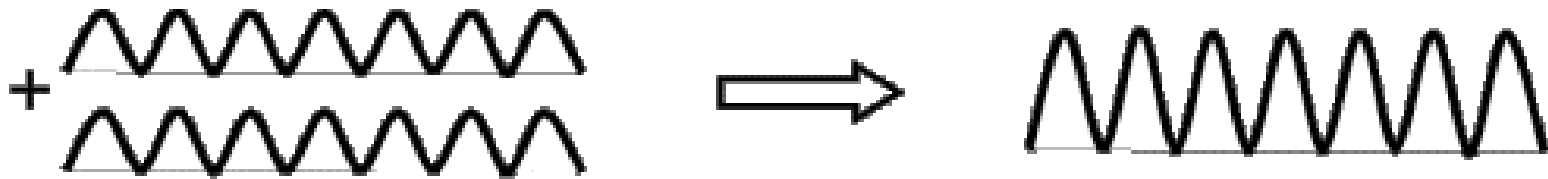
DIFFRACTION IMAGE FROM CCD DIFFRACTOMETER



- The geometry of the diffraction pattern (i.e., where the diffracted beams emerge) depends on the size and shape of the unit cell.
- The intensities of the diffracted beams depend on the contents of the unit cell.

We will use the **reciprocal lattice** as a tool for interpreting the diffraction geometry.

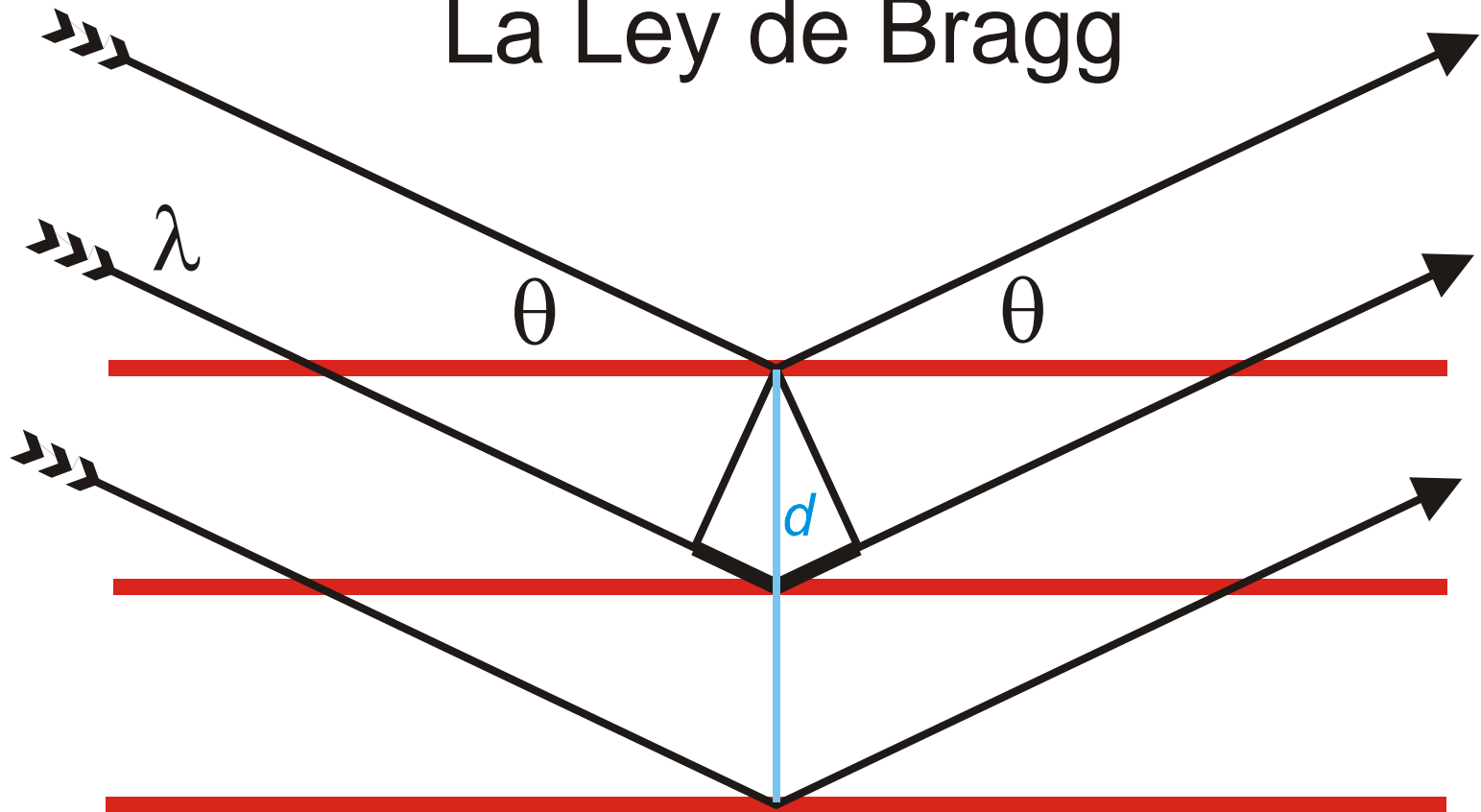
interference between waves



Bragg's Law



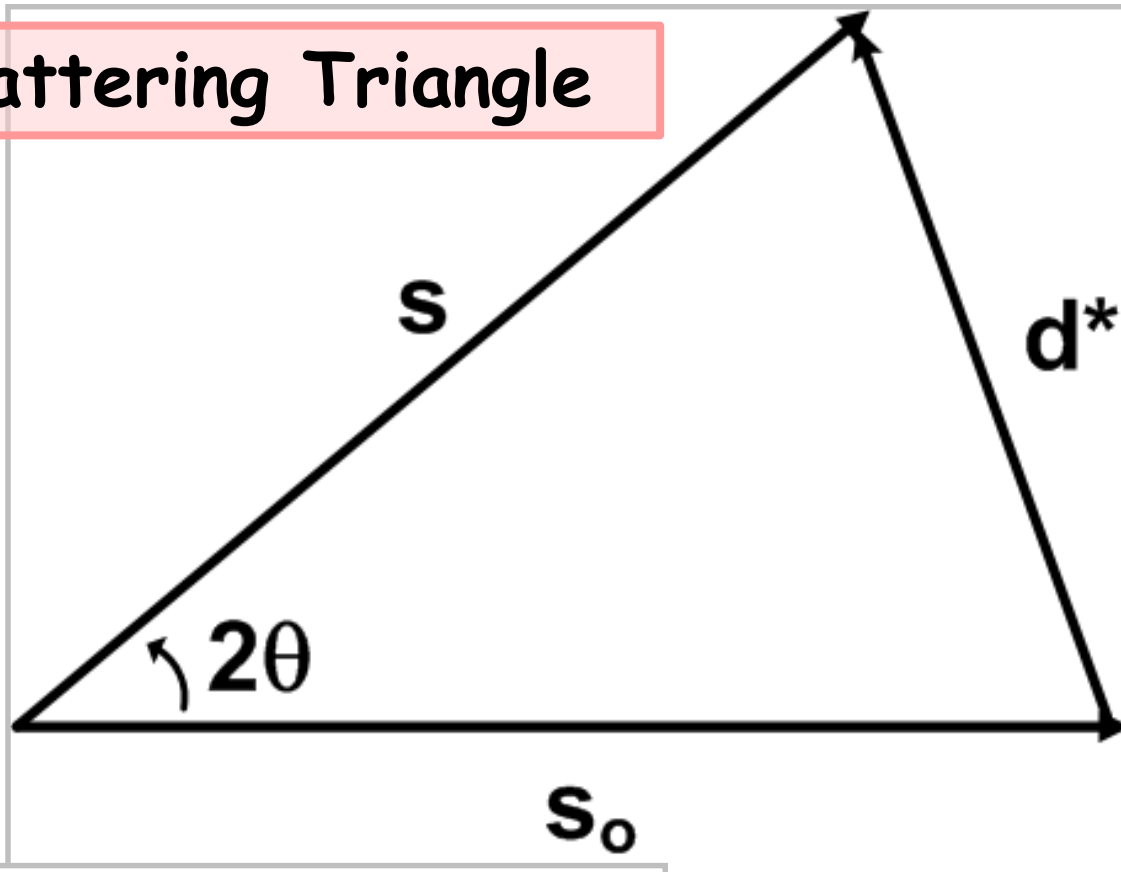
La Ley de Bragg



$$n\lambda = 2d \sin \theta$$

$$n\lambda = 2d \sin \theta$$

The Scattering Triangle



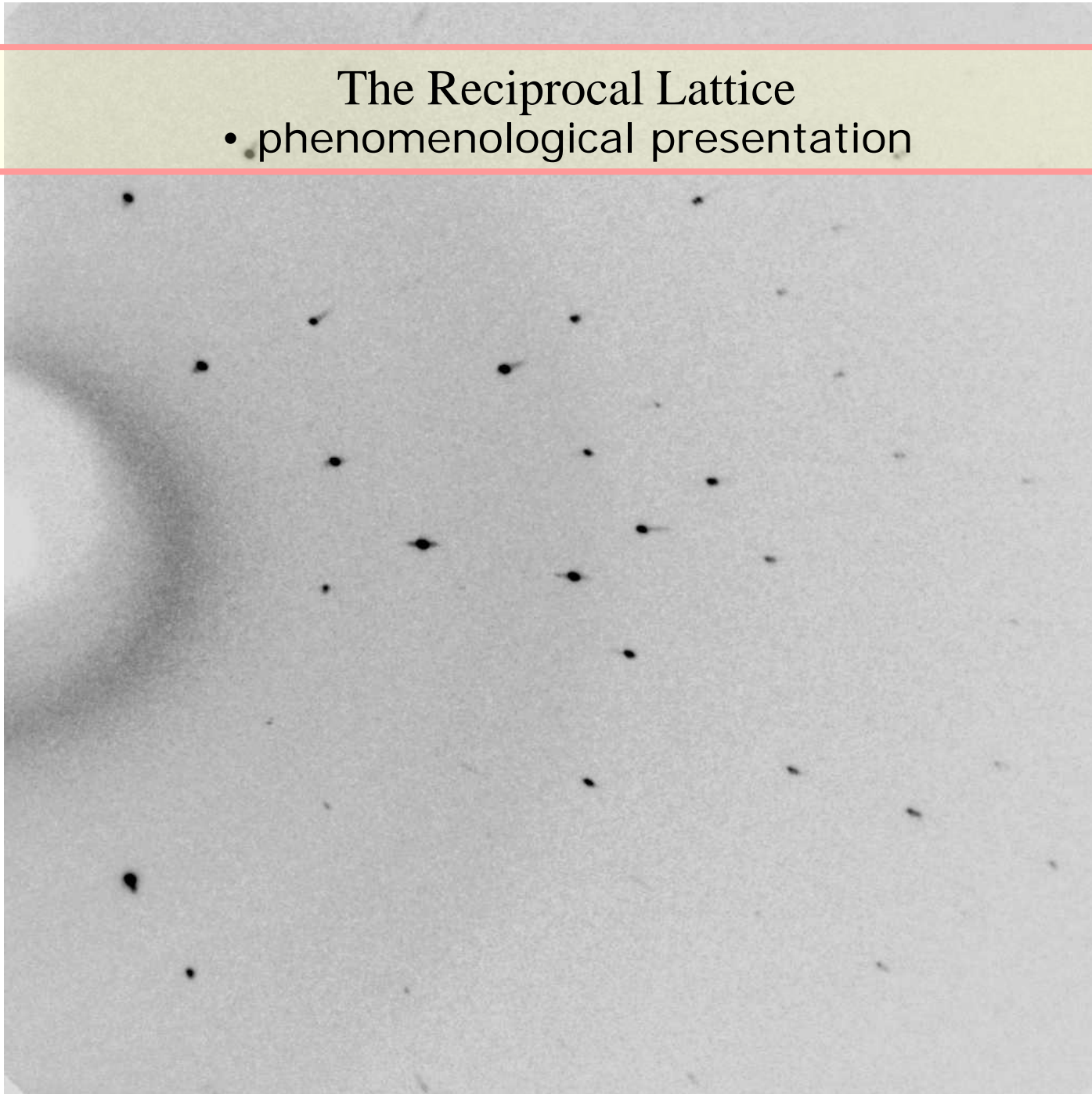
s_0 – incident beam momentum
 s – scattered beam momentum
 d^* -- “scattering vector”
 2θ – scattering angle

$$|s| = |s_0| = 1 / \lambda$$

$$|d^*| = 2\sin\theta / \lambda$$

The Reciprocal Lattice

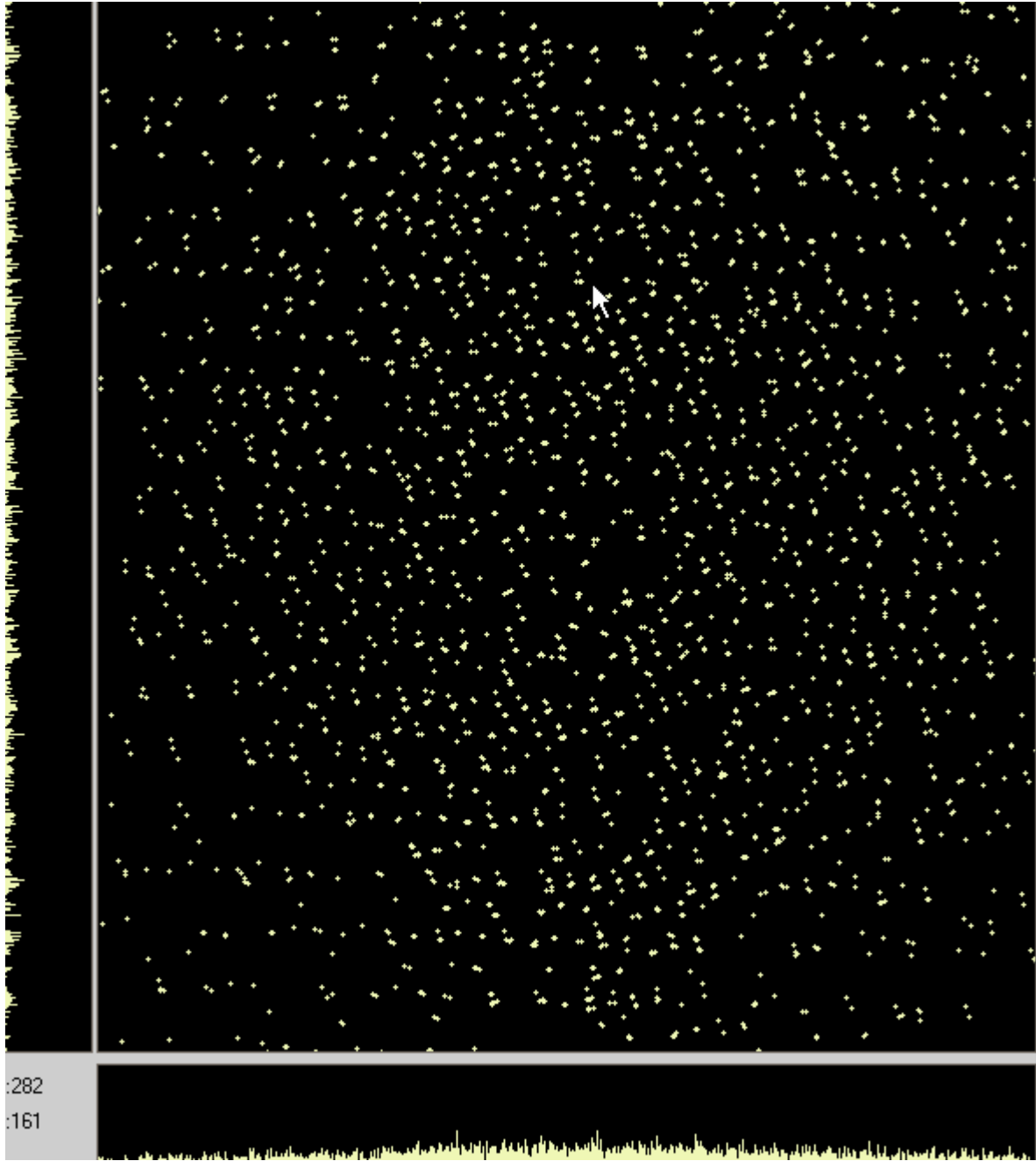
- phenomenological presentation



The Reciprocal Lattice

- phenomenological presentation





:282

:161

<http://en.wikipedia.org/wiki/Photon>

The energy and momentum of a photon depend only on its **frequency** (ν) or conversely, its **wavelength** (λ):

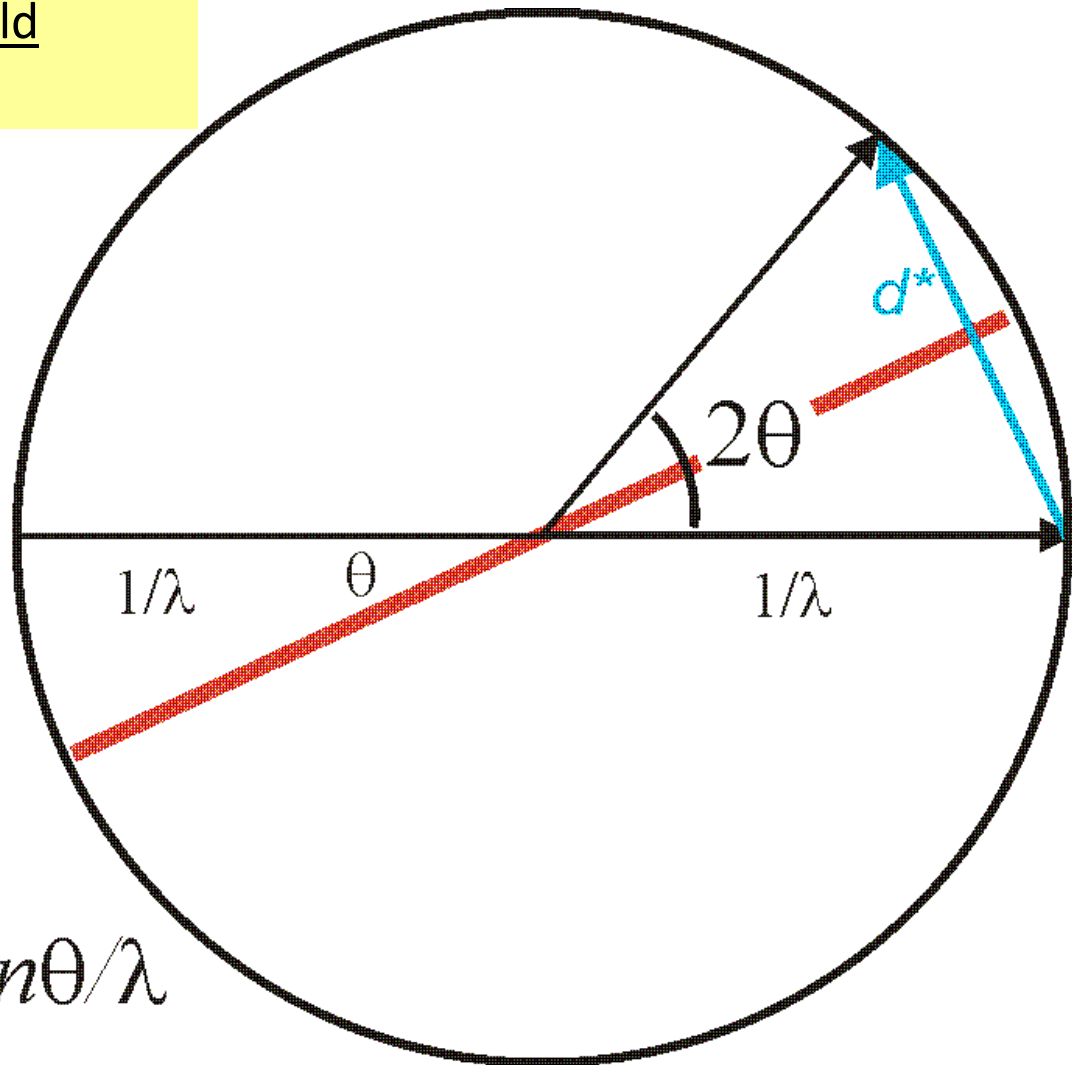
$$E = h \nu = hc / \lambda$$

$$p = \hbar k = h \nu / c = h / \lambda$$

\mathbf{p} is the momentum (a vector). \mathbf{k} is the wave vector. The wave number (magnitude of the wave vector) is:

$$k = |\mathbf{k}| = 2 \pi / \lambda$$

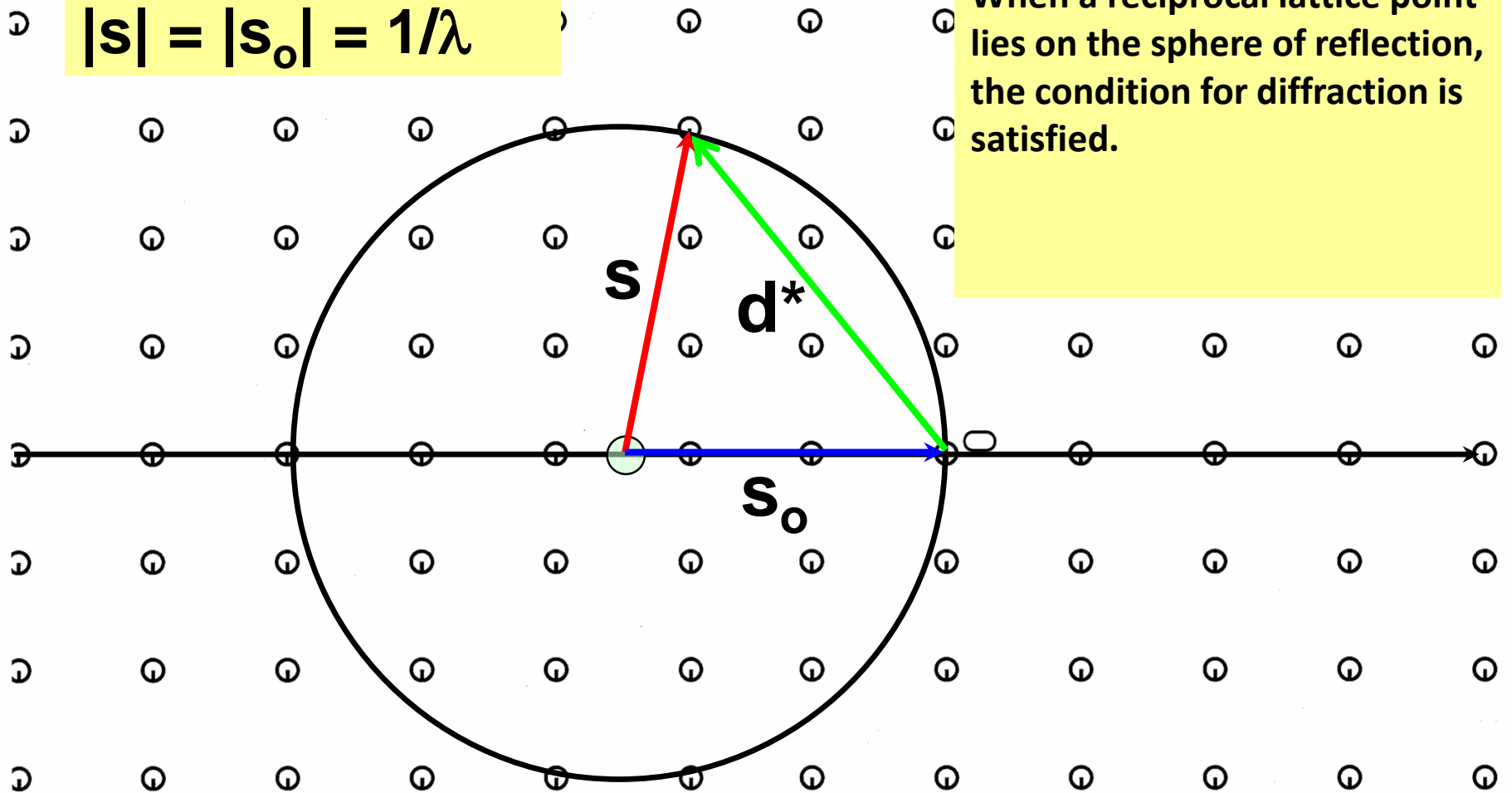
The locus of all of the scattered beam vectors, \mathbf{s} , is a sphere – the sphere of reflection or Ewald sphere.



$$d^* = 2\sin\theta/\lambda$$

$$|\mathbf{s}| = |\mathbf{s}_0| = 1/\lambda$$

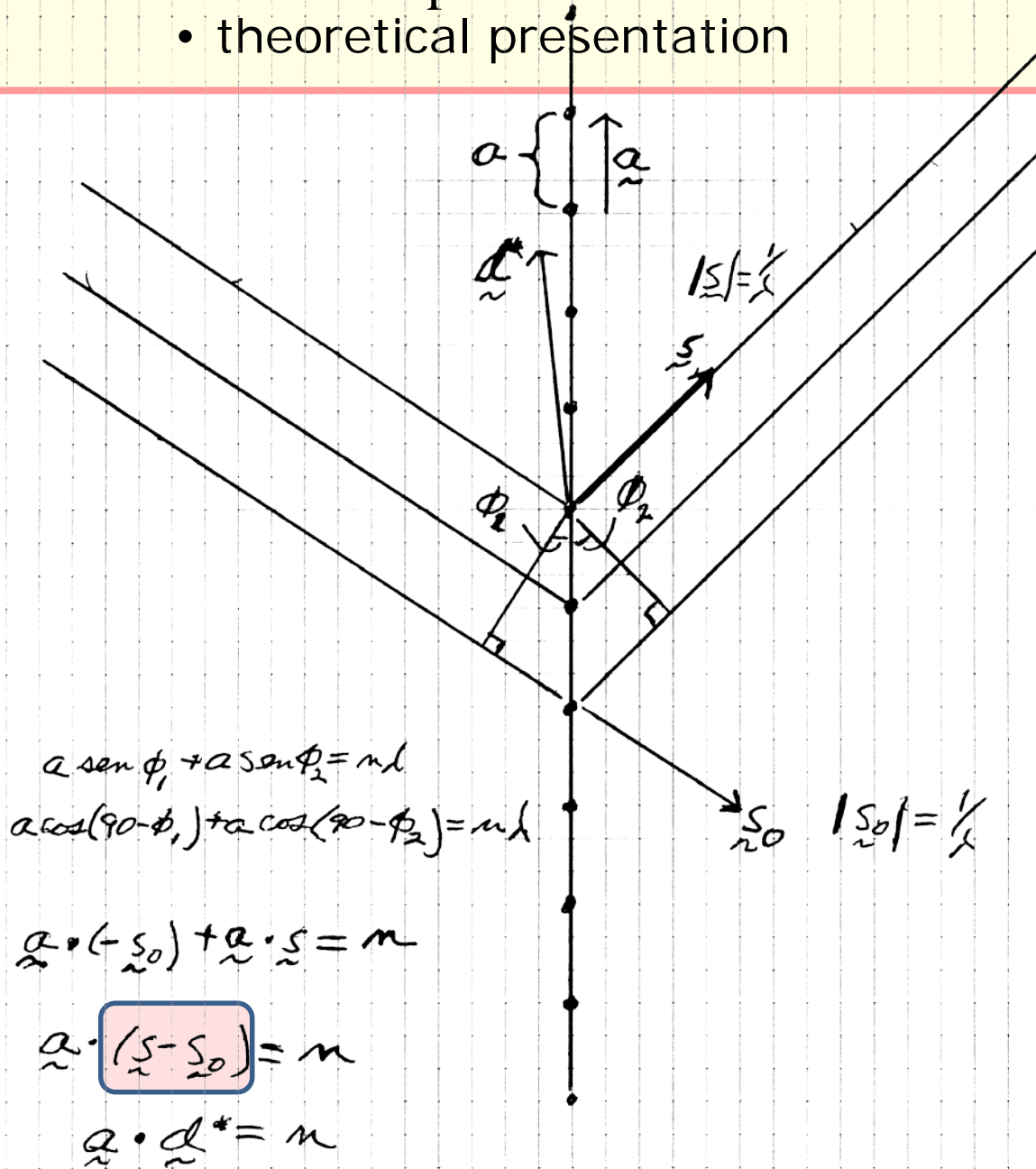
When a reciprocal lattice point lies on the sphere of reflection, the condition for diffraction is satisfied.



This construct is geometrically equivalent to Bragg's Law.

The Reciprocal Lattice

- theoretical presentation





Direct / reciprocal lattice relationships – scalar and vector

Relationships between the real and reciprocal cell axes

The "real" cell is defined by its parameters $a, b, c, \alpha, \beta, \gamma$.

The "reciprocal" cell is defined by its parameters $a^*, b^*, c^*, \alpha^*, \beta^*, \gamma^*$.

In this table, the letters refer to the real and reciprocal cell vectors.

$$a \cdot a^* = 1 \qquad a \cdot b^* = 0 \qquad a \cdot c^* = 0$$

$$b \cdot a^* = 0 \qquad b \cdot b^* = 1 \qquad b \cdot c^* = 0$$

$$c \cdot a^* = 0 \qquad c \cdot b^* = 0 \qquad c \cdot c^* = 1$$

Table 2.3 Triclinic Direct/Reciprocal Relationships

$$a^* = \frac{bc \sin \alpha}{V}$$

$$a = \frac{b^*c^* \sin \alpha^*}{V^*}$$

$$b^* = \frac{ac \sin \beta}{V}$$

$$b = \frac{a^*c^* \sin \beta^*}{V^*}$$

$$c^* = \frac{ab \sin \gamma}{V}$$

$$c = \frac{a^*b^* \sin \gamma^*}{V^*}$$

$$V = \frac{1}{V^*} = abc \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$V^* = \frac{1}{V} = a^*b^*c^* \sqrt{1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma}$$

$$\cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

$$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma}$$

$$\cos \beta = \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*}$$

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta}$$

$$\cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*}$$

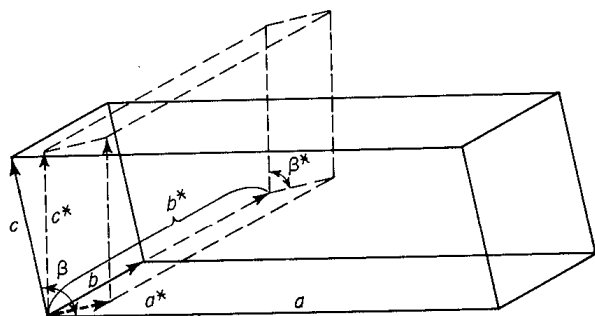
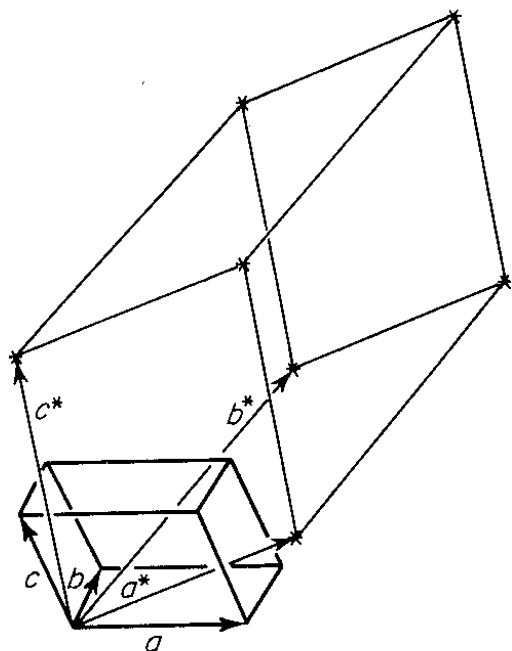


Figure 2.18. Monoclinic direct and reciprocal cells.

Direct / reciprocal lattice relationships

$$V = \vec{a} \cdot \vec{b} \times \vec{c}$$

$$\vec{a}^* = \frac{\vec{b} \times \vec{c}}{V}, \quad \vec{b}^* = \frac{\vec{c} \times \vec{a}}{V}, \quad \vec{c}^* = \frac{\vec{a} \times \vec{b}}{V}$$

$$\vec{a} = \frac{\vec{b}^* \times \vec{c}^*}{V^*}, \quad \vec{b} = \frac{\vec{c}^* \times \vec{a}^*}{V^*}, \quad \vec{c} = \frac{\vec{a}^* \times \vec{b}^*}{V^*}$$

Diffraction analysis: How symmetry is used at the beginning of a single-crystal study.

When you perform a diffraction analysis, you first scan several (digital) photos to find reflections; then the reciprocal lattice is constructed (by the computer). Then the crystal (direct) unit cell parameters are calculated. On the basis of these parameters, you can make a good determination of the crystal system, Laue group and lattice type. The computer aids in this process by reporting the reduced cell and the most likely conventional cell.

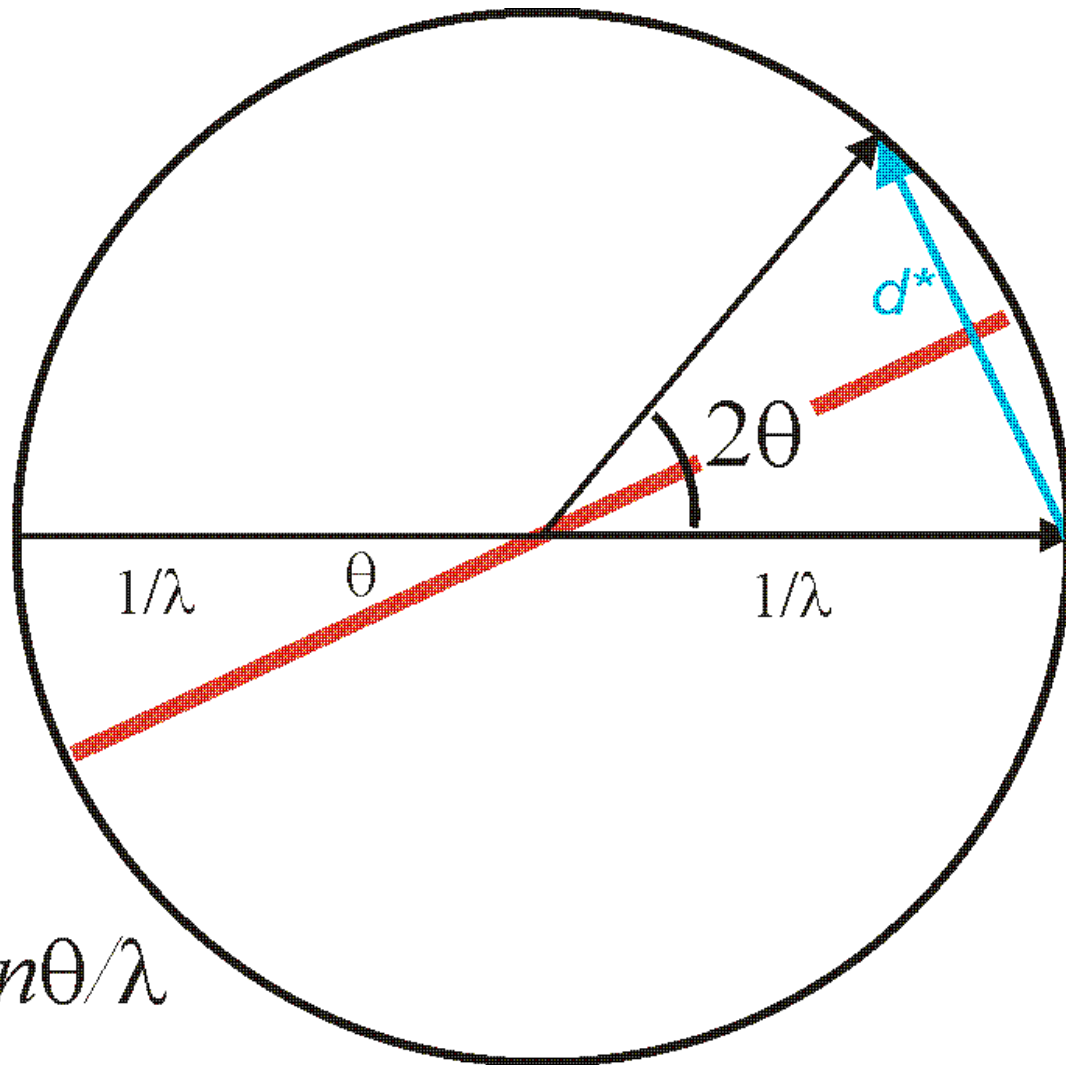
THE 32 THREE-DIMENSIONAL POINT GROUPS

THE 32 THREE-DIMENSIONAL POINT GROUPS

	Triclinic	Monoclinic (1st setting)	Tetragonal	Trigonal	Hexagonal	Cubic	
X	 1	 2	 4	 3	 6	 23	X
\bar{X} (even)	—	 $\bar{2}$	 $\bar{4}$	—	 $\bar{6}$	—	\bar{X} (even)
X (even) plus centre and \bar{X} (odd)	 $\bar{1}$	 $2/m$	 $4/m$	 $\bar{3}$	 $6/m$	 $m\bar{3}$	X (even) plus centre and \bar{X} (odd)
$X2$	 2	 222	 422	 32	 622	 432	$X2$
Xm	 m	 $mm2$	 $4mm$	 $3m$	 $6mm$	—	Xm
$\bar{X}2$ (even) or $\bar{X}m$ (even)	—	—	 $\bar{4}2m$	—	 $\bar{6}2m$	 $\bar{4}2m$	$\bar{X}2$ (even) or $\bar{X}m$ (even)
$X2$ or Xm plus centre and $\bar{X}m$ (odd)	 $2/m$	 mmm	 $4/mmm$	 $\bar{3}m$	 $6/mmm$	 $m\bar{3}m$	$X2$ or Xm plus centre and $\bar{X}m$ (odd)

stereograms of poles of general equations of sections, and symmetric elements of each of the 32 point groups (c and n normal to the paper in all drawings)

Sphere of reflection, or Ewald sphere



$$d^* = 2\sin\theta/\lambda$$

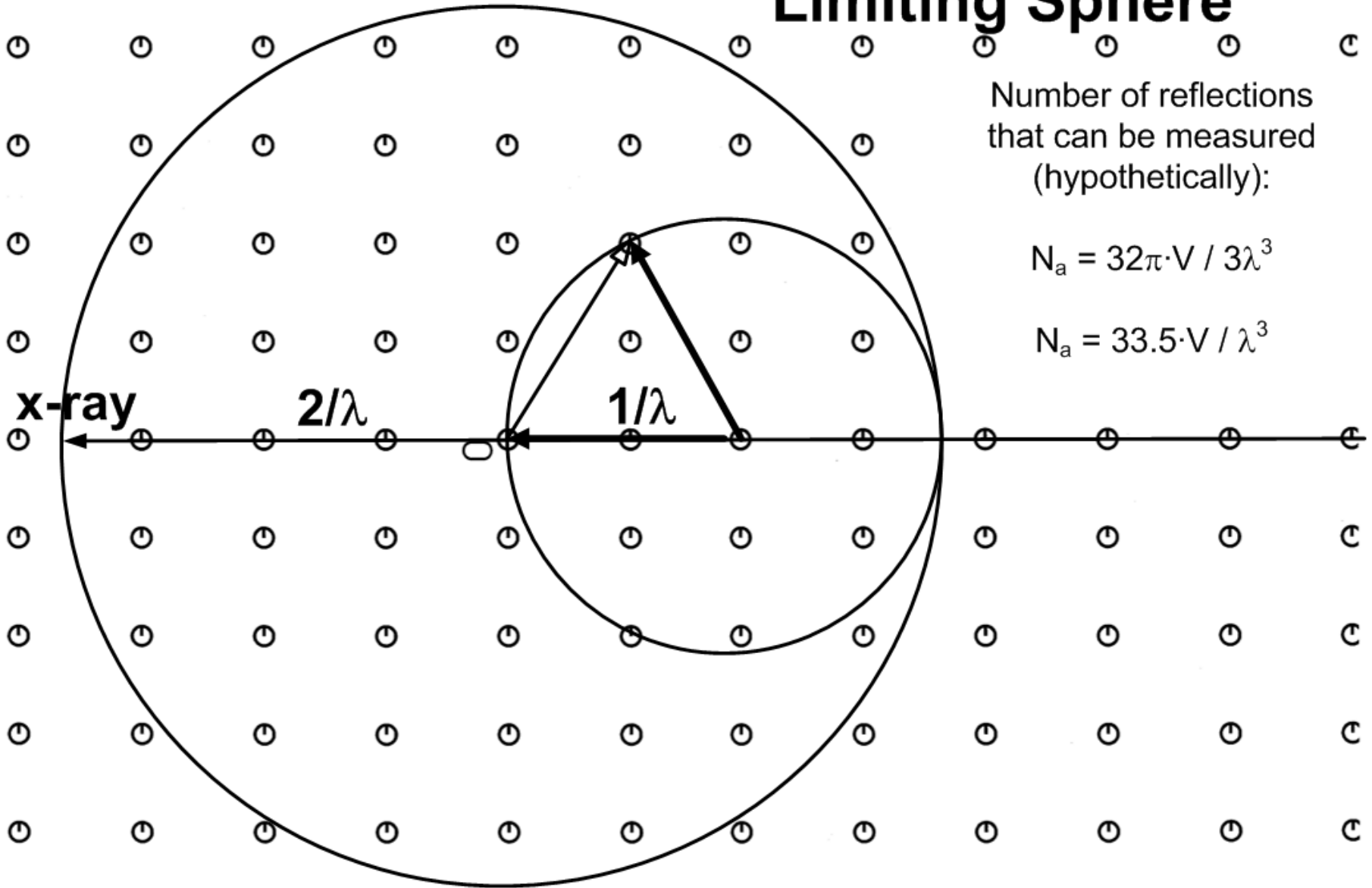
How many data can we measure from a single-crystal sample?

“Limiting Sphere”

Number of reflections that can be measured (hypothetically):

$$N_a = 32\pi \cdot V / 3\lambda^3$$

$$N_a = 33.5 \cdot V / \lambda^3$$



“Resolution,” “coverage,” “completeness”

The **“resolution”** of a single-crystal diffraction analysis is a number with dimensions of distance (Å), which gives an indication of how well the analysis permits the distinction of fine details of the structure.

The resolution is the minimum value of the Bragg plane spacing d corresponding to any of the diffraction data used in the analysis. Since the following three relations hold:

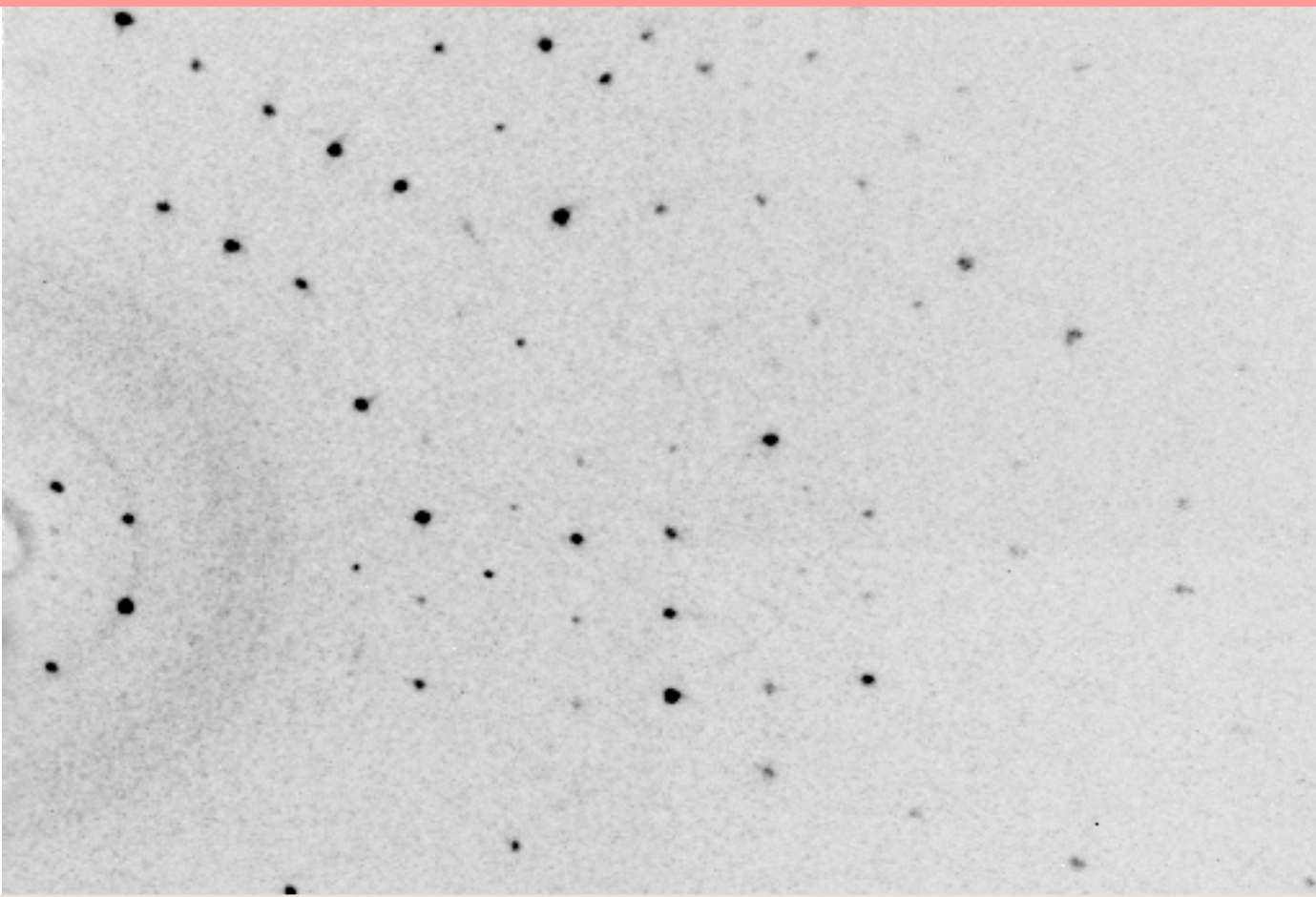
$$n\lambda = 2d \sin \theta \quad d^* = 2 \sin \theta / \lambda \quad 2\theta = 2 \sin^{-1} (\lambda d^* / 2)$$

$d(\min)$, $|d^*|(\max)$, $\theta(\max)$ and $2\theta(\max)$ are all used as indicators of resolution.

For a data set with a given resolution or $2\theta(\max)$, **“coverage”** is the fraction that has been measured, of all available reciprocal lattice points.

For a data set with a given resolution or $2\theta(\max)$, **“completeness”** is the fraction that has been measured, of all symmetry-independent reciprocal lattice points.

DIFFRACTION IMAGE FROM CCD DIFFRACTOMETER



- The geometry of the diffraction pattern (i.e., where the diffracted beams emerge) depends on the size and shape of the unit cell.
- The intensities of the diffracted beams depend on the contents of the unit cell.

We will use the **structure factor** for understanding the diffracted intensities.

The structure factor is the nexus of union between experimentally determined diffracted intensities and the internal structure of the unit cell.

$$F_{calc,hk\ell} = \sum_{atoms\ j} f_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + \ell z_j]}$$

$$T = 2\pi i [h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + \ell^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2h\ell a^* c^* U_{13} + 2k\ell b^* c^* U_{23}]$$

Scattering from a single electron -- Thomson Scattering:

$$P = \frac{8\pi}{3} \left(\frac{e^2}{4\pi\epsilon_0 c^2 m} \right)^2 I_o$$

P = power scattered by one electron

e = charge

ϵ_0 = electric permittivity of free space

c = speed of light

m = mass of the scatterer

Thomson scattering is coherent; there is a fixed relationship between the phase of the incident photon and the phase of the scattered photon.

(Compton Scattering involves electron recoil and is incoherent.)

Coherent scattering from one atom -- the atomic scattering factor:

$$f_a = 4\pi \int_{r=0}^{\infty} \rho_a(r) r^2 \frac{\sin 2\pi r s}{2\pi r s} dr = \sum_{j=1}^Z (p_s)_j$$

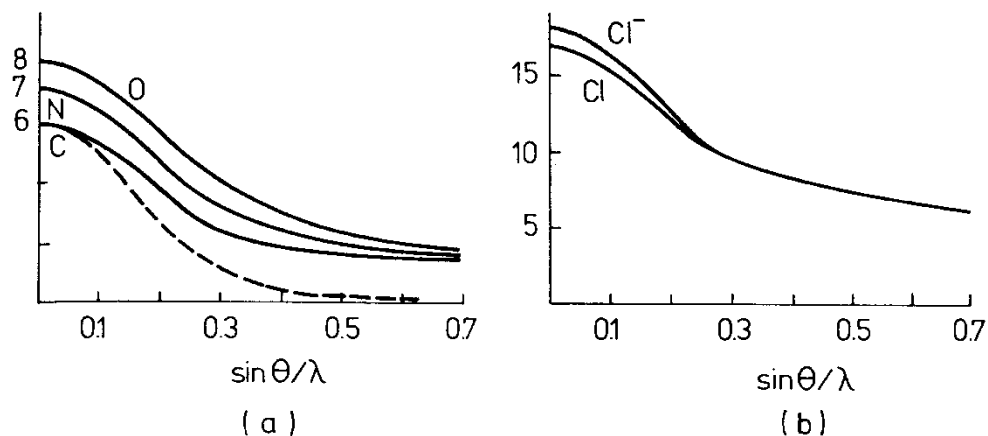
f_a = atomic scattering factor for atom **a** and scattering vector **s**

$\rho_a(r)$ = electron density in atom **a** at radius **r** from the center

$(p_s)_j$ = amplitude scattered by electron **j** (relative to that which would be scattered by a point charge at the center of the atom) for scattering vector **s**.

This expression assumes that the atom is spherical.

Diffraction of X-Rays by Crystals



J. D. Dunitz, *X-Ray Analysis and the Structure of Organic Molecules*

Figure 1.11. Form factors for isolated atoms at rest. (a) C, N, and O. (b) Cl and Cl^- . In (a) the scattering factor is also shown for a carbon atom with mean-square vibration amplitude of 0.1 \AA^2 .

An important fact in x-ray diffraction analysis is that the scattering strength of an atom, which is f_j in the structure factor equation below, diminishes as the scattering angle 2θ increases.

An important fact in any diffraction analysis (x-ray, neutron or other) is that thermal motion and other sources of displacement attenuate the atomic scattering factor [dashed curve in (a) above].

$$F_{calc,hkl} = \sum_{atoms\ j} f_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + lz_j]}$$

In x-ray diffraction, the atomic scattering factor decreases in value as the scattering angle 2θ increases, because the extent of the electron cloud is comparable to the wavelength of the radiation. So interference is produced.

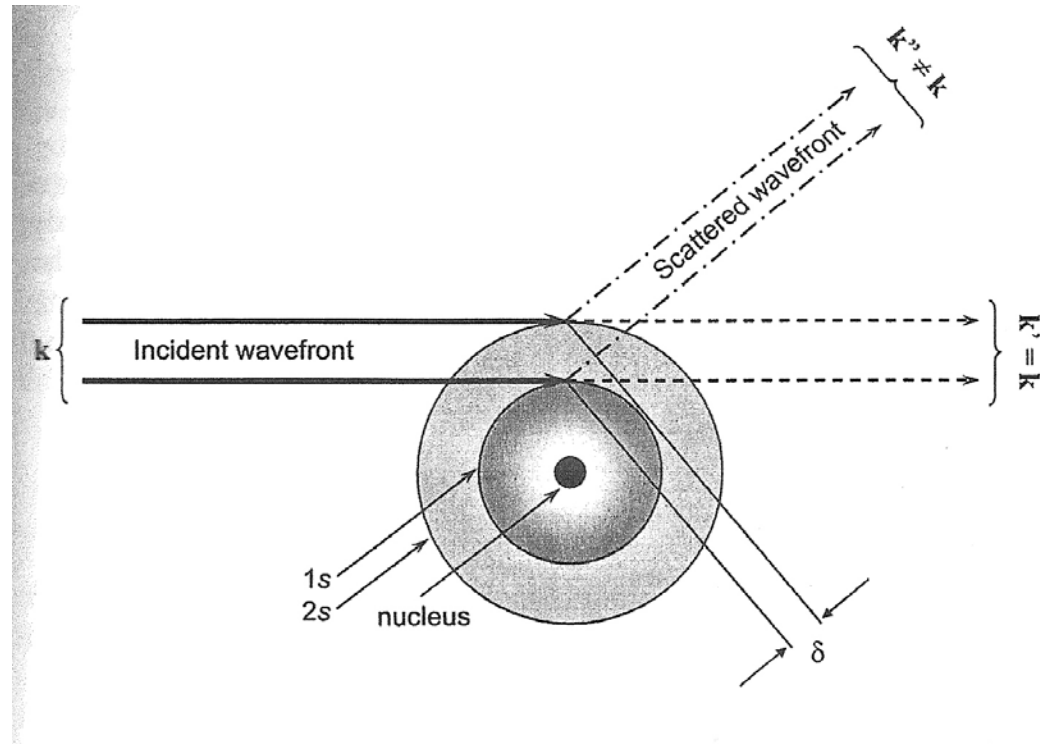
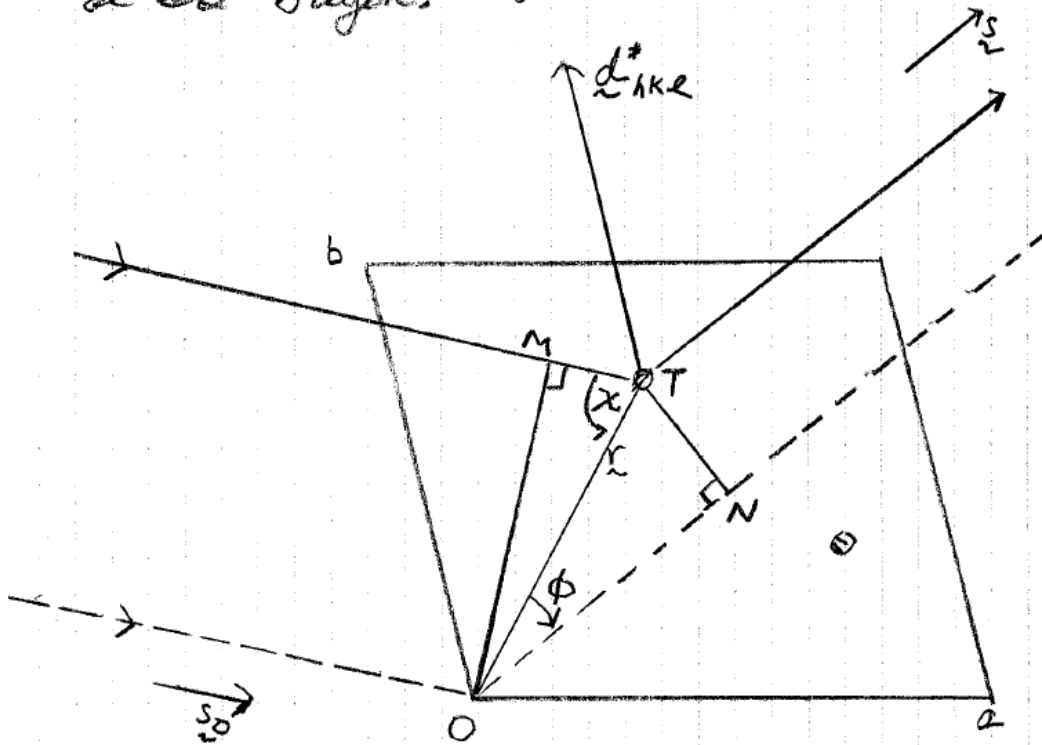


Figure 2.24. The schematic of the elastic scattering of x-rays by s electrons illustrating the introduction of a path difference, δ , into the wavefront with a propagation vector k' , when it is different from the propagation vector, k , of the incident beam. The distribution of electrons in two s -orbitals is determined from the corresponding wave functions.

Pecharsky, V. K & Zavalij, P. Y., *Fundamentals of Powder Diffraction and Structural Characterization of Materials*. Springer, 2005. e-ISBN: 0.387-2456-7

Path length difference between a wave scattered from atom T and a wave scattered from a hypothetical atom at the origin.



Path length difference:

$$ON - MT$$

$$ON = r \cos \phi$$

$$= \underline{r} \cdot \underline{s}$$

$$MT = r \cos \chi$$

$$= -\underline{r} \cdot -\underline{s}_0$$

$$= \underline{r} \cdot \underline{s}_0$$

$$ON - MT = \underline{r} \cdot \underline{s} - \underline{r} \cdot \underline{s}_0$$

$$= \underline{r} \cdot (\underline{s} - \underline{s}_0)$$

$$= \underline{r} \cdot \underline{d}_{hkl}^*$$

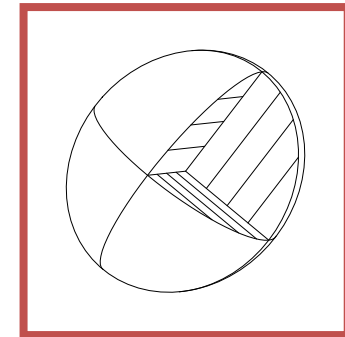
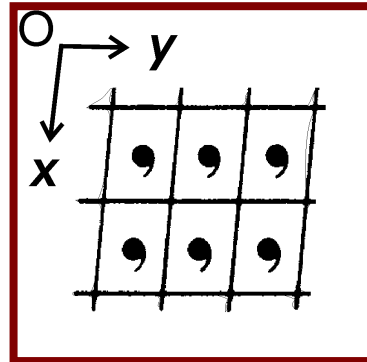
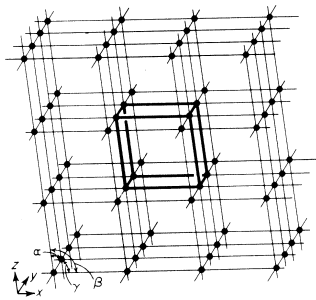
$$F_{calc, hkl} = \sum_{\text{atoms } j} f_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + lz_j]}$$

The structure factor, the diffraction data, and the structural model



$$F_{calc,hkl} = \sum_{atoms\ j} f_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + \ell z_j]}$$

$$T = 2\pi i [h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + \ell^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2h\ell a^* c^* U_{13} + 2k\ell b^* c^* U_{23}]$$

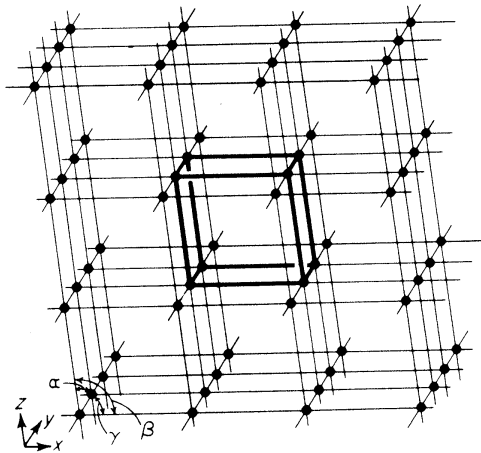


$$F_{obs,hkl} \propto \sqrt{I_{obs,hkl}}$$

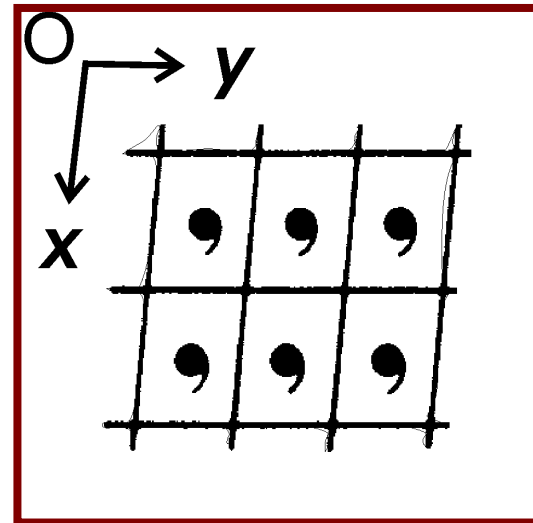


Electron density as a Fourier transform. The phase problem.

$$\rho_{xyz} = \sum_{hkl} |F_{obs,hkl}| \cdot \exp^{i\phi} \cdot \exp^{-2\pi i [hx_j + ky_j + \ell z_j]}$$



j
 i



The phase problem dictates our mode of operation. ✓

- (1) Measure diffracted intensities.
- (2) “Derive” (invent?) a structural model and calculate the data that would be produced by that model.
- (3) Compare the observed and calculated data.

$$(1) \quad \boxed{F_{obs,hkl} \propto \sqrt{I_{obs,hkl}}}$$

$$(2) \quad F_{calc,hkl} = \sum_{atoms\ j} f_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + \ell z_j]}$$

$$(3) \quad R1 = \frac{\sum_{hkl} \left| |F_{obs,hkl}| - |F_{calc,hkl}| \right|}{\sum_{hkl} |F_{obs,hkl}|}$$

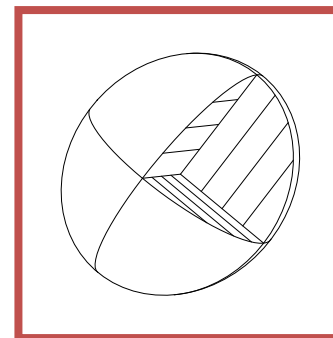
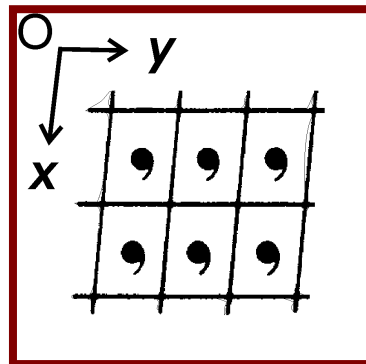
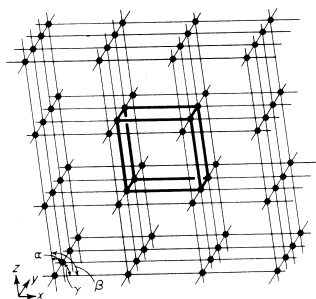
If the R-factor is small, the structural model is taken to be "correct."

The structure factor, the diffraction data, and the structural model, which is **parametric**. ✓

*
$$F_{calc,hkl} = \sum_{atoms\ j} f_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + lz_j]}$$

$$T = 2\pi i [h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2hka^* b^* U_{12} + 2hla^* c^* U_{13} + 2klb^* c^* U_{23}]$$

* F_{hkl} **calculated** from the structural model



* F_{hkl} derived from **measured** diffracted intensities

*
$$F_{obs,hkl} \propto \sqrt{I_{obs,hkl}}$$

Since the structural model is parametric, and there are usually many more data than parameters, least-squares analysis is used to derive the ideal values of the parameters.

$$F_{calc,hkl} = \sum_{\text{all atoms } j} f_j \exp^{2\pi i(hx_j + ky_j + lz_j)}$$

Minimize:

“Refinement on F”

$$D = \sum_{\text{all data } hkl} w_{hkl} \left(F_{obs,hkl} - F_{calc,hkl} \right)^2$$

“Refinement on F²”

$$D = \sum_{\text{all data } hkl} w_{hkl} \left(F_{obs,hkl}^2 - F_{calc,hkl}^2 \right)^2$$

Structure refinement by least squares.

$$F_{calc,hkl} = \sum_{\text{all atoms } j} f_j \exp^{2\pi i(hx_j + ky_j + lz_j)}$$

Least-squares principle -- For the “best” result, minimize this:

$$D = \sum_{\text{all data } hkl} w_{hkl} \left(F_{obs,hkl} - F_{calc,hkl} \right)^2$$

Modern practice -- minimize this:

$$D = \sum_{\text{all data } hkl} w_{hkl} \left(F_{obs,hkl}^2 - F_{calc,hkl}^2 \right)^2$$

$$D = \sum_{\text{all data } hkl} w_{hkl} \left(F_{obs,hkl} - \sum_{\text{all atoms } j} f_j \exp^{2\pi i(hx_j + ky_j + lz_j)} \right)^2$$

Crystallographic least-squares refinement

$$D = \sum_{\text{all data } hkl} w_{hkl} \left(F_{\text{obs},hkl} - \sum_{\text{all atoms } j} f_j \exp^{2\pi i(hx_j + ky_j + lz_j)} \right)^2$$

To minimize D: $\frac{\partial D}{\partial x_1} = 0$

More generally: $\frac{\partial D}{\partial p_1} = 0 \quad \frac{\partial D}{\partial p_2} = 0 \quad \frac{\partial D}{\partial p_3} = 0 \quad \dots \quad \frac{\partial D}{\partial p_n} = 0 \quad \text{etc.}$

If we have n parameters, we thus create n equations. With some approximations and some reorganization, we arrive at a set of n linear equations in n unknowns.

$$\begin{bmatrix} M_{11} & M_{12} & \cdots & M_{1,(n-1)} & M_{1n} \\ M_{21} & & & & M_{2n} \\ \vdots & & \ddots & & \vdots \\ M_{(n-1),1} & & & & M_{(n-1),n} \\ M_{n1} & & \cdots & M_{n,(n-1)} & M_{nn} \end{bmatrix} \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_{(n-1)} \\ \varepsilon_n \end{bmatrix} = \begin{bmatrix} g_1 \\ g_2 \\ \vdots \\ g_{(n-1)} \\ g_n \end{bmatrix}$$

$$M_{ij} = \sum_{hkl} w_{hkl} \left(\frac{\partial F_{calc,hkl}}{\partial p_i} \right) \left(\frac{\partial F_{calc,hkl}}{\partial p_j} \right)$$

$$g_i = \sum_{hkl} w_{hkl} \left(\frac{\partial F_{calc,hkl}}{\partial p_i} \right) (F_{obs,hkl} - F_{calc,hkl})$$

The quantity ε_i is the shift to be applied to parameter i . This set of equations is solved for the ε_i .

Crystallographic least-squares refinement

More briefly:
$$[M_{ij}][\varepsilon_j] = [g_i]$$

Note : $[M_{ij}]$ and $[g_i]$ can be calculated.

So the parameter shifts are obtained as:

$$[\varepsilon_j] = [M_{ij}]^{-1} [g_i]$$

We (actually, the program) apply the shifts to the parameters and begin again with the new structural model.



Crystallographic Least Squares – Agreement Indices

Traditional R-factor, using “observed” data [$I > 2\sigma(I)$, usually]:

$$R1 = \frac{\sum_{\text{all data } hkl} \left| |F_{obs,hkl}| - |F_{calc,hkl}| \right|}{\sum_{\text{all data } hkl} |F_{obs,hkl}|}$$

Weighted R-factor, using all data (statistically significant):

$$wR2 = \left\{ \frac{\sum_{\text{all data } hkl} w_{hkl} (F_{obs,hkl}^2 - F_{calc,hkl}^2)^2}{\sum_{\text{all data } hkl} w_{hkl} (F_{obs,hkl}^2)^2} \right\}^{1/2}$$

“Quality of fit,” “goodness of fit,” “GOOF”:

$$q.o.f. = \left\{ \frac{\sum_{\text{all data } hkl} w_{hkl} (F_{obs,hkl}^2 - F_{calc,hkl}^2)^2}{(N_{\text{observations}} - N_{\text{parameters}})} \right\}^{1/2}$$

Convergence, Standard Uncertainty, Correlation

$$\sigma^2(p_i) = \frac{M_{ii}^{-1} \sum_{\text{data } hkl} (F_{obs,hkl}^2 - F_{calc,hkl}^2)^2}{(N_{observations} - N_{parameters})}$$

$$\sigma^2(p_i p_j) = \frac{M_{ij}^{-1} \sum_{\text{data } hkl} (F_{obs,hkl}^2 - F_{calc,hkl}^2)^2}{(N_{observations} - N_{parameters})}$$

A crystallographic least-squares refinement is considered to have **converged** when no parameter changes by as much as ± 0.01 times its estimated standard deviation (standard uncertainty).

Difference Fourier Map

$$\rho - \rho_{calc, partial}(xyz) = \sum_{hkl} \left| F_{obs, hkl} \right| - \left| F_{calc, (partial), hkl} \right| \exp^{i\phi_{calc(partial), hkl}} \exp^{-2\pi i(hx+ky+lz)}$$

The Fourier transform using phases calculated from the model structure and, as coefficients, the differences between F_{obs} and F_{calc} will give, under favorable conditions, the part of the “full” structure that is not yet included in the model.

The difference Fourier map is used to find atoms that have not yet been incorporated into the structural model.

It is also used as a test of whether all atoms have been found.

Crystallographic Information File (CIF)



<http://www.iucr.org/iucr-top/cif/>

Acta Cryst. (1991). A47, 655-685

data_x2

```
_audit_creation_method          SHELXL-97
_chemical_name_systematic
;
?
;
_chemical_formula_sum
  'C8 H12 N6 O4 Zn'
_chemical_formula_weight        321.61

_cell_length_a                   9.3896(7)
_cell_length_b                   6.9093(10)
_cell_length_c                   19.3766(16)
_cell_angle_alpha                90.00
_cell_angle_beta                 90.951(8)
_cell_angle_gamma                90.00
_cell_volume                     1256.9(2)
_cell_formula_units_Z            4
_cell_measurement_temperature    150(2)
_cell_measurement_reflns_used    ?
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loop_

_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
_atom_site_symmetry_multiplicity
_atom_site_calc_flag
_atom_site_refinement_flags
_atom_site_disorder_assembly
_atom_site_disorder_group

Structural Results:

Atomic Coordinates (CIF format)

```
Zn1 Zn 0.86552(6) 0.14715(7) 0.60752(3) 0.01304(16) Uani 1 1 d . . .  
N11 N 0.6883(4) -0.0015(5) 0.58618(18) 0.0136(8) Uani 1 1 d . . .  
C12 C 0.7004(5) -0.1394(7) 0.5366(2) 0.0149(10) Uani 1 1 d . . .  
O12 O 0.8068(3) -0.1547(5) 0.49967(15) 0.0172(7) Uani 1 1 d . . .  
N13 N 0.5882(4) -0.2676(6) 0.52820(18) 0.0140(8) Uani 1 1 d . . .  
H13 H 0.596(5) -0.357(7) 0.501(2) 0.017 Uiso 1 1 d . . .  
C14 C 0.4612(5) -0.2611(7) 0.5632(2) 0.0140(10) Uani 1 1 d . . .  
O14 O 0.3674(3) -0.3850(5) 0.55053(16) 0.0196(8) Uani 1 1 d . . .  
C15 C 0.4523(5) -0.1090(7) 0.6121(2) 0.0175(10) Uani 1 1 d . . .  
H15 H 0.366(5) -0.092(7) 0.636(2) 0.021 Uiso 1 1 d . . .  
C16 C 0.5656(5) 0.0084(7) 0.6217(2) 0.0181(10) Uani 1 1 d . . .  
H16 H 0.567(5) 0.107(7) 0.654(2) 0.022 Uiso 1 1 d . . .  
N21 N 0.8113(5) 0.6163(5) 0.7455(2) 0.0192(9) Uani 1 1 d . . .  
H21 H 0.812(6) 0.728(8) 0.740(3) 0.023 Uiso 1 1 d . . .
```

Structural Results:

Atomic Displacement Parameters

(ADP's)

loop_
_atom_site_aniso_label
_atom_site_aniso_U_11
_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12

Zn1 0.0151(3) 0.0100(3) 0.0140(3) -0.0011(2) 0.0012(2) -0.0026(3)
N11 0.012(2) 0.0105(18) 0.0181(19) -0.0012(16) -0.0006(16) -0.0012(16)
C12 0.015(2) 0.015(2) 0.015(2) 0.002(2) 0.0001(19) 0.000(2)
O12 0.0141(17) 0.0194(17) 0.0183(15) 0.0006(14) 0.0037(13) -0.0016(15)
N13 0.016(2) 0.015(2) 0.0114(18) -0.0051(16) 0.0000(16) -0.0019(18)
C14 0.013(2) 0.015(2) 0.015(2) 0.0004(19) -0.0005(19) 0.001(2)
O14 0.0156(17) 0.0197(19) 0.0236(17) -0.0054(14) 0.0020(14) -0.0066(15)
C15 0.013(2) 0.017(3) 0.022(2) -0.005(2) 0.002(2) 0.000(2)
C16 0.020(3) 0.013(2) 0.021(2) -0.007(2) 0.003(2) 0.000(2)
N21 0.033(3) 0.0043(18) 0.020(2) -0.0025(17) 0.0024(18) 0.0022(19)
C22 0.017(2) 0.008(2) 0.020(2) -0.0038(19) -0.005(2) -0.001(2)
O22 0.039(2) 0.0078(16) 0.0199(17) 0.0030(13) 0.0030(16) -0.0030(16)
N23 0.014(2) 0.0093(19) 0.0155(18) -0.0023(15) 0.0020(16) 0.0002(16)
C24 0.018(3) 0.011(2) 0.015(2) 0.0003(19) 0.0003(19) 0.000(2)
O24 0.027(2) 0.0083(16) 0.0180(16) 0.0019(14) -0.0029(15) -0.0011(15)
C25 0.022(3) 0.021(3) 0.014(2) -0.001(2) 0.005(2) 0.005(2)
C26 0.024(3) 0.014(3) 0.018(2) -0.006(2) 0.006(2) 0.002(2)
N1 0.016(2) 0.012(2) 0.017(2) -0.0032(17) -0.0012(17) 0.0008(18)
N2 0.020(2) 0.013(2) 0.016(2) -0.0034(17) 0.0014(17) -0.0021(19)



Presentation of Results

A numerical value is presented with its standard uncertainty in parentheses. The standard uncertainty is expressed in units of the final digit given for the datum. Rounding is done in such a way that the standard uncertainty has a value between (2) and (19).

Numerical results obtained for N11:

N11	0.68828	-0.00148	0.58618	0.01357	<i>x, y, z, Uiso</i>
	0.00039	0.00053	0.00018	0.00081	s.u.'s of <i>x, y, z, Uiso</i>

Presentation:

N11 N 0.6883(4) -0.0015(5) 0.58618(18) 0.0136(8) Uani 1 1 d . . .

For N11, the x-coordinate has a value of 0.6883 with a standard uncertainty of 0.0004. The z-coordinate has a value of 0.58618 with a standard uncertainty of 0.00018.

Numerical results obtained for N13:

N13	0.01580	0.01491	0.01136	-0.00508	-0.00004	-0.00192
	0.00205	0.00203	0.00180	0.00163	0.00158	0.00179

Presentation:

N13 0.016(2) 0.015(2) 0.0114(18) -0.0051(16) 0.0000(16) -0.0019(18)

For N13, U_{11} has a value of 0.016 with an s.u. of 0.002. U_{13} has a value of 0.0000 with s.u. of 0.0016.

Derived Parameters

Most commonly calculated entities:

- distance: two atoms
- angle: three atoms
- torsion angle: four atoms
- plane: three or more atoms
- dihedral angle: two planes
- interplanar spacing
- etc.

The metric tensor is used in the calculation of distances and related **derived parameters** in crystallographic reference frames.

Distance between atoms at (x_i, y_i, z_i) and (x_j, y_j, z_j) :

$$d_{ij}^2 = (\Delta x, \Delta y, \Delta z) \begin{bmatrix} \underline{a \cdot a} & \underline{a \cdot b} & \underline{a \cdot c} \\ \underline{a \cdot b} & \underline{b \cdot b} & \underline{b \cdot c} \\ \underline{a \cdot c} & \underline{b \cdot c} & \underline{c \cdot c} \end{bmatrix} \begin{pmatrix} \Delta x \\ \Delta y \\ \Delta z \end{pmatrix}$$

$$d_{ij}^2 = (x_j - x_i, y_j - y_i, z_j - z_i) \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ab \cos \gamma & b^2 & bc \cos \alpha \\ ac \cos \beta & bc \cos \alpha & c^2 \end{bmatrix} \begin{pmatrix} x_j - x_i \\ y_j - y_i \\ z_j - z_i \end{pmatrix}$$

Unit cell vectors: \underline{a} , \underline{b} , \underline{c}

Unit cell scalars: a , b , c , α , β , γ

loop_

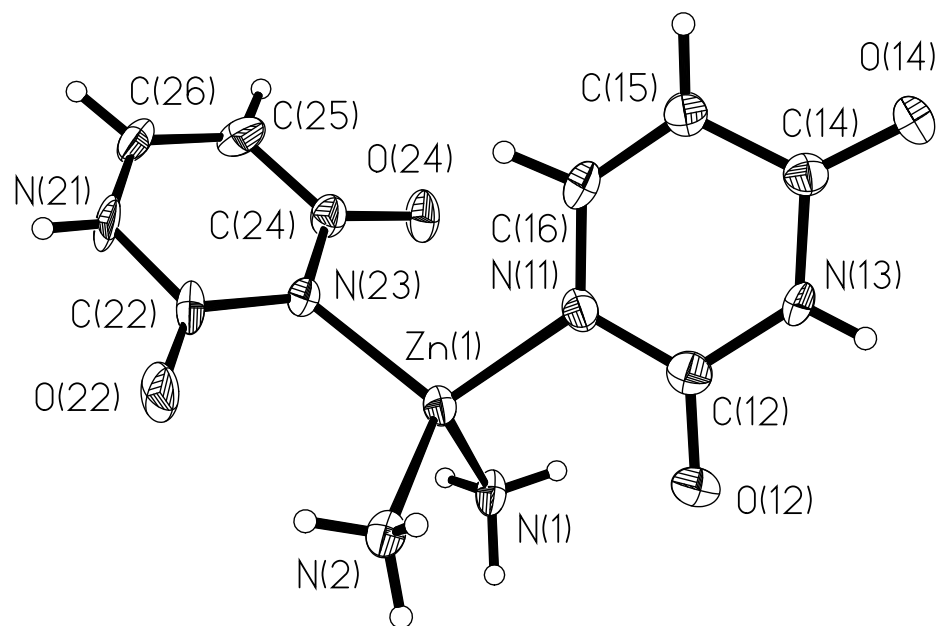
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Zn1 N11 1.993(4) . ?
Zn1 N2 2.006(4) . ?
Zn1 N23 2.011(4) . ?
Zn1 N1 2.015(4) . ?

loop_

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N11 Zn1 N2 107.67(16) . . ?
N11 Zn1 N23 109.66(15) . . ?
N2 Zn1 N23 108.71(16) . . ?
N11 Zn1 N1 110.06(16) . . ?
N2 Zn1 N1 107.04(18) . . ?
N23 Zn1 N1 113.50(16) . . ?





Public Domain Software (partial list)

SHELX: <http://shelx.uni-goettingen.de/>

CRYSTALS: <http://www.xtl.ox.ac.uk/crystals.html>

SHELXle: <https://www.shelxle.org/shelx/eingabe.php>

WinGX: <http://www.chem.gla.ac.uk/~louis/software/wingx/>

ORTEP for Windows: <http://www.chem.gla.ac.uk/~louis/software/ortep/index.html>

PLATON: <https://www.platonsoft.nl/platon/pl000000.html>

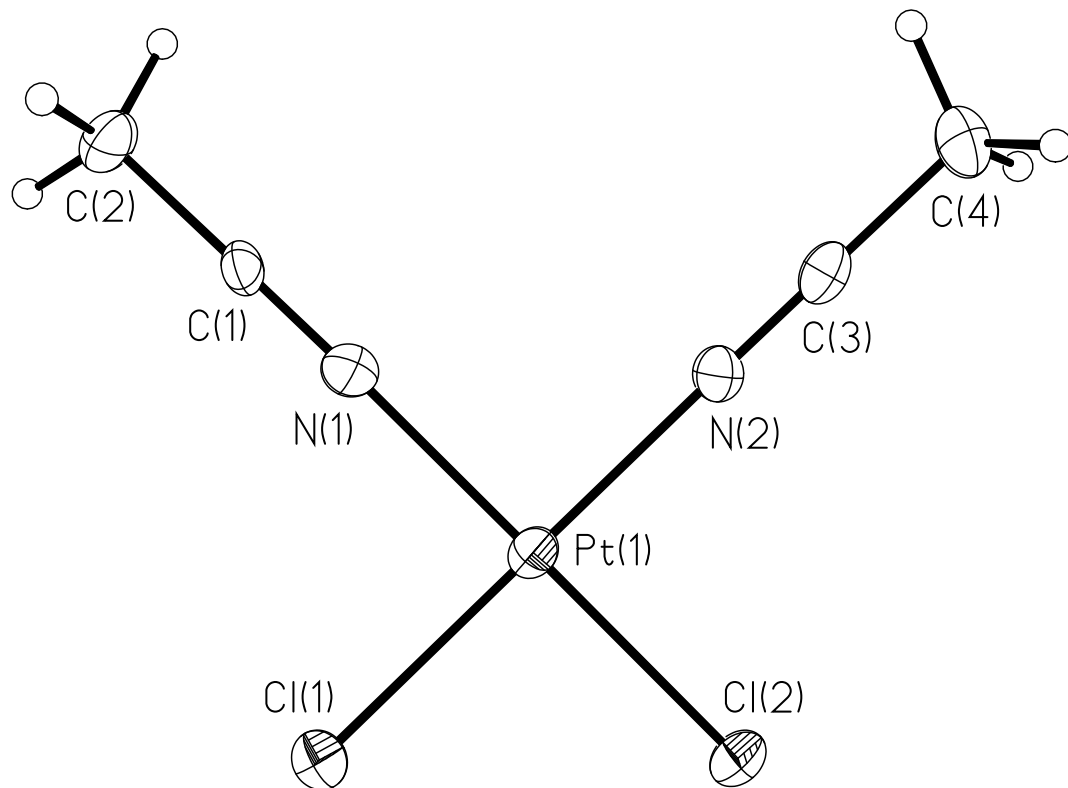
PLATON for Windows: <http://www.chem.gla.ac.uk/~louis/software/platon/index.html>

OLEX2: <http://www.olexsys.org>

FULLPROF: <http://www.ill.eu/sites/fullprof/>

GSAS-II: <https://subversion.xray.aps.anl.gov/trac/pyGSAS>

The observation and its referent.



distances, Å

Pt1 N2: 1.975(5)

Pt1 N1: 1.979(5)

Pt1 Cl1: 2.2679(17)

Pt1 Cl2: 2.2716(15)

N1 C1 1.138(8)

N2 C3 1.128(8)

angles, °

N2 Pt1 N1 91.1(2)

N2 Pt1 Cl1 178.46(16)

N1 Pt1 Cl1 88.81(16)

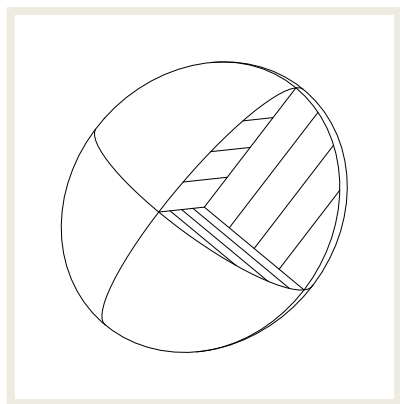
N2 Pt1 Cl2 89.24(15)

N1 Pt1 Cl2 177.52(16)

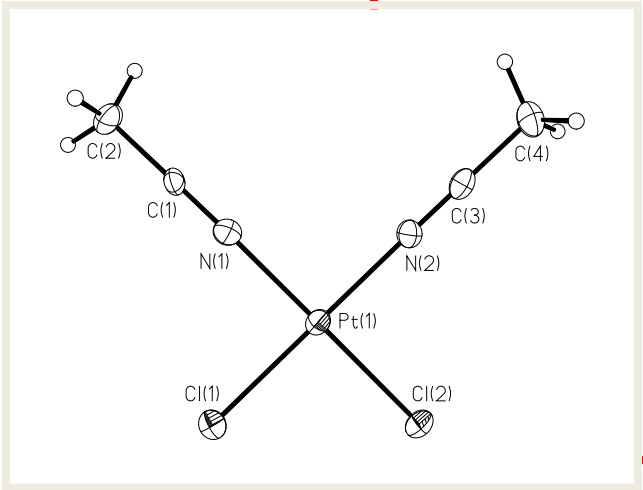
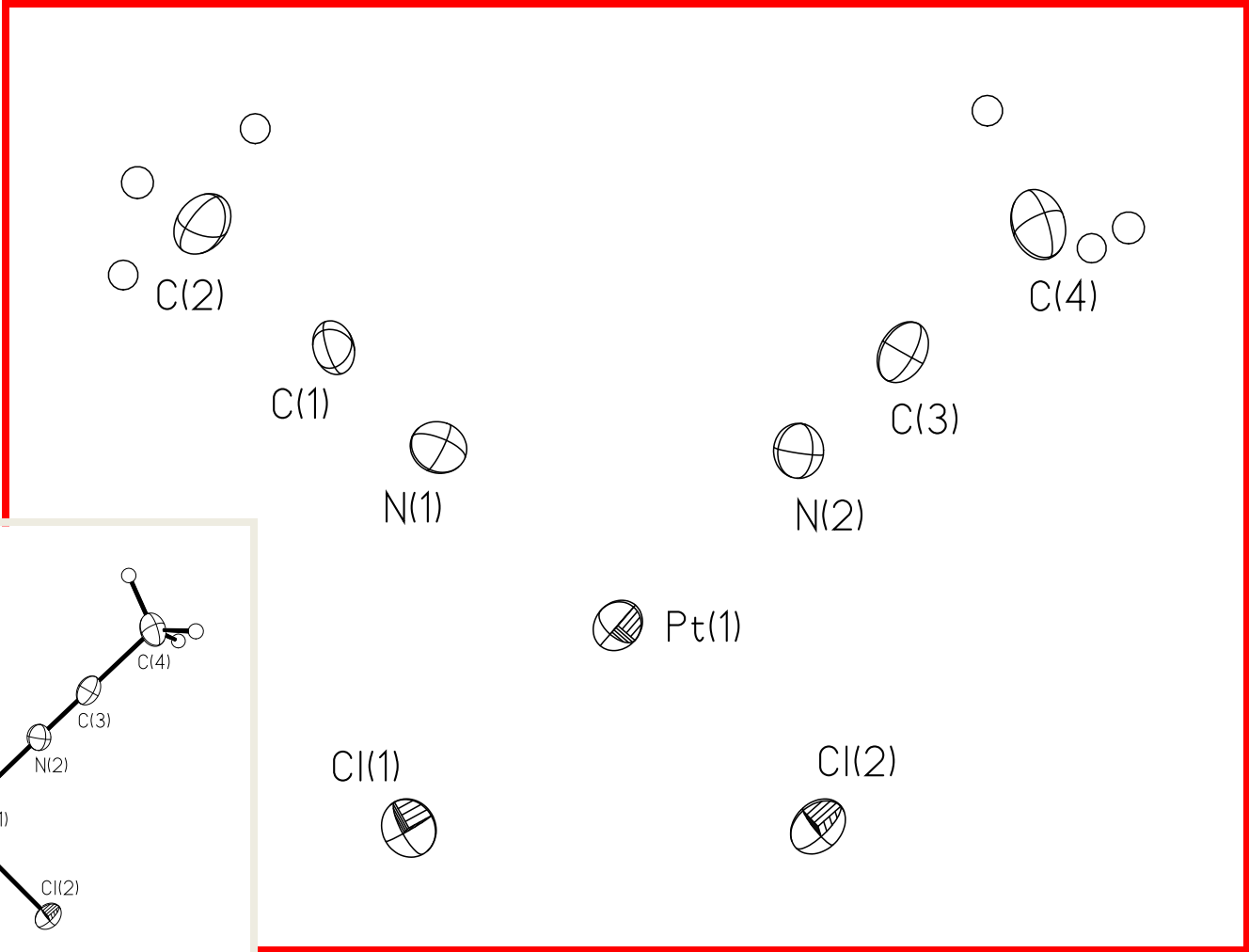
Cl1 Pt1 Cl2 90.87(6)

C1 N1 Pt1 174.1(5)

C3 N2 Pt1 178.4(5)



The Structural Model





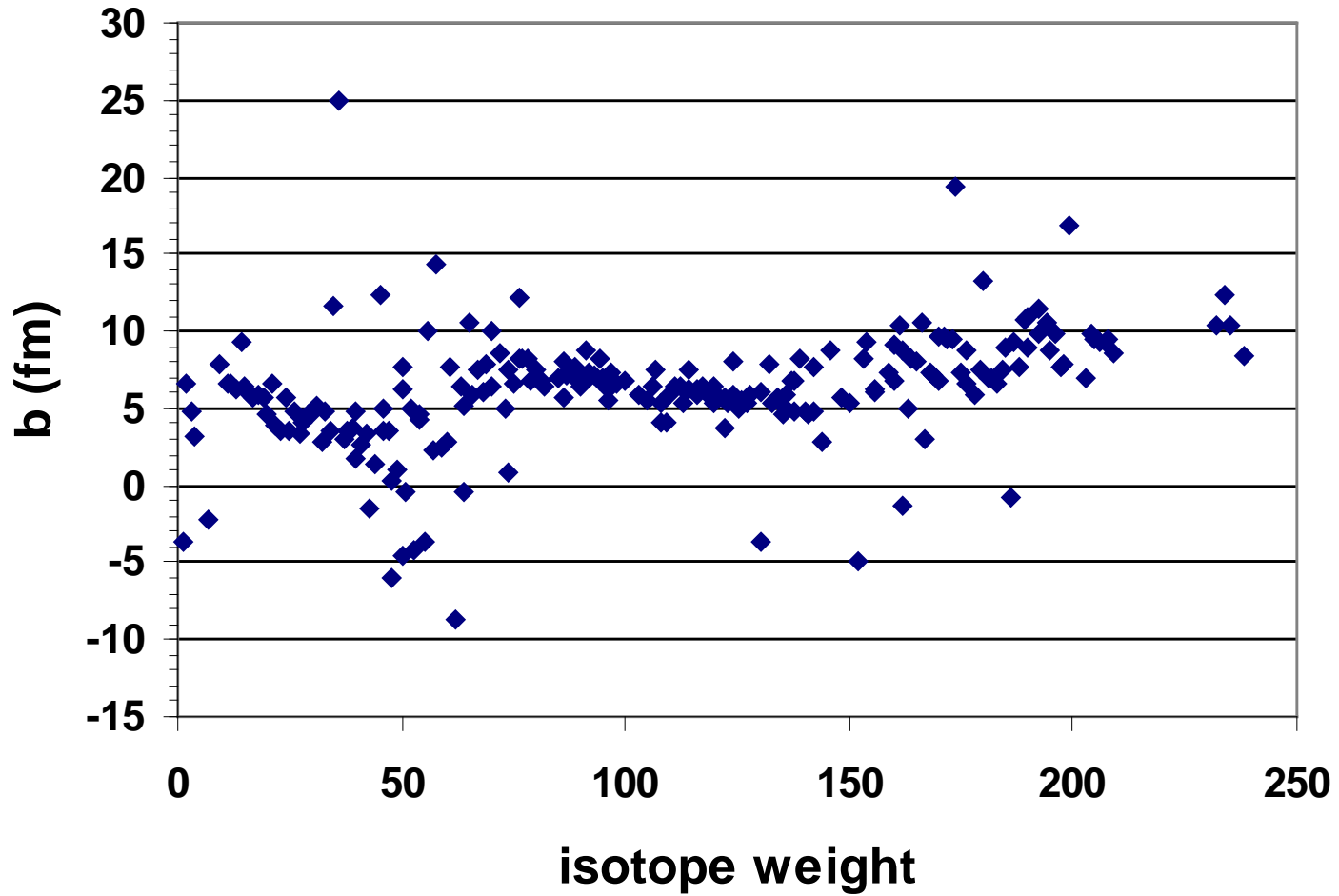
neutron diffraction

<https://www.ill.eu/neutrons-for-society/about-neutrons/>

<https://neutrons.ornl.gov/science>

<http://www.isis.stfc.ac.uk/about-isis/aboutisis.html>

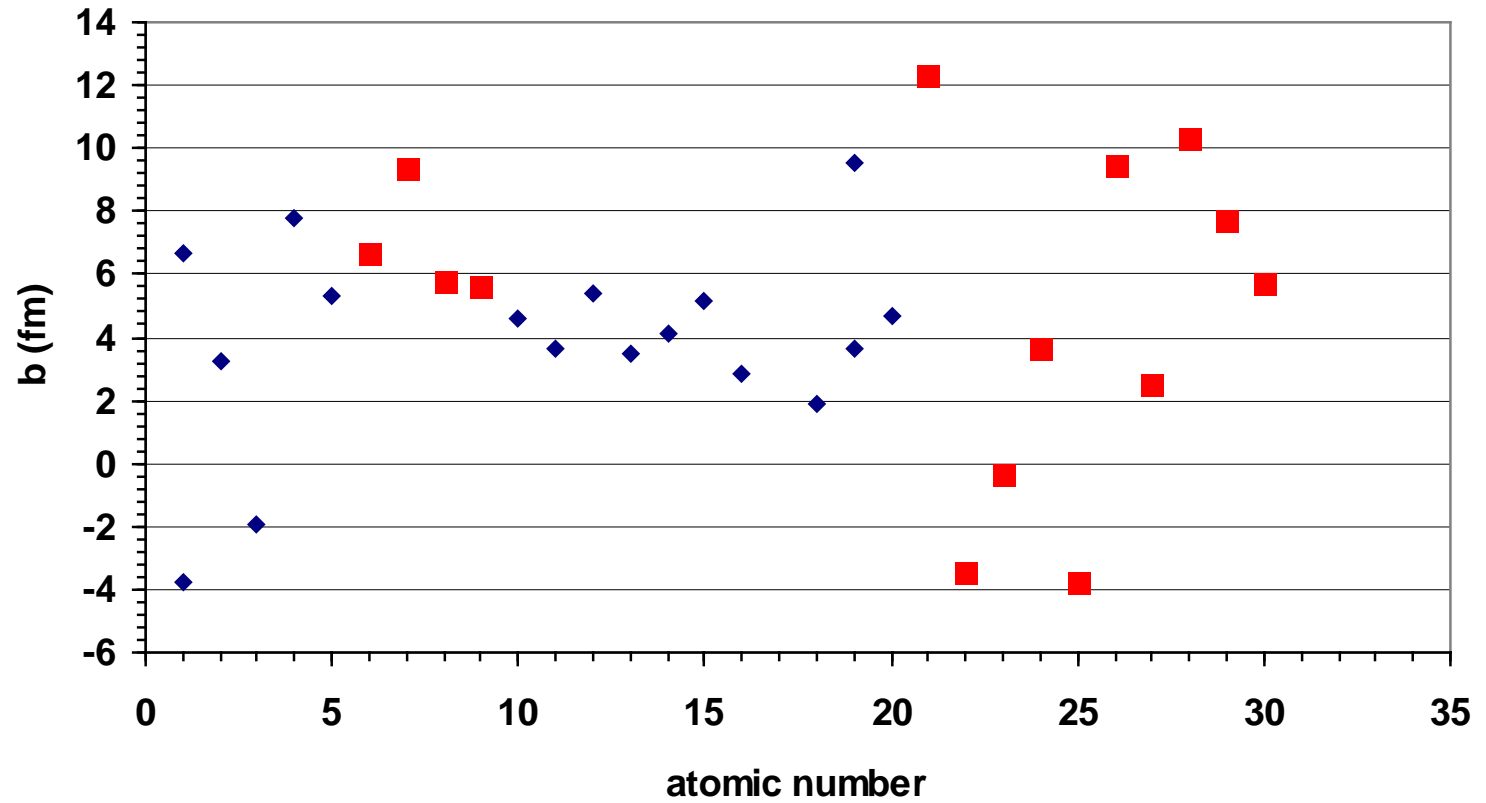
Bound Scattering Length vs. Isotope Weight



Source: <http://webster.ncnr.nist.gov/resources/n-lengths/>



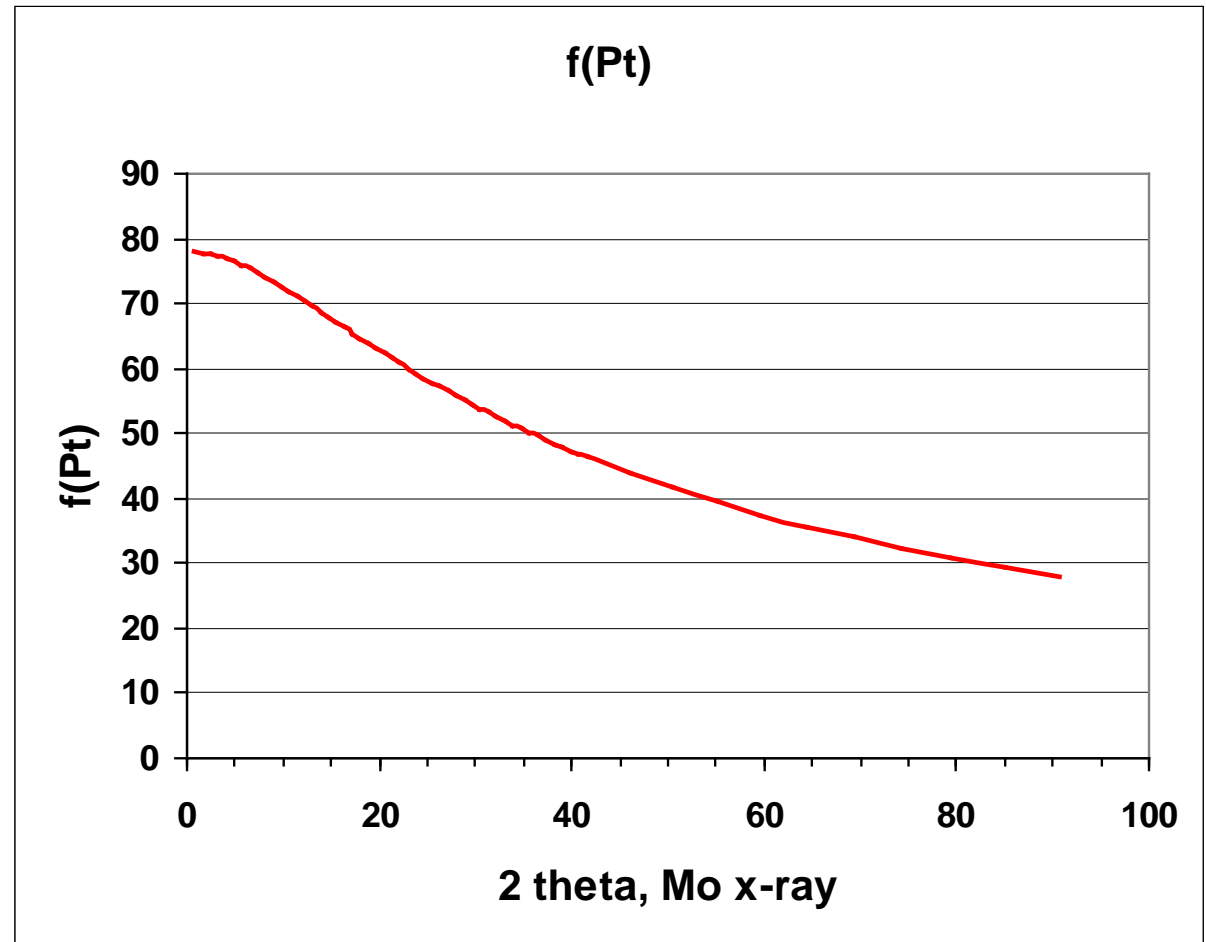
Bound Scattering Lengths vs. Z



$$F_{calc,hk\ell} = \sum_{atoms\ j} f_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + \ell z_j]}$$

X-Ray scattering factors decrease with increasing scattering angle, for a given wavelength.

Neutron scattering lengths do not.



The diffracted **intensities** depend on the contents of the unit cell.

$$F_{calc,hk\ell} = \sum_{atoms\ j} b_j \exp^{-T} \cdot \exp^{2\pi i [hx_j + ky_j + \ell z_j]}$$

The structure factor expression describes the diffracted intensities produced by a given unit-cell content.

When we analyze a structure, we start from the structure factors, or their squares, the measured intensities, and we want to calculate the unit-cell contents.

$$\rho_{xyz} = \sum_{hk\ell} |F_{obs,hk\ell}| \cdot \exp^{i\phi} \cdot \exp^{-2\pi i [hx_j + ky_j + \ell z_j]}$$



What is unique to single-crystal **neutron** diffraction?

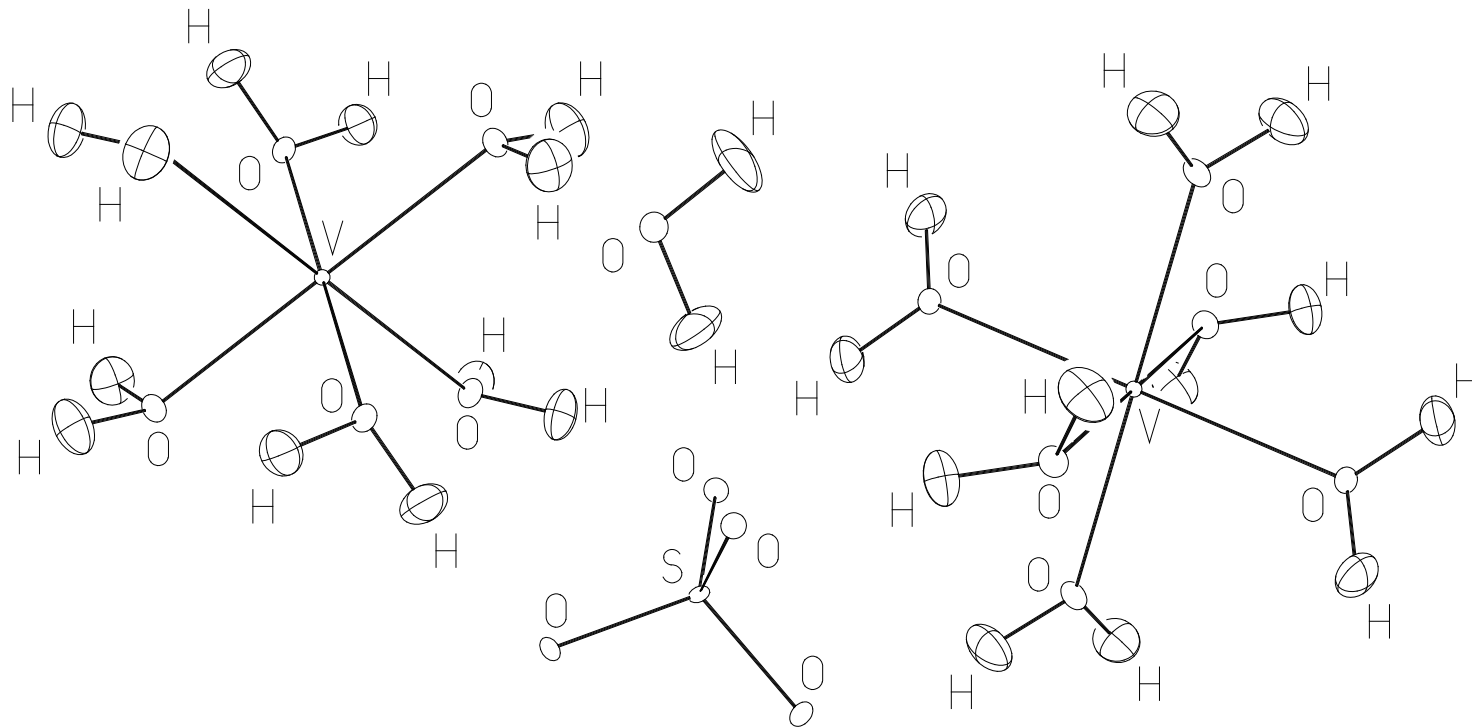
- *b*
- **sample size**
- **accessibility**
- **energy**
- **special environments**
- **spin**
- **Laue technique with time-of-flight**
- **absorption and extinction properties**

It is because of the properties of b as a function of element and isotope that single-crystal neutron diffraction has acquired its best-known application – the location of hydrogen atoms.

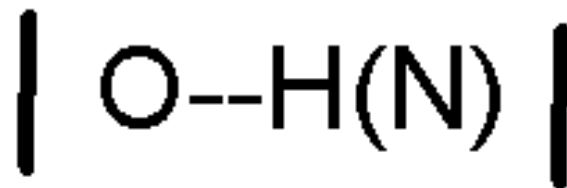
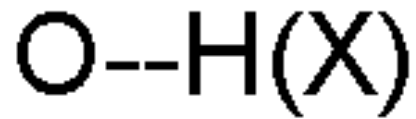
However, the properties of b also enable other applications, for example:

- “neutron distances” for bonds involving hydrogen atoms (*vide infra*)
- distinguishing the elements of the first d-block series
- distinguishing C from N, and N from O (*vide infra*)
- anisotropic displacement parameters of H
- crystallographic tricks, such as the correct use of two different space groups for the same structure (*vide infra*)

$\text{VSO}_4 \cdot 7\text{H}_2\text{O}$



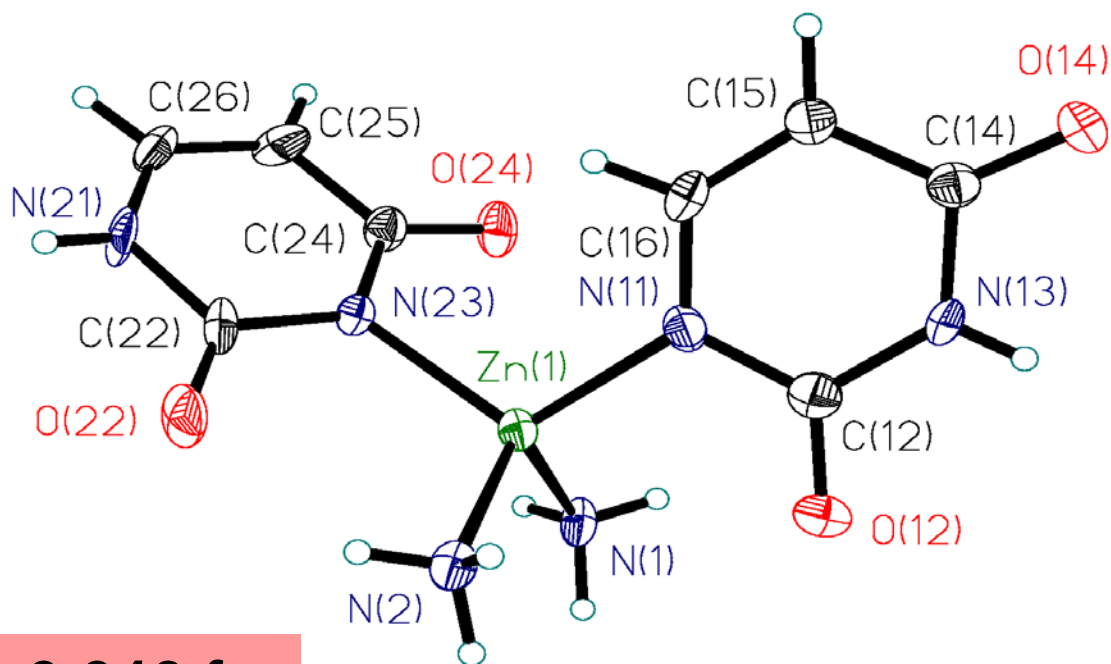
“X-Ray Distance” and “Neutron Distance”



VSO₄·7H₂O Hydrogen-Bond Geometry (X-Ray and Neutron)

D—H...A "coords. Å"	D...A Å	D—H Å	H...A Å	D—H...A (°)
O(1w) - H(11) ... O(1) "x, y, z"	2.757(3) 2.758(4)	0.81(4) 0.990(7)	1.96(4) 1.788(7)	166(4) 165.7(6)
O(1w) - H(12) ... O(2) "x, 1/2 - y, -1/2 + z"	2.739(3) 2.729(3)	0.74(4) 0.970(5)	2.00(4) 1.762(6)	177(3) 174.3(7)
O(2w) - H(21) ... O(2) "x, -1 + y, z"	2.777(3) 2.776(4)	0.79(3) 0.984(8)	2.02(3) 1.809(7)	162(3) 167.1(6)
O(2w) - H(22) ... O(4) " x, y, z"	2.877(3) 2.893(4)	0.78(3) 0.984(7)	2.11(3) 1.923(7)	169(3) 168.0(7)
O(3w) - H(31) ... O(2) "x, y, z"	2.945(3) 2.859(4)	0.88(4) 0.966(8)	2.10 (4) 1.907(7)	162(4) 168.1(6)
O(3w) - H(32) ... O(1) "-x, 1 - y, -z"	2.863(3) 2.828(4)	0.82(3) 0.968(7)	2.05(4) 1.861(7)	174(3) 176.9(6)
O(4w) - H(41) ... O(3) "x, y, z"	2.798(3) 2.793(3)	0.78(4) 0.971(6)	2.02(4) 1.826(6)	177(4) 173.8(7)

Distinguishing Carbon and Nitrogen



C: $b = 6.646$ fm
N: $b = 9.36$ fm

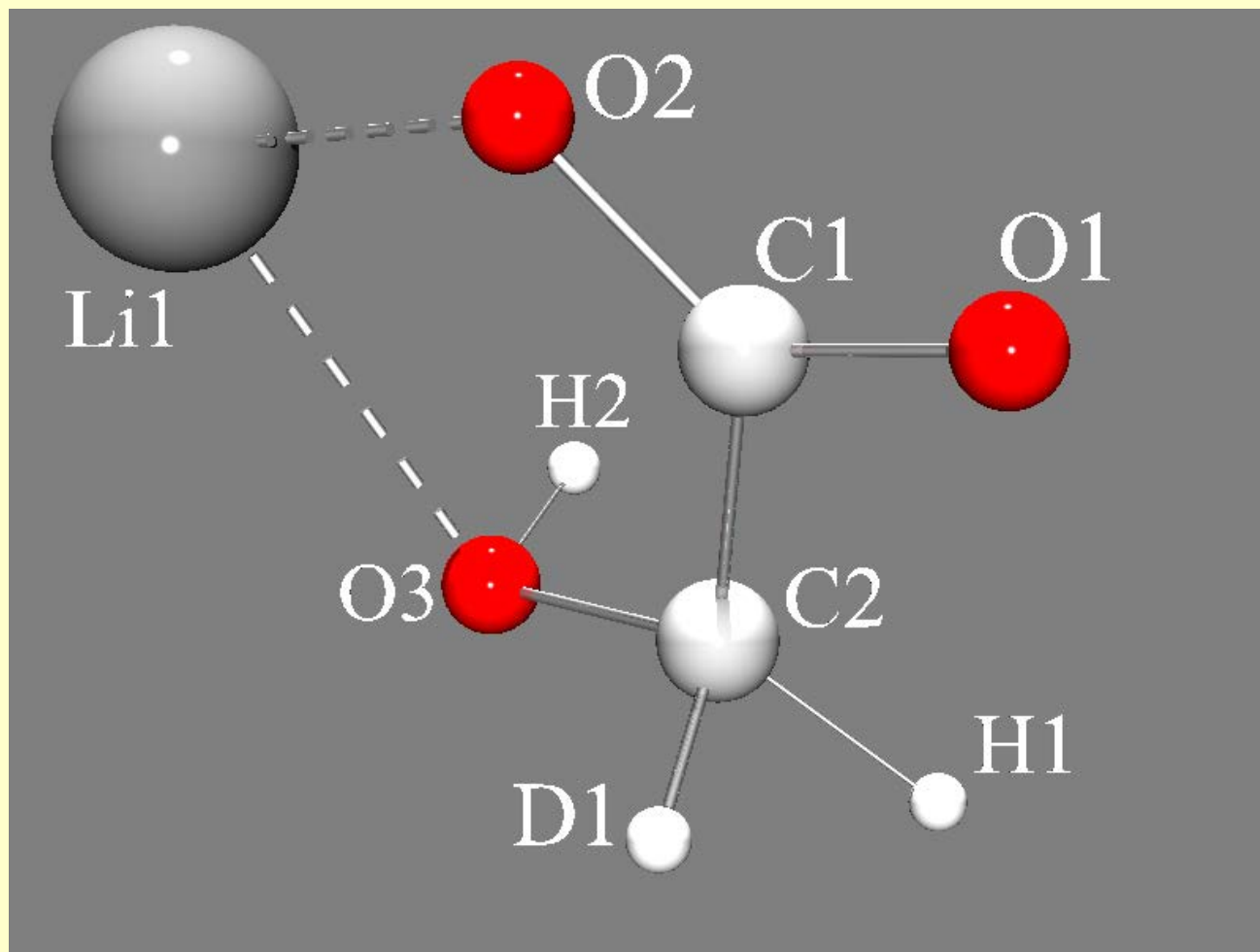
Two Space Groups for the Same Structure: Li α -deuteroglycollate

Johnson, C. K., Gabe, E. J., Taylor, M. R., Rose, I. A. (1965). *J. Am. Chem. Soc.* 87, 1802.

X-ray: $P2_1/n$

Neutron: $P2_1$

$Z = 4$



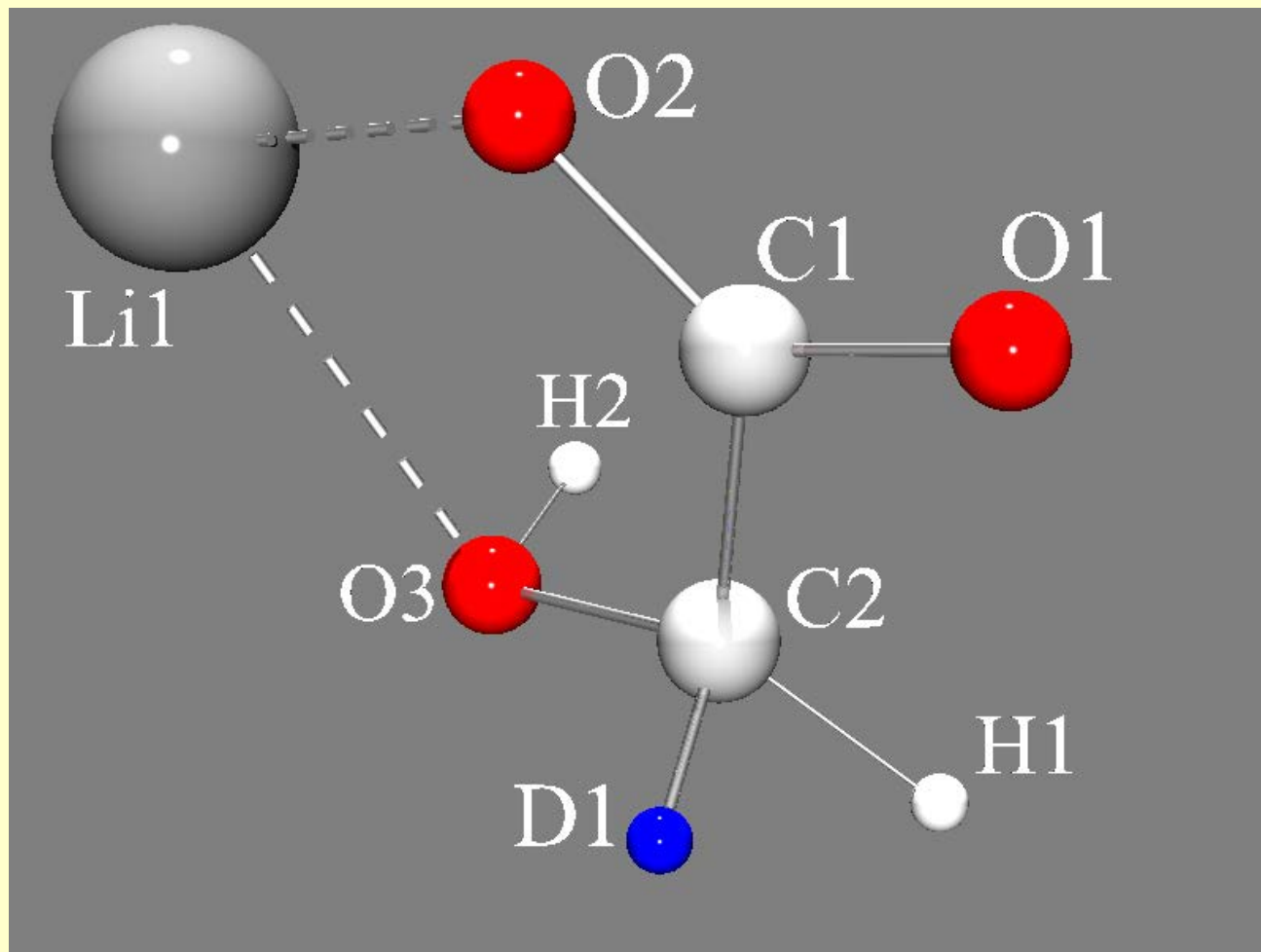
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Neutron: $P2_1$

Z = 4





ENERGY: Neutrons vs. X-Rays

For $\text{MoK}\bar{\alpha}$ x-radiation ($\lambda = 0.71069 \text{ \AA}$):

$$E = h\nu = \frac{hc}{\lambda} = 2.795 \times 10^{-15} \text{ J} = 17440 \text{ eV} = 17.4 \text{ keV}$$

For $\text{CuK}\bar{\alpha}$ x-radiation ($\lambda = 1.5418 \text{ \AA}$):

$$E = h\nu = \frac{hc}{\lambda} = 1.288 \times 10^{-15} \text{ J} = 8040 \text{ eV} = 8.04 \text{ keV}$$

For neutrons with $\lambda = 0.71069 \text{ \AA}$:


$$\lambda = \frac{h}{p} = \frac{h}{mv} \quad v = \frac{h}{m\lambda} = 5566 \text{ m/s}$$

$$E_n(\text{meV}) = 81.8/\lambda^2 (\text{\AA}^2)$$

$$E = \frac{1}{2}mv^2 = 2.594 \times 10^{-20} \text{ J} = 0.162 \text{ eV} = 162 \text{ meV} \quad \sim 1300 \text{ cm}^{-1}$$

For neutrons with $\lambda = 1.5418 \text{ \AA}$: $v = 2566 \text{ m/s}$

$$E = 5.514 \times 10^{-21} \text{ J} = 0.0344 \text{ eV} = 34.4 \text{ meV} \quad \sim 280 \text{ cm}^{-1}$$



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Nanostructured Materials for Nanotechnology Applications

Materiales Nanoestructurados para Aplicaciones en Nanotecnología

Module 4 -- Characterization I: Physical-Chemical Techniques

Diffraction

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