nanomat

Nanostructured Materials for Nanotechnology Applications

Materiales Nanoestructurados para Aplicaciones en Nanotecnología

Module 4 -- Characterization I: Physical-Chemical Techniques

Diffraction

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Powder Diffraction

Powder diffraction is used in many contexts, and especially in industrial applications such as quality control.

-- qualitative phase analysis

-- quantitative phase analysis, or composition

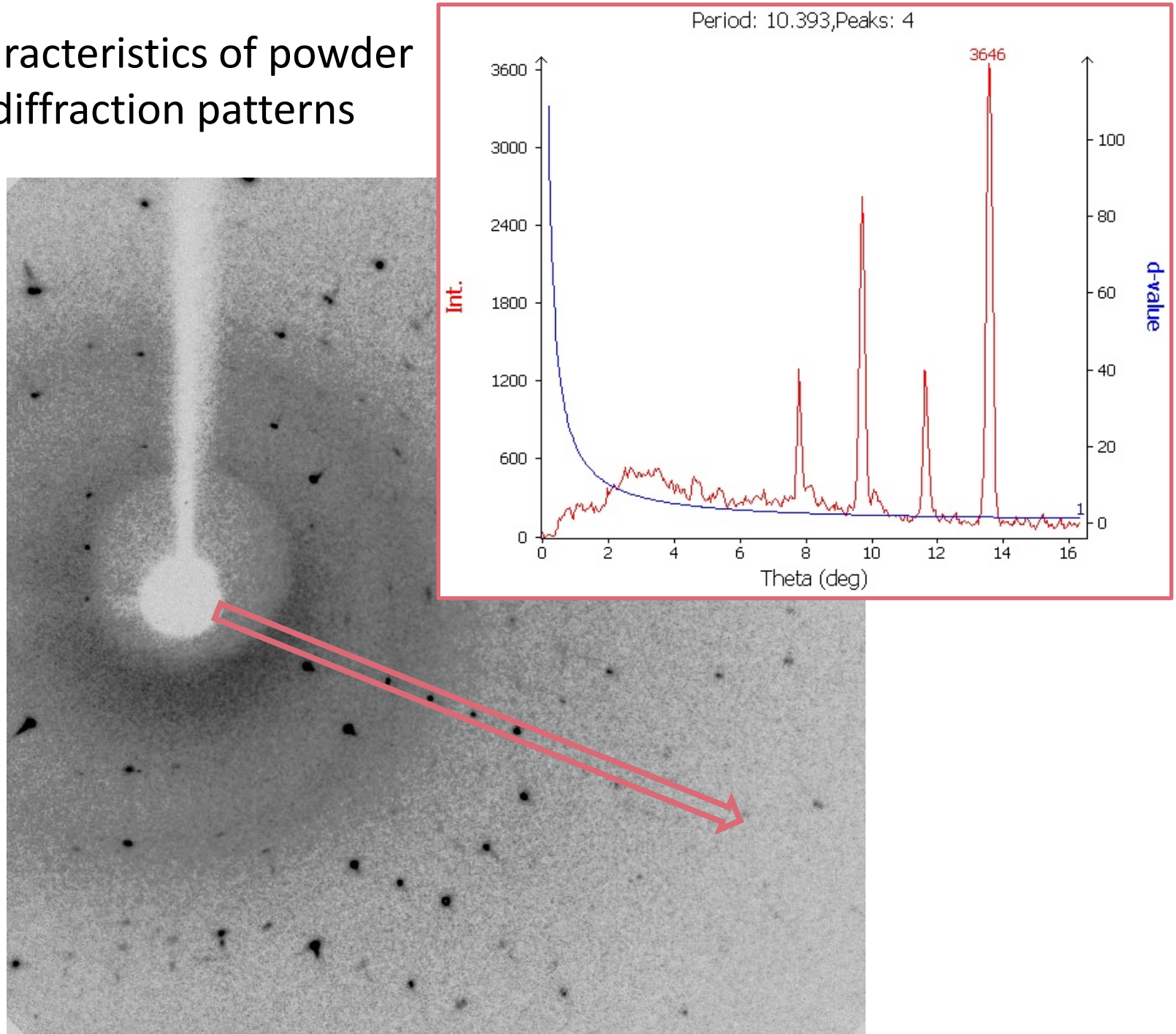
-- lattice parameters

-- refinement of structural parameters, for a variation on a known structure

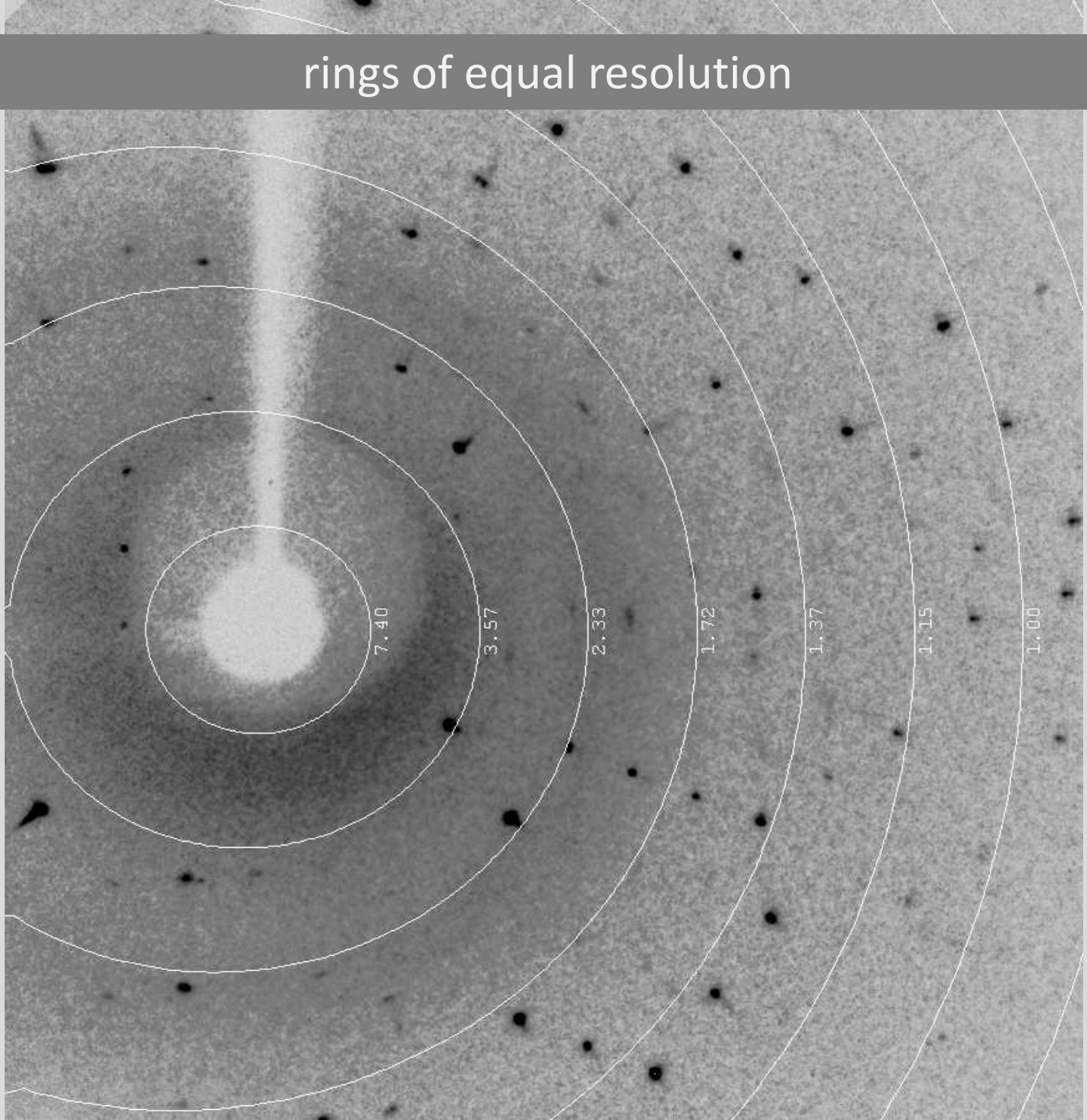
-- *ab initio* determination of structure, with refinement

-- physical properties, stress, texture, lattice defects, domain size

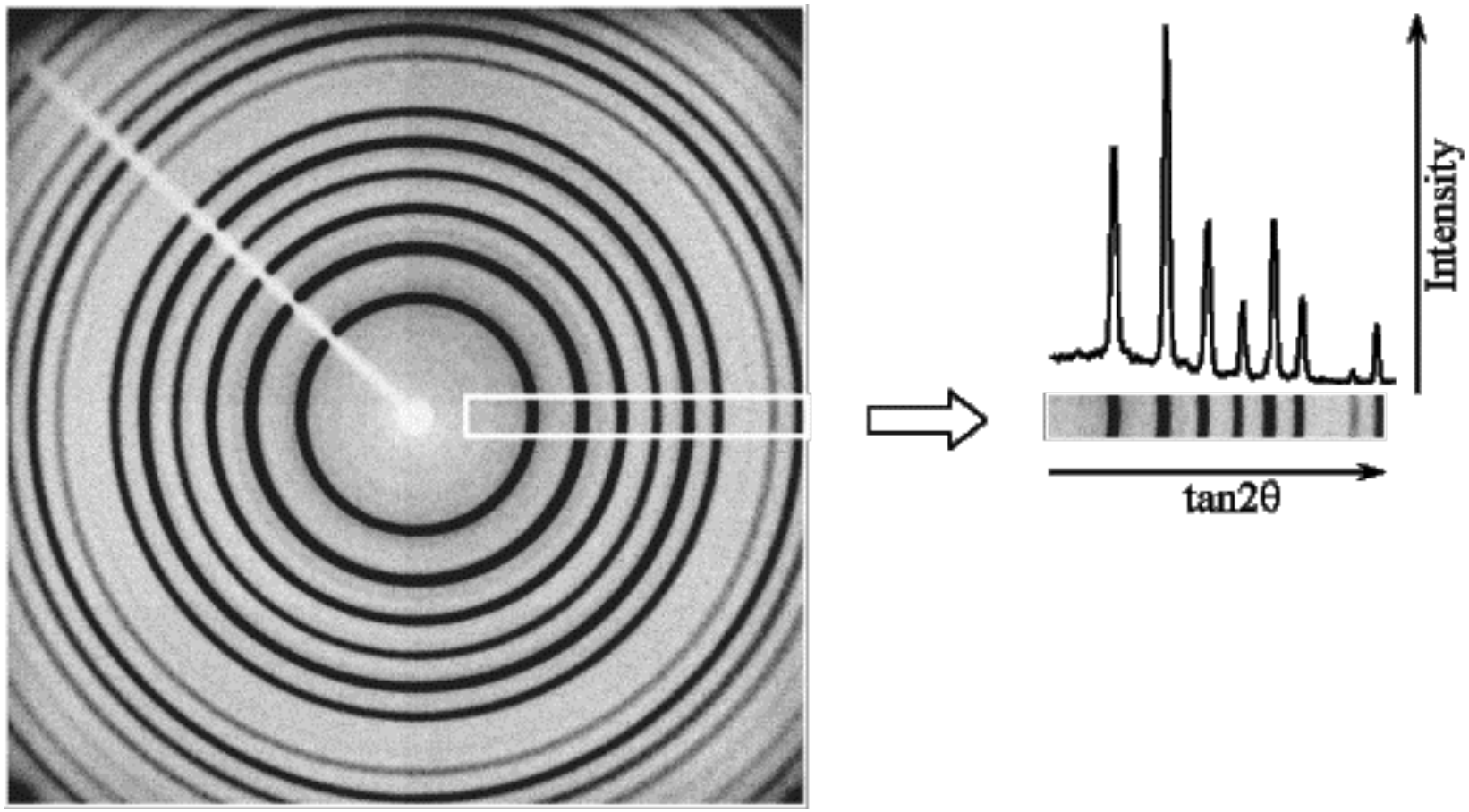
Characteristics of powder diffraction patterns



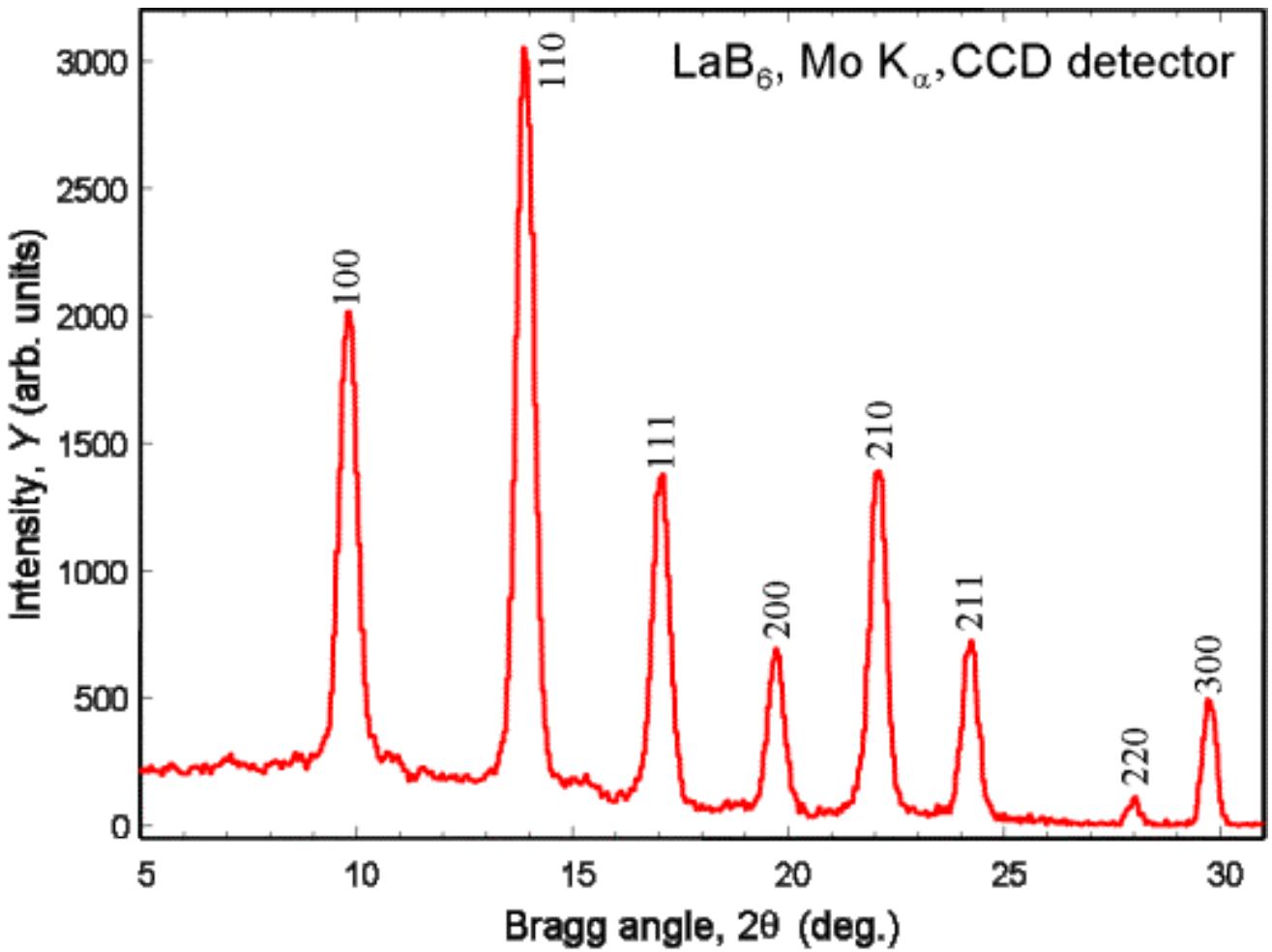
rings of equal resolution



powder diffraction pattern



powder diffraction pattern



V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005.

XRD for the analyst: Getting acquainted with the principles
Martin Ermrich & Detlef Opper
PANalytical, GmbH, 2011

2nd revised edition (2013)

X-Ray Powder Diffraction
Abraham Clearfield & Nattamai Bhuvanesh
Encyclopedia of Inorganic and Bioinorganic Chemistry
2008. John Wiley & Sons, Ltd.
Online 2011. John Wiley & Sons, Ltd.
First publisned in the Encyclopedia of Inorganic Chemistry, 2008.
John Wiley & Sons, Ltd.
DOI: 10.1002/9781119951438.eibc0307

Rietveld Refinement

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - Y_i^{calc} \right)^2$$

n -- the number of points in the diffraction pattern
Y_i -- the intensity at point i
w_i -- weighting factor for point i
b_i -- background intensity at point i
K -- phase scale factor if more than one phase is present

$$\Phi = \sum_{i=1}^{n} w_i \left(Y_i^{obs} - \left[b_i + K \sum_{j=1}^{m} I_j \, y_j \left(x_j \right) \right] \right)^2$$

m -- the number of reflections contributing intensity to point i
I_j -- integrated intensity of the jth Bragg reflection
$y_j(x_j)$ -- peak shape function

von Dreele, R. B., *Rietveld Refinement,* in *Powder Diffraction, Theory and Practice,* Ed. Binnebier, R. E. and Billinge, S. J. L. RSC Publishing, 2008. ISBN 978-0-85404-231-9

Pecharsky, V. K. & Zavalij, P. Y., *Fundamentals of Powder Diffraction and Structural Characterization of Materials,* Springer, 2005. ISBN 0-387-24147-7

Factors which may enter into the calculation of Y_i^{calc}

peak shape

$$y_i = I_k exp\left[\frac{-4ln\,(2)}{H_k^2}\,(2\theta_i - 2\theta_k)^2\right]$$

peak asymmetry

$$A_s = 1 - \left[\frac{sP\,(2\theta_i - 2\theta_k)^2}{tan\theta_k}\right]$$

peak width

$$H_k^2 = U\ \tan^2\ \theta_k\ + V\ \tan\theta_k\ +\ W$$

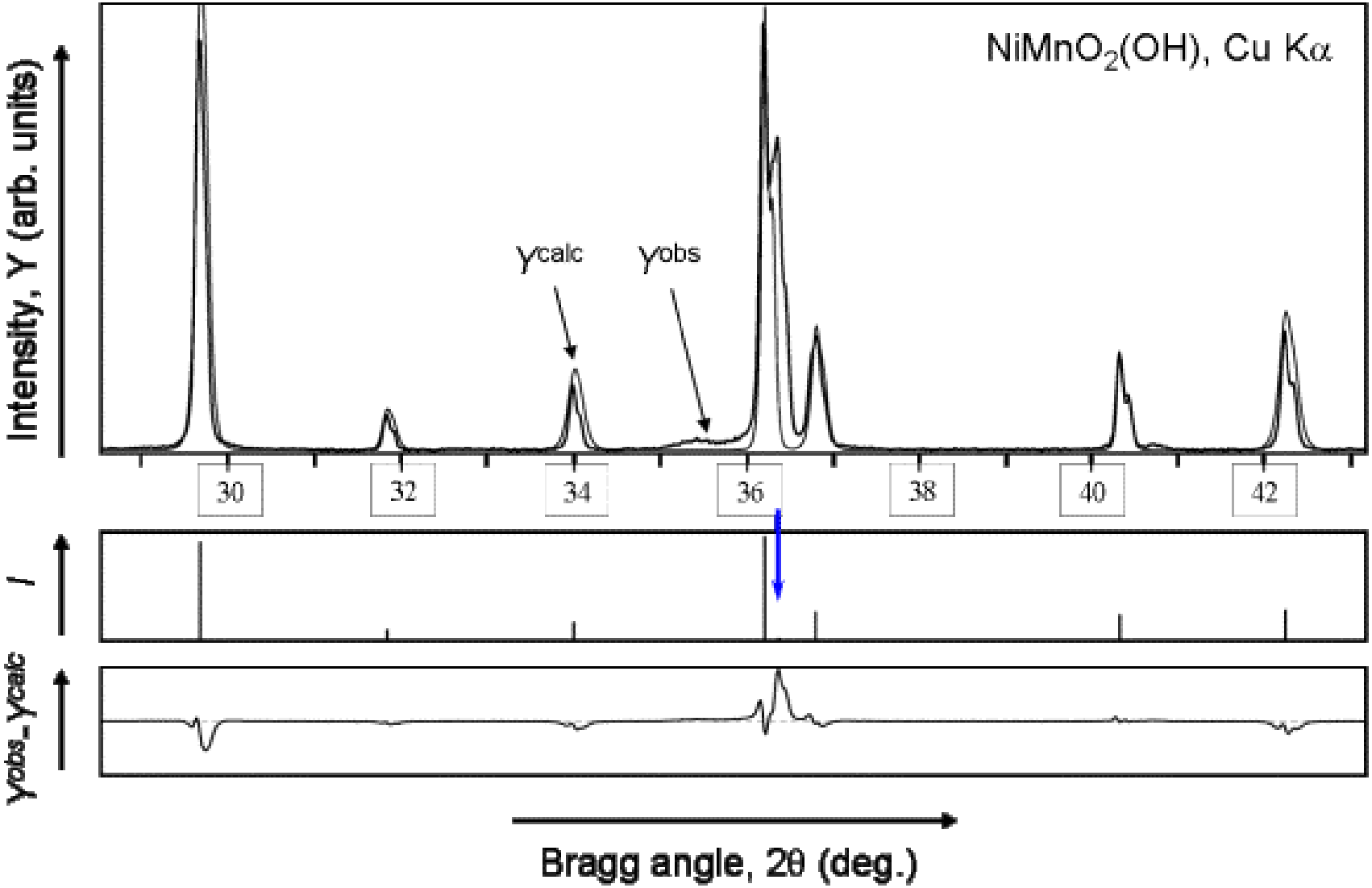
preferred orientation

$$I_{corr} = I_{obs}\exp\left(-G\alpha^2\right)$$

... and others

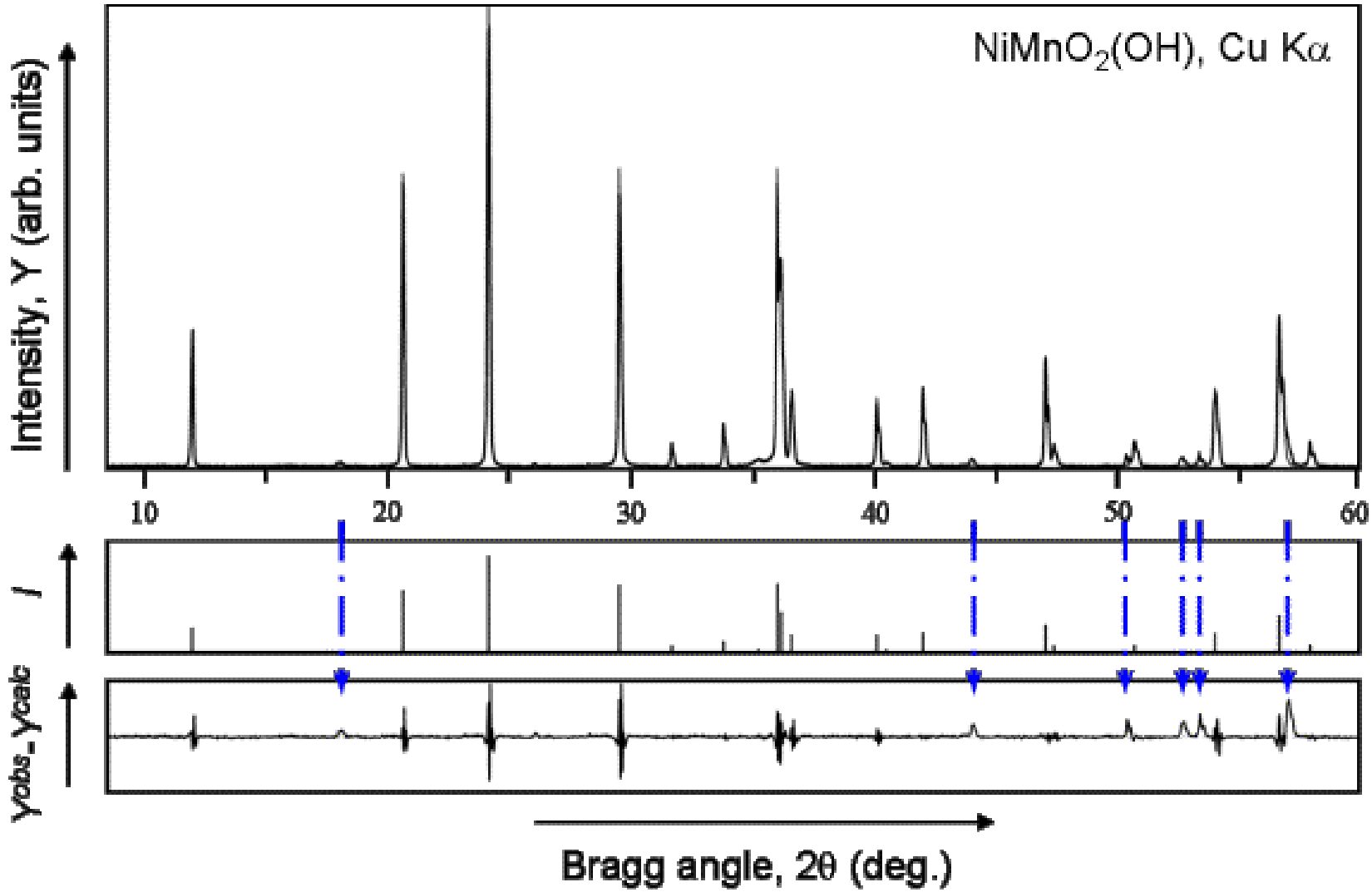
from Wikipedia

powder diffraction -- results



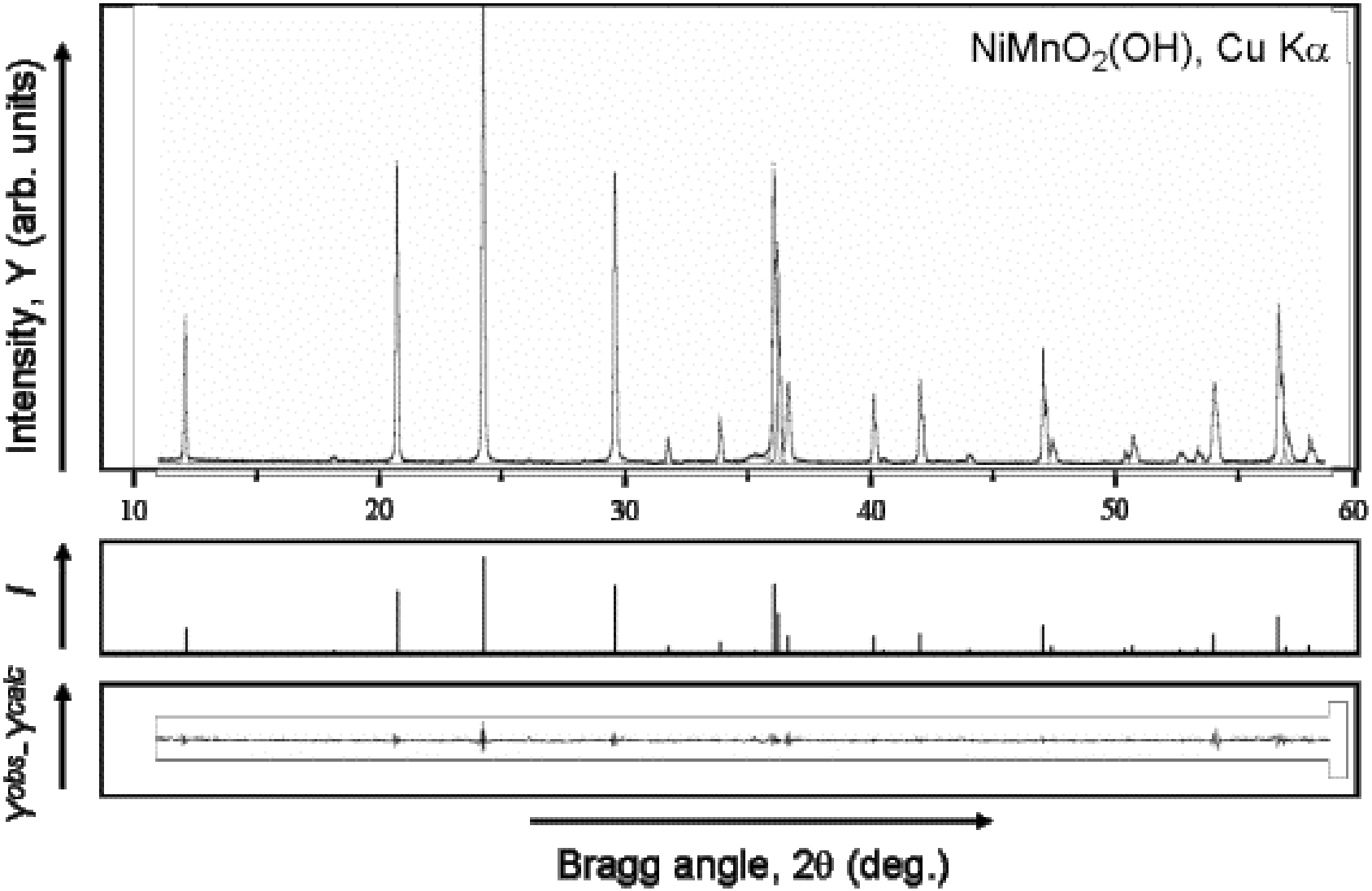
V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005. Fig. 4.9.

powder diffraction -- results



V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005. Fig. 4.14. Blue arrows indicate peaks that are still not included in the fit.

powder diffraction -- results



V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005. Fig. 4.16. End of refinement.

Peak Shape Analysis

- Peak broadening comes from several sources
  - Instrumental effects
  - Finite crystallite (not particle) size (< 100-500 nm)
  - Strain (atoms deformed from ideal positions in a non-uniform manner)
  - Extended defects (terminate "crystal" and lead to size broadening)
- Methods of extracting size & strain information
  - Scherrer formula (average size, neglects strain)
  - Integral breadth methods (provide average values of size and strain)
  - Peak shape methods (provide size and strain distributions)

http://www.chemistry.ohio-state.edu/~woodward/chem_995.htm

Size Broadening

- Scherrer (1918) first observed that small crystallite size could give rise to line broadening. He derived a well known equation for relating the crystallite size to the broadening, which is called the "Scherrer Formula"

$$D_v = K\lambda/\{\beta \cos \theta\}$$

- D_v = Volume Weighted crystallite size
- K = Scherrer constant, somewhat arbitrary value that falls in the range 0.87-1.0. I usually assume K = 1.
- λ = The wavelength of the radiation
- β = The integral breadth of a reflection (in radians 2θ) located at 2θ.

Stress and strain

-- **Stress** can be applied by an external action. Stress can also be "residual," that is, a physical potential within the sample as a result of previous action or deformation.

-- **Strain** is the deformation that occurs in response to stress. Strain modifies the spacing between Bragg planes, so it modifies the angle 2θ observed in a powder diffraction pattern.

Stress and strain

Strain modifies the Bragg plane spacing *d* and affects the diffraction pattern in two ways.

-- Considering a given reflection, if the average Bragg plane spacing *d* (averaged over all the crystallites in the sample) for this reflection is changed by strain, then there is a peak shift. The mean value of 2θ for the reflection in question is changed.

-- If the dispersion of the Bragg plane spacing for a reflection is modified by strain, then there is a change in the width of the peak -- usually peak broadening.

Welzel, U., Ligot, J., Lamparter, P., Vermeulen, A. C., and Mittemeijer, E. J., J. Appl. Cryst. (*2005*), *38*, 1 - 29.

Stress and strain

Stress and strain are symmetrical second-rank tensors.

Popa, N. C., *Microstructural Properties: Texture and Macrostress Effects,* in *Powder Diffraction, Theory and Practice,* Ed. Binnebier, R. E. and Billinge, S. J. L. RSC Publishing, 2008.

Scardi, P., *Microstructural Properties: Lattice Defects and Domain Size Effects,* in *Powder Diffraction, Theory and Practice,* Ed. Binnebier, R. E. and Billinge, S. J. L. RSC Publishing, 2008.

Texture analysis

The goal of texture analysis is to establish the orientation distribution function (ODF).

-- Using Euler angles to define the orientation of a crystallite relative to a global reference frame for the sample, the ODF is a description of the volume fraction of particles lying within each incremental range of the Euler angles.

-- Sometimes the ODF is the object of the measurements.

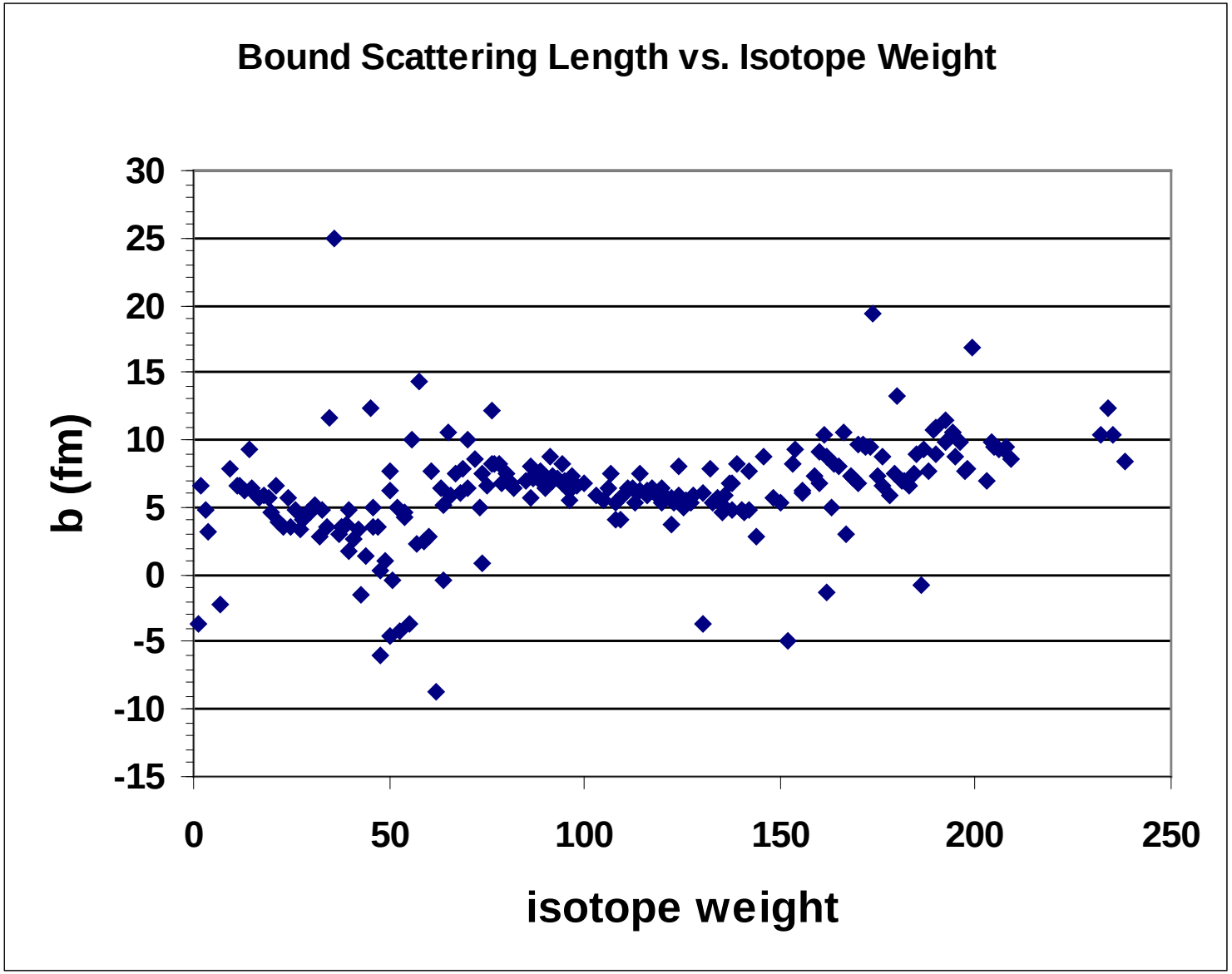
-- Sometimes the ODF is needed as a parametric addition to Rietveld refinement.

neutron diffraction

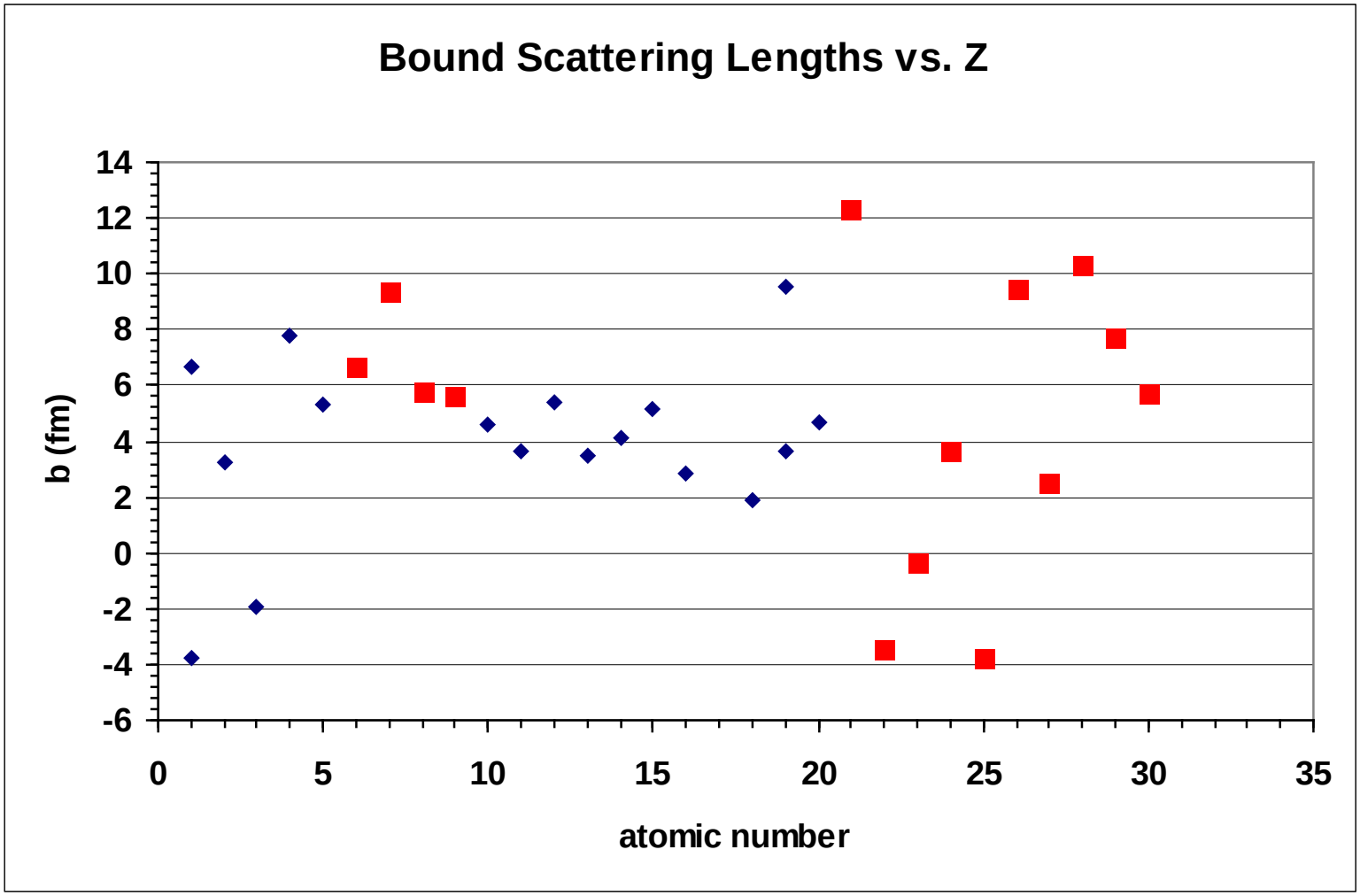
http://www.ill.eu/science-technology/why-use-neutrons/

http://www.sns.gov/science/aboutneutrons.html

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



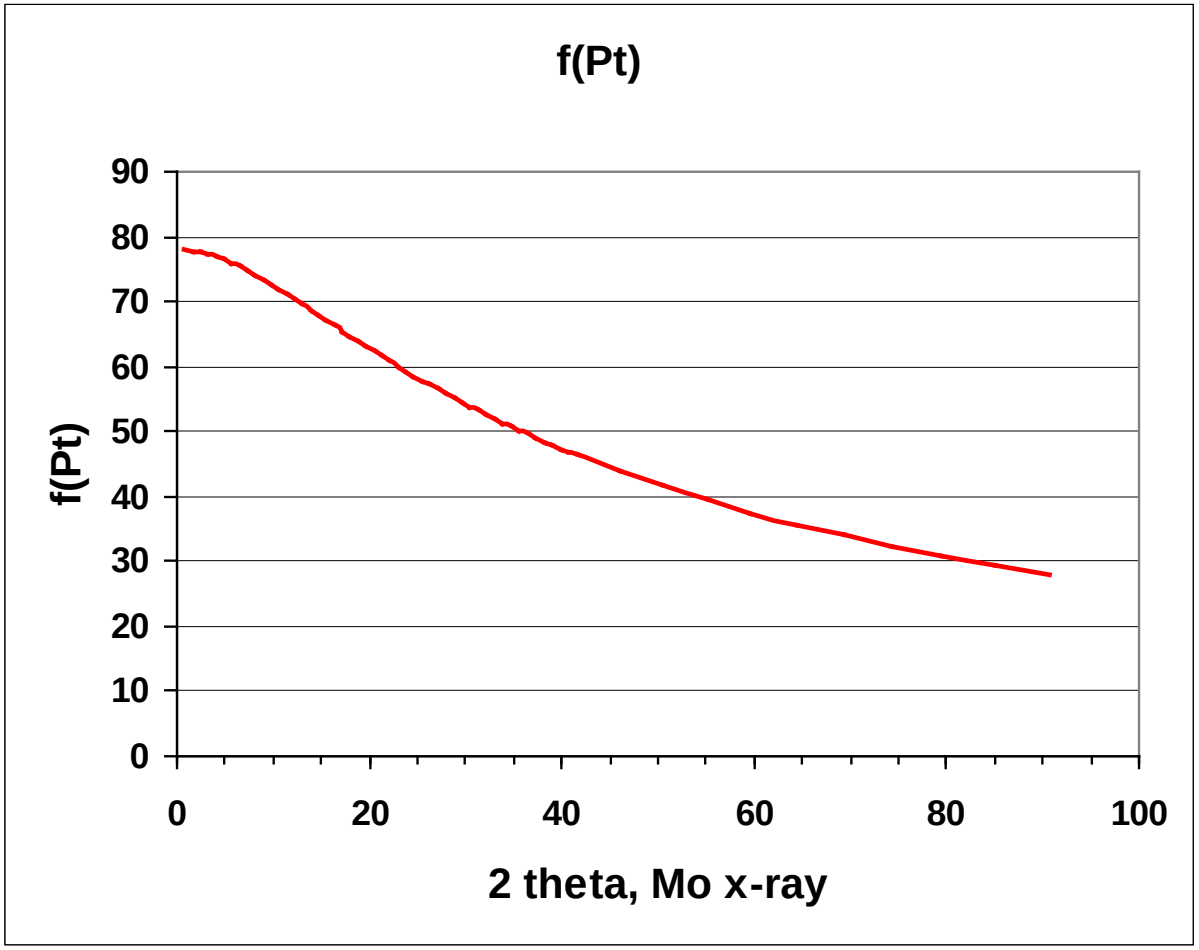
Source: http://webster.ncnr.nist.gov/resources/n-lengths/


Bound Scattering Lengths vs. Z
b (fm)
14
12
10
8
6
4
2
0
-2
-4
-6
0
5
10
15
20
25
30
35
atomic number

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

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.

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

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)*

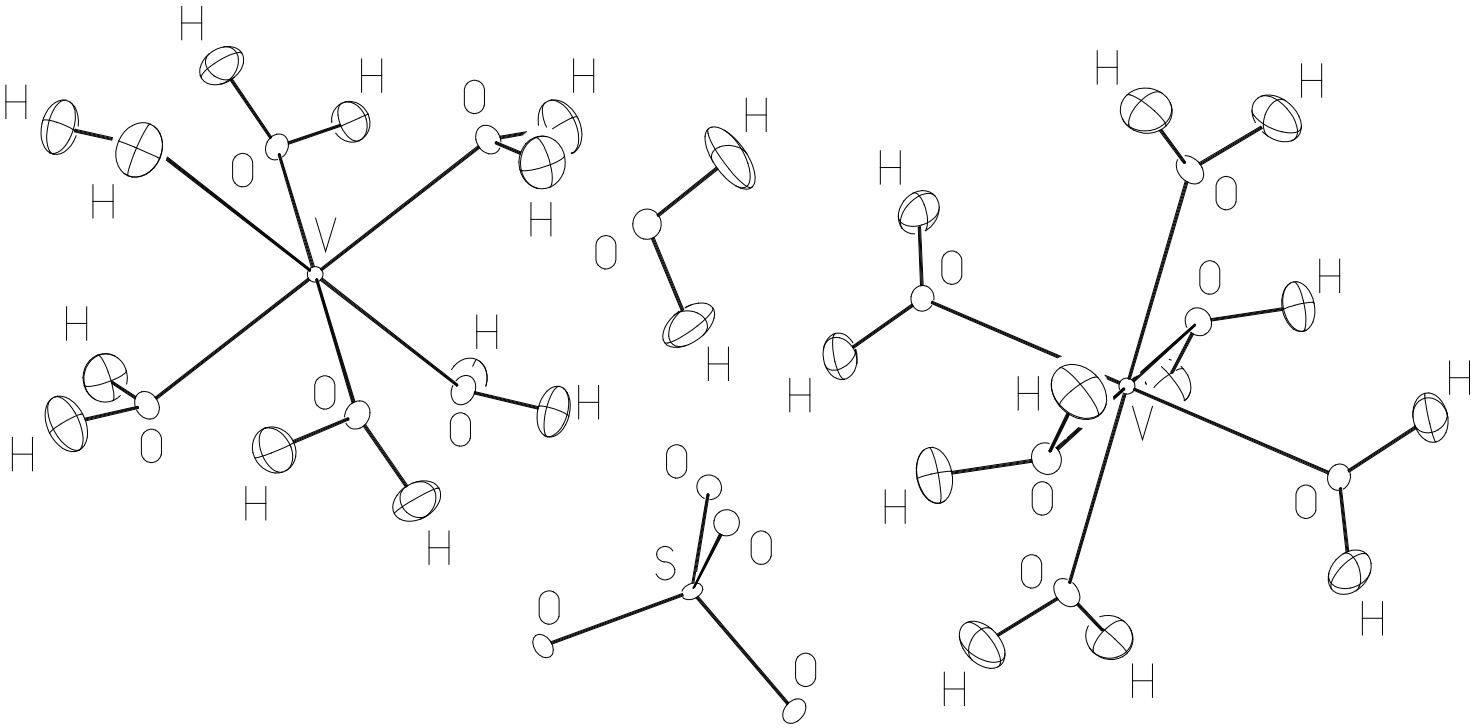
• distinguishing the elements of the first d-block series

• distinguishing C from N, and N from O *(vide infra)*

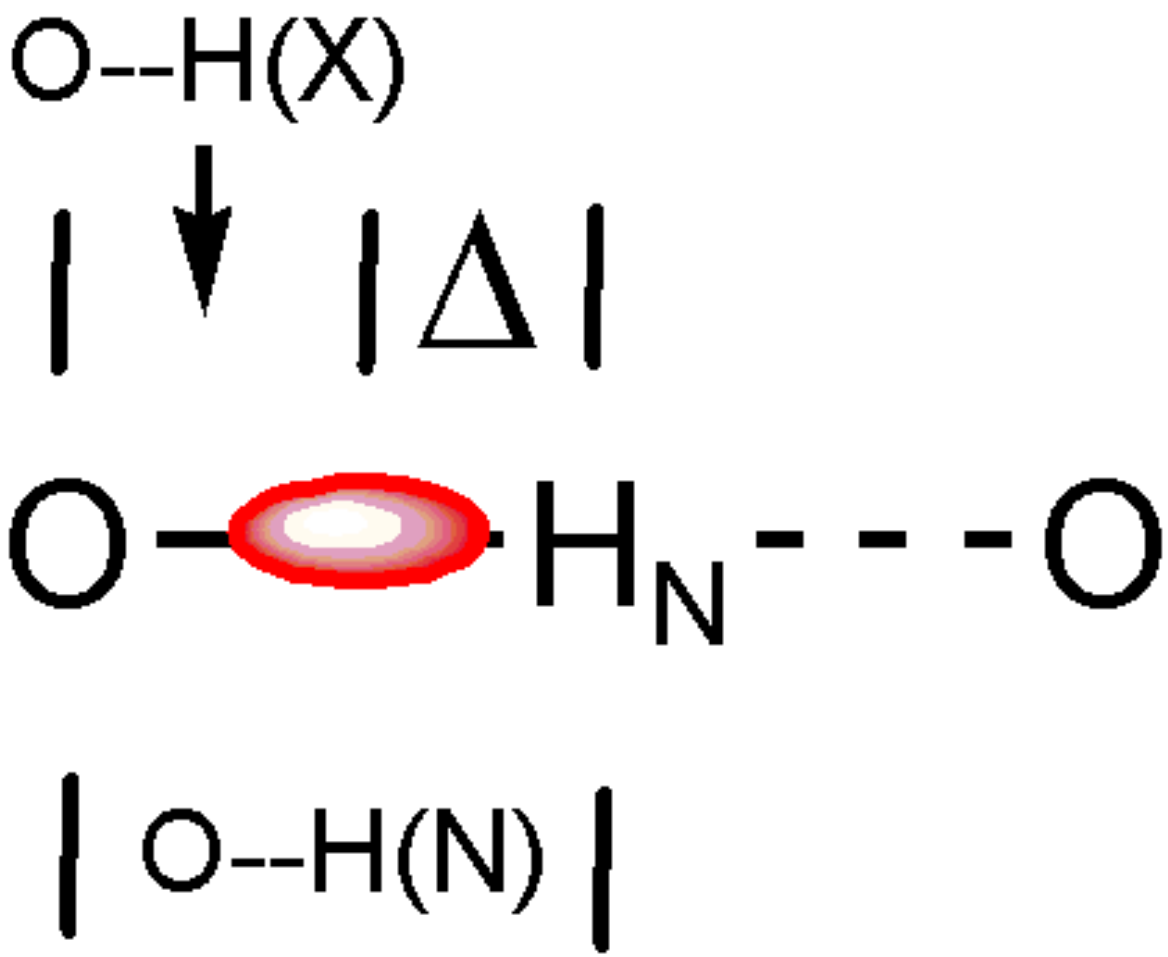
• anisotropic displacement parameters of H

• crystallographic tricks, such as the correct use of two different space groups for the same structure *(vide infra)*

$VSO_4 \cdot 7H_2O$



“X-Ray Distance” and “Neutron Distance”

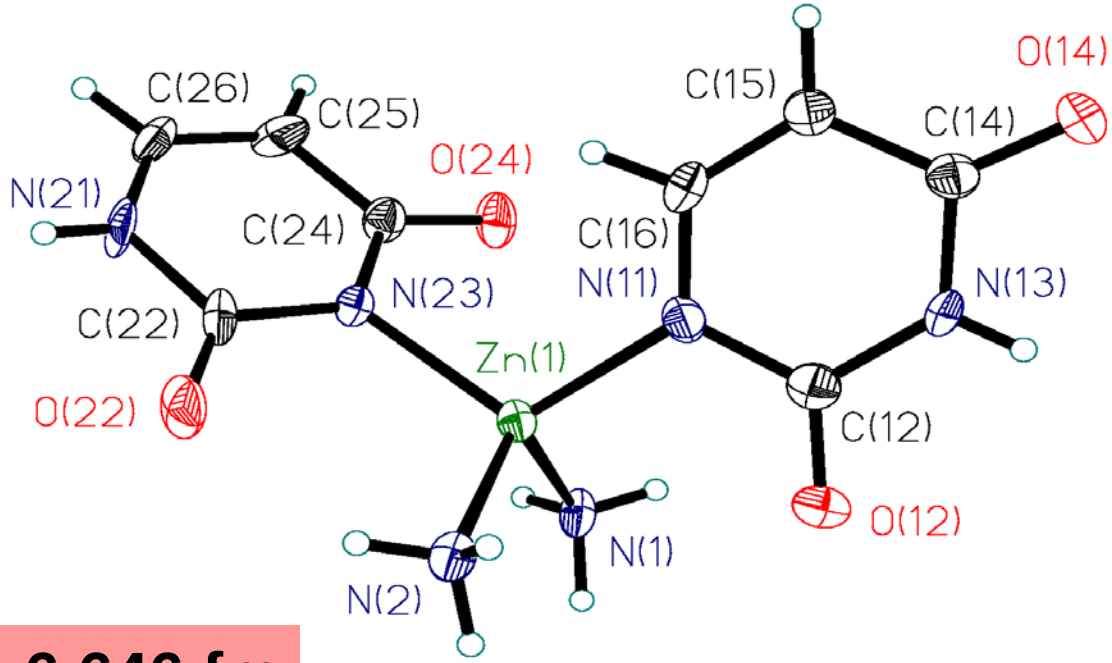


$VSO_4 \cdot 7H_2O$ Hydrogen-Bond Geometry
(X-Ray and Neutron)

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

Distinguishing Carbon and Nitrogen

$[Zn(urac\text{-}\kappa N^1)(urac\text{-}\kappa N^3)(NH_3)_2]$



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

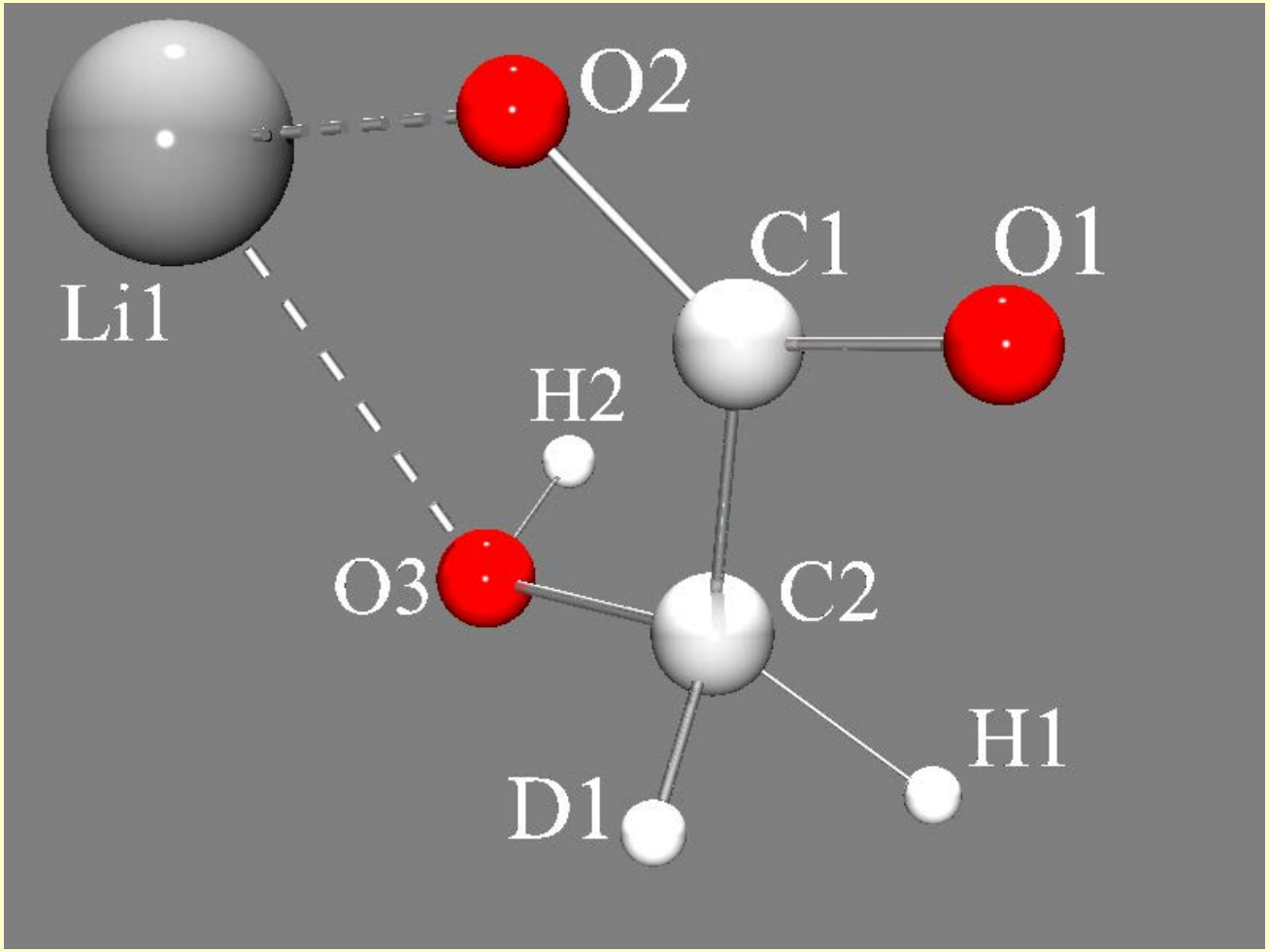
Two Space Groups for the Same Structure: Li α-deuteroglycollate

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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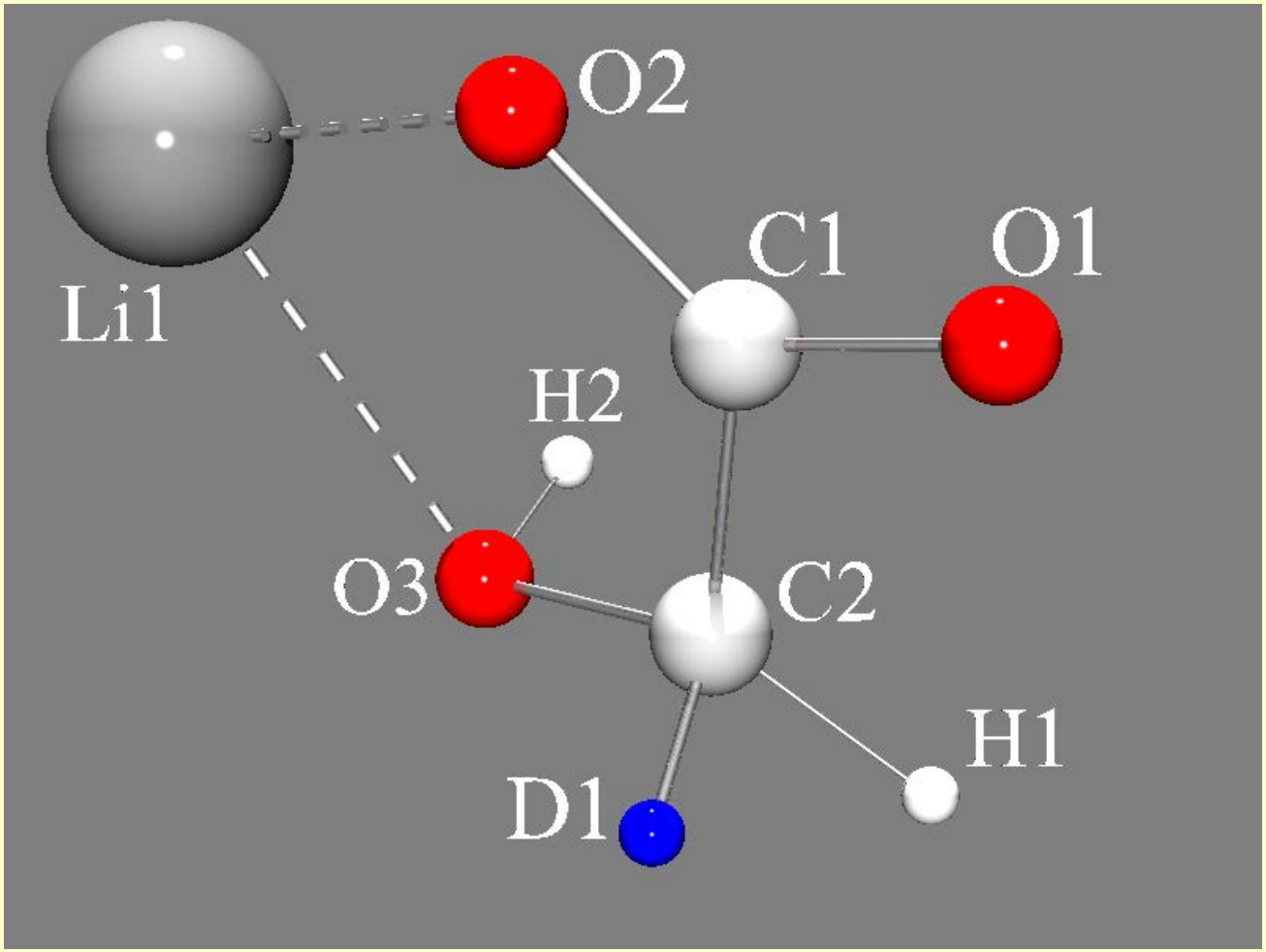


ENERGY: Neutrons vs. X-Rays

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

$$E = h\nu = hc/\lambda = 2.795\times10^{-15}\ J = 17440\ ev = 17.4\ keV$$

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

$$E = h\nu = hc/\lambda = 1.288\times10^{-15}\ J = 8040\ ev = 8.04\ keV$$

$$For\ neutrons\ with\ \lambda = 0.71069 A:$$

$$\lambda = h/p = h/mv \qquad v = h/m\lambda = 5566\ m/s$$

$$E = \frac{1}{2}mv^2 = 2.594\times10^{-20}\ J = 0.162\ eV = 162\ meV$$

$$For\ neutrons\ with\ \lambda = 1.5418\ A: \quad V = 2566\ m/s$$

$$E = 5.514\times10^{-21}\ J = 0.0344\ eV = 34.4\ meV$$

E_n(meV)=81.8/λ^2 (Å^2)

~1300 cm^{-1}

~280 cm^{-1}

Absorption and Extinction Properties

$$\mu = \mu_s + \mu_a \left(\lambda(\text{Å}) / 1.8\text{Å} \right)$$

$$A = I / I_o = \exp(-\mu\tau)$$

$$A = I / I_o = \frac{1}{V} \int_{crystal} \exp(-\mu\tau) dV$$

Absorption and Extinction Properties

$$\mu = \mu_s + \mu_a \left(\lambda(\text{Å}) / 1.8\text{Å} \right)$$

$$\mu_s = \frac{Z}{V} \sum \sigma_s$$

σ_s: total scattering cross section, tabulated in units of 100 fm^2

μ_s (cm^{-1}); V ($Å^3$)

summation over one formula weight, Z = number of formulas per unit cell, V = unit cell volume

$$\mu_a = \frac{Z}{V} \sum \sigma_a$$

σ_a: absorption cross section, (100 fm^2), tabulated for 1.8 Å neutrons

μ_s (cm^{-1}); V ($Å^3$)

σ_s and σ_a: *International Tables, Vol. C*, Table 4.4.4.1.

Experimental Determination of Spin Densities

$$f_p\left(\bar{s}\right) = \sum_{\ell=0}^{L} \sum_{m=-\ell}^{\ell} i^{\ell} M_{\ell}^{m} N_{\ell}^{m} \left\langle j_{\ell} \right\rangle Z_{\ell}^{m}\left(\theta_s, \phi_s\right)$$

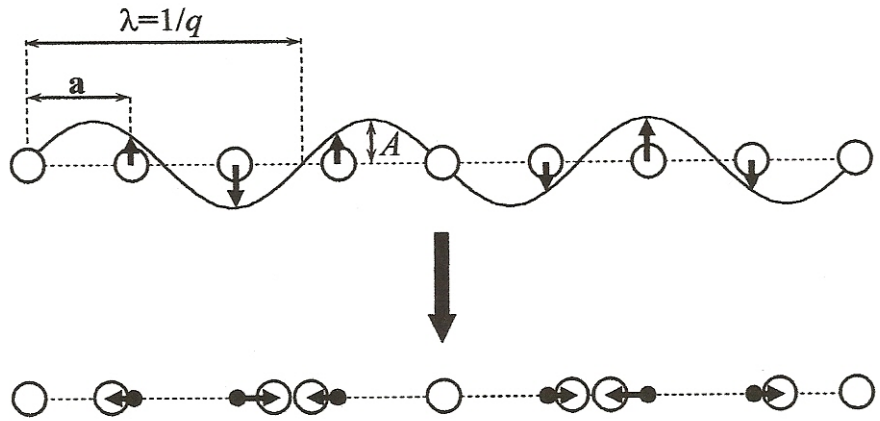
(This same scheme is used in the experimental determination of charge densities by x-ray diffraction.)

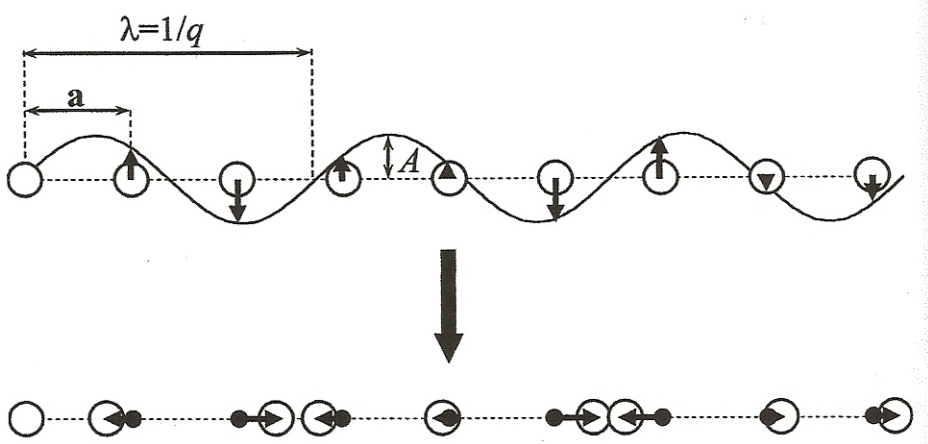
Sub-periodic crystals

Incommensurate modulations

Composite crystals

Quasi-crystals





take-home points

single-crystal diffraction
-- structure analysis
powder diffraction
-- phase identification (qualitative)
-- composition analysis (quantitative phase analysis)
-- Rietveld refinement (variation on known structure)
-- ab initio structure analysis and Rietveld refinement

radiation:
-- in-house x-rays (usually Cu or Mo sources)
-- synchrotron radiation (x-rays)
-- neutrons (reactor or spallation)

take-home points

defining formula and Z
calculate density
different ways of representing symmetry
origins of diffraction
-- scattering interaction (x-rays - electron, neutrons - nucleus)
-- atomic scattering factor
-- structure factor

Bragg's law
Laue equation
reciprocal lattice / Ewald sphere
number of reflections that can be measured (single crystal)
resolution of a diffraction analysis

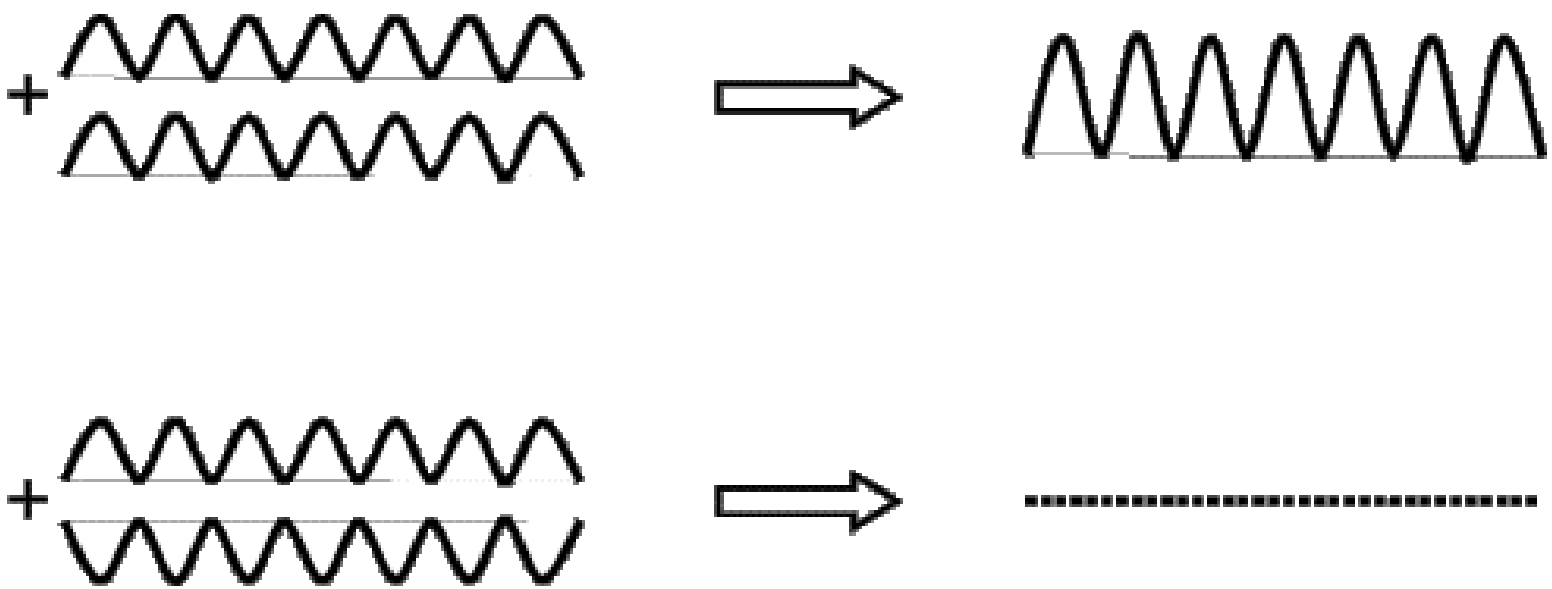
take-home points

least-squares refinement of structural parameters
-- single crystal
-- powder (Rietveld)

reporting diffraction results
-- CIF for some applications
-- rounding numbers derived by least-squares
-- calculating distances in crystallographic reference frames

stress and strain
texture
particle size

interference between waves



V. K. Pecharsky & P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials, Springer, 2005.

density

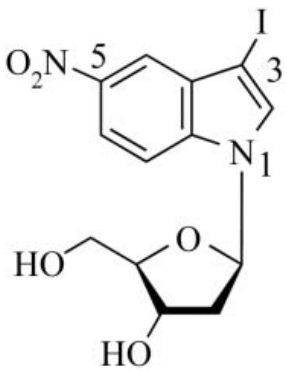
The density of a crystalline solid is calculated this way:

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

The origin of the formula is this:

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

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 Å^3 per non-H atom is used. (For a pure inorganic, this number will not provide a good estimate.)



(I)

$\rho = 1.972\ g \cdot cm^{-1}$

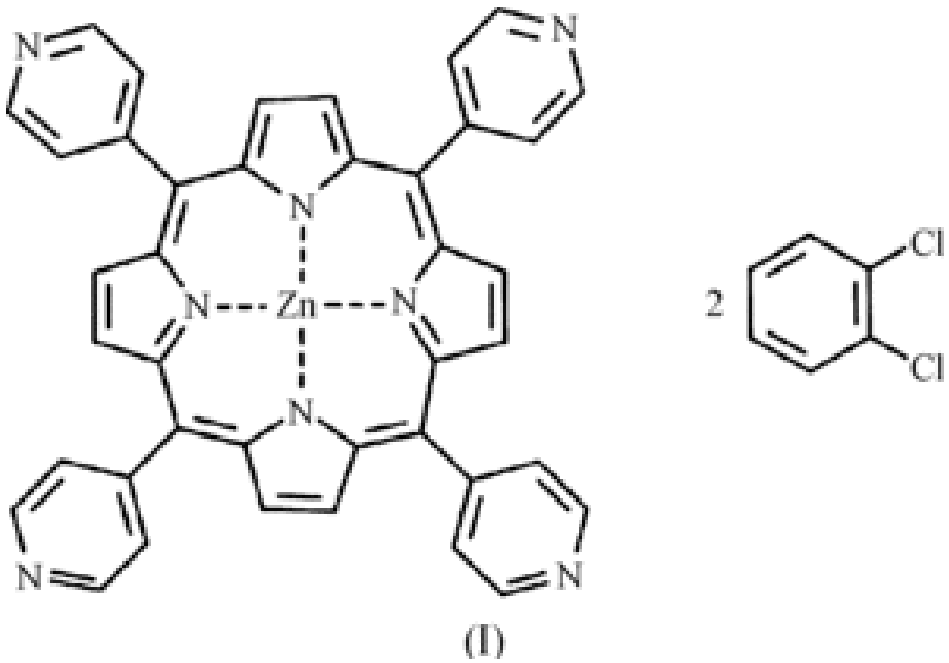
$C_{13}H_{13}IN_2O_5$

M_r = 404.15

a = 17.549 b = 7.0981 c = 10.9242 Å $\alpha = \beta = \gamma$ = 90º V = 1360.8 A^3

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

Acta Cryst., Section C (2009). C65, o100-o102.



$\rho = 1.502\ g \cdot cm^{-1}$

$[Zn(C_{40}H_{24}N_8)] \cdot 2C_6H_4Cl_2$

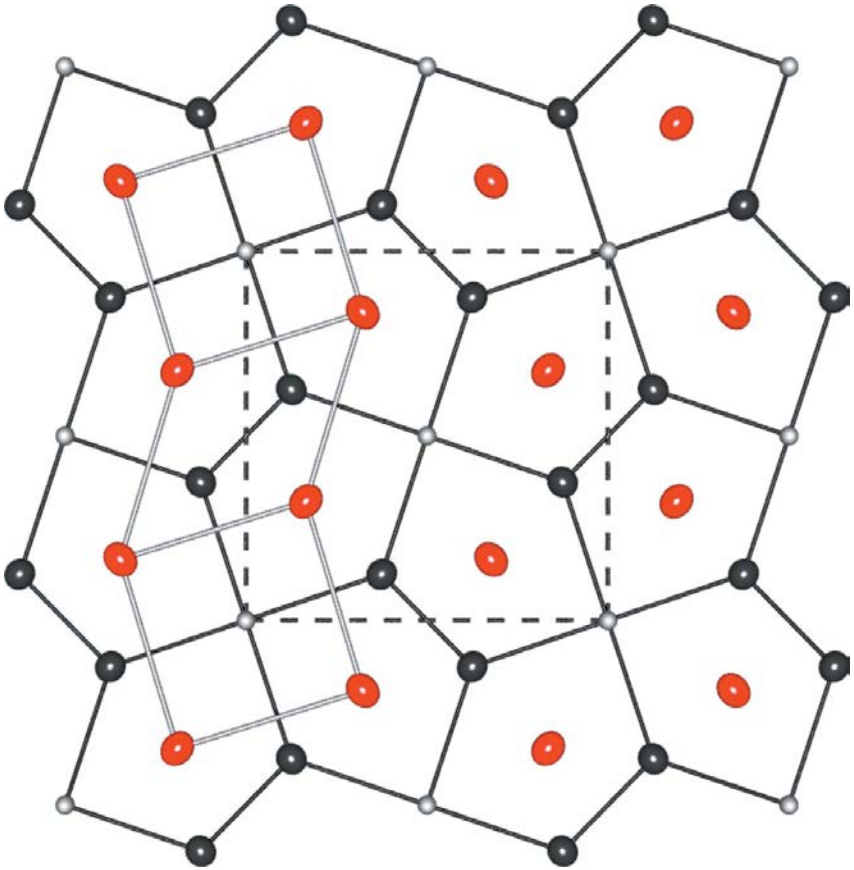
Mr = 976.03

a = 11.0295 b = 13.8207 c = 14.1529 Å

$\alpha = \gamma = 90º$ $\beta = 90.2382$ V = 2157.39 A^3

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

Acta Cryst., Section C (2009). C65, m139-m142.



Sc_2MgGa_2

M_r = 253.67

a = b = 7.1577 c = 3.9166 Å

$\alpha = \beta = \gamma = 90º$ V = 200.66 $Å^3$

Mg: white

Ga: black

Sc: red

Z = 2

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

Acta Cryst., Section C (2009). C65, i7-i8.

Panalytical document, page 25, “Discussion of Bragg’s Law”:

4. Resolution can be defined as the lowest measurable *d*-value for a used wavelength, for sin q = 1 follows $d_{min} = \lambda/2$.

5. Varying of λ causes:

- The number of measurable reflections to vary, and
- The angular position of the reflections to vary; also,
- The separation between two neighboring reflections is changed.