Basics of X-ray diffraction: From symmetry to structure determination

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Matter : ***Gases, Liquids and Solids***

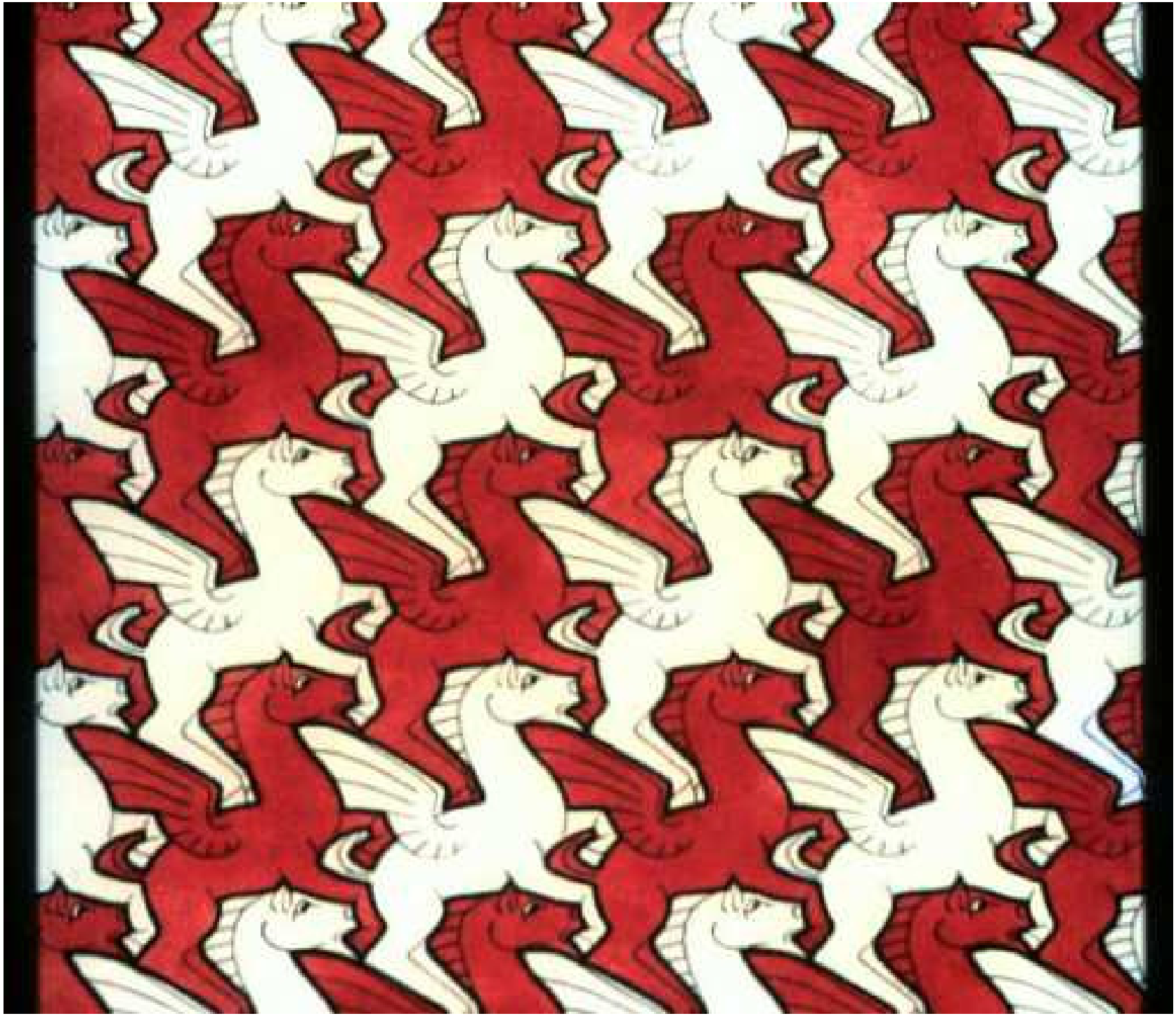
The 3-d world we live in

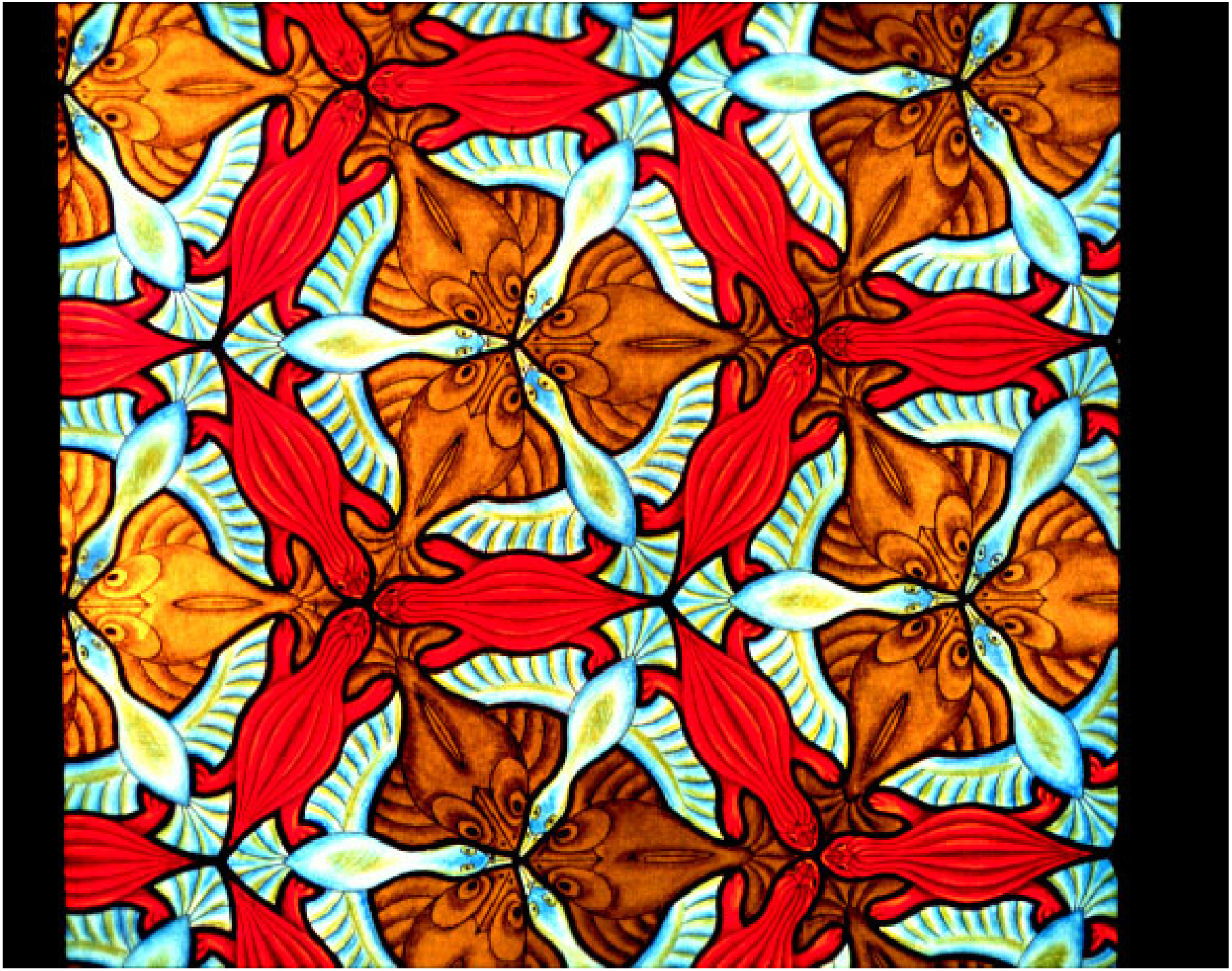
Love of symmetry and Mankind

Basic mistake: Joining school

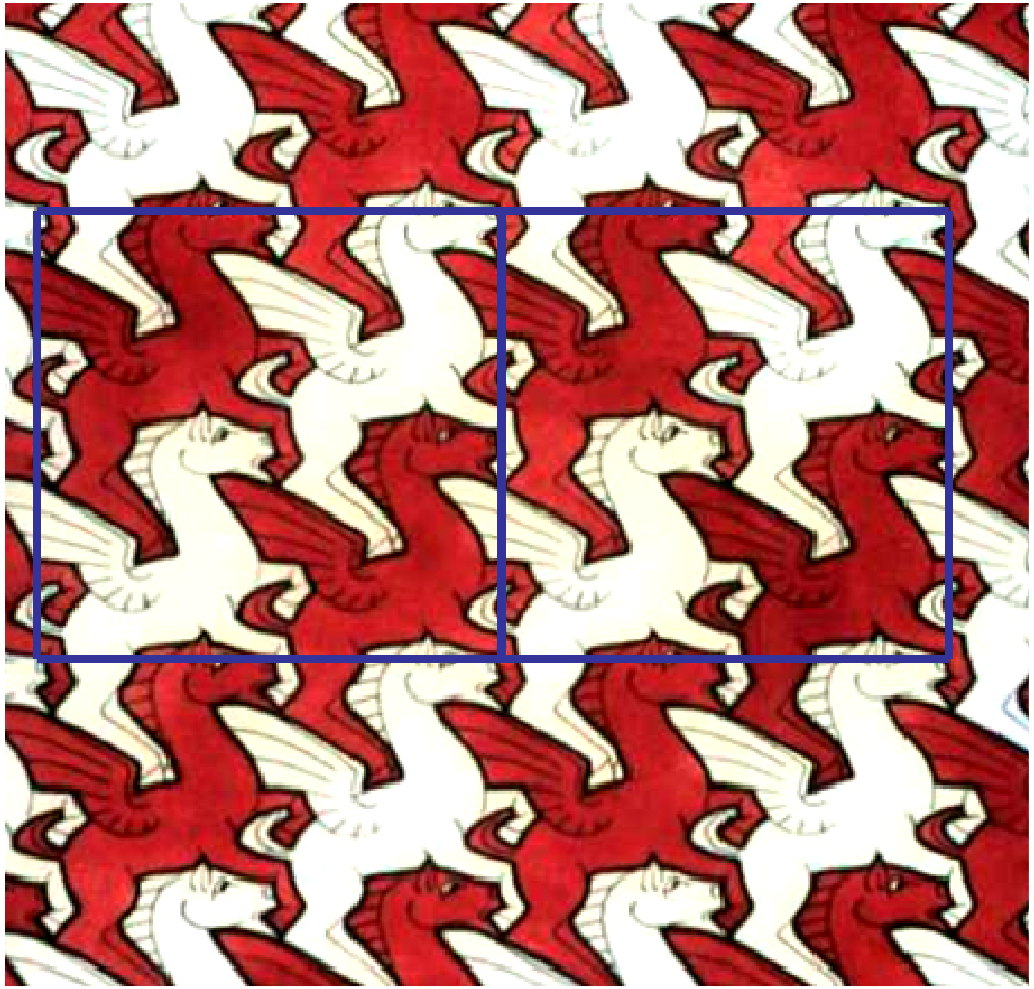
Stereographic projection

Rubens Aguilon Stereographic Projection

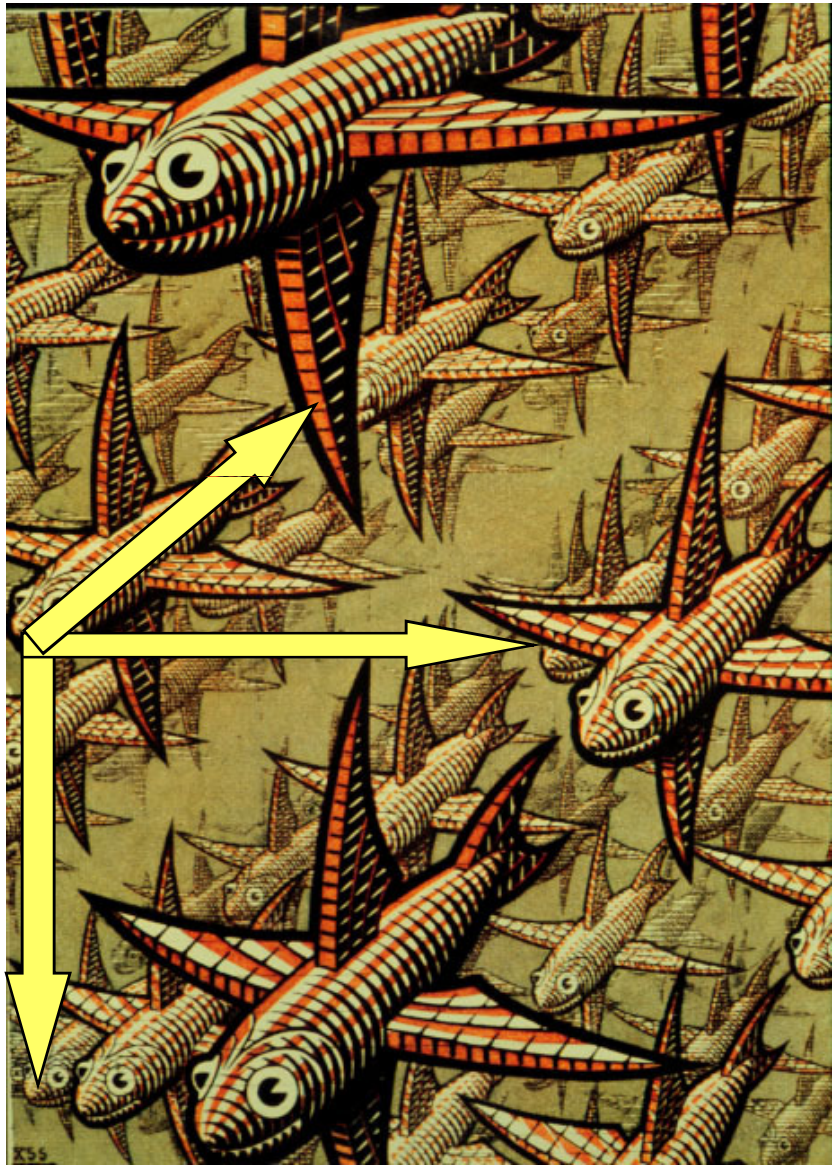




Similar cells can be drawn in all the other repeating (wall-paper) patterns that we saw previously.

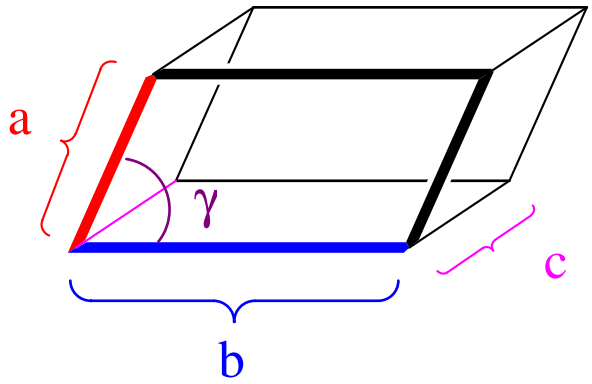


Crystals are built in a similar manner, with regularly repeating cells. Only now these cells regularly repeat in three dimensions to produce a box called a unit cell.



Crystals use (7) different shapes of regular box to build up into a crystal. Actually there are only (5) unique shapes, the other two are special cases of one of the five. The five shapes are:

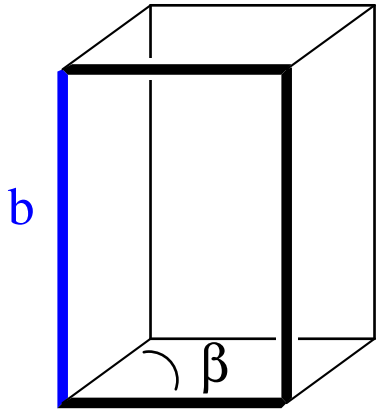
Triclinic



The box has edges of length (a), (b), and (c); and the angles between the edges are (α), (β) and (γ)

In triclinic:
$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma \neq 90^o$

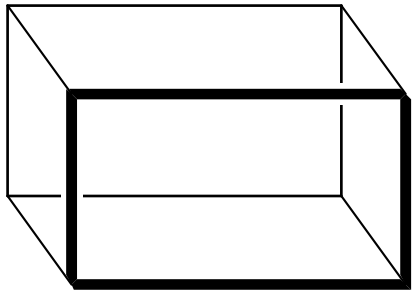
Monoclinic



In monoclinic
$a \neq b \neq c$
$\alpha = \gamma = 90^o;\ \beta \neq 90^o$

(A squished book)

Orthorhombic



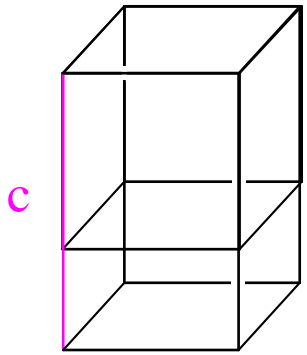
In orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^o$

(A shoe box)

Crystals use (7) different shapes of regular box to build up into a crystal. Actually there are only (5) unique shapes, the other two are special cases of one of the five. The five shapes are:

Tetragonal

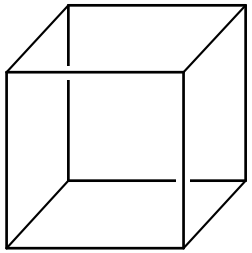
A stretched cube



In tetragonal
a=b ≠c
$\alpha = \beta = \gamma = 90^o$

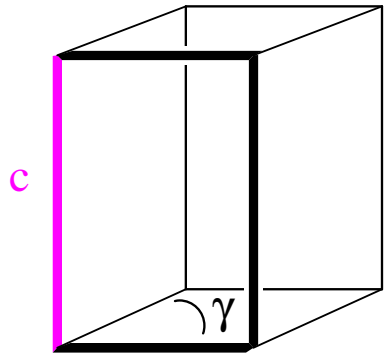
(a column or pillar)

Cubic



In cubic
a=b =c
$\alpha = \beta = \gamma = 90^o$

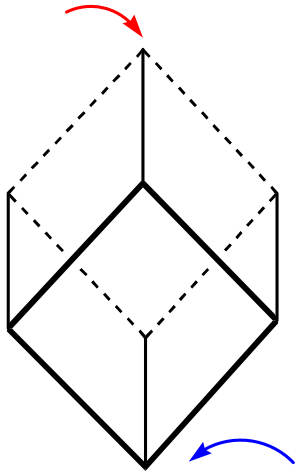
Hexagonal



In hexagonal a=b ≠c
$\alpha = \beta = 90^o$ $\gamma = 120^o$

Rhombohedral

a=b =c
$\alpha = \beta = \gamma \neq 90^o$

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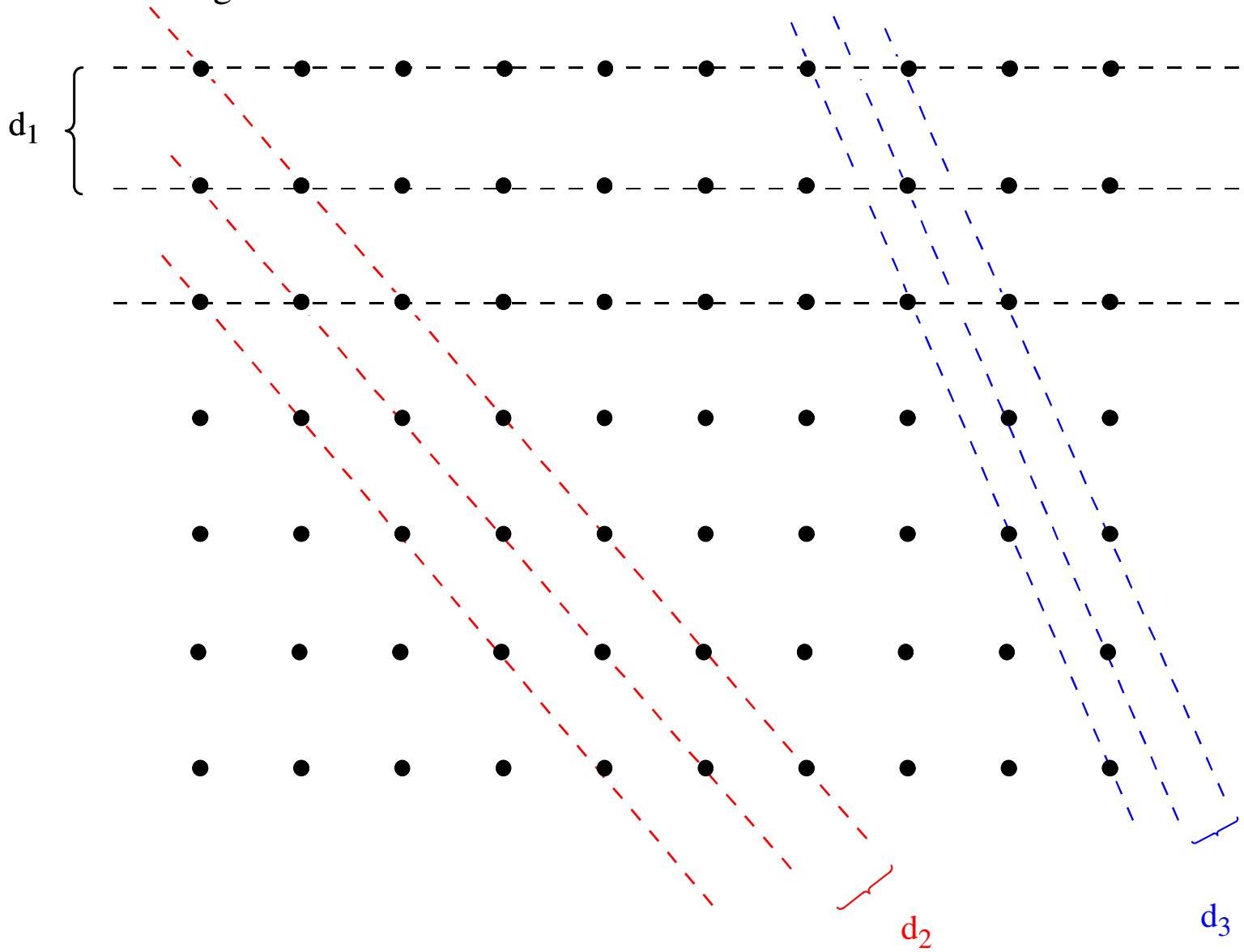
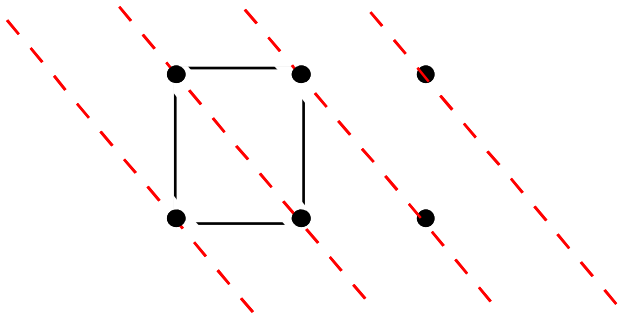
Miller Indices

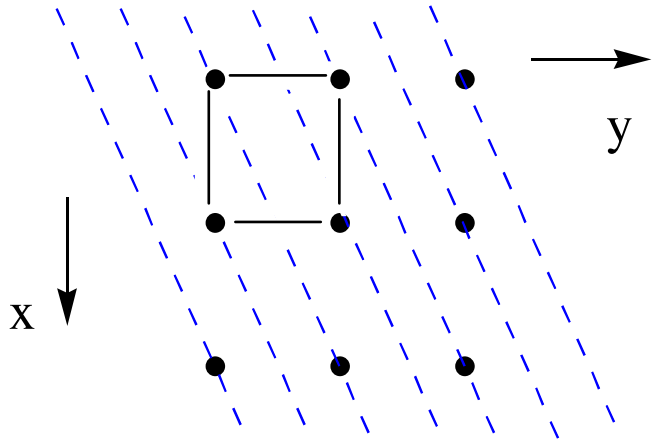
Take a simple structure, there are an of infinite number of planes that can be constructed through it.



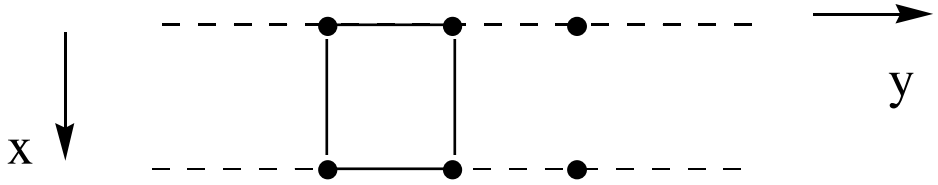
Miller Indices



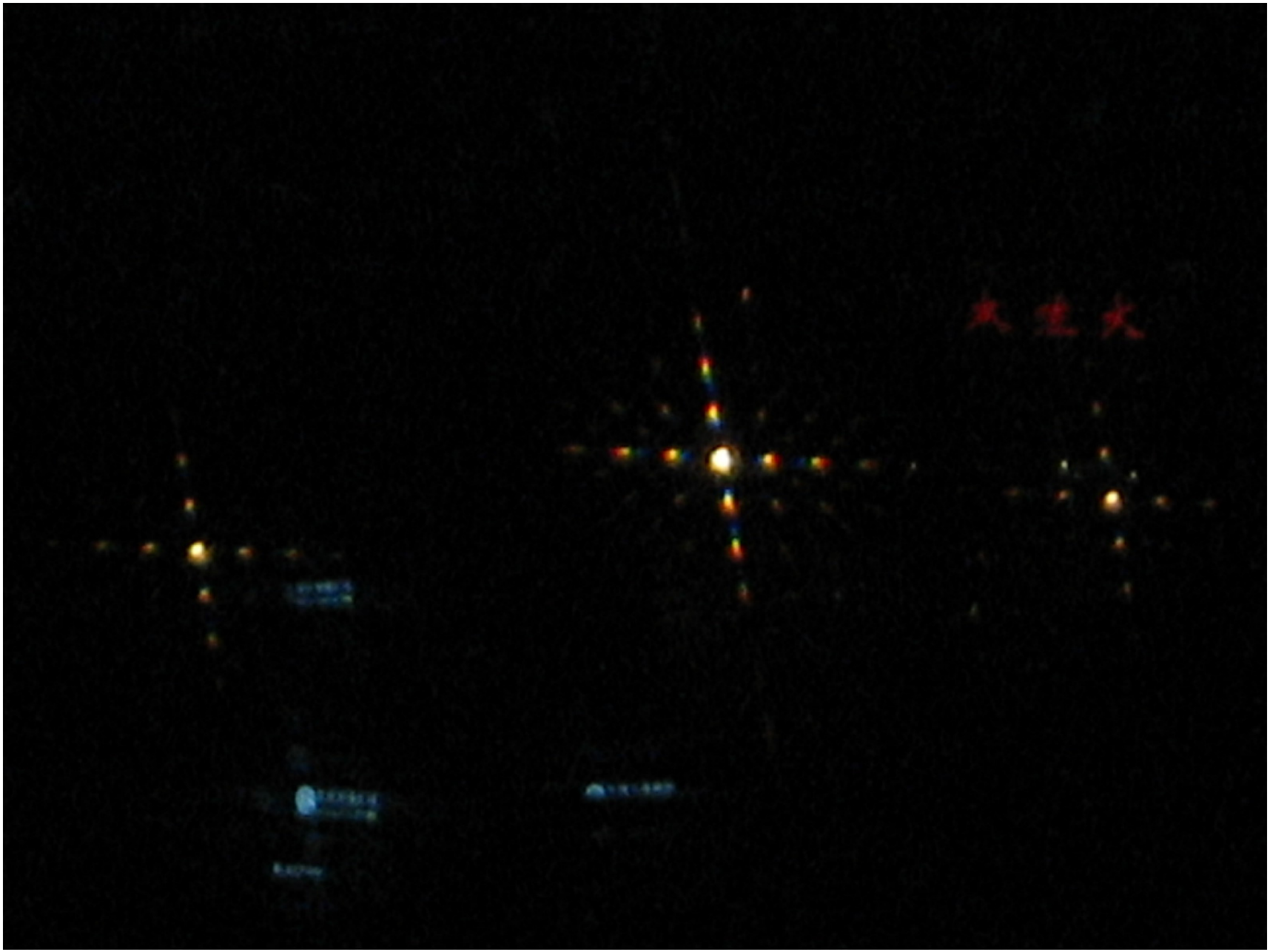
The plane cuts each cell edge once and is the (1,1) plane.



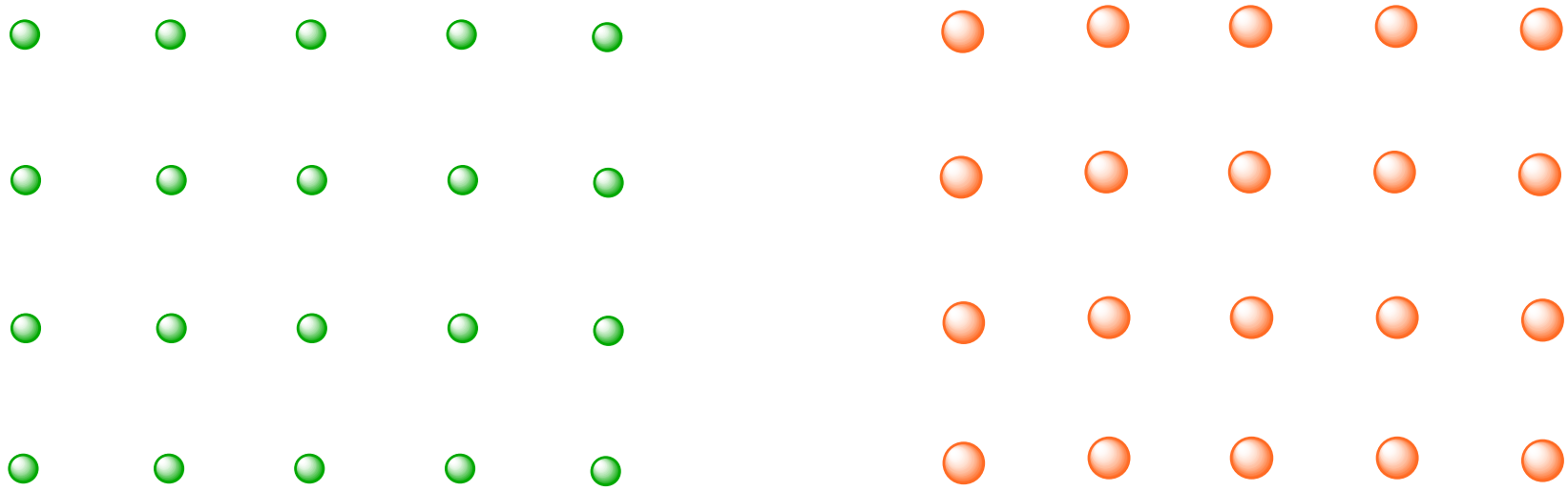
This is the (1,2) plane



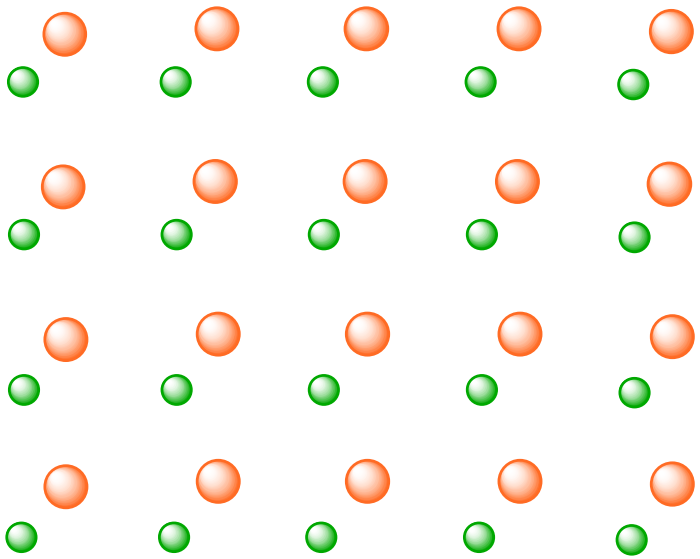
This is the (1,0) plane, it never cuts the (y) axis



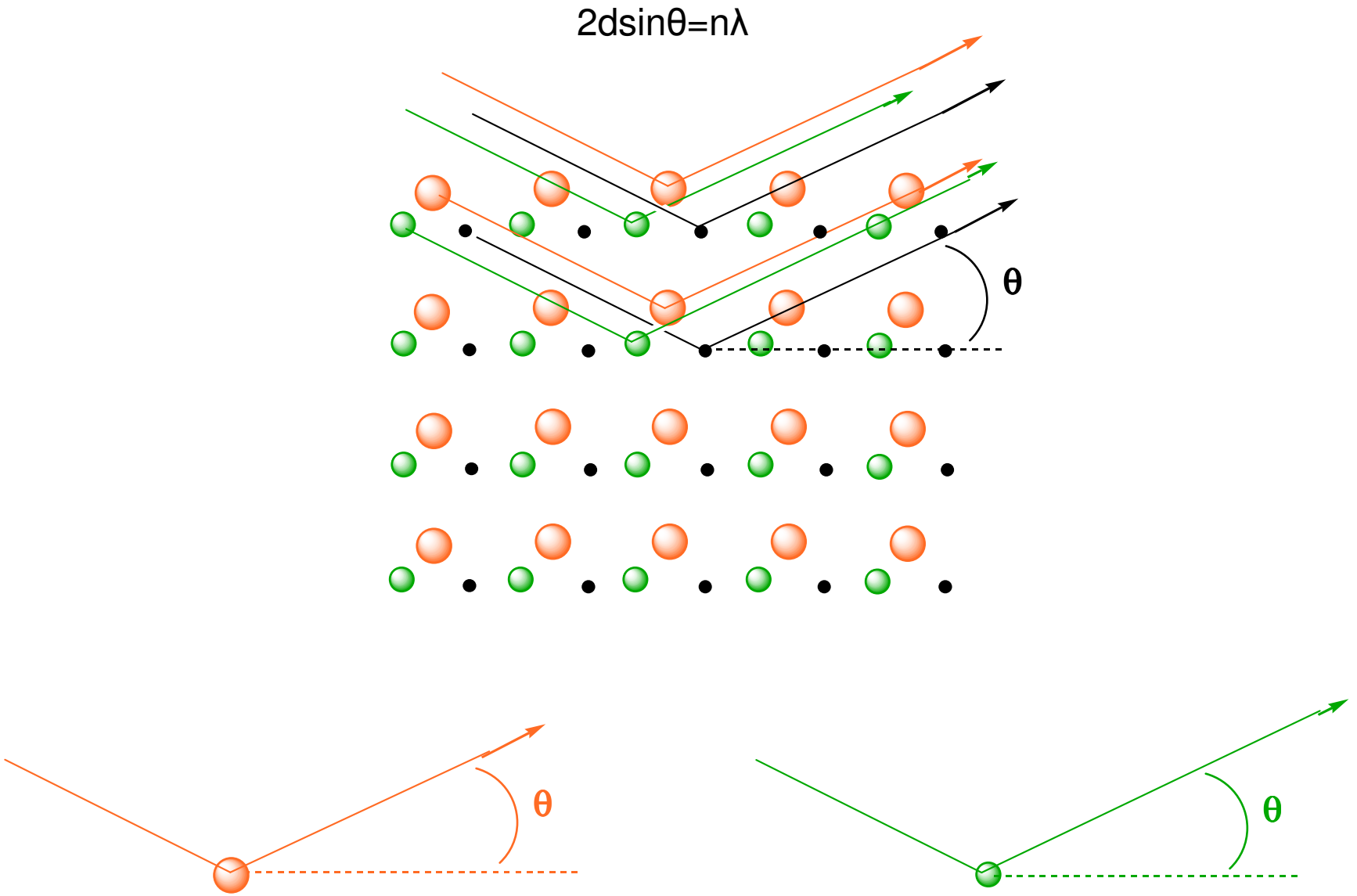
When there is more than one type of atom in the crystal, each atom forms its own separate array.



When there is more than one type of atom in the crystal, each atom forms its own separate array within the crystal.

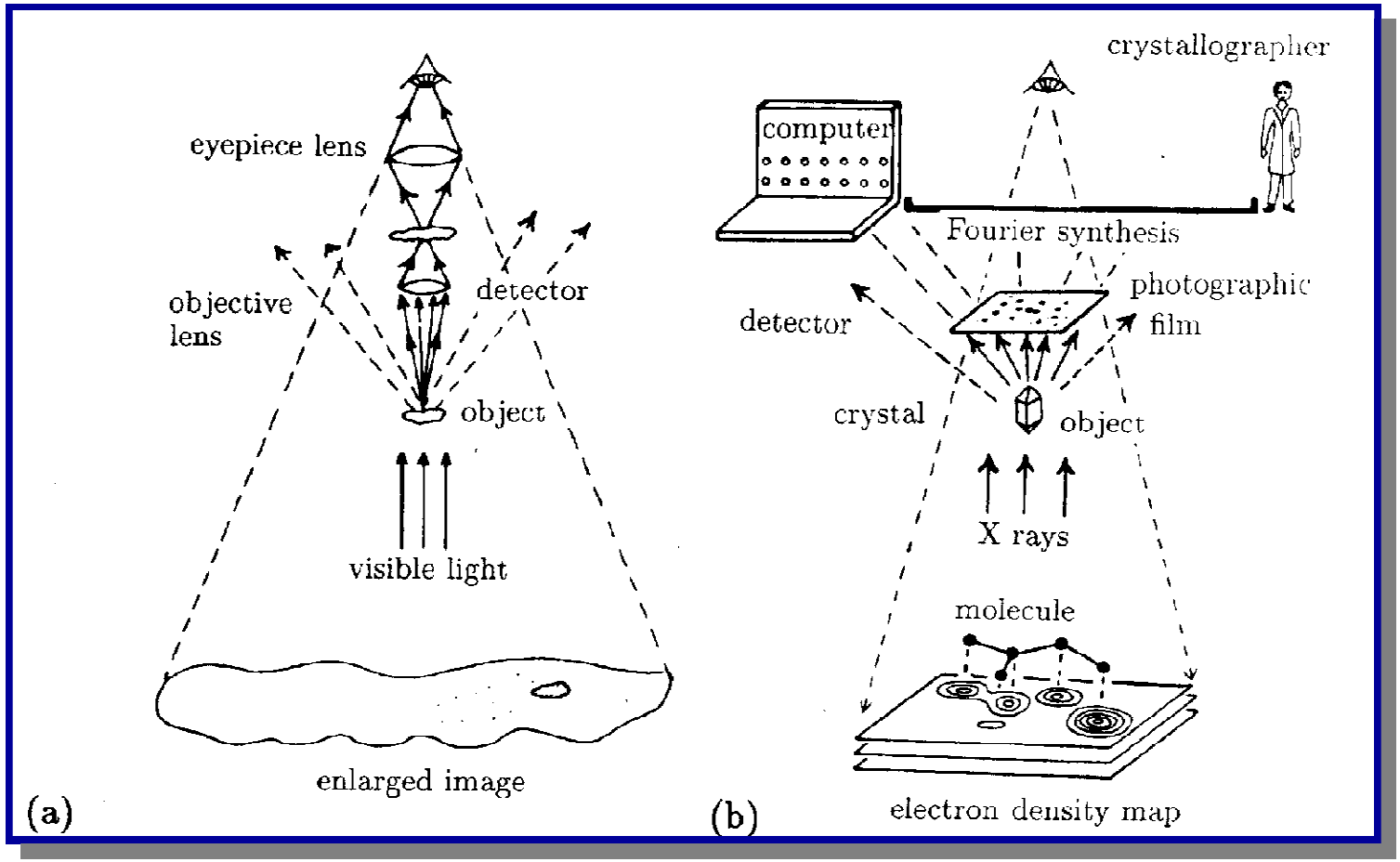


When there is more than one type of atom in the crystal, each atom forms its own separate array and each array separately satisfies the Bragg equation.



How can we "*see*" atoms?

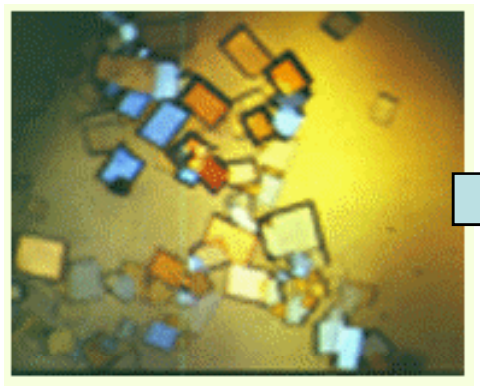
"supermicroscope" *via* X-ray



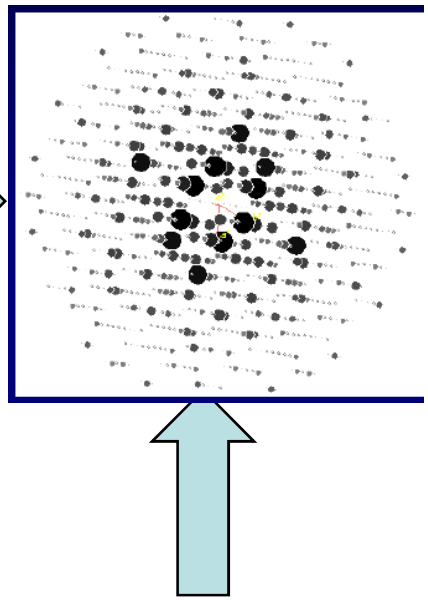
Microscope

X-ray diffraction

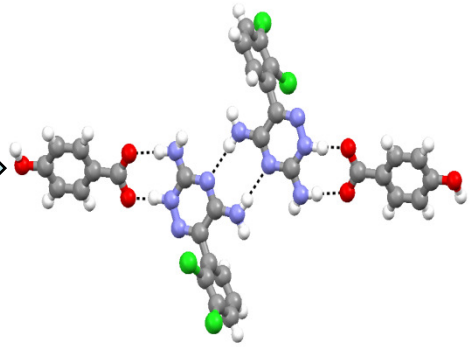
Single Crystal X-Ray Structure Determination



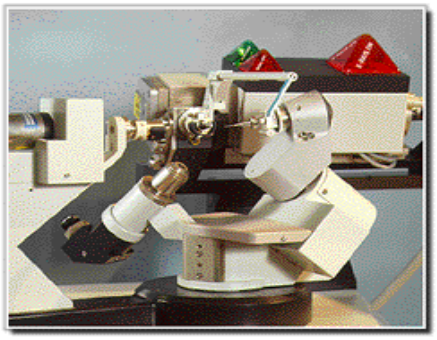
Single Crystals



X-Ray Diffraction Experiment



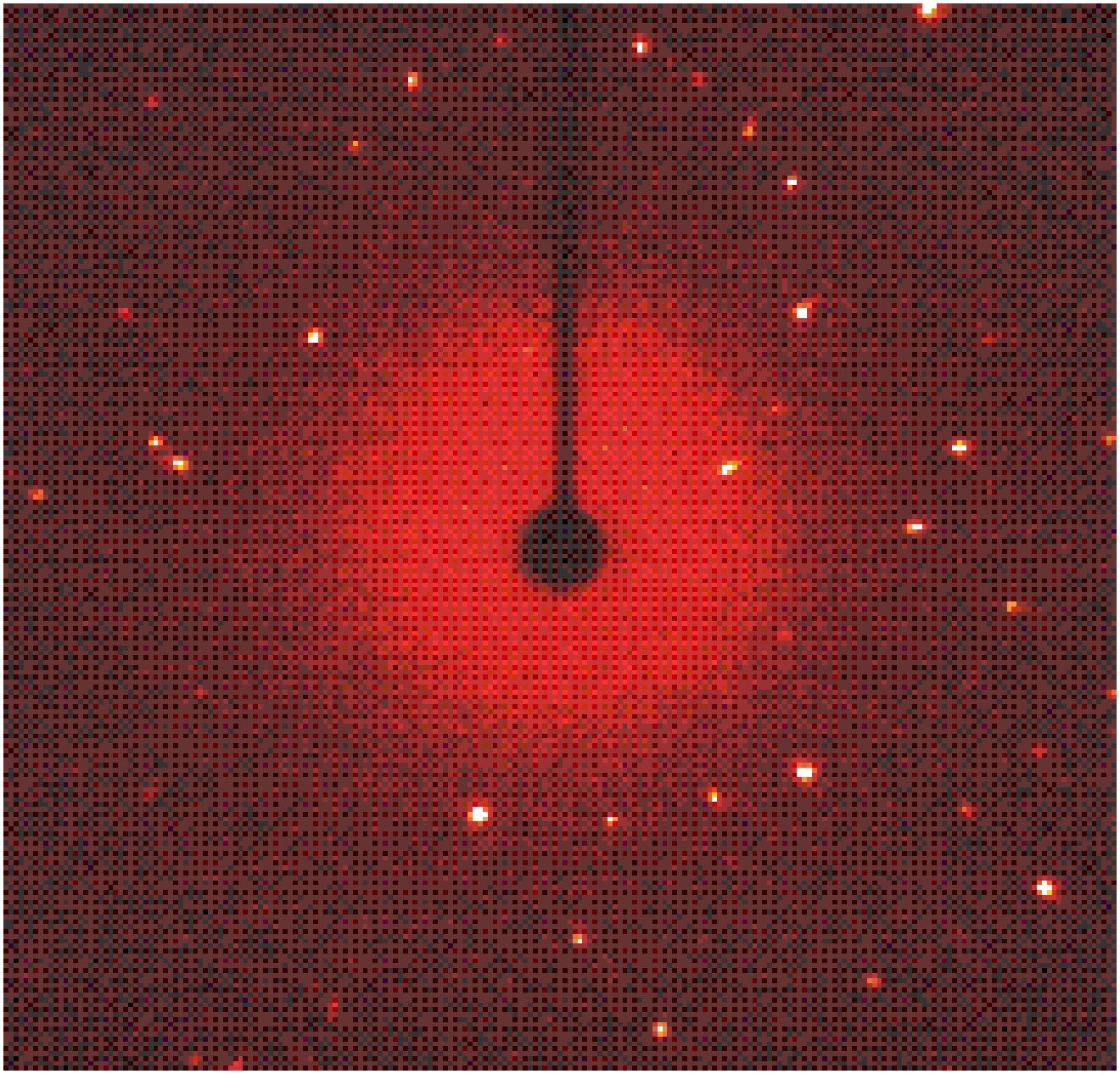
Crystal structure



Tabletop ‘Black Box’ – Smart X2S

Crystal

Structure ?



One of the several hundreds of CCD images with diffraction spots

Determination of the Space Group

- Cell Dimensions, Laue Symmetry, Intensity Statistics (Centro/Non-Centro), Systematic Extinctions

Structure Determination

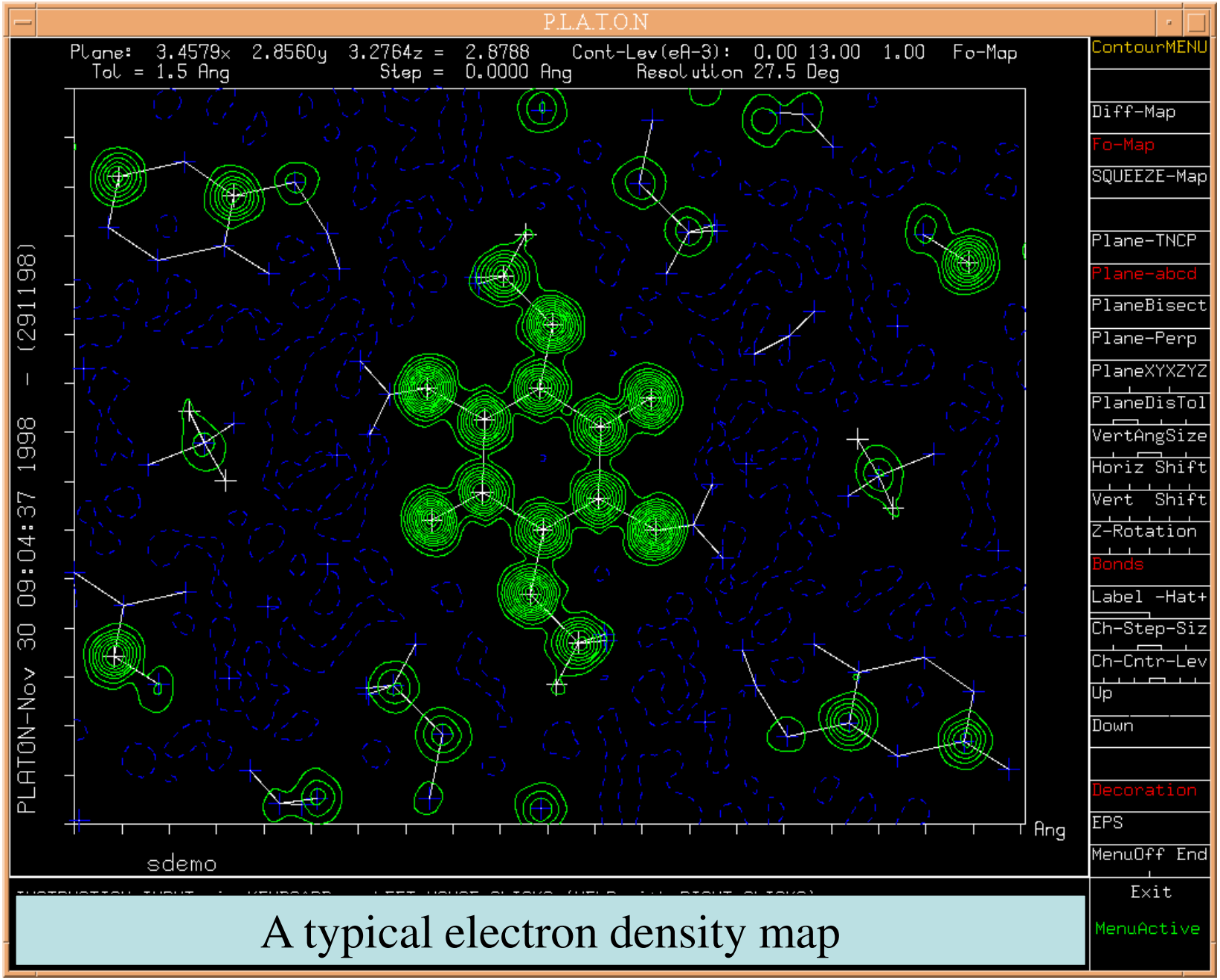
- Experiment ➔ I_{hkl} ➔ $|F_{hkl}| = \mathrm{Sqrt}(I_{hkl})$
- Needed for 3D structure (approximate) Phases: ϕ_{hkl}

  $|F_{hkl}| + \phi_{hkl} = F_{hkl}$ ➔ 3D-Fourier Synthesis

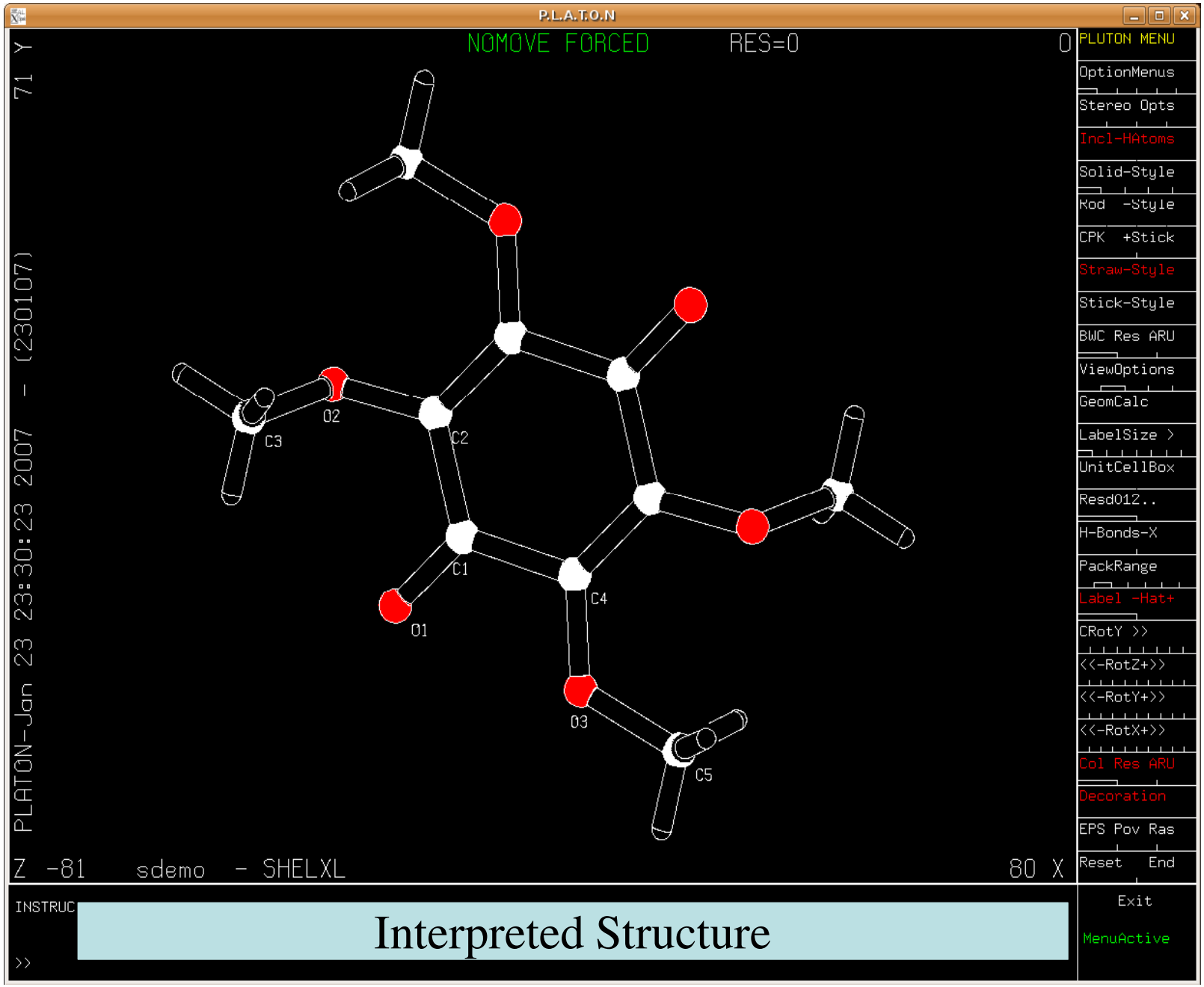
  $\rho(x,y,z) = [\ \Sigma_{hkl}\ F_{hkl}\ exp\{-2\pi\imath(hx + ky + lz)\}] / V$

  x,y,z are fractional coordinates (range 0 → 1)

Phase problem



A typical electron density map



Interpreted Structure

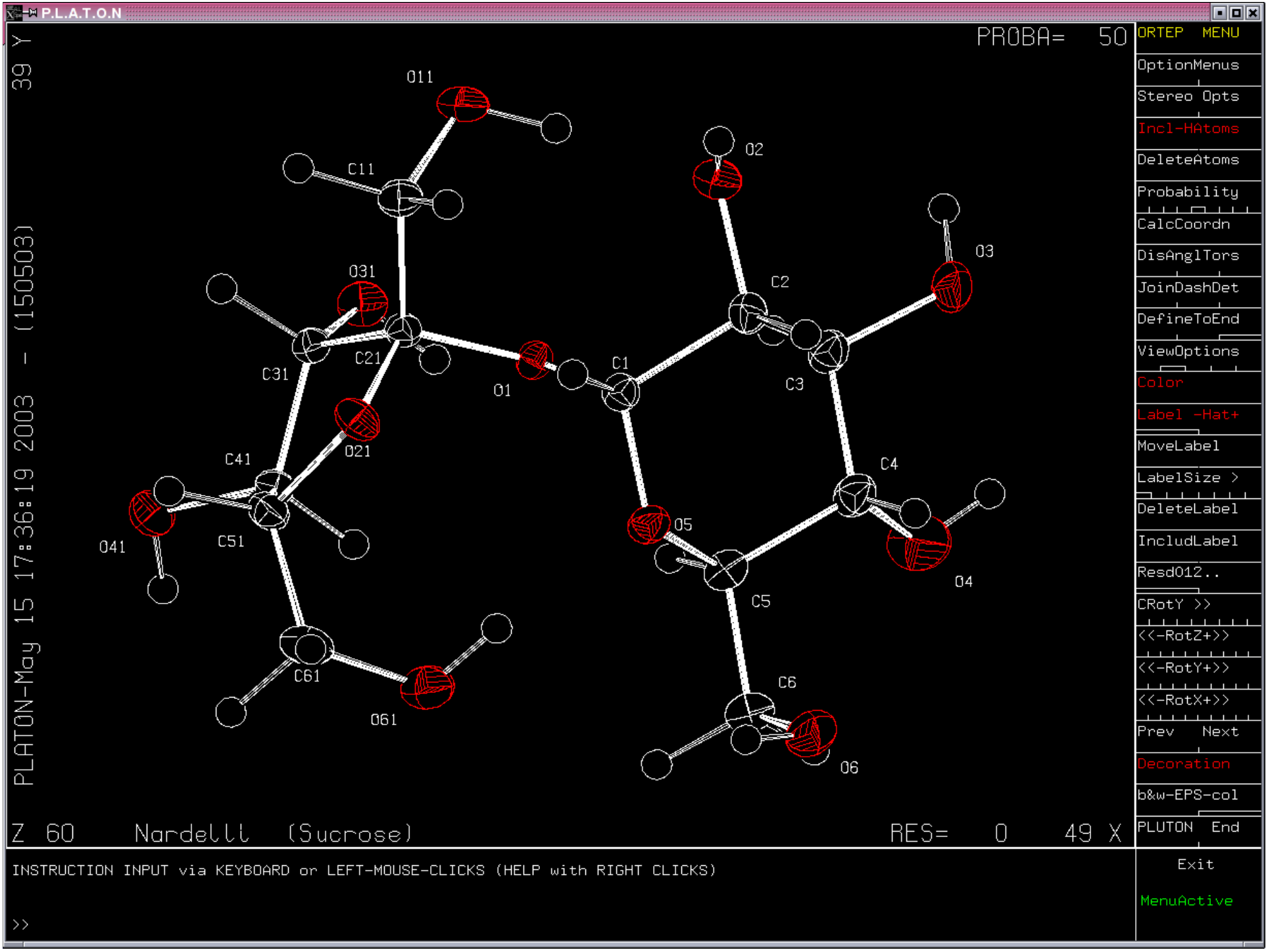
Structure Completion

- Extract the 3D Coordinates (x, y, z) of the atoms.
- Assign Atom Types (Scattering type C, O etc.)
- Assign Additional Parameters to Model the ***Thermal Motion*** (T) of the Atoms.
- Other Parameters: Extinction, Twinning, Flack x
- Model: $F_{hkl} = S_{j=1,n}\, f_j\, T \exp\{2\pi i(hx + ky + lz)\}$
- Non-linear Least-squares Parameter Refinement until Convergence.
- Minimize: $S_{hkl}\; w\,[(F_{hkl}^{obs})^2 - (F_{hkl}^{calc})^2]^2$
- Agreement Factor: $R = S\,|F^{obs} - F^{calc}| \,/\, S|F^{obs}|$

Refinement of the Structural Model

Refinement Steps (Programs SHELXL, Crystals, XTAL etc)

1. Refine positional parameters + isotropic U
2. Refine positional + anisotropic parameters
3. Introduce H-atoms
4. Refine H-atoms with x,y,z,U(iso) or riding on their carrier atoms
5. Refine weighting scheme
6. ORTEP presentation ➔


P.L.A.T.O.N
PROBA= 50
O11
C11
O2
O3
O31
C2
C21
C31
O1
C1
C3
O21
C41
C4
O41
C51
O5
O4
C5
C61
C6
O61
O6
Z 60 Nardelli (Sucrose)
RES= 0 49 X
39 Y
PLATON-May 15 17:36:19 2003 - (150503)
ORTEP MENU
OptionMenus
Stereo Opts
Incl-HAtoms
DeleteAtoms
Probability
CalcCoordn
DisAnglTors
JoinDashDet
DefineToEnd
ViewOptions
Color
Label -Hat+
MoveLabel
LabelSize >
DeleteLabel
IncludLabel
Resd012..
CRotY >>
<<-RotZ+>>
<<-RotY+>>
<<-RotX+>>
Prev Next
Decoration
b&w-EPS-col
PLUTON End
INSTRUCTION INPUT via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)
>>
Exit
MenuActive

Analysis of the Geometry and Intermolecular Interactions

Programs: PLATON, PARST etc

- Bond distances, angles, torsion angles, ring (puckering) geometry etc.
- Intermolecular Contacts

Structure validation

- Refinement results in CIF File format.
- Final Fobs/Fcalc data in FCF File Format
- IUCr CHECKCIF tool
- PLATON Validation Tool
- Check in Cambridge Crystallographic Database for similar structures.

Hydrogen Bonds (O-H..O, N-H..O, O-H..π)

Technical Problems

- Poor crystal quality (e.g. fine needle bundles)
- Determination of the correct Space Group Symmetry
- Pseudo-Symmetry
- Absolute Structure of light atom structures
- Twinning
- Positional and substitutional disorder of part (or even the whole) molecule
- Disordered Solvent
- Incommensurate structures
- Diffuse scattering, streaks, diffuse layers

SOLUTION

A solution for the structure validation problem was pioneered by the *International Union of Crystallography*

- Provide and archive crystallographic data in the computer readable CIF standard format.
- Offer Automated validation, with a computer generated report for authors and referees.
- Have journals enforce a structure validation protocol.
- The IUCr journals and most major journals now indeed implement some form of validation procedure.

THE CIF DATA STANDARD

- Driving Force: Syd Hall (IUCr/ Acta Cryst C)
- Early Adopted by XTAL & SHELX(T)L.
- Currently: WinGX,Crystals,Texsan, Maxus etc.
- Acta Cryst. C/E – Electronic Submission
- Acta Cryst.:Automatic Validation at the Gate
- CIF data available for referees for detailed inspection (and optional calculations).
- Data retrieval from the WEB for published papers
- CCDC – Deposition in CIF-FORMAT.

VALIDATION QUESTIONS

Single crystal validation addresses three simple but important questions:

1 – Is the reported information complete?
2 – What is the quality of the analysis?
3 – Is the Structure Correct?

IUCr CHECKCIF WEB-Service

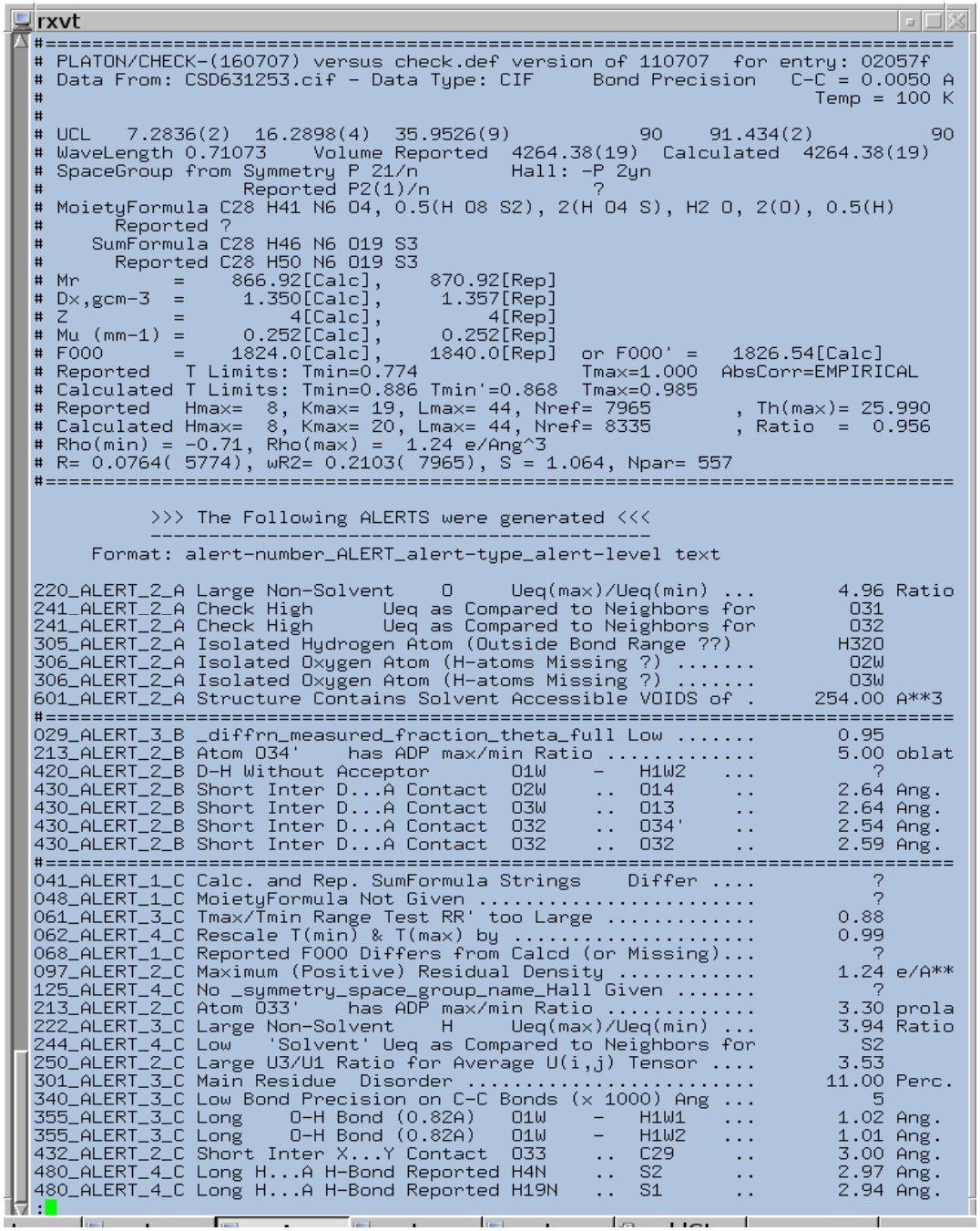
http://checkcif.iucr.org reports the outcome of:

- IUCr standard tests

  Consistency, Missing Data, Proper Procedure, Quality etc.
- + Additional PLATON based tests

  Missed Symmetry, Twinning, Voids, Geometry, Displacement Parameters, Absolute Structure etc.

- ALERT A – Serious Problem
- ALERT B – Potentially Serious Problem
- ALERT C – Check & Explain
- ALERT G – Verify or Take Notice



EXAMPLE OF PLATON GENERATED ALERTS FOR A RECENT PAPER PUBLISHED IN J.Amer.Chem.Soc. (2007)

Attracted special attention in Chemical and Engineering News

Properly Validated ?

THE MESSAGE

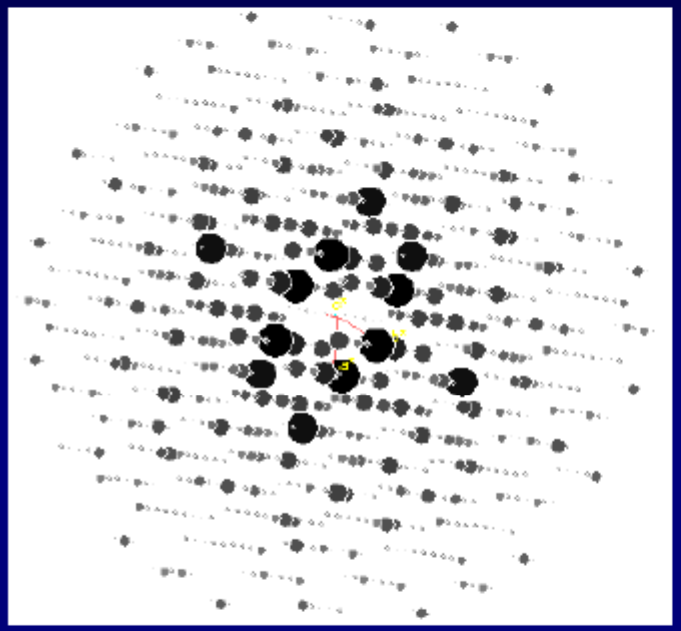
- Validation should not be postponed to the publication phase. All validation issues should be taken care of during the analysis.
- Everything unusual in a structure is suspect,

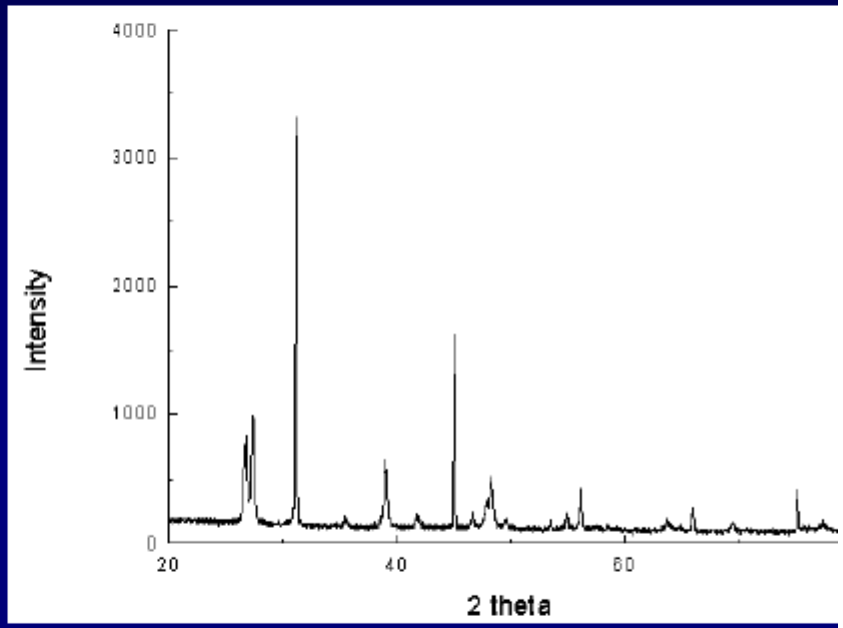
  mostly incorrect (artifact) and should be investigated and discussed in great detail and supported by additional independent evidence.
- The CSD can be very helpful when looking for possible precedents

Validation Procedures are excellent Tools to:

- Set Quality Standards (Not just on R-Value)
- Save a lot of Time in Checking, both by the Investigators and the Journals (referees)
- Point at Interesting Features (Pseudo-Symmetry,

  short Interactions etc.) to be discussed.
- Surface a problem that only an experienced Crystallographer might be able to Address
- Proof of a GOOD structure.





3D Single Crystal

1D Powder

1. Sample preparation
2. Method - λ used (Source)
3. Mode of Data Collection

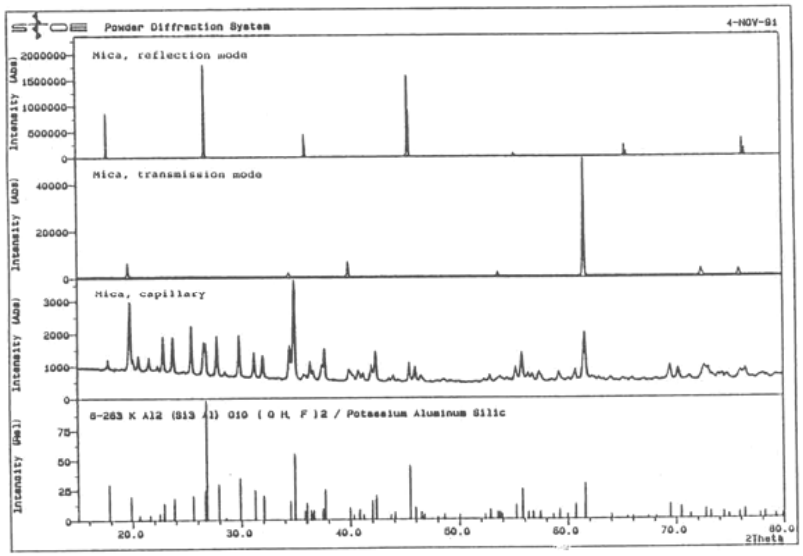


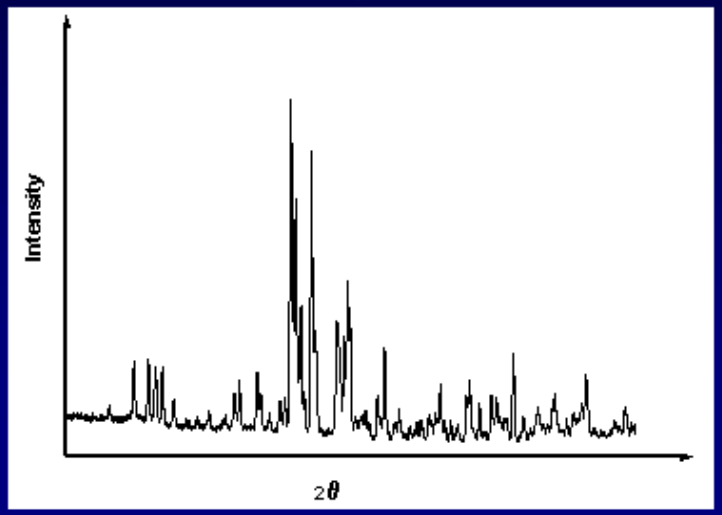
Fig. 35

Fig. 35 shows the results for mica in reflection, transmission and from a capillary, together with the 6-263 JCPDS file of mica.

0.02 ° in 2θ →~5000 Data Points in the Range 1-100 °

0.005 ° in 2θ →~20,000 Data Points in the Range 1-100 °

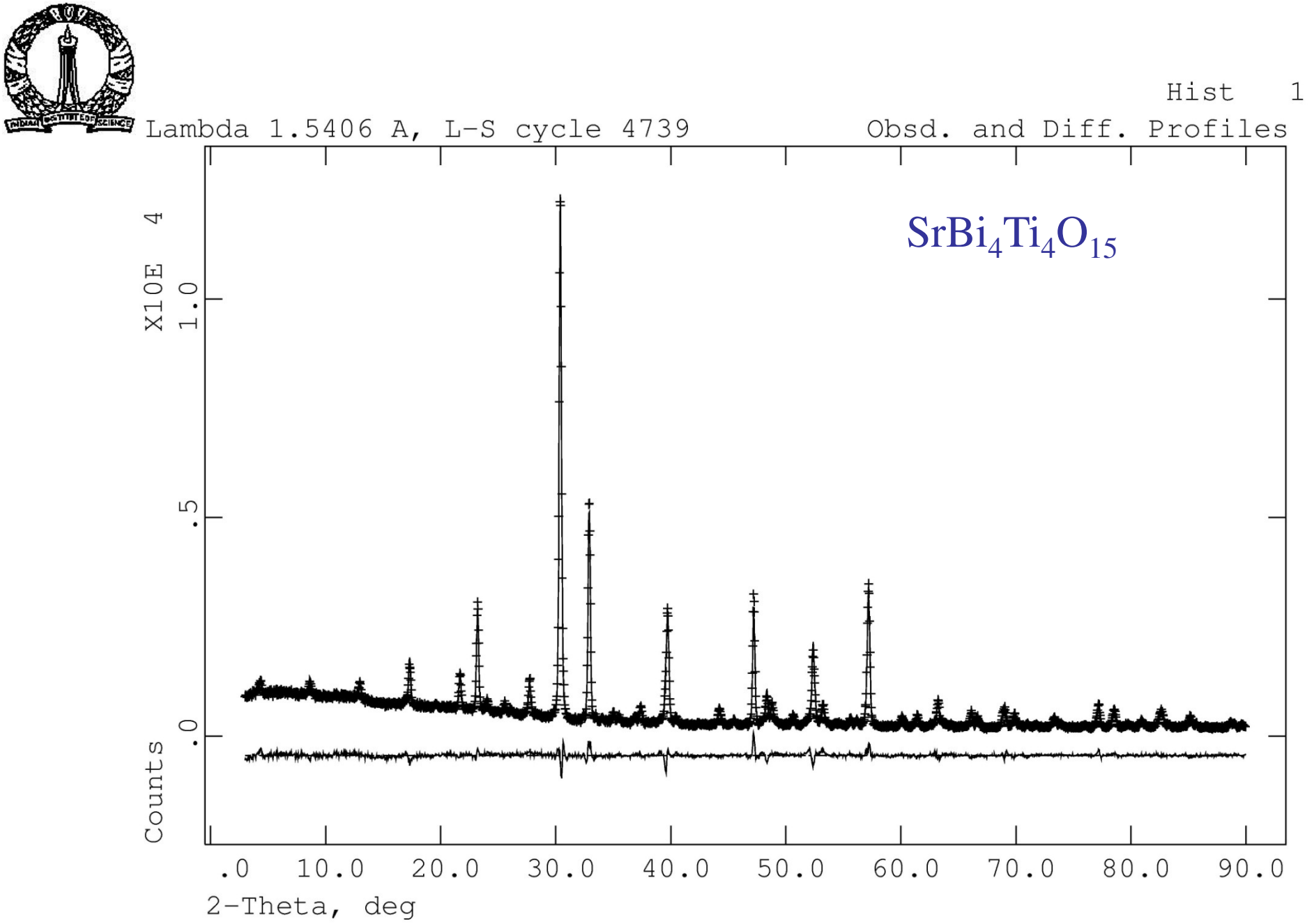
Experimental powder diffraction pattern

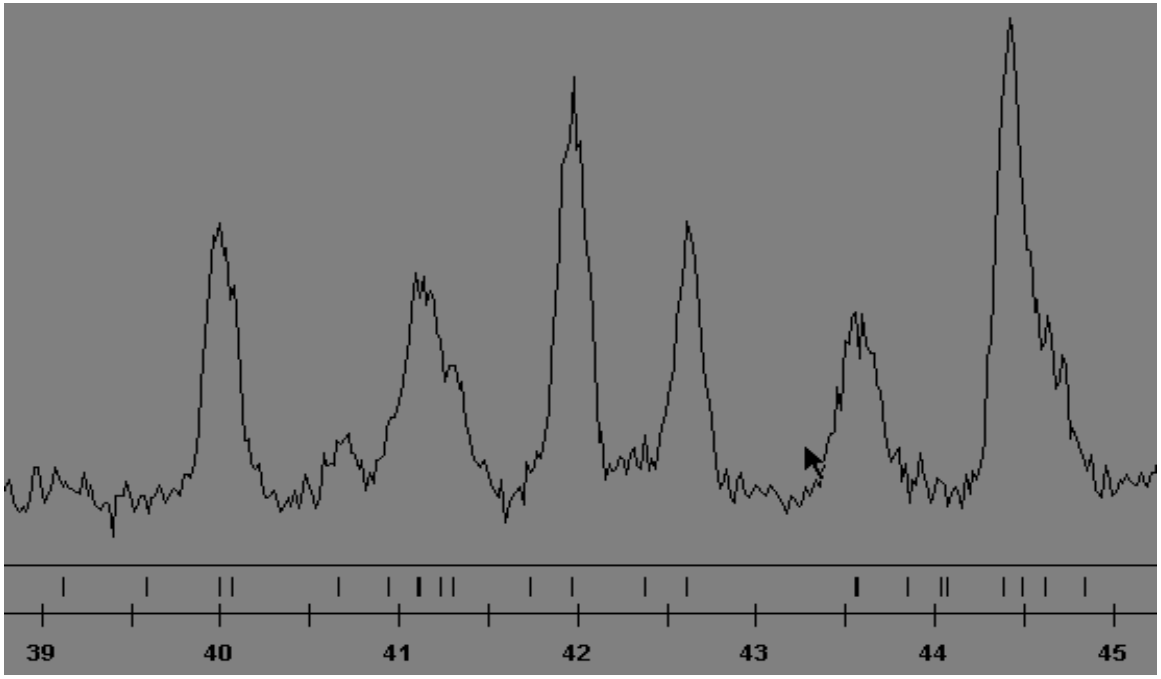


Unit cell dimensions, space group
unit cell content

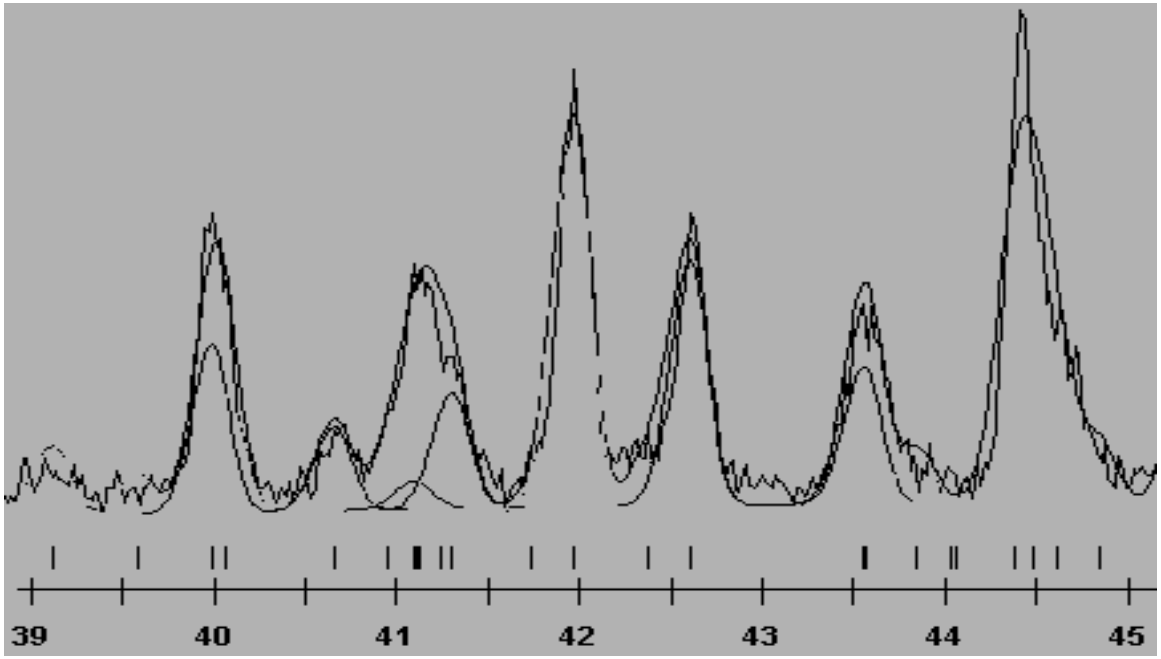
Structure solution

Initial structure model → Rietveld refinement → Final crystal structure


Hist 1
Lambda 1.5406 A, L-S cycle 4739
Obsd. and Diff. Profiles
$SrBi_4Ti_4O_{15}$
X10E 4
1.0
.5
.0
Counts
.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
2-Theta, deg



X-ray powder pattern



X-ray powder pattern
after decomposition

Least Square Refinement: (Rietveld protocol)

$$S_y = \sum_i w_i (y_i - y_{ci})^2$$

$w_i = 1/y_i$, y_i = observed Intensity, y_{ci} = Calculated intensity

Where the entire powder diffraction pattern is taken as a whole.

$$Y_{ci} = s \sum_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) P_k A + y_{bi}$$

s=scale factor K=Miller indices(h k l) ϕ =Reflection profile Function

A=Absorption factor, L_k= Lorentz , polarization and multiplicity factors

P_k=Preferred orientation function, F_k=Structure factor for the K_{th}Bragg reflection, Y_{bi}=Background intensity at the i_{th} step

Profile functions Examples

Function

$[C_o^{1/2} / H_k\pi^{1/2}] \exp(-C_o(2\theta_i - 2\theta_k)^2/H_k^2)$ Gaussian (G)

$(C_1^{1/2}/\pi H_k)\ 1/\ [1+C_1(2\theta_i - 2\theta_k)^2/H_k^2]^2$ Lorentzian (L)

$(2C_2^{1/2}/\pi H_k)\ 1/\ [1+C_2(2\theta_i - 2\theta_k)^2/H_k^2]^2$ Mod 1 Lorentzian

$(C_3^{1/2}/2H_k)\ 1/\ [1+C_3(2\theta_i - 2\theta_k)^2/H_k^2]^{3/2}$ Mod 2 Lorentzian

$\eta\ L + (1-\eta)G$ pseudo-Voigt

The mixing parameter η can be refined as a linear function of 2θ wherein the refinable variables are NA and NB.

$\eta = NA + NB * 2\theta$

Refinable Parameters

Structural parameters

Profile parameters

2θ-Zero

Instrumental profile

Profile asymmetry

Background

Crystallite size and microstrain(through profile parameters)

Specimen-profile breadth parameters

Lattice parameters

Specimen displacement

Specimen transparency

Absorption

$$R_F = \sum \left| (I_{k(obs)})^{1/2} - (I_{k(calc)})^{1/2} \right| \Big/ \sum (I_{k(obs)})^{1/2}$$ (Residual structure factor)

$$R_B = \sum \left| (I_{k(obs)}) - (I_{k(calc)}) \right| \Big/ \sum (I_{k(obs)})$$ (Residual Bragg)

$$R_p = \sum \left| (Y_{i(obs)}) - (Y_{i(calc)}) \right| \Big/ \sum (Y_{i(obs)})$$ (Residual pattern)

$$R_{wp} = \left[\sum w_i \{ (Y_{i(obs)}) - (Y_{i(calc)}) \}^2 \Big/ \sum w_i (Y_{i(obs)})^2 \right]^{1/2}$$ (Residual weighted pattern)

$$R_e = \left[N-P \Big/ w_i (Y_{i(obs)})^2 \right]^{1/2}$$ (Residual expected)

$$S = R_{wp/} R_e = \chi$$ (Goodness of fit)

$$d = \sum (\Delta y_i - \Delta y_{i-1})^2 / \Delta(\prod_{i=1}^{N} y_i)$$ (Durbin-Watson statistic)

Crystal structure of α-$NaBi_3V_2O_{10}$

- New phase - $NaBi_3V_2O_{10}$ in Na_2O-Bi_2O_3-V_2O_{10} system (D C Sinclair *et.al*, J Mater. Chem. 1998, 8 (2), 281-282)

- Oxide ion conductor, conductivity = 1.5mS cm^{-1} at 675°C

- Synthesized at 600°C from Na_2O, Bi_2O_3, V_2O_5

$NaBi_3V_2O_{10}$ (single phase) $\xrightarrow{700°C}$ $NaBi_3V_2O_{10}$ + minor phase

$\xrightarrow{775°C}$ $NaBi_3V_2O_{10}$ (melts) $\xrightarrow{cool}$ two phases

- Phase transition at 575°C
  - -DTA analysis
  - -High temperature powder XRD

$NaBi_3V_2O_{10}$ $\underset{\text{phase transition}}{\overset{575°C}{\rightleftharpoons}}$ $NaBi_3V_2O_{10}$

Crystal Data for α-$NaBi_3V_2O_{10}$

Formula	$NaBi_3V_2O_{10}$
Formula weight	911.804
Color	Yellow
Space group	$P\bar{1}$
Z	1
λ (Å)	1.54056
2θ	3-100.42°
Number of Structural parameters	41
Profile function	Pseudo-Voigt
a(Å)	7.1964(4)
b(Å)	7.0367(3)
c(Å)	5.5139(2)
α°	84.440(3)
β°	113.462(2)
γ°	112.319(2)
V(Å^3)	236.46(2)
R_{wp}	13.14%
R_p	9.91%
R(I,hkl)	8.68%

Results of the EXTRA pattern decomposition module

$2\theta = 3.00$ to 100.42°
498 reflections generated
$R_p = 11.55\%$ $R_{wp} = 15.80\%$

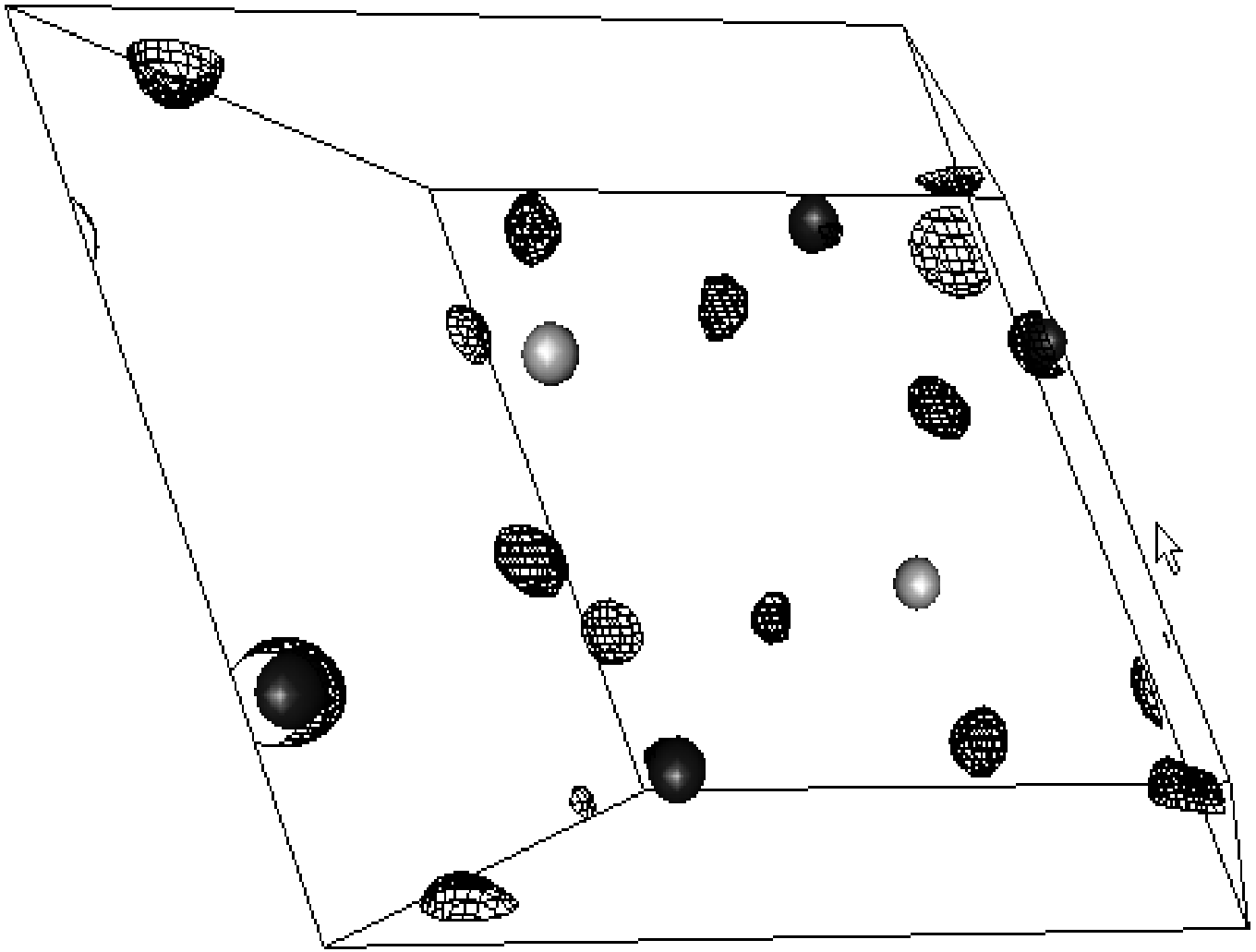
Result of the SIRPOW97 structure solution module

Positional parameters of two Bismuth atoms and one Vanadium atom were found

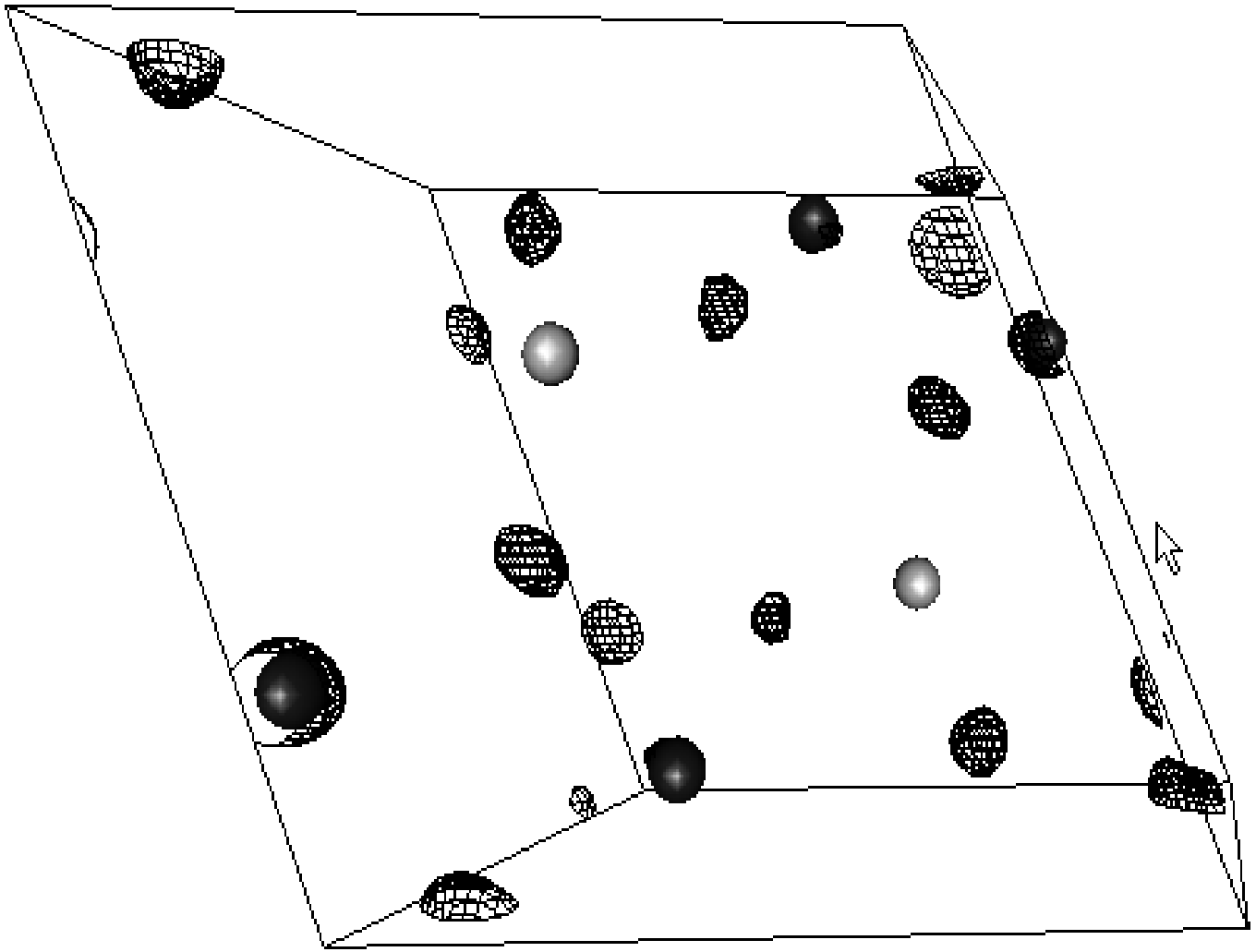
Difference Fourier analysis was used to locate remaining atoms

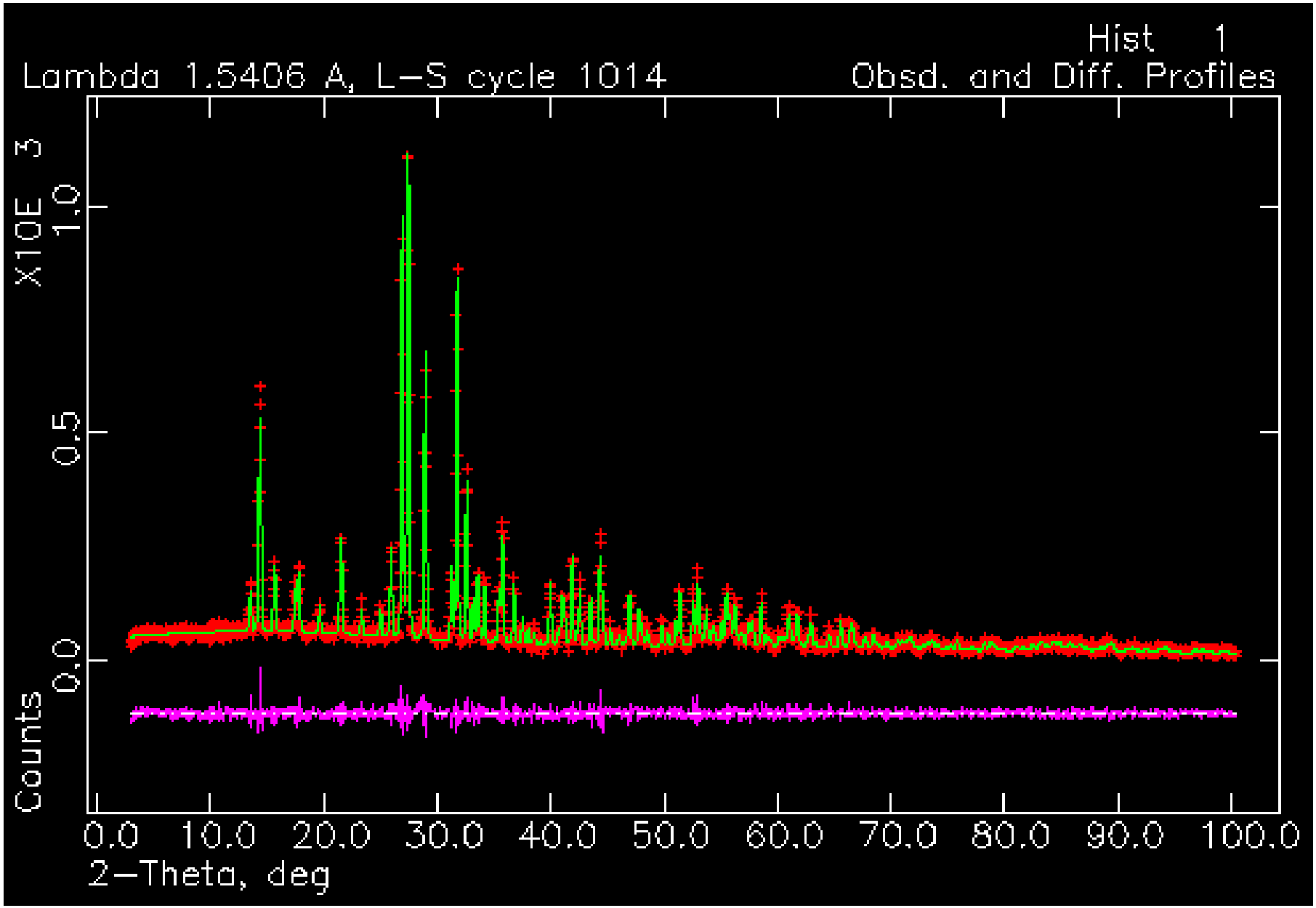
GSAS was used for Rietveld refinement

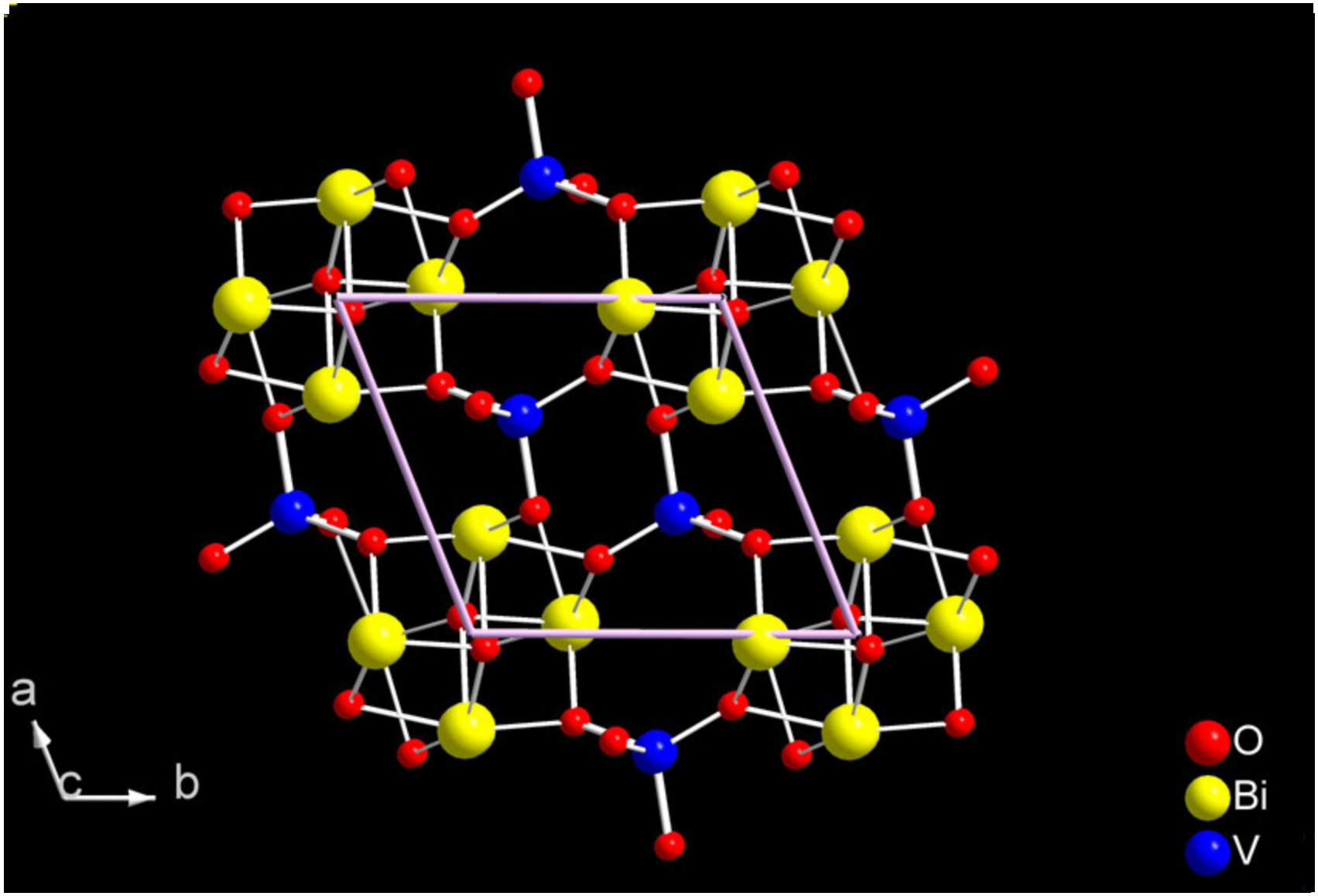
Difference Fourier map



Difference Fourier map




Hist 1
Lambda 1.5406 A, L-S cycle 1014
Obsd. and Diff. Profiles
X10E 3
1.0
0.5
0.0
Counts
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
2-Theta, deg


a
c
b
O
Bi
V

Methods and Strategy

* **Traditional approach**

-pattern decomposition (Pawley,Le Bail method)

-structure solution → model (Direct,Patterson method)

-structure completion (difference Fourier technique)

-Rietveld refinement

* **Direct Space approach**

-trial structures are generated independent of powder pattern,

-compare calculated pattern with experimental powder pattern

(Monte Carlo, simulated annealing, grid search)

Step-1

Determine the unit cell

$\Rightarrow$ Crysfire, Macmallie, Grid search.

Step-2

Decomposition of Powder pattern into integrated intensities $\Rightarrow$ LeBail or Pawley approach [X-pert high score plus, EXPO ..]

Step-3

Assignment of space group from systematic absences [X-pert high score plus, EXPO, Chekcell ..]

Step-4 Reciprocal Lattice methods: Solution of phase problem by Patterson (for inorganic) or direct methods (organic) (GSAS)

Step-5 Use of Monte-Carlo algorithm with Simulated annealing technique (FOX)

Step-6 Rietveld refinement of structure with GSAS by applying different soft constraints, planarity, rigid body etc.

Direct Space approach

The most preferred approach for organic compounds- Drugs

The methodology

1. Trial crystal structures need to be generated in direct space
2. Calculated powder pattern compared with observed powder pattern
3. R and R wp give guidelines How and Why?
4. Aim is to identify the trial structure with lowest R value
5. Any technique for global optimization may be used
   Monte Carlo
   Simulated annealing
   grid search
   genetic algorithm
6. Cell dimensions and experimental pattern are prerequisites
7. Unit cell contents are known (structural formula)
8. Molecular dimensions are optimized and known partly or fully

Solving a structure from powder diffraction data

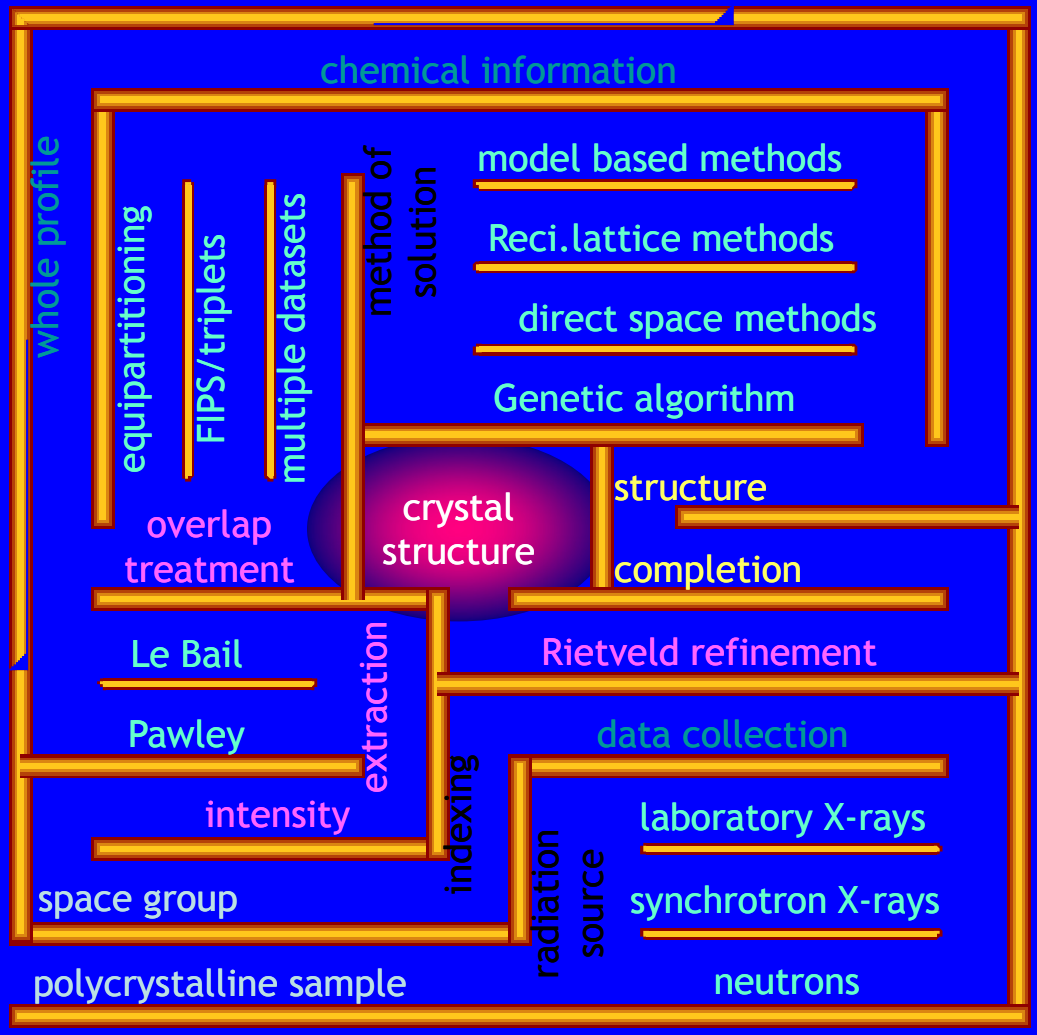
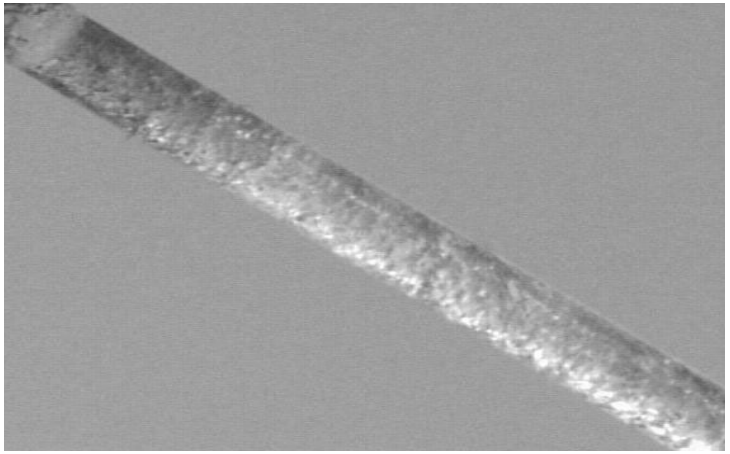
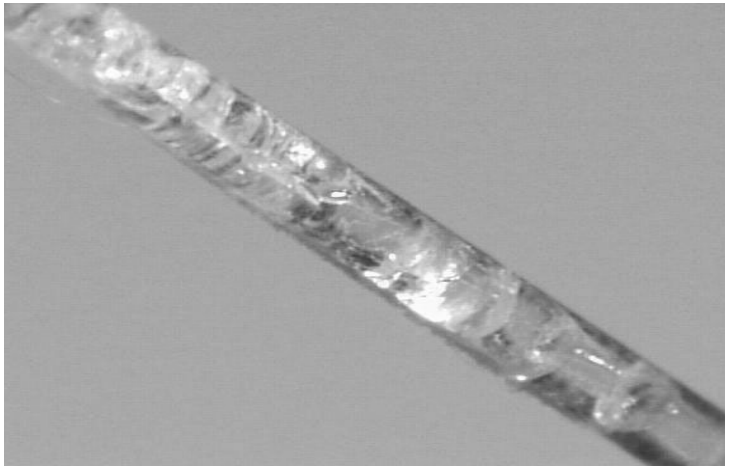


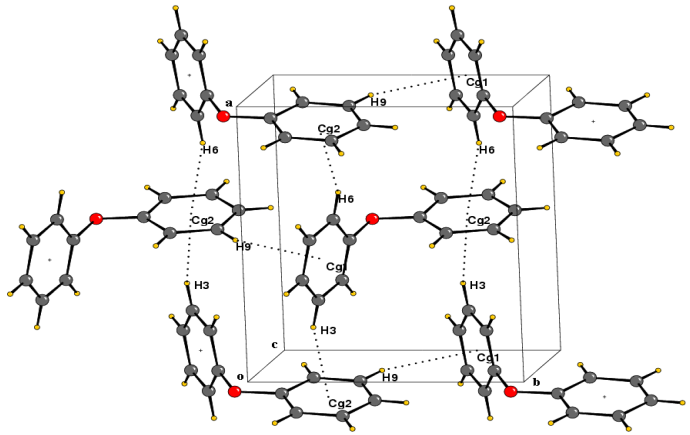
Figure 3: Bruker *SMART APEX CCD* area detector, Oxford nitrogen cryosystem, goniometer attachment with liquid mounted in a capillary.

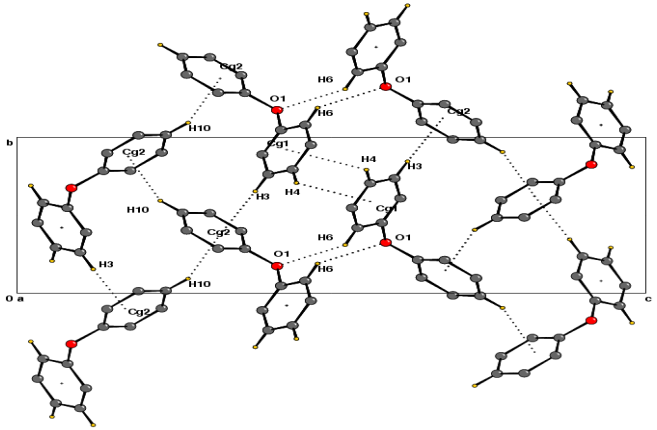
A. R. Choudhury, K. Islam, M. T. Kirchner, G. Mehta, T. N. Guru Row, *J. Am. Chem. Soc.(communication)*, **2004**, 126(39), 12274-12275.

In situ cryo-crystallization of diphenyl ether

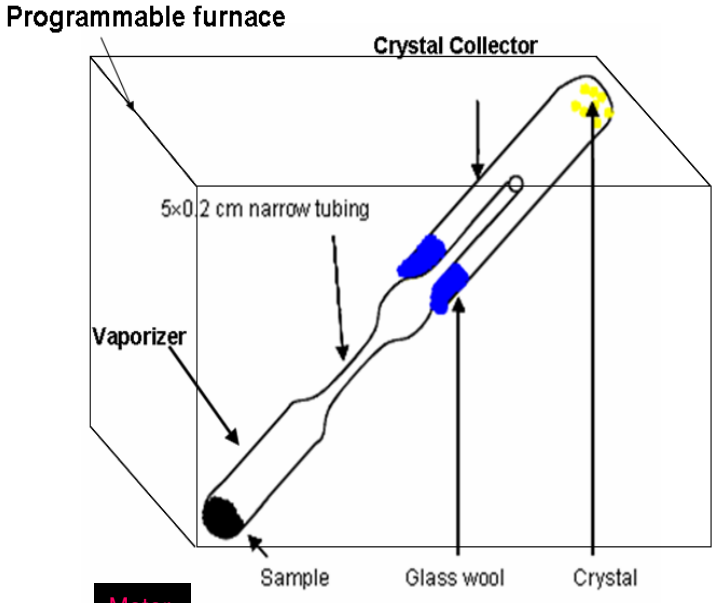


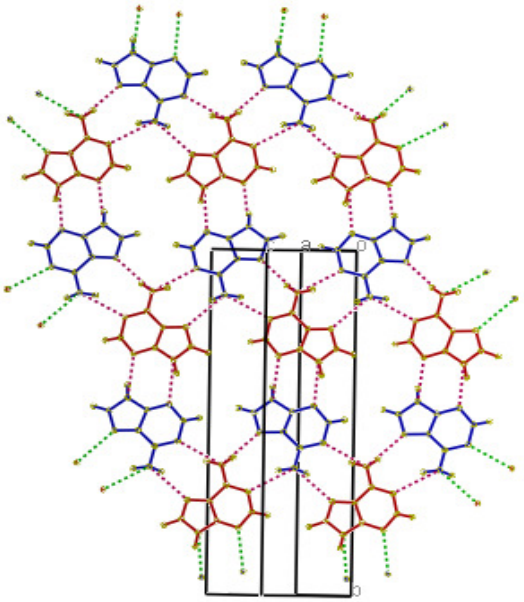


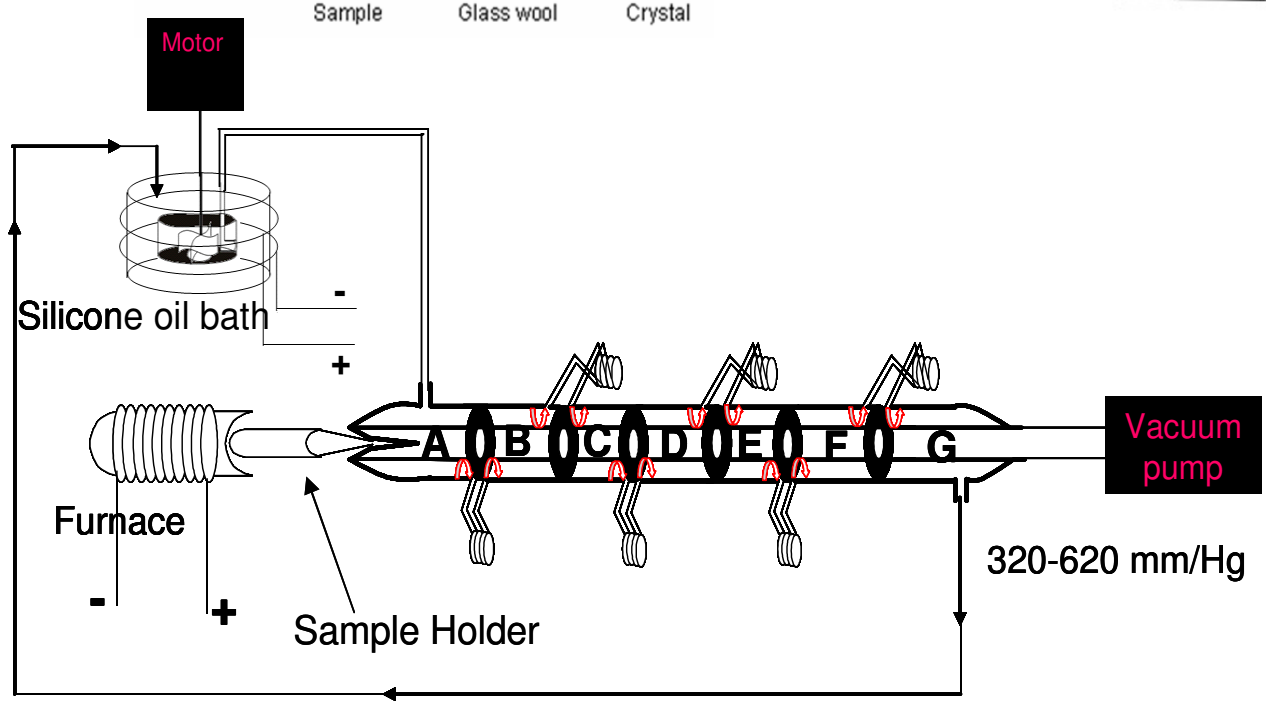


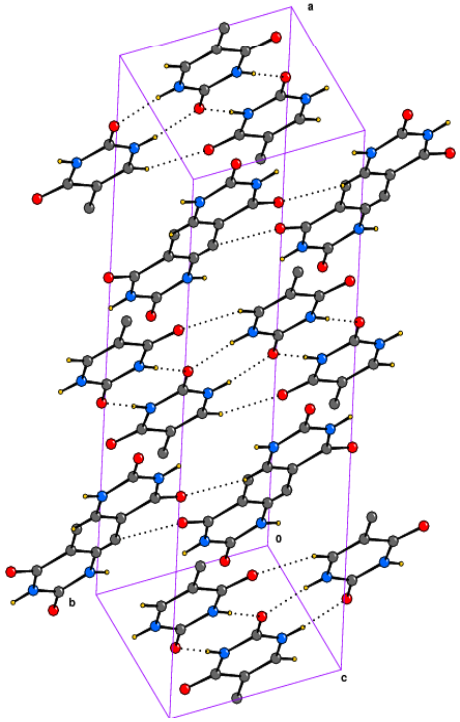


Set up used for Crystallization









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My students, post-docs and project assistants

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