62th Annual Conference on Applications of X-ray Analysis: SAND2013-6234C
Denver X-ray Conference Workshop
5 August 2013, 9AM-Noon, Meadowbrook, Westin Westminster Hotel

BASIC TO INTERMEDIATE XRD ANALYSIS

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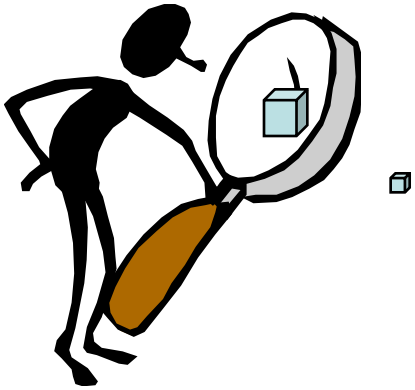
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

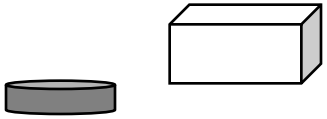
What kinds of samples can we measure?



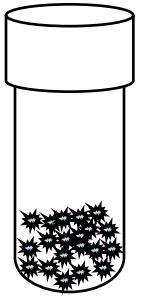
Single crystals

100 - 500 μm

Thin films

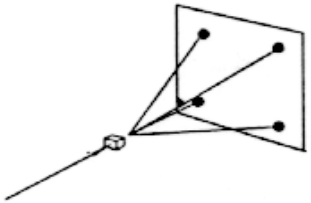


Bulk samples

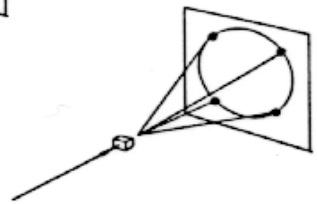


Powders

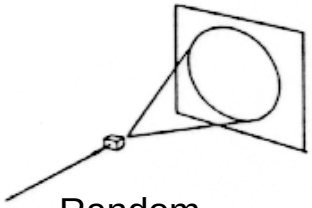
1 mg - 5 gms



Single Crystal

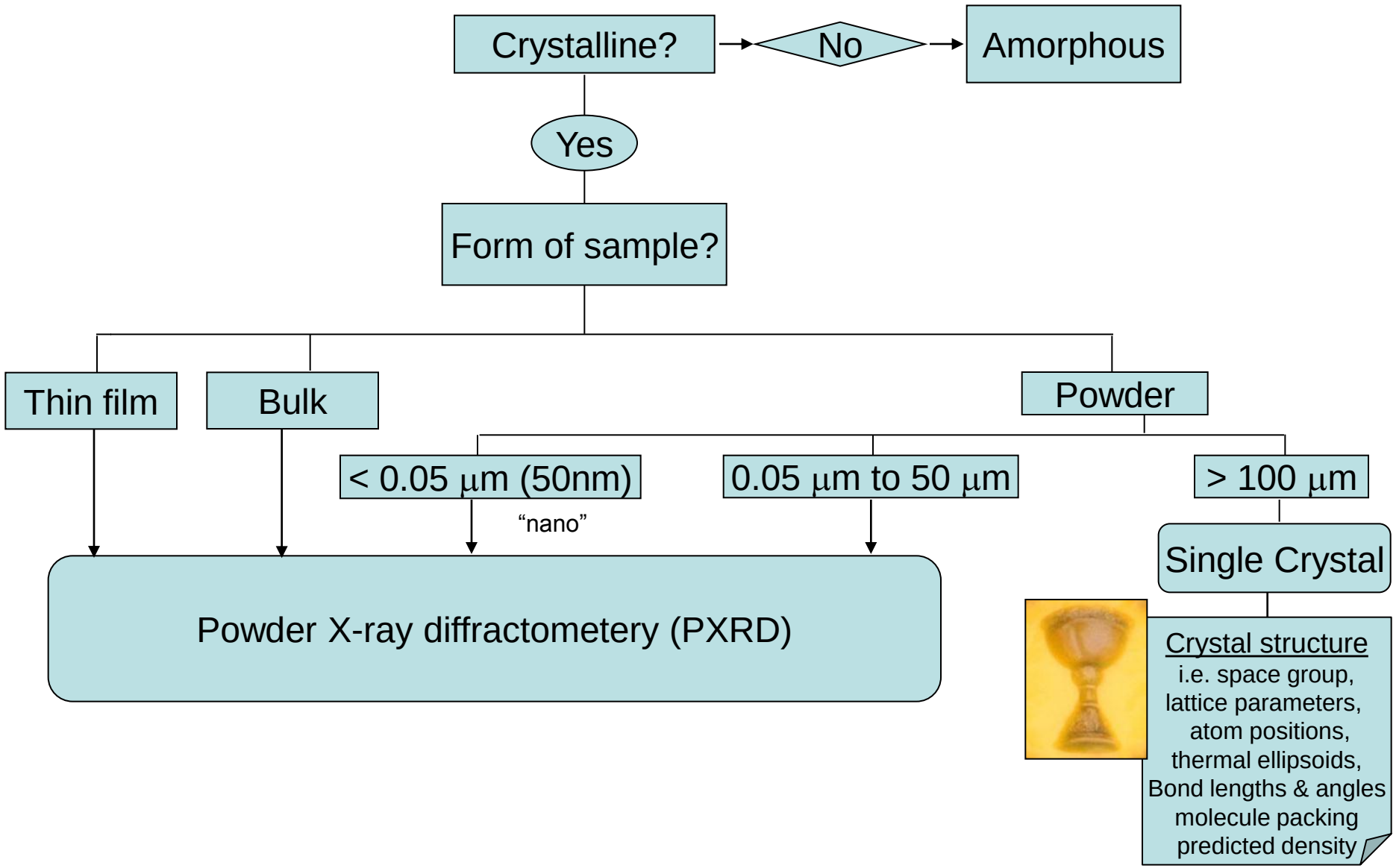


Textured



Random

XRD flow chart



Standard XRD

Powder

0.05 μm to 50 μm

Powder X-ray diffractometery (PXRD)

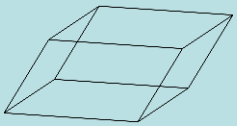
Phase identification: *What is this stuff?*

Phase fraction quantification via RIR: *How much is there?*

Out-of-plane preferred orientation: *Is sample non-random?*

crystallite size / micro-strain: *What can I learn about the crystallites?*

Lattice parameter indexation / cell refinement: *What is the cell?*



Known structure?

No

Yes

Structure Solution from Powder Data (SSPD)

model

Rietveld refinement

Phase fraction
space group,
lattice parameters,
atom positions,
site occupancy,
thermal ellipsoids,
Bond lengths & angles
molecule packing
predicted density
size/strain

Nano-crystalline

Powder

< 0.05 μm (50nm)

Mo tube: λ = 0.7107 Å

Powder X-ray Diffractometery (PXRD)

Phase identification?

Out-of-plane preferred orientation:

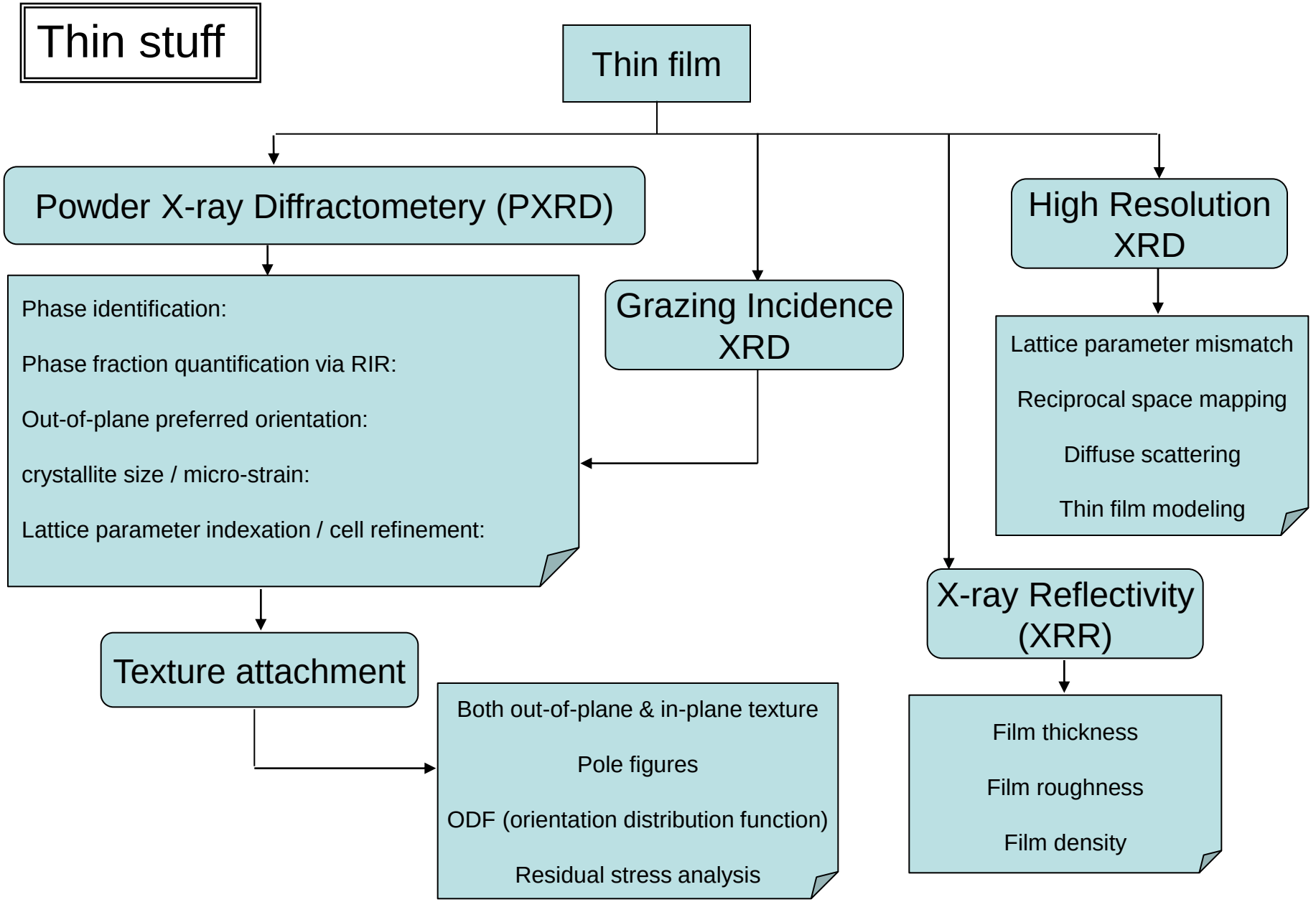
crystallite size / micro-strain:

Atomic pair distribution function (aPDF)

Known structure?

aPDF refinement

space group,
lattice parameters,
atom positions,
site occupancy,
thermal ellipsoids,
Bond lengths & angles
molecule packing
predicted density
size/strain


Thin stuff
Thin film
Powder X-ray Diffractometery (PXRD)
Phase identification:
Phase fraction quantification via RIR:
Out-of-plane preferred orientation:
crystallite size / micro-strain:
Lattice parameter indexation / cell refinement:
Grazing Incidence XRD
High Resolution XRD
Lattice parameter mismatch
Reciprocal space mapping
Diffuse scattering
Thin film modeling
Texture attachment
Both out-of-plane & in-plane texture
Pole figures
ODF (orientation distribution function)
Residual stress analysis
X-ray Reflectivity (XRR)
Film thickness
Film roughness
Film density

Bulk

Can’t grind it

Powder X-ray Diffractometery (PXRD)

Phase identification:

Phase fraction quantification via RIR:

Out-of-plane preferred orientation:

crystallite size / micro-strain:

Lattice parameter indexation / cell refinement:

Random?

No

Texture attachment

Both out-of-plane & in-plane texture

Pole figures

ODF (orientation distribution function)

Residual stress analysis

Yes

Known structure?

No

Yes

Structure solution
From powder (SSFP)

model

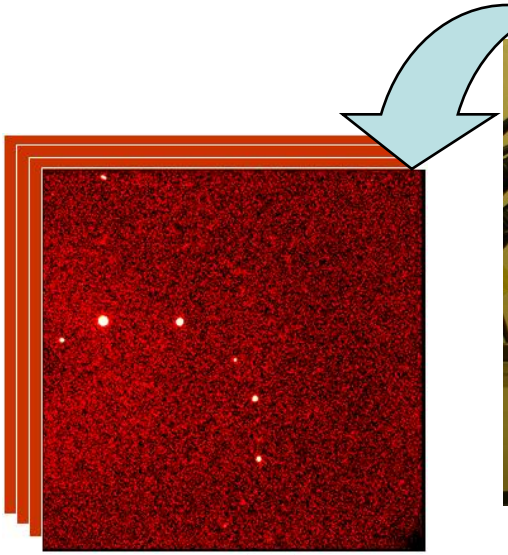
Rietveld
refinement

Phase fraction
space group,
lattice parameters,
atom positions,
site occupancy,
thermal ellipsoids,
Bond lengths & angles
molecule packing
predicted density
size/strain

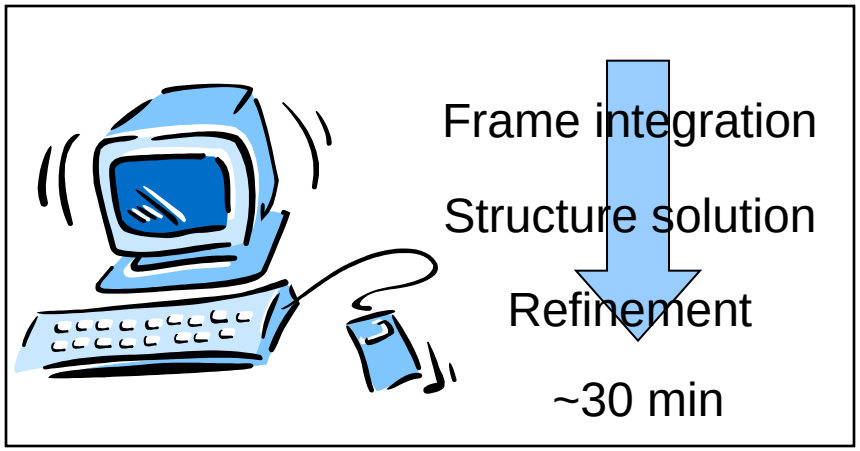
Single Crystal

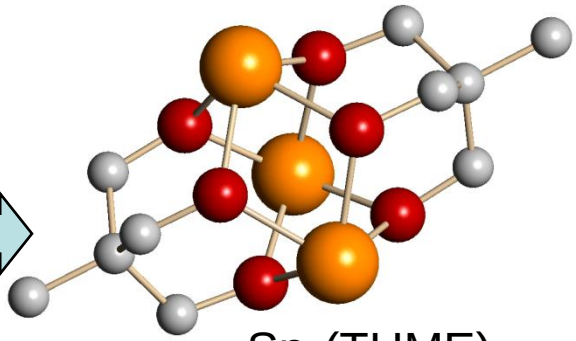
Single-Crystal XRD is a reasonably mature science and is becoming routine for many materials systems

3 hour automated data collection ~1 Gb



Bruker Single-Crystal diffractometer with Apex CCD detector





$Sn_3(THME)_2$

Solved Structure in < 4 hrs

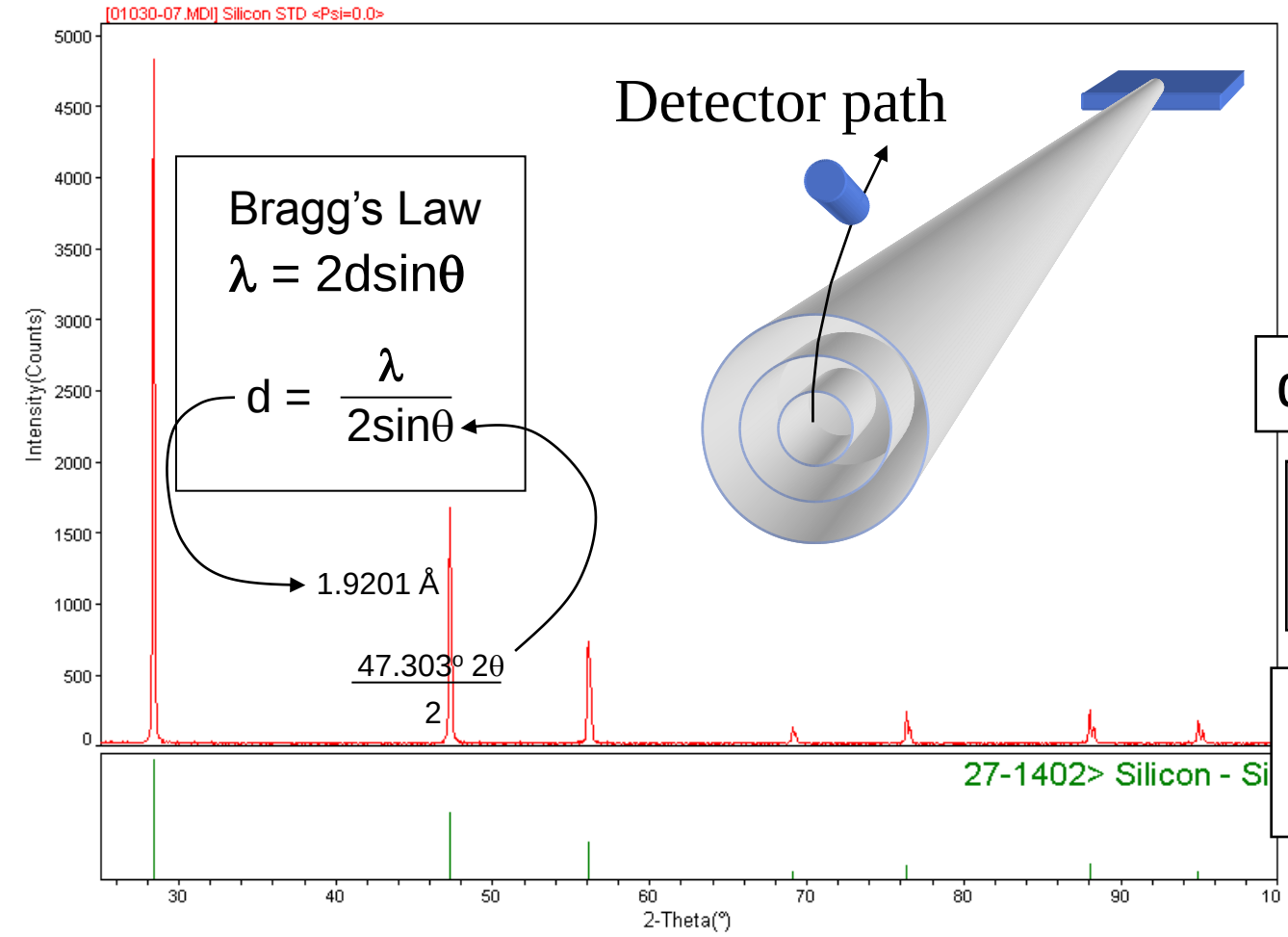
Powder

For the **rest of us** who have something other than a big single crystal, there is the world of **powder diffraction** characterization

Powder

0.05 μm to 50 μm

Anatomy of a powder XRD pattern



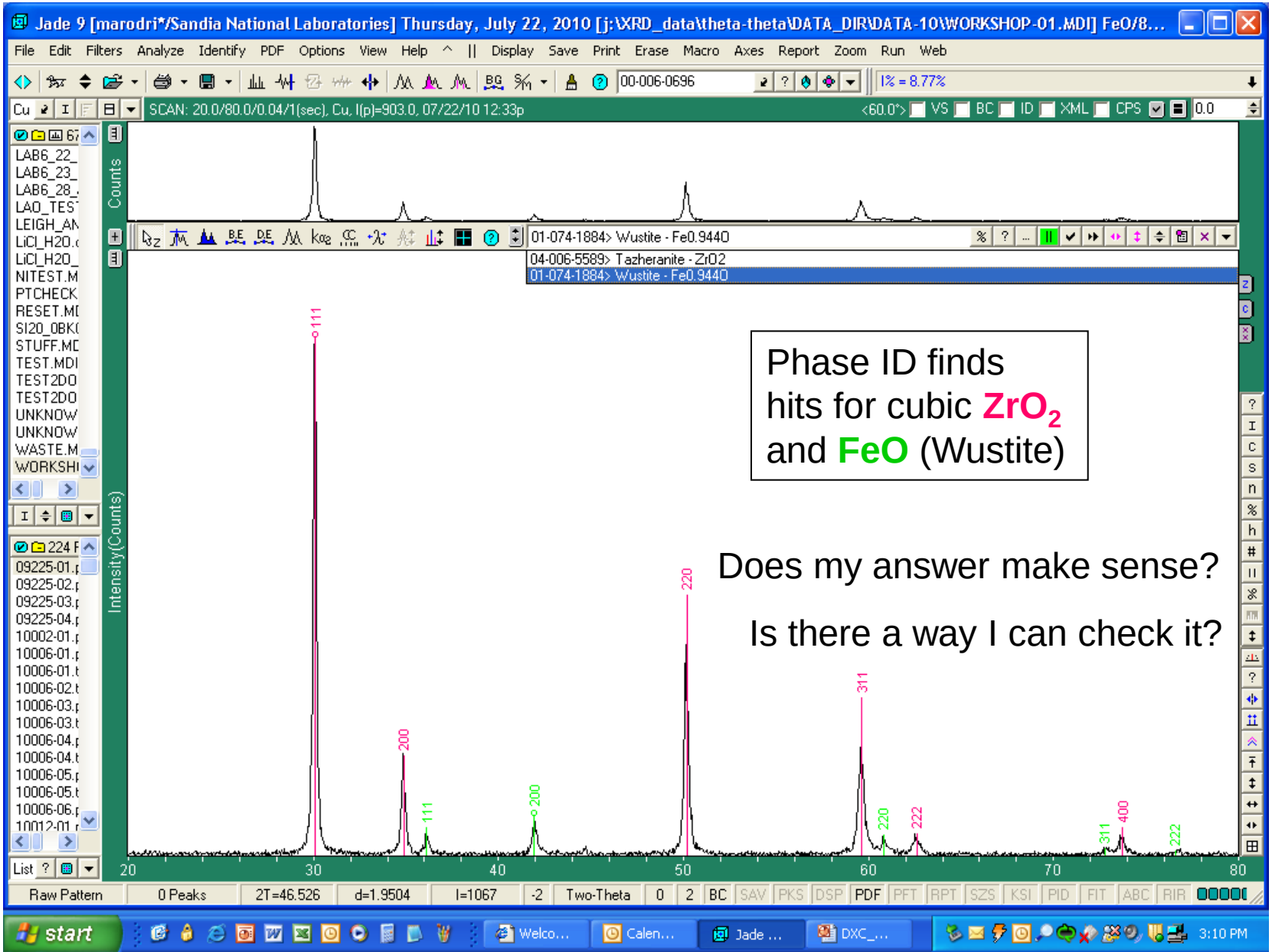
d, I "Fingerprint" ⇨ phase

d ⇨ index & unit cell

I ⇨ site occupancy & phase fraction

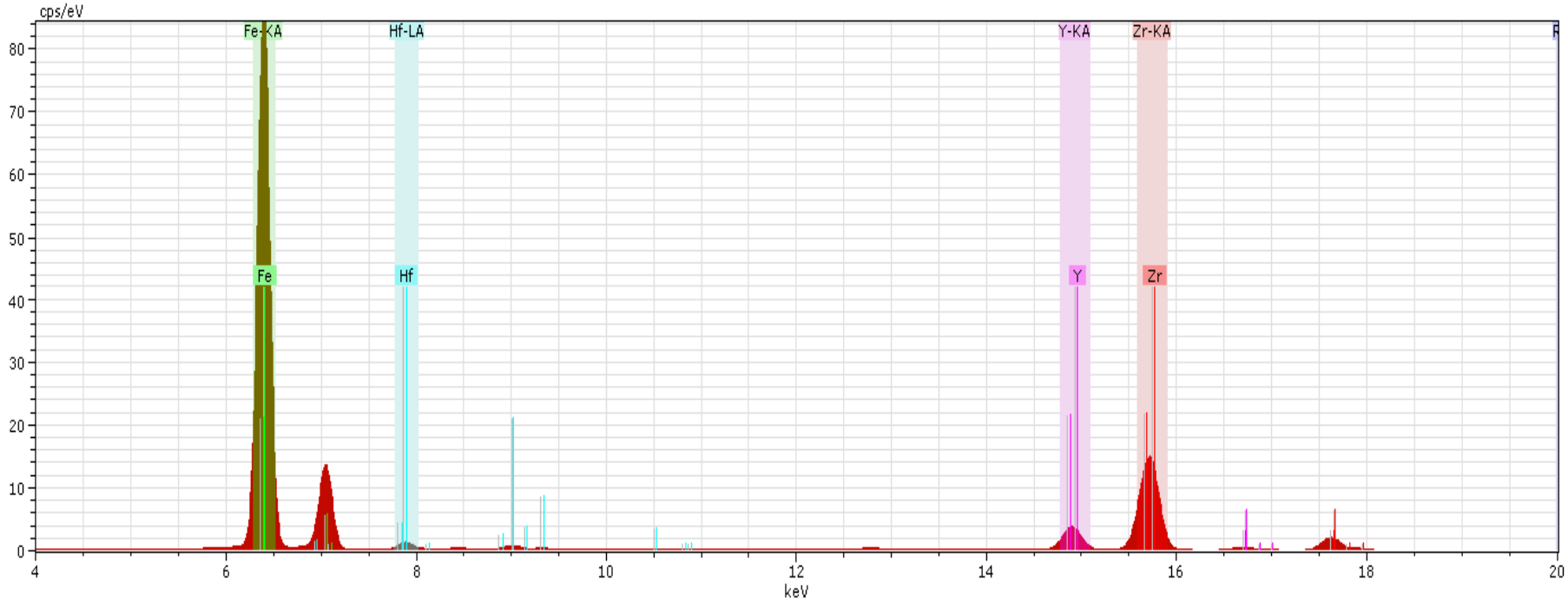
FWHM ⇨crystallite size & micro-strain

First step in a typical analysis is the straightforward qualitative phase ID.



XRF can be used for a quick check of the chemistry for the specimen.

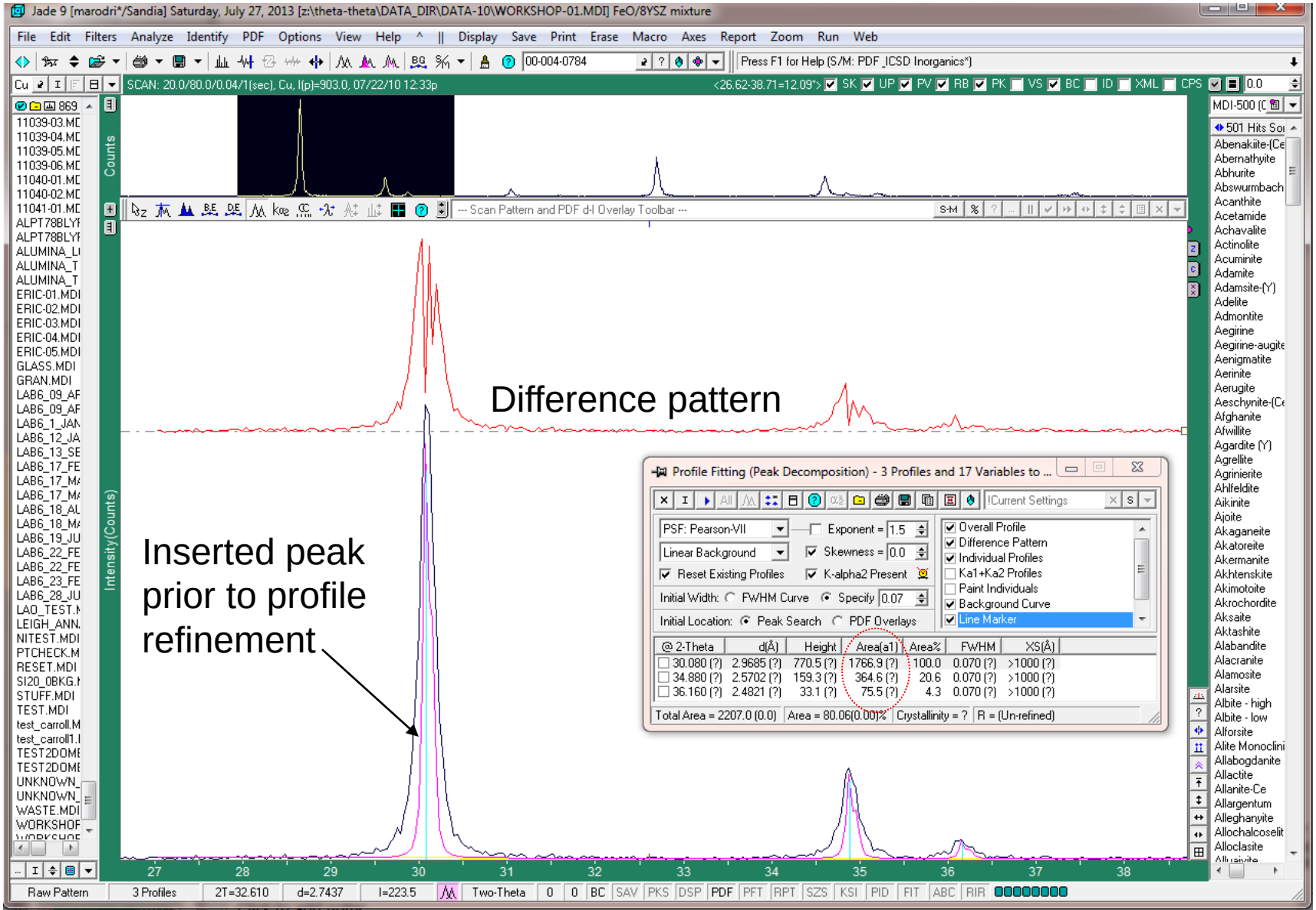
XRF shows strong signal for Fe and Zr elements



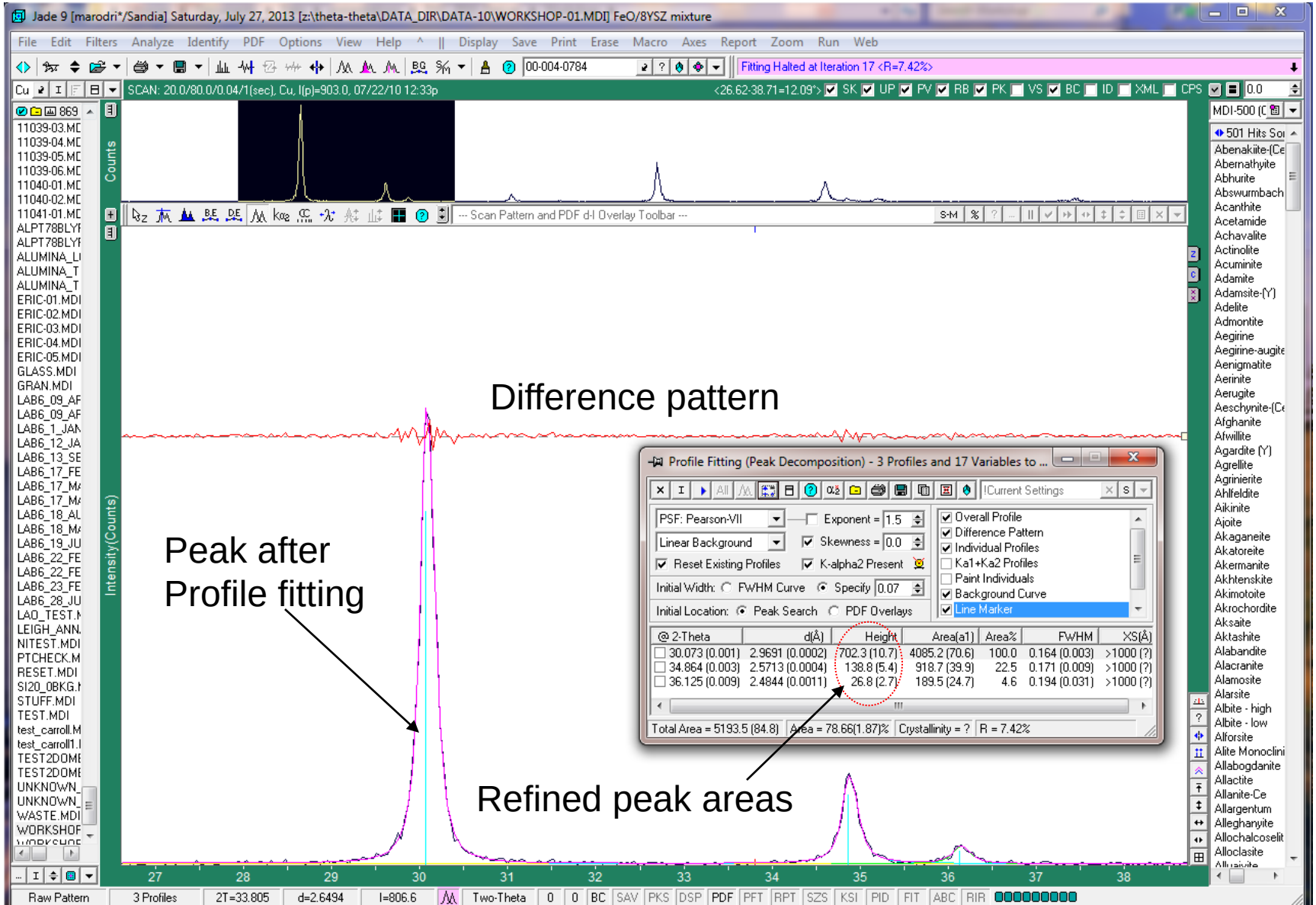
There is also the presence of Hf and Y as well.
You might need to do some investigating…..

Y is used to stabilize the cubic ZrO_2 phase.
Hf is likely a contaminant in the Zirconia.

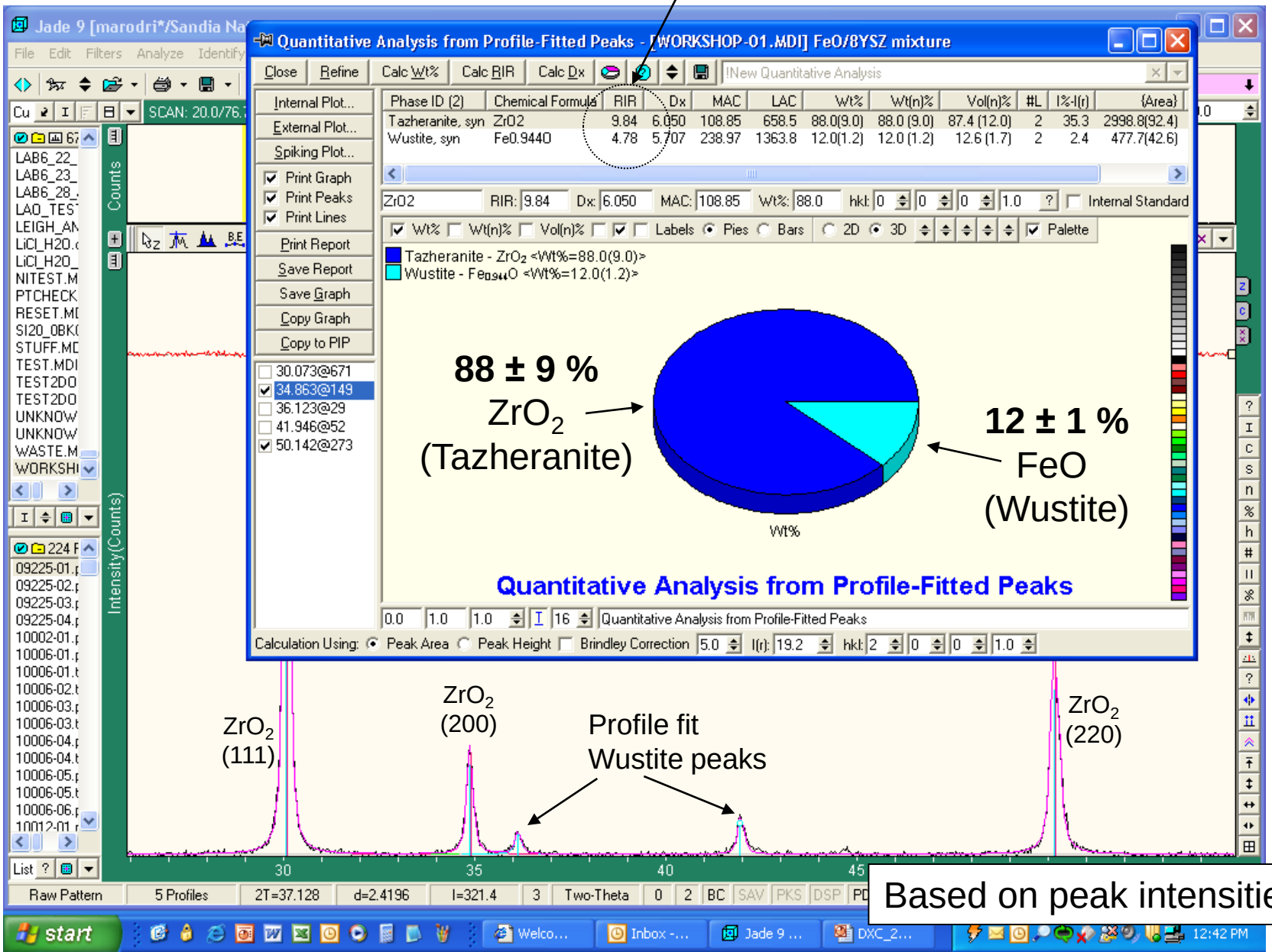
Typically, analysis software allows you to fit the peak profiles. This is important because quantitative phase fraction depends on **relative peak areas**, and accurate 2θ positions (i.e. d values) will improve lattice parameter refinements.



After profile fitting, the difference pattern looks essentially flat, indicating that the peak areas are modeled well. This information can be now used for quantitative analysis.

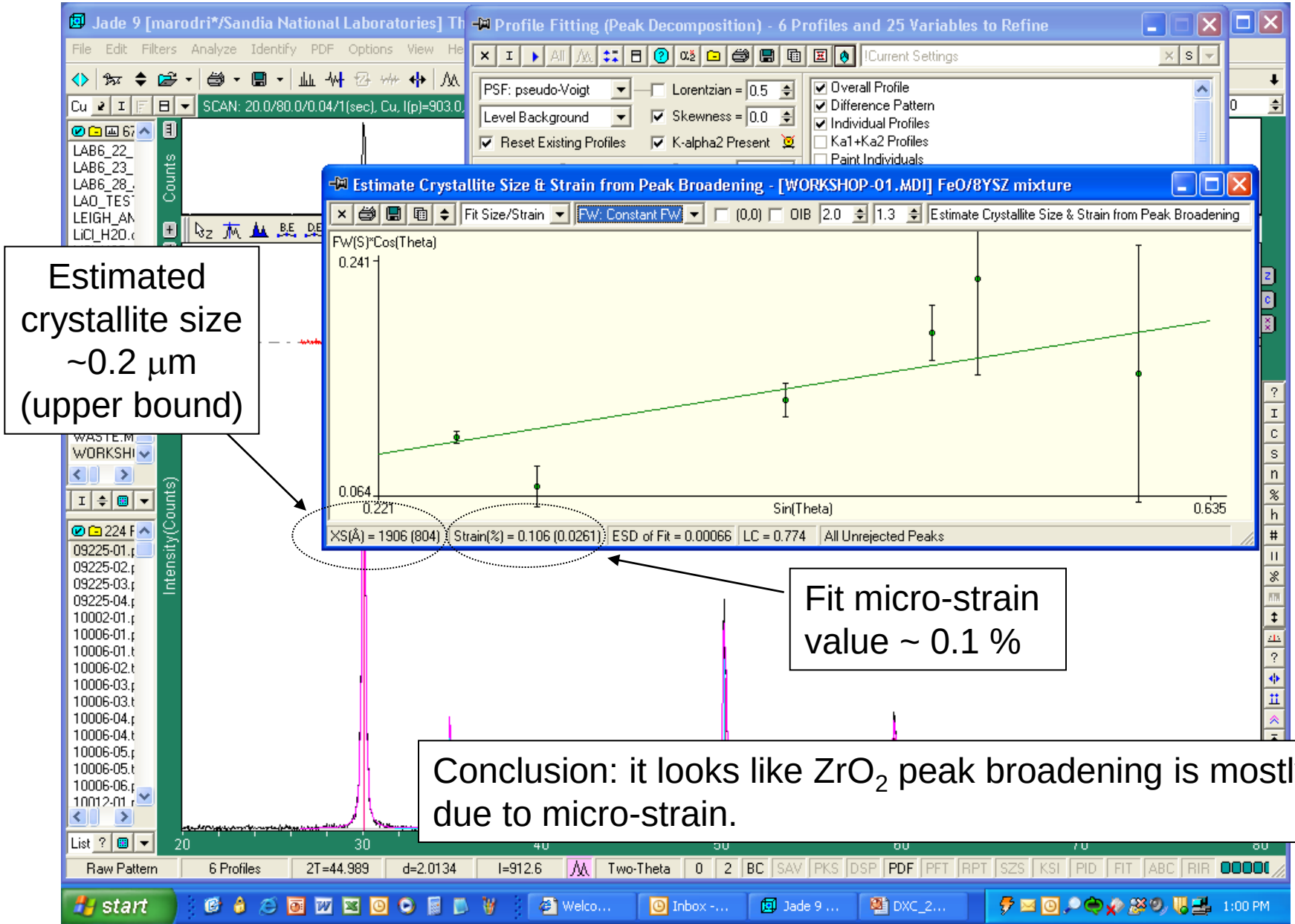


Semi-quantitative analysis via Reference Intensity Ratios ($I/I_{corundum}$) can be generated in most software via reported RIR values from the PDF database.



Based on peak intensities

Separation of micro-strain broadening from crystallite size broadening can be done based on FWHM changes with 2θ angle.

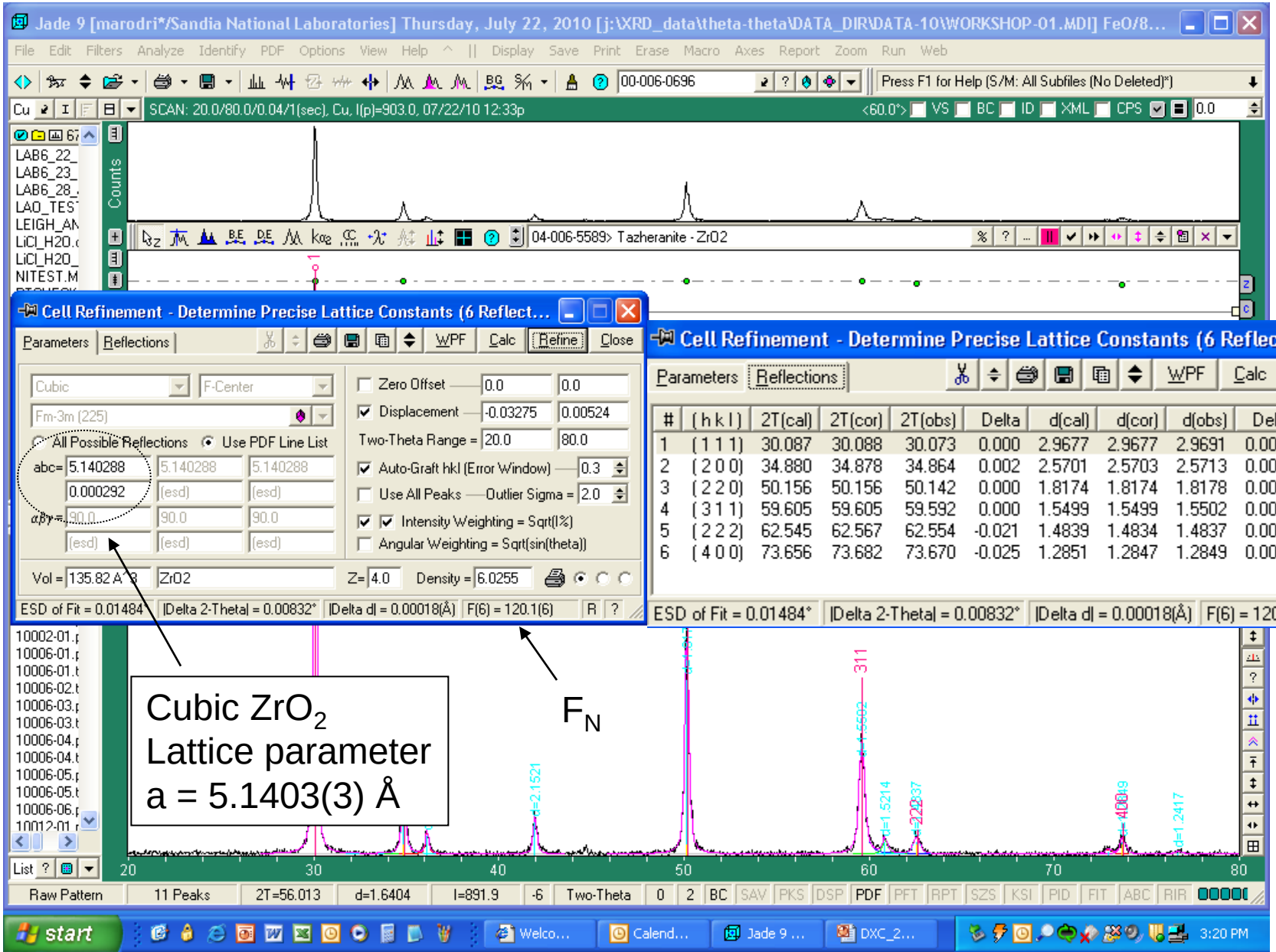


Estimated crystallite size ~0.2 μm (upper bound)

Fit micro-strain value ~ 0.1 %

Conclusion: it looks like ZrO_2 peak broadening is mostly due to micro-strain.

If the unit cell is known from the PDF entry, you can usually perform a lattice parameter refinement based on peak positions for a given phase.

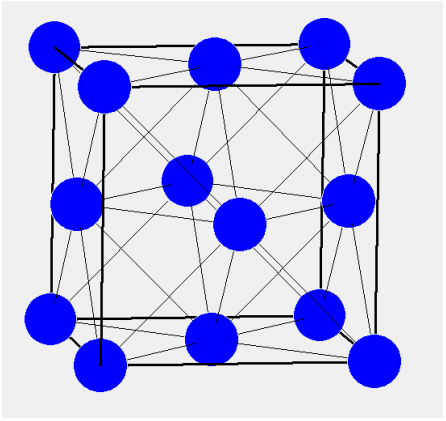


Lattice parameters and Vegard's Law

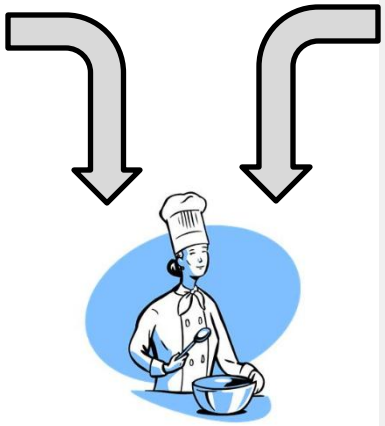
The idea behind Vegard's law is based on the concept of Solid-Solution.

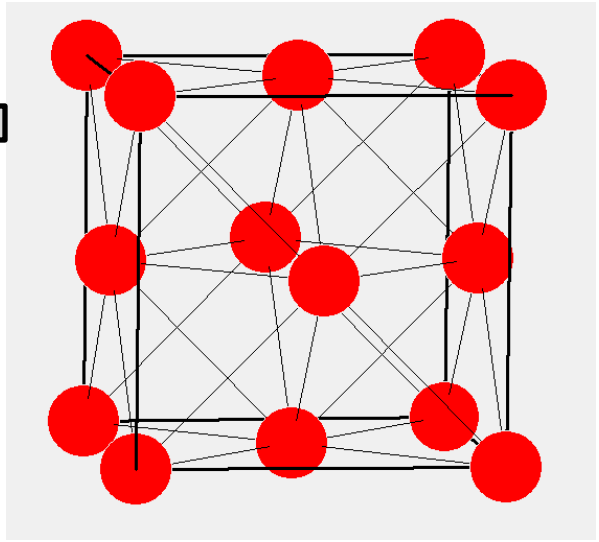
Imagine I am making an alloy from two pure metals of similar structure.

Nickel cubic Fm3m



a_{Ni} = 3.524 Å

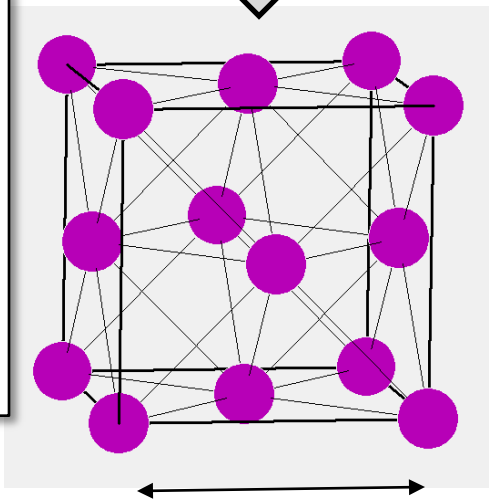




Copper cubic Fm3m

a_{Cu} = 3.615 Å

The lattice parameter of the synthesized alloy will fall between the end members as an "**atomic**" weighted average of the mixed metals.

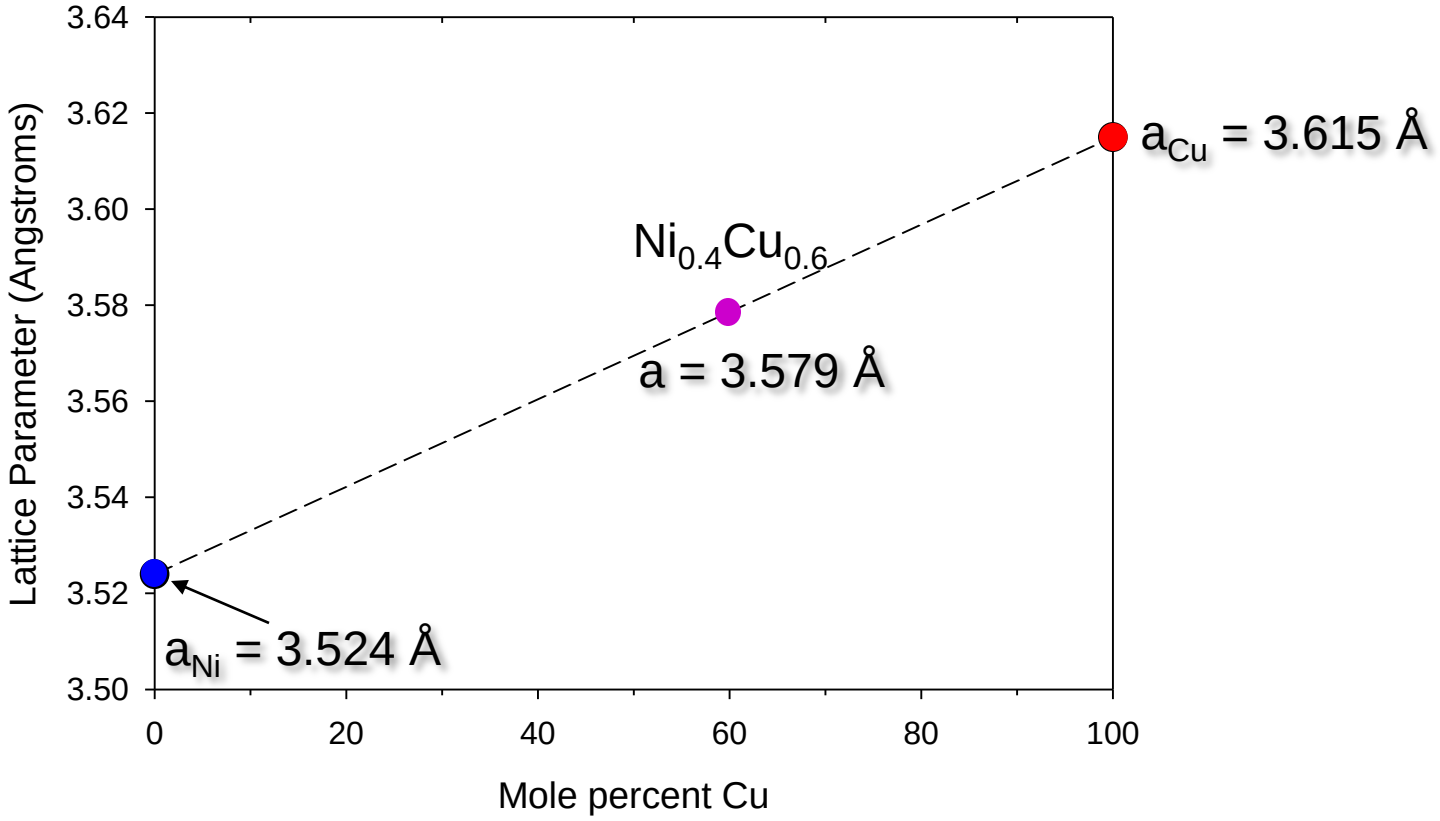


$a_{Ni} < a_{alloy} < a_{Cu}$

$a_{alloy} = (x)\ a_{Ni} + (1\text{-}x)\ a_{Cu}$

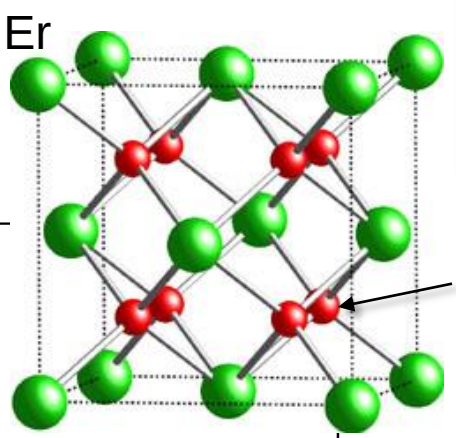
Where **x** is the <u>atomic</u> fraction of each constituent.

Therefore, if we plot the lattice parameter vs. mole percent of the mixture we should be able to predict what the lattice parameter will be at any given composition for an alloy of Ni_xCu_{1-x}

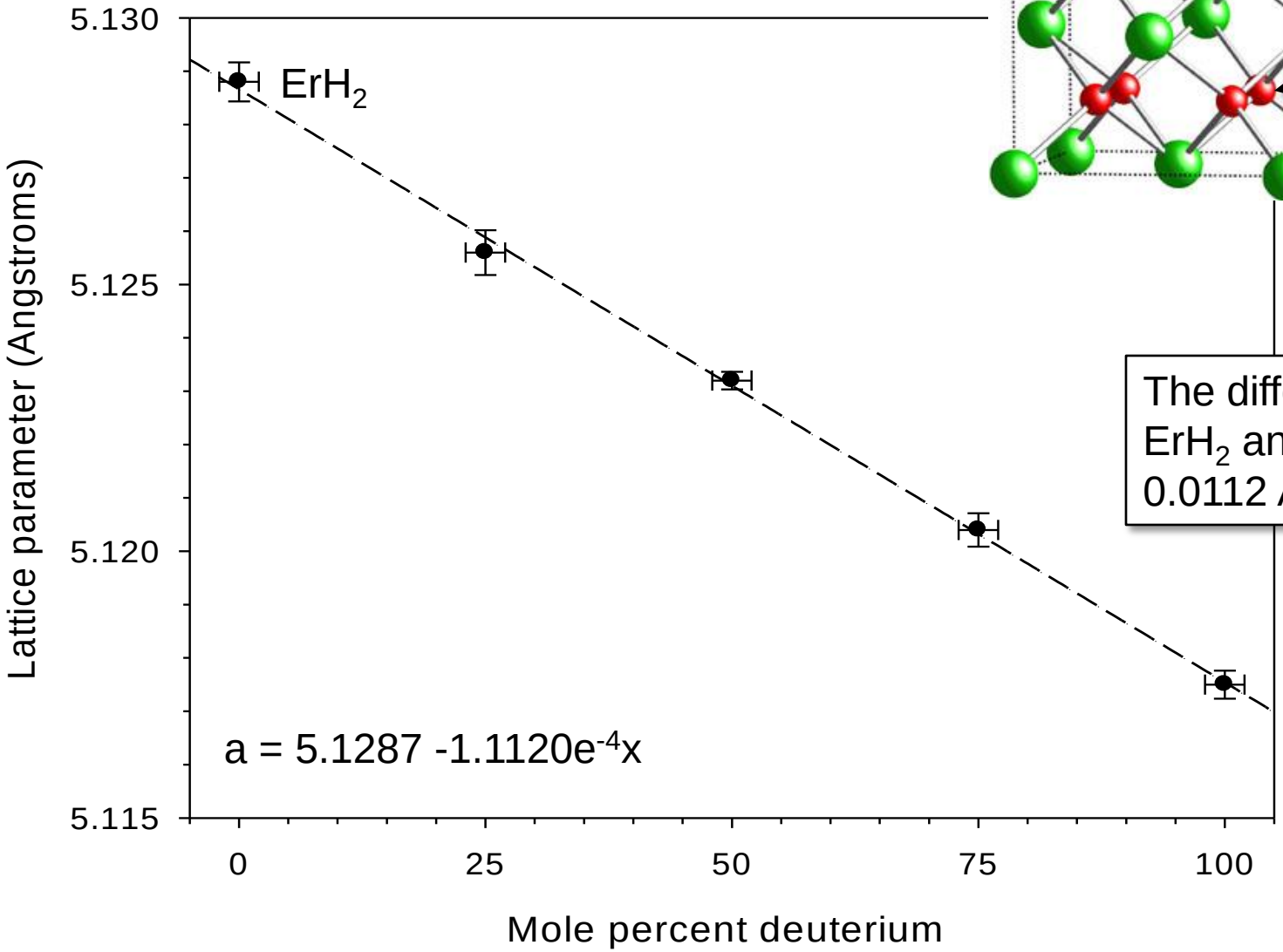


Likewise, if we measure the lattice parameter of an alloyed mixture we should be able to *predict its chemical composition*.

Here is an example of Vegard's law in a series of $ErH_{2-x}D_x$ compositions.



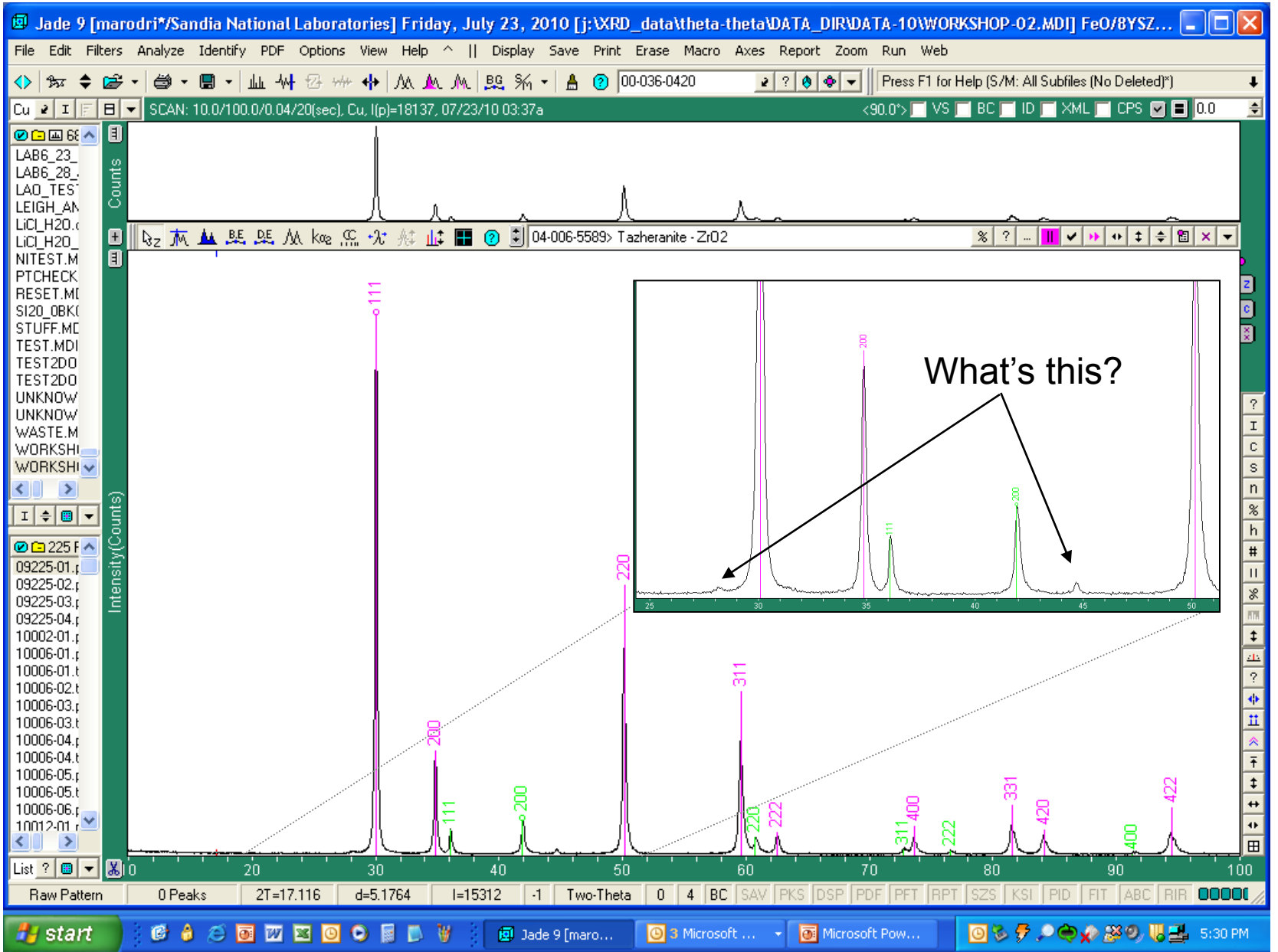
ErH_2 Fluorite structure



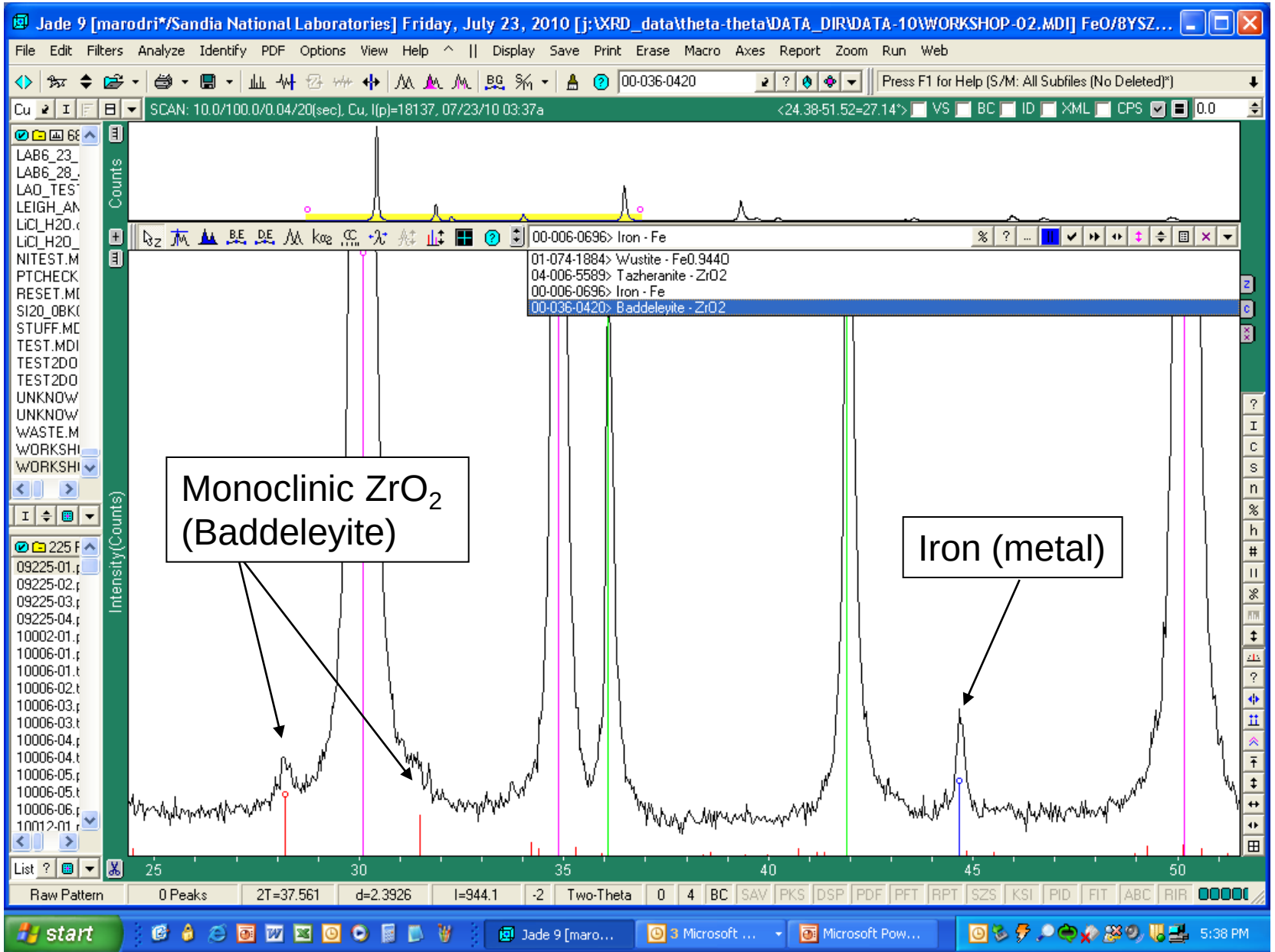
The difference between ErH_2 and ErD_2 is only 0.0112 Angstroms!!

Rodriguez, *et al,* (2008) *Powder Diffraction* **23** 259-264.

For Rietveld structure refinement a high-quality dataset is usually required so I ran the sample overnight.

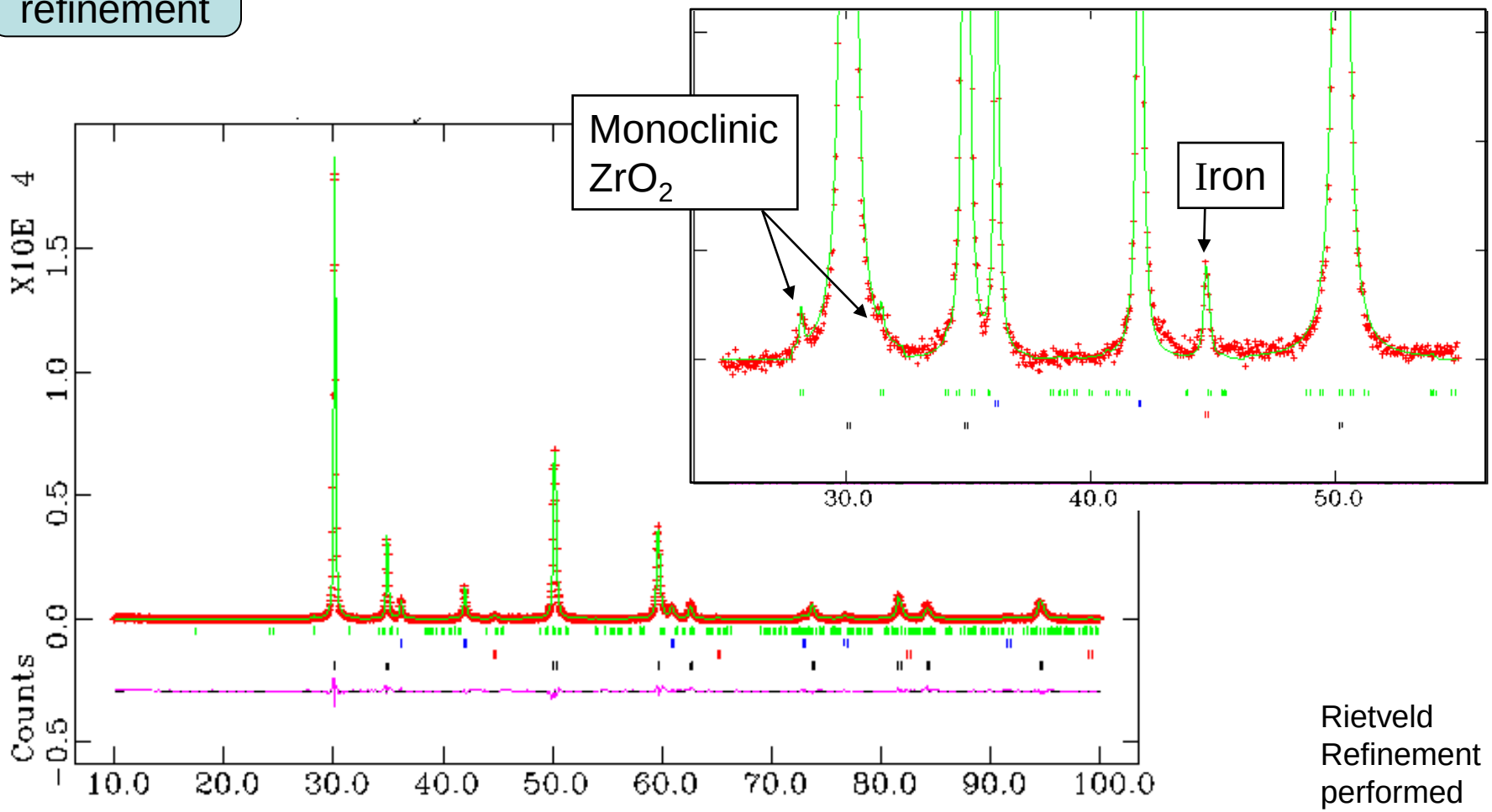


The overnight scan picked up two more phases that are present at low concentrations as seen in this zoomed range.



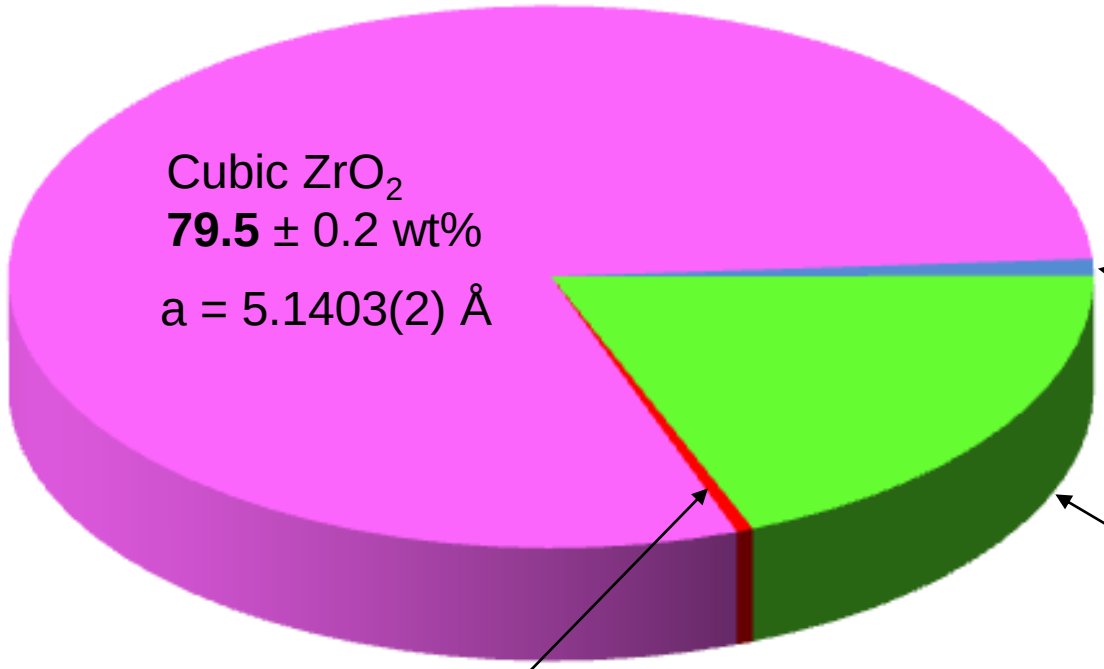
For low concentration phases it is *very* important to make sure the small peak profiles are fit properly for accurate phase fraction quantification.

Rietveld refinement



Rietveld Refinement performed using GSAS

Rietveld structure refinement yields much more accurate quantitative analysis along with structural parameters and even sensitivity to Fe deficiency in FeO.



Cubic ZrO_2
79.5 ± 0.2 wt%
a = 5.1403(2) Å

Iron
1.0 ± 0.2 wt%
a = 2.866(2) Å

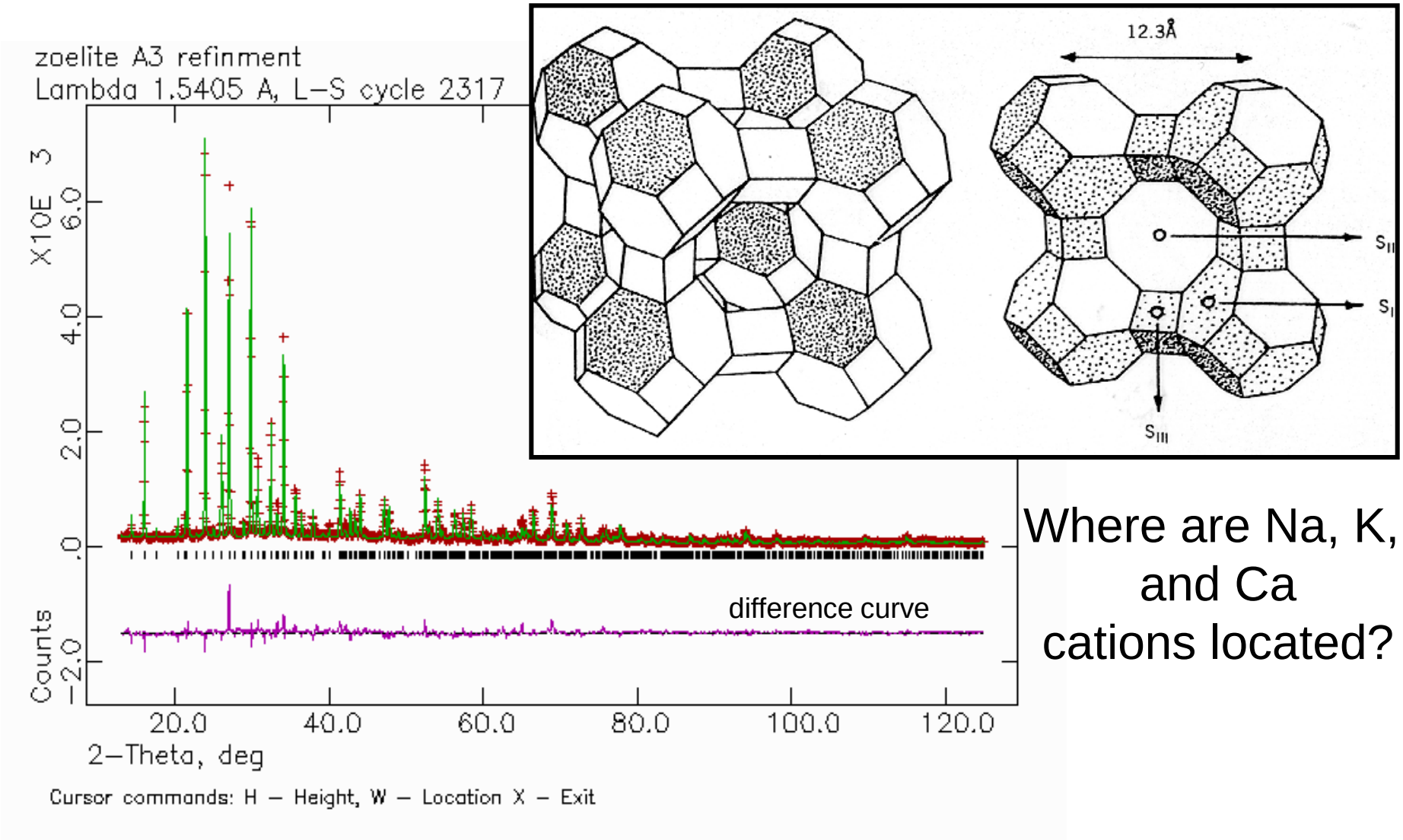
$Fe_{0.87}O$
19.0 ± 0.2 wt%
a = 4.3022(6) Å

Monoclinic ZrO_2
0.5 ± 0.2 wt%
a = 5.17(3) Å
b = 5.19(3) Å
c = 5.32(1) Å
β = 99.2(2) °

This is about as good as you will get to the grail for this sample

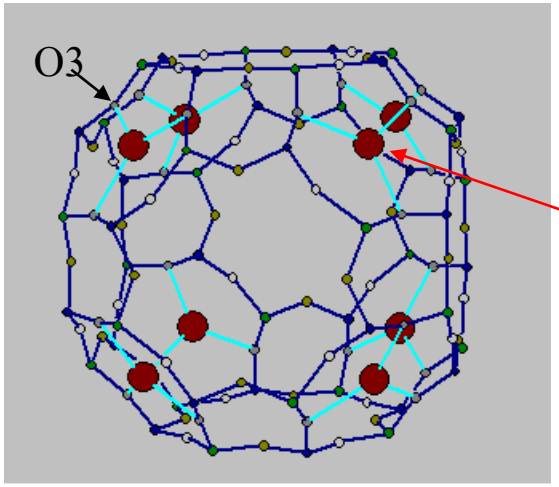
Rietveld structure refinement was used to find cations in Zeolite 3A powder.

I was given ICP results



Where are Na, K, and Ca cations located?

Rietveld Refinement results matched well with ICP analysis.

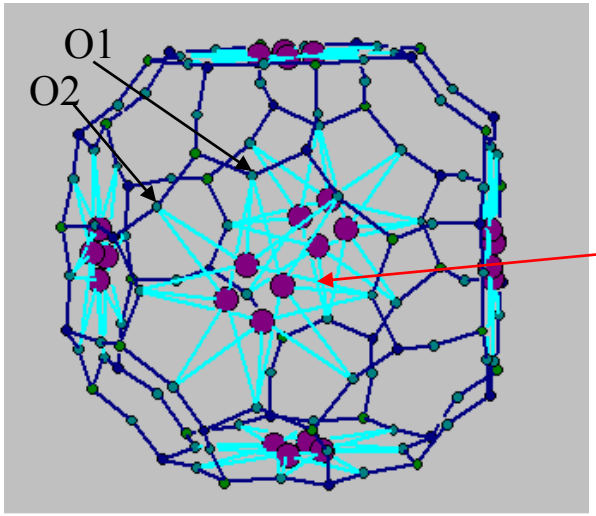


Molar content

Na

ICP 0.37

XRD 0.40(3)

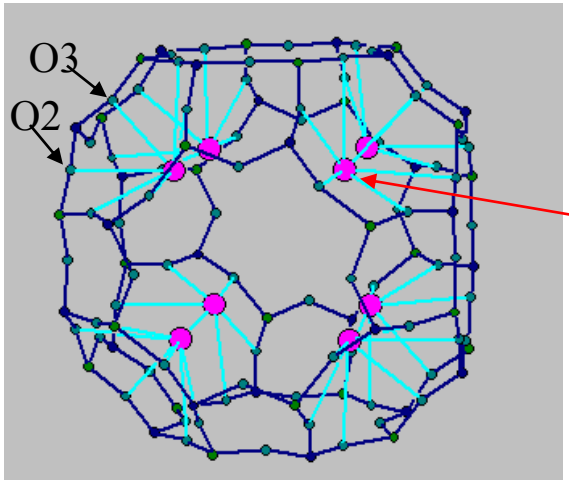


Molar content

Ca

ICP 0.13

XRD 0.14(2)

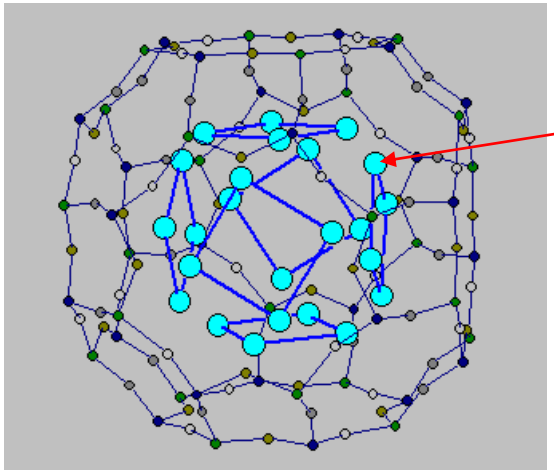


Molar content

K

ICP 0.34

XRD 0.32(3)

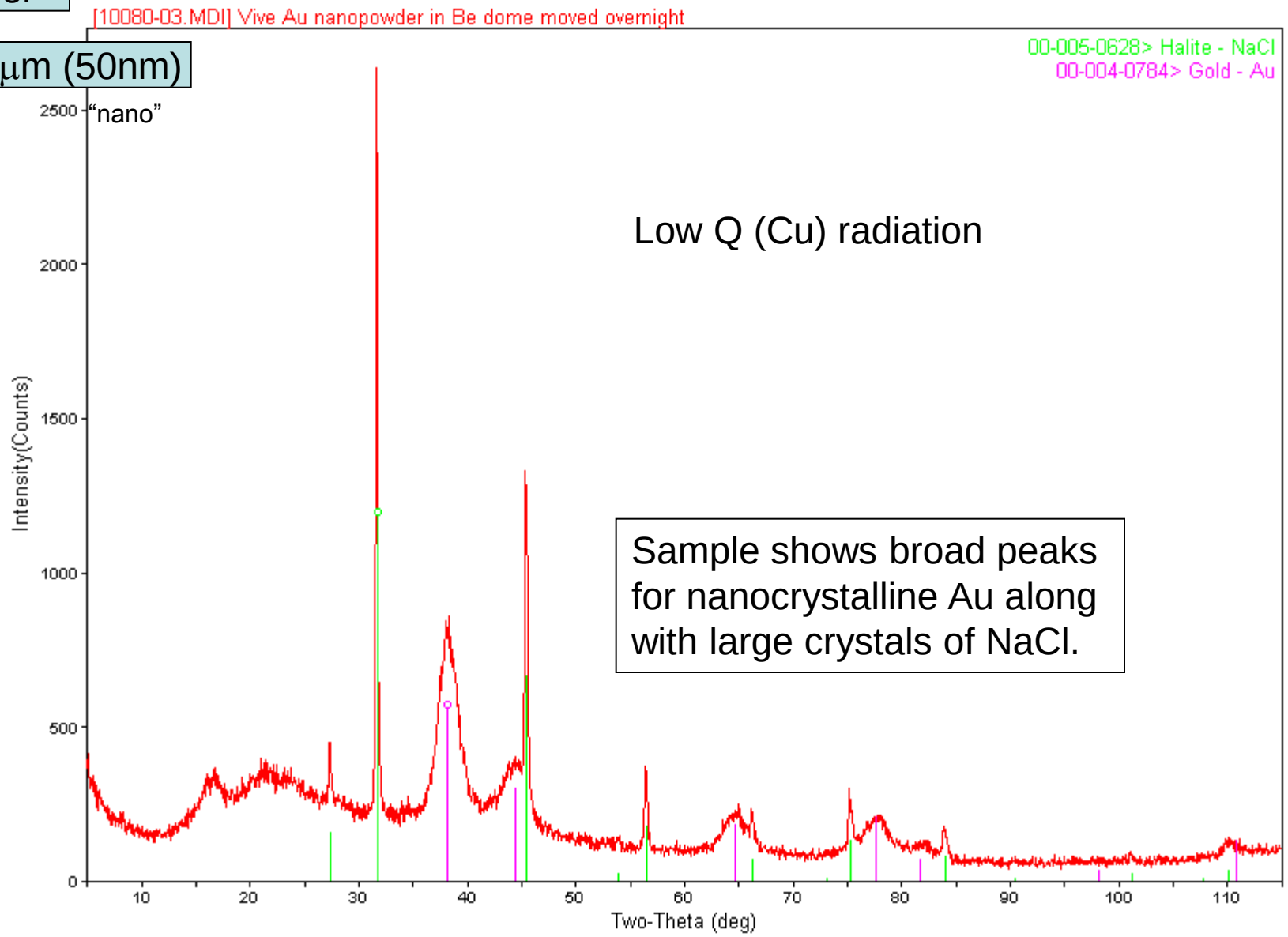


Water molecules

Here is an example of nanocrystalline Au powder contaminated with salt.

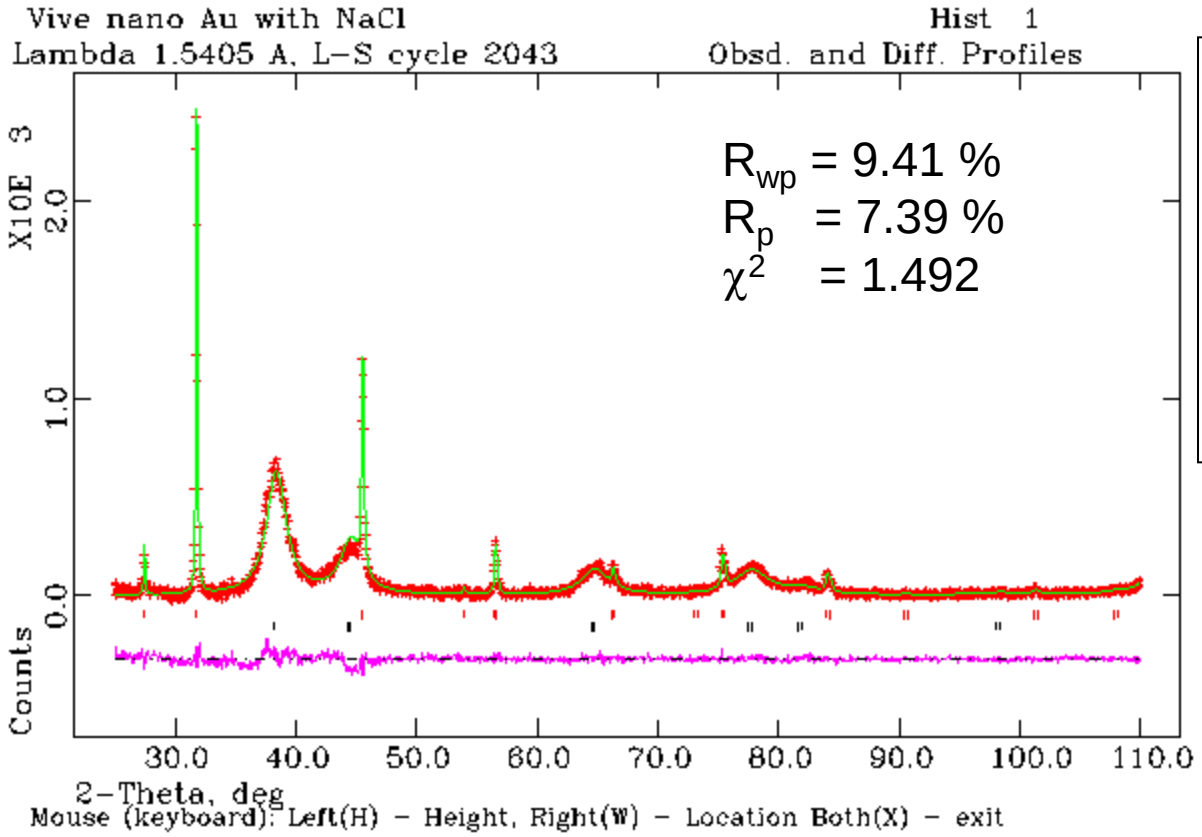
Powder

< 0.05 μm (50nm)



[s877989|marodri]<j:\XRD_data\theta-theta\DATA_DIR\DATA-10> Monday, February 15, 2010 04:46p (MDI/JADE9)

A Rietveld structure refinement of powder data reported the expected lattice parameter values for Au and NaCl phases.



R_{wp} = 9.41 %
R_p = 7.39 %
χ^2 = 1.492

expected

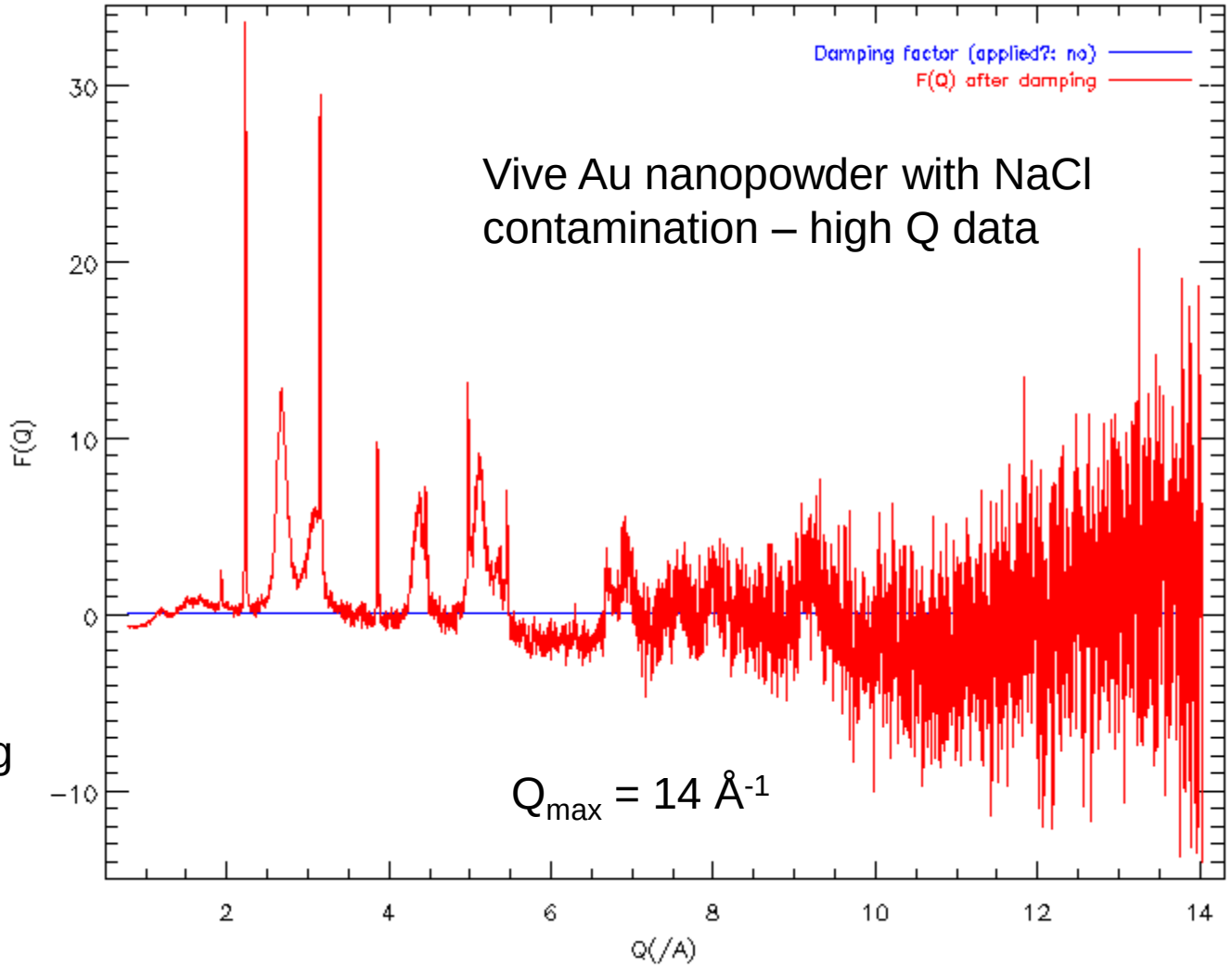
Au	a = 4.078(2) Å	4.079
Au	vol = 67.8(1) Å^3	
Au	B_{iso} = 0.6 Å^2	
NaCl	a = 5.639(1) Å	5.640
NaCl	vol = 179.3(1) Å^3	
NaCl	B_{iso} = 2.1 Å^2	

Wt fraction:
Au: 34.6(5) %
NaCl: 65.4(5) %

Crystallite size for Au ~8 nm.

High Q XRD data can be measured for the purposes of generating an atomic Pair-Distribution Function (aPDF).

F(Q) is the total scattering structure function

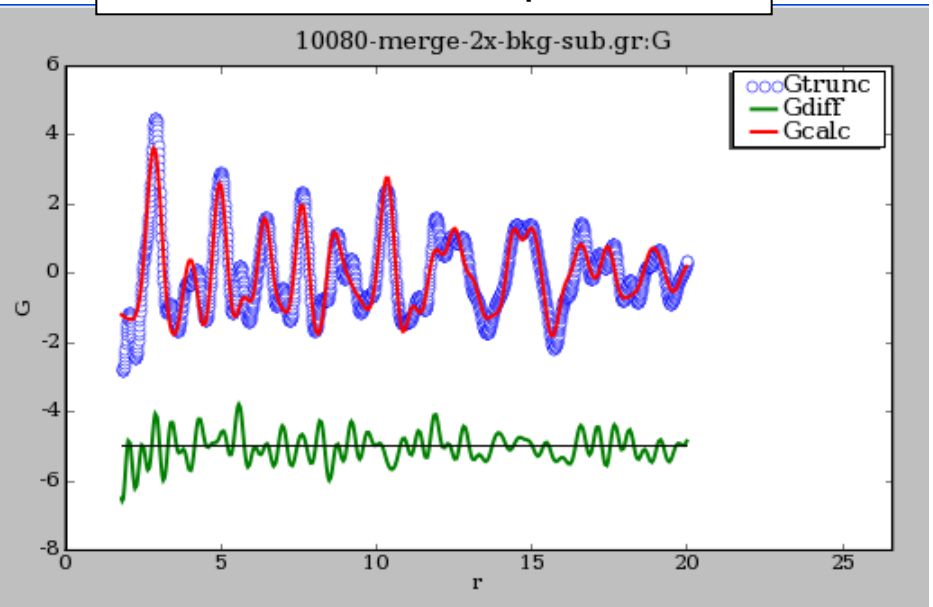


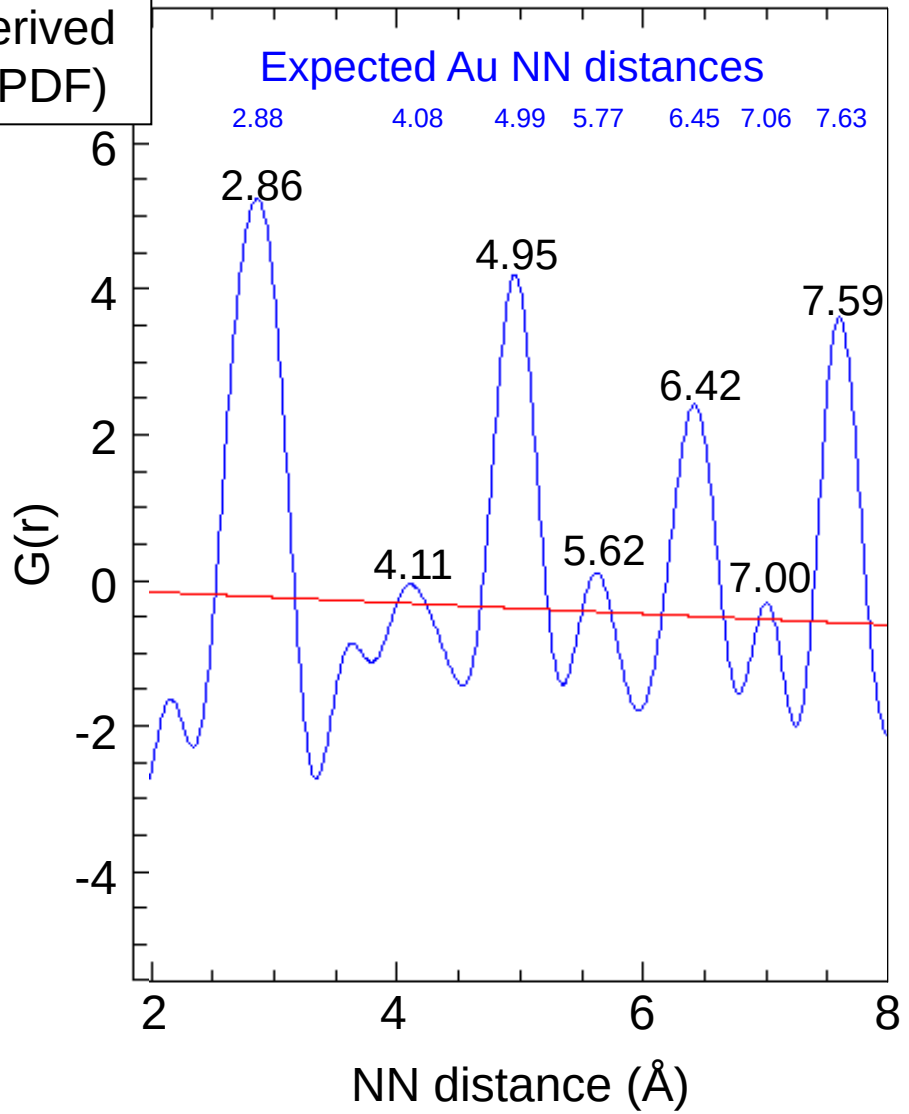
The atomic pair distribution function (aPDF) of a nanomaterial can be helpful for characterization purposes.

Nearest neighbor (NN) distances can be derived from the atomic pair distribution function (aPDF)

Helpful for determining coordination

G(r) function can be refined in a similar fashion as Rietveld refinement of XRD pattern

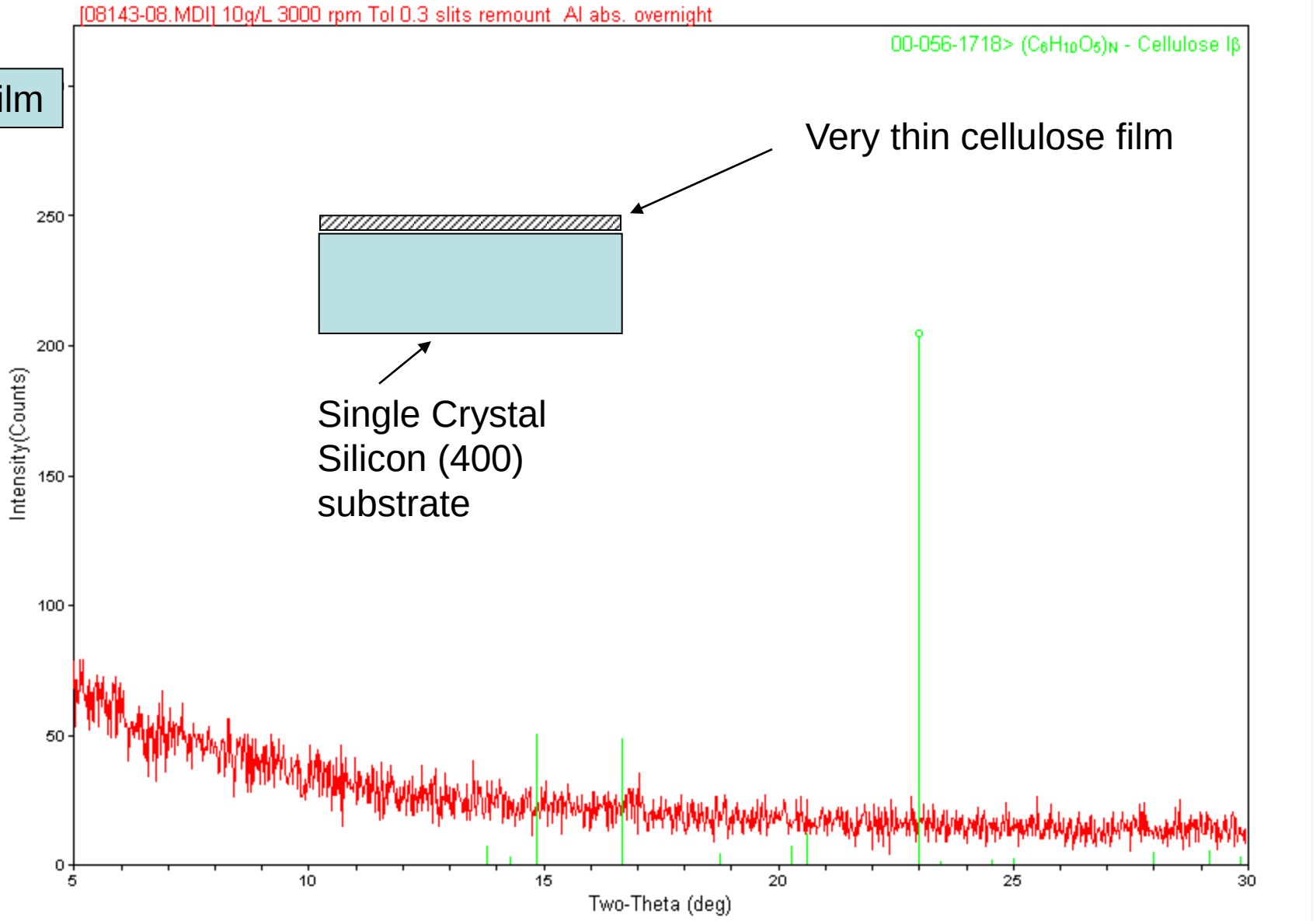




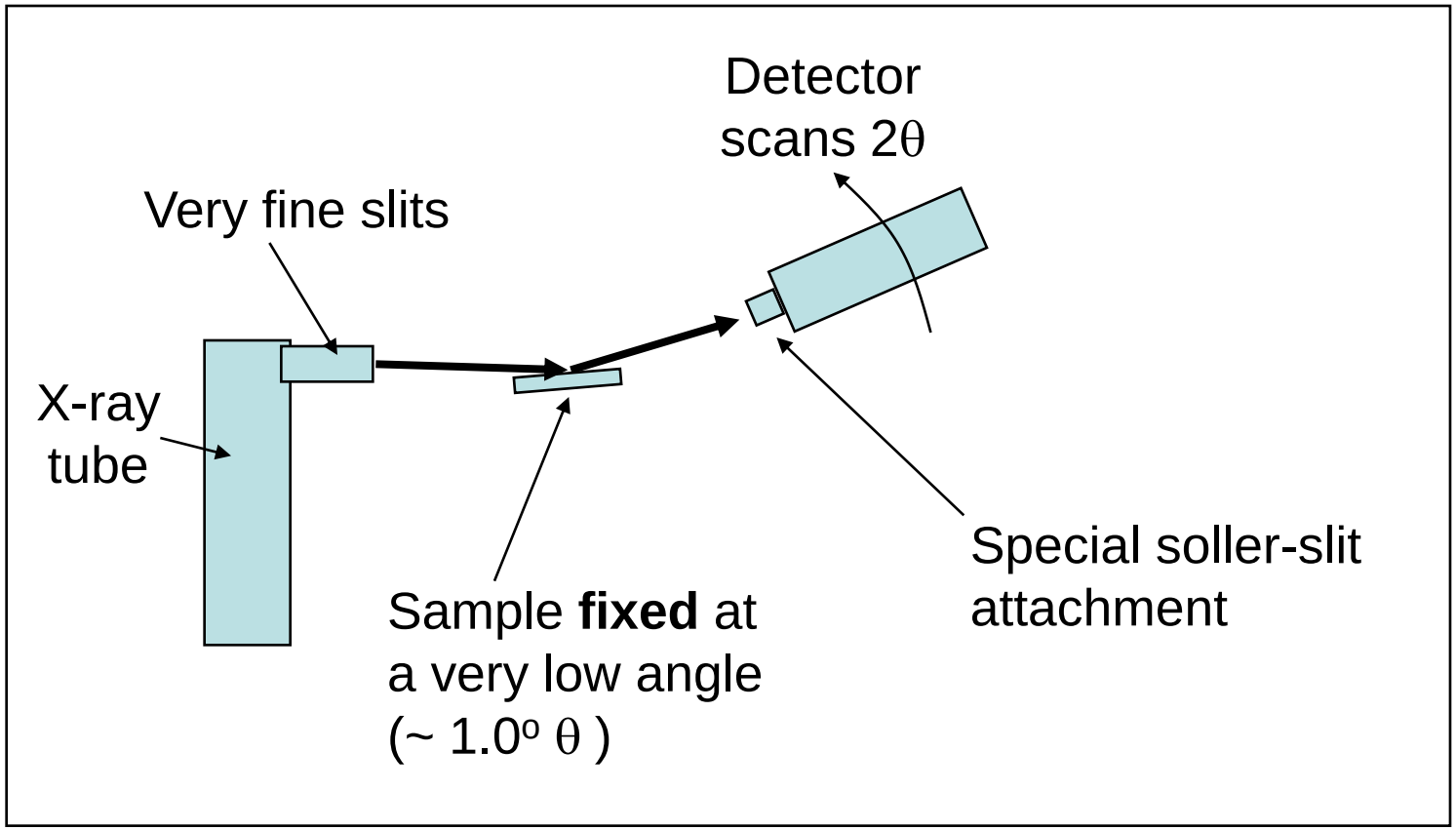
Thin Films

Even running this film sample **overnight** in standard θ–2θ configuration does not reveal any signal for a crystalline film presence on the Silicon substrate.

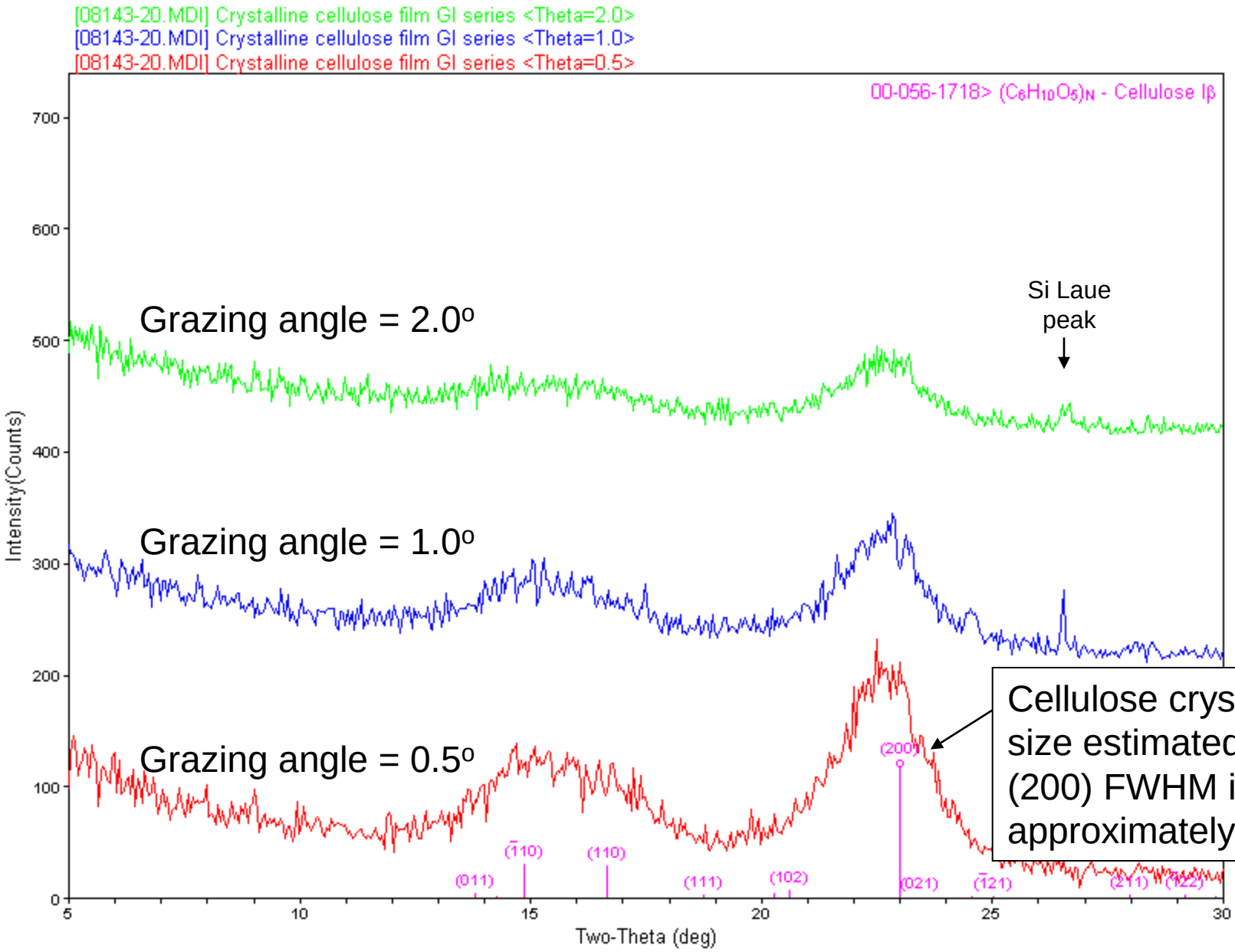
Thin film



Setup of Grazing Incidence X-ray Diffraction (GIXRD) employs parallel beam optics.

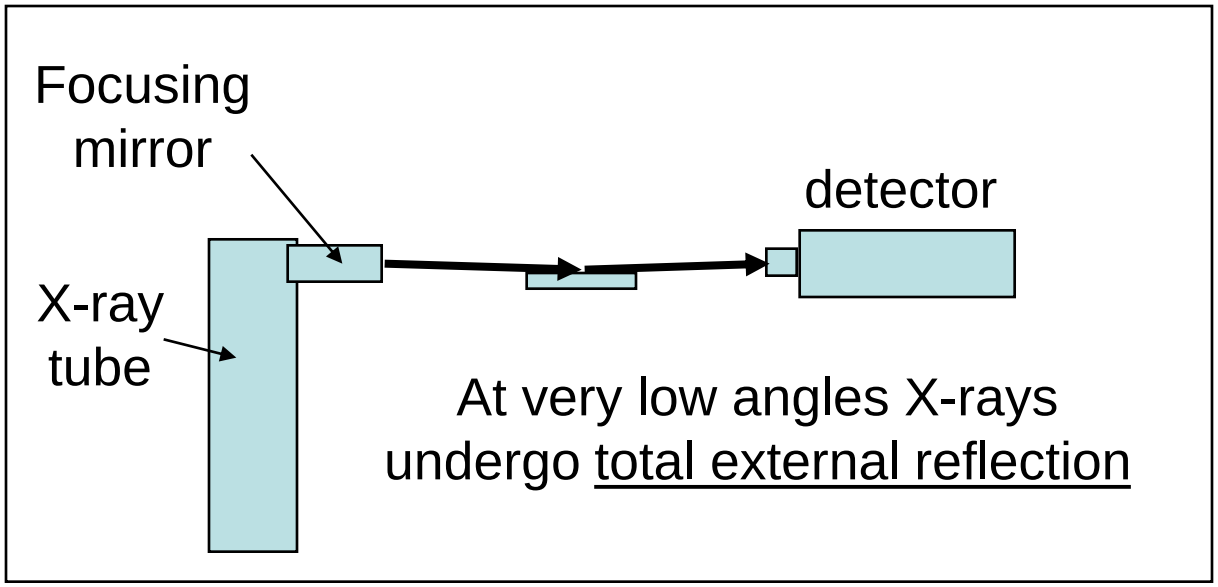


GIXRD analysis of film shows reasonable match to cellulose Iβ.

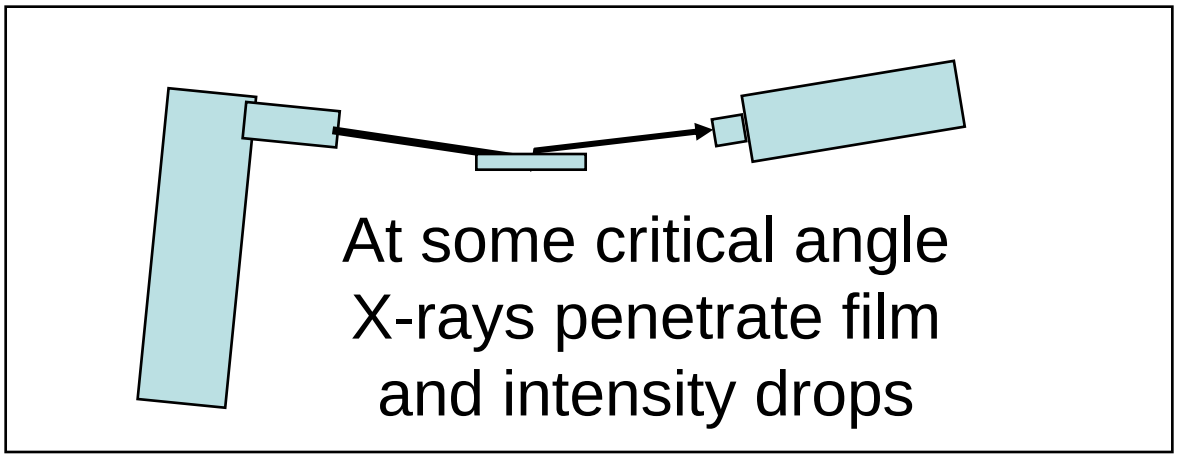


08143

Reflectivity is a low-angle technique for analysis of thin films



Film density determines critical angle

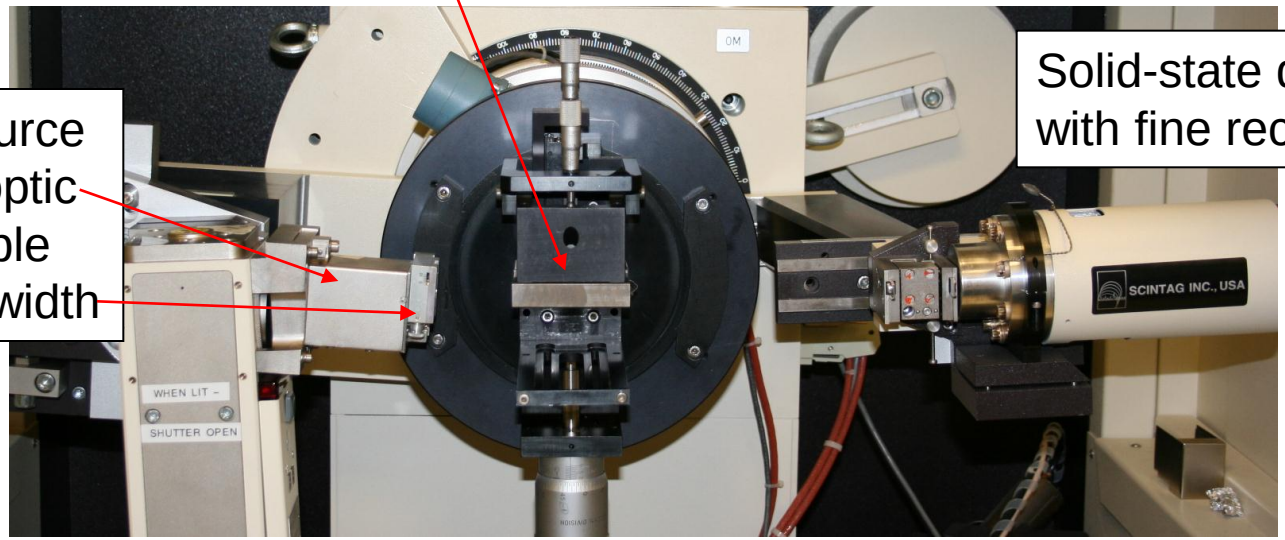


Reflectivity setup

Sample stage with height, level, and knife edge adjustment

Cu X-ray source with mirror optic and adjustable incident slit width

Solid-state detector with fine receiving slits



Scintag X_1 diffractometer system

Note: **alignment is very important**. Specimen film must be centered at the maximum of the specular reflection intensity, which is usually < 0.2º wide.

Here is an example of successfully modeling reflectivity data from a very thin Silane film on a Si wafer.

Silane film Density

1.81 g/cm^3

Silane film Roughness

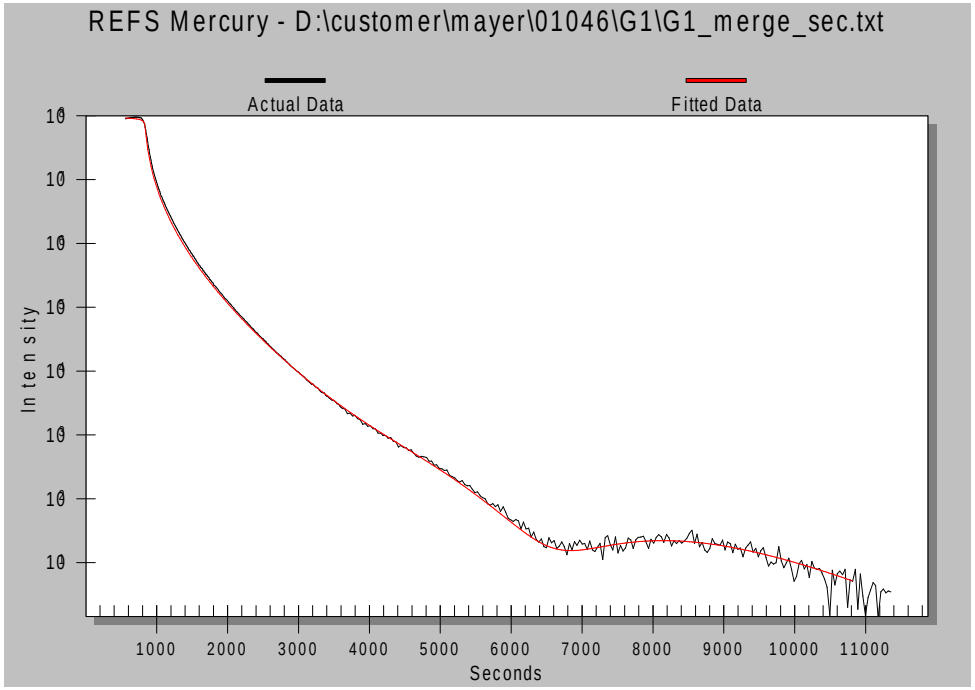
6.5 Å

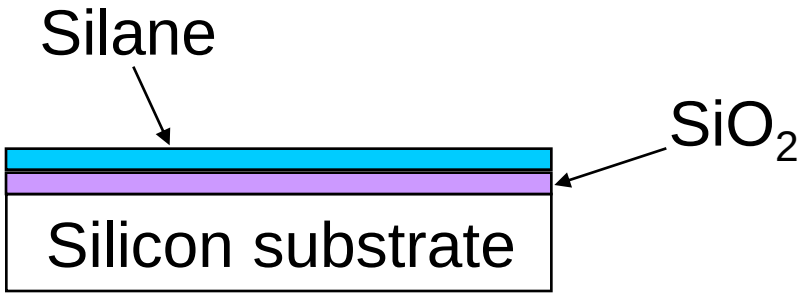
Silane Film thickness

15.5 Å

Film thickness from Ellipsometry

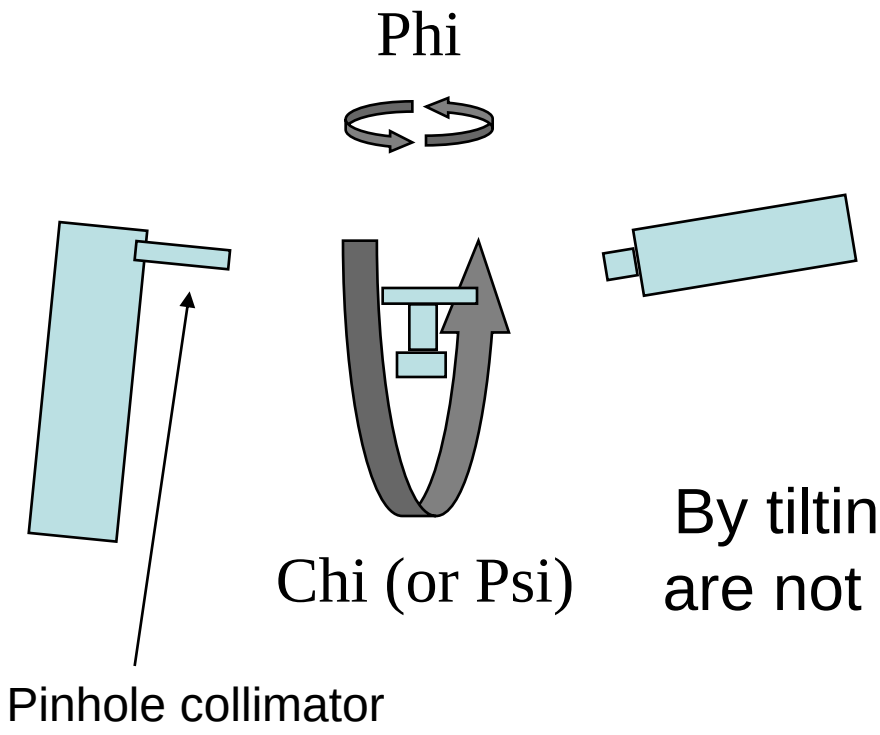
13.1 Å

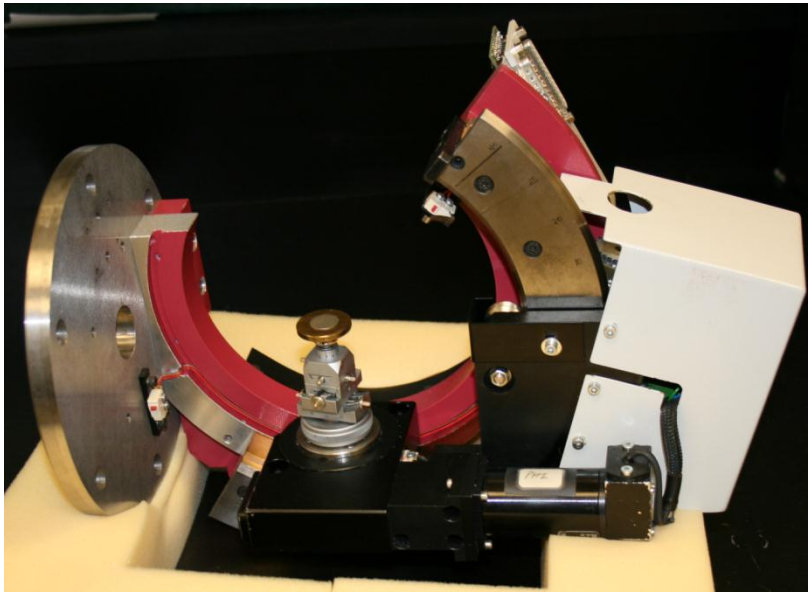




Pole-figure analysis can be a big help in characterizing films and textured metals

Texture cradle adds two additional degrees of freedom (Chi, Phi)





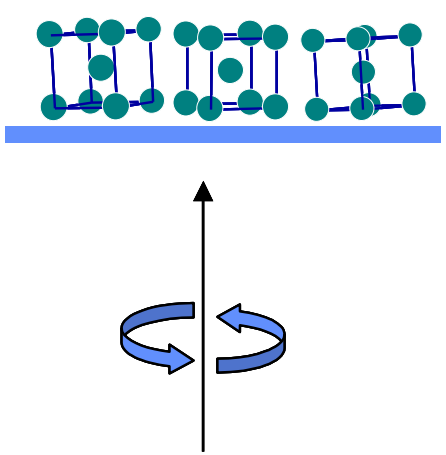
Scintag Texture Cradle Attachment

By tilting, we can look at grains that are not normal to the sample surface

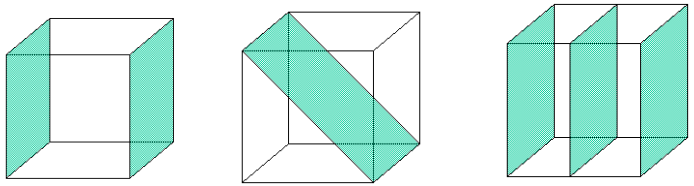
Texture definitions

Random grain orientation = no texture

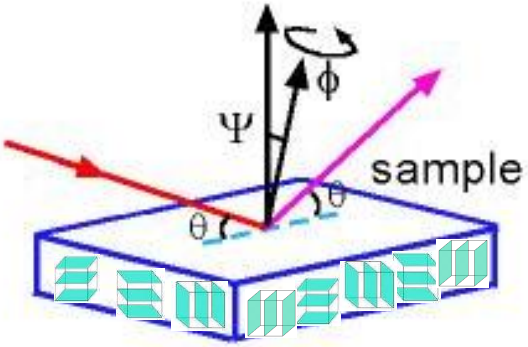
Fiber	Rolling Texture	Bi-Axial
out-of-plane (YES) in-plane (NO)	out-of-plane (YES) in-plane: 1-dimension of freedom, other fixed	out-of-plane (YES) in-plane (YES)



Pole figure represents a distribution in space of a given set of lattice planes (hkl).

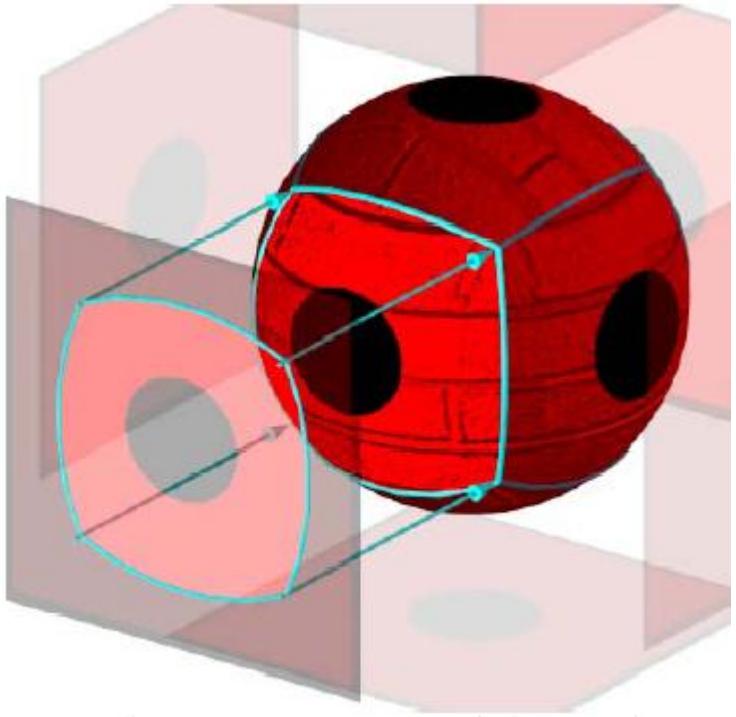


(100) (110) (200)



Pole Figure Measurement

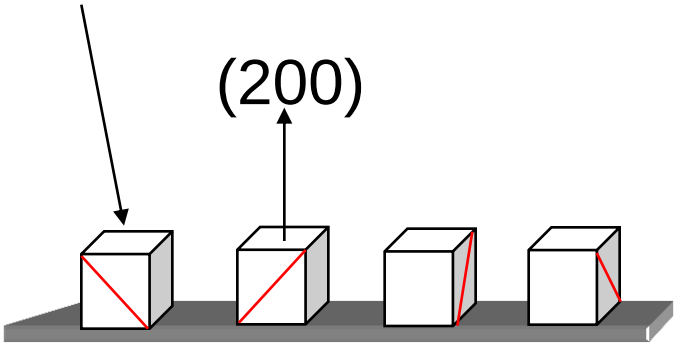
http://www.mrl.ucsb.edu/mrl/centralfacilities/xray/xray-basics/index.html#x4



All possible orientations of a selected hkl plane are plotted on a hemisphere that is then projected onto a planar surface (i.e. pole figure)

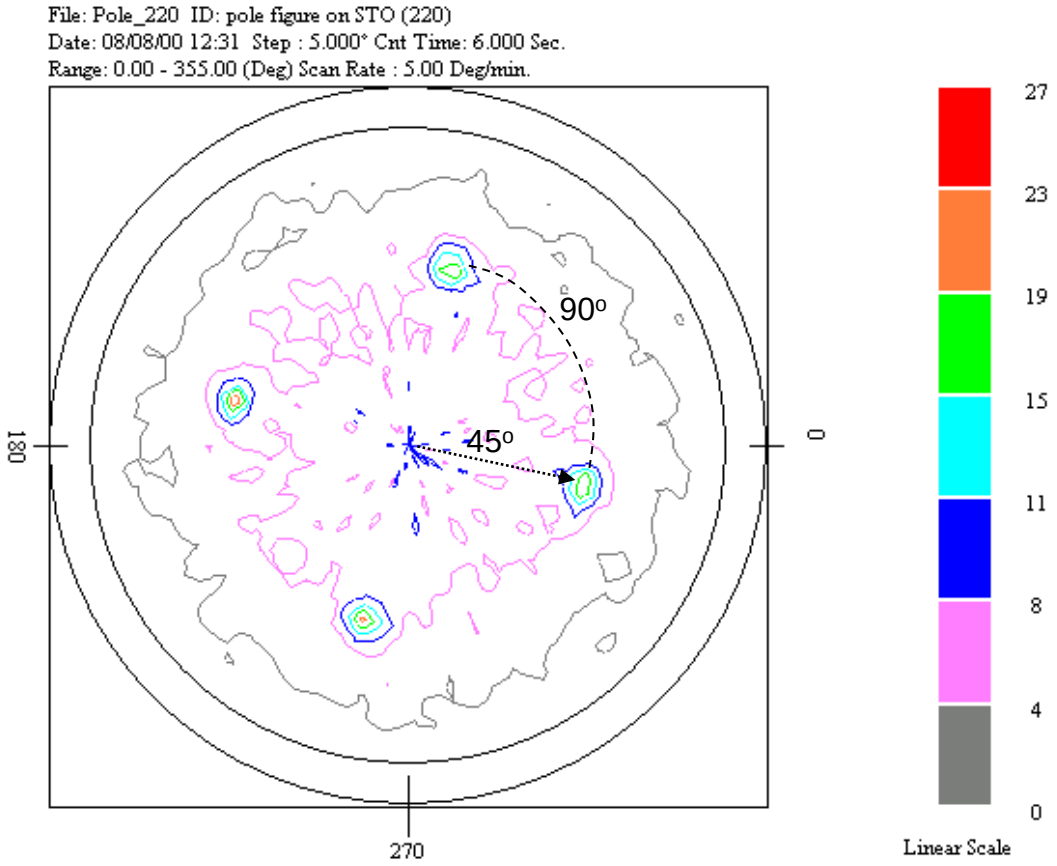
Texture analysis is useful for confirming bi-axial texturing of $SrTiO_3$ on (200) Ni metal.

Bi-axially oriented $SrTiO_3$ crystals



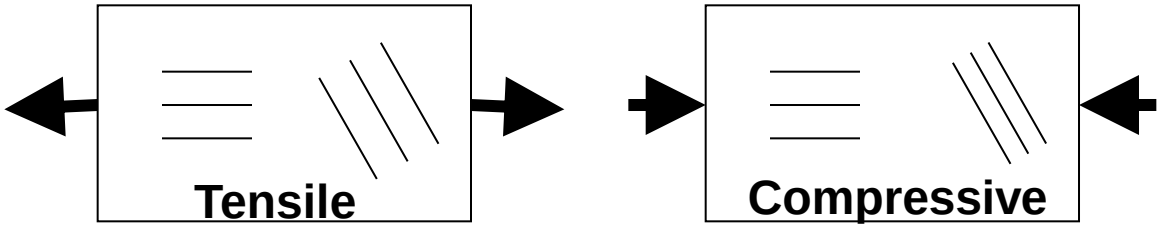
Ni substrate

(220) planes shown in red will diffract at 45° from (200), each separated by 90°

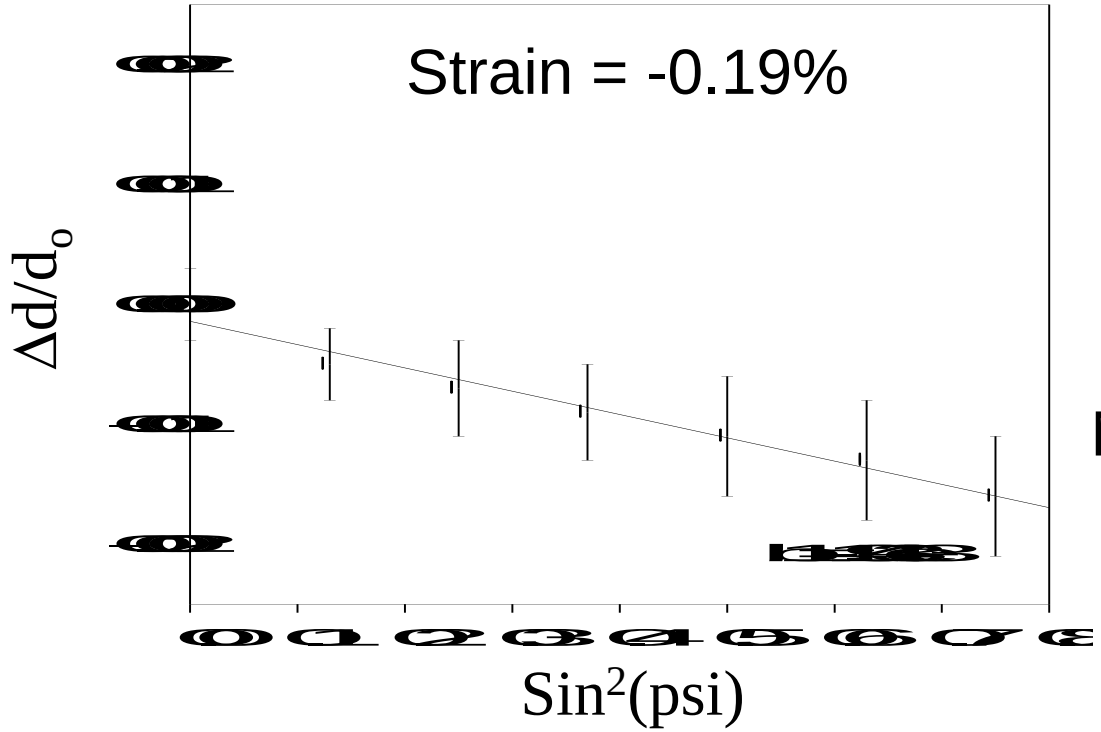


$SrTiO_3$ (220) pole figure

Tilting the sample can also make it possible to measure in-plane strains.



Data for ErD_2 thin film



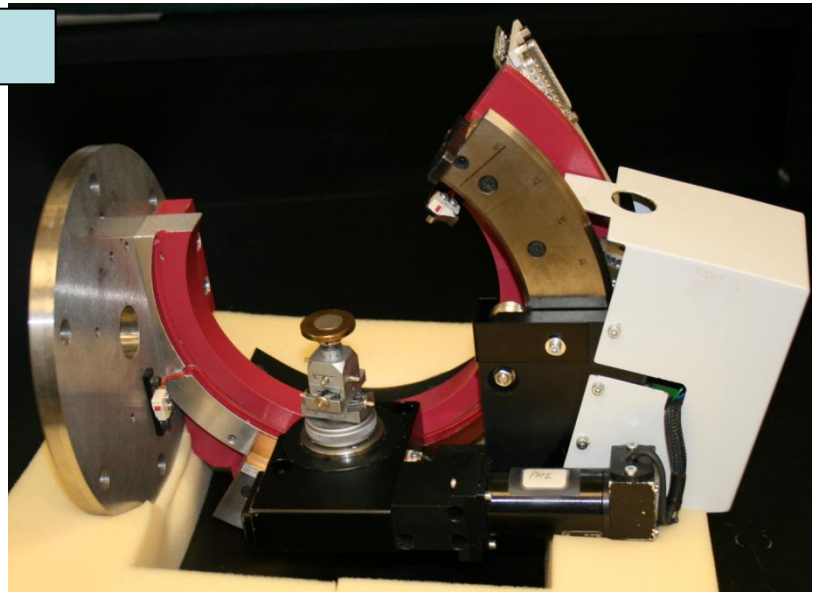
Positive slope: tension

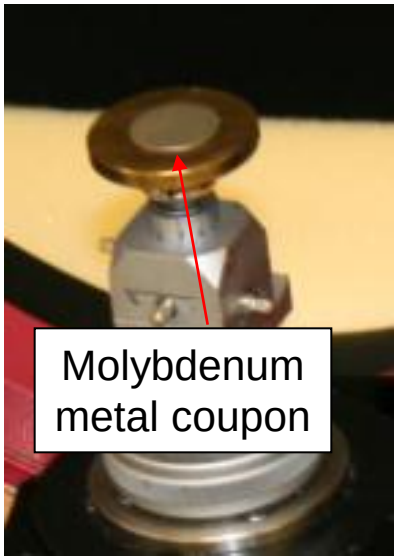
Negative slope: compression

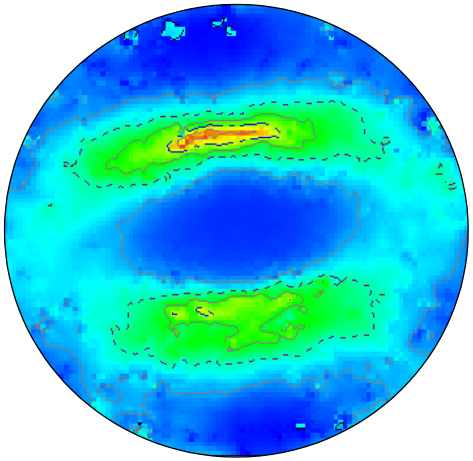
Bulk

Bulk Sample of Molybdenum for Texture Analysis

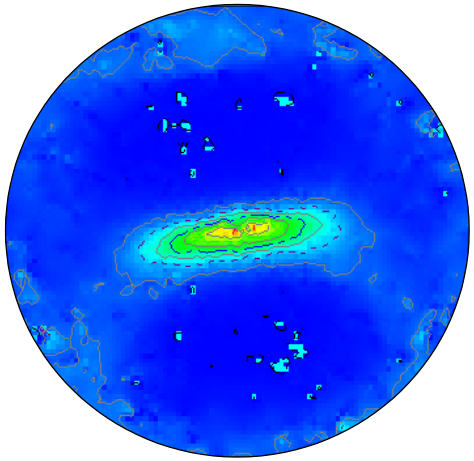
Bulk



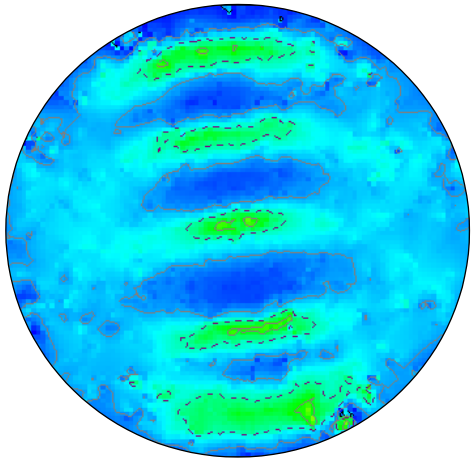




(110)



(200)



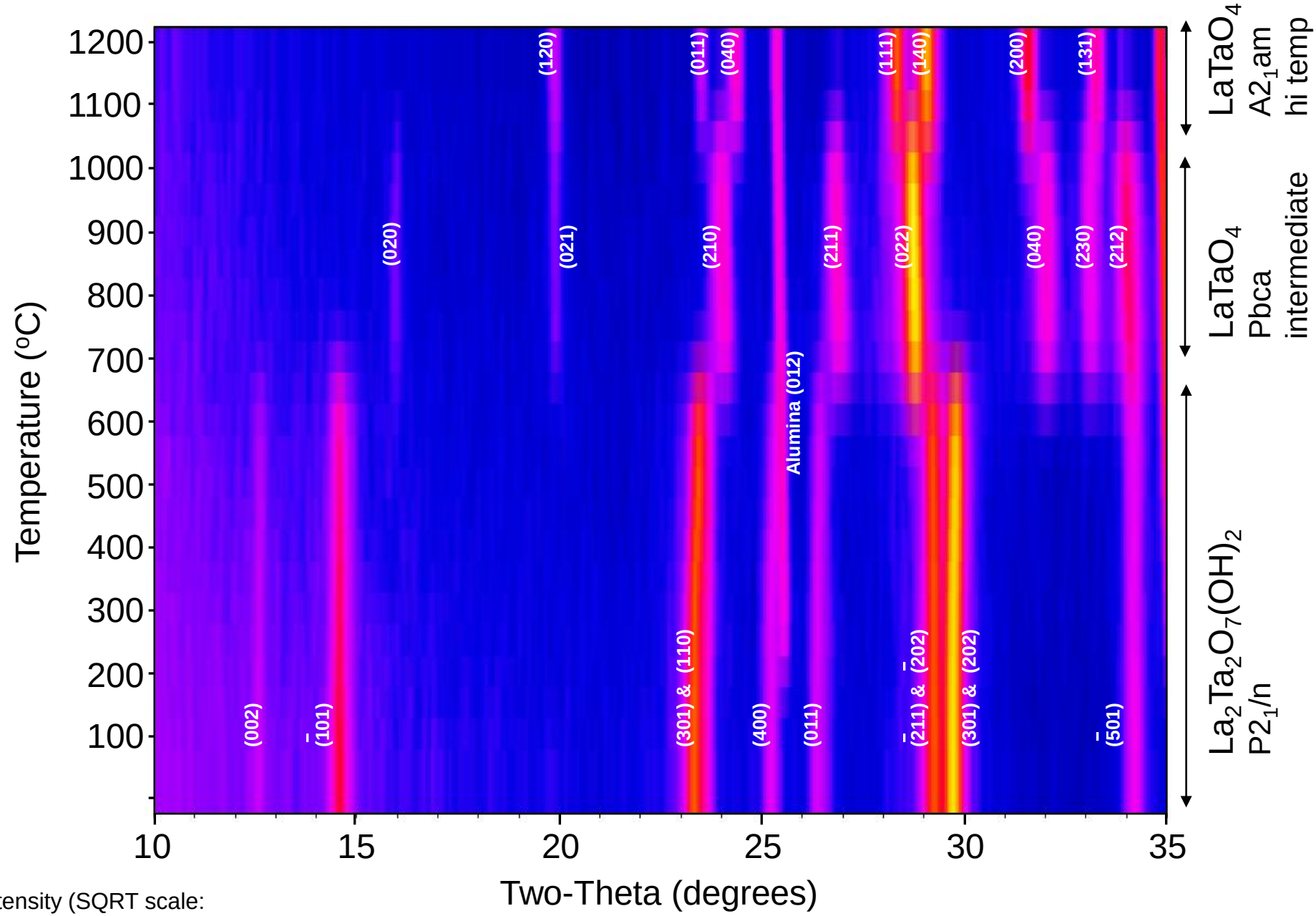
(211)

Molybdenum pole-figures showing rolling texture

SSPD

(structure solution from powder data)

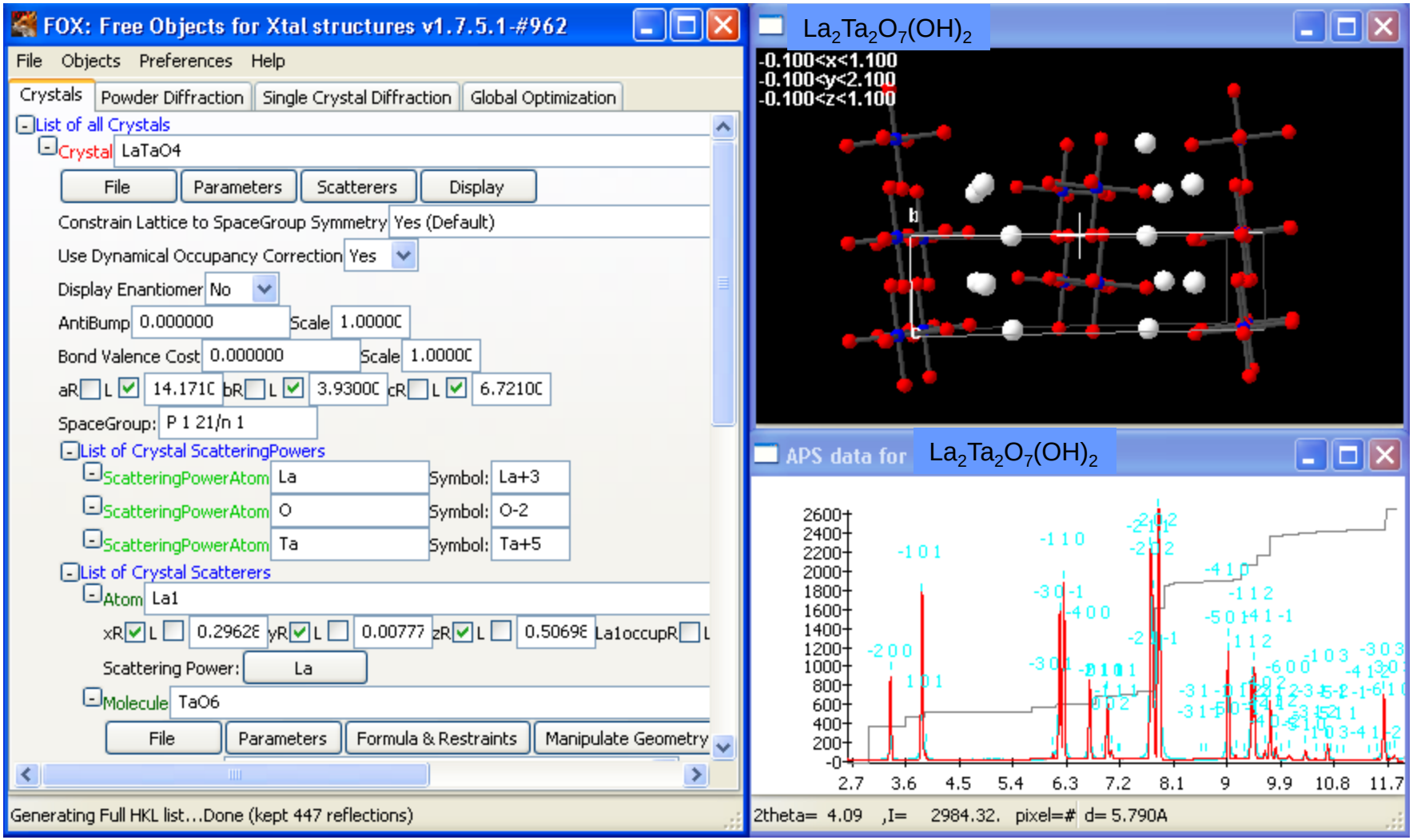
Sometimes we come across new phases that have no ID



Intensity (SQRT scale:
yellow =high, blue=low)

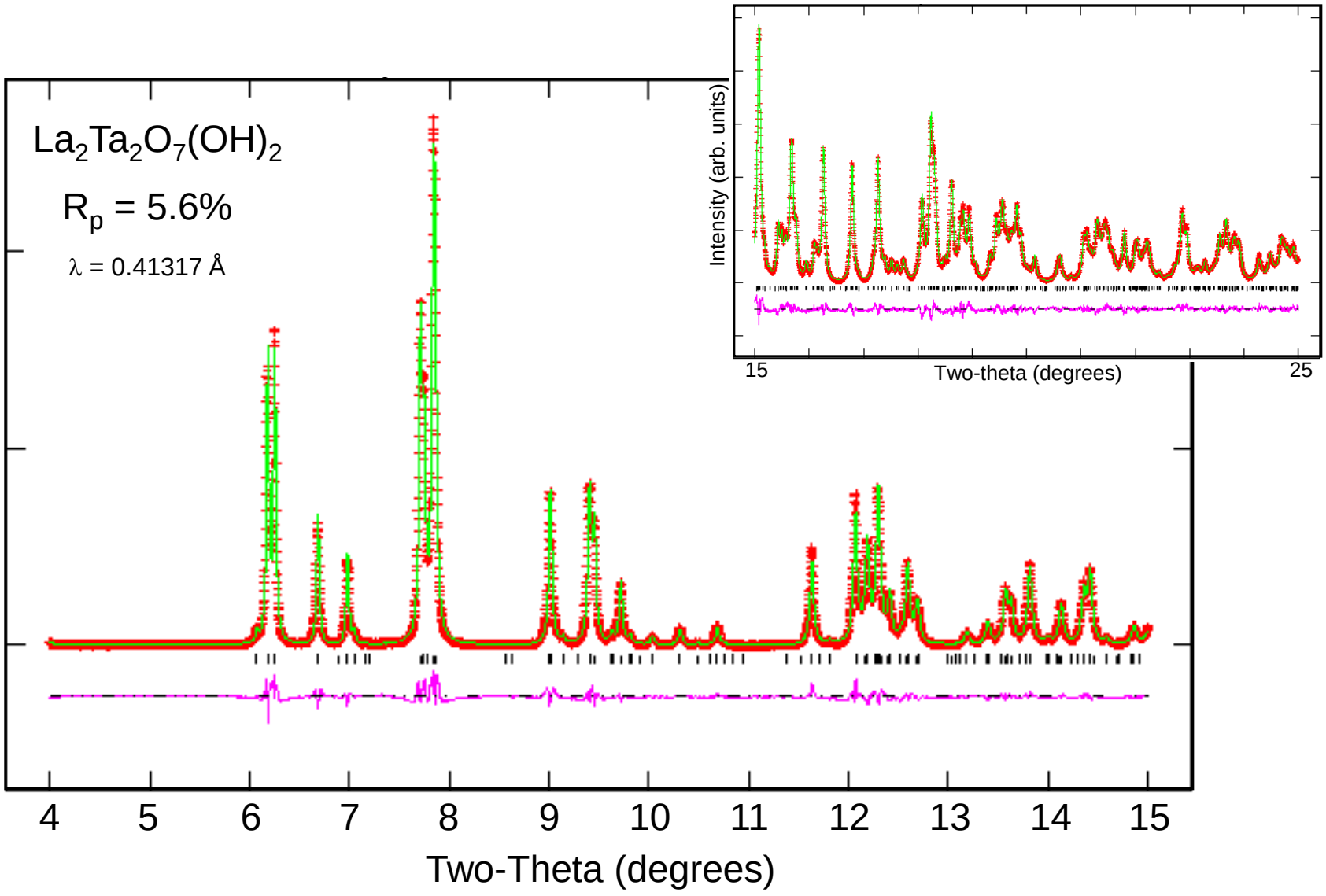
High resolution powder data was collected at APS 11-BM* and structure was derived from indexed powder diffraction pattern.

I knew the approximate composition and assumed Ta was in TaO_6 building blocks



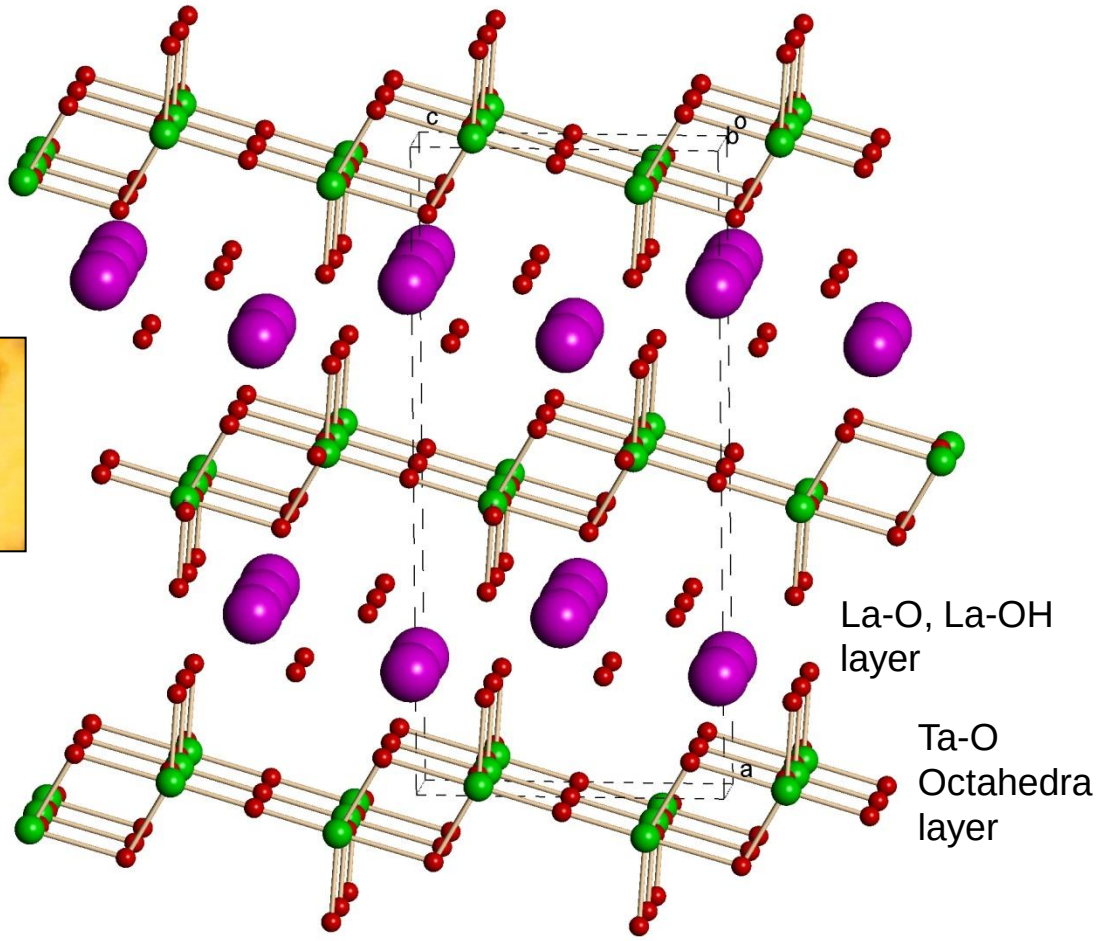
*http://11bm.xor.aps.anl.gov/

Refinement of high resolution powder data yields excellent quality structural information.



It is possible to derive the structure from the powder pattern. But it is not by any means an easy task. Any ability to isolate the compound's chemistry, density, symmetry, properties, etc., will aid in directing the crystal solution.

formula	$La_2Ta_2O_7(OH)_2$
Space group	$P2_1/n$
a (Å)	14.1711(6)
b (Å)	3.9303(2)
c (Å)	6.7201(3)
β (°)	91.08
Vol	374.22
Z	2
R_p	0.056
La (x, y, z)	0.299 0.005 0.502
Ta	0.538 0.494 0.729
O1	0.579 0.488 0.419
O2	0.544 0.026 0.712
O3	0.5 0.5 0
O4	0.174 0.015 0.252
OH5	0.198 0.522 0.625



Model of $La_2Ta_2O_7(OH)_2$

Questions?