Società Italiana Luce di Sincrotrone

"Gilberto Vlaic" XVII School on Synchrotron Radiation: Fundamentals, Methods and Applications

Muggia (Italy), 16 - 26 September 2024

Elettra Sincrotrone Trieste

Analysis of diffraction data

Marco Merlini

Earth Science Department
Università degli Studi di Milano (Italy)

UNIVERSITÀ DEGLI STUDI DI MILANO

1) GEOMETRY of diffraction (powder diffraction experiments)

1.1) Monochromators
1.2) Calibration of beamline parameters

1.3) Use of unit cell volume for determination of bulk properties (i.e. thermal expansion, etc.)
1.4) Microstructure (i.e. crystallite size)

2) INTENSITY of diffraction

2.1) Quantitative analysis
2.2) Structure determination (powder and syngle crystals)

3) EXAMPLES

3.1) Diffraction tomography
3.2) Single crystal at extreme conditions
3.3) Single crystal data processing

1) GEOMETRY of diffraction (powder diffraction experiments)

Bragg's law

1.1) Monochromators
1.2) Calibration of beamline parameters

Laue equations

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Rietveld fit

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Software:

Fit2D
Dioptas

GSAS
GSAS-II

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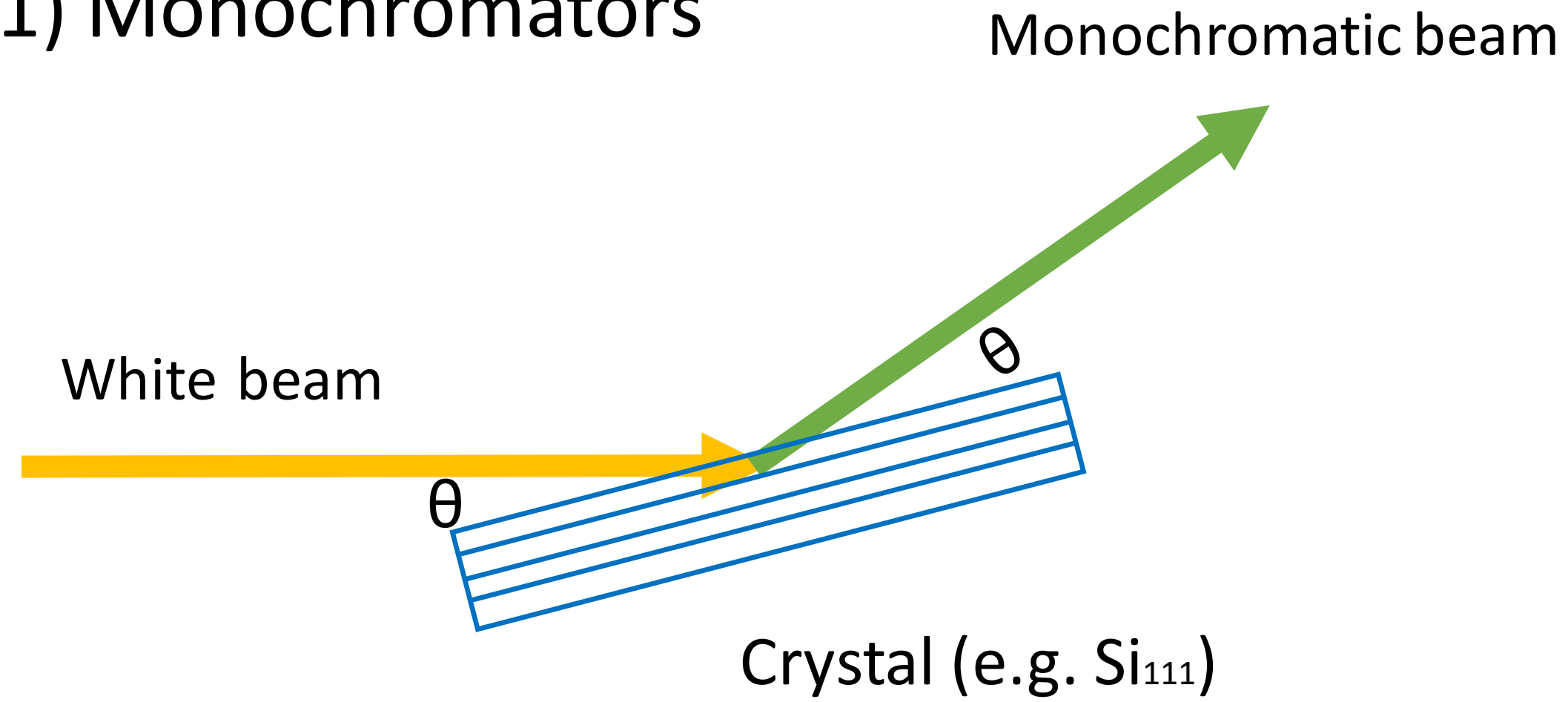
Crystal structure database (American Mineralogist database)

Single crystal data reduction (multipurpose – inorganic)

1.1) Monochromators



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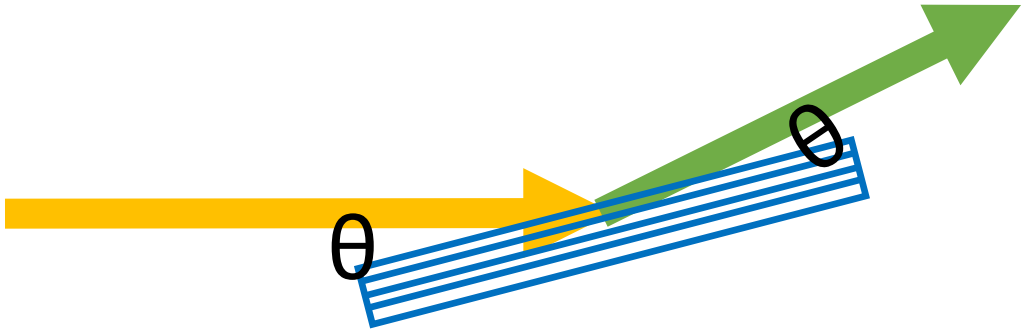
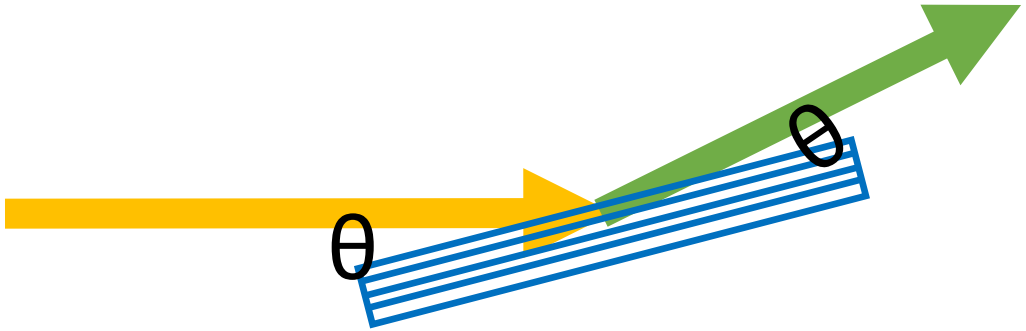


At which theta angle should be set a Si_{111} monochromator to get 30keV ?

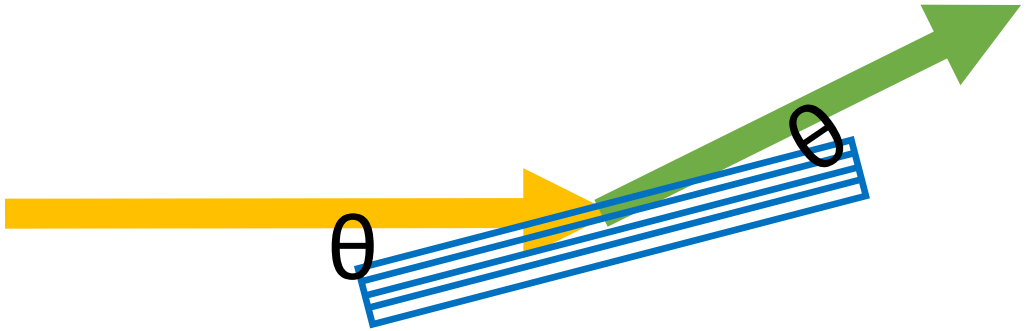
1.1) Monochromators



At which theta angle should be set a Si_{111} monochromator to get 30keV ?

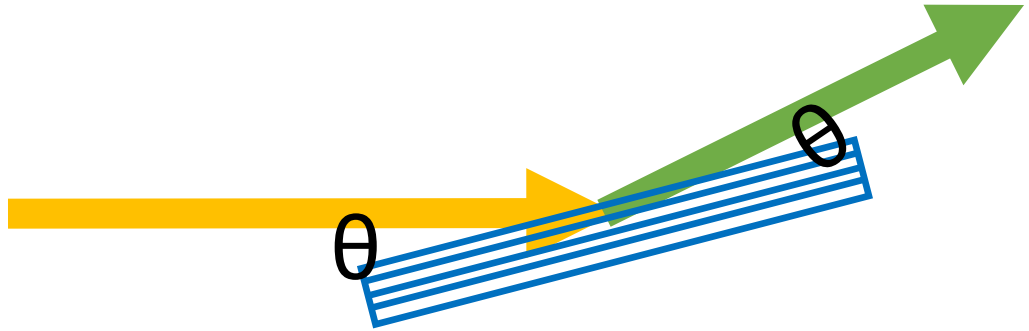
- Need Bragg's law and crystallographic (unit cell) parameters of crystalline silicon

1.1) Monochromators



Bragg's law: $2d_{hkl}\ \text{sen}\theta = (n)\lambda$

1.1) Monochromators



Bragg's law: $2d_{hkl}\ \mathrm{sen}\theta = (n)\lambda$

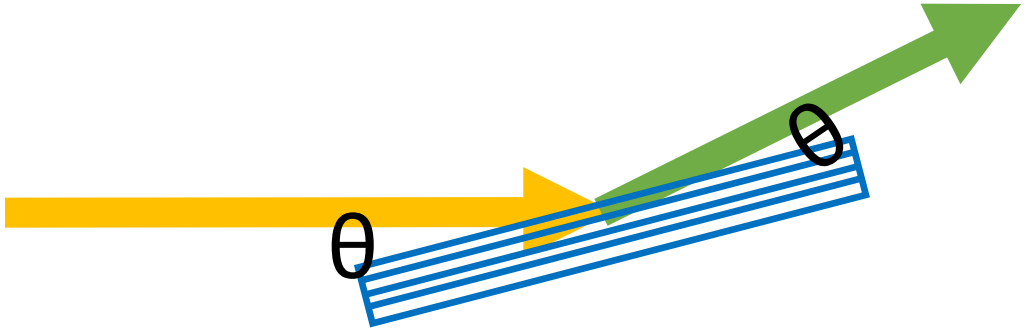
$E=h\upsilon=hc/\lambda$

$E(keV)=12.4 / \lambda(Å)$

12.398…

12.39841930…

1.1) Monochromators



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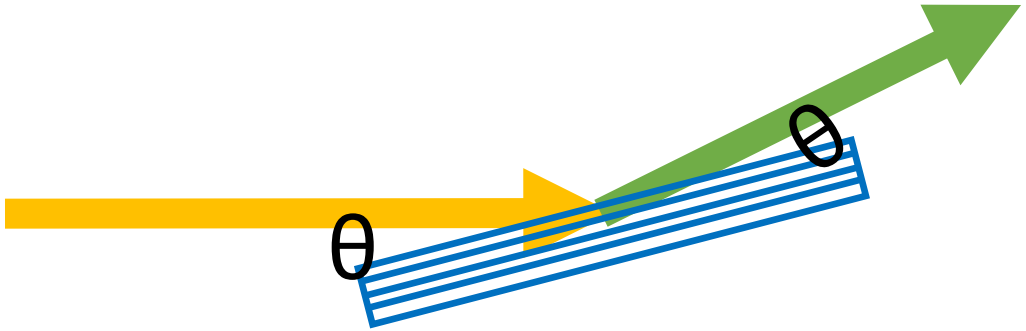
12.398…

12.39841930…

30 keV : $\lambda = 0.41328$ Å

1.1) Monochromators



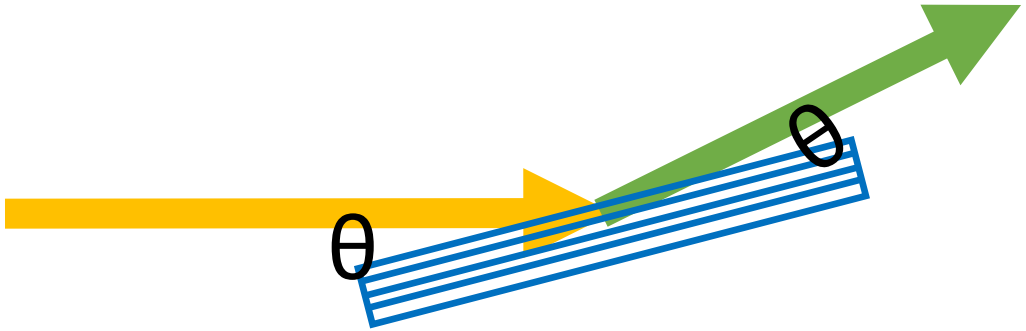
Bragg's law: $2d_{hkl}\,\mathrm{sen}\theta = (n)\lambda$

Silicon: cubic, a= 5.43102 Å

$1/d^2=(h^2+k^2+l^2)/a^2$

d_{111} = 3.13560 Å

1.1) Monochromators



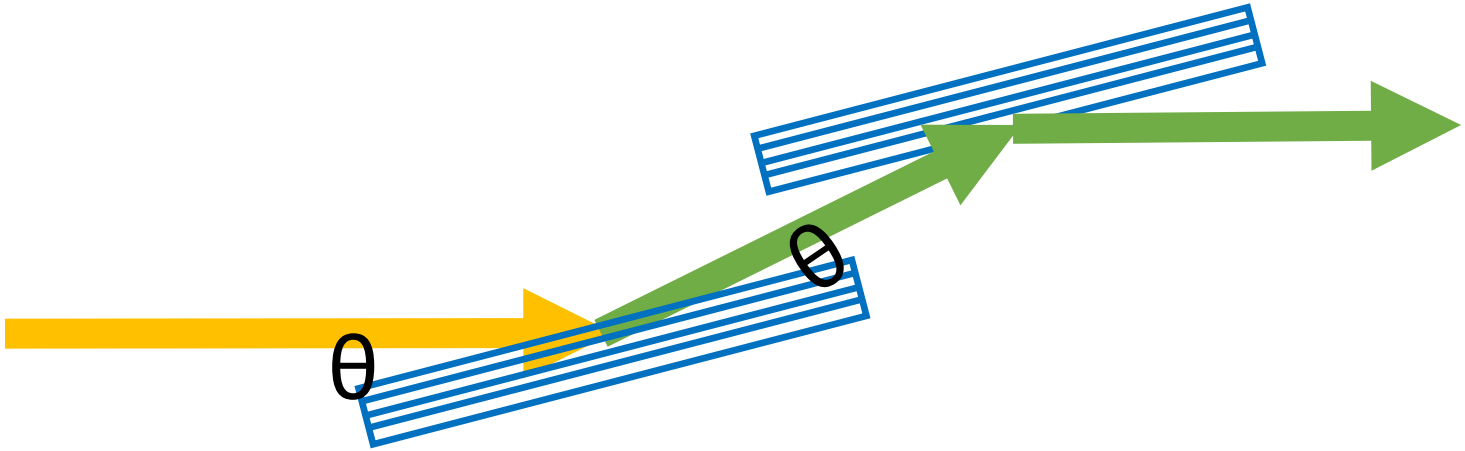
Bragg's law: $2d_{hkl}\ \text{sen}\theta = (n)\lambda$

$\lambda = 0.41328$ Å

$d_{111} = 3.13560$ Å

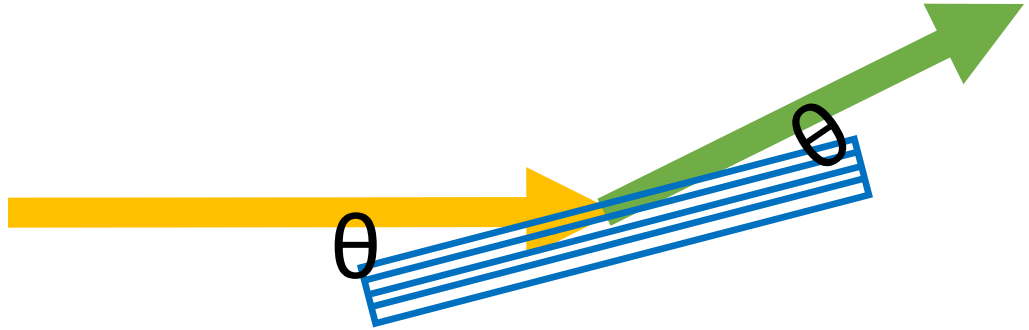
$\Theta = 3.7786°$

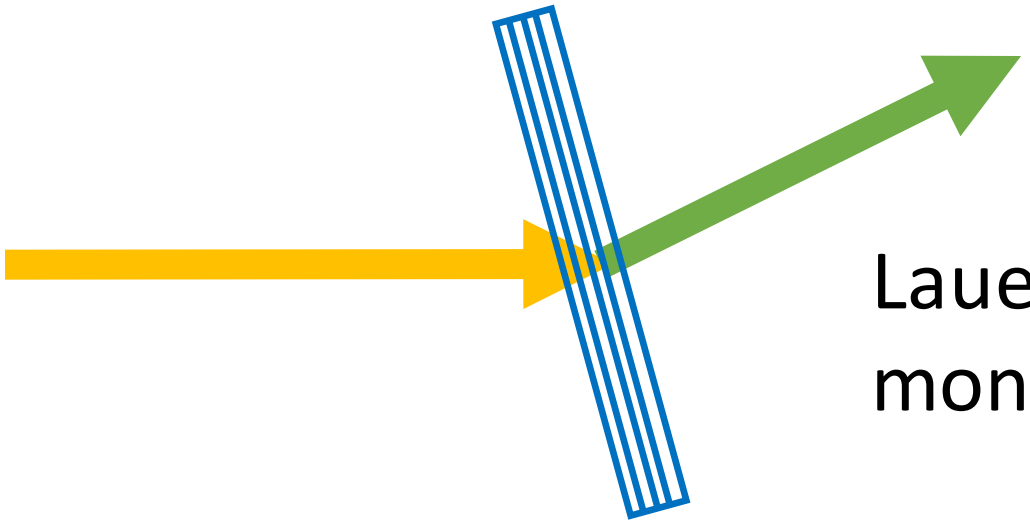
1.1) Monochromators



Double parallel monochromators

1.1) Monochromators

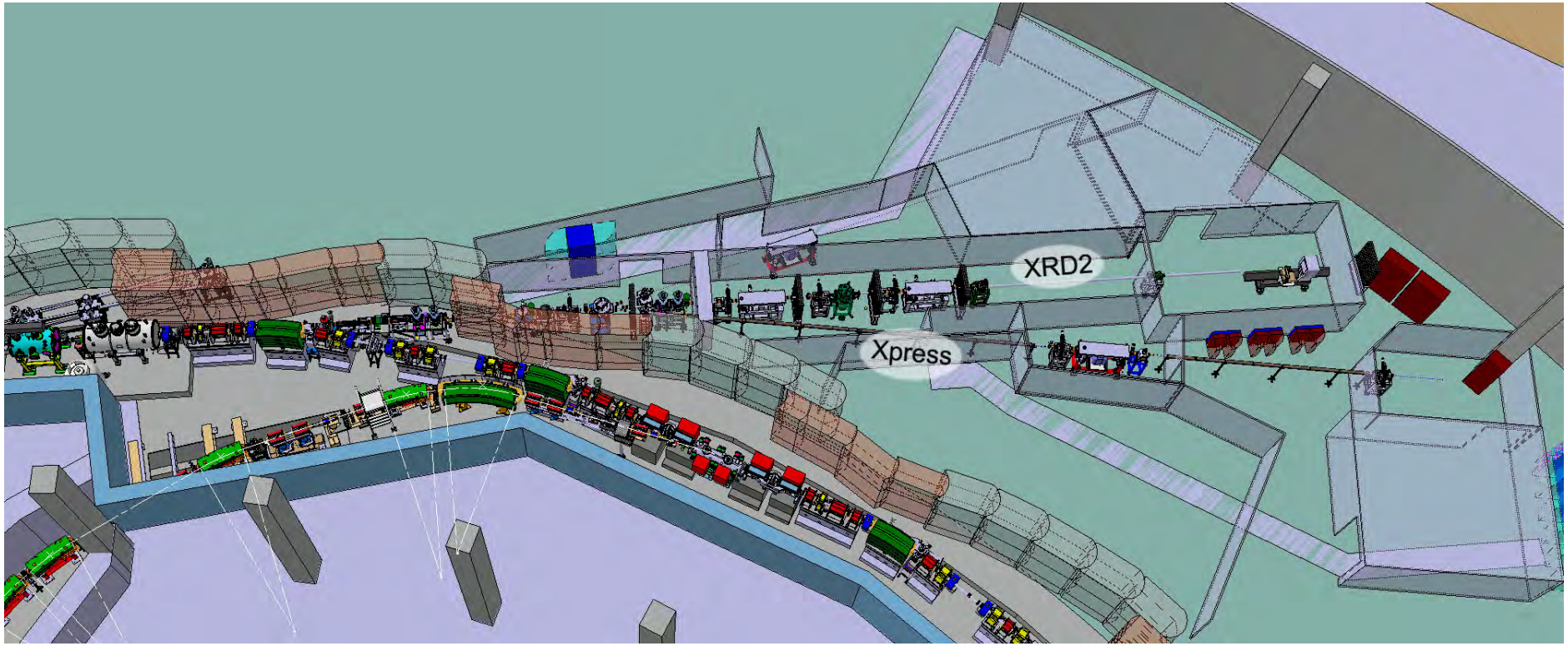




Laue geometry monochromator

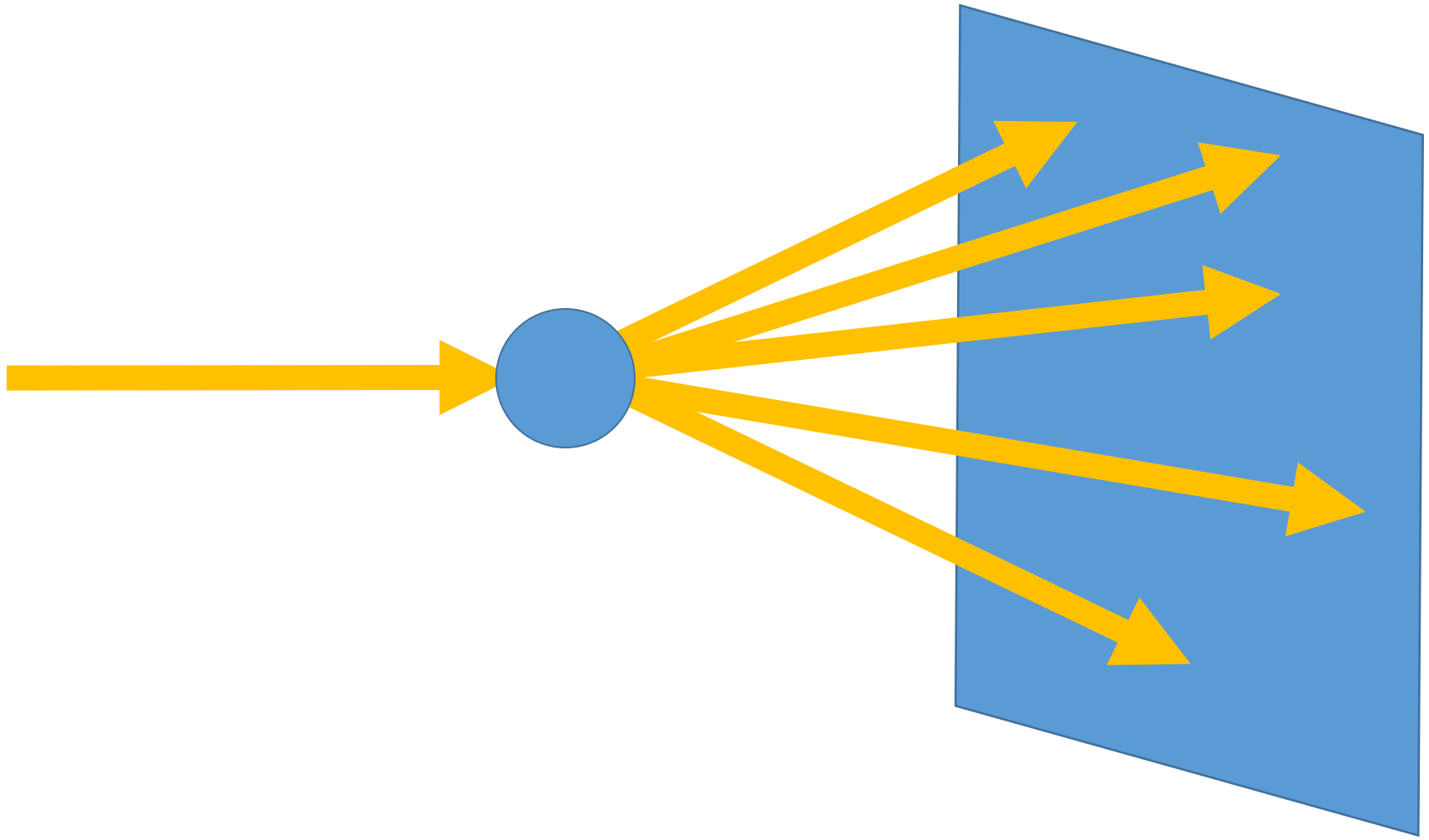
Or single monochromator for specific purposes (i.e. two beamlines on single source)

1.1) Monochromators

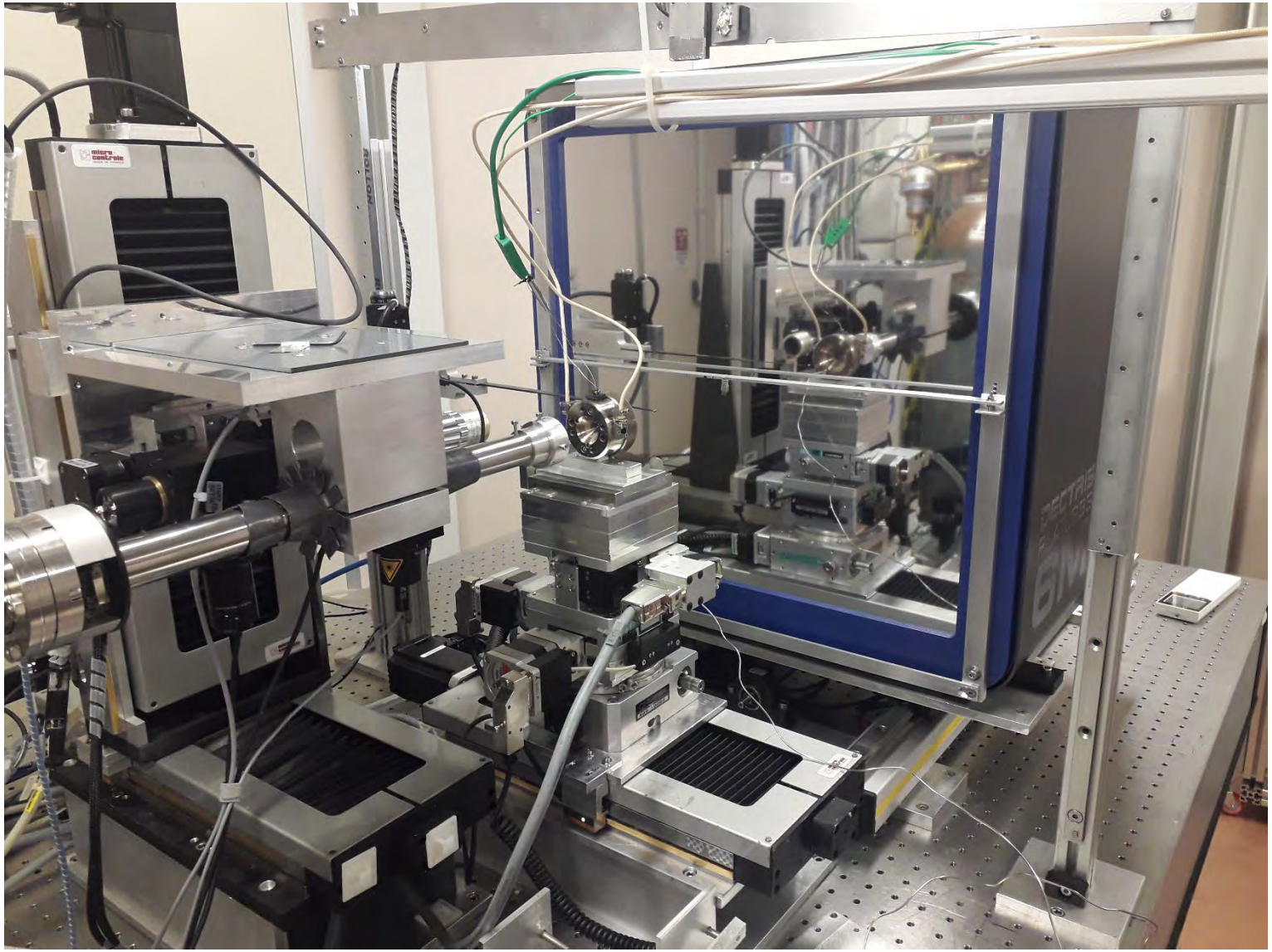


Courtesy of A. Lausi & P. Lotti

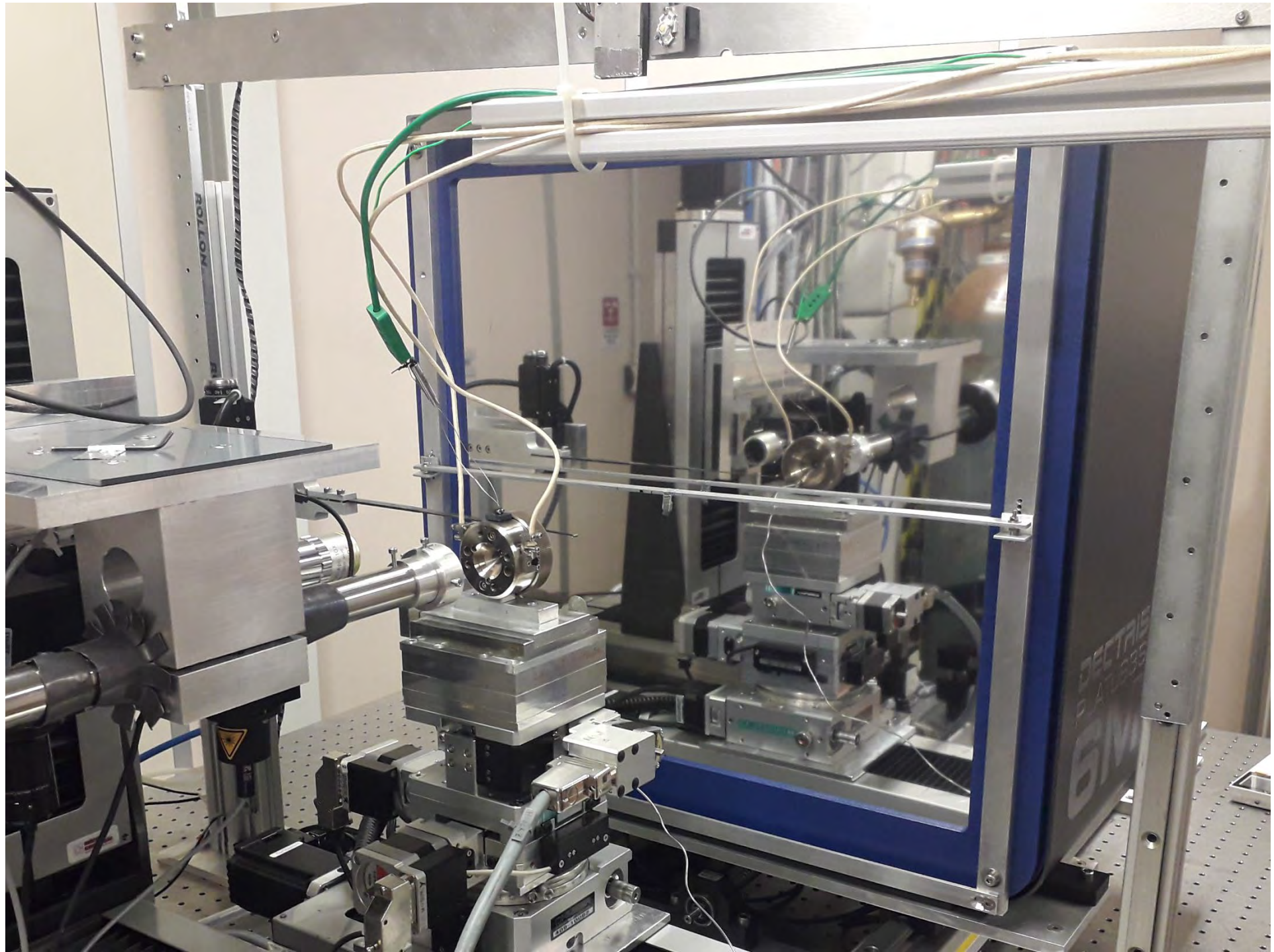
1.2) Calibration of beamline parameters

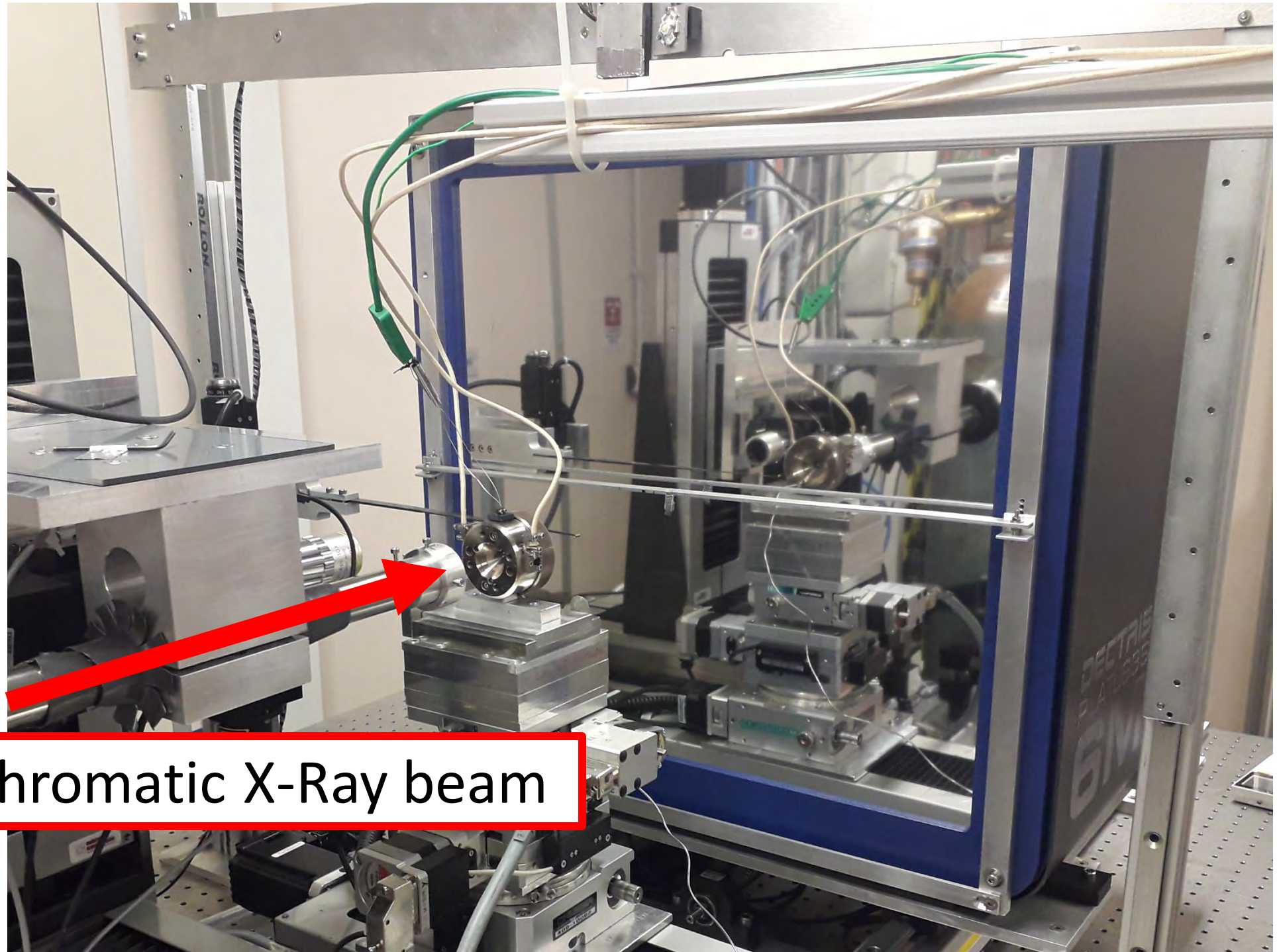


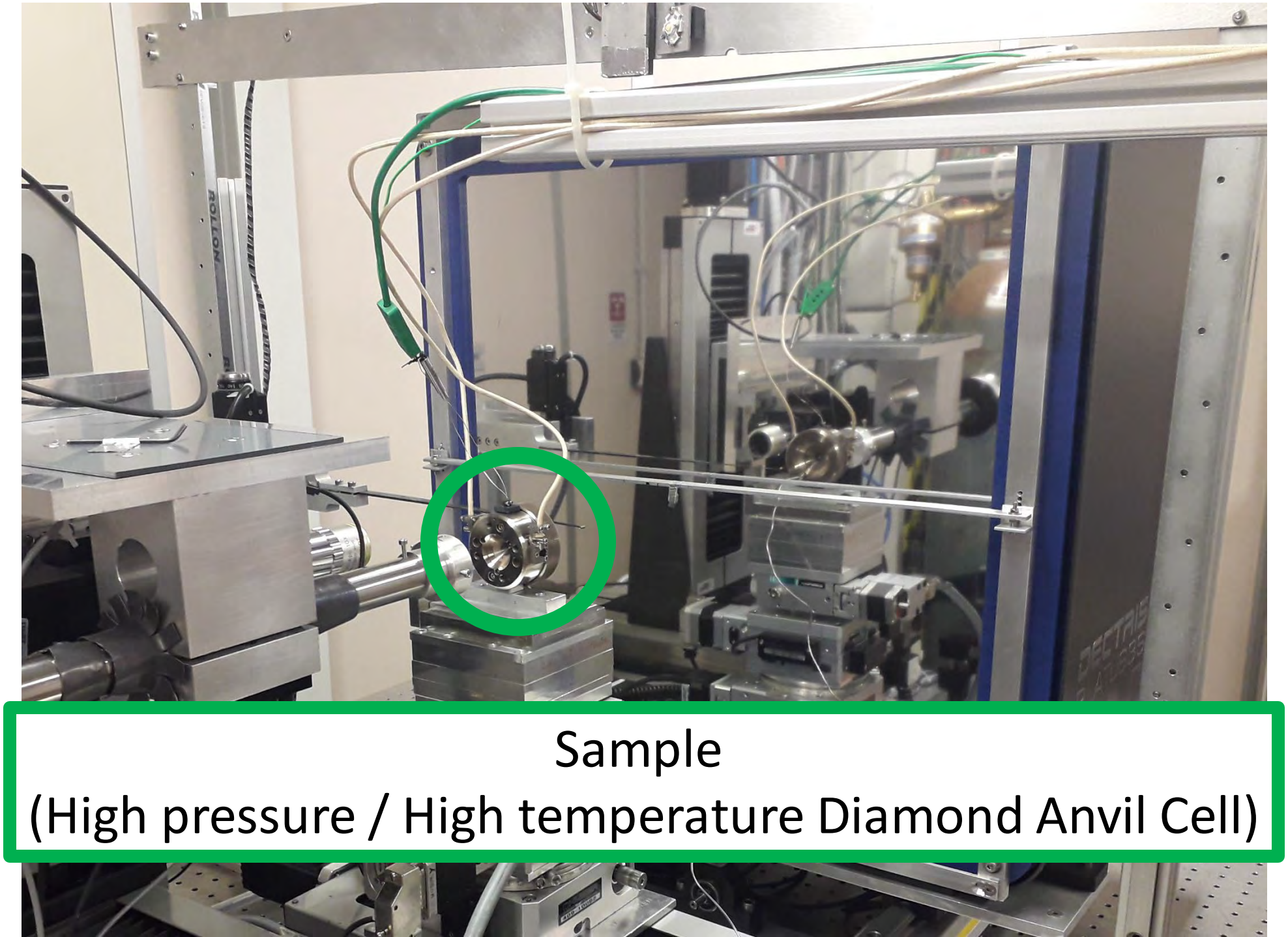
1.2) Calibration of beamline parameters



XPRESS @ Elettra

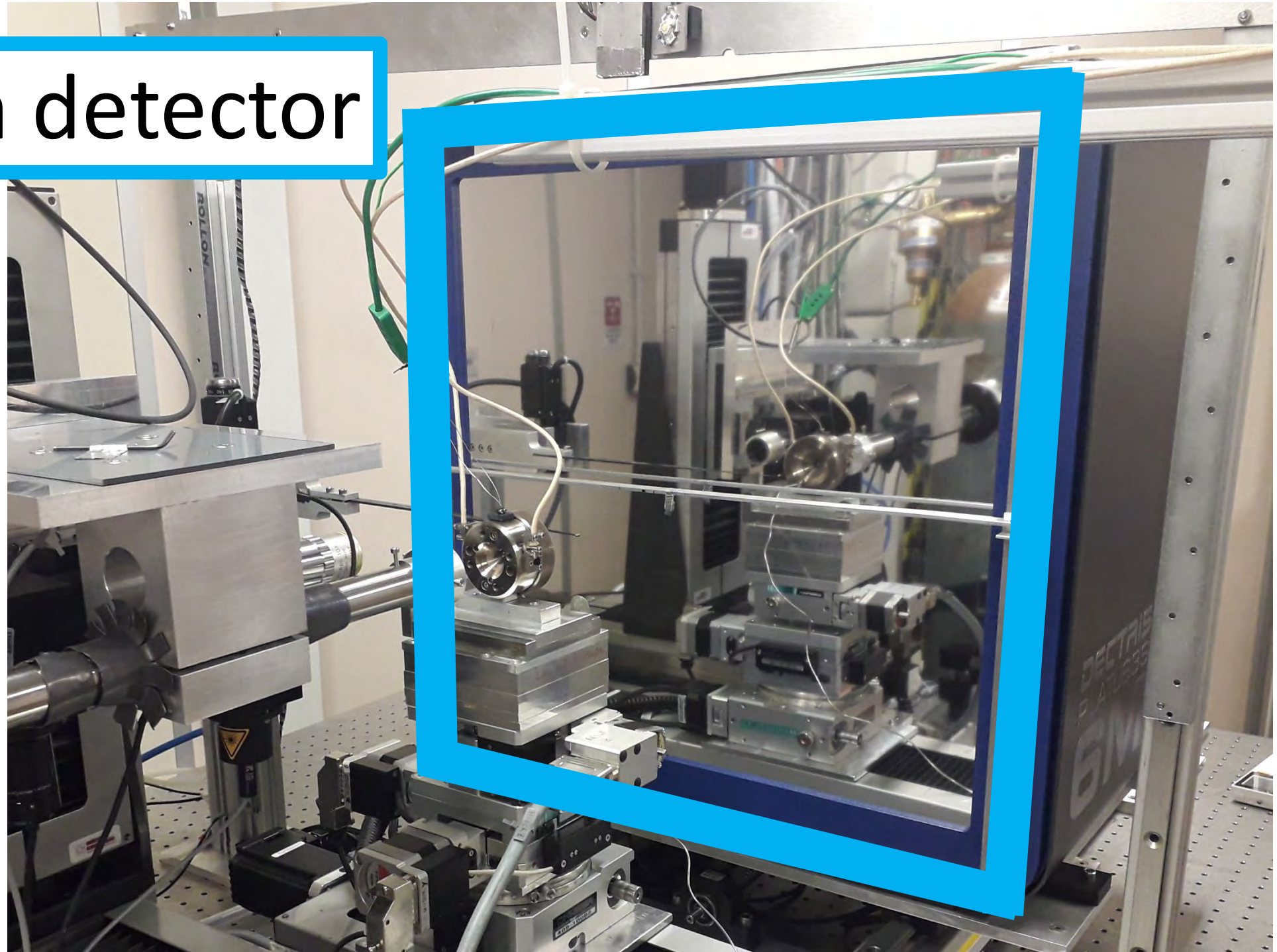

ROLLON


ROLLON
Monochromatic X-Ray beam

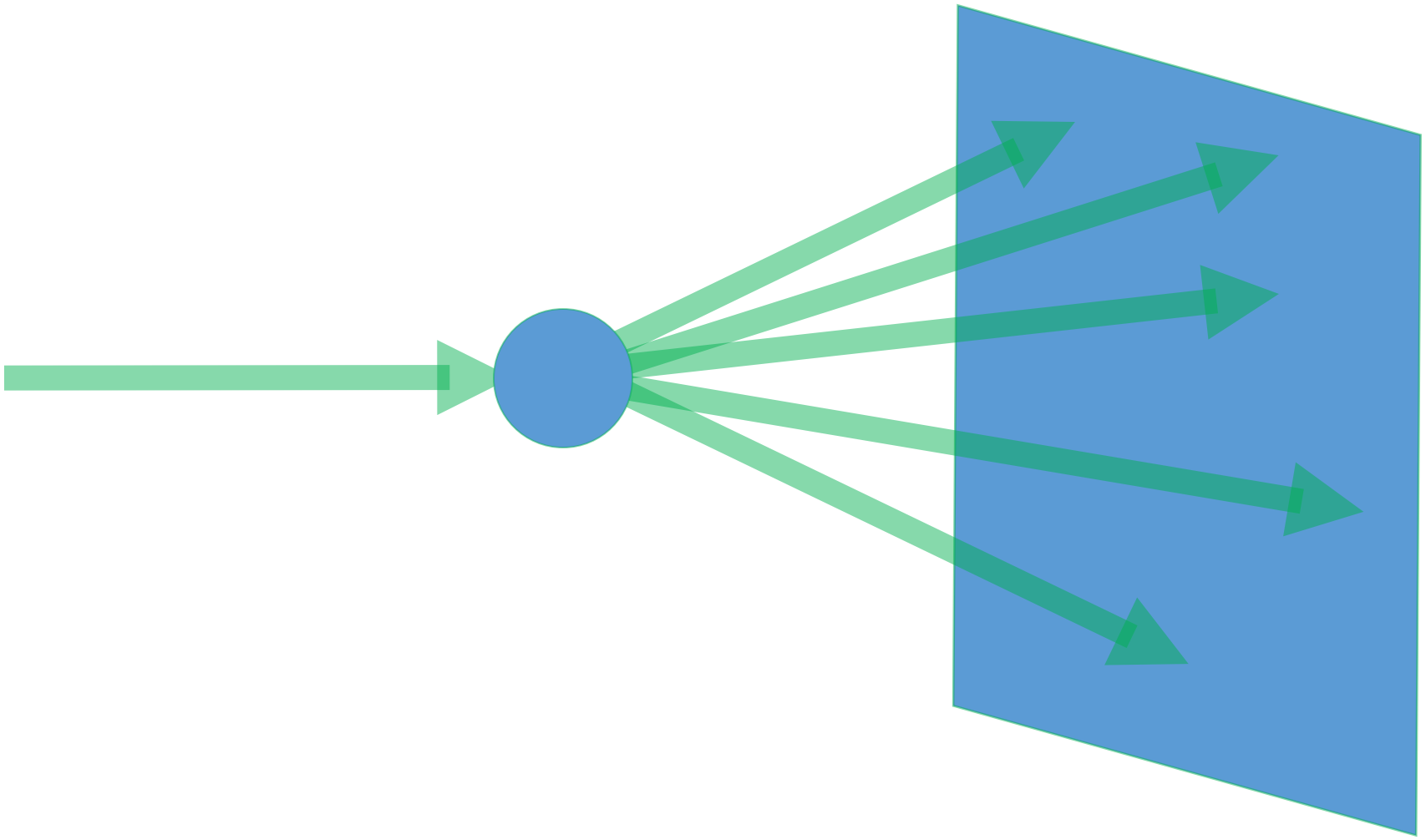


Sample
(High pressure / High temperature Diamond Anvil Cell)

Area detector



1.2) Calibration of beamline parameters



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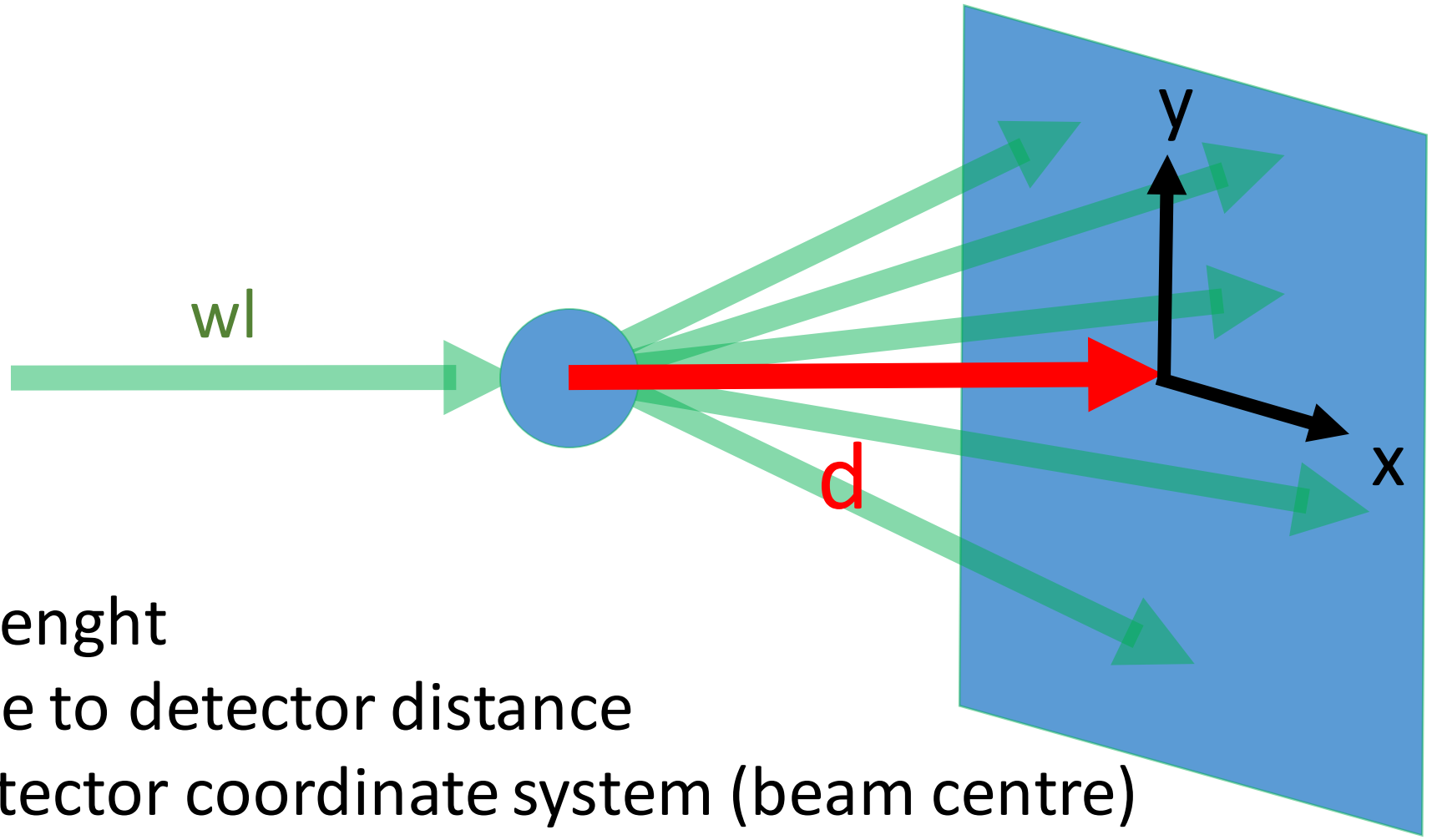
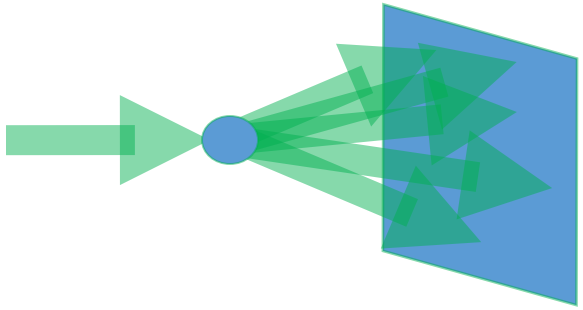


- Wavelenght
- Sample to detector distance
- X,Y detector coordinate system (beam centre)
- Detector tilt

1.2) Calibration of beamline parameters

- Calibration against a powder (single crystal) reference sample with well known lattice parameter



- Operation normally done by beamline staff, but users should know how to do

- Standards: Silicon, LaB_6, CeO_2…..

- Software: FIT2D, Dioptas

1.2) Calibration of beamline parameters

1 of 1

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Fit2D

High Pressure Research
Volume 14, Issue 4-5, 1996, Pages 235-248

Two-dimensional detector software: From real detector to idealised image or two-theta scan (Article)

Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N., Häusermann, D.

Europ. Synchrt. Radiation Facility, BP 220, 38043 Grenoble Cedex, France

Abstract

View references (32)

Detector systems introduce distortions into acquired data. To obtain accurate angle and intensity information, it is necessary to calibrate, and apply corrections. Intensity non-linearity, spatial distortion, and non-uniformity of intensity response, are the primary considerations. It is better to account for the distortions within scientific analysis software, but often it is more practical to correct the distortions to produce 'idealised' data. Calibration methods and software have been developed for single crystal diffraction experiments, using both approaches. For powder diffraction experiments the additional task of converting a two-dimensional image to a one-dimensional spectrum is used to allow Rietveld analysis. This task may be combined with distortion correction to produce intensity information and error estimates. High-pressure experiments can introduce additional complications and place new demands on software. Flexibility is needed to be able to integrate different angular regions separately, and to produce profiles as a function of angle of azimuth. Methods to cope with awkward data are described, and examples of the techniques applied to data from high pressure experiments are presented.

Metrics View all metrics >

3054 Citations in Scopus

99th Percentile

5.46 Field-Weighted Citation Impact

PlumX Metrics

Usage, Captures, Mentions, Social Media and Citations beyond Scopus.

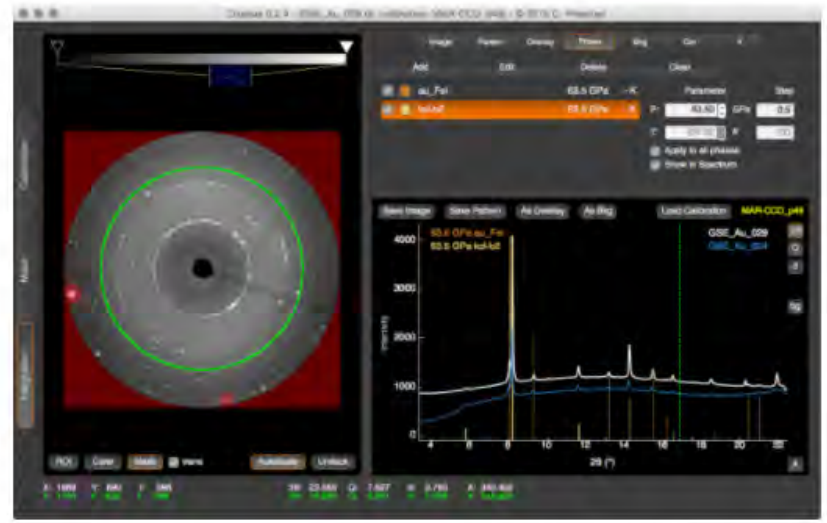
Cited by 3054 documents

Investigation of the precipitation of Na2SO4 in supercritical water

Voisin, T. , Erriguible, A. , Philippot, G. *(2017) Chemical Engineering Science*

The critical role of Si doping in enhancing the stability of M6C carbides

Dioptas



Dioptas is a Python-based program for on-the-fly data processing and exploration of two-dimensional X-ray diffraction area detector data. It is specifically designed for the large amount of data collected at XRD beamlines at synchrotrons. Its fast data reduction algorithm and graphical data exploration capabilities make it ideal for online data processing during XRD experiments and batch post-processing of large numbers of images.

Dioptas is written with interactivity and speed in mind while still being as versatile as possible. It employs an algorithm for calibration of any possible detector geometry, features easy-to-use masking tools, and offers very fast data exploration and phase analysis capabilities. The tunable calibration procedure enables the calibration of even the most complex geometries, including very large detector tilts, the primary beam being outside of the image and very spotty diffraction pattern of the calibrant. The main part of the software is the opportunity to interactively explore the 2d image and integrated pattern at the same time. The very fast integration algorithm (around 0.1s for an 2048px X 2048px image), a reliable tunable automatic background subtraction algorithm and the possibility to display phase lines make it a viable tool for realtime processing online at the beamline. Thus, enabling very fast decision making during the course of the experiment.

Distribution

Dioptas is mainly distributed via an open-source repository at http://github.com/Dioptas/Dioptas. However, since some of the required packages can be hard to install on some operating systems by non-expert end-users, we also provide executable packages which can be downloaded by using the link below. Dioptas is cross-platform compatible and has been tested on Windows 7, Windows 8, 10, Mac OS X and Linux Debian systems. Dioptas has a very fast-growing user base and is currently employed for online data processing and post experiment data analysis at CARS(Sectors 13-15, APS), HPCAT (Sector 16, APS), ID27 (ESRF), ID9 (ESRF), ID31 (ESRF) and ECB P02.2 (Petra III). Furthermore, non-high pressure beamlines and in-house laboratories are starting to adapt it.

Publications

A paper about Dioptas has been published in High Pressure Research:

- **Prescher, C.**, Prakapenka, V.B., 2015. DIOPTAS : a program for reduction of two-dimensional X-ray diffraction data and data exploration. ***High Press. Res.*** 35:3, 223-230. link

- Silicon NIST collected at XPRESS beamline (Elettra)

- Pilatus 6M area detector

- Approximate sample to detector distance: 250 mm (from uncalibrated motor position)

- Beam energy: ~ 25 keV (i.e. ~ 0.495)

- Pixel size: 0.172x0.172 mm

    - Using Fit2D and Dioptas to calibrate experimental geometry and integrate powder diffratcion from samples

Light Graphics Window
fit2d
big photo crusher
Copyright 1987-2016 Andy Hammersley / ESRF
Use of FIT2D implies acceptance of
the " Conditions of Use "
(Click on "CONDITIONS")
Note: The text window can
contain important
information !
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CONDITIONS
I ACCEPT
HELP
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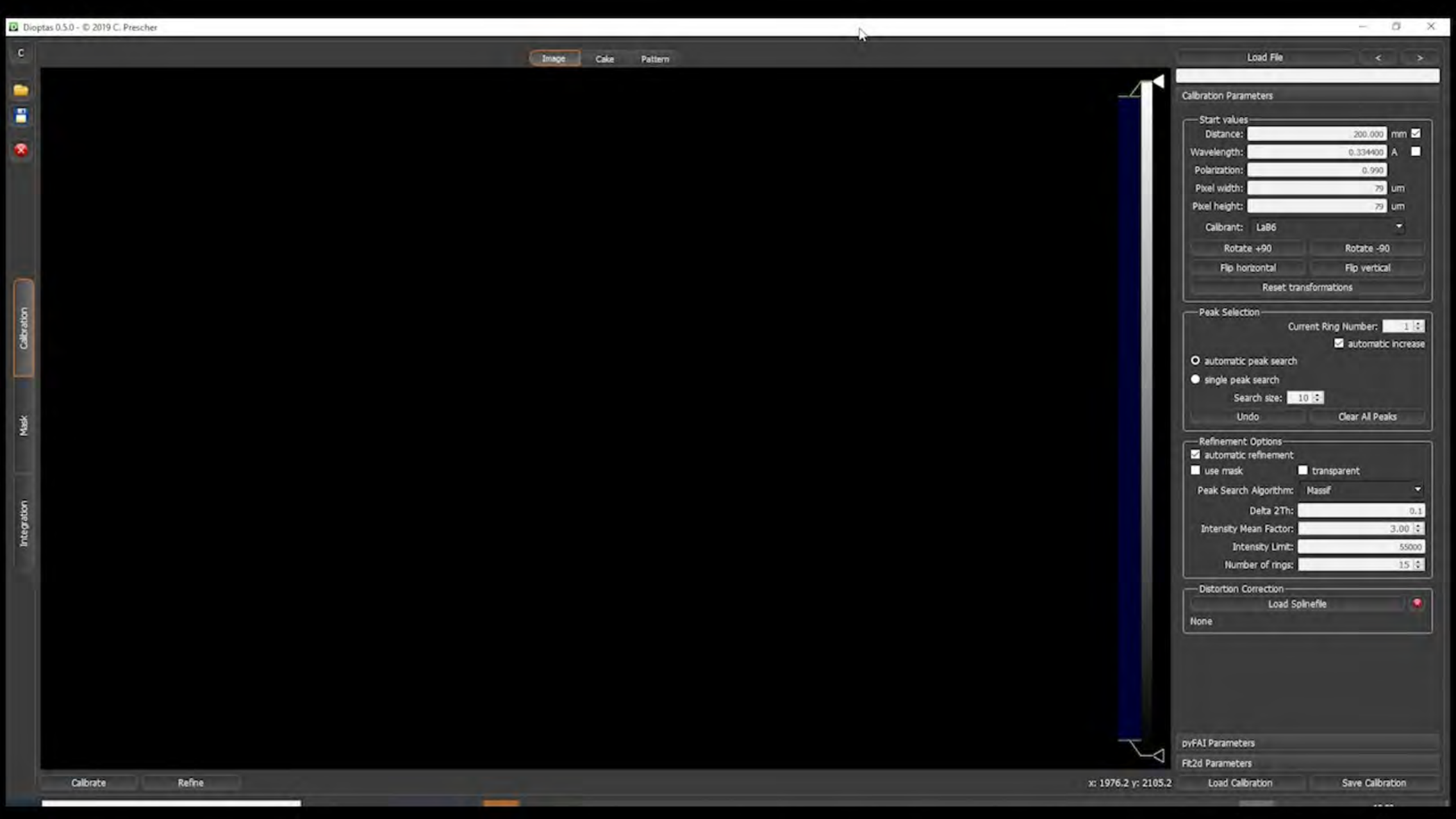
Dioptas 0.5.0 - © 2019 C. Prescher
C
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Calibration Parameters
Start values
Distance:
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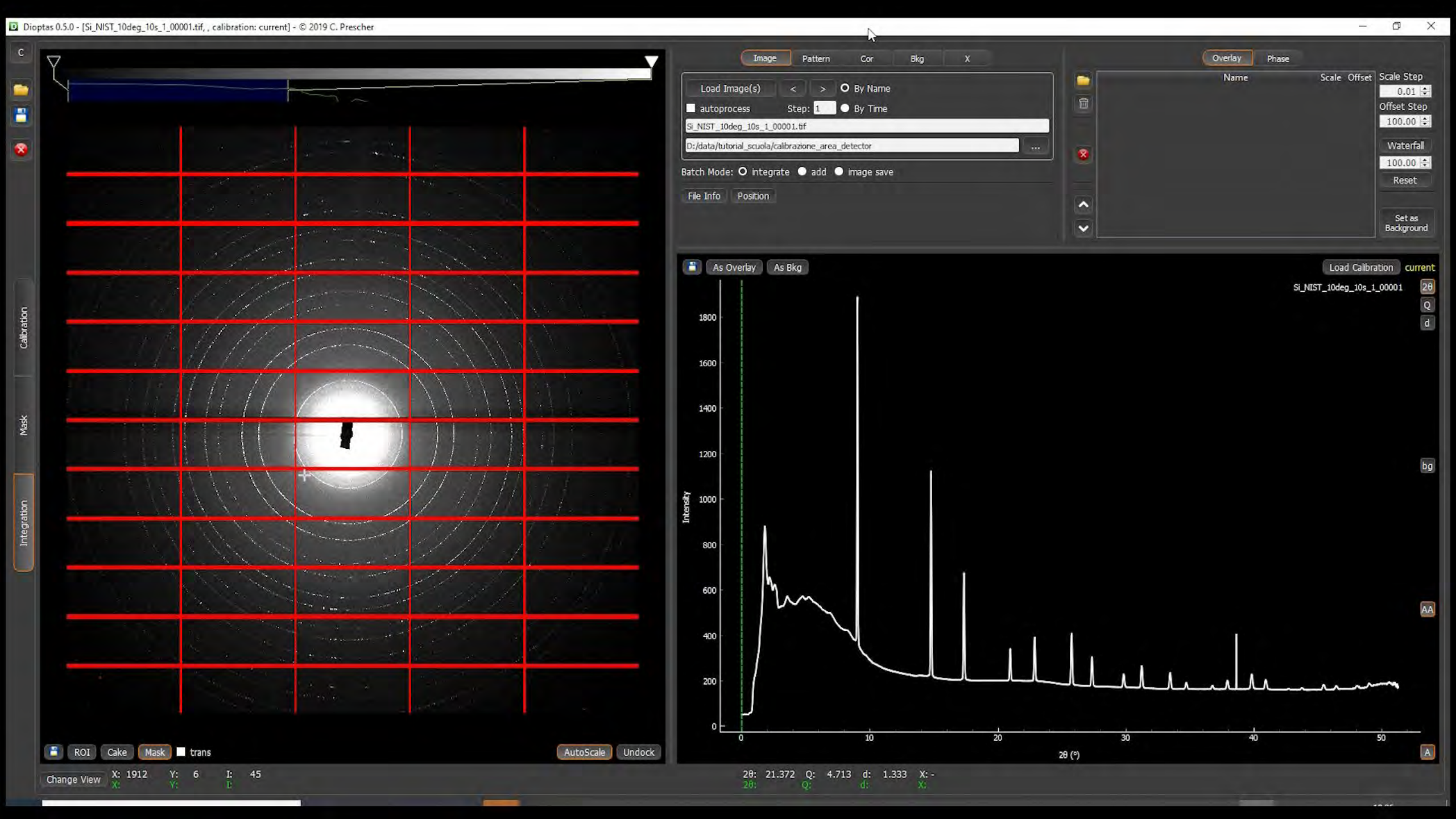
A
Polarization:
0.990
Pixel width:
79
um
Pixel height:
79
um
Calibrant:
LaB6
Rotate +90
Rotate -90
Flip horizontal
Flip vertical
Reset transformations
Peak Selection
Current Ring Number:
1
automatic increase
automatic peak search
single peak search
Search size:
10
Undo
Clear All Peaks
Refinement Options
automatic refinement
use mask
transparent
Peak Search Algorithm:
Massif
Delta 2Th:
0.1
Intensity Mean Factor:
3.00
Intensity Limit:
55000
Number of rings:
15
Distortion Correction
Load Splinefile
None
Calibration
Mask
Integration
Calibrate
Refine
x: 1976.2 y: 2105.2
pyFAI Parameters
Fit2d Parameters
Load Calibration
Save Calibration

Integration of sample XRPD


Dioptas 0.5.0 - [Si_NIST_10deg_10s_1_00001.tif, , calibration: current] - © 2019 C. Prescher
C
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Phase
Name
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Offset
Scale Step
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Offset Step
100.00
Waterfall
100.00
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As Bkg
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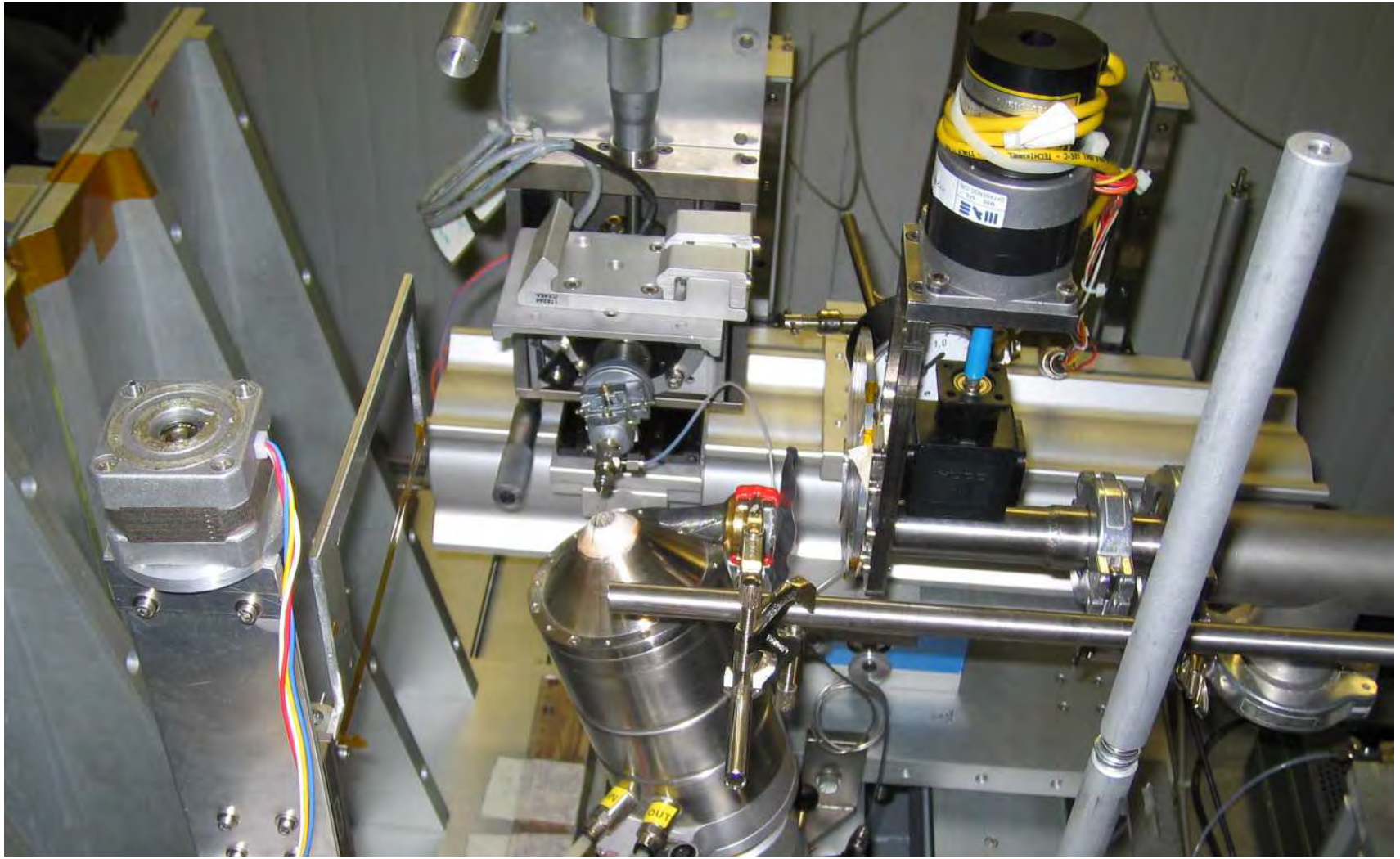
Si_NIST_10deg_10s_1_00001
2θ
Q
d
bg
AA
A
Intensity
2θ (°)
Change View
X: 1912
Y: 6
I: 45
2θ: 21.372
Q: 4.713
d: 1.333
X: -

1.3) Use of unit cell volume for determination of bulk properties: thermal expansion

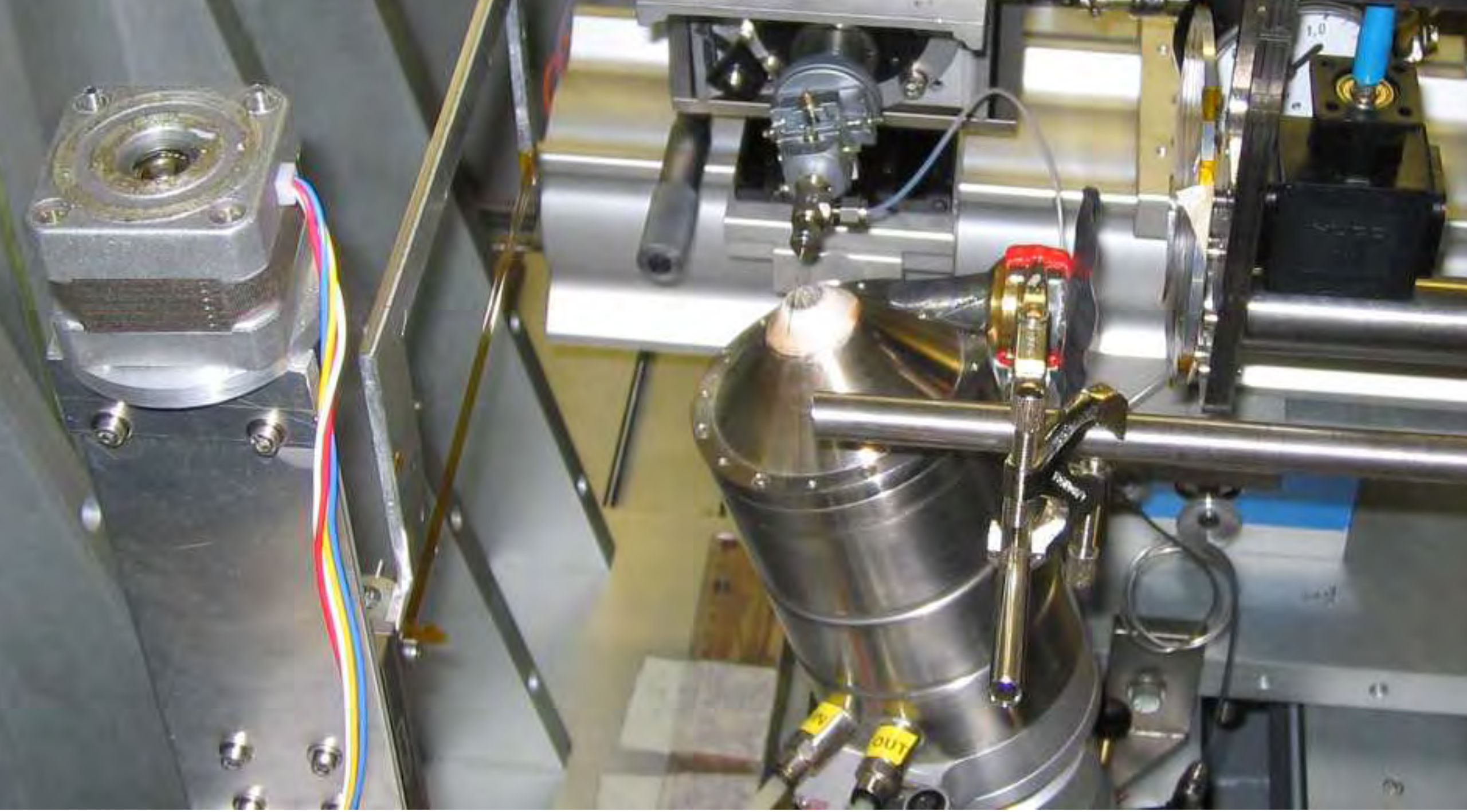
Thermal expansion: $\alpha = 1/V \, (\partial V/\partial T)$

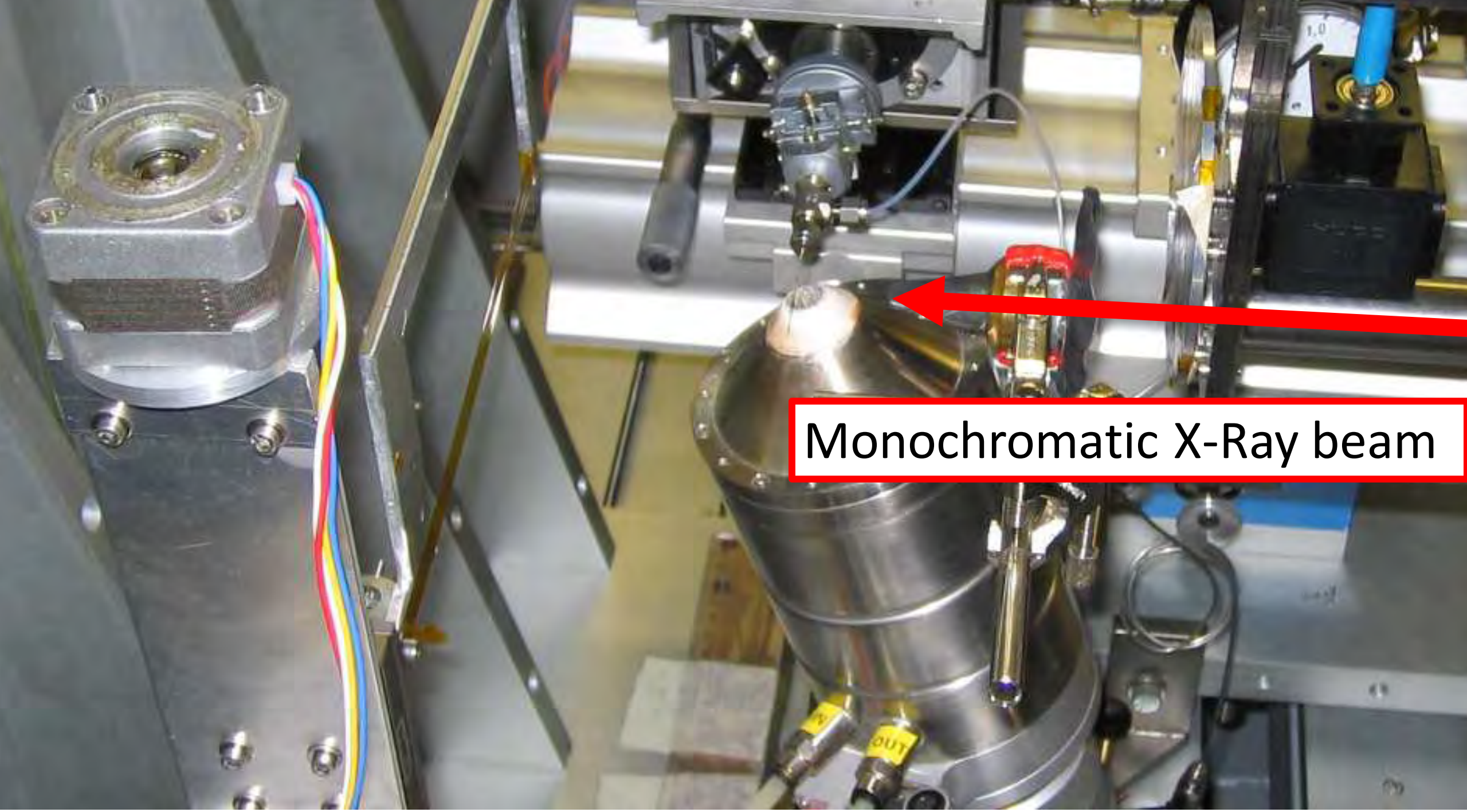
$= \partial \ln V/\partial T$

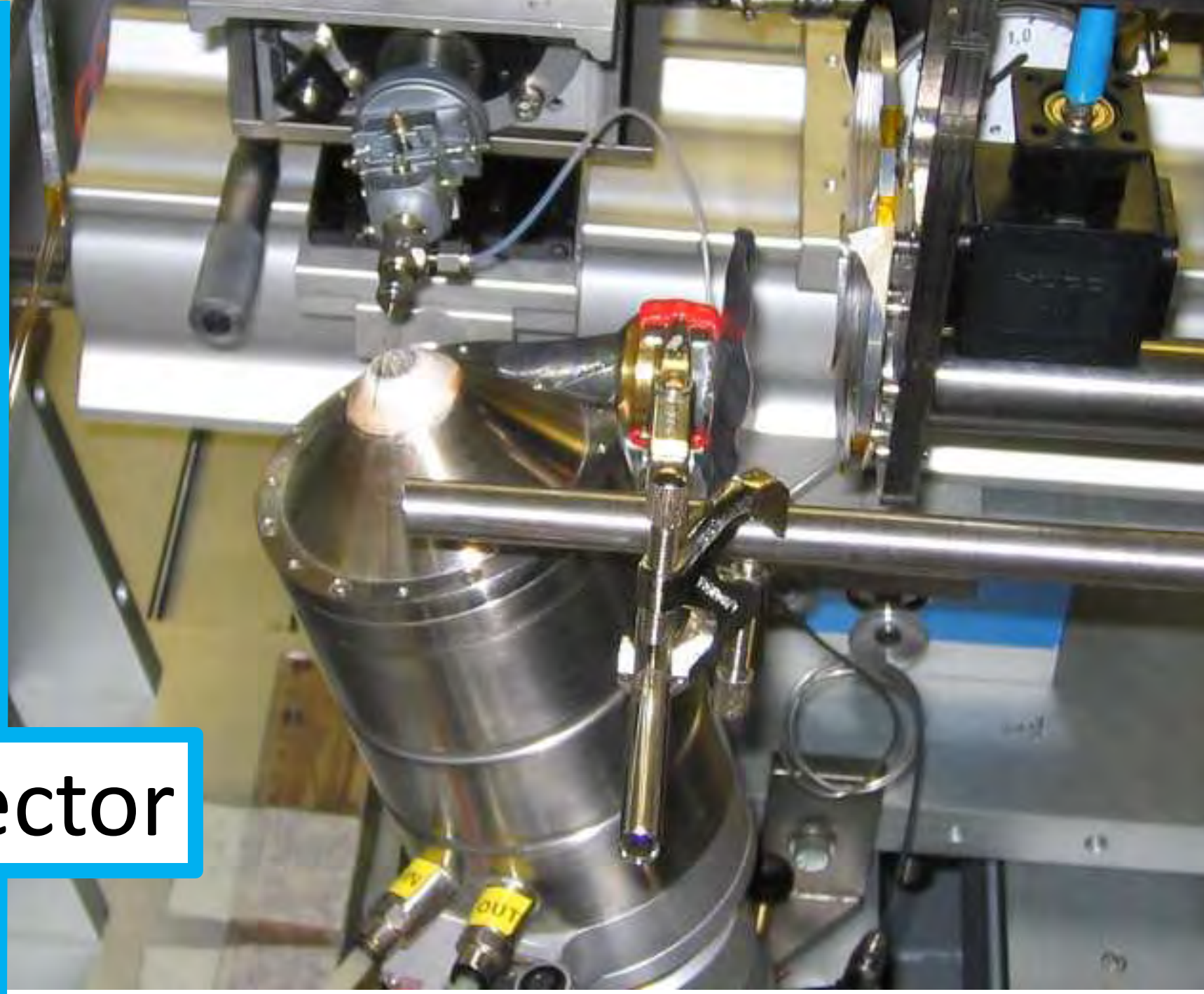
Determination of unit cell volume at different temperatures



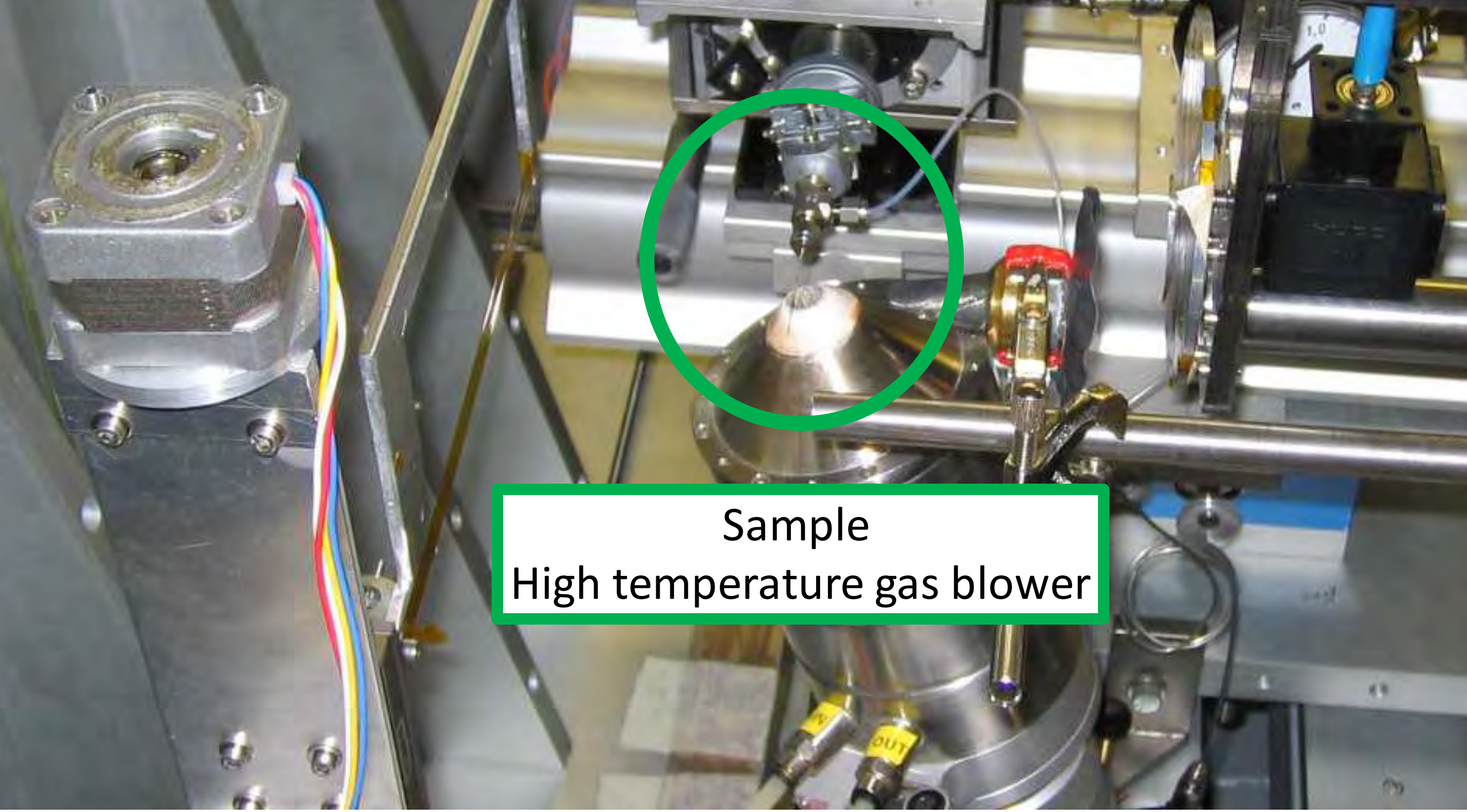
«Hystorical» (2005) beamline setup for HT X-ray powder diffraction @ GILDA beamline (CRG beamline – ESRF, now LISA beamline)


IN
OUT


Monochromatic X-Ray beam

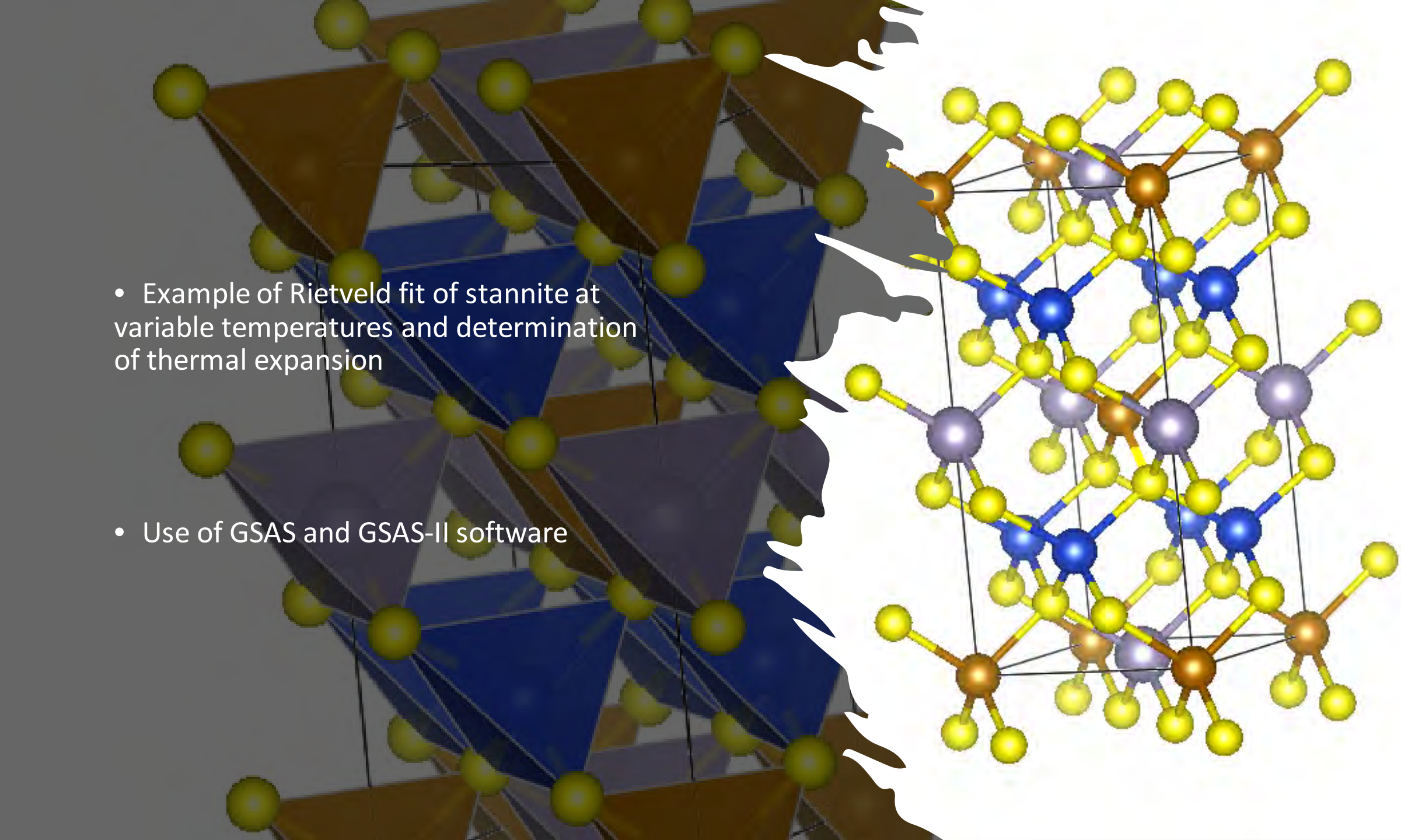


Area detector


Sample
High temperature gas blower

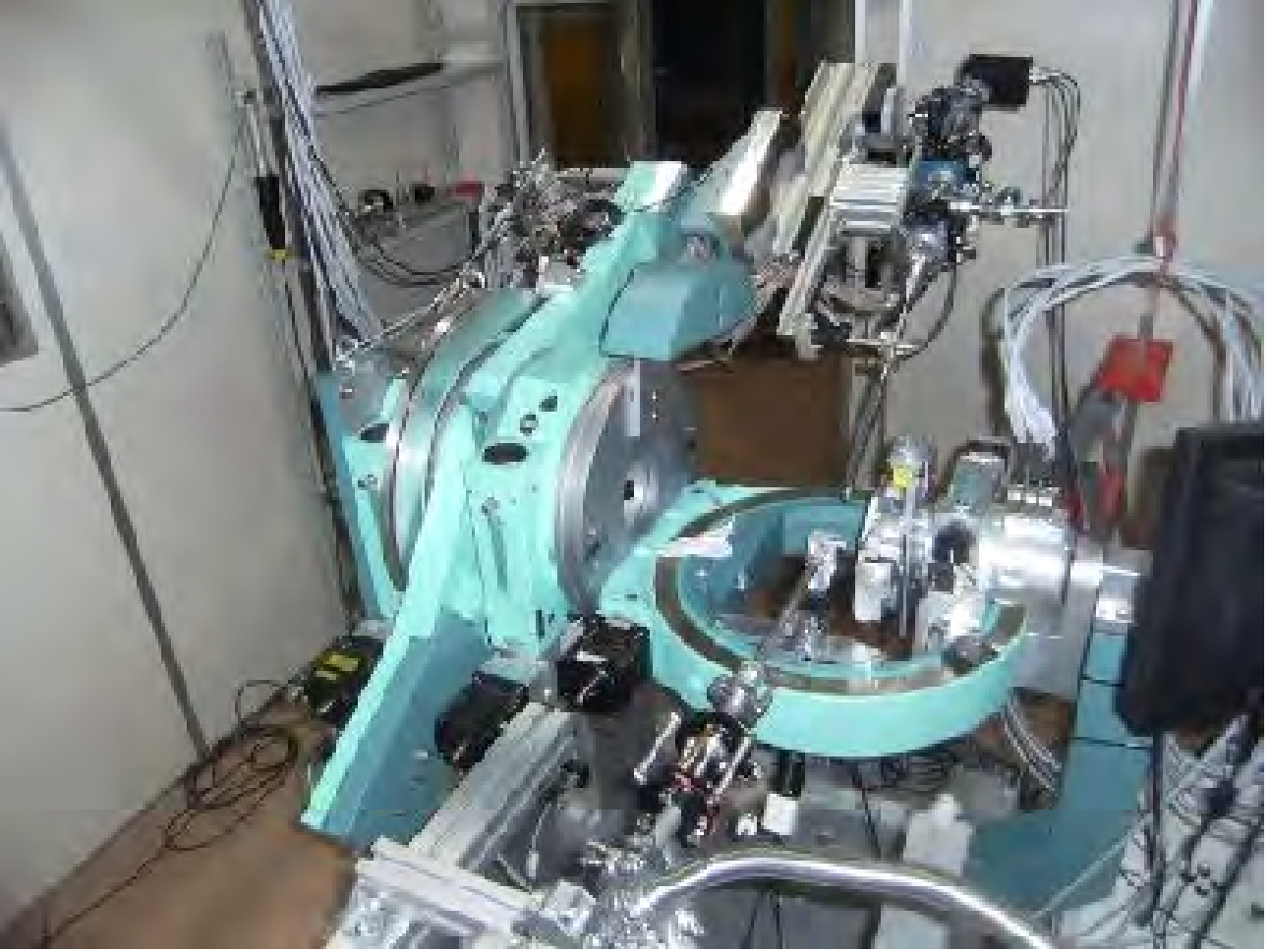
Example: thermal expansion of stannite, Cu_2FeSnS_4

- Ore mineral for tin, together with cassiterite SnO_2
- Important structure in material science together with kesterite, Cu_2ZnSnS_4 (for photovoltaic application)
- In the last decade increase of publication on synthesis of these materials. The knowledge of structural behaviour as function of temperature, chemistry, etc… is relevant for stabilization of phases with specific properties



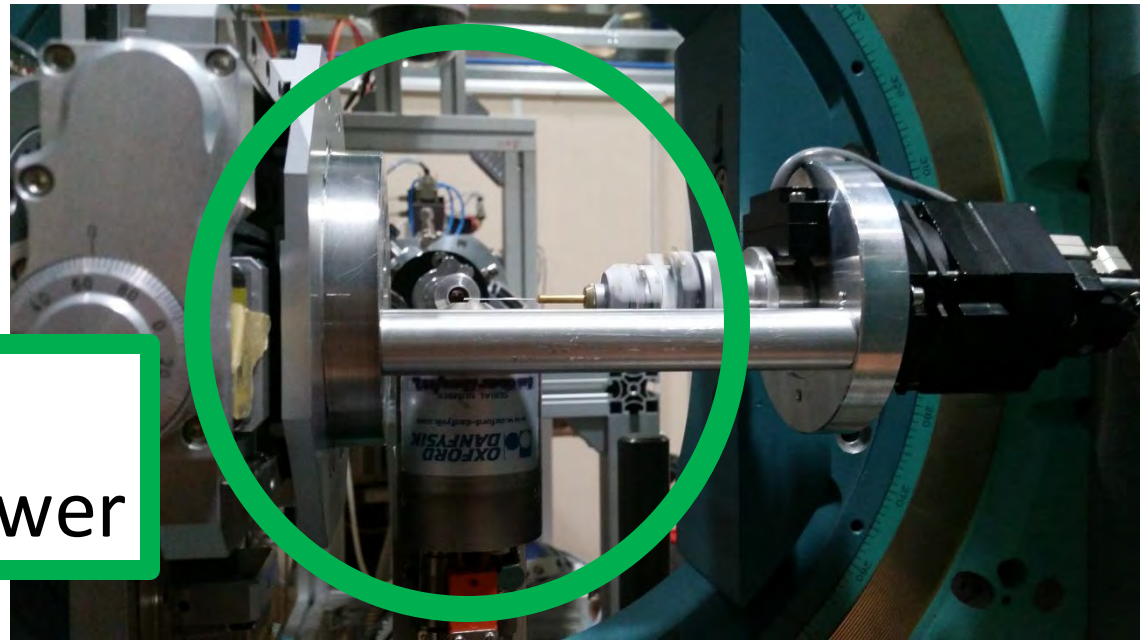
- Example of Rietveld fit of stannite at variable temperatures and determination of thermal expansion

- Use of GSAS and GSAS-II software



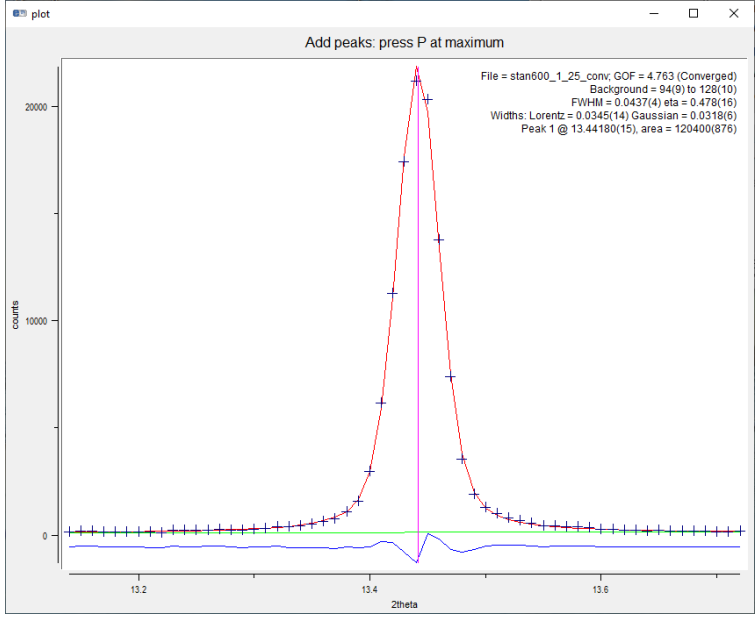
Data collected @ MCX beamline (Elettra)

High resolution powder diffraction

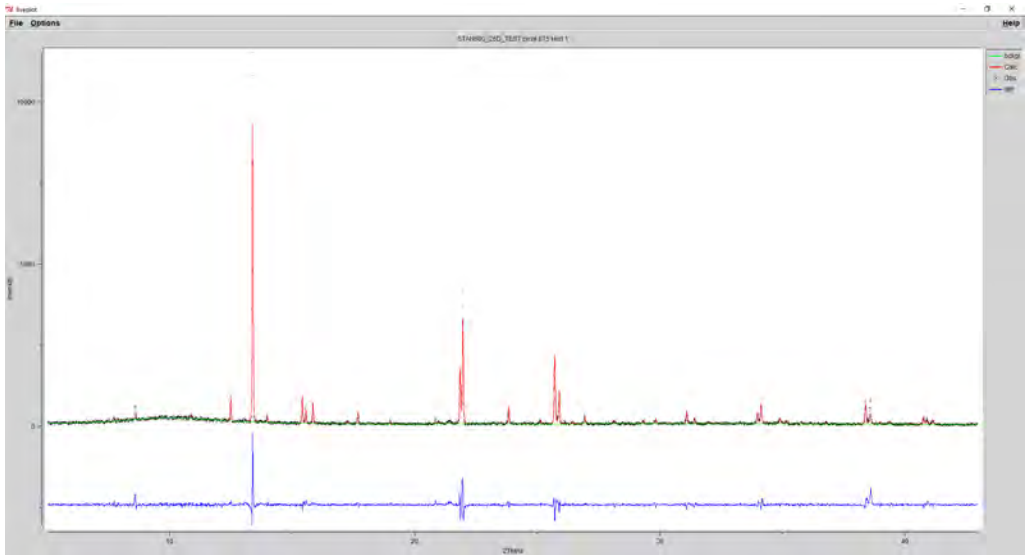


Sample
High temperature gas blower

Single peak fit: fast, useful for preliminary information on unit cell

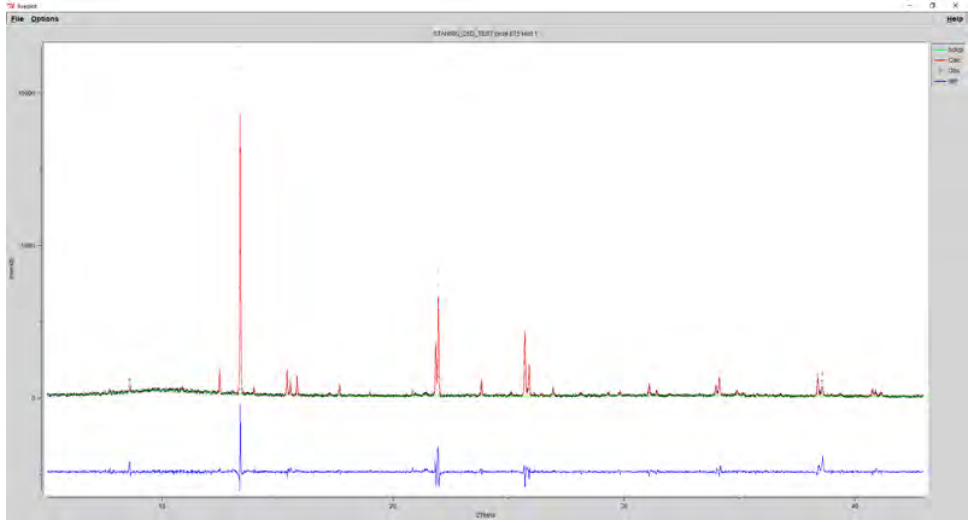


Full profile fit: more accurate lattice parameter determination. It allows also structural and microstructural analysis, quantitative analysis…



Rietveld fit

Rietveld fit



Simulation of powder pattern
Least square minimization on experimental pattern

Refinable parameters:

Unit cell
Scale factor
Crystal structure
Peak shape
Background

Other parameters (i.e. preferred orientation….)

Information needed:

1) Experimental pattern

2) Wavelenght

3) Crystal structure (unit cell, symmetry and atomic coordinates)

(eventually other parameters, i.e. instrumental resolution…)

http://www.minsocam.org/msa/Crystal_Database.html

Mineralogical Society of America, Founded December 30, 1919

The American Mineralogist Crystal Structure Database

The Crystal Structure Database has been compiled by Bob Downs and Paul Heese of the University of Arizona. It includes every structure published in both the American Mineralogist, The Canadian Mineralogist, the European Journal of Mineralogy and is beginning to include structures from Physics and Chemistry of Minerals.

The database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada, and financed by the National Science Foundation.

The data is retrieved via a compound query using pop-up windows with the fields "Mineral Name", "Author", "Title", "Year", or "Volume".

A complete description of the American Mineralogist crystal structure database and use with interactive software is available (pdf, 156 K)

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American Mineralogist Crystal Structure Database

This site is an interface to a crystal structure database that includes every structure published in the American Mineralogist, The Canadian Mineralogist, European Journal of Mineralogy and Physics and Chemistry of Minerals, as well as selected datasets from other journals. The database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada, and financed by the National Science Foundation.

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This material is based upon work supported by the National Science Foundation under Grant Nos. EAR-0112782. and EAR-0622371. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation.

Should the use of the database require a citation, then please use: Downs, R.T. and Hall-Wallace, M. (2003) The American Mineralogist Crystal Structure Database. American Mineralogist 88, 247-250. (pdf file)

Contact Robert T Downs for suggestions and corrections.

Stannite

Bonazzi P, Bindi L, Bernardini G P, Menchetti S

The Canadian Mineralogist 41 (2003) 639-647

A model for the mechanism of incorporation of Cu, Fe and Zn in the stannite - kesterite series, Cu2FeSnS4 - Cu2ZnSnS4

Sample: Fe100

_database_code_amcsd 0005838

5.4495 5.4495 10.726 90 90 90 I-42m

atom	x	y	z	Uiso
Cu(4d)	0	1/2	1/4	.01924
Fe(2a)	0	0	0	.01219
Sn(2b)	0	0	1/2	.01025
S(8i)	.75581	.75581	.87012	.01134

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Download diffraction data (View Text File)

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Unit cell and spacegroup

Stannite

Bonazzi P, Bindi L, Bernardini G P, Menchetti S

The Canadian Mineralogist 41 (2003) 639-647

A model for the mechanism of incorporation of Cu, Fe and Zn in the stannite - kesterite series, Cu2FeSnS4 - Cu2ZnSnS4

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Atomic coordinates

Atomic displacement parameters

Stannite

Bonazzi P, Bindi L, Bernardini G P, Menchetti S

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CIF:
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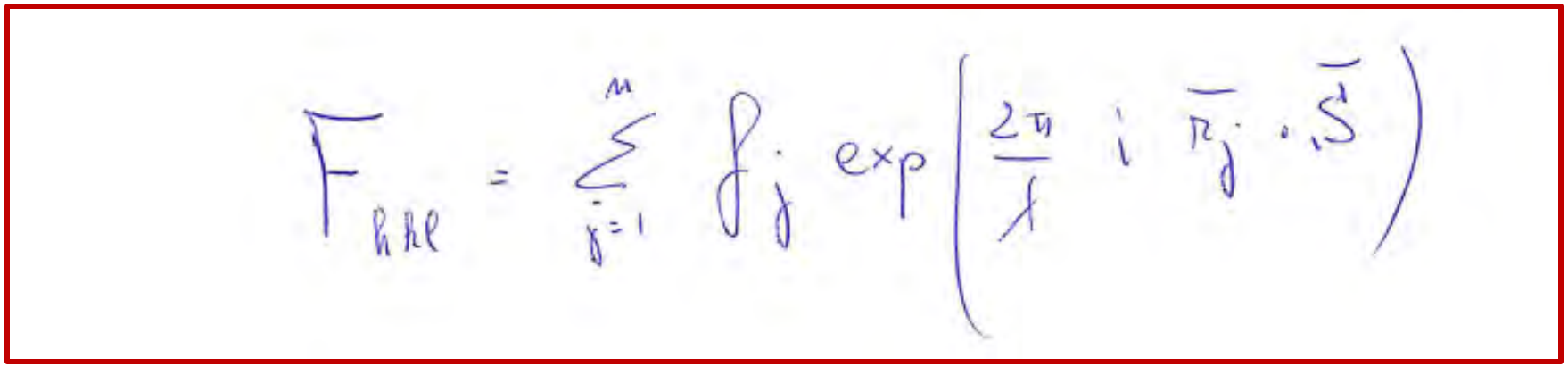
Calculation of powder pattern

$$2d_{hkl}\ \text{sen}\theta = (n)\lambda$$

Bragg's law + structure factor



Calculation of diffraction angle as function of hkl (Miller index) + calculation of intensity of each diffraction

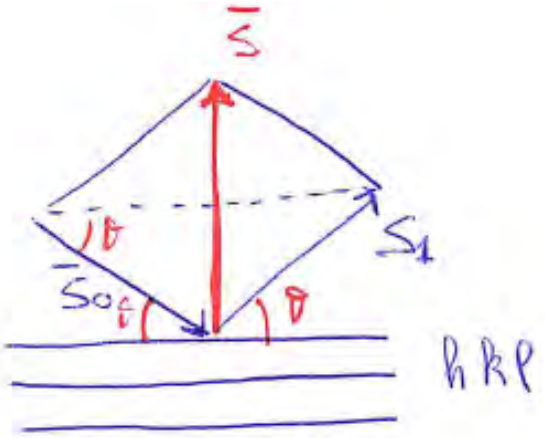
Structure factor

Intensity of diffraction: function of atomic species and structure

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp\left(\frac{2\pi}{\lambda} i \left(\bar{r}_j \cdot \bar{S}\right)\right)$$

fj = atomic scattering factor

rj= atomic position vector (i.e. atomic coordinates)



S = scattering vector (s_1-s_0) s_1: direction of diffracted beam

s_0: direction of primary beam

Peak list

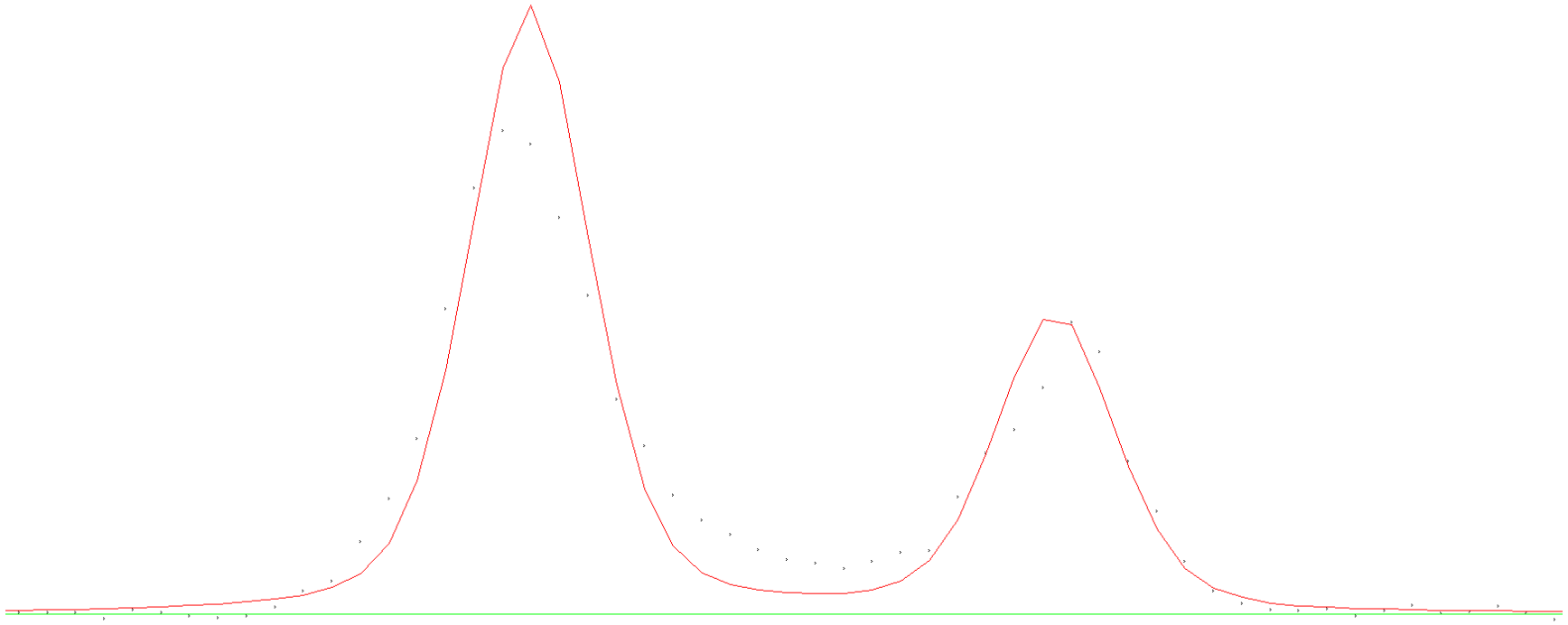
No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	0	0	2			
2	1	0	1			
3	1	1	0			
4	1	1	2			
5	1	0	3			
6	2	0	0			
7	0	0	4			
8	2	0	2			
9	2	1	1			
10	1	1	4			
11	2	1	3			
12	1	0	5			
13	2	2	0			
14	2	0	4			
15	2	2	2			
16	3	0	1			
17	3	1	2			
18	1	1	6			
19	2	2	4			
20	3	2	1			
21	3	1	4			
22	4	0	0			
23	0	0	8			
24	2	2	6			
25	3	3	2			
26	3	1	6			
27	4	0	4			
28	2	0	8			
29	4	2	4			
30	2	2	8			

Peak list

No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	0	0	2	5.36700	7.788	
2	1	0	1	4.85700	8.608	
3	1	1	0	3.85200	10.860	
4	1	1	2	3.12900	13.379	
5	1	0	3	2.99000	14.004	
6	2	0	0	2.72400	15.380	
7	0	0	4	2.68300	15.616	
8	2	0	2	2.42900	17.261	
9	2	1	1	2.37640	17.646	
10	1	1	4	2.20220	19.054	
11	2	1	3	2.01380	20.856	
12	1	0	5	1.99800	21.023	
13	2	2	0	1.92580	21.821	
14	2	0	4	1.91240	21.975	
15	2	2	2	1.81360	23.189	
16	3	0	1	1.79130	23.481	
17	3	1	2	1.64090	25.669	
18	1	1	6	1.62320	25.954	
19	2	2	4	1.56520	26.933	
20	3	2	1	1.49620	28.200	
21	3	1	4	1.45030	29.112	
22	4	0	0	1.36250	31.034	
23	0	0	8	1.34220	31.515	
24	2	2	6	1.31140	32.275	
25	3	3	2	1.24930	33.927	
26	3	1	6	1.24150	34.147	
27	4	0	4	1.21500	34.915	
28	2	0	8	1.20440	35.233	
29	4	2	4	1.10990	38.344	
30	2	2	8	1.10170	38.641	

Peak list

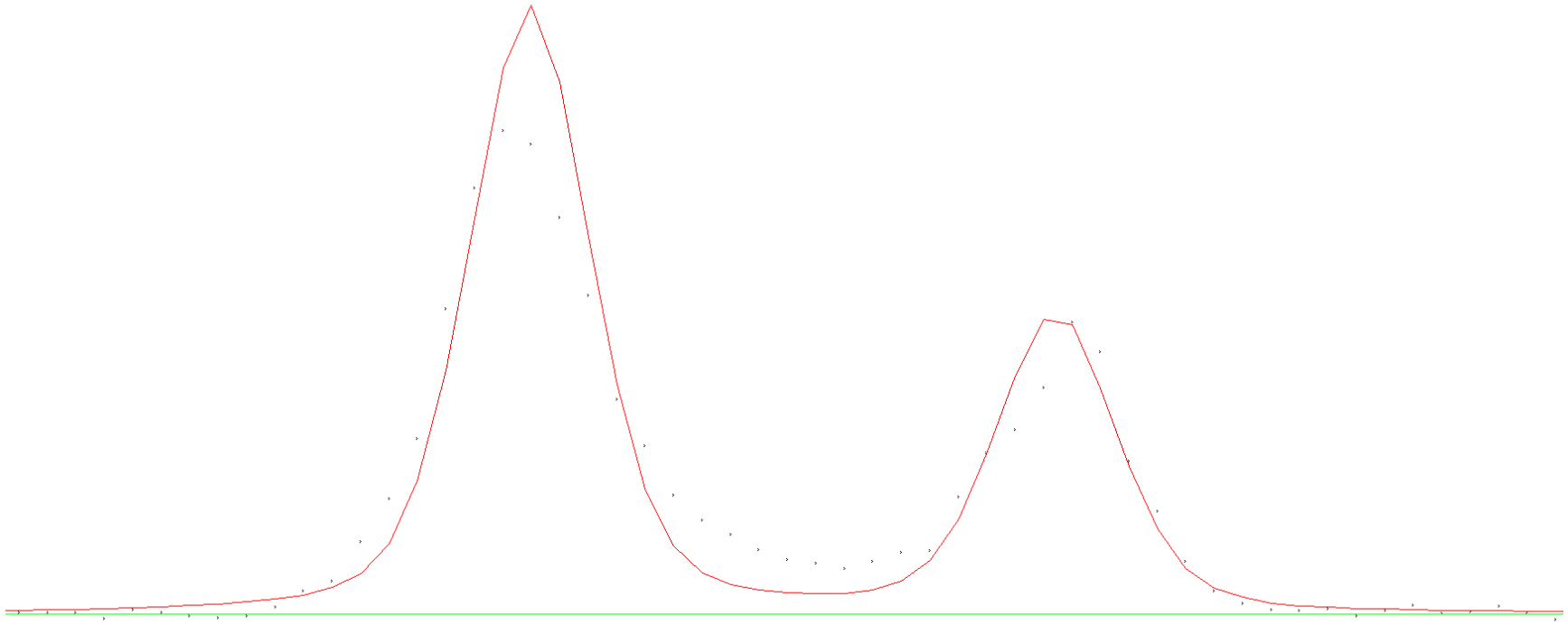
No.	h	k	l	d [A]	2Theta[deg]	I [%]
1	0	0	2	5.36700	7.788	2.0
2	1	0	1	4.85700	8.608	3.0
3	1	1	0	3.85200	10.860	2.0
4	1	1	2	3.12900	13.379	100.0
5	1	0	3	2.99000	14.004	1.0
6	2	0	0	2.72400	15.380	6.0
7	0	0	4	2.68300	15.616	4.0
8	2	0	2	2.42900	17.261	2.0
9	2	1	1	2.37640	17.646	2.0
10	1	1	4	2.20220	19.054	1.0
11	2	1	3	2.01380	20.856	1.0
12	1	0	5	1.99800	21.023	1.0
13	2	2	0	1.92580	21.821	15.0
14	2	0	4	1.91240	21.975	27.0
15	2	2	2	1.81360	23.189	1.0
16	3	0	1	1.79130	23.481	1.0
17	3	1	2	1.64090	25.669	13.0
18	1	1	6	1.62320	25.954	7.0
19	2	2	4	1.56520	26.933	2.0
20	3	2	1	1.49620	28.200	1.0
21	3	1	4	1.45030	29.112	1.0
22	4	0	0	1.36250	31.034	2.0
23	0	0	8	1.34220	31.515	1.0
24	2	2	6	1.31140	32.275	1.0
25	3	3	2	1.24930	33.927	2.0
26	3	1	6	1.24150	34.147	3.0
27	4	0	4	1.21500	34.915	1.0
28	2	0	8	1.20440	35.233	1.0
29	4	2	4	1.10990	38.344	3.0
30	2	2	8	1.10170	38.641	2.0



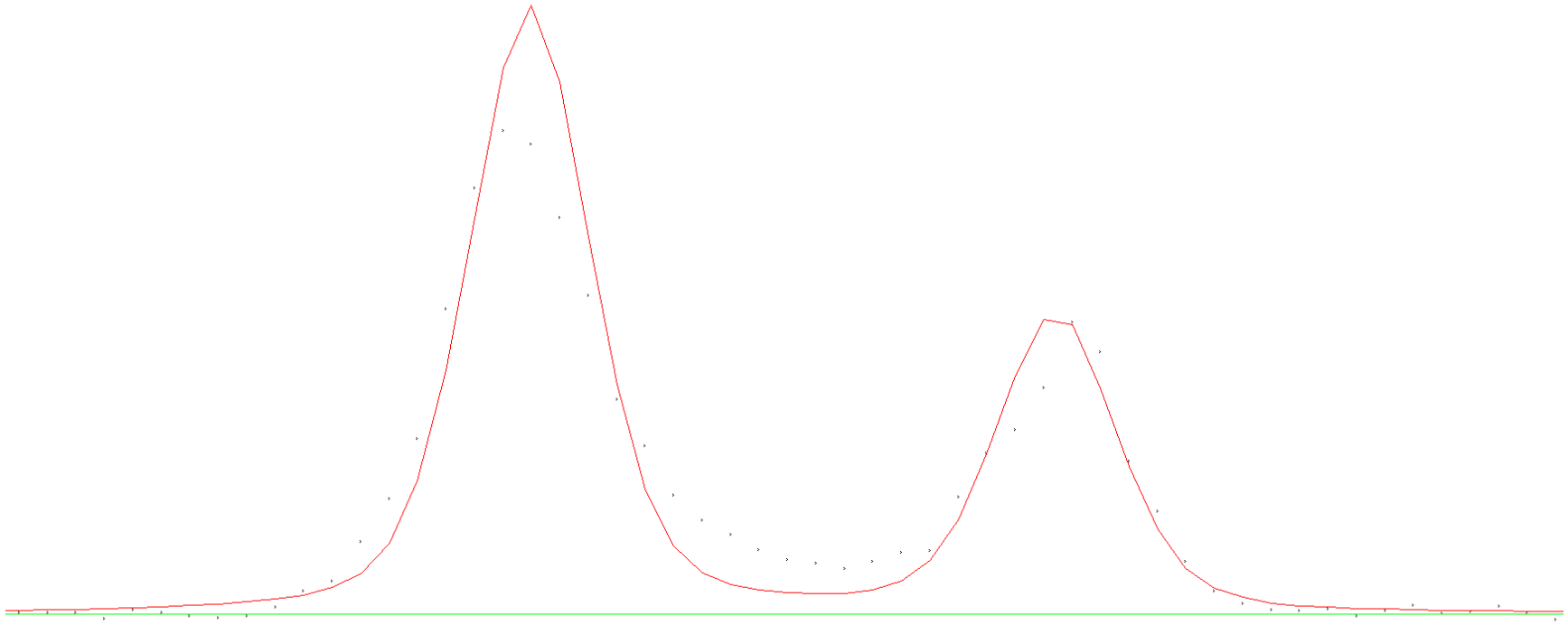
Simulation of diffraction:

Sum of simulated peaks

Peak position (bragg’s law) + peak scale factor (Structure factor) + peak shape



Peak position: bragg’s law

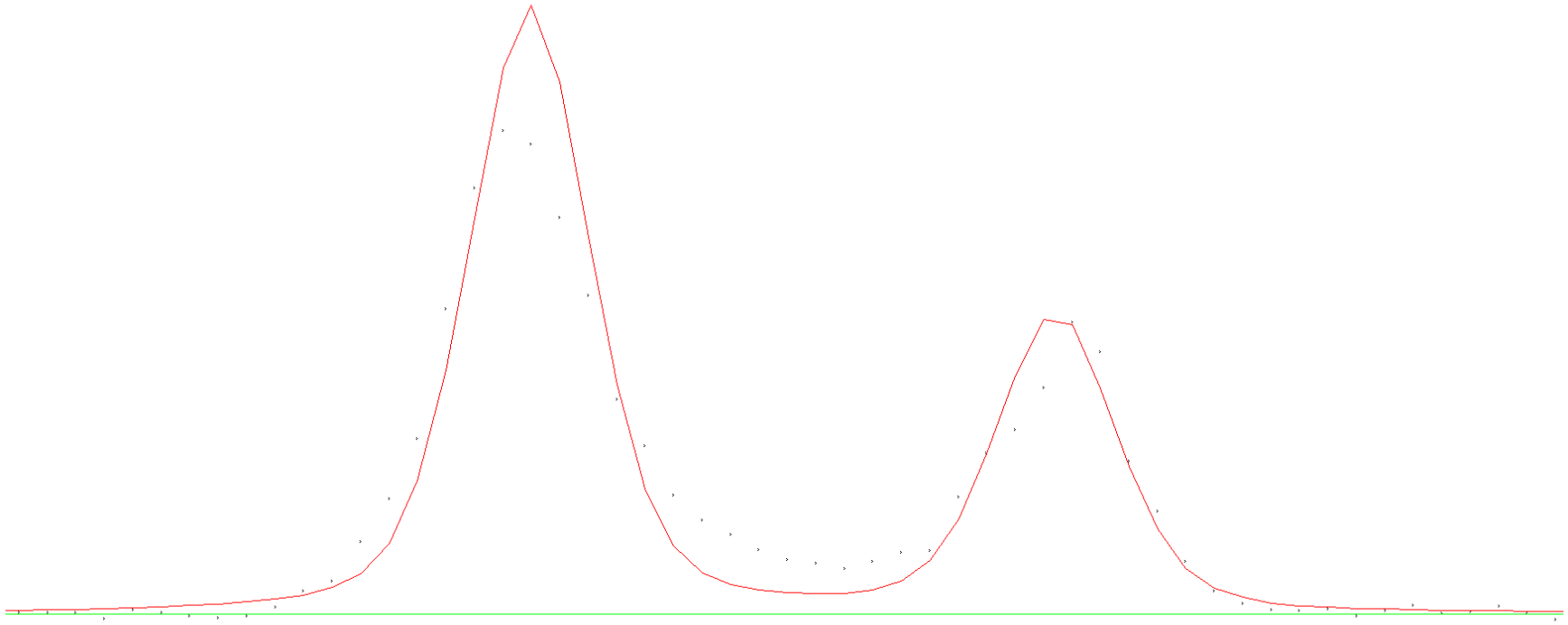


Scale factor (proportional to squared structure factor)

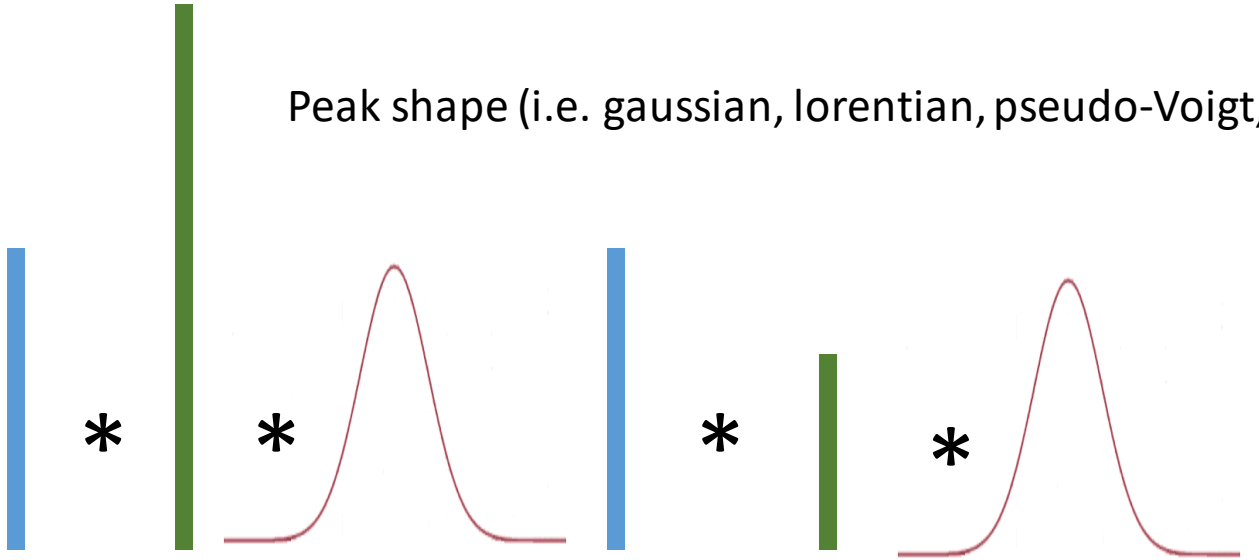
Peak position: bragg’s law

h1 k1 l1

h2 k2 l2

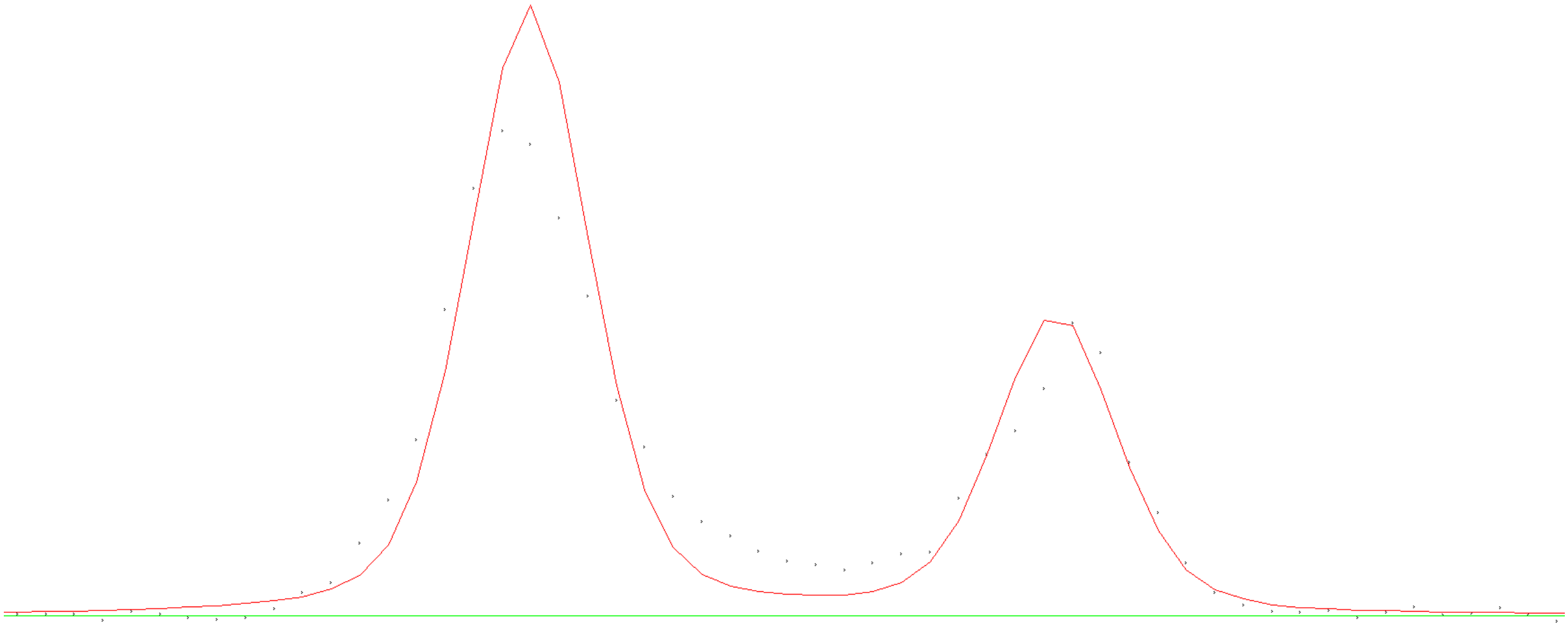


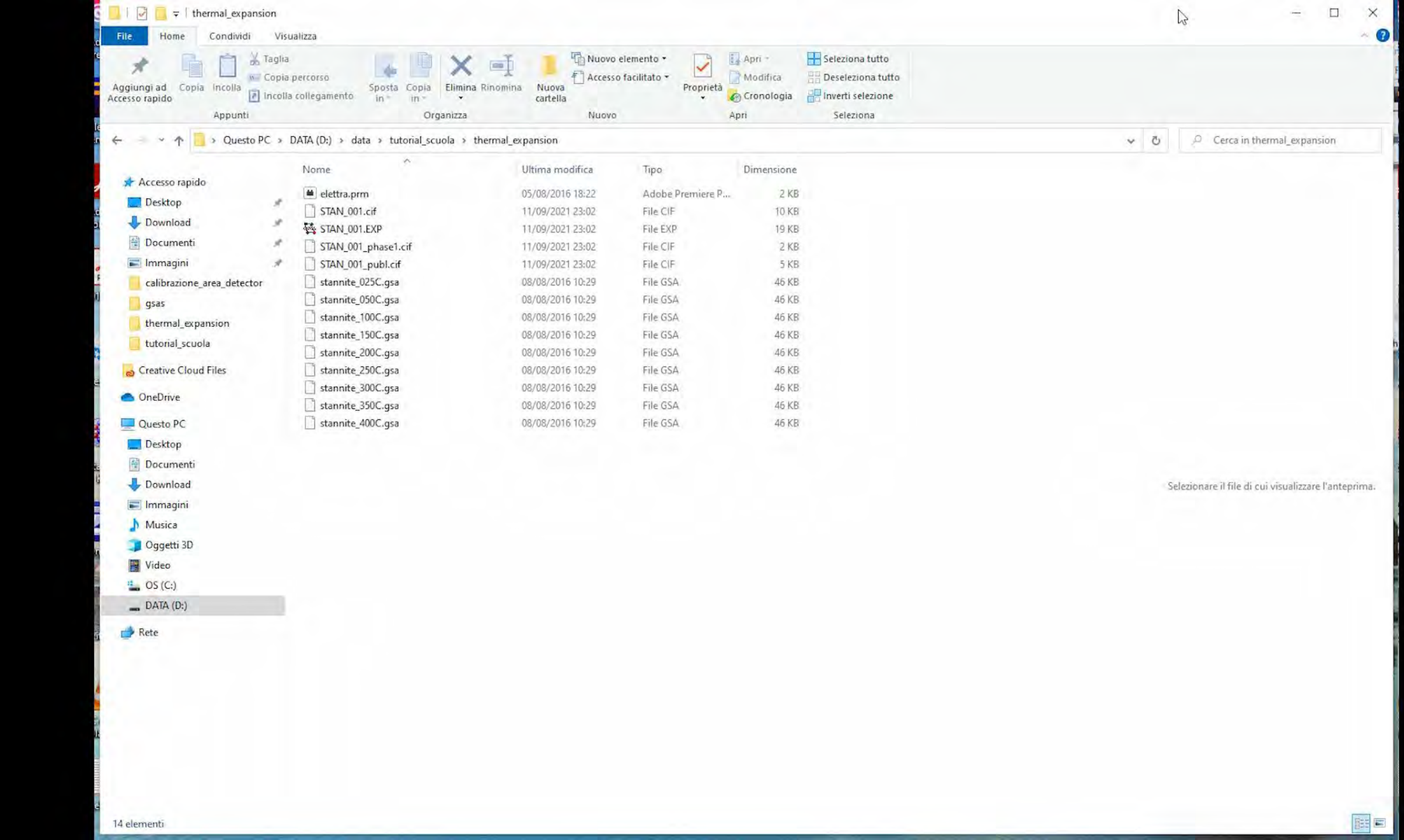
Peak shape (i.e. gaussian, lorentian, pseudo-Voigt, etc…)



h1 k1 l1

h2 k2 l2

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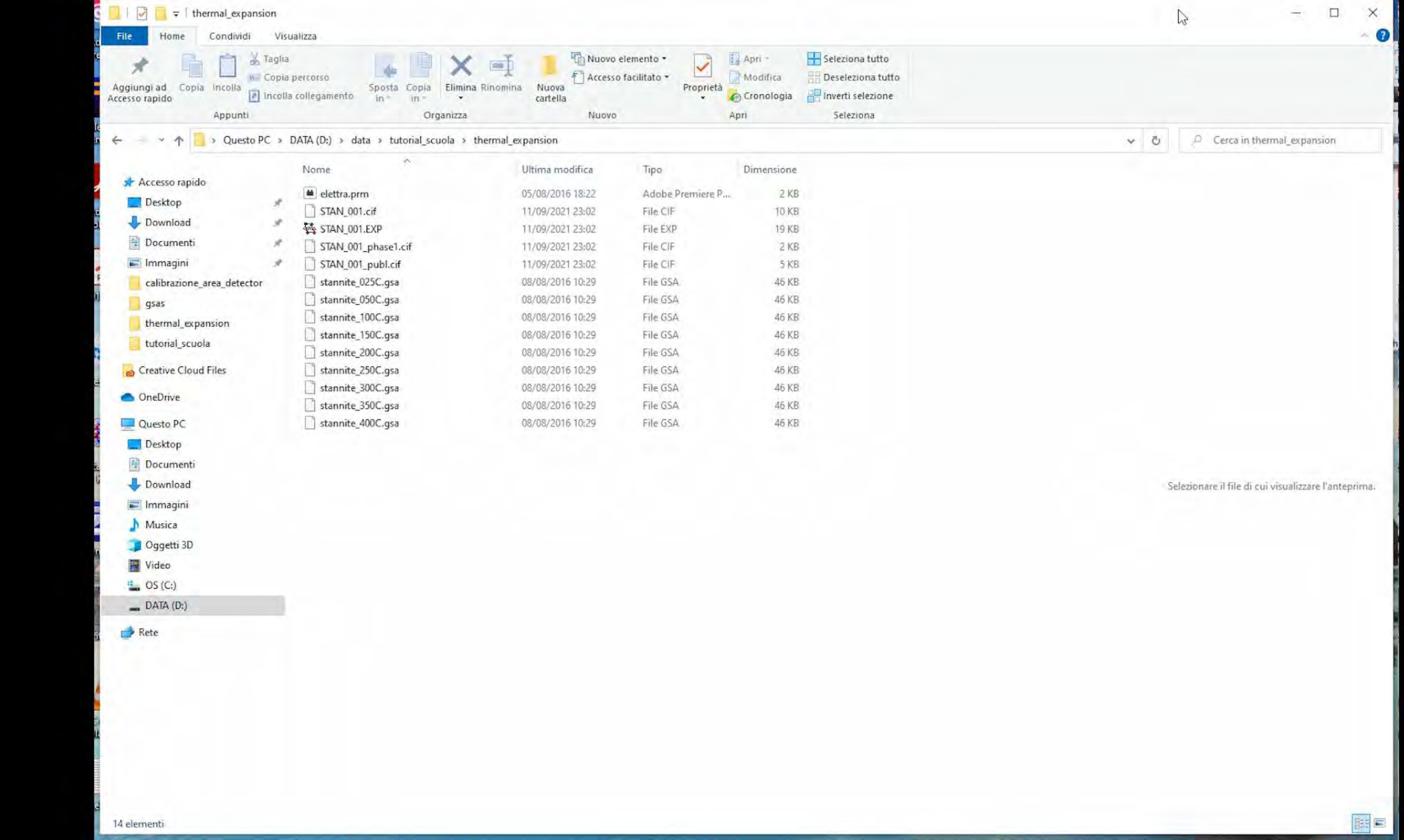
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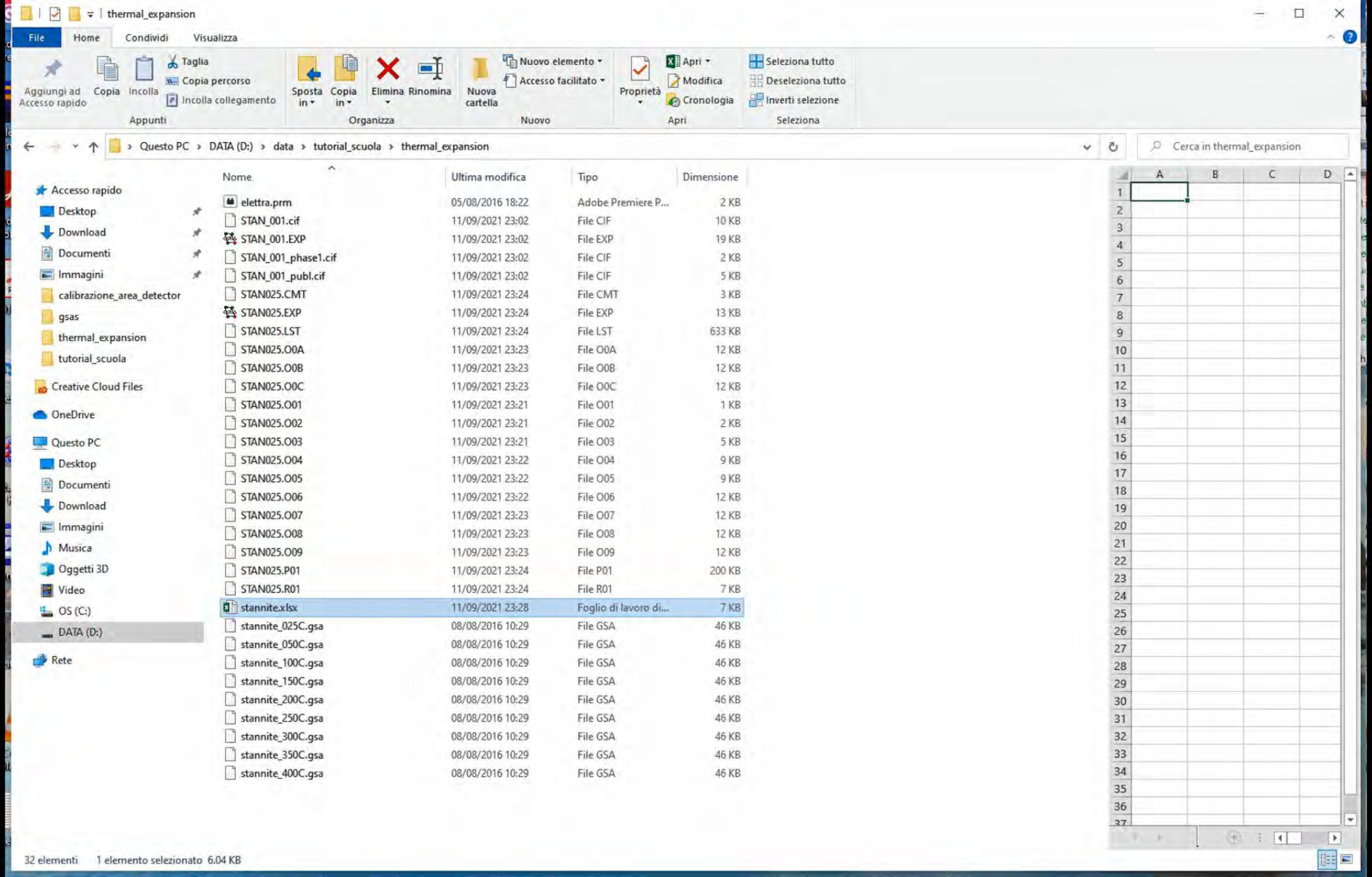
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stannite_350C.gsa 08/08/2016 10:29 File GSA 46 KB
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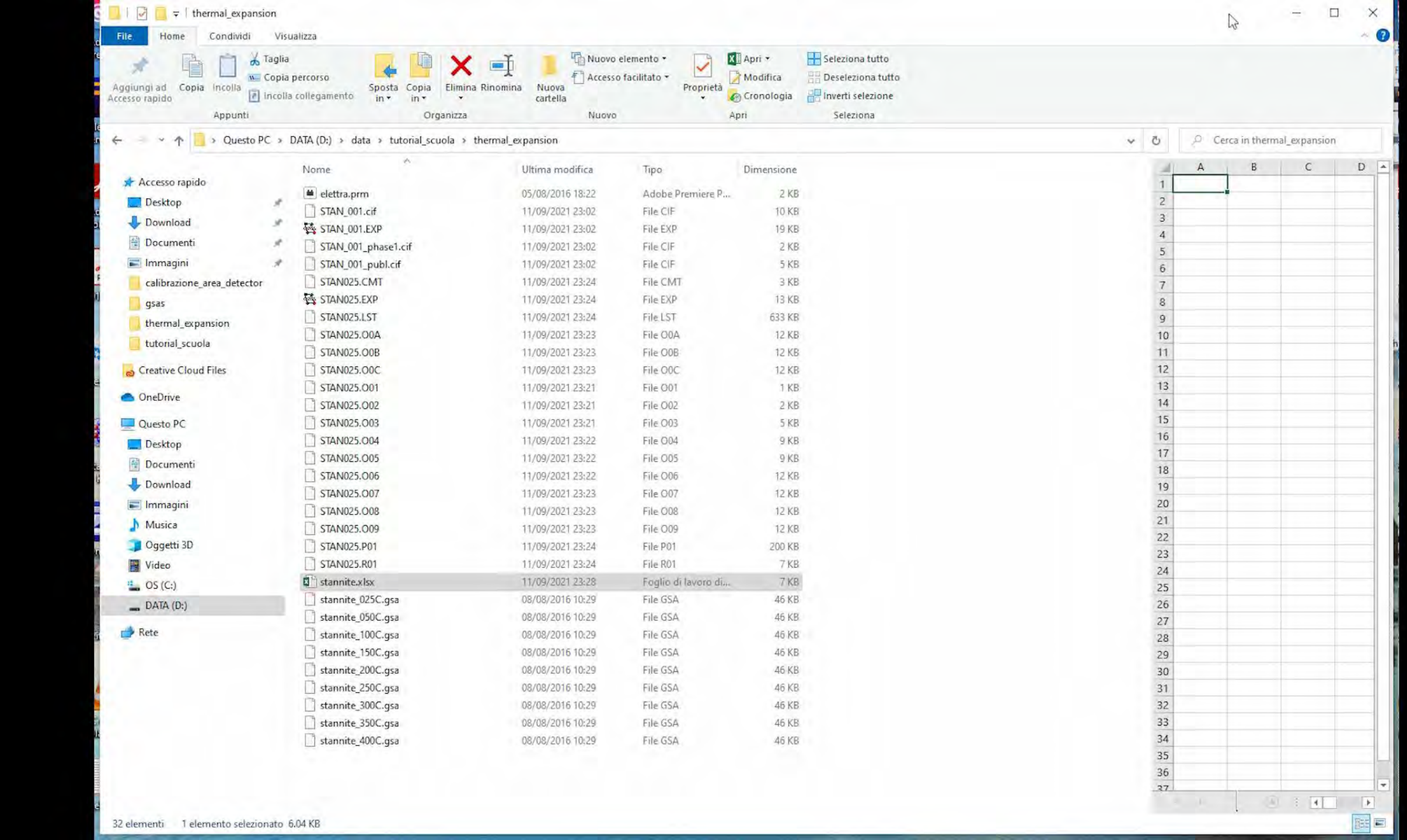
A B C D
32 elementi 1 elemento selezionato 6.04 KB


thermal_expansion
File
Home
Condividi
Visualizza
Aggiungi ad Accesso rapido
Copia
Incolla
Taglia
Copia percorso
Incolla collegamento
Appunti
Sposta in
Copia in
Elimina
Rinomina
Nuova cartella
Organizza
Nuovo elemento
Accesso facilitato
Nuovo
Proprietà
Apri
Modifica
Cronologia
Apri
Seleziona tutto
Deseleziona tutto
Inverti selezione
Seleziona
Questo PC › DATA (D:) › data › tutorial_scuola › thermal_expansion
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OS (C:)
DATA (D:)
Rete
Nome
Ultima modifica
Tipo
Dimensione
elettra.prm 05/08/2016 18:22 Adobe Premiere P... 2 KB
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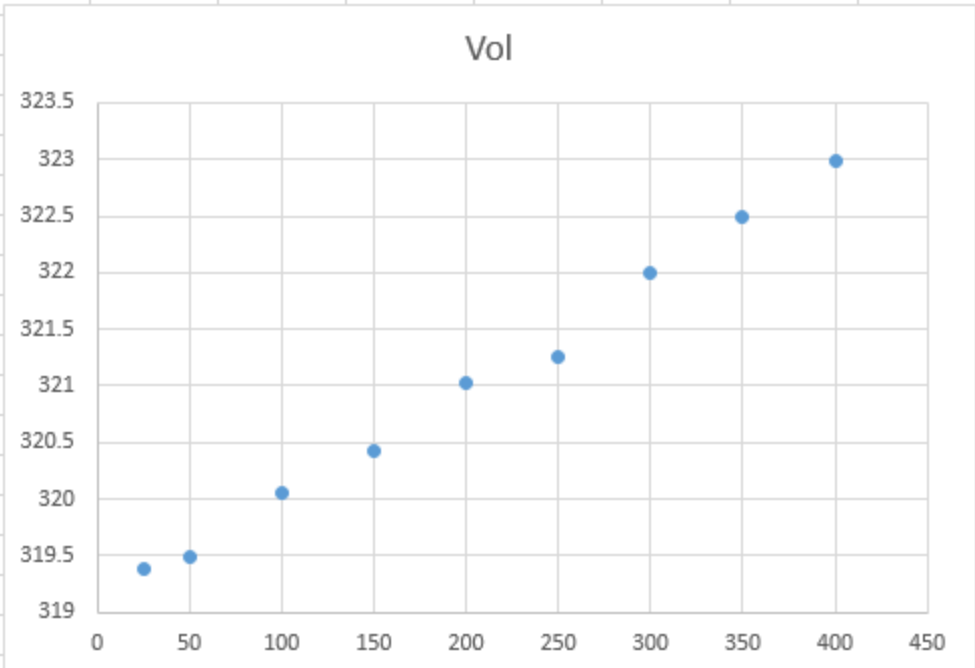
stannite_350C.gsa 08/08/2016 10:29 File GSA 46 KB
stannite_400C.gsa 08/08/2016 10:29 File GSA 46 KB
32 elementi
1 elemento selezionato 6.04 KB
A
B
C
D

	A	B	C	D	E
1	T (°C)	a	c	Vol	ln (vol)
2	25	5.454544	10.73457	319.3754	5.766367
3	50	5.454919	10.73675	319.4844	5.766708
4	100	5.457446	10.74581	320.0501	5.768478
5	150	5.458938	10.75228	320.4179	5.769626
6	200	5.461257	10.76374	321.0322	5.771541
7	250	5.461492	10.77052	321.2618	5.772257
8	300	5.46261	10.79057	321.9918	5.774526
9	350	5.460221	10.81703	322.4992	5.776101
10	400	5.454249	10.85706	322.9848	5.777605



$$\alpha = 1/V\,(\partial V/\partial T) = \partial \ln V/\partial T$$

Linear thermal expansion: $\alpha = 30.4*10^{-6}\ (K^{-1})$

	A	B	C	D	E
1	T (°C)	a	c	Vol	ln (vol)
2	25	5.454544	10.73457	319.3754	5.766367
3	50	5.454919	10.73675	319.4844	5.766708
4	100	5.457446	10.74581	320.0501	5.768478
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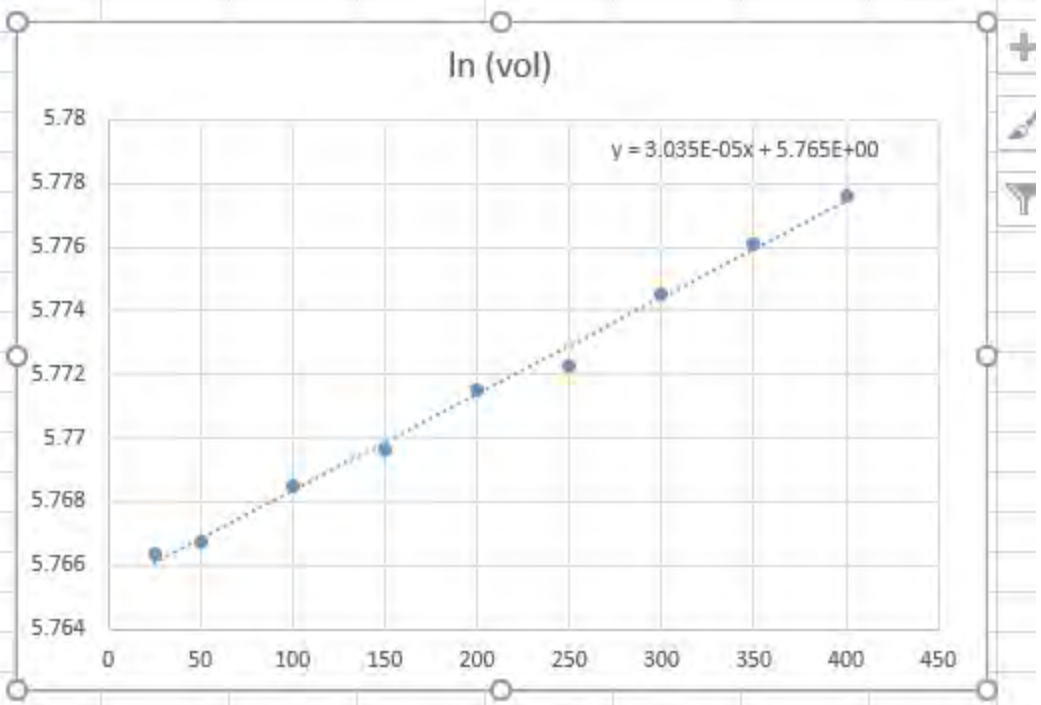
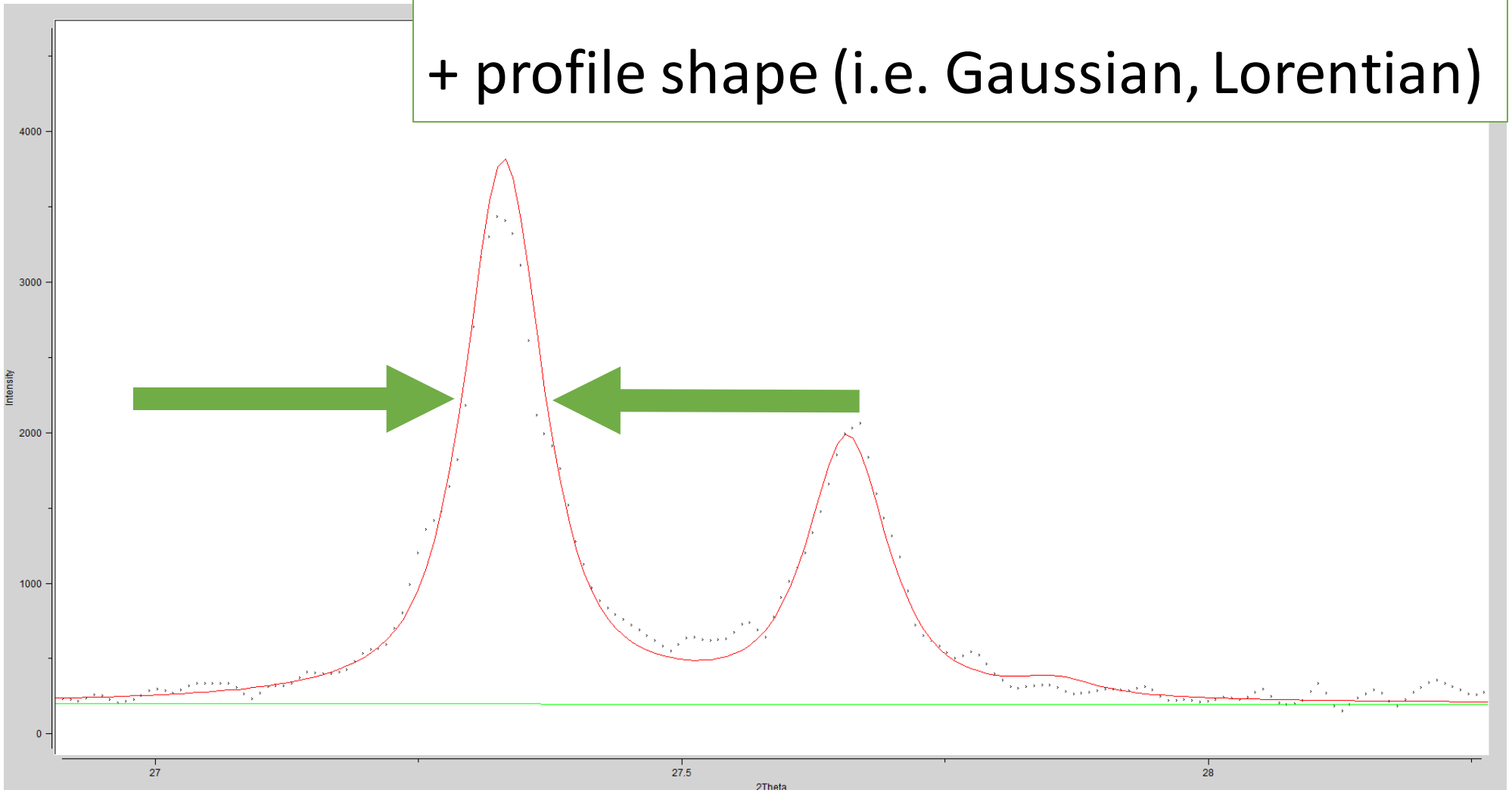
10	400	5.454249	10.85706	322.9848	5.777605



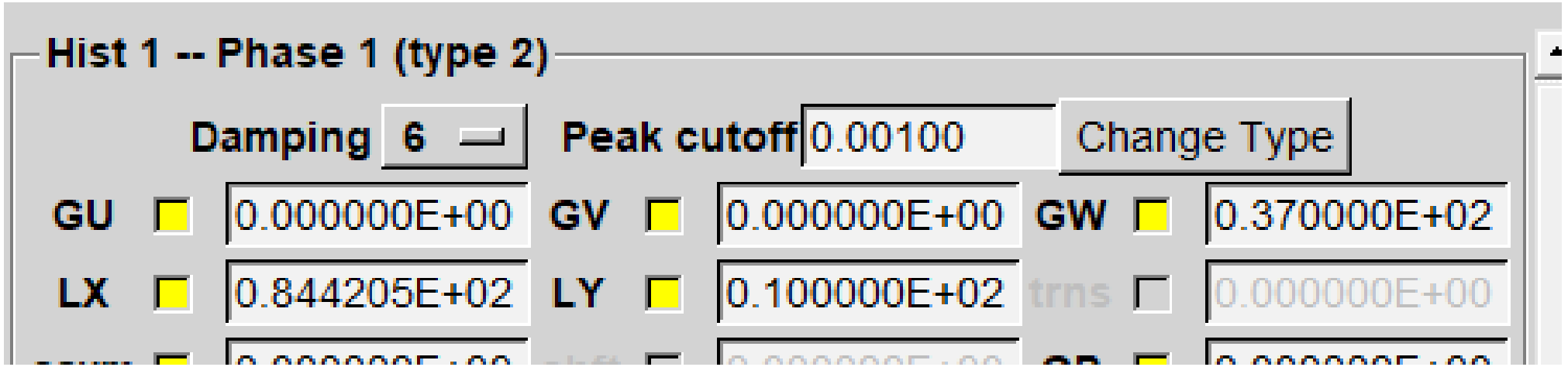
Peak profile

FWHM (Full width at Half Maximum)

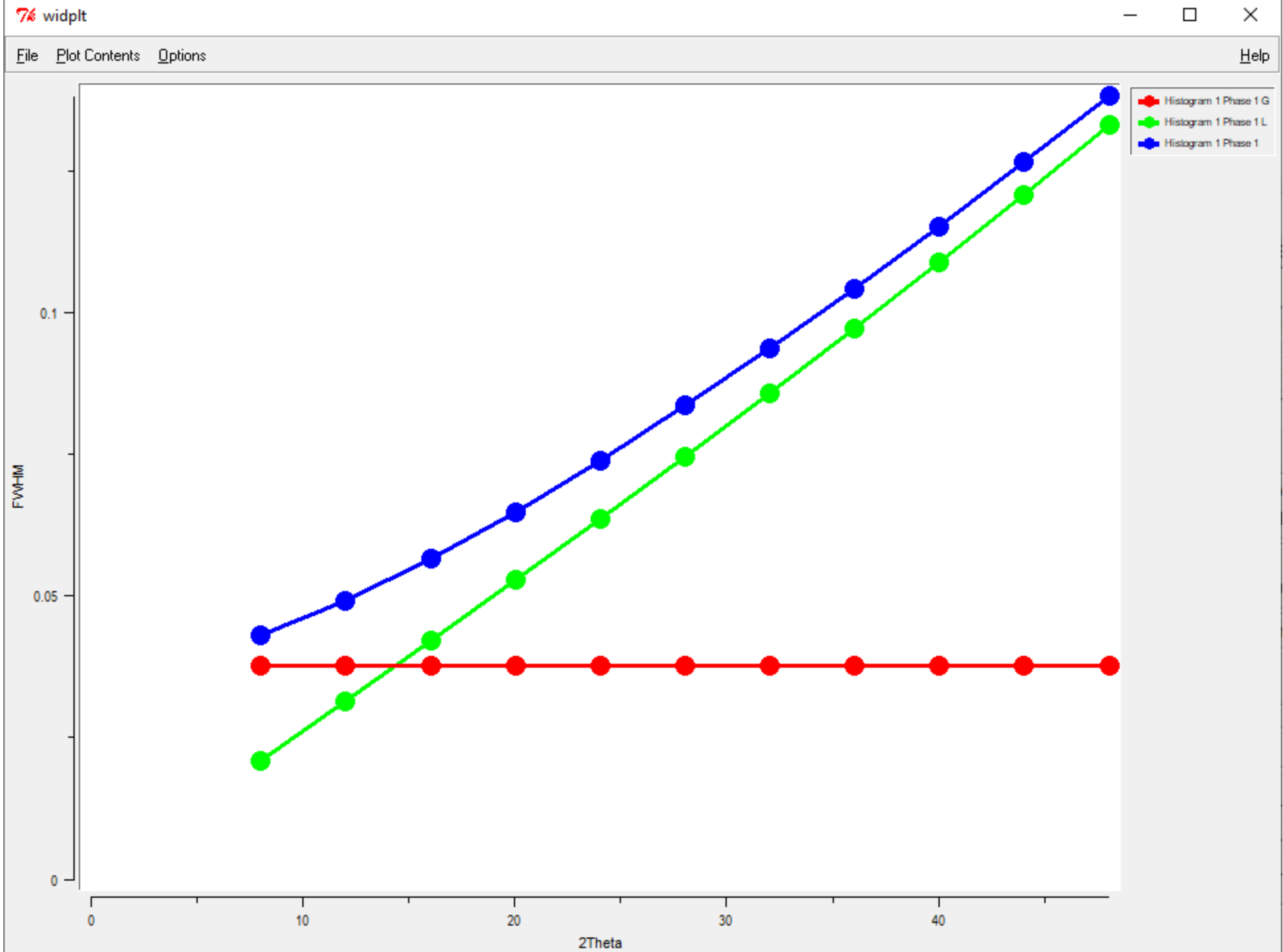
+ profile shape (i.e. Gaussian, Lorentian)

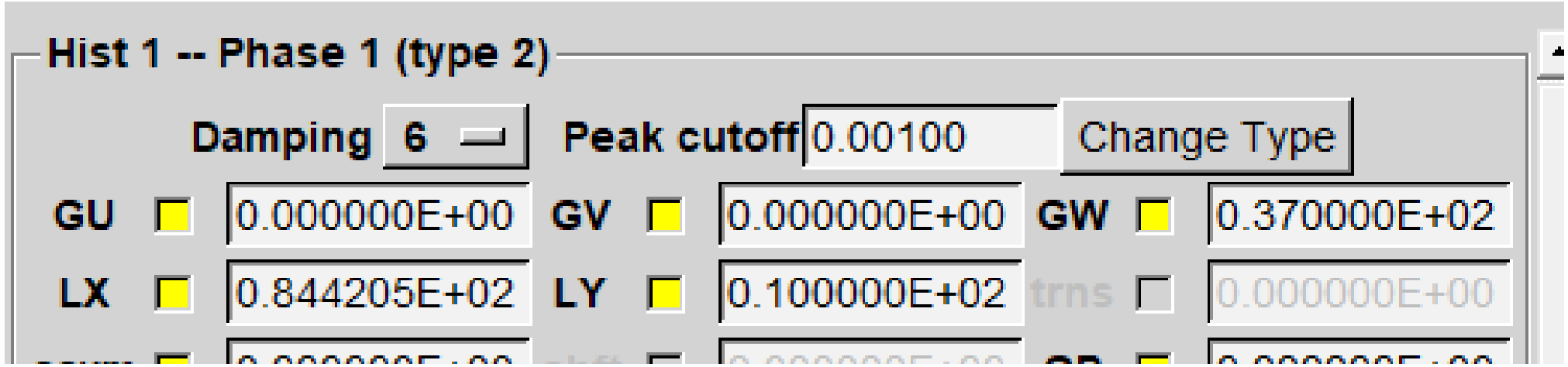


Pseudo-Voigt: Gaussian (G) +Lorentian (L)



GU, GV, GW and LX, LY describe the variation of FWHM of a Gaussian and a Lorentian as function of 2theta angle


widplt
File
Plot Contents
Options
Help
Histogram 1 Phase 1 G
Histogram 1 Phase 1 L
Histogram 1 Phase 1
FWHM
0.1
0.05
0
0
10
20
30
40
2Theta


Hist 1 -- Phase 1 (type 2)
Damping
6
Peak cutoff
0.00100
Change Type
GU
0.000000E+00
GV
0.000000E+00
GW
0.370000E+02
LX
0.844205E+02
LY
0.100000E+02
trns
0.000000E+00

From GSAS manual

The variance of the peak, σ_2, varies with 2Θ as

$$\sigma^2 = U\,tan^2\,\Theta + V\,tan\,\Theta + W + P/cos^2\,\Theta$$

where U, V and W are the coefficients described by Cagliotti, Pauletti and Ricci in 1958 (Nucl. Instrum.,**3**, 223) and P is the Scherrer coefficient for Gaussian broadening. The Lorentzian coefficient, γ, varies as

$$\gamma = \frac{X + X_e\,cos\,\phi}{cos\,\Theta} + \left(Y + Y_e\,cos\,\phi + \gamma_L d^2\right)tan\,\Theta$$

The first term is the Lorentzian Scherrer broadening and includes an anisotropy coefficient, X_e. The second term describes strain broadening and also includes an anisotropy coefficient. If a sublattice is defined by use of "stacking fault vectors", then

Example: estimation of crystallite size in cubic ZrO2 (nominally 5 nm by TEM)

- Determination of experimental broadening using a standard (i.e. LaB6, Silicon)

- Profile fitting of ZrO2 (using GSAS-II software, which has implemented the deconvolution of sample broadening from instrumental broadening)

GSAS-II project: test_silicon.gpx

File Data Calculate Import Export | Operations | Help

- Project: D:\data\tutorial_scuola\
  - Notebook
  - Controls
  - Covariance
  - Constraints
  - Restraints
  - Rigid bodies
  - Phases
    - Silicon
  - PWDR silicon3.gsa Bank 1
    - Comments
    - Limits
    - Background
    - Instrument Parameters
    - Sample Parameters
    - Peak List
    - Index Peak List
    - Unit Cells List
    - Reflection Lists

Histogram Type: PXC Bank: 1

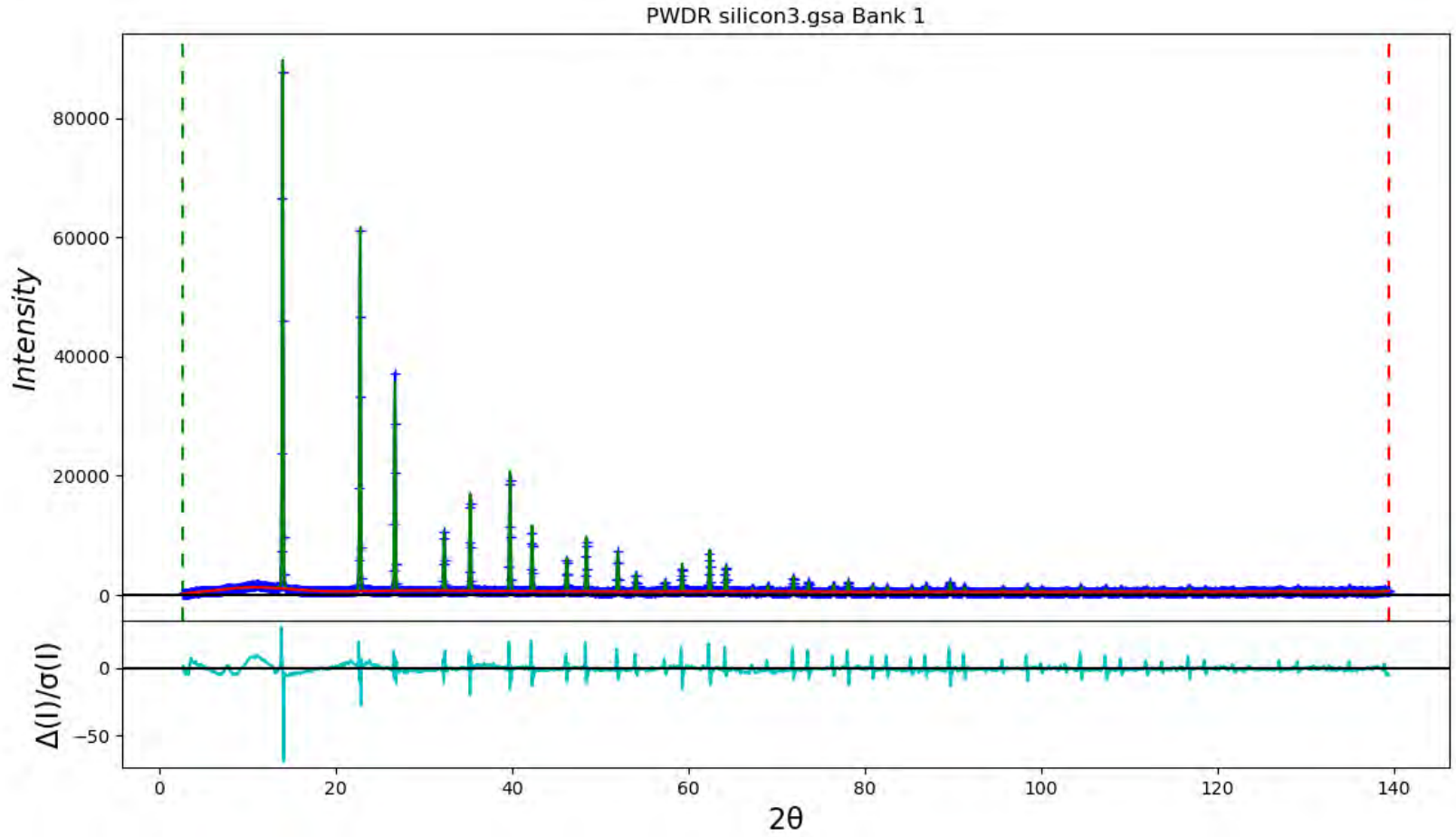
Name (default)	Value	Refine?
Azimuth:	0.00	
Lam (Å): (0.729320)	0.747631	☑
Zero (0.0000):	0.259	☑
Polariz. (0.9600):	0.96	☐
U (0.000):	0.0	☐
V (0.000):	0.0	☐
W (5.402):	33.843	☑
X (0.000):	0.0	☐
Y (0.000):	0.0	☐
Z (0.000):	0.0	☐
SH/L (0.00200):	0.002	☐

Mouse RB drag/drop to reorder

NB: Azimuth is used for polarization only

GSAS-II plots: test_silicon.gpx

Peak Widths | Powder Patterns



zoom rect

2-theta = 7.738 d= 5.73164 Q= 1.09623 Intensity = -44.89

GSAS-II project: test_silicon.gpx

File Data Calculate Import Export | Operations | Help

- Project: D:\data\tutorial_scuola\
  - Notebook
  - Controls
  - Covariance
  - Constraints
  - Restraints
  - Rigid bodies
  - Phases
    - Silicon
  - PWDR silicon3.gsa Bank 1
    - Comments
    - Limits
    - Background
    - Instrument Parameters
    - Sample Parameters
    - Peak List
    - Index Peak List
    - Unit Cells List
    - Reflection Lists

Histogram Type: PXC Bank: 1

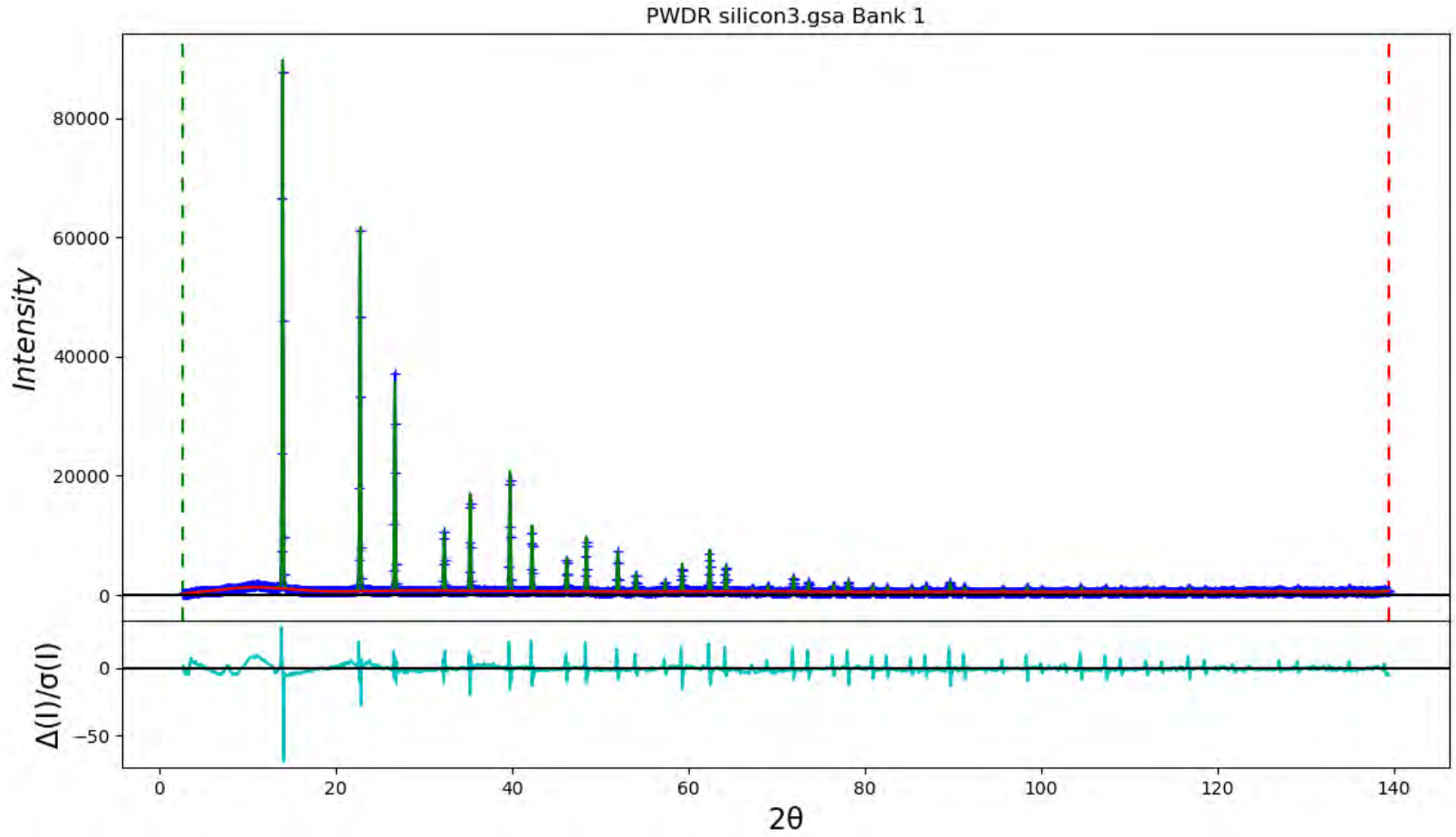
Name (default)	Value	Refine?
Azimuth:	0.00	
Lam (Å): (0.729320)	0.747631	☑
Zero (0.0000):	0.259	☑
Polariz. (0.9600):	0.96	☐
U (0.000):	0.0	☐
V (0.000):	0.0	☐
W (5.402):	33.843	☑
X (0.000):	0.0	☐
Y (0.000):	0.0	☐
Z (0.000):	0.0	☐
SH/L (0.00200):	0.002	☐

Mouse RB drag/drop to reorder

NB: Azimuth is used for polarization only

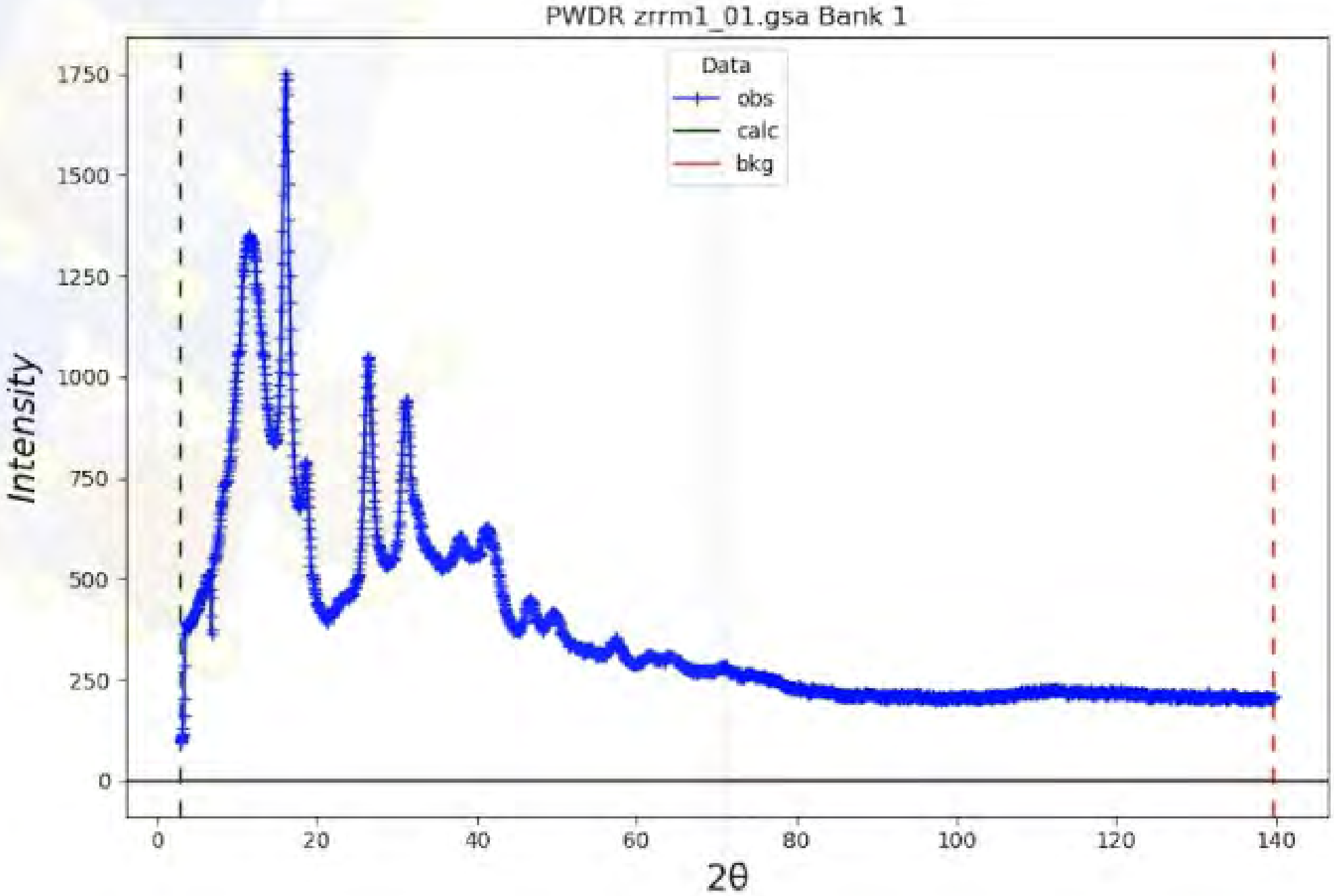
GSAS-II plots: test_silicon.gpx

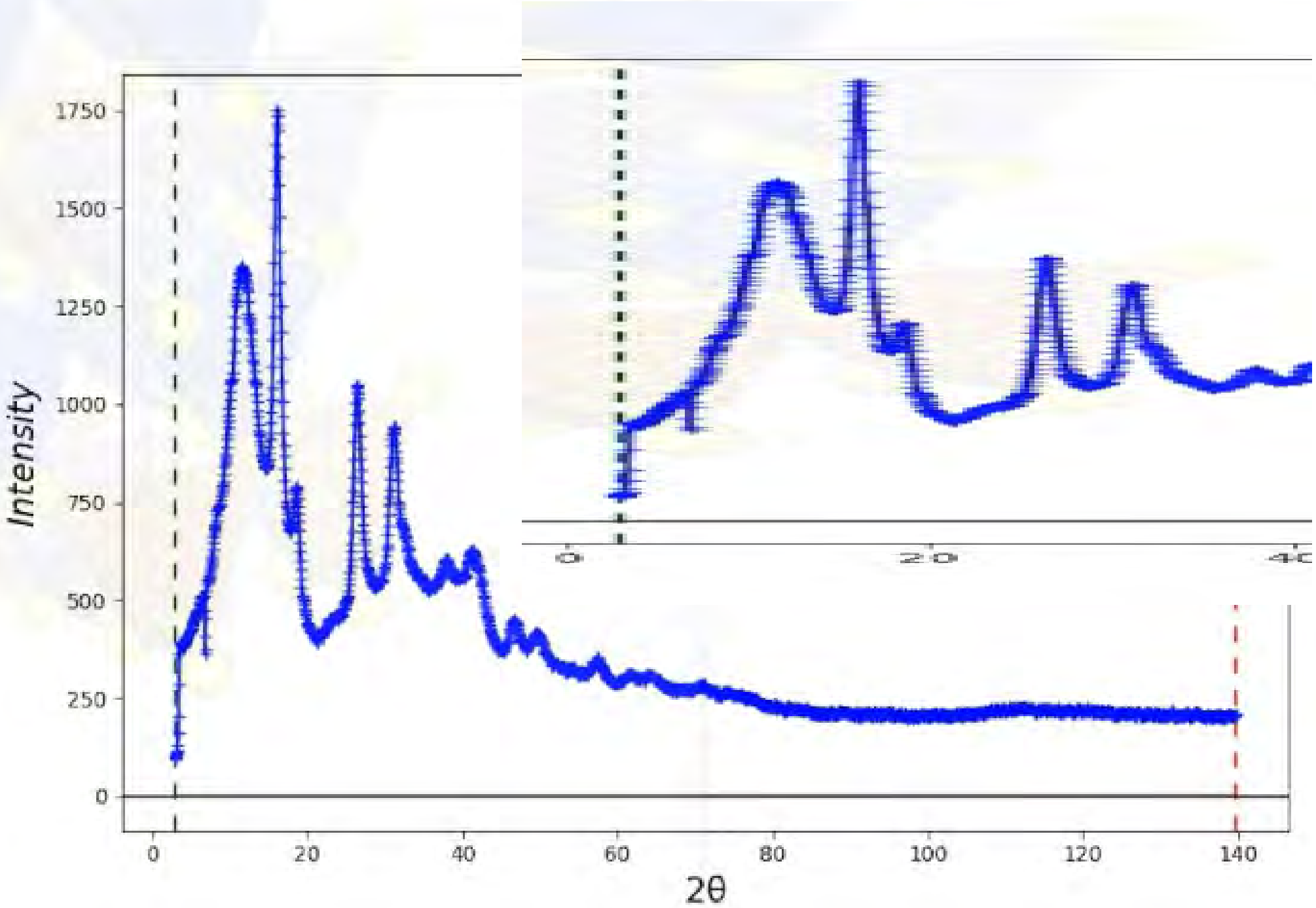
Peak Widths | Powder Patterns

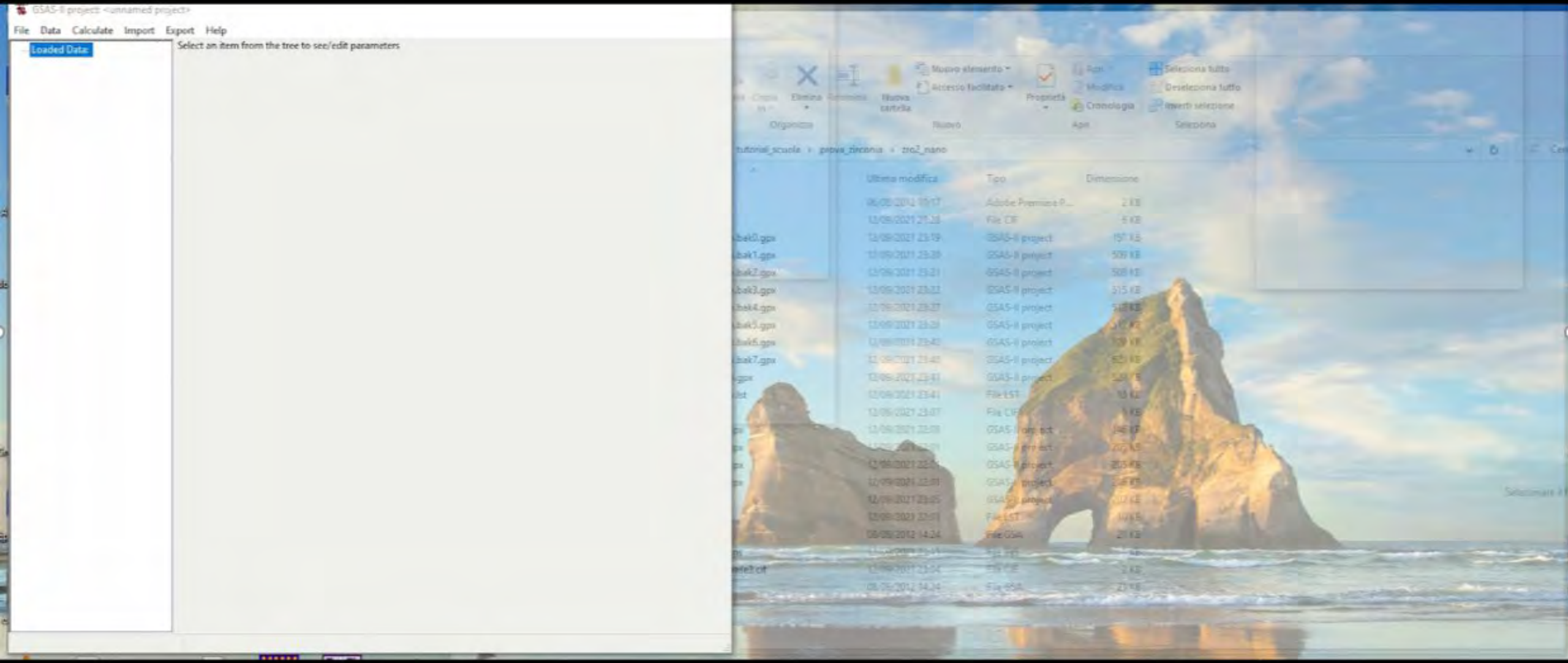


zoom rect

2-theta = 7.738 d= 5.73164 Q= 1.09623 Intensity = -44.89


PWDR zrrm1_01.gsa Bank 1
Data
obs
calc
bkg
Intensity
1750
1500
1250
1000
750
500
250
0
0
20
40
60
80
100
120
140
2θ


Intensity
1750
1500
1250
1000
750
500
250
0
0
20
40
60
80
100
120
140
2θ

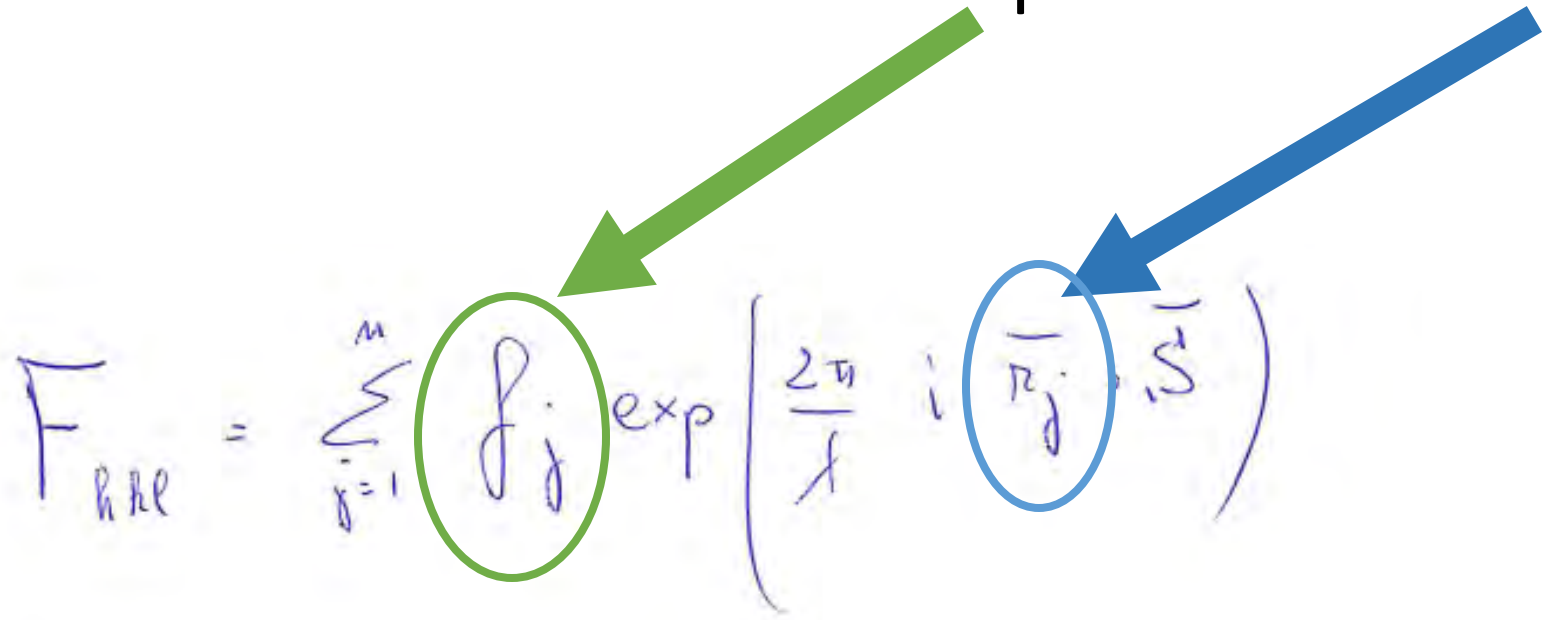

GSAS-II project: <unnamed project>
File Data Calculate Import Export Help
Loaded Data:
Select an item from the tree to see/edit parameters

2) Intensity of diffraction: function of atomic species and structure

$$F_{hkl} = \sum_{j=1}^{n} f_j \exp\left(\frac{2\pi}{\lambda} i \vec{r}_j \cdot \vec{S}\right)$$

Structure factor

Intensity of diffraction: function of atomic species and structure

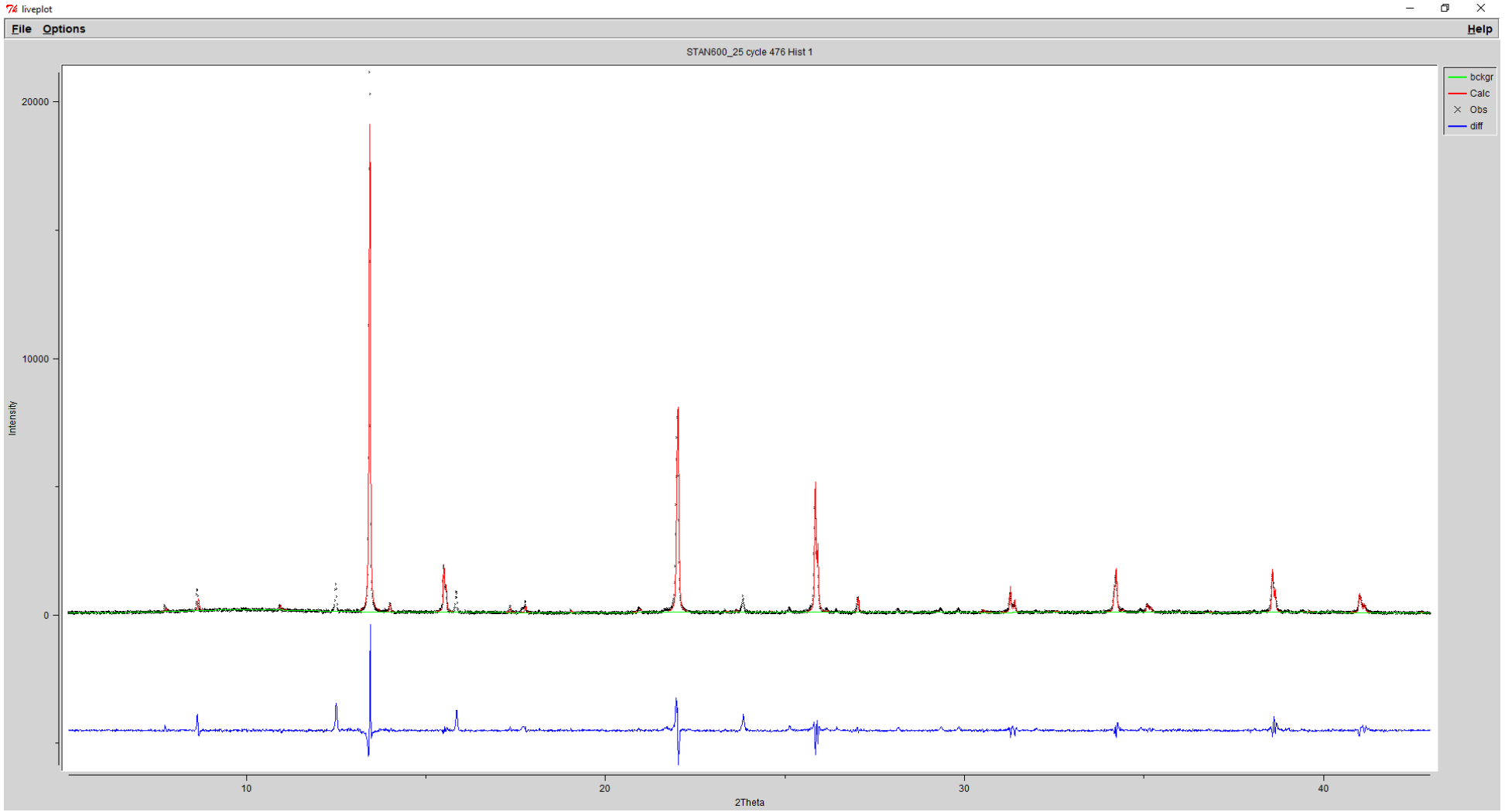


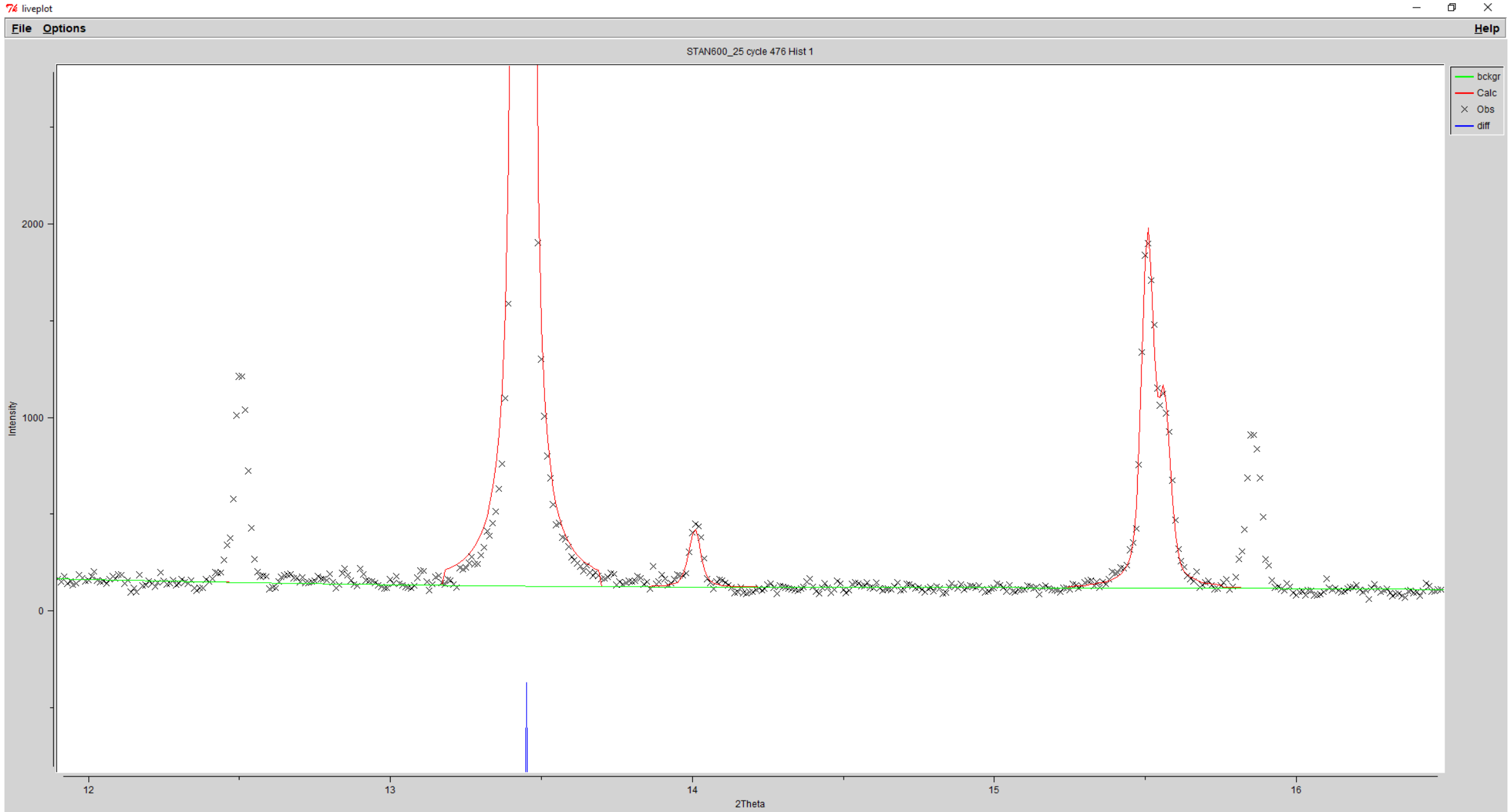
Structure factor

- Use of intensity for quantitative analysis and for structure determination

Quantitative analysis:

Stannite Cu2FeSnS4 – Rietveld fit – few peaks not fitted

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File Options
Help
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Obs
diff
Intensity
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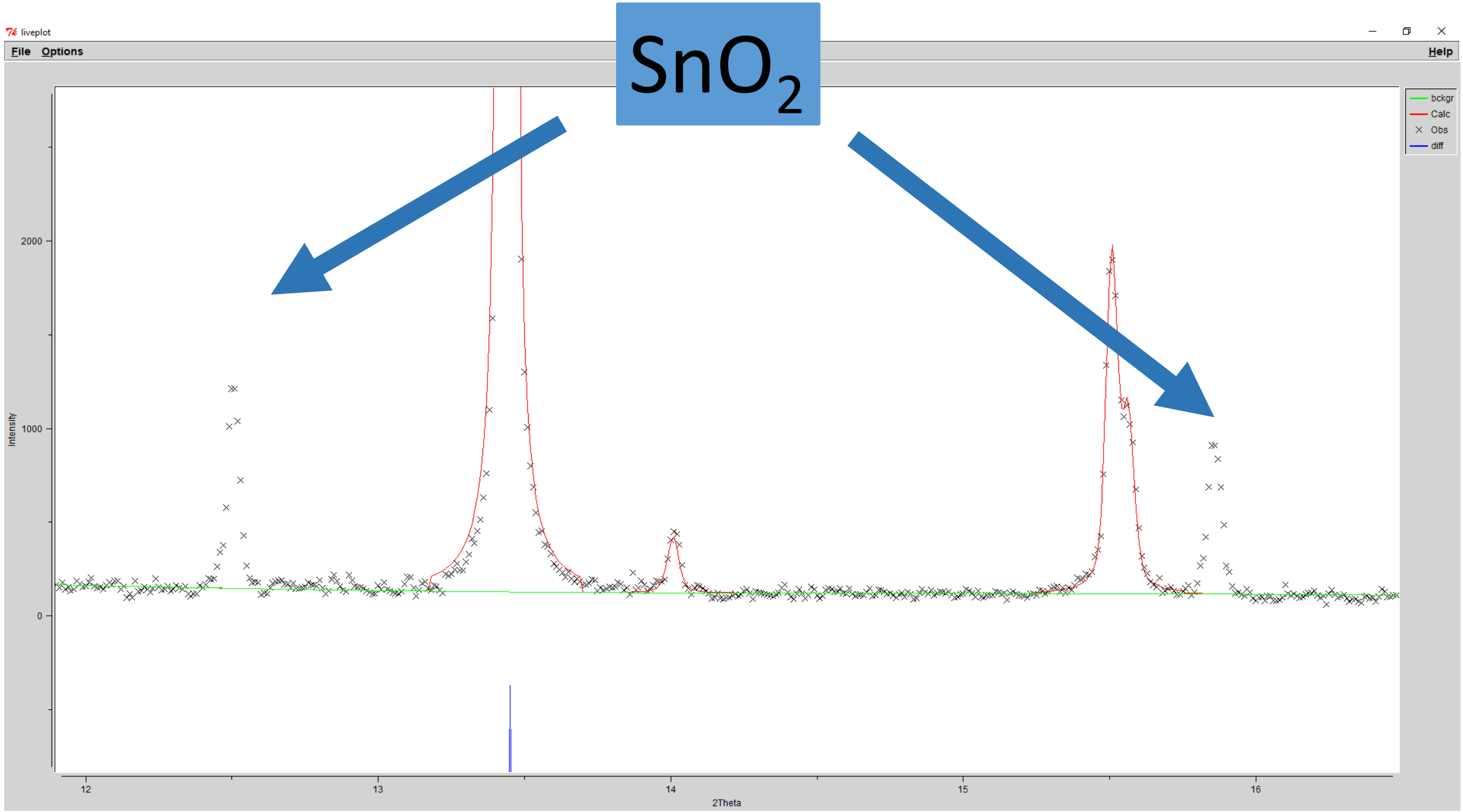
1000
0
12
13
14
15
16
2Theta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Help
SnO_2
bckgr
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Obs
diff
Intensity
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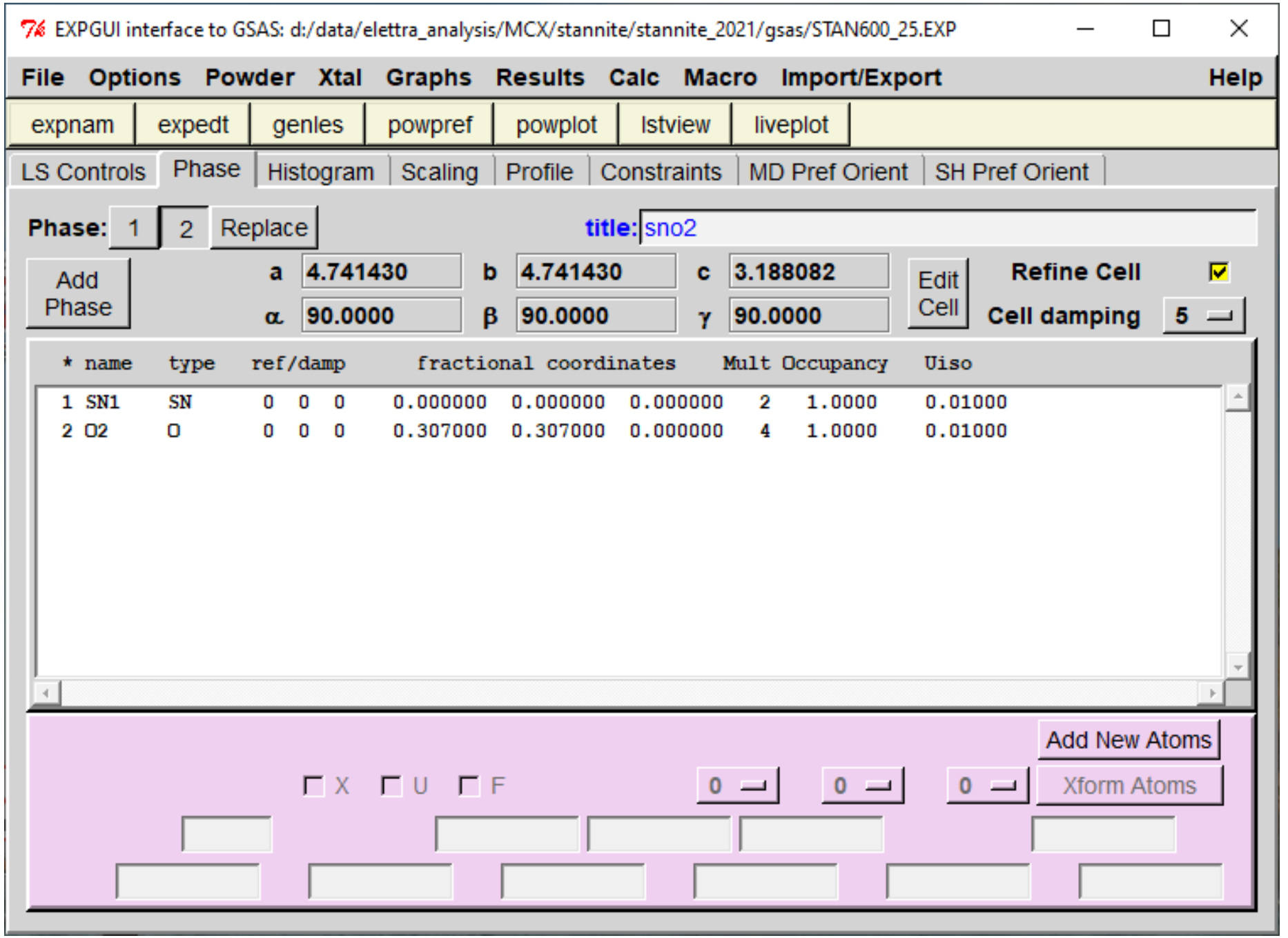
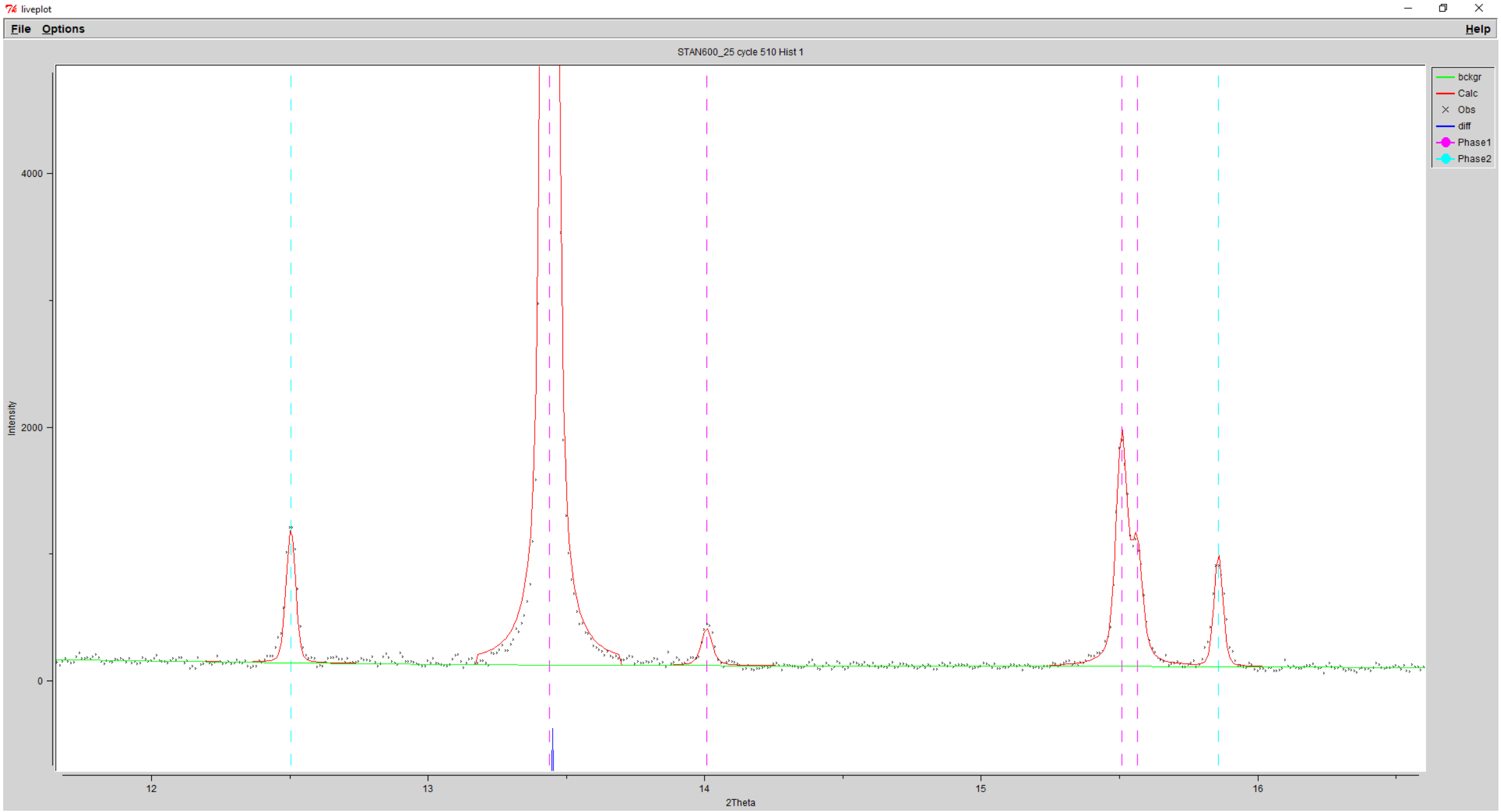
1000
0
12
13
14
15
16
2Theta


EXPGUI interface to GSAS: d:/data/elettra_analysis/MCX/stannite/stannite_2021/gsas/STAN600_25.EXP
File Options Powder Xtal Graphs Results Calc Macro Import/Export Help
expnam expedt genles powpref powplot lstview liveplot
LS Controls Phase Histogram Scaling Profile Constraints MD Pref Orient SH Pref Orient
Phase: 1 2 Replace
title: sno2
Add Phase
a 4.741430 b 4.741430 c 3.188082
α 90.0000 β 90.0000 γ 90.0000
Edit Cell
Refine Cell
Cell damping 5
* name type ref/damp fractional coordinates Mult Occupancy Uiso
1 SN1 SN 0 0 0 0.000000 0.000000 0.000000 2 1.0000 0.01000
2 O2 O 0 0 0 0.307000 0.307000 0.000000 4 1.0000 0.01000
Add New Atoms
X U F
0 0 0
Xform Atoms


liveplot
File
Options
Help
STAN600_25 cycle 510 Hist 1
bckgr
Calc
Obs
diff
Phase1
Phase2
4000
2000
0
Intensity
12
13
14
15
16
2Theta

View STAN600_25.LST

File Edit Go To Options Font: Courier Help

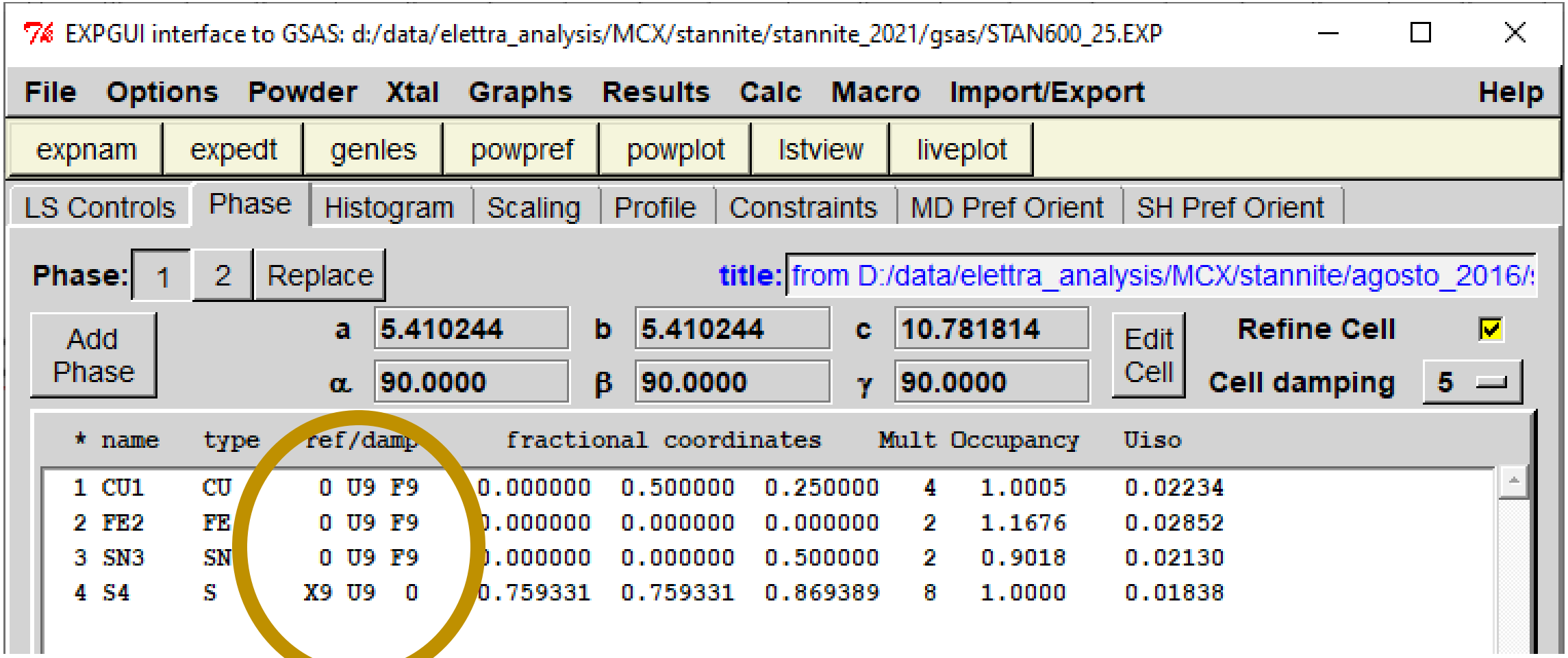
```
Calculated unit cell formula weight:   301.376, density:  6.982gm/cm**3

Phase/element fractions for phase no.  1

Hist Elem:      1 1 PXC
Fraction :    2.26796
Sigmas   :   0.775638E-01
Shift/esd:       0.00
Wt. Frac.:    0.96004
Sigmas   :   0.131197E-02

Phase/element fractions for phase no.  2

Hist Elem:      1 1 PXC
Fraction :   0.267887
Sigmas   :   0.666184E-02
Shift/esd:       0.00
Wt. Frac.:    0.39959E-01
Sigmas   :   0.953988E-03
Phase/element fraction sum(shift/error)**2 :      0.00

Lattice parameters for powder data:
Phase  1
```

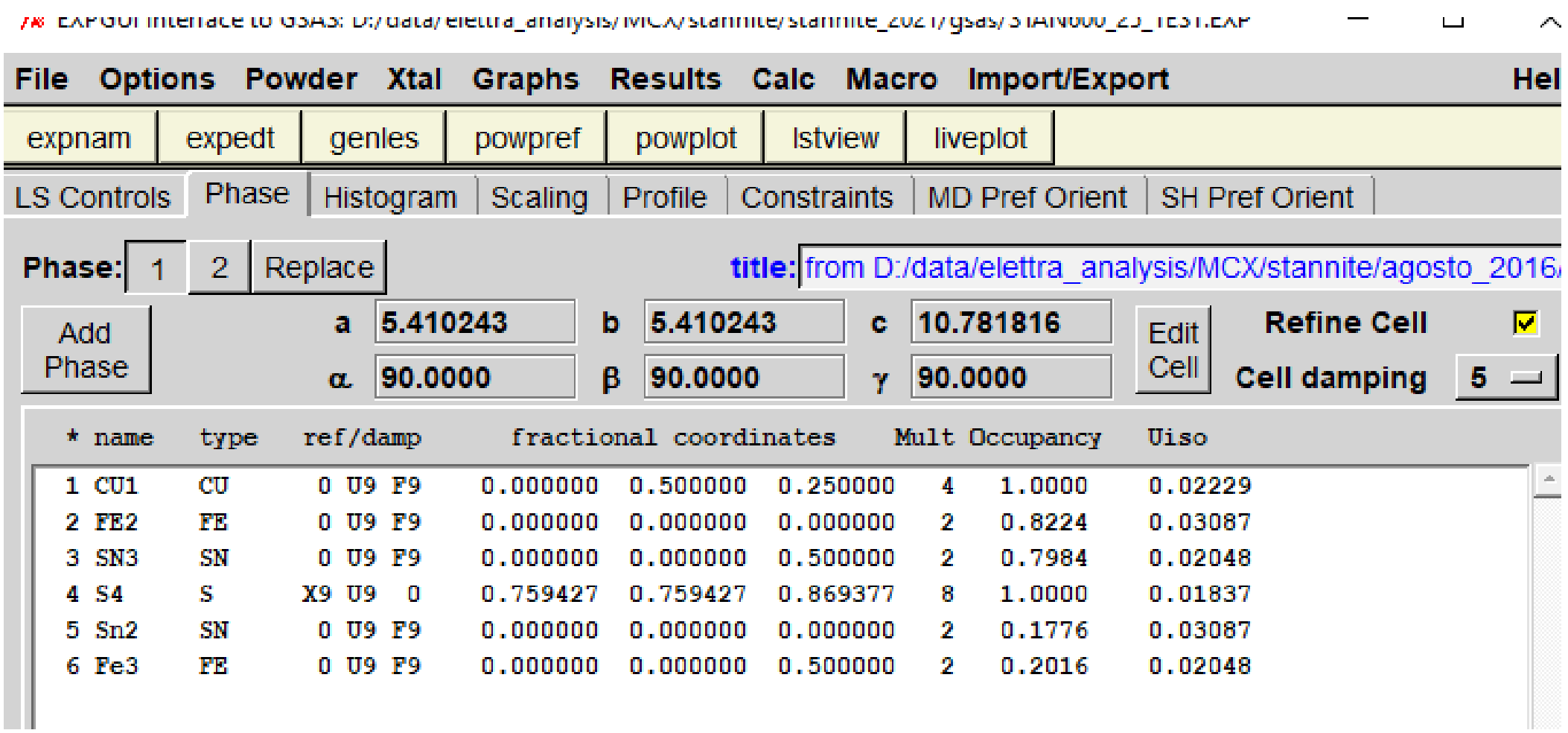
96 % Stannite

4 % SnO_2

Cycle 510 | Chi**2 8.123 | Shift/SU 0.01

Structure determination / refinement




EXPGUI interface to GSAS: D:/data/elettra_analysis/MCX/stannite/stannite_2021/gsas/STAN000_23_1E31.EXP
File Options Powder Xtal Graphs Results Calc Macro Import/Export Hel
expnam expedt genles powpref powplot lstview liveplot
LS Controls Phase Histogram Scaling Profile Constraints MD Pref Orient SH Pref Orient
Phase: 1 2 Replace
title: from D:/data/elettra_analysis/MCX/stannite/agosto_2016/
Add Phase
a 5.410243 b 5.410243 c 10.781816
α 90.0000 β 90.0000 γ 90.0000
Edit Cell
Refine Cell
Cell damping 5
* name type ref/damp fractional coordinates Mult Occupancy Uiso
1 CU1 CU 0 U9 F9 0.000000 0.500000 0.250000 4 1.0000 0.02229
2 FE2 FE 0 U9 F9 0.000000 0.000000 0.000000 2 0.8224 0.03087
3 SN3 SN 0 U9 F9 0.000000 0.000000 0.500000 2 0.7984 0.02048
4 S4 S X9 U9 0 0.759427 0.759427 0.869377 8 1.0000 0.01837
5 Sn2 SN 0 U9 F9 0.000000 0.000000 0.000000 2 0.1776 0.03087
6 Fe3 FE 0 U9 F9 0.000000 0.000000 0.500000 2 0.2016 0.02048

STAN600_25_1.ins - VESTA

File Edit View Objects Utilities Help

a b c a* b* c* Step (°): 0.5 Step (px): 10 Step (%): 10

Tools Style Objects

Structural models
- [x] Show models
- [ ] Show dot surface

Style
- ( ) Ball-and-stick
- ( ) Space-filling
- (•) Polyhedral
- ( ) Wireframe
- ( ) Stick

Volumetric data
- [ ] Show sections
- [ ] Show isosurfaces
- [ ] Surface coloring

Style
- (•) Smooth shading
- ( ) Wireframe
- ( ) Dot surface

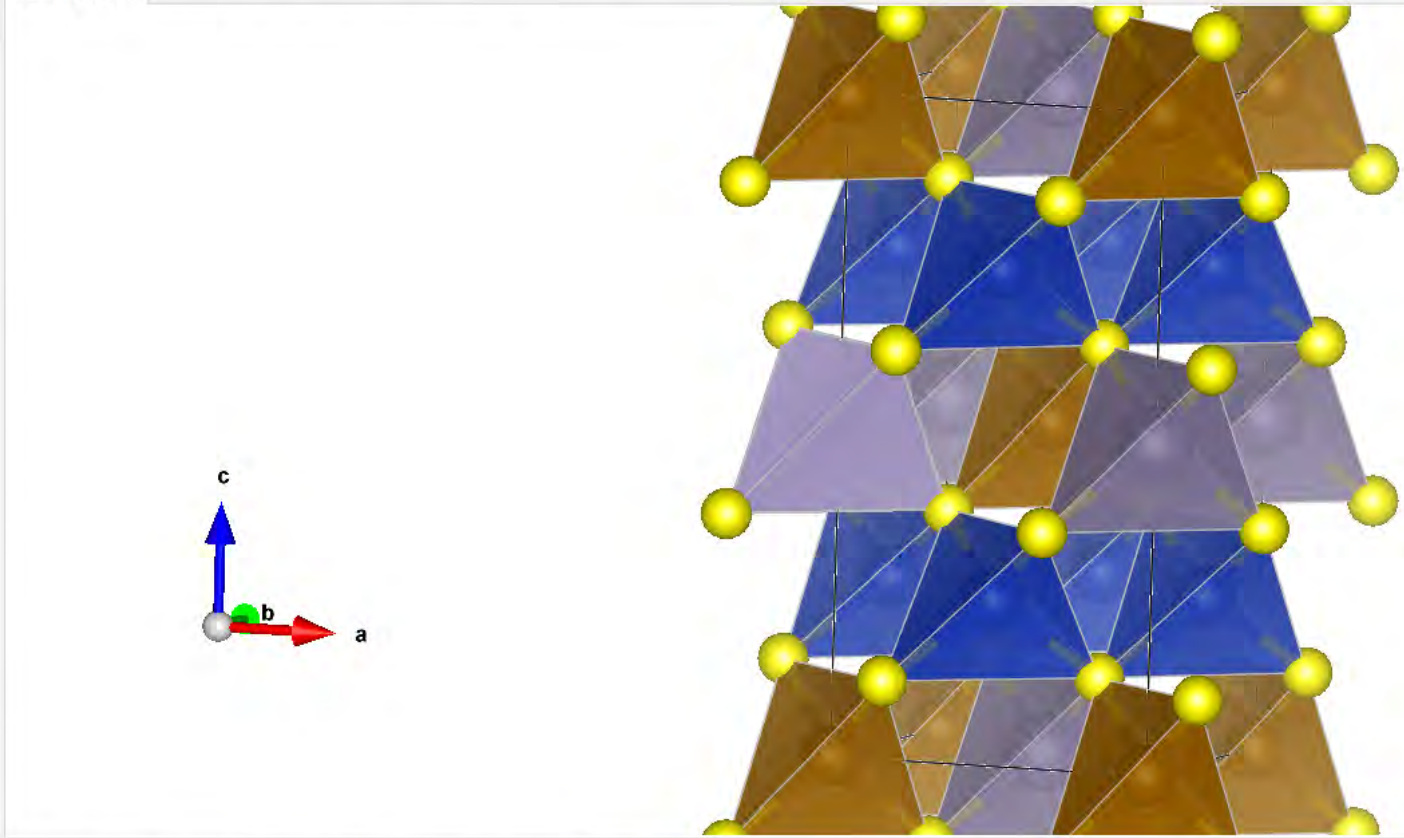
Crystal shapes
- [ ] Show shapes

Style
- (•) Unicolor
- ( ) Custom color
- ( ) Wireframe

Properties...

Boundary... Orientation...

STAN600_25_1.ins




```
   4      S1  S -0.26080 -0.26080  0.36936  ( 0, 0,-1)+ -x+1/2, -y+1/2, z+1/2
   4      S1  S -0.26080  0.26080  0.63064  ( 0,-1, 1)+ -y+1/2, x+1/2, -z+1/2
   4      S1  S  0.26080 -0.26080  0.63064  (-1, 0, 1)+ y+1/2, -x+1/2, -z+1/2
   4      S1  S  0.26080  0.26080  0.36936  (-1,-1,-1)+ x+1/2, y+1/2, z+1/2
--------------------------------------------------------------------------

l(SN1-S1) =  2.44289(0) Å
l(SN1-S1) =  2.44289(0) Å
l(SN1-S1) =  2.44289(0) Å
l(SN1-S1) =  2.44289(0) Å
---------------------------------------
Average bond length =  2.4429 Å
Polyhedral volume =  7.4817 Å^3
Distortion index (bond length) = 0.00000
Quadratic elongation =  1.0000
Bond angle variance =  0.0047 deg.^2
Effective coordination number =  4.0000
```

Output Summary Comment

Press "Del" to delete selected objects, "Esc" to reset deleted objects.

Summary

- Accuracy (and precision) in geometrical parameters (i.e. peak position, lattice parameter) is function of calibration
- Synchrotron experiments (especially in Bragg-Brentano – transmission -geometry) can result in improved accuracy compared to laboratory sources

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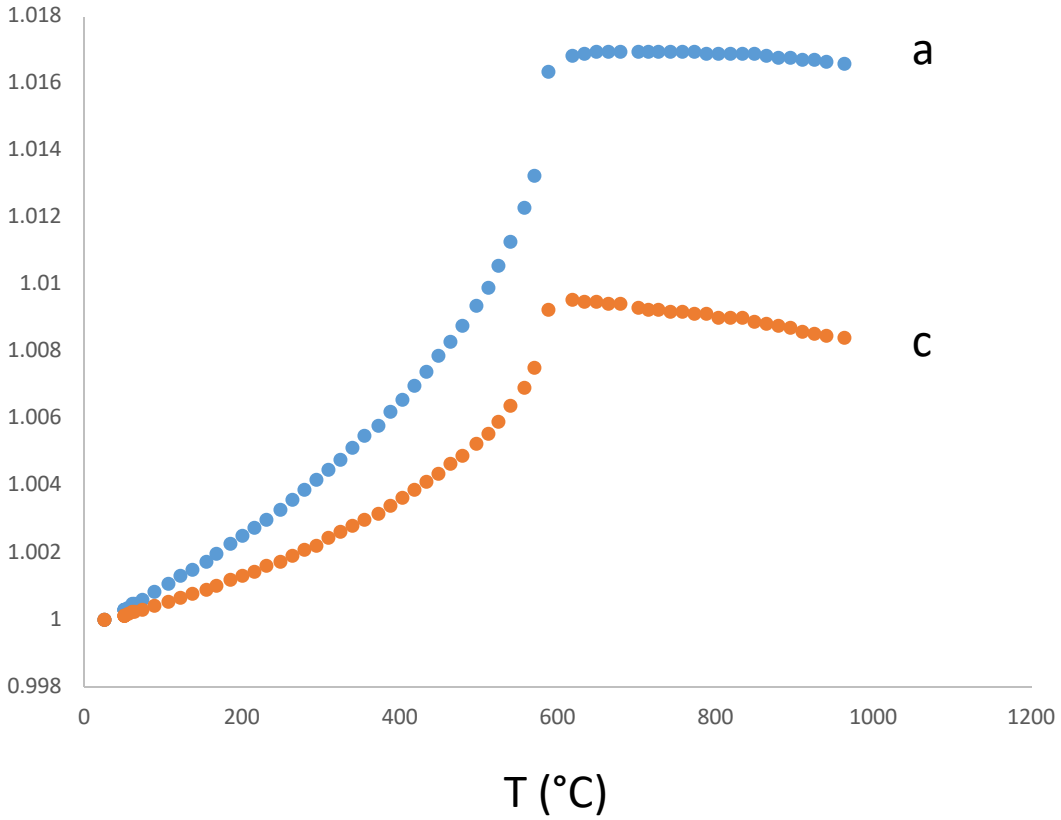

Thermal expansion of SiO2 quartz

Normalized lattice parameters

Summary

- Synchrotron high resolution beamlines: improved angular resolution compared to laboratory sources
- Accurate determination of microstructural parameters (i.e. crystallite size, microstrain)

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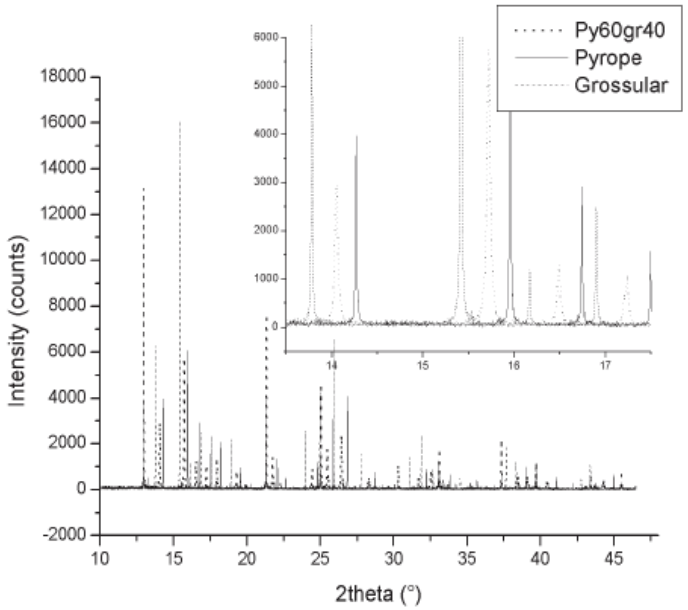


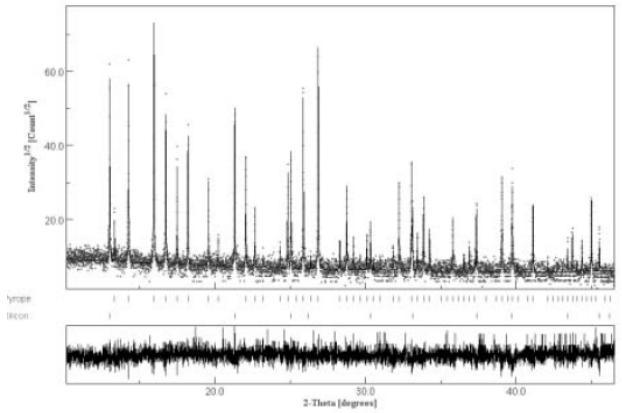
American Mineralogist, Volume 90, pages 506–509, 2005

LETTER

Microscopic strain in synthetic pyrope-grossular solid solutions determined by synchrotron X-ray powder diffraction at 5 K: The relationship to enthalpy of mixing behavior

MONICA DAPIAGGI,[1,*] CHARLES A. GEIGER,[2] AND GILBERTO ARTIOLI[1]

[1]Dipartimento di Scienze della Terra "A. Desio", Università degli Studi di Milano, I-20133 Milano, Italy
[2]Institut für Geowissenschaften, Christian-Albrechts-Universität, D-24098 Kiel, Germany



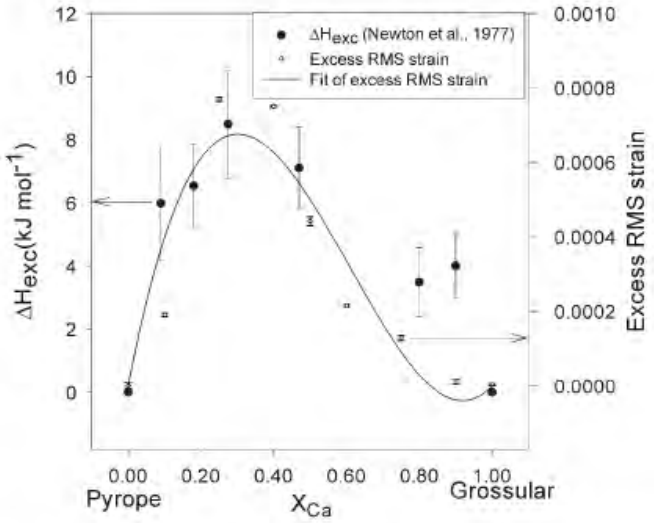


FIGURE 3. Experimental values of the excess enthalpies of mixing (open squares from Newton et al., 1977) and the excess RMS strain (black circles). The error bars represent 2σ variations in the determinations. The solid line is a two parameter asymmetric fit (Eq. 4) to the excess RMS strain data.

Summary

- Synchrotron diffraction with tunable energy – high energy can result in minimization of absorption effects. Useful for structure determination of sample with atomic species with significant different atomic numbers
- Diffraction in complex environments
- Large experimental space for ad-hoc experimental setup

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- Diffraction in complex environments
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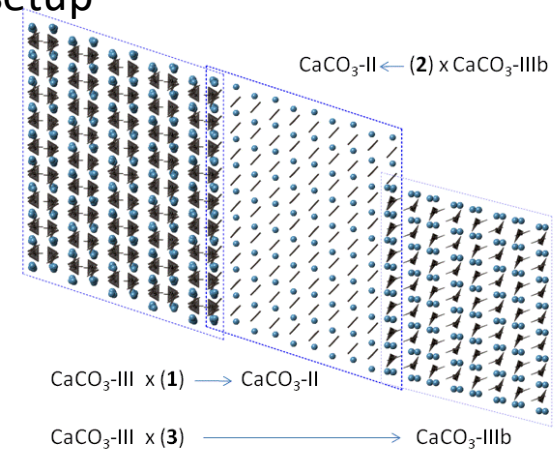
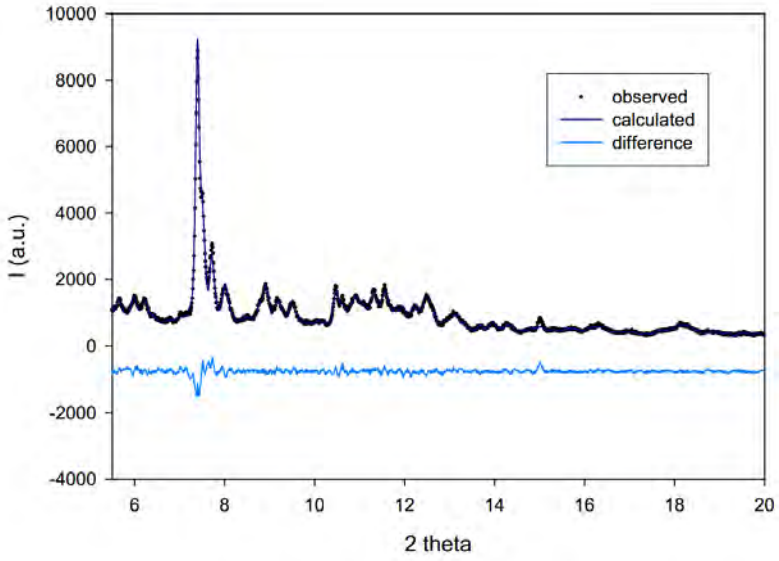
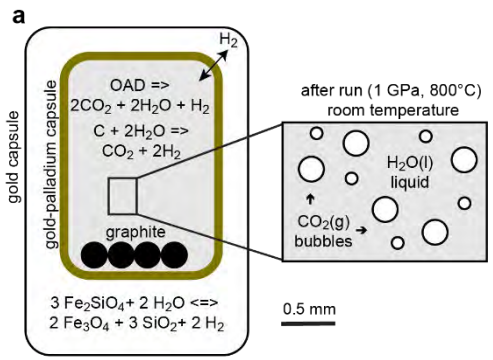
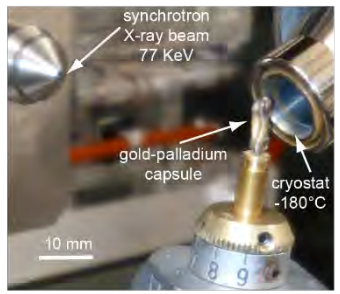
LVP – Large Volume Press @ ESRF ID06 beamline

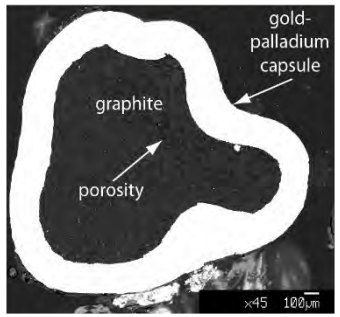


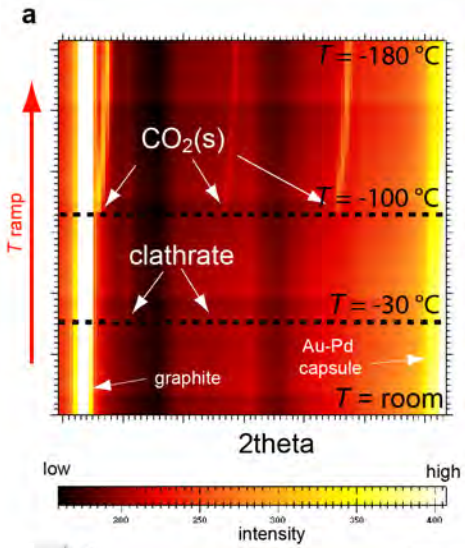


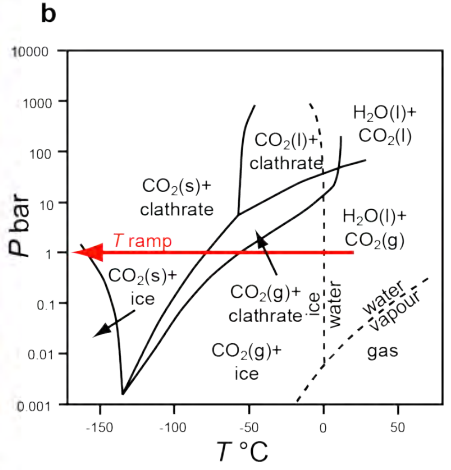
Rietveld fit of complex structural intergrow of different domain in high pressure phase

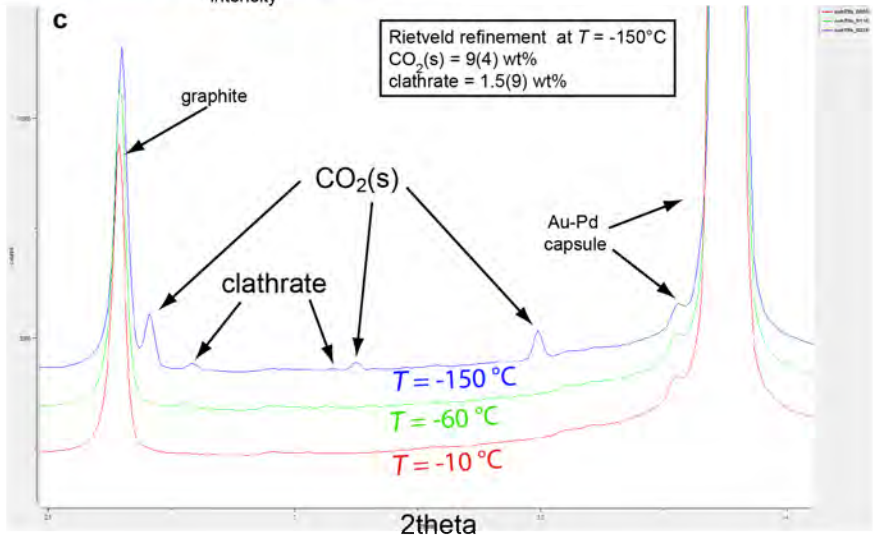

a
gold capsule
gold-palladium capsule
H2
OAD =>
2CO2 + 2H2O + H2
C + 2H2O =>
CO2 + 2H2
graphite
3 Fe2SiO4+ 2 H2O <=>
2 Fe3O4 + 3 SiO2+ 2 H2
after run (1 GPa, 800°C)
room temperature
H2O(l)
liquid
CO2(g)
bubbles
0.5 mm

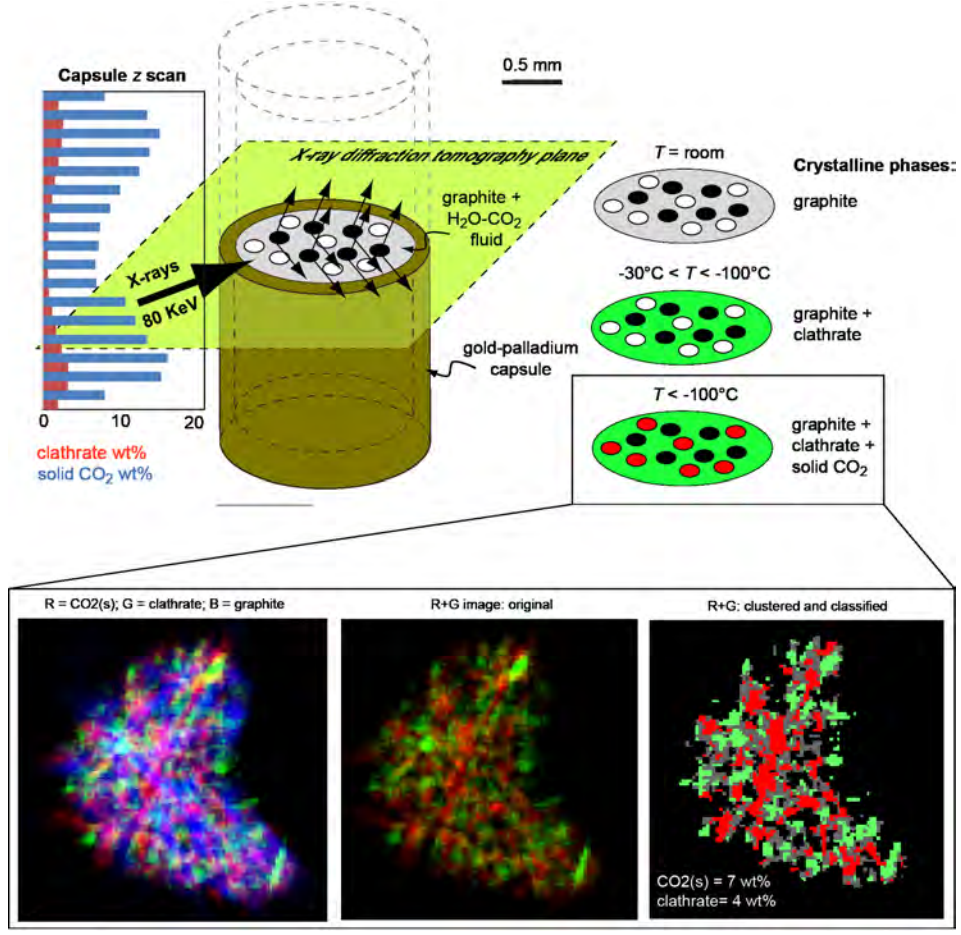

b
synchrotron
X-ray beam
77 KeV
gold-palladium
capsule
cryostat
-180°C
10 mm


c
gold-
palladium
capsule
graphite
porosity
x45 100µm


a
T = -180 °C
CO2(s)
T = -100 °C
clathrate
T = -30 °C
Au-Pd
capsule
graphite
T = room
T ramp
2theta
low
high
intensity

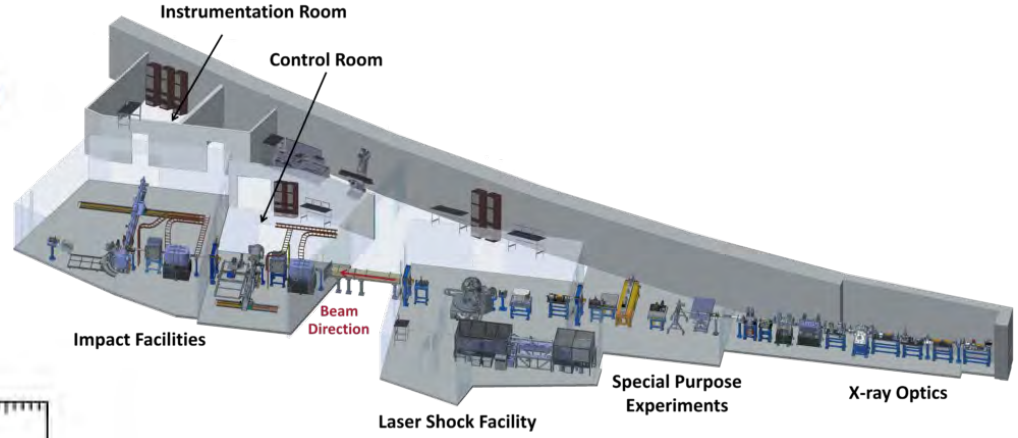

b
P bar
T °C
T ramp
CO2(s)+
clathrate
CO2(l)+
clathrate
H2O(l)+
CO2(l)
H2O(l)+
CO2(g)
CO2(s)+
ice
CO2(g)+
clathrate
CO2(g)+
ice
ice
water
water
vapour
gas

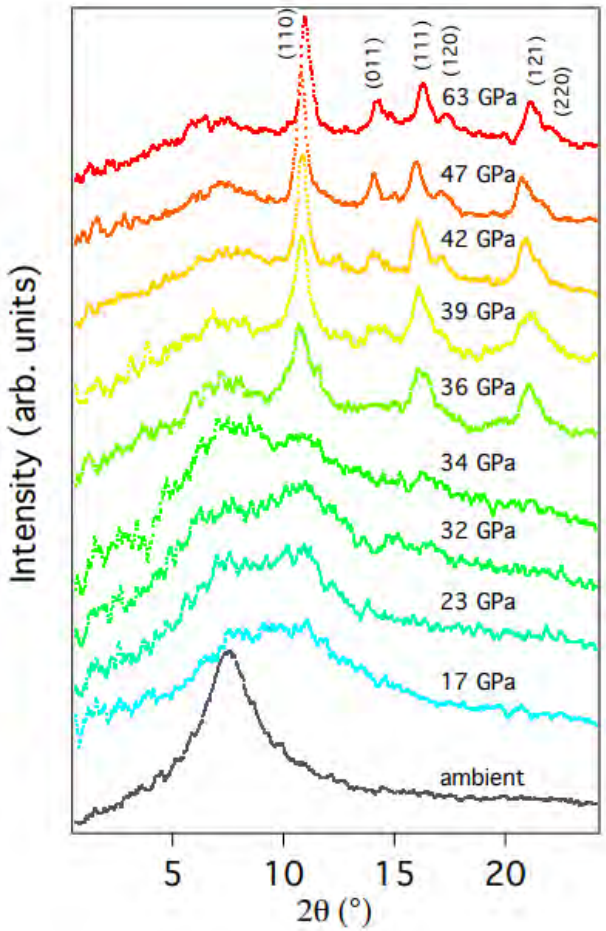

c
Rietveld refinement at T = -150°C
CO2(s) = 9(4) wt%
clathrate = 1.5(9) wt%
graphite
CO2(s)
clathrate
Au-Pd
capsule
T = -150 °C
T = -60 °C
T = -10 °C
2theta

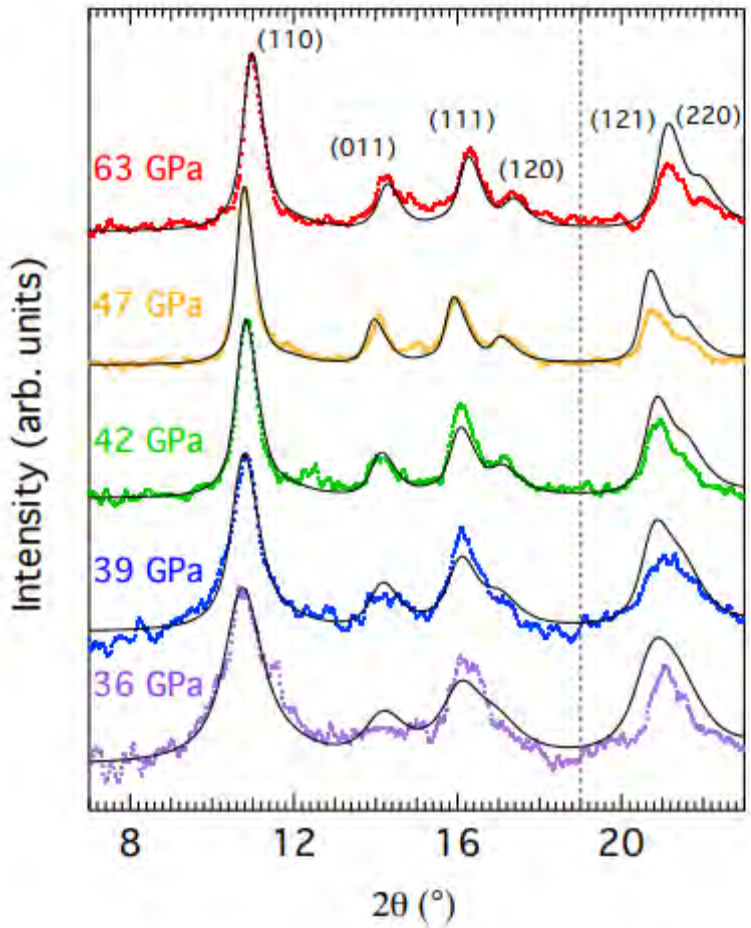

Capsule z scan
clathrate wt%
solid CO2 wt%
0.5 mm
X-ray diffraction tomography plane
graphite +
H2O-CO2
fluid
X-rays
80 KeV
gold-palladium
capsule
T = room
Crystalline phases:
graphite
-30°C < T < -100°C
graphite +
clathrate
T < -100°C
graphite +
clathrate +
solid CO2
R = CO2(s); G = clathrate; B = graphite
R+G image: original
R+G: clustered and classified
CO2(s) = 7 wt%
clathrate= 4 wt%

In situ X-Ray Diffraction of Shock-Compressed Fused Silica

Sally June Tracy, Stefan J. Turneaure, and Thomas S. Duffy
Phys. Rev. Lett. **120**, 135702 – Published 29 March 2018







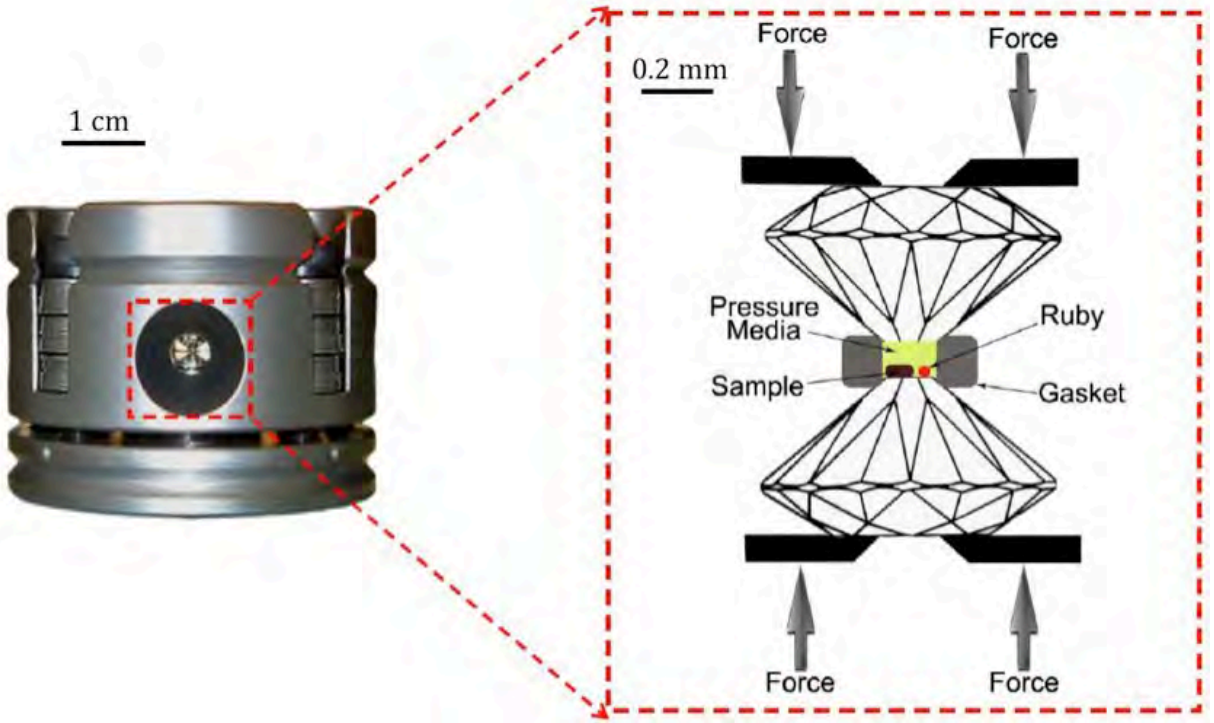
The diffraction data are combined with continuum-level measurements to reveal a complete picture of the material response from the atomic length scale to the continuum level, allowing for the unambiguous determination of the phase(s) formed at ~100 ns timescales from 12 to 63 GPa.

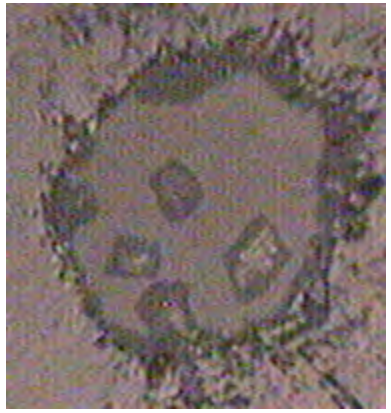
Plate impact experiments were carried out at the Dynamic Compression Sector of the Advanced Photon Source (APS). Planar shock waves in fused silica were generated using LiF impactors accelerated in a polycarbonate projectile to a velocity of 1.8–5.6 km/s using either a single-stage propellant gun or a two-stage light gas gun. A schematic of the impact

3) EXAMPLE of crystal structure determination from single crystals at «extreme conditions»

High-pressure and high-temperature

Diamond anvil cell



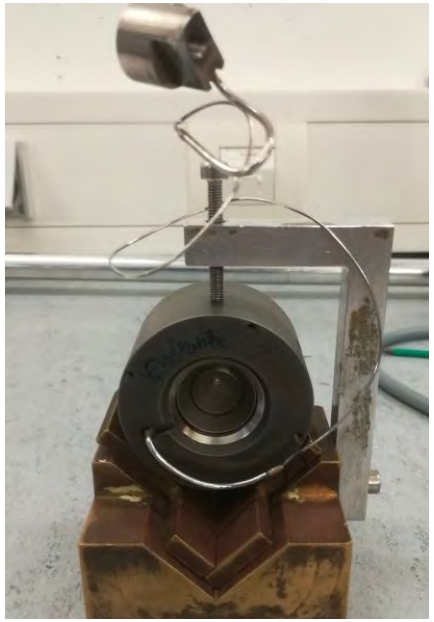


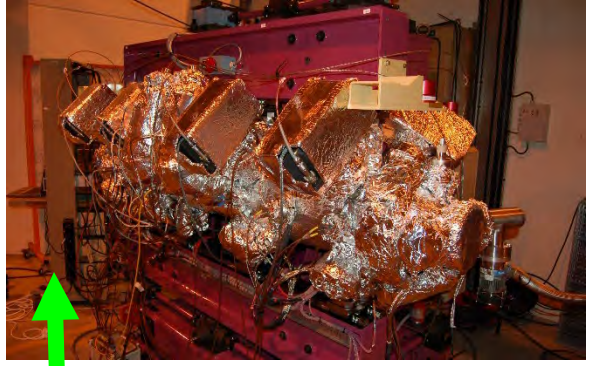
Diamond culet diameter	max pressure
1 mm	2 GPa
0.6 mm	20 GPa
0.3 mm	60 Gpa
0.125 mm	> 100 GPa

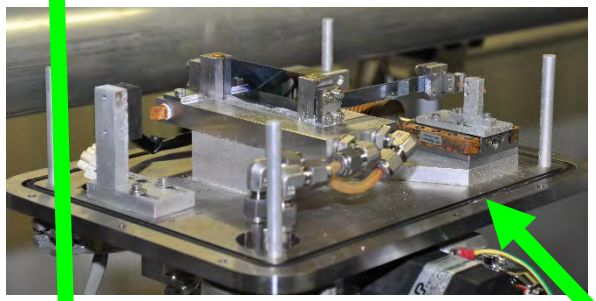
Force:

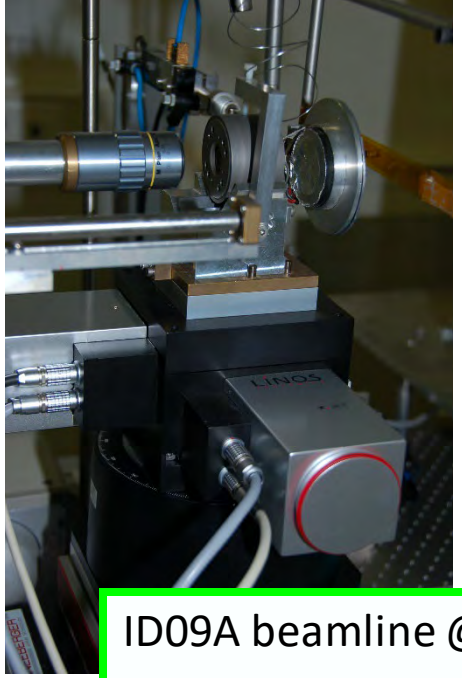
screws

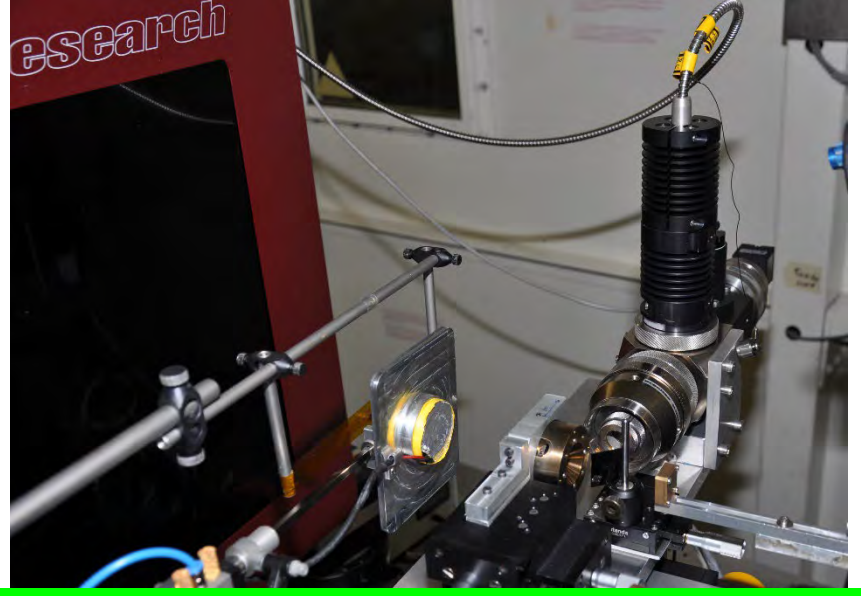
Gas under pressure
(0-200 bar)
and expanding
metallic membrane





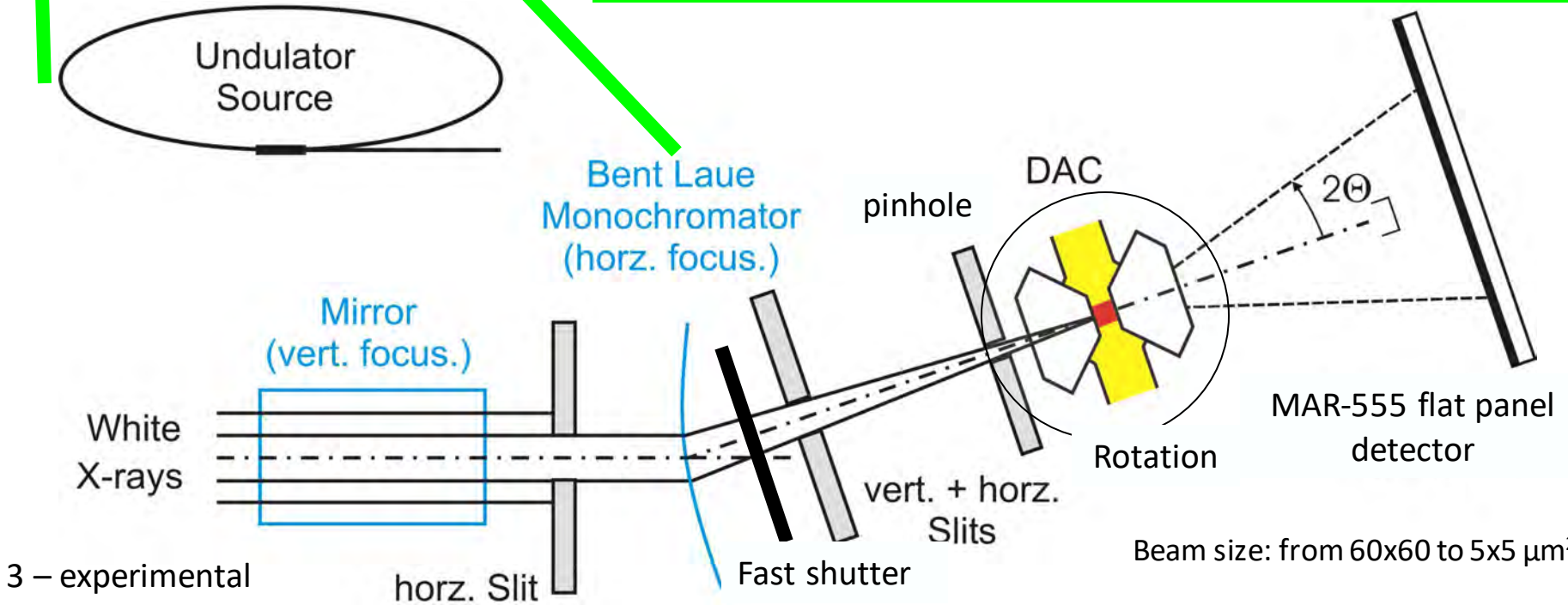






ID09A beamline @ ESRF (Grenoble, France)

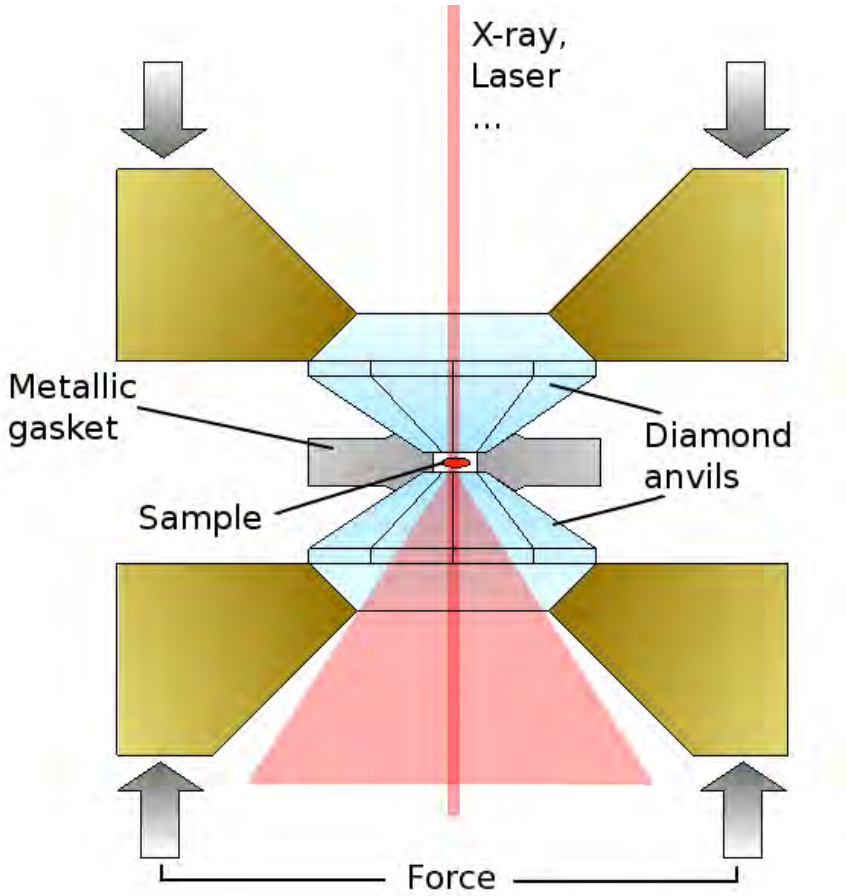
European Synchrotron Radiation Facility



Beam size: from 60x60 to 5x5 μm^2

Diamond Anvil Cell (DAC) +/- resistive heating +/- laser heating

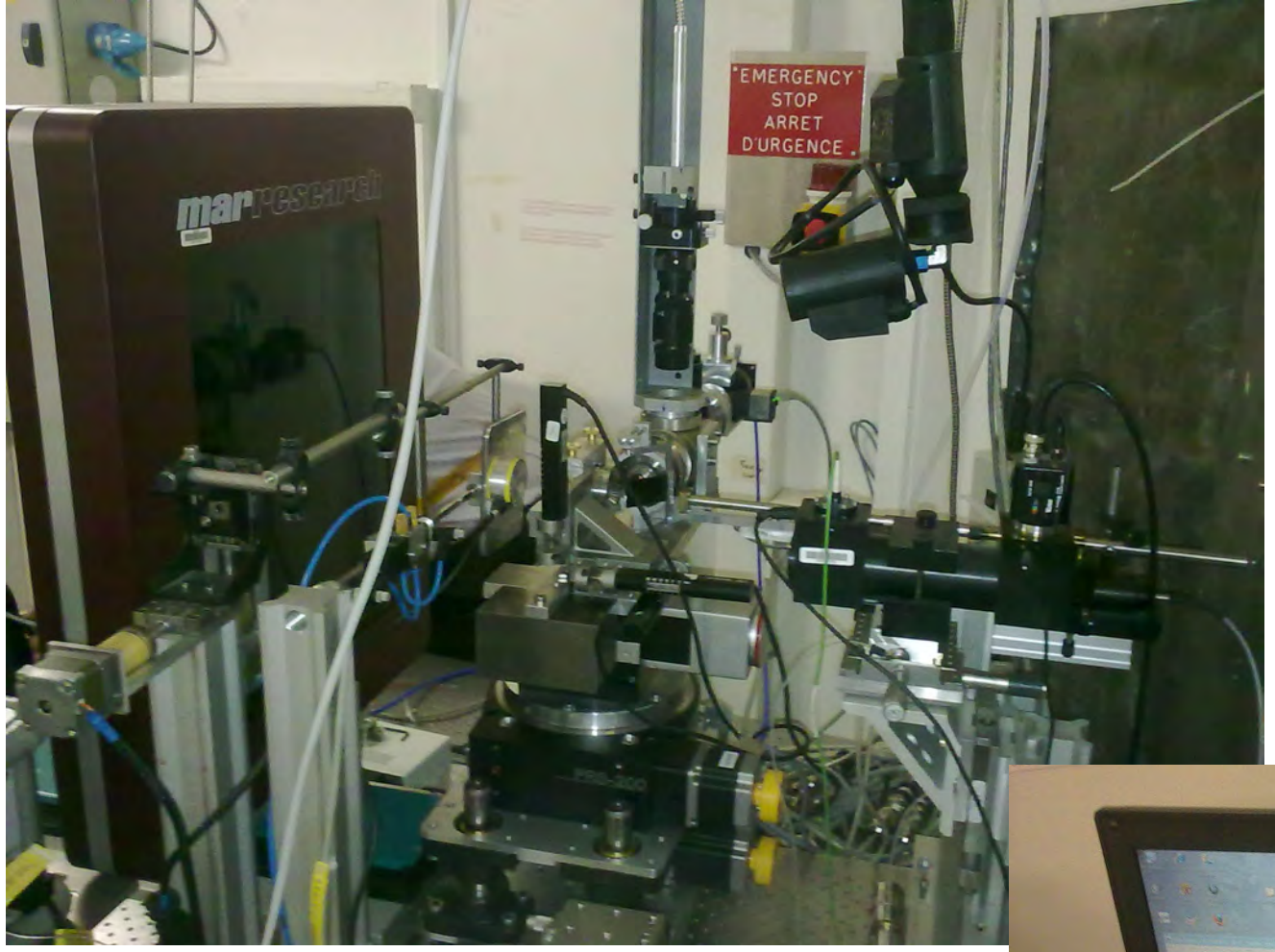
P max: «routine» 1.5 Mbar – possible experiments up to 6 Mbar
T max: cryostat + resistive: 5-1000 K; laser heating: up to 6000 K

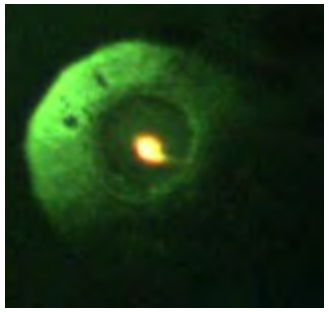


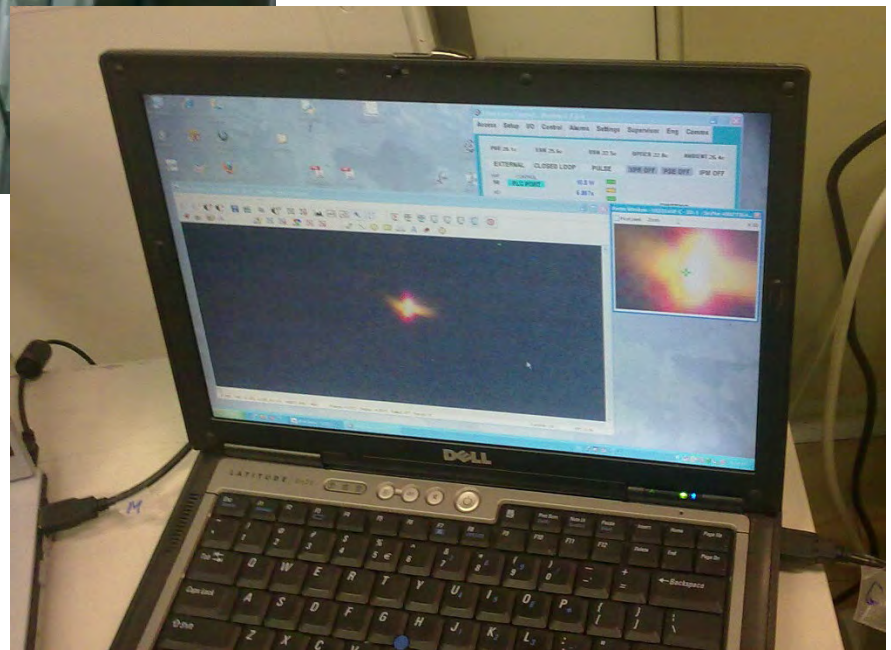
X- ray diffraction
(powder, single crystal)

X-ray scattering

X-ray spectroscopy

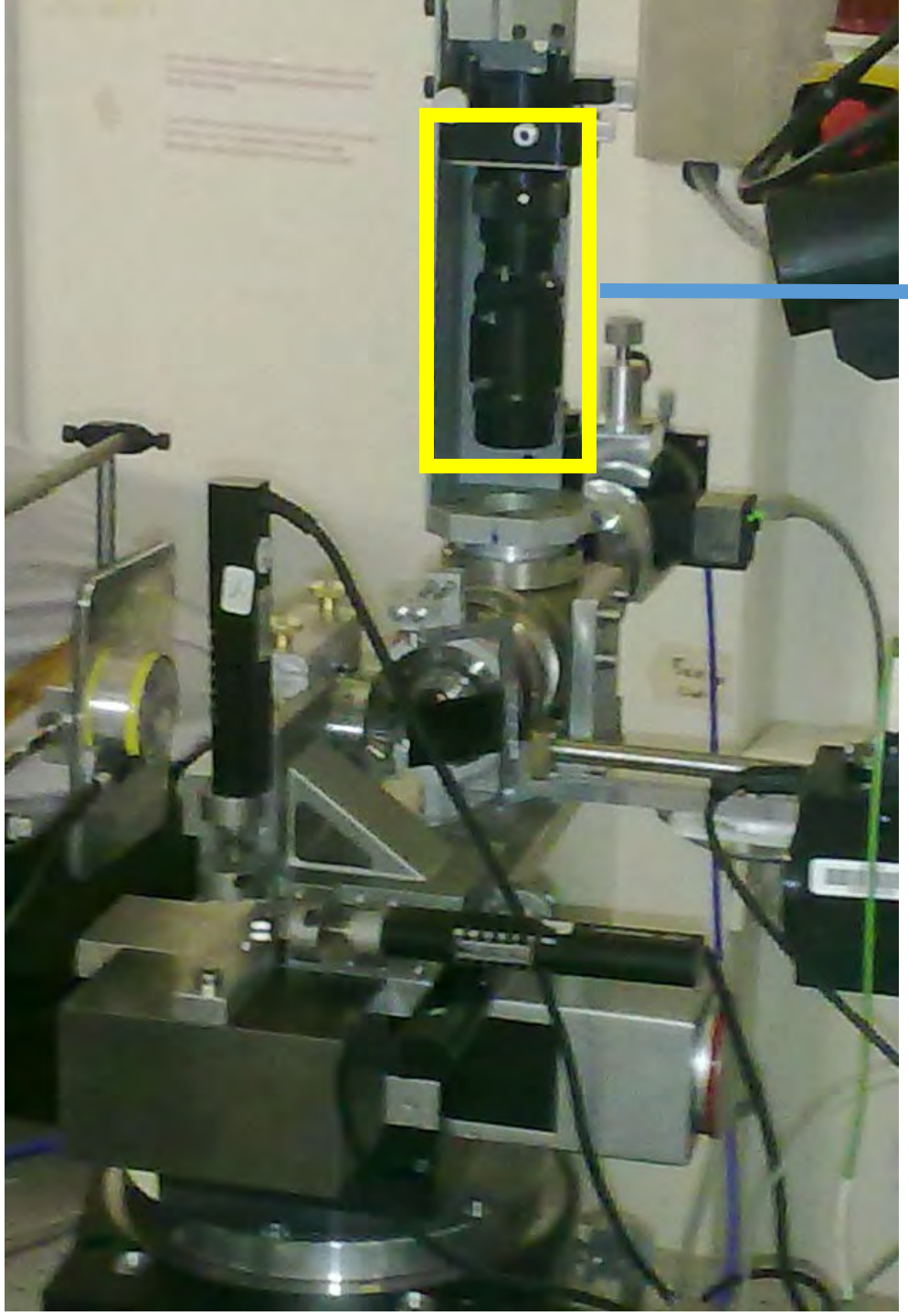




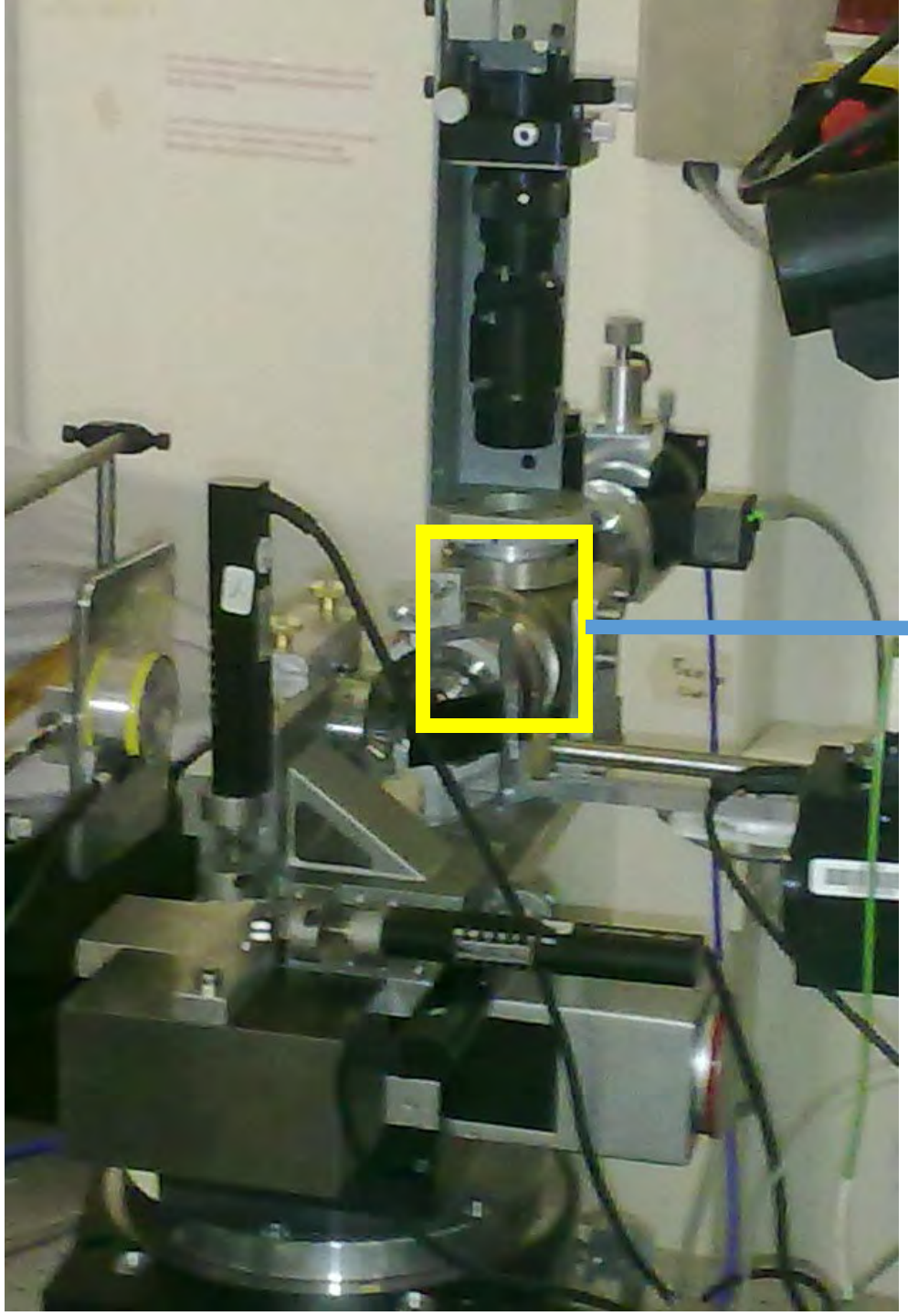


Portable laser heating system for single crystal diffraction

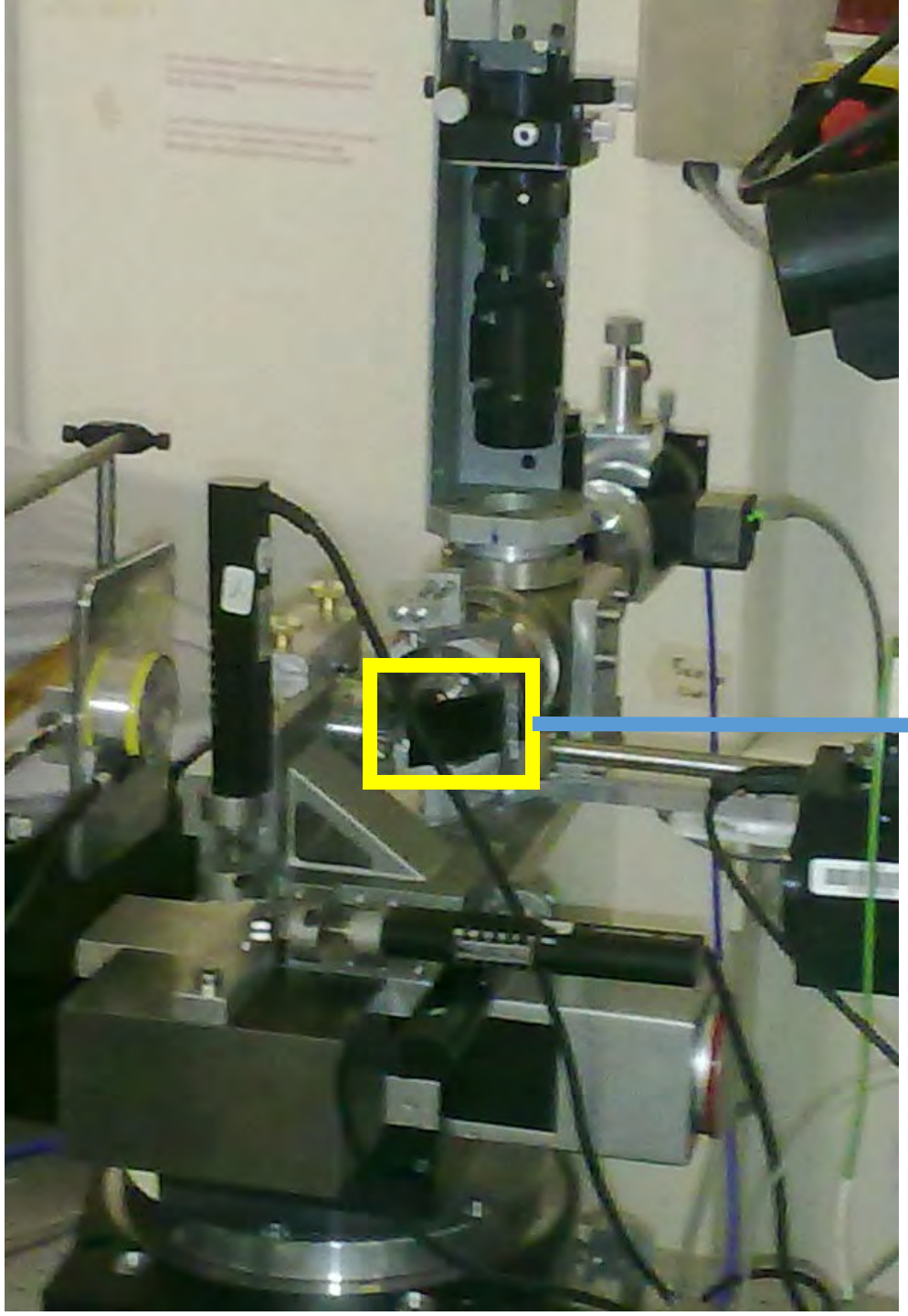
Dubrovinsky et al., HPR 2010

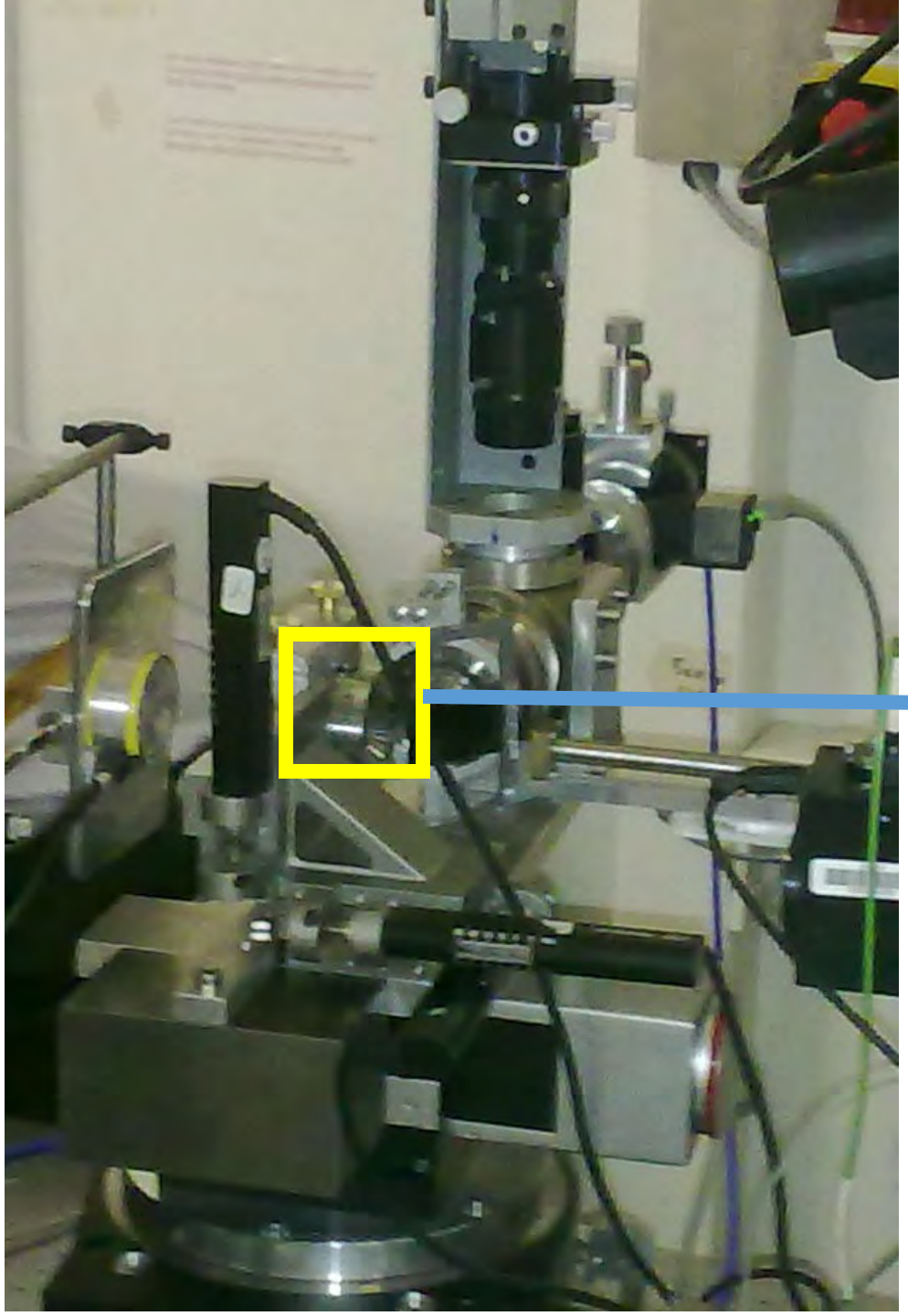


Incoming laser beam

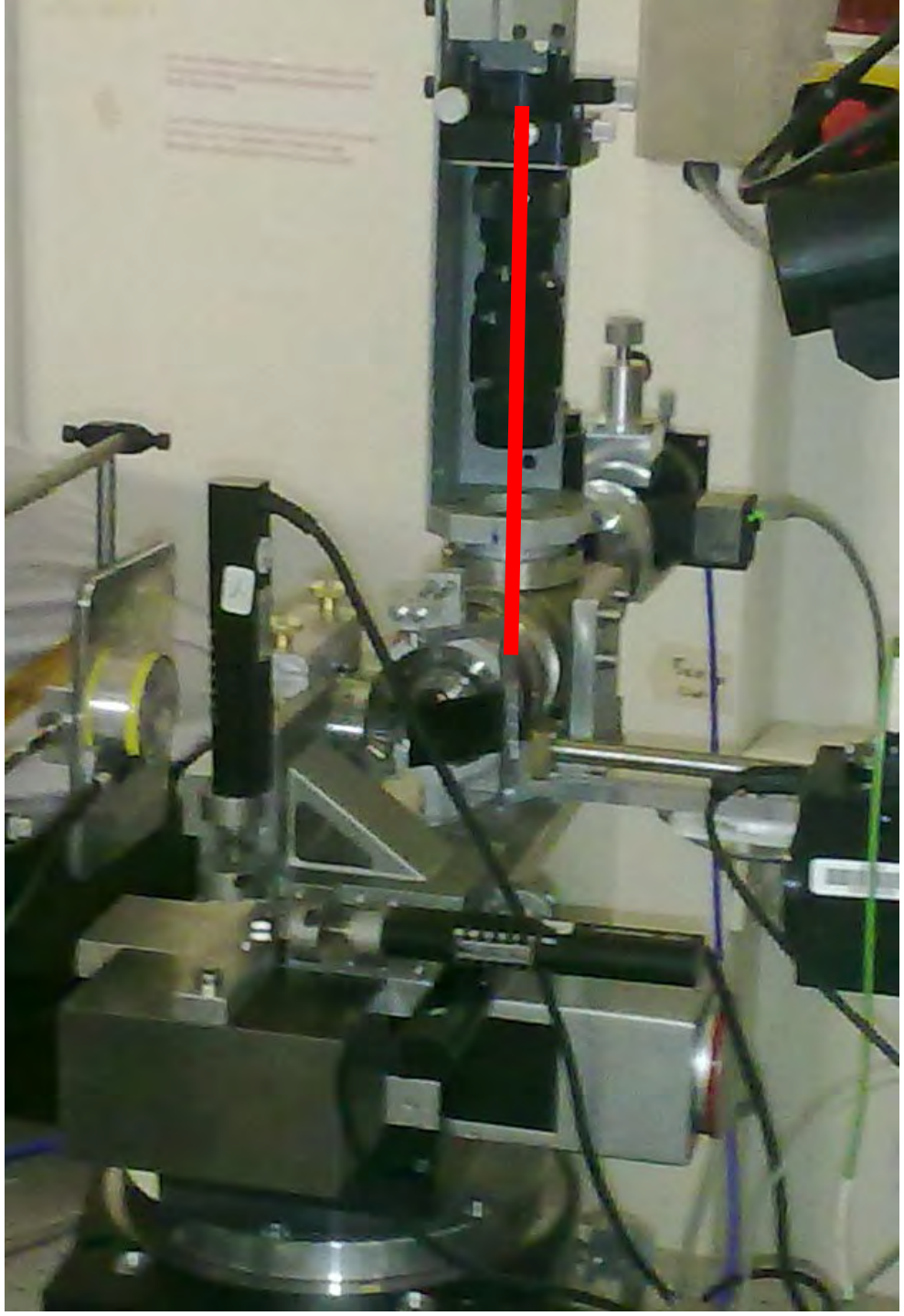


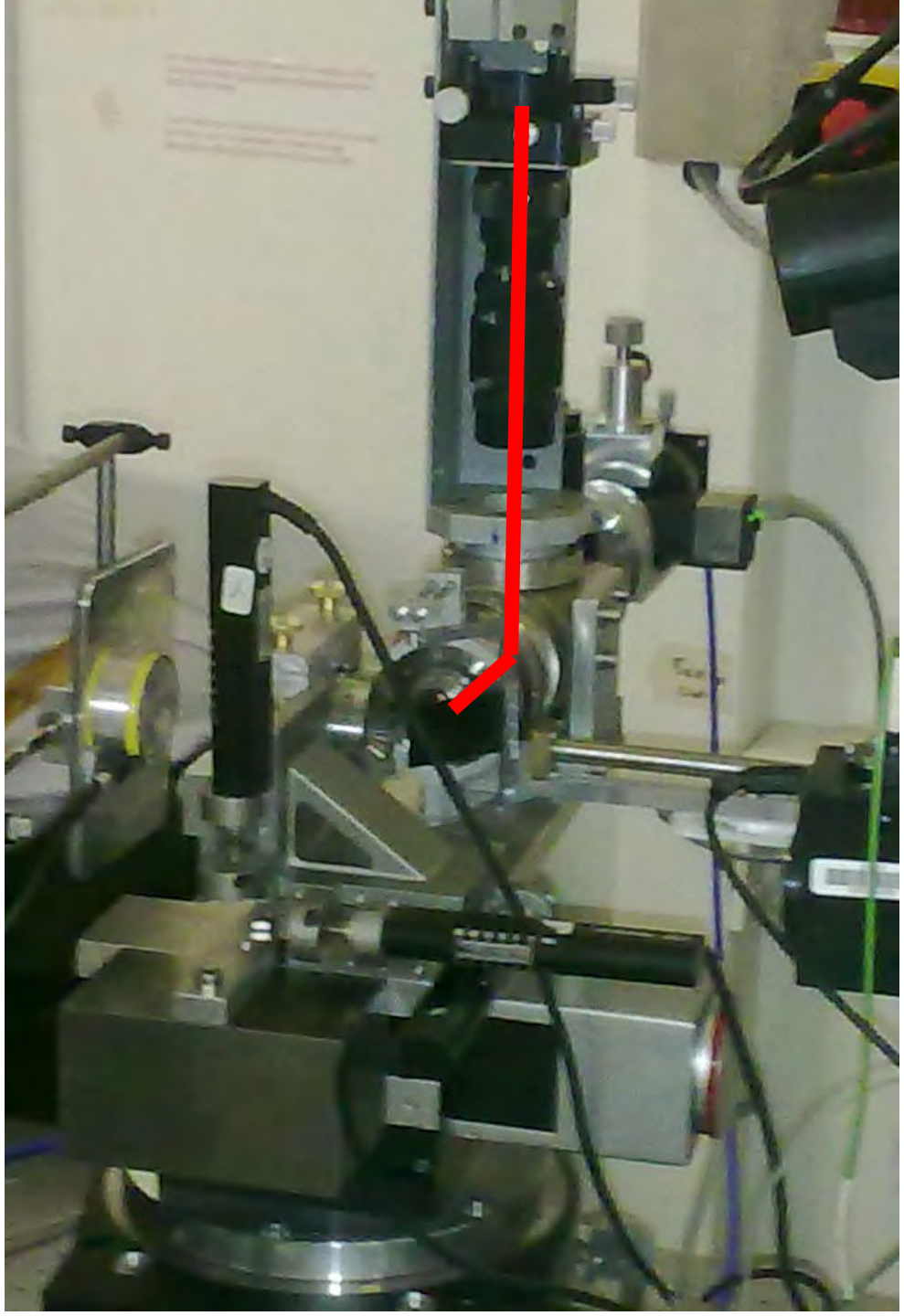
Mirror and lens

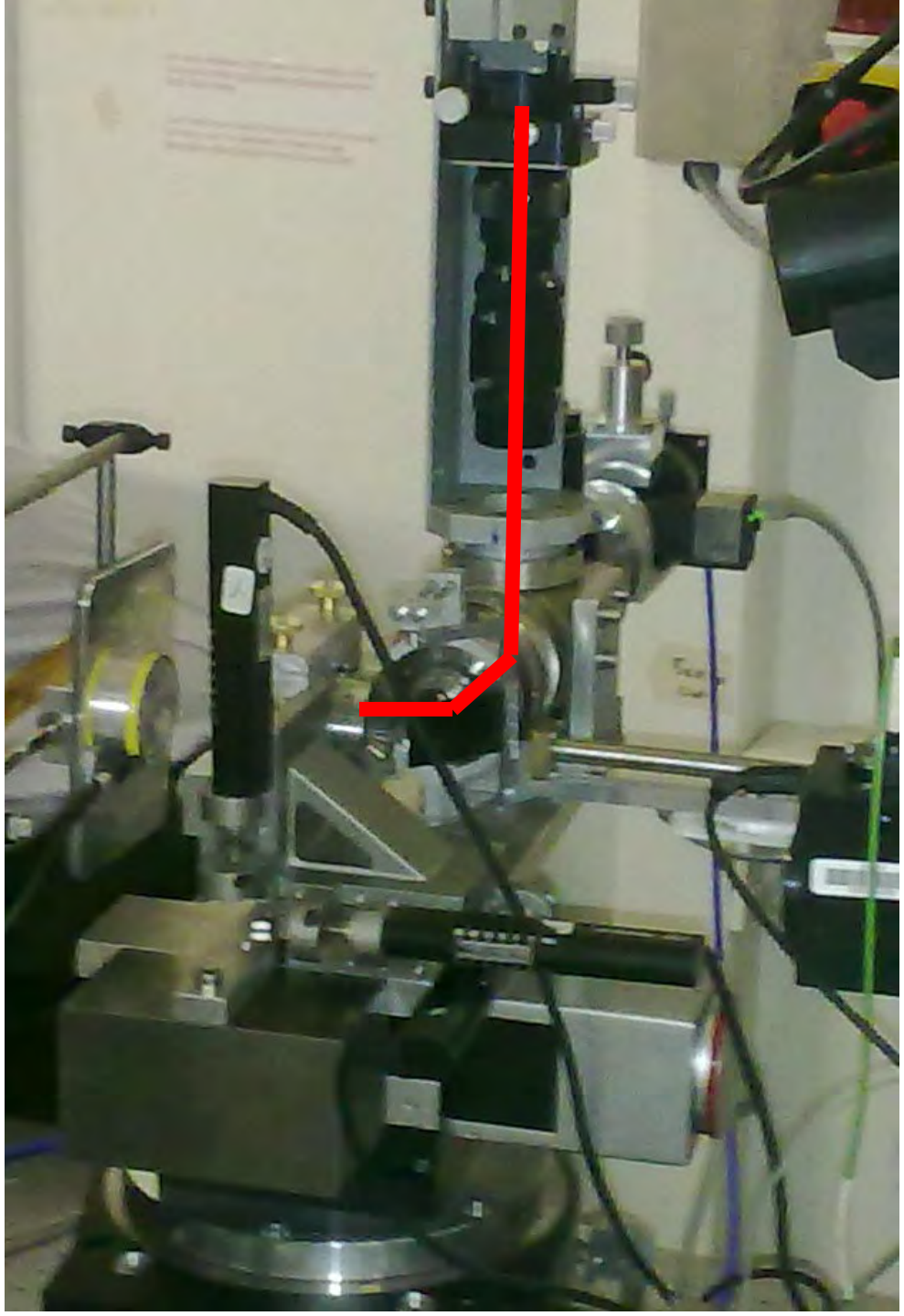

Mirror



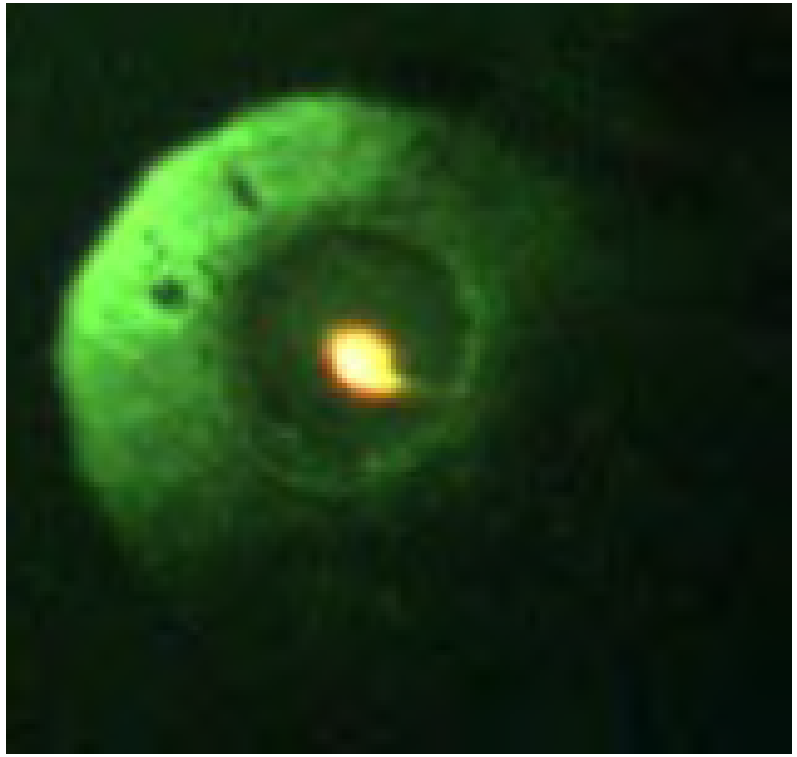
Diamond Anvil Cell

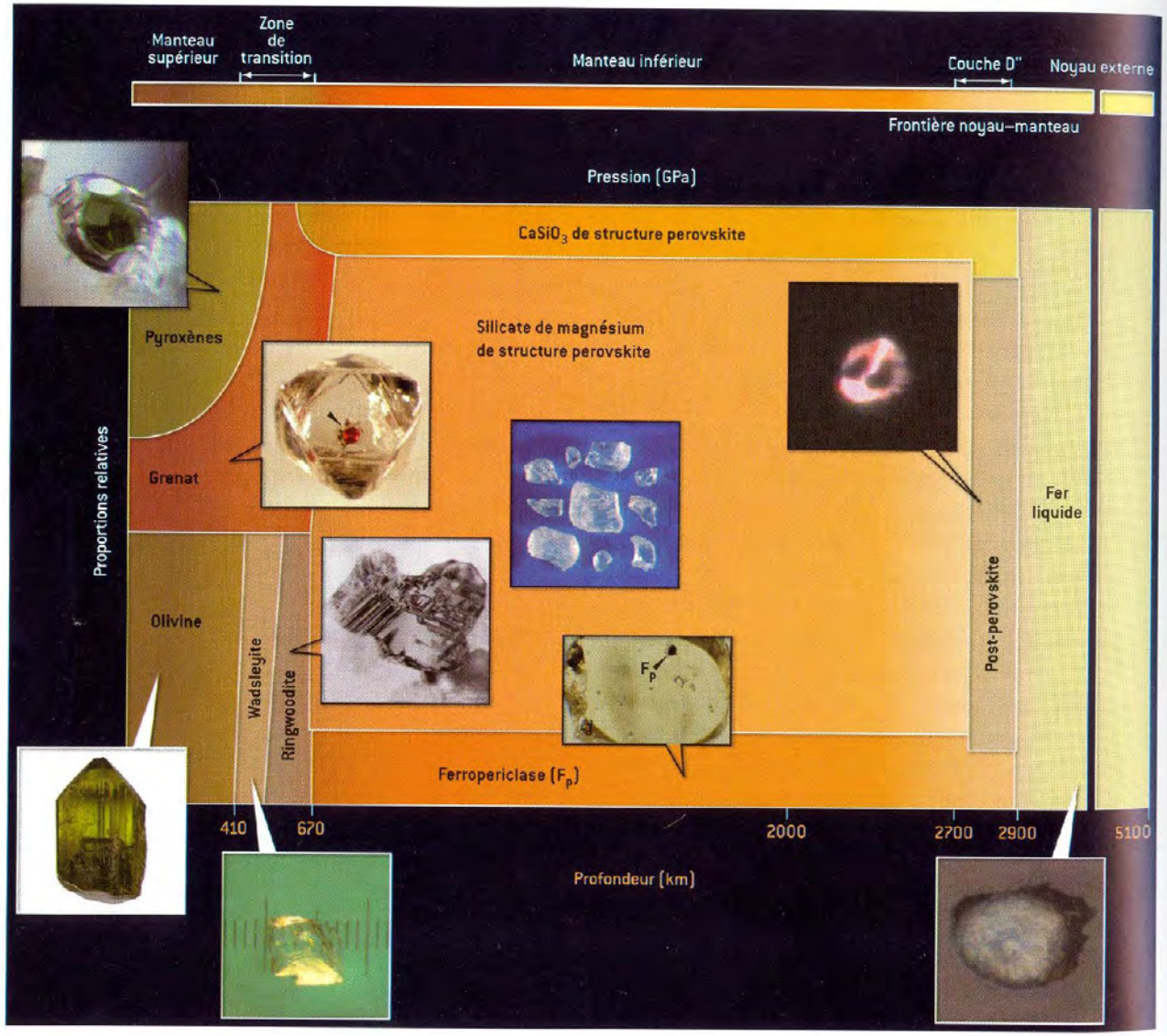






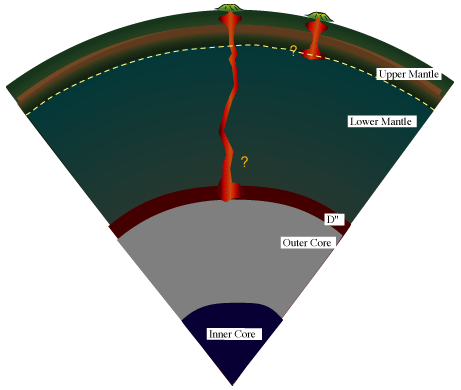
Single crystal laser heating
+ rotation of all the stage
for single crystal diffraction
data collection in situ @
HP/HT

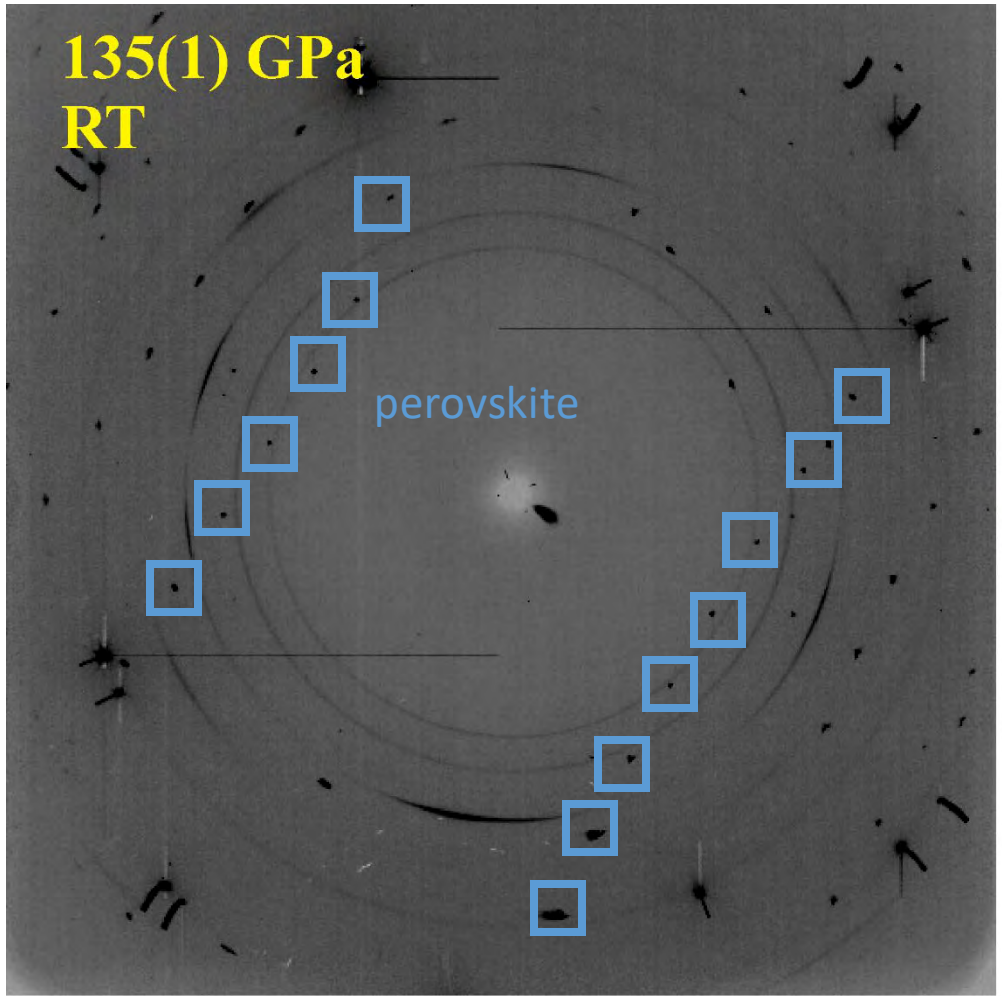


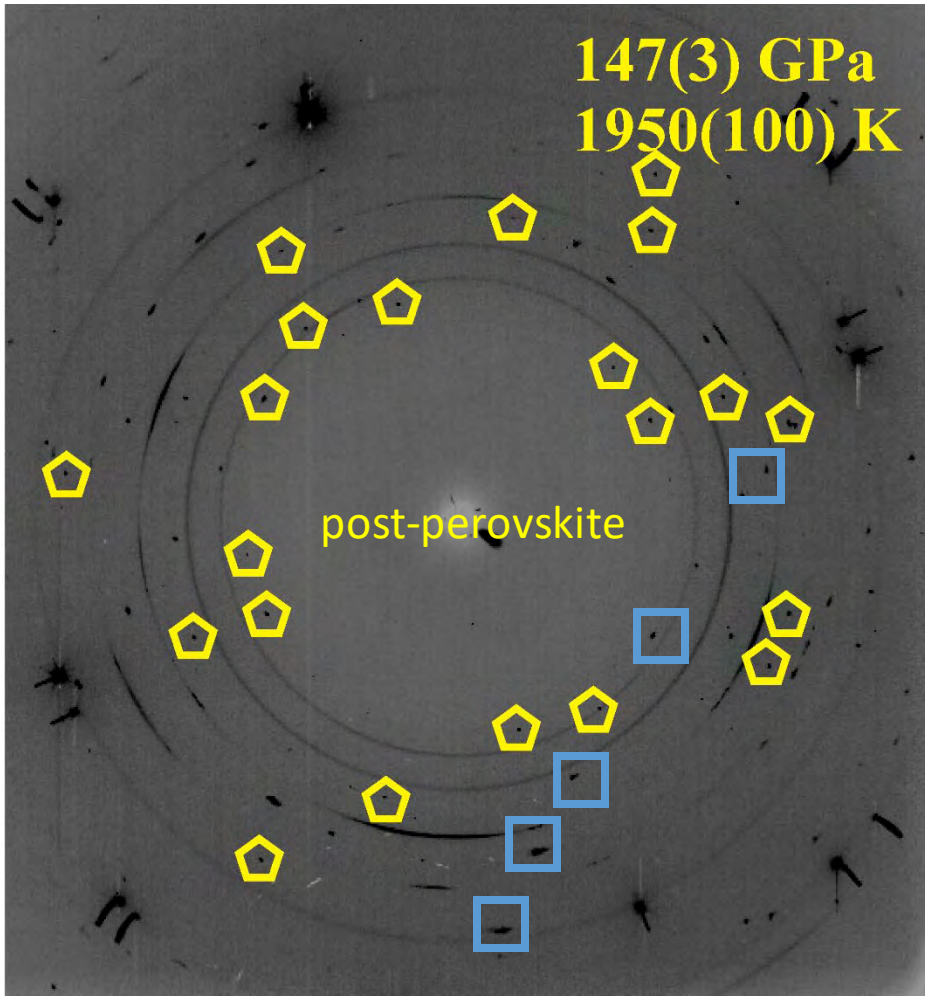

Manteau supérieur
Zone de transition
Manteau inférieur
Couche D"
Noyau externe
Frontière noyau–manteau
Pression (GPa)
$CaSiO_3$ de structure perovskite
Silicate de magnésium de structure perovskite
Pyroxènes
Grenat
Olivine
Wadsleyite
Ringwoodite
Ferropericlase (F_p)
Post-perovskite
Fer liquide
Proportions relatives
410
670
2000
2700
2900
5100
Profondeur (km)

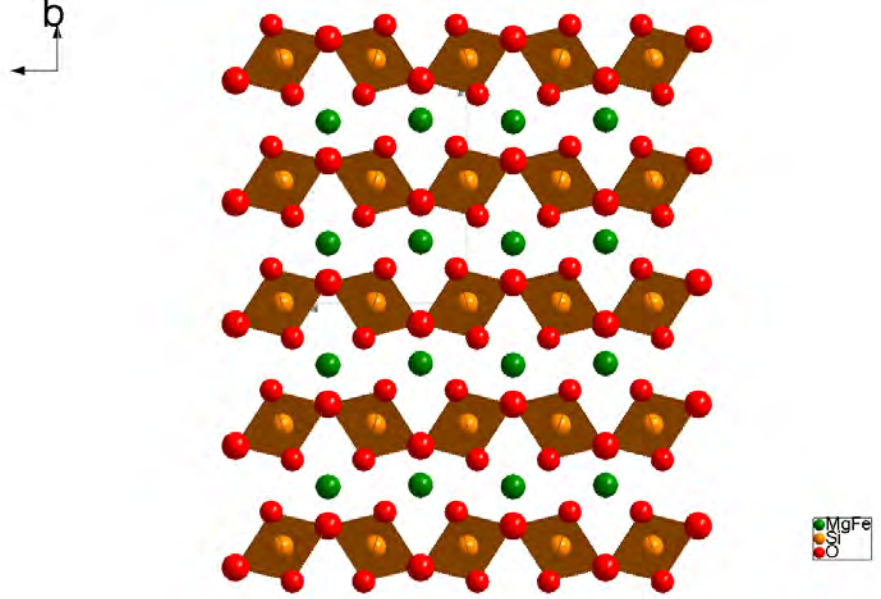
Single crystal diffraction

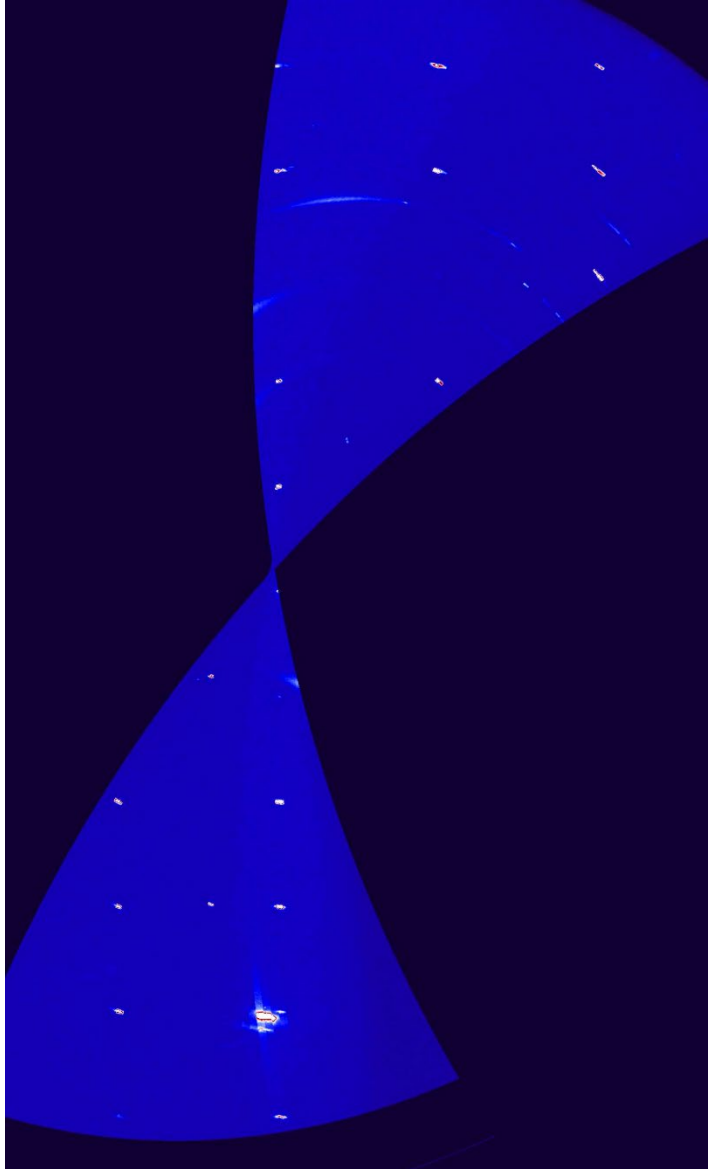
In-situ growing of post-perovskite @ 150 Gpa & 2000 K











Post-perovskite,

struttura a
140 Gpa e 2000K

Crystal data

Formula sum	$Fe_1 Mg_1 O_1 Si_1$
Crystal system	orthorhombic
Space group	*C* m c m (no. 63)
Unit cell	*a* = 2.477(7) Å
	b = 8.03(2) Å
	c = 6.109(13) Å
Cell volume	121.51(50) $Å^3$
Z	16
Pearson code	oC20

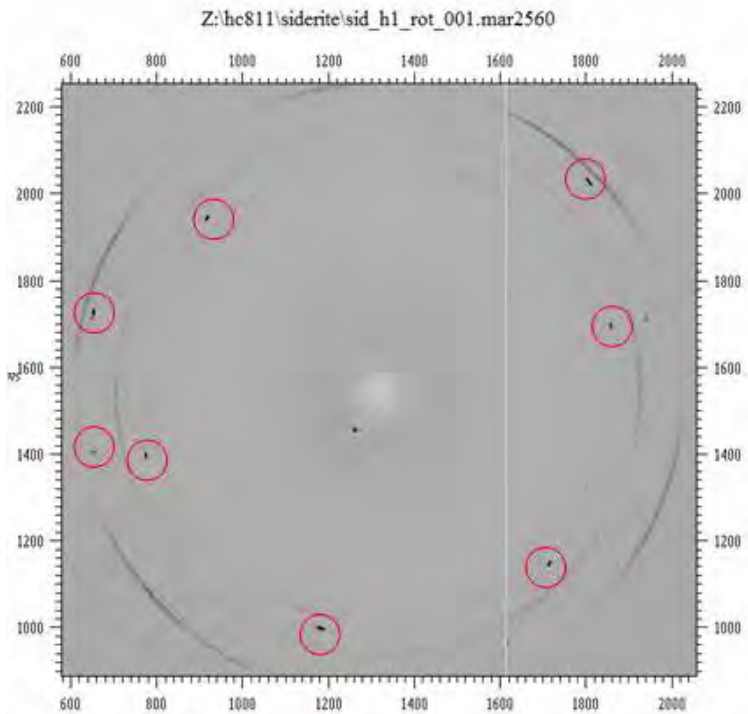
Atomic coordinates and isotropic displacement parameters (in $Å^2$)

Atom	Wyck.	Occ.	x	y	z	U
Mg1	4*c*	0.703	0	0.25346	1/4	0.0149
Fe1	4*c*	0.297	0	0.25346	1/4	0.0149
Si	4*a*		0	0	0	0.0126
O1	4*c*		0	0.91453	1/4	0.0187
O2	8*f*		0	0.64244	0.44277	0.0130

$FeCO_3$

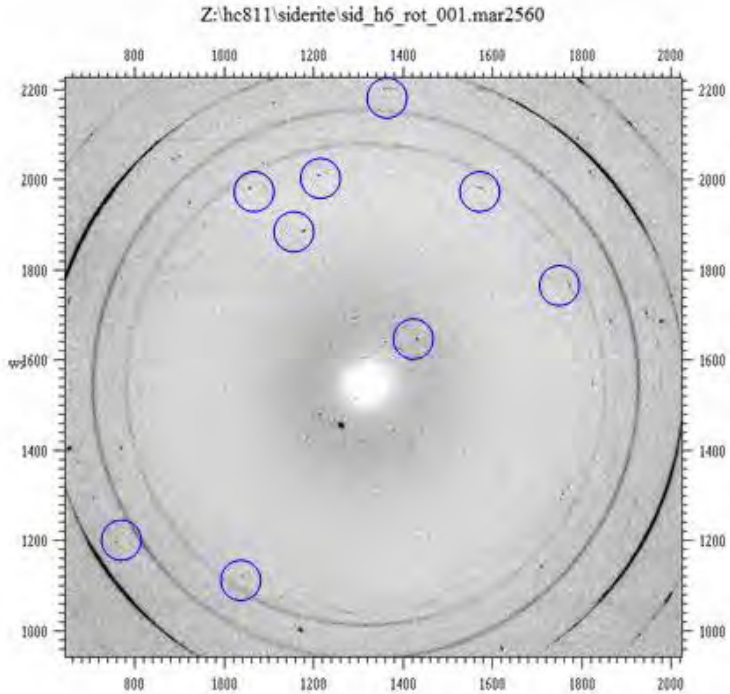
(Experiment with L. Dubrovinsky,
In-situ laser heating single crystal)

1Mbar, start heating



Low pressure FeCO3

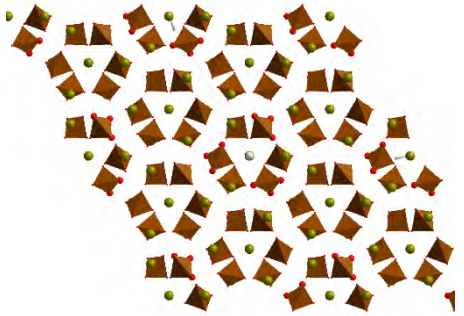
1 Mbar, 2500 K

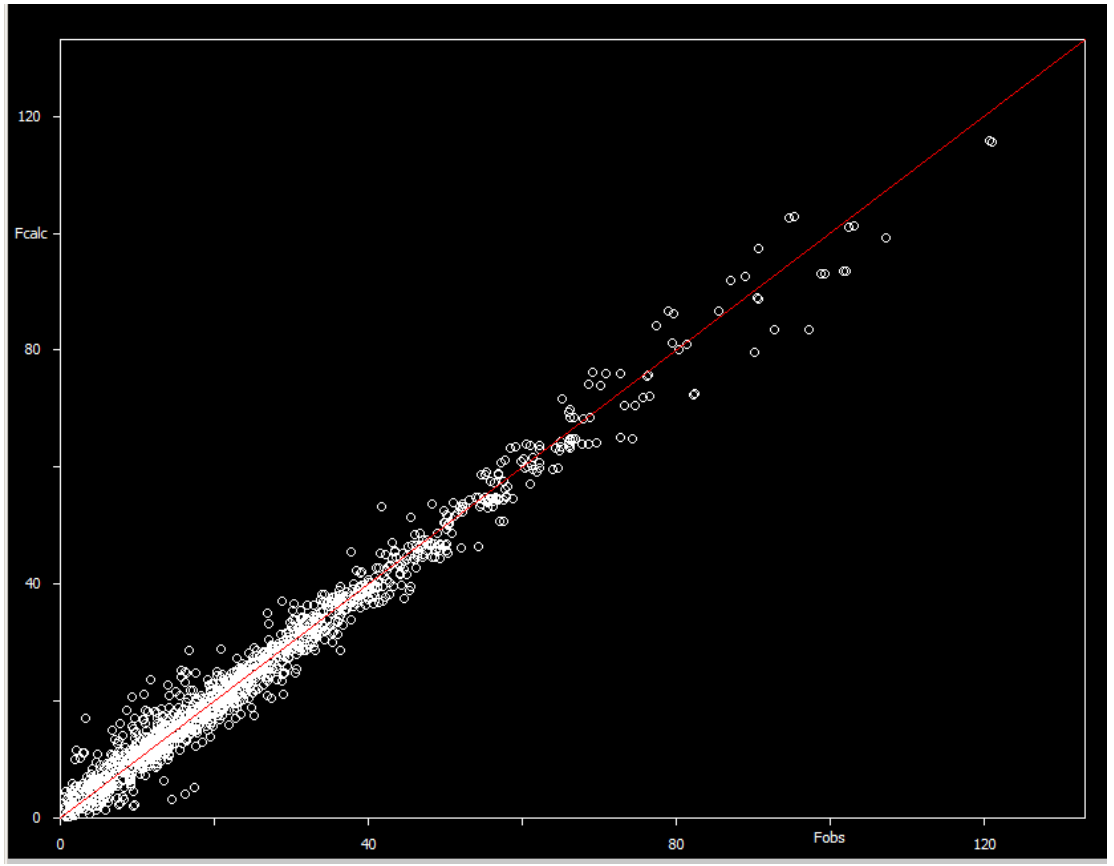


New single crystal diffraction of high pressure Fe-carbonate single crystal

$Fe_4C_3O_{12}$

Dataset collected at 1Mbar and ambient T





Fcalc

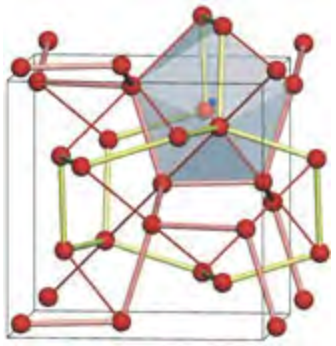
Fobs

Solved and refined in P1, pseudo symmetry elements which suggests possible HT R3c symmetry

1116 obs
151 refined parameters
R(obs) 7 %
R(all) 8 %

```
|R factors : [1338=1116+222/151],    Damping factor:   0.9000          |
|GOF(obs)=  4.44    GOF(all)=  4.03                                    |
|Number of reflections excluded due to refinement options: 22+0        |
|R(obs)=   6.94    wR(obs)=   7.22    R(all)=    8.03    wR(all)=   7.27 |
|Last wR(all):  7.27                                                   |
|Maximum change/s.u. :    0.0083 for z[C2]                           |
```

Complex structures of metals @ High Pressure



Letters to Nature

Nature **408**, 174-178 (9 November 2000) | doi:10.1038/35041515; Received 22 May 2000; Accepted 20 September 2000

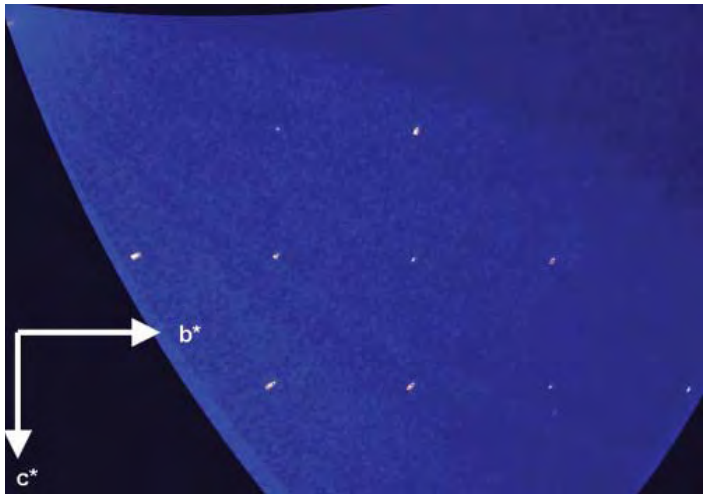
New high-pressure phases of lithium

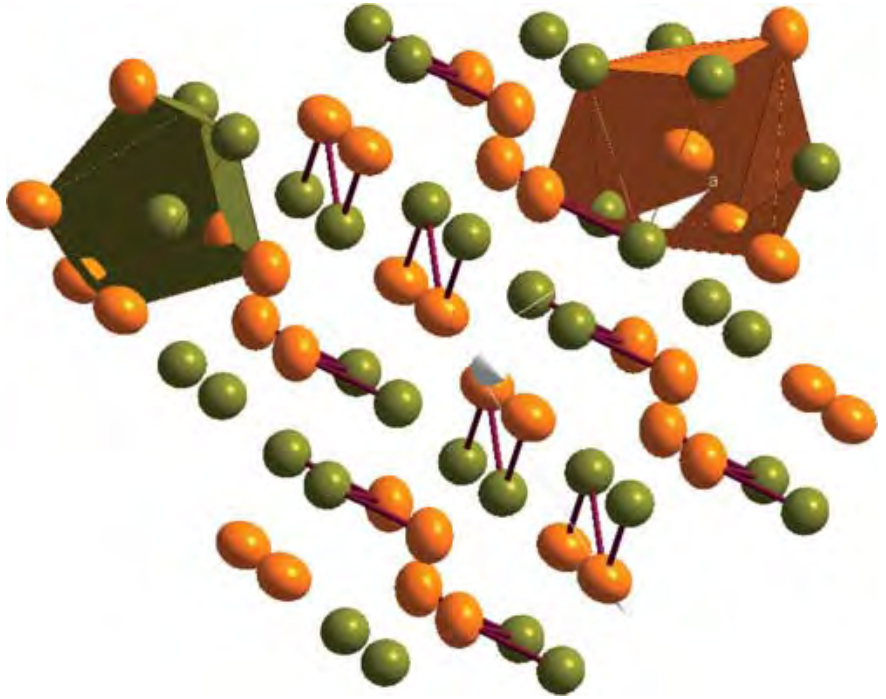
M. Hanfland[1], K. Syassen[2], N. E. Christensen[3] & D. L. Novikov[4]

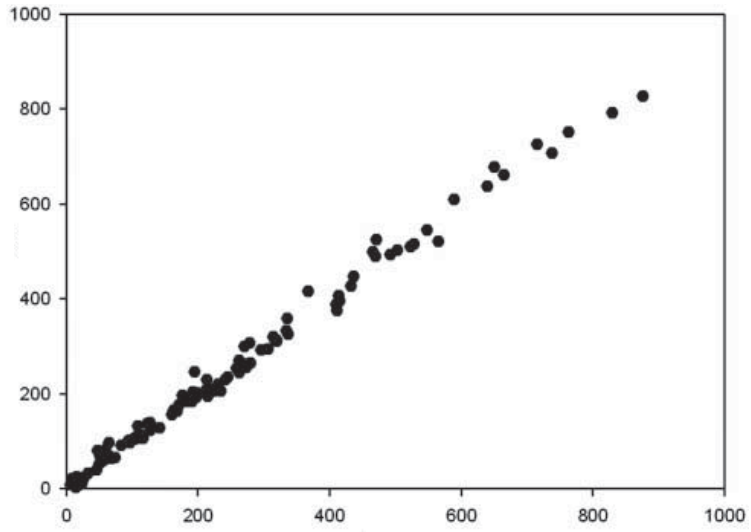
atomic cores. It was recently predicted[1] that at pressures below 100 GPa, dense Li may undergo several structural transitions, possibly leading to a 'paired-atom' phase with low symmetry and near-insulating properties. Here we report synchrotron X-ray diffraction measurements that confirm that Li undergoes pronounced structural changes under pressure. Near 39 GPa, the element transforms from a high-pressure face-centred-cubic phase, through an intermediate rhombohedral modification, to a cubic polymorph with 16 atoms per unit cell. This cubic phase has not been observed previously in any element; unusually, its

The predictions by Neaton and Ashcroft[1] are in sharp contrast to intuitive expectation that the application of hydrostatic pressure favours high-coordination crystal structures with metallic properties. In their theoretical simulations of dense Li, which are based on first principles band structure theory, they compare the relative stability of a number of crystal structures common among elemental solids. Their results clearly indicate a strong preference of dense Li to form low-symmetry structures. Therefore, experiments aimed at structure determinations of compressed Li are highly desirable. Furthermore, experimental high-pressure studies of Li are of fundamental interest, because they are expected to reveal new aspects relevant for the theoretical modelling of other light elements, including hydrogen[2], at high density.

Na oP8 structure determined at 118 GPa

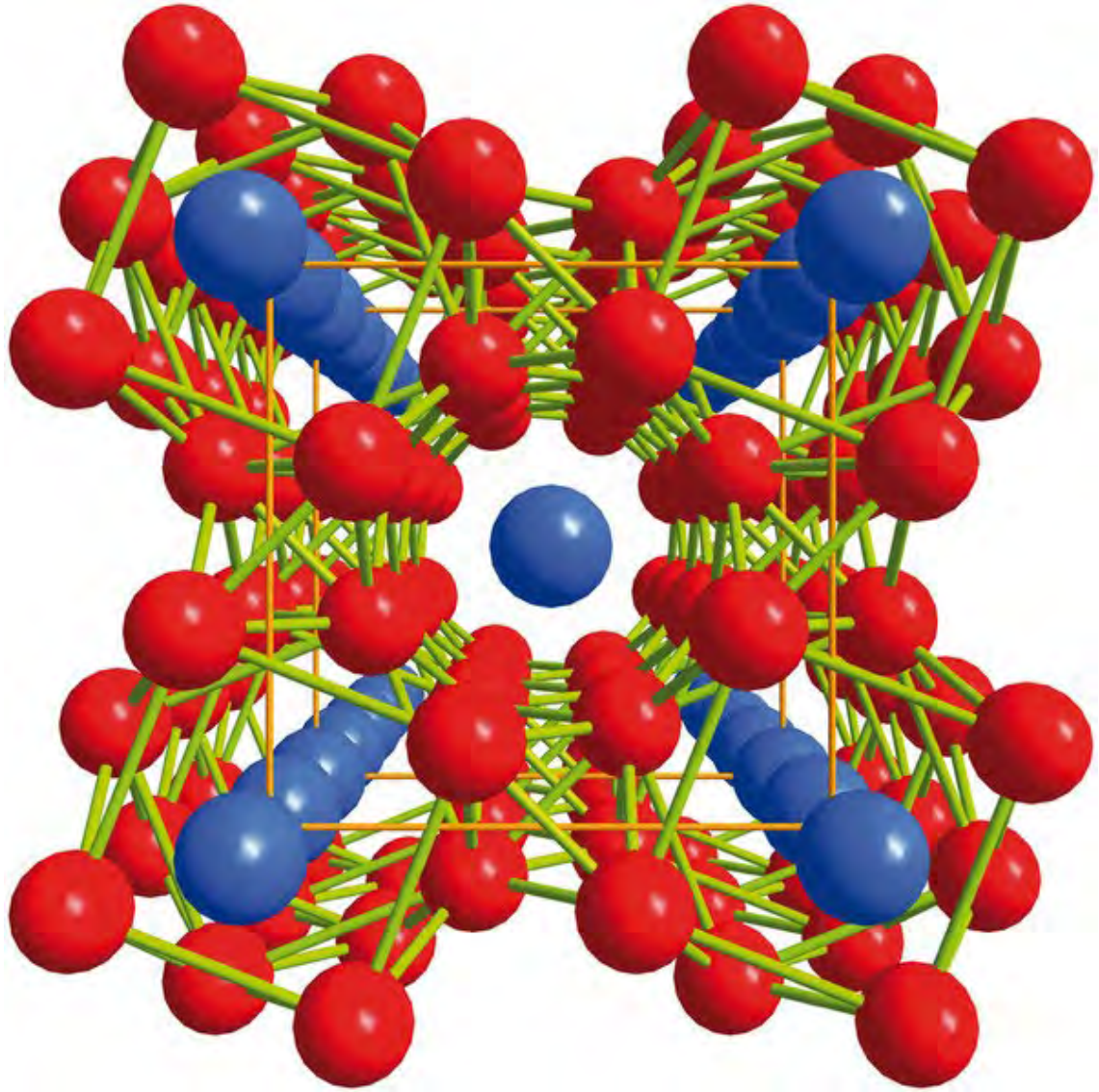






MnP type structure

Single atomic species, but binary compound type structure

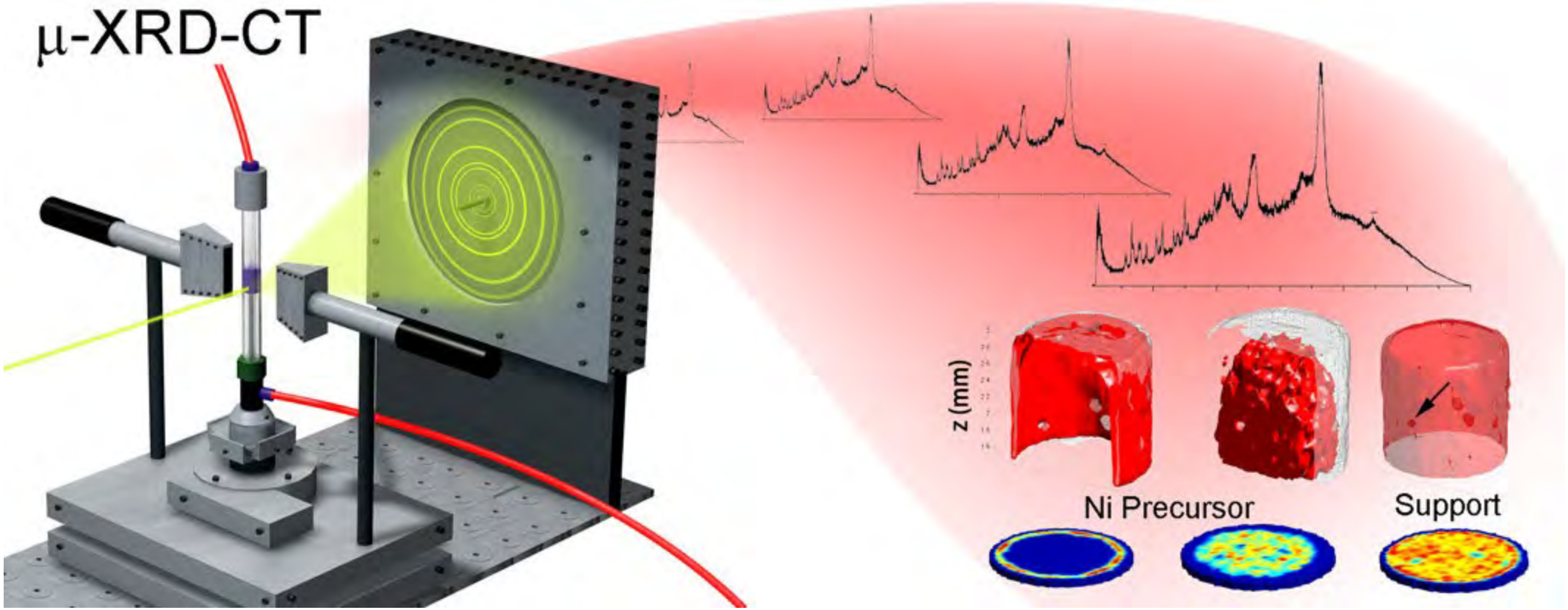


Na – host-guest structure P > 125 GPa

- Single crystal diffraction on crystals with size down to 0.005x0.005x0.005 mm (almost routine) and even less

- Possibility to have structural information from single crystal data at non ambient conditions, not only with static measurements (i.e high pressure) but also during dynamic processes (i.e. variable magnetic field, temperature, etc) on second time scale

3) EXAMPLE: Diffraction tomography



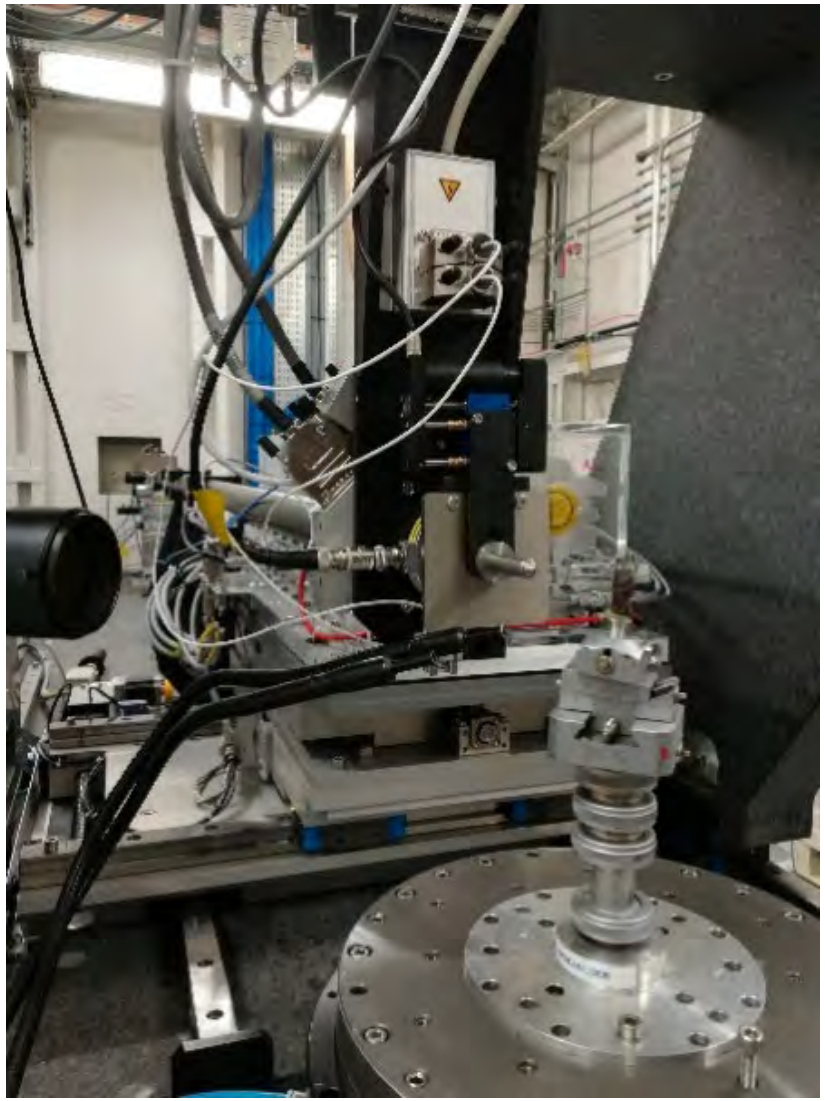
ESRF, ID15A

Courtesy of Marco Di Michiel

Experimental setup

Energy	90 KeV
(ʎ)	0.137 Angstrom
Sample to detector distance	1.00/1.40 m
Data collection	Continuous rotation

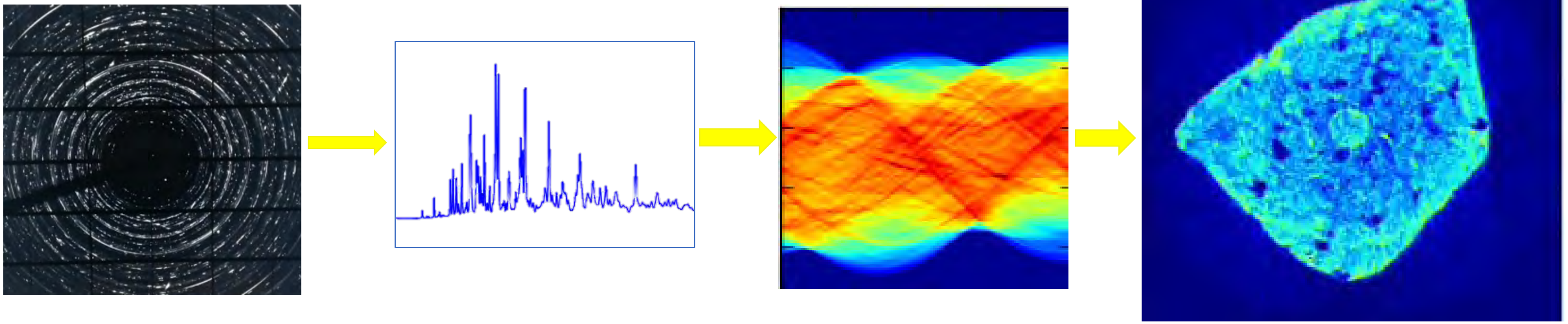
- Monochromatic beam
- Continuous translation and rotation of the sample
- Diffraction data collection during translation and rotation



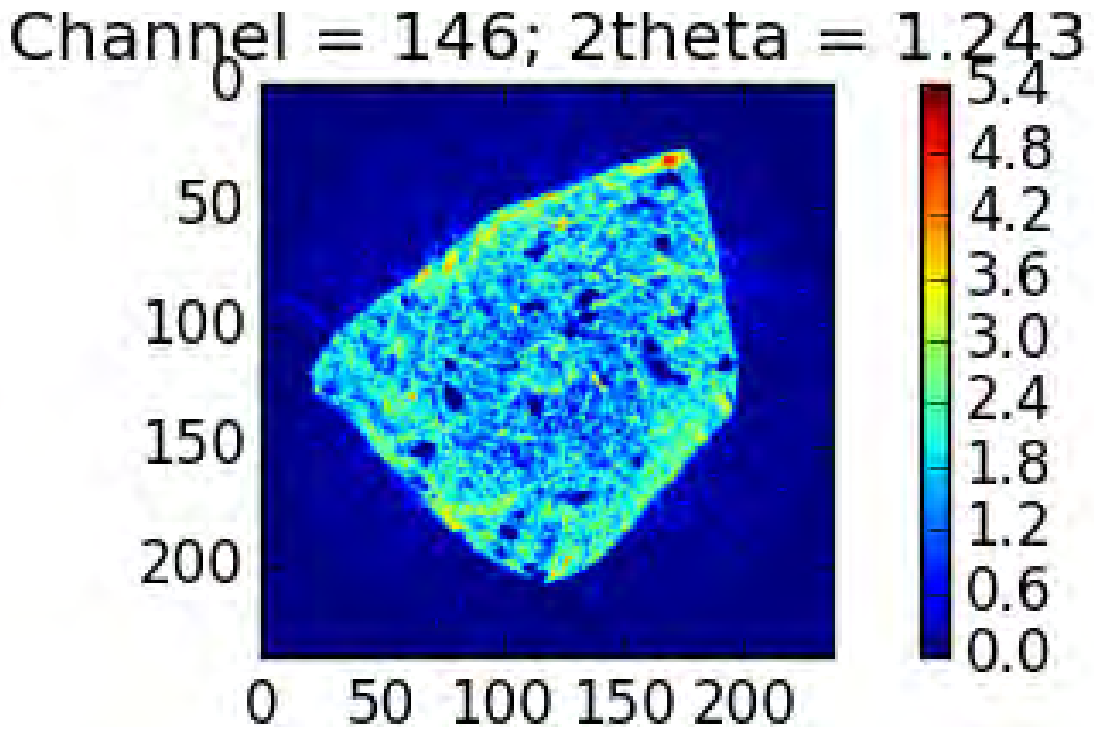
Courtesy of Laura Leone

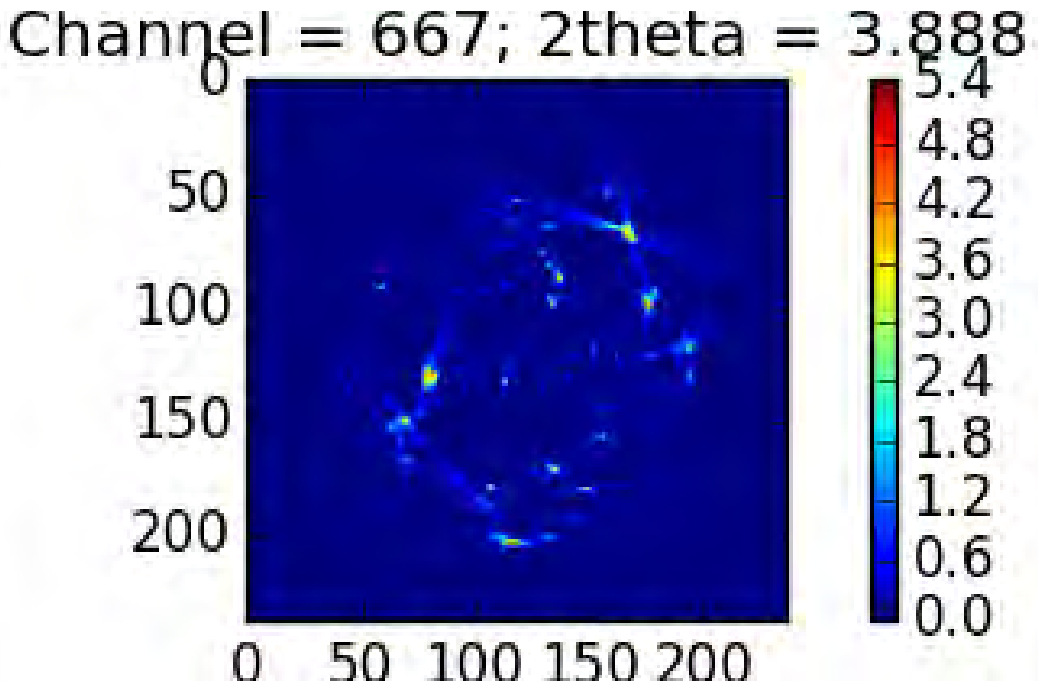
COSA SI OTTIENE?

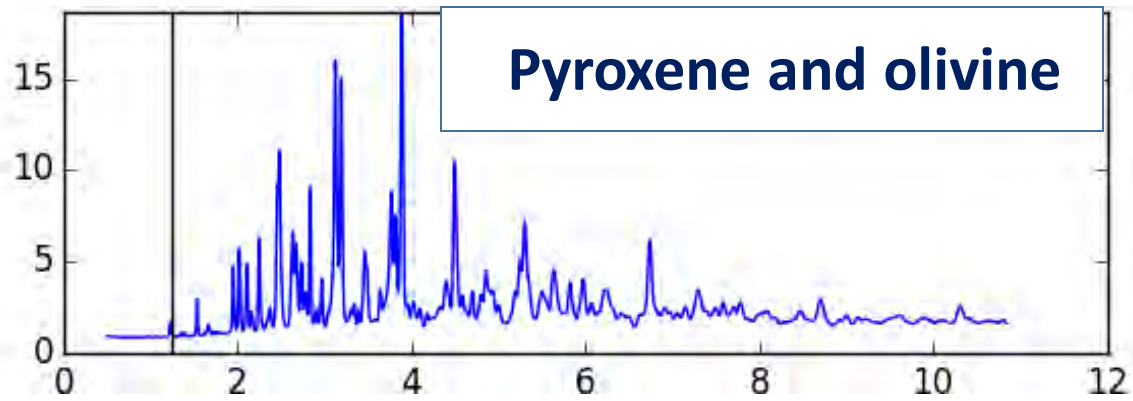
- 2D diffraction
- Integration → from 2D to 1D powder pattern
- «Elaboration» of pattern (synogram)
- «Slices»

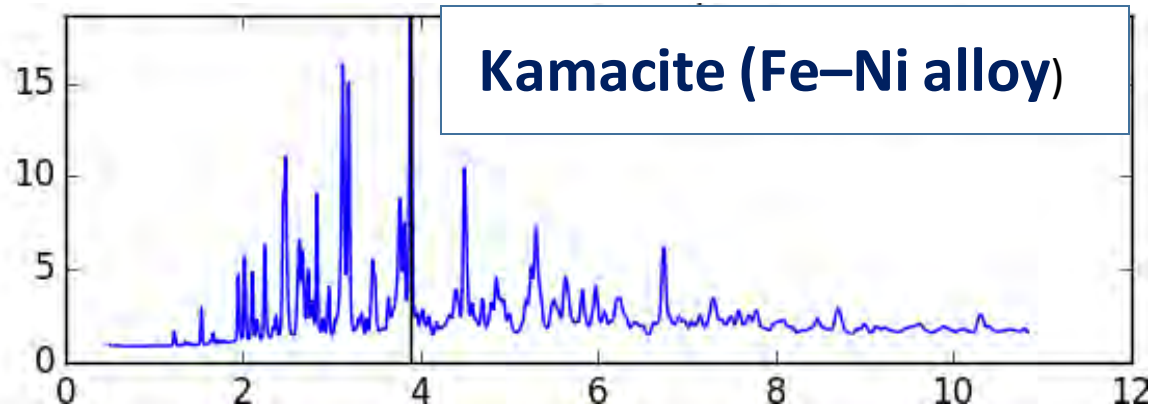


METEORITE from museum collection

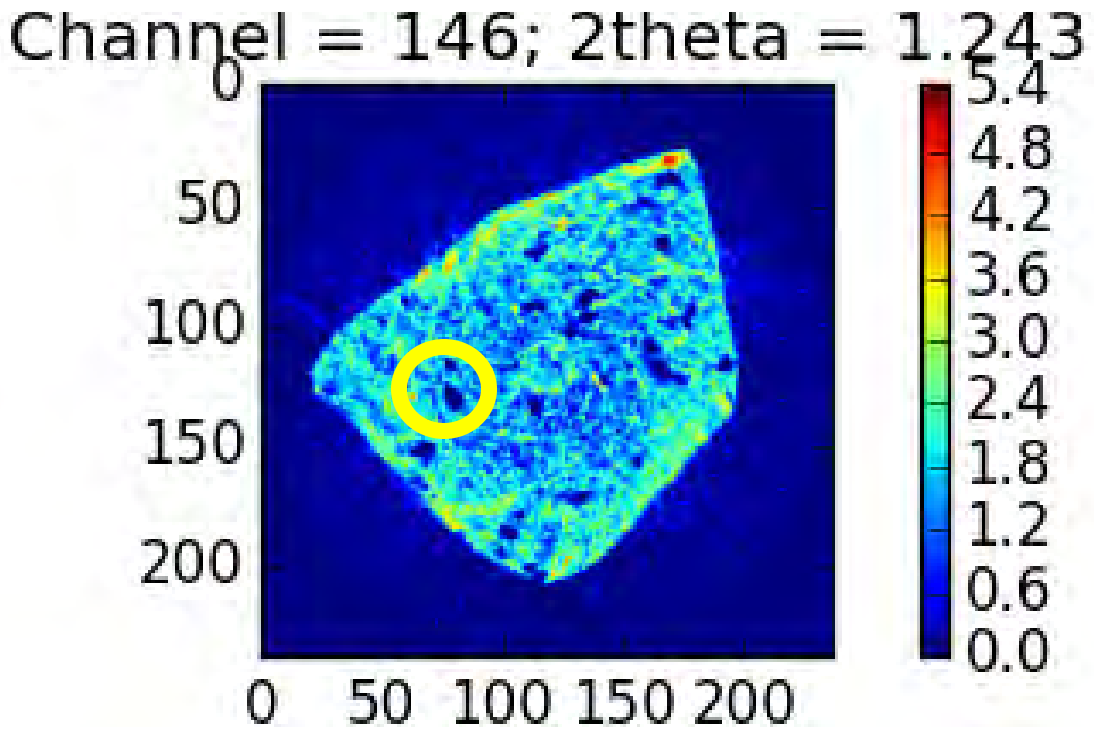


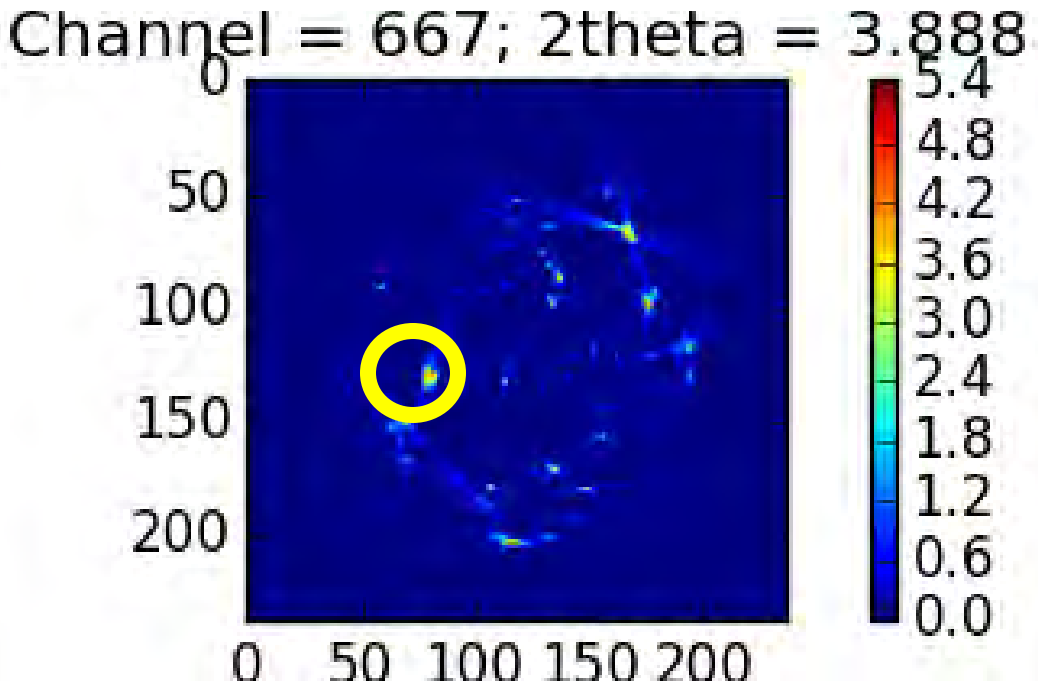


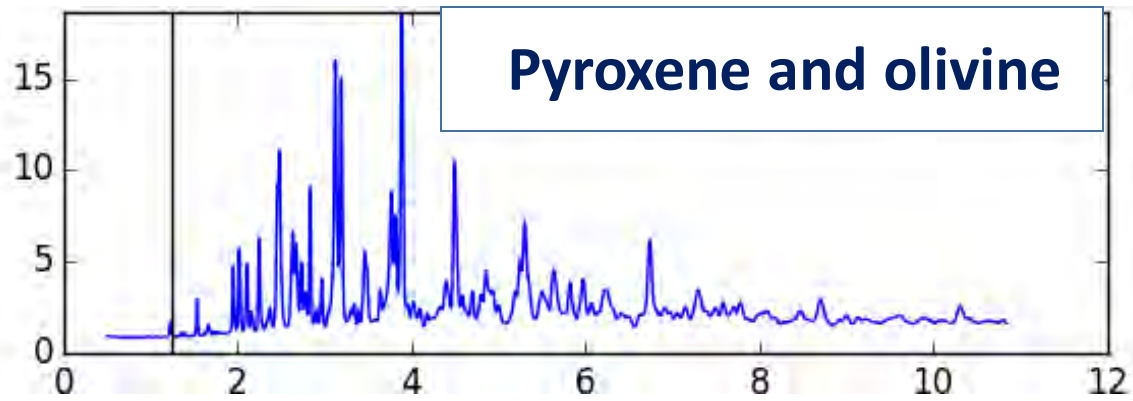


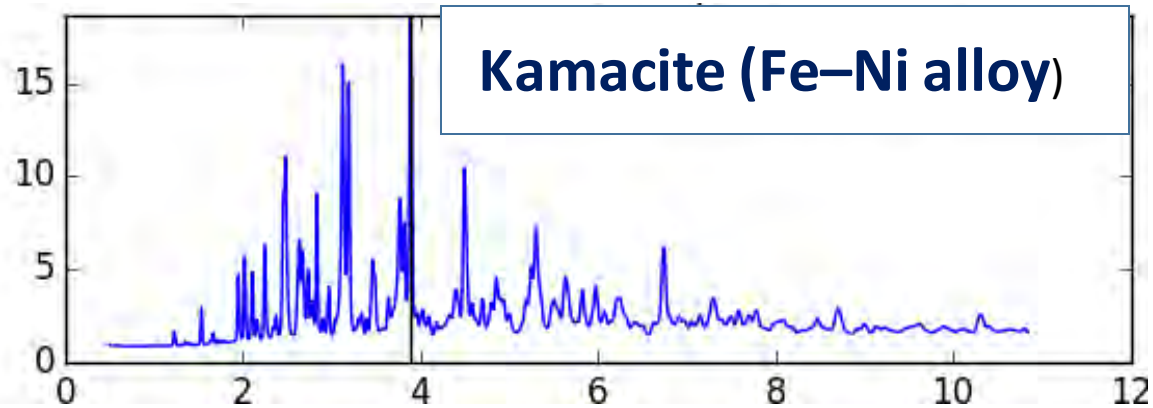


METEORITE from museum collection

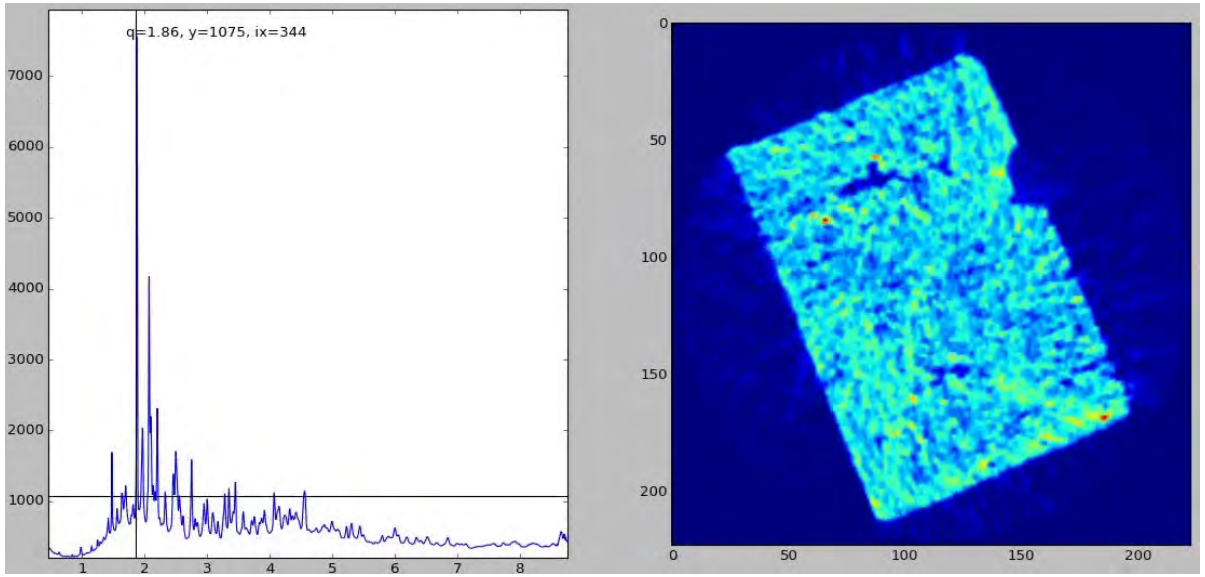




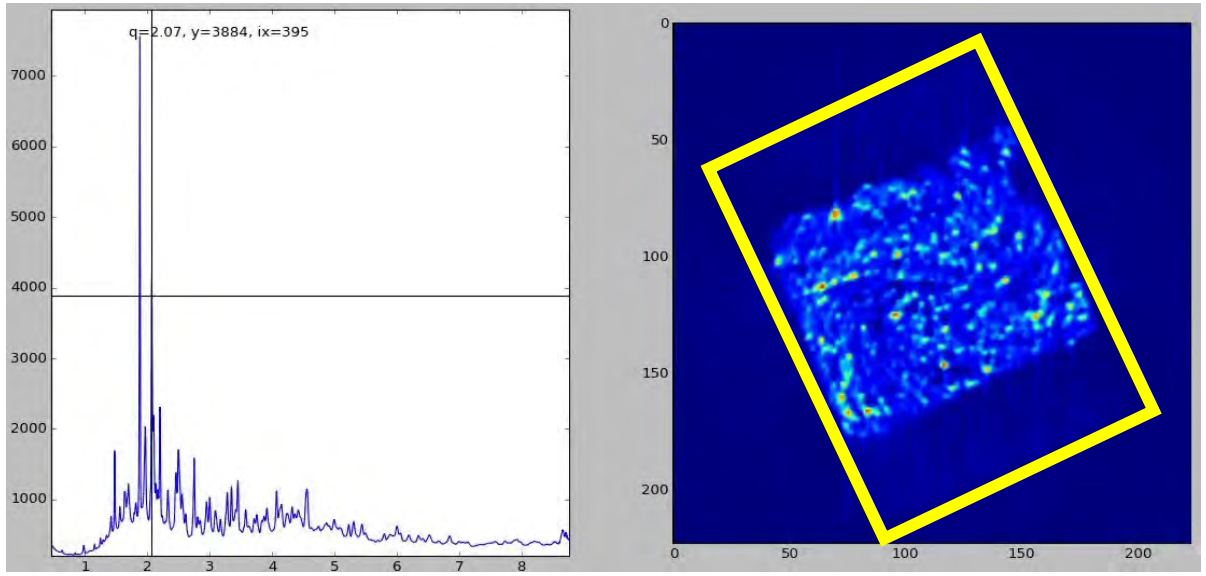




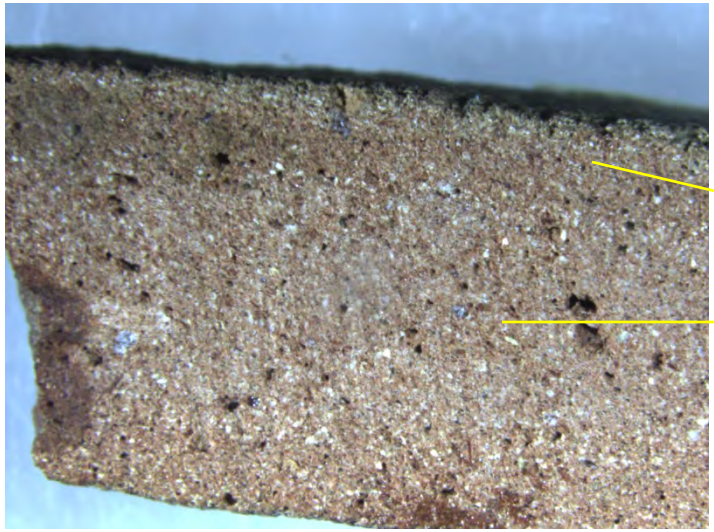
Archaeological sample: ceramic from northern Africa, Roman period (apx. 2000 year ago)



Quartz (SiO_2)

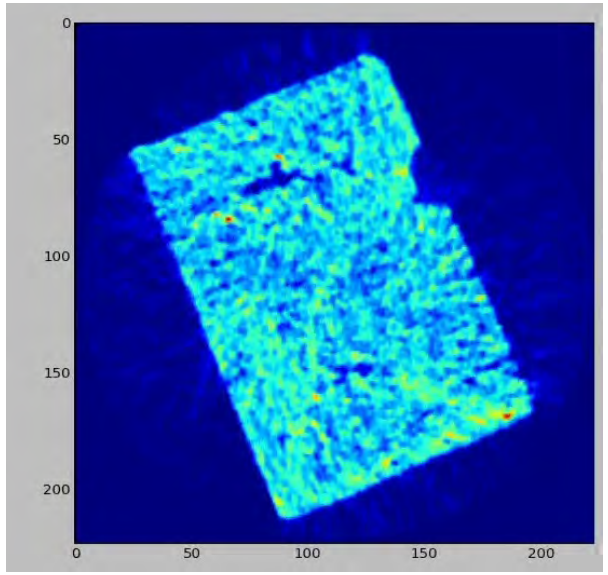


Calcite ($CaCO_3$)

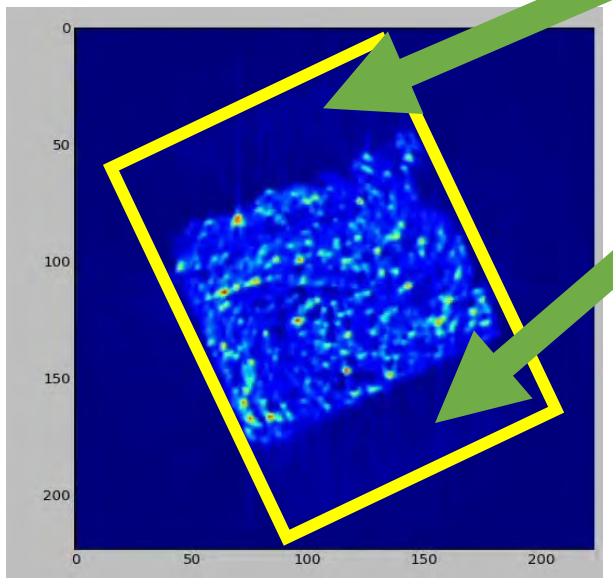


Different granulometry and calcite distribution

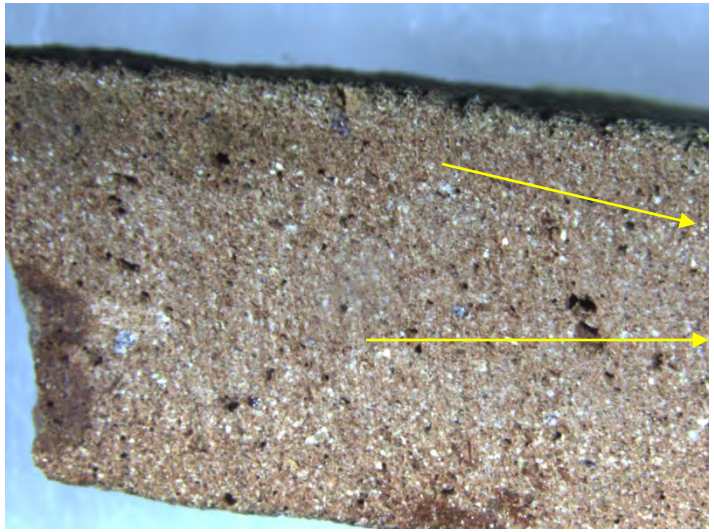
Archaeological sample: ceramic from northern Africa, Roman period (apx. 2000 year ago)



Quartz (SiO2)



Missing calcite in external portion of ceramic:
«Sandwitch» preparation
With different clay composition



Different granulometry and calcite distribution

Journal of
Synchrotron Radiation

ISSN 0909-0495

Single-crystal diffraction at the Extreme Conditions beamline P02.2: procedure for collecting and analyzing high-pressure single-crystal data

André Rothkirch, G. Diego Gatta, Mathias Meyer, Sébastien Merkel, Marco Merlini and Hanns-Peter Liermann

J. Synchrotron Rad. (2013). **20**, 711–720

Commercial softwares (i.e. scientists and engeneer working full time for software development, maintainance and upgrades) for single crystal data reduction from area detectors work much better than in-house written codes

XDS, Crysalis, etc… are normally available at synchrotron beamlines and universities/research center

PETRA III, DESY, is presented. A new data image format called 'Esperanto' is introduced that is supported by the commercial software package *CrysAlis*^{Pro} (Agilent Technologies UK Ltd). The new format acts as a vehicle to transform the most common area-detector data formats *via* a translator software. Such a conversion tool has been developed and converts tiff data collected on a Perkin Elmer detector, as well as data collected on a MAR345/555, to be imported into the *CrysAlis*^{Pro} software. In order to demonstrate the validity of the new