Elettra Sincrotrone Trieste

Powder diffraction at Synchrotrons

J.R. Plaisier

Elettra Sincrotrone Trieste

Synchrotron Radiation

Nan ED

Light is used by the researchers to study the properties of matter on the scale of atoms and molecules.

The information that can be obtained are related to several different fields: electronics, earth sciences, biology, environmental research, material engineering, medicine, nanotechnology …

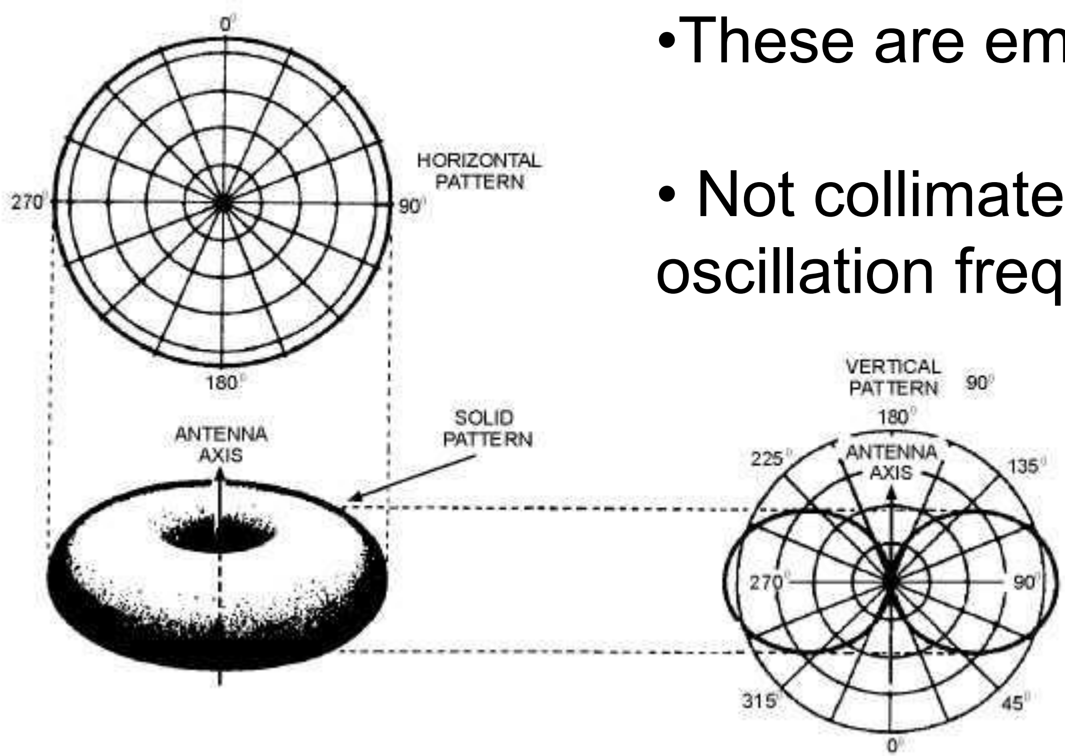
Synchrotron Radiation

•Accelerating charged particles emit light

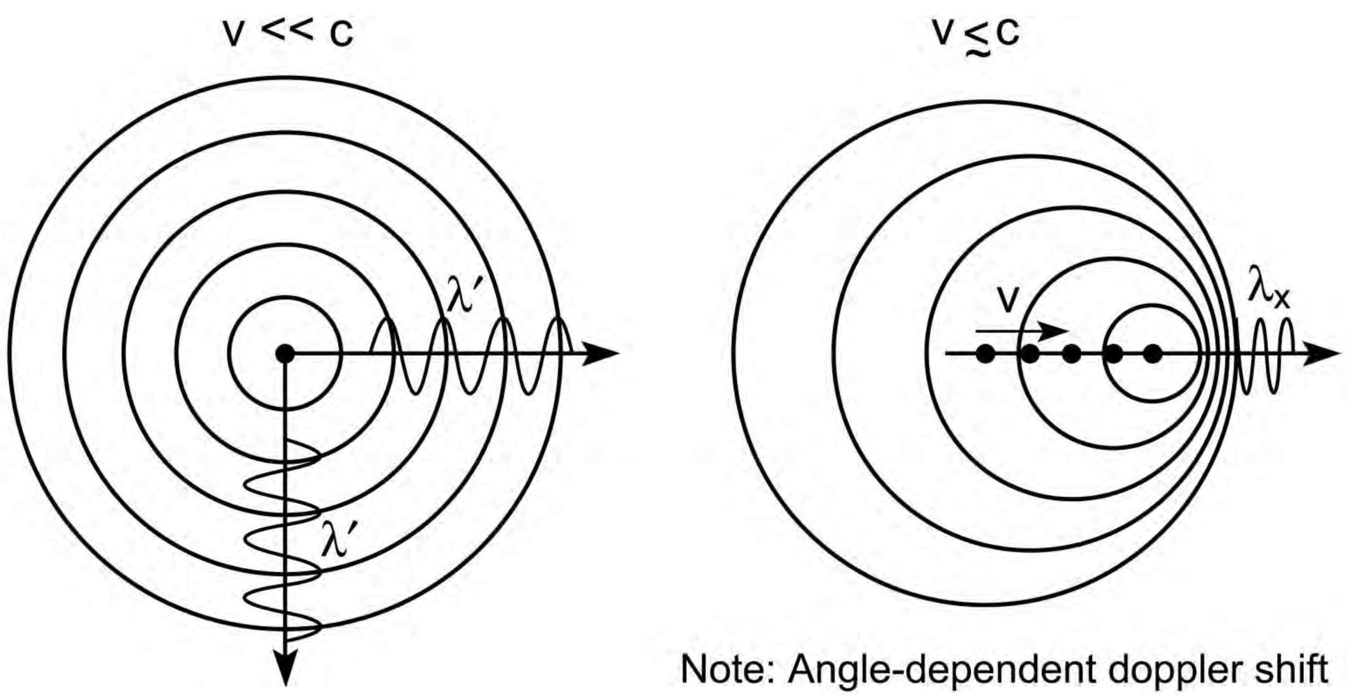
• radio, microwave, infrared, visible, UV X-rays

•These are emitted in a dipole pattern

• Not collimated - frequency is same as oscillation frequency



Synchrotron Radiation

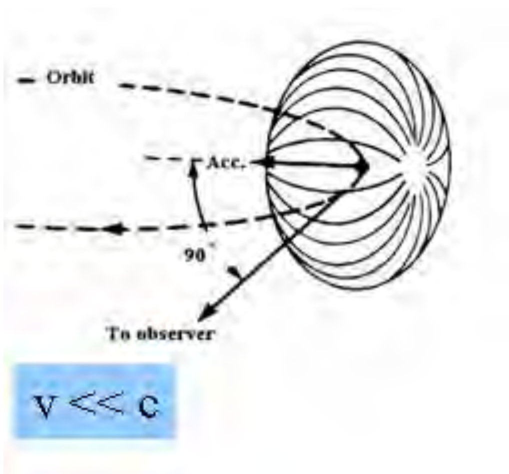


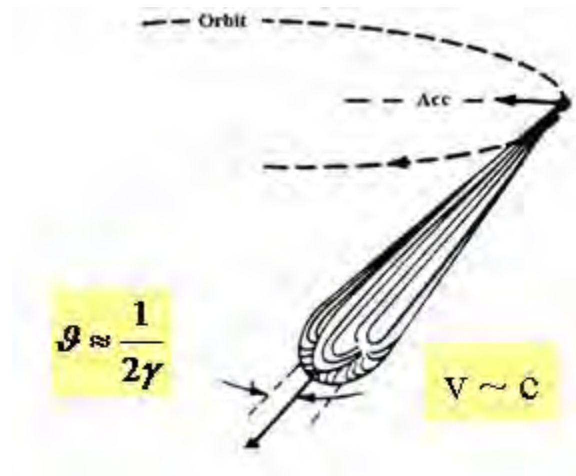
$$\lambda = \lambda' \left(1 - \frac{v}{c}\cos\theta\right) \qquad \lambda = \lambda' \gamma \left(1 - \frac{v}{c}\cos\theta\right)$$

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}$$

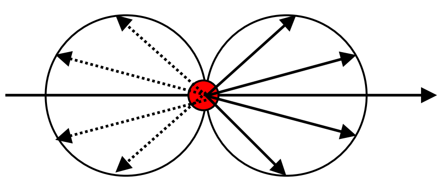
The Lorentz factor or Lorentz term is the factor by which time, length, and relativistic mass change for an object while that object is moving. The expression appears in several equations in special relativity, and it arises in derivations of the Lorentz transformations. The name originates from its earlier appearance in Lorentzian electrodynamics – named after the Dutch physicist Hendrik Lorentz.

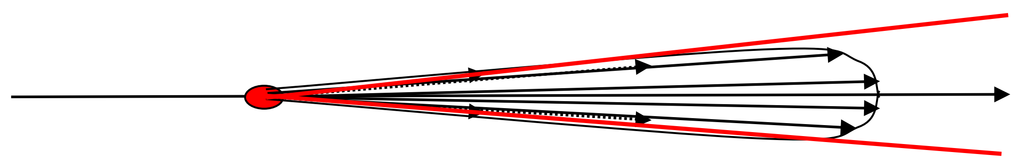
Synchrotron Radiation





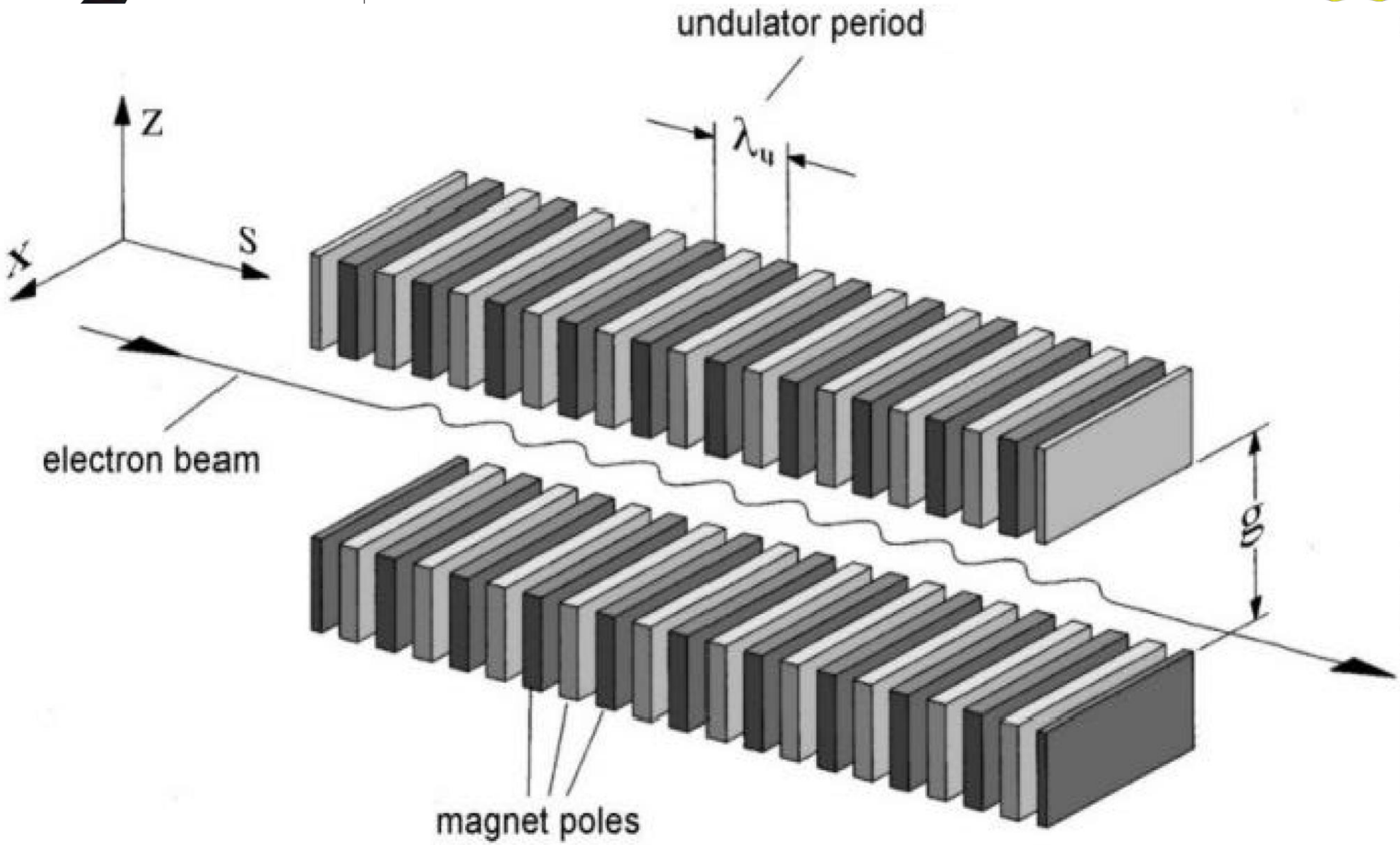
$\gamma = \frac{E}{mc^2}$



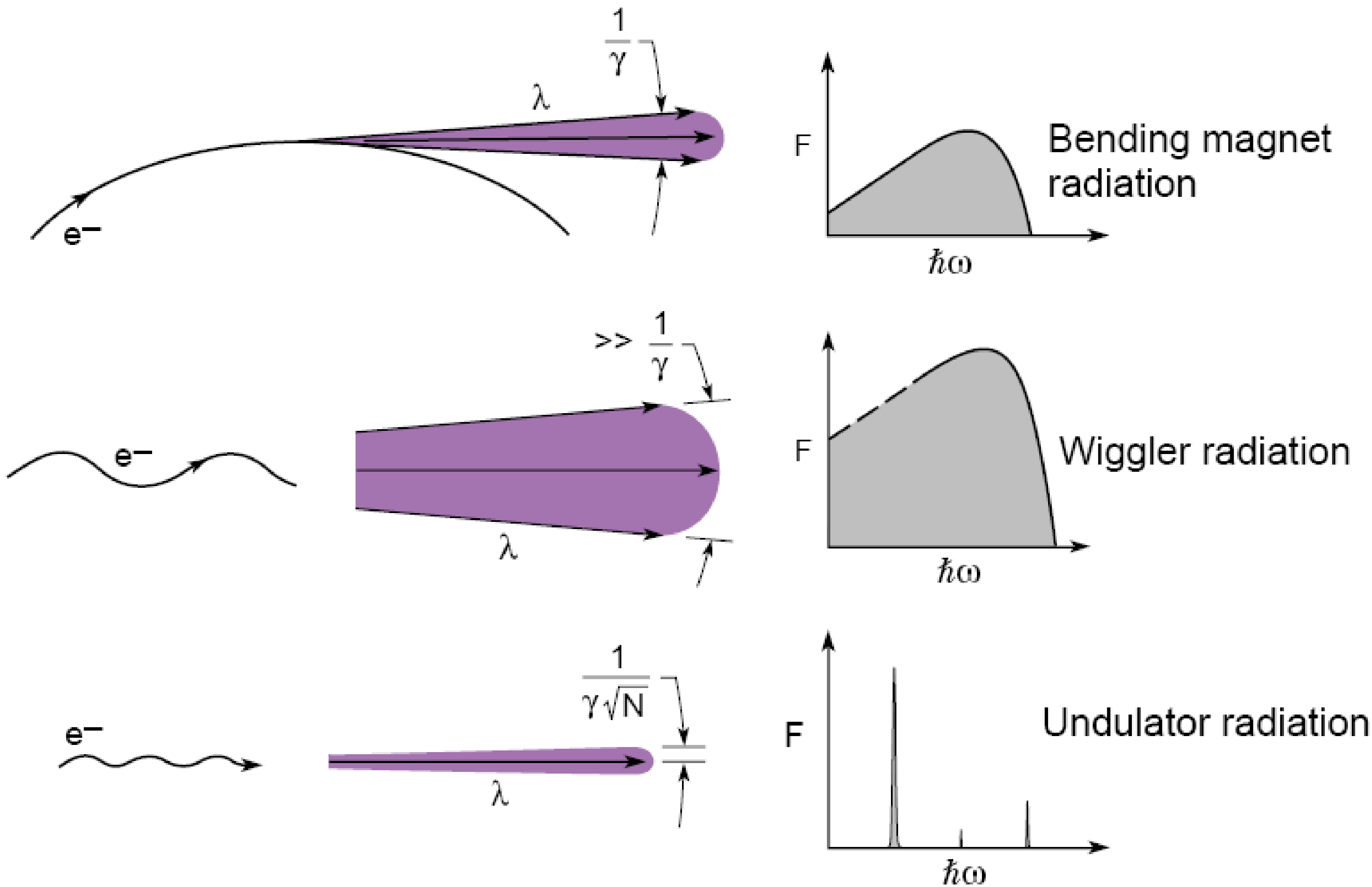


(E=2GeV → θ=0.12mrad=0.007°)

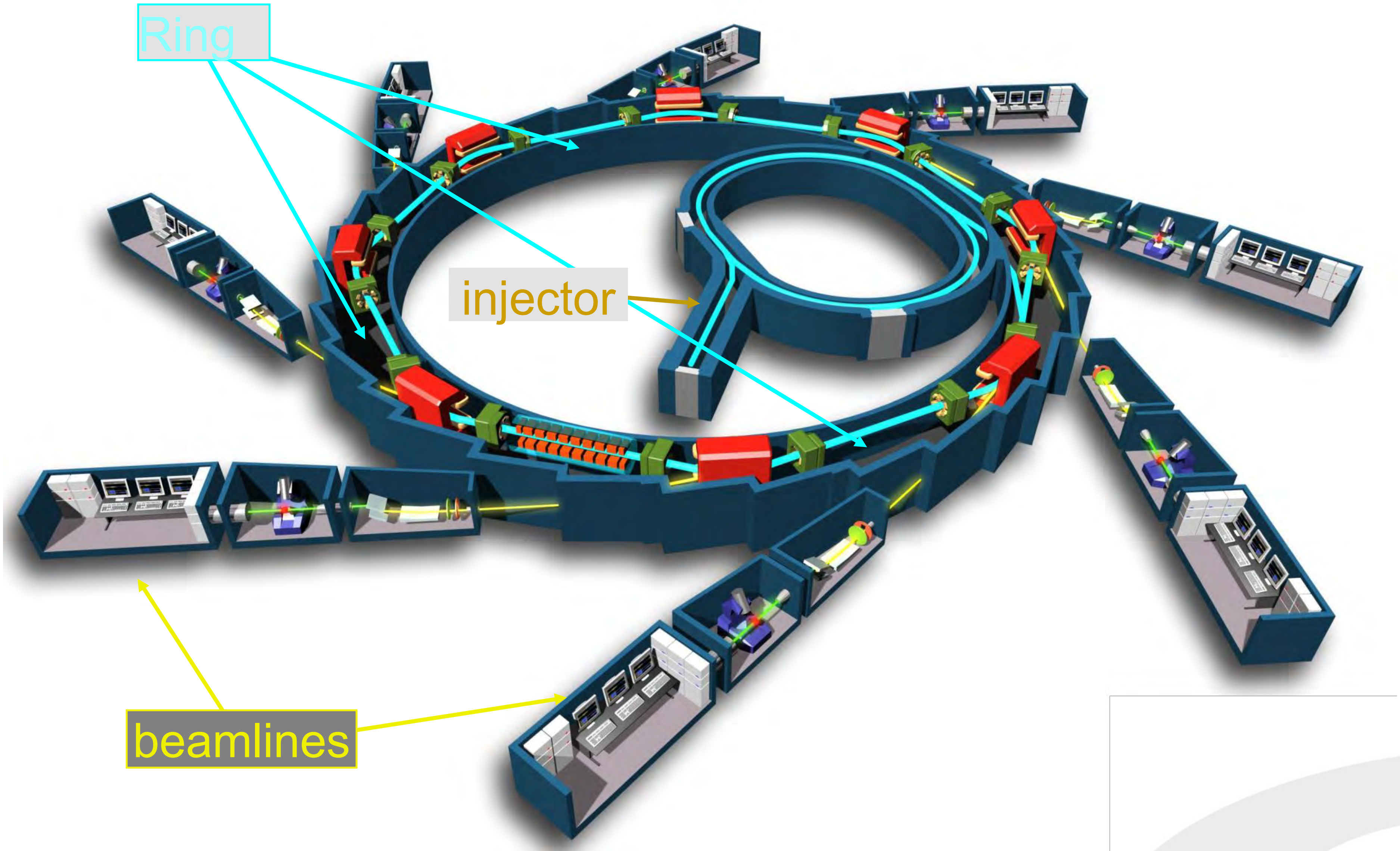
Synchrotron Radiation



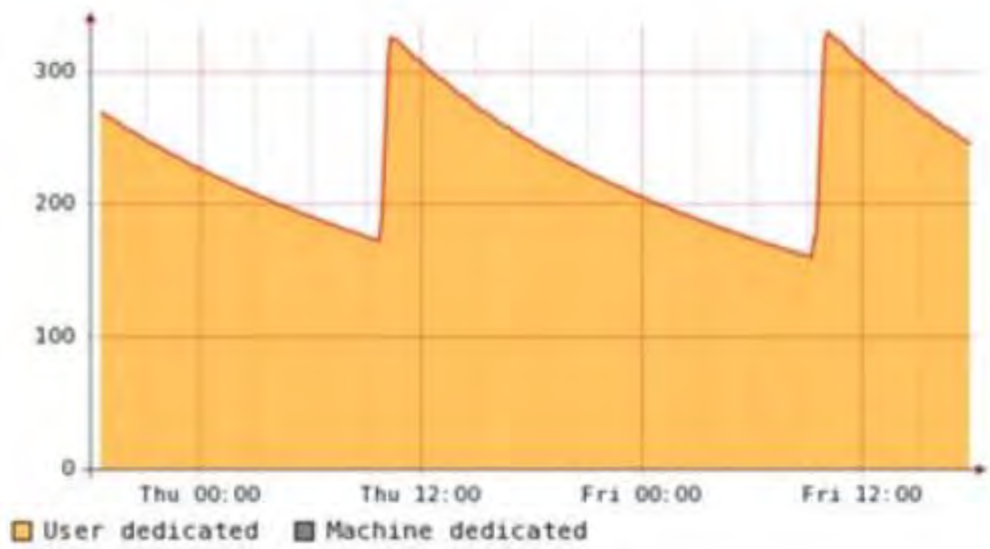
Synchrotron Radiation

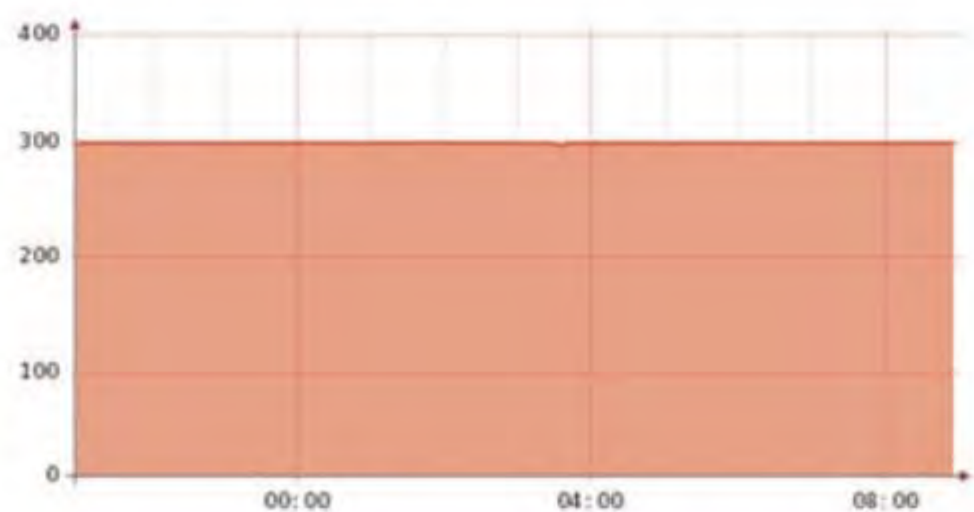


Synchrotron Radiation



Synchrotron Radiation





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Powder diffraction at Synchrotrons

CERTIFIED MANAGEMENT SYSTEM
CQY CERTIQUALITY
UNI EN ISO 9001:2015
UNI ISO 45001:2018

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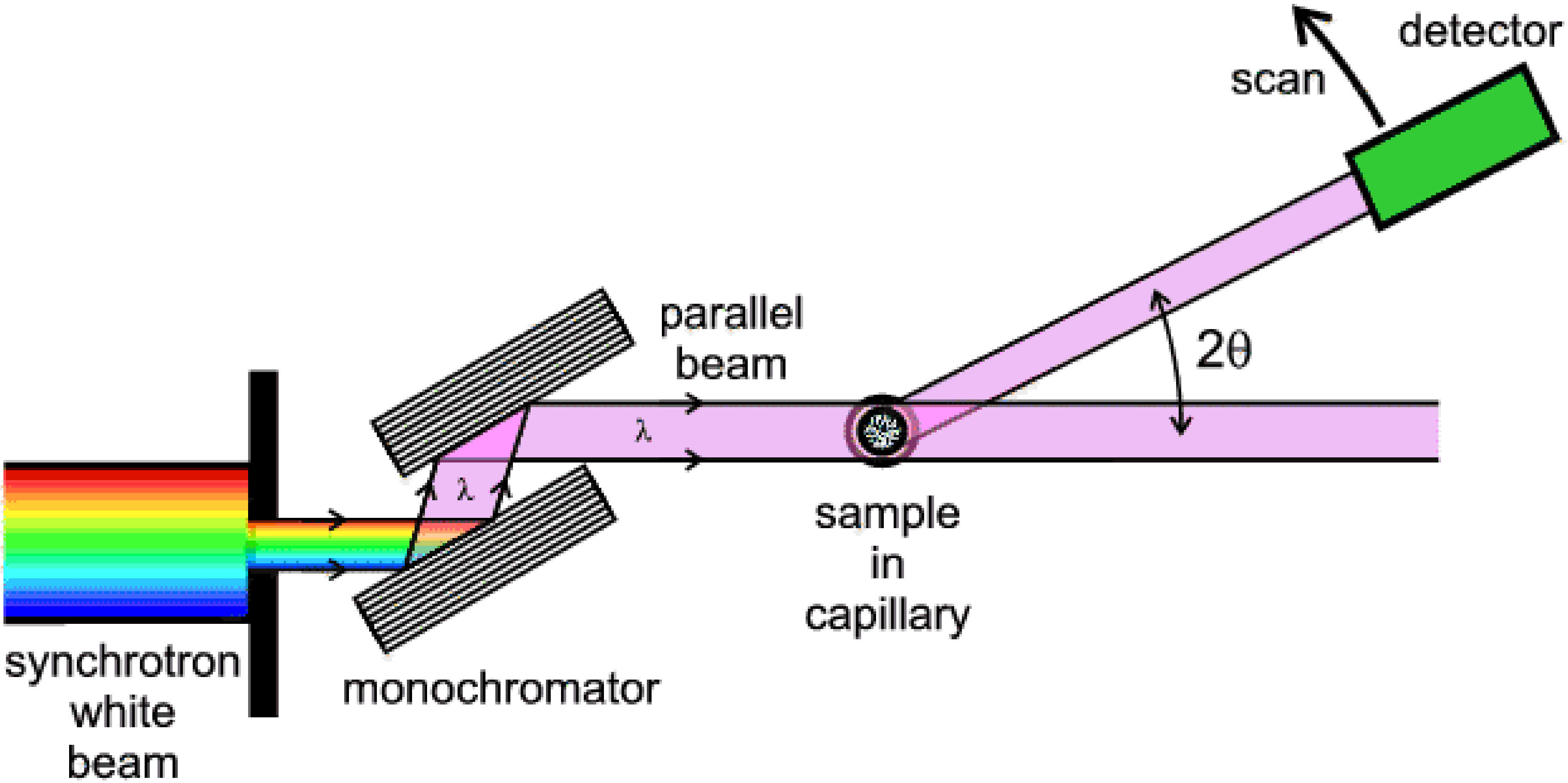
Synchrotron Powder Diffraction



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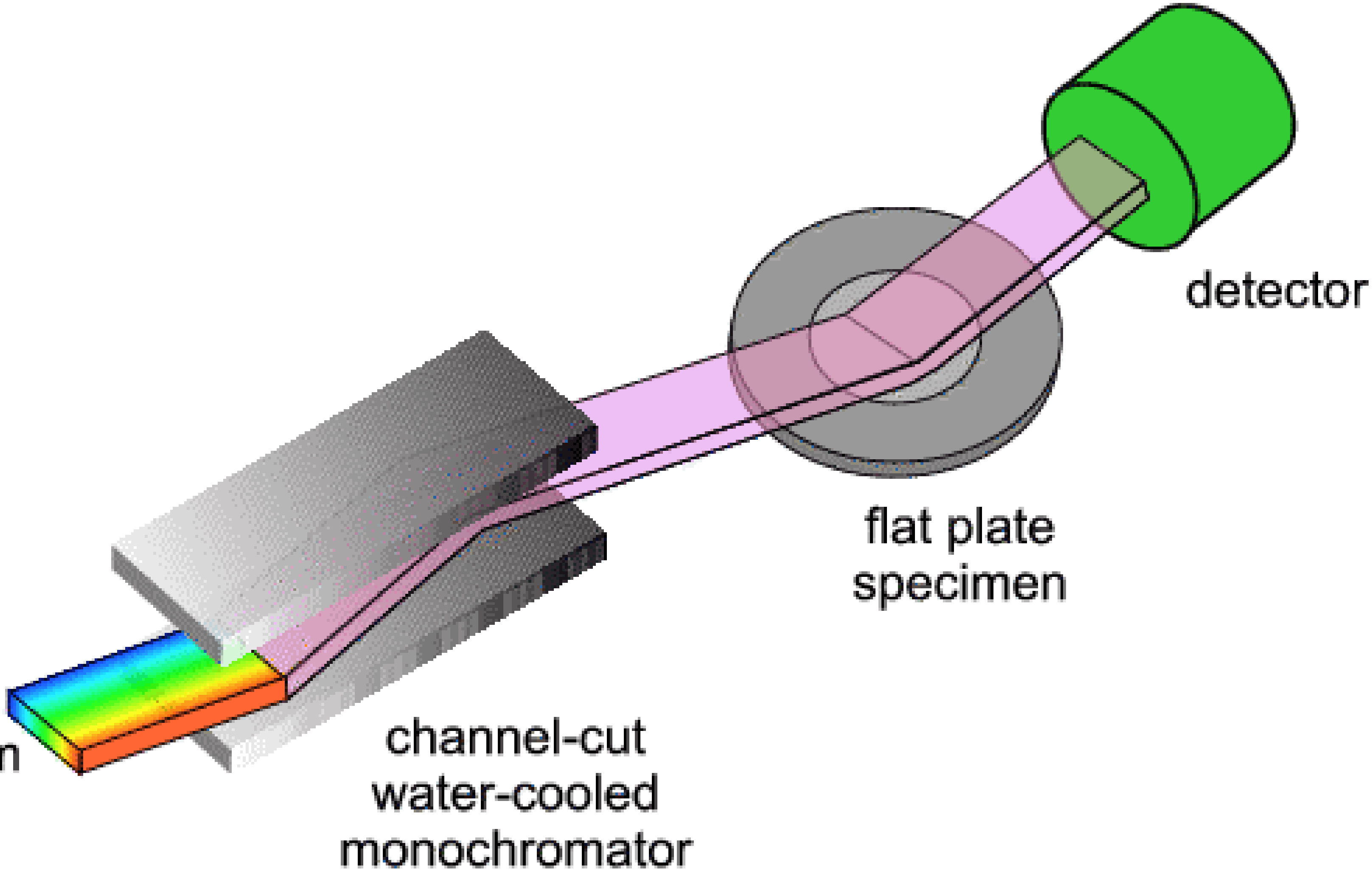
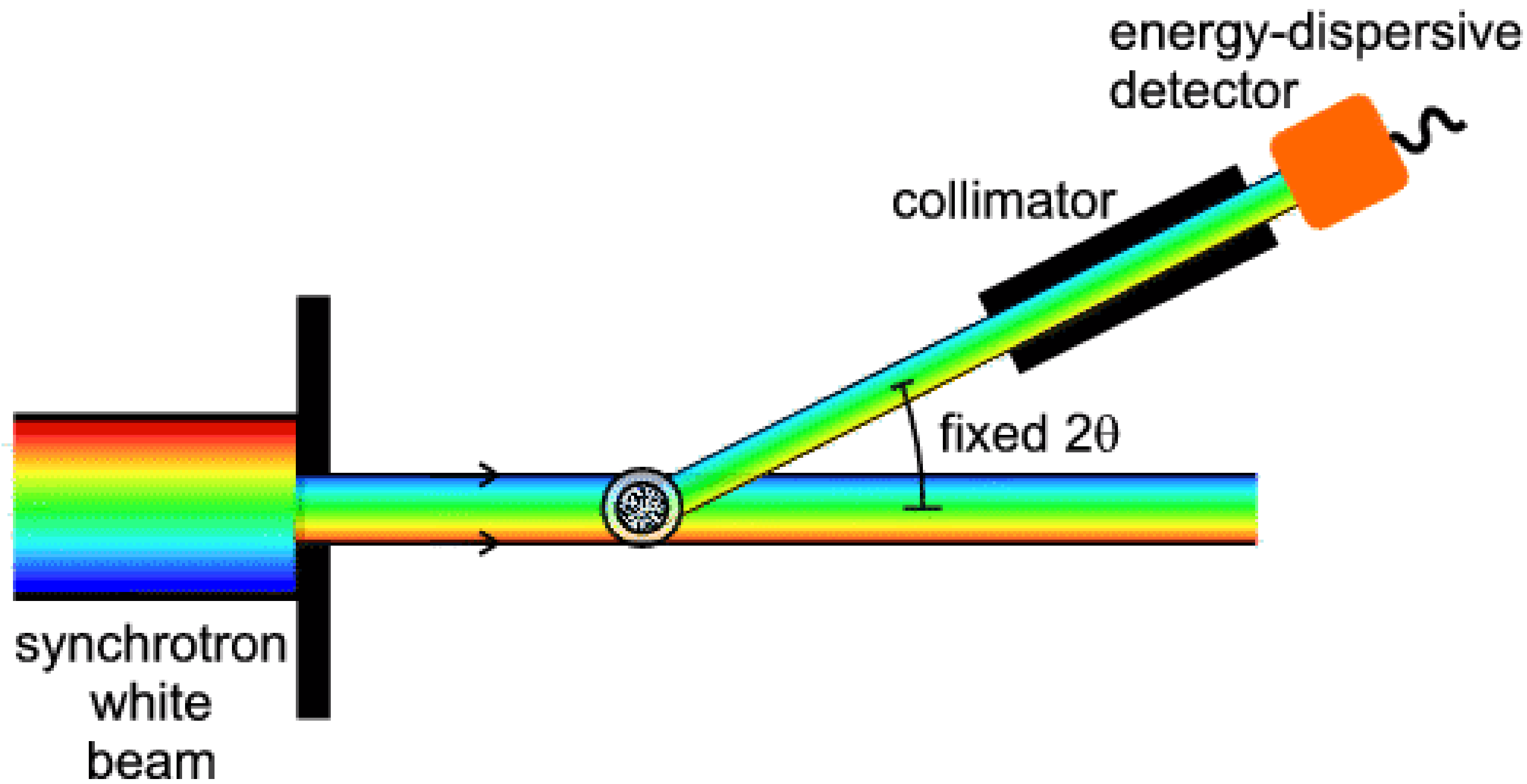
Synchrotron Powder Diffraction



Synchrotron Powder Diffraction



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

scanned variable (by ED detector)

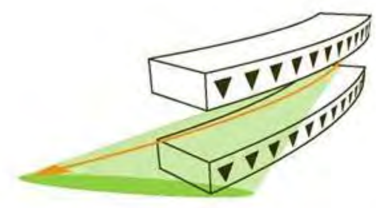
determined variable

fixed (by collimator)

Synchrotron Powder Diffraction

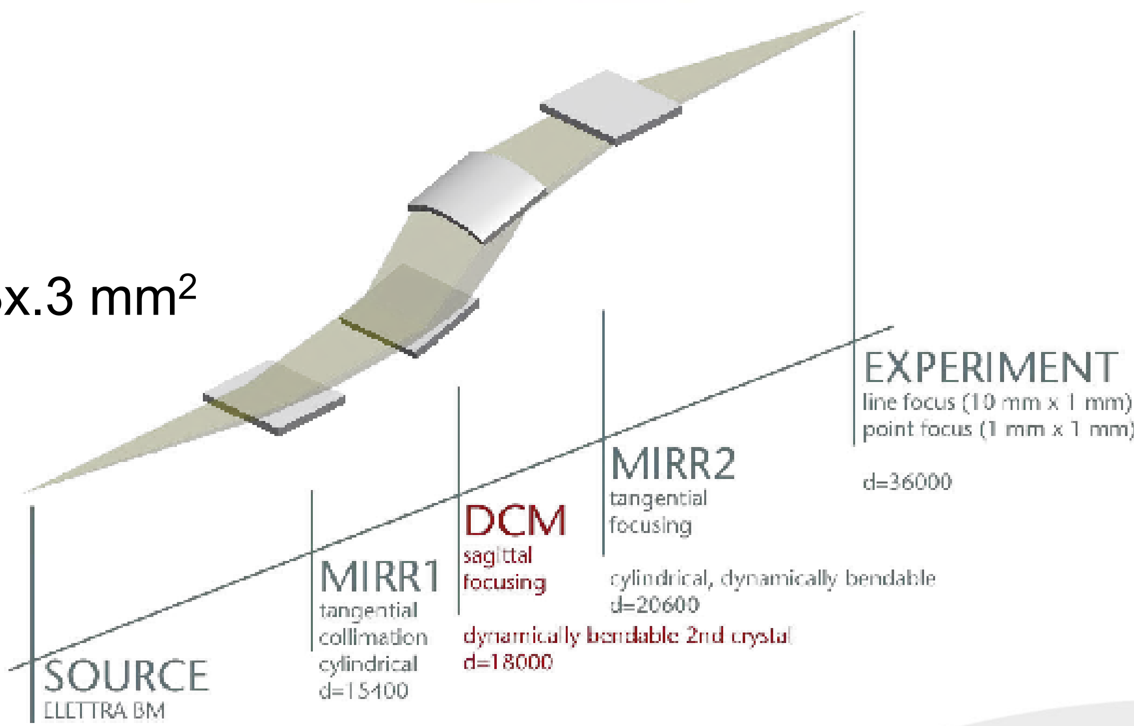
Light Source:

- Bending magnet
- Critical energy : 3.2keV (2.0) , 5.5keV (2.4)



X-rays at sample:

- Energy range : 6-20 keV
- Photon flux : 10^{11} photons/sec
- Beam size at sample : 10x1 - .3x.3 mm^2
- Energy resolution : $\Delta E/E$ $2x10^{-4}$



Synchrotron Powder Diffraction

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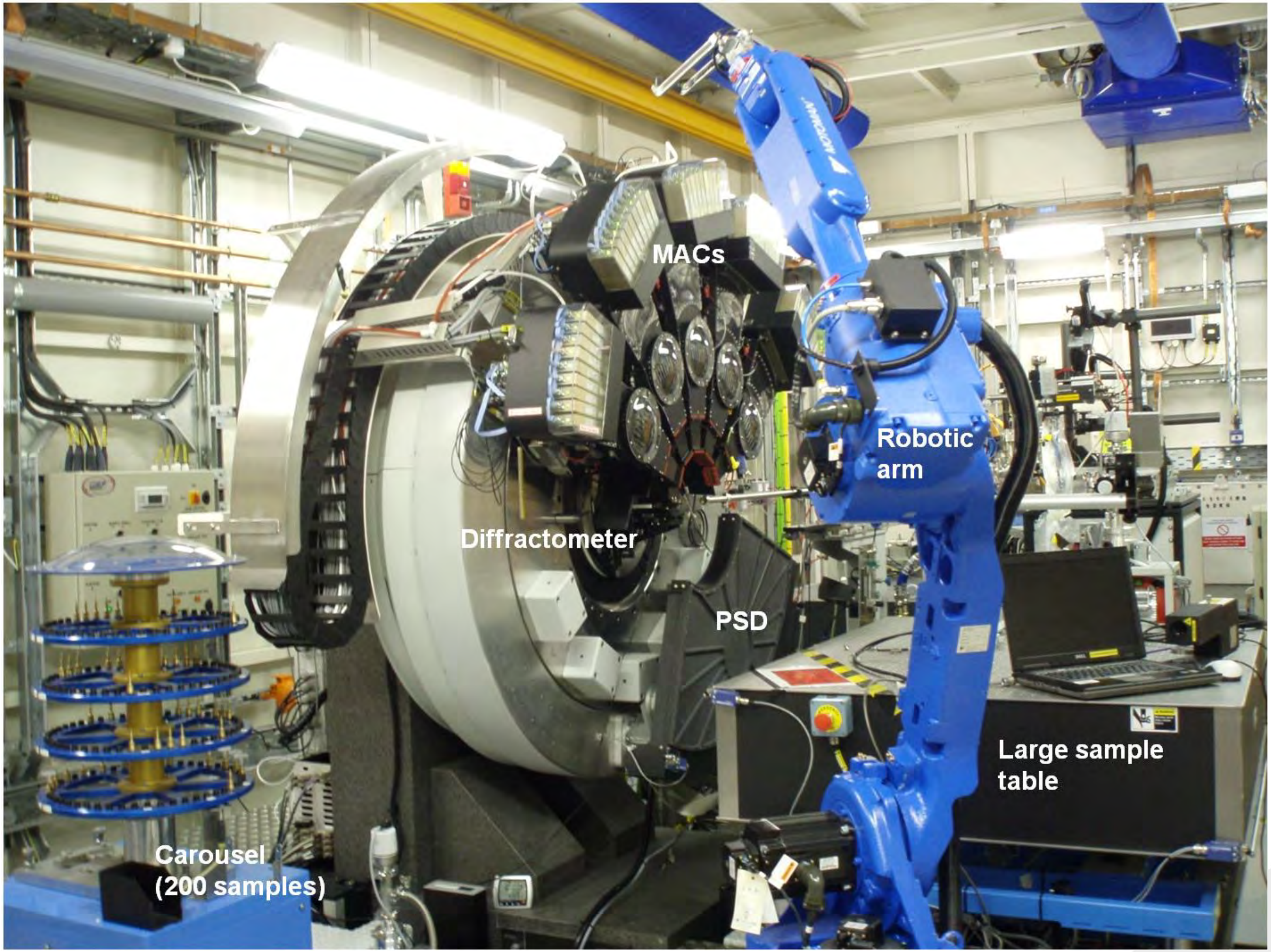

Synchrotron Powder Diffraction

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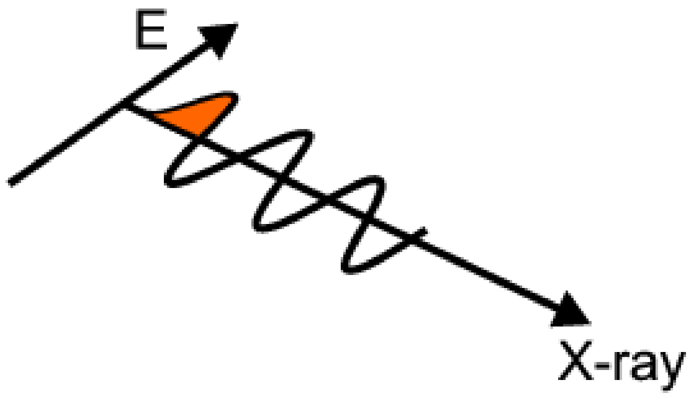
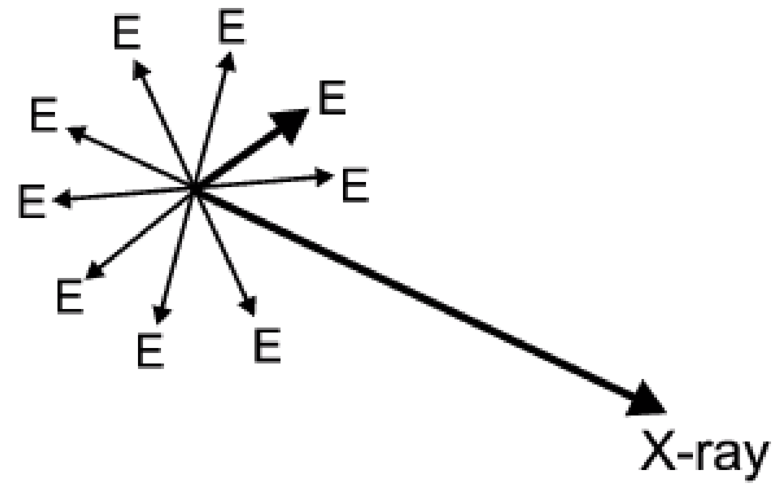
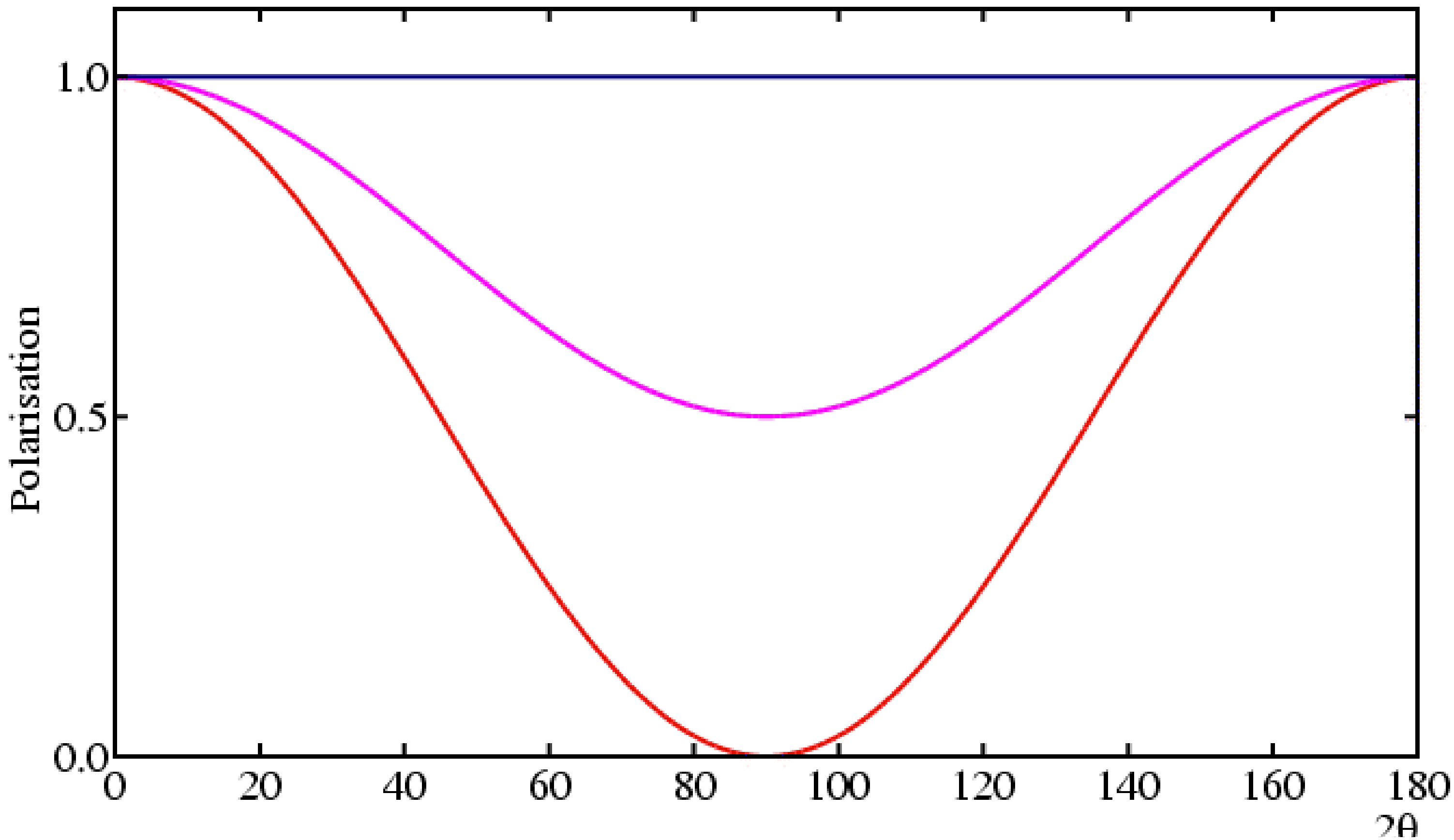




Synchrotron
Radiation is horizontally polarised in the plane of the electron orbit

Laboratory source
Unpolarised radiation

Synchrotron Powder Diffraction



Red: Polarisation in plane of scattering $P = \cos^2 2\theta$

Blue: Polarisation perpendicular to plane of scattering $P = 1$

Pink: Unpolarised X-rays $P = (1 + \cos^2 2\theta)/2$

Synchrotron Powder Diffraction

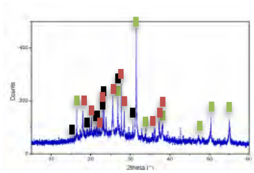
- **High X-ray flux** : Millions count counting statistics in reflection (Bragg-Brentano) as well as in transmission (Debye-Scherrer) modes even with low quantities of powder available

- **Highly collimated photon beam**: angular resolution better due to narrow instrumental profile. FWHM better than 0.01° 2θ obtained with new generation solid state microstrip detectors and down to 0.002° 2θ using multicrystal analyser detectors

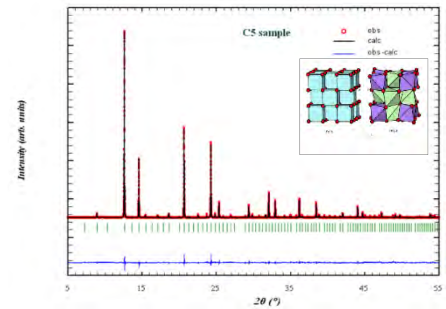
- **Tunable photon energy up to high energies:**
  - anomalous scattering experiments
  - collect fluorescence-free XRPD data
  - Extension of d-space that can be probed.
  - depth analysis by varying energy

MCX @ Elettra

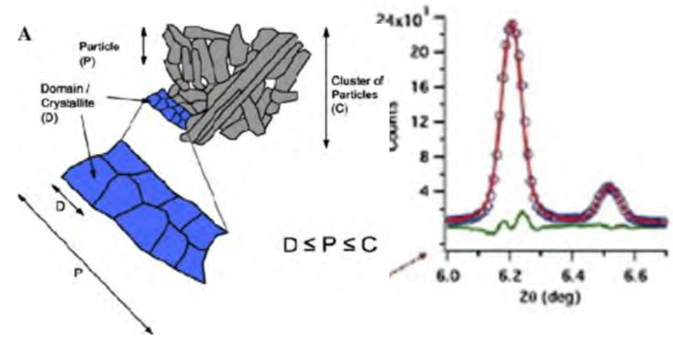
Phase Identification



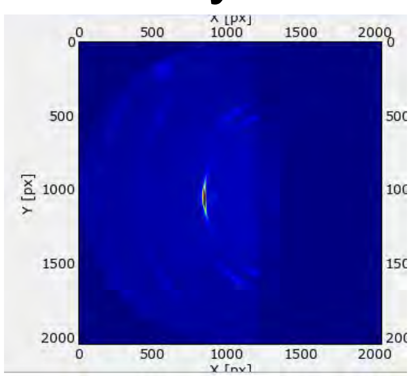
Structure Determination



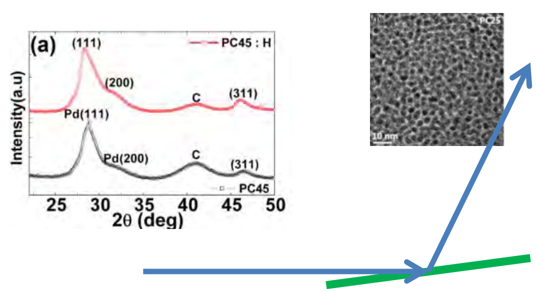
Line Profile Analysis



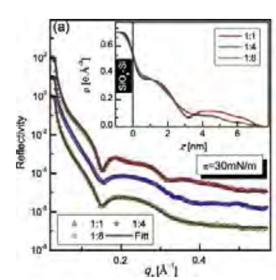
Texture Analysis

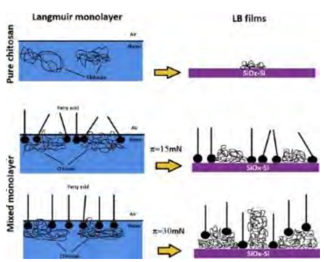


Grazing Incidence Diffraction



X-ray Reflectivity





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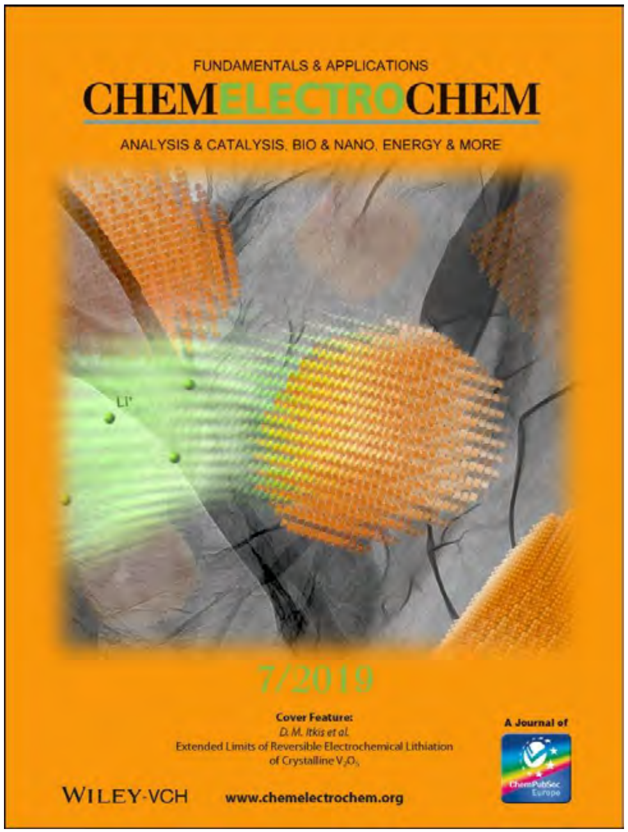
Operando batteries V_2O_5 - RGO



ChemElectroChem
Chemistry Europe
European Chemical Societies Publishing

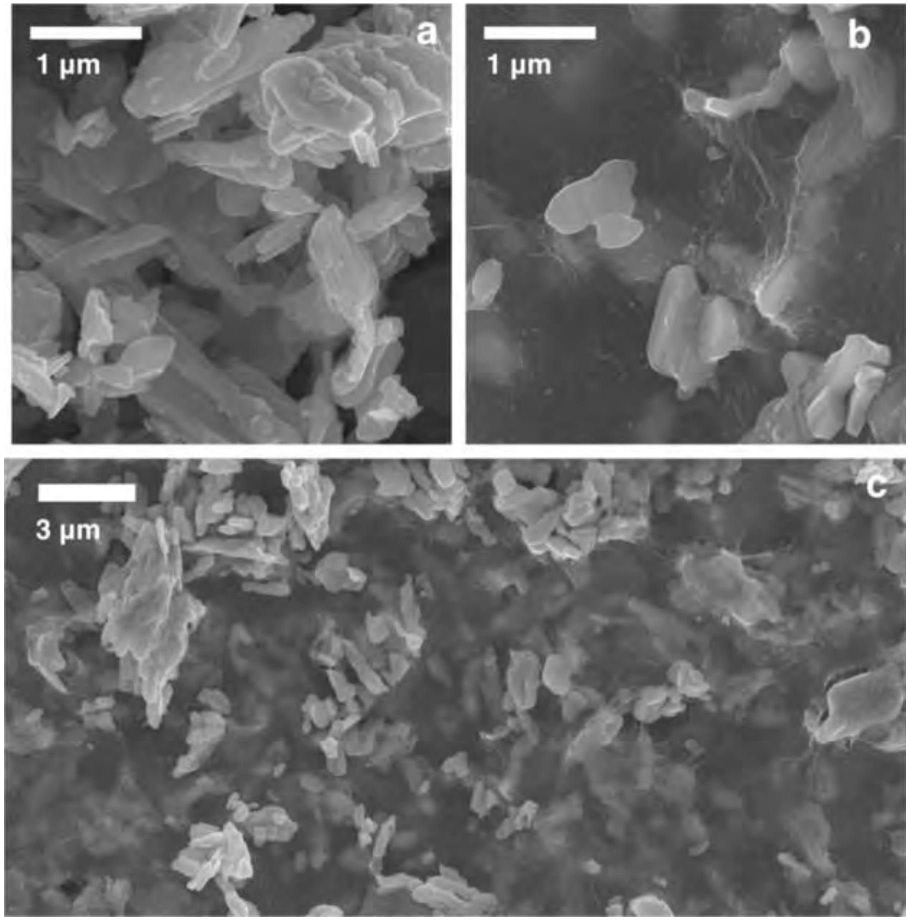
Article

Extended Limits of Reversible Electrochemical Lithiation of Crystalline V_2O_5

Dr. Daniil M. Itkis, Dr. Victor A. Krivchenko, Anna Ya. Kozmenkova, Margarita S. Pakhotina, Filipp S. Napolskiy, Lara Gigli, Jasper Plaisier, Dr. Nellie R. Khasanova, Prof. Dr. Evgeny V. Antipov

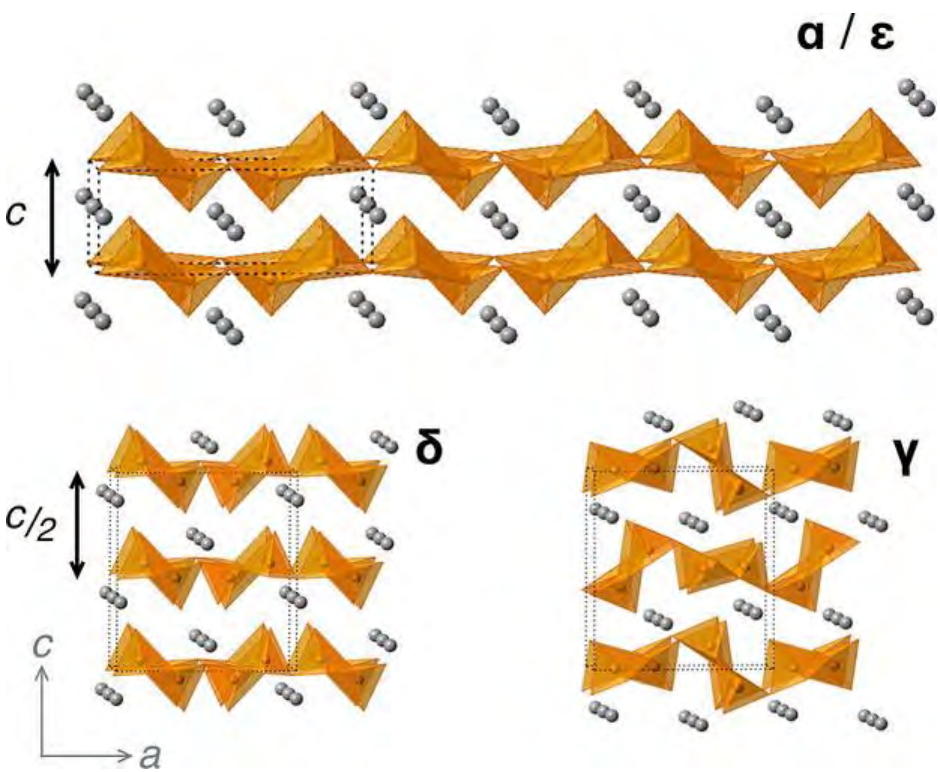
First published: 14 January 2019 | https://doi.org/10.1002/celc.201801638 | Citations: 2

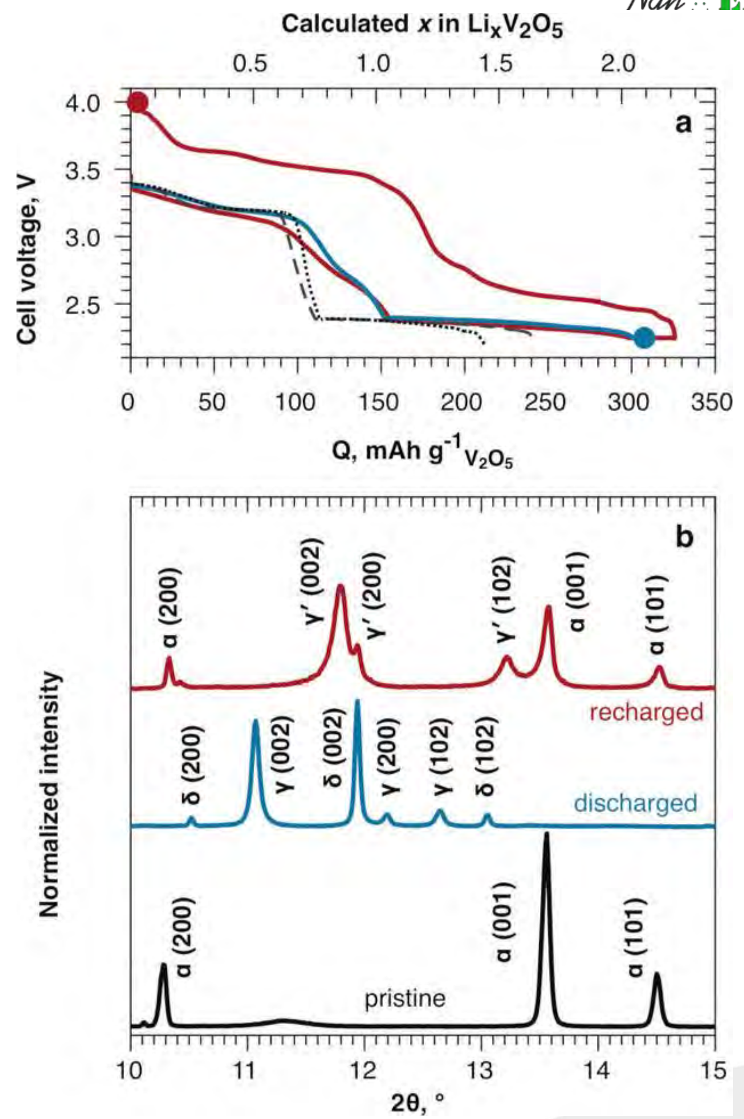
Operando batteries



- Vanadium (V) oxide was suggested as an attractive host for electrochemical lithium yet in 1970s due to ability of multielectron redox in layered V_2O_5
- Insertion of extremely high amounts of lithium (up to 3 moles per mole of oxide) is possible, however, it is believed that insertion/extraction of about 1.8 moles of Li^+ can enable sustainable cycling.

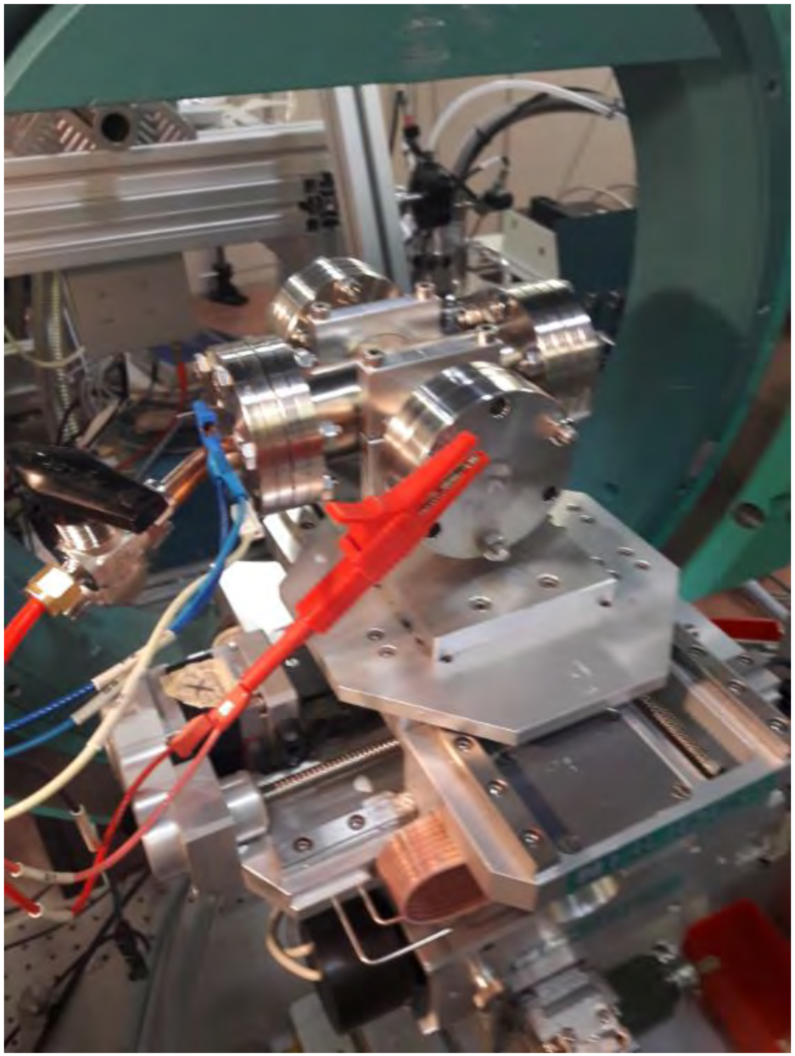
Operando batteries V_2O_5 - RGO

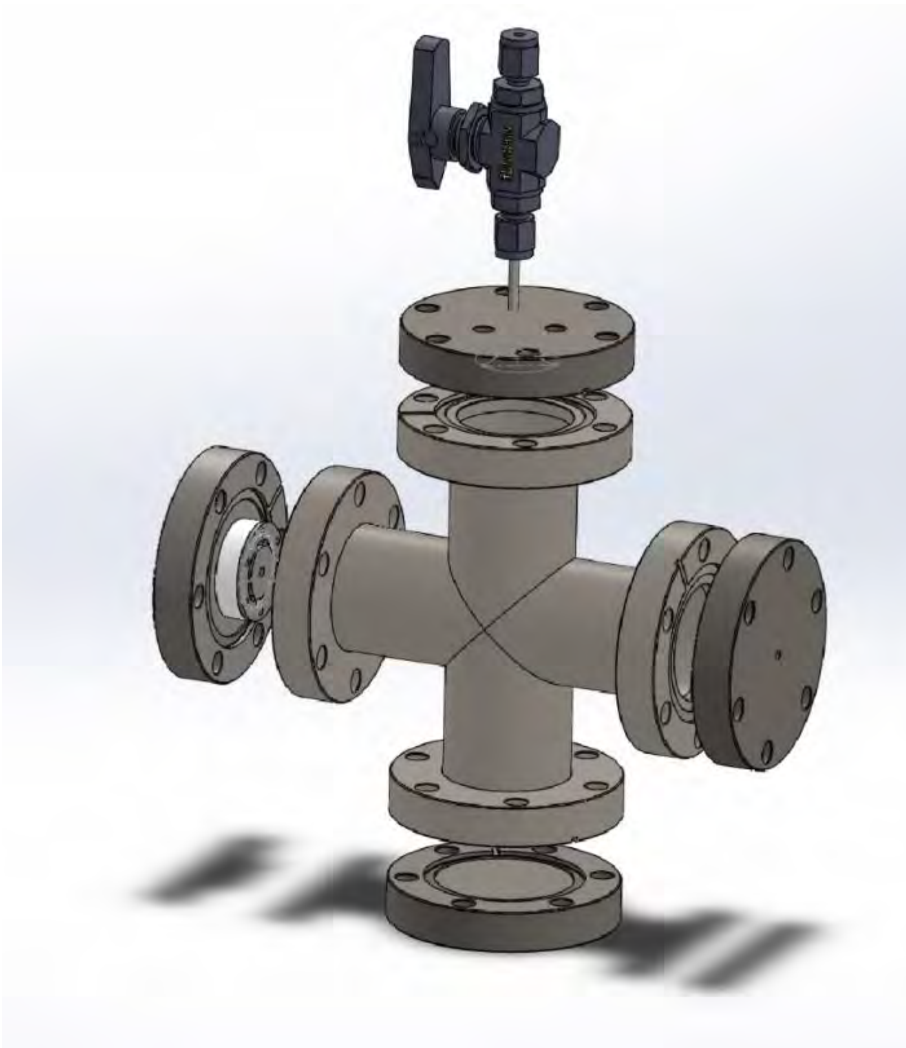




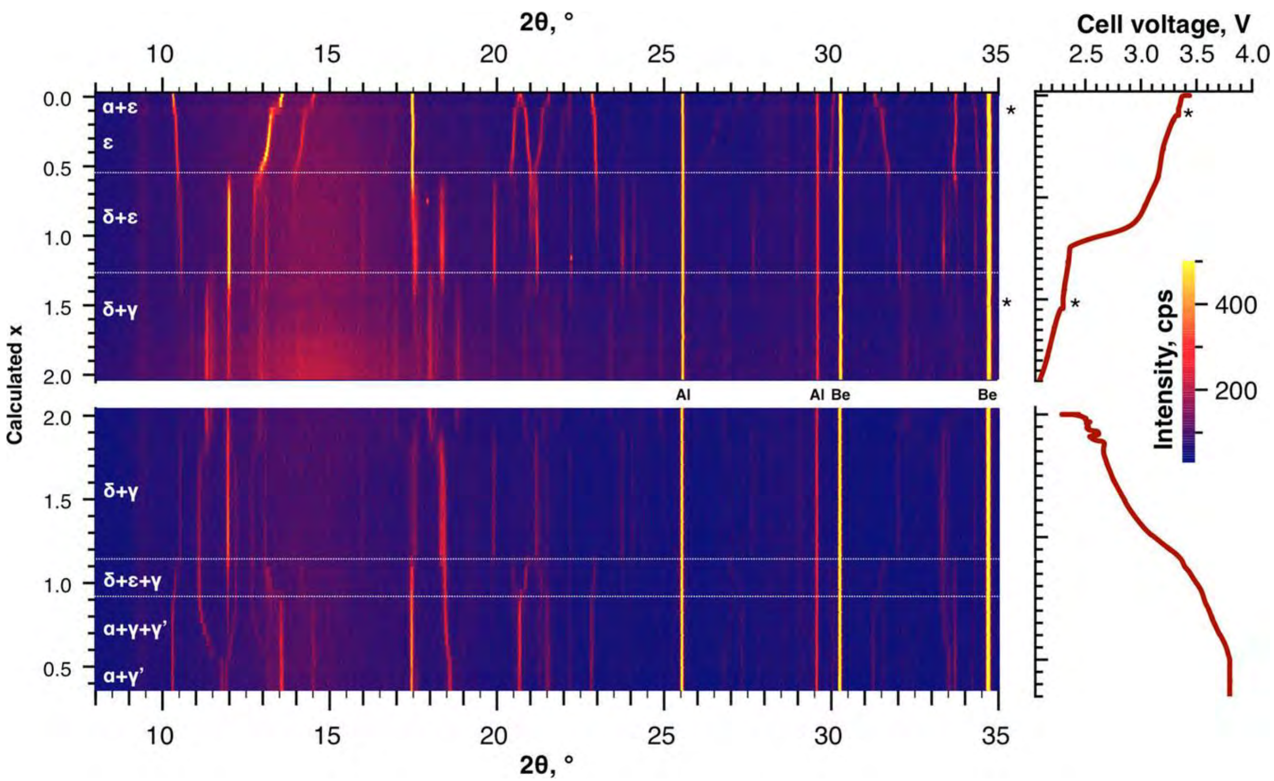
$V_2O_5 + xLi^+ + xe^- \leftrightarrows Li_xV_2O_5$ (0 < x < 3)

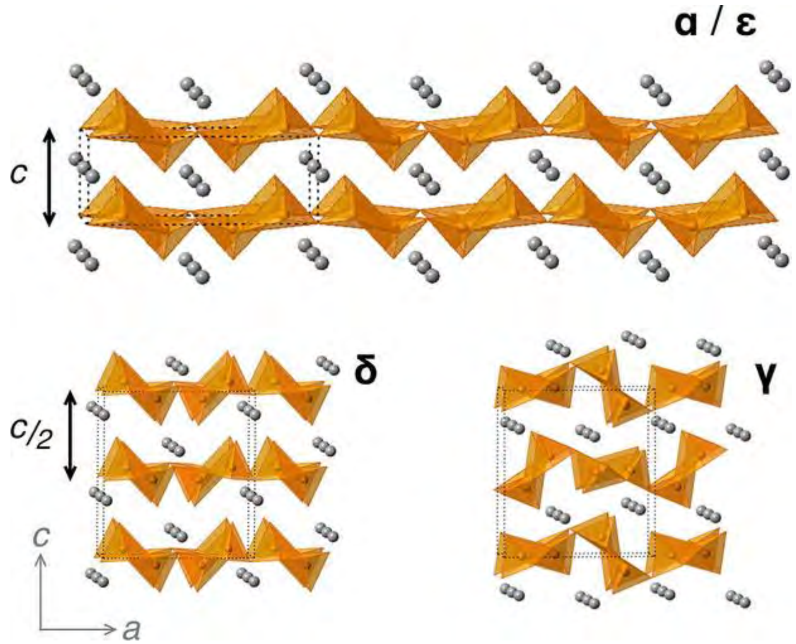
Operando batteries V_2O_5 - RGO



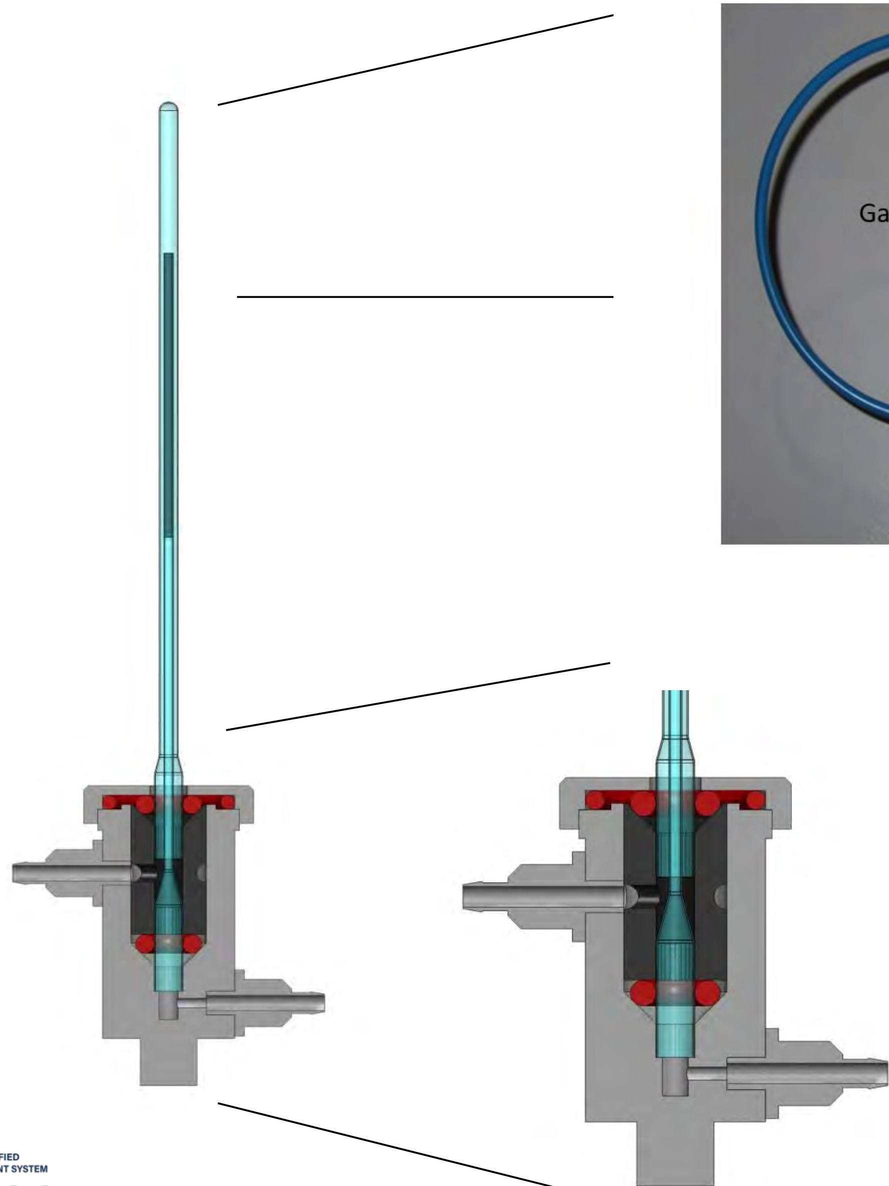


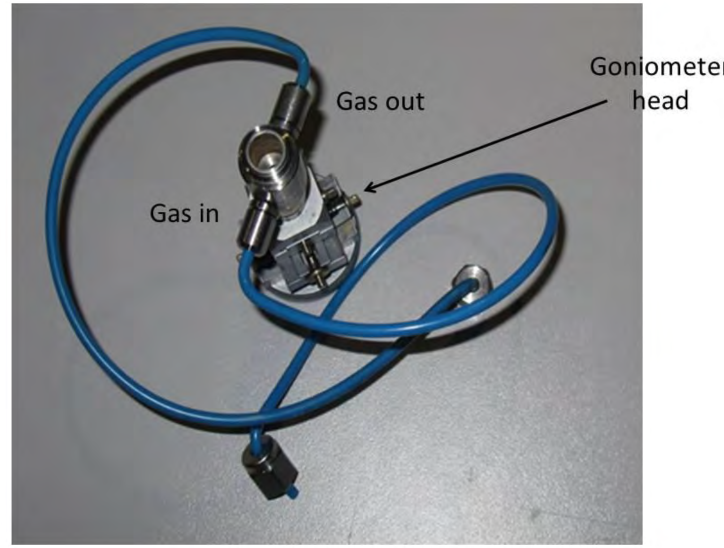
Operando batteries V_2O_5 - RGO

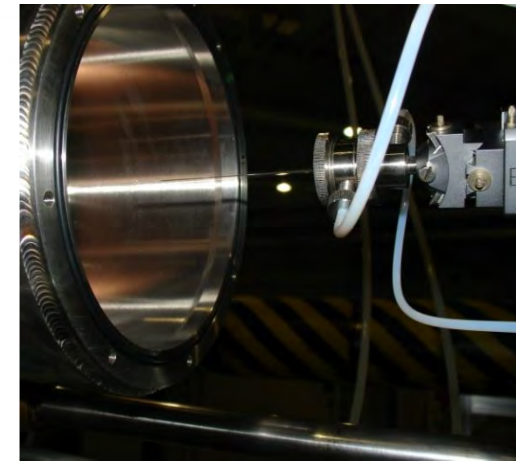


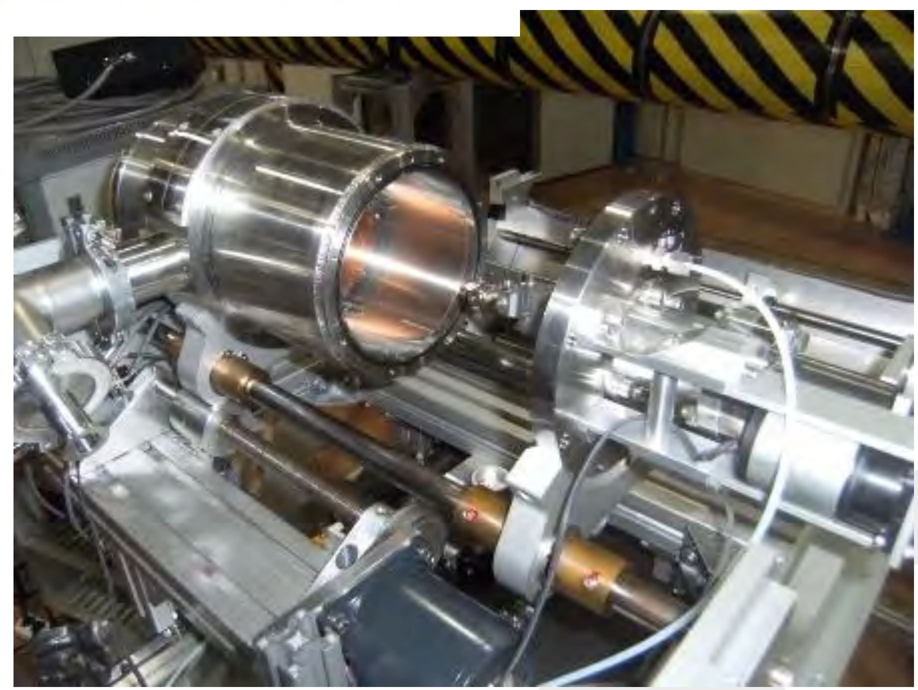


XRPD in non ambient conditions









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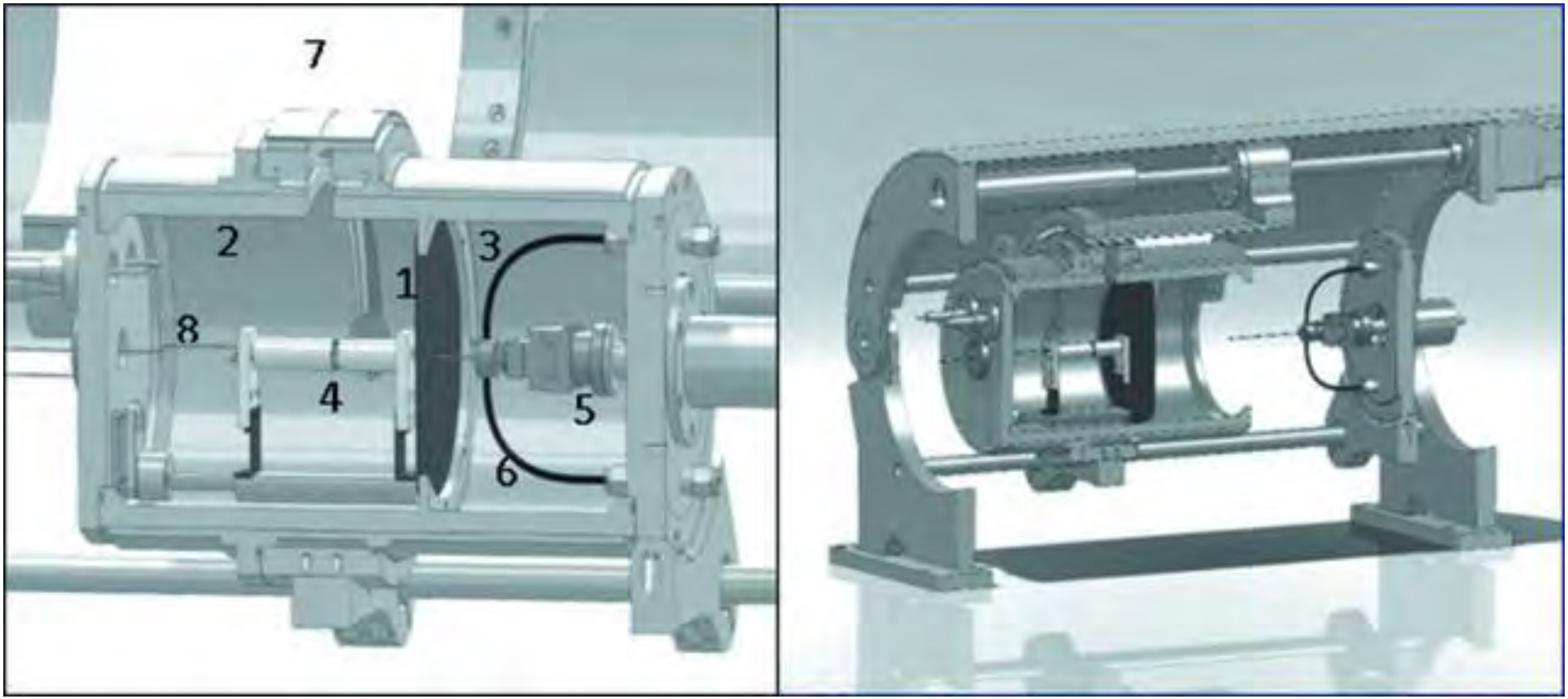
Furnace Design



In situ reaction furnace for real-time XRD studies

Riello P., Lausi A., MacLeod J., Plaisier J.R., Zerauschek G., Fornasiero P.

196 (201

2D-3D transition In Cu–TiS_2 system

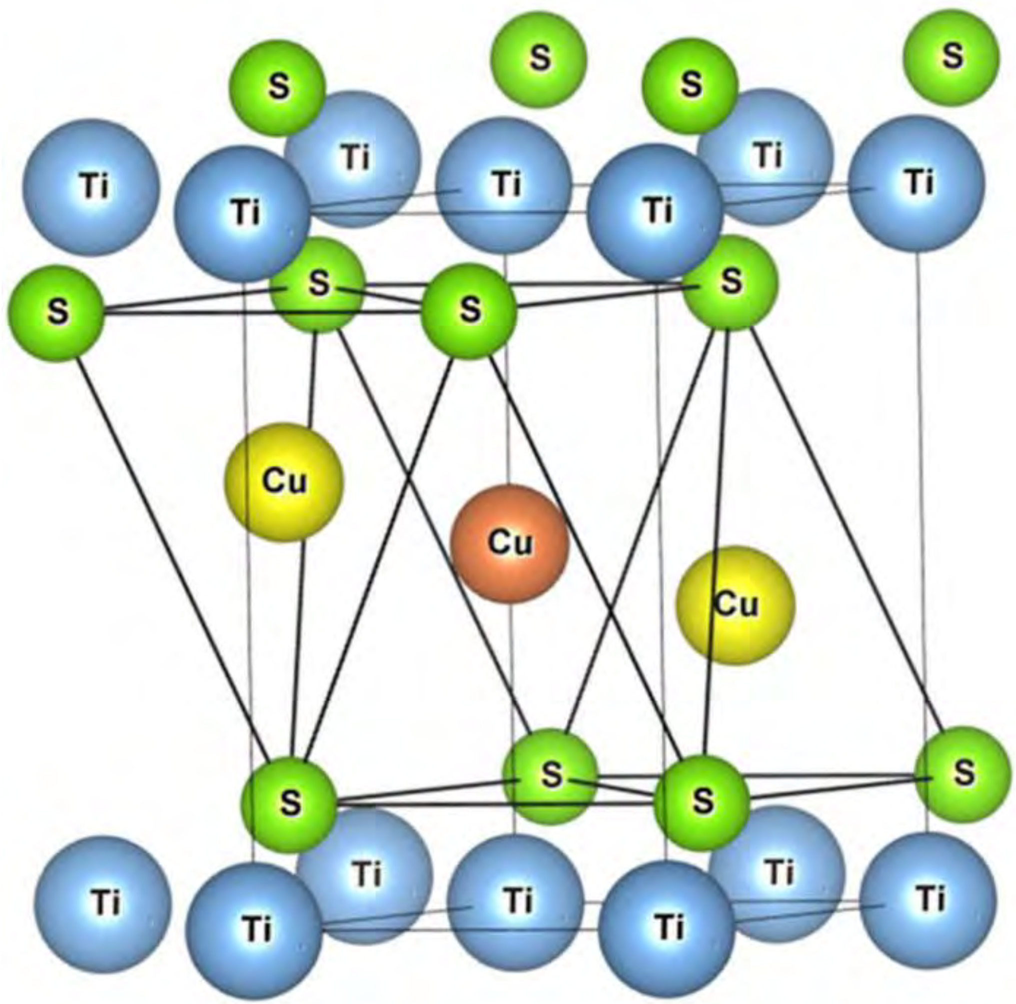
- Phase transitions between 2D (layered) and 3D (cubic) phases in Cu_xTiS_2 (x = 0-0.5) intercalation compounds have been studied ***in situ*** by the X-ray diffraction technique in the temperature range 20–1000 ° C.

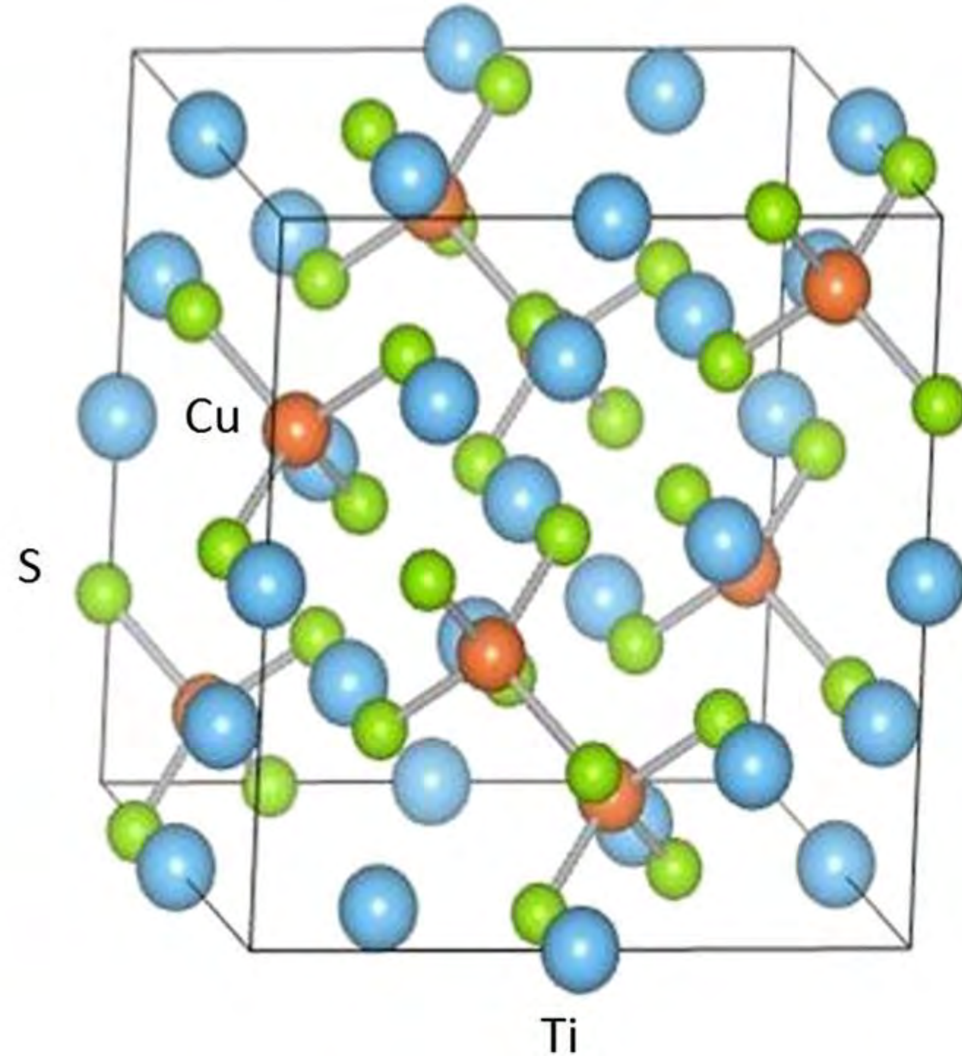
- The discovery of CDW (charge density wave) quantum states and superconductivity in the Cu–$TiSe_2$ system arouses interest to isostructural materials, but known phase transformations to the spinel structure make comparison difficult.

- Samples were prepared by intercalation of Cu at room temperature. All samples had the layered hexagonal structure.

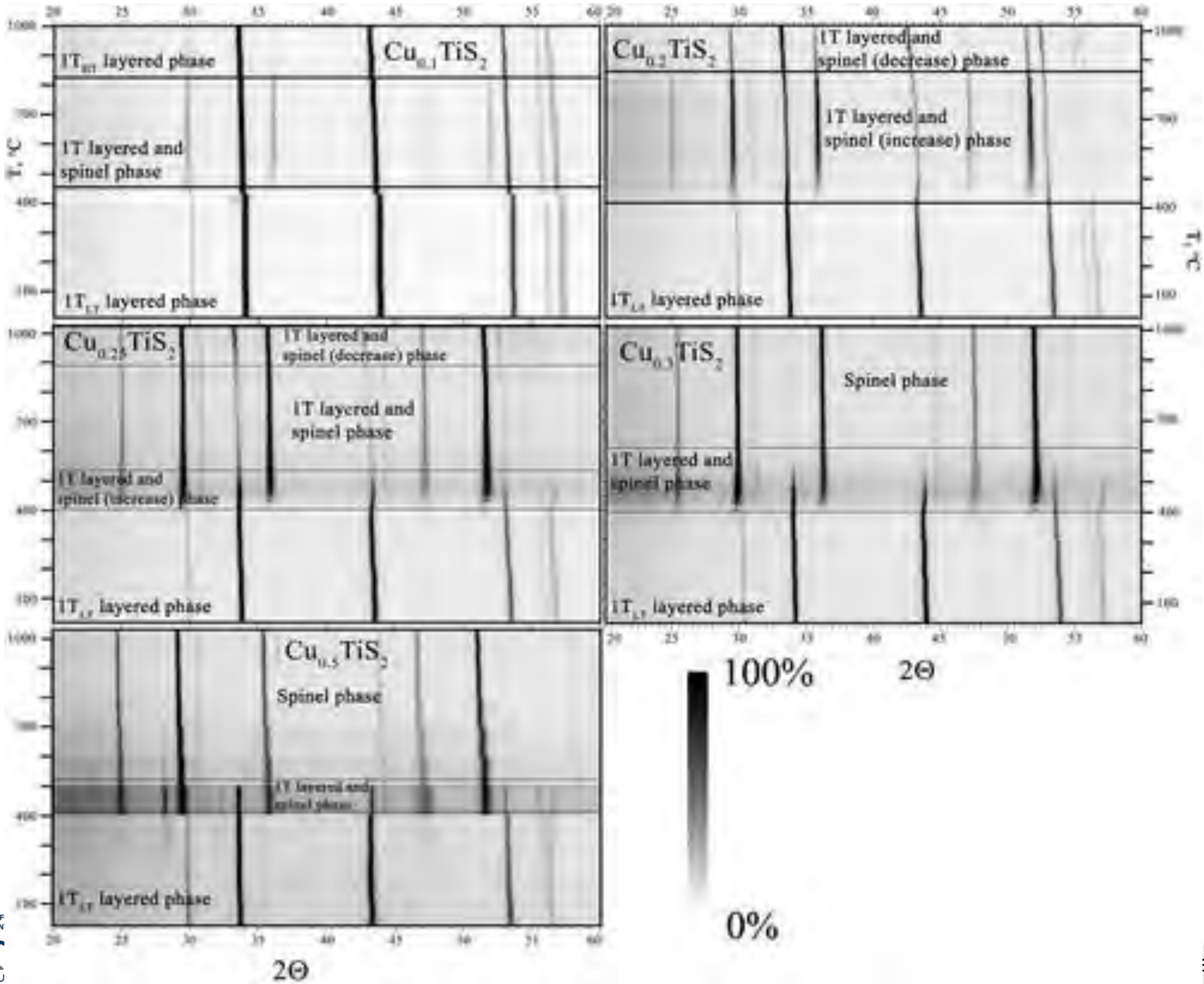
2D-3D transition in Cu–TiS_2 system
Shkvarina EG, Titov AA, Doroschek AA, Shkvarin AS, Starichenko DV, Plaisier JR, Gigli L, Titov AN.
The Journal of Chemical Physics 147, 044712 (2017)

2D-3D transition In $Cu–TiS_2$ system





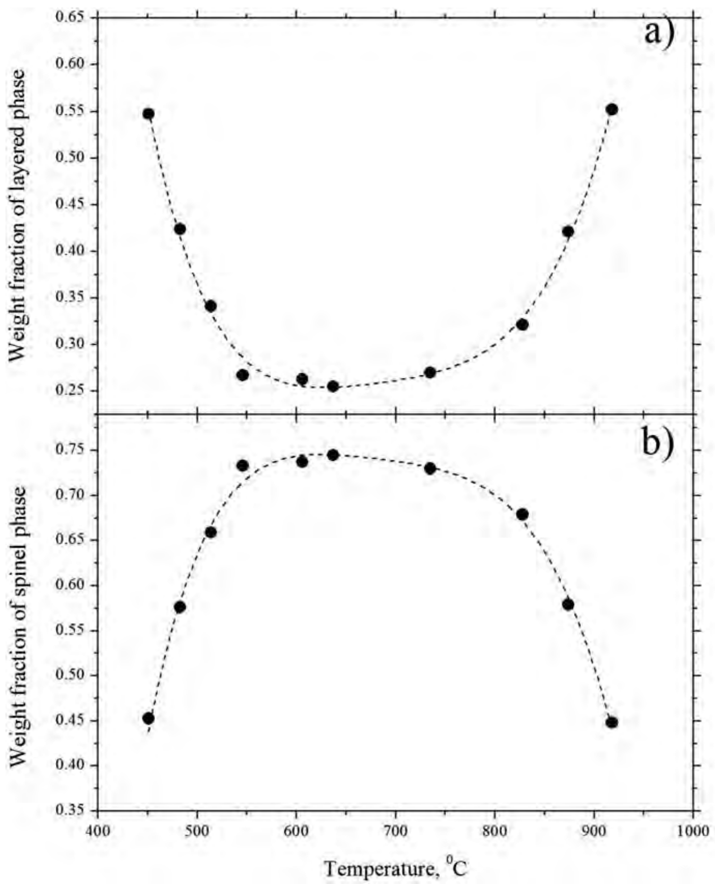
2D-3D transition In Cu–TiS_2 system

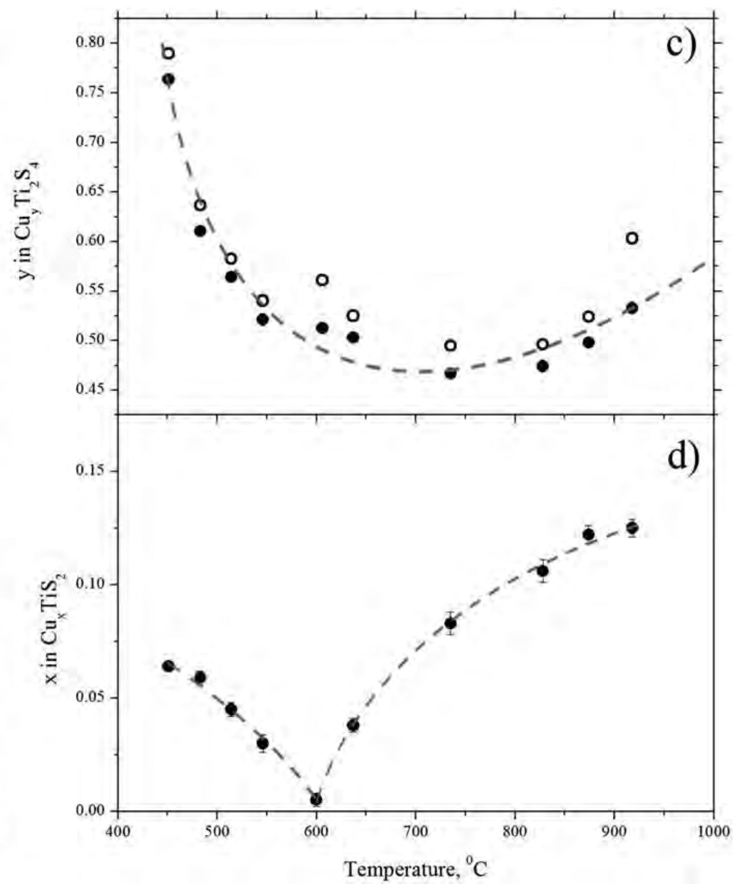


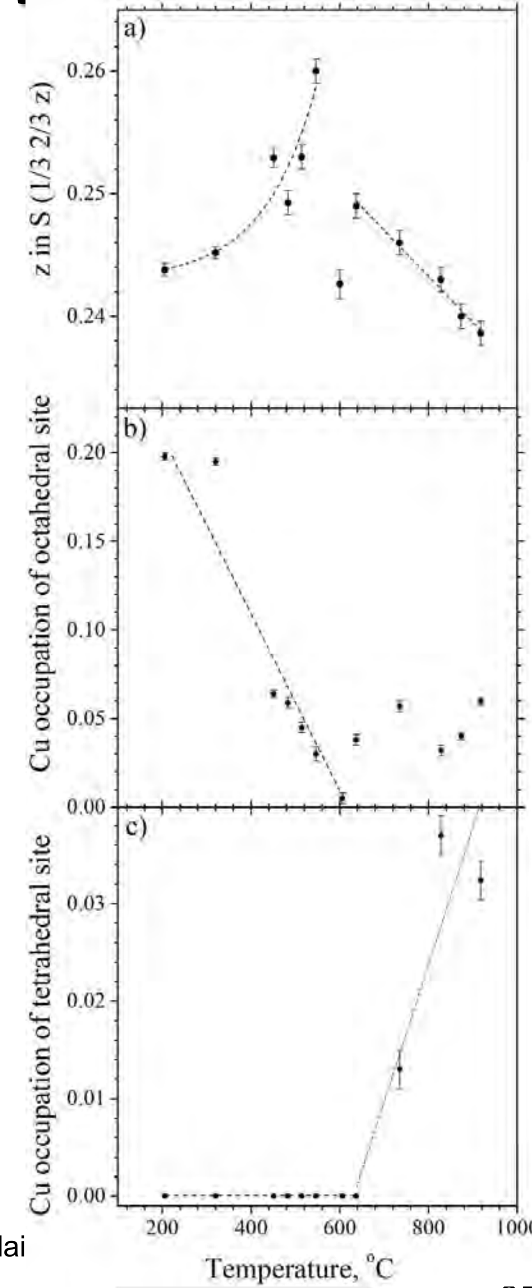
2D-3D transition In Cu–TiS_2 system

T (°C)	1T layered phase							Cubic spinel phase			R_F^2 (%)	χ^2
	a	c	S (⅓ ⅔ z)	Cu (0 0 ½)	Cu (⅓ ⅔ z)		Ti (0 0 ½)	a	Cu (⅛ ⅛ ⅛)	S (x x x)		
			z	Occupation	z	Occupation	Occupation		Occupation	x		
$Cu_{0.2}TiS_2$												
206	3.4269(1)	5.8106(2)	0.2438(5)	0.198(2)	...	...	...	...	...	...	5.96	1.880
320	3.4331(1)	5.8252(2)	0.2452(5)	0.195(2)	...	...	...	...	...	...	6.44	1.688
451	3.4401(1)	5.8037(2)	0.2593(8)	0.064(2)	...	...	0.005(3)	9.9816(4)	0.763(8)	0.2502(5)	3.90	1.123
483	3.4405(1)	5.7942(3)	0.249(1)	0.059(3)	...	...	...	9.9631(3)	0.611(5)	0.2526(3)	2.89	1.136
514	3.4421(1)	5.7937(3)	0.253(1)	0.045(3)	...	...	0.017(4)	9.9592(2)	0.564(4)	0.2530(2)	3.18	1.064
546	3.4441(1)	5.7982(4)	0.260(1)	0.030(4)	...	...	0.018(5)	9.9604(2)	0.521(3)	0.2529(3)	2.78	1.138
606	3.4482(1)	5.8083(4)	0.243(1)	0.005(3)	...	...	0.074(6)	9.9642(1)	0.512(3)	0.2536(2)	4.55	1.107
637	3.4498(1)	5.8133(4)	0.249(1)	0.038(3)	...	...	0.018(5)	9.9660(1)	0.503(3)	0.2532(1)	1.86	1.105
735	3.4543(1)	5.8365(4)	0.246(1)	0.057(3)	0.45(3)	0.013(2)	0.020(5)	9.9726(1)	0.467(3)	0.2538(2)	2.89	1.565
828	3.4603(1)	5.8677(3)	0.243(1)	0.032(3)	0.454(7)	0.037(2)	0.029(4)	9.9846(1)	0.474(3)	0.2536(2)	2.72	1.296
874	3.4626(1)	5.8881(2)	0.240(1)	0.040(2)	0.431(6)	0.041(2)	0.031(4)	9.9908(1)	0.498(4)	0.2535(2)	2.92	1.770
918	3.4654(1)	5.9051(3)	0.239(1)	0.060(2)	0.445(8)	0.032(2)	0.001(4)	9.9662(4)	0.533(6)	0.2540(3)	4.12	2.410
$Cu_{0.1}TiS_2$												
525	3.4422(1)	5.7990(2)	0.2460(6)	0.044(2)	0.35(2)	0.013(2)	0.024(3)	9.9701(8)	0.66(2)	0.2547(8)	8.16	5.921
647	3.4494(1)	5.8129(2)	0.2448(6)	0.038(2)	0.37(2)	0.015(2)	0.023(4)	9.9690(4)	0.50(2)	0.2544(6)	7.05	5.813
918	3.4650(1)	5.8691(2)	0.2428(7)	0.055(2)	0.42(2)	0.020(3)	0.002(4)	...	...	...	9.65	10.47
$Cu_{0.25}TiS_2$												
918	3.4664(2)	5.9140(8)	0.236(2)	0.009(6)	0.46(1)	0.052(4)	...	10.0075(1)	0.512(4)	0.2531(2)	6.42	10.81

2D-3D transition In Cu–TiS_2 system







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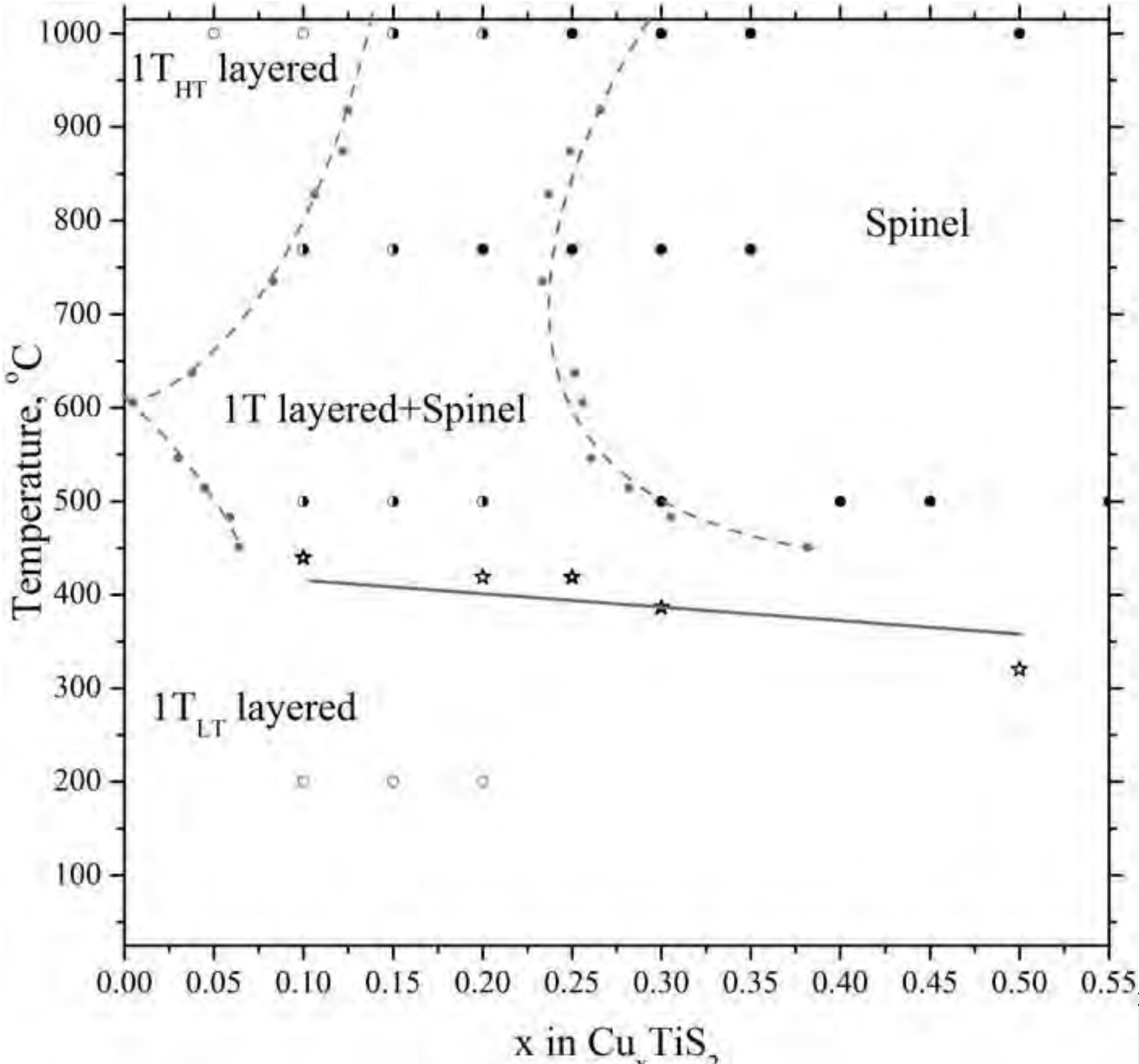
2D-3D transition In Cu–TiS_2 system



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Trieste

2D-3D transition In Cu–TiS_2 system

- It has been found that the stability of the layered phase is determined by the distribution of copper atoms between the octahedral and tetrahedral crystallographic sites.
- The occupation of octahedral sites dominates at low temperatures.
- Upon heating, tetrahedral site occupation is limited and the layered phase becomes unstable and transforms to the spinel.
- Further heating allows the distribution of copper between octahedral and tetrahedral sites; the layered phase becomes stable again.

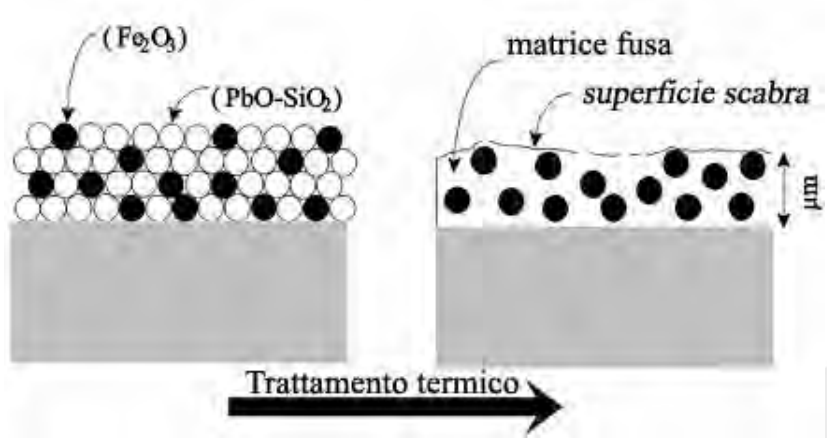
CERTIFIED MANAGEMENT SYSTEM
CERTIQUALITY
UNI EN ISO 9001:2015
UNI ISO 45001:2018

Phase identification - example

Phase identification - example

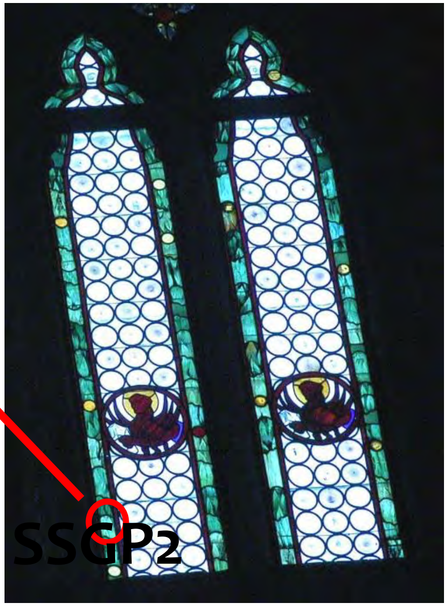
Glass samples: Grisaille

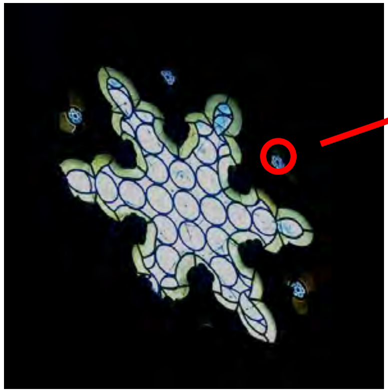
- Low melting glass (SiO_2, PbO,)
- Pigment (metal oxides)
- Paint medium (water, vinegar, oil)
- Firing to fuse the grisaille on the glass



Phase identification - example

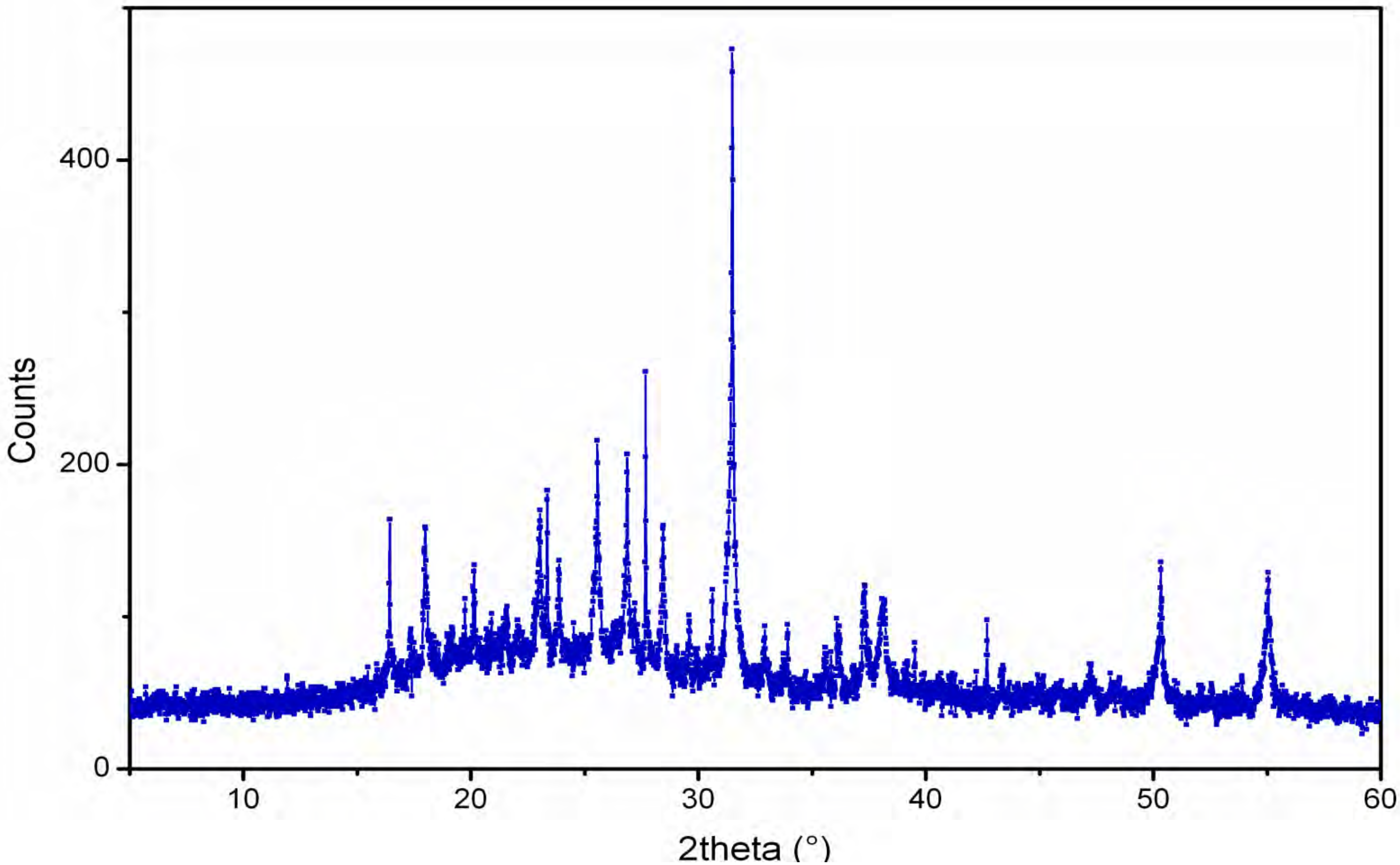
SSGP1/2





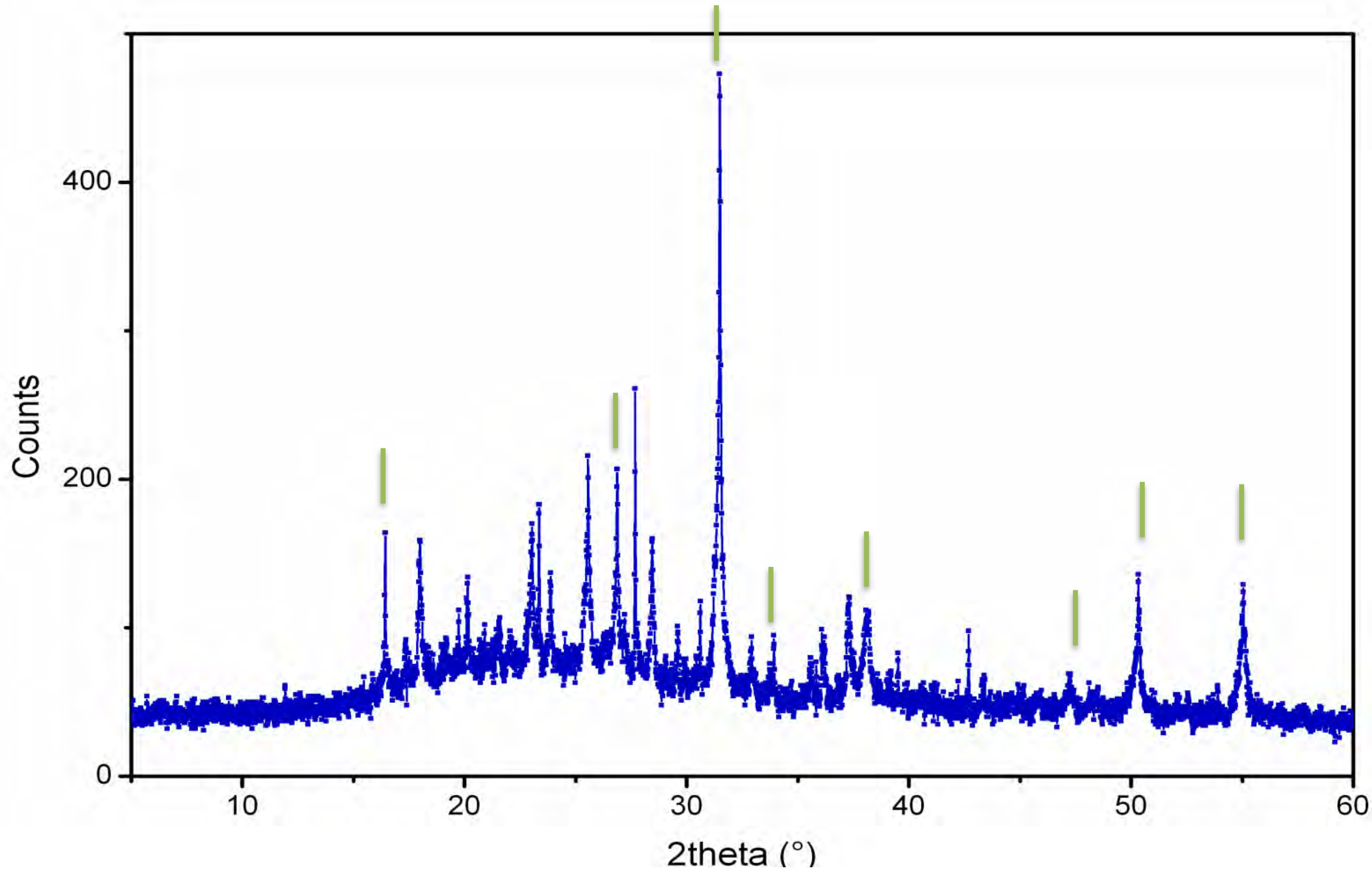
SSGP3

Phase identification - example



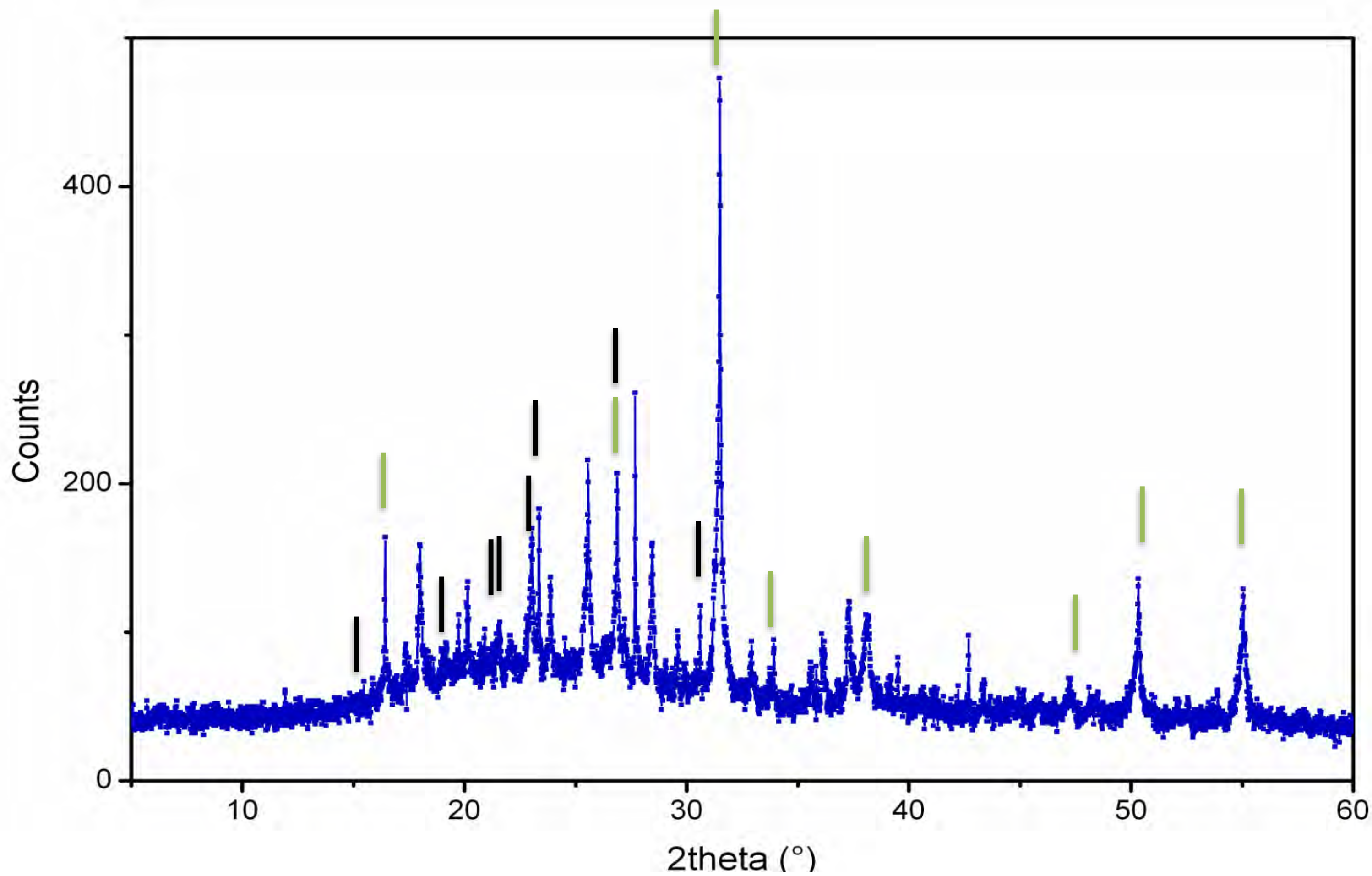
E = 9.4 keV
λ = 1.319Å

Phase identification - example



Spinel
$CoAl_2O_4$
01-082-2422

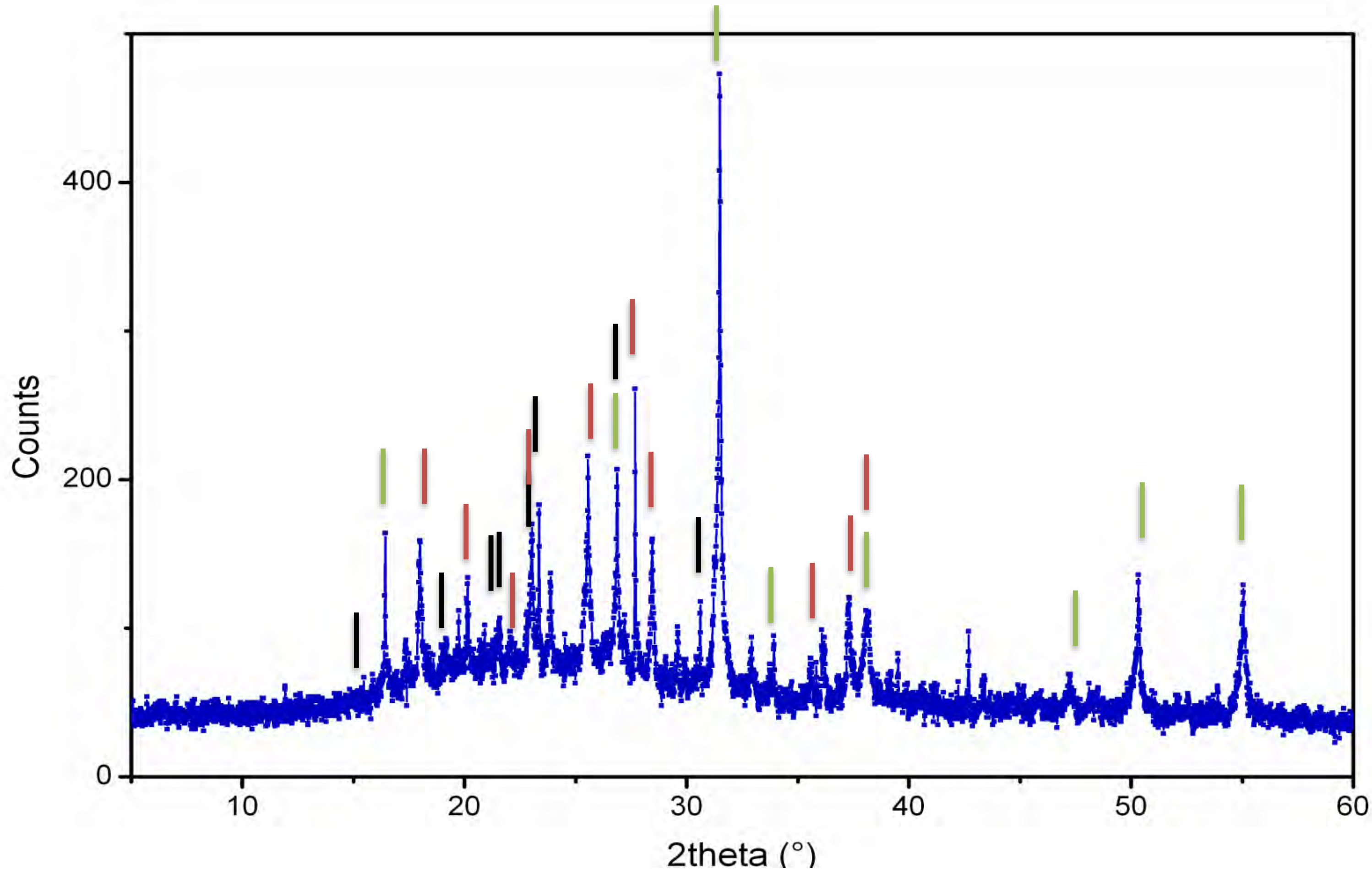
Phase identification - example



Spinel
$CoAl_2O_4$
01-082-2422

Laurionite
$PbCl(OH)$
04-012-3672

Phase identification - example



Spinel
$CoAl_2O_4$
01-082-2422

Laurionite
PbCl(OH)
04-012-3672

Anglesite
$PbSO_4$
04-008-8386

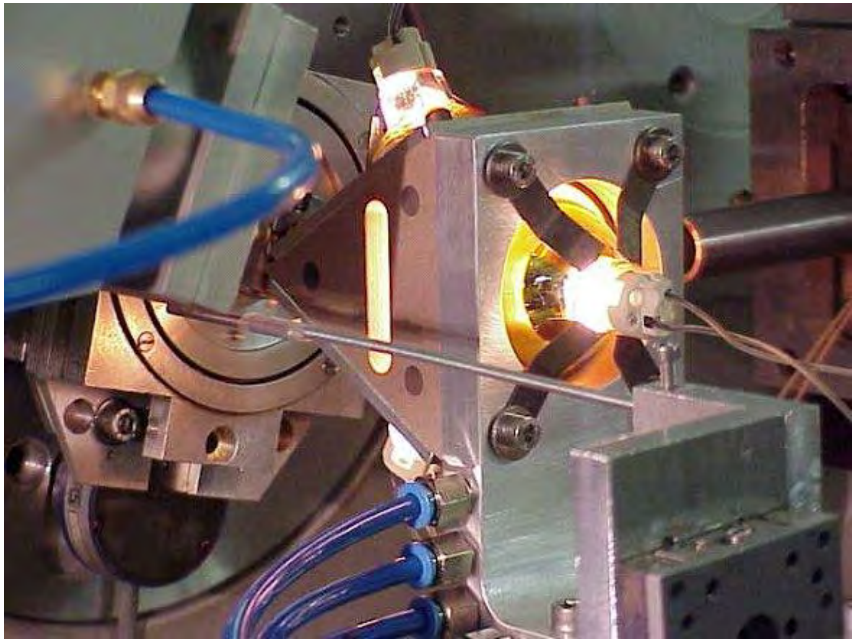
Phase identification - example

	GRISAGLIA	PATINA
	$CoAl_2O_4$; $PbSO_4$; $Pb(OH)Cl$	Amorphous
	$Pb_2Sb_2O_7$; $PbSO_4$; $CaSO_4(H_2O)_2$; $CaAl_2Si_2O_8$	$FeO(OH)$; $FeSO_4(OH)(H_2O)_2$ $PbSO_4$; $CaSO_4(H_2O)_2$; $Al_2Si_2O_5(OH)_4$
	$CoAl_2O_4$; $PbSO_4$; $CaPO_3(OH)_2H_2O$	SiO_2; PbS; $PbSO_4$; $CaCO_3$ (vat), $CaPO_3(OH)_2H_2O$

Phase identification - example

- **$Pb_2Sb_2O_7$** : original pigment
- **SO_4^{2-}, S^{2-}, CO_3^{2-}** : alteration product seawater-aerosol , acid rain
- **$FeO(OH)$; $FeSO_4(OH)(H_2O)_2$** : alteration product of original pigments
- **CO_3^{2-},PO_3^{3-}**: biological origin
- **$CoAl_2O_4$** : intervention at later date?

XRPD in non ambient conditions

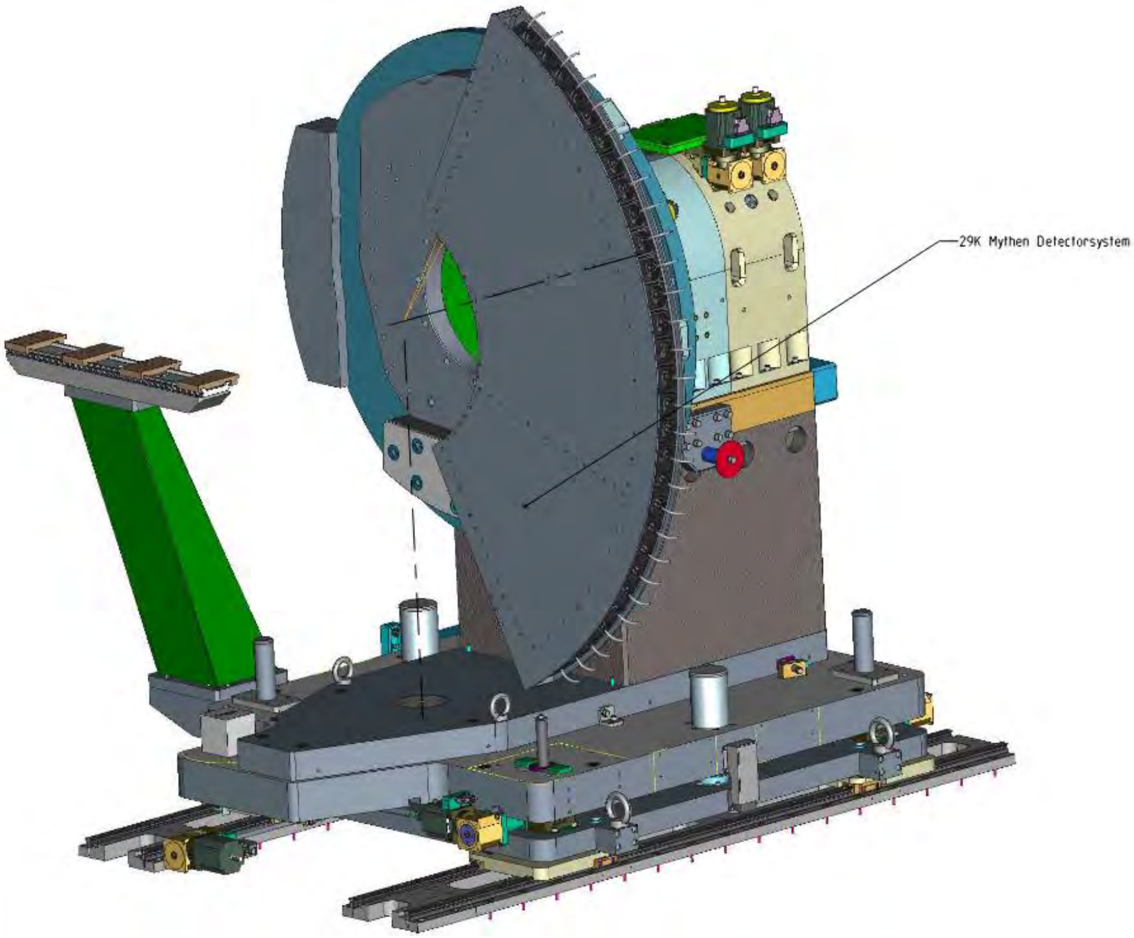


MCX: major upgrades

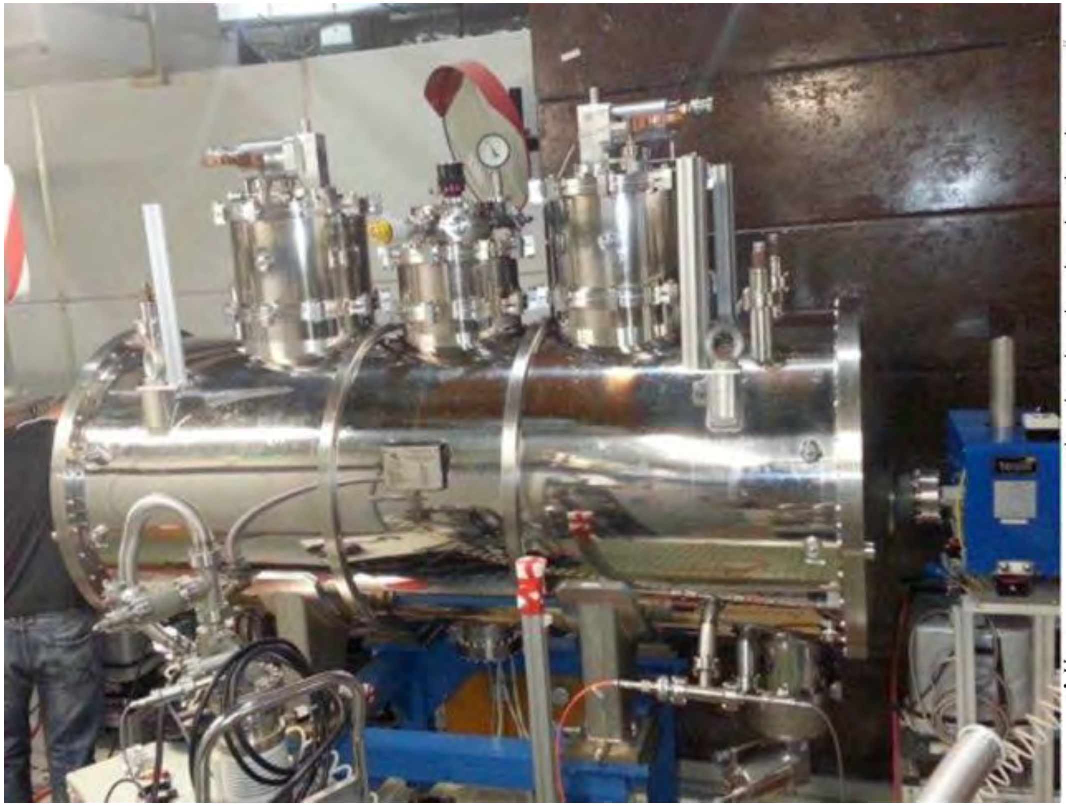
✓ Early 2022 a new diffractometer equiped with a mythen detector covering 120° was ordered

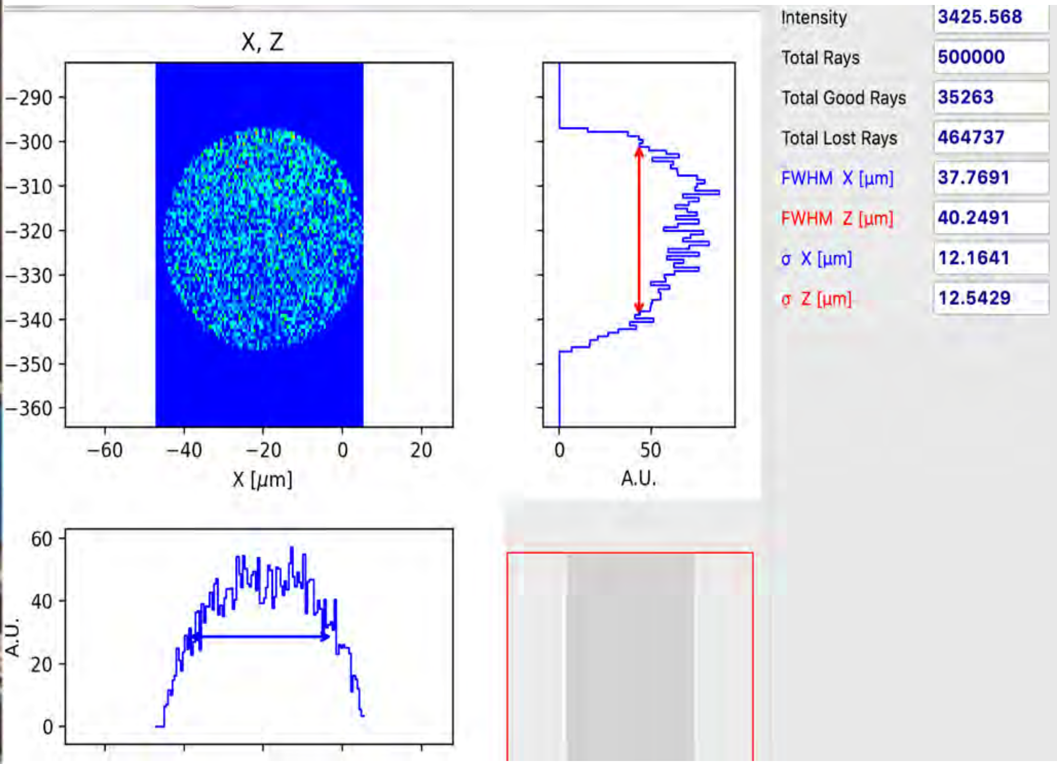
.

✓ Estimated installation November 2023.



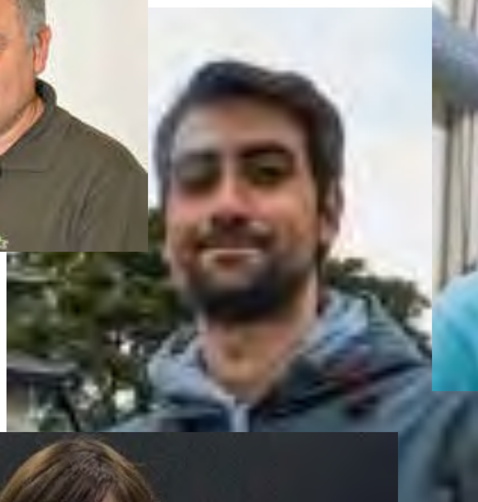
MCX: major upgrades

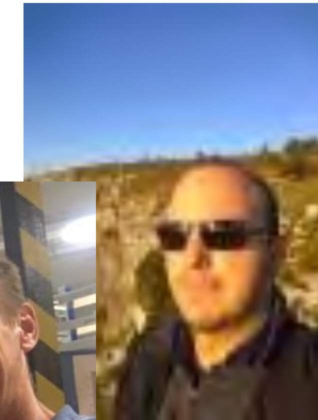
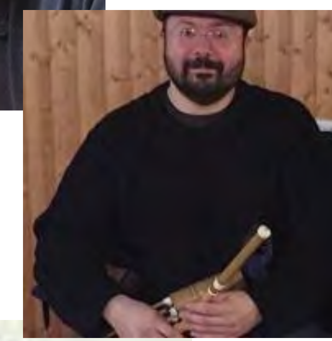




IMG_9920.jpg

MCX: The people

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Thank you!

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