LCC X-ray diffraction analysis platform

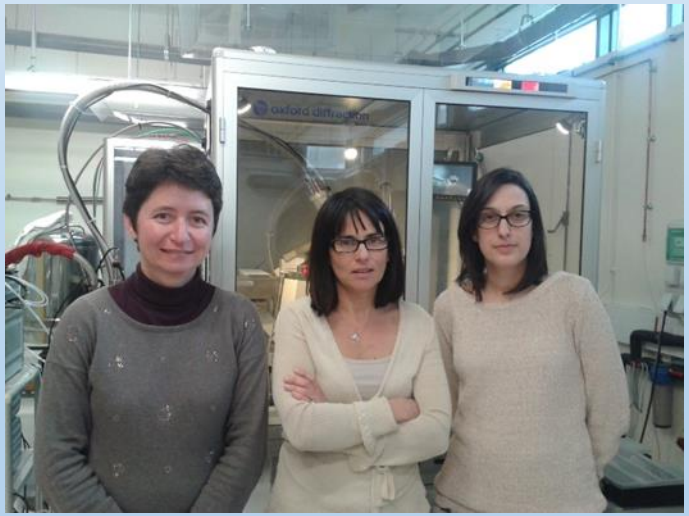
- **Staff :**

  3 CNRS Research Engineers

  Carine Duhayon

  Sonia Mallet-Ladeira

  Laure Vendier



Equipements:

Five diffractometers:

- Two single crystal diffractometers (Mo and Cu micro source X-rays tubes), liquid nitrogen cryostats (100-400K), high pressure cell (4 GPa).

- Three multi-configuration powder diffractometers: reflection, transmission on capillaries, CHT°, GIXRD, Cu or Mo anodes.

FIT24

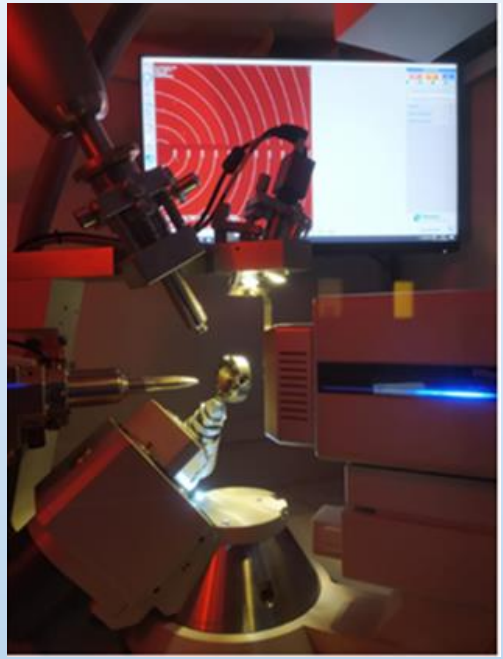
Nanomat PRRI 2020 project: collaboration Rigaku/LCC

Regional project dedicated to platforms (CASTAING/CIRIMAT/LCC and JEOL/RIGAKU/EDEN INSTR)

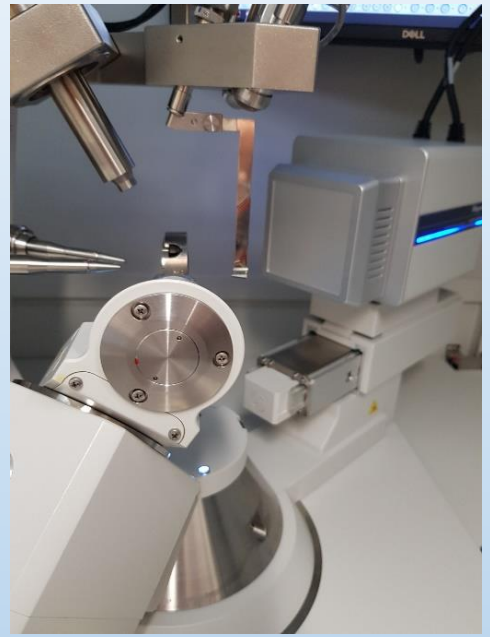
- Two new diffractometers: a Rigaku Single Crystal XtaLab Synergy-S Diffractometer and a Rigaku Smartlab Diffractometer.
- High pressure set up on the Synergy
- New DAC: Almax EasyLab One20DAC, opening angle 120°
- High pressure expert engineer financed by Rigaku : choice and implementation of the DAC on the Synergy, training of LCC XRD department staff, Dr Damian Paliwoda,

Projet NanoMAT
Plateforme Régionale de Recherche et d'Innovation

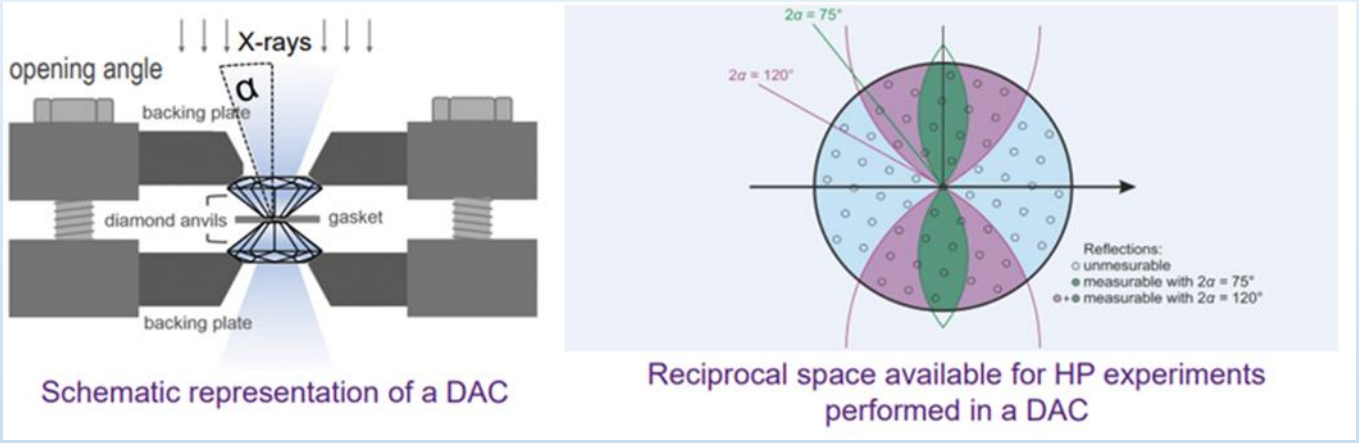
High pressure set up on the Synergy



- DAC mounted on a regular goniometer head
- Smaller collimators
- Adapted beam stop
- Cryostream raised to high position
- Benefits of small X-rays beam from micro-focus tube
- New DAC: Almax EasyLab One20DAC, opening angle 120°:crystal structures of low symmetry

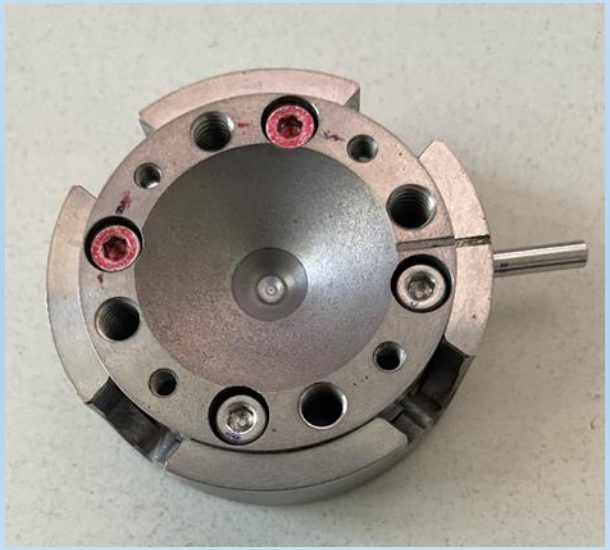


Almax EasyLab One20DAC, opening angle 120°



Schematic representation of a DAC

Reciprocal space available for HP experiments performed in a DAC



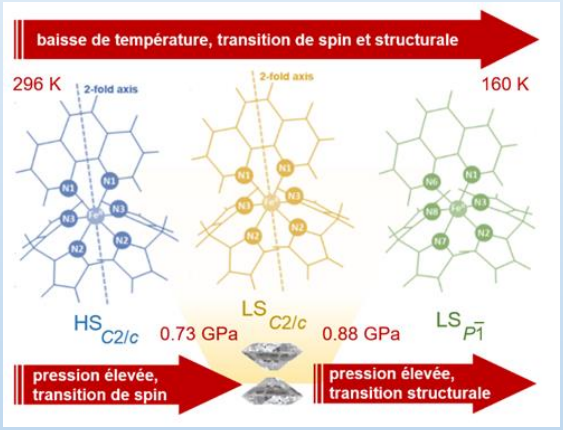
Unique cell with a physical angle of 120 degrees on both sides, particularly suited for single crystal diffraction.
Allows a large access to the reciprocal space whilst carrying out measurements at high pressure.

XRD studies under pressure: how to better understand the structure-property relationships of materials?

- Pressure: a thermodynamic parameter that significantly influences material properties.
- Its effect on chemical reactions, material properties and their electronic structure relatively poorly understood until now: lack of experimental data.
- This lack of high pressure (HP) information, compared to the large amount of low and high temperature data, is due to HP technical requirements.
- DAC design made possible the development of HPs as a powerful tool for spectroscopic and X-ray diffraction studies.
- Thanks to our new type of DAC with a large opening angle (120°), we were able to determine crystal structures of low symmetry, which is extremely rare for laboratory (not Synchrotron) experiments.

Low-Temperature and High-Pressure XRD Study of Molecular Fe(II) Complex

- Coupling mechanism between the spin transition and a structural transition, accompanied by symmetry breaking, in the molecular complex [Fe(H2B(pz)2)2(phen)]



Spin state	HS	LS	LS
pressure GPa	0.40 GPa	0.73 GPa	2.15 GPa
space group, Z	*C*2/*c*, 4	*C*2/*c*, 4	$P\bar{1}$, 2
a, Å,	17.027(3)	16.745(10)	11.5110(9)
b, Å	15.7475(9)	15.390(3)	10.3137(11)
c, Å	10.4279(11)	10.272(4)	10.1045(10)
α, °	90	90	70.202(9)
β, °	121.274(16)	120.27(6)	111.176(8)
γ,°	90	90	94.264(8)
V, Å^3	2389.8(6)	2286(2)	1050.92(19)
R_{int}	0.0476	0.1075	0.0728
GOF on F^2	1.024	1.003	1.156
R_1 [I > 2σ(I)]	0.0499	0.0813	0.0795
R_1 (all data)	0.1000	0.2493	0.1602
wR_2 (all data)	0.1395	0.2667	0.2858
completness to theta max	78.2 %	65.2 %	49.6 %
Av. Fe-N distance, Å	2.167(2)	2.040(5)	1.962(9)

- Coupling between the two phenomena can be controlled by the external stimulus. Particularly under pressure, the spin transition can be separated from the structural transition phenomenon, which is not possible to detect at low temperature.

References

1. Pressure Tuning of Coupled Structural and Spin State Transitions in the Molecular Complex [Fe(H2B(pz)2)2(phen)], Paliwoda D., Vendier L., Nicolazzi W., Molnar G., Bousseksou A., Inorg. Chem. 2022, 61, 40, 15991–16002.
2. Decoupling Spin-Crossover and Structural Phase Transition in Iron(II) Molecular Complex Damian Paliwoda, Poster, ECM33, Versailles 2022

Financial support from from the European Research Council (ERC) (grant agreement N° 101019522), the Region Occitanie and the company Rigaku Corporation (PRRI project NANOMAT) is gratefully acknowledged.