

PSICHÉ

CAESAR data acquisition on the PSICHE beamline

X-ray diffraction at extreme conditions from large volumes cells

The name of PSICHE (in French), Pressure, Structure and Contrast Imaging at High Energy, sums up the thematics of the beamline: X-ray diffraction under extreme pressure conditions (whether or not coupled with temperature) and X-ray absorption wide-field tomography (3-D imaging). Here, we will focus on the first application.

Energy dispersive X-ray diffraction

The Bragg law describes the relationship between the distance between the crystallographic lattice planes, the diffraction angle and the wavelength of the diffracted photons.

$2d \sin\theta = \lambda$ which can be re-written introducing the energy E of photons (keV) $d = 6.199/(E \sin\theta)$.

We can see here that the energy and the sine of the diffraction angle play a similar role. Classical diffraction (angular dispersion) fixes the energy, and allows to vary. In energy dispersive diffraction, the angle is fixed, and the

energy allowed to vary. To achieve this, all energies must be present in the beam (as is the case for the PSICHE white beam), and the detector needs to be capable of analyzing the energy of the diffracted photons at a certain angle (it is the case for the Germanium (Ge) detector used on PSICHE which, coupled to a multi-channel analyzer, allows us to count the number of events at a given energy.

Figure 2 shows the energy dispersion diffraction display mounted on the CAESAR system. You can see the inlet and outlet slits which define the incident beam and the diffraction angle,

the Paris-Edinburgh high-pressure cell and the Ge detector which analyzes the photon energies and counts them. The CAESAR system allows the diffraction angle to be varied between 0 and 30° with a circle of confusion inferior to 20 μm. By performing an energy dispersion acquisition for each angular step, we obtain a 3-dimension diagram, in which the axes are the diffraction angle, the energy of the photons and the diffracted intensity (figure 3 top). It can be read by extracting a profile at a given angle (energy dispersion), at a given energy (angular dispersion) or, by using the Bragg Law to transform the energy axis into d-spa-

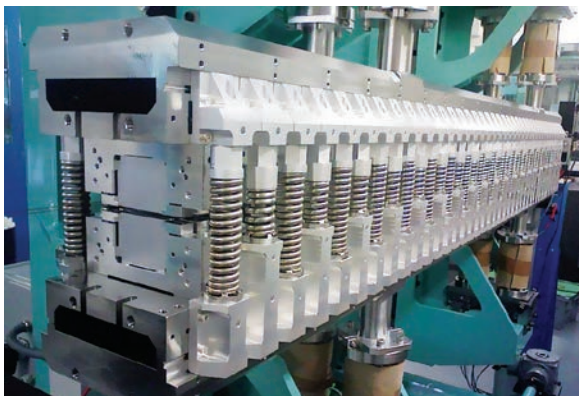


Figure 1. Multi-pole wiggler WS50.

The PSICHE beamline at SOLEIL is characterized by having as its source a multi-pole vacuum wiggler (on the left), designed by the Insertion group of the Source and Accelerator division¹. The intrinsic properties of the wiggler as the insertion element offer the beamline particular characteristics in terms of bandwidth, flux and critical energy. In particular, the possibility of using a white beam with photons up to 80keV opens up perspectives unique in SOLEIL for X-ray diffraction as well as in tomography. Moreover, the beamline can also produce a monochromatic beam up to an energy of more than 50keV, which also offers the beamline specific possibilities.

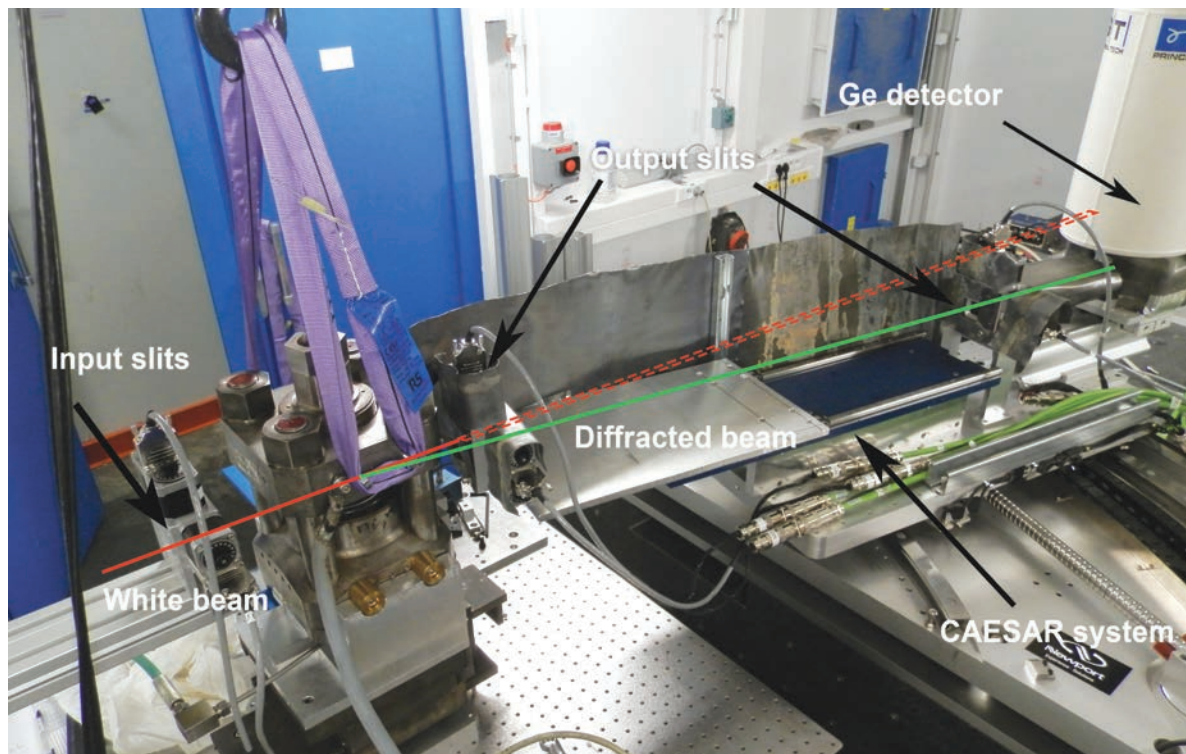


Figure 2. Energy dispersion diffraction display mounted on its CAESAR system.

cing (figure 3, middle, logarithmic coordinates). From this transformed data a classical diffraction spectrum is obtained, which intensity varies as a function of the interplanar distance; it gathers all of the data obtained at every angle and every energy (figure 3 bottom).

We see that it is possible to record spectra either by using the CAESAR system, or simply in energy dispersion. This last mode is much faster (a few seconds can suffice in some cases). When experimenting with pressure, energy dispersion spectra are enough to determine the evolution of the lattice parameters of the compressed material, because these depend only of the position of the diffraction peaks. On the other hand, if a new structure appears (modification of the diffraction peaks), then the energy dispersion is no longer ideal because the intensities of the diffraction peaks obtained are not suitable for use in a Rietveld refinement. In this case, as we will see later on, it is possible to use the CAESAR

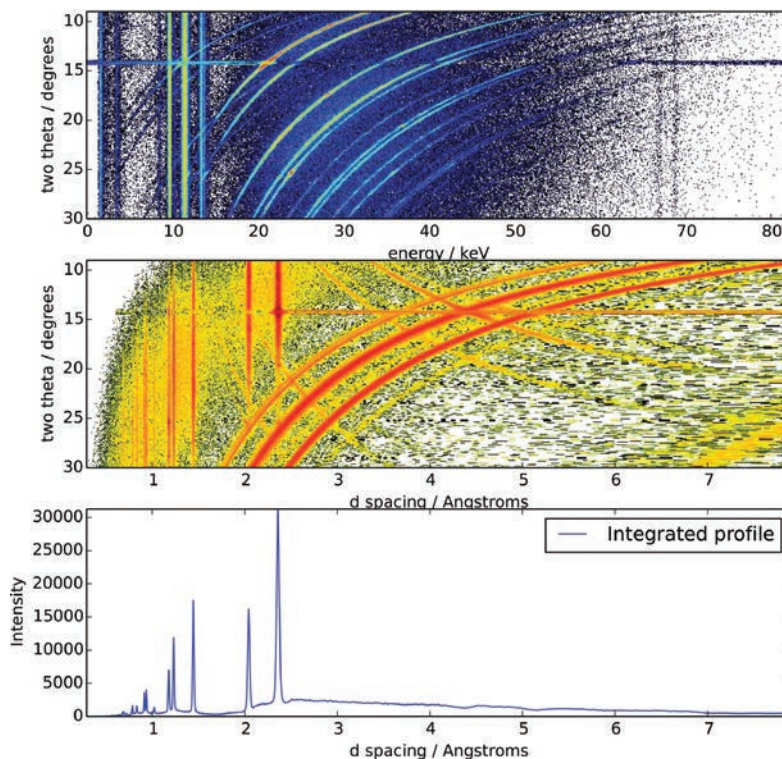


Figure 3. "CAESAR" acquisition of a gold leaf between 4° and 14°.

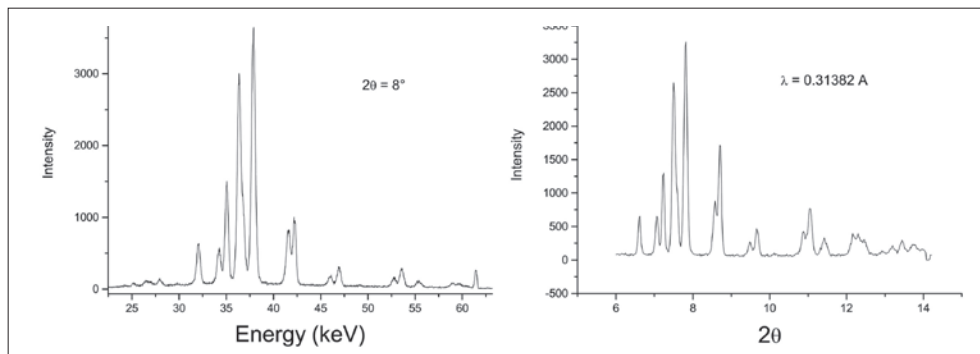


Figure 4. Energy dispersion and angular dispersion X-ray diffraction spectra, of a magnesium carbide sample under high pressure and high temperature (O. Kurakevych and Y. Le Godec).

system to obtain an angular dispersion spectrum and perform a Rietveld refinement to find the new structure. In addition, this angular dispersive spectrum can be obtained much faster than in a classical monochromatic experiment.

Synthesis of new magnesium carbide

Magnesium carbides are interesting components, both from the fundamental and applied point of view. From an advanced new materials research standpoint, the Mg-C system appears promising (polymerized carbon chains, magnesium-intercalated graphite, carbon clathrate...). However, at ambient pressure, reactions between carbon and magnesium are not favorable. That is why the IMPMC, UPMC team (O. Kurakevych, Y. Le Godec²), in collaboration with the PSICHE team, has developed high pressure magnesium carbide synthesis methods in a Paris-Edinburgh cell, by following *in situ* the reactions between materials with X-ray diffraction.

Figure 4 displays the same spectrum in both energy dispersion (for $2\theta=8^\circ$) and angular dispersion (for $\lambda=0.313\text{\AA}$) of a sample synthesized under high pressure in a Paris-Edinburgh cell, measured with the CAESAR system on the PSICHE beamline. One can notice the similarity between spectra, but can also observe that the background is flat for the angular dispersion spectrum. The latter can be used to perform a Rietveld refinement, which has been

done, revealing the existence of a new form of magnesium carbide (figure 5).

All this proves that CAESAR system is very well suited for following the structure modifications and new materials synthesis, *in situ*. The possibility to perform different pressure and temperature measurements is an essential step towards optimizing the most efficient thermodynamic path to the final product. The time-saving compared to a post-mortem analysis is huge, and allows the consideration of syntheses in which 3 parameters are altered: composition, temperature and pressure.

It is clear that the CAESAR acquisition system developed on the PSICHE beamline using a white beam is perfectly adapted to diffraction measurements at high pressure and high temperature in large-volume cells. It has been shown here with a Paris-Edinburgh cell. Other experiments were conducted in a multi anvil cell, specially designed for the beamline, which allows performing higher pressure measurements. Recently, a team from the Magmas and Volcanoes Laboratory of the Clermont-Ferrand University has been able to achieve pressures of 25GPa à 2300°, and observe the melting of an Earth's mantle compound in these thermodynamic conditions.

→ Contacts:
jean-paul.itie@sncrotron-soleil.fr
nicolas.guignot@sncrotron-soleil.fr

References:
¹O. Marcouille et al.
 Phys. Rev. ST Accel. Beams 16,
 art. 050702 (2013).
²T.A. Strobel et al.
 Inorg. Chem 53 (13), 7020 (2014).

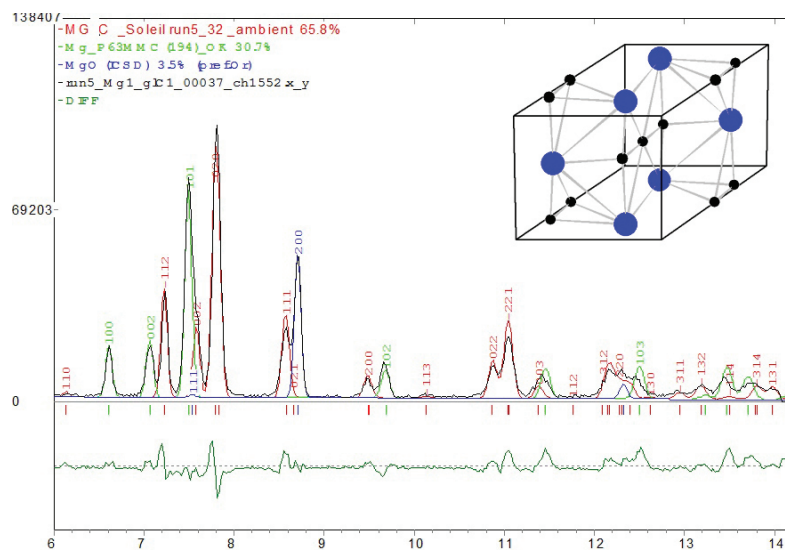


Figure 5. Rietveld refinement of the magnesium carbide monoclinic phase in the HP cell².