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# Light-irradiation at 700 MPa down to 1.5 K for neutron diffraction

**P Parisiades<sup>1,2,\*</sup>, C Payre<sup>2</sup>, J P Gonzales<sup>2</sup>, J L Laborier<sup>2</sup>, J P Bidet<sup>2</sup>, P Guionneau<sup>3</sup>, P Rosa<sup>3</sup>, E Lelièvre-Berna<sup>2</sup> and M H Lemée-Cailleau<sup>2</sup>**

<sup>1</sup>European Synchrotron Radiation Facility, CS 40220, 38043 Grenoble Cedex 9, France

<sup>2</sup>Institut Laue-Langevin, CS 20156, 38042 Grenoble Cedex 9, France

<sup>3</sup>CNRS, Univ. Bordeaux, ICMCB, UPR 9048, 33600 Pessac, France

Email: [parisiad@esrf.fr](mailto:parisiad@esrf.fr)

**Abstract.** We present a new high-pressure cell for neutron diffraction made from TiZr ‘null-matrix’ alloy that combines high mechanical resistance below 100°C and negligible coherent neutron scattering. This pressure cell can operate at a maximum pressure of 700 MPa down to a temperature of 1.5 K. A sapphire optical window allows simultaneous illumination of the sample over the broad wavelength range ~0.4 to almost 5 μm. The pressure is applied with Fluorinert 770 or helium gas to ensure the best possible hydrostatic conditions at cryogenic temperatures. We present the design, the FE calculations and the first neutron data collected with this pressure cell on the spin-crossover dinuclear iron (II) complex system.

**Keywords.** 75.30.Wx, 78.20.Ls, 74.62.Fj

## 1. Introduction

The spin crossover (SCO) phenomenon, where low spin (LS) and high spin (HS) states can be exchanged upon the application of external perturbations (temperature, pressure, magnetic field or light irradiation), has greatly been reported for transition metal complexes with  $d^4$  to  $d^7$  electronic configurations [1-7]. Of special interest are SCO materials with cooperative behavior, where hysteresis effects can make them ideal candidates for applications in optical switches, sensors and memory devices [5, 8-10]. The LS and HS states can manifest differences in magnetic, dielectric and optical properties, as well as in color and structure. Photo-irradiation in particular has attracted great attention as an external stimulus to drive and control spin transitions. Usually two methods are employed. Ultrafast spectroscopy using fs lasers is very useful to distinguish individual dynamics of order parameters that are strongly tied to each other in the static state, such as charge orbital ordering and collective Jahn-Teller distortion [11]. On the other hand, continuous laser irradiation is more appropriate for SCO systems since it can induce reactions requiring slow kinetics such as spin transitions [8, 12].

Neutron diffraction is an ideal experimental tool for the study of such systems thanks to its sensitivity to light elements and atomic magnetic moments. While low-temperature / high-pressure measurements are routinely carried out at neutron facilities, light irradiation under high-pressure and low temperature is not common because of several technical impediments. The powder or single crystalline sample is placed in a cell made from materials having appropriate neutron properties (e.g. transparency, low neutron background) and filled generally with Fluorinert 770 or He gas by an external pressure intensifier. In comparison with Paris-Edinburgh presses, opposed-anvil or clamped cells, the main advantage of these cells is the precise control of pressure [13], even at low temperature. Moreover, their small size makes them fit inside most cryostats and significantly reduces the cool-down time. However, the energy stored in gas cells is huge and limits their operation to low-pressure ranges. The maximum possible pressure is usually 700 MPa when using hard Al alloys for the vessel material [13, 14]. TiZr and hardened CuBe alloys exhibit better mechanical performances [15, 16] and higher pressures can be achieved [16, 17]. In more recent developments, double-layered cell designs have demonstrated maximum pressures of 1.8 GPa [18] or even 2.5 GPa [19] at ambient temperature.

The provision of an optical access to the sample within a high-pressure cell brings obviously some difficulties. Clamped cells with optical access for ruby fluorescence in-situ pressure measurements [20] are routinely used in many laboratories. Neutron facilities also use to provide 200 - 300 MPa pressure cells with sapphire windows on small angle scattering instruments [21, 22]. But these cells host liquids, have small angular openings, are limited to pressures lower than  $\sim 500$  MPa and used at near-ambient temperatures. Here we present a new liquid- or gas-loaded pressure cell designed for neutron diffraction, operating at up to 700 MPa at temperatures below 100°C (down to 1.5 K) and featuring in-situ light irradiation of the sample through a sapphire optical window. We also report first measurements on a spin-crossover dinuclear Fe(II) system to illustrate the performance of the device.

## 2. Technical challenges and considerations

For SCO systems with slow kinetics, it is important to track spin transitions with irradiation time [5, 7]. Given the relatively low flux of neutron sources compared to synchrotrons, we decided to take advantage of the quickest crystallography technique i.e. Laue diffraction. The detectors of the ILL Laue single crystal diffractometers VIVALDI [23] or CYCLOPS [24] cover large solid angles requiring wide horizontal access in the equatorial plane as well as below and above this plane. So obviously the pressure cell should have a cylindrical geometry.

The cell itself will attenuate the beam and scatter neutrons. Thus, the amount of cell material in the beam path should be minimized and the material of the cell body should have a very weak coherent neutron scattering length to avoid the presence of unwanted Bragg spots. The coherent scattering contribution being the most prominent issue, CuBe and Aluminum alloys are less good candidates than the 'null-matrix' TiZr

alloy whose mechanical properties match the required pressure and temperature ranges:  $p < 700$  MPa and  $T < 100^\circ\text{C}$ . Ti and Zr nuclei scatter neutrons in opposite phases with coherent scattering lengths being respectively  $-3.44$  fm and  $+7.16$  fm. A solid solution with mass composition 52.2% Ti / 47.8% Zr gives rise to a null coherent neutron scattering [27, 28]. Like CuBe and Al alloys, TiZr is non-magnetic and therefore allows the investigation of magnetic samples under magnetic fields with polarized neutrons.

As previously mentioned, one of the great advantages of gas cells is the ease with which one controls the pressure with an accuracy better than 1 bar up to 700 MPa or even more. Helium is an ideal pressure transmitter since it is transparent to neutrons and retains its fluidity at high pressures down to a lower temperature than any other substance (freezing temperature  $\sim 50$  K at 700 MPa). Moreover, the pressure loss along an isochoric when cooling below the freezing point is smaller for helium than any other gas [25]. However, helium is very compressible and thus hard to pressurize but not impossible. Sealing helium gas inside a pressure cell is also a difficulty to consider with care.

The injection of light to the sample region requires an optical window that withstands high pressures at both ambient and cryogenic temperatures. The dimensions of this window should be large enough to ensure efficient irradiation of the sample. Differential strains under pressure between the window and the various metallic parts of a pressure cell assembly can increase linearly with dimensions [26] and should be avoided. A simple and reliable sealing technique must thus be adopted. Sapphire having excellent transparency for a wide range of wavelengths (UV, visible and near-IR) and great mechanical properties over a wide temperature range, we chose to use a sapphire window sealed with optically polished surfaces.

### **3. Design and construction**

A cross-section of the pressure cell assembly including all individual components is shown in figure 1. Following reasons given above, the cell has a cylindrical symmetry matching the detector coverage of ILL Laue diffractometers. The body is made from TiZr null-matrix alloy prepared by Timet (Titanium Metals Corporation, Henderson Technical Laboratory, USA) following a double vacuum-arc melting process using nuclear grade sponges of Titanium and Zirconium.

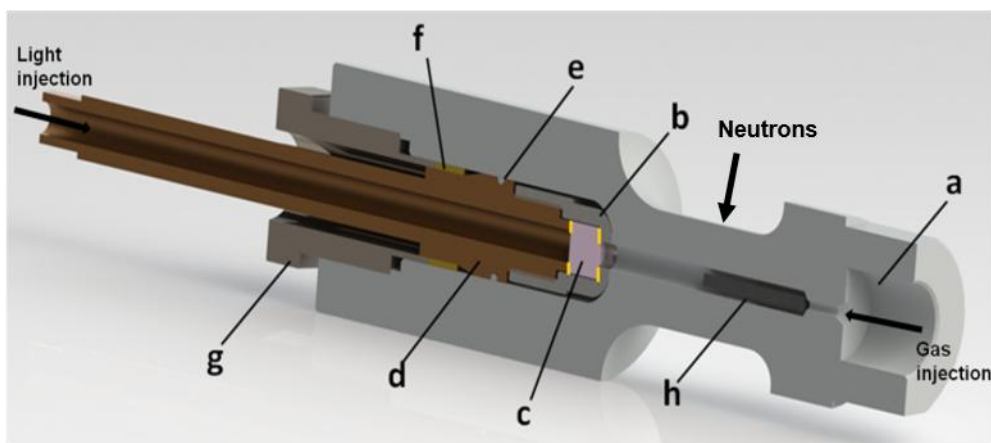


Figure 1: Pressure cell complete assembly: a) cell body, b) sapphire window nut/housing, c) sapphire window, d) Cu-Be guide, e) rubber O-ring, f) copper ring, g) closing nut, h) vanadium sample holder.

The sample is introduced into the central thinner part of the cell body crossed by the neutron beam (left side on figure 1). Its position is tuned with a sample holder (h) made from Vanadium, which is a very weak incoherent neutron scatterer. A sapphire window (c) closes one end of the CuBe guide (d) in which the optical fiber will be introduced. This window is maintained in position with a nut/housing (b) made from non-magnetic stainless steel 316L (or 304L) and drilled to the diameter of the sample space for transmission of the light. The unsupported and outer diameters of the window are respectively 4 and 8 mm and the window thickness is 8 mm. With such dimensions, the maximum allowed pressure is about 1 GPa with a safety factor of 4 [29]. The faces of (c) and (d) are optically polished to 300 nm and the window surfaces are oriented perpendicularly to the crystallographic *c* axis within  $\pm 0.5^\circ$  since such orientation provides the highest mechanical strength [26]. The Sapphire window with surfaces parallelism better than  $0.2^\circ$  was produced by RSA Le Rubis (Jarrie, France) and surfaces were coated with anti-reflective  $\text{MgF}_2$  to increase the transmission up to 99% through the entire visible spectra and near-IR regions.

The polishing serves as a first level of sealing since the contact pressure of the mating surfaces is greater than the gas pressure due to the unsupported area principle. When the pressurized gas is driven inside the pressure cell, it pushes the Sapphire window on the CuBe tube and travels up to the rubber O-ring (e) ensuring the leak-tight sealing in the lower pressure range. For higher pressures up to the maximum of 700 MPa, the copper ring (f) ensures metal-to-metal contact with the CuBe tube (d) closed with the maraging steel nut (g).

A technical drawing of a cross-section of the cell plugged to the high-pressure capillary is presented in figure 2. The body is 39 mm maximum in diameter and 123 mm long. The sample chamber is large enough to host crystals of several  $\text{mm}^3$  in the inner hollow cylinder 4 mm in diameter. The cell is screwed at the bottom of the sample stick of a top-loading Orange cryostat (left side on figure 2). The optical fiber bringing light down into the cell is protected with a  $\varnothing 4$  mm tube inside the main stainless-steel inner tube of the stick and escapes the cryostat through a He-tight connector.

The solid angle access to the detector is slightly reduced because of the presence of the capillary (dark angle). Of course, it should not be in the incident beam path because that would produce a considerable background signal. Concerning the out-of-plane access, the sample position inside the cell is managed carefully during sample mounting so that the maximum possible angular opening for neutron diffraction is attained. On the VIVALDI instrument, a maximum of  $\pm 52^\circ$  is achieved [23].

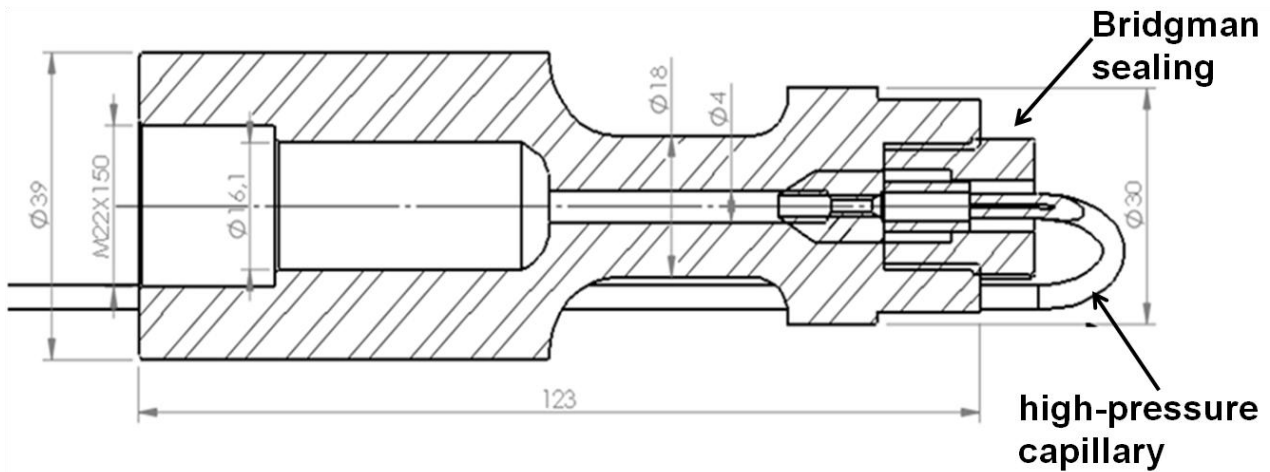


Figure 2: Schematic drawing of the pressure cell. The high-pressure capillary and the Bridgman seal are also shown. The light is brought through the cryostat sample stick from the left side.

In order to prevent any mechanical failure of the pressure cell and minimize the amount of material in the neutron beam, we have optimized the dimensions of the body using ANSYS® finite element analysis software. After application of the appropriate cylindrical boundary conditions, the stress distribution on the pressure cell was analyzed. Figure 3 shows the stresses (a) and deflections (b) resulting from the axisymmetric FEA simulations at the maximum load of 700 MPa. As expected, the highest observed stresses occur on the inner wall of the pressure cell. The maximum stress is found to be 760 MPa. In all cases the maximum expected stress is well below the break limit of the TiZr alloy (860-920 MPa), but the elastic limit varies between 680 and 760 MPa and is surpassed in a particular region. Thus a small plastic deformation on the order of 31  $\mu\text{m}$  is expected. The pressure cell exhibits better mechanical resistance upon cooling, since at cryogenic temperatures the tensile strength of the TiZr alloy rises significantly. Ultimate tensile strengths for this material are around 1300 MPa at 4 K [30].

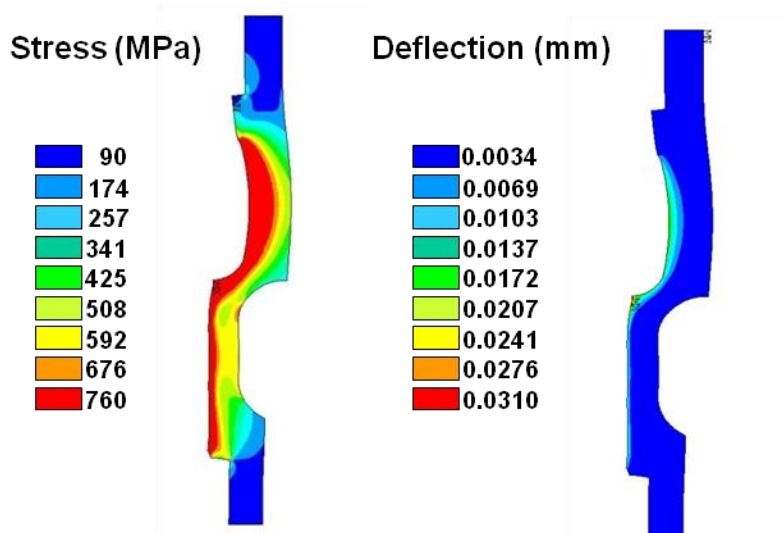


Figure 3: Stress and deflection of the pressure cell under the maximum load of 700 MPa.

With regard the injection of the transmitting media; the capillary is plugged to the cell using the standard Bridgman sealing used in most gas- or liquid-operated pressure cells of ILL. This high-pressure capillary mounted along the stainless steel tubes of the sample stick passes close to the liquid N<sub>2</sub> reservoir of the Orange cryostat. To avoid blockages when using transmitting media freezing at nitrogen temperature, a Thermocoax heater is wound and glued around the capillary. The heating is controlled with a standard temperature controller reading a Pt100 sensor placed at the coldest point of the stick i.e. at the height of the top of the liquid N<sub>2</sub> bath.

The light irradiation is achieved with a simple setup using laser diodes (as of now wavelengths of 660 and 852 nm have been implemented). The laser light passes through a set of collimators and is then inserted in a set of two optical fibers. The first fiber is a common polymer-coated 10 m long multimode fiber, while the second one is a 2 m long aluminum-coated special multimode fiber designed for cryogenic temperatures down to 4 K without loss of transmission or possibility of cracking. The numerical aperture and core sizes of the fibers have been selected so as to illuminate the whole sample surface. In order to fit inside the protective tube, the end of the aluminum-coated optical fiber has a flat-cleave ferrule-only finish.

#### 4. Results

Initially the empty pressure cell was installed on the VIVALDI instrument at ILL in order to measure the neutron background at ambient pressure with a thermal beam flux of  $1.2 \times 10^8 \text{ n.cm}^{-2}.\text{s}^{-1}$ . As expected with TiZr alloy, the coherent contribution is negligible while some incoherent scattering is observed at low angles (figure 4). Whereas CuBe cells would give rise to a significant scattering [31], TiZr gives the most uniform background.

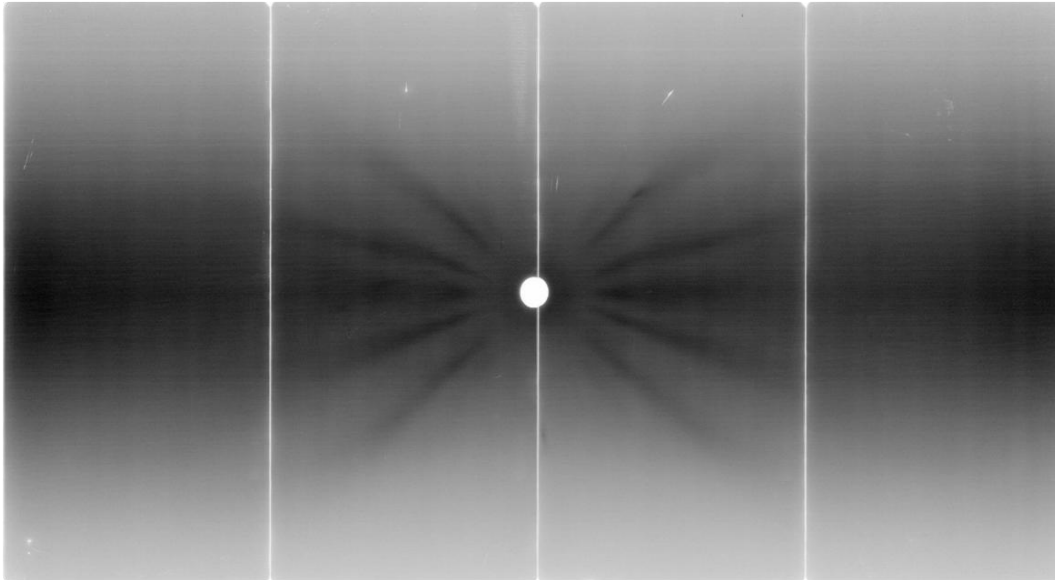


Figure 4: Neutron scattering from the empty pressure cell at ambient pressure inside an Orange cryostat. The image corresponds to 30 min of exposure time.

The cell was also checked in terms of mechanical integrity and sealing efficiency at the maximum working pressure. During its assembly, the copper ring shown in figure 1 was sunk in an indium solution in order to improve its sealing performance. As shown in figure 5, Helium gas was pressurized into the cell in steps with a two-stage system: a Nova-Swiss gas compressor increased the pressure up to  $\sim 300$  MPa and an intensifier increased it further up to its maximum capability of 500 MPa. The steps at 350 and 400 MPa were intentionally done to check the absence of leaks. Similarly, we injected Fluorinert 770 with a manual rig. After a first step to 300 MPa, we increased the pressure by steps of  $\approx 50$  MPa up to 700 MPa. No failure of sapphire window was observed. The deformation of the interior walls of the pressure cell was measured after a few applications of pressure at room temperature. After the first run up to 700 MPa, a deformation of  $\sim 36$   $\mu\text{m}$  was observed, close to what is expected from the calculations (figure 3). Successive measurements led to smaller deformations, with a modification of only 13  $\mu\text{m}$  at 700 MPa.

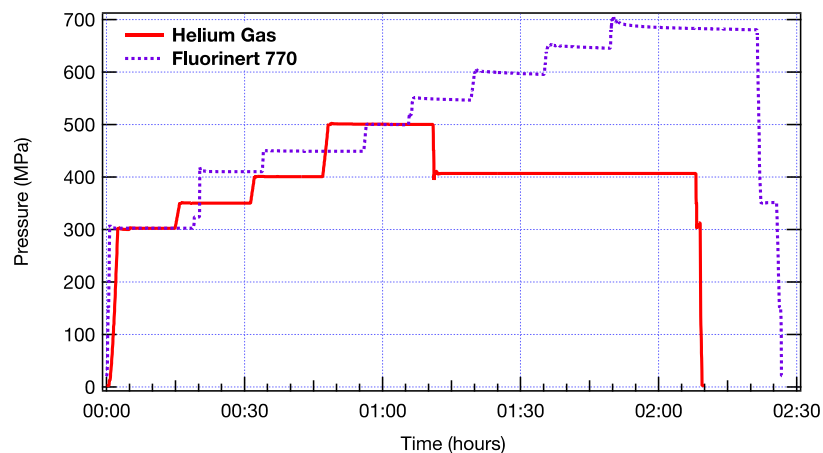


Figure 5: Step by step increase of pressure versus time using helium and Fluorinert 770. The gas pressure intensifier limited the tests performed with helium to 500 MPa.



Some high-pressure studies on spin-transition systems have been previously performed using many different techniques such as magnetization [2, 32], x-ray diffraction [33, 34], or XANES [35, 36], but high-pressure data on neutron diffraction have only recently started to appear [37, 38]. After these successful tests, we performed the first Laue neutron diffraction experiment on high quality single crystals of the spin-crossover complex  $[\{\text{Fe}(3\text{-bpp})(\text{NCS})_2\}_2(4,4'\text{-bipyridine})] \cdot 2\text{CH}_3\text{OH}$  [7]. This system is expected to undergo two phase transitions on cooling: a) a transition from *phase I* to *phase II* at 161 K, corresponding to the quadrupling of unit cell volume and b) a transition from *phase II* to *phase III* at 113K, which corresponds to unit cell reduction and a spin transition from the HS to a mixed HS-LS phase. Laser irradiation of the samples reverts the material back to the HS state, with a slight modification of the lattice parameters (*phase III\**). The expected effect of pressure was to shift the temperature of these transitions, while a complete LS state is expected at much higher values ( $> 2$  GPa).

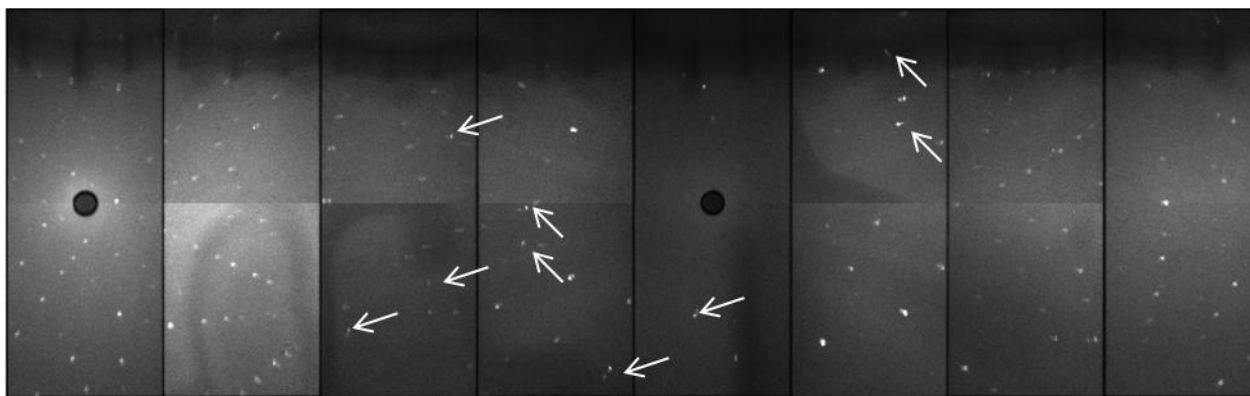


Figure 6a: Diffraction pattern of  $[\{\text{Fe}(3\text{-bpp})(\text{NCS})_2\}_2(4,4'\text{-bipyridine})] \cdot 2\text{CH}_3\text{OH}$  at 10 K and 200 MPa, before laser irradiation. The white arrows indicate spots that are not present in the irradiated pattern (fig. 6b).

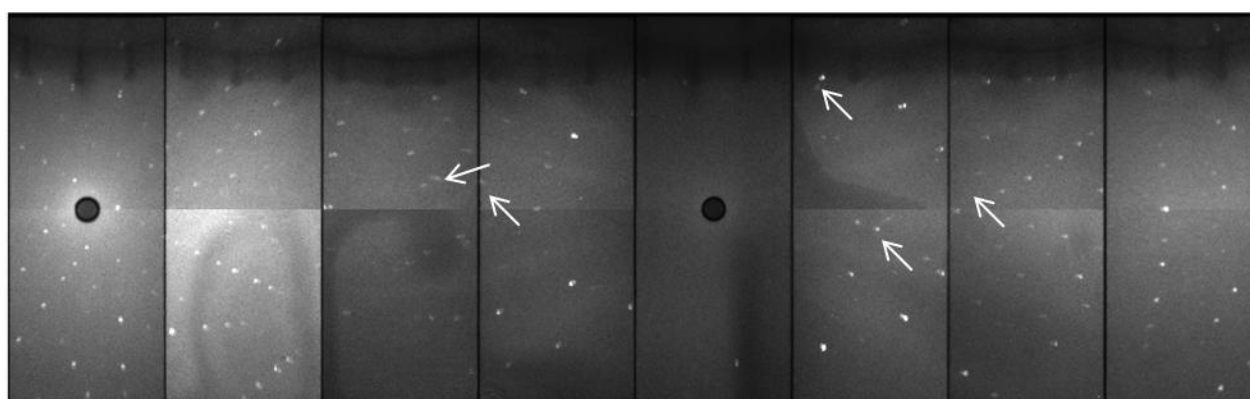


FIG 6b. Diffraction pattern of  $[\{\text{Fe}(3\text{-bpp})(\text{NCS})_2\}_2(4,4'\text{-bipyridine})] \cdot 2\text{CH}_3\text{OH}$  at 10 K and 200 MPa after light irradiation. The white arrows indicate spots that are not present in the non-irradiated pattern (fig. 6a).

The experiment was performed on the CYCLOPS instrument at the ILL. The pressure inside the cell was increased with He to 200 MPa at room temperature. After cooling to 10 K, we measured the neutron

diffraction pattern shown in figure 6a before illumination, which corresponds to *phase III*. The light irradiation of the samples was carried out using a CW laser diode at 660 nm wavelength and a fluency of 5 mW/cm<sup>2</sup>. The diffraction patterns were collected every 30 minutes of illumination at constant temperature and pressure, thus allowing us to track any possible change with respect to time. After 1.5 hours of laser irradiation, we observed the different pattern presented in figure 6b and which corresponds to the HS *phase III\**. It is clear that many spots appear or disappear during irradiation and that some singlet spots in figure 6a split as doublets in figure 6b and vice versa. Although more data would be required to complete the analysis, signs of structural and/or magnetic transition are present, probably to the HS state due to laser irradiation. These results will be presented in detail in another article.

## 7. Conclusion

We have successfully designed and constructed a new gas- or liquid-operated 700 MPa pressure cell for neutron experiments. This cell combines low temperatures (1.5 to 380 K) and light irradiation (UV to almost 5  $\mu$ m). The cell produces negligible coherent scattering and is optimized for diffraction. It offers a wide angle of detection, making it suitable for both monochromatic and white beam techniques. The performance of the cell was demonstrated by a Laue neutron diffraction experiment on a spin-crossover dinuclear iron (II) complex system and is now available to users.

## 8. Acknowledgments

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