Full description of the behavior of a Molecular Switch probed by Single Crystal and Powder XRD under pressure at variable temperature

M. Marchivie[1*], E. Tailleur[1,2], P. Rosa[1], J.P Itié[3], M. Probert[4] and P. Guionneau[1]

[1] *CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB, UMR 5026, F-33600 Pessac, France*
[2] *LLB, CEA-Saclay, 91191 Gif-Sur-Yvette Cedex*
[3] *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, F-91192 Gif-sur-Yvette Cedex, France*
[4]*Chemistry, School of Natural and Environmental Sciences, Newcastle University, Kings Road, Newcastle NE1 7RU, UK*

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*e-mail: mathieu.marchivie@icmcb.cnrs.fr

Since the development of the first Diamond anvil cell (DAC) in 1958[1], and the development of DAC well adapted to commercial diffractometers 20 year latter[2], the investigations of materials under high pressure did not stop to increase. Nevertheless, obtaining **high-pressure structural data** is, as a general matter in Science, still a challenge especially when combining several thermodynamic variables such as **pressure and temperature**, or when data are recorded on **molecular materials**. Crystal structure investigations under pressure performed on molecular systems significantly starts only in the early 2000s and represent only about 0.2% of the CSD database. Addressing the additional difficulties due to molecular compounds necessary includes instrumental and methodology developments in order to access to a reliable characterization, taking account their specificities such as low symmetries, poor crystallinity and relatively low and narrow pressure working range. Surprisingly, though the scientific community still develops new technics to get accurate data at very high pressure for inorganic materials, working with soft molecular material at pressure bellow 1 GPa is still challenging especially on a laboratory X-ray source. Despite a significant improvement of X-ray diffraction methods and an increasing number of crystal structures under high pressure, the crystallographic investigations on molecular compounds under pressure remain scarce despite the new, unexplained or very rare behaviors observed in numerous examples. Typically, despite the crucial role of polymorphism on such materials, (P, T) **phase-diagrams of molecular compounds are almost unexplored**. In this communication, we will present a full structural description of a Spin Crossover Compounds (SCO) compound along its transition that occurs at relatively low pressure, ca. 1.6 kbar, opening potential piezo-switch based applications[3,4]. This work aimed to determine the structural properties under pressure at **different scales**, from the coordination sphere of the metal center to the crystal packing scale by **in situ single-crystal and powder X-Ray Diffraction** to correlate them to magnetic properties. Moreover, **in situ high-pressure Powder X-ray diffraction** (PXRD) revealed the behaviour of this compound along the phase transition including **piezo-hysteresis**[4]. Additionally, experiments combining **high pressure and variable temperature PXRD** lead to the determination of the bulk moduli of both HS and LS phase

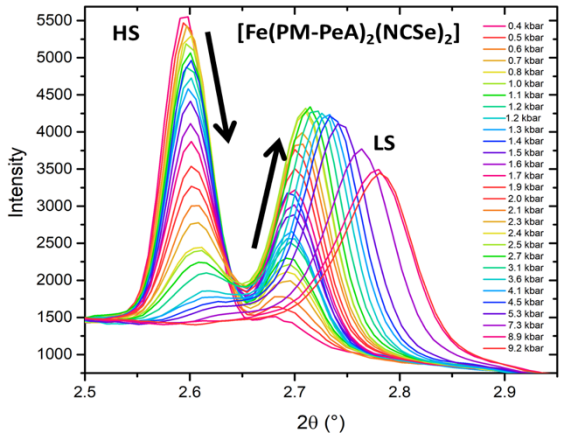

Figure: Pressure-induced Spin-CrossOver shown by the modification of the Bragg peaks intensity

at different temperature, and constitutes one of the rare experimental validation of the Clausius-Clapeyron low for SCO molecular material. Finally, we will show how powerful is PXRD under pressure and at variable temperature to (i)precisely determine the complicated phase diagram of molecular switches like SCO compounds and (ii) to reveal original effect like strong negative linear compressibility.

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