ESRF	**Experiment title:** Understanding Elastically Driven Cooperativity in Molecular Photomagnetic Materials	**Experiment number**: hc3439
Beamline: ID09	**Date of experiment**: from: 31/01/2018 to: 06/02/2018	**Date of report**: 01/03/2019
Shifts: 18	**Local contact(s)**: Matteo Levantino (matteo.levantino@esrf.fr)	*Received at ESRF:*

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Report:

With the advent of ultrashort lasers pulses (typically femtosecond), light excitation has been added to the panel of available techniques for materials control. One possible approach to amplify the photoresponse is based on the material elastic properties. This was demonstrated for a light-sensitive and volume-changing Spin Crossover (SCO) material, a molecular crystal in which the unit cell is built with SCO molecule(s) [1]. In this molecule, the ligand field causes splitting of the 3d levels of the metal ion (FeIII) into low energy and high energy ones. The population of high energy levels (at high temperature) changes the spin state and is accompanied by strong changes in Fe-ligand distances (and thus unit cell volume).

Quasi instantaneous generation (via a laser pulse) of a high enough fraction of photo-excited molecules (switched from Low Spin (LS) to High Spin (HS) state) creates local negative pressure. This drives lattice expansion that can induce additional switching of neighboring molecules through positive feedback effect. This cooperative effect is associated as expected with a well-defined threshold mechanism [1,2].

In hc3439, we performed time resolved powder diffraction at different temperatures (set by the nitrogen cryostream) and excitation energies by standard pump and probe approach. The repetition rate of the experiment was set to 40 Hz to allow full relaxation of the sample before the next pump and probe cycle. The sample was a thin film of Fe(salen) microcrystals, dispersed in a PVP matrix and deposited on a thin glass slide (fig.1). The sample has optical density of only 0.3 OD at the pump energy wavelength assuring a homogenous excitation throughout the full depth. The laser beam was delivered from the top and focused in the plane of the sample, such that its footprint matches the x-ray one. Scattering patterns were measured using

the Rayonix 170HS detector. One image needs about 500 shots (i.e. ~12.5 sec at 40Hz). The ⅞+1 bunch mode benefitted the experiment ran at low repetition rate.

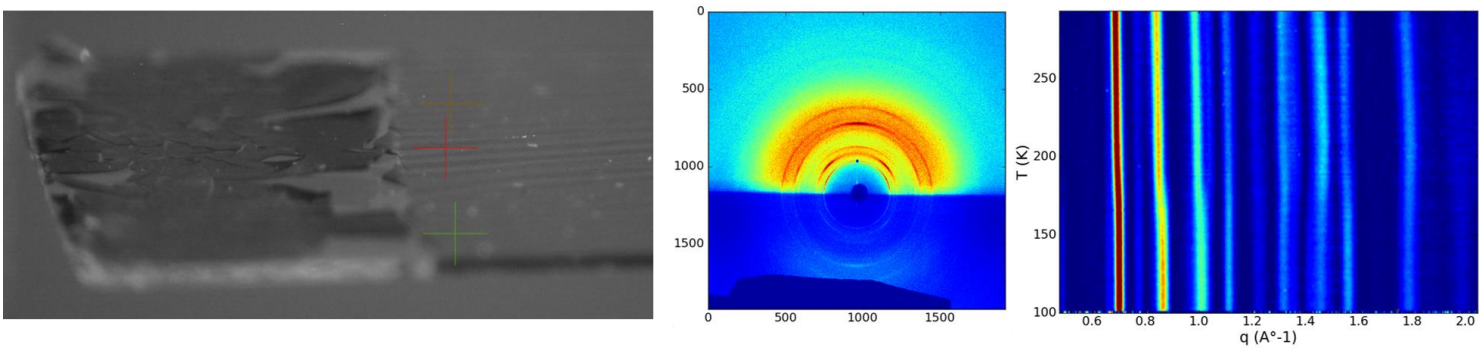

Fig. 1 Picture of the sample (microcrystals polydispersed in a polymer and deposited on a glass substrate) (left). Diffraction image (center) and evolution of the diffraction pattern in temperature (right)

Static measurements in temperature show a transition around 150-170 K, with subsequent Bragg peaks shift (fig.1) and in accordance with values from the literature (fig.3b).
Under laser excitation, this peak-shift is clearly resolved on time resolved data (fig.2), thus bearing a strong evidence of the photo-induced spin transition.

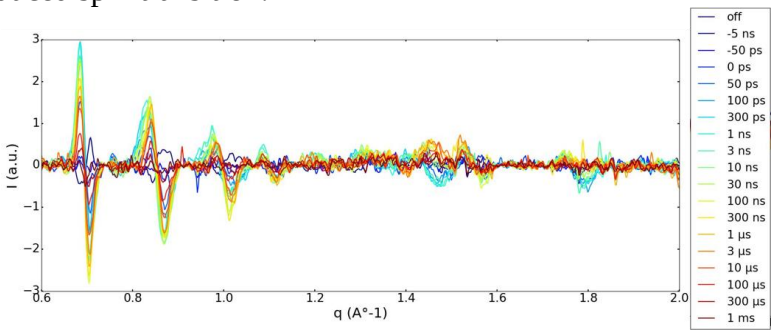

Fig. 2: Difference between patterns at different delays and a reference pattern (-5 ns). Experiment performed under laser excitation, at 120 K.

In the context of what we called “elastically driven cooperativity” this experiment aimed at unambiguously discriminating between spin state conversion and volume change, at different temperatures, on the very same samples studied with ultrafast optical spectroscopy. Full analysis of the whole diffraction patterns (fig.3a) allowed for real time observation of both unit cell volume expansion and spin state, showing that volume dilation precedes spin state switching amplification (fig.3c).

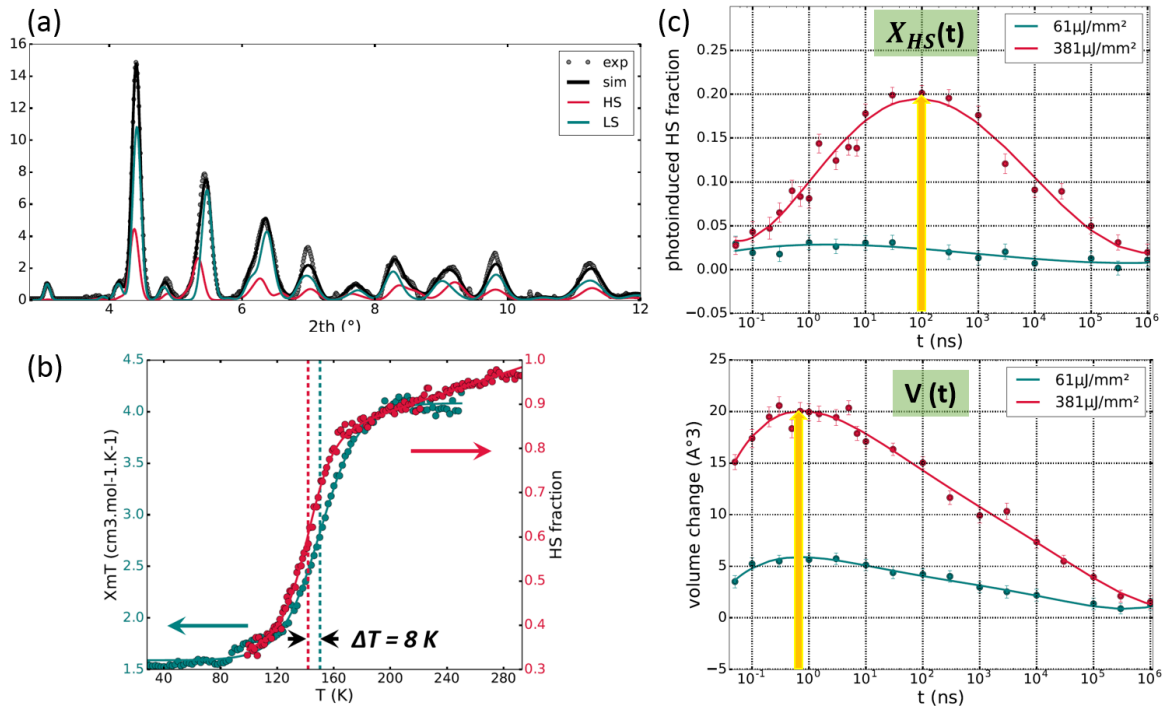

Figure 3: Diffraction pattern with assocated phases weights (a) at 99 K.(b) Evolution of the HS fraction with T, extracted from diffraction patterns and compared with SQUID measurements. (c) Photoinduced HS fraction and volume increase (circles: experimental data, lines: guides for the eye), extracted from diffraction patterns for different laser fluences. Yellow arrows emphasize curves maxima.

[1] R.Bertoni, M.Lorenc, H.Cailleau, A.Tissot, J.Laisney, M. Boillot, L. Stoleriu, A. Stancu, C.Enachescu & E.Collet. Elastically driven cooperative response of a molecular material impacted by a laser pulse,Nature Materials 15, 606–610, (2016)

[2] R. Bertoni, M. Lorenc, T. Graber, R. Henning, K. Moffat, J.-F. Létard, and E. Collet, Cooperative elastic switching vs laser heating in [Fe(phen)2(NCS)2] spin-crossover crystals excited by a laser pulse. Cryst.Eng.Comm. 18, 7269-7275 (2016)