ESRF	**Experiment title:** Dynamical limits upon downsizing in thin films of SCO nanocrystals with controlled morphology	**Experiment number**: hc4689
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Report:

In hc4689, we studied nanocrystals undergoing molecular spin transition in a form of oriented thin films [Ridier2019] (figure1a). Newly synthesised crystals of [Fe(HB(tz)3)2] (tz = 1,2,4-triazol-1-yl) [Shalabaeva2017] exhibit an extremely abrupt first order, isostructural spin transition above room temperature (334 K) (figure2a), associated with an exceptionally high resilience upon repeated switching (>10^7).
We performed time-resolved X-ray diffraction, by the excitation of a d-d transition of [Fe(HB(tz)3)2] at 535 nm, applying a routine pump and probe setup on ID9. The excitation of this weakly authorised transition ensured an homogeneous excitation of the layers. We used the pink x-ray beam at 15 keV in order to maximize the flux. The repetition rate of the experiment was set to 1 kHz. Co-proposers from LCC-Toulouse provided films of oriented crystallites (1cm x 1cm), with well-defined thicknesses (174 - 212 nm) and the size of the crystallite of around 20 nm. Several substrates (Si, SiO2, quartz) were also tested. Diffraction patterns (figure1c) were measured in reflection geometry at low angle (1.5°), to reduce the contribution from the substrate. Measurements were performed at controlled temperature, across the transition temperature range, using a heating device developed in collaboration with the sample environment group from ESRF (figure1b).

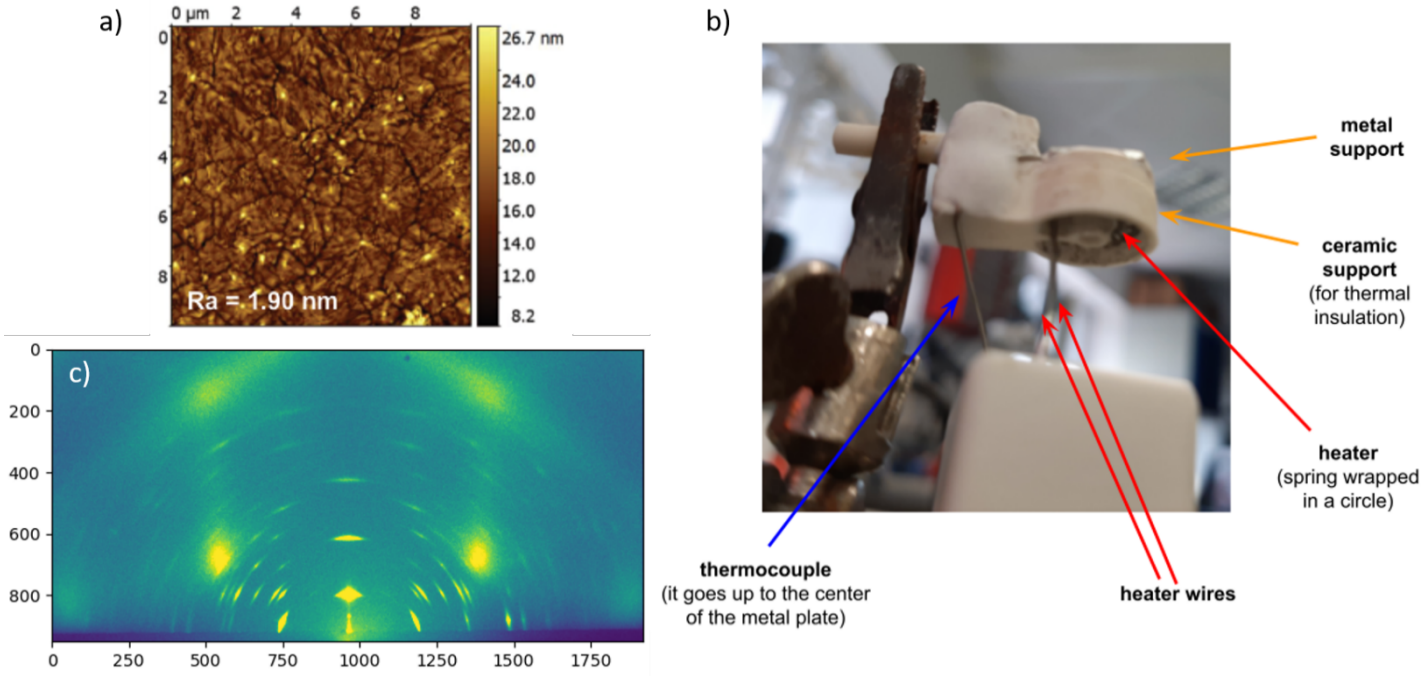

Figure 1:a) Atomic force microscopy topography of the film (image size is 10x10 µm^2). b) Descriptive picture of the heating device, designed in collaboration with the sample environment group at ESRF. The metallic support is here to ensure homogeneous temperature over the sample area. Its size is maller than the sample (9x9mm^2), to prevent X-rays from hitting the metallic surface. c) Diffraction image from a 174nm film on Si substrate, measured at ID9.

The measured diffraction patterns allowed to extract very accurately the evolution of the c unit cell parameter dynamics, related to the shift of 00l Bragg peaks. XRD was first measured as a function of temperature on the different samples for benchmarking. The extracted temperature evolution (figure2a) shows extremely good correlation with measurements performed on a single crystal.

Since the measurements were very sensitive to x-ray beam drift, the time-resolved measurements were systematically performed with interleaved references (without laser). This allowed to extract measure very accurately the strain dynamics from 100 ps to few 10ns. The dynamics observed at ns time scale (figure2b) correlates very well with what was observed at similar laser fluences by optical pump-probe experiments [Ridier2019]. The observed signal enhancement at long time scale appears to be strongly dependent on the substrate nature and initial temperature.

Interestingly at short time scale (below 1 ns), strain oscillations are clearly observed in all samples (figure2c). This behaviour is attributed to laser-induced strain build-up into the thin film [Schick2014], inducing a "breathing" of this SCO layer. Finite-elements simulations of strain in a film on a substrate (figure2d) nicely reproduce the experimental data and corroborate this hypothesis.

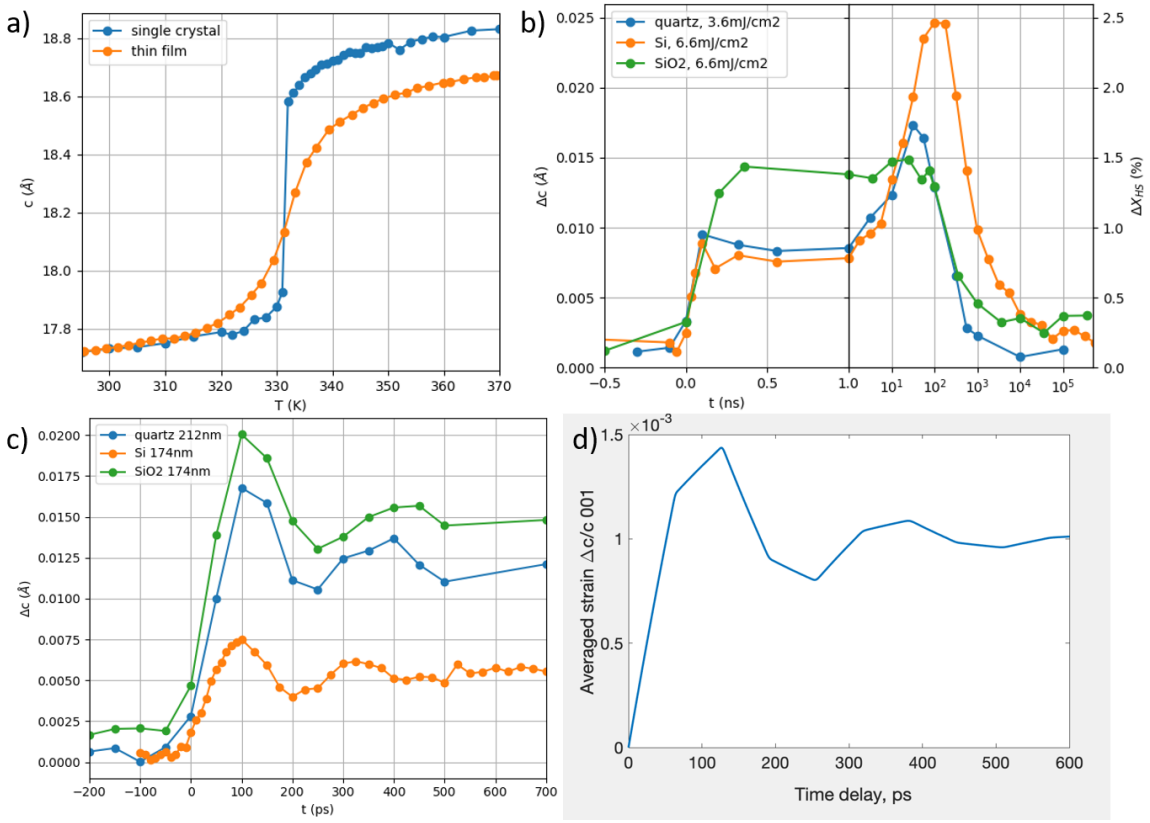

Figure 2: a) c parameter versus temperature, measured on a single crystal at Institut de Physique de Rennes (in blue) and on a 212nm film on quartz at ID9 (in orange), showing comparable evolutions. b) Variation of c parameter and estimated high spin fraction, for films on various substrates. The ns dynamics strongly depends on substrate nature. c) variation of c parameter at sub-ns time scale, for films on different substrates. Observed oscillations are attributed to laser-induced strain propagation from the film surface. d) Finite elements simulations of strain propagation in a film on quartz substrate reproduce the observed oscillations at sub-ns time scale.

References

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[Schick2014] *Structural Dynamics 1, 064501 (2014)*, doi.org/10.1063/1.4901228