	Experiment title: Influence of the shell microstructure on the mechanical coupling strength in photostrictive/magnetostrictive core-shell heterostructures based on Prussian blue analogues	**Experiment number**: MA-3212
Beamline: BM1A	**Date of experiment**: from: 26/10/2016 to: 31/10/2016	**Date of preliminary report**: 02/03/2020
Shifts: 9	**Local contact(s)**: Dmitry CHERNYSHOV, dmitry.chernyshov@esrf.fr	*Received at ESRF: 06/03/2020*

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Report:

This experiment was specifically aimed at understanding the influence of the shell-to-core volume ratio and of the shell morphology on the strain field in epitaxial core-shell particles combining a photoactive (photostrictive) charge-transfer compound and an optically-inactive ferromagnetic Prussian blue derivative. The strain fields before and after laser irradiation (690 nm, 3 Watt.cm^{-2}) were characterized by x-ray powder diffraction (XRPD) measurements in transmission geometry using a Pilatus 2M pixel-array detector, a helium cryostream unit for sample cooling and a laser diode illumination set-up. Powder samples were mounted in 0.1 mm diameter capillaries, and rocked by 10° only during x-ray exposure to avoid powder moving during data collection. The major difficulty encountered during this experiment was ice formation on the capillary, and eventually on the beam stopper. Additional data sets were measured with the Oxford N_2 cryostream unit of the beamline to investigate the lattice expansion (80-293 K range) for selected single-phase compounds and core-shell heterostructures.

Most of the XRPD data collected during the MA-3212 experiments are included in the PhD manuscript of A. Adam (HAL Id: tel-01661397, https://hal.archives-ouvertes.fr/tel-01661397/). Data related to the influence of the volume ratio between the magnetic shell and the active core material are included in a paper in preparation (see title and abstract below), which also combines XAFS measurements carried out on the BM30B workstation (expt. MA-2966). Experiments related to the impact of the shell morphology still need to be complemented by simulations.

Impact of the shell-to-core volume ratio in mechanically coupled Prussian blue analogue heterostructures

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In this work, we investigate the influence of the shell-to-core volume ratio on the photomechanical response of heterostructures made of photostrictive/magnetostrictive core-shell particles. These functional architectures provide a versatile approach to optically control magnetic properties through a strain-mediated mechanism, but optimization of their response still requires a screeening of the parameters which govern the coupling strength. Herein, heterostructures are formed of a $Rb_{0.5}Co[Fe(CN)_6]_{0.8}.zH_2O$ photoactive core and ferromagnetic nickel hexacyanochromate shells. The shell-to-core volume ratio is tuned by changing either the core size, from 25 to 140 nm, or the shell thickness in the 3-40 nm range. Synchrotron X-ray powder diffraction combined with X-ray absorption spectroscopy under visible light irradiation are used to monitor the transfer of elastic stresses across the interface and the mechanical counteraction of the shell. We report on a unique behaviour when the core size is decreased or when the shell thickness is increased, leading to a reduction of the amplitude of the core photostriction. There is a clear cut-off as a function of the Ni/Co atomic ratio, at a value of about 2.25, above which the core dilatation is suppressed. This scaling law is in fair agreement with simulations and should have a large impact for mininiaturization strategies. Nevertheless, this cut-off behaviour is system-dependent and, to some extent, it is controlled by the mismatch between the core and shell lattices. In addition, the strain field within the magnetic shell is strongly dependent on the shell-to-core volume ratio, with either a main contibution in dilatation or in compression.

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Below selected figures from the MA-3212 experiment:

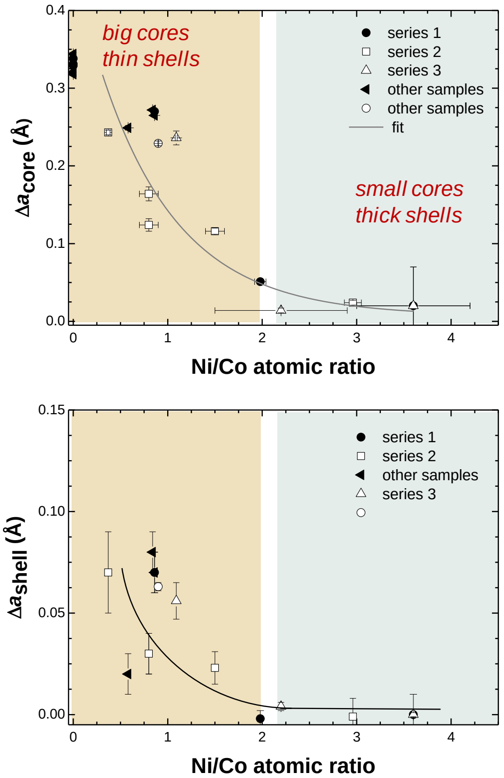

Fig 1: Maximum photo-striction recorded for the core (top) and shell (bottom) compounds in different series of core-shell particles. Series **1** correspond to heterostructures made from 25, 45 or 140 nm cores with a similar a 10-15 nm shell thickness. Series **2** and **3** were prepared by varying the shell thickness starting from 140 nm or 25 nm cores, respectively.

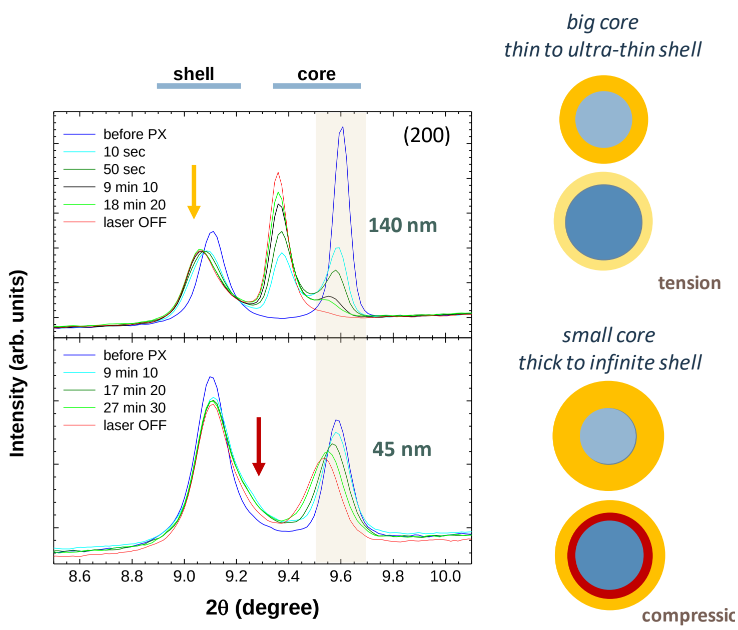

Fig 2: Time evolution of the (200) Bragg reflections of the core and shell components under continuous laser irradiation for two samples of series **1** made from 45 nm or 140 nm $Rb_{0.5}Co[Fe(CN)_6]_{0.8}.zH_2O$ photoactive cores. Arrows indicate the main change of the shell lattice that correspond to expansion (top panel) or contraction (bottom panel) depending on the shell-to-core volume ratio.