ESRF	**Experiment title:** Mechanical coupling in switchable core-shell nanoparticles	**Experiment number**: HC-3375
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Report:

Recently, finite-size effects in spin transition materials have attracted much attention [1] due to their broad range of potential applications at the nanoscale such as photoswitches [2] or electronic/spintronic switches [3], molecular memory devices [4] or actuators [5]. Very recently, we succeeded in synthesizing an original family of core-shell nanoparticles [6], which couple a ferromagnetic shell with a spin transition core (see Figures). Due to strong interface mechanical coupling, the magnetic properties of the shell can be controlled by light- or temperature-induced switching of the core. This synergistic property opens new engineering pathways and provides a unique opportunity to better understand the role of interface phenomena governing the phase stability of these materials at the nanoscale [7]. In this context, determination of the iron density of phonon states (Fe-DOS) of the core by Nuclear Inelastic Scattering shows promising results to understand how interfacial mechanical coupling affects lattice dynamics and, as a consequence, the spin transition and the magnetic properties [8].

Nuclear Scattering was performed at ID18 at two different temperatures for three samples (cf. table 1). The Nuclear Forward Scattering (NFS) and Nuclear Inelastic Scattering (NIS) spectra were recorded. For the sake of the simplicity, only the results of **C224** and **C224@S9** are described. It is important to note this technique allows to probe only the iron atoms and thus the core part. From the spectra, the first result we can extract is the effect of the spin transition on the vibrational density of states (DOS) and on the NFS spectra. In NFS spectra, the quadrupole splitting, which leads to oscillation in the time spectra, when going from the low spin (LS) to the high spin (HS) state is a clear evidence of the charge-transfer-induced spin transition. More interesting, Figure 1(a) displays the DOS. A global blue shift of the vibrational modes occurs in the LS state meaning a stiffening of the lattice. This is particularly pronounced for the FeC stretching mode around 60-80 meV.

Sample name	Core size	Shell size
C224	224 nm	0 nm
C224@S9	224 nm	9 nm
C443@S7	443 nm	7 nm

Table 1. Core@Shell samples of $RbCo[Fe(CN)_6]@KNi[Cr(CN)_6]$.

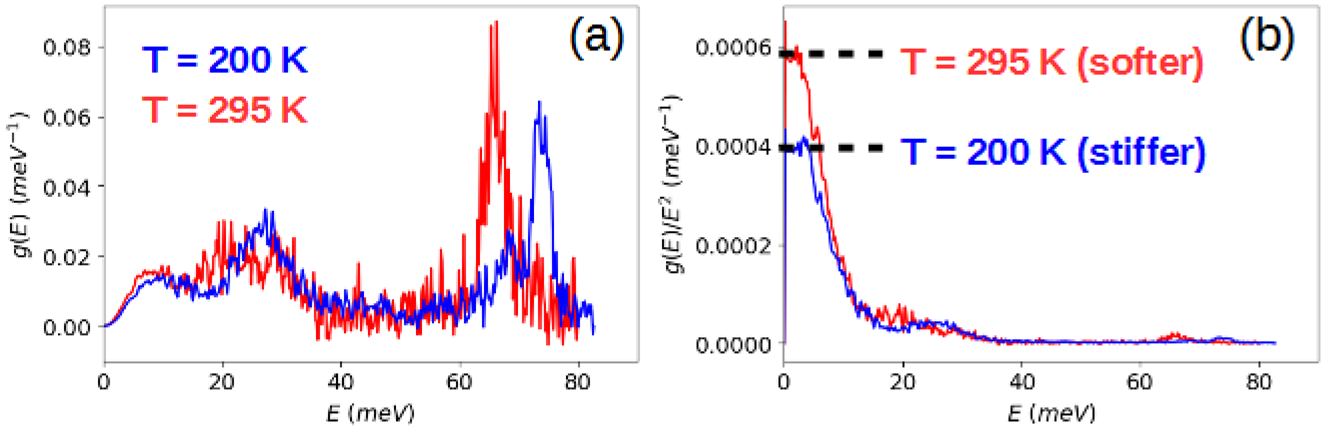

Figure 1. (a) Fe-DOS at two different temperatures of **C224**. (b) Reduce density of states at two different temperatures of **C224**.

Using the Debye model, we can extract the sound velocities from the low energy part which is directly proportional to $[E^2/g(E)]^{1/3}$ (cf. fig 1b). In addition, the Young's moduli can be extracted from the Debye sound velocity as described in ref. [8]. We can thus quantify the stiffening when going from the HS to the LS state (cf. table 2). An increase of the Young's modulus of 35% is observed when going from the HS to the LS state.

The second important result is the investigation of the mechanical coupling between the core and the shell. A clear increase of the sound velocity in the core surrounded by the shell in respect with the core alone is observed (cf. Table 2). This stiffening is interpreted as the effect of the stress due to the lattice mismatch between the core and the shell and affects mainly the acoustic part of the DOS leading to an increase of the Young's modulus of 22% and 9% in the HS and in the LS state, respectively. This is worthwhile to note that the stiffening due to the shell is more important in the HS state. In first approximation, this can be understood due to the higher elastic modulus of the core in the LS state. We were not able to measure the thick-shell samples due to the important decrease of the amount of resonant atoms in these samples (Fe are only in the core). This issue could be solved using enriched samples which were not available yet.

Sample	***C224***		***C224@S9***	
T	200 K	295 K	200 K	295 K
ρ (kg.m^{-3})	1994±60	1795±54	1985±60	1832±55
v (m.s^{-1})	2785±54	2527±55	2920±86	2773±60
Y (GPa)	33±3	24.5±2.7	36.1±3.6	30±2.9

Table 2. ρ, v and Y are the estimated mass density, the sound velocity and the Young's modulus assuming a Poission's ratio of 0.35±0.02 [9]. Uncertainties will be improved by XRD measurements.

In summary, this experiment allowed us to extract the Young's modulus of RbCoFe-PBA in the two spin states, which is a very useful information. In addition, we were able to quantify the effect of the shell for three core-shell ratio samples through the change of the Debye sound velocity and the effective Young's modulus. Simulations (molecular dynamics and finite-element analysis) and X-ray diffraction under pressure (at ID27) are expected to bring out complementary information and to give a global understanding of the phenomenon.

[1] *Bousseksou et al.* Chem. Soc. Rev. **2011**, 40, 3313.

[2] *Bertoni et al.* Nature Materials **2016**, 15, 606; *Bairagi et al.* Nature Comm. **2016**, 7, 12212.

[3] *Miyamachi et al.* Nature Comm. **2012**, 3, 938; *Lefter et al.* Adv. Mater. **2016**, 28, 7508.

[4] *Holovchenko et al.* Adv. Mater. **2016**, 28, 7228; *Dugay et al.* Adv. Mater. **2015**, 27, 1288.

[5] *Shepherd et al.* Nature Comm. **2013**, 4, 2607; *Frisenda et al.* Nano Letters, **2016**, 16, 4733.

[6] *Felts et al.* J. Phys. Chem. C **2016**, 120, 5420; *Pajerowski et al.* J. Am. Chem. Soc. **2010**, 132, 4058

[7] *Félix et al.* Phys. Rev. Lett. **2013**, 110, 235701.

[8] *Félix, et al.* Phys. Rev. B **2015**, 91, 024422.

[9] *Félix, et al.* Eur. J. Inorg. Chem. **2017** *'Elasticity of Prussian blue analogue nanoparticles'*