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Report:

Nanoscale spin transition materials have received much attention [1] recently due to their potential applications as photoswitches [2], electronic switches [3], memory devices [4], and actuators [5]. At this scale, surface and interface effects have an outsize role in determining the character of the spin transition [6]. We have recently synthesized a series of core-shell nanoparticles [7], using the same batch of cores, but varying the shell thickness. An unprecedented finding is a dramatic enhancement of the rate of the core's optically-induced spin transition relative to an uncoated particle. With the use of an electro-elastic model [8], the behavior was attributed to a change in the elastic properties of the core due to the interface-induced stress. This discovery hints at the promise of engineering desired properties in spin transition heterostructures through elastic interactions. In order to obtain a more complete understanding, we carried out Nuclear Inelastic Scattering at ID18 in order to determinate the density of phonon states (DOS) and to probe the elastic changes in the core responsible for the change in spin transition rate and elucidate how interfacial mechanical coupling affects lattice dynamics.

The DOS of five enriched samples at two different temperatures were obtained (cf. table 1). Figure 1 shows the sample dependence of the Debye level and the mean force constant extracted from the DOS. The Debye level D is directly related to the Debye sound velocity v_D by:

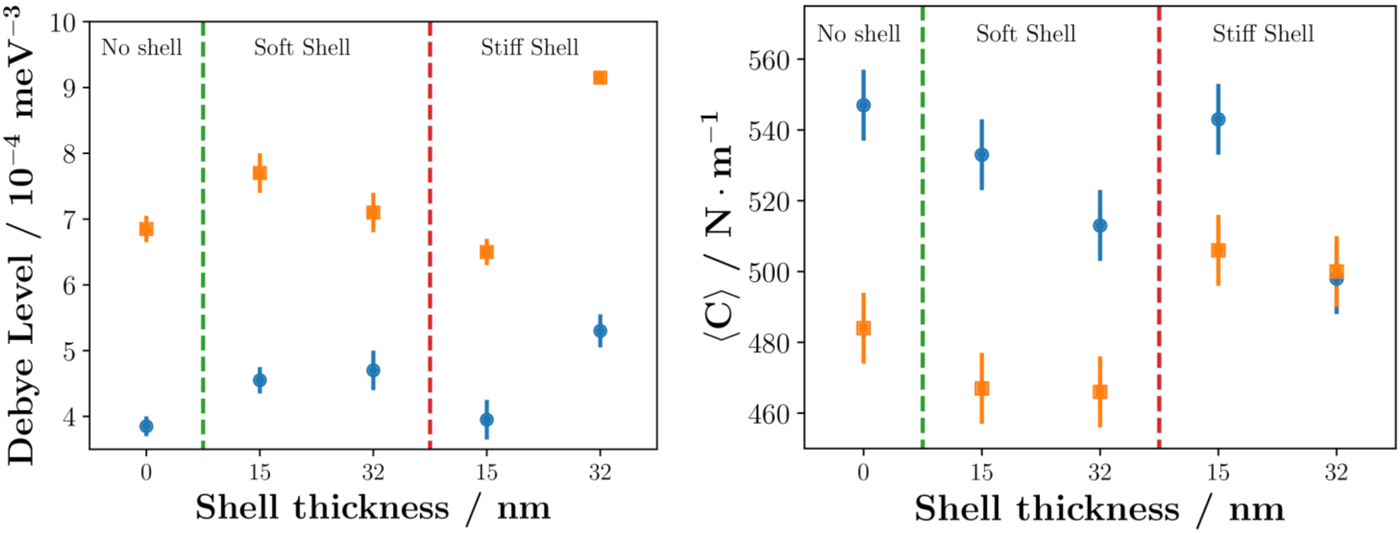
$$D = \frac{g_D(E)}{E^2} = \frac{m_{Fe}}{2\,\pi\rho\,\hbar^3 v_D^3}$$

Where E is the phonon energy, g_D is the Debye density of state, m_{Fe} is the mass of iron, ρ is the mass density and $\hbar$ the reduced Planck constant. While the sound velocity and, by extension the Debye level, tells us about the stiffness of the low energy acoustic modes, the mean force constant informs us about the optical modes.

Name	Shell size	a_S (Å)	*Shell*
JC04	0 nm	-	
JC05	15 nm	10.45	***KCo[Cr(CN)$_6$]***
JC02	32 nm	10.45	***KCo[Cr(CN)$_6$]***
JC06	15 nm	10.65	***KNi[Cr(CN)$_6$]***
JC07	32 nm	10.65	***KNi[Cr(CN)$_6$]***

Table 1. Core@Shell samples of RbCo[Fe(CN)$_6$ core in different shell

When going from the HS to the LS state, a clear stiffening appear (decrease of the Debye level and increase of the mean force constant). On the other hand, the effect of the shell is not as strong as expected from preliminary data. In the case of



Debye level (left) and mean force constant (right) of the core for different shells in the low temperature phase (blue full circle) and high temperature phase (orange full square)

$KNi[Cr(CN)_6]$ shell, a softening of both optical and acoustic modes occurs. This is not clear in the case of the X shell.

This phenomenon can be attributed to the shell due to a tensile stress applied on the core. This tensile stress/strain has probably two main consequences: a softening of the core due to the mechanical coupling and the presence of HS residual fraction in the low temperature phase due to an electronical interfacial relaxation. This HS fraction can also contribute to the softening of the core but also plays an important role in the enhancement of the rate of the optically-induced spin transition relative to the uncoated particle.

In addition of the effect of the shell on the core, this experiment has allowed us to characterize the elastic properties (Young's Modulus) of the core. These results are going to be combined with bulk moduli of both core and shell extracted from X-ray diffraction under high pressure, and by this way, obtain a full mechanical characterization of sub-micrometric objetcs (Poisson's ratio, shear modulus…).

In summary, this experiment allowed us to extract the elastic properties of RbCoFe in the two spin states, which is a very useful information for applicative propects. In addition, we were able to quantify the effect of different shells on the core through the change of the Debye level (and Debye sound velocity) and mean force constants. This study will be completed with other characterization such as X-ray diffraction under pressure and combined with physical modelling.

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