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## Report:

Spin crossover (SCO) materials can exhibit a reversible switching between the molecular low-spin (LS) and high-spin (HS) states upon the application of an external perturbation such as the temperature, the pressure, and light irradiation. The strong electron-phonon coupling in these systems leads to a memory effect displaying by a hysteresis in thermal curves. With the diminution of size, SCO materials show a loss of the memory effect [1], explained by a coordination defect and a residual HS fraction at the surface [2-3]. However, very small nanoparticles (~2-4 nm) exhibit a surprising hysteresis [4]. We suggested that this effect occurs due to a stiffening of the particle with the diminution of the size [3], but this hypothesis has not been demonstrated experimentally.

The objective of this beam time session was to measure the phonon density of states (DOS) of spin crossover coordinate nanoparticles as a function of their size (4 nm, 15 nm, 50 nm), by Nuclear Inelastic Scattering (NIS). With these spectra, we are able to compare the difference of vibrational frequencies between the two spin states. Moreover, for the first time in the SCO field, we can extract from these spectra the sound velocity $v$ as a function of size, and by the way the stiffness of the particles.

In our team, we have developed different experimental protocols which permit to control the size (from 4 nm until 150 nm) of coordinate nanoparticles [5]. This method was also adapted to obtain the corresponding nanoparticles enriched with $^{57}$Fe. These samples are well characterised by TEM, Raman, FTIR, Mössbauer spectroscopy and magnetic measurements.

The figure 1a) shows spectra at 50 K and 310 K for the 50 nm particles, which represent the LS and HS DOS, respectively. The magnetic measurements and Mössbauer spectroscopy show that the spin transition is complete, which means there is no residual LS and HS fraction at high or low temperature, respectively. The HS state is characterized by one large optical vibrational mode around 30 meV. With the spin transition the iron environment becomes stiffer, and logically the optical mode shifts to the higher energies, accompanied by a lifting of degeneracy. The spin transition leads to a stiffening of the lattice, which can be directly inferred from the DOS/$E^2$ curve (see figure 1b), with the low energy part which is proportional to $1/v^3$.

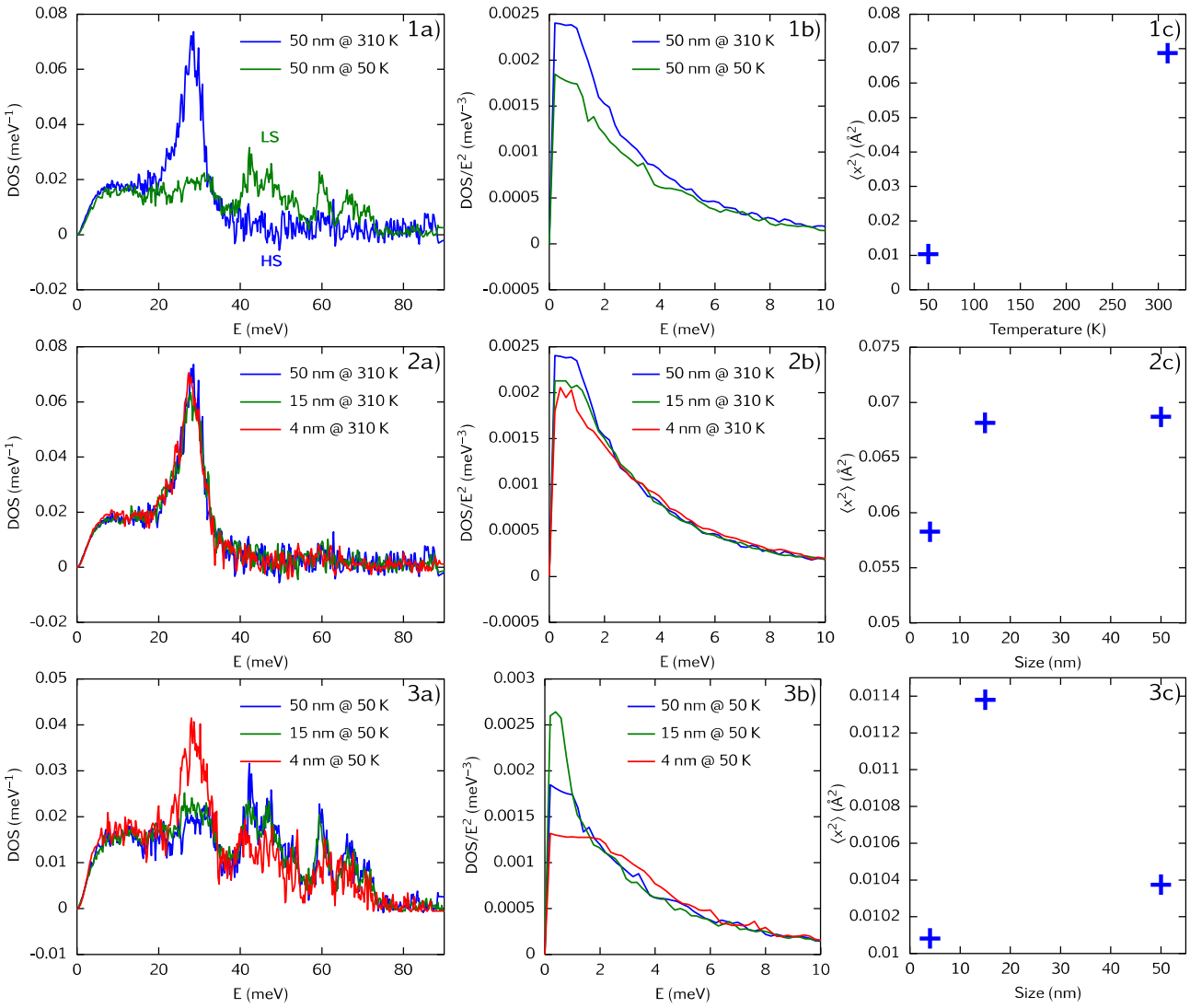
Figure 2a) represents the phonon DOS at 310 K for different sizes of Fe(pyrazine)[$Ni(CN)_4$] nanoparticles. In comparison with the 50 nm particles at 310 K, the 15 nm and 4 nm particles have the same HS DOS spectrum. In general, in metallic particles, there is a diminution of the sound velocity with the diminution of the size [6]. However in our case, the diminution of the size leads to an enhancement of the sound velocity (see figure 2b). This phenomenon has an important impact on the phase stability in SCO compounds [3].

Another interesting physical ingredient which can be extracted from this measurement is the mean square displacement $\langle x^2 \rangle$. This value characterizes the displacement around the equilibrium position of the iron atoms. This parameter follows a linear tendency with the temperature. A diminution of this term indicates a

stiffening of the material. Figure 2c) shows clearly a diminution of $\langle x^2 \rangle$, which indicates once again a stiffening of the particles when decreasing the size.

To confirm the change of stiffness in both spin states, the same measurements were repeated at 50 K. Figure 3a) shows a difference between the DOS spectra for the different sizes. The 4 nm and 15 nm particles display less intense LS modes, with a conservation of the HS mode. This result indicates a residual HS fraction, with inactive iron localized at the nanoparticle surface. In other words, the diminution of the size leads to an increase of the HS residual fraction at low temperature. This HS residual phase, which is softer than the LS state, results in the diminution of the sound velocity between the 50 nm and the 15 nm particles (see figure 3b). However at very small sizes the diminution of the sound velocity due to the rising of the HS fraction is compensated by the augmentation of the nanoparticle stiffness and leads to the highest sound velocity in the 4 nm particles. $\langle x^2 \rangle$ shows the same tendency (see figure 3c).

The measurement of the sound velocity as a function of the particle spin state represents new important data for our community. This result will be the subject of a publication on near future, which should also include a study of the vibrational entropy. On the other hand, the increase of the sound velocity in very small SCO nanoparticles revealed by NIS acquisition is a significant breakthrough. More data is needed on the 2-20 nm size range and at different temperatures, in order to better understand the physics governing the elasticity of small nanoparticles. For this reason, we will apply for additional beamtime, which should allow us to publish this remarkable result in a high impact factor journal.





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