

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Nuclear Inelastic Scattering study of spin crossover nanoparticles: determination of the relationship between size and stiffness at the nanometer scale	Experiment number: HC-1669
Beamline: ID18	Date of experiment: from: 29/11/2014 to: 03/12/2014	Date of report: 19/02/2015
Shifts: 12	Local contact(s): Aleksandr CHUMAKOV	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Mirko MIKOLASEK ^{*,a,b} , Gautier FÉLIX ^{*,b} , Sylvain RAT ^{*,a} , Haonan PENG ^{*,a} , Lionel SALMON ^a and Gábor MOLNÁR ^a ^a CNRS-Laboratoire de Chimie de Coordination, Toulouse, France ^b Institut Charles Gerhardt. Université Montpellier 2. Montpellier. France		

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 (hysteresis). With the diminution of size, SCO materials show a loss of the memory effect [1], explained by the coordination defects and the 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 clearly demonstrated experimentally.

Our previous session at ID18 allowed us to obtain the phonon density of states (DOS) of spin crossover coordinate nanoparticles in the two spin states for 4 nm, 6 nm, 15 nm and 50 nm. From the 50 nm spectra, we were able to extract important parameters [5] such as mean force constant C , sound velocity v_s or Young's modulus Y . The objective of this beam time session was to complete our size study using a better beam (hybrid mode) and to understand the mechanisms behind the stiffening of the particles with the size reduction.

In our team, we have developed different experimental protocols which permit to control the size (from 2 nm until 150 nm) of coordination nanoparticles [6]. This method was also adapted to obtain the corresponding nanoparticles fully enriched with ^{57}Fe . These samples are well characterized by TEM, Raman, FTIR, Mössbauer spectroscopy and magnetic measurements. Figure 1a) shows the structure of Fe(pyrazine) $[\text{Ni}(\text{CN})_4]$ complex.

Figure 1b) shows the size-dependence of the sound velocity in the LS (green square) and in the HS (blue circle) states. The sound velocity v_s has been extracted from the low energy part of the DOS/E^2 which is proportional to $1/v_s^3$ [5]. An increase of the sound velocity with decreasing size is observed. Since the Young's modulus is directly depending on the sound velocity, $Y \sim \rho v_s$ (ρ is the density), we deduce the particles become stiffer with the size reduction (below ca. 10 nm). This important result brings out the increase of the particle stiffness with the size reduction in the both spin states.

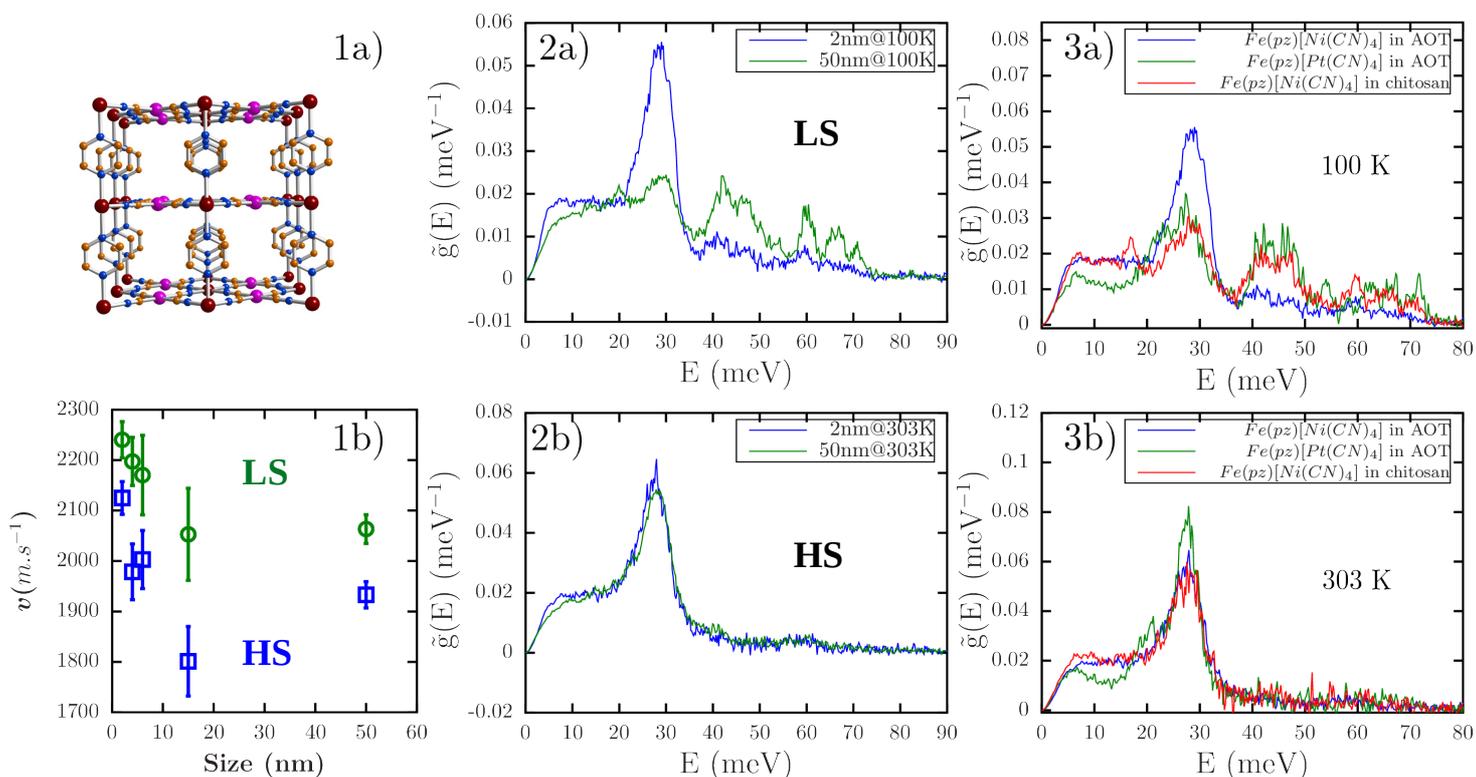
Figures 2a) and 2b) show spectra at 100 K and at 303 K respectively, for both 50 (green) and 2 (blue) nm particles of Fe(pyrazine) $[\text{Ni}(\text{CN})_4]$. In the 50 nm particles, the magnetic measurements and Mössbauer spectroscopy show that the spin transition is complete, which means there is no residual LS and HS fraction at high or low temperature. 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. In the 2 nm particles, the magnetic measurements and Mössbauer spectroscopy show that there is a important residual HS fraction at low temperature. Indeed, the low temperature spectrum of the 2 nm particles is very similar to its high temperature spectrum except the

small high energy peaks. Despite this residual HS fraction, the sound velocity of the 2 nm particles is higher than the 50 nm ones.

The other important result of this beam time session is the observation of novel low frequency modes in the 2-4 nm particles. In figure 2), we can observe a 7-8 meV peak in the 2 nm particle spectra, which does not appear in 50 nm particle spectra.

Figures 3a) and 3b) show spectra at 100 K and 303 K respectively, for Fe(pyrazine)[Ni(CN)₄] (blue) and Fe(pyrazine)[Pt(CN)₄] (green) of 2 nm particles in AOT (Dioctyl sulfosuccinate sodium salt) matrix and 3 nm Fe(pyrazine)[Ni(CN)₄] in chitosan matrix (red). A low frequency peak is also observed for the 3 samples in the two spin states. This mode seems to be dependent on the sample and could be a surface or a confined acoustic mode. An additional theoretical investigation could highlight the mechanisms at the origin of this phenomenon and bring out the role of the surfaces and the environment in the spin transition at the nanoscale. The measurement of the sound velocity as a function of the particle size represents new important data for our community. The increase of the sound velocity in very small SCO nanoparticles revealed by NIS acquisition is a significant breakthrough. These results will be the subject of a publication on near future. Whenever, we will be able to analyze the vibrational entropy of particles of different size.

The next step is the investigation of the surface/interface effects at the nanoscale which are expected to strongly affect the physical properties of the particle and consequently change the phonon DOS. The study of the role of the surface, supported by theoretical calculations and molecular simulations, will be able to highlight the mechanisms underlying the stiffening and open new interesting perspectives such as the study of hybrid nano-objects. For this reason, we will apply for additional beamtime, which should allow us to highlight the matrix dependence of phonon DOS in nanoparticles.



Legend: 1a) The structure of Fe(pyrazine)[Ni(CN)₄]. 1b) Size-dependence of the sound velocity in LS (green circle) and HS (blue square) phases. 2) Phonon density of states of 50 nm (blue) and 2 nm (green) particles in polymeric matrix in LS (a) and HS (b) states. 3) Phonon density of states of Fe(pyrazine)[Ni(CN)₄] (blue) and Fe(pyrazine)[Pt(CN)₄] (green) of 2 nm particles in polymeric matrix and 3 nm Fe(pyrazine)[Ni(CN)₄] in chitosan matrix (red) in LS (a) and HS (b) states.

References:

- [1] Volatron et al. Inorg. Chem. (2008), **47**, 6584-6586
- [2] Félix, et al. Phys. Chem. Chem. Phys. (2014), **16**, 7358
- [3] Félix, et al. Phys. Rev. Lett. (2013), **110**, 235701.
- [4] Larionova et al. Angew. Chem. Int. Ed. 2008, **47**, 8236–8240
- [5] Félix, et al. Phys. Rev. B (2015), **91**, 024422.
- [6] Peng, et al. Angew. Chem. Int. Ed. (2014), **53**, 10894–10898