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ESRF

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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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.

ESRF	**Experiment title:** XAS study of the local structure of two families of polymeric spin-crossover compounds	**Experiment number**: 25-01-686
Beamline: BM25A	**Date of experiment**: from: 21-10-2008 to: 24-10-2008	**Date of report**: 30-03-2009
Shifts: 9	**Local contact(s)**: Félix Jiménez Villacorta	*Received at ESRF:*

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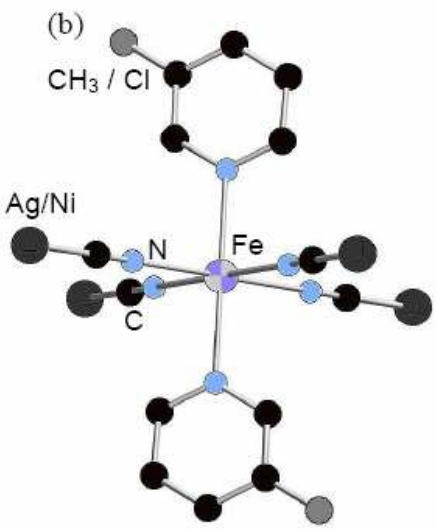
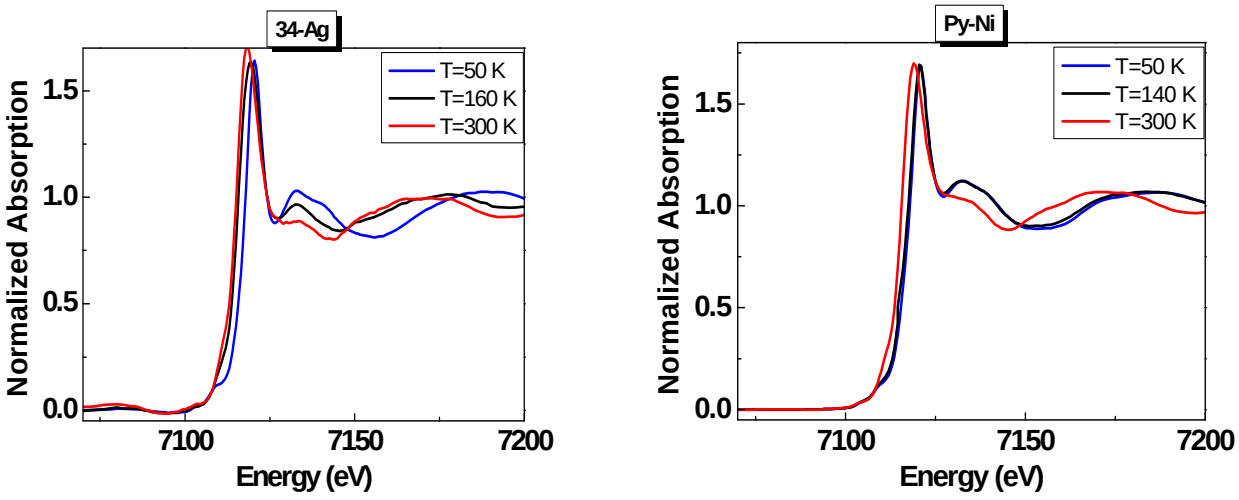
Report:

In this experiment, we have performed x-ray absorption spectroscopy measurements of Fe-polymeric spin-crossover compounds. The purpose was to observe the variation of the local structure around the magnetic Fe ions and also of their electronic structure with the temperature. This evolution in the structural and electronic properties should be directly linked with the transition from low-spin (LS) state at low temperatures to high-spin (HS) state at room temperature in such magnetic systems.

Two families of spin-crossover compounds were measured: $Fe(X\text{-}py)_2[Ag(CN)_2]_2$ and $Fe(X\text{-}py)_2[Ni(CN)_4]$. X-ray absorption spectra have been collected in the transmission mode, using partially filled gas ionization chambers to detect the incident and the transmitted beam. A continuous flow He-cryostat belonging to the beamline was used to measure the compounds at three temperatures, 15 K, 150 K and 300 K. Some of the samples have an intermediate step in the spin-state transition at around 150 K, and it was our interest to determine the local origin of this intermediate step.

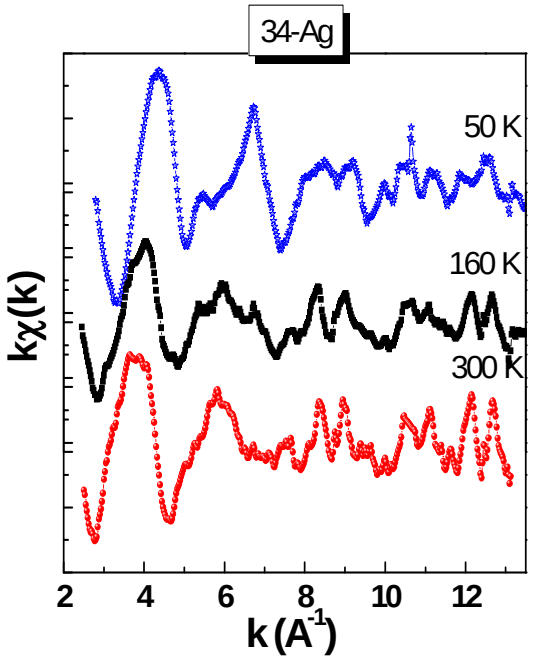


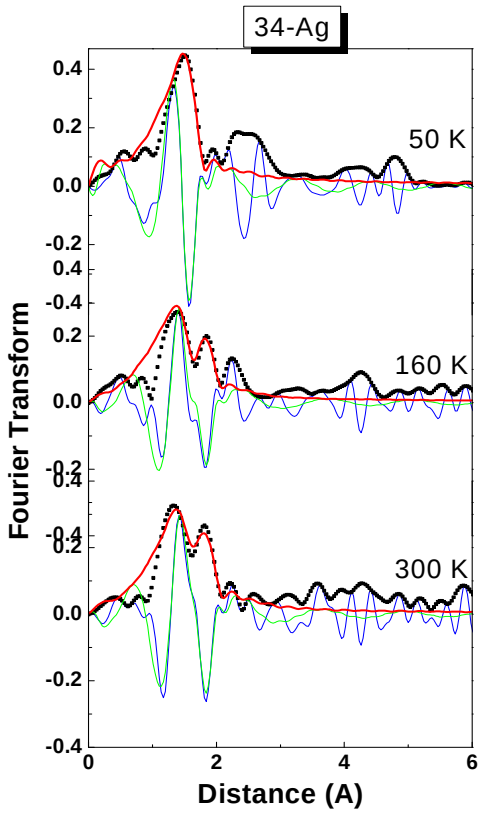
Results show a progressive shift of the edge position while increasing the temperature for all the cases. This reduction in the oxidation state of iron (always around Fe^{2+}) is accompanied by the suppresion of the pre-edge feature at room temperature. This evolution in the electronic structure observed by the evolution of the edge spectra can be fully explained with the transition from LS to HS states. The spin transition comes together with a variation in the metal-ligand distances at different spin states. At short Fe-N distances, the crystal field leads to 3d splitting (in t_{2g} and e_g sublevels), resulting in a LS configuration of the initial $3d^6$ state of Fe^{2+}). However, at larger Fe-N distances, the effect of the Hund splitting could be larger than the crystal field splitting, and the final electronic configuration of the iron centers result in HS state.

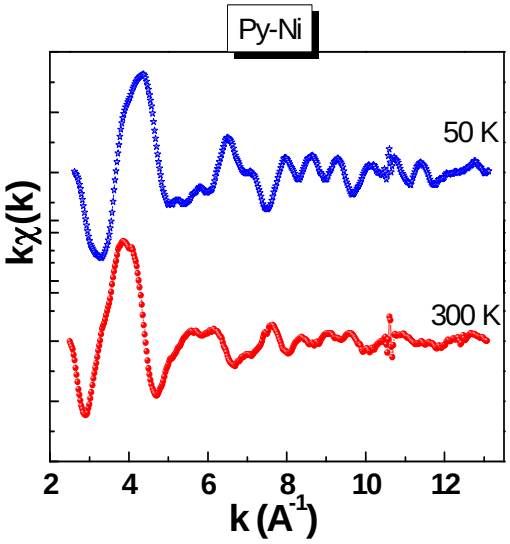


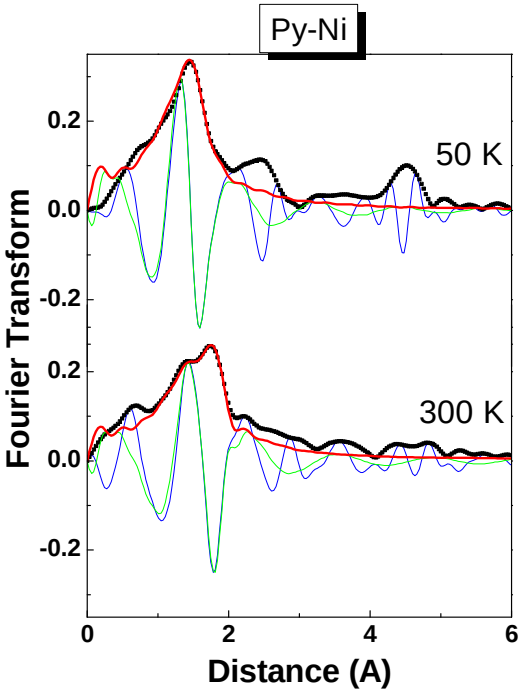
EXAFS analysis will give us information about the evolution of the Fe-N distances with temperature. It is worth to point that for the analysis, a broad k-range of around 13 $Å^{-1}$ has been used for all the spectra and all the samples. Results confirm the idea suggested from the XANES observation. At low temperatures, the six N from the FeN6 octahedra are at the same distance, less than 2 Å for all the samples. With increasing temperatures, a splitting of the Fourier transform first peak is observed, suggesting a larger distance of the Fe-N bond

due to distortion of the FeN6 octahedra. This effect is observed, whether the compounds are polymerized with Ag or Ni, though slight differences between the two families should be considered.









These results confirm the effect of the local structure in the spin state of Fe and its crossover from low temperature LS state (with very weak magnetization values) to room temperature HS state (with a remarkable increase of the magnetization at intermediate temperatures).

Moreover, from the quantitative analysis of the EXAFS oscillations and the observation of the XANES spectra, it can be concluded that the intermediate state at around 150 K in Ag-compounds is a combination of LS and HS states. These results by themselves will be the subject of a next paper submitted to an international journal to be considered for publication.

Other analogue phenomenon which provide a similar spin crossover effect in such compounds is the excitation of the samples with light. These light-induced spin-crossover effect can be precisely determined by x-ray absorption spectroscopy, and a forthcoming proposal should be submitted for consideration of the ESRF committee next run.