Electronic supplementary information for

A detailed investigation of the core@shell structure of exchanged coupled magnetic nanoparticles after performing solvent annealing

Kevin Sartori,[1,2,3] Dris Ihiawakrim,[1] Christophe Lefèvre,[1] Solenn Reguer,[2] Cristian Mocuta[2], Sylvie Bégin-Colin,[1] Fadi Choueikani,[2] Benoit P. Pichon[*,1,3]

[1] Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, F-67000 Strasbourg, France

[2] Synchrotron SOLEIL, L'Orme des Merisiers, Saint Aubin – BP48, 91192 Gif-sur-Yvette, France

[3] Institut Universitaire de France, 1 rue Descartes, 75231 Paris Cedex 05

Corresponding Author

E-mail: Benoit.Pichon@unistra.fr

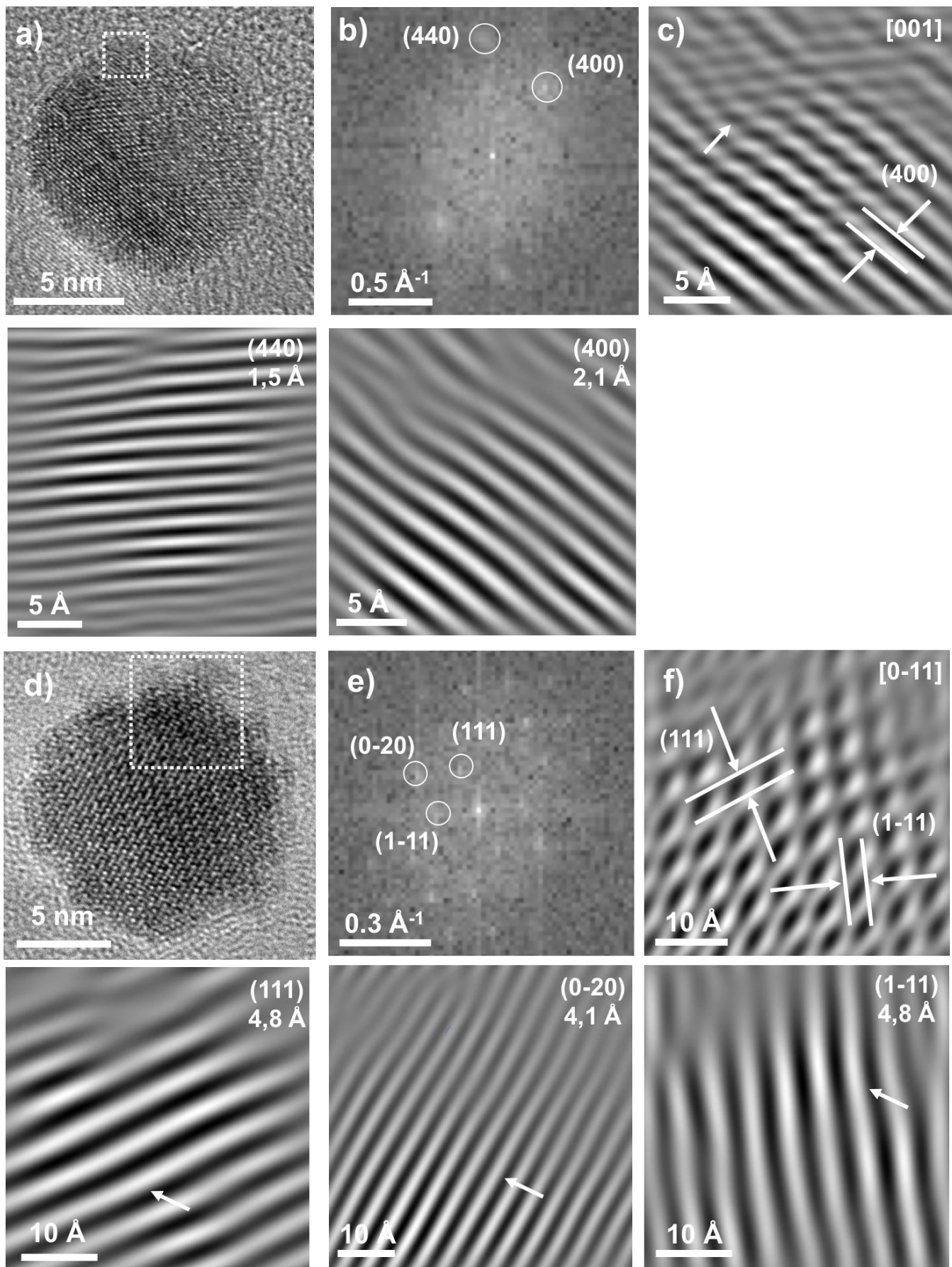Tel: 0033 (0)3 88 10 71 33, Fax: 0033 (0)3 88 10 72 47

a) 5 nm

b) (440) (400) 0.5 Å⁻¹

c) [001] (400) 5 Å

(440) 1,5 Å 5 Å

(400) 2,1 Å 5 Å

d) 5 nm

e) (0-20) (111) (1-11) 0.3 Å⁻¹

f) [0-11] (111) (1-11) 10 Å

(111) 4,8 Å 10 Å

(0-20) 4,1 Å 10 Å

(1-11) 4,8 Å 10 Å

Figure 1S. Study of the local structure of the edges of CS and CSR nanoparticles. a,b,c) CS, d,e,f) CSR. a,d) HR-TEM micrographs. b,e) FFT corresponding to the region of interest (white square) in HR-TEM micrographs. c,f) Reverse FFT calculated from the FFT after applying a Bragg filter. *hkl* reflections (circles in the FFT) were indexed by measuring the distances between lattices fringes that were observed in reverse FFT. Pictures in rank 2 and 4 correspond to reverse FFTs that were calculated separately for each *hkl* reflection indexed in b) and e), respectively. The [uvw] indexes in the upper right corner correspond to the zone axis.
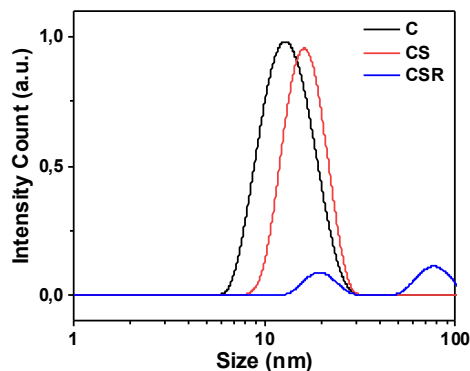

Figure 2S. Distributions of hydrodynamic diameters of nanoparticles suspended in chloroform plotted as a function of intensity counts.

Extraction and refinement of the DANES spectra

1. Extraction of the measured scattered intensity *vs.* the scattering angle

The XPAD detector[39,40] was used to record the diffraction rings of powdered samples at different energies corresponding to Fe K-edge (7.11 keV) and Co K-edge (7.71 keV). Series of scans were performed in a range from -50 eV to +50 eV relative to the K-edges with a step of 1 eV. Each scan consists in recording 26 images in order to cover a 2θ angular range of 10 – 90°. All the recorded images are encompassed in a Nexus file, (h5py type). A Python script was developed for the data extraction and geometrical corrections, as well as for the azimuthal regrouping of the data and to obtain the intensity *vs.* 2θ diffraction pattern (Figure 3S) at each energy step of DANES scan.[70,71]
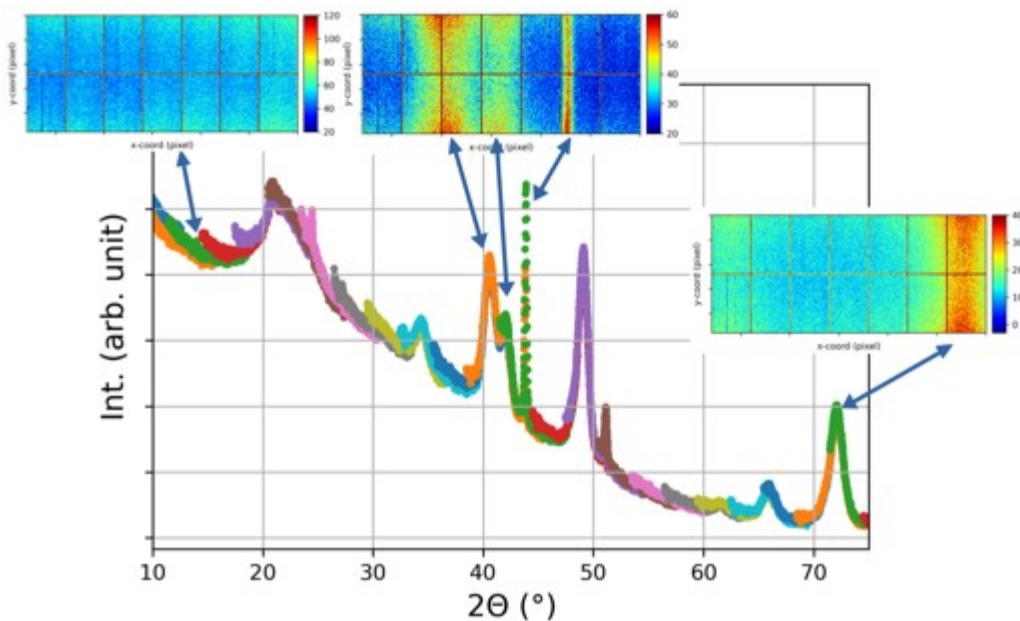
Figure 3S. Example of integration of the powder diffraction rings at selected energy. Flat corrected images correspond to selected 2Θ ranges.

This process allows to obtain a 2D maps (intensity versus 2Θ and Energy) of the sample. As an example, the 2d map of CS at Fe and Co K-edges are shown in Figure 4S.
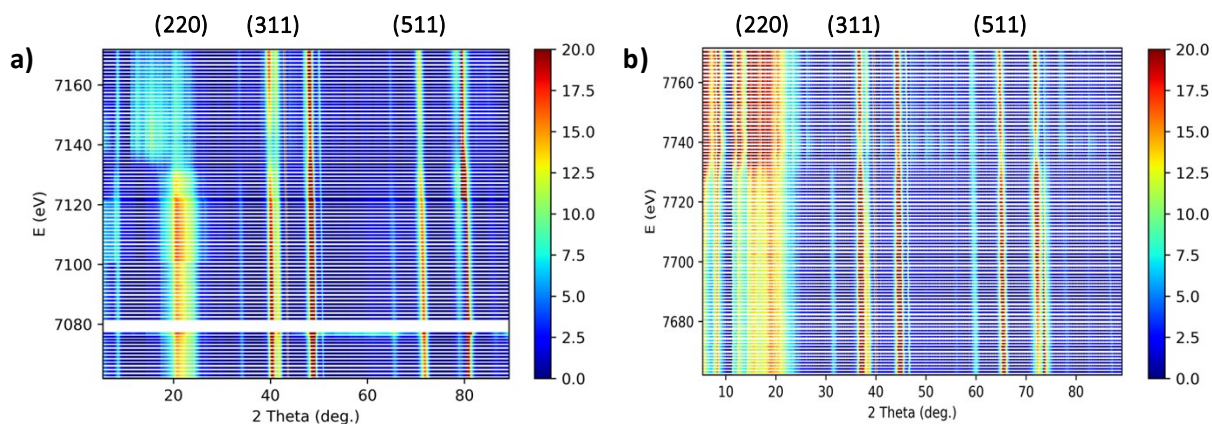

Figure 4S. Patterns recorded for CS at different energies around the Fe and Co K-edges. Variations of intensity are clearly noticeable at Fe-K-edge (7.13 keV) and Co K-edge (7.74 eV).

2. Extraction of the DANES

Profile refinement was performed for each energy via a cycling mode owing to a dedicated python script. The used profile function for the different refinement was composed of a quadratic function for the background and a person-VII function for the diffraction peak. Then, DANES spectra were obtained by computing the integrated surface area of each (*hkl*) peak in order to plot it as a function of the energy.

3. Refinement of the spinel contribution

DANES spectra showed important variations of intensity at both the Fe and Co edges which is ascribed to the occupancy of nodes by Fe and Co (Figure 5S). (*220*), (*311*) and (*511*) Bragg peaks being specific to the spinel structure (no contribution wüstite), refinement of DANES spectra allowed quantifying the occupancy of T_d and O_h sites by Fe and Co (Table 1S). It is worth noting that the (*220*) node corresponding only to Td sites, both Fe and Co cations are distributed between Td and Oh sites.
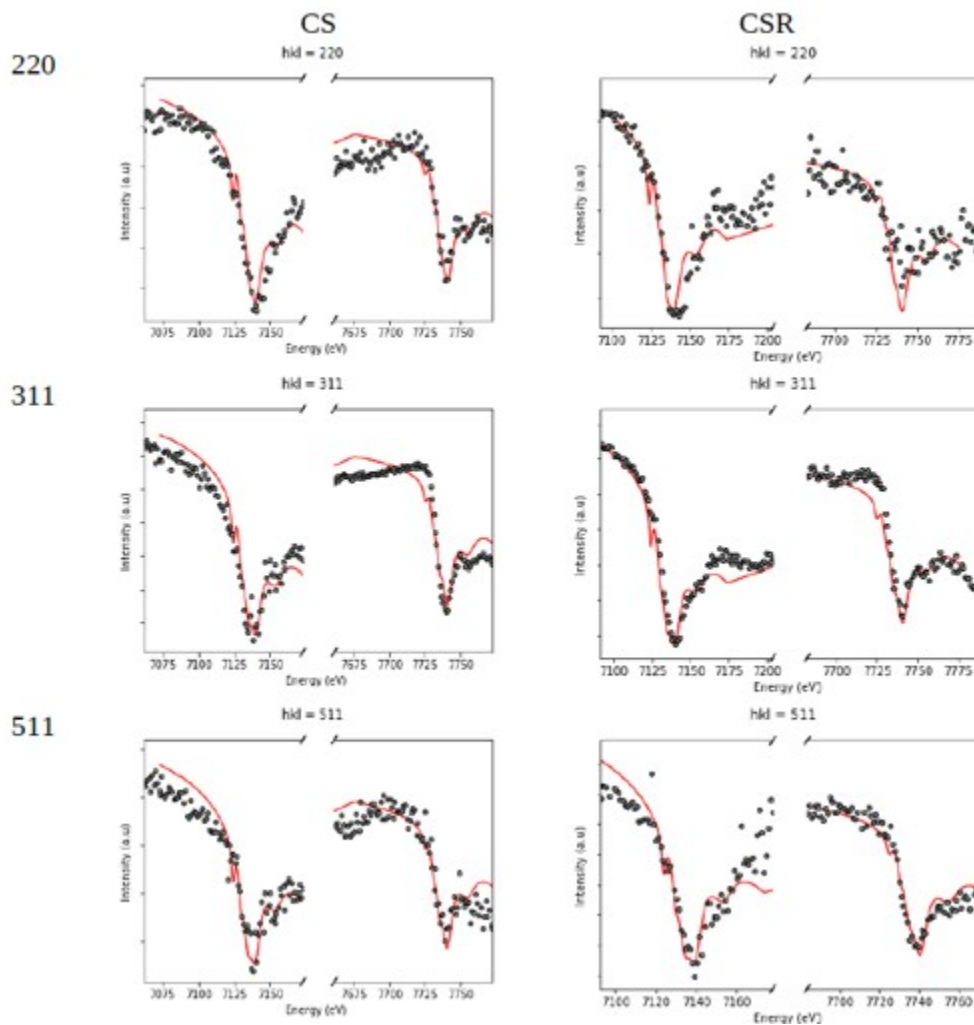

Figure 5S. Refined DANES spectra of the integrated surface area of peaks ascribed to the (220), (311) and (511) Bragg peaks of the spinel structure as a function of energy for CS (left) and CSR (right).

Table 1S. Chemical compositions of the spinel and wüstite structure in CS and CSR obtained by the refinement of DANES spectra and the core/shell volume ratio (ρ).

Sample	Spinelle phase	Wüstite phase	Spinelle/Wüstite volume ratio
CS	$(Fe_{0.89}Co_{0.11})[Fe_{0.91}Co_{0.09}]_2O_4$	$Fe_{0.09}Co_{0.91}O$	0.44
CSR	$(Fe_{0.77}Co_{0.23})[Fe_{0.80}Co_{0.20}]_2O_4$	$Fe_{0.03}Co_{0.97}O$	0.62

4. Refinement of the wüstite contribution

DANES spectra corresponding to the (111) node of the wüstite phase also includes the (222) node of the spinel phase cannot be refined by considering a wüstite phase as CoO (figure 6S). It suggests that the wüstite phase consists in a binary oxide, i.e. that Fe diffused into the wüstite phase.
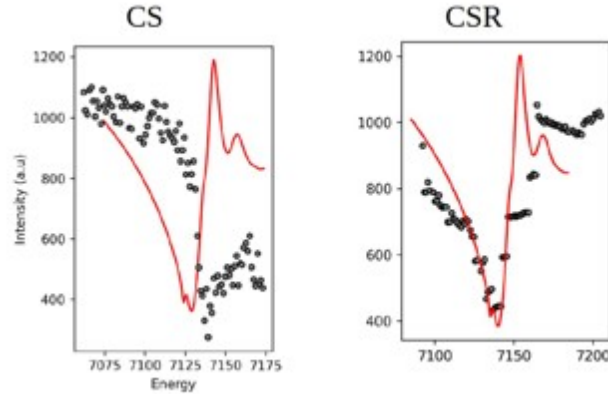

Figure 6S. DANES spectra corresponding to the (222) node recoded for CS and CSR.

Indeed, linear combinations of DANES spectra corresponding to the (111) reflection of pure CoO and FeO phases showed that better refinements of were obtained by increasing to component corresponding to the FeO fraction (Figure 7S).
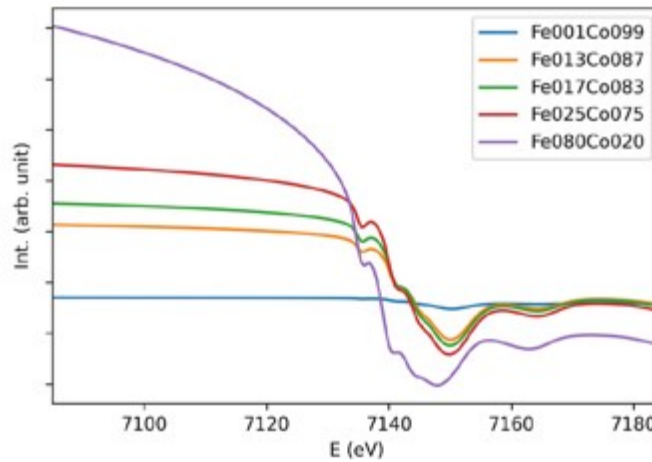

Figure 7S. Theoretical spectra corresponding to the (111) reflection of $Co_{1-x}Fe_xO$ at the Fe edge as a function of the Fe content.

Therefore, the chemical composition of the wüstite phase ($Co_{1-x}Fe_xO$) was calculated by performing linear combinations in order to refine DANES spectra corresponding to (222) spinel + (111) wüstite reflections as follows:

$$I_{exp} = p I_{Core} + (1-p) I_{Shell} \quad \text{with } I_{Shell} = I_{Fe_xCo_{1-x}O}$$

Core corresponds to the spinelle phase and shell corresponds to the wüstite phase.

p corresponds to the core/shell volume ratio. From the TEM observation, one obtains V_{core} = 288 nm³, V_{shell} = 371

nm^3 for CS and V$_{core}$ = 288 nm^3, V$_{shell}$ = 175 nm^3 for CSR. Finally, the figure of merit χ2 was computed considering all possibilities of the Fe content within the shell (Figure 9S).
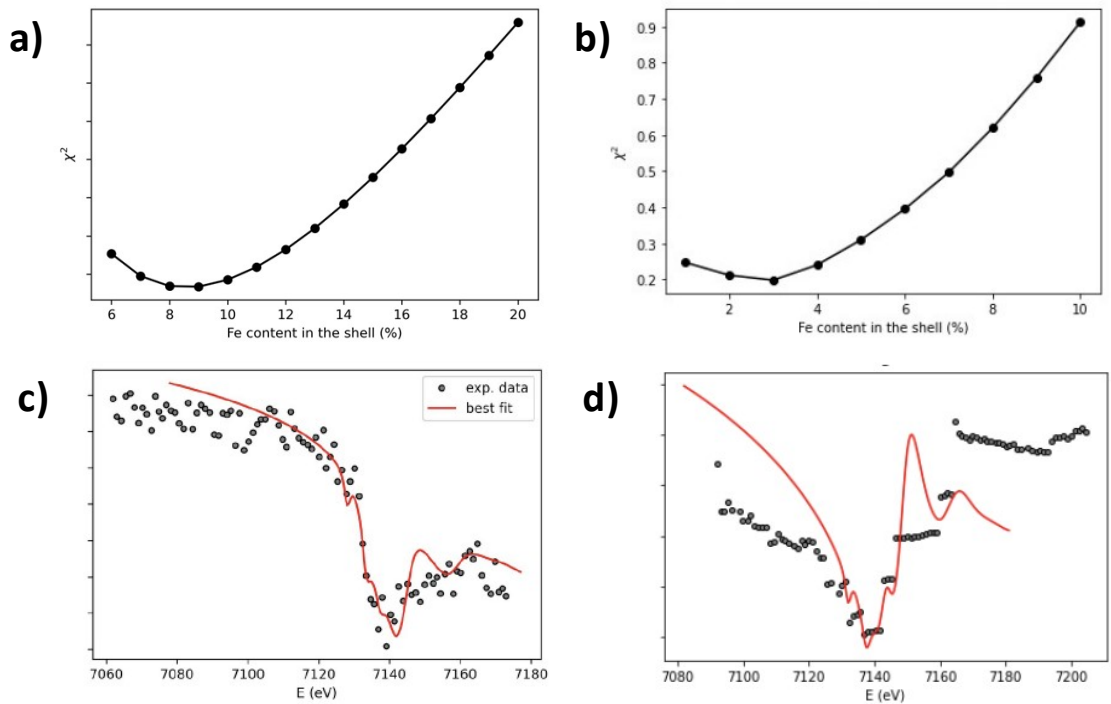

Figure 8S. Variation of χ2 value as a function of Fe content in the Co$_{1-x}$Fe$_x$O shell for a) CS and b) CSR. Refinement of DANES spectra corresponding to (222)$_{spinel}$ and (111)$_{wüstite}$ nodes for c) CS and d) CSR. The "stair profile" in d) corresponds to low signal of the sample.