

Electronic Supplementary Information for:

Anatase-driven charge transfer involving a spin transition in cobalt iron cyanides nanostructures.

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Sample preparation

Samples have been prepared by following the method by Berrettoni et al.¹ Briefly, iron hexacyanocobaltate and cobalt hexacyanoferrate were chemically synthesized by precipitation mixing 0.05 M water solution of FeCl₂ or CoCl₂ drop wise to an equivalent amount of K₃[Co(CN)₆] or K₃[Fe(CN)₆] and stirring at room temperature. TiO₂-FeHCC and TiO₂-CoHCF were obtained by following the previous procedure being the first step the preparation of a TiO₂ suspension to which a water solution of FeCl₂ or CoCl₂ and an equivalent amount of K₃[Co(CN)₆] or K₃[Fe(CN)₆] were added. Table S1 indicates the investigated samples together with their chemical analysis and XRD data (cell parameter *a* of a *Fm3m* structure).

Table S1 List of the investigated compounds: stoichiometry and cell parameter *a*.

Compounds (formal stoichiometry from chemical analysis)	Cell parameter <i>a</i>	
	From XRD powder, Å (±0.05)	From EXAFS, Å (±0.02)
(I) TiO ₂ -K _{1.2} Co _{1.3} Fe(CN) ₆	10.07	9.86
(II) K _{0.4} Co _{1.4} Fe(CN) ₆	10.34	10.28
(III) TiO ₂ - K _{0.6} Fe _{1.1} [Co(CN) ₆]	10.33	10.28
(IV) K _{0.5} Fe _{1.3} [Co(CN) ₆]	10.31	10.22

XAS measurements

Samples for XAS measurements were solid pellets, prepared by mixing the material (15 mg) with cellulose filler (100 mg). X-Ray absorption measurements have been recorded at the XAFS beamline at Elettra Synchrotron (Basovizza, Trieste, Italy). The storage ring operated at 2.0 GeV in top up mode with a typical current of 300 mA. Data were recorded at Fe K-edge (7112 eV) and Co K-edge (7709 eV) in transmission mode using ionization chamber filled with a mixture of Kr, Ar, N₂ and He in order to have 20%, 70% and 95% of absorption in the I0, I1 and I2 ion chambers, for all working energy range. The beam was monochromatized using a fixed exit monochromator equipped with a pair of Si(111) crystals. For the XANES recording a pair of Si(311) crystals were used. Harmonics were rejected by using the cut-off of the reflectivity of the Platinum mirror placed at 3 mrad with respect to the beam upstream the monochromator and by detuning the second crystal of the monochromator by 30% of the maximum. The energy was defined by assigning to 7112 eV and 7709 eV the first inflection point of the spectrum of iron and cobalt foil, respectively. The spectra of metallic Fe or Co were collected simultaneously to those of the samples. This allowed us a continuous monitoring of the energy scale during consecutive scans. No energy drifts of the

monochromator were observed during the experiments. Spectra were collected with 2 s/point acquisition time.

XAS Data Analysis

XAS spectra were deglitched, calibrated, and normalized using the Athena program.² The pre-edge background was removed by subtraction of a linear function extrapolated from the pre-edge region, and the raw spectra were normalized to the unity by extrapolation of the atomic background evaluated using a polynomial function.

XANES spectra were normalized to an edge jump of unity. A prior removal of the background absorption was done by subtraction of a linear function extrapolated from the pre-edge region. The EXAFS analysis was performed using the GNXAS package^{3,4} which is based on Multiple Scattering (MS) theory. The method is based on the decomposition of the EXAFS signals into a sum of several contributions, the n-body terms. It allows the direct comparison of the raw experimental data with a model theoretical signal. The procedure avoids any filtering of the data and allows a statistical analysis of the results. The theoretical signal is calculated *ab-initio* and contains the relevant two-body $\gamma^{(2)}$, the three-body $\gamma^{(3)}$, and the four-body $\gamma^{(4)}$ multiple scattering (MS) terms⁵.

The two-body terms are associated with pairs of atoms, probing their distances and variances. The three-body terms are associated with triplets of atoms and probe angles, bond-bond, and bond-angle correlations. The four-body terms are associated to chains of 4 atoms, and probe distances and angles in between, and bond-bond, and bond-angle correlations. In this paper, however, because of the linearity of the –Fe-C-N-Co- chains, all the angles are set to be 180° and hence the actual number of parameters used to define the $\gamma^{(3)}$ or the $\gamma^{(4)}$ peak is reduced by symmetry. Deviations from the planarity can be neglected; therefore the corresponding correlations are set to be zero. For instance, this is the case of the bond-angle correlations. Bond-bond correlation has not taken into account, considering the magnitude of the signal-to-noise ratio of the measurements. The straightforward use of all the correlation concerning the four body contribution is beyond the aim of the present work and more details can be found in the references above.

Data analysis is performed by minimizing a χ^2 -like residual function that compares the theoretical signal, $\alpha_{\text{mod}}(E)$, to the experimental one, $\alpha_{\text{exp}}(E)$. In the case of the multiple edge fitting, the χ^2 -like residual function is used to perform a simultaneous structural

refinement over a selected number M of independent a-ray absorption spectra related to the same system:

$$R(\{\lambda\}) = \sum_{j=1}^M \sum_{i=1}^{N_j} \frac{[\alpha_{\text{exp}}^i(E_i) - \alpha_{\text{mod}}^i(E_i; \lambda_1, \lambda_2, \dots, \lambda_p)]^2}{\sigma_{i,j}^2}$$

where the index i runs over the number N_j of experimental energy points E_i of each absorption spectrum j . $\sigma_{i,j}^2$ is the variance associated with the $\alpha_{\text{exp}} - \alpha_{\text{mod}}$ random variable. In most cases $\sigma_{i,j}^2$ can be directly estimated from the experimental spectrum and a k^m weighting (with $m = 2, 3, \dots$) results in a good approximations. As in the usual single-edge case, the use of the equation specified above allows us to perform a statistical analysis of the structural results. The optimal best-fit values of the p parameters to be refined ($\lambda_1, \lambda_2, \dots, \lambda_p$) along with their statistical error including correlation among different parameters can be evaluated as illustrated elsewhere.⁶ Typical errors in the 0.001-0.01 Å range for the first neighbor bond distances have been found using such a *ab-initio* multiple scattering calculation of the x-ray absorption cross section.

Data analysis is performed by minimizing a χ^2 -like residual function that compares the theoretical signal, $\alpha_{\text{mod}}(E)$, to the experimental one, $\alpha_{\text{exp}}(E)$. The phase shifts for the photoabsorber and backscatterer atoms

were calculated starting from the structural model.⁷ They were calculated according to the muffin-tin approximation and allowing 10% overlap between the muffin-tin spheres. The Hedin-Lundqvist complex potential⁸ was used for the exchange-correlation potential of the excited state. The core hole lifetime, Γ_c , was fixed to the tabulated value⁹ and was included in the phase shift calculation. The experimental resolution used in the fitting analysis was about 1 eV, in agreement with the stated value for the beam line used. The amplitude correction factor S_0^2 were identified to be 0.75(5) for the Fe K-edge and in the 0.73(6) - 0.81(5) range for the Co K-edge. The multiple-edge fitting procedures at the Fe and Co K-edge were conducted including the relevant set of multiple scattering paths that originates from the typical structure of metal hexacyanoferrates, as previously specified by Giorgetti et al.¹⁰. The theoretical signals included in the fitting procedures for Fe K-edge are the following: the two-atom contributions $\gamma_1^{(2)}$ Fe-C with degeneracy of 6, the three-body contribution $\eta_1^{(3)}$ Fe-C-N with degeneracy of 6 and the four body contribution $\eta_1^{(4)}$ Fe-C-N-Co with degeneracy of 6. It is worth noting that the inclusion of the three-body term $\eta_1^{(3)}$ allows monitoring the shells beyond the first one by using

the same three-atom coordinates both for the two-atom and the three-atom contributions. In fact, the three-body signal $\eta_1^{(3)}$ Fe-C-N includes both $\gamma^{(2)}$ Fe-N and $\gamma^{(3)}$ Fe-C-N contributions.

Similarly, the $\eta_1^{(4)}$ MS signal includes two three-body contributions, the $\gamma^{(3)}$ Fe-C--Co and the $\gamma^{(3)}$ Fe--N-Co and the interaction Fe--Co through the $\gamma^{(2)}$ Fe--Co signal. In addition, a $\gamma_1^{(2)}$ Fe-K signal, due to the contribution of the interstitial alkali cations was considered as well. On the other hand, signals associated to the Cu K-edge included in the fit are: $\gamma^{(2)}$ Co-N with starting degeneracy of 4.5; $\eta_1^{(3)}$ Co-N-C with starting degeneracy of 4.5 and the $\eta_1^{(4)}$ Co-N-C-Fe with starting degeneracy of 4.5. Also, a second $\gamma^{(2)}$ signal, the $\gamma_2^{(2)}$ Co-O with starting degeneracy of 1.5, was necessary in order to take into account the “insoluble” structure of metal hexacyanoferrates¹¹. These two starting path degeneracy of 4.5 and 1.5 (which are actually coordination numbers), were called CN1 and CN2 in the fitting procedure.

According to this model, the total number of parameters employed in the fitting procedure (including the structural and non-structural terms, namely E_0 and S_0^2 , and the experimental resolution) depends on the compounds investigated as well as on the fitting strategy. The total number of parameters

was 20 for double-edge fitting. Besides, it is worth mentioning that in all cases the number of fitting parameters did not exceed the estimated “number of independent data points” $N_{ind} = \frac{2 \cdot \delta k \cdot \delta R}{\pi} + 2$, thus ensuring that the fit is well constrained and does not lead to parameters with very large errors, which, in turn, confirms the reliability of the minimization.

Table S2 Structural parameters from EXAFS fitting results of samples I-IV. The estimated parameter errors are indicated in parentheses.

	I	II	III	IV
Fe-C / Å	1.872(6)	1.892(5)		
Co-C / Å			1.868(2)	1.859(4)
σ^2 Fe-C / Å ²	0.0016(5)	0.0010(6)		
σ^2 Co-C / Å ²			0.0023(7)	0.0018(5)
C≡N / Å	1.171(5)	1.166(5)	1.19(1)	1.19(1)
σ^2 C≡N / Å ²	0.009(2)	0.008(2)	0.006(1)	0.006(1)
Co-N / Å	1.891(7)	2.084(5)		
Fe-N / Å			2.087(3)	2.061(4)
σ^2 Co-N / Å ²	0.003(1)	0.004(1)		
σ^2 Fe-N / Å ²			0.007(1)	0.005(2)
Co-O / Å	2.16(2)	2.22(1)		
Fe-O / Å			2.11(1)	2.058(5)
σ^2 Co-O / Å ²	0.03(1)	0.008(2)		
σ^2 Fe-O / Å ²			0.009(3)	0.006(2)
σ^2 the1 / deg ²	5(3)	5(3)	10(3)	5(3)
σ^2 the2 / deg ²	6(3)	5(2)	6(4)	6(4)
E0 Fe	7118.3(8)	7118.9(5)	7121.4(3)	7124.1(4)
E0 Co	7718.2(6)	7721.9(8)	7717.2(2)	7716.7(5)
CN 1	4.3(2)	3.7(2)	3.7(2)	2.8(2)
CN 2	2.0(5)	2.2(2)	1.7(2)	2.3(2)
S02 Fe	0.75(3)	0.75(3)	0.71	0.70
S02 Co	0.81(4)	0.73(3)	0.70	0.73
$a/2$ / Å	4.93	5.14	5.14	5.11
χ^2 -like residual / (10 ⁻⁶)	4.0	2.4	6.5	8.4

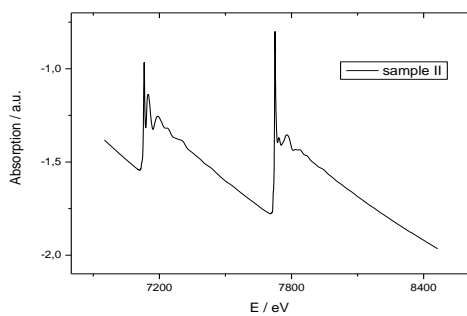


Fig. S1 Raw experimental spectrum of sample I as example. The close Fe and Co K-edge requires a specific analysis, based on Multiple Edge EXAFS, as specified in the Experimental Section.

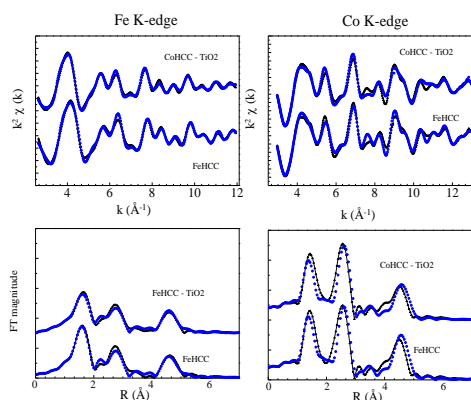


Fig. S2. Comparison of the experimental (-) and theoretical (...) k^2 -weighted EXAFS signals (upper panels) and the corresponding Fourier Transform (FT) of the k^2 -weighted EXAFS for samples III and IV at the two different metals K-edges. The Multiple-edge fitting approach, although allowing a strong reduction of the structural parameters for the fittings, causes little discrepancy at the Co K-edge respect to the Fe K-edge.

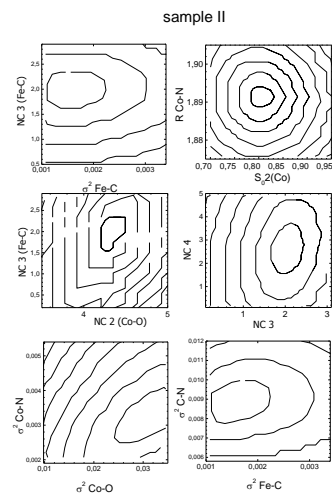
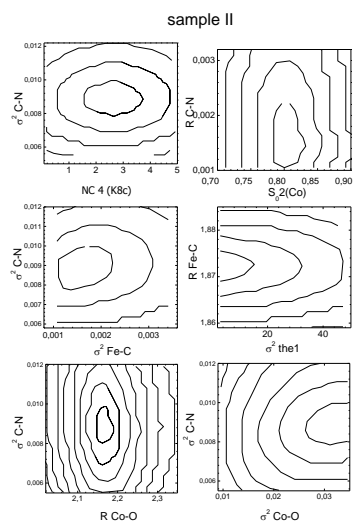
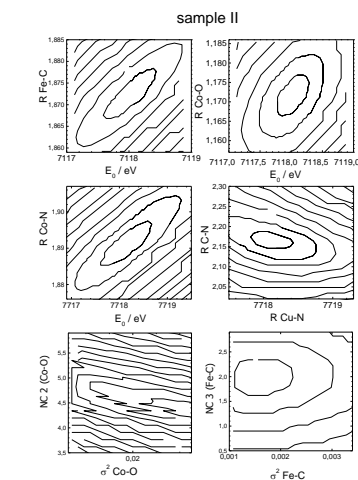
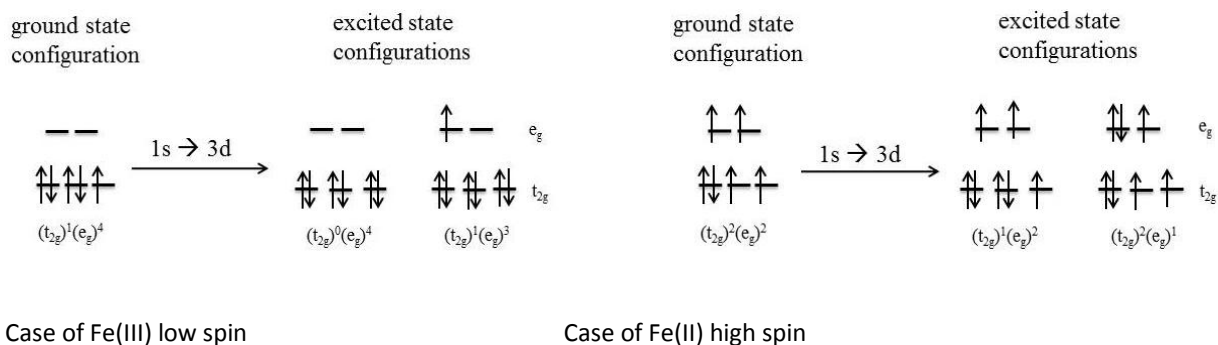
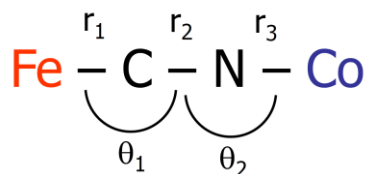


Fig. S3 Examples of the two dimensional section of the parameter space (contour plots) for sample II. These plots were selected among the

parameters having strong correlation to reflect the highest error. The inner elliptical contour corresponds to the 95% confidence level.



Scheme S1 1s-3d transition for the Fe(III) low spin and Fe(II) high spin.



Scheme S2. Chain structure of the cobalt hexacyanoferrate with the involved structural parameters that have been fitted during the EXAFS analysis. r_1 , r_2 and r_3 indicate the Fe-C, C=N, and Co-N interatomic distances, respectively.

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