EXAFS and XANES simulations of Fe/Co hexacyanoferrate spectra by GNXAS and MXAN

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Abstract. In the present paper Full Multiple Scattering (FMS) theory has been applied to analyse the cobalt hexacyanoferrate XANES spectra. The use of the MXAN program has permitted to calculate the edge spectra and to perform a fitting procedure with the experimental data, obtaining a set of structural parameters. A previously reported EXAFS analysis (which includes terms up to four-body MS calculations) was performed via the GNXAS program, by a Multiple Edge approach of both Fe/Co K-edges and Fe/Co/Ni K-edges, and using the same structural parameters for all edges. The XANES data of Fe and Co K-edges are independently analysed here. An excellent reproduction of the XANES spectra, and a good agreement with the previous EXAFS results is obtained. The CN bond length using EXAFS has been determined with a statistical error of few thousandths of Å, whereas structural parameter using MXAN are probed within a 0.01-0.03 Å accuracy.

1. Introduction

Renewed attention to metal hexacyanoferrate is based on their use as magnetic devices, and in particular, on the discovery of the photoinduced magnetization effects in some of these compounds [1, 2]. From the structural viewpoint these complexes are characterized by a rigid three dimensional cubic network (although other crystal symmetries are found in a few other hexacyanoferrates) of repeating -NC-Mₐ-CN-MₐCN- units where Mₐ is Fe and Mₐ Co and/or Ni. Iron and cobalt sites are typically octahedral, and the sites at the cube centre are occupied by water (zeolitic water) as well as counterions as necessary to achieve charge neutrality (see figure 1). Depending on the method of preparation, these compounds also feature structural defects. Particularly, the presence of Fe(CN)₆ vacancies and the partial occupancy of zeolitic water contribute to obtain compounds with unique magnetic and physical-chemistry properties.

In a previous EXAFS investigation [3], via multiple-edge analysis using the GNXAS program [4], we have determined the structural parameters of crystalline Co/Fe hexacyanoferrates, underlying the potentiality of the EXAFS probe when the multiple edge approach is applied on compounds having the peculiar characteristic of sharing the entire structural parameters. Moreover a XANES study [5] done on a simple hexacyanoferrate demonstrated the reliability of the MXAN method [6] to fit this kind of systems.
In the present work, the MXAN analysis has been applied to Co/Fe hexacyanoferrate by obtaining excellent agreement with the GNXAS results. The joint use of XANES and EXAFS analysis can give an insight into the possible markers probing the presence of structural defects and Fe(CN)₆ vacancies, and their relative concentration.

2. Methods
Solid samples of mixed hexacyanoferrates were prepared by precipitation method of the appropriate solutions, following the preparation described in reference [3]. All chemicals were reagent grade and were used as received. All solutions were prepared using fresh prepared doubly distilled water. The samples considered in the present paper are Na₂Co⁰Fe⁰(CN)₆ (sample I), NaCo⁰Fe⁰(CN)₆ (sample II).

![Figure 1. A ball and stick sketch of the typical fcc structure of metal hexacyanoferrates. Fe and Co atoms are in the corner of each cube, occupying the 4a and 4b crystallographic sites of the Fm3m space group. The interstitial 8c position are occupied by water as well as countercations (soluble structure). The insoluble structure is formed when Fe(CN)₆ vacancies are present, and the N empty sites are occupied by O of coordinated water.](image)

The Fe and Co K-edge XAS spectra were collected in absorption mode at SRS, Daresbury Laboratory, England. The spectra were calibrated by assigning the first inflection point of the Fe and Co foil spectra to 7112 eV and 7709 eV, respectively. Calculation and fitting of XANES spectra was carried out via the MXAN program [6] which is based on the full multiple scattering (MS) approach (i.e. exact calculation of the scattering matrix) in the framework of the muffin tin (MT) potential approximation. MXAN also takes into account inelastic processes by means of a Lorentzian broadening function [7, 8]. During the first fitting cycles the MT potential is optimized by refining two parameters: ovlp (overlap between atomic MT spheres) and V₀ (the zero-energy of the photo-electron). The EXAFS analysis was performed using the GNXAS package [4] which is based on Multiple Scattering (MS) theory (i.e. truncated series expansion of the scattering matrix). 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. Full details concerning the data analysis are available in [3], including the number and the type of the included n-body contributions and the minimization procedures. The phase shifts for the photoabsorber and backscatterer atoms were calculated ab-initio starting from the structural model reported in [9], according to the muffin-tin approximation and allowing for 10% overlap between the muffin-tin spheres. The Hedin-Lundqvist complex potential [10] was used for the exchange-correlation potential of the excited state. The core hole lifetime, Γ_c, was fixed to the tabulated value [11] and included in the phase shift calculation.

3. Results and Discussion
The typical fcc structure shown in figure 1 is the so called soluble one when applied to the metal hexacyanoferrates, i.e. the cobalt and the iron site are both octahedral, coordinated by six nitrogens
and six carbons, respectively. In the presence of Fe(CN)$_6$ vacancies, the octahedral symmetry around the cobalt is broken, leading to two different sites: CoN$_6$ and CoN$_4$O$_2$. The structure in this case is called *insoluble*. It is generally acknowledged that hole doping at the iron site is a powerful tool to control the material properties in this class of compounds, for instance magnetism [12], electrochromism [13], and sensing capabilities [14].

Figure 2 shows the comparison of the theoretical best fit and the experimental EXAFS signal for compounds (I) and (II) at the Fe and Co K-edges, respectively, obtained by using the GNXAS program. A previous EXAFS study, made by using a variable coordination number at the cobalt site, coupled with stoichiometric data [3], had suggested a *soluble*, vacancies-free arrangement for compound (I), and an *insoluble* structure for compound (II). Thus, the various MS contribution to the theoretical EXAFS signals for the fitting procedure are chosen according to this result: the EXAFS spectrum of the compound (I) has been successfully analysed with the *soluble* model of the figure 1 whereas compound (II) matches well with an *insoluble* model with vacancies.

The structural parameters obtained from the GNXAS fitting procedures are displayed in table 1. Figure 3 (right) displays the relevant MS signals contributing to the total theoretical EXAFS signal for compounds (I), at the Co K-edge. This figure underlines one peculiarity of the present EXAFS data analysis: the large contribution of the three- and four body signals, whose intensities are comparable to the first shell signal. Indeed, as pointed out in the literature [9], the particular atomic arrangement of the cobalt hexacyanoferrate that are characterized by an almost perfect Fe-C-N-Co linear chain, a short distance between the two metal center and a high degeneracy of the chains makes the four body Co-N-C-Fe contribution a strong one.

![Figure 2](image.png)

*Figure 2.* Comparison of the experimental (-) and theoretical (…) $k^2$-weighted EXAFS signals for compounds (I), (II) at Fe (left) and Co (right) metals K-edges. Compound (I) is vacancies-free with a Fm$ar{3}$m fcc structure. Compound (II) is characterized by the presence of Fe(CN)$_6$ vacancies.

With the aim to improve our knowledge of the relationships between magnetochemical properties, based on the presence of vacancies, and the structure of these compounds, in this work we have started a preliminary XANES study of the *soluble* compound (I) to test both the accuracy of the MXAN
analysis, and the theoretical XANES sensitivity to the presence of a fraction of vacancies in this compound.

A close inspection of the figure 1 reveals that the presence of Fe(CN)$_6$ vacancies affects the cobalt sites more than the iron one, and thus it might affects the Co K-edge XANES spectrum of the compound (II) with respect to the vacancies-free compound (I). For this reason, in the present work we have tested if the Co K-XANES changes are reproducible by theory and are compatible with the presence of a certain fraction of vacancies.

First we have calculated the Co K-edge XANES spectrum of the metal hexacyanoferrate with a typical fcc structure, sample (I), as a function of the cluster size surrounding a Co atom. In figure 3 (left) the result of such calculations is shown.

![Graph showing Co K-edge XANES theoretical spectrum](image)

Figure 3. Co K-edge XANES theoretical spectrum of Na$_2$Co(II)Fe(II)(CN)$_6$ (compound I) hexacyanoferrate as a function of the cluster size, and using the MXAN program (left). The final 5-shell cluster corresponds to a cluster radius of 8.2 Å. On the right: details of the EXAFS analysis at of the same compound using the GNXAS program. The individual (not cumulative) EXAFS contributions, the two-, three, and four body signals, corresponding to the first, second and third shell around the cobalt site, are shown.

According to these calculations, the XANES spectrum mainly reflects the 2-shell cluster arrangement, including the strong 3-body multiple scattering terms due to the 6 CN groups. The sensitivity of the XANES spectrum to the 6 Fe atoms in the 3rd shell is weaker than in the EXAFS range (see the high amplitude of the corresponding EXAFS signal in the figure 3 right), having some influence above 100 eV. Further shells seem to have second order effects on the XANES features.

As a second step, we have tried to fit the Co and Fe K-edge XANES spectra of the same vacancies-free compound (I), using the MXAN program. In Table 1, a comparison is shown between the XANES (this work) and EXAFS [3] fits, the latter done via the GNXAS program. In Figure 4, the best fitting XANES spectra are superimposed to the experimental data, for both edges, Fe and Co. As seen from the figure, the XANES theoretical signal matches well with the experimental ones.
Table 1. Comparison between XANES (MXAN) and EXAFS (GNXAS) fits of \( \text{Na}_2\text{Co}^{III}\text{Fe}^{III}(\text{CN})_6 \) (sample I) at both Co and Fe K-edges. EXAFS results are based on single-edge refinements.

|                | Co K-edge | Fe K-edge |
|----------------|------------|------------|
|                | MXAN\(^a\) | GNXAS\(^d\) | MXAN\(^b\) | GNXAS\(^e\) |
| \( d(\text{Co-N})/\text{Å} \) | 2.15(1)    | 2.10(1)    | 2.09(2)    |            |
| \( d(\text{C-N})/\text{Å} \)  | 1.16(1)    | 1.18(1)    | 1.23(1)    | 1.19(1)    |
| \( d(\text{Co-C})/\text{Å} \)  | 3.31(1)    | 3.28\(^c\) | 3.28\(^d\) |            |
| \( d(\text{Co-Fe})/\text{Å} \) | 5.18(6)    | 5.15\(^c\) | 5.17(6)    | 5.15\(^e\) |
| \( d(\text{Fe-N})/\text{Å} \)  | 3.05\(^c\) | 3.10(1)    | 3.05\(^e\) |            |
| \( d(\text{Fe-C})/\text{Å} \)  | 1.87(1)    | 1.87(1)    | 1.864(5)   |            |

\(^a\) MXAN potential parameters: ovlp=-0.07, \( V_0=-7.3 \text{ eV} \). \(^b\) MXAN potential parameters: ovlp=0.12, \( V_0=-16.7 \text{ eV} \). \(^c\) Data obtained from geometrical consideration. \(^d\) Data obtained at Co K-edge. \(^e\) Data obtained at Fe K-edge.

As shown in Table 1, the MXAN results on the vacancies-free compound are in good agreement with those found by the EXAFS single-edge refinement, with a maximum discrepancy of 0.03 Å beyond the statistical errors. Also the Co-Fe distance is probed by XANES with 0.06 Å accuracy. It is worth noticing that the multiple-edge approach in the EXAFS analysis leads to better shorter statistical errors, being less than one hundredth of an Å [3]. For instance the CN bond length has found to be quoted 1.183(5) Å in the compound (I).

In figure 4 (left), the theoretical Co K-edge spectrum of Figure 4 (soluble structure), reported without broadening terms, is compared to the spectrum obtained by substituting two of the C-N chains with two oxygen atoms, i.e. by simulating the presence of water containing vacancies (the insoluble structure). This accounted for samples that are characterized by the presence of Fe(CN)\(_6\) vacancies. The main changes observed going from a CoN\(_6\) site to a CoN\(_4\)O\(_2\) site are a decrease of the intensity of the white line and of the main oscillating features between 25 and 80 eV beyond the edge. This test confirms the dependence of the XANES characteristic to check the possible soluble to insoluble transformation. Figure 5 (right) displays a comparison of the XANES experimental spectra taken at the Co K-edge for compound (I) and (II). A close inspection of the two curves reveals differences on both white line intensity and in the features between 25 and 80 eV beyond the edge. Because
compound (I) is vacancies-free with a Fm3m fcc structure and compound (II) are characterized by the presence of Fe(CN)$_6$ vacancies, the comparison may underline an experimental evidence of their intrinsic soluble or insoluble structure. Combined XANES and EXAFS simulation and fitting procedure are in progress to clarify this issue.

![Figure 5](image)

**Figure 5.** Comparison of ‘vacancies’ and ‘vacancies-free’ theoretical Co K-edge XANES spectra of compound (I) (left). Comparison of the XANES experimental spectra taken at the Co K-edge for compound (I) and (II) (right).

4. Conclusions

This work presents the potentiality of the combined XANES and EXAFS fitting approach which, taking advantage of modern data analysis techniques, allows a detailed study of the structural properties of metal hexacyanoferrates.

The XANES simulations and fitting procedures confirm the structural results obtained by EXAFS and thus make available an important probe for checking the role of the vacancies in metal hexacyanoferrates, i.e., the Prussian Blue like compounds. The joint XANES – EXAFS fitting approach in these systems is recommended, especially in the case of dilute systems, where the XANES spectra is more easily carried out. This is the case, for instance, of electrochemical devices with little concentration of the active material (metal hexacyanoferrate).

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