Self-consistency, spin-orbit and other advances in the FDMNES code to simulate XANES and RXD experiments

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Abstract. A user friendly tool allowing the simulation of x-ray absorption near edge structure (XANES) spectra and Resonant X-ray Diffraction (RXD) peak intensity is necessary for many purposes. We present the actual developments of the FDMNES code which realizes this task in a mono-electronic approach. The code uses both the multiple-scattering theory and the finite difference method in a fully relativistic frame, including thus the spin-orbit interaction. In diffraction, the resonant and non-resonant, magnetic and non-magnetic components are all included, allowing an easy use by non experts of the code. In the same idea, the automatic analysis of the unit cell (or molecule) symmetry greatly simplifies the user’s work. Summation on and energy shift between the different absorption sites are automatically included. Comparison with experiment in order to fit parameters is also possible. The last advances with the self-consistent calculations are discussed. It is shown that within the multiple-scattering theory, using the muffin-tin approximation on the shape of the potential, the improvement is not high for non magnetic situation and limited to the pre-edge region. The improvements coming from the non-muffin-tin corrections are notably higher. More improvement results from self-consistency for the magnetic NdMg system. Various examples in oxides and metal in RXD and XANES are given showing the potentiality of the code. The fit procedure is applied in the magnetite low temperature phase case.

1. Introduction

X-ray Absorption Near Edge Structure (XANES), as well as the related spectroscopies like RXD (Resonant X-ray Diffraction, also called RXS for Resonant X-ray Scattering) and XMCD (X-ray Magnetic Circular Dichroism), are powerful means of probing the electronic and geometric structure around the absorbing atoms. To help understand what is measured and for extracting relevant parameters, there is a great need of codes which are able to reproduce the experimental spectra within a reasonable calculation time and permitting an easy use. When the probed states are localized and in interaction with the core-hole, multi-electronic tools are necessary[1]. Otherwise, the mono electronic approach is most often sufficient. It is this latter case which concerns the K-edges of most chemical species and the L₂₃ edges of the heavy elements, which is the subject of this paper. Many codes working in reciprocal space [2–4] or in direct space already exist [5–8]. The key point in these calculations concerns the final states evaluation. Once the final states are calculated, the computation of the matrix terms giving the electron transition
amplitude, then the absorption cross section and/or the resonant scattering amplitudes, is a relatively easy task and in any case, not a CPU consuming operation. Another step not conceptually complex but very useful for the users is the proper summation over equivalent and non-equivalent atoms in the unit cell or in the cluster to get at the end the spectra to compare with the experiment. All this work can eventually be integrated in a fit procedure of some parameters by comparison of the set of simulated spectra with the experimental ones as it is possible for example with MXAN[7] or FDMNES[5].

In this context, we want to present in this paper several new advances in the FDMNES code. The first one is the introduction of self-consistency in the evaluation of the final states. Such an advance has already been implemented in the FEFF8 code[8, 9]. Nevertheless, the comparison of the improvement given by this procedure with the one given by other advances in the calculation must be made. This question is presented after some keypoints in the methodology (Sec. 3.2), then the application, firstly in XANES case in metal and oxides, secondly in RXD case with an NdMg study (section 4). Another important advance concerns the use of a good fit procedure. Fitting parameters with a supposedly ab initio code can sound contradictory. In this case, of course, the simulation will not be completely “first principle”. Nevertheless, a part of some fixed parameters, as for example the atom positions, all the remaining can be calculated ab initio. In the context of charge ordering we can also use the fact that our spectroscopy is not necessarily very sensitive to the very small energy range around the Fermi level, but uses a relatively wide energy range, say 60 eV, above it. In this range, and contrary to the total energy evaluation, the spectra shape can be evaluated by less sophisticated calculations neglecting, for example, multi-electronic phenomena, but using nonetheless some effects which are thus parametrized, in the electronic structure. It is in this way that in the last section we show a quantitative analysis of the charge and geometric ordering in the Cc unit cell of the low temperature phase of magnetite. Before presenting the code, we briefly recall the basic equations in XANES and RXD in the following section.

2. Equations of XANES and RXD

Absorption and resonant diffraction’s main featured quantities are respectively the cross section \(\sigma(\omega)\) and the structure factor \(F(Q,\omega)\), both normalized with respect to the unit cell:

\[
\sigma(\omega) = 4\pi^2\alpha\hbar\omega \sum_{j} |\langle \psi_f^{(j)} | \hat{O} | \psi_g^{(j)} \rangle|^2 \delta(\hbar\omega - (E - E_g^{(j)}))
\]

\[
F(Q,\omega) \propto \sum_{j} e^i Q \cdot \mathbf{R}_j \left(f_{0j} + f_j^*(\omega) + i f_j''(\omega)\right)
\]

with \[10\]:

\[
f_j^*(\omega) = \frac{m_e}{\hbar^2} \sum_{j,g} \frac{(E - E_g^{(j)})^2 \langle \Psi_g^{(j)} | \hat{O}_{\text{out}}^* | \Psi_f \rangle \langle \Psi_f | \hat{O}_{\text{in}} | \Psi_g^{(j)} \rangle}{\hbar\omega - (E - E_g^{(j)}) + i \frac{1}{2}}
\]

Here \(\alpha\) is the fine structure constant, \(m_e\) the electron mass, \(\hbar\omega\) the photon energy, \(\delta(E)\) the electronic density of states, \(E_F\) the Fermi energy, \(E_g\) and \(E\) are the energies of the ground state \(\Psi_g^{(j)}\) and photo-excited state \(\Psi_f\), respectively. X-ray absorption requires a core, localized level as a ground state, thus we introduced the index \(j\) describing the atom. The summation over \(j\) adds the contributions of all the atoms in the unit cell. The final state \(\Psi_f\) is an unoccupied state above \(E_F\); we omit its \(j\) index. \(Q\) is the diffraction vector and \(\mathbf{R}_j\) is the position vector of atom \(j\) in the unit cell. \(\Gamma_f\) is the sum of the inverse of the final state and the core hole lifetimes, and thus depends on the chemical type of the absorber and the edge considered. The atomic structure factors intervening in (2) are, respectively, the off-resonant, nearly isotropic,
energy independent Thomson term \( f_{0j} \) and the complex resonant contribution \( f_j'(\omega) + if_j''(\omega) \).

We agree to use a sign convention in (3) such that \( f''(\omega) > 0 \) and \( f'(\omega) \) is most often negative. For the diffraction part, as we deal with a scattering process, we need to distinguish between the incoming photon field operator \( \hat{O}_{in} \) and the outgoing one \( \hat{O}_{out} \).

The electron - photon interaction is described classically by means of the field operator \( \hat{O} \). In the X-ray regime, the magnetic part of the electromagnetic field can be neglected and the remaining electric part is satisfactorily described by the first two terms of the multipolar expansion, corresponding to the excitations of the electric dipole and of the electric quadrupole:

\[
\hat{O} = \epsilon \cdot r \left( 1 + \frac{i}{2} k \cdot r \right)
\]

where \( r \) is the position from the absorbing ion, \( \epsilon \) the polarization of the photon and \( k \) its wave vector.

3. The FDMNES code

The FDMNES (standing for Finite Difference Method Near Edge Structure) package is an ab-initio, free and open source code, parallelled under MPI, which calculates the XANES, RXD and XMCD spectra. FDMNES works in real space, whether we deal with a molecule or a periodic system. It builds clusters around the absorbing atoms performing several independent calculations when there are several non equivalent absorbing atoms.

3.1. General frame

All the sequences of the spectra calculations can be summarized in the following way: 1) From the molecule or the unit cell atom positions the code evaluates the non-equivalent and equivalent atoms with the symmetry operation relating them to each other. 2) For each non-equivalent and absorbing atom a cluster is formed around it with a radius chosen by the user. The point group is evaluated, giving the shape of the scattering tensors and the useful representation to calculate. 3) For each cluster the final states are calculated. From the superposed first guess atomic density the Poisson equation is solved to get the Coulomb potential; the energy dependent exchange-correlation potential is evaluated using the local density approximation (LDA), using either the Perdew and Wang [11] or the real Hedin-Lundquist [12, 13] formulations. Once the potential has been constructed we solve the Schrödinger-like equation (SE) or the Dyson equation to get the electronic structure which can be the final states when there is a transition. There is now the possibility for having this step self-consistent. In this case from the electronic structure a new potential is calculated and so on, up to convergence. Note that the calculated cluster is embedded in a wider cluster to calculate the potential properly at its border. 4) From this electronic structure, matrix elements governing the transition depending on the polarization condition are evaluated. These matrix elements are summed and multiplied in order to get the tensorial expressions of the scattering-absorption properties of the absorbing atom in its cluster. 5) The contributions of the different absorbing atoms are then summed up with, in the diffraction case, the Bragg term taken into account. 6) The convolution in XANES and the summation over energy in RXD gives the absorption cross-section spectra and the anomalous scattering amplitudes respectively. The latter is summed with the non-resonant contribution to obtain the diffracted peak intensity spectra.

All these steps can be included in a fit procedure where some parameters are chosen to vary in some range. An automatic comparison with experimental spectra is then performed to propose a best model with the corresponding spectra. For this purpose different comparison criteria are proposed, such as metric distances or confident R-factor. More confidence in the result is reached when the number of parameters is not too high in comparison with the number of independent
experimental data. In this context, fit procedures are easier in RXD because one can have a relatively large number of spectra whereas in XANES one has just one or two.

Note also that FDMNES allows a full analysis of both cartesian and spherical tensors which can be helpful in the context of magneto-electric studies.

FDMNES features two ways of calculating $\Psi_f(r)$: the finite differences method (FDM) and the multiple scattering theory (MST), the latter within the limits of the muffin-tin approximation (MT). MT assumes a crystal potential that has spherical symmetry around the atoms (the so-called “muffin-tin” spheres) and is constant in the remaining space. The FDM can use the full potential and consists of constructing a space grid and discretizing the SE on the points of this grid. FDM does not introduce any approximation of the form of the potential and therefore provides a more accurate, but more time consuming, description of the electronic structure in both occupied and non occupied states and thus of the absorption-scattering phenomena. In this paper we shall not explain in detail the FDM and MST method (see Ref. [5] and [14]). We present the philosophy of our self-consistent calculation (SCF) in the next section.

3.2. Implementation of the self-consistency

We introduced the self-consistency within the multiple-scattering frame. As in any self-consistent calculation from a first guess electronic density, the SE equation is solved to get new states and thus new electronic density. The procedure is repeated until convergence is achieved. Once we are sure to have the correct electronic levels, we perform a last iteration which calculates the absorption spectra (1) in either the MST or the FDM approach. In this last case, the difference between the muffin-tin SCF and muffin-tin non-SCF potential is added to the non-SCF non-muffin-tin potential. We note that the cluster’s radius for this last calculation is not necessarily the same as the one used in the previous iterations.

A priori it is not sure that a self-consistent calculation must give a better result than a non self-consistent one. Indeed one has to recall that the photo electron probes an excited state and the density functional theory (DFT) is not an appropriate theory in this case. This is even more true when, as in our case, one uses a mono electronic approach following the LDA. The key point is wether the final states must be calculated with the core-hole or without. We know empirically that in most cases, when calculations are not self-consistent, the results are usually better when the potential is calculated with a core-hole and a full (or nearly full) screening, placing an extra electron on the first non-occupied state. The absorbing atom remains neutral (or nearly neutral). In a self-consistent calculation the neighboring atoms can participate in the core-hole screening by a charge transfer. In this case one supposes that the photo-electron probes an already relaxed electronic state. On the contrary, if one imagines that the photo-electron probes non-relaxed states, the potential must be calculated without the core-hole. It is the so called ”initial state rule”. The essential difference between these two schemes is linked to the difference in the time scales associated with the two main processes involved: the passage of the photo-electron and the response of the electron cloud surrounding the absorber. The electrons either adjust instantaneously to the perturbed structure, in which case the first scheme is appropriate, or their reactivity is slow with respect to the advent of the photo-electron, in which case the second scheme is more accurate.

To study this we shall compare simulations using these two schemes, that is (a) assuming a non-excited electronic configuration for the absorber during the entire calculation and (b) assuming an excited absorber, i.e. in the presence of a core hole and with an extra electron on the first available valence level. We shall also introduce a third scheme (c) corresponding to an intermediate situation between (a) and (b): the self-consistency is performed on a non-excited atom, in order to get the accurate electronic structure; it is only at the last iteration (that is when calculating the final states in the XANES energy range) that we take into account the excited electronic structure of the absorber. In practice, at the beginning of the absorption
calculation, we add the difference between the atomic density corresponding to an excited atom and the one for the non-excited case to the self-consistent electronic density of the absorber. We note that both in (b) and in (c) we introduce by default a full screening to calculate absorption.  

First, the electron density is integrated in the cluster of calculation in order to get the reference number of charge. This step is not straightforward because it requires the definition of atomic radii. A bad choice can lead to uncertainty in the results. We note that the atomic radii are usually larger than the muffin-tin radii. At each energy grid point, after having calculated all the electronic states, the number of electrons per unit energy is evaluated by integration over the atoms of the cluster. Then the total number of electrons in the cluster is obtained by integration over energy up to the current energy value. When this number of electrons is equal to the reference charge, the current cycle stops giving the Fermi energy. Note also that the energies of the calculation are chosen to have a small (0.1 eV) imaginary part. This is needed in order to broaden the localized electronic levels, otherwise we would need an extremely small energy step to properly count the electrons in these orbitals. We therefore also need to calculate in the MST frame the irregular solution of the radial SE in all the atoms of the cluster. In practice, as usual, we perform a weighting of the charge density from the previous iteration (that we used in the beginning of the cycle in order to calculate the Coulomb potential) with the current one. The experience tells us that the current calculation needs to have a rather small weight (0.1 at most) for convergence to be achieved. The interpolation parameter is set up dynamically, i.e. we decrease it by a factor 2 in case of a beating convergence parameter. We inject the weighted charge density into the next cycle and we repeat the calculation until the convergence is achieved. At the end of each cycle the total energy is calculated. Convergence is achieved when the difference with the previous cycle is beneath a fixed value.

We note that the automatic setting of the Fermi level is a very convenient and user-friendly feature of the self-consistent calculation. For the codes where this is not the case, the Fermi level is set ad-hoc and thus the elimination of occupied states is spurious. In the case of sparse structures (as one will see in the next section), the calculated Fermi level and the cut-off of the absorption spectrum may differ. Nevertheless the former still gives valuable information (within \( \approx 1-5 \) eV).

4. Results on selfconsistency  
In this section we aim to answer several questions linked to the pertinence of applying a self-consistent procedure to an X-ray absorption calculation. In particular, we are interested in detecting the structures where a self-consistent calculation can improve the non self-consistent results. Another issue is whether one could afford a smaller calculation radius for the self-consistent part than for the absorption calculation, with the purpose of saving computation time. Moreover, we wish to indicate what is the best self-consistent approach among the ones presented in the previous section. To begin with, we shall study copper Cu and other simple metal cases. We also discuss the results of calculations run on the rutile TiO\(_2\), the boron nitrate BN and the calcium oxide CaO. In a last step we study a magnetic system: the low temperature phase of NdMg studied by RXD.

4.1. Absorption K-edges of simple metal  
We performed a series of simulation of the copper K-edge in its FCC structure. Convergence is achieved at 6.76 Å (i.e. 135 atoms). In Fig. 1 we show the simulations after convolution for several self-consistent and non-self-consistent calculations. The self-consistent calculations have been performed in several manners (a,b,c), according to the procedures described above. Among these, one notices that procedure (c) is the most appropriate with respect to the agreement with the experiments [15], as it improves the ratio of intensities of the structures after the edge. Unlike scheme (b), non-excited self-consistent procedures (a) and (c) do not influence the position of
the structures preceding the white line, as compared to both the non-self-consistent case and the experiment. We therefore conclude that the assumption we had made to get the (b) spectrum (i.e. the response of the electron cloud surrounding the absorber to the passage of the photo-electron is adiabatic) is not valid at the K-edge, as confirmed by our further examples.

Figure 1. Calculation and experimental data for absorption at copper’s K edge, for a 6.76 Å cluster. For what self-consistent calculations are concerned, we tested the three different procedures: full non-excited calculation (a), full excited calculation (b) and hybrid (c), i.e. self-consistency is performed on the non-excited absorber while the absorption takes into consideration the excited electronic structure.

We ran calculations on the 3d and 4d series by using the standard crystallographic structure. We encountered no particular difficulty, either in achieving convergence, or in obtaining the correct cut-off for the convolution and, thus, the elimination of the occupied states. In the cases where the (b) and (c) self-consistent schemes give different results (Ag,Ni,Cu), the best agreement is achieved by using the last procedure. In other cases (Fe,Ti) this difference is not at all noticeable. We inferred that the (c) self-consistent scheme is the best choice when dealing with the K-edge. Our general conclusion is that the self-consistency brings no major change at high energies, as compared to the non self-consistent calculations. In some cases (Fe, Ni), one can see a shift in the position of the low-energy peaks. Self-consistent effects occur mostly in the vicinity of the Fermi level.

To conclude, one may state that the self-consistency does not have a major influence in the case of simple metal systems. Nevertheless, it provides the Fermi level, which in practice is a very useful information for comparison with the experiment.

4.2. The rutile TiO₂
TiO₂ is an interesting structure because at the rising edge, it features several pre-edge peaks of both dipolar and quadrupolar origin[5, 15]. A priori one would expect benefits from a self-consistent calculation, as it is supposed to act especially on the localized 3d states in the vicinity of the Fermi level.

We performed SCF and non-SCF simulations using the (b) and (c) procedures and with XANES calculation using the FDM or the MST technique. All calculations were performed with different radii up to 5.51 Å which corresponds to 75 atoms and complete octahedra surrounding the central TiO₆ octahedron. This radius is necessary to get the pre-edge structures. In figure 2 we show these simulations and compare them to the experimental data of Poumellec et al. [15]. We show the signal obtained for one orientation of the polarization and the wave vector: \((\epsilon, k) = ([1-10], [110])\). (b) and (c) procedures give nearly the same result so we only show
As compared to the non-self-consistent calculation, the SCF succeed in shifting the pre-edge structures towards the smaller energies, although this shift is not enough to give a perfect agreement with the experiments. One can see that all MST calculations fail to describe the double structure at the edge (4980 - 4990 eV). This is due to the MT approximation. Moreover, the ratio of the intensities of the pre-edge structures is improved using the FDM. To get a better agreement with the experiments one should implement a full potential self-consistent calculation.

**Figure 2.** Ti K-edge in rutile TiO$_2$ for the polarization ($\epsilon,k$) = (110,110). The experiment [15] (dotted) is compared with simulations all performed with a 5.51 Å cluster radius. Bottom are the simulation using the finite difference method and top the one using the MST-MT technique. Full lines correspond to self-consistent simulations, and dashed ones to non-self-consistent calculations. FDM simulations are better. SCF improve slightly the agreement at low energy, shifting the pre-edge structure by some fraction of eV. This shift is nevertheless not sufficient to have a perfect agreement.

### 4.3. CaO and BN

At the K edge of Ca in CaO and of B in BN, we compared the self-consistent and the non-self-consistent results (Fig. 3) with the experiments [8, 9]. Among the self-consistent calculations, schemes (b) and (c) give similar results and we chose to show the former one. Simulations were performed respectively with 6.9 Å and 4.7 Å cluster radii, that is 93 atoms for CaO and 87 atoms for BN. For these particular materials, the calculated Fermi level is not the same with the cut-off we used for the convolution. We explain this inadequacy by the fact that our assumption of sphericity (the MT approximation) prevents us for counting all the electrons, provided that we are not allowed to exceed an upper limit of the overlap of the integration spheres. This energy shift does not usually appear if the compound is a compact structure, as non-spherical effects are negligible, but may be significant if one deals with a sparse structure, like BN or CaO. We note that it is still the self-consistent calculation that gives a more reasonable result with respect to the Fermi level evaluation.

In the case of BN, one can see practically no difference between the self-consistent and the non-self-consistent calculations, whether the last iteration was performed in the FDM or in the MST-MT frame. Moreover, the agreement with the experiment is obviously better in the case of the FDM calculations. One concludes that it is crucial for this particular material to be treated with a full potential method, whereas the fact that the calculation is self-consistent or not does not make any difference.
Figure 3. Comparison between the self-consistent (solid line) and non-self-consistent (dashed line) calculations with the experimental data [9] (with dots), for the calcium oxide CaO (left) and BN (right), with the absorption calculation performed in the FDM (below) and in the MST-MT (above). There is little difference between SCF and non-SCF simulations. In both cases FDM is better than MST.

As CaO is concerned, one notices an improvement provided by the self-consistent calculations in both MST-MT and FDM cases. Nevertheless we are still unable to get a perfect agreement for the modulations in the range 4060-4070 eV. One can see a better agreement in the case of a non-self-consistent FDM absorption calculation than for the self-consistent MST-MT one. This leads us to the conclusion that taking into account the effects of non-sphericity is more important than the amelioration given by the self-consistent procedure, as implemented in the FDMNES (i.e. in the spherical potential approximation).

4.4. RXD magnetic case, the NdMg
The NdMg compound crystallizes in the cubic CsCl-type structure. At $T_R = 35$ K one observes a spontaneous magnetic transition that corresponds to the change into a double-$k$ structure with non-collinear moments perpendicular to the $c$-axis (see Fig. 4). The existence of charge satellites associated to this new periodicity in the crystal is also observed by x-ray diffraction experiments in non-resonant conditions [16, 17].

The purpose here is simply to compare simulations with measured diffracted peaks in order to show the influence of self-consistency. In this case, magnetic calculation including spin-orbit are mandatory. We show in Fig. 4 some of the reflections calculated with and without self-consistency. In the experiment, peaks were recorded along specific polarization conditions. Here we show some of the magnetic peaks (for which only one index is half-integer) in the $\pi-\sigma$ polarization condition and one non-magnetic, but forbidden, reflection in the $\pi-\pi$ channel (for which two indices are half-integer). This last is a signature of the orbital ordering. It is interesting to note that the MST-MT simulation gives a non-zero intensity for the latter reflection thanks to the spin-orbit. Nevertheless, a better agreement would need a non-muffin calculation because the asphericity of the potential is not taken into account before solving the Dyson equation. It is clear that the SCF procedure improves the agreement with the experiment in this case. Our conclusion is that in the magnetic case an SCF calculation can be very useful.
Figure 4. Fluorescence and resonant diffraction spectra at the Nd L₂ edge in NdMg. The (5/2, 0, 0) and (5/2, 0, 3) are pure magnetic reflections. The (5/2, 1/2, 0) is an electric reflection due to the orbital ordering. This one can be simulated due to the spin-orbit which tends to align the 4f orbital along the magnetic moment. Dotted is the experiment, full line the SCF simulation and dashed the non-SCF simulation. In this case the SCF is better than the non-SCF calculation. On the right is shown the superstructure due to the magnetic ordering. At the corners stand the Nd elements, the arrows showing the orientation of the magnetic moments. The Mg (not shown here) is a the center of the parallelograms.

5. Fit procedure and charge and geometrical ordering in magnetite

We want to show that by using a fit procedure, it is possible to extract new pieces of information on a very complex compound. Indeed because the effect of self-consistency is just in the first eV of the edge, the use of a fit by comparison with experimental spectra minimizing confidence factor can be easier than the minimization of a total energy which can be difficult to calculate. The low temperature phase of magnetite is a very good candidate for such study. Indeed its structure is not well known and its associate charge ordering is still a subject of debate [18]. We propose here an analysis of the geometry and charge pattern of magnetite. The sensitivity of resonant diffraction to charge ordering comes from the fact that atoms with closely related site symmetries but with barely different charges exhibit resonances at slightly different energies. For some reflections the Bragg factor makes these slightly different atoms nearly subtract in the atomic structure factor. Such reflections, usually weak in intensity, are consequently sensitive to tiny differences between the charge state of the resonant specie. In addition, the influence of the often associated geometrical distortions has to be disentangled from pure charge effect.

The valence state of the resonant atom is seen through the energy shift of its main absorption edge. The energy shift, Δ, of the core state \( E_g^{(j)} \) in equation 3 is directly related to the variation of the atomic electronic occupancy rate, δ, with respect to a nominal value. In the case of magnetite we already noted [19] that a \( \Delta = +0.8 \) eV shift corresponds to \( \delta = -0.1 \) electron difference and this relation is roughly linear. Such linear relation is valid because the local octahedral structure is hardly modified through the phase transition. Once summed over the different sites, this simple shift of the atomic scattering factors can give rise to specific features in the spectra which are a signature of charge disproportion. Peaks sensitive to charge disproportion will be such that the atoms of the same charge are out of phase with respect to the atoms with a different charge. Most often, charge effect and the related atomic displacement
Table 1. Fitted Iron atom positions and charges given in the Cc cell. The sites with index $n$ between 9 and 16 correspond to the sites 3 and 4 in Pmca standing at $z \approx 3/8$ and $z \approx 5/8$. The position, in cell units is relative to the Pmca structure. The charge disproportion, $\delta$charge, is relative to $+2.5$.

| Cc index | $\delta x$ | $\delta y$ | $\delta z$ | $\delta$charge |
|----------|------------|------------|------------|----------------|
| 9        | 0.0020     | 0.0015     | 0.000      | 0.025          |
| 10       | 0.0020     | 0.0015     | 0.000      | 0.050          |
| 11       | -0.0020    | -0.0015    | 0.000      | -0.025         |
| 12       | -0.0020    | -0.0015    | 0.000      | -0.050         |
| 13       | 0.0020     | 0.0015     | 0.000      | 0.000          |
| 14       | -0.0020    | -0.0015    | 0.000      | 0.025          |
| 15       | -0.0020    | -0.0015    | 0.000      | 0.000          |
| 16       | 0.0020     | 0.0015     | 0.000      | -0.025         |

seen through the Bragg factor contribute to the structure factor; sometimes both effects add, sometimes they subtract. The maximum of the charge effect is where the derivative of the spectra is large, more than 8 eV above the Fermi level in this example. There a mono-electronic calculation generally suffices.

At room temperature magnetite displays a cubic structure of space group $Fd\bar{3}m$ and lattice parameters $a_c = 8.394$ Å. It has two non-equivalent iron sites, one in a slightly distorted octahedral environment and the other in a tetrahedral coordination. In a pure ionic description the octahedral iron is in a $+2.5$ charge state, the tetrahedral one is $+3$. The Verwey transition leads to a lowering of the symmetry of the unit cell, at least down to Cc. Despite numerous efforts and attempts in the past to refine the low temperature structure, only an approximate structure in a smaller unit cell has been completely refined. Until now the Pmca space group is supposed to give the best agreement [20] with experiment. The new unit cell is rotated by 45°, ($Fd\bar{3}m \rightarrow Pmca$, and $a_c \times a_c \times a_c \rightarrow a_c/\sqrt{2} \times a_c/\sqrt{2} \times 2a_c$) which generates 6 non-equivalent iron sites, 4 of them possessing a distorted octahedral environment. Each site possesses a multiplicity equal to four. Note that Wright and collaborators found $\beta = 90.2363^\circ$ so that monoclinic $P2/1c$ is a better description of the unit cell. Under this symmetry lowering the two first octahedral iron sites split into 4 non-equivalent positions of multiplicity 2.

In the present study we have measured peaks not allowed in the Pmca (or P2/1c) which are compatible with the 4 times larger unit cell corresponding to the Cc space group. From the Pmca unit cell, the Cc unit cell has its $a$ and $b$ cell parameters doubled. Consequently the new unit cell parameters are $a = 11.888814$ Å, $b = 11.849402$ Å, $c = 16.775150$ Å, $\alpha = 90^\circ$, $\beta = 90.2363^\circ$, and $\gamma = 90^\circ$ with 24 non equivalent iron atoms of multiplicity 4.

We do not give the details of the study which has already been published [21] in this paper but focus on the potentiality of the fit procedure. This was not easy because, due to the large number of non-equivalent atoms, there are many parameters. From a previous study[19] we knew that most uncertainty on the charge and positions was standing at 8 of the 16 octahedral sites. We thus focused primarily on these sites. We also checked the other sites and determined that their influence was less important.

It has been very difficult to find a pattern of charge and displacements which permits improvement in all the measured spectra. The best result is given in Fig. 5 and the refined parameters (position and charge of the atoms) are given in Table 1. The charge ordering on the Fe1 - Fe8 sites (corresponding to the sites 1 and 2 in Pmca) remain at $\pm 0.10$, very close to our previous results [19].

We come back to the a priori considerations concerning the possible influence of the other atoms on the diffracted Cc intensities. We already noticed that the small displacements of the
iron atoms in $Cc$ do not change sufficiently their anomalous scattering factor to modify the calculated intensity. The same occurs for the surrounding oxygen atoms because the important parameter is the relative position of both species. The constant factor resulting from the Thomson part must be smaller than the one due to the iron atoms. It is difficult to imagine that adding a relatively small constant can change drastically the shape of the $Cc$ spectra and thus the conclusion on the pattern and charge. In the same way as for the octahedral sites, we have carried out a simulation of the charges and displacements at the tetrahedral Fe sites and at the Fe$_1$ - Fe$_8$ octahedral iron sites. In this case, keeping the octahedral sites at their original $Pmca$ positions, we always found a poor agreement. Charge ordering at these sites can be ruled out at the tetrahedral sites and is very small, if it exists, at the Fe$_1$ - Fe$_8$ octahedral iron sites. Small displacements on these sites cannot be completely excluded, although their contribution is not going to be sizable on the majority of the measured peaks. Therefore the conclusion for the Fe$_9$ - Fe$_{16}$ octahedral sites remains valid.

From all these simulations, we do not pretend to have solved completely the $Cc$ structure. A complete quantitative evaluation of all these parameters would need a concomitant fit of all of them, a situation that is not possible today. The points we think safe in our model are: 1) the pattern of displacement of the Fe$_9$ - Fe$_{16}$ sites with the corresponding charge disproportions, 2) the absence of charge disproportion on the tetrahedral sites, 3) the displacements of the Fe$_1$ - Fe$_8$ and Fe$_{17}$ - Fe$_{24}$ sites and the charge disproportions of the Fe$_1$ - Fe$_8$ sites are smaller than the ones of the Fe$_9$ - Fe$_{16}$ sites. Starting from our best model, a fit of the parameters of the other iron sites would lead to a model with uncertainties larger than their variation from the original $Pmca$ model.

Figure 5. Energy variation of the simulated intensities (full line) and measured spectra at 50 K (dotted) of Bragg reflections corresponding to the $Cc$ space group around the Fe K-edge. The simulation is performed with the structural and charge model given in Table 1.
6. Conclusions
One concludes that at the K-edge the effects of self-consistency (in terms of the positions of the peaks) are restrained to the pre-edge structures, close to the Fermi level. For some materials, a slight redistribution of the intensities can be noticed at high energies. In the cases where non-spherical effects are expected, performing calculations with a full potential method is more important than the benefits one gets by means of the self-consistency in the MST-MT frame. The value of the Fermi level is a very useful information one gets from a self-consistent calculation, as it is essential for the identification of the occupied states and thus for the comparison with the experimental spectra. This cut-off of the spectra is correctly estimated for the compact structures, but is liable to adjustment in the case of materials where non-spherical effects are important. We have proved that the self-consistency brings practically no change for the compact structures, in which case one should be content to run the self-consistent part of the calculation at a lower radius than the one used for the absorption part. Oxides require that one uses the same cluster sizes for the two stages of the calculation in the purpose of improving the description of pre-edge structures. We have also shown that a fit procedure in the RXD case can give very important information on material without self-consistent calculation. We chose the low temperature \textit{Cc}\textsuperscript{2} \times \textit{Cc}\textsuperscript{2} larger unit cell. In addition, and by taking advantage of the possibilities of RXD concerning the determination of the charge, we have completed the charge ordering pattern previously initiated in ref. [19].

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