



# **Pre-edge XAFS simulations for the $SrTiO_3$ and $TiO_2$ crystals**

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## **Abstract**

In this study X-ray absorption spectroscopy simulations were performed. FEEF 9.6 was used to this aim in order to study the quadrupole transitions on  $SrTiO_3$  and the  $TiO_2$  crystals and their dependence with the orientation of the incident beam. Results show a privileged direction for the electric field in which an enhancement of the quadrupole peak is noticeable for both compounds.

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# 1 X-ray Absorption Spectroscopy

## 1.1 X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is a material characterization technique. From the spectral is possible to obtain oxidation state, coordination chemistry, distances, coordination number and species of atoms immediately surrounding the selected element. Also this technique is chemically selective. Importantly, crystallinity is not required for XAFS measurements. There are obtained by synchrotron radiation, which provide intense and **tunable** x-ray beams, with energies ranging from  $\sim 500$  eV to 500K eV. Light is absorbed by all matter through the *photoelectric effect*. In this process, an x-ray photon is absorbed by an electron in a tightly bound quantum core level of an atom.

The energy of the incident photon must be higher than the binding energy of the electronic core level, so that an absorption event of the element under study takes place. If the binding energy is greater than the energy of the x-ray, the bound electron will not be perturbed from the well-defined quantum state and will not absorb the x-ray. If the incident x-ray has an energy equal to that of the binding energy an electron, there is a sharp rise in absorption, this is the so called *absorption edge* and is when the photoelectron is ejected to the continuum. The name of each *edge* correspond to the transition that takes place inside the atom: For example the K edges refers to transitions that excite the innermost 1s electron. Also it is possible that the photoelectron does not have enough energy to go to the continuum but it can pass at a higher empty level. This is the absorption for a dipolar and/or quadrupolar transitions, of course it follows the selection rule.

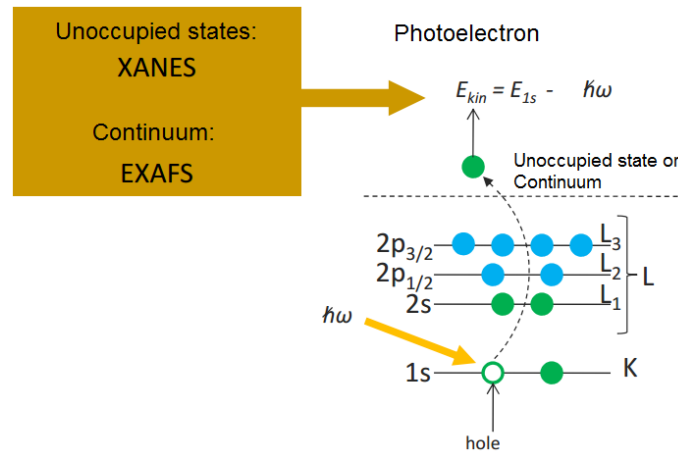


Figure 1: Photoelectric effect.

Following an x-ray absorption event there are two main mechanisms for the decay of the excited atomic state. The first of these is x-ray fluorescence in which a higher energy

electron core-level electron fills the deeper core hole, ejecting an x-ray of well-defined energy. The fluorescence energies emitted in this way are characteristic of the atom, and can be used to identify the atoms in a system, and to quantify their concentrations. The second process is the Auger Effect, in which an electron drops from a higher electron level and a second electron is emitted into the continuum (and possibly even out of the sample). In the hard x-ray regime ( $> 2$  keV), x-ray fluorescence is more likely to occur than Auger emission, but for lower energy x-ray absorption, Auger processes dominate. Either of these processes can be used to measure the absorption coefficient  $\mu$ . The absorption coefficient  $\mu$ , gives the probability that x-rays will be absorbed according to Beers Law:

$$I = I_0 e^{-\mu t} \quad (1)$$

where  $I_0$  is the x-ray intensity incident on a sample,  $t$  is the sample thickness, and  $I$  is the intensity transmitted through the sample. The x-ray intensity is proportional to the number of x-ray photons. At most x-ray energies, the absorption coefficient  $\mu$  is a smooth function of energy, with a value that depends on the sample density  $\rho$ , the atomic number  $\mathbf{Z}$ , atomic mass  $A$ , and the x-ray energy  $E$ : as approximation:

$$\mu \approx \frac{\rho Z^4}{AE^3} \quad (2)$$

The strong dependence of  $\mu$  on both  $\mathbf{Z}$  and  $E$  is a fundamental property of x-rays.  $\mu$  is determined from the decay in the x-ray beam intensity  $I$  with distance  $x$ .

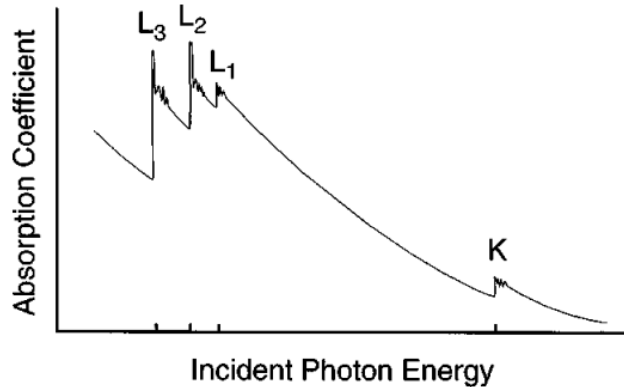


Figure 2: Absorption edge energy.

X-ray absorption spectroscopy measures the absorption of x-rays as a function of x-ray energy  $E = \hbar\omega$ . If  $\mu$  is plotted as a function of  $E$  (Fig.2), the experimental data show three general features:

- An overall decrease in x-ray absorption with increasing energy.

- The presence of a sharp rise at certain energies called edges, which roughly resembles step-function increases in the absorption.
- Above the edges, a series of wiggles or oscillatory structure that modulate the absorption, typically by a few percent of the overall absorption cross section.

## 1.2 Main regions on spectrum

### 1.3 Extended X-ray Absorption Fine Structure (EXAFS)

The Extended X-ray Absorption corresponds to the oscillatory part of the spectrum for energies above the absorbing edge. These oscillations are understood in terms of the wave behavior of the photoelectron<sup>1</sup> which takes place in a scattering process with neighboring atoms. The fine structure is in fact a finger print of the structural information of the material.

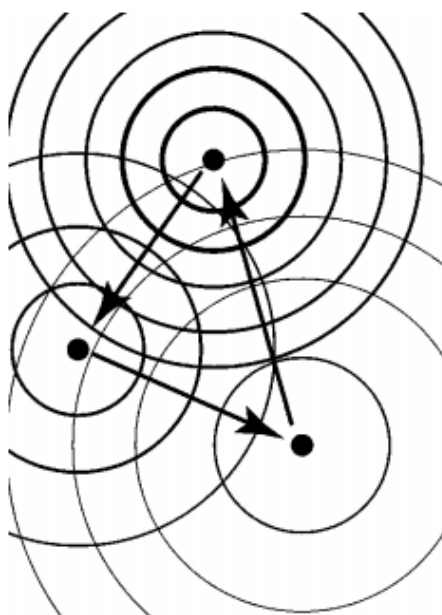


Figure 3: Scattering by photoelectron with neighboring atoms.

### 1.4 X-ray Absorption Near-edge Structure (XANES)

The XANES region, starting about 5 eV beyond the absorption edge, gives information about density of states unoccupied, chemical species and oxidation state. In the region

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<sup>1</sup>created by absorption process

of pre-edge<sup>2</sup> dipolar and quadrupolar transitions take place. The **quadrupolar** transition has a special feature in crystals, the intensity of its peak can be increased when the electric field has a particular direction, this means that contrary to the dipole the quadrupole depends on the direction of the electric field.

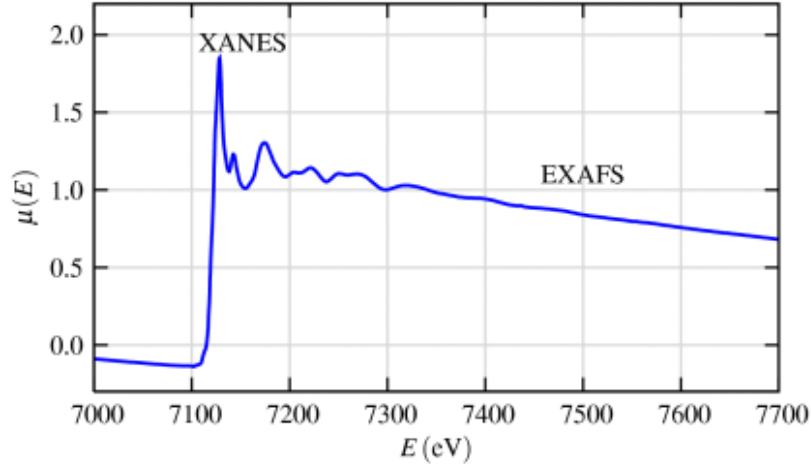


Figure 4: XANES and EXFAS region.

The full implications of this process when applied to molecules, liquids, and solids will give rise to XAFS.

## 2 Quadrupolar simulations

Simulations of the X-ray absorption spectroscopy aims at a better understanding of the phenomena and allow experimenters to fit their data and to find structural and chemical information they seek. There are several programs like FEFF available to perform such calculations.

In this project we seek a better understanding of the programs FEFF in terms of their CARDS and we make special focus on the pre-edge region and the quadrupole transitions for the  $SrTiO_3$  and  $TiO_2$  crystals.

### 2.1 FEFF

For accurate XANES calculations of crystals it is necessary to use the following parameters in the FEFF input file *feff.inp*:

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<sup>2</sup>which is a part of the XANES

Define the edge energy under study and the parameter  $S_0^2$ . The later one corresponds to the square of the determinant of overlap integrals for core orbitals calculated with and without core hole.

EDGE	K
S02	1.0

Where  $S_0^2 = 1.0$  because the K-edge was chosen. If the simulation is done with another edge the table 4.1 in the User's Guide of FEFF [3] could be useful.

The **CONTROL** card is used to selectively run parts of FEFF, and the **PRINT** card controls which output files are written. The \* symbol is used for comment the line.

*	pot	xsph	fms	paths	genfmt	ff2chi
CONTROL	1	1	1	1	1	1
PRINT	1	0	0	0	0	0

The **SCF** card controls FEFF's automated self-consistent potential calculations. It is mandatory to use *rfms1* (rscf) which species the radius of the cluster for full multiple scattering during the self-consistency loop. This value is smaller than the value *rfms* used in the FMS card. The **XANES** card is used when a calculation of the near edge structure including the atomic background and absolute energies is desired. The **FMS** card computes full multiple scattering within a sphere of radius *rfms* centered around the absorbing atom. The *rfms* module sums all MS paths within the specified cluster.

SCF	4.0
XANES	4.0
FMS	4.29551

SCF is equal to 4.0 due to it correspond at a sphere which including 2 shells. FMS needs to be larger than SCF. XANES *kmax* must be smaller than FMS for a good results when these cards are used.

The **EXCHANGE** card species the energy dependent exchange correlation potential to be used for the fine structure and for the atomic background, *ixc* is an index specifying the potential model to use for the near edge structure. The **LDOS** card is useful when examining densities of states and if one calculates the LDOS of a crystal in real space, it will always be broadened due to the effect of finite cluster size. **RPATH** card determines the maximum effective (half-path) distance.

*ixc* equal to 0 means to use Hedin-Lundqvist potential. The *emin*, *emax*, *eimag* are energy grid over which to calculate DOS functions.

```

*          emin  emax  eimag
LDOS      -30   20   0.1
EXCHANGE   0
RPATH      0.1

```

The **MULTIPOLE** card species which multipole transitions to include in the calculations. The **POLARIZATION** card species the direction of the electric field of the incident beam, or the main axis of the ellipse, in the case of elliptical polarization. The **ELLIPTICITY** card is used with the POLARIZATION card.

```

MULTIPOLE      2    0
POLARIZATION   1.0  1.1  0.0
ELLIPTICITY    1.0  0.0  0.0 -2.0

```

The MULTIPOLE card defines desired combinations between dipole and quadrupole transitions (electric or magnetic), in our case quadrupole and dipole are included. The POLARIZATION card gives the direction of the electric field in z axis. The ELLIPTICITY is the average over linear polarization in the xy-plane.

The **POTENTIALS** card is followed by a list which assigns a unique potential index to each distinguishable atom. The potential index *ipot* is the index of the potential to be used for the phase shift calculation. The **ATOMS** card species the cartesian coordinates (in angstroms) and unique potential indices of each atom in the cluster, one atom per line.

```

POTENTIALS
*      ipot  z  element
      0  22  Ti
      1  38  Sr
      2  22  Ti
      3   8   o

ATOMS
*      x      y      z      ipot  tag      distance
0.00000  0.00000  0.00000  0    Ti      0.00000  0
1.95250  0.00000  0.00000  3    o      1.95250  1
-1.95250  0.00000  0.00000  3    o      1.95250  2
0.00000  1.95250  0.00000  3    o      1.95250  3
0.00000 -1.95250  0.00000  3    o      1.95250  4
0.00000  0.00000  1.95250  3    o      1.95250  5
0.00000  0.00000 -1.95250  3    o      1.95250  6
1.95250  1.95250  1.95250  1    sr      3.38183  7
-1.95250  1.95250  1.95250  1    sr      3.38183  8

```

*ipot=0* corresponds the absorbing atom must be given unique potential index 0. The list of the atomic position was generated with the *WebAtoms* page [4]. It is an extension of FEFF.



To run FEFF for the first time with a cluster of atoms, it is necessary to run only the POTENTIAL card and ATOMS card<sup>3</sup> in order to create the necessary files to run XANES calculations. On the other hand, if FEFF is run again the output file `xmu.dat` must be erased, because the previous one can generate inconsistencies.

### 2.1.1 SrTiO<sub>3</sub> Crystal

Strontium titanate is an oxide of strontium and titanium with the chemical formula SrTiO<sub>3</sub>. This belongs a space group: Pm3m, cubic. With unit cell constants  $a = 3.9050 \text{ \AA}$  and atomic positions: Sr: 0, 0, 0; Ti: 1/2, 1/2, 1/2; O: 1/2, 1/2, 0; O: 1/2, 0, 1/2; O: 0, 1/2, 1/2. These information was used to run **WebAtoms**.

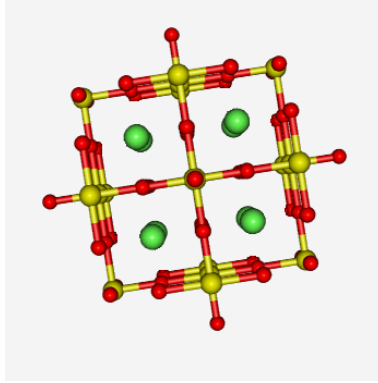


Figure 5: Crystalline structure of SrTiO<sub>3</sub>.

The following plot was developed for the XANES region, where Ti is the element which absorbs the x-ray energy. The MULTIPOLE, POLARIZATION, ELLIPTICITY cards were not considered in the *feff.inp* file (Fig.5).

Now the effect of implementation of MULTIPOLE, POLARIZATION, ELLIPTICITY cards will be discussed.

The blue plot shows two peaks (figure 6.), they correspond to the dipole and quadrupole transitions. This plot was obtained by using only a MULTIPOLE card, and is in good agreement with the results expected from the experiments.

The MULTIPOLE card will make spherical average of the sample without any special orientation of the incident electric field. Adding the ELLIPTICITY and POLARIZATION<sup>4</sup> cards an increase in the quadrupolar transition is observed. This result is in good agreement with the one obtained experimentally by Dr. Martin Tolkiehn which is shown in the red plot (figure 7.) (experimentally the electric field direction is represented by

<sup>3</sup>Without the inclusion of the rest of the parameters

<sup>4</sup>described in section 3.1

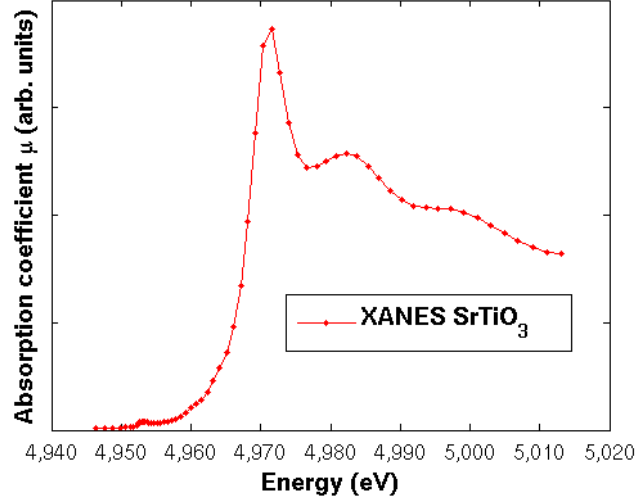


Figure 6: XANES of  $\text{SrTiO}_3$ ; with absorption center in Ti.

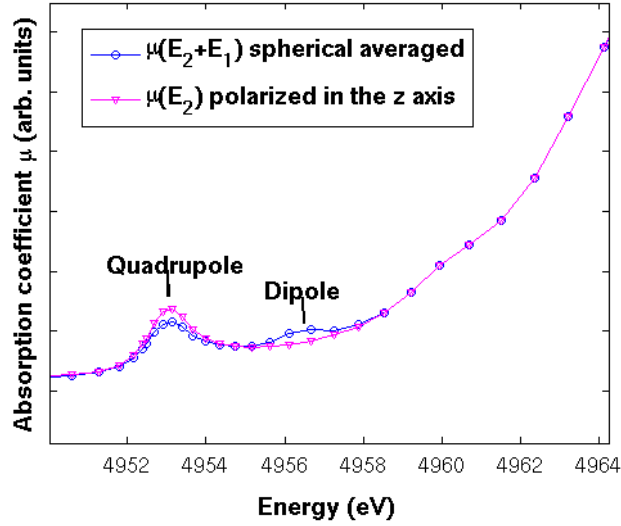


Figure 7: Magenta plot shows the effects caused by choice of the electric field's direction. Blue plot quadrupole and dipole presence by activated MULTIPOLE card.

different Bragg planes of the crystal). The quadrupole transition exhibits an increment when orienting the electric field in the  $z$  direction of the crystal (figure 6.), this is due to the fact that the nature of the quadrupole transitions is dependent on the direction of the electric field.

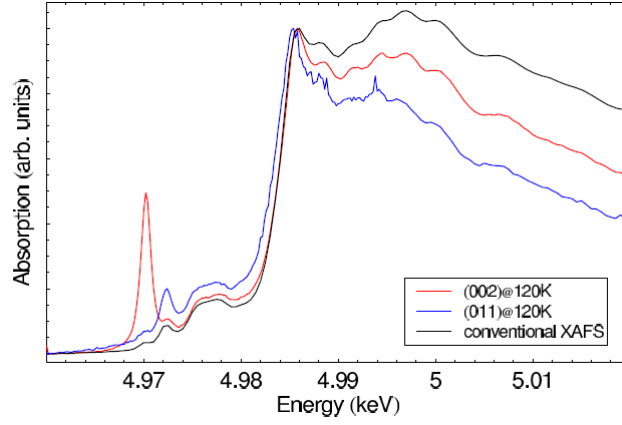


Figure 8: Red plot is the experimental results of the quadrupole increase upon the choice of an electric field direction.

### 2.1.2 $\text{TiO}_2$ Crystal

Titanium dioxide, also known as titanium(IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula  $\text{TiO}_2$ . This compound belongs the space group:  $I 41/a m d$ . With unit cell constants  $a = 3.785 \text{ \AA}$  and atomic positions: Ti: 0.00000, 0.25000, -0.12500; O: 0.00000, 0.25000, 0.08160. This information was used to run **WebAtoms**.

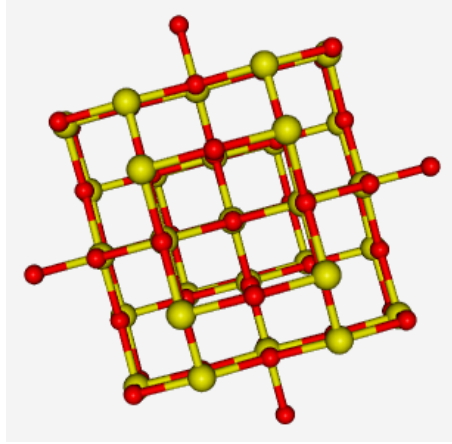


Figure 9: Crystalline structure of  $\text{TiO}_2$ .

The following plot was developed for the XANES region. The MULTIPOLE, POLARIZATION, ELLIPTICITY cards were not considered in the *feff.inp* file. Now the effect of implementation of MULTIPOLE, POLARIZATION, ELLIPTICITY cards will be discussed.

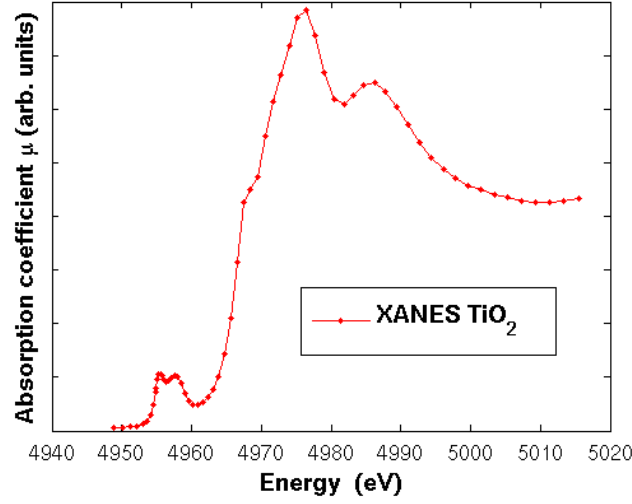


Figure 10: XANES of  $\text{TiO}_2$ ; with absorption center in Ti.

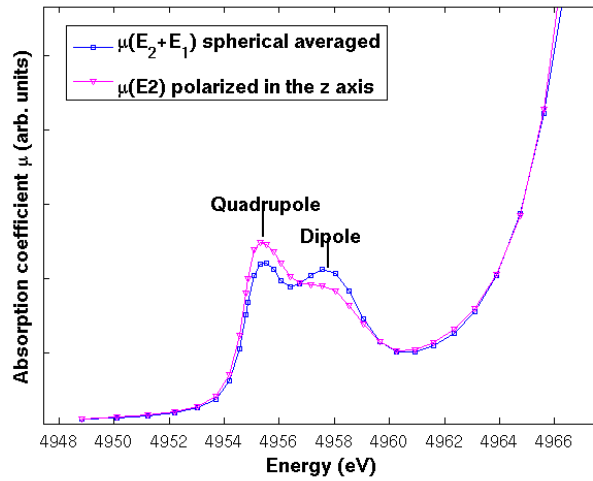


Figure 11: Magenta plot shows the effects caused by choice of the electric field's direction. Blue plot quadrupole and dipole presence by activated MULTIPOLE card.

There one can find the dipole and quadrupole transitions as well. This plot was obtained using only a MULTIPOLE card (Figure 9.) The ELLIPTICITY and POLARIZATION<sup>5</sup> cards were added and, again, we find an increase in the quadrupolar transition (Figure 10). This result is in good agreement with the one obtained experimentally.

<sup>5</sup>They were described in the Section 3.1

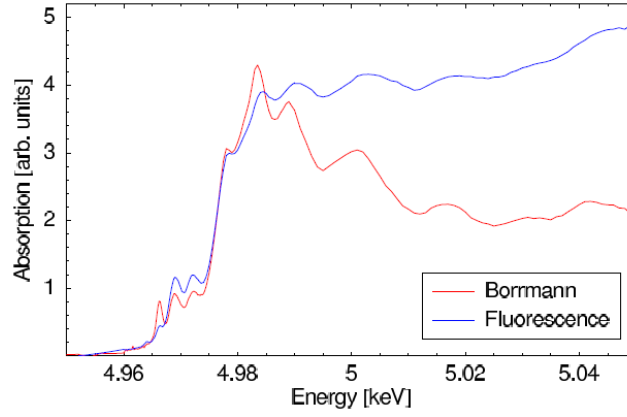


Figure 12: Red plot is the experimental results of the quadrupole increase upon the choice of an electric field direction.

### 3 Conclusions

From this work, it is possible to conclude that FEFF is in fact a suitable program to simulate the pre-edge region of XAFS throw the MULTIPOLE card to simulate the pre-edge transitions under an spherical average and throw the POLARIZATION and ELLIPTICITY cards to obtain a desirable direction for the incident electrical field. The pre-edge region should be simulated under the XANES regime and for that reason the SCF card plays an important role.

From the comparison between experimental plots and theoretical plots it is possible to conclude that the direction of polarization makes the quadrupole transition peak increases for both crystals and this direction is along the z axis of the crystal. This could be seen experimentally when looking at the 002 Brag planes of the crystal  $SrTiO_3$ .

There is an energy shift between the experimental and the theoretical quadrupolar peak simulated by FEFF 9.6 For the  $SrTiO_3$  the energy is 17 eV and energy for  $TiO_2$  it is 13 eV. This shifts could be a calibration problem with the monochromator.

## 4 Acknowledgments

*I would like to thank my supervisors for giving me the opportunity to work in their team and for all the time they dedicated to help me understanding XAFS simulations. I would like to thank also DESY summer student program organizers for making of this summer such a nice experience for my life. An finally but not less important thanks to all desy summer students for all the nice moments.*

## References

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