Modeling of XANES-Spectra with the FEFF-Program

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Abstract. The aim of this project is the calculation of the absorption coefficient $\mu$ of x-ray absorption spectra as a function of energy and a comparison with experimental data. A characteristic fine structure can be found in x-ray absorption spectra (XAS) consisting of the XANES (X-Ray Absorption Near Edge Structure) and the EXAFS (Extended X-Ray Absorption Fine Structure) region. XANES is characterized by multiple scattering and provides information about coordination chemistry and bonding angles of the irradiated sample. The program FEFF 8.4 was used for the calculations of the absorption K-edge spectra. FEFF was generated for ab initio multiple scattering calculations of X-ray Absorption Fine Structure (XAFS) of atom-clusters. The code yields scattering amplitudes, phases and other quantities. We computed $\mu$ at the K-edge of several elements like Ti, S and Fe. For this purpose, clusters of $Na_2SO_4$, $Ba_2TiO_4$, $FeS_2$, $CaSO_4 \cdot 2(H_2O)$ were used, working with several space groups. Some of the calculations are consistent with the results of the experiments, but others show energy shifts in the range of some eV. In summary, the FEFF calculations and the experimental data exhibit similarities as well as deviations. By using trimming parameters, deviations could be eliminated to a certain extent, which will be presented.

1. Introduction
The aim of this project is the calculation of the absorption coefficient $\mu$ of x-ray absorption spectra as a function of energy and a comparison with experimental data. If the experimental data agree well with the simulated data, additional knowledge about the sample could be obtained, or one could predict the characteristics of a sample to a certain extent [7], [8]. X-ray absorption spectroscopy is the measurement of the absorption of x-rays as a function of x-ray energy. In a plot of the absorption coefficient $\mu$ as a function of the x-ray energy the characteristic oscillations above the absorption edge (fig. 2, solid line) known as fine structure can be distinguished.

2. Theory
The fine structure of the XANES region can be explained as follows. An incident x-ray photon is absorbed by an atom (fig. 1, grey) and causes either fluorescence- or the Auger effect. After interaction the photoelectron wave of the emitted photoelectron propagates. It is scattered at the neighbouring atoms (fig. 1, white), which cause multiple scattering. The multiple scattering paths are illustrated with arrows. The outgoing and the backscattered photoelectron wave result in interference, which is observable as fine structure near the absorption edge [1]. Such XANES
Figure 1. The absorber atom (grey) is surrounded by several neighbouring atoms (white) on the first and second coordination shell (dashed lines). The arrows describe the direction of the propagation of the photoelectron wave along the multiple scattering paths [1].

spectra provide information about coordination chemistry, bonding angles, bonding types (e.g. C=C, C≡C, C≡C) and oxidation number of the irradiated sample.

3. FEFF 8.4
FEFF 8.4 [2] is a program for the calculation of multiple scattering in order to simulate XAFS-spectra. The potential geometry of the crystal lattice is approximated by a muffin-tin like shape. FEFF calculates with the Hartree-Fock method self-consistent orbitals to obtain the scattering potentials. Some quantities, which are calculated by FEFF, are the scattering amplitude and the wave number of the photoelectron wave, the phase shift between outgoing and backscattered wave, the absorption coefficient and the multiple scattering paths.

4. Results and comparison with measured data
With the calculated data the absorption coefficient \( \mu \) as a function of the photon energy \( E \) can be plotted for comparison with measured spectra. Fig. 3 shows spectra taken at the sulfur K-edge of \( FeS_2 \) where the number of scatteres has been increased. In Fig. 4 spectra of \( CaSO_4 \cdot 2(H_2O) \) are shown where by the use of a so-called correction card the peak positions could be manipulated. In the diagrams the calculated absorption is normalized to the measured absorption.

For \( FeS_2 \) the calculated K-edge (peak A) of S agrees with the measured data. The fine structure (C’ and D’) above the edge first appears at a cluster size of 21 atoms and the B’ peak first at 103 atoms (not shown here). Calculations with more than 167 atoms did not lead to better conformity with the experiment. The shoulder B of the measured XANES-spectrum is recognizable as B’ in the spectra of the two largest atom clusters. The peaks C’ and D’ are approximately at the same position as in the measured spectrum. However, the heights of the peaks C’ and D’ do not agree with the experiment very well. The proportion of A to C is not verified in the calculations, but the proportion of C to D (reduction of about 1/5) is. With FEFF the relative positions (on the energy scale) of the peaks and the relative absorption maxima can be calculated quite reliable, but the absolute energy values are often inconsistent as can be seen in the figures.

Due to an energy shift of about 11 eV regarding the K-edge position, the computed XANES-spectrum of \( CaSO_4 \cdot 2(H_2O) \) (dashed line) does not agree with the measured data. Energy shifts of the calculated K-edge were frequently observed, independently of the analyzed substance or the element of the absorber atom. In addition, a double peak feature (A’) is noticeable, which
Figure 3. Measured (solid line) [5] and calculated (dashed and dotted) XANES-spectra of the S K-edge of FeS$_2$

Figure 4. Measured (solid line) [5] and calculated (dashed and dotted) XANES-spectra of the S K-edge of CaSO$_4$ (2H$_2$O)

can be generally assessed as a numerical artefact. With correction parameters these deviations could be eliminated to a certain extent (dotted line). In this case the absorption edge was shifted by 10 eV to higher energies and the atomic coordinates were multiplied by the value 0.9 to reduce the interatomic distances, which means that the cluster shrinks to 90% of its original size. Fig. 2 shows spectra taken at the titanium K-edge of Ba$_2$TiO$_4$ where the calculated spectra agree well with the measured data.

In general, there is always a difference between the well known model substance and the measured sample, because a real sample never has the perfect structure of the model and this results in diverse spectra. To sum up, in some cases the computed spectra verify the experiment without further manipulations and in other cases correction parameters are necessary to reduce differences to the measured spectra to a certain extent. Thus, FEFF might not be able to predict characteristics of a sample from the environment.

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