Availability of the FEFF Simulations to K-edge XANES spectra in the soft X-ray region

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Abstract

Availability of the FEFF simulations to K-edge X-ray absorption near edge structure (XANES) spectra of the third-row elements has been investigated. The FEFF simulations well reproduced the spectra from simple substances (Al, Mg, Si, P and S), but did not always reproduce those from chemical compounds containing the third row elements. The FEFF simulation has a tendency to underestimate the white line intensity of the XANES spectra in these compounds. This was because the potential by the effect of the core hole was not reproduced well. This situation is much improved by the Z+1 approach, in which the central atom is replaced by the atom with the atomic number larger by one.

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1. Introduction

X-ray absorption near-edge structure (XANES) spectra are well-known to contain information of the local atomic and electronic structures around an X-ray absorbing atom. Many theoretical approaches to XANES spectral analyses have been performed. They can be mainly classified to three groups; those based on the molecular orbital (MO) method, density functional theory (DFT), and multiple-scattering (MS) method. Among them, the MS method is the most popularly used. It is also applied to the analysis of the spectra in extended X-ray absorption fine structure (EXAFS) region.

The FEFF program code is based on the real-space full multiple-scattering (FMS) theory, which has been developed by Rehr's group, and brushed up to a sophisticated program with quick and easy calculations [1, 2]. The FEFF program has been popularly used not only for EXAFS analysis, but also for XANES spectral analysis, especially from those of heavy elements.

In fact, the FEFF well reproduces XANES spectra quite satisfactorily [3]. It was also applied to those of lighter elements. Some reproduce observed spectra well [4], but some are far from the observed ones. Most critical problem must be the muffin tin potential and one electron approximation. The core hole in a FEFF simulation is sometimes too much screened. One possible way to mitigate this problem is the "Z+1 approach", in which the input atomic number of the X-ray absorbing atom is replaced by Z+1. Although this approach is not physically sound since the core hole is already taken into account in the FEFF program, Prado and Frank demonstrated that this approach works effectively for Na K-edge XANES [5]. However there has been no extensive study to verify how much the FEFF simulation works for the light elements.

In this paper, we have studied K-edge XANES spectra composed of the third row elements in the soft X-ray region, which is the available energy region at BL-10, in order to know the reliability of the FEFF simulation for lighter elements.

2. Experimental

We have chosen simple substances and several compounds containing the third row elements; Mg and Al metals, crystalline Si, black phosphorus, α-S_8, crystalline $LaAlO_3$, 6H-SiC and InP, powders of NaF, NaCl, Na_2SO_4, MgO, $Mg(OH)_2$, MgF_2, $MgCl_2$, LTA Zeolite (Zeolite), α-Quartz, α-Cristobalite, AlN, β-Si_3N_4, KH_2PO_4, $FePO_4$, ZnS, $CaSO_4$, Na_2SO_4, K_2SO_4, $NaClO_4$, KCl, $CuCl_2$. Most of K-edge XANES spectra of these

samples have been published elsewhere, but we measured their spectra again to discuss the spectra with same energy resolution and calibration. Observed results of other works were used for the spectra of black phosphorus (black P), NaF, $Mg(OH)_2$, MgF_2, AlN, $NaClO_4$ and α-Cristobalite [5-11].

The experiments were performed at BL-10 of the SR center, Ritsumeikan University. It consists of a pre-focusing Ni toroidal mirror, a Golovchenko-type double-crystal monochromator, an I_0 monitor of a Cu mesh, and a sample chamber. The available photon energy covers from about 1000 to 4000 eV by exchanging a pair of several monochromatizing crystals, such as beryl($10\bar{1}0$), KTP(011), InSb(111), and Ge(111). Energy calibration was performed as follows. For the Na K-edge, the white line of NaCl was calibrated at 1076.6 eV [12]. For Mg, Al, and Si K-edges, the energies at the first maximum of the first derivative of Mg metal, Al metal, and Si wafer were calibrated to 1303.0 eV[13], 1560.0 eV[14], and 1839.0 eV[15], respectively. For P, S and Cl K-edges, the white lines of $FePO_4$, K_2SO_4 and NaCl were calibrated at 2153.0 eV[16], 2481.7 eV [17] and 2828.4 eV [17], respectively. All the observed spectra were background-subtracted and normalized by the edge jump height, if not specified.

3. Calculation

The *ab-initio* FEFF-8.4 program [18] was used in all XANES simulations in this paper. In the FEFF program, there are only limited input parameters; the type of the exchange potential, the ranges of FMS and self-consistent field (SCF) muffin tin potential calculations, and the maximum angular quantum number, and the atomic numbers of the X-ray absorbing central atom and surrounding atoms, and their coordinates. We have tested several exchange potentials, and adopted Hedin-Lundqvist potential, since no significant differences were obtained. An amplitude reduction factor S_o^2 was set to 1.0, More than 200 atoms and more than 30 atoms are taken into account for FMS and SCF calculations, respectively.

As described above, the Z+1 approach is to replace the atomic number Z of the central atom by the Z+1 atom in an FEFF input file. If the Z+1 approach applied to Al K-edge XANES, the Al atom of a central atom is replaced by a Si atom. It appears to be same as “equivalent core approximation [19]”, but if not specified with a NOHOLE card in the FEFF input file, the effect of the core hole is already taken into consideration. Thus, the Z+1 approach is not theoretically based in the FEFF program.

The purpose of the Z+1 approach is to enhance the core hole potential more than the conventional FEFF program. The conventional FEFF calculation will be called hereafter as the Z approach to discriminate from the Z+1 approach.

Energies of simulated spectra were shifted so as to fit each simulated curve to the corresponding observed spectra.

4. Results and discussion

4.1 Effect of changing a core potential

The effect of changing a core potential in the FEFF simulation is clearly demonstrated in Figure 1, which shows the Al K-edge XANES spectral change of α-Al_2O_3 by replacing the input atomic number of the central atom, Z (13: Al, labeled 'Z' in Figure 1) to Z-1 (12: Mg, labeled 'Z-1'), and Z+1 (14: Si, labeled 'Z+1') with a core hole (a) and without a core hole (b). Close resemblance between the simulated spectra of the Z approach with a core hole and that of the Z+1 approach without a core hole means that the equivalent core approximation is justified. At lower Z, the first absorption band is diffused, but with increase of Z, the band is narrowed. Increasing Z means the increase of a core potential which enhances the intensities of the lower features, especially that of the white line. This is a typical result for an insulator, such as α-Al_2O_3.

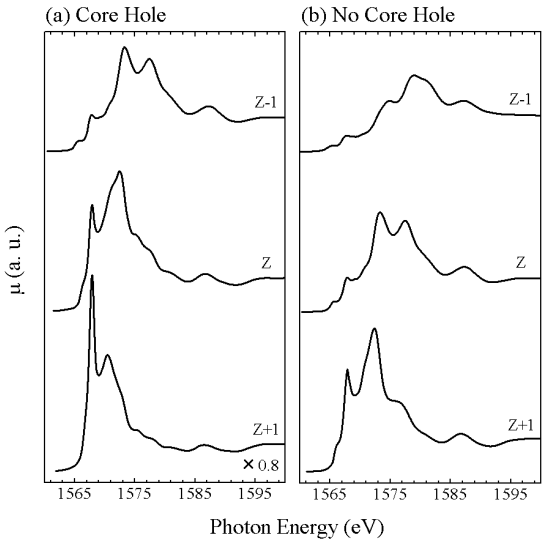

Figure 1. Effect of changing a core potential for simulated Al K-edge XANES spectra from α–Al_2O_3 with a core hole (a) and without core hole (b). For comparison, simulated spectra were shifted by 261.4 (a) and 258.3 eV (b) for 'Z−1', 3.5 (a) and 2.8 eV (b) for 'Z', and −274.4 (a) and −275.1 eV (b) for 'Z+1' approaches respectively.

4.2 K-edge XANES spectra of simple substances

Figure 2 shows experimental and theoretical results for K-edge XANES spectra from simple substances of the third row elements. For Mg and Al metals, the FEFF simulations with the Z approach are in good agreement with the observed spectra, better than the Z+1 approach. These results suggest that the conventional FEFF simulation well reproduces spectra of metals, in which the core hole is highly-screened. For Si (semiconductor) and P (semi-metal), simulated spectra with the Z approach are in agreement with the observed spectra, comparable with the Z+1 approach. α-S_8 is a typical molecular compound and its S K-edge XANES spectrum shows a strong white line, which might be ascribed to the transition to π^* like orbital. In general, the FEFF simulation does not reproduce π^* transitions, located below the vacuum level. In fact, the Z approach does not reproduce the observed one. Simulation with the Z+1 approach is even worse; the first peak is more suppressed in the Z+1 approach. This result seems contradicted to the general tendency of the effect of the core potential. In general, the Z approach works well for K-edge XANES simulation of the simple substances of the third row elements.

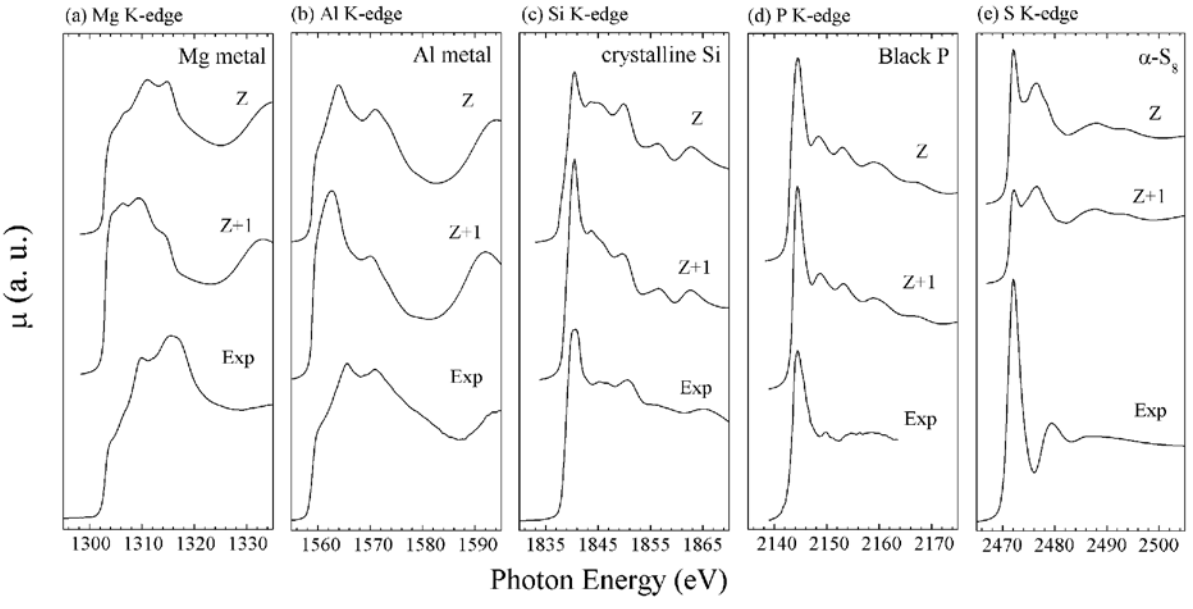

Figure 2. K-edge XANES spectra from simple substances: comparison between observed ('Exp') and simulated spectra using the Z approach ('Z') and Z+1 approach ('Z+1'). Observed spectrum of black phosphorus ('Black P') was cited from reference [6]. Simulated spectra were shifted so as to fit the corresponding observed spectra.

4.3 K-edge XANES spectra of oxides

Figure 3 shows XANES spectra from typical oxides of the third row elements, all of which exhibit sharp white lines. The Z approach fails to give intense white line features, especially in the lower elements. This situation is almost overcome by using the Z+1 approach. Simulated XANES spectra from MgO and α-Al_2O_3 are surprisingly in good agreement with the observed ones. These oxides are typical insulators and the core holes generated by X-ray absorption are poorly screened. In the FEFF program, the core hole potential of these insulators seem underestimated and as a result of it, the white line peak intensity is much suppressed in the Z approach. This situation is improved with the Z+1 approach by enhancing the core hole potential.

For higher Z elements, the increase of the core potential does not affect the simulated results so much. Conventional FEFF simulation gives tolerable spectra. Disagreement of the Si K-edge XANES spectrum from α-Quartz might be due to different reason, as described below.

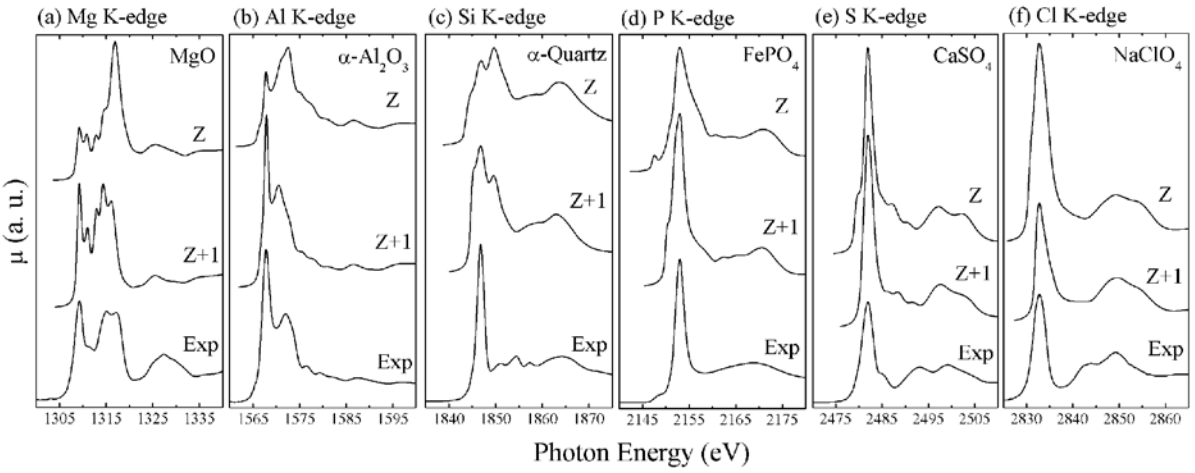

Figure 3. K-edge XANES spectra from typical oxides: comparison between observed and simulated spectra. Observed spectrum of $NaClO_4$ is cited from reference [10]. Simulated spectra are shifted so as to fit the corresponding observed spectra.

4.4 K-edge XANES spectra of other compounds

Three typical compounds containing Na, Mg, Al, Si, P, S and Cl atoms are chosen and their K-edge XANES spectra are compared with simulations with the Z and Z+1 approaches, as shown in Figure 4. The effect of changing a core potential is more

significant for the lower Z elements and there is no big difference for the higher Z elements. In fact, the Z and Z+1 approaches give almost same simulated curves for Cl K-edge XANES. This indicates that the larger Z has more electrons, mitigating the core hole effect. But, in general, the Z+1 approach reproduce the observed spectra, better than the Z approach for these oxides.

It is intriguing why the simulated spectrum from K_2SO_4 is different from that from Na_2SO_4, in spite of the same nearest neighbor structure, SO_4. This might come from a specific higher order structure of K_2SO_4, in which the atomic arrangement of S-O-K is almost linear and the multiple scattering along this line is highly enhanced and causes the doublet white line. However, the observed spectrum shows just a single sharp white line. This might be either due to a wrong crystal structure, or due to overestimation of the multiple scattering.

In Figure 4, Si K-edge XANES simulation well reproduces the spectrum of 6H-SiC, but is quite different from that of β-Si_3N_4, although both are typical insulators. The situation must be same as that for α-Quartz. Many works have been published for spectral analysis of SiO_2 [11, 20, 21]. To examine why such discrepancy comes, we studied the cluster size dependences of α-Cristobalite, α-Quartz and β-Si_3N_4, as shown in Figure 5. Both α-Cristobalite and α-Quartz are SiO_2 with the same nearest structure, surrounded by four O atoms. Only difference is the Si-O-Si angle, which is 146.5° and 143° for α-Cristobalite and α-Quartz, respectively. By increasing the cluster size more than 53 atoms for α-Quartz, the first band is broadened with a side band, which is clearly due to the multiple scattering effect. On the other hand, no side band appears for α-Cristobalite. Such a drastic difference of the simulations comes from a small difference of the Si-O-Si angle. The observed spectra of these two SiO_2 polymorphs are quite similar to each other, showing a sharp white line. Similar situation happens for β-Si_3N_4. Simulation with a cluster smaller than the second nearest neighbor atoms gives better agreement with the observed one, while extra peak appears by taking account of surrounding atoms further. These results suggest that the FEFF simulation has a tendency to overestimate the multiple scattering for some cases.

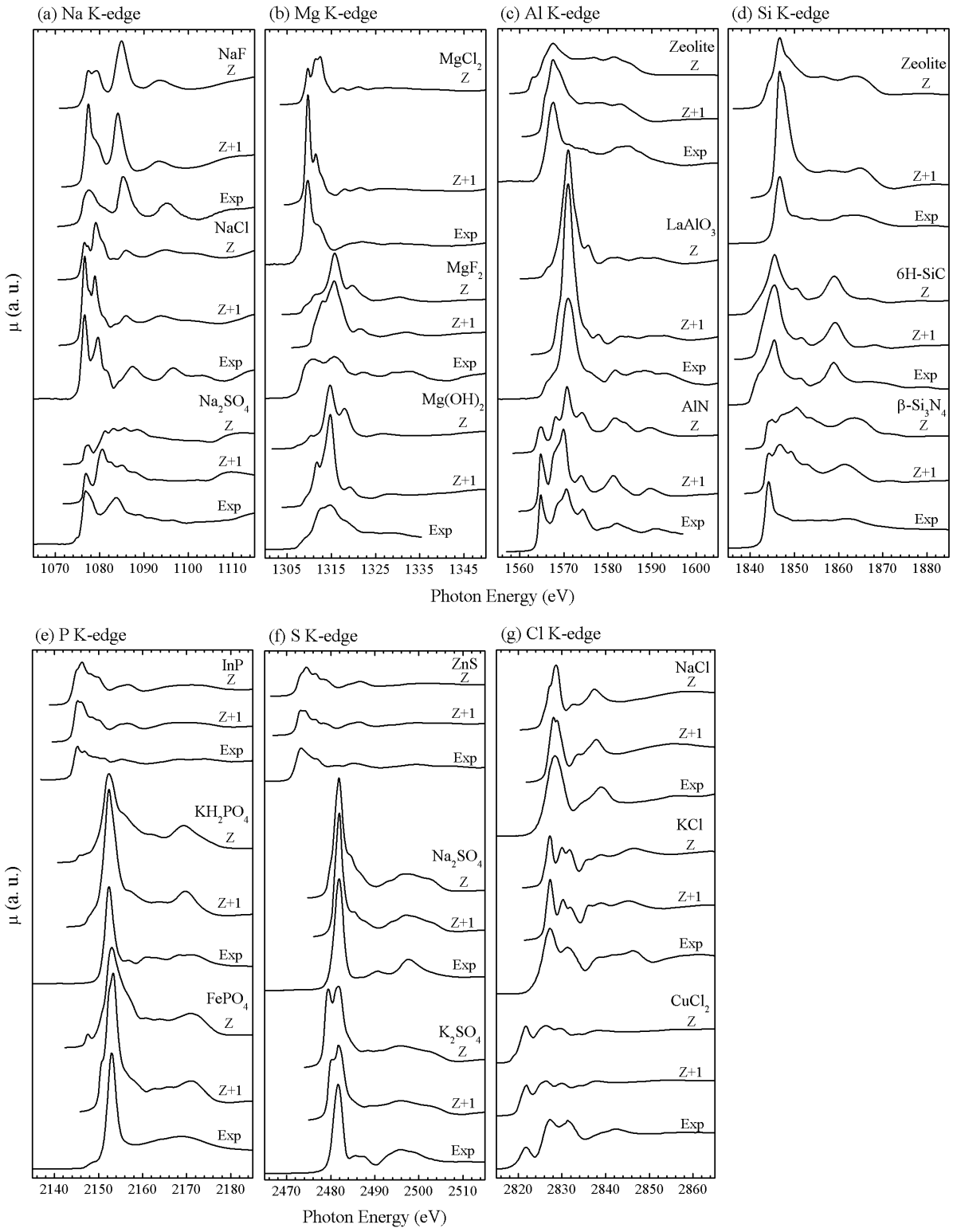

Figure 4. K-edge XANES spectra from compounds containing the third row elements: Comparison of observed and simulated spectra. Observed spectra of NaF, $Mg(OH)_2$, MgF_2, and AlN are cited from reference [5, 7, 8, 9] respectively. Simulated spectra are shifted so as to fit the corresponding observed spectra.

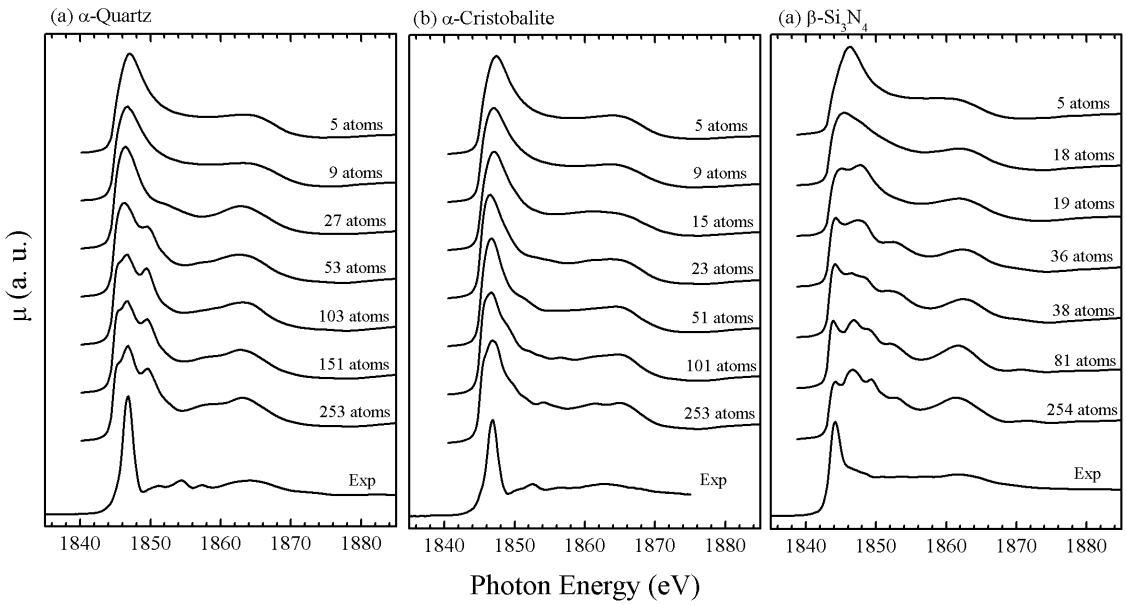

Figure 5. Cluster size effect to the Si K-edge XANES simulations with the Z+1 approach. Observed spectrum of α-Cristobalite is cited from reference [11].

5. Summary

We investigated the applicability of the FEFF simulations for K-edge XANES spectra from the third row elements. The Z+1 approach generally improves the spectral simulation, meaning that larger core potential is necessary to obtain better results.

This tendency is mitigated at larger Z with more electrons, but the Z+1 approach still works well. Some simulated spectra do not agree with observed ones due to overestimation of multiple scattering. Some idea to reduce the effect of multiple scattering might be necessary for further improvement of the FEFF simulation.

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