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# Verification of the FEFF simulations to K-edge XANES spectra of the third row elements

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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 reproduce the spectra from simple substances (Al, Mg, Si, P and S) well, but do 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 situation is much improved by the  $Z + 1$  approach, in which the central atom is replaced by an atom with the atomic number larger by one.

## 1. Introduction

X-ray absorption near-edge structure (XANES) spectra are widely 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 into 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 popular. It has also been applied to the analysis of the spectra in the 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 evolved to a sophisticated program with quick and easy calculations [1, 2]. The FEFF program has been widely used not only for EXAFS analysis, but also for XANES spectral analysis, especially from those of heavy elements.

In fact, the FEFF reproduces XANES spectra quite satisfactorily [3]. It was also applied to those of lighter elements. Some reproduce the observed spectra well [4], but some are far from the observed ones. The most critical problem might be the muffin tin potential and one electron approximation. The core hole in a FEFF simulation is sometimes overly screened. One possible way to mitigate this problem is the ' $Z + 1$  approach', in which the input atomic number  $Z$  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 and investigated the reliability of the FEFF simulation in these compounds.

## 2. Experimental details

We have chosen simple substances and several compounds containing the third row elements; Mg and Al metals, crystalline Si, black phosphorus,  $\alpha$ -S<sub>8</sub>, crystalline LaAlO<sub>3</sub>, 6H-SiC and InP, powders of NaF, NaCl, Na<sub>2</sub>SO<sub>4</sub>, MgO, Mg(OH)<sub>2</sub>, MgF<sub>2</sub>, MgCl<sub>2</sub>, LTA zeolite (zeolite),  $\alpha$ -quartz,  $\alpha$ -cristobalite, AlN,  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>, FePO<sub>4</sub>, ZnS, CaSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, NaClO<sub>4</sub>, KCl and CuCl<sub>2</sub>. Most of the K-edge XANES spectra of these samples have been published elsewhere, but we measured their spectra again to obtain spectra with the same energy resolution and calibration. The observed results in other works were used for the spectra of black phosphorus (black P), NaF, Mg(OH)<sub>2</sub>, MgF<sub>2</sub>, AlN, NaClO<sub>4</sub> and  $\alpha$ -cristobalite [5–11].

The experiments were performed at BL-10 of the SR center, Ritsumeikan University. The instrumentation 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(1010), 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 the 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 the P, S and Cl K-edges, the white lines of FePO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> 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, 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 the Hedin–Lundqvist potential, since no significant differences were obtained. An amplitude reduction factor  $S_0^2$  was set to 1.0. More than 200 atoms and more than 30 atoms are taken into account for the FMS and SCF calculations, respectively.

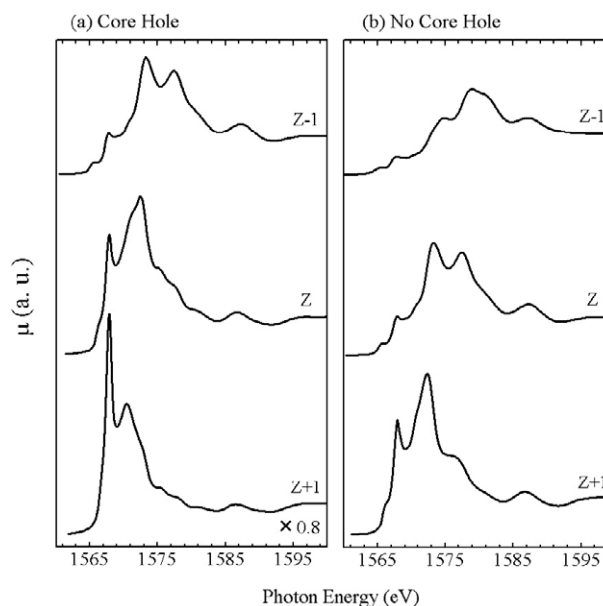
As described above, the  $Z + 1$  approach is to replace the atomic number  $Z$  of the central atom by the  $Z + 1$  atom in the FEFF input file. If the  $Z + 1$  approach is applied to the Al K-edge XANES, the Al atom of a central atom is replaced by a Si atom. It appears to be the same as the ‘equivalent 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 the  $Z$  approach to discriminate it 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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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). The close resemblance between the simulated spectra of the  $Z$  approach with a core hole and that

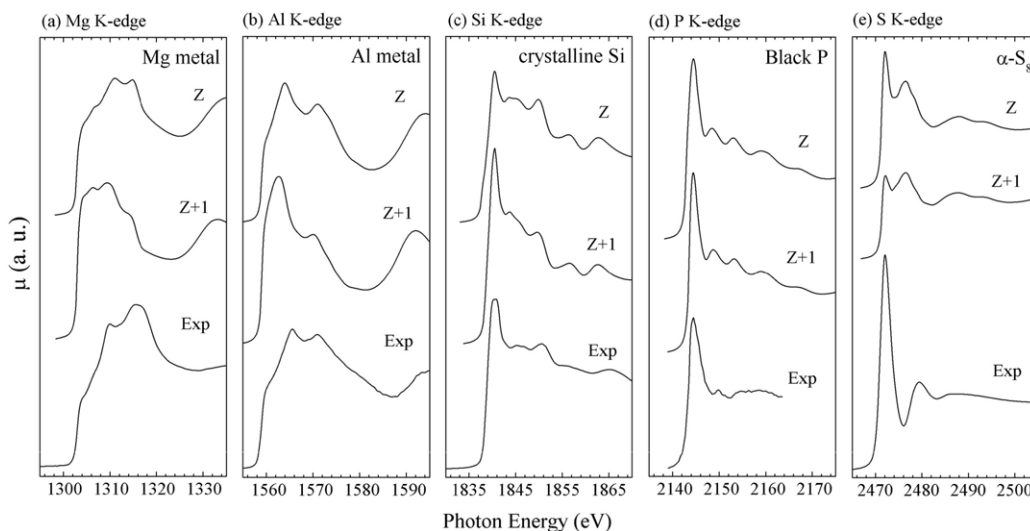


**Figure 1.** Effect of changing a core potential for the simulated Al K-edge XANES spectra from  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with a core hole (a) and without core hole (b). For comparison, simulated spectra are shifted by 261.4 (a) and 258.3 eV (b) for ‘ $Z - 1$ ’, 3.5 (a) and 2.8 eV (b) for ‘ $Z$ ’, and  $-274.4$  (a) and  $-275.1$  eV (b) for ‘ $Z + 1$ ’ approaches, respectively.

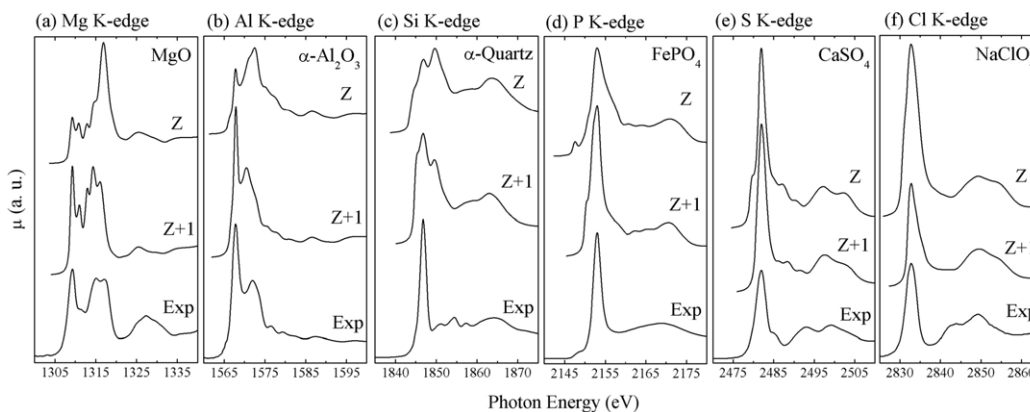
of the  $Z + 1$  approach without a core hole means that the equivalent core approximation is justified. At lower  $Z$ , the first absorption band is diffused, but with an increase of  $Z$ , the band is narrowed. Increasing  $Z$  means the increase of a core potential which enhances the intensities of the lower features, especially that of the white line. This is a typical result for an insulator, such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

### 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, and better than the  $Z + 1$  approach. These results suggest that the conventional FEFF simulation reproduces the spectra well for metals in which the core hole is highly screened. For Si (semiconductor) and P (semi-metal), the simulated spectra with the  $Z$  approach are in agreement with the observed spectra, comparable with the  $Z + 1$  approach.  $\alpha$ -S<sub>8</sub> 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  $\pi^*$  like orbital. In general, the FEFF simulation does not reproduce  $\pi^*$  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. This result seems contradictory to the general tendency of the effect of the core potential. In general, the  $Z$  approach works well for the K-edge XANES simulation of 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'). The observed spectrum of black phosphorus ('Black P') is cited from [6]. Simulated spectra are shifted so as to fit the corresponding observed spectra. The shifted energy values are listed in table 1.



**Figure 3.** K-edge XANES spectra from typical oxides: comparison between observed and simulated spectra. (a) MgO, (b)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (c)  $\alpha$ -quartz, (d) FePO<sub>4</sub> and (e) CaSO<sub>4</sub>, (f) NaClO<sub>4</sub>. The observed spectrum of NaClO<sub>4</sub> is cited from [10]. Simulated spectra are shifted so as to fit the corresponding observed spectra. The shifted energy values are listed in table 1.

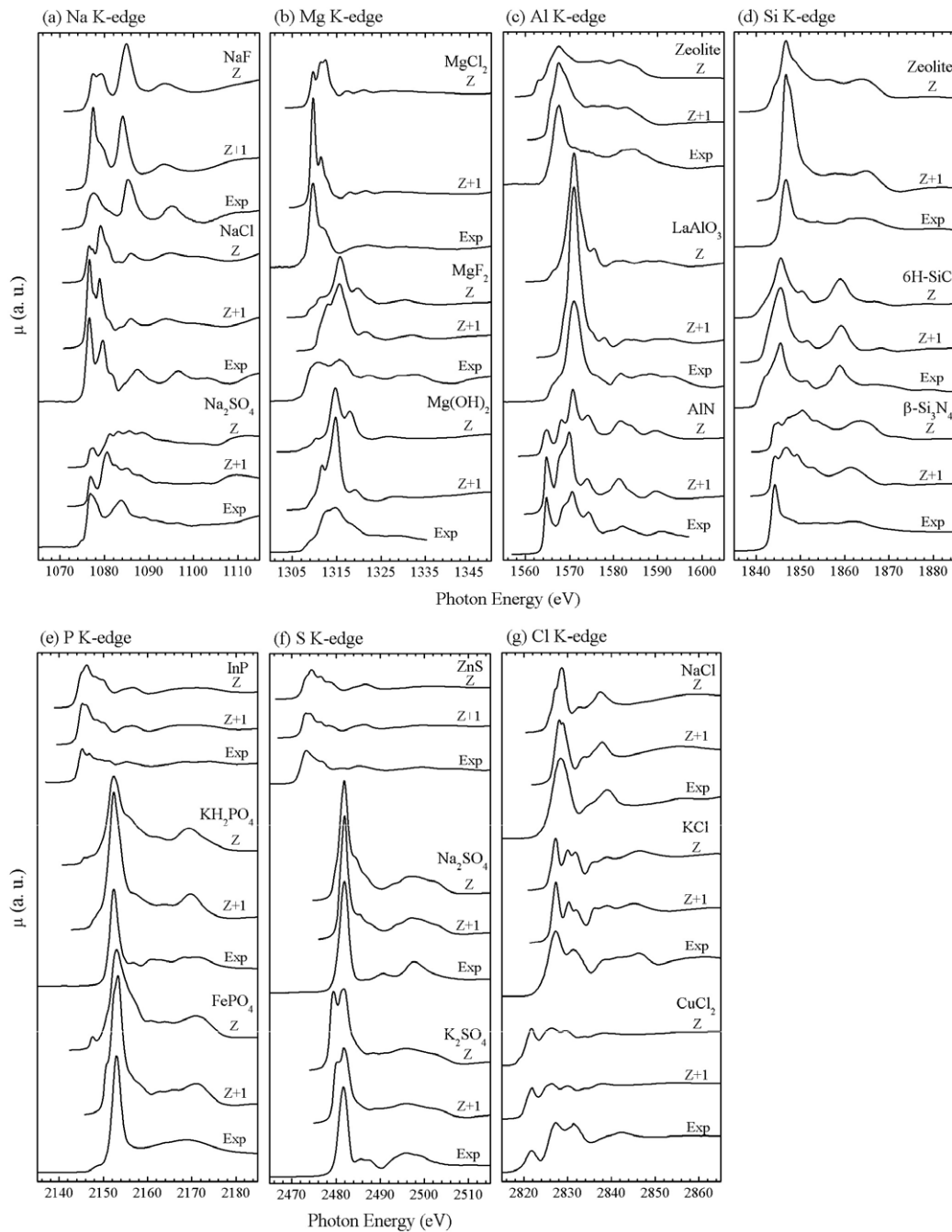
#### 4.3. K-edge XANES spectra of oxides

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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are in surprisingly 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 potentials of these insulators seem to be underestimated and as a result of it, the white line peak intensity is overly 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 as much. Conventional FEFF simulation gives tolerable spectra. The disagreement of the Si K-edge XANES spectrum from  $\alpha$ -quartz might be due to a different reason, as described below.

#### 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 using 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 not a great difference for the higher Z elements. In fact, the Z and Z + 1 approaches give almost the 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 reproduces the observed spectra better than the Z approach for these oxides. It is intriguing why the simulated spectrum from K<sub>2</sub>SO<sub>4</sub> is different from that of Na<sub>2</sub>SO<sub>4</sub>, in spite of the same nearest neighbor structure, SO<sub>4</sub>. This might be due to the specific higher order structure of K<sub>2</sub>SO<sub>4</sub>, in which the atomic arrangement of S–O–K is almost linear and the multiple scattering along this line is highly enhanced, causing a doublet white line. However, the observed spectrum shows just a single



**Figure 4.** K-edge XANES spectra from compounds containing the third row elements: comparison of observed and simulated spectra. (a) Na K-edge (NaF, NaCl, Na<sub>2</sub>SO<sub>4</sub>) (b) Mg K-edge (MgF<sub>2</sub>, MgCl<sub>2</sub>, Mg(OH)<sub>2</sub>), (c) Al K-edge (Zeolite-Al, LaAlO<sub>3</sub>, AlN), (d) Si K-edge (zeolite-Si, 6H-SiC,  $\beta$ -Si<sub>3</sub>N<sub>4</sub>), (e) P K-edge (InP, KH<sub>2</sub>PO<sub>4</sub>, FePO<sub>4</sub>), (f) S K-edge (ZnS, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>), (g) Cl K-edge (NaCl, KCl, CuCl<sub>2</sub>). The observed spectra of NaF, Mg(OH)<sub>2</sub>, MgF<sub>2</sub>, and AlN are cited from [5, 7–9], respectively. Simulated spectra are shifted so as to fit the corresponding observed spectra. The shifted energy values are listed in table 1.

sharp white line. This might be either due to a wrong crystal structure, or due to overestimation of the multiple scattering.

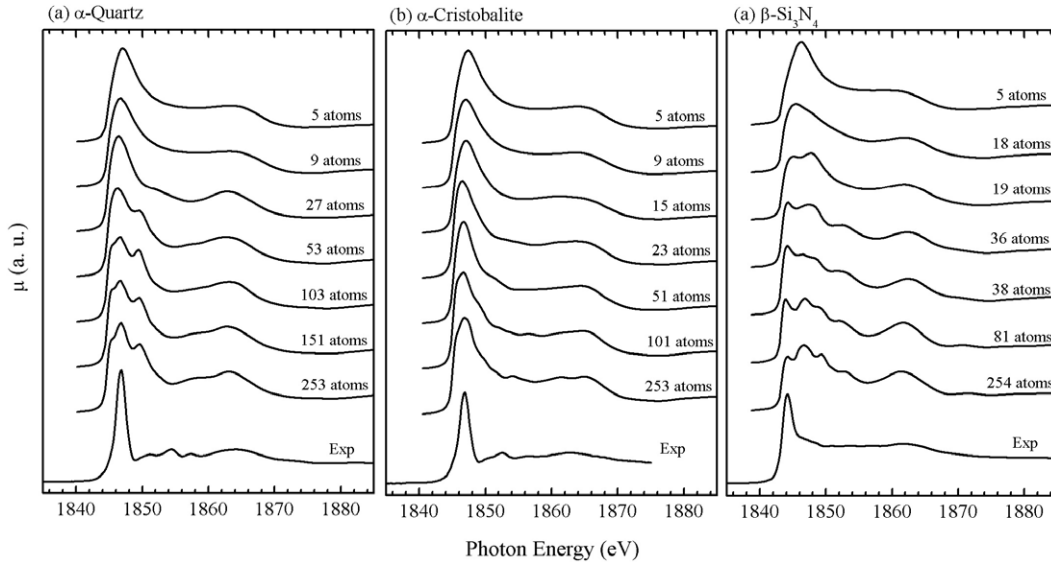
#### 4.5. Calculated energies

As described above, each spectrum is shifted so as to get the best agreement with the observed one of the corresponding material. The energy ‘zero’ is referred to as the muffin tin potential  $V_0 < 0$  below the vacuum level and is not always the same for all compounds. Even considering this situation,

the shifted energies are fairly variable. Although it is difficult to derive a systematic energy shift, we can find some general tendencies. First, the energy shift of each simple substance (if they are) is generally smaller, compared with those of chemical compounds. Second, the energy shift is larger for the compounds associated with a large charge transfer, such as the S of SO<sub>4</sub> and the Cl of ClO<sub>4</sub>. This might reflect a large shift of the  $V_0$  value. At present, it is difficult to say something from the absolute calculated energies.

**Table 1.** Shifted energies of simulated spectra for simple substances and chemical compounds of the third row elements in figures 2–4. In the ‘relative  $Z + 1$ ’ columns, relative values of  $Z + 1$  to standard materials in the first row of each element are listed.

Element	Material	Z (eV)	Z + 1 (eV)	Relative Z + 1 (eV)	Element	Material	Z (eV)	Z + 1 (eV)	Relative Z + 1 (eV)
Na	NaF	0.0	-227.8	0.0	P	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	2.8	-299.7	5.0
	NaCl	0.5	-227.8	0.0		$\alpha$ -quartz	2.7	-298.1	6.6
	Na <sub>2</sub> SO <sub>4</sub>	1.6	-226.9	0.9		Black P	-0.1	-325.1	0.0
Mg	Mg metal	-1.8	-260.3	0.0	InP	0.1	-325.0	0.1	
	Mg(OH) <sub>2</sub>	2.2	-254.2	6.1	KH <sub>2</sub> PO <sub>4</sub>	1.7	-321.9	3.2	
	MgO	2.5	-255.7	4.6	FePO <sub>4</sub>	3.6	-318.7	6.4	
	MgF <sub>2</sub>	4.2	-251.9	8.4	S	$\alpha$ -S <sub>8</sub>	3.2	-346.0	0.0
	MgCl <sub>2</sub>	4.8	-253.0	7.3		ZnS	0.6	-348.1	-2.1
	Al	Al metal	-2.7	-281.2		0.0	K <sub>2</sub> SO <sub>4</sub>	8.5	-339.8
Zeolite		-0.1	-275.8	5.4	CaSO <sub>4</sub>	8.7	-339.0	7.0	
AlN		0.7	-276.5	4.7	Na <sub>2</sub> SO <sub>4</sub>	9.9	-338.0	8.0	
LaAlO <sub>3</sub>		0.0	-275.0	6.2	Cl	NaCl	6.6	-377.8	0.0
Si	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3.5	-274.5	6.7		KCl	6.7	-378.5	-0.7
	Crystalline Si	-3.1	-304.7	0.0		CuCl <sub>2</sub>	0.9	-383.5	-5.7
	6H-SiC	-2.0	-302.3	2.4		NaClO <sub>4</sub>	12.2	-372.1	5.7
	Zeolite	-0.5	-298.7	6.0					

**Figure 5.** Cluster size effect to the Si K-edge XANES simulations with the  $Z + 1$  approach. (a)  $\alpha$ -quartz, (b)  $\alpha$ -cristobalite and (c)  $\beta$ -Si<sub>3</sub>N<sub>4</sub>. The observed spectrum of  $\alpha$ -cristobalite is cited from [11]. Simulated spectra were shifted by  $-298.1$  (a),  $-297.8$  (b),  $-299.7$  eV (c), respectively.

#### 4.6. Effect of cluster size

In figure 4(d), the Si K-edge XANES simulation reproduces the spectrum of 6H-SiC well, but does not reproduce that of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, although both are typical insulators. The situation must be the same as that for  $\alpha$ -quartz. Many works have been published for spectral analysis of SiO<sub>2</sub> [11, 20, 21]. To examine why such a discrepancy occurs, we studied the cluster size dependences of  $\alpha$ -cristobalite,  $\alpha$ -quartz and  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, as shown in figure 5. Both  $\alpha$ -cristobalite and  $\alpha$ -quartz are SiO<sub>2</sub> with the same nearest structure, surrounded by four O atoms. The only difference is the Si–O–Si angle, which is 146.5° and 143° for  $\alpha$ -cristobalite and  $\alpha$ -quartz, respectively. By increasing the cluster size to more than 53 atoms for  $\alpha$ -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  $\alpha$ -cristobalite. Such a drastic difference in the simulations comes from a small difference of the Si–O–Si angle. The observed spectra of these two SiO<sub>2</sub> polymorphs are quite similar to each other, showing a sharp white line. A similar situation happens for  $\beta$ -Si<sub>3</sub>N<sub>4</sub>. A simulation with a cluster smaller than the second nearest neighbor atoms gives better agreement with the observed one, while an extra peak appears when taking account of further surrounding atoms. These results suggest that the FEFF simulation has a tendency to overestimate the multiple scattering in some cases.

## 5. Summary

We investigated the applicability of the FEFF simulations for K-edge XANES spectra of the third row elements. The  $Z + 1$

approach generally improves the spectral simulation, meaning that a 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 the observed ones due to overestimation of the multiple scattering. Some new ideas to reduce the effect of multiple scattering might be necessary for further improvement of the FEFF simulation.

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