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Oxygen K x-ray-absorption near-edge structure of alkaline-earth-metal and 3d-transition-metal oxides

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The oxygen K x-ray-absorption near-edge structure of alkaline-earth-metal and 3d-transition-metal oxides has been measured by means of the photoelectric yield method. The short-range order multiple scattering calculations for O K-edge spectra of CaO and TiO have also been performed. From comparison of the observed spectra with the calculated results, the effective cation charge is estimated with $q=0.7$ for CaO. In the case of 3d-transition-metal oxides, the calculated results are sensitive not only to the cation charge but also to the 3d electron number (d). For TiO, the effective cation charge and the number of 3d electrons are estimated with $q=0.7-0.8$ and $d=1.8-2.0$.

I. INTRODUCTION

In general, x-ray-absorption spectra (XAS) are classified into two regions, namely, x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS). XANES spectrum means the structure in the energy region from the absorption edge to about 30 eV above the edge, while EXAFS spectrum is extended about 1000 eV above the edge. We can get the information about the interatomic distances and coordination numbers around the absorbing atom from EXAFS. On the other hand, we can obtain the information about the geometric and the electronic structures from XANES. The distinction between them is in the scattering strength of the ejected photoelectrons.

It is well known that the XANES spectra reflect the projected unoccupied density of states restricted by the dipole selection rule. This traditional picture of XANES is well applied for metallic compounds as studied by Müller *et al.*[1] Another method of analyses is also widely used based on the multiple-scattering (MS) approach;[2–5] the ejected photoelectrons are strongly scattered by valence electrons. Therefore XANES spectra give us the information on the chemical bonding effect and the effective charge density around the x-ray-absorbing atom. For example, we have measured the fluorine K XANES spectra of alkali[6] and alkaline-earth fluorides[7] in high resolution and analyzed the spectra by use of the short-range-order full-multiple-scattering theory. By comparing the observed spectra with the calculated results, we can estimate the effective cation and anion charge distribution.

A considerable amount of work has been carried out to clarify the electronic structure of various metal oxides. For example, Lindner *et al.*[8] have measured both the Mg and O K-edge spectra of MgO with the aid of the transmission mode electron-energy-loss spectra. They have analyzed the spectra by the application of the MS theory to the cluster model and have shown that the observed near-edge structures are in good agreement with both the structures calculated by the MS theory and the symmetry-projected local density of states derived from the band calculation. However, they have given no discussion on the charge density of this compound from the analysis of the XANES spectra. They tentatively interpret the small peak which was observed at the onset of the absorption edge, but which did not appear in the calculated spectra at all, to be a core exciton. Norman *et al.*[9] calculated the cation K-edge spectra for a series of crystalline oxides of the 3d transition metals from Ca to Cu by using the one-electron multiple-scattering computational scheme and compared them with their experimental data. Their overall agreement between theory and experiment is satisfactory. The cation K-edge XANES spectra reflect the density of the unoccupied p-symmetry state around the metal atom. The electronic structure of these compounds is dominated by the $3d$-electron density of states near the Fermi level. CaO is a diamagnetic ionic insulator, while TiO is metallic and NiO is an antiferromagnetic Mott insulator. Therefore, the electronic structure does not influence their cation K-edge XANES and the spectra are rather similar. The shoulder structures on the low-energy sides of the largest peaks in the experimental spectra for MnO, FeO, CoO, and CuO were interpreted to be excitons.

We thought it would be very interesting to study whether core excitons appear in the O K-edge spectra of the other alkaline-earth oxides as observed in MgO and whether the anion K-edge spectra of $3d$-transition-metal oxides are influenced by the $3d$ electron density of states in contrast with the cation K-edge XANES spectra. With these points in mind, we measured the O K-edge spectra of the alkaline-earth metal oxides MgO, CaO, SrO, and BaO and the $3d$-transition-metal oxides TiO, MnO, FeO, NiO, and CuO. These oxides were crystallized in rocksalt structure except for CuO. For CaO and TiO, O K-edge XANES have also been calculated by means of the full-multiple-scattering theory.

II. EXPERIMENT

Measurements were carried out with a 10 m grazing incidence monochromator by the use of synchrotron radiation (SR) from the 2.5-GeV electron-storage ring at Photon Factory of National Laboratory for High Energy Physics (KEK-PF). An Au coated replica grating with 2400 grooves per mm of 10-m radius was used at the incident angle of 89°. The width of entrance and exit slits was 10 μm. In this condition the energy resolution of this monochromator was about 0.1 eV at the O K edge. Further detailed descriptions of this monochromator are described elsewhere.[10] Spectra were recorded by the total electron yield method. The ejected photoelectrons from the sample surface were detected by a Channeltron (CEM4700). The samples of the $3d$-transition-metal oxides were available as single crystals and obtained from the Nakazumi Earth Jewelry Co. Ltd. Clean surfaces were prepared *in situ* by diamond filing. The oxides of alkaline-earth metals were of the commercial reagent grade and were studied in powdered form. The sample chamber was evacuated to the vacuum of 1.3×10^{-7} Pa. The Ceratron electron multiplier was used as a monitor counter and monitored the intensity of the photoelectron emitted from the Au mesh which was arranged in the x-ray path. The accumulation of the data and the control of the stepping motor for scanning the monochromator were done by a microcomputer system (AIDACS-3000).

III. METHOD OF CALCULATION

The XANES theory used in this study is based on the short-range-order full-multiple-scattering theory proposed by the present authors.[3,4] In this study we define the quantity $\chi(k)$ which is the same as the EXAFS function,

$$\chi(k)=\Delta\sigma(k)/\sigma_0(k),\quad \Delta\sigma=\sigma-\sigma_0\ , \tag{1}$$

where σ_0 is the photoabsorption cross section of a core orbital of a free atom, $\Delta\sigma$ is the correction term to the cross section σ_0 due to the presence of surrounding atoms, and k is the wave vector of the ejected photoelectron. For photoionization from a deep s orbital, the explicit formula of $\chi(k)$ is given in Ref. 3. The phase shifts considered in the numerical calculations are computed in the Hartree-Fock approximation by use of Pendry's method.[11] In the case of the semiconductors and insulators considered here, core holes are not fully screened and the hole potential felt by a photoelectron is not neglected.[5] One of the simple approximate hole potentials is the $Z+1$ potential.[12] Previous results on alkali[6] and alkaline-earth fluorides[7] show that it is important to use the $Z+1$ potential for the interpretation of XANES spectra of such compounds.

The scattering property of each atomic sphere is described by a set of scattering phase shifts which reflect the electronic structure in each atom. Thus information on the charge distribution around the x ray absorbing atom can be obtained if we compare the XANES spectra with the full-multiple-scattering calculations. So far we have applied this method to the determination of the net charge on cations or anions in semiconductors,[13,14] alkali fluorides,[6] and alkaline-earth fluorides.[7] For these systems we do not need to pay attention to the evaluation of d electron numbers. However, we have to investigate the sensitivity of the calculated XANES to d electron numbers for transition-metal oxides such as TiO considered here. Of course the number of electrons in each atomic region depends on the definition of the space separation into metallic and oxygenic regions. The radii of the spherical charge distributions representing the various atoms or ions should be determined as the distances from the nuclei out to the minimum of the charge densities between the atoms. Once the charge distribution is assumed, the radii are uniquely determined. In general, these radii are not always the same as either the atomic or ionic radii, so they should be determined separately for each system.[15]

If $\chi(k)$ is not so large, the calculated XANES can be directly compared with the observed XANES. However, we have to precisely determine the σ_0 to compare these calculated results with the experimental results for large $\chi(k)$ as obtained in this work. From Eq. (1) and the calculated $\chi(k)$, we can calculate σ_0 which usually does not show a smooth curve. Then we get the smooth σ_0 by a computer smoothing procedure, and finally $\chi(k)$ can be calculated using the $\chi(k)$ and σ_0 obtained here.

IV. RESULTS AND DISCUSSION

Figure 1 shows the O K-edge spectra of alkaline-earth oxides. These spectra show systematical change in the near-edge structure, that is, the intensity of the first peak increases when atomic number Z increases from the third to the fourth period of the Periodic Table as ob-

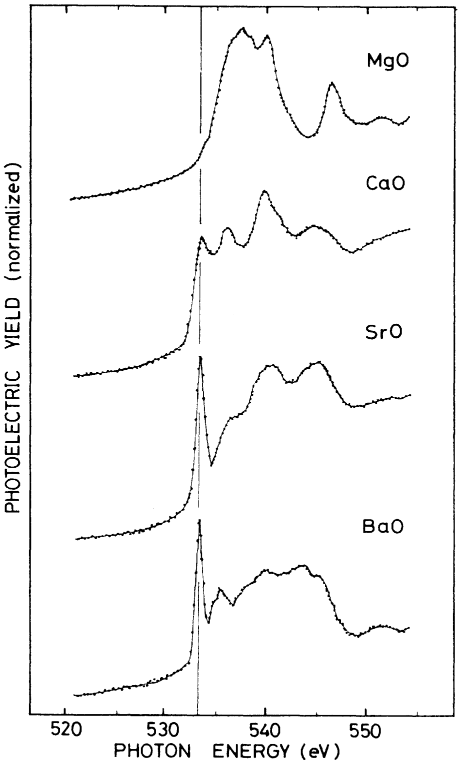

FIG. 1. O *K*-edge spectra of alkaline-earth oxides MgO, CaO, SrO, and BaO.

served for alkaline-earth fluorides. The width of the first peak becomes considerably narrow when one goes from CaO to BaO, but the chemical shift of the first peak is not observed.

Now we will analyze the XANES and discuss the electronic structure of CaO. So far various kinds of techniques have been used to determine the effective static charge q ($q>0$) on a metal cation. One of the simplest methods to evaluate the charge distribution in ionic compounds is Pauling's method[16] of using electronegativities of two different atoms; this predicts that $q=0.79$ for this compound. The modified version was also presented by Hannay and Smyth,[17] which predicts that $q=0.62$. The values estimated by thermochemical data and atomization energy are about 1.1–1.2.[18] Some band calculations have been done for this system: Springborg *et al.* estimated q at 0.87 by use of self-consistent linear muffin-tin orbitals (LMTO) method.[19]

Figures 2(a) and 2(b) show the calculated XANES spectra for the $O^{*}Ca_6O_{12}Ca_8O_6$ (33-atom) cluster compared with the experimental result of CaO, where O* is the x-ray-absorbing atom replaced by the $Z+1$ atom. Ca_6 means that there are six Ca atoms in the first shell around O*, and so on. The calculated results are shown for $q=0.6$–0.95; they are sensitive to the charge distribution. When we assume that q is equal to 0.70, the best agreement between the theory and experiment is obtained. Even in that case, the first peak cannot be predicted; it is probably due to the excitation to the local-

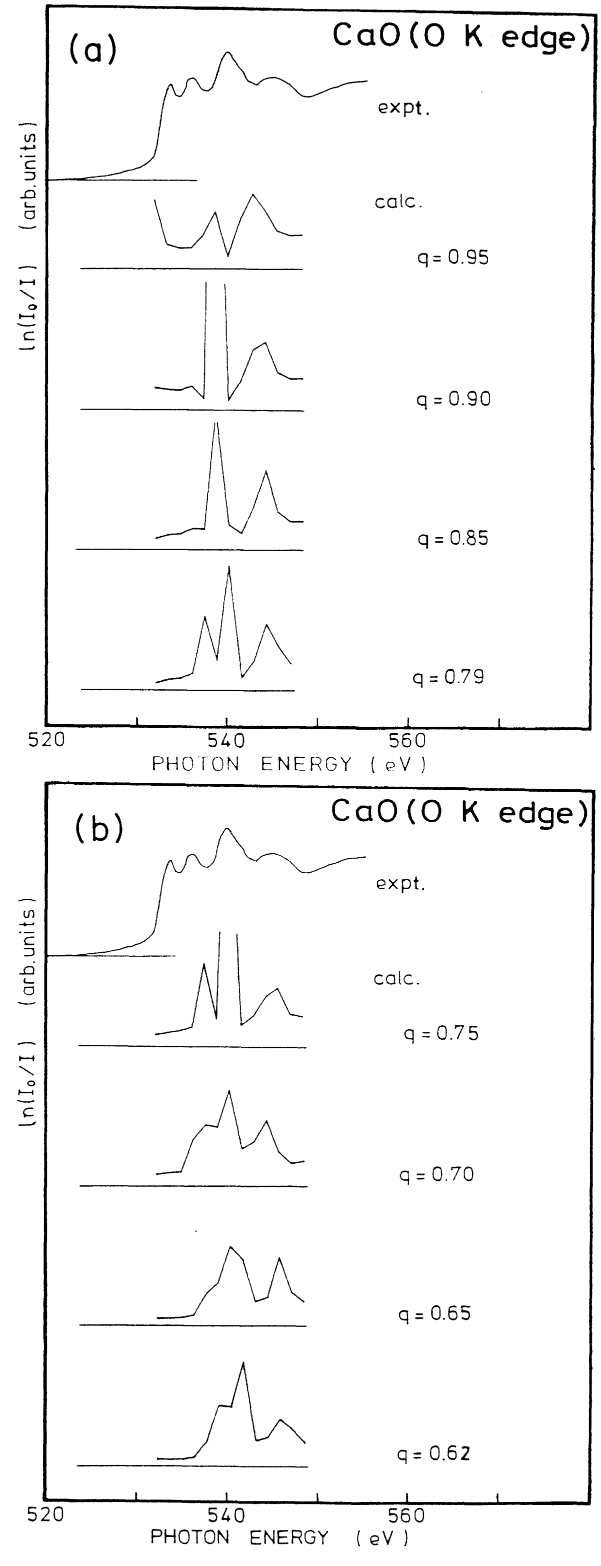

FIG. 2. (a) Calculated XANES spectra for the $O^{*}Ca_6O_{12}Ca_8O_6$ (33-atoms) cluster compared with the experimental results of CaO. The calculated results are shown for $q=0.95$, 0.90, 0.85, and 0.79. (b) Calculated XANES spectra of CaO compared with the experimental one. The calculated results are shown for $q=0.75$, 0.70, 0.65, and 0.62.

ized bound state (core exciton) which cannot be considered in this calculation. This feature is consistent with the result obtained by Lindner *et al.*[8] for MgO. The obtained q value is slightly smaller but comparable with the values predicted by simple methods based on electronegativities and the self-consistent LMTO method.

Next we will investigate the electronic structure of $3d$-transition-metal oxides by comparing the calculated results with the experimental result. Figure 3 shows the O K-edge spectra of $3d$-transition-metal oxides. The spectral profiles are different from each other even though they have a same rocksalt crystal structure except for CuO. The oxygen K edge in FeO, NiO, and CuO has previously been measured using electron-energy-loss spectroscopy (EELS) by Grunes *et al.*[20] The spectra in the present work appear to be very similar to their spectra but of much higher resolution. In the cation K-edge spectra of TiO, MnO, FeO, NiO, and CuO, near-edge profiles are rather similar;[9] on the other hand, as seen in Fig. 3, the anion K-edge spectra show quite different features. Therefore, it seems that the O K-edge spectra of these oxides are strongly affected by the electronic states of $3d$ electrons which dominate the various properties of these oxides. In this paper we especially consider the O K-edge XANES spectrum of TiO. Pauling's method predicts $q=0.70$ for TiO, while Hannay and Smyth's method predicts $q=0.52$. Neckel *et al.* calculated the self-consistent band structures for TiO by using the APW method in connection with the $X\alpha$ method for exchange.[21] Their result shows that the total charge in the oxygen sphere is 7.99 and the number of $3d$ electrons in the Ti sphere is 1.85, but there are 2.04 electrons outside the atomic spheres. If we equally divide these 2.04 electrons into Ti and O regions because of nearly equal atomic spheres used by them, then we can approximately represent the charge distribution as $Ti^{1.0}O^{-1.0}$. They also applied the Slater-Koster linear combination of atomic orbitals (LCAO) interpolation scheme, and then obtained the charge distribution $Ti^{1.45}O^{-1.45}$ with 2.55 d electrons on Ti. In the procedure, however, the metal $4s$ and $4p$ states were not taken into account within the LCAO tight-binding method, so the problem of determining these values still remains. Figure 4 shows the experimental O K-edge XANES of TiO compared with calculated ones for different d values 1.6–2.2, where q is fixed at 0.9. None of the calculated spectra show good agreement with the experimental spectrum. Figure 5 is similar, but q is fixed at 0.8. In the first two-peak region, good agreement is obtained for $d=2.0$, but the second broad peak region observed in the range 537–547 eV is not well reproduced. In this region we get a considerably good result for $d=1.8$. Therefore we can predict that $1.8<d<2.0$ for $q=0.8$. Figure 6 is similar, but q is fixed at 0.7. The calculated first two-peaks are too strong, but two of the three peaks are predicted at the second broad peak region at 537–547 eV, if we use d equals 2.0. Figure 7 is similar with $q=0.6$–0.9, but d is fixed at 2.0. If q is changed for fixed d, we observe the rapid change again

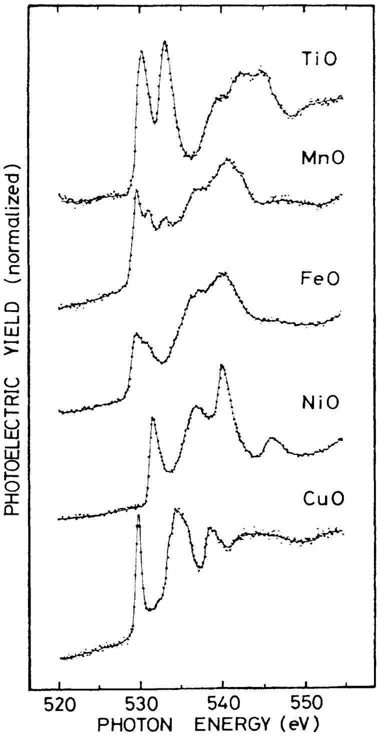

FIG. 3. O K-edge spectra of $3d$-transition-metal oxides TiO, MnO, FeO, NiO, and CuO.

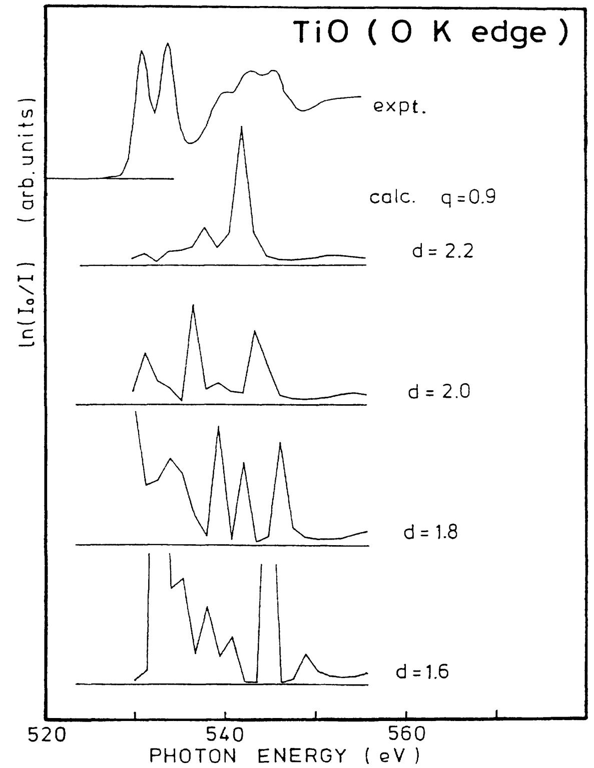

FIG. 4. Experimental O K-edge XANES of TiO compared with calculated ones for different d values 1.6–2.2, where q is fixed at 0.9.

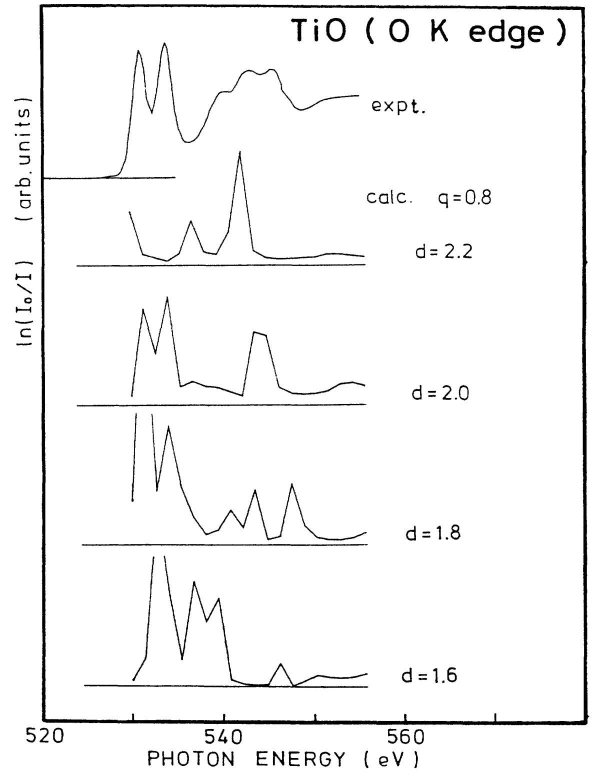

FIG. 5. Experimental O *K*-edge XANES of TiO compared with calculated ones for $d = 1.6-2.2$, where q is fixed at 0.8.

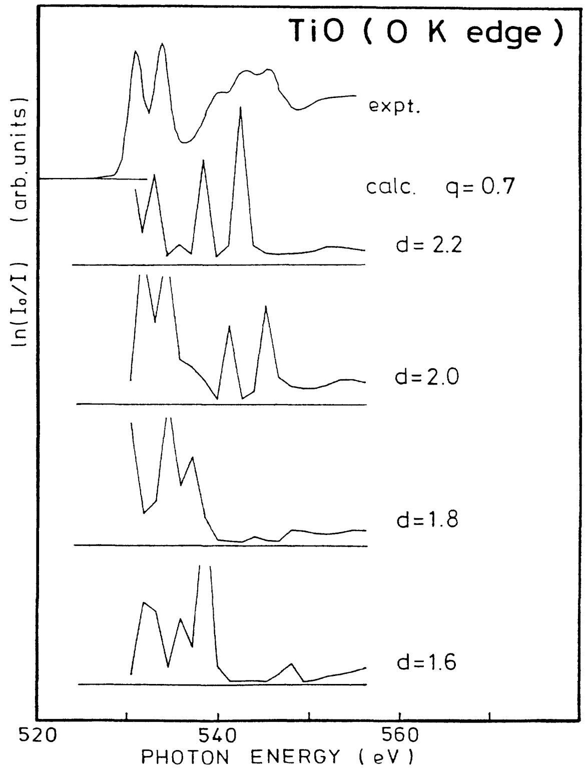

FIG. 6. Experimental O *K*-edge XANES of TiO compared with calculated ones for $d = 1.6-2.2$, where q is fixed at 0.7.

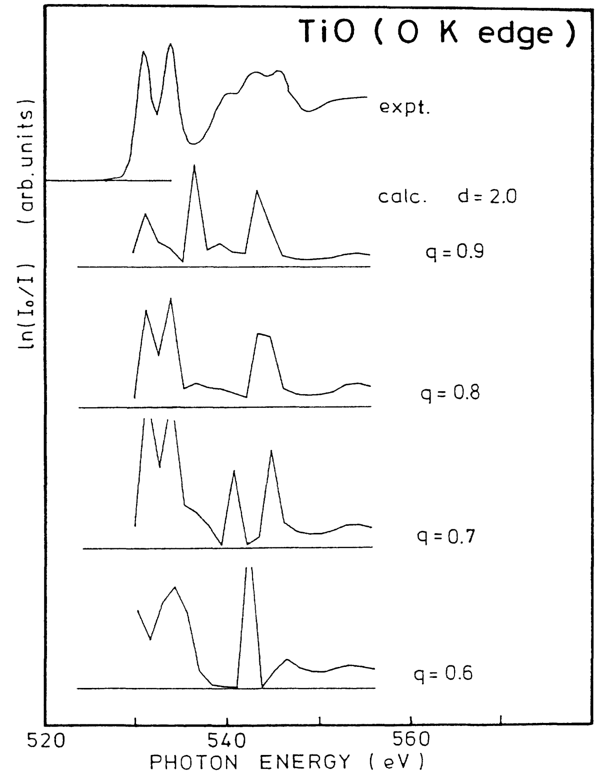

FIG. 7. Experimental O *K*-edge XANES of TiO compared with calculated ones for $q = 0.6$, 0.7, 0.8, and 0.9; the value of d is fixed at 2.0.

as observed earlier for d variation. The first two-peaks around 530 and 533 eV are well predicted, if we use $q = 0.8$ and 0.7. The second peak region at 537–547 eV is also sensitive to q values. The calculated result for $q = 0.8$ cannot predict the shoulder peak around 540 eV, and the one for $q = 0.7$ shows two peaks that are too sharp in this region. Although the calculated results shown here are too sensitive for both q and d for us to agree completely, we have obtained a satisfactory agreement. Defects usually prepared in this compound would have an important effect on the observed XANES.[22] For better agreement, this effect should be taken into account. However, we can predict that $q = 0.7-0.8$ and $d = 1.8-2.0$. These values are close to the ones predicted by Pauling's method, and by the APW method if we equally divide the electrons outside the atomic spheres ($q = 1.0$, $d = 1.85$).[21]

V. CONCLUSION

The O *K*-edge XANES spectra of alkaline-earth metal and 3*d*-transition-metal oxides have been measured with high resolution by the use of synchrotron radiation. Furthermore, the full-multiple-scattering calculations for the O *K*-edge spectra of CaO and TiO have been performed. By comparison of experimental and theoretical spectra, we can estimate the effective cation charge distribution with $q = 0.7$ for CaO. The first peak of CaO is attributed to the core exciton absorption as observed for

MgO. In the oxides of $3d$ transition metals, the cation K-edge XANES are not so sensitive to the number of $3d$ electrons,[9] while the anion K-edge XANES calculated by us are very sensitive to not only the anion or cation charge density but also to the $3d$ electron numbers on metals. For TiO, we can predict the effective cation charge and the number of $3d$ electrons with $q = 0.7-0.8$ and $d = 1.8-2.0$.

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