

Influence of the muffin-tin approximation on the simulation of titanium *K*-edge X-ray absorption spectra of TiO₂ (rutile and anatase phases)

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ARTICLE INFO

Article history:

Received 8 June 2009

Received in revised form

28 September 2009

Accepted 28 September 2009

PACS:

61.05.cj

Keywords:

Titanium oxides

XANES

Muffin-tin approximation

ABSTRACT

X-Ray absorption near-edge structure (XANES) spectra at the Ti *K*-edge of TiO₂ (rutile and anatase phases) have been analyzed. Theoretical analyses of the experimental data have been performed on the basis of both real-space full multiple scattering theory with muffin-tin approximation for potential shape and full-potential (beyond muffin-tin approximation) finite difference method. A full potential is required to satisfactorily reproduce experimental Ti *K*-edge XANES spectra in the TiO₂.

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1. Introduction

X-ray absorption near-edge structure (XANES) spectroscopy [1] is a fruitful tool providing information about the 3D local atomic structure and the distribution of unoccupied electronic states in the bottom of conduction band of compounds in condensed state. To obtain this information from XANES spectra, experimental XANES must be interpreted using theoretical analysis.

In this study, we present experimental and theoretical Ti *K*-edge XANES spectra of rutile and anatase phases of titanium dioxide (TiO₂). Experimental Ti *K*-XANES spectra of rutile and anatase have been already measured previously [2–7], and some simulations of XANES spectra near the Ti *K*-edge of rutile and anatase have been performed [3–4,6–10]. We provide a detailed theoretical analysis of the Ti *K*-edge XANES using different theoretical methods and determine the influence of the muffin-tin approximation.

2. Experiment and method of calculation

TiO₂ (rutile and anatase) samples were received from Alfa Aesar Company. The samples were examined by X-ray Diffraction

(XRD) analysis. The XANES spectra near the Ti *K*-edge of rutile and anatase were measured at the SuperXAS beamline of the Swiss light source (SLS) (Villigen, Switzerland), which operated at 2.4 GeV in top-up mode at a current of 400 mA. The spectra were collected in transmission mode at room temperature using a Si(111) monochromator. The spectra were collected with an energy resolution $\Delta E/E$ equal to 2×10^{-4} .

Theoretical analysis of the Ti *K*-XANES spectra was performed using two methods: real-space full multiple scattering (FMS) theory using the FEFF8.4 [11] and FDMNES2007 [12] codes and the finite difference method (FDM) using the FDMNES2007 code. FEFF8.4 code uses the muffin-tin approximation [13] for the shape of crystal potential. FDMNES2007 code has an advantage over FEFF8.4 program as it allows carrying out calculations using the so-called 'full potential' beyond the muffin-tin approximation. The results of the different approximations were compared to each other. It is necessary to mention that in recent years a full potential multiple scattering scheme was developed for the interpretations of X-ray spectroscopies [14,15].

For the simulations of XANES spectra of rutile and anatase the structural information from Ref. [16] was used.

An important step in the FMS analysis of XANES data is the determination of the minimum size of the atomic cluster around the absorbing Ti atom, within which the scattering of the photoelectron can reproduce the entire fine structure of the XANES. So, the comparison of the experimental Ti *K*-XANES of rutile with the theoretical those calculated by FEFF8.4 code for different

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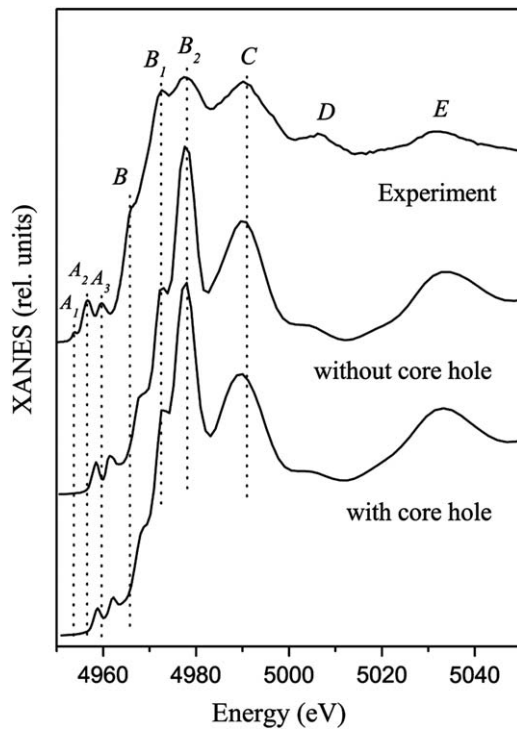


Fig. 1. Experimental Ti *K*-XANES spectrum of the TiO₂ (rutile) compared with theoretical spectra simulated by FEFF8.4 code with taking into account the presence of core hole and without it. Theoretical spectra are aligned in energy scale relative to the position of peak B₁ of the experimental spectrum.

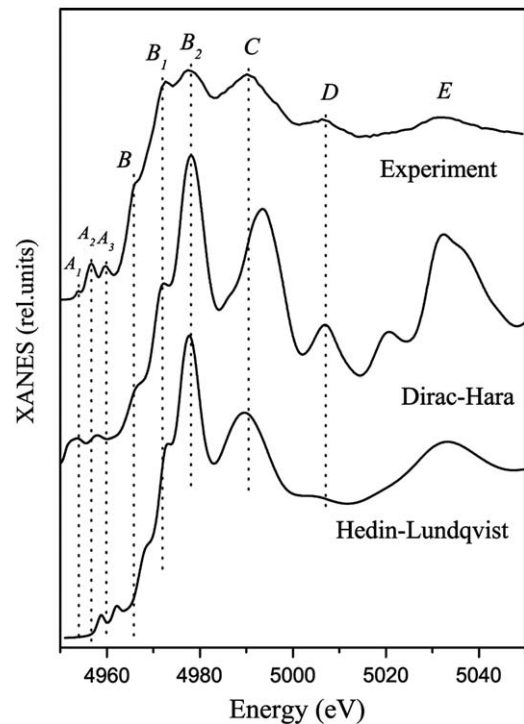


Fig. 2. Experimental Ti *K*-XANES spectrum of the TiO₂ (rutile) compared with theoretical spectra calculated by FEFF8.4 taking into account different models of exchange potential (Hedin–Lundqvist and Dirac–Hara models). The spectra are aligned relative to the energy position of peak B₁ of the experimental spectrum.

cluster sizes has been performed. It was found that the convergence of theoretical XANES is already observed for the cluster containing 153 atoms (radius of the cluster is 7.2 Å). Nevertheless, in the paper we present the XANES spectra of rutile calculated using FEFF8.4 code for the atomic cluster of 397 atoms (10 Å). For FEFF8.4 calculation of XANES spectrum of anatase an atomic clusters of 395 atoms with a radius of 10.3 Å was taken into consideration. As the finite difference method demands higher computational time and resources for XANES simulation, the FDMNES calculations of Ti *K*-XANES of both rutile and anatase were carried out for a cluster containing 153 atoms, which corresponds to a cluster radius of about 7.2 Å for rutile and 7.6 Å for anatase.

3. Results and discussion

In Fig. 1 we compare the experimental Ti *K*-XANES spectrum of rutile with theoretical ones calculated by FEFF8.4 program code with taking into account the presence of core hole created by electronic transition and without it. The spectra were calculated using Hedin–Lundqvist model of the exchange potential. It can be seen from Fig. 1 that the theoretical spectra are almost identical. This means that in the case of Ti *K*-XANES of rutile a core hole does not influence significantly the spectral shape. Nevertheless, all following XANES spectra for both rutile and anatase were simulated taking into account the presence of the core hole. Fig. 1 shows that the XANES spectrum calculated by FEFF8.4 program reproduces all main features of the experimental spectrum—A₂, A₃, B, B₁, B₂, C, D, E, but that there is a some disagreement with the experiment concerning the energy positions of pre-peaks A₂ and A₃ and the relative intensity of the spectral features.

In Fig. 2 a comparison of theoretical Ti *K*-XANES spectra of rutile simulated by FEFF8.4 code using different models of

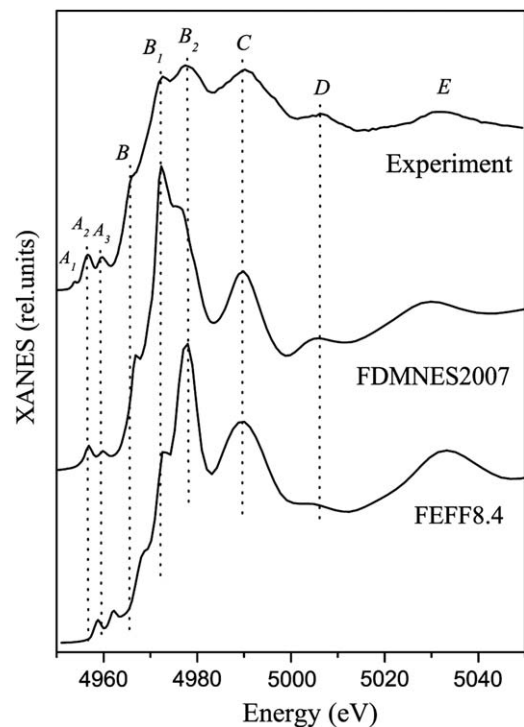


Fig. 3. Comparison of the experimental Ti *K*-XANES spectrum of the TiO₂ (rutile) with the theoretical spectra calculated using FMS within MT approximation for potential shape (FEFF8.4 code) and full-potential FDM (FDMNES2007 code). The spectra are aligned relative to the energy position of peak B₁ of the experimental spectrum.

exchange potential (Hedin–Lundqvist and Dirac–Hara) is shown. It can be seen that using of Dirac–Hara model of exchange potential instead of Hedin–Lundqvist does not lead to a better

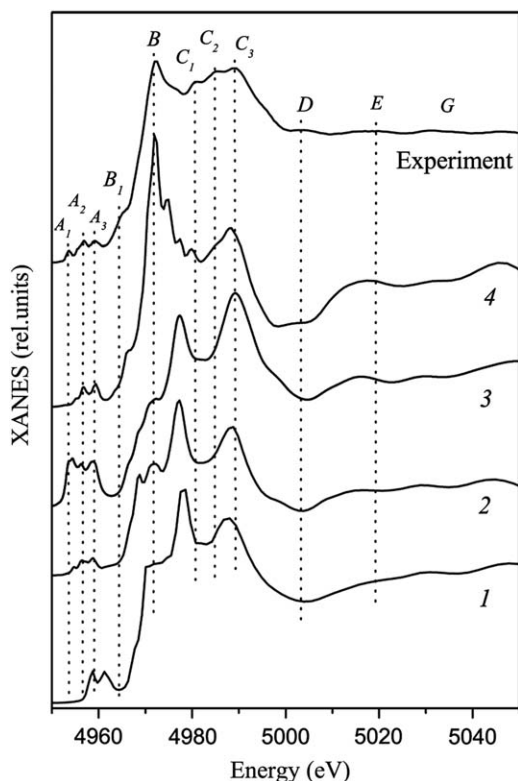


Fig. 4. Comparison of the experimental Ti *K*-XANES spectrum of TiO₂ (anatase) with the theoretical those. Curves 1 and 2 correspond to the theoretical XANES calculated on the basis of FMS theory within MT approximation using codes FEFF8.4 and FDMNES2007, correspondently. The spectrum calculated by FDMNES2007 program on the basis of FDM within the MT approximation is labeled as 3. Spectrum 4 corresponds to the simulation carried out using full-potential FDM method (FDMNES2007 program). Theoretical spectra are aligned relative to the position of peak C₃ of the experimental XANES.

agreement with the experimental XANES: there is a disagreement not only in the energy positions of the pre-peak features (A₂, A₃), but also in the energy positions of the main maxima (C, E).

Fig. 3 compares the experimental Ti *K*-XANES of rutile with the theoretical spectra calculated on the basis of two theoretical approaches: full-multiple scattering (FMS) theory within the muffin-tin (MT) approximation for potential shape (FEFF8.4 code) and the full-potential finite difference method (FDM) (FDMNES2007 code). It can be seen that the spectrum obtained by using the FDMNES2007 code demonstrate an excellent agreement with the experimental energy positions of all peaks. Only the low-intensity pre-peak feature A₁ is not reproduced in the theoretical spectrum.

The FMS theory within MT approximation for potential simulation (FEFF8.4 program) and full-potential FDM approach

(FDMNES2007 code) were applied to calculate the Ti *K*-XANES spectrum of anatase. Fig. 4 compares the theoretical spectra (curves 1 and 4) with the experimental one. The theoretical spectrum calculated by FEFF8.4 (curve 1) has a shape that disagrees significantly with the shape of the experimental XANES: for example, the experimental peak B is absent in the theoretical spectrum. The spectrum calculated using the FDMNES2007 program (curve 4) agrees well with the experimental one regarding energy position and relative intensity of all the peaks.

To understand if the reason of the disagreement between the experimental XANES and the theoretical spectrum calculated by the FEFF8.4 code was the theoretical method used (FMS theory) or the MT approximation itself, additional calculations of the Ti *K*-XANES of anatase were performed. The FDMNES program allows to perform calculations not only on the basis of the FDM approach, but also on the basis of the FMS theory; it is also possible to carry out not only the ‘full-potential’ calculations, but also to use the MT approximation within FDM method. So, the XANES spectrum near the Ti *K*-edge of anatase was also simulated by FDMNES2007 code using the MT approximation for potential shape within both the FMS theory (curve 2 of Fig. 4) and the FDM approach (curve 3 of Fig. 4). XANES simulations within the MT approximation for potential shape carried out by both FMS and FDM methods failed to agree satisfactory with the experiment. So, a good agreement with the experimental spectrum was obtained only in the case of the full potential calculations (curve 4 of Fig. 4).

Thus, simulations of the Ti *K*-XANES spectra for TiO₂ let us to conclude that the adequate description of the Ti *K*-XANES spectrum of TiO₂ demands calculations within a full potential (i.e., beyond the MT approximation) for the crystal potential shape.

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