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Electronic structure of germanium dioxide with rutile structure according to ab initio computer simulation data

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Abstract

The article focuses on the electronic structure of the tetragonal crystalline modification of germanium dioxide. The electronic structure was theoretically studied by means of the full-potential linearized augmented plane wave method using the Wien2k software.

Total and partial densities of electronic states were calculated. The spectra of the X-ray absorption near edge structure were simulated for various absorption edges of germanium and oxygen atoms. The Z+1 approximation method was used to calculate Ge K-, Ge L₃- and O K absorption edges for the tetragonal modification of GeO₂. The result obtained for the Ge K absorption edge is in good agreement with the experimental data.

The Ge L₃ spectrum was calculated for the first time, and the result is of predictive nature. In order to obtain a better agreement with the experimental calculations of the oxygen K absorption edge, besides the Z+1 approximation method, we also used the core hole method, including the simulation of a partial core hole. The study demonstrated that the use of a core hole with an electron charge of 0.7 results in a better agreement between the calculations and the experiment.

Keywords: Computer simulation, Germanium dioxide, Electronic structure, Density of states, XANES, Core hole, Rutile

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1. Introduction

Germanium dioxide is a wide bandgap semiconductor [1] used in optoelectronics, solar energy, and catalysis [2–5]. Normally, germanium dioxide exists in two stable crystalline modifications: a hexagonal q -GeO₂ (quartz structure) and a tetragonal r -GeO₂ (rutile structure) [6].

Due to several reasons, the electronic structure of the tetragonal phase of germanium dioxide is of great scientific interest. Firstly, there are a lot of studies focusing on the synthesis and analysis of nanomaterials based on GeO_x compounds [3, 4, 7, 8]. Secondly, r -GeO₂ is one of oxide materials that have a rutile-type spatial structure [9]. These materials have similar parameters of their crystal lattices and can therefore be used to synthesise new functional materials in the form of interfaces and heterostructures based on them [10]. In both cases, an accurate analysis and interpretation of the experimentally determined properties of such materials requires understanding of the specifics of the electronic structure of r -GeO₂.

X-ray absorption near edge structure (XANES) is one of the methods commonly used in experimental studies of the atomic and electronic structure of materials [11]. XANES spectra provide researchers with information about the distribution of the density of the unoccupied electronic states in the conduction band of solids. They are also highly sensitive to the thin layers on the material's surface and to the short-range order in the spatial distribution of atoms of the studied material.

Analyses of the experimental spectra of the studied samples usually involve their comparison with the spectra of well-studied materials considered as reference materials. For the materials of the Ge – O system, one of such reference materials is r -GeO₂. There have been a number of studies obtaining experimental XANES spectra of the r -GeO₂ phase. Several works [12–14] demonstrate the K edge X-ray absorption spectra of germanium and [15, 16] demonstrate the K edge X-ray absorption spectra of oxygen. Some studies use the Ge K edge as a reference when analysing the spatial structure of the studied samples of the Ge – O system [13, 14, 17]. However, the existing literature provides no theoretical, neither experimental

information about the L₃ edge absorption spectra of germanium in r -GeO₂.

At the same time, the results of computer simulation, as well as the results of experiments, can be used as reference spectra [18]. Although there are quite a number of works focusing on the tetragonal GeO₂ electronic structure modelling [5, 16, 19, 20–23], they do not contain the Ge K edge and Ge L₃ edge XANES spectra calculations results. Apparently, up to now there have been no publications providing such information. There has only been a study focusing on the calculation of the K edge absorption spectrum of oxygen in r -GeO₂ [15]. The results of this study are in good agreement with the experimental results. However, they demonstrated some significant differences in the intensity ratios of the structural features of the spectrum.

Therefore, it is important to perform first-principles calculations of the tetragonal phase of GeO₂ and calculate the XANES spectra, which was the purpose of our study.

2. Calculation methodology

The tetragonal phase of germanium dioxide has a rutile-type spatial structure with the space group P4₂/mnm [19]. In our study, we used the experimental values of unit cell parameters presented in [24] analogous to the calculations performed in [5, 23]. The appearance of the r -GeO₂ unit cell is given in Fig. 1. The parameters of the crystal structure are given in Table 1.

The electronic structure was calculated using a Wien2k program package [25] based on a full-potential linearized augmented plane wave method (LAPW). Within the framework of the density functional theory, generalized gradient

Table 1. Parameters of the r -GeO₂ crystal lattice

Space group	P4 ₂ /mnm		
Unit cell parameters a, b, Å	4.40656		
Unit cell parameter c, Å	2.86186		
Atomic position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Ge ₁	0.5	0.5	0.5
Ge ₂	0.0	0.0	0.0
O ₁	0.806	0.806	0.5
O ₂	0.194	0.194	0.5
O ₃	0.694	0.306	0.0
O ₄	0.306	0.694	0.0

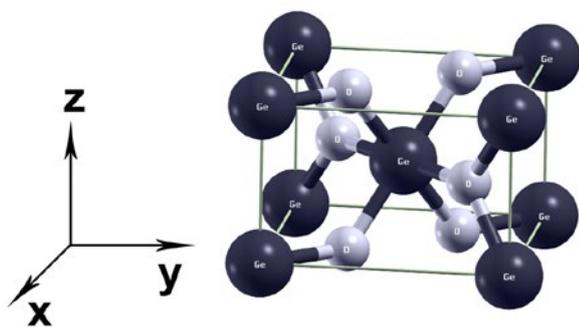


Fig. 1. r - GeO_2 unit cell. The Ge atom is dark-grey, the O atom is light-grey

approximation (GGA) was used for the exchange-correlation energy. The muffin-tin radii of Ge were 1.85 a.u., and the muffin-tin radii of O were 1.67 a.u.

The XANES spectra were simulated using the core hole method and the $Z+1$ approximation method. The formalism of each of these methods is slightly different. Both methods are based on the idea that it is necessary to perform the calculation of excited state when simulating the electronic structure of the conduction band in order to compare the result with experimental XANES spectra [26, 27]. The experimental studies of the conduction band were performed using the XANES method, with high-energy X-ray photon beam aimed at a sample whose core electrons absorb energy and pass to the conduction band. This means that it is necessary to calculate the band structure of the material in this particular electronic configuration: with a $+1e$ positive charge on the atomic core and a $-1e$ negative charge in the conduction band. For this, the core hole method can be used [26–28]. It involves removing a core electron from a previously selected atom A, whose spectrum needs to be calculated. This electron passes to the conduction band to maintain electroneutrality. The core hole is simulated on the same energy level, where the electron vacancy occurs during the experiment. When the $Z+1$ approximation method is used [28], atom A is replaced with an atom of the next chemical element with the charge number $Z+1$. We should note that for both methods atom A is a part of a supercell, whose volume is several times larger than the unit cell volume. All the other atoms in the supercell

are in a ground energy state. At the same time, the supercell volume should be large enough to prevent the interaction between neighbouring atoms with core holes or the charge number $Z+1$ [26, 27]. In our study, we used $2 \times 2 \times 3$ supercells analogous to the calculations performed in [15, 29]. With these parameters the shape of the supercell is close to cubic, and the minimum distance between two excited atoms is $\sim 8.585 \text{ \AA}$. When the spectra of germanium were calculated using the $Z+1$ approximation method, one of the germanium atoms in the supercell was replaced with an arsenic atom. Similarly, when the oxide spectra were calculated, one of oxygen atoms was replaced with a fluorine atom. Thus, we performed theoretical calculations of the absorption spectra of Ge K, Ge L_3 , and O K.

3. Results and discussion

3.1. The density of electronic states of r - GeO_2

The calculated total $N(E)$ and partial $n(E)$ densities of electronic states (DOS) of r - GeO_2 in the ground state are given in Fig. 2. The beginning of the energy scale was the valence band top. The bandwidth of the valence band was 10.4 eV. The curve of the total DOS of the valence band has a three-peak structure characteristic of the other oxides of elements in group 14 of the periodic table that have a rutile-type spatial structure [29, 30]. The intensity of peaks of the DOS grows from the bottom to the top of the valence band. The peak at -9.65 eV is equally contributed to by the $4s$ states of germanium and the $2p$ states of oxygen. The peak in the middle of the valence band at -5.4 eV is mainly formed by the $2p$ states of oxygen with a small part by the $4p$ states of germanium. The most intensive peak at a distance of -1.2 eV from the top of the valence band is almost completely formed by the $2p$ states of oxygen atoms. The dominance of the occupied electronic states of oxygen in the valence band can be explained by a greater electronegativity of oxygen atoms as compared to germanium atoms.

Below the valence band there are two narrow subvalent groups: Ge $3d$ in the energy range from -24.8 to -23.8 eV and O $2s$ in the energy range from -21.3 to -16.7 eV (they are not shown in the figure). The valence band is divided from the conduction band by a band gap, whose width is 1.996 eV , which is lower than the experimental value 4.680 eV [1]

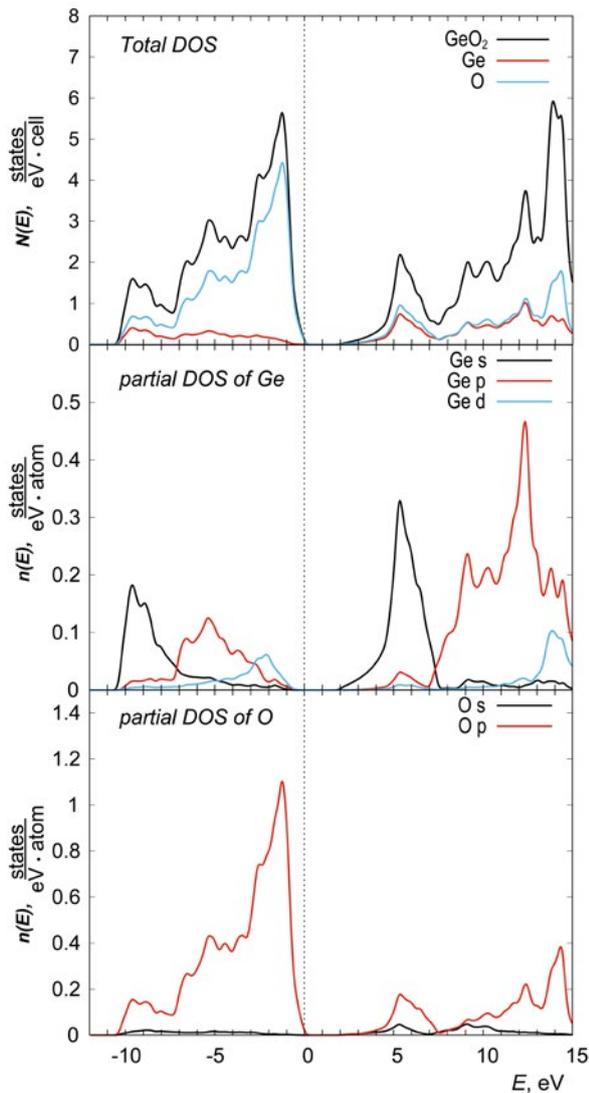


Fig. 2. Total $N(E)$ and partial $n(E)$ densities of electronic states of $r\text{-GeO}_2$.

due to the fact that it was calculated using GGA, which tends to underestimate the bandwidth of the band gap in semiconductors and dielectrics [31]. An analysis of the conduction band demonstrated that the contribution of germanium and oxygen states are practically the same in a wide energy range up to 15 eV.

We should also note that the results of our calculation of the DOS of $r\text{-GeO}_2$ are in good agreement with the calculations presented in [5, 16, 20–22].

3.2. XANES spectra of $r\text{-GeO}_2$

Fig. 3 demonstrated a Ge K edge XANES spectrum calculated using the Z+1 approximation. The Ge K spectrum shows the density of

unoccupied Ge p states in the conduction band. We compared the model spectrum to the experimental spectrum described in [14]. The spectra were compared using a single energy scale based on the position of the main peak at $E \sim 11110$ eV. The comparison showed that the shape and position of the main energy features, including several low-intensity peaks in the range of 50 eV from the absorption edge, correspond well to the experimental ones. This confirms the accuracy of the calculations and the validity of the Z+1 approximation method and makes it possible to use this method when modelling other absorption edges of $r\text{-GeO}_2$.

Fig. 4 demonstrates the results of calculations of a Ge L_3 edge XANES spectrum by means of the Z+1 approximation. The Ge L_3 spectrum shows the density of unoccupied Ge s - and d - states in the conduction band. The existing literature does not provide any data regarding the experimental calculations of the Ge L_3 absorption edge in $r\text{-GeO}_2$. Therefore, we compared the calculated spectrum to the theoretical and experimental Sn L_3 spectra in rutile-type SnO_2 described in [32]. The spectra were aligned along the position of the peak at ~ 11 eV using the energy scale corresponding to the model Ge L_3 spectrum. The germanium spectrum is quite similar to the tin spectrum with regard to the shape and the location of the main structural features. The main difference is that the germanium spectrum has a single main peak, while in the tin spectrum the main peak is bifurcated. This is explained by the difference in the energy distribution of Ge $4d$ and Sn $5d$ states that form the considered spectra. The result obtained for the Ge L_3 absorption edge is of predictive nature and can be used to analyse

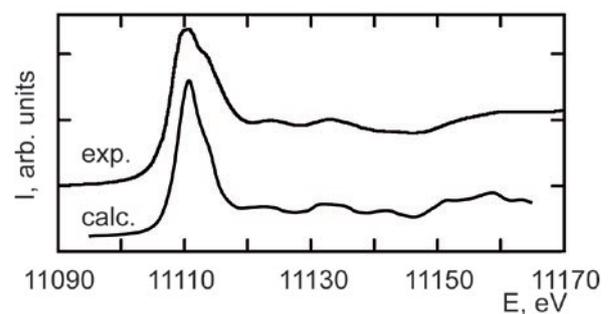


Fig. 3. Calculated (calc.) Ge K absorption spectrum in comparison with the experimental (exp.) spectrum presented in [14]

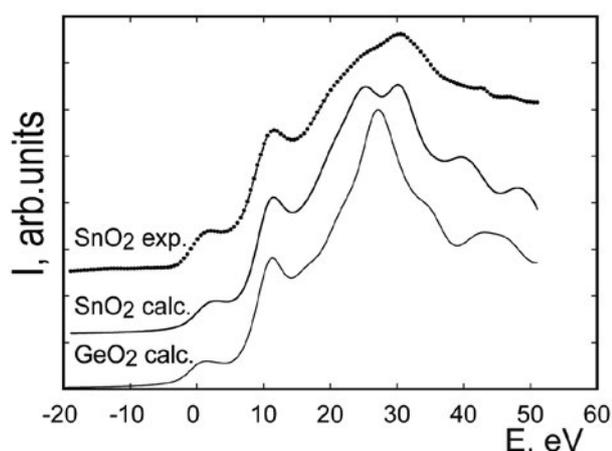


Fig. 4. Calculated (GeO_2 calc.) Ge L_3 absorption spectrum in comparison with the calculated (SnO_2 calc.) and experimental (SnO_2 exp.) Sn L_3 spectra in SnO_2 [32]

experimentally studied samples of the Ge – O system.

Then we calculated the O K absorption edge. Fig. 5 demonstrates the calculated spectra in comparison with the experimental and model spectra presented in [15]. We compared the calculated spectra to the experimental ones based on the position of the main peak at 535 eV on the energy scale. In general, the results of our calculations performed by means of the Z+1 approximation method agree well with the experiment [15]. However, similar to the theoretical calculations [15], the obtained spectrum demonstrated a redistribution of the intensity of the spectrum's thin structure in the range of 540–545 eV as compared to the experimental intensity. In [15], this is explained by the too attractive potential of the core hole. This is why we also calculated the O K XANES spectrum using the core hole method, including by introducing a partial core hole. A similar approach was used to calculate the XANES spectra in [28] and helped to enhance the agreement between the calculated and experimental results. Fig. 5 demonstrates the spectra calculated for the full core hole and core holes with charges 0.8e and 0.7e (1.0 ch, 0.8 ch, and 0.7 ch respectively). The result obtained for the full core hole is practically the same as the result obtained using the Z+1 approximation method. A decrease in the charge of the core hole results in changes in the intensity ratio of the structural features of the calculated absorption spectrum in the region of 540–545 eV.

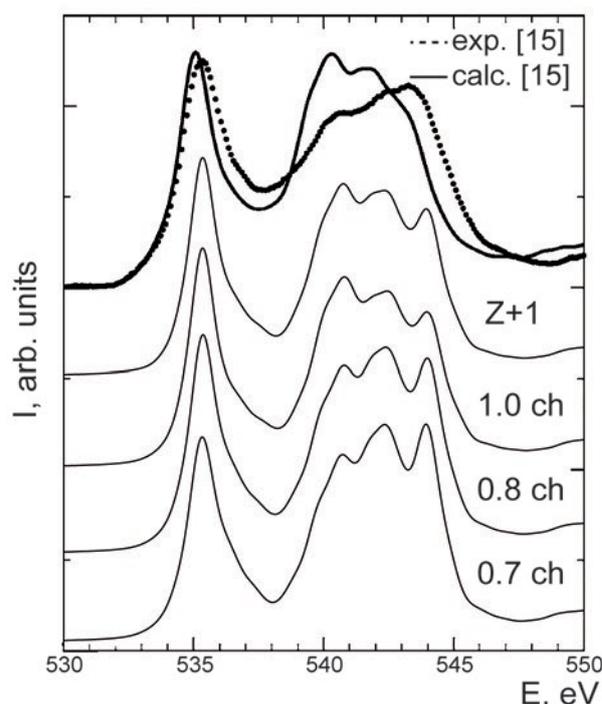


Fig. 5. O K XANES absorption spectra calculated using various methods in comparison to the results presented in [15]

The theoretical spectrum obtained using the core hole with the 0.7e charge demonstrated a better agreement with the experiment.

4. Conclusions

A linearised augmented plane wave method was used to study the electronic structure of the tetragonal crystalline modification of germanium dioxide.

Ge K and Ge L_3 XANES absorption spectra were calculated for the first time using the Z+1 approximation method.

O K XANES spectrum was for the first time calculated using the partial core hole method. The model spectrum obtained using the core hole with the 0.7e charge demonstrated a better agreement with the experiment.

The obtained results can be used to analyse experimentally studied specimens of the Ge – O system.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal

relationships that could have influenced the work reported in this paper.

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