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Electronic Properties of 3d-Metal-Doped Zirconia Nanotubes

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Abstract—The electronic structure of hexagonal ZrO₂ nanotubes doped by 3d-metal atoms was calculated by the linearized augmented cylindrical wave (LACW) method. The calculated densities of electronic states indicate that partial substitutions of zirconium atoms by transition metals (Sc, Ti, Mn, Co, and Zn) decrease the optical gap of (4,4) ZrO₂ nanotubes from 3.7 to 2–2.3 eV. Doping of nanotubes shifts optical absorption from the UV to the visible, and the nanotubes themselves become candidate materials for design of electrodes for electrochemical water photolysis.

Keywords: nanotubes, zirconia, electronic properties, doping, 3d metals, photocatalysis of water, linearized augmented cylindrical waves

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Zirconia ZrO₂ thanks to its high chemical durability, mechanical strength, and biocompatibility [1–3] is used in optoelectronics, as an industrial catalyst for catalytic decomposition, neutralization of organic eco-toxicants [4–13], as a biomedical material [14], and for other purposes [15–17]. One of the promising uses of ZrO₂ is the production of hydrogen by the water–gas shift reaction on the oxide surface under the action of sunlight [18–21]. However, this has not been widely developed due to the large bandgap width of zirconia, for this reason absorbing only in the ultraviolet region of light, which accounts for about 5% of the solar energy. The visible region of light accounts for about ~50% of the solar energy. Therefore, there is a topical problem of searching for the methods of doping ZrO₂ [20–26] that would decrease the optical gap to the energies of the visible region of sunlight. In addition, in order for the photocatalytic water–gas shift reaction to occur, the oxidation and reduction potentials of water should fall within the catalyst bandgap. These requirements can be satisfied by materials having bandgap widths of 1.23–2.5 eV. Since the reaction proceeds on the catalyst surface, nanomaterials with large surface areas have a preference over crystals. It is known that ZrO₂ nanotubes are manufactured by a hydrothermal method, metal-doped nanotubes are manufactured by alloy anodizing, and cations doped into ZrO₂ samples modify the physical and chemical properties of the compound and can enhance their required characteristics [21–31].

The goal of this work is to calculate the electronic structure of 3d-metal-doped ZrO₂ nanotubes.

COMPUTATIONAL DETAILS

All calculations were performed by the linearized augmented cylindrical wave (LACW) method for a ZrO₂ (4,4) nanotube that contained seven zirconium atoms, one 3d impurity, and sixteen oxygen atoms per unit cell. The LACW method is an expansion of the linearized augmented plane wave method to apply to systems having a tubular geometry [32–35]. This theory uses the local density functional approximation, and the electronic potential is built to be spherically symmetrical in the region of atoms and constant in the space between them up to the two impermeable barriers that separate the tube from the vacuum regions outside and inside the tube. The electronic structure of a nanotube is determined by the unconfined motion of electrons through the inter-sphere region, scattering of electrons by atoms, and reflection from the barriers. The method requires a single parameter, namely, Δ , the cylindrical layer thickness, which is common for all nanotubes and is selected so that the bandgap width in ZrO₂ would be 3.7 eV. Band structure calculations for crystalline zirconia are documented, but neither pristine, nor doped ZrO₂ nanotubes have been calculated as yet.

RESULTS AND DISCUSSION

Figure 1 shows the partial densities of electronic states calculated by the LACW method for a pristine ZrO₂ (4,4) nanotube; they can be compared to the band structure of the cubic phase of the compound that was calculated by the linearized augmented plane

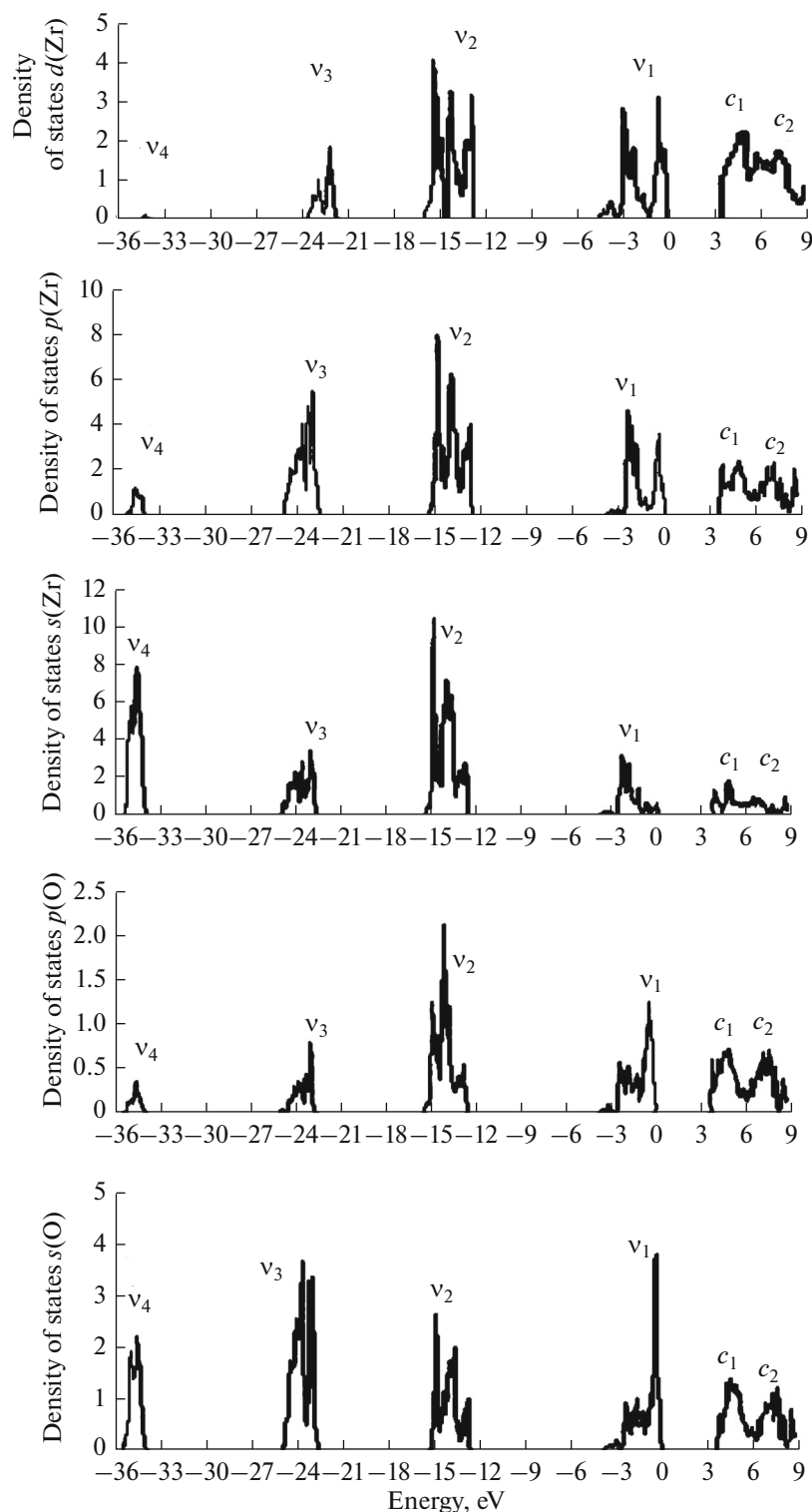


Fig. 1. Partial densities of states of a ZrO_2 (4,4) nanotube calculated by the linearized augmented cylindrical wave method.

wave method [22] and shown in Fig. 2. For the nanomaterial and a bulk ZrO_2 crystal, the band v_1 having a width of 4.5 and 6 eV, respectively, is observed on top of the valence band, being separated by a wide gap

from the inner levels. The narrowing of this band in going from a crystalline phase to a nanotube reflects the lower CN values of Zr and O atoms in a nanotube compared to a crystal. In a crystal, the band v_1 is sep-

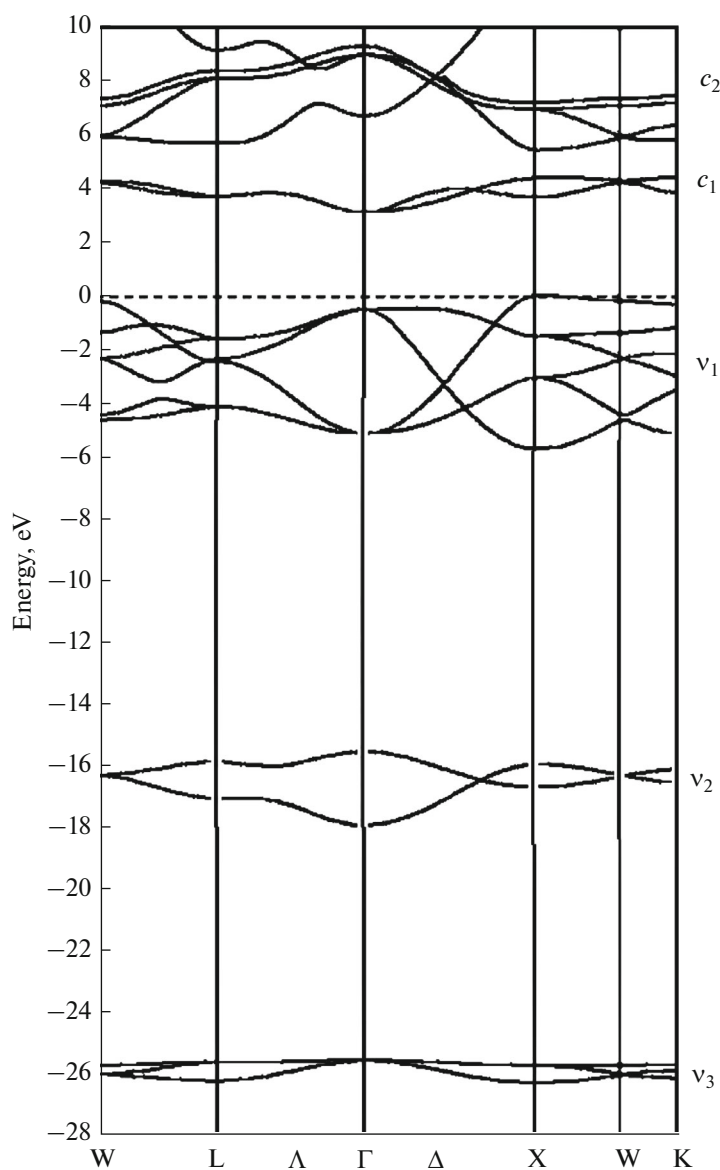


Fig. 2. Band structure of cubic ZrO₂ obtained by the linearized augmented cylindrical wave method [22].

arated from the conduction band by a 3-eV gap, while in a nanotube, the bandgap is 0.7 eV wider. In the conduction band of a crystal there are bands c_1 and c_2 with energies of 3–4 eV and of 5 eV or higher. In the density of states of a nanotube, the bands c_1 and c_2 appear as two bands peaking near 5 and 7 eV. The positions and widths of the bands v_2 and v_3 of the density of states of nanotubes coincide with the dispersion curves v_2 and v_3 in a crystal, except for an expected small shift. Thus, there is a close qualitative and semiquantitative analogy between the electronic structures of zirconia nanotubes and crystals. The dimensional effects arising from the transition from a crystal to a nanotube cause relatively small perturbations of the density of states in zirconia. The effect of $3d$ -doping is illustrated

by Fig. 3. This figure shows the full densities of states for ten doped nanotubes having one impurity atom in one Zr atom position in each unit cell, which corresponds to about 4 at % of the impurity. The substitution of one Zr atom by a $3d$ metal induces a considerable change in the electronic structure of the nanotube in the bandgap region, this change being stronger than upon the transition from a crystal to a nanotube. In all cases, doping is accompanied by a broadening of the edges of the valence and conduction bands. These effects alone are sufficient for causing the bandgap width to narrow from 3.7 to 2.2, 2.0, 3.0, 2.6, and 2.3 eV in the compounds doped by Sc, Ti, Cr, Cu, and Zn, respectively. When a ZrO₂ nanotube is doped with V and Fe, a new impurity band about 0.5 eV wide appears in the center of the bandgap of the nanotube,

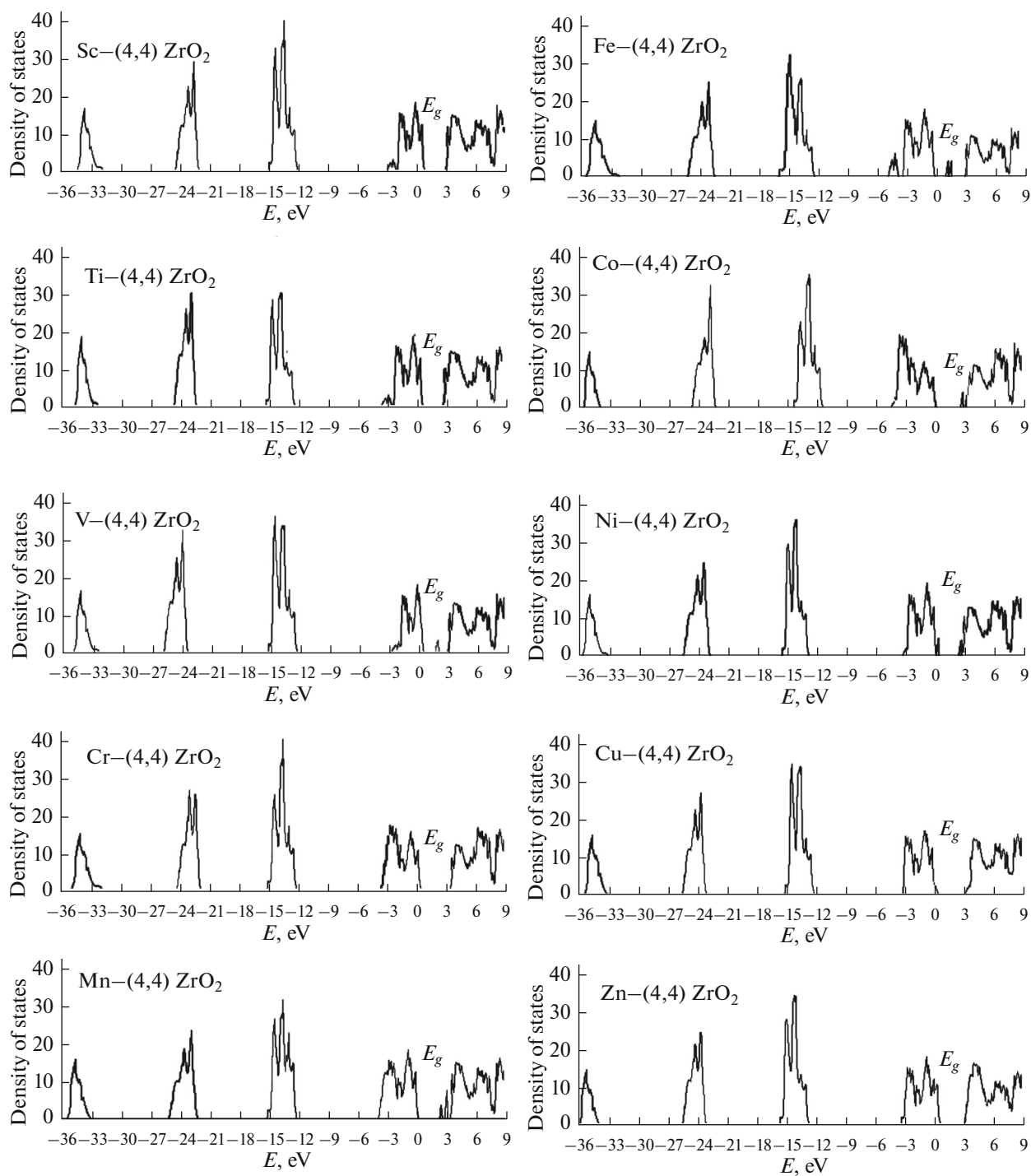


Fig. 3. Full densities of state of ZrO_2 (4,4) nanotubes doped by 3d metals calculated by the linearized augmented cylindrical wave method.

so the optical gap of the material narrows by more than twice: to 1.4 and 1.2 eV. When Zr is substituted by Mn and Co, additional density of states peaks appear immediately under the conduction band top, and optical gaps shift to the visible, decreasing to 2.2–2.4 eV. An about 2.0-eV bandgap is in the nickel compound,

where the gap is narrowed due to the formation of two impurity bands, one lying above the valence band top and the other under the conduction band bottom.

The described narrowing of the bandgap in doped ZrO_2 nanotubes and enhancement of catalytic activity agree with the magnetic measurements of nanotubes

with an admixture of Fe atoms [36] and with an enhanced activity of manganese-doped nanostructured $\text{ZrO}_2/\text{TiO}_2$ photocatalysts [13].

CONCLUSIONS

The density of electronic state proves that doping with Sc, Ti, Mn, Co, and Zn narrows the optical gap of ZrO_2 (4,4) nanotubes from 3.7 to 2–2.3 eV. Optical absorption in these nanotubes shifts from the UV to the visible, and the nanotubes themselves become candidate materials for design of electrodes for electrochemical water photolysis.

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REFERENCES

1. P. F. Manicone, P. R. Iommetti, and L. Raffaelli, *J. Dentistry* **35**, 819 (2007).
2. A. W. Amer, S. M. Mohamed, and A. M. Hafez, *RSC Adv* **4**, 36336 (2014).
3. M. B. Suresh and R. Johnson, *Intern. J. Energy Res.*, 1291 (2012).
4. L. N. Wang and J. L. Luo, *Electrochem. Commun.* **12**, 1559 (2010).
5. F. Vacandio, M. Eyraud, P. Knauth, and T. Djenizian, *Electrochem. Commun.* **13**, 1060 (2011).
6. J. L. Zhao, X. X. Wang, and L. B. Zhang, *J. Hazard. Mater.* **188**, 231 (2011).
7. R. Hahn, S. Berger, and P. Schmuki, *J. Solid State Electrochem.* **14**, 285 (2010).
8. X. X. Wang, J. L. Zhao, X. R. Hou, et al., *React. Kinet., Mechanisms Catal.* **104**, 227 (2011).
9. V. Vishwanathan, H. S. Roh, and J. W. Kim, *Catal. Lett.* **96**, 23 (2004).
10. M. Alvarez, T. Lopez, and J. A. Odriozola, *Appl. Catal. B* **73**, 34 (2007).
11. C. Karunakaran and S. Senthilvelan, *J. Mol. Catal. A: Chem.* **233**, 1 (2005).
12. G. Guo and Y. Chen, *Physica A* **84**, 431 (2006).
13. H. Chen, G. Jiang, T. Jiang, et al., *MRS Commun.* **5**, 525 (2015).
14. L. M. Guo, J. L. Zhao, X. X. Wang, et al., *Mater. Sci. Eng. C* **29**, 1174 (2009).
15. F. W. Guo and P. Xiao, *J. Eur. Ceram. Soc.* **32**, 4157 (2012).
16. T. Tsoncheva, L. Ivanova, D. Paneva, et al., *Microporous Mesoporous Mater.* **120**, 389 (2009).
17. L. F. Chen, J. C. Hu, and R. M. Richards, *Chem. Phys.* **9**, 1069 (2008).
18. R. Wang, G. Jiang, and Y. Ding, *ACS Appl. Mater. Interfaces* **3**, 4154 (2015).
19. Z. Li, W. Renata, and K. Witold, *ACS Appl. Mater. Interfaces* **4**, 4499 (2012).
20. J. A. Navio, M. C. Hidalgo, and G. Colon, *Langmuir* **17**, 202 (2001).
21. M. Alvarez, T. Lopez, and J. A. Odriozola, *Appl. Catal. B* **73**, 34 (2007).
22. J. C. Garcia, L. M. Scolfaro, and A. T. Lino, *J. Appl. Phys.* **100**, 104103 (2006).
23. N. Fu, X. Wang, Y. Ma, et al., *J. Phys. D: Appl. Phys.* **49**, 135105 (2016).
24. Y. S. Vidya, K. S. Anantharaju, H. Nagabhushana, et al., *Spectrochim. Acta A* **135**, 241 (2015).
25. H. W. Zhang, X. Y. Fu, S. Y. Niu, et al., *J. Non-Cryst. Solids* **354**, 1559 (2008).
26. X. Qu, D. Xie, L. Cao, et al., *Ceram. Int.* **40**, 12647 (2014).
27. B. Neppolian, Q. Wang, and H. Yamashita, *Appl. Catal. A* **333**, 264 (2007).
28. N. Fu, X. Wang, L. Guo, et al., *J. Mater. Sci.-Mater. Electron.* doi 10.1007/s10854-017-6407-7
29. M. Garcia-Hipolito, R. Martinez, and O. Alvarez-Fregoso, *J. Lumin.* **93**, 9 (2001).
30. N. Bashrom, K. A. Razak, and Z. Lockman, *Surf. Coat. Technol.* **320**, 371 (2017).
31. W. Jiang, J. He, J. Zhong, et al., *Appl. Surf. Sci.* **307**, 407 (2014).
32. P. N. D'yachkov, O. M. Kepp, and A. V. Nikolaev, *Dokl. Akad. Nauk* **365**, 215 (1999).
33. O. M. Kepp and P. N. D'yachkov, *Dokl. Akad. Nauk* **365**, 354 (1999).
34. P. N. D'yachkov, *Electronic Properties and Applications of Nanotubes* (Laboratoriya Znaniy, Moscow, 2012) [in Russian].
35. P. N. D'yachkov, *Int. J. Quantum Chem.* **116**, 174 (2016).
36. M. Guo, J. Zhao, X. Xu, et al., *Mater. Lett.* **111**, 93 (2013).

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