Electronic Structure and Optical Properties of Zirconia
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Abstract—The effects of substitutional impurities and oxygen vacancies on the electronic structure and optical properties of cubic zirconia were studied using band-structure calculations. It is shown that oxygen vacancies produce additional states near the Fermi level, whereas impurity atoms make an insignificant contribution to the states in the valence band and at the bottom of the conduction band, and their effect has a predominantly electrostatic character. The mechanisms of the stabilization of the high-temperature ZrO$_2$ polymorphs are elucidated. The calculation results agree well with x-ray photoelectron spectroscopy and optical data.

INTRODUCTION

There is currently considerable research interest in zirconia-based ceramics engendered by the various technological applications of these materials. Understanding the physical nature of the phase transformations in zirconia in the context of first-principles theoretical studies continues to be a challenge. ZrO$_2$ is known to exist in three polymorphs: monoclinic (M), tetragonal (T), and cubic (C). The high-temperature phases C and T can be stabilized to lower temperatures by the introduction of other metal oxides, e.g., Y$_2$O$_3$, MgO, and CaO. Crucial for understanding the structural, thermodynamic, and spectroscopic properties of zirconia on a microscopic scale are detailed studies of its electronic structure. Although the band structure of zirconia was investigated in many works with the use of various band approaches, most calculations, except those reported in [1-4], were focused on undoped phases. The results of band-structure calculations were discussed in [1, 5]. French et al. [6], carried out, along with band-structure calculations, an optical study of the three ZrO$_2$ polymorphs. However, their calculations were concerned with undoped structures, while the experimental study was performed on Y$_2$O$_3$-stabilized materials. It appears interesting to compare results on the electronic structure of doped materials with experiment. In the present paper, we address this issue.

CALCULATIONAL APPROACH

The electronic structure of the undoped C and T phases was calculated by the linearized muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA) [7]. In the case of doped phases, we considered periodically situated supercells each containing 12 atoms. The drawbacks to this approach are obvious: there is no way to model structural disordering, and there are certain difficulties in calculations for low concentrations of vacancies and impurities. At the same time, this approach is justified if the results are used to analyze characteristics that are only weakly dependent on disordering. Moreover, as shown earlier [8], LMTO-ASA results agree with the results provided by the KKR-CA method. To model vacancies, we replaced one or a few of the eight oxygens by empty spheres. As substitutional impurities, we considered yttrium and magnesium. Calculations were performed for 10 and 20 k points along symmetry lines in the Brillouin zone. These numbers of k points were found to ensure well-converged total energy, which increased by 0.005 Ry when the number of points was increased and differed by 0.008 Ry from the value calculated for an fcc cell (C phase, three atoms per cell) at 161 k points. All of the energy parameters of the C phase calculated in our approach are in good agreement with those obtained for the fcc cell. The observed slight differences originate from the reduction in the number of points in the Brillouin zone in view of the larger number of atoms in the unit cell, which leads to extremely time-consuming computations. Note also that our energy-band results for yttria-stabilized zirconia differ only little from those obtained by the LMTO method (program configured at the Theoretical Department, Lebedev Institute of Physics, Russian Academy of Sciences) based on a complex of 24 atoms per cell [4]. We used metal and oxygen spheres of the same radius and a basis function set corresponding to $l_{\text{max}} = 2$. Exchange-correlation effects were included in the Ceperley–Alder approximation [9].

RESULTS AND DISCUSSION

Figure 1 displays the density-of-states (DOS) results for undoped and doped cubic zirconia. The calculation results for undoped C and T phases were discussed in detail elsewhere [1, 5]. Note good agreement with the OLCAO energy-band results reported by Zandiehnaden et al. [10], who carried out self-consistent calculations for the cubic phase only. The dielectric
gap of 4.167 eV obtained for the $T$ phase agrees well with the results reported in [10] (4.11 eV) and [11] (4.35 eV) and recent OLCAO calculations [6]. However, whereas the calculations by French et al. [6] predict an increase in the gap in going from the higher symmetry, tetragonal phase to the lower symmetry, monoclinic phase (from 4.28 to 4.46 eV), in accordance with their experimental results (5.78–5.83 or 6.62–7.09 eV), a larger gap was obtained for the cubic phase (theoretical prediction, 4.93 eV; experimental value, 6.01–7.08 eV). The last result is in conflict with the general trend revealed in our earlier study [5] and also with the results obtained in [10, 11]. Furthermore, French et al. [6] report the value of the direct gap calculated at point $\Gamma$ of the Brillouin zone, whereas their dispersion curves (Fig. 6 in [6]) indicate an indirect gap ($X-\Gamma$), which is narrower by at least 1 eV. The scatter in the measured gap (e.g., 5.78 and 6.62 eV for the $T$ phase) originates from the procedure used to determine the direct band gap—extrapolation of the optical absorption curve. Note also that our results on the width of the valence bands in the $C$ and $T$ phases are in reasonable agreement with experimental data [6]: the calculated width of the O 2p band is 6.77 eV in the $C$ phase and 5.23 eV in the $T$ phase; the experimental values are 7 and 6 eV, respectively.

Consider in greater detail the experimental results obtained for zirconia in [6]. The measured spectra of the three zirconia polymorphs show a strong absorption, designated $E_1$ [6], around 8 eV (0.59 Ry): a sharp peak for the $C$ phase, a broad maximum for the $T$ phase, and a plateau extending from 8 to 10 eV for the $M$ phase. Below $E_1$, the optical conductivity of the $C$ phase rises faster than those of the other two phases. French et al. [6] also observed a small shoulder at 6.5 eV (0.48 Ry), which becomes more prominent in going from the $C$ to $M$ phase. Their calculations indicate the presence of a finer structure in optical conductivity curves, in line with our findings (Fig. 2). Both their and our calculations show that, in addition to the major peak, there is a weaker peak which is stronger for the $T$ and $M$ phases. It is this peak that manifests itself as the $E'_1$ shoulder in the experimental curves. The predicted absorption minimum at 14 eV (1 Ry) is observed at 15 eV (1.1 Ry). In principle, comparison of theoretical predictions with experimental data at high energies requires two-panel LMTO calculations with an increased basis function set, to more accurately assess the structure of unoccupied bands. Our calculations, encompassing 60 bands, allow nevertheless all of the observed high-energy peaks to be revealed. As in the calculations by French et al. [6], peak $E_2$ (16.7 eV, 1.22 Ry) appears as a doublet in the range 15–18 eV (1.1–1.3 Ry), the position of peak $E_3$ (21.5 eV, 1.58 Ry) agrees with that of the theoretical doublet at 21–23 eV (1.54–1.69 Ry), and peak $E_4$ (33.5 eV, 2.46 Ry) is reproduced by a peak at 30 eV (2.2 Ry). As might be expected, the agreement with experiment becomes poorer with increasing energy. Yet another important point warrants mention. In both present and earlier calculations [6], the theoretical curves are shifted to lower energies as compared to experimental data. This is related to the use of the local-density-functional approximation. As is well known, calculations in this approach yield dielectric gaps underrated by ~1 eV.

Calculations for C-ZrO$_2$ containing oxygen vacancies (Fig. 3) reveal additional bands lying in the gap between the valence and conduction bands and also in the gap within the conduction band of the undoped $C$ phase. With increasing vacancy concentration, the peaks below $E_F$ become stronger (Fig. 4). The vacancy-related states result from a distortion of the band structure of undoped compounds, breaking the symmetry of the nearest neighbor environment of metal atoms. As shown earlier [8], the appearance of two vacancies in the oxygen coordination of a metal atom reduces symmetry from Oh to D$_{4h}$ and gives rise to an additional splitting of $t_{2g}$ and $e_g$ levels, thereby producing additional levels. Note also that the removal of an oxygen atom reduces the numbers of states and electrons in the O 2s band and O(2p)–Zr(4d) complex, the number of states decreasing faster than the number of electrons.