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Structure and Positron Characteristics of Basic Open Volume Defects in Zirconia

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Abstract. In this contribution we report on the theoretical study of basic vacancy-like defects in cubic zirconia and yttria stabilized zirconia. In particular, we concentrate on oxygen vacancy, zirconium vacancy and oxygen vacancy – yttrium complex. Relaxed atomic configurations of studied defects are obtained by means of an ab initio pseudopotential method within the supercell approach. Positron characteristics, like positron lifetime and binding energy to defects, are calculated using self-consistent electron densities and potentials taken from ab initio calculations.

Introduction

Zirconia (ZrO_2) based materials are promising for many practical applications, including heat-resistance structural and functional ceramics, solid oxide fuel cells, oxygen sensors, as well as applications in nuclear fuel and waste confinement. For such applications it is often necessary to employ the cubic zirconia phase that can be stabilized at ambient temperature by adding yttria. Due to such doping oxygen vacancies are present in yttria stabilized zirconia (YSZ) in a large amount. An aggregation of oxygen vacancies was also detected experimentally and confirmed by simulations. Nevertheless, the role of point defects in YSZ is yet far from being understood. Dominant positron trapping sites in YSZ are supposed to be associated with the oxygen vacancy – yttrium complex ($Y'_{Zr}V_O^{\bullet\bullet}Y'_{Zr}$) due to the neutralization of positively charged oxygen vacancies ($V_O^{\bullet\bullet}$) by negatively charged substitutional yttrium atoms in their neighborhood [1]. Positron trapping at negatively charged zirconium vacancies (V_{Zr}''''), is neglected due to the observation of their extremely low concentration in YSZ [1]. This interpretation was used in several other works on YSZ [2, 3, 4], but the value of the positron lifetime that should be associated with such a complex and ability of these complexes trap positrons is still under question. In our previous work [5] we calculated positron lifetimes (τ) and high momentum profiles for the perfect lattice and selected non-relaxed defect configurations in three ZrO_2 polymorphs. However, the quantitative agreement between calculated and experimental lifetimes was not reached. In this work we performed the structural relaxations of several types of vacancy-like defects in ZrO_2 and calculated positron characteristics for them.

Computational methods

The Vienna ab initio simulation package [6] (VASP) considering the local density approximation (LDA) and generalized gradient approximation (GGA) pseudopotentials, within the projected augmented wave framework, supplied along with the package was employed in order to obtain relaxed defect geometries. 96-atom supercells containing studied defects were used in the course of minimization of the total energy with respect to atomic positions. Calculations were performed for the cubic ZrO_2 phase with the lattice parameter 5.08 Å [7]. The starting defect configurations for studied vacancy-like defects were obtained by removing appropriate atoms from the ZrO_2 lattice. Oxygen

vacancy – yttrium complex was modelled by removing an oxygen atom and substituting two Zr atoms by Y in sites that are next-nearest-neighbors of the vacancy [8].

Two approaches were employed for the calculation of positron parameters for the relaxed defects: (i) Ion positions for relaxed defect were treated by conventional atomic superposition (ATSUP) method [9], i.e. the effective positron potential was constructed from superposition of electron densities of free atoms located at the relaxed positions. Hence, the charge transfer is neglected in this approach, and (ii) the Schrödinger equation for positron was solved using an effective potential obtained from the self-consistent electron density and Coulomb potential calculated by VASP for the relaxed defect geometry. This means that the charge transfer between cations and anions, which is an important effect in oxides, is taken into account.

In the positron lifetime calculations the electron-positron correlations were treated according to Boroński-Nieminen (BN) [10] with the correction [11] for incomplete positron screening with a dielectric constant of $\varepsilon_\infty = 4.6225$ and the gradient-correction (GC) scheme of Barbiellini et al. [12].

For the purpose of positron calculations, the relaxed VASP supercells were extended to a total of 768 atoms by adding atoms at sides of VASP supercells. Such added atoms are arranged in the form of the regular ZrO_2 lattice. The positron lifetimes for bulk ZrO_2 and studied defects were calculated [13] using corresponding ground state positron wave functions and considering the abovementioned approaches to electron-positron correlations. The positron binding energy E_B to a defect was determined as a difference of the ground state positron energies for the bulk and corresponding defect.

Results and discussion

The following defects have been studied (the Kröger-Vink notation is used): zirconium vacancy ($V_{Zr}^{''''}$), oxygen vacancy ($V_O^{\bullet\bullet}$), and oxygen vacancy – yttrium complex ($Y_{Zr}^{'}V_O^{\bullet\bullet}Y_{Zr}^{'}$). Calculated positron bulk lifetime (bulk) and lifetimes and binding energies both for relaxed and non-relaxed defect configurations in cubic ZrO_2 phase are given in Table 1.

Table 1. Calculated positron lifetimes (τ) and binding energies (E_B) for various positron states.

Positron state, pseudopotential	Charge transfer neglected				Charge transfer included	
	τ [ps] BN	E_B [eV] BN	τ [ps] GC	E_B [eV] GC	τ [ps] BN	E_B [eV] BN
Bulk	138	-	146	-	-	-
Bulk, LDA	-	-	-	-	134	-
Bulk, GGA	-	-	-	-	133	-
$V_O^{\bullet\bullet}$, non-relaxed	140	0.02	149	0.03	-	-
$V_O^{\bullet\bullet}$, LDA	139	0.01	148	0.02	135	–0.20
$V_O^{\bullet\bullet}$, GGA	139	0.01	147	0.02	132	–0.12
$Y_{Zr}^{'}V_O^{\bullet\bullet}Y_{Zr}^{'}$, non-relaxed	139	<0.01	148	0.02	-	-
$Y_{Zr}^{'}V_O^{\bullet\bullet}Y_{Zr}^{'}$, LDA	167	0.34	175	0.34	141	0.05
$Y_{Zr}^{'}V_O^{\bullet\bullet}Y_{Zr}^{'}$, GGA	164	0.30	173	0.40	139	0.04
$V_{Zr}^{''''}$, non-relaxed	196	2.71	222	2.44	-	-
$V_{Zr}^{''''}$, LDA	223	2.85	244	2.72	226	2.81
$V_{Zr}^{''''}$, GGA	216	2.75	238	2.60	220	2.80

The open volume of $V_O^{\bullet\bullet}$ was reduced in the relaxed configuration due to an inward relaxation of both O and Zr neighbors. Thus, $V_O^{\bullet\bullet}$, which was found to be unable of positron trapping in the rigid lattice geometry [5], is even less attractive for positrons, in the relaxed configuration. The positively charged $V_O^{\bullet\bullet}$ repels the positron and forces it to sample regions with higher electron density causing

thus a shortening of the positron lifetime as well as an increase of the positron energy. In fact, the positron annihilates in a delocalized state, but the lattice differs from the true bulk.

The open volume of the $Y'_{Zr}V_O^{\bullet\bullet}Y'_{Zr}$ complex increases due to an outward relaxation of the nearest neighbor Zr atoms in <111> directions, but the charge transfer diminishes this effect. Hence, the neutral complex $Y'_{Zr}V_O^{\bullet\bullet}Y'_{Zr}$ cannot be considered as a positron trap within the current approach. This defect is often assumed to be responsible for positron trapping in YSZ (see e.g. [2, 3, 4]). Further refinement of theoretical positron calculations for defects in YSZ should consider the positron-induced forces [14]. Such a refined approach could modify results given here, especially regarding the $Y'_{Zr}V_O^{\bullet\bullet}Y'_{Zr}$ complex, which could contribute to the solution of the question whether this defect can act as a positron trap.

The open volume of V''''_{Zr} becomes larger in the relaxed configuration due to an outward relaxation of the nearest neighbor O atoms in <111> directions. Thus, relaxed V''''_{Zr} represents a deep positron trap. Considering charge transfer does not have a pronounced effect for V''''_{Zr}.

Further details concerning the structure of studied defects, computation methods as well as the comparison with experimental lifetime data will be published elsewhere.

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