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2010 J. Phys.: Conf. Ser. 225 012035

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## Investigation of hydrogen interaction with defects in zirconia

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**Abstract.** Defect studies of a  $\text{ZrO}_2 + 9 \text{ mol. \% Y}_2\text{O}_3$  single crystal were performed in this work using a high resolution positron lifetime spectroscopy combined with slow positron implantation spectroscopy. In order to elucidate the nature of positron trapping sites observed experimentally, the structural relaxations of several types of vacancy-like defects in zirconia were performed and positron characteristics for them were calculated. Relaxed atomic configurations of studied defects were obtained by means of *ab initio* pseudopotential method within the supercell approach. Theoretical calculations indicated that neither oxygen vacancies nor their neutral complexes with substitute yttrium atoms are capable of positron trapping. On the other hand, zirconium vacancies are deep positron traps and are most probably responsible for the saturated positron trapping observed in yttria stabilized zirconia single crystals. However, the calculated positron lifetime for zirconium vacancy is apparently longer than the experimental value corresponding to a single-component spectrum measured for the cubic  $\text{ZrO}_2 + 9 \text{ mol. \% Y}_2\text{O}_3$  single crystal. It was demonstrated that this effect can be explained by hydrogen trapped in zirconium vacancies. On the basis of structure relaxations, we found that zirconium vacancy – hydrogen complexes represent deep positron traps with the calculated lifetime close to the experimental one. In zirconium vacancy – hydrogen complexes the hydrogen atom forms an O-H bond with one of the nearest neighbour oxygen atoms. The calculated bond length is close to 1 Å.

### 1. Introduction

Zirconia ( $\text{ZrO}_2$ ) exhibits a high thermal stability and a low thermal conductivity together with good mechanical properties (high strength and enhanced fracture toughness). Zirconia-based materials are promising for the use in a large area of industrial applications including refractory materials, ceramic glazes, oxygen sensors, solid oxide fuel cells etc [1]. Three zirconia polymorphs are known to exist at ambient pressure [2]. The high temperature cubic phase is stable at temperatures above 1380 °C. At lower temperatures zirconia transforms into a tetragonal and subsequently into a monoclinic phase.

The high temperature cubic phase can be stabilized down to room temperature by addition more than 8 mol % of trivalent yttria ( $\text{Y}_2\text{O}_3$ ) [2]. Such system is then called yttria stabilized zirconia (YSZ). An embedment of  $\text{Y}_2\text{O}_3$  into the  $\text{ZrO}_2$  host lattice leads to a deviation from stoichiometry resulting in the creation of a high amount of native oxygen vacancies. Hence, vacancies play certainly a very important role in physical properties of YSZ.

High quality YSZ single crystals are nowadays commercially available. As vacancies strongly influence properties of YSZ, it is very important to characterize in detail vacancies in YSZ crystals. It

this work we investigated vacancies and vacancy-like defects using positron annihilation spectroscopy (PAS), which is a well established experimental technique with a high sensitivity to open volume point defects like vacancies. In order to facilitate interpretation of experimental PAS data, we performed also theoretical modeling of defects in YSZ by state-of-art *ab initio* electronic structure calculations including ionic relaxations.

## 2. Experimental

A commercially available  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  single crystal with dimensions  $10 \times 10 \times 0.5 \text{ mm}^3$  supplied by Crystec GmbH, Berlin was investigated in the present work. Surfaces of YSZ crystals were optically polished.

A digital positron lifetime (LT) spectrometer [3] with an excellent time resolution of 145 ps (FWHM  $^{22}\text{Na}$ ) was employed for LT studies. The decomposition of experimental LT spectra to individual components was performed by a maximum likelihood-based procedure [4].

Slow positron implantation spectroscopy (SPIS) was performed on a magnetically guided variable energy slow positron beam SPONSOR [5]. The energy of incident positrons can be varied in the range from 0.03 to 36 keV. Doppler broadening (DB) of annihilation profile was measured by high purity Ge detector with an energy resolution of  $(1.06 \pm 0.01) \text{ keV}$  at 511 keV. The shape of broadened annihilation profile was analyzed using the  $S$  parameter and the dependence of the  $S$  parameter on the positron energy was fitted by the VEPFIT code [6].

## 3. Theoretical calculations

As lattice relaxations around defects are known to be rather high in semiconductors including oxides [7], it is important to calculate positron characteristics for relaxed defect geometries. *Ab initio* calculations of atomic relaxations around defects and determination of the relaxed defect geometry having the lowest energy was performed using the Vienna *ab initio* simulation package (VASP) [8]. The calculations were performed using the generalized gradient approximation (GGA) projector augmented-wave (PAW) pseudopotential.  $4s$ ,  $4p$ ,  $5s$  and  $4d$  Zr electrons and  $2s$  and  $2p$  O electrons were included in the *ab initio* VASP pseudopotential calculations of electronic structure and ion relaxations. For calculations of vacancy-hydrogen complexes  $1s$  H electron was included in the VASP calculations as well. Defects were modeled using 96 atom-based supercells employing  $2 \times 2 \times 2$   $k$ -mesh sampling centered at the  $\Gamma$  point. Cubic  $\text{ZrO}_2$  (fluorite) lattice with lattice parameter  $a = 5.08 \text{ \AA}$  [9] was assumed in calculations.

Positron lifetimes and positron binding energies to defects were calculated in the limit of vanishing positron density within the so called ‘conventional scheme’ described in ref. [10], which becomes nowadays a standard for calculations of positron parameters. Note that positron binding energy to a defect is defined as

$$E_B = E_f - E_d, \quad (1)$$

where  $E_f$  is the ground state energy of a free, delocalized positron in the perfect  $\text{ZrO}_2$  lattice and  $E_d$  is the ground state energy of a positron trapped at a particular defect.

The electron density needed for the construction of the effective positron potential was calculated using two approaches:

- (i) The atomic superposition (ATSUP) method [11] which uses superimposed atomic electron densities calculated by a self-consistent relativistic atomic code [12]. The ATSUP approach *neglects* charge transfer in crystals, but it is a very fast method which can be used even for very large supercells.
- (ii) The self-consistent valence electron density calculated by VASP was used in positron calculations. In this approach frozen-core electron orbitals, which are unaffected by crystal bonding, were added to the self-consistent VASP valence electron density. Hence in this approach charge transfer is *included* in calculations of positron parameters.

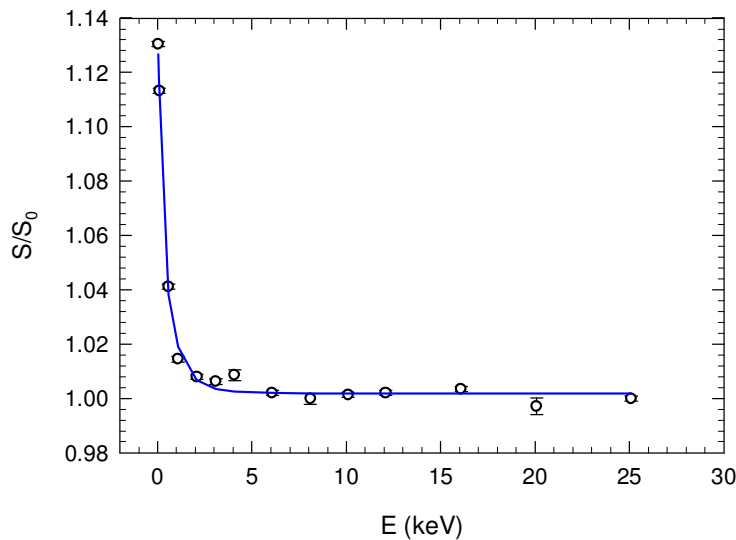
Two approaches were used also for the correlation part of the positron potential:

- (i) The local-density approximation (LDA) using results of Arponen and Pajanne [13] parametrized by Boroński and Nieminen [14] taking into account incomplete positron screening [15] considering a high frequency dielectric constant  $\epsilon_\infty = 4.62$ , and
  - (ii) A GGA scheme for electron-positron correlations as formulated by Barbiellini et al. [16].
- Combination of the approaches described above results in four various schemes how to calculate positron parameters denoted here: ATSUP-LDA, ATSUP-GGA, VASP-LDA, and VASP-GGA.

#### 4. Results and discussion

##### 4.1. Experimental results

LT measurements revealed that the  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  crystal exhibits a single component spectrum (apart from the source component) with a lifetime of  $(175 \pm 1) \text{ ps}$ . This lifetime is remarkably longer than the calculated lifetime of for free positrons in zirconia (see Table 1). Hence, this result suggests that virtually all positrons in the studied YSZ crystal are trapped at certain defects (saturated positron trapping).



**Figure 1.** Dependence of the  $S$  parameter (open circles) on the positron energy the  $E$  for the  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  single crystal. The  $S$  parameter was normalized to the bulk value  $S_0$  measured at  $E = 25 \text{ keV}$ . The solid line shows a model curve fitted by the VEPFIT.

Figure 1 shows dependence of the  $S$  parameter on the positron energy  $E$  measured on the  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  crystal by SPIS. The solid line plotted in the figure is a model function calculated by the VEPFIT software assuming a single layer model. A very short positron diffusion length  $L_+ = (8.6 \pm 0.4) \text{ nm}$  was obtained from fitting. This gives a strong evidence that positrons are trapped at certain lattice defects. Note that similar result was obtained by Gryzspan et al. [17] on another cubic  $\text{ZrO}_2$  crystal.

The concentration of positron traps can be estimated from SPIS results using the relation

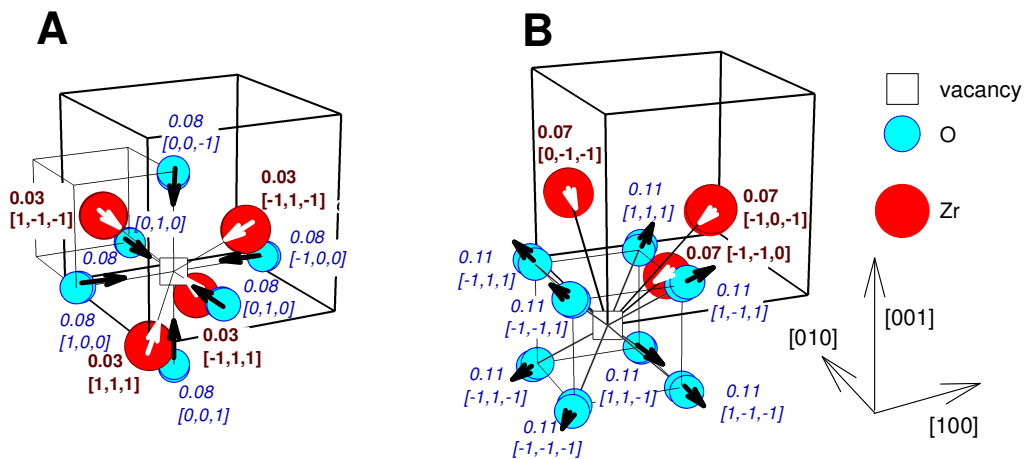
$$c = \frac{1}{\nu \tau_B} \left( \frac{L_{B,+}^2}{L_+^2} - 1 \right), \quad (2)$$

where  $\tau_B$  and  $L_{B,+}$  denote the free-positron lifetime and diffusion length in a perfect  $\text{ZrO}_2$  lattice, while  $L_+$  is the mean positron diffusion length measured in the sample. Here we used  $\tau_B \approx 150 \text{ ps}$  calculated using the VASP-GGA approach (see Table 1) and  $L_{B,+} \approx 150 \text{ nm}$ , which is a typical mean positron diffusion length in similar materials [18]. The symbol  $\nu$  denotes the specific positron trapping rate to defects of given type. Using  $\nu \approx 10^{14} \text{ at. s}^{-1}$ , which is a typical value for monovacancies in most solids [10], we estimated the defect concentration in the studied crystal to be  $c \approx 2 \text{ at.}\%$ . Despite of uncertainties of input quantities, Eq. (2) implies a very high defect concentration comparable in order

of magnitude with the concentration of substitutional yttrium atoms in the crystal (5.5 at.%). This testifies that the defects responsible for positron trapping in the  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  single crystal must be of a structural origin.

#### 4.2. Theoretical modeling of vacancies

Calculated relaxed geometries of the oxygen and zirconium vacancies are shown in figures 2A and 2B, respectively. Calculated positron parameters for the defect-free crystal and various defects are listed in Table 1. One can see in figure 2A that in the case of the oxygen vacancy the nearest neighbor Zr ions and also the second nearest neighbor O ions relax towards the vacancy, i.e. the free volume of the oxygen vacancy is *reduced*. It was shown [19] that even in a rigid lattice the oxygen vacancy represents a too shallow potential well that is unable to confine a positron. The same conclusion holds for the relaxed oxygen vacancy, which due to the inward relaxation of neighbors becomes even a shallower well. Inability of the oxygen vacancy to trap positrons is demonstrated by the positron lifetime which approaches the bulk lifetime and a very low or even a negative positron binding energy (see Table 1).



**Figure 2.** Relaxed defect geometries for (A) oxygen vacancy, (B) zirconium vacancy. The values given are atomic displacements in Å and displacement directions.

On the other hand, the zirconium vacancy is a deep positron trap even in the rigid  $\text{ZrO}_2$  lattice. Figure 2B shows that the nearest neighbor oxygen anions relax outward, i.e. the open volume of the zirconium vacancy is *increased* due to relaxation. Hence the relaxed zirconium vacancy is even a deeper positron trap than the zirconium vacancy in a rigid lattice. This is reflected by a significantly increased lifetime of trapped positrons and a high positron binding energy.

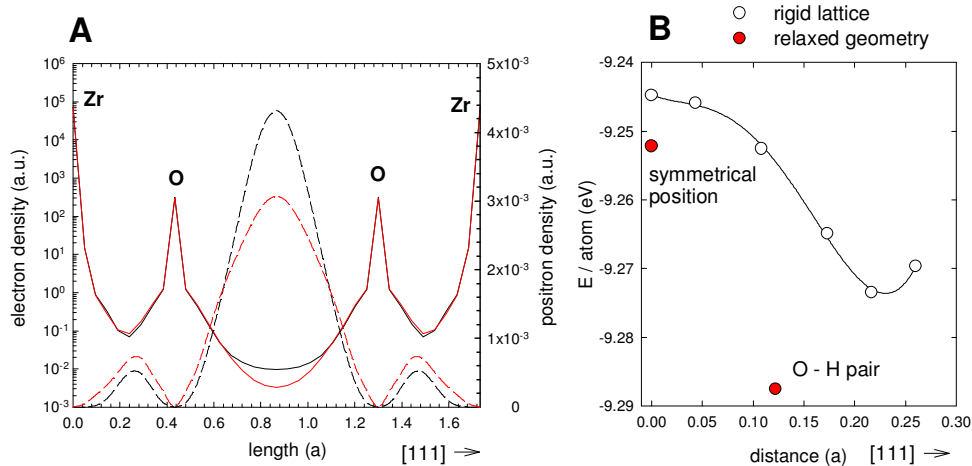
One can see in Table 1 that results for the same defect may considerably differ when calculated by various approaches. It should be mentioned that the precision of the approaches used here is not the same. It is well known [16] that LDA approximation of electron-positron correlation overestimates annihilations with core electrons. This drawback is to some extent compensated if electron density is constructed by superposition of atomic densities and charge transfer is neglected [20]. Hence lifetimes calculated using VASP-LDA approach are usually shorter than experimental values and better agreement with experiment is obtained employing a simpler ATSUP-LDA approach. The GGA approximation of electron-positron correlations is more sensitive to details of electron density [16] and atomic superposition is not precise enough for the GGA scheme. As the consequence, the ATSUP-GGA approach over estimates positron localization and lifetimes calculated within this scheme are often found to differ from experimental values. On the other hand, positron lifetimes calculated within the GGA scheme with self-consistent electron density (i.e. including the charge transfer) are in very

good agreement with experiment for most chemical elements [16,21]. In any case, the suitability of both the LDA and GGA approaches for ZrO<sub>2</sub> and other oxides needs to be further investigated and we refer readers also to ref. [22] for further discussion.

**Table 1.** Positron lifetimes  $\tau$  and positron binding energies  $E_B$  for various positron states calculated within the four various approaches described in section 3. Two different configurations of zirconium vacancy with hydrogen are described in the text.

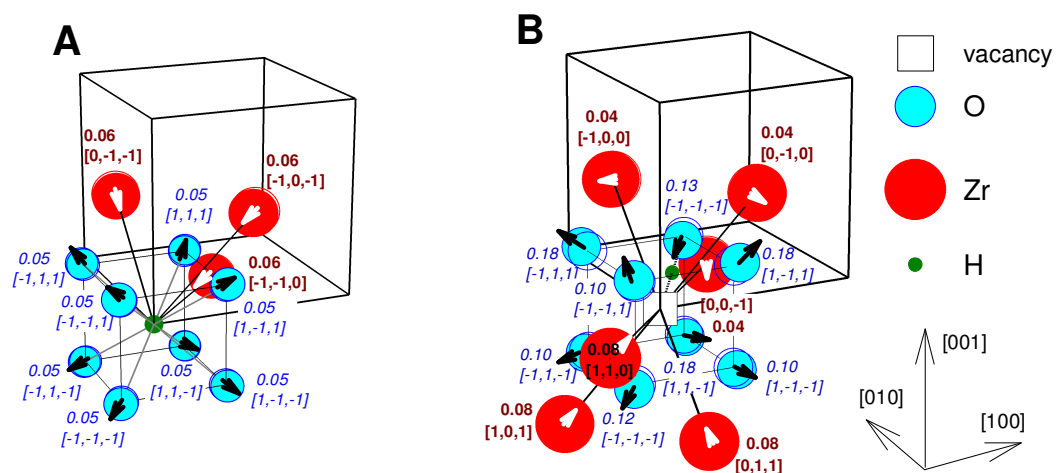
	<i>charge transfer neglected</i>		<i>charge transfer included</i>		<i>charge transfer neglected</i>		<i>charge transfer included</i>	
	ATSUP-LDA		VASP-LDA		ATSUP-GGA		VASP-GGA	
	$\tau$ (ps)	$E_B$ (eV)	$\tau$ (ps)	$E_B$ (eV)	$\tau$ (ps)	$E_B$ (eV)	$\tau$ (ps)	$E_B$ (eV)
Bulk	138	-	133	-	147	-	151	-
O-vacancy	139	0.01	132	-0.12	147	0.02	153	0.05
Zr-vacancy	216	2.75	220	2.80	238	2.60	287	2.33
Zr-vacancy with H (i) symmetrical position	164	1.87	167	0.89	178	1.75	195	1.08
Zr-vacancy with H (ii) O-H pair	197	2.37	171	1.44	211	2.28	175	1.83

Moreover, due to the ionic nature of bonding, the effect of charge transfer in ZrO<sub>2</sub> is relatively important. This is demonstrated in figure 3A which compares the electron and positron density in a perfect ZrO<sub>2</sub> crystal calculated within the ATSUP scheme, i.e. neglecting the charge transfer, and using the VASP-GGA approach when the charge transfer was included. The electron density in the interstitial region among oxygen anions was reduced due to the charge transfer from Zr atoms to O anions. As the positron density has a maximum in these interstitial regions, the positron annihilation rate (and thereby the lifetime) is very sensitive to the electron density there and its decrease caused by charge transfer leads to a longer bulk positron lifetime calculated within the VASP-GGA approach.



**Figure 3.** (A) Calculated electron density (solid lines) and positron density (dashed lines) in the [111] direction in a perfect ZrO<sub>2</sub> crystal. The results obtained when charge transfer was neglected are plotted by black lines. Red lines show results of calculations with charge transfer included. (B) The supercell energy per atom as a function of the hydrogen distance from the center of the vacancy. Open circles show results for hydrogen moved in the [111] direction from the vacancy center towards the nearest neighbour oxygen atom in the rigid lattice. Full red circles are energies of relaxed configurations (i) and (ii) described in the text.

Our results showed that oxygen vacancies even if present in a high concentration cannot explain the component with the lifetime 175 ps determined by LT spectroscopy. Note that complexes of oxygen vacancies with yttrium atoms were proposed by some authors as possible positron traps in YSZ, see e.g. [23,24]. A variety of these complexes, which can be expected to be formed in YSZ, were investigated in ref. [25]. However, none of them was found to be really capable of positron trapping. Thus, we can conclude that positron traps found in  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  crystal should be related to the zirconium vacancy. However, the zirconium vacancy is too deep positron trap characterized by a lifetime, which is remarkably longer than the 175 ps experimental value. Shortened lifetime of trapped positrons could be explained by some impurity associated with zirconium vacancies and reducing their free volume. Such an impurity could also reduce the formation energy of the zirconium vacancy, which is known to be rather high in pure  $\text{ZrO}_2$  [26]. When considering possible impurities, hydrogen can be considered as the most promising candidate. First, the presence of hydrogen can hardly be avoided in any experimental technique of YSZ crystal growth. Second, hydrogen is highly mobile and can be relatively easily incorporated into  $\text{ZrO}_2$  structure due its tendency to bind with oxygen. Indeed, it was found on the basis of our theoretical calculations that hydrogen in a perfect  $\text{ZrO}_2$  crystal becomes bound to one of the nearest neighbor oxygen anions and forms an O-H pair with a bonding length of  $\approx 1 \text{ \AA}$ .



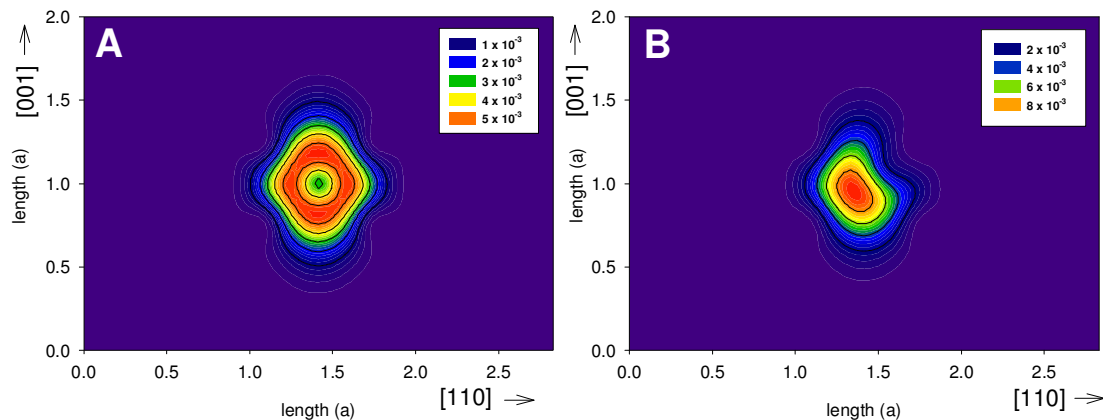
**Figure 4.** Relaxed defect geometries for two configurations of the zirconium vacancy containing a hydrogen atom: (A) “symmetrical case” with retained cubic symmetry and hydrogen in the center of vacancy, (B) the lowest energy geometry where hydrogen is displaced 1.13 Å from the centre of vacancy towards a nearest neighbour O atom and forms O-H pair with bonding length of 0.96 Å. The values given in the figure are atomic displacements in Å and displacement directions.

Our calculations showed that hydrogen is trapped in the zirconium vacancy. Figure 4 shows the relaxed geometry of the zirconium vacancy containing hydrogen. Two cases were considered:

- (i) “symmetrical position” of hydrogen in the zirconium vacancy keeping the cubic symmetry of the  $\text{ZrO}_2$  lattice (see figure 4A) and
- (ii) the lowest energy geometry where the requirement of cubic symmetry was released. This configuration is shown in figure 4B.

In the case (i) hydrogen is located in the center of the zirconium vacancy and the nearest neighbor oxygen anions relax outward from the center of vacancy, i.e. in the similar manner as in the case of a plain zirconium vacancy only with lowered magnitude of their displacements. When the symmetry restriction is released, i.e. the case (ii), hydrogen moves towards a nearest neighbor oxygen anion and forms an O-H pair with bond length of  $\approx 1 \text{ \AA}$ . The relaxation of other nearest neighbor oxygen anions

is unequal and depends on the distance of oxygen anion from the O-H pair. Nevertheless in general, the nearest neighbor oxygen anions (except the one which formed the O-H pair) relax outward the center of the vacancy. To obtain a rough picture about hydrogen energies in the  $\text{ZrO}_2$  lattice with the zirconium vacancy we calculated energy of a rigid supercell with hydrogen atom moving from the center of the vacancy towards one of the nearest neighbor oxygen anions. The calculated energy per atom is plotted in figure 3B as a function of the hydrogen distance from the center of the vacancy. Clearly the minimum in energy corresponds to hydrogen displaced from the center of the vacancy towards oxygen and the formation of the O-H pair. The red points in Figure 3B show the energy of relaxed geometry in the case (i) and (ii). Obviously the case (ii), i.e. formation of O-H pair, represents the lowest energy configuration of the zirconium vacancy containing hydrogen.



**Figure 5.** Positron density in (110) plane calculated using VASP-GGA approach for relaxed zirconium vacancy with hydrogen: (A) “symmetrical case” with retained cubic symmetry and hydrogen in the center of vacancy, (B) the lowest energy geometry where hydrogen forms O-H pair with a nearest neighbor oxygen anion

Figures 5 A and B show the calculated positron density for the configurations (i) and (ii), respectively, while calculated positron characteristics are listed in Table 1. One can clearly see that the zirconium vacancy containing a hydrogen atom is capable of positron trapping. Moreover, the presence of hydrogen in the zirconium vacancy leads in both cases considered here to a shortening of lifetime of trapped positrons (see table 1). Interestingly, positron lifetime calculations within the VASP-GGA scheme for the lowest energy configuration of the zirconium vacancy containing hydrogen, i.e. the case (ii), results in a positron lifetime of 175 ps which agrees very well with the lifetime measured on the YSZ single crystal. Hence, we suggest that experimental data measured on the  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  single crystal can be explained by positron trapping at zirconium vacancies containing hydrogen. We note that similar defects were recently identified in hydrothermally grown ZnO crystals [22]. This result emphasizes necessity to determine experimentally the hydrogen content in YSZ single crystals and compare it with the estimated concentration of zirconium vacancies.

## 5. Conclusions

Investigations of defects in  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  single crystal were performed by positron lifetime measurements combined with slow positron implantation spectroscopy. The interpretation of experimental data was made with the aid of *ab initio* modeling of vacancies and vacancy-like defects in  $\text{ZrO}_2$ . It was found that oxygen vacancies are too shallow and are unable to confine positrons. On the other hand, zirconium vacancies are deep positron traps. Experimental data testified that the  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  single crystal contains a high density of defects because virtually all positrons annihilate from the trapped state. However, the experimental lifetime 175 ps is shorter than the calculated



lifetime of positrons trapped at the zirconium vacancy. Extended *ab initio* modeling of zirconium vacancy-hydrogen complexes revealed that hydrogen forms an O-H pair with one of the nearest neighbor oxygen anions. It was demonstrated that presence of hydrogen in the zirconium vacancy leads to a shortening of the positron lifetime and, in principle, can explain experimental data measured on the  $\text{ZrO}_2 + 9 \text{ mol.}\% \text{ Y}_2\text{O}_3$  single crystal.

### Acknowledgments

We are grateful to M.J. Puska for his ATSUP code that served as a basis for further developments. This work was supported by the Academy of Science of the Czech Republic (project KJB101120906) and the Ministry of Schools, Youths and Sports of the Czech Republic through the research plan No MSM 0021620834 and the project COST OC 165.

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