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Positron annihilation in three zirconia polymorphs

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Positron lifetimes and high momentum profiles both for the perfect lattice and selected defects are calculated in three (cubic, tetragonal and monoclinic) zirconia polymorphs using the atomic superposition method. Theoretical data are compared with the measured positron lifetime for cubic and tetragonal monocrystals of yttria-stabilized zirconia (YSZ) and coincidence Doppler broadening measurements on tetragonal monocrystals of YSZ. Positron lifetime spectra of YSZ monocrystals exhibit a single component spectrum with lifetimes 178 ps and 174 ps for cubic and tetragonal phases, respectively. Possible interpretations of measured lifetime and Doppler data are discussed.

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1 Introduction Zirconia (ZrO_2) based materials are promising for many practical applications, including heat-resistant structural and functional ceramics, solid oxide fuel cells and oxygen sensors, as well as applications in nuclear fuel and waste confinement. Positron annihilation may bring important information on defects in this class of materials, which is a substantial prerequisite for understanding zirconia properties in general.

At room temperature pure ZrO_2 exhibits the monoclinic baddelyite structure (m-ZrO_2, space group $P2_1/c$ [1]) with the Zr^{4+} ion in a distorted seven-fold coordination. On increasing the temperature, the structure transforms into a tetragonally distorted fluorite structure (t-ZrO_2, $P4_2/nmc$ [1]) at $T \sim 1370$ K, with Zr^{4+} surrounded by eight anions, but with two slightly different $Zr^{4+} - O^{2-}$ distances. Perfect eight-fold coordination is achieved at $T \sim 2643$ K with a transformation to a cubic fluorite structured phase (c-ZrO_2, $Fm\bar{3}m$ [1]), followed by melting at $T \sim 2988$ K. High-temperature c-ZrO_2 and t-ZrO_2 structures can be stabilized at room temperature by an addition of yttrium oxide (Y_2O_3). These so-called "yttria-stabilized zirconia" (YSZ) materials are stable over the following ranges: up to ~3 mol % Y_2O_3 for the monoclinic phase (m-YSZ), between approximately 2 mol % Y_2O_3 and 9 mol % Y_2O_3 for the tetragonal phase (t-YSZ) and between approximately 4 mol % Y_2O_3 and 30 mol % Y_2O_3 for the cubic phase (c-YSZ) [1]. Such an addition leads to the formation of structural oxygen vacancies in the ZrO_2 lattice which have a significant impact on physical properties of YSZ (see e.g. [2]).

Obviously, positron annihilation spectroscopy (PAS) has a high potential for the investigation of defects in YSZ. However, the assignment of experimental results to corresponding defect configurations is still on the level of hypotheses without direct and convincing confirmation. Dominant positron trapping sites in YSZ are supposed to be associated with complexes ($\mathrm{Y}_{\mathrm{Zr}}^{1-}V_{\mathrm{O}}^{2+}\mathrm{Y}_{\mathrm{Zr}}^{1-}$) due to the neutralization of positively charged oxygen vacancies (V_{O}^{2+}) by negatively charged substitutional yttrium atoms ($\mathrm{Y}_{\mathrm{Zr}}^{1-}$) in

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their neighbourhood [3]. Positron trapping at negatively charged zirconium vacancies (V_{Zr}^{4-}) is neglected due to the observation of their extremely low concentration in YSZ [3]. This interpretation was used in several other works on YSZ [4–6], but the value of the positron lifetime that should be associated with such a complex is still under question. It should be mentioned that in [3, 4] sintered powders of *c*-YSZ were investigated and spectra with at least two-components were obtained with mean lifetimes in the range 214-248 ps [3] and 193 ps [4]. The authors argue that grain boundaries in YSZ make no contribution to the PAS signal due to positively charged grain-boundary interfaces and positrons are trapped at ($\mathrm{Y}_{\mathrm{Zr}}^{1-}V_{\mathrm{O}}^{2+}\mathrm{Y}_{\mathrm{Zr}}^{1-}$) complexes. Contrary, Garay et al. [6] argue that the negatively-charged grain-boundary space regions act as positron trapping centres. Trapping at the grain-boundaries is also found in our measurement on YSZ powders [7]. Therefore an association of the above lifetimes with $\mathrm{Y}_{\mathrm{Zr}}^{1-}V_{\mathrm{O}}^{2+}\mathrm{Y}_{\mathrm{Zr}}^{1-}$ complexes is problematic. PAS measurements on *c*-YSZ monocrystal before and after ion irradiation are referred to at [5]. One lifetime component was detected in un-irradiated samples (179.5 ± 1 ps), and a second weak (~7%) component (312 ± 14 ps) evolved after irradiation. The value of the short component remains unchanged (179.6 ± 2 ps) and was connected with saturated positron trapping at $\mathrm{Y}_{\mathrm{Zr}}^{1-}V_{\mathrm{O}}^{2+}\mathrm{Y}_{\mathrm{Zr}}^{1-}$ complexes.

Theoretical calculations of basic positron characteristics of various defects in YSZ seem to be essential in order to interpret the experimental data unambiguously. Thus, the aim of the present work is to calculate positron lifetimes (τ) and high momentum profiles (HMP) for the perfect lattice and selected defects in three $\mathrm{ZrO_2}$ polymorphs. Theoretical data are compared with positron annihilation lifetime (PAL) and coincidence Doppler broadening (CDB) measurements carried out on selected monocrystals of zirconia.

2 Computational and experimental methods Positron calculations were performed employing the so-called atomic superposition (ATSUP) method [8]. Lattice parameters used in calculations were a = 5.15 Å; b = 5.21 Å; c = 5.32 Å; β = 99.2° [2] for *m*-$\mathrm{ZrO_2}$; a = 3.60 Å; c = 5.18 Å [2] for *t*-$\mathrm{ZrO_2}$; and a = 5.08 Å [2] for *c*-$\mathrm{ZrO_2}$. In these calculations 768 atom-based supercells (4 × 4 × 4 unit cells[**] of $\mathrm{ZrO_2}$) were used.

In the positron lifetime and HMP calculations the electron-positron correlations were treated according to Boroński-Nieminen (BN) [9] with the correction [10] for incomplete positron screening with a dielectric constant of $\varepsilon_\infty = 4.62$ and the gradient-correction (GC) scheme of Barbiellini et al. [11]. The scheme described in [12] was utilized for calculations of HMPs of the momentum distribution of annihilation photons. The calculated spectra were convoluted with a Gaussian function with a width of $4.9 \times 10^{-3}\, m_e c$ (full width at half maximum), which corresponds to the experimental energy resolution of our CDB spectrometer. (Kr) orbitals were considered as core states for Zr and Y and (He) + 2*s* for O.

Monovacancies were created by removing one O or Zr atom. For *m*-$\mathrm{ZrO_2}$ both non-equivalent oxygen positions were considered in calculations. In the case of *t*-$\mathrm{ZrO_2}$ $\mathrm{Y}_{\mathrm{Zr}}^{1-}V_{\mathrm{O}}^{2+}\mathrm{Y}_{\mathrm{Zr}}^{1-}$ complexes were modelled by removing an oxygen atom and substituting Zr by Y in the first nearest-neighbour (NN) position. As for *c*-$\mathrm{ZrO_2}$, the highest binding energies for $\mathrm{Y}_{\mathrm{Zr}}^{1-}V_{\mathrm{O}}^{2+}$ complexes occur when $\mathrm{Y}_{\mathrm{Zr}}^{1-}$ is in the second NN position relative to V_{O}^{2+} [13], so that $\mathrm{Y}_{\mathrm{Zr}}^{1-}V_{\mathrm{O}}^{2+}\mathrm{Y}_{\mathrm{Zr}}^{1-}$ complexes with Y in the second NN position were also calculated for this phase. For *c*-$\mathrm{ZrO_2}$ and *t*-$\mathrm{ZrO_2}$, a bulk lattice with a high amount of V_{O}^{2+} was modelled by removing one O atom from the 12 atom cell of $\mathrm{ZrO_2}$ considering periodic boundary conditions (i.e. V_{O}^{2+} defects constitute a superstructure). No relaxations of defect configurations and no charged defect states were considered (therefore, in the next section charge states of defects are omitted).

PAL measurements were performed on commercial *c*-YSZ (9.5 mol % $\mathrm{Y_2O_3}$) and *t*-YSZ (3 mol % $\mathrm{Y_2O_3}$) monocrystals. In addition CDB measurements were carried out on *t*-YSZ (3 mol % $\mathrm{Y_2O_3}$) monocrystals and well-annealed yttrium. Further details of the sample preparation and experimental setup are given in [7].

[**] In the case of the tetragonal phase the unit cell was doubled.

3 Results and discussion Theoretical calculations of the positron bulk lifetime (τ_{bulk}) and lifetimes and binding energies for selected defect configurations in *c*-ZrO$_2$, *t*-ZrO$_2$ and *m*-ZrO$_2$ phases are given in Tables 1 and 2 . There is only a slight difference between τ_{bulk} for *c*-ZrO$_2$ and *t*-ZrO$_2$ (see Table 1). On the other hand, the *m*-ZrO$_2$ exhibits remarkably higher τ_{bulk} (see Table 2) because the interstitial space is structured in a different way than in other polymorphs, and, in addition, *m*-ZrO$_2$ has also a larger volume per formula unit (35.23 Å^3 [14]) compared to *t*-ZrO$_2$ (33.07 Å^3 [14]) and *c*-ZrO$_2$ (32.97 Å^3 [14]). Our calculations further show that neither V_{O} nor $\mathrm{Y}_{\mathrm{Zr}}V_{\mathrm{O}}\mathrm{Y}_{\mathrm{Zr}}$ defects are able to trap positrons, but introducing a high amount of V_{O} can prolong the lifetime of free positrons due to enlarging the interstitial (open) volume in the bulk. Zr vacancies and their complexes with V_{O} can be efficient positrons traps. Substitutional yttrium (Y_{Zr}) seems to repel positrons and does not change τ_{bulk}. It should be mentioned, however, that the influence of lattice relaxations around defects usually cannot be neglected in oxides and the presented results should be considered as preliminary only.

Table 1 Results of positron calculations for bulk and vacancy like defects in *c*-ZrO$_2$ and *t*-ZrO$_2$. τ stands for the positron lifetime and E_b designates the positron binding energy to defects (the positive sign means attraction, negative repulsion. 1NN (2NN) means the first (second) nearest neighbor configuration.

Defect	ATSUP-BN		ATSUP-GC		ATSUP-BN		ATSUP-GC	
	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)
Bulk	138	–	146	–	141	–	150	–
V_{O}	140	0.02	149	0.03	142	0.02	152	0.03
$\mathrm{Y}_{\mathrm{Zr}}V_{\mathrm{O}}\mathrm{Y}_{\mathrm{Zr}}$ (1NN)	138	<0.01	147	<0.01	141	<0.01	150	<0.01
$\mathrm{Y}_{\mathrm{Zr}}V_{\mathrm{O}}\mathrm{Y}_{\mathrm{Zr}}$ (2NN)	139	0.01	148	0.02	–	–	–	–
V_{Zr}	196	2.72	222	2.44	198	2.56	224	2.28
$V_{\mathrm{O}}V_{\mathrm{Zr}}$ (1NN)	215	2.96	239	2.79	223	2.85	247	2.72
Y_{Zr}	138	–0.002	146	–0.003	141	–0.003	150	–0.003
V_{O} superstructure	153	–	159	–	156	–	163	–
	c-ZrO$_2$		*c*-ZrO$_2$		*t*-ZrO$_2$		*t*-ZrO$_2$	

Table 2 Results of positron calculations for *m*-ZrO$_2$ (for explanations see Table 1).

Defect	ATSUP-BN		ATSUP-GC	
	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)
Bulk	160	–	170	–
V_{O} (1)	162	0.02	174	0.04
V_{O} (2)	161	0.01	170	0.01
V_{Zr}	202	1.80	229	1.53
$V_{\mathrm{O}}V_{\mathrm{Zr}}$ (1) (1NN)	234	2.13	258	2.03
$V_{\mathrm{O}}V_{\mathrm{Zr}}$ (2) (1NN)	227	2.06	252	1.92

PAL measurements on *t*-YSZ and *c*-YSZ monocrystals exhibit single component spectra with lifetimes 174±1 ps and 178.3±0.3 ps , respectively. These lifetimes lie between the calculated bulk lifetimes and lifetimes for V_{Zr} . In principle, there are two possibilities for the interpretation of this component:

(i) It can be saturated trapping in defects (the concentration should be at least 10^{-4} at.$^{-1}$ in order to observe saturated trapping). However, the nature of such defects is unknown because – as discussed above – the concentration of V_{Zr} is supposed to be negligible and complexes $\mathrm{Y}_{\mathrm{Zr}}V_{\mathrm{O}}\mathrm{Y}_{\mathrm{Zr}}$ are not able to trap positrons according to our calculations.

(ii) Positrons annihilate from the free state. But measured lifetimes in *t*-YSZ and *c*-YSZ monocrystals are significantly higher than the calculated values for pure *t*-ZrO$_2$ and *c*-ZrO$_2$ phases. The explanation could be that the lifetime increases due to an open volume introduced by V_{O} . This hypothesis is sup-

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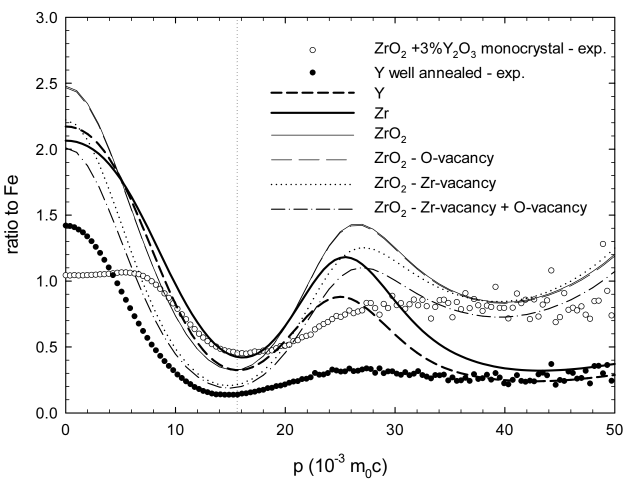

Fig. 1 Ratio curves of measured CDB spectra for *t*-YSZ monocrystal and pure Y to pure α-Fe are compared with calculated ratio of HMPs for Y, Zr and bulk and selected defects in *t*-ZrO_2.

ported by the fact that the *c*-YSZ monocrystal exhibits a higher lifetime than the *t*-YSZ monocrystal due to a higher amount of V_O as well as by the comparison of the low-momentum part of CDB curves measured on nanopowders and the monocrystal of *t*-YSZ, which indicates that majority of positrons in nanopowder compacts are trapped at open volume defects, while in the monocrystal positrons seem to annihilate from the free state (see Fig. 1 in [7]). However, quantitative agreement between calculated and experimental lifetimes is not reached.

The comparison of the calculated HMP's for *t*-ZrO_2 and Y with profiles measured on the *t*-YSZ monocrystal and pure Y is given in Fig. 1. The experimental HMP curves exhibit a good qualitative agreement with the corresponding calculated profiles. Unfortunately, the similarity of electronic structures of Y and Zr atoms makes it impossible to distinguish between positron annihilations with Zr and Y electrons by CDB.

In conclusion, positron annihilation in zirconia and YSZ still represents a puzzling problem and further theoretical and experimental work is necessary to elucidate the nature of positron annihilation sites in such materials.

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