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Positron annihilation in oxides

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Positron annihilation in oxides

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Outline

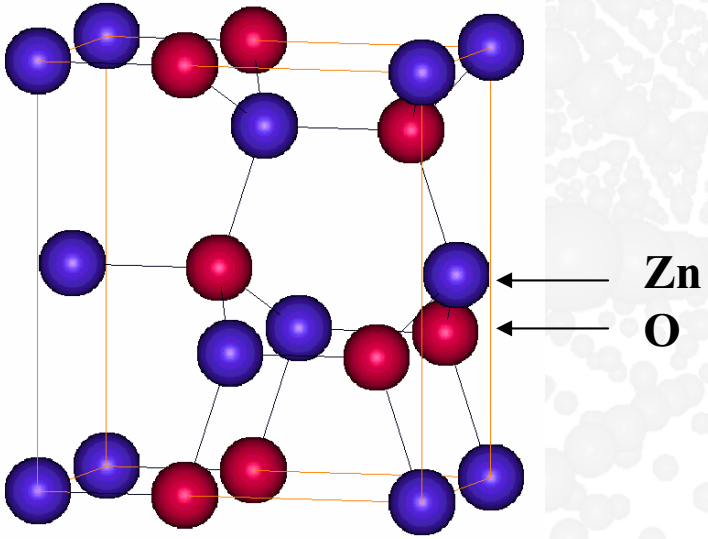
- ZnO
- ZrO_2 (YSZ)

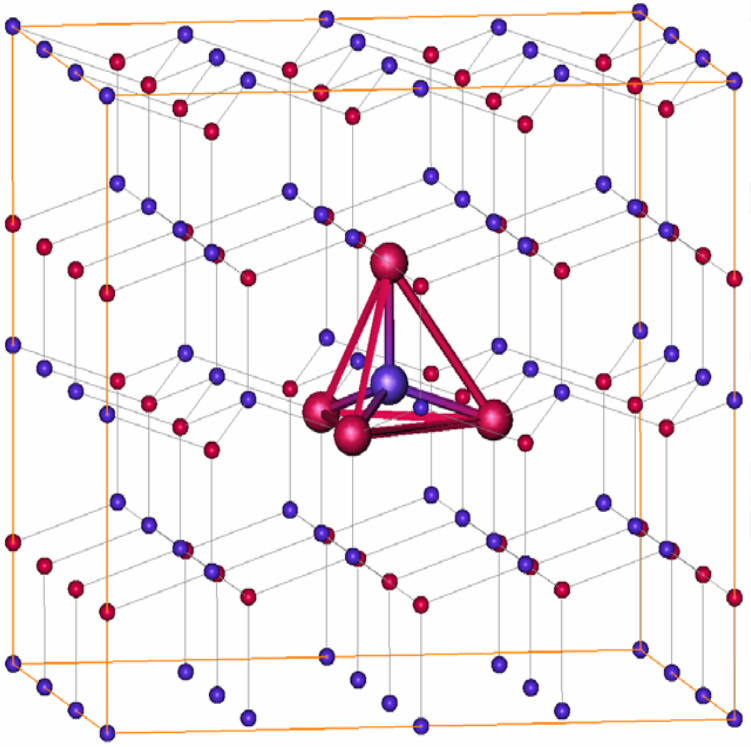
ZnO-motivation

- ZnO is a wide band gap semiconductor (~3.4 eV).
- Defect identification in ZnO is of great importance because of prospective applications in electronics.
- Positrons may help to identify open volume defects.
- ZnO contains large amount of hydrogen and studying H-related defects is necessary.
- Most of commercial ZnO materials are of n-type and p-type doping is problematic
  - origin: V_O, Zn_i, H-related defects
- We concentrate on nominally undoped materials and grown in defects.

ZnO-structure

- ZnO exhibits hexagonal wurtzite structure
  - it is useful to view the structure in terms of ZnO_4 tetrahedra interconnected at corners





ZnO–chemical analysis

- Nuclear reaction analysis (NRA) measurement of H content in ZnO single crystals revealed the presence of at least 0.3 at.% of H.

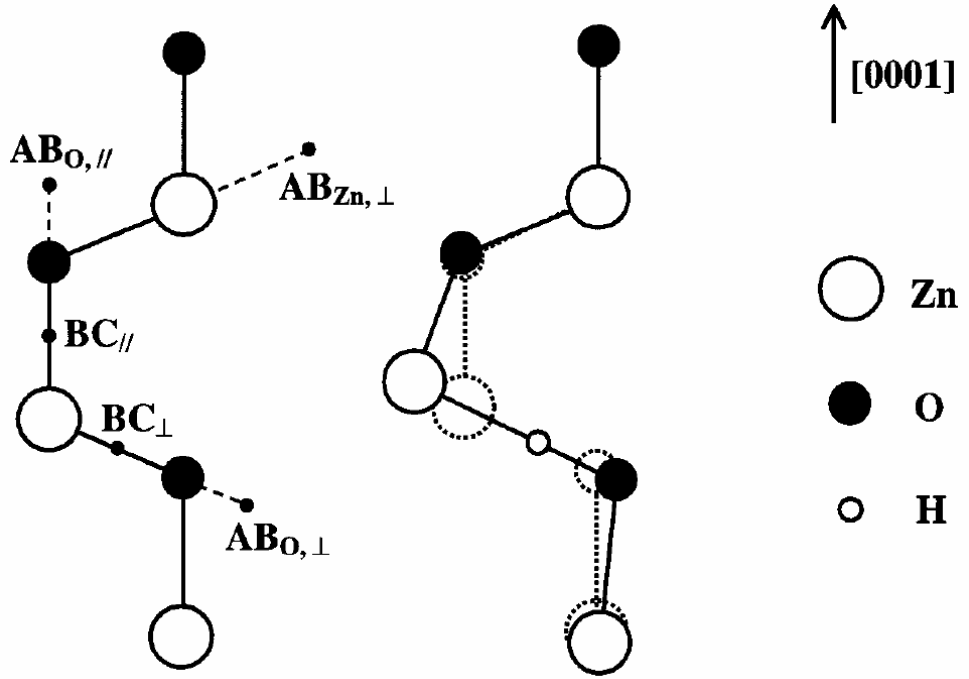
- Concentrations of other impurities (obtained via ICP-MS) are small.

G. Brauer et al., PRB **79** (2009) 115212

ZnO + H

H in ZnO lattice

- Interstitial H may act as a donor
  - Van de Walle, PRL 85 (2000) 1012
- Bond center and antibonding positions



Zn-methods

- Obtaining defect configurations in ZnO:
  - VASP (=Vienna ab initio simulation package)
  - projected augmented wave (PAW) pseudopotentials
  - valence electrons: Zn – $4s^2$, $3d^{10}$; O – $2s^2$, $2p^4$
  - local density approximation
  - 96 atom based supercells used
  - 2 x 2 x 2 k-points in the whole BZ (symmetry switched off)
  - vacancies created by removing corresponding atoms
  - H atoms added to positions predicted by Van de Walle
  - the total energy of studied defect configurations relaxed with respect to atomic positions (all atoms allowed to move)

ZnO-methods

- Positron induced forces:
  - treated within the scheme developed by Makkonen et al., PRB 73 (2006) 035103
  - conventional scheme for positron calculations considered
  - Hellman-Feynman theorem used to calculate forces

$$\mathbf{F}_j = -\langle \psi_+ | \nabla_j V_+(\mathbf{r}, \{\mathbf{R}_i\}) | \psi_+ \rangle$$

  - V_+ is constructed using atomic (Coulomb) potentials and densities and force calculation is thus very fast
  - such forces added to ionic forces calculated by VASP and atomic positions where total forces vanish are found
  - though the method is not fully self-consistent and does not use TCDFT, it is sufficient to get reliable results

ZnO-results

- Bulk lifetime:
  - Calculated:

154 ps (SC) 153 ps (SC, LMTO) 159 ps (NS)

  - Experimental:

151, 155-158, 161, 166, 169-173, 176-183 ps

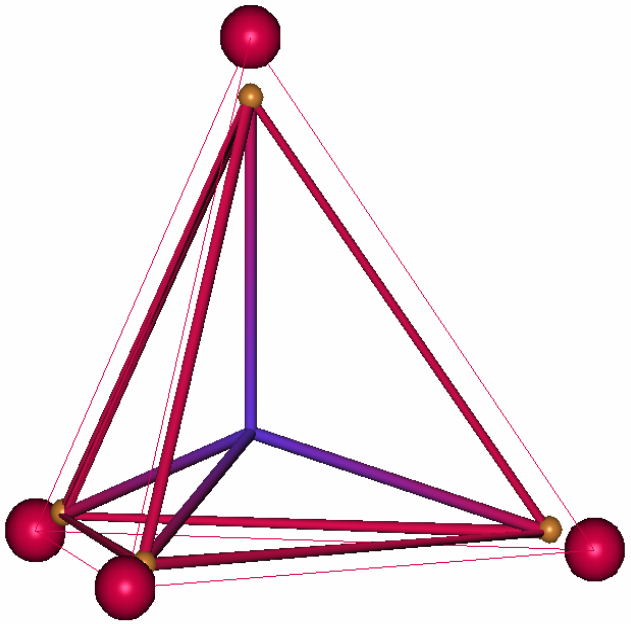
  - Plausible assumption: the bulk lifetime is 150-160 ps

ZnO-results

- Oxygen vacancy:
  - There is no positron trapping
  - Removing oxygen atom is not enough to create sufficiently deep potential well to trap positrons.

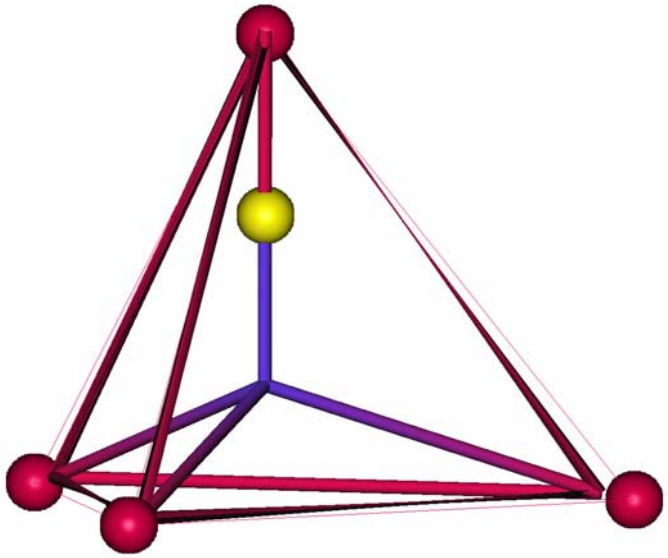
ZnO-results

- Zinc vacancy:
  - NR NS 194 ps 0.35 eV
  - RE NS 231 ps 0.60 eV
  - RE SC 246 ps 1.25 eV
  - RE SC PF 207 ps 1.11 eV
  - Calculated lifetime can be compared with a lifetime of 207 ps observed in electron irradiated ZnO.



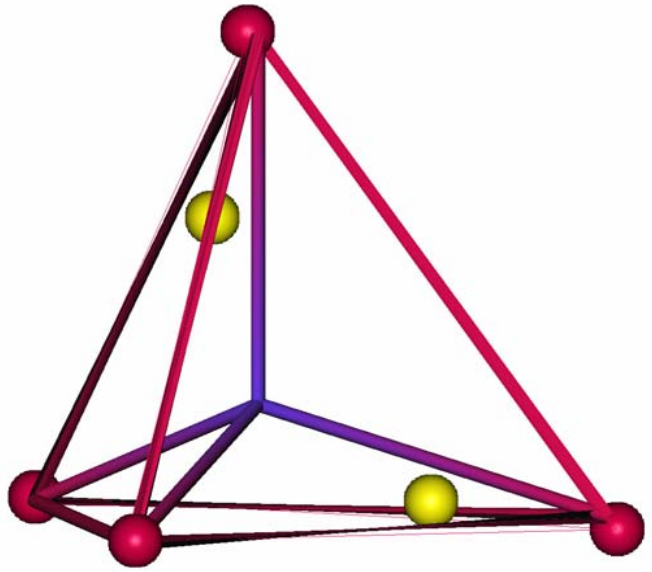
ZnO-results

- V_{Zn}+1H:
  - NR NS 179 ps 0.12 eV
  - RE NS 190 ps 0.19 eV
  - RE SC 199 ps 0.48 eV
  - RE SC PF 177 ps 0.25 eV
  - Calculated lifetime can be compared with 169-183 ps measured in various ZnO materials indicating presence of V_{Zn} – H complexes.
  - Second configuration:
    RE SC PF 179 ps 0.30 eV



ZnO-results

- V_{Zn}+2H:
  - NR NS 161 ps ~0 eV
  - RE NS 163 ps 0.01 eV
  - RE SC 164 ps 0.03 eV
  - RE SC PF 156 ps ~0 eV
  - This case demonstrates that already 2 H atoms probably fill up zinc vacancy and no trapping is possible.
  - Second configuration:
    RE SC PF 156 ps ~0 eV



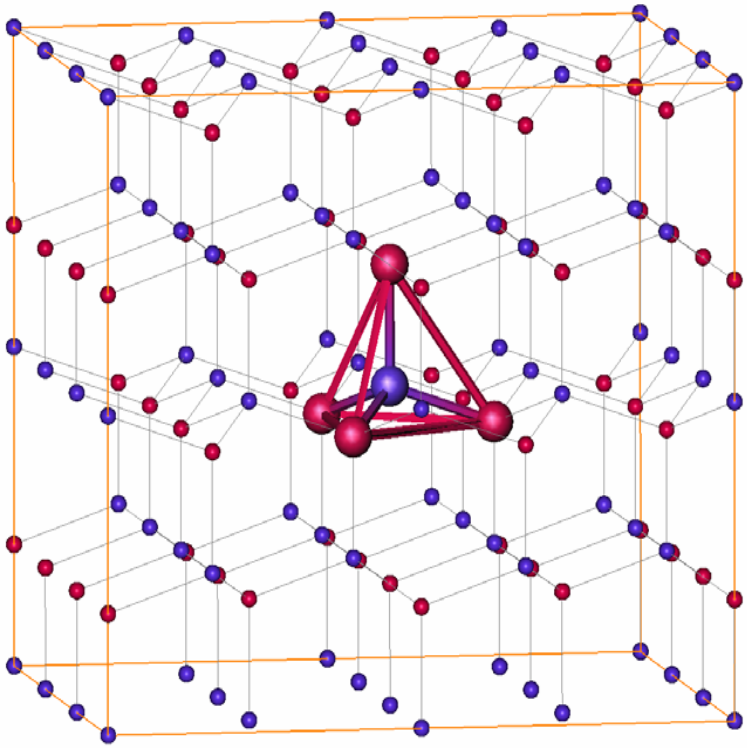
ZnO-results

- Further observations:
  - The H_2 molecule is neither stable in V_{Zn} nor in V_{Zn+O}.
  - H-related defects that involve antibonding sites are not stable or have much larger energies than those corresponding to BC sites.
  - H binding energies to V_{Zn}
    - ~ 3 eV for 1H
    - ~ 6 eV for 2H
    - ~ 7 eV for 3H
    - ~ 7 eV for 4H

    with respect to H_i positions.

ZnO-results

- Configurations examined:
  - V_{Zn+O}
  - V_{Zn+O}+1H OV
  - V_{Zn+O}+1H Oab
  - V_{Zn+O}+1H Oc
  - V_{Zn+O}+2H OabV
  - V_{Zn+O}+2H OcV
  - V_{Zn+O}+2H Oab
  - V_{Zn+O}+2H Oabc



ZnO-results

- Positron lifetimes and binding energies:

ZnO bulk	154 ps	
V_{Zn+O}	225 ps	1.0 eV
V_{Zn+O}+1H OV	220 ps	0.9 eV
V_{Zn+O}+1H Oab	211 ps	0.8 eV
V_{Zn+O}+1H Oc	208 ps	0.7 eV
V_{Zn+O}+2H OabV	185 ps	0.4 eV
V_{Zn+O}+2H OcV	184 ps	0.4 eV
V_{Zn+O}+2H Oab	156 ps	~0 eV
V_{Zn+O}+2H Oabc	156 ps	~0 eV

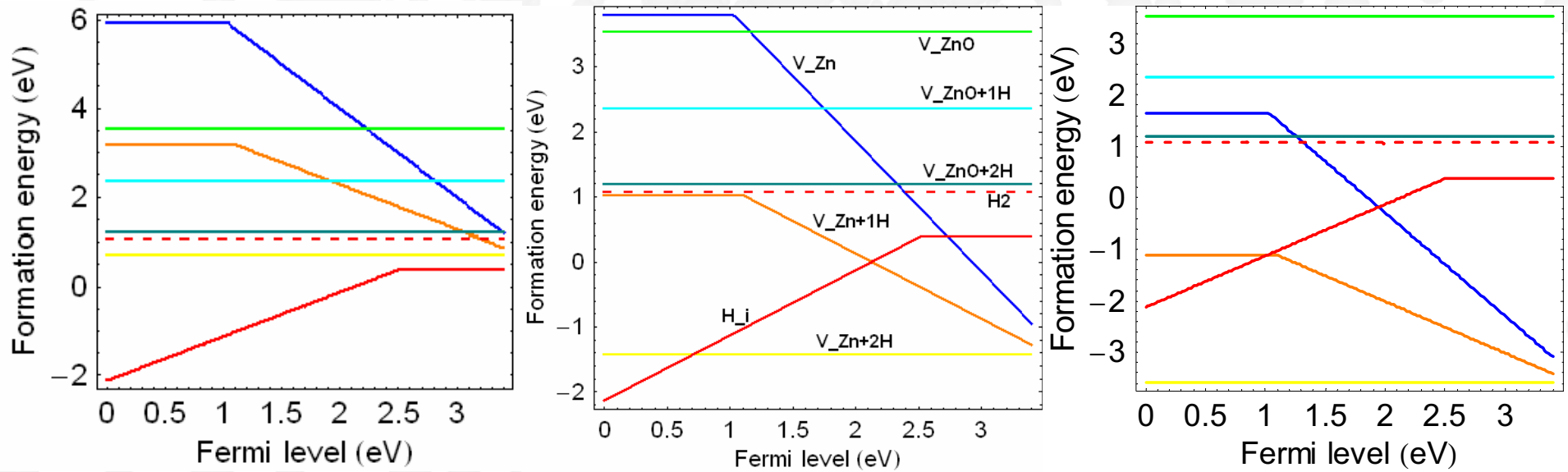
ZnO-results

- Energies of configurations (low, high):

V_{Zn+O}+1H OV	220 ps	(1.7eV)
V_{Zn+O}+1H Oab	211 ps	
V_{Zn+O}+1H Oc	208 ps	
V_{Zn+O}+2H OabV	185 ps	(0.2eV)
V_{Zn+O}+2H OcV	184 ps	(0.2eV)
V_{Zn+O}+2H Oab	156 ps	
V_{Zn+O}+2H Oabc	156 ps	

ZnO-results

- Defect formation energies:



Zn rich conditions

intermediate

Zn poor conditions

ZnO-conclusions

- Both the charge transfer between cations and anions as well as relaxations of defect configurations including positron induced forces are important to get reliable results.
- Oxygen vacancy does not trap positrons.
- One hydrogen atom reduces significantly the positron lifetime of the zinc vacancy.
- Two hydrogen atoms fill up V_{Zn} so that positron trapping is not possible.

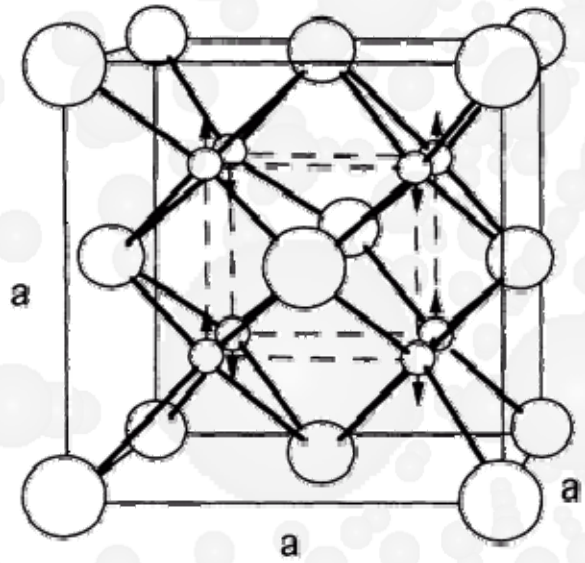
ZnO-conclusions

- V_{Zn+O} is a deep positron trap and its positron lifetime is very close to lifetimes observed in some experiments.
- When one H atom is bound inside V_{Zn+O} the positron lifetime is reduced significantly and is close to that for V_{Zn}.
- Some of V_{Zn+O}+2H complexes trap positrons, but their energy is relatively high so that they may not contribute to positron annihilation response from ZnO samples.

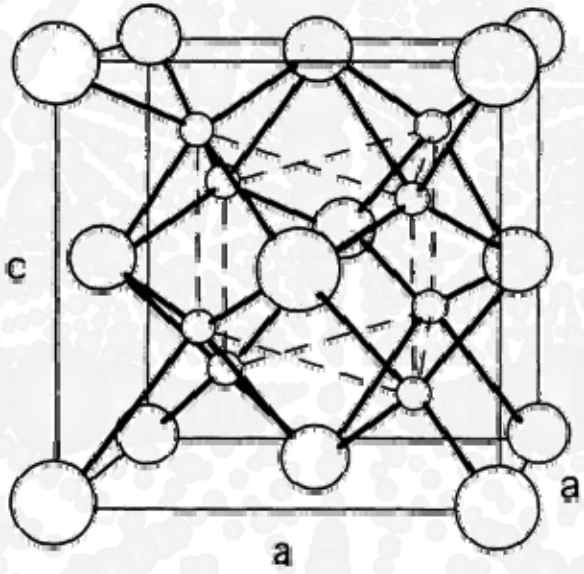
- Defects in various charge states need to be studied.

ZrO_2-structure

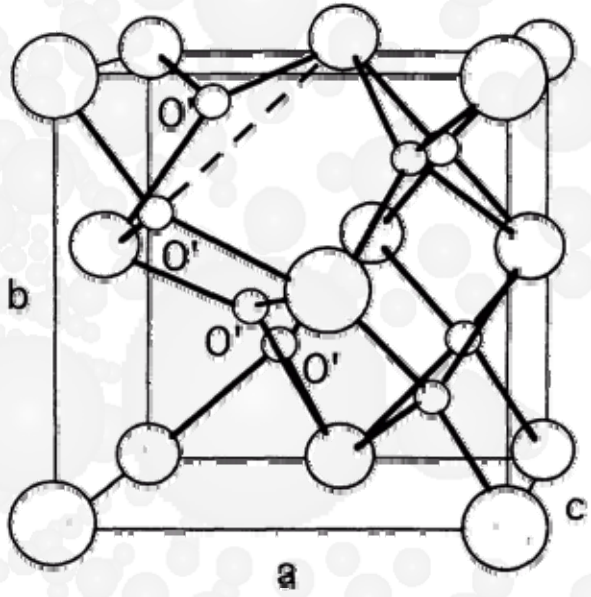
- Three structures of ZrO_2 at ambient pressure:



cubic structure (CaF_2)
above ~1380 °C



tetragonal structure
above ~1200 °C



monoclinic structure

ZrO_2-introduction

- ZrO_2 (zirconia):
  - high melting point (2700 °C)
  - low thermal conductivity
  - good oxygen-ion conductivity (higher temperatures)
  - high strength
  - enhanced fracture toughness

- For applications stabilization of the tetragonal or cubic phase is necessary.
- Zirconia is often stabilized by yttria (Y_2O_3) → yttria stabilized zirconia (YSZ)

ZrO_2-introduction

- Zr has +4 charge state ($Zr^{''''}$) and Y is +3 only ($Y^{'''}$), i.e. -1 with respect to the lattice
- $\Rightarrow$ compensation by O vacancies having +2 charge state ($V_O^{\bullet\bullet}$)
- there are two $Y^{'''}$ per one $V_O^{\bullet\bullet}$

- stability ranges:
  - > 8 mol% of $Y_2O_3 \rightarrow$ cubic phase
  - > 3 mol% of $Y_2O_3 \rightarrow$ tetragonal phase
- $\Rightarrow$ large amount of vacancies in YSZ materials

ZrO_2-recent results

- Cubic YSZ single crystal (8 mol% of Y_2O_3) $\rightarrow$ 175 ps positron lifetime.

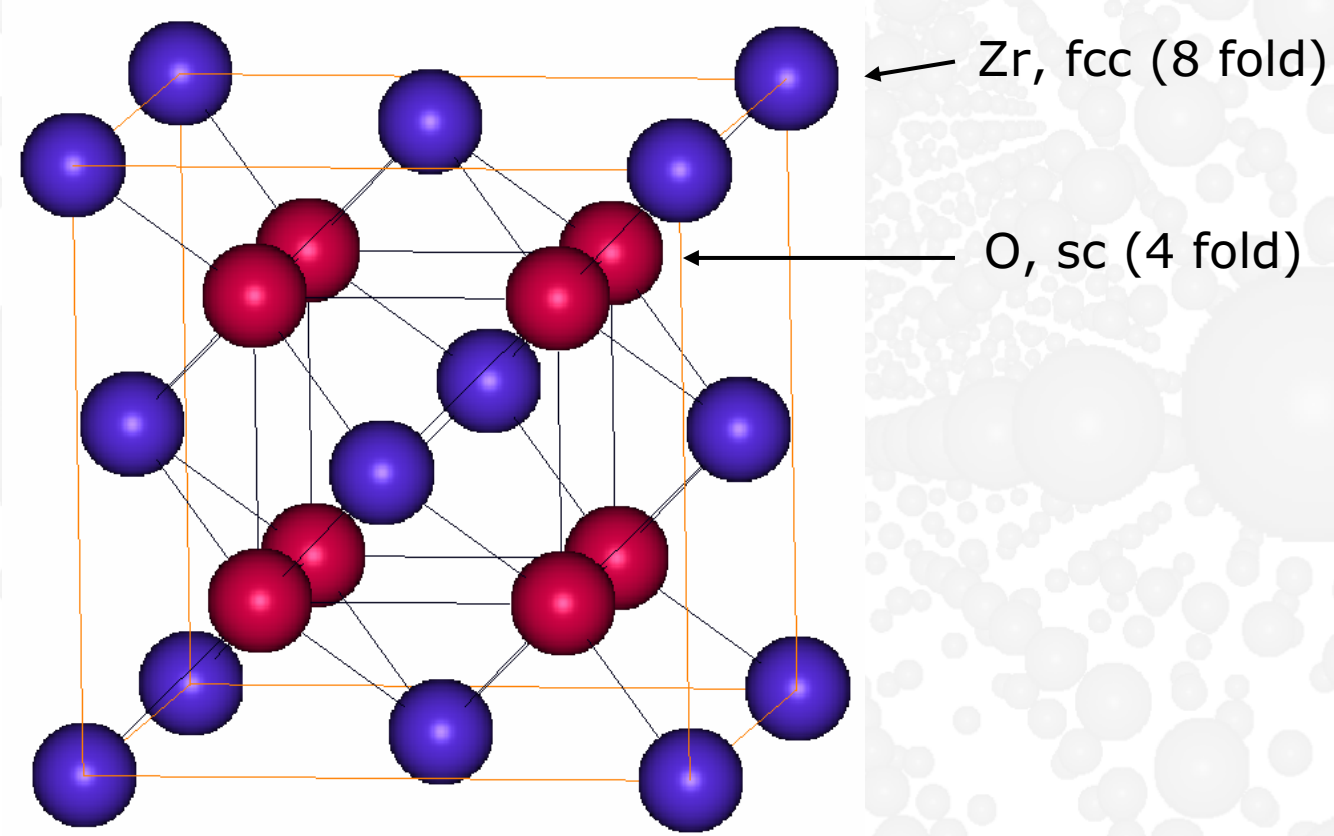
- Before we studied the following vacancy-like defects:
  - V_{Zr}, V_O, V_O-2Y, $2V_O$-4Y (V_O's along [111] direction)
  - positron trapping at V_{Zr} only (but too long lifetime)

ZrO_2-motivation

- H is everywhere …
- First NRA results indicate that we have appreciable amount of H in our sample.
- What are the positions of H in ZrO_2 lattice.

ZrO_2-structure

- ZrO_2 (CaF_2) structure:

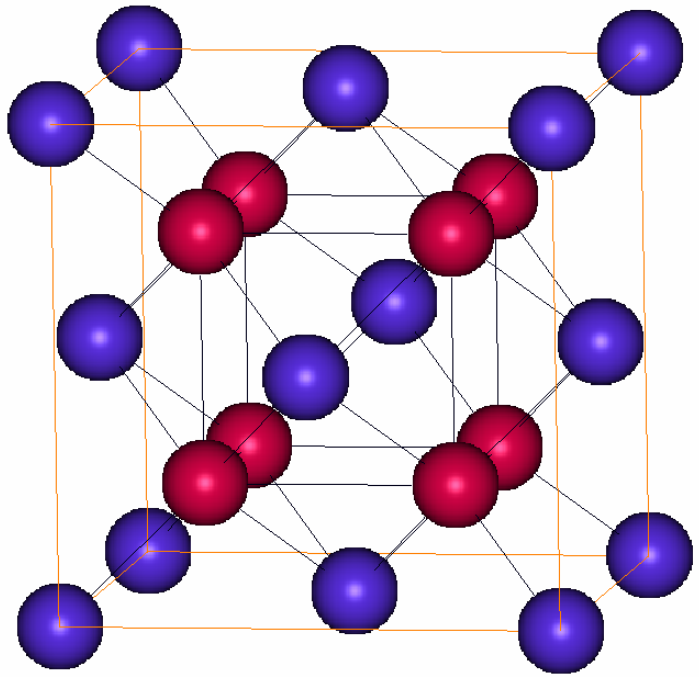


ZrO_2-methods

- Defect configurations:
  - obtained using VASP-PAW, LDA & GGA
  - 96 atom based supercells
  - total energy of studied defect configurations relaxed with respect to atomic positions
  - cubic structure unstable (without Y) !!

ZrO_2-methods

- Configurations examined:
  - Interstitial hydrogen
  - Hydrogen in V_{Zr}



ZrO_2-results

- Cubic phase:

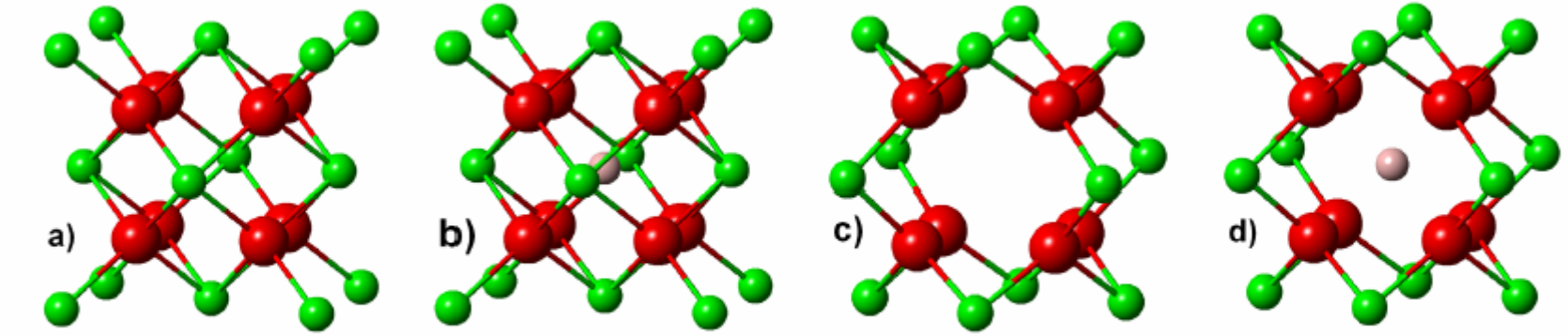


Figure 1. Cubic ZrO_2: a) perfect lattice, b) H in the O_8 interstitial space, c) V_{Zr}, and d) H in the center of V_{Zr}. Red, green, and pink spheres represent, respectively, O, Zr, and H atoms.

ZrO_2-results

- Tetragonal phase:

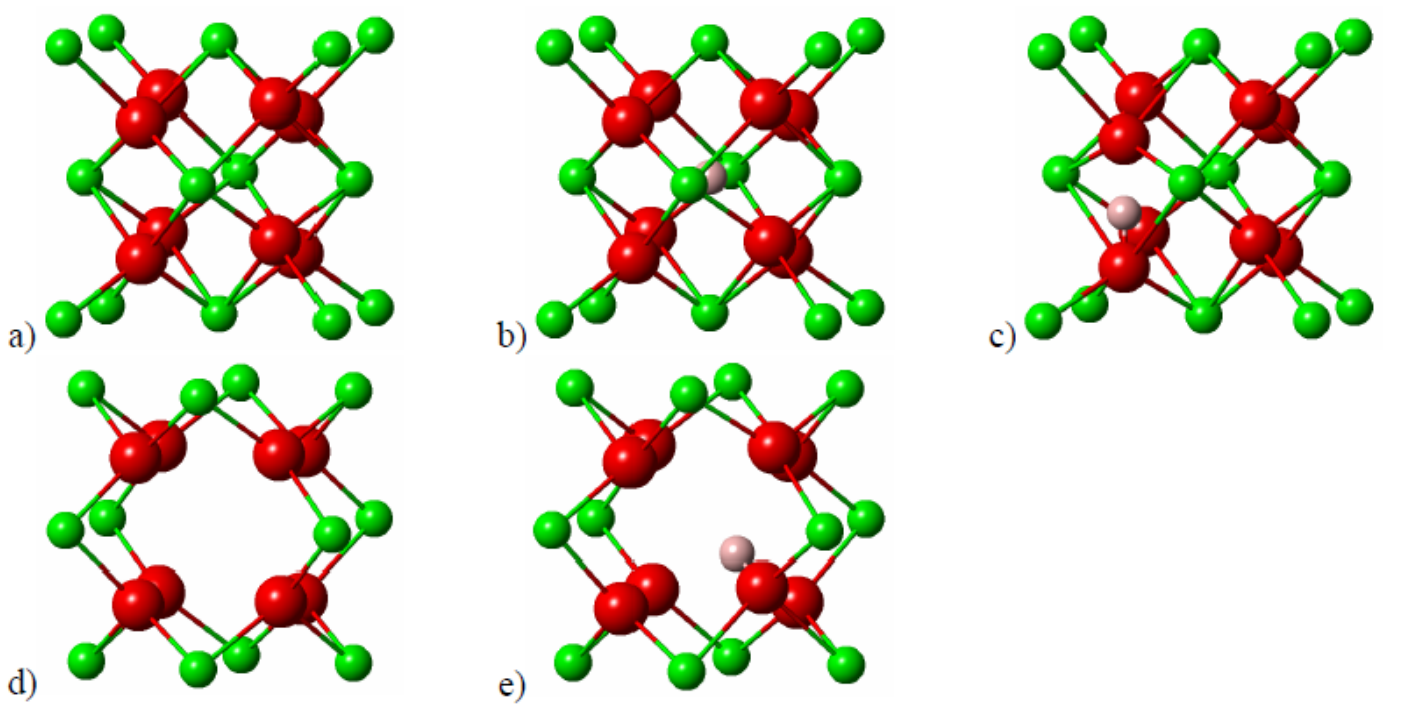


Figure 2. Tetragonal ZrO_2: a) perfect lattice, b) H in the center of the interstitial space, c) H bound to an oxygen atom, d) V_{Zr}, and e) H in V_{Zr}. Sphere designation is the same as in figure 1.

ZrO_2-results

- Positron lifetimes and binding energies (LDA/GGA):

Table I. Positron characteristics of studied open volume defects.

	BN		GC		BN		GC	
Configuration	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)	τ (ps)	E_b (eV)
Cubic phase								
Bulk	138	–	146	–	133	–	157	–
V_{Zr}	216	2.75	238	2.60	220	2.81	291	2.42
V_{Zr}+1H (center)	169	1.76	181	1.68	167	1.28	199	1.31
Tetragonal phase								
Bulk	138	–	146	–	133	–	158	–
V_{Zr}	216	2.74	238	2.59	219	2.76	291	2.37
V_{Zr}+1H	189	2.23	204	2.12	189	1.76	237	1.54
	ATSUP				ATSUP+VASP			

H in V_{Zr} can in principle explain lifetime data !!

ZrO_2-conclusions

- We have studied H positions in the zirconia lattice.
- In the case of the interstitial H the lowest energy configuration is for H bound to an O atom near the center of the interstitial space (tetragonal, O-H bond formed).
- As for the V_{Zr} , H prefers position close to a neighboring O atom (tetragonal, O-H bond formed).

- The latter defect traps positrons and could be responsible for the observed positron lifetime.

ZrO_2-outlook

- More H-related configurations needed.
- The question of the cubic YSZ structure needs to be solved.

Thank you!