

Positron annihilation at planar defects in oxides

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Abstract. Planar defects may exhibit free volumes which, in principle, are detectable using positron annihilation spectroscopy. In this contribution, we present a preliminary theoretical study of positron trapping at stacking faults in zinc oxide and at a grain boundary in zirconia. In particular, we calculate the positron lifetime and positron binding energy to such defects. In the case of the grain boundary in zirconia, the influence of the yttrium segregation on the GB structure and positron characteristics is also examined. Calculated structural and positron characteristics are critically compared with experimental and other calculated data.

Introduction

Transition metal oxides are interesting materials with important existing and further prospective applications. Planar defects like stacking faults (SFs) and grain boundaries (GBs) are often present in such materials and may affect their properties. These lattice imperfections exhibit free volumes which, in principle, are detectable using positron annihilation spectroscopy. In particular, it has recently been shown that a zinc oxide (ZnO) single crystal contains a large amount of SFs [1]. We examine several SFs in ZnO with respect to their ability to trap positrons, following their structural investigation presented in [2]. Furthermore, nanocrystalline (nc) materials based on zirconia (ZrO₂) are also frequently studied and their characteristics are significantly influenced by GBs. Positron trapping at GBs in nc yttria stabilized zirconia (YSZ) materials was detected [3], but the character of trapping sites at GBs remains unclear. Here we selected to study the symmetrical tilt $\Sigma 5$ (310) [001] GB in cubic ZrO₂. This GB has already been studied experimentally [4] and also theoretically [5], which provides a basis for the current study.

Computational methods

In order to obtain realistic atomic configurations of studied planar defects, the Vienna ab initio simulation package (VASP) [6] was employed within the framework of the projected augmented wave method (PAW) [7]. The PAW pseudopotentials [8] supplied along with the VASP package were utilized. In the case of ZnO, the local density approximation [9] was employed, whereas the generalized gradient approximation [10] was utilized for ZrO₂. The selected approaches are known to reproduce reasonably well basic structural characteristics for respective systems. Positron characteristics were calculated using the atomic superposition method (ATSUP) [11] employing relaxed atomic configurations from VASP. The positron correlation potential and enhancement factor from [12] were taken considering the correction for incomplete positron screening. We refer readers to [13] for further details regarding positron calculations.

ZnO exhibits a wurtzite type structure which is hexagonal. The VASP optimized lattice parameters are $a = 3.195 \text{ \AA}$ and $c = 5.158 \text{ \AA}$. They are slightly smaller than experimental ones [14] and result in about 4% lower unit cell volume, which also affects calculated positron characteristics. Here we study four types of SFs parallel to the hexagonal basal plane. They are described in detail in [2] and are marked in the following correspondingly by I, II, III and E, the last one being an abbreviation of the so called extrinsic SF. For instance, if the basic stacking sequence of ZnO along the c -axis is ...AaBbAaBb... ('Aa' and 'Bb' being different sequences of dual Zn-O layers), then a type I SF can be described with a sequence ...AaBbAaBbCcBbCcBb..., 'Cc' being another sequence of Zn-O layers. Fig. 1 shows an example of the type I and type III SFs. The corresponding supercells for studying I and III type SFs contained 6 double layers, whereas 8 double layer supercells were employed for II and E type SFs. The just described supercells were optimized with respect to atomic positions and the cell dimension along the hexagonal axis using VASP.

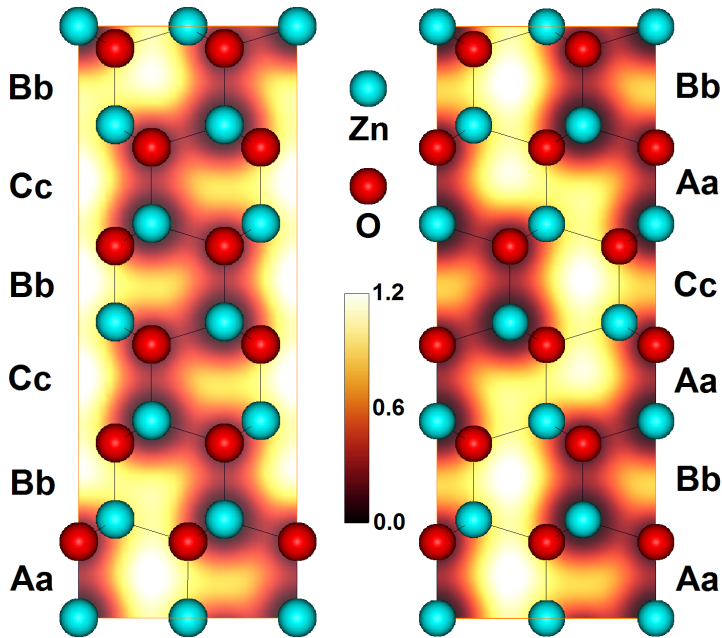


Fig. 1: Examples of stacking faults in ZnO: type I (left) and III (right). Positron density (in $10^{-3} \text{ a.u.}^{-3}$ units) at the supercell face is also shown in the form of shading.

structures exist. The optimized lattice constant 5.146 \AA for cubic ZrO_2 agrees well with other calculation [15] and with experiment (see [16] and references therein). The starting configuration of the $\Sigma 5$ (310) [001] GB was obtained using the coincident site lattice principle. In the course of calculations, we considered yet another GB configuration which was obtained from the previous one by shifting the upper part of the GB supercell along the direction lying in the GB plane and perpendicular to the tilt axis in order to decrease the distance between atoms of the same type at the GB, which should lower the energy. These configurations will be further denoted as GB1 and GB2, and their corresponding supercells were relaxed using VASP with respect to atomic positions and the cell dimension perpendicular to the GB plane (310). In order to study the influence of yttrium on the GB properties, a Zr atom at the GB was substituted by Y at two different positions for each GB configuration studied. The presence of oxygen vacancies, which are known to be associated with Y atoms in YSZ, was not considered at this stage of research, which could slightly affect energy considerations.

Results and discussions

Stacking faults in ZnO. Calculated SF energies agree well with those obtained in [2] though they are by about 15 % smaller, which can be attributed to a different exchange-correlation potential and supercell size used. For example, the SF energy for the E-type SF amounts to 71 mJ/m^2 (or 4.4 meV/\AA^2) and represents the largest value among the studied SFs. These are very small energies and typical grain boundary energies in materials are one order of magnitude higher. This also explains why there is a large amount of SFs in ZnO materials, as suggested in [1]. When the excess free volume due to the lattice expansion along the c -axis is investigated, it is found -- in agreement with very low SF energies -- that these volumes are also very small and fall into the $0.03 \text{ -- } 0.05 \text{ \AA}^3/\text{\AA}^2$ range.

As for positron characteristics, the calculated bulk positron lifetime (τ_b) using the ATSUP method is 152 ps and is somewhat shorter than reported in [17] (158 ps) due to the contraction of the relaxed lattice, as mentioned above. We shall not discuss here the issue of the bulk positron lifetime in ZnO, which is still debated in the literature. A detailed survey on this subject is given in [17]. Positron lifetime calculations for the studied SFs give positron lifetimes which are usually 0.1 -- 0.2 ps longer than τ_b . The only exception is the E-type SF which exhibits by 0.1 ps shorter lifetime compared to τ_b , because of a special atomic arrangement at the SF. If the positron binding energy to SFs is formally calculated as a difference of positron energies corresponding to the bulk material and to SFs, values around 0.02 eV are obtained (including E-type SF). In any case, the inspection of the positron density (see Fig. 1) shows that no positron trapping occurs at the studied SFs and the just reported lifetime prolongation and positive 'binding energies' are due to a different atomic arrangement compared to bulk.

Grain boundary in ZrO₂. Configurations GB1 and GB2 relaxed with VASP are shown in Fig. 2. The corresponding grain boundary energies are 2.20 and 1.56 J/m² (i.e. 137 and 97 meV/Å²). These values are indeed more than 10 times larger than SF energies discussed above. We note that a configuration having even lower GB energy than GB2 has been found in [5]. Both GB configurations studied here exhibit quite large free volume at the GB region (see Fig. 2). This free volume is somewhat larger for GB1 compared to GB2, according to the visual inspection. This is confirmed by the fact that the calculated excess free volumes are 0.99 and 0.91 Å³/Å² for GB1 and GB2, respectively. This is in accordance with GB energy results, i.e. a larger GB energy implies a larger excess free volume (and, consequently, a larger expansion along the direction perpendicular to the GB plane).

When an Y atom substitutes a Zr atom, it can be shown that Y is attracted to the GB in agreement with experimental [4] and computational [5] segregation studies. In particular, the calculated binding energies of Y atoms to the $\Sigma 5$ (310) GB configurations studied are 1.86 and 0.57 eV for GB1 and 0.22 and 0.02 eV for GB2, for two distinct Y atom positions (see Fig. 2). It is interesting to note that one of the GB1+Y configurations changed its structure to a GB2+Y one during relaxation.

Concerning positron results, the calculated bulk positron lifetime is 143 ps. There is no precise experimental value, but a value around 140 ps is suggested in [3] on the basis of results obtained for a sintered nc YSZ sample. The relaxed GB1 and GB2 configurations yield lifetimes 235 and 217 ps, respectively, with appreciable localization at the GB region (see Fig. 2 and compare it with the SF case shown in Fig. 1). It is worth mentioning that these lifetimes are close to ~ 220 ps calculated for a Zr vacancy in ZrO₂ [3]. Experimentally detected lifetimes corresponding to GBs in compacted and sintered nc samples are between 180 and 200 ps. This suggests that open volumes detected at GBs in nc samples could be due to a relatively open GB structure rather than due to vacancies, i.e. missing atoms, at the GB. Here we study only one special GB and in reality much more different GB types exist in nc YSZ materials, which may result in somewhat different lifetimes than calculated in this study.

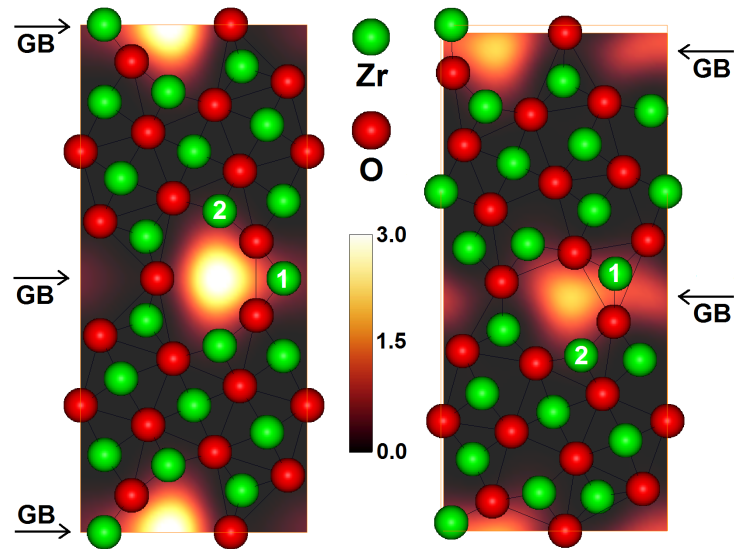


Fig. 2: Two configurations of $\Sigma 5$ (310): GB1 (left) and GB2 (right). Positron density (in 10^{-3} a.u.⁻³ units) at a plane inside the supercell is also shown in the form of shading. Zr atoms substituted by Y in the segregation study are labelled '1' and '2'.

When Y substitutes a Zr atom at the GB, the lifetimes vary in the range 217 to 250 ps depending on the configuration. Positron binding energies to the clean and segregated GB are around 3 eV implying again a deep positron trap.

Concluding remarks

It is found that the studied SFs, which are parallel with the hexagonal basal plane of the wurtzite structure of ZnO, do not trap positrons. It is supposed that such SFs may attract other defects (both intrinsic and extrinsic) to segregate there, including hydrogen. These effects need to be further investigated, though positron characteristics of open volume defects will be probably affected to a very small extent because the environment of atomic sites at SFs differs only slightly from those in the ZnO bulk undisturbed by SFs. In this respect, other planar defects in ZnO like inversion domain boundaries should be also examined.

The studied $\Sigma 5$ (310) GB in cubic zirconia exhibits apparent large volumes with the corresponding positron lifetime similar to that of Zr vacancy. Yttrium doping and segregation may cause a GB structure change. Positron lifetime values for segregated GB are similar or slightly exceed those for clean GB configurations. This result suggests that positron trapping at GBs in YSZ may occur in free volumes that are inherent to GBs rather than in absent atomic sites at the GB, as it is usually interpreted. This can be further elucidated by analogy with the difference between the close-packed and open type crystalline structures. Open type structures usually exhibit longer lifetimes compared to close-packed atomic arrangements. This is not due to some vacant atomic sites in open structures, but it is caused by looser atomic arrangement relative to close-packed structures. The studied GB is of very special type and further computational and experimental studies are necessary in order to clarify the structure of more general GBs in nc YSZ and the origin of positron trapping sites in such materials. Notably, the situation differs from metals where GBs have apparently a more compact structure because of a different type of bonding among atoms compared to zirconia (and oxides in general) [18].

From the quantum mechanical view point, both types of studied interfaces should represent two-dimensional potential wells for positrons. Any two-dimensional potential well must have a bound state (see e.g. [19]), which was not observed for the case of ZnO SFs studied here, in contrast to the selected GB in zirconia where positron trapping was clearly detected. This can be related to the fact that we are using a real space method to solve the positron Schrödinger equation and the spatial mesh used is rather coarse in comparison with the size of the potential well in the case of SFs in ZnO. In any case, one can expect nearly negligible differences between true bulk and SF positron characteristics, based on the results presented here.

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