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Vacancy-hydrogen Complexes in ZnO

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Abstract. Hydrogen is an important impurity in zinc oxide and can be incorporated into the lattice in several ways. Hydrogen can be also bound by vacancies that can be studied using positron annihilation techniques. Here we examine theoretically oxygen and zinc vacancies in ZnO, the latter also with hydrogen atoms inside. Several computational approaches are employed to determine the defect geometries and related positron characteristics. Positron-induced forces are also taken into account. Calculated positron lifetimes are compared with those observed in experiment, which gives an indication of the presence of zinc vacancy-hydrogen complexes in ZnO materials.

Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor with a promising potential for many applications, mainly in electronics. Recent experiments suggest that commercially available, hydrothermally grown ZnO materials contain an appreciable amount of hydrogen. The concentration measured using nuclear reaction analysis is of the order of 0.1 at.% [1]. In this respect, it is useful to briefly summarize suggestions from the literature how hydrogen atoms can be incorporated into the ZnO lattice. The ZnO structure is enlightened in Fig. 1a and it is useful to consider this structure as a network of ZnO_4 tetrahedra interconnected at their corners.

Van de Walle [2] examined theoretically interstitial hydrogen and found that H atoms can be located in several positions in the lattice. First, these are ‘bond-center’ positions in which H atoms are located approximately in the middle of the original Zn-O bonds (inside corresponding ZnO_4 tetrahedron; see Fig. 1b), which causes a substantial lattice distortion at the place of defects. Second, there also exist ‘antibonding’ positions where the H bond is located outside ZnO_4 tetrahedra. Furthermore, hydrogen atoms may occupy vacancies on both Zn and O sublattices as suggested in [3,4]. In addition, weakly bound H atoms (in the form of H_2 molecules) may reside in ‘channels’ (along the hexagonal axis) in the ZnO structure [2]. Hydrogen atoms can also be bound to other impurities, but this is not a subject of the present study. We also note that hydrogen impurities in ZnO were recently identified as a source of its *n*-type conductivity [2,4]. On the other hand, the role of H in ZnO is yet far from being well understood and the identification of point defects related to hydrogen is of crucial importance for applications.

Positron annihilation spectroscopy is sensitive to open volume defects and it is, therefore, appropriate for studying vacancy-hydrogen complexes. In the present study we investigate theoretically the simplest vacancy-hydrogen complexes in ZnO. Realistic atomic configurations of studied defects are found using an ab initio method. The positron distribution in defects as well as the positron lifetime and binding energy to defects are determined using self-consistent electron densities and potentials taken from ab initio calculations. The effect of lowering the vacancy open volume due to hydrogen incorporation is discussed. The lifetime results are compared with existing experimental data.

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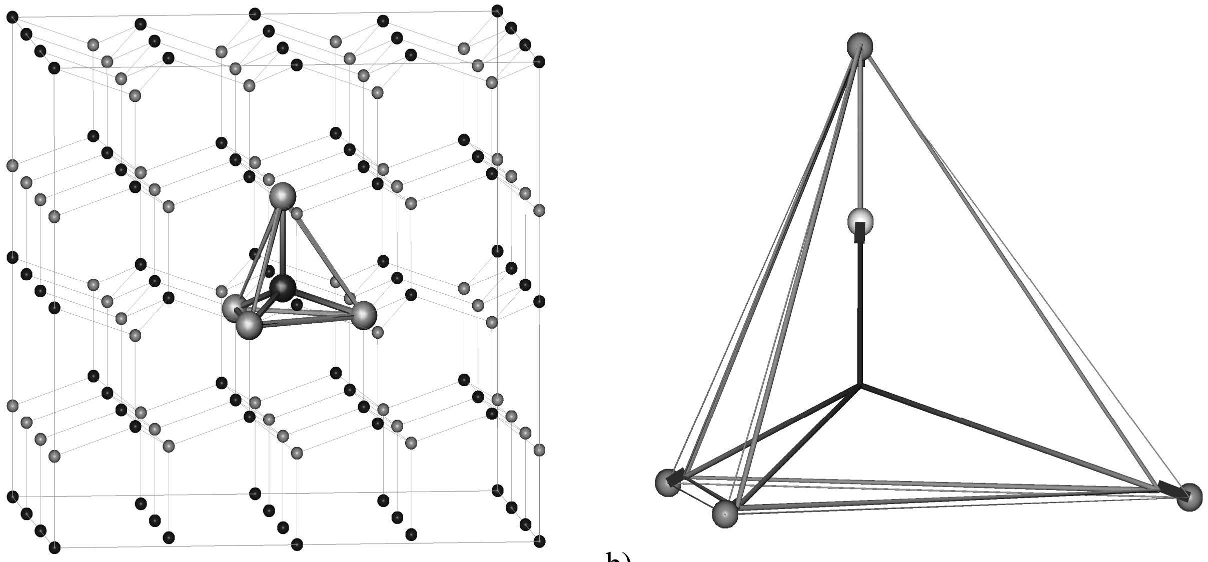
Computational methods

Realistic defect configurations were obtained by means of relaxing the total energy of appropriate supercells with respect to atomic positions. For this purpose, the Vienna ab initio simulation package (VASP) [5] was employed. In the course of calculations, projector augmented-wave potentials within the local density approximation were used [6]. 96 atom based supercells containing defects were utilized. Starting configurations of studied defects were prepared as follows: Vacancies were created by removing the corresponding atoms, whereas H atoms were placed into positions inside vacancies as suggested in [2]. In particular, we studied the oxygen vacancy (V_{O}) as well as the zinc vacancy with no, one and two hydrogen atoms (V_{Zn}, V_{Zn}+1H, V_{Zn}+2H, respectively). In the cases of V_{Zn}+1H, the hydrogen atom was incorporated into the BC$_{\parallel}$ position (see Fig 1b). The BC$_{\parallel}$ position and one of (three equivalent) BC$_{\perp}$ positions were occupied in the V_{Zn}+2H defect. At this stage of research we considered the neutral charge state of defects only. As a reference, the perfect ZnO lattice was also considered.



a) b)

Figure 1: (a) The ZnO perfect lattice (hexagonal, wurtzite) together with a ZnO_4 tetrahedron. Light (dark) spheres mark O (Zn) atoms. (b) The atomic configuration of the V_{Zn}+1H defect (H atom in the BC$_{\parallel}$ position). The original (non-relaxed) ZnO_4 tetrahedron is plotted by solid lines (as in figure (a)). Spheres and another tetrahedron (thin lines) indicate relaxed positions. Thicker dark bars show atomic shifts due to positron-induced forces.

Positron calculations were performed using a real space method as implemented in the atomic superposition method [7]. Two approaches were adopted: (i) self-consistent valence charge densities and Coulomb potentials as produced by VASP were considered for valence electrons, whereas the superposition of atomic densities and potentials was considered for core electrons (abbreviated further as the SC case) and (ii) superimposed atomic densities and potentials were employed to approximate the electron density and Coulomb potential for both valence and core electrons (NS case). Furthermore, we took into account non-relaxed (NR) and relaxed (RE) defect configurations, the former being starting defect configurations described above. In order to study the effect of various approximations, for each defect we performed a set of positron calculations described as follows: NS NR, NS RE and SC RE.

Finally, positron-induced forces acting on atoms around the defect were implemented according to the scheme developed by Makkonen et al. [8]. In such calculations, the so called conventional scheme [8,9] for positron calculations is considered, which means that the electronic structure is not primarily influenced by the presence of the positron trapped in a defect. On the other hand, the positions of ions

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(Zn, O and H) are influenced by the presence of the positron through positron-induced forces (PF). These forces are calculated using the Hellman-Feynman theorem employing atomic densities and Coulomb potentials, but the positron density is calculated within the SC scheme described above. In positron calculations the approach of Boroński-Nieminen [10] to the electron-positron correlations and enhancement factor – with the correction [11] for incomplete positron screening with the high frequency dielectric constant $\varepsilon_\infty = 4$ – was used.

As many defects in ZnO are not deep positron traps and supercells used in VASP calculations are rather small, VASP supercells were extended by adding atoms at sides of such supercells when calculating the final positron lifetime and positron energy. Such added atoms are arranged in the form of the regular ZnO lattice. Usually, 2592 atom supercells were used. In addition, the procedure according to Korhonen et al. [12] was used to minimize the effect of the finite supercell size on calculated positron properties. The positron binding energy to a defect was obtained as a difference of the ground state positron energies for bulk and the corresponding defect.

We further refer readers to [8,9] concerning theoretical background of positron calculations and to [13] regarding our previous calculations for ZnO. Further computational details of our current method will be given elsewhere.

Results and discussions

Calculated positron lifetimes and binding energies for bulk ZnO and studied defects are given in Table 1.

Table 1: Results of positron calculations for selected defects; τ and E_b are, respectively, the positron lifetime and binding energy and are given in ps and eV units.

	NS NR		NS RE		SC RE		SC RE PF	
Case	τ	E_b	τ	E_b	τ	E_b	τ	E_b
Bulk	—	—	159	—	154	—	—	—
V_O	159	~0	159	~0	154	~0	154	~0
V_{Zn}	197	0.34	231	0.60	246	1.25	207	1.11
V_{Zn}+1H	177	0.12	190	0.19	199	0.48	177	0.25
V_{Zn}+2H	161	~0	163	0.01	164	0.03	156	~0

We first discuss the bulk positron lifetime. The calculated values are 159 and 154 ps for NS and SC computational schemes, respectively (we note that the perfect wurtzite lattice of ZnO was also relaxed with respect to internal degrees of freedom (u-parameter)). In the literature one can find many different experimental values ranging from 151 to 185 ps (see [14] for a review) claimed to correspond to the bulk lifetime in ZnO. This range is obviously too wide and all the values may hardly be considered as the lifetime of delocalized positrons in ZnO even if corresponding experimental uncertainties are taken into account. These facts allow us to conclude that the bulk positron lifetime should rather correspond to the lower end of the given range and a lifetime of 150-160 ps represents a plausible assumption about the bulk positron lifetime in ZnO, in our opinion. At the same time, the above mentioned calculated values fit well into this narrower range. Considering the finding that the lowest 'bulk' values [13,15,16] from the wide range (151-185 ps) correspond to an estimate using the simple trapping model, it becomes clear that ZnO materials without an appreciable amount of free volume defects have not been used for measurements so far. Thus, an experimental lifetime value exceeding ~ 160 ps very probably corresponds to positron trapping in certain open volume defects (or their mixture). We also note that the gradient correction scheme [17] might not be appropriate to calculate positron properties of ZnO and we refer to the discussion in [13].

Next, we come to the defects. As for V_O, there is no positron trapping regardless of the computational approach used (see Table 1 and [13]). The positron potential well originating from a

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removed oxygen atom is rather shallow and its depth is not sufficient to trap positrons. When charge effects are taken into account, V_O becomes effectively positively charged and the corresponding potential well becomes even shallower, also due to an inward shift of nearest neighbor Zn atoms. Positron-induced forces do not change this picture though they move neighboring Zn atoms outward. The positron wave function is rather delocalized in all cases and the positron binding energy to the defect is zero (within the numerical precision of our calculations). If hydrogen would reside inside V_O [4], one can also expect no positron trapping in such a defect as the corresponding free volume is even smaller compared to the 'bare' oxygen vacancy (see also [18]) .

When V_{Zn} is considered, it is interesting to see the effect of various approximations employed in calculations (Table 1). Within the NS scheme relaxations affect strongly the lifetime (see also [13]) due to a large outward shift of O atoms surrounding the vacancy. When the charge transfer among atoms is taken into account, the lifetime is even longer as positrons are attracted to oxygen anions next to the vacancy. Switching on positron forces results in an inward shift of these anions (as well as of neighboring cations), which reduces the lifetime to 207 ps. This value can be well compared with defect lifetimes (202-209 ps) observed in electron irradiated ZnO [15,16]. The calculated positron binding energy slightly exceeds 1 eV (SC RE PF scheme).

Furthermore, we study hydrogen atoms inside the zinc vacancy. First, it is the V_{Zn}+1H defect. The effect of relaxations and self-consistency can be qualitatively described as in the V_{Zn} case, except the H atom is bound to the neighboring O atom in the *c*-axis direction (see Fig. 1b). The O-H bond length is ~1 Å, like for the interstitial hydrogen [2]. When positron forces are considered, the O-H pair moves slightly towards the vacancy center (as do neighboring cations) and the positron lifetime is reduced compared to the SC RE case. This means that the positron lifetime is reduced by about 30 ps with respect to the V_{Zn} value due to the effect of filling up the vacancy free volume by hydrogen. Also the positron binding energy is now much smaller (0.25 eV) than for the 'bare' zinc vacancy. The resulting calculated lifetime (177 ps) can be compared with often observed experimental lifetimes in the range ~ (170-185) ps [1,14]. Such lifetimes are usually interpreted as bulk lifetimes, but as we explained above, they should rather correspond to certain open volume defects and current calculations suggest that the V_{Zn}+1H defect could be one of them.

V_{Zn}+2H is the last defect studied. In this case, there is no positron trapping for the NS NR scheme, whereas we can observe very weak positron trapping for NS RE and SC RE cases. Positron-induced forces move two oxygen atoms with no bound hydrogen inwards so that no positron trapping occurs. This means that already two hydrogen atoms inside V_{Zn} result in a substantial reduction of the vacancy free volume and, as a consequence, the defect becomes invisible to positrons.

Conclusions

For ZnO, we studied theoretically clean single vacancies as well as zinc vacancies containing hydrogen atoms. Both the charge transfer between cations (Zn) and anions (O) as well as relaxations of defect configurations including positron-induced effects are important to get reliable results.

The calculated bulk lifetime amounts to 154 ps (SC RE scheme) and compares well with experimental data. As shown already earlier [13,18], oxygen vacancies do not constitute positron traps, which is not affected by considering positron-induced forces. The calculated positron lifetime of the clean zinc vacancy is 207 ps. If one hydrogen atom is located inside the vacancy (in the position described above), the positron lifetime is reduced to 177 ps. The V_{Zn}+2H defect does not trap positrons anymore. These findings demonstrate the effect of gradual filling up the zinc vacancy with the increasing number of hydrogen atoms. The calculated lifetimes can be associated with certain lifetimes observed in experiment, which also indicates that zinc vacancy-hydrogen complexes are present in ZnO materials. Nevertheless, further work is needed to identify positron trapping sites in ZnO more precisely. To this end, calculations for further H-related defects in ZnO are in progress, considering also appropriate defect charge states.

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