A comprehensive ab initio study of doping in bulk ZnO with group V elements

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Despite the lack of reproducible experimental confirmation, group V elements have been considered as possible sources of p-type doping in ZnO in the form of simple and complex defects. Using ab initio calculations, based on state-of-the-art hybrid exchange-correlation functional, we studied a wide range of defects and defects complexes related with N, P, As and Sb impurities. We show that none of the candidates for p-type doping can be considered a good source of holes in the valence band due to deep acceptor levels and low formation energies of compensating donor defects. In addition, we discuss the stability of complexes in different regimes.

Zinc oxide has attracted a considerable interest as promising material for optoelectronics applications, like light-emitting diodes and solar cells, due to its large band gap and large exciton binding energy. The actual possibility of successfully employing ZnO in these kind of devices relies on the ability of preparing stable p-type as well as an n-type ZnO. Unfortunately, like other wide band gap semiconductors, ZnO suffers from a doping asymmetry problem and, while n-type ZnO has been easily obtained, reliable p-type ZnO has not been produced yet.

One of the most common ways to overcome this difficulty has been to incorporate group V elements, in the hope that they could substitute oxygen in ZnO crystal and provide shallow enough acceptor levels. In particular, nitrogen has played the role of the favorite dopant, owing to its atomic size close to that of oxygen. Experimentally, despite the great deal of effort devoted to the topic, only few successes in achieving p-type ZnO have been reported with this kind of doping and up to now none of them has eventually led to further development.

From a theoretical point of view, the understanding of these results and the proposition of other ways of obtaining p-type doping by means of density functional theory (DFT) calculations is a challenging task as well. In fact, the problem of the band gap underestimation related to the local or semi-local approximations of the exchange correlation functional is particularly relevant in the case of ZnO, with a calculated gap of only ~0.8 eV. Calculations performed within these approximations have shown for example a transition level of 0.4 eV for N_{o2}^\text{Zn} and shallow levels for complexes of the form X_{Zn}^2Zn_{o2}^\text{Zn}, but, in light of the severe gap underestimation, these results should be considered with care. Recently, some of these calculations have been updated with the introduction of hybrid functionals, which use an admixture of exact and local exchange, giving larger values of the band gap and providing more reliable results. According to the latest evaluation with hybrid functionals for some group V related defects, the results indicate that the acceptor levels are much deeper than expected from previous calculations, suggesting that these are not good candidates for achieving p-type doping. Anyway, these calculations have been carried out with different approximations and several of the possible defects have not been considered, making it difficult to draw a uniform conclusion about the doping with group V elements. To fill this gap, in this letter we consider the problem of ZnO doping with N, P, As and Sb in the most relevant defect configurations by means of DFT calculations based on hybrid functionals. We will show that it is unlikely to obtain good acceptor states from these elements and finally we will discuss the possibility to actually observe complex defects in doped samples.

Our calculations have been performed in the framework of plane-wave pseudopotential DFT as implemented in the Quantum ESPRESSO package. Norm-conserving pseudopotentials have been employed for all the atoms, with the semicore Zn 3d states included in the valence electrons, and the energy cutoff has been set to 80 Ry. The exchange correlation potential has been treated with the hybrid functional of Heyd, Scuseria and Ernzerhof (HSE), based on the Perdew, Burke, and Ernzerhof (PBE) where a fraction α of the exchange is replaced by Hartree-Fock (HF) exchange. However, the problem of choosing the α parameter to get accurate defect levels is still under debate and its value has been set based on several schemes. Since we are dealing with transition energies that span all the band gap, we have set α = 0.45. This allows us to correctly reproduce the experimental value of the band gap of 3.44 eV and gives lattice parameters a = 3.23 Å, c = 5.19 Å and u = 0.38, in good agreement with the experiments. Such a large value of α may affect the transition levels due to the relation between the valence band maximum (VBM) and the α parameter itself, but this should not alter the general conclusions drawn in the following. The calculations have been carried out in a 72 atoms supercell with a 2\times2\times2 Monkhorst-Pack grid to sample the Brillouin zone and a 1\times1\times1 Q-point grid. The formation energies of defect D in charge state q have been calculated according to the formula

\[ E_f(D, q) = E_{\text{tot}}(D, q) - E_{\text{tot}}(\text{bulk}) - \sum_i n_i \mu_i + q(\epsilon_v + \epsilon_F + \Delta V) + \Delta E_{\text{el}}(q), \]

where \( E_{\text{tot}}(D, q) \) and \( E_{\text{tot}}(\text{bulk}) \) represent the total energy of the supercell with and without the defect, \( \epsilon_v \) is the energy of the VBM, \( \epsilon_F \) indicates the value of the Fermi level inside the band gap and \( \Delta V \) is a potential
alignment term. The electrostatic correction $\Delta E_{el}(q)$ is calculated as the monopole Madelung term in the generalized case when anisotropy in the screening requires that the dielectric constant $\varepsilon$ is replaced by a tensor $\varepsilon_{\parallel}$. In the case of ZnO $\varepsilon = \text{diag}(\varepsilon_{\perp}, \varepsilon_{\perp}, \varepsilon_{\parallel})$ with $\varepsilon_{\perp} = 7.77$ and $\varepsilon_{\parallel} = 8.91$. Finally, for each species $i$, $n_i$ is the change in the total number of atoms to create defect $D$ and $\mu_i$ is the corresponding chemical potential, which is constrained by the growth conditions. In particular $\mu_{\text{Zn}} = \mu_{\text{Zn}}^0 + \Delta H_f$ and $\mu_{\text{O}} = \mu_{\text{O}}^0/2$ for O-rich environment, while $\mu_{\text{Zn}} = \mu_{\text{Zn}}^0$ and $\mu_f = \mu_{\text{O}}^0/2 + \Delta H_f$ for Zn-rich conditions. Here $\Delta H_f = -2.96$ eV is the calculated ZnO enthalpy of formation. If needed, also the chemical potentials of the group V dopants should be constrained as well. The results shown are under the dopant rich condition, using molecular N$_2$ and P$_4$O$_{10}$, and solid As$_2$O$_3$ and Sb$_2$O$_3$ as dopant sources.

In our simulations, we have considered several species of defects, identified as promising for p-type doping in the literature. These include simple substitutional defects X$_0$ and X$_{Zn}$ (X=N, P, As, Sb) and complexes of the form X$_{Zn}$-2V$_{Zn}$ and X$_{Zn}$-V$_{Zn}$, which have been proved to be binding in ZnO. To evaluate the binding energies of the complexes the isolated Zn vacancy V$_{Zn}$ has been isolated as well. In addition, given the stability of the N$_2$ molecule and their importance for p-type doping, we have included the (N$_2$)$_O$ and (N$_2$)$_Zn$ defects.

In order to discuss the relative stability of the different kind of defects and the charge transition energies, we report the formation energies $E_f$ as a function of $\epsilon_F$ in Figs. 1 and 2. The former deals with the simple substitutional defects under Zn-rich growth condition and the latter focuses on complexes under O-rich conditions. As it is immediately evident, in most cases, defects of the same kind display the same qualitative behavior for all the dopants, and for P, As and Sb a quantitative agreement can be recognized. We thus begin analyzing each specie of defect. Simple oxygen substitutional defects X$_O$ are single acceptors due to the missing electron in group V elements compared to O. From a structural point of view, when using hybrid functionals the hole present in the neutral charge state is localized on one of the four bonds, producing a non symmetric configuration. It has been shown that N$_O$ with the hole localized along the bond parallel to the c axis (N$_O$$_{||}$) is the most stable configuration and gives good agreement with electron paramagnetic resonance (EPR) measurements. Our calculations confirm these results, with N$_O$$_{||}$ configuration having a 45 meV lower energy than the one with the hole localized along a bond perpendicular to the c axis (N$_O$$_{\perp}$), highlighting the ability of hybrid functionals to correctly describe this kind of defects. For P$_O$, As$_O$ and Sb$_O$ we found the same tendency to hole localization, with the difference that X$_O$$_{||}$ is unstable and only configurations of the type X$_O$$_{\perp}$ have been observed and with a much smaller asymmetry in the bond lengths. Although defects of this kind have a stable negative charge state configuration, they fail to be good sources of holes.

When substituting Zn atoms, group V elements are instead triple donors. According to our hybrid functional results, P and Sb bear positive charge state for all the values of $\epsilon_F$ making them good donors and in agreement with some experimental results, while N and As has rather deep transition energies $\epsilon(0/+) = 0.39$ eV and $\epsilon(0/3+) = 0.73$ eV from the top of the conduction band, respectively. However, in this context it is important that, when $\epsilon_F$ is close to the valence band maximum, X$_3$$^{2+}$ have a very small formation energy and therefore will certainly contribute to compensate the effect of acceptor impurities that one wants to create.

Also in this case, due to its smaller atomic radius, N$_O$ has a different structure compared to P, As and Sb. For the 0 and + charge states it forms an isolated NO molecule, while for 2+ and 3+ charge states it forms a NO$_3$ molecule bounded to one of the neighboring Zn atoms. The other elements form a symmetric configuration after relaxation, except for As$_2$O$_{3Zn}$, where As is strongly bound to just three O atoms.

Since we have just shown that the isolated dopant are ineffective for p-type doping, let us now move to analyze complex defects, starting from the N$_2$ molecule, which can substitute an O or a Zn atom as recently identified in Ref.24. In the former case each N atom binds with two surrounding Zn and the molecule acts as a strong double donor. It is also quite stable, compared with N$_O$ and even N$_{2Zn}$, and this provides a further reason for the dif-

![Figure 1. Formation energy $E_f$ of simple substitutional defects as a function of the Fermi level in Zn-rich conditions. The Zn-rich conditions were chosen so to best stabilize the oxygen substitution. The zero of the Fermi level has been set to the valence band maximum.](image-url)
ficulty of obtaining p-type from N\textsuperscript{23}. On the other hand, \((\text{N}_2)\text{zn}\) could be a double acceptor. Recently, Lambrecht and Boonchum\textsuperscript{24} have studied the \((\text{N}_2)\text{zn}\) molecule in an isolated configuration, excitingly concluding that it has a relatively shallow transition energy \(\epsilon(0/-)\) for both PBE and HSE calculations. According to our results, however, in the 0 charge state the system has two competing configurations, one with the \(\text{N}_2\) forming a bridge across two O atoms and one in the \(\text{N}_2\) isolated molecule configuration with a S=1 spin configuration, with the former being slightly more stable\textsuperscript{25}. With our calculation parameters, both of them have relatively low formation energies, making the transition level very deep \(\epsilon(0/-) = 1.92\) eV, at variance with what has been observed in Ref. 24. In addition \((\text{N}_2)\text{zn}\) is also less stable than \((\text{N}_2)\text{O}\), even in O-rich conditions, and thus unlikely to be a good acceptor.

Given the difficulties of finding a shallow acceptor among simple donors configurations, complexes of the form \(\text{X}_\text{zn}-2\text{V}_\text{zn}\) have been studied, since they were expected to be stable acceptors due to reaction \(\text{X}_\text{zn}^+ + 2\text{V}_\text{zn}^– \rightarrow (\text{X}_\text{zn} – 2\text{V}_\text{zn})^–\). Since the first time they were proposed\textsuperscript{26} due to the results of semilocal functional calculations\textsuperscript{27} these complexes have been believed to be shallow acceptors and have often been used to justify the observation of p-type doping in experiments. Only recently Puchala and Morgan\textsuperscript{28} have shown that \(\text{As}_\text{zn}-2\text{V}_\text{zn}\) is instead a deep acceptor according to hybrid DFT calculations.

Several inequivalent configurations can be found removing three Zn atoms and adding one impurity. We explored several of them and selected those with lower formation energies\textsuperscript{29}. The results are shown in Fig. 2. It can be argued that the small sizes of the supercell could play a role in determining the most favorable configuration, since the complex is quite extended and this could actually be the case, as demonstrated in some cases\textsuperscript{22}. However, the differences in the formation energies between the various configurations are usually below few hundreds of meV, a quantity that will only marginally affect the values of formation and binding energies.

These defects require several missing Zn, therefore the O-rich conditions should make them more stable. It can be seen in Fig. 2 that, in this limit, \(\text{X}_\text{zn}-2\text{V}_\text{zn}\) is the acceptor with the lowest formation energy, even if still larger than that of \(\text{X}_\text{zn}\) for a wide range inside the band gap. Note also that while P, As and Sb have a close behavior, N is much less stable compared to them. Despite their relatively low formation energies, we are faced again with the problem of deep values of the ionization energies \(\epsilon(0/-)\) for all the group V elements: 1.53 eV, 1.48 eV, 1.50 eV and 1.69 eV for N, P, As and Sb, respectively. Unlike for \(\text{XO}\) defects, the transition energies are approximately the same for all X and much smaller, but still too deep to provide good acceptor levels.

Since \(\text{X}_\text{zn}-2\text{V}_\text{zn}\) are complex defects that involve three atoms, it is necessary to study the properties of its simpler components, namely \(\text{X}_\text{zn}-\text{V}_\text{zy}\) and \(\text{V}_\text{zn}\). Complexes with only one vacancy \(\text{X}_\text{zn}-\text{V}_\text{zn}\) are quite stable as well, but they do not undergo strong deformation. They are just hold together by the attractive coulomb interaction between \(\text{X}_\text{zn}^+\) and \(\text{V}_\text{zn}^–\) and, as expected from this, they are donors. Like before, \(\text{N}_\text{zn}-\text{V}_\text{zn}\) has a larger formation energy, compared to the other elements, which are instead quite similar. Finally, it can be seen that Zinc vacancy is a double acceptor, but with a deep transition level \(\epsilon(0/-) = 1.68\) eV and a high formation energy close to the VBM. Note that, like in the isolated molecule configuration of \((\text{N}_2)\text{zn}\), the 0 charge state is more stable in a spin polarized configuration.

Up to now we have shown that these complexes should not be suitable to create p-type ZnO. Nonetheless there have been some speculations about their possible presence in experiments\textsuperscript{28,29} and so it is interesting to check whether these kind of defects are likely to be found or not. In order for the cluster to form, it is essential that their binding energy \(E_b = E_f(X) + nE_f(V_{zn}) - E_f(X-nV_{zn})\) is positive and large enough to favor the complexes over the single components. The values of \(E_b\) for all the kind of dopants are shown in Fig. 3 as a function of the Fermi level. The complexes including N are much less binding than those for the other group V elements, and in particular \(\text{N}_\text{zn}-\text{V}_\text{zn}\) is almost never binding. As a further confirmation of the scarce utility of the complexes we can see that they are just loosely binding in the p-type regime, while the binding energy grows rapidly with \(\epsilon_f\) and could remain as large as 5 eV up to the conduction band minimum (CBM) for \(\text{P}_\text{zn}-2\text{V}_\text{zn}\). This suggests that it should possible to observe them for large enough values of \(\epsilon_f\). To further investigate this possibility, we consider the case when the defects are formed out of equilibrium in the crystal during the growth and the total amounts of dopants and vacancies remain fixed during the cooling down of the sample. In this process the defects could reorganize in complexes and the evolution of the concentrations as function of the temperature \(T\) is governed by the mass-action law:

\[
[X-nV_{zn}] = |X||V_{zn}|^n \exp(E_b/k_BT), \quad n = 1, 2
\]
Figure 3. Binding energy $E_b$ of complex defects as a function of the Fermi level.

Figure 4. Phase diagram showing the prevalent configuration of the zinc vacancy configurations as a function of temperature and Fermi level. Black V$_{Zn}$, gray X$_{Zn}$-V$_{Zn}$ and white X$_{Zn}$-2V$_{Zn}$.

where [X-nV$_{Zn}$], [X] and [V$_{Zn}$] are the defect concentrations and $k_B$ is the Boltzmann constant. The experimentally reported densities of group V elements are quite variable in the range 10$^{15}$-10$^{20}$ cm$^{-3}$, while Zn vacancies could be found with a density of 10$^{15}$-10$^{16}$ cm$^{-3}$. Thus we fix the total concentrations to $[X]_{tot}=1 \times 10^{17}$ cm$^{-3}$ and $[V_{Zn}]_{tot}=1 \times 10^{16}$ cm$^{-3}$, with the comment that a change of few orders of magnitude does not alter qualitatively our findings. Solving the system for $E_b(\epsilon_F)$ and $T$ down to room temperature, we verified that the concentrations tend to saturate quite fast with one of the defect among X$_{Zn}$-2V$_{Zn}$, X$_{Zn}$-V$_{Zn}$ and V$_{Zn}$ dominating the others. Of course in our configuration the limiting factor for complex total concentration is $[V_{Zn}]_{tot}$, while the group V elements are supposed to be present in abundance. The phase diagrams reporting the defect with the highest concentration are shown in Fig. 4 and confirm that both X$_{Zn}$-2V$_{Zn}$ and X$_{Zn}$-V$_{Zn}$ could be obtained, depending on the value of $\epsilon_F$. It should be pointed out that the dependence of the defects diffusivity on $\epsilon_F$ and $T$ could hinder the reorganization of the defects into complexes when decreasing too quickly the temperature.

In conclusion, we studied the properties of ZnO doped with group V elements as possible candidates to provide p-type doping. We have shown that none of the defect configurations considered so far are likely to provide a good source of holes, due to the defects being too deep or to their tendency to behave like donors. We have also considered the complexes X$_{Zn}$-2V$_{Zn}$ and X$_{Zn}$-V$_{Zn}$ and we have provided a possible justification to the experimental observation of these kind of defects.

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See supplemental material for detailed information about (N₂)₂α and X₂α-2V₂α defect structure.

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SUPPLEMENTAL MATERIAL

I. DETAILS FOR THE (N\textsubscript{2})\textsubscript{Zn} DEFECT

When substituting a Zn atom, the N\textsubscript{2} molecule can be found in two different configurations, illustrated in Fig. 5. One has the molecule isolated from all the O nearest neighbors, while in the other one the N\textsubscript{2} forms a bridge between two O atoms. We found that the most stable configuration among the two is charge state dependent. In particular, for the neutral defect the bridge configuration is more stable by 0.25 eV. The opposite is true for the 1− and 2− charge states, where the isolated configuration is much more favorable. Anyway, in both cases the configuration with higher energy is metastable. The same trends are observed within PBE calculations, even if the formation energy differences are smaller in this case.

It should be noted that the neutral isolated configuration is in a spin polarized state with spin S=1, as it happens for the V\textsubscript{Zn} defect. This, along with the similar behavior for the transition energies of (N\textsubscript{2})\textsubscript{Zn} and V\textsubscript{Zn}, could suggest that the N\textsubscript{2} molecule remains quite inert with respect to the environment and that the (N\textsubscript{2})\textsubscript{Zn} defect acts basically as a Zn vacancy.

II. THE X\textsubscript{Zn}-2V\textsubscript{Zn} DEFECTS STRUCTURE

Removing three zinc atoms and adding one from the group V, it is possible to find several inequivalent configurations for the resulting complex defect. We have thus considered four of them, shown in Fig. 6 with the following different qualitative peculiarities: (1) the two vacancies placed at opposite sites with respect to the dopant\textsuperscript{1}, (2) two neighboring vacancies next to the dopant\textsuperscript{2}, and two neighboring vacancies with the dopant shifted in (3) tetrahedral and (4) octahedral interstitial positions\textsuperscript{3}. For N the most stable structure is obtained starting from configuration (3), but it ends up in a distorted configuration, with N bound to only three O atoms. When the dopant is P or As configurations (2) and (3) are the most favorable and almost equivalent in energy, with (2) being slightly favored. Sb, having a larger size, prefers configuration (4).

In the paper only the values of these most stable configurations are reported. Anyway, the differences between the formation energies between different configurations are too small to alter relevant conclusions of our work, like the transition energies being too deep and the formation energies of X\textsubscript{Zn}-2V\textsubscript{Zn} defects being much larger than those of X\textsubscript{Zn}-V\textsubscript{Zn} close to the VBM.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Possible configurations for the N\textsubscript{2} molecule on Zn site in 0 charged state. (a) The isolated configuration: the molecule is isolated from the neighboring O atoms. (b) The bridge configuration: the molecule is bonded to two O atoms. N, Zn and O are shown as gray, violet and red spheres, respectively.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{The four different starting configurations considered for the X\textsubscript{Zn}-2V\textsubscript{Zn} defects. X, Zn and O are shown as yellow, violet and red spheres, respectively, while the blue spheres represent the removed Zn atoms.}
\end{figure}

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