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# The role of the $V_{Zn}-N_O-H$ complex in the p-type conductivity in ZnO

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Past research efforts aiming at obtaining stable p-type ZnO have been based on complexes involving nitrogen doping. A recent experiment by (J. G. Reynolds *et al.*, *Appl. Phys. Lett.*, 2013, **102**, 152114) demonstrated a significant ( $\sim 10^{18} \text{ cm}^{-3}$ ) p-type behavior in N-doped ZnO films after appropriate annealing. The p-type conductivity was attributed to a  $V_{Zn}-N_O-H$  shallow acceptor complex, formed by a Zn vacancy ( $V_{Zn}$ ), N substituting O ( $N_O$ ), and H interstitial ( $H_i$ ). We present here a first-principles hybrid functional study of this complex compared to the one without hydrogen. Our results confirm that the  $V_{Zn}-N_O-H$  complex acts as an acceptor in ZnO. We find that H plays an important role, because it lowers the formation energy of the complex with respect to  $V_{Zn}-N_O$ , a complex known to exhibit (unstable) p-type behavior. However, this additional H atom also occupies the hole level at the origin of the shallow behavior of  $V_{Zn}-N_O$ , leaving only two states empty higher in the band gap and making the  $V_{Zn}-N_O-H$  complex a deep acceptor. Therefore, we conclude that the cause of the observed p-type conductivity in experiment is not the presence of the  $V_{Zn}-N_O-H$  complex, but probably the formation of the  $V_{Zn}-N_O$  complex during the annealing process.

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## 1 Introduction

There are many well-known n-type transparent conducting oxides (TCOs), but the lack of good p-type TCOs limits the manufacturing of active devices based on transparent conducting elements. Finding appropriate acceptor dopants for semiconductors that are transparent in the optical frequency range is therefore a very active field of research. Both single atoms and complexes of atoms have been considered as potential candidates in the past. Complexes of dopants are particularly promising, since the interaction between donor and acceptor dopants might limit compensation and lower the acceptor level formation energy, providing a more stable system compared to the corresponding isolated dopants.

N-doping has been used to make p-type ZnO by many groups,<sup>1–4</sup> and hole concentrations of  $\sim 10^{16} \text{ cm}^{-3}$  have been achieved in ZnO films. It was shown theoretically that the p-type conductivity of N-doped ZnO can originate from the shallow acceptor complex  $V_{Zn}-N_O$ , which actually evolves from the double-donor state of  $V_O-N_{Zn}$ .<sup>5</sup> Recently, it has also been shown experimentally that a much higher hole concentration ( $\sim 10^{18} \text{ cm}^{-3}$ ) can be reached in N-doped ZnO under appropriate annealing.<sup>6</sup> Several characterization techniques indicate that a  $V_{Zn}-N_O-H$  defect complex is the cause of this behavior and that it acts as a shallow acceptor with an

ionization energy of 130 meV. The doping process in this experiment is not straightforward. Different techniques are used and the doping process is mainly divided into three steps. First, N-doped ZnO films are annealed at low Zn partial pressure to induce the formation of  $V_{Zn}$ . Incorporation of N atoms (originating from  $N_2$  gas, nitric oxide (NO) and nitrous oxide ( $N_2O$ )) causes the formation of a substitutional N on the Zn sublattice ( $N_{Zn}$ ). In the second step, high Zn partial pressure is used for the formation of oxygen vacancies ( $V_O$ ). Finally, by further annealing the obtained complex, a  $V_O-N_{Zn}$  double donor is converted into  $V_{Zn}-N_O-H$ , which is claimed to be the origin of the heavy p-type behavior at room temperature.

In order to shed more light on the role of the  $V_{Zn}-N_O-H$  complex in the p-type conductivity observed in ZnO, we investigate in the present paper the formation of the (charged) complex and its acceptor behavior by means of first principles calculations.

## 2 Computational details

We perform spin polarized density functional theory (DFT) calculations, as implemented in the Vienna ab initio simulation package.<sup>7,8</sup> Since the introduction of (charged) defects can involve the occupation of levels in the band gap, a correct value of the formation energy depends sensitively on the correct position of the defect levels and thus on the value of the band gap. This poses a major hurdle to standard DFT defect calculations using the LDA or GGA functionals.<sup>9</sup> On the other hand, the hybrid HSE06

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functional<sup>10</sup> does not suffer from the band gap problem and has proven to be reliable to obtain realistic defect formation energies.<sup>9,11,12</sup> Therefore, the formation energy calculations are performed using the HSE06 functional. We use an optimized 37.5% Hartree–Fock exchange mixing in the HSE06 functional. This mixing correctly reproduces the experimental value of the band gap in ZnO.<sup>13</sup> Electron–ion interactions are treated using projector augmented wave potentials.<sup>14–16</sup> A large supercell consisting of 108 atoms is used ( $3 \times 3 \times 3$  unit cells). Therefore, the concentration is equivalent to the dilute limit and defects act basically as isolated entities. The Zn ( $4s^2 3d^{10}$ ), H ( $1s^1$ ), N ( $2s^2 2p^3$ ), and O ( $2s^2 2p^6$ ) electrons are treated as valence electrons. Wave functions are expanded using plane wave basis sets up to a cutoff energy of 400 eV, and the Brillouin zone is sampled using a  $k$ -point grid of  $2 \times 2 \times 2$ . Convergence of the self-consistent iterations is assumed when the total energy difference between cycles is less than  $10^{-4}$  eV, and the atomic positions are relaxed until the magnitude of residual forces on the atoms is less than  $0.05 \text{ eV } \text{\AA}^{-1}$ .<sup>†</sup> A single N atom is chosen to substitute an O atom and one of its Zn nearest neighbors is removed to have a Zn vacancy. For the H atom, an extensive number of positions around the substituted N element are considered. The formation energy is calculated for the most stable configuration of each charge state.

## 3 Results and discussion

### 3.1 Structural properties

The doped ZnO structure is shown schematically in Fig. 1. For the interstitial hydrogen  $H_i$  defect, for all charge states, the lowest formation energy is obtained when the H atom is located in between N and the Zn vacancy atom. The formation energy for the H atom between O and the Zn vacancy is higher by at least 0.39 eV. With H at other interstitial positions the difference between the formation energies is larger than 2 eV. The N–H distance in the three charge states (0, +1, and –1) is about  $1.03 \text{ \AA}$ , which is consistent with the N–H bond length observed in experiment.<sup>6</sup> This indicates the formation of a bond between N and H atoms.

### 3.2 Formation energy calculations

The formation energy of a point defect or impurity is a key quantity, playing a central role in the determination of its thermodynamic stability and its equilibrium concentration. The formation energy of a defect or impurity  $D$  in charge state  $q$  is defined as<sup>17,18</sup>

$$E_f[D^q] = E_{\text{tot}}[D^q] - E_{\text{tot}}[\text{bulk}] + \sum_i n_i \mu_i + q[E_F + E_V + \Delta V]. \quad (1)$$

where  $E_{\text{tot}}[D^q]$  is the total energy obtained from a supercell calculation with one impurity  $D$  in the cell and  $E_{\text{tot}}[\text{bulk}]$  is the

<sup>†</sup> We have verified that this is sufficient for the purposes of the present work by performing the relaxation in a few cases with  $0.01 \text{ eV } \text{\AA}^{-1}$  as a force criterion. We found that the changes in total energy were at most of the order of a few meV.

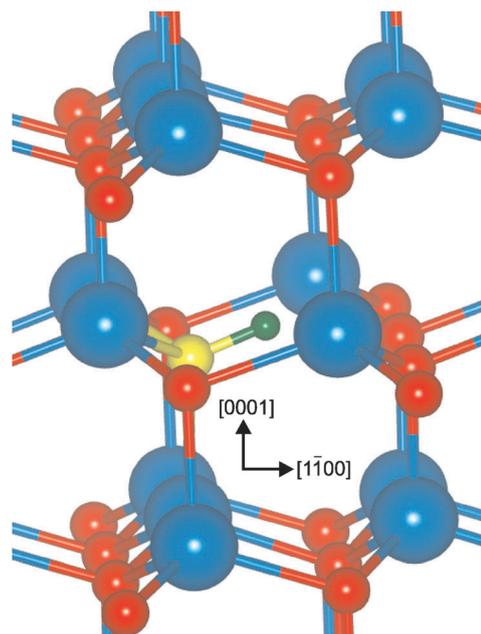


Fig. 1 N–H neutral complex. The blue atom is Zn, the red atom is O, the yellow atom is N, and the green atom is H.

total energy of the equivalent perfect supercell.  $n_i$  indicates the number of atoms of type  $i$  that has been added ( $n_i < 0$ ) or removed ( $n_i > 0$ ) from the supercell and  $\mu_i$  is the chemical potential of the corresponding species.  $E_F$  is the Fermi level with respect to the top of the valence band,  $E_V$ .  $\Delta V$  aligns the potentials in the perfect and doped supercells in a region far from the defect.<sup>19,20</sup> We calculate  $\Delta V$  following the procedure introduced in ref. 20.

Eqn (1) indicates that the defect formation energy depends sensitively on the chemical potential of both atomic species and electrons (often referred to as the Fermi energy  $-E_F$ ). This is because in forming the defect, atoms are exchanged between the host material and the chemical reservoirs. These chemical potentials depend on the experimental growth conditions, which can be either Zn-rich, O-rich, or anything in between. As mentioned in the Introduction, different techniques are used in the formation process of the  $V_{\text{Zn}}\text{--}N_{\text{O}}\text{--}H$  complex.<sup>6</sup> These techniques are meant to optimize the formation of the final complex in the material. Therefore, we consider thermodynamically most favorable conditions (which lower the formation energy of the  $V_{\text{Zn}}\text{--}N_{\text{O}}\text{--}H$  complex in ZnO) in our calculations. The enthalpy of formation of bulk ZnO is given by

$$\Delta H_f[\text{ZnO}] = E[\text{ZnO}] - \mu_{\text{Zn}}^{\text{Zn bulk}} - \mu_{\text{O}}^{\text{O}_2 \text{ mol}} \quad (2)$$

where  $E[\text{ZnO}]$  is the total energy of bulk ZnO,  $\mu_{\text{Zn}}^{\text{Zn bulk}}$  is the chemical potential of Zn from Zn bulk, and  $\mu_{\text{O}}^{\text{O}_2 \text{ mol}}$  is the chemical potential of O from the  $\text{O}_2$  molecule. Through the thermodynamic stability conditions,  $E[\text{ZnO}]$  is related to the chemical potentials by  $E[\text{ZnO}] = \mu_{\text{Zn}} + \mu_{\text{O}}$ . Calculations show that the lowest formation energies for the different charge states of the complex require extreme Zn-rich conditions. These conditions correspond to the upper limit of the

Zn chemical potential, given by  $\mu_{\text{Zn}}^{\text{max}} = \mu_{\text{Zn}}^{\text{Znbulk}}$ . This upper limit for Zn leads to the lower limit for the O chemical potential through the above stability conditions for ZnO, resulting in

$$\mu_{\text{O}}^{\text{min}} = \mu_{\text{O}}^{\text{O}_2\text{mol}} + \Delta H_{\text{f}}[\text{ZnO}]. \quad (3)$$

The chemical potentials of N and H are also coupled with the O chemical potential. Indeed, the limits of the chemical potentials of N and H are determined by the enthalpies of formation of  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and NO, which can be written as

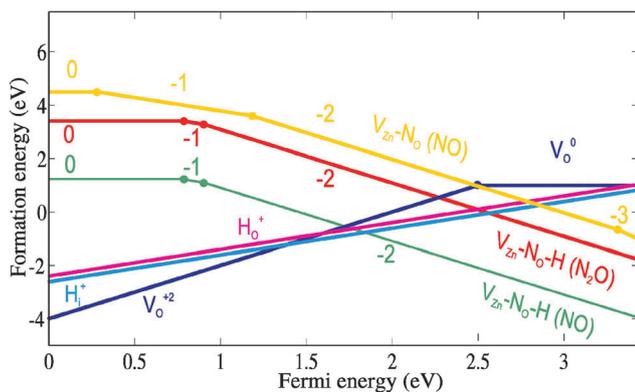
$$\begin{aligned} \Delta H_{\text{f}}(\text{H}_2\text{O}) + \mu_{\text{H}}^{\text{H}_2\text{mol}} + \mu_{\text{O}}^{\text{O}_2\text{mol}} &= 2\mu_{\text{H}} + \mu_{\text{O}} \\ \Delta H_{\text{f}}(\text{N}_2\text{O}) + \mu_{\text{N}}^{\text{N}_2\text{mol}} + \mu_{\text{O}}^{\text{O}_2\text{mol}} &= 2\mu_{\text{N}} + \mu_{\text{O}} \\ \Delta H_{\text{f}}(\text{NO}) + \mu_{\text{N}}^{\text{N}_2\text{mol}} + \mu_{\text{O}}^{\text{O}_2\text{mol}} &= \mu_{\text{N}} + \mu_{\text{O}}. \end{aligned} \quad (4)$$

Table 1 shows the calculated enthalpies of formation for different considered compounds, with the corresponding experimental values. In ref. 6 annealing is done in  $\text{N}_2\text{O}$ . However, since we are interested in the possibility of forming a  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}\text{-H}$  complex, for N we also consider the chemical potential determined by NO. As seen in Table 1, the latter has a higher enthalpy of formation compared to  $\text{N}_2\text{O}$  and can therefore shift down the formation energy of the complex.

Fig. 2 shows the formation energy of the complex  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}\text{-H}$  as a function of Fermi level  $E_{\text{F}}$  for the most stable charge states, 0, -1 and -2, for two different N chemical potentials and under Zn-rich (O-poor) conditions. (Under O-rich conditions the formation energies increase because of the higher chemical

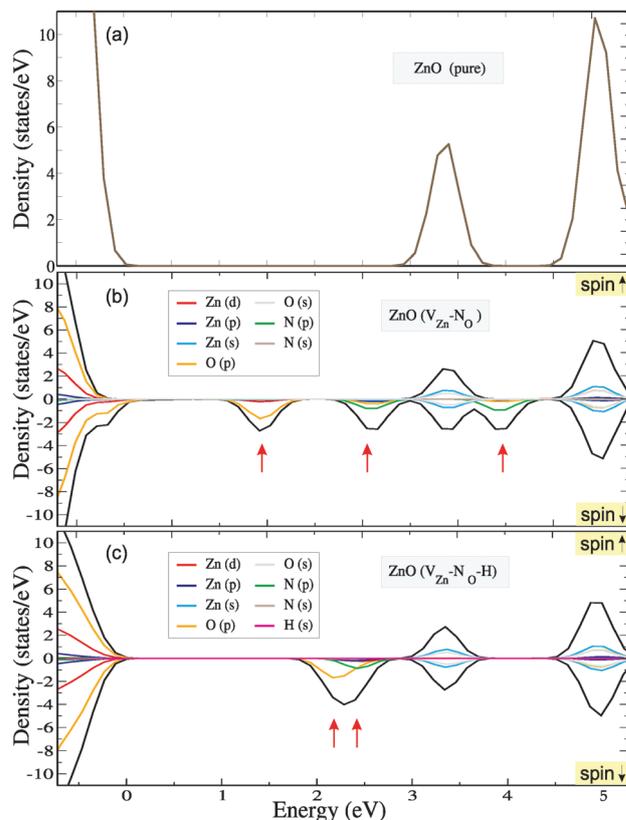
**Table 1** Calculated and experimental enthalpies of formation for different considered structures

Oxide	Experimental (eV) <sup>21</sup>	HSE06 (eV)
$\Delta H(\text{ZnO})$	-3.60	-3.12
$\Delta H(\text{H}_2\text{O})$	-2.96	-2.72
$\Delta H(\text{N}_2\text{O})$	0.85	0.62
$\Delta H(\text{NO})$	0.94	0.93



**Fig. 2** Calculated formation energies as a function of Fermi energy for the complex  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}\text{-H}$  in ZnO under O-poor conditions for two different conditions of nitrogen (NO and  $\text{N}_2\text{O}$ ), together with the formation energies of some individual defects such as  $\text{V}_{\text{O}}$ ,  $\text{N}_{\text{O}}$ ,  $\text{H}_{\text{i}}$ ,  $\text{H}_{\text{O}}$  and also the  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}$  complex in ZnO.

potential of O, making the formation of the complex less likely.) The transition point, indicated with a dot in Fig. 2, between the neutral and negative charge states is about 0.77 eV above the valence band maximum (VBM). Therefore, the complex does not have the potential to act as a shallow acceptor in ZnO. To understand the reason for the deep acceptor behavior of the  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}\text{-H}$  complex, it is useful to compare it with the  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}$  complex. As mentioned in the Introduction, it was shown before that the  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}$  complex itself acts as a shallow acceptor in ZnO, and can be the cause of p-type conductivity of N-doped ZnO.<sup>5</sup> As shown in Fig. 2, we find indeed that the transition level (0,-) for this complex is 0.28 eV above the VBM. A similar value is found in ref. 22. We further find that the (-1, -2) and (-2, -3) transitions occur at 1.2 eV and 3.3 eV, respectively. The origin of these transition levels can be understood by analyzing the electronic structure of the complex. An inspection of the occupancy of bands for spin-up and spin-down states in the  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}$  complex shows that there are 3 electrons more with spin up than with spin down at the  $\Gamma$  point. The missing electrons stem from the  $\text{V}_{\text{Zn}}$  (2) and  $\text{N}_{\text{O}}$  (1) defects. To characterize the three empty spin-down states we consider the projected density of states at the  $\Gamma$  point. Fig. 3(a) presents the density of states of pure ZnO, for reference, with the peak at around 3.4 eV corresponding to the conduction band minimum. Fig. 3(b) clearly shows



**Fig. 3** Density of states at the  $\Gamma$  point: (a) total for the pure ZnO, (b) partial for the spin-up and spin-down states of the  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}$  complex and (c) partial for the spin-up and spin-down states of the  $\text{V}_{\text{Zn}}\text{-N}_{\text{O}}\text{-H}$  complex. VBMs are aligned at 0 eV.

three empty localized spin-down states, of mainly Op and Np character (indicated by arrows in the figure).<sup>23</sup> These empty states give rise to optical transition levels, but at the same time are at the origin of the (thermodynamic) transition levels in Fig. 2 (the latter are shifted with respect to the former because of relaxation of atomic positions). Turning to  $V_{\text{Zn}}\text{-N}_\text{O}\text{-H}$ , we plot its projected density of states in Fig. 3(c). It shows that adding H to  $V_{\text{Zn}}\text{-N}_\text{O}$  results in filling the lowest hole by the H electron, leaving the two higher spin-down states empty. These states are reconstructed as two nearly degenerate states in the gap, indicated by arrows in Fig. 3(c). This explains the deep acceptor nature of  $V_{\text{Zn}}\text{-N}_\text{O}\text{-H}$ .

It is also necessary to consider the formation energy of the above complexes in relation to the formation energy of other defects.<sup>24</sup> For instance, although  $V_{\text{Zn}}\text{-N}_\text{O}$  is a relatively shallow acceptor, its formation energy is high compared to the formation energy of compensating defects like the O vacancy, H interstitial or H substitutional. These have rather low formation energies and are likely to form.<sup>25–27</sup> The formation energies of these defects are also shown in Fig. 2, indeed indicating that they behave as hole “killer” defects. This result is in contrast to the claim by Liu and co-workers that the  $V_{\text{Zn}}\text{-N}_\text{O}$  complex is free from compensation due to spontaneous intrinsic donors.<sup>5</sup> They attributed the origin of the p-type conductivity in the ZnO p–n junction to the  $V_{\text{Zn}}\text{-N}_\text{O}$  complex achieved by Tsukazaki *et al.*<sup>2</sup> This might well be the case, but the reported p-type behavior is unstable, as later discussed by the same group.<sup>28</sup> In this perspective, it is of interest to note that the formation energy of the  $V_{\text{Zn}}\text{-N}_\text{O}\text{-H}$  complex is about 0.57 eV lower than the sum of the formation energies of the  $V_{\text{Zn}}\text{-N}_\text{O}$  complex and the  $\text{H}_\text{i}$  defect separately. This shows that adding H to the  $V_{\text{Zn}}\text{-N}_\text{O}$  complex results in a complex with lower formation energy, tending to stabilize it and making it easier to form. This is a step in the right direction, but unfortunately at the same time the acceptor level becomes deep, as shown above.

## 4 Conclusions

To summarize, we have studied using first principles calculations the complex  $V_{\text{Zn}}\text{-N}_\text{O}\text{-H}$  in ZnO using DFT with the HSE06 functional. We first show that this complex will indeed tend to form, as its formation energy is lower than the sum of the formation energies of the isolated dopants. We further show that the presence of H is important, in that it results in a complex of lower formation energy compared to the H-free complex,  $V_{\text{Zn}}\text{-N}_\text{O}$ . However, having H in the system adds one more electron to the complex and fills an empty state which turns it from a shallow acceptor into a deep acceptor. Moreover, the formation energy values depend highly on the chemical potentials of the species and even under the optimal experimental conditions that we considered in our calculations, the obtained formation energies are still high with respect to the formation energy of native compensating donor defects. Thus, the stabilizing effect of H is thus not strong enough. Our results indicate that the  $V_{\text{Zn}}\text{-N}_\text{O}\text{-H}$  complex itself cannot be the cause

of the significant p-type behavior observed in experiment. Instead, the annealing process could lead to the formation of the shallow acceptor  $V_{\text{Zn}}\text{-N}_\text{O}$  complex, resulting in the observed conductivity. In any case, because of their high formation energy compared to that of compensating defects, it is very unlikely that these complexes can act as a lasting source of any conductivity in ZnO under standard conditions.

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- 24 We also compared the stability of the  $V_{\text{Zn}}\text{-N}_{\text{O}}$  and  $V_{\text{Zn}}\text{-N}_{\text{O}}\text{-H}$  complexes with respect to each other and to the individual defects (representing noninteracting defects, far from each other). The formation energy of the  $V_{\text{Zn}}\text{-N}_{\text{O}}\text{-H}$  complex (in the neutral charge state) is about 2.27 eV lower than the sum of the formation energies of the  $V_{\text{Zn}}$ ,  $\text{N}_{\text{O}}$ , and  $\text{H}_{\text{i}}$  defects separately at  $E_{\text{F}} = 0$  (for  $V_{\text{Zn}}$  and  $\text{N}_{\text{O}}$  the formation energy is lowest in the neutral charge state Liu 2012, while for  $\text{H}_{\text{i}}$  it is lowest in the positive charge state<sup>26</sup>). Similarly, the formation energy of the  $V_{\text{Zn}}\text{-N}_{\text{O}}$  complex is about 1.70 eV lower than the sum of the formation energies of the individual defects at  $E_{\text{F}} = 0$ .
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