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# Hydrogen multicenter bond mediated magnetism in Co doped ZnO

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## Abstract

Magnetism in Co doped ZnO (ZnO:Co) is strongly affected by the presence of the ZnO's extrinsic impurities, such as unintentional hydrogen dopants. Our *ab initio* investigation reveals that in ZnO:Co the formation of substitutional H ( $H_O$ ) with four-fold hydrogenic bonds is favored over interstitial hydrogen ( $H_I$ ) by 0.4 eV. It is found that  $H_O$  is trapped by Co ions to form highly stable Co– $H_O$ –Co complexes.  $H_O$  also mediates a strong short-ranged ferromagnetic interaction between Co dopants via short-range exchange interaction which induces room temperature ferromagnetism.

(Some figures in this article are in colour only in the electronic version)

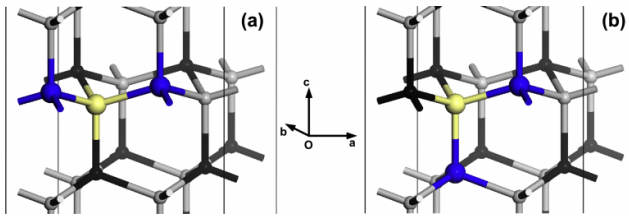
## 1. Introduction

As unique spintronic materials with potential technological applications, ZnO-based diluted magnetic semiconductors (DMSs) have recently attracted enormous scientific interest [1, 2]. In particular, due to its high Curie temperature, the ZnO:Co system is promising for applications requiring ferromagnetism above room temperature [3, 4]. Despite many works focusing on the ZnO:Co DMS, the origin of its ferromagnetism is not well understood yet and is a matter of heated debate [3, 4]. Originally Dietl *et al* proposed a carrier mediated mechanism based on the Zener model of p-type DMSs. [5]. This was followed by a series of predictions based on density functional theory (DFT) of the possibility of achieving high temperature DMSs in p-type ZnO [6]. However, the experimental difficulties in fabricating p-type ZnO shifted the theoretical and experimental trend to focus on n-type ZnO DMSs in which electrons instead of holes mediate the magnetic interactions. Most recently a work by Walsh *et al* predicted the stabilization of a ferromagnetic phase in ZnO:Co by doping 0.5 electrons per Co [7]. However, no ferromagnetic trace was observed in highly conductive ZnO:Co samples [8]. Considering the lack of an unambiguous correlation between carrier concentration and magnetism in experimental findings, structural defects were proposed to be behind the presence or absence of magnetism [9]. Among the extrinsic impurities of ZnO, unintentionally doped hydrogen is believed to occur in high concentrations depending on the growth conditions.

Theoretical investigations suggest that interstitial hydrogen ( $H_I$ ) enhances the magnetic properties of ZnO:Co by opening a channel for a spin–spin interaction among Co ions [10]. Furthermore, hydrogen in ZnO, besides the interstitial site where it forms a hydrogen bond with O, can also substitute for oxygen ( $H_O$ ) and form multicenter bonds where a hydrogen ion bonds equally to all the surrounding Zn ions, becoming four-fold coordinated [11].  $H_O$  is the dominant form of hydrogen impurity in ZnO samples grown in oxygen-poor conditions. Furthermore, high concentration Co can be incorporated in the ZnO host lattice in oxygen-poor conditions as well [12]. This motivated the authors to systematically investigate the role of  $H_O$  on magnetism in ZnO:Co within the framework of DFT.

## 2. Method

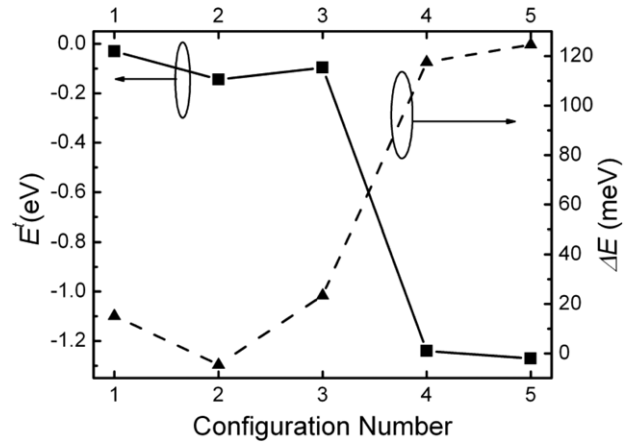
Total energy density functional calculations were performed using the plane-wave pseudopotential approach as implanted in the CASTEP code [13]. The energy cut-off and  $k$ -point mesh were set to be 800 eV and  $3 \times 3 \times 1$ , respectively. The density-mixing scheme was applied for electronic minimization during which the formal spin numbers of all ions were fixed to their formal values. Convergence tests were performed by increasing the  $k$ -point mesh to  $4 \times 4 \times 2$  and the energy cut-off to 900 eV. It was found that the total energy differed only by 0.025 meV/atom. Thus the results are well converged. For the exchange correlation functional, both the local density



**Figure 1.** (a) The Co–H<sub>0</sub>–Co complex within the *ab* plane in Configuration 4. (b) The Co–H<sub>0</sub>–Co complex along the *c* direction in Configuration 5. Small black, big blue and big yellow balls stand for Zn, Co and H<sub>0</sub>, respectively.

approximation (LDA) and generalized gradient approximation (GGA) based on the Perdew and Wang formalism [14, 15] were employed on pure ZnO. Both functionals gave very good lattice constants. Pure ZnO has a wurtzite structure with  $a = 3.253$  and  $c = 5.205$  Å [16]. The LDA results underestimated both quantities by 2% and 1.5%, and the GGA overestimated them by 0.9% and 1.5%, respectively. It should be noted that this minor expansion (contraction) in lattice constants is attributed to the nature of GGA (LDA) in softening (hardening) chemical bonds [17]. With smaller mismatch the GGA was used in the rest of calculations. Regarding the lattice constants, in order to avoid the artificial hydrostatic stress in doped structures lattice parameters were fixed to the calculated values and all internal atomic coordinates were relaxed until the Cartesian force components were smaller than  $0.05$  eV Å<sup>-1</sup>. To simulate doped structures, a 32-atom  $2a \times 2a \times 2c$  ZnO supercell was adopted for calculations with two Co ions substituting Zn sites and one H ion substituting an O site.

In order to systematically investigate the distribution pattern of Co ions in the presence of H<sub>0</sub> and its effect on magnetism, two Co ions and one H<sub>0</sub> substituted the original lattice sites of Zn and O, respectively. In total, five different typical configurations were considered in which the dopant ions were arranged to constitute a variety of complexes. The total energy of each configuration was calculated once for ferromagnetic spin alignment ( $E_{\text{Conf.No.}}^{\text{FM}}$ ) and once again for antiferromagnetic spin alignment ( $E_{\text{Conf.No.}}^{\text{AFM}}$ ) of Co ions being in the high-spin state. The lower one of them is referred to as the total energy ( $E_{\text{Conf.No.}}^{\text{t}}$ ) of every particular configuration.  $\Delta E_{\text{Conf.No.}}$  is defined to be  $(E_{\text{Conf.No.}}^{\text{AFM}} - E_{\text{Conf.No.}}^{\text{FM}})/2$  as an indicator of ferromagnetic phase stabilization. In Configuration 1 Co ions are located at the greatest possible distance in the supercell with a separation of 6.269 Å while the H<sub>0</sub> is situated far from both Co ions with a separation of 3.300 and 2.863 Å from each Co ion, representing a scattered pattern for the distribution of defects where none is in nearest neighbor configuration. In Configuration 2 Co ions form a Co–O–Co complex within the *ab* plane while H<sub>0</sub> is separated by 6.001 and 5.028 Å from Co ions being located at the maximum distance possible from Co ions. In Configuration 3 Co ions form a Co–O–Co complex along the *c* direction with H<sub>0</sub> being separated by 3.890 and 5.999 Å from Co ions. In Configurations 4 and 5 Co ions and H<sub>0</sub> form a Co–H<sub>0</sub>–Co complex within the *ab* plane and along the *c* direction, as shown in figures 1(a) and (b), respectively.



**Figure 2.** Total energy,  $E_{\text{Conf.No.}}^{\text{t}}$ , and difference in total energy between AFM and FM,  $\Delta E_{\text{Conf.No.}}$ , versus configuration number. For all configurations total energies are presented with respect to an arbitrarily chosen reference which places the total energy of the least stable configuration at zero.

In these two configurations the distance between H<sub>0</sub> and Co ions is the length of the Co–H<sub>0</sub> bonds. The calculated Co–H<sub>0</sub> bond in Configuration 4 is 1.738 Å, which is 13% shorter than the original Zn–O bond (1.992 Å). In Configuration 5 the length of the Co–H<sub>0</sub> bond along the *c* direction is 1.684 Å, 17% shorter than the original Zn–O bond along the *c* direction which is 2.021 Å. The shrinkage in Co–H<sub>0</sub> bonds is attributed to the smaller radius of the divalent high-spin Co in tetrahedral coordination compared to the divalent Zn rather than the radius difference between H<sub>0</sub> and O. In Configurations 1–3, the Zn–H<sub>0</sub> bond length was calculated to be 2.037 Å within the *ab* plane and 2.048 Å along the *c* direction, where both bonds slightly expand by ~2% while similar shrinkage occurs in Co–O bonds. This indicates that the expansion strain caused by the incorporation of H<sub>0</sub> ions into substitutional O sites is vanishingly small and unlike H<sub>1</sub> it does not lead to remarkable lattice relaxations [18].

### 3. Results and discussion

The calculated  $E_{\text{Conf.No.}}^{\text{t}}$  and  $\Delta E_{\text{Conf.No.}}$  are presented in figure 2. It can be clearly observed that Configuration 1 scores the highest total energy followed by Configurations 3 and 2 with  $E_3^{\text{t}}$  and  $E_2^{\text{t}}$  of  $-0.1$  and  $-0.14$  eV, respectively. This is an indication of a slight stabilization gained by the aggregation of Co ions into Co–O–Co complexes compared to the scattered pattern. Configurations 4 and 5 are much further stabilized with  $E_4^{\text{t}}$  and  $E_5^{\text{t}}$  of  $-1.23$  and  $-1.27$  eV, respectively, indicating that H<sub>0</sub> is trapped by Co ions to form the highly stable Co–H<sub>0</sub>–Co complexes. Configuration 5 is notably the most stable one in which Co and H<sub>0</sub> ions are arranged in a Co–H<sub>0</sub>–Co complex along the *c* direction with the minimum possible separation among dopant ions, while Configuration 1 stands as the highest ground state energy in which Co ions and H<sub>0</sub> are far from each other. This strongly suggests a clustering tendency among Co ions and H<sub>0</sub>. In thermodynamic equilibrium, the concentration of a complex

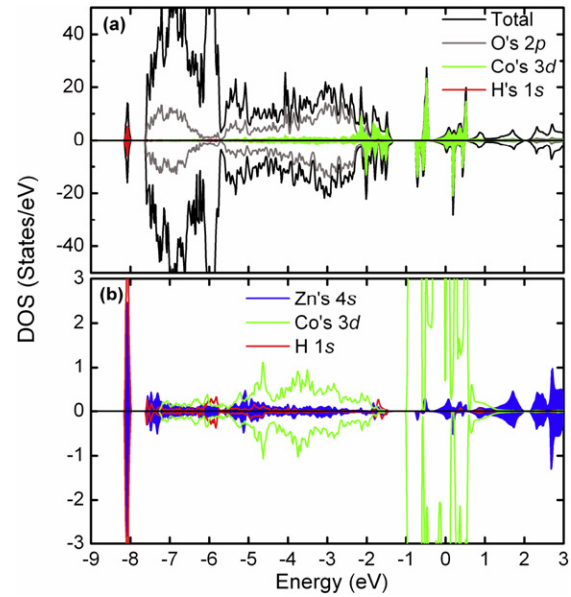
(*c*) is proportional to  $N \exp(-E^f/k_B T)$  in which  $N$  is the number of realizations of the complex in the supercell,  $E^f$  is the complex formation energy,  $k_B$  is Boltzmann's constant, and  $T$  is temperature. Since all configurations studied have the same chemical composition and charge states the relative concentration is given by the following expression:

$$\frac{c_x}{c_y} = \frac{N_x}{N_y} \exp\left(-\frac{E_x^f - E_y^f}{k_B T}\right). \quad (1)$$

According to equation (1), the relative concentration of Configurations 5 and 4, the first and second most stable configurations, is compared at room temperature,  $T = 300$  K, as  $c_5/c_4 = 3$ . This trend clearly indicates that Configuration 5 is the dominant complex consisting of two Co ions and one  $H_O$  with the minimum possible separation in the ZnO host lattice, while all other complexes, if present, make up a small portion.

Magnetically in Configuration 1, in which Co ions and  $H_O$  are scattered with the maximum separation between Co ions, the ferromagnetic phase is slightly stabilized as  $\Delta E_1$  equals 15 meV/Co. However, as mentioned above, Co dopants and the  $H_O$  defect are not likely to be in this particular arrangement in thermodynamic equilibrium. By moving to more compact complexes as in Configurations 2 and 3, in which  $H_O$  is not yet in the vicinity of Co ions, slight ferromagnetic phase stabilization occurs as  $\Delta E_2$  and  $\Delta E_3$  are 4 and 23 meV/Co, respectively. Notable ferromagnetic phase stabilization occurs in Configurations 4 and 5, where Co ions and  $H_O$  form Co– $H_O$ –Co complexes as  $\Delta E_4$  and  $\Delta E_5$  are 117 and 125 meV/Co, respectively. The complex in Configuration 5 with minimum formation energy and maximum ferromagnetic phase stability is predicted to dominate the room temperature ferromagnetism in the ZnO:Co system where  $H_O$  is present.

To reveal the cause of the strong magnetic interaction in the ZnO:Co +  $H_O$  system, the total and partial density of states (DOS) of the most stable configuration, i.e. Configuration 5, in the ferromagnetic state were calculated and are presented in figures 3(a) and (b). According to figure 3(a) major hybridizations occur between the Co 3d and the O 2p orbitals, forming bonding  $t^b$  and antibonding  $t^a$  states with nonbonding  $e$  states lying between the two states.  $t^b$  states are extended along the valence band while  $e$  and  $t^a$  states are located within the bandgap. The H 1s states are mainly concentrated in a sharp peak which is located 8 eV below the Fermi level, while the rest of states are extended in a long tail that hybridizes with valence band states as shown in figure 3(b). The position of the H 1s states with respect to the Fermi level in ZnO:Co +  $H_O$  is in good agreement with previous calculations on ZnO: $H_O$  [11], which implies that Co doping does not alter the electronic behavior of H. In figure 3(b) a closer picture of the hybridization of the H 1s states with the Co 3d states in the valence band is presented. As p–d hybridization between the Co 3d and O 2p states does not stabilize ferromagnetic interaction between Co ions [19], the cause of magnetism should be sought in the overlap between the H 1s states and the Co 3d binding states in the valence band. In order to investigate the actual charge distribution among the ions quantitatively, Mulliken population analyses



**Figure 3.** Total and partial density of states (DOS) of the ferromagnetic ZnO:Co +  $H_O$  system in Configuration 5. Total, O 2p, H 1s and Co 3d (shaded) DOS are presented in (a). The Zn 4s (shaded), Co 3d and H 1s neighboring H are presented in (b).

were performed on the same configuration. The localized charge on Zn(O) ions was calculated to be  $+1.6(-1.6)e$  which is in good agreement with the ionic nature of ZnO. The charge on the Zn d orbitals was  $9.98e$  indicating the  $sp^3$  nature of the Zn–O bond with no significant engagement of d electrons in the bonding process. Co ions, on the other hand, show a different behavior. The localized charge on the Co 3d orbitals was  $7.53e$ , which is higher than the nominal number of 3d electrons existing on a free Co(II) ion which is just  $7e$  considering the  $3s^2 3p^6 3d^7$  electronic configuration. The excess charge in the Co d shell can be attributed to charge transfer from neighboring  $H_O$  which has a total charge of only  $0.30e$ . This is consistent with the fact that H in ZnO is positively charged. Therefore the excess charge in the Co d shell results from charge transfer from the H 1s orbital to the Co empty  $t_{2g}$  spin-minority orbitals. This charge transfer stabilizes the ferromagnetic spin alignment of Co ions via hydrogen mediated superexchange interaction, similar to bridge-bond-mediated d–d interaction [10]. However, it also leads to lower magnetization per Co ( $2.35 \mu_B$ ) as a portion of magnetization of Co is compensated by excess charge which is transferred to spin-minority states.

In Configurations 1–3 where no Co– $H_O$  bond exists, the removal of an oxygen atom creates four Zn dangling bonds with a doubly occupied electronic state located in the bandgap of the ZnO:Co system. When H sits at an O vacancy, the  $H_O$  1s orbital strongly interacts with these states and thus forms a fully symmetric state located deep beneath the valence band and an antibonding state that is orthogonal to the fully symmetric one in the conduction band. Out of three electrons (one from hydrogen and two from the four Zn dangling bonds) two occupy the low-energy fully symmetric orbital deep inside the valence band and stabilize the center and

the third electron would occupy the antibonding state in the conduction band. Therefore  $H_O$  acts as a shallow donor in the ZnO:Co system and facilitates the carrier mediated magnetism in configurations 1–3.

Finally the likelihood of the formation of  $H_O$  versus  $H_I$  in ZnO:Co was analyzed. The energy required to replace an O by a  $H_O$  or to introduce  $H_I$  in the ZnO:Co system is given by

$$E^f = E^t(\text{ZnO:Co} + \text{H}) - E^t(\text{ZnO}) - 2\mu_{\text{Co}} + 2\mu_{\text{Zn}} - \mu_{\text{H}} + n\mu_{\text{O}} + E_{\text{F}} \quad (2)$$

in which  $E^t$ ,  $\mu$  and  $E_{\text{F}}$  represent total energy, chemical potential for respective elements and Fermi energy, respectively.  $\mu_{\text{Co}}$  and  $\mu_{\text{Zn}}$  are set to be the calculated energies of metallic Zn and Co per element, while  $\mu_{\text{H}}$  is set to be half of the energy of a  $H_2$  molecule.  $n$  is zero (one) in the case of  $H_I$  ( $H_O$ ). Due to the metal-excess nature of ZnO,  $\mu_{\text{O}}$  was calculated for oxygen-poor environments where  $\mu_{\text{O}} = E^t(\text{O}_2)/2 + \Delta H^f(\text{ZnO})$ , in which  $\Delta H^f(\text{ZnO})$  is the formation enthalpy of ZnO and was calculated to be  $-3.55$  eV. Since both  $H_I$  and  $H_O$  were positively charged, the formation energy is also proportional to the Fermi energy. Additionally  $E^f$  is highly sensitive to the position of the H in the lattice. In order to make a realistic comparison of formation energy, the formation energy of the most stable configurations of the dopants in both ZnO:Co +  $H_I$  [19] and ZnO:Co +  $H_O$  systems were calculated and compared against each other. It was found that the formation energy of  $H_O$ ,  $E^f(H_O)$  was  $1.11 + E_{\text{F}}$  eV while  $E^f(H_I)$  was  $1.51 + E_{\text{F}}$  eV, which indicates that  $H_O$  is more stable by 0.4 eV in ZnO:Co for the entire range of bandgaps. Considering this difference in  $E^f$ ,  $H_O$  is predicted to be the dominant form of hydrogen in ZnO:Co under oxygen-poor conditions.

#### 4. Conclusion

In summary first-principles density functional calculations have demonstrated that the formation energy of  $H_O$  in ZnO:Co is 0.4 eV lower than  $H_I$ .  $H_O$  is trapped by Co ions to form highly stable Co– $H_O$ –Co complexes along the  $c$  direction. In

such complexes  $H_O$  opens a channel for strong ferromagnetic coupling by short-range exchange interaction with Co ions.

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