

## Role of diatomic hydrogen in electronic structure of ZnO

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According to traditional point of view interstitial H in ZnO is a shallow donor. We report that the feature can be inhibited by another interstitial H. Although there is a chemical bonding between the two H atoms, they can not necessarily be considered as a H<sub>2</sub> molecule: one of the H atoms is tightly bonded into the nearest O and forms the O-H complex, the other H atom forms chemical bond with nearest Zn and these bonds are stronger than the H-H bond. The defect molecule can be called as  $H_2^*$  complex and it forms deep energy level in the band gap. At Fermi levels closer to the conduction band minimum, the complex is found to be more stable than the two distant H atoms. We discuss the role of  $H_2^*$  in electronic structure, optical and electrical properties of ZnO. In particular, formation of the  $H_2^*$  complex provides a natural limitation for the *n*-type doping of ZnO by H.

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## 1. Introduction

Hydrogen is one of the commonly used impurities in wide band gap semiconductors.<sup>1-7</sup> Distinct from its amphoteric behaviour in other semiconductors, in ZnO H possesses the unique feature such as always being a shallow donor and enhance electrical conductivity when it is at the interstitial site around O atom<sup>1-3, 8, 9</sup> and at the O vacancy site,<sup>1, 10, 11</sup> being an acceptor when it substitutes Zn site, a passivator of shallow acceptors of Li<sup>12</sup> and N.<sup>13</sup> H is found to exist in hidden form also, which can not be detected by infra-red (IR) spectroscopy and does not give rise to free carriers at room temperature.<sup>14-16</sup> Several other experimental findings are suggested to be caused by the “hidden H”. Some of them are: (i) decrease of the concentration of the O-H complex responsible for shallow donor level and bimolecular character of the decrease,<sup>14, 16</sup> (ii) discrepancy in concentration of H determined by SIMS from that of free electrons measured by Hall method,<sup>17</sup> a flat region in the dependence of concentration of free electrons on pressure of the H<sub>2</sub> gas.<sup>17</sup> The reason why electron concentration in the near-surface regions of the H plasma treated thin films of and crystalline ZnO<sup>18</sup> is larger than that in the bulk crystalline ZnO is not clear. Although it was shown recently that H diffuses from ZnO at temperatures  $\geq 600$  °C,<sup>19</sup> the  $I_4$  line exits at the elevated temperatures and the result has been ascribed to thermally stable H or H trapped at secondary defect.<sup>7</sup>

It should be noted that H<sub>2</sub> molecule are suggested to be the candidate for the “hidden H”.<sup>15, 16</sup> However, in IR spectroscopy, no line near 4000 cm<sup>-1</sup> corresponding to the H<sub>2</sub> was observed.<sup>15, 20</sup> Furthermore, formation energy of both  $H_2^*$  complex<sup>21</sup> and H<sub>2</sub><sup>3</sup> in ZnO is shown to be large and therefore, to be unstable. The diatomic H complexes

have been studied before in other semiconductors also, such as, e.g., Si,<sup>22-25</sup> GaP,<sup>26</sup> and GaAs<sup>27</sup> and it is found to be unstable in the latter two compounds. Incorporation of N into GaAs and GaP is predicted to increase stability of  $H_2^*$  and  $H_2$ .<sup>26, 27</sup> Experimental and theoretical results suggest (see, e.g., Refs.<sup>23, 25, 28, 29</sup> and references therein) that in hydrogenated amorphous (*a*-Si:H) and crystalline Si hydrogen predominantly bonds to the Si network in diatomic pairs. The  $H_2^*$  configuration consisting of a bond centered H and a H located at a adjacent antibonding site is found to be low in energy and play important role in electronic structure of Si by forming the Si{111} platelet structures and be responsible for metastability of *a*-Si:H. It should be noted that at Fermi levels close to conduction band (CB) minimum the diatomic H complex in ZnO can be even more stable than positively charged H.<sup>3, 21</sup> For this particular case role of the H complex in electronic structure, electrical and optical properties of ZnO was not studied. In this paper we explore this problem. We found that: (i) although there is a chemical bonding between two H atoms, they can not necessarily be considered as a  $H_2$  molecule, because the Zn-H and O-H chemical bonding is stronger than the H-H bond, (ii) the defect molecule can be called as  $H_2^*$  complex, which can form a deep trap level, (iii) at Fermi levels closer to CB minimum formation of the  $H_2^*$  complex is energetically more preferable than two distant H atoms, and (iv) in strained part of ZnO, e.g. around voids, grain boundaries, the distant H is energetically more preferable than  $H_2^*$ .

## 2. Computational details

The computations have been performed using the Vienna *ab initio* simulation package (VASP).<sup>30, 31</sup> We use the generalized-gradient approximation (GGA) following

the Perdew-Bueke-Ernzerhof scheme (PBE),<sup>32</sup> for the exchange-correlation functional and with the multiorbital mean-field Hubbard potential GGA+ $U$ . Non-norm-conserving pseudopotentials generated in accordance to the projector-augmented-wave (PAW) method<sup>33, 34</sup> have been used. It allowed us to construct orthonormalized all-electron-like wave functions for the Zn- $3d$ , - $4s$ , O - $2s$  and - $2p$ , H- $1s$  valence electrons.

The lattice was fully relaxed using the conjugate gradient method. Plane-wave cut-off of 500 eV is employed to ensure the convergence in our calculations which is found to be sufficient to reproduce ground state and high pressure structural properties. The convergence was achieved when the forces acting on the atoms were smaller than 10 meV  $\text{\AA}^{-1}$  and the total energy difference between two consecutive iterations were  $<10^{-6}$  eV.

It is well known that in the calculations by density/functional theory (DFT) within GGA the Zn  $3d$  bands are located inappropriately close to the topmost valence band (VB) of ZnO, hybridizing with the O  $2p$  band, falsifying the band dispersion, reducing the band gap, modifying the spin-splitting and crystal-field energies, changing the order of states at the topmost valence band. The problem has partially been solved<sup>35-37</sup> by using the GGA + $U$ ,<sup>33, 34</sup> which requires explicit values of the parameters  $U$  and  $J$  are required as input. Analysis of literature (see, e.g. Refs.<sup>35-37</sup>) shows that the calculated band parameters can be more within reasonable limit for  $U=6$  eV and  $J=1$  eV.

The changes of energy levels of the  $H_2^*$  in the band gap  $E_t^{GGA}$  and  $E_t^{GGA+U}$  coming out from GGA and GGA+ $U$  reflect their character relative to valence band (VB) and conduction band (CB). Therefore, to estimate correct value of energy level  $E_t$  of  $H_2^*$  we use the following extrapolation

$$E_t = E_t^{GGA+U} + \frac{E_t^{GGA+U} - E_t^{GGA}}{E_g^{GGA+U} - E_g^{GGA}} \times (E_g^{Expt} - E_g^{GGA+U}). \quad (1)$$

Here  $E_g^{GGA}$  and  $E_g^{GGA+U}$  are the band gaps obtained from calculations within GGA and GGA+U, whereas  $E_g^{Expt}$  is the experimental band gap of ZnO. The Eq. (1) has previously been used by many authors (see, e.g., Ref. <sup>38</sup>) for calculation the defect transition level. The computations have been performed for  $2 \times 2 \times 2$ ,  $3 \times 3 \times 2$  (Fig. 1),  $3 \times 3 \times 3$ , and  $4 \times 3 \times 2$  supercells, which correspond to H concentrations of  $4.9 \times 10^{21}$ ,  $2.2 \times 10^{21}$ ,  $1.5 \times 10^{21}$ , and  $1.7 \times 10^{21} \text{ cm}^{-3}$ , respectively.

Formation energy of  $H_2^*$  in ZnO has been calculated as<sup>38</sup>

$$E^f(D^q) = E_{tot}(D^q) - E_{tot}(ZnO, bulk) - n_H \mu_H + qE_F. \quad (2)$$

Here  $E_{tot}(D^q)$  and  $E_{tot}(ZnO, bulk)$  are the total energy of the lattice with an impurity  $D$  in charge state  $q$  and of the perfect ZnO, respectively.  $E_F$  is the Fermi energy.  $\mu_H$  is the chemical potential of H and  $n_H$  is the number of H atoms in the supercell. Dissociation energy for  $H_2^*$  has been calculated as difference of  $E_{tot}(D^q)$  for ZnO with  $H_2^*$  from that with two distant H atoms.

### 3. Results

We have performed structural study for the following three models with two H atoms (H1 and H2) in a unit cell. One of them, to be called hereafter as two distant H, H1 and H2, have been located at two different Zn-O bonds aligned with the  $c$ -axis and located each from other at a distance of  $9.98 \text{ \AA}$ . Electronic studies show that the two

distant H atoms form shallow donor level in the band gap, in agreement with the theoretically and experimentally established result (see, e.g., Ref. <sup>39</sup>).

The other model is similar to  $\beta$ - $H_2^*$  modification of diatomic H in GaP.<sup>26</sup> In the model H1 is located at Zn-O bond centre whereas H2 is at antibonding site near to Zn (Fig. 1 (a)). Upon relaxation, H1 has been shifted closer to nearest O, thus forming O-H complex and H2 has been moved toward nearest Zn atoms (Fig. 1 (b)). Total energy for  $\beta$ - $H_2^*$  is smaller than that for two distant H to  $\sim 0.06$  eV and is also donor.

In the third model, to be called hereafter as  $H_2^*$  complex, both H1 and H2 of the unrelaxed lattice are located in the close vicinity of the same O atom (Figs. 1 (c) and (e)). Upon relaxation H1 has been moved to the Zn-O bond along  $c$ -axis, whereas H2 has been shifted to antibonding site closer to H1 (Figs. 1 (d) and (f)). Total energy of the system is smaller than that with two distant H atoms to  $\sim 0.5$  eV. In the configuration H1 and H2 remind a  $H_2$  molecule. However, as we show later it can be called a  $H_2^*$  complex rather than  $H_2$  molecule. The nearby Zn and O atoms have been shifted drastically out of their position in the equilibrium lattice. The displacements of the O, Zn1, and Zn2 atoms from their position corresponding to ideal lattice as well as bond lengths for Zn1-H2, H2-Zn2, H1-O, and H1-H2 have been presented in Table I. Analysis of Table I shows that the H1-H2 bond calculated in the present work is larger than  $0.798 \text{ \AA}$ ,<sup>3</sup>  $0.770 \text{ \AA}$ ,<sup>20</sup> and  $0.782 \text{ \AA}$  for the free  $H_2$  molecule. Also, in all the supercells considered the Zn1-H2, O-H1, and H1-H2 bond lengths are almost the same. As we demonstrate later, the calculated energy band of the diatomic H complex is also almost the same for all the supercells considered. This indicates that the Zn1-H2, O-H1, and H1-H2 bonds can be responsible for the H diatomic complex bands.

To know influence of the  $H_2^*$  complex on electronic structure of ZnO we have studied total density of states (DOS) (Fig. 2). It is seen that a deep well-localized band has been formed. From computations within GGA and GGA+ $U$  it is found using the Eq. (1) that the band is located at 0.75 eV above the VB of ZnO. Width of the band is 0.70 eV and it is completed by electrons. Analysis of orbital and site projected density of states shows that H1, H2, and the O atom located near to H1 are responsible for the deep trap derived band. The above result can be consistent by several experimental findings. One of them is the result related to H related deep trap<sup>39</sup> located at 0.90 eV found from deep level transient spectroscopy (DLTS) measurements and wide defect green band located in the energy range from 2.0-2.8 eV determined from micro-cathodoluminescence studies. The other one is the reduction of the intensity of near gap emission by more than three orders of magnitude in room temperature cathodoluminescence of ZnO even for a dose of  $10^{15} \text{ cm}^{-2} \text{ } ^1\text{H}^+$  ions.<sup>40</sup> The increase of electrical resistance by about 7 orders of magnitude experimentally observed in Ref. <sup>41,42</sup>, which has been explained by generation of ion irradiation-induced traps. The  $H_2^*$  complex can be a candidate for the traps.

Although the spatially well separated H atoms are shallow donors, those located very close to each other in pure stoichiometric ZnO, can passivate each other and form deep energy levels in the band gap. So, such a  $H_2^*$  complex can, probably, be one of the candidates for the “hidden H”. It can also explain the reason of the experimental results as to: (i) why the concentration of H atoms determined from secondary ion mass spectroscopy (SIMS) is larger than that of free electrons found by Hall measurements<sup>17</sup> and (ii) why the concentration of the O-H shallow donor complexes decreases with increasing the time.<sup>16</sup>

To clarify whether H1 and H2 in Fig. 1(d) is a molecule or not we have analyzed charge density and electron localization function (ELF) (Fig. 3 (a) and (b)). It is seen that chemical bonding of ZnO in close vicinity of H1 and H2 has been basically reconstructed. The Zn1-O bond has been broken and the strong H1-O complex has been formed (Fig. 3 (a)), thus, weakened the Zn2-O bond. The H2 atom forms chemical bond with the nearest Zn atom and these bonds are stronger than the H1-H2 bond. Analysis of Fig. 3 (a) shows that both H1 and H2 are negatively charged. ELF analysis (Fig. 3 (b)) confirms this point and is in agreement with orbital and site projected DOS analysis. In Fig. 3 (a) and (b) one can see Zn1-H2-Zn2, H1-H2, Zn2-O, and H2-O bonds. In the  $3 \times 3 \times 2$  supercell only one Zn1-H2 bond has been formed. These analyses show that the defect molecule in Figs. 1 (d) and (f) can be called as  $H_2^*$  complex rather than  $H_2$  molecule. For quantitative analysis we have calculated the charge around the atoms incorporated into the  $H_2^*$  complex. We found that the charge is equal to +1.16 for Zn1, +1.20 for Zn2, -0.57 for H1, -0.68 for H2 as well as -0.23 for O atoms.

For analysis of stability, we have studied dependence of total energy  $E_{tot}$  on volume  $V$  (Fig. 4 (a)) for ZnO with  $H_2^*$  complex and two distant H atoms. It is seen that the former is more stable than the latter. Consequently, the  $H_2^*$  complex is the energetically preferable state for H atoms. This result explains the reason of experimental findings of Ref. <sup>16</sup> regarding why concentration of the O-H complex decreases according to bimolecular model.

Analysis of Fig. 4 (a) shows that at large volumes, the two dependencies  $E_{tot}(V)$  intersect each other. It indicates that when ZnO is well strained, the H-related complex can become less stable than the distant ones. Consequently, one can expect that the  $H_2^*$



complex can exist only in that part of ZnO, which is not strained well. Around voids, grain boundaries, dislocations, etc., which can be the source of the strained ZnO with elongated Zn-O bonds, formation of the  $H_2^*$  complex is less probably. In such places for H the preferable configuration is existence separately each from other. This result explains the reason of the experimentally established findings of Refs. <sup>39, 40</sup> as to why concentration of electrons in the near-surface regions of the H plasma treated n-ZnO crystals and thin films is considerable larger than that in the bulk. Furthermore, concentration of electrons in the surface region of H plasma treated good quality ZnO is found<sup>40</sup> to be in one-to-one correspondence with the H concentration determined from SIMS. However, in the bulk ZnO, H concentration found from SIMS is much larger than free electron concentration found from Hall measurements.

Figure 4(b) displays formation energy calculated by Eq. (2) for  $H_2^*$  complex and single H. It is seen that at high doping levels by H corresponding to location of Fermi level considerable close to CB minimum,  $H_2^*$  becomes more stable than positively charged single H. This result is in agreement with that of Refs. <sup>3, 20, 21</sup>.

Figure 4 (c) demonstrates dissociation energy  $\Delta E_d$  calculated as the difference of total energies for the unit cell with the H-related complex and separated from each other H as a function of the H-H  $L_{H-H}$  distance. It is seen that absolute value of  $\Delta E_d$  decreases with increasing  $L_{H-H}$ . However, at small H-H distances  $\sim 1.2 \text{ \AA}$ ,  $\Delta E_d \approx 0.92 \text{ eV}$ . This result is in agreement with that of Refs. <sup>43, 44</sup>, which reported about  $\sim 1.0 \text{ eV}$  diffusion activation energy of H derived from effusion data. Furthermore, an increase in electrical conductivity of ZnO has been observed<sup>45, 46</sup> at temperatures  $>200 \text{ }^\circ\text{C}$  due to indiffusion of H with activation energy  $0.91 \text{ eV}$ <sup>46</sup> and  $1.12 \text{ eV}$ .<sup>45</sup> The large value of the binding energy

indicates that annealing of ZnO even at  $\sim 600$  °C can be insufficient to remove H completely. Hence, the  $H_2^*$  complex can be one of the candidates, which is responsible for reduction of the intensity of near-gap photoluminescence after 700 °C anneals. Such complex previously has been ascribed to the H implantation-induced recombination centres.<sup>40</sup> The  $I_4$  line of the bound-exciton luminescence, which has been reduced at  $> 600$  °C,<sup>47</sup> can be attributed to stable H complex, which can be the  $H_2^*$ .

Since single H atoms are mobile at moderate temperatures, they can easily form the quite stable  $H_2^*$  complexes with large dissociation energy. As a result surface blistering in ZnO can require larger fluencies of H than those in Si. This suggestion is consistent with recent experimental finding of the hydrogen-implantation-induced exfoliation of ZnO at  $\geq 2.8 \times 10^{17} \text{ cm}^{-2}$ .<sup>48</sup>

The above results related to inhibition of shallow donor feature of the interstitial H by another interstitial H in ZnO are similar to those well known as passivation of donors by H in Si,<sup>49-52</sup> dilute nitrides,<sup>53</sup> etc.

#### 4. Conclusion

In conclusion, we have found that the shallow donor feature of interstitial H can be inhibited by another interstitial nearby H. It is shown that although there is a chemical bonding between two H atoms, they can not necessarily be considered as a  $H_2$  molecule, because the Zn-H and O-H bonds are stronger than the H-H bond. The defect molecule can be called as  $H_2^*$  complex, which can form a deep trap level in the band gap and be responsible for modulation of electrical and optical properties of ZnO. At Fermi levels closer to CB minimum formation of the  $H_2^*$  complex is energetically more preferable

than two distant H atoms. We show that in strained part of ZnO, e.g. around voids, grain boundaries, the distant H atoms are energetically more preferable than the  $H_2^*$  complex. Formation of the complex can be one of the reasons for the doping limit in ZnO saturated by atomic H and for high H fluencies to cause hydrogen-implantation-induced exfoliation.

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Table I. Calculated displacements  $\Delta$  (in Å) of Zn and O atoms located in close vicinity of the diatomic H complex as well as bond lengths  $d$  (in Å) for Zn1-H2, Zn2-H2, O-H1, and H1-H2.

	O	$\Delta_{\text{Zn1}}$	$\Delta_{\text{Zn2}}$	$d_{\text{Zn1-H2}}$	$d_{\text{Zn2-H2}}$	$d_{\text{O-H1}}$	$d_{\text{H1-H2}}$
2×2×2	0.70	0.47	0.19	1.625	1.939	1.009	1.280
3×3×2	0.58	0.52	0.22	1.652	2.674	1.029	1.258
4×3×2	0.49	0.49	0.22	1.675	2.727	1.028	1.271
3×3×3	0.62	0.45	0.11	1.645	2.240	1.012	1.301



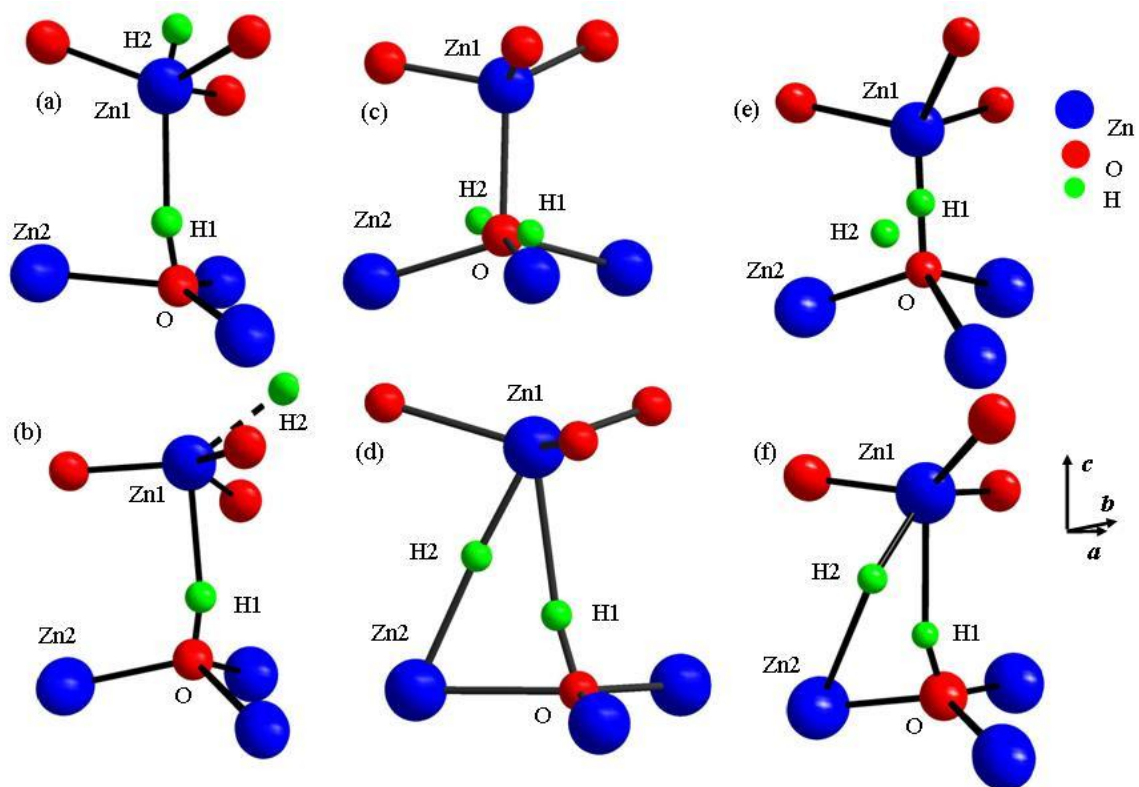


Fig. 1 Schematic presentation of (a), (c), (e) unrelaxed and (b), (d), (f) relaxed lattices of ZnO with two H atoms for (a)-(d)  $2 \times 2 \times 2$  and (e), (f)  $3 \times 3 \times 2$  supercells.

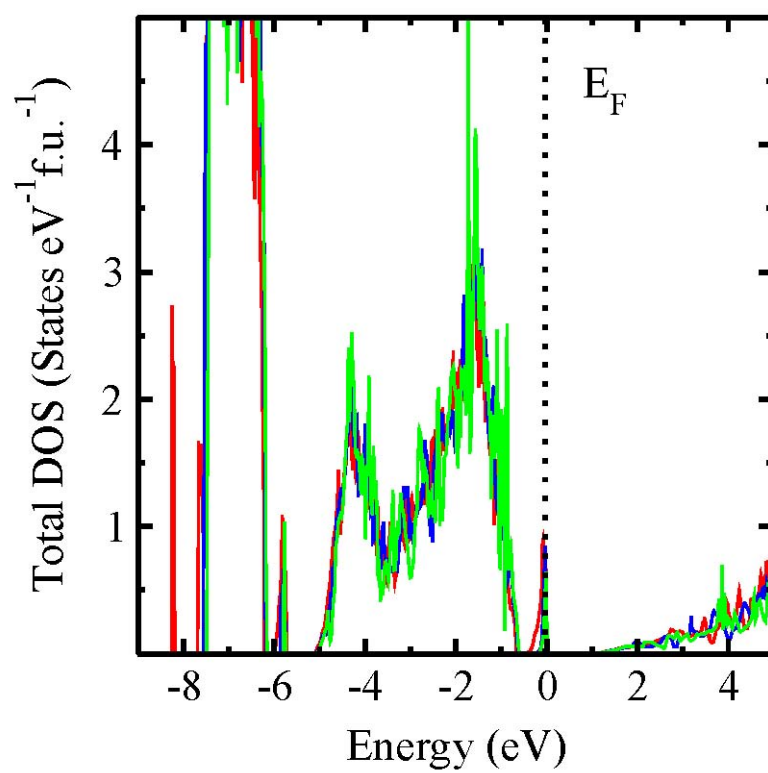


Fig. 2. Total DOS for optimized ZnO unit cells with two H atoms located closely to each other for the 2×2×2 (red color), 3×3×2 (blue color), and 3×3×3 (green color) supercells.

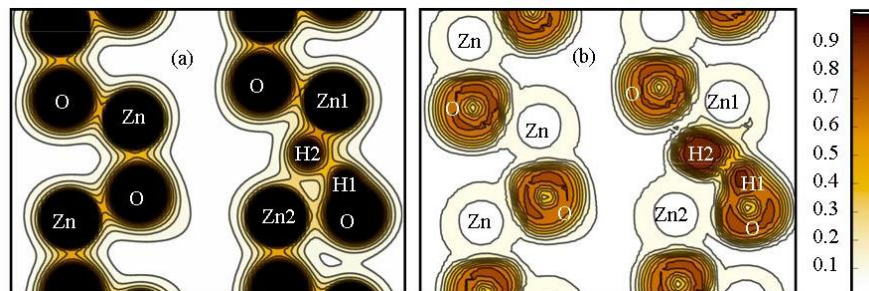


Fig. 3. (a) Charge density and (b) ELF for  $2 \times 2 \times 2$  supercell of ZnO with two H atoms located closely to each other.

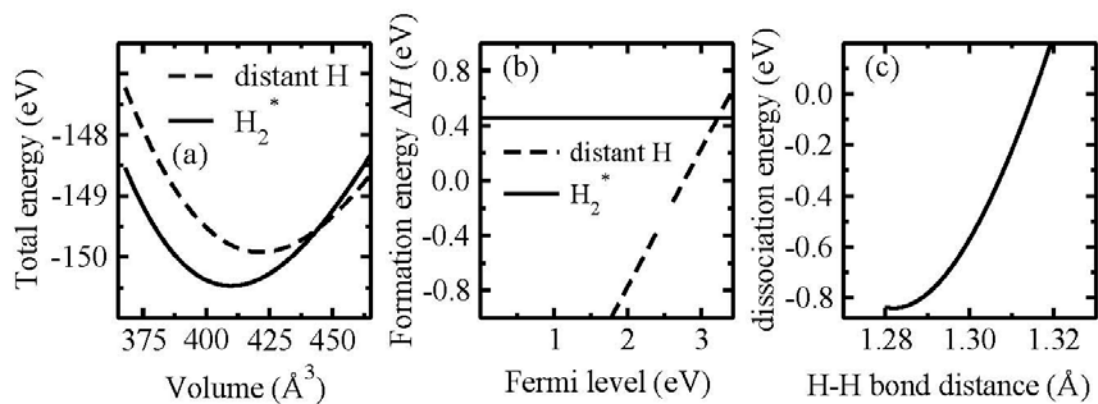


Fig. 4. (a) Dependence of total energy on volume for two types of unit cells of ZnO with H-related complex and two spatially well separated H atoms. (b) Formation energies of  $H_2^*$ -complex and single H in ZnO as a function of Fermi level. (c) Dependence of dissociation energy of the  $H_2^*$ -complex on H-H bond distance.