Resolving hydrogen binding sites by pressure—A first-principles prediction for ZnO

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The binding sites and vibrational frequencies ω of H in ZnO are studied by first-principles total-energy calculations. In the past, different experiments have observed different primary H vibrational modes, making the comparison with theory, and hence the identification of the most favorable H site, difficult. Here, we show that by applying a hydrostatic pressure, one should be able to make an unambiguous distinction, in particular, between the bond center sites and antibonding sites. This is because ω should *increase* with pressure for the former but *decrease* for the latter with the magnitude of calculated slopes about 4 cm^{-1}/GPa, which should be large enough to measure. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1900935]

Recently, ZnO has attracted a lot of attention due to its potential for blue light optoelectronics. If reasonably good *p*-type conductivity can be achieved, ZnO could eventually emerge as a superior alternative to GaN. Hydrogen is one of the most common impurities in semiconductors. It is abundant in air, used in the various growth techniques, and generally has a rather high diffusivity inside semiconductors. Usually, H is an amphoteric impurity, namely, acting either as a donor or an acceptor depending on the Fermi level. However, ZnO is an exception[1] for which isolated interstitial is predicted to be the predominant form of H (Ref. 2), and H acts only as a shallow donor.[1–5] Both first-principles calculations and local vibration measurements indicate that hydrogen prefers to bond with oxygen. However, what is the most favorable geometry is still under intensive debate.[2–8]

In a tetrahedrally coordinated semiconductor, a hydrogen atom can bind to an anion atom predominantly in two ways: in the bond center (BC) site or in the antibonding (AB) site. Due to the low symmetry of the ZnO wurtzite crystal, however, there are two types of orientations ($\parallel$ and $\perp$) for each site above, as shown in Fig. 1(a). First-principles calculations suggested that all four sites have relatively low energies with the global-minimum BC$_\parallel$ site lower than the AB$_O$ sites by less than 0.2 eV. The occupation of the BC sites by an H atom requires large displacements of the host atoms, which may rarely happen due to their relatively large masses with respect to that of H. Therefore, from a kinetic point of view, the H atom might occupy the AB$_O$ sites, instead, despite their slightly higher energies. In cases like this, often, a calculation of the local vibrational modes (LVMs) could differentiate among the structures. Indeed, the calculated H stretch frequencies for the BC and AB$_O$ sites differ by about 300 cm^{-1}. However, the measured *primary* frequencies for interstitial H by different groups also differ by this amount. This makes the assignment difficult because assigning the modes to different sites would contradict energetic argument in favor of kinetic argument. Therefore, it is highly desirable

to have another experimental means to independently confirm the assignment.

In this letter, we predict, based on first-principles calculations, that an experiment on the LVMs (e.g., IR, Raman, or inelastic neutron scattering) under pressure should independently provide the critical test of the H binding sites, differentiating between BC and AB$_O$. The reason is because the O-H bond length for the BC sites decreases under pressure, resulting in an increase in the LVM frequencies. In contrast, the O-H bond length for the AB$_O$ sites increases under pressure, resulting in a decrease in the LVM frequencies. Frequency shifts ($\Delta\omega$), as much as ±35 cm^{-1}, are predicted over a pressure range of 8 GPa, at which phase transition takes place.[9] These shifts should be large enough to be readily detected by experiments.

We used the density-functional theory, within the local-density approximation (LDA), and the Vanderbilt-type ultra-soft pseudopotentials,[10] as implemented in the VASP code.[11] Zinc 3*d* states are treated as valence states. The cutoff energy for the plane-wave expansion is 400 eV, with additional tests carried out at 515 eV. The calculated equilibrium lattice constant of ZnO is only 1.4% shorter than experiment. We used a supercell approach with a Monkhorst-Pack *k*-point mesh
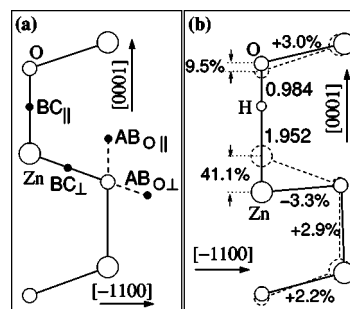

FIG. 1. (a) Schematic representation of the four H sites in ZnO and (b) calculated atomic positions for H$^+$ at the BC$_\parallel$ site, in the (11–20) plane. The dashed circles and dashed lines indicate bulk atomic positions and bonds, respectively. Distances are given in unit of Å and percentage changes are with respect to the bond length of bulk ZnO.

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TABLE I. Calculated formation energy with respect to that of BC∥ and the O-H bond length for H+ in ZnO.

Site	ΔE (eV)			$d_{\text{O-H}}$ (Å)	
	Present	Ref. 2	Ref. 6	Present	Ref. 6
BC∥	0.00	0.00	0.0	0.986	0.990
BC⊥	0.15	−0.02	0.1	0.982	
AB$_{\text{O}∥}$	0.17	0.23	0.1	1.003	1.006
AB$_{\text{O}⊥}$	0.14	0.04	0.1	1.003	

for Brillouin-zone integration ($2 \times 2 \times 2$ for the 36-atom cell and $1 \times 1 \times 1$ for the 96-atom cell). For charged H, we use a jellium background. All atoms in the supercell are allowed to relax in the structural optimizations. A test using the 96-atom cell shows that the energy difference between the two BC configurations in the 36-atom calculations are converged to within 0.01 eV. The smaller supercell is used for extracting the energy difference needed for LVM calculation.

We simulate the stretch frequency by tracing the potential energy curve of the vibration. This has been carried out by calculating the energy as a function of H displacement in both compression (toward O) and extension (away from O) directions. Because (1) H is much lighter than the host atoms and (2) the LVM of the O-H bond (around 3000 cm^{-1}) is much higher than the crystal phonon modes, the displacement of the host atoms during the vibration can thus be neglected. A previous study[12] has explicitly compared the LVMs obtained by freezing host atoms and the LVMs obtained from dynamic matrix approach. A good agreement was found provided that the reduced mass of the anion-H pair is used. Due to the light mass of the H atom, anharmonic contribution ($\tilde{\omega}_{\text{AC}}$) could also be important.[13] We include $\tilde{\omega}_{\text{AC}}$ in our calculation by fitting the calculated energy curve as a function of the H displacement with a fourth-degree polynomial, i.e.,

$$V(x) = \frac{k}{2}x^2 + \alpha x^3 + \beta x^4. \tag{1}$$

To solve the Schrödinger equation with such a potential, we used a perturbation theory[14] to obtain an approximate analytical solution, which reads

$$\tilde{\omega} = \tilde{\omega}_{\text{Har}} + \tilde{\omega}_{\text{AC}} = \sqrt{\frac{k}{\mu}} - 3\frac{\hbar}{\mu}\left(\frac{5\alpha^2}{2k^2} - \frac{\beta}{k}\right). \tag{2}$$

Table I shows the calculated energy for the four H sites and the corresponding O-H bond lengths. It suggests that BC∥ is the most stable H configuration, in agreement with the recent results by Lavrov *et al.*[6] Figure 1(b) shows the atomic geometry of the fully relaxed BC∥. We see that, with respect to ideal ZnO, the Zn atom adjacent to the H atom has relaxed away from the H through the basal plain defined by the three remaining oxygen atoms by as much as 41.1%. As a result, the three remaining Zn-O bonds are compressed by 3.3%. Our calculated O-H bondlengths ($d_{\text{O-H}}$) agree with those in Ref. 6 to within 0.005 Å.

Table II shows the calculated LVM frequencies, $\tilde{\omega}_{\text{Har}}$, $\tilde{\omega}_{\text{AC}}$, and $\tilde{\omega}$, as defined in Eq. (2). The anharmonic contribution $\tilde{\omega}_{\text{AC}}$, for example, −282 cm^{-1} for BC∥ and −352 cm^{-1} for AB$_{\text{O}∥}$, is typically 8–10 % of the corresponding harmonic contribution $\tilde{\omega}_{\text{Har}}$, 3659, and 3370 cm^{-1}, respectively, and the two have opposite signs. It appears that the difference in $\tilde{\omega}$ between the ∥ and ⊥ modes are relatively small, typically 40 cm^{-1}, with the latter being slightly larger. We may expect some errors in our calculated $\tilde{\omega}$'s, as $\tilde{\omega}$ for the free water molecule in Table II is lower than experiment[15] by $\omega_{\text{ER}} = 98$ cm^{-1}. The error is most likely systematic because the calculated O-H bond lengths are consistently longer than experiment by about 2%. We have therefore corrected the errors for all the $\tilde{\omega}$'s by adding ω_{ER} to obtain ω. The same procedure, but with $\omega_{\text{ER}} = 51$ cm^{-1}, is applied to the calculated results in Ref. 6. After the correction, the average values for the BC and AB$_{\text{O}}$ modes are $\omega(\text{BC}) = 3497$ and $\omega(\text{AB}_{\text{O}}) = 3135$ cm^{-1}, respectively. These can be compared with the corrected values in Table II for Ref. 6, $\omega(\text{BC}) = 3551$ and $\omega(\text{AB}_{\text{O}}) = 3259$ cm^{-1}. Thus, theories agree to within $3551 - 3497 = 54$ cm^{-1} for $\omega(\text{BC})$ and $3259 - 3135 = 124$ cm^{-1} for $\omega(\text{AB}_{\text{O}})$. These differences, 54 and 124 cm^{-1}, are significantly smaller than the calculated splitting between the BC and AB$_{\text{O}}$ modes: 362 (present) and 292 cm^{-1} (Ref. 6). It comes to our attention that the measured LVM frequencies in Refs. 6,8 differ by 285 cm^{-1}, suggesting that one of them could be the BC mode whereas the other is the AB$_{\text{O}}$ mode.

More definitive identification of the experimental LVMs may be obtained by pressure measurement. This is possible because the neighboring atoms of the BC and AB$_{\text{O}}$ sites are different, which could result in different responses to external pressure. To simulate the pressure effect, we need the total energy as a function of volume, from which the

TABLE II. Stretch modes for interstitial H+ in ZnO, in units of cm^{-1}. $\tilde{\omega}_{\text{Har}}$, $\tilde{\omega}_{\text{AC}}$, and $\tilde{\omega}$ are described in Eq. (2), whereas the calculated ω's (columns 4 and 5) include the systematic error correction, as described in the text.

Site	Present			Ref. 6 $\omega(\tilde{\omega})$	Measured ω
	$\tilde{\omega}_{\text{Har}}$	$\tilde{\omega}_{\text{AC}}$	$\omega(\tilde{\omega})$		
BC∥	3659	−282	3475 (3377)	3551 (3500)	3611[a]
BC⊥	3706	−285	3519 (3421)		
AB$_{\text{O}∥}$	3370	−352	3116 (3018)	3259 (3208)	3326[b]
AB$_{\text{O}⊥}$	3379	−323	3154 (3056)		
H$_2$O	3815	−257	3657 (3559)	3657 (3606[d])	3657[c]

[a]Reference 6.
[b]Reference 8.
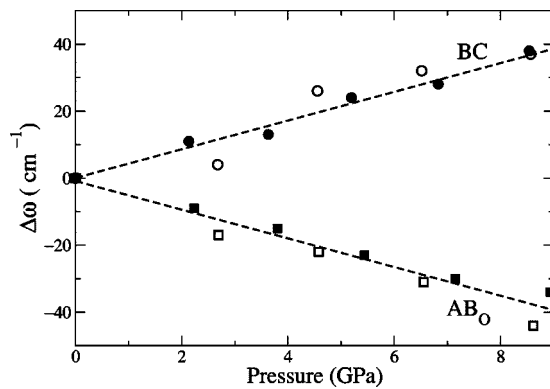[c]Reference 15.
[d]Calculated using FHI98 codes.

FIG. 2. The shifts in the stretch mode frequencies of the O-H bonds for the four H sites in Fig. 1, as a function of the external pressure. Two possible orientations of the O-H bonds in the crystal are coded with solid ($\parallel$) and open ($\perp$) symbols. The lines are least-square fits to the calculated data.

pressure $P(V)$ as a function of V is obtained through $P(V) = -dE(V)/dV$. Next, we need the frequency as a function of volume, $\omega(V)$. From $\omega(V)$ and $P(V)$, we can deduce $\omega(P)$. The above calculation should be straightforward if we use very large supercells. In practice, we use a finite-size 36-atom supercell, which might introduce errors both in $P(V)$ and $\omega(V)$. To minimize the error in $P(V)$, we calculate instead $dE(V)/dV$ using a primitive cell for the reasons that P is an intensive quantity and that in the dilute limit the effect of the defect should diminish. To minimize the error in $\omega(V)$, we did selectively 96-atom cell calculations to adjust the 36-atom cell results. The correction on ω was found to be rather small, whose main role was to eliminate the artificial small splitting between the $\parallel$ and $\perp$ modes due to the specific shape of the 36-atom cell. Figure 2 shows the calculated ω for the four H binding sites, as a function of P. We see clearly the qualitative difference between the LVMs for the BC and AB_O sites: while $\omega(BC)$ increases with pressure, $\omega(AB_O)$ decreases, instead. In spite of that, $\omega(BC)$ and $\omega(AB_O)$ have, fortuitously, a similar magnitude of slope around 4.2 cm^{-1}/GPa.

The distinct pressure dependences in Fig. 2 may be qualitatively understood by the change of the O-H bond length (d_{O-H}) under pressure, namely, a decrease in d_{O-H} would correspond to an increase in ω, as demonstrated in Ref. 13. Here, d_{O-H} for AB_O monotonically increases with P, which explains why ω decreases in Fig. 2, e.g., at $P = 5.4$ GPa, $\Delta d_{O-H} = 0.0013$ Å whereas $\Delta\omega = -23$ cm^{-1} for $AB_{O\parallel}$. On the other hand, d_{O-H} for BC monotonically decreases with P, which explains why ω increases in Fig. 2: at $P = 5.2$ GPa, $\Delta d_{O-H} = -0.0021$ Å whereas $\Delta\omega = +22$ cm^{-1} for BC$_\parallel$. We speculate that the change in d_{O-H} for AB_O under pressure is because of the compression of the neighboring Zn-O bonds. To test this hypothesis, we have calculated an acetylene molecule (H-C-C-H) and found that indeed if we compress the C-C bond by 0.02 Å, both of the C-H bonds will increase, as expected, by about 0.001 Å. Concerning the change in d_{O-H} for BC under pressure, we note that the H atom sits between an O and a Zn atom. When the O-Zn distance is reduced due to the external pressure, the O-H distance (d_{O-H}) is also reduced.

A recent experiment showed that the 3326 cm^{-1} frequency corresponds to an H mode in the $\perp$ direction, whose frequency changes with pressure by a negative slope,

−1.5 cm^{-1}/GPa (Ref. 16). This mode has also been assigned to hydrogen on the $AB_{O\perp}$ sites. In fact, this assignment agrees with our present calculation where the $AB_{O\perp}$ site should have a negative pressure slope, as well as a slightly lower formation energy than that of the $AB_{O\parallel}$ site (see Table I). Even the measured slope, −1.5 cm^{-1}/GPa, is within a factor of 3 of the calculated one, −4.2 cm^{-1}/GPa. Note that to calculate the small changes in ω accurate to within 10 cm^{-1} requires a very high convergence to at least within 0.001 Å in the atomic positions and 1 meV in energy. Hence, such a deviation from experiment is not at all surprising. Also, while both the measured 3326 and 3611 cm^{-1} modes in Table II have been previously assigned to interstitial H, there is always the concern whether they belong to some hydrogen/(unknown)-defect complexes, instead. We believe that the pressure dependence of the LVMs should not depend very sensitively on the complex formation. In other words, the pressure coefficient should still be positive if the H in a complex can be described as a bond-center H, but negative if the H can be described as an antibonding H.

In conclusion, first-principles studies predict that hydrostatic-pressure experiments could be an important tool for making unambiguous identification of interstitial H in ZnO; in particular, showing a clear, qualitative difference between the bond center and antibonding sites. The frequency ω for the former should increase with pressure, but ω for the latter should decrease, with a slope of 4.2 cm^{-1}/GPa. The magnitude of the calculated slopes qualitatively agrees with the only known experiment.

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