Uncovering the Complex Behavior of Hydrogen in Cu$_2$O

David O. Scanlon[*] and Graeme W. Watson[†]

School of Chemistry, Trinity College Dublin, Dublin 2, Ireland
(Received 15 July 2010; published 3 May 2011)

The behavior of hydrogen in p-type Cu$_2$O has been reported to be quite unusual. Muon experiments have been unable to ascertain the preferential hydrogen site within the Cu$_2$O lattice, and indicate that hydrogen causes an electrically active level near the middle of the band gap, whose nature, whether accepting or donating, is not known. In this Letter, we use screened hybrid-density-functional theory to study the nature of hydrogen in Cu$_2$O, and identify for the first time the "quasiatomic" site adopted by hydrogen in Cu$_2$O. We show that hydrogen will always act as a *hole killer* in p-type Cu$_2$O, and is one likely cause of the low performance of Cu$_2$O solar cell devices.

The behavior of hydrogen in semiconductors has been investigated for decades [1]. It was thought that interstitial hydrogen behaved only as an *amphoteric* impurity in semiconductors, acting as a donor in p-type materials and as an acceptor in n-type materials [2]. However, in 2000, Van de Walle demonstrated using first-principles methods that hydrogen could act as a shallow donor in wide-band-gap n-type ZnO [3]. This was subsequently verified by many experimental studies, e.g., Ref. [4], and it has been demonstrated that hydrogen can act as a shallow donor *and* is a source of n-type conductivity in other wide-band-gap n-type oxide semiconductors [5]. The behavior of hydrogen in p-type oxides, however, has not been elucidated.

Cu$_2$O is a native p-type semiconducting oxide with many applications, including catalysis, gas sensing, and photovoltaics [6]. Because of its abundance, nontoxicity, and direct fundamental band gap of 2.17 eV, it has been regarded as particularly promising for photovoltaic solar cells [6]. The p-type nature of Cu$_2$O stems from cation deficiency which manifests itself as copper vacancies (V_{Cu}) and to a much lesser extent oxygen interstitials (O$_i$) [7–9]. A recent muon spectroscopy study has indicated that hydrogen in Cu$_2$O has "*quasiatomic*" character and causes an electrically active level ~1 eV above the valence band maximum (VBM) [10]. However, this study could not identify whether the transition level represents hole or electron ionization, and could not infer any site identification [10].

In this Letter, we present a hybrid-density-functional-theory examination of the geometry and electronic structure of hydrogen in Cu$_2$O. We show (i) in stoichiometric Cu$_2$O, hydrogen preferentially occupies the tetrahedral interstitial position, explaining for the first time the quasiatomic nature of hydrogen in Cu$_2$O as indicated by Muon spectroscopy, (ii) hydrogen acts as an amphoteric defect in stoichiometric Cu$_2$O, and is *not* a cause of n-type conductivity, and (iii) hydrogen will bind into any V_{Cu} in the system and *kill* p-type conductivity. In light of these results

we discuss strategies to remove hydrogen from the system and increase Cu$_2$O device performance.

Method.—All calculations were performed using the VASP code [11], with the projector augmented wave approach [12], and utilizing the screened hybrid functional as proposed by Heyd, Scuseria, and Ernzerhof (HSE) [13]. The value of exact nonlocal exchange (α) chosen was 27.5%, which yielded a band gap of 2.12 eV, in excellent agreement with the experimentally measured band gap of 2.17 eV [6]. HSE has previously been shown to produce improved structural data and more accurate band gaps than standard density functionals [e.g., local density approximation (LDA), generalized gradient approximation (GGA), metaGGA, etc.] [14–17]. The defect formation energy, $\Delta H_f[(D), q]$, of a defect D in charge state q, and the thermodynamic ionization (transition) levels (TLs) of a given defect, $\epsilon_D(q/q')$, are calculated as a function of E_F, using the computational approach and parameters as detailed in Ref. [9]. Supercell convergence tests were carried out using GGA $+ U$ on V_{Cu} and H$_i^{tet}$ in 48, 162, and 384 atom supercells, which showed that the formation energies in a 384 atom cell varied by less than 0.05 eV, with TLs varying by less than 0.09 eV from the 48 atom cell. Extra constraints on the chemical potentials limits are caused by the introduction of hydrogen into the system, namely, the formation of H$_2$O in both the Cu-rich–O-poor and Cu-poor–O-rich limits. The chemical potential limits for hydrogen, $\Delta\mu_H$, were calculated to be -0.54 eV for Cu-rich–O-poor and -0.66 eV for Cu-poor–O-rich. The numbers shown are relative to half the energy of H$_2$, and represent the upper limits of the hydrogen chemical potentials.

We have examined the stability of interstitial hydrogen, H$_i$, in stoichiometric Cu$_2$O in both the tetrahedral, H$_i^{tet}$, and octahedral, H$_i^{oct}$, interstitial positions, in the so-called bond center (H$_i^{BC}$) position and in two anion antibonding configurations (H$_i^{AB1}$ and H$_i^{AB2}$), as shown in Fig. 1. From the formation energies listed in Table I, it is clear that the most favorable position for H$_i$ in Cu$_2$O is the H$_i^{tet}$ position.
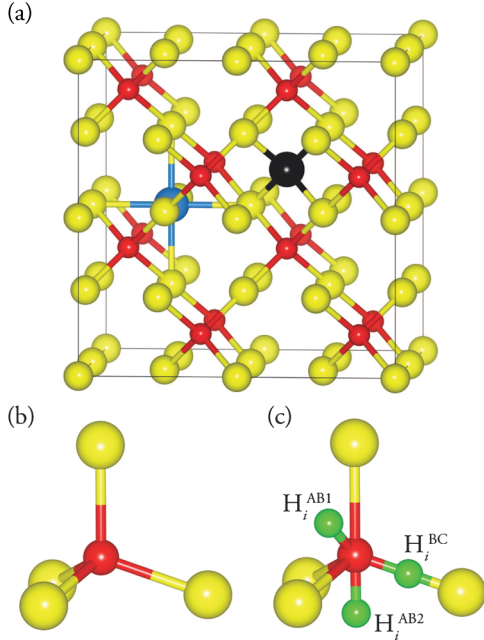
(a)

(b)   (c)

H_i^{AB1}

H_i^{BC}

H_i^{AB2}

FIG. 1 (color online). (a) Octahedral [large light gray (blue) sphere] and tetrahedral (large black sphere) interstitial positions in Cu$_2$O, (b) coordination around an O atom in Cu$_2$O, and (c) possible sites for interstitial H (H_i^{BC}, H_i^{AB1}, and H_i^{AB2}) around the tetrahedral O in Cu$_2$O.

This is surprising, as in many oxides and nitrides [3,18,19], H preferentially occupies a position next to the anions in either a bond center or anion antibonding configuration. This result explains the uncertainty about the preferred lattice site for H in Cu$_2$O found in the muon study by Cox *et al.* Analyzing the charge density distribution of the H_i^{tet}, Fig. 2, we can see that the electron from the interstitial hydrogen is donated to the four cation nearest neighbors and to the interstitial itself, in a "quasiatomic" manner. The tetrahedral interstitial position was first proposed by Cox *et al.* as a possible explanation for their experimental results [10]. This view was recently supported by the GGA

TABLE I. HSE calculated formation energies in the neutral charge state, $\Delta H_f[(D), 0]$, for H defects in Cu$_2$O in Cu-rich–O-poor conditions. O-H and Cu-H bond lengths are given where appropriate.

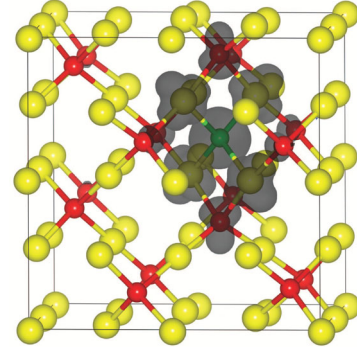| Defect	$\Delta H_f[(D), 0]$ (eV)	$d_{\text{O-H}}$ (Å)	$d_{\text{Cu-H}}$ (Å)
H_i^{oct}	2.21	2.37	1.76
H_i^{tet}	1.64	2.47	1.80
H_i^{BC}	1.98	0.99	⋯
H_i^{AB1}	2.32	0.98	⋯
H_i^{AB2}	1.93	0.98	⋯
H_O	2.26	⋯	1.66
$(H_2)_i^{oct}$	2.41	⋯	⋯
$(H_2)_i^{tet}$	2.25	⋯	⋯
$(H_i - V_{Cu})$	0.17	0.98	⋯

FIG. 2 (color online). HSE ($\alpha = 27.5\%$) spin density for H_i^{tet} in Cu$_2$O. The small dark gray (red), large light gray (yellow), and medium-sized medium gray (green) spheres denote O, Cu, and H, respectively. The black isosurface is shown at $0.01e$ Å^{-3}.

calculations of Catlow *et al.* [20], where GGA calculations did not find the H_i^{tet} to be the lowest energy configuration, but it was proposed as the minimum energy structure based on *a posteriori* corrections.

When examining the interaction of H with defective Cu$_2$O, we have only considered H interacting with V_{Cu} and V_O, as the formation energy of both anion and cation interstitials is very high [7]. We tested H on both the perfect Cu and O crystallographic sites, and then offset from these sites, finding that for H_O, hydrogen wished to sit on the perfect lattice site. For H interacting with a V_{Cu}, H wanted to distort from the perfect Cu site and move towards one of the two three-coordinate oxygens left behind upon V_{Cu} formation, forming an O-H bond. The formation energy of the resulting (H-V_{Cu}) complex was found to be only 0.17 eV, making it the most stable defect considered, Table I.

Defect energetics and transition levels.—Figure 3 shows a plot of formation energy as a function of Fermi-level position for all intrinsic defects and H related impurities for
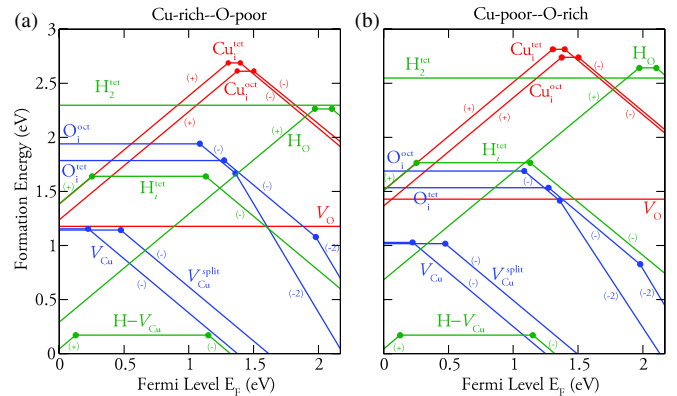

FIG. 3 (color online). HSE ($\alpha = 27.5\%$) calculated formation energies for intrinsic *p*-type (blue), *n*-type (red), and hydrogen impurity (green) defects in Cu$_2$O in (a) Cu-rich–O-rich conditions and (b) Cu-poor–O-rich conditions. The solid dots denote the transition levels $\epsilon(q/q')$.

both Cu-rich–O-poor and Cu-poor–O-rich regimes. For most of the H related defects, all three charge states ($-$, 0, and $+$) are stable within the band gap. This type of behavior has not been reported thus far for H in oxides. *All* H_i defects act as deep *amphoteric* impurities under both sets of conditions, meaning that H_i will effectively kill both *p*-type and *n*-type conductivity in the system. We find that H_O^+ is the most stable charge state for H_O over the majority of the band gap, and should oppose *p*-type conductivity under all growth conditions, but interestingly, H_O is also an amphoteric defect. This behavior is very different from the behavior of H_O in other wide-band-gap *n*-type oxides, where it is found to act only as a shallow donor [21], with the H_O^0 or H_O^- charge states rarely reported. H_O^0 induces a singly occupied, single particle level (SPL) in the band gap, 1.68 eV above the VBM. The H_O^- charge state is made possible by the presence of a doubly occupied, spin-paired, SPL in the band gap, 1.82 eV above the VBM, which can be thought of as an extra electron pairing with the singly occupied SPL produced by H_O^0. Amphoteric behavior for H_{anion} has, however, been predicted for some zinc blende chalcogenides [22], and all three charge states for H_{anion} have been found to be stable in the band gap for H_{Te} in CdTe [23], but to the best of our knowledge, never for oxides.

Surprisingly, the ($H - V_{Cu}$) complex possesses a $0/-1$ TL near midgap, which upon further investigation was found to be mediated by a singly occupied SPL at ~ 1.0 eV above the VBM. This SPL is found to be primarily of Cu *d* character, and is delocalized over all the Cu sites in the supercell. It is therefore probable that the TL seen by Cox *et al.* is actually the $0/-$ transition, for the ($H - V_{Cu}$ defect, which occurs at ~ 1.15 eV above the VBM. Thus we have identified that the TL seen in muon spectroscopy most likely represents hole ionization. The already deep TLs of V_{Cu} are thus passivated, with the TL for ($H - V_{Cu}$) being *ultra* deep in the band gap, severely affecting the *p*-type ability of Cu_2O under all growth conditions.

Acceptor reactivation.—The calculated binding energy of the ($H_i - V_{Cu}$) complex is given by

$$E_b = \Delta H_f[(V_{Cu}), 0] + \Delta H_f[(H_i), 0]$$
$$- \Delta H_f[(H_i - V_{Cu}), 0], \quad (1)$$

where $\Delta H_f[(H_i - V_{Cu}), 0]$ is the formation energy of the complex in the neutral charge state. A positive E_b indicates that the complex ($H_i - V_{Cu}$) is lower in energy than the isolated H_i and V_{Cu}. We obtain an E_b of 2.62 eV, which is large when compared with the binding energy for other hydrogen-acceptor complexes, e.g., in $SnO_2 : IIIA$ [24] (0.22–0.53 eV) or in GaN:Mg [25] (0.7 eV). The high binding energy is most likely due to the fact that in Cu_2O, H actually binds into a *vacancy*, whereas in SnO_2 and GaN, H binds onto anions neighboring the acceptor dopants. This suggests that the passivating effect of H

binding into V_{Cu} in Cu_2O will be more evident than for H in GaN:Mg.

Using the nudged elastic band method we have calculated the migration barrier for H_i in Cu_2O to be ~ 0.18 eV, which is very low compared to the calculated migration barriers in other oxides, e.g., SnO_2 (0.57 eV) [26]. In other oxides and nitrides, H_i exists as H_i^+, bonded to the anions [3,19]. The reason for this low migration barrier is that as H_i is most stable in the H_i^{tet} position, and not in an AB or BC configuration, it does not have to break any strong O-H bonds, and is free to move from tetrahedral hole to tetrahedral hole. Cox *et al.* have also noted that muonium can diffuse quite easily in Cu_2O, with a hop rate activation energy of ~ 0.1 eV [10], which is in reasonable agreement with our migration barrier of ~ 0.18 eV.

Experimentally the removal of hydrogen and reactivation of acceptors in GaN:Mg is possible with thermal annealing [27]. This begs the question: can H be annealed out of Cu_2O to reactivate the intrinsic acceptors and increase *p*-type conductivity? Based on our results for the migration barrier of H_i, we can calculate the temperatures at which we expect H_i to become mobile using transition state theory as outlined by Van de Walle and co-workers [28,29]. From this analysis we define an annealing temperature T, which is the T at which the H jump rate is $1/s$. This yields an annealing temperature for H_i of 72 K, which indicates that H_i will be annealed out well below room temperature.

However, H trapped in a V_{Cu} will be much more difficult to remove. Approximating the activation energy for dissociation of the ($H_i - V_{Cu}$) complex to be equal to the binding energy for the complex (2.62 eV), we can estimate an annealing temperature for the removal of all H from the system of 943 K. This result gives good agreement with experiment, as the disappearance of the muonium signal in Cu_2O was noted to occur at around 900 K [10].

In the literature, annealing studies on Cu_2O samples have resulted in remarkable decreases in resistivity [30,31]. Annealing thin films of Cu_2O at 623 K has been reported to result in a decrease in resistivity by 4 orders of magnitude compared to as-prepared films [30], with the increase attributed to increased crystallinity from the annealing process. Onimisi has reported a decrease in resistivity of Cu_2O solar cell samples by $\sim 36\%$ upon annealing at 773 K, and the higher output performance of annealed Cu_2O solar cells over that of unannealed samples [31]. Similarly $CuAlO_2$, a wide-band-gap transparent conducting oxide (TCO) whose defect chemistry is very similar to that of Cu_2O [32] experiences a decrease in resistivity of 3 orders of magnitude upon postannealing [33]. $SrCu_2O_2$, another *p*-type TCO, also experiences a decrease in resistivity upon postannealing [34].

It is surprising that these reported increases in conductivity upon postannealing have not been linked to the possible removal of H, and subsequent reactivation of

acceptors in these systems, especially since H is ubiquitous in most materials. In fact H is known to passivate p-type defects in $CuInSe_2$ and $CuGaSe_2$ solar cell absorbers [35], and can even reverse the polarity of conductivity in $CuInSe_2$ [36]. In light of our results, we propose that postannealing be adopted to increase Cu_2O's p-type conductivity, as any H in the Cu_2O system will effectively act as *hole killers*, and impair device performance.

Conclusions.—We have revealed the quasiatomic nature of H_i^{tet} in the Cu_2O crystal structure, and found that contrary to most oxides and nitrides, H_i in stoichiometric Cu_2O does not favor formation of a H-anion bond. H binds into V_{Cu} under all growth conditions, and acts to kill p-type conductivity. As H is an ever-present impurity in oxide materials, and the defect chemistry of the Cu^I-based TCOs are similar to that of Cu_2O, it is expected that H will behave similarly in Cu^I-based p-type oxide materials. Thus we propose that postannealing to remove H in these materials will be necessary for increased performance.

*scanloda@tcd.ie

†watsong@tcd.ie

[1] C. G. Van de Walle, Phys. Status Solidi B **235**, 89 (2003).
[2] J. I. Pankove and N. M. Johnson, *Hydrogen in Semiconductors, Semiconductors and Semimetals* (Academic, Boston, 1991), Vol. 34.
[3] C. G. Van de Walle, Phys. Rev. Lett. **85**, 1012 (2000).
[4] S. F. J. Cox *et al.*, Phys. Rev. Lett. **86**, 2601 (2001).
[5] P. D. C. King *et al.*, Phys. Rev. B **80**, 081201(R) (2009).
[6] S. Kale, S. Ogale, S. Shinde, M. Sahasrabuddhe, V. Kulkarni, R. Greene, and T. Venkatesan, Appl. Phys. Lett. **82**, 2100 (2003).
[7] H. Raebiger, S. Lany, and A. Zunger, Phys. Rev. B **76**, 045209 (2007).
[8] D. O. Scanlon, B. J. Morgan, and G. W. Watson, J. Chem. Phys. **131**, 124703 (2009).
[9] D. O. Scanlon, B. J. Morgan, G. W. Watson, and A. Walsh, Phys. Rev. Lett. **103**, 096405 (2009).
[10] S. F. J. Cox, J. S. Lord, S. P. Cottrell, J. M. Gil, H. V. Alberto, A. Keren, D. Prabhakaran, R. Scheuermann, and A. Stoykov, J. Phys. Condens. Matter **18**, 1061 (2006).
[11] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
[12] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[13] S. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
[14] J. P. Allen, D. O. Scanlon, and G. W. Watson, Phys. Rev. B **81**, 161103(R) (2010).
[15] J. Paier, R. Asahi, A. Nagoya, and G. Kresse, Phys. Rev. B **79**, 115126 (2009).
[16] B. G. Janesko, T. M. Henderson, and G. E. Scuseria, Phys. Chem. Chem. Phys. **11**, 443 (2009).
[17] D. O. Scanlon and G. W. Watson, J. Phys. Chem. Lett. **1**, 3195 (2010).
[18] S. Limpijumnong, J. E. Northrup, and C. G. Van de Walle, Phys. Rev. B **68**, 075206 (2003).
[19] S. Limpijumnong, P. Reunchan, A. Janotti, and C. G. Van de Walle, Phys. Rev. B **80**, 193202 (2009).
[20] C. R. A. Catlow, Z. X. Guo, M. Miskufova, S. A. Shevlin, A. G. H. Smith, A. A. Sokol, A. Walsh, D. J. Wilson, and S. M. Woodley, Phil. Trans. R. Soc. A **368**, 3379 (2010).
[21] A. Janotti and C. G. Van de Walle, Nature Mater. **6**, 44 (2006).
[22] M. H. Du and D. J. Singh, Phys. Rev. B **79**, 205201 (2009).
[23] Z. Rak, S. D. Mahanti, and K. C. Mandal, J. Electron. Mater. **38**, 1539 (2009).
[24] J. B. Varley, A. Janotti, A. K. Singh, and C. G. Van de Walle, Phys. Rev. B **79**, 245206 (2009).
[25] J. Neugebauer and C. G. Van de Walle, Phys. Rev. Lett. **75**, 4452 (1995).
[26] A. K. Singh, A. Janotti, M. Scheffler, and C. G. Van de Walle, Phys. Rev. Lett. **101**, 055502 (2008).
[27] W. Götz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, Appl. Phys. Lett. **68**, 667 (1996).
[28] A. Janotti and C. G. Van de Walle, Phys. Rev. B **76**, 165202 (2007).
[29] A. Janotti, E. Snow, and C. G. Van de Walle, Appl. Phys. Lett. **95**, 172109 (2009).
[30] T. Mahalingham, J. S. P. Chitra, J. P. Chu, S. Velumani, and P. J. Sebastian, Solar Energy Mater. Sol. Cells **88**, 209 (2005).
[31] M. Y. Onimisi, Int. J. Phys. Sci. **3**, 194 (2008).
[32] D. O. Scanlon, K. G. Godinho, B. J. Morgan, and G. W. Watson, J. Chem. Phys. **132**, 024707 (2010).
[33] W. Lan, W. L. Cao, M. Zhang, Z. Q. Liu, Y. Y. Wang, E. Q. Xie, and H. Yan, J. Mater. Sci. **44**, 1594 (2009).
[34] J. Liu, S. Lee, and C. Yang, Mater. Trans., JIM **49**, 1694 (2008).
[35] Ç. Kiliç and A. Zunger, Phys. Rev. B **68**, 075201 (2003).
[36] K. Otte, G. Lippold, D. Hirsch, R. K. Gebhardt, and T. Chassé, Appl. Surf. Sci. **179**, 203 (2001).