Modeling the polaronic nature of *p*-type defects in Cu$_2$O: The failure of GGA and GGA+*U*

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The exact nature of the hole traps reported deep in the band gap of Cu$_2$O has been a topic of vigorous debate, with copper vacancies and oxygen interstitials both having been proposed as the relevant defects. In this article, the electronic structure of acceptor-forming defects in Cu$_2$O, namely, copper vacancies and oxygen interstitials, is investigated using generalized gradient approximation (GGA) and GGA corrected for on-site Coulombic interactions (GGA+*U*). GGA produces notionally semimetallic defect complexes, which is not consistent with the experimentally known polaronic nature of conduction in Cu$_2$O. GGA+*U* also predicts a semimetallic defect complex for the "simple" copper vacancy but predicts the "split" vacancy and both oxygen interstitials are characterized by localized polarons, with distinct single particle levels found in the band gap. For both methods, however, the positions of calculated transition levels are inconsistent with experimental ionization levels. Hence neither GGA nor GGA+*U* are successful in modeling *p*-type defects in Cu$_2$O. © *2009 American Institute of Physics*. [doi:10.1063/1.3231869]

I. INTRODUCTION

Cuprous oxide (Cu$_2$O) is an abundant, low cost, non-toxic semiconductor material with a direct band gap of 2.17 eV.[1] Interest in this prototypical *p*-type conducting oxide is due to its potential use for photovoltaic powercell applications[2] and as a possible *p*-type host for dilute semiconductor ferromagnetism when doped with magnetic ions.[3] The recent explosion of interest in *p*-type transparent conducting oxides (TCOs) such as Cu*M*O$_2$ (*M*=Al, Cr, B, Ga, In) (Ref. 4) and SrCu$_2$O$_2$ (Ref. 5) has also refocused attention on the chemistry of Cu(I) oxides, as the *p*-type properties of these materials are thought to be similar.[6]

p-type conduction in Cu$_2$O is caused by oxygen excess, which results in the formation of hole (acceptor) states above the valence band.[6] The valence bands of most wide band gap metal oxides are composed of O 2*p* states, leading *p*-type doping to often result in localized oxygen holes deep in the band gap, associated with poor *p*-type conduction. In Cu$_2$O, the top of the valence band is dominated by Cu 3*d* states, with some O 2*p* mixing.[7] Upon hole formation, oxidation of 3*d*^{10} Cu(I) to 3*d*^{9} Cu(II) occurs, with the corresponding acceptor levels being formed primarily on the Cu *d* states.[8]

The band gap of Cu$_2$O is not sufficiently large for transparency in the visible spectrum (band gaps greater than 3.1 eV ensure transparency), making Cu$_2$O itself unsuitable for TCO applications. The small band gap is thought to be due to the three-dimensional interactions between 3*d*^{10} electrons on neighboring Cu(I) ions.[9] These three-dimensional interactions are a consequence of the crystal structure, which can be constructed as two interpenetrating cristobalite lattices,[10,11] as shown in Fig. 1. It was proposed by Kawazoe *et al.* that maintaining the *p*-type nature of Cu$_2$O is necessary for the

development of Cu-based *p*-type TCOs, and this was incorporated in a set of design rules for TCOs, called the "chemical modulation of the valence band."[12] This approach aims to maintain the valence band properties of Cu$_2$O while increasing the band gap by alloying with other oxides, such as Al$_2$O$_3$ or SrO, to form CuAlO$_2$ or SrCu$_2$O$_2$, respectively. These ternary oxides decrease the dimensionality of the Cu–Cu interactions, resulting in band gaps large enough for TCO applications.[5,13,14] The defect chemistry of Cu$_2$O and these technologically useful daughter compounds is expected to be similar; thus developing an understanding of the *p*-type behavior of Cu$_2$O is an important step toward understanding the chemistry of Cu-based TCOs.

Although the *p*-type conduction properties of Cu$_2$O have been studied extensively for decades,[15–19] the exact nature of the hole states found in the forbidden energy gap of Cu$_2$O has been a source of much controversy, with acceptorlike states being reported in the range 0.12–0.70 eV.[20–27] Deep level transient spectroscopy (DLTS) has shown the presence of hole traps 0.40–0.55 eV above the top of the valence band maximum (VBM).[26,28] These hole traps have been attributed to structural anomalies such as CuO "islands."[26] Similar conclusions were reached regarding the acceptor levels in DLTS study of Cd-doped Cu$_2$O.[29]

A recent DLTS study, with a broader temperature range of 100–350 K, reported two trap levels.[27] The first trap at 0.45 eV above the VBM was attributed to copper vacancies, while a second trap at 0.25 eV was tentatively assigned as a Cu divacancy. The trap at 0.25 eV becomes the dominant feature with increasing oxygen flow rate, possibly indicating that the formation of Cu divacancies is facilitated by increasing Cu monovacancy formation. The authors excluded the possibility of the trap at 0.25 eV being due to oxygen interstitials, as they reasoned interstitial oxygen would be unlikely to act as an acceptor.

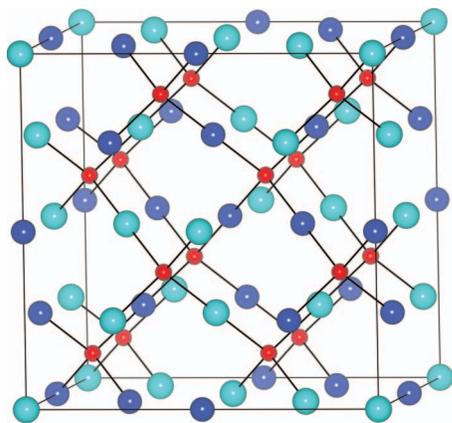[a]Electronic mail: scanloda@tcd.ie.
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FIG. 1. A $3 \times 3 \times 3$ supercell of cubic Cu_2O showing the two interpenetrating cristobalitelike structures. Dark blue and light blue spheres indicate the copper atoms associated with the different cristobalite sublattices, and the red spheres are oxygen.

Deep acceptor states are also observed with photoinduced current transient spectroscopy, with the defect states having activation energies ranging 0.12–0.63 eV above the VBM.[25] The acceptor state at 0.63 eV was assigned as a copper vacancy defect with an acceptor-type charge state. None of the other defect levels were assigned.

The presence of more than one acceptor level has also been noted by Pollack and Trivich.[20] Samples of cuprous oxide were prepared using a high-temperature equilibration and quenching technique designed to "freeze in" any nonstoichiometry. For a sample equilibrated at 1373 K at an oxygen partial pressure placing its composition in a region near the $CuO–Cu_2O$ phase boundary, an acceptor level at 0.4 eV was found, but the relevant defect was not assigned.[20] Another sample was equilibrated at 1373 K, at an oxygen partial pressure placing it near the $Cu–Cu_2O$ phase boundary, and two acceptor levels were found. Only one could be accurately resolved at 0.16 eV above the VBM.[20] The nature of this defect level was again not assigned. An acceptor defect level at 0.16 eV has also been reported in a photoluminescence study of polycrystalline n-type Cu_2O, but this defect level was not assigned since previous studies had shown that copper vacancies give much deeper acceptor levels.[23]

The existence of multiple acceptor levels was given further support in a study of the Poole–Frenkel (PF) conduction mechanism of $Mo–Cu_2O–Au$ thin film structures,[22] which suggested that PF conduction is governed by two temperature dependent mechanisms. In the low-temperature range of 78–230 K, conduction is due to a field assisted lowering of the ionization energy of an acceptor level 0.12 eV above the VBM, and in the range of 231–321 K conduction is related to an acceptor level at 0.70 eV.[22] The nature of these distinct acceptor levels was not discussed.

Additional studies include those of Peterson and Wiley and Porat and Reiss.[30] In the former, a defect model involving copper vacancies, holes, and singly ionized oxygen interstitials was obtained by fitting to tracer diffusion data and the conductivity data of Maluenda *et al.*[16] combined with the stoichiometry data of O'Keefe and Moore.[17,31] Porat and Reiss studied the defect chemistry of $Cu_{2-y}O$ at elevated tem-

peratures and suggested that above 1150 K the dominant ionic defect is the doubly charged oxygen interstitial, whereas at temperatures below 950 K the singly charged copper vacancy dominates.[30]

The existence of defect levels in Cu_2O systems is therefore not in doubt, although the source of these acceptor levels still remains uncertain. It has been known for decades that Cu_2O conducts via a polaronic, hole-hopping mechanism,[32–34] which is governed by an activated Arrhenius-type behavior.[15,16,18,35] This type of conductivity is consistent with localized single particle levels (SPLs or raw eigenvalues of the hole states) deep in the band gap of the material.

Cu vacancies in Cu_2O have not received much theoretical attention.[36–39] Wright and Nelson studied the energetics of Cu vacancies in Cu_2O using density functional theory (DFT)-local density approximation (LDA), finding that a "simple" vacancy, V_{Cu}, in which one Cu is removed leaving two three-coordinate oxygen atoms, is less stable than a "split" vacancy, V_{Cu}^{split}, where one remaining Cu moves toward the simple vacancy and into a tetrahedrally coordinated site.[36] Divacancies were also examined but only to compensate for the substitution of Al or In into a Cu position, and the electronic structure of these defects was not analyzed.[36]

Cu vacancies were also studied by Nolan and Elliot using DFT within the generalized gradient approximation (GGA) and with GGA supplemented by an on-site Coulomb correction (GGA$+U$).[37] For both GGA and GGA$+U$ (where a U of 7 eV was applied to the Cu d states), a delocalized state was reported for the simple vacancy, with the defect band crossing the Fermi level, giving a metallic system. Based on the equivalence of the GGA and GGA$+U$ results for the simple vacancy it was argued that GGA$+U$ is unnecessary for modeling Cu vacancies in Cu_2O. The split vacancy was also described as corresponding to a delocalized state, although no detailed analysis of the electronic structure was presented. The simple vacancy was 0.06 eV more favorable than the split vacancy. The authors interpreted their results as showing the presence of an acceptor level at 0.2 eV and were suggested to be consistent with the hole traps seen at 0.45–0.55 eV in DLTS experiments.[26,29] Transition levels were not calculated, however, and the presented band structures show a spin-paired system with the Fermi level 0.2 eV below the top of the VBM, with no empty states in the gap. It appears that this analysis compares a calculated SPL to the experimental transition level, even though they are distinctly different properties.[40] The formation of oxygen interstitials was not considered in this work.

Raebiger *et al.* employed GGA, with a GGA$+U$ correction to the energetics, to study Cu vacancies in Cu_2O.[38] They proposed cation vacancies as the most likely cause of p-type conduction due to the preferential formation of this defect. The calculated transition level for the simple V_{Cu} was ~ 0.28 eV, which compares well to the trap at 0.25 eV in the DLTS study of Paul *et al.*[27] It should be noted, however, that these calculated levels are subject to a rigid shift of 0.32 eV applied to the VBM of the GGA calculation, derived from a reference bulk calculation using GGA$+U$ with $U=5$ eV applied to the Cu d states, without which the transition levels

would be resonant in the valence band. It was postulated that the most probable explanation for the deep hole trap levels reported in the literature is the presence of interstitial oxygen. Detailed electronic structures were not reported for the simple and split vacancies or for the oxygen interstitial.

Soon *et al.* used GGA to study the formation of defects in the bulk and on the surfaces of Cu$_2$O.[39] In the bulk, the formation of Cu vacancies was favorable under all conditions but the calculated transitions levels for the Cu vacancy and the split vacancy were in the valence band. The same shift of 0.32 eV was applied to the transition levels as used in the study by Raebiger *et al.*[38] making their transition levels appear in the band gap. This study did not consider CuO formation as the limit of Cu-poor/O-rich growth conditions, and thus the Cu-poor/O-rich results are probably for an unphysical composition.[39]

From both the previous experimental and theoretical work, it is clear that there is a pressing need for a reexamination of these defect levels within the band gap of Cu$_2$O. In this article we attempt to answer two questions: (i) Can GGA or GGA+U reproduce the polaronic nature of defective Cu$_2$O, with distinct localized defect SPL? (ii) Can either method successfully reproduce deep acceptor levels seen experimentally, and thus elucidate the nature of these levels? We present a comprehensive first principles examination of the electronic structure and geometry of acceptor-level-forming defects in Cu$_2$O using GGA and GGA+U. We find the following: (i) for the first time in a DFT-based study of Cu$_2$O distinct acceptor level bands split off from the valence band for the split vacancy and oxygen interstitials using GGA+U, thus reproducing the expected polaronic nature of the system, (ii) the application of a rigid shift to the GGA calculated transition levels is not equivalent to the application of a +U correction in all calculations, and its use therefore can give misleading results, and (iii) the positioning of calculated transition levels for the defects investigated using both GGA and GGA+U cannot reproduce the experimentally seen hole trap positions due to the partially delocalized nature of these defect states, and hence neither GGA nor GGA+U are sufficient to model these acceptorlike states in Cu$_2$O.

II. THEORETICAL METHODS

The periodic DFT code VASP (Refs. 41 and 42) was employed for all our calculations, in which a plane wave basis set describes the valence electronic states. The Perdew–Burke–Ernzerhof[43] (PBE) gradient corrected functional was used to treat exchange and correlation. Interactions between the cores (Cu:[Ar] and O:[He]) and the valence electrons were described using the projector-augmented wave[44] method. The defect calculations were fully spin polarized to describe the unpaired electrons produced upon defect formation.

Structural optimizations of bulk Cu$_2$O were performed using GGA and GGA+U at a series of volumes to calculate the equilibrium lattice parameters. The U value applied to the Cu d states was 5.2 eV, which closely reproduces the X-ray photoelectron spectroscopy valence band features of

Cu$_2$O (Refs. 6 and 45) and has also accurately reproduced the valence band features of CuMO_2 (M=Al, Cr).[46,47] The validity of the GGA+U approach has been demonstrated in providing improved descriptions of a wide range of localized electronic defect systems including reduced cations[48–51] and oxygen holes.[52,53]

In each case the atomic positions, lattice vectors, and cell angles were allowed to relax, while the total volume was held constant. The resulting energy-volume curves were fitted to the Murnaghan equation of state to obtain the equilibrium bulk cell volume.[54] This avoids the problems of Pulay stress and changes in basis set that can accompany volume changes in plane wave calculations. Convergence with respect to k-point sampling and plane wave energy cutoff were checked, and for both methods a cutoff of 500 eV and a k-point sampling of $8 \times 8 \times 8$ were used. Structural optimizations were deemed to be converged when the force on every ion was less than 0.01 eV Å^{-1}. The minimum lattice parameters for both GGA and GGA+U were then used for all subsequent reduced system calculations, with the same calculation parameters and convergence criteria. Supercells of 162 atoms were used in all defect calculations, with a $3 \times 3 \times 3$ k-point mesh, centered at the Γ point. The defects considered are copper vacancies in both the simple and split configurations,; V_{Cu} and V_{Cu}^{split}, and oxygen interstitials in octahedral and tetrahedral sites, O_i^{oct} and O_i^{tet}.

So that consistent energies could be used in the calculation of defect formation energies, GGA calculations were performed on molecular oxygen, and GGA+U and GGA calculations were performed on Cu metal and CuO using equivalent convergence criteria and calculation parameters.

III. DEFECT METHODOLOGY

A. Formation enthalpy of neutral defects

The formation enthalpy of a neutral defect can be calculated from

$$\Delta H^f(D,0) = (E(D,0) - E^H) + \sum_i n_i E_i + n_i \mu_i, \qquad (1)$$

where E^H is the total energy of the stoichiometric host supercell and $E(D,0)$ is the total energy of the neutral (charge state 0) defective cell. Calculations on the constituent elements of the material in their standard states, in this case O$_2$ and Cu metal, give the elemental energies, E_i, with n being +1 or −1 if an atom is added to or removed from an external reservoir.

Varying the chemical potentials, μ_i of each species can reflect specific equilibrium growth conditions, within the global constraint of the calculated enthalpy of the host; in this instance Cu$_2$O. Using GGA+U, with U applied to the d states of all species containing Cu, this gives

$$2\mu_{Cu} + \mu_O = \Delta H_f^{Cu_2O} = -1.55 \text{ eV}.$$

The lower limit of μ_O, which would indicate a Cu-rich/O-poor environment, is limited by Cu metal formation:

$$\Delta\mu_{Cu} = 0 \text{ eV}, \quad \Delta\mu_O = -1.55 \text{ eV}.$$

The upper bound of μ_O (Cu poor/O rich) is limited by CuO formation:

$$\mu_{Cu} + \mu_O \leq \Delta H_f^{CuO} = -1.36 \text{ eV},$$

giving

$$\Delta\mu_{Cu} = -0.19 \text{ eV}, \quad \Delta\mu_O = -1.17 \text{ eV}.$$

Similar chemical potential analysis using GGA gives

$$\Delta H_f^{Cu_2O} = -1.23 \text{ eV}, \quad \Delta H_f^{CuO} = -1.15 \text{ eV},$$

which produces a Cu-rich/O-poor environment with

$$\Delta\mu_{Cu} = 0 \text{ eV}, \quad \Delta\mu_O = -1.23 \text{ eV}$$

and a Cu-poor/O-rich environment of

$$\Delta\mu_{Cu} = -0.08 \text{ eV}, \quad \Delta\mu_O = -1.07 \text{ eV}.$$

The formation energies of both CuO and Cu_2O calculated using GGA+U are considerably closer to the experimental values of ~ -1.60 and ~ -1.73 eV, respectively, than their GGA calculated counterparts.[55] As the correct description of CuO can be problematic for GGA,[37] and even for GGA+U, we have also tested the chemical limits using the experimental formation energies, as outlined in Secs. V B and VI B.

B. Formation enthalpy of charged defects

The formation enthalpy of a defect in a charge state q is

$$\Delta H^f(D,q) = \Delta H^f(D,0) + q[\Delta E_F + \epsilon_{VBM}^H + \Delta v(D)]. \quad (2)$$

The last term in Eq. (2) is the Fermi energy $E_F = \Delta E_F + \epsilon_{VBM}^H + \Delta v(D)$, which ranges from the VBM ($E_F = 0$ eV) to the conduction band minimum (CBM) ($E_F = 2.17$ eV). ϵ_{VBM}^H is the VBM eigenvalue of the host bulk and Δ_v aligns the VBM in the defective and stoichiometric supercells. This alignment correction is necessary as ϵ_{VBM}^H for the stoichiometric supercell cannot be directly applied to the defective supercell. This is due to the long range nature of the Coulombic potential and the periodic boundary conditions of the supercell approach.[56] This is addressed by inspecting a core level (in this case the O 1s core states) in the supercell far away from the impurity and aligning it with the core level in the stoichiometric supercell to define the shift in the reference level, given by

$$\Delta v(D) = \epsilon_{core,1s}^{far}(D,q) - \epsilon_{core,1s}^H,$$

where $\epsilon_{core,1s}^{far}(D,q)$ is the O 1s core energy level of the furthest O atom from the defect location, and $\epsilon_{core,1s}^H$ is the O 1s core energy level of the bulk host.

C. Transition levels

Thermodynamic ionization (transition) levels of a given defect, $\epsilon_D(q/q')$, are defined as the Fermi level for which the charge states q and q' have equal total energy. These transition levels can be calculated using

TABLE I. Comparison of the lattice constant a, Cu–O bond lengths, and fundamental band gaps (E_g) of bulk Cu_2O from previous theoretical and experimental studies and those from the current GGA and GGA+U calculations. Bond distances and lattice parameters are given in Å and E_g is measured in eV.

	a	Cu–O	E_g
LDA[a]	4.18	$\cdots$	$\cdots$
GGA-PBE[b]	4.29	1.86	0.47
GGA-PBE[c]	4.32	$\cdots$	0.46
GGA-PBE[d]	4.31	$\cdots$	0.43
GGA-PBE[e]	4.31	1.86	0.44
GGA-PBE+U [e]	4.28	1.85	0.67
Expt.[f]	4.27	1.85	2.17

[a]Reference 36.　　　　[d]Reference 38.
[b]Reference 37.　　　　[e]This study.
[c]Reference 39.　　　　[f]Reference 59.

$$\epsilon_D(q/q') = \frac{\Delta H^f(D,q) - \Delta H^f(D,q')}{q' - q} \quad (3)$$

and can be directly compared to the trap levels reported in experiments where the final charge state can relax to its equilibrium configuration after the transition.[57] DLTS is therefore an excellent spectroscopic technique with which to compare our calculated transition levels.[27,58]

IV. GGA AND GGA+U BULK CU_2O

Table I lists the calculated lattice parameters, equilibrium Cu–O bond distances, and fundamental band gaps for the stoichiometric bulk Cu_2O using GGA and GGA+U. The GGA and GGA+U lattice parameters and bond lengths are in good agreement with previous GGA results[37] and with known experimental values.[59] The GGA band gap (0.44 eV) is severely underestimated compared to experiment (2.17 eV),[6] but this is a known feature of GGA/LDA functionals.[46] Although the addition of the +U correction increases the band gap (to 0.67 eV), it is still severely underestimated. This is to be expected as GGA+U should not be used to fit to band gaps, except in the case where the VBM and CBM are of the same localized orbitals, as in the case of Mott insulators.[60]

V. GGA p-TYPE DEFECTS

A. Single particle levels

The SPL Fermi offsets (Fig. 2) for both V_{Cu} and V_{Cu}^{split} show no distinct acceptor bands in the band gap. For both vacancies the defect levels cross the Fermi level, giving semimetallic defect complexes. Raebiger $et\ al.$ suggested that this delocalization of defect states is the main difference between hole states in Cu(I)-based materials and hole states in native n-type materials.[38]

In typical n-type oxides such as ZnO, the O(p) dangling bond states of V_{Zn} occur deep in the band gap. In contrast, the delocalized nature of the GGA SPLs for V_{Cu} has been interpreted by Raebiger $et\ al.$ as holes residing in "delocalized, valence-band-like perturbed-host states" (PHSs) and not as split off "defect-localized" states.[38] It was reported
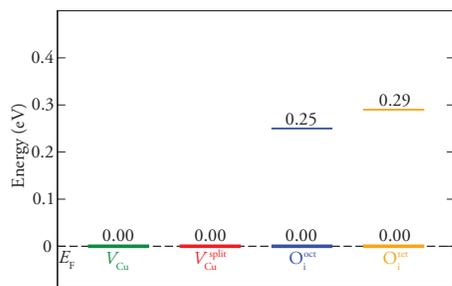
FIG. 2. Offsets of the hole SPL from the Fermi energy for the *p*-type defects studied using GGA. The Fermi energy does not represent the VBM in the cases of the oxygen interstitials.

that the dangling bond states of the unrelaxed V_{Cu} are 4 eV below the VB and "float up" to occupy a delocalized PHS just above the VBM, thus giving rise to *p*-type conductivity. Nolan and Elliot[37] also found delocalized hole states predicted by their GGA calculations and similarly suggested this explains the *p*-type conductivity in Cu₂O. Delocalized SPLs were also described by Soon *et al.*[39] This description of metallic defect-derived conductivity in Cu₂O, however, is in apparent contradiction to the activated, polaronic, hopping mechanism identified experimentally.[33,34] The relatively high resistivity observed for bulk Cu₂O of 35 Ω cm (Ref. 61) is also atypical for metallic-type conduction and suggests caution in interpreting the delocalized electronic states predicted with GGA as the source of *p*-type conductivity.

For an interstitial in an octahedral site, O_i^{oct}, GGA predicts that one defect band crosses the Fermi level and one distinct acceptor level lies 0.25 eV above the VBM. For an interstitial in a tetrahedral site, O_i^{tet}, one defect band crosses the Fermi level, and one acceptor level lies 0.29 eV above the VBM. These results are again at variance with the known polaronic nature of conductivity in Cu₂O, as the description of the electronic structure of both oxygen interstitials using GGA indicates semimetallic conductivity.

B. Energetics and transition levels

Figure 3(a) shows the calculated formation enthalpies of all the intrinsic *p*-type defects for different charge states calculated with GGA under Cu-rich/O-poor conditions. V_{Cu} has the lowest formation enthalpy; $\Delta H^f(V_{Cu}, 0) = 0.41$ eV. The formation energy of V_{Cu}^{split} is considerably higher with
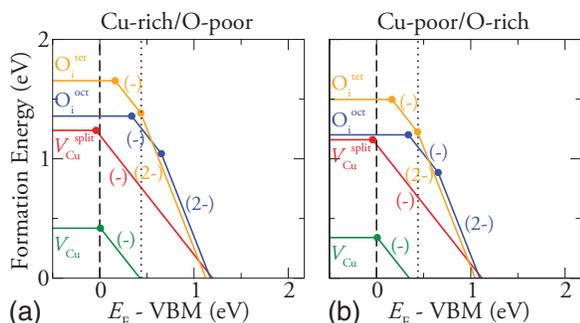

FIG. 3. Formation energies for intrinsic *p*-type defects in Cu₂O in (a) Cu-rich/O-poor conditions and (b) Cu-poor/O-rich conditions calculated using GGA. The solid dots denote the transition levels $\epsilon(q/q')$. The dashed and the dotted lines indicate the position of the VBM and the CBM, respectively.

$\Delta H^f(V_{Cu}^{split}, 0) = 1.24$ eV. This is significantly different to the results of Nolan and Elliott,[37] who found V_{Cu} to be only 0.06 eV more favorable than V_{Cu}^{split}, and to those of Raebiger *et al.* and Soon *et al.*, who found V_{Cu} to be 0.30 and 0.31 eV more stable than V_{Cu}^{split}, respectively.[38,39] The formation enthalpies of O_i^{oct} and O_i^{tet} are 1.36 and 1.65 eV, and as such are considerably higher in energy than the V_{Cu}. This trend is maintained under Cu-poor/O-rich conditions. The formation enthalpy all defects is lowered, but V_{Cu} and V_{Cu}^{split} remain more stable than the O_{int}. This is consistent with the results of Raebiger *et al.* and Soon *et al.*[38,39] It should be noted, however, that neglecting the formation of CuO when defining the limiting chemical potential means Soon *et al.* predicted that under Cu-poor/O-rich conditions the formation energy of V_{Cu} is exothermic, indicating V_{Cu} would form spontaneously.[39] This is unsurprising since Cu₂O is chemically unstable with respect to CuO under these conditions, and the formation of copper vacancies drives the system toward the more stable CuO phase. Using the experimental formation energies for Cu₂O and CuO, we find that only the oxygen interstitial formation energy is strongly affected by the change in chemical potential under both growth conditions, with increases in energy of ∼0.5 eV in both cases. The formation energy of both copper vacancies under Cu-poor/O-rich conditions are only increased by ∼0.06 eV. As these results clearly show that the defect chemistry of Cu₂O will be dominated by copper vacancies, this change in the formation energy of the oxygen interstitials is irrelevant.

The calculated $\epsilon(0/-)$ transition levels for V_{Cu} (0.01 eV) and for V_{Cu}^{split} (−0.04 eV) are not consistent with the trap levels reported in the DLTS study of Paul *et al.* which are 0.25 and 0.45 eV above the VBM.[27] Such shallow $\epsilon(0/-)$ transition levels would be indicative of a conduction process that is thermally activated at room temperature and is not consistent with the known activated nature of conduction in Cu₂O.[15,16,18,35] The transition levels for the oxygen interstitials are deep in the band gap, with the $\epsilon(0/-)$ transition levels at 0.16 and 0.34 eV and the $\epsilon(-/-2)$ transition levels 0.43 and 0.65 eV above the VBM for O_i^{oct} and O_i^{tet}, respectively. Raebiger *et al.* suggested that the deeper trap levels (0.45 eV) as seen in DLTS experiments can be explained by the $\epsilon(0/-)$ transition levels of the O_{int}.[38]

VI. GGA+U p-TYPE DEFECTS

A. Single particle levels

The GGA+U description of V_{Cu} is similar to that for GGA. The defect SPL again crosses the Fermi energy, producing a semimetallic defect complex, Fig. 4, as noted previously by Nolan and Elliott.[37] The GGA+U description of V_{Cu}^{split}, however, is notably different to the GGA description. The defect SPL for V_{Cu}^{split} is split off from the VBM by 0.04 eV, indicative of a polaronic defect center and in better agreement with the activated conduction behavior seen experimentally. Interestingly, Nolan and Elliot reported GGA and GGA+U both predicted a *delocalized* description for V_{Cu}^{split}.[37] Their use of a larger value of U of 7 eV than the present study, however, would suggest that the defect state ought to be more split off than described here.
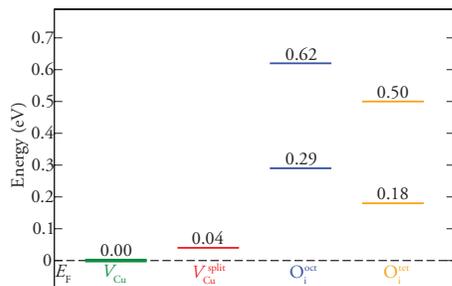
FIG. 4. Offsets of the hole SPL from the Fermi energy for the p-type defects studied using GGA+U. The Fermi energy does not represent the VBM for the oxygen interstitials.

Both O_i^{oct} and O_i^{tet} produce two distinct acceptor SPLs above the VBM, with one positioned deep in the band gap and one in the conduction band. This is again more consistent with an activated, polaronic conduction mechanism than the GGA description. The position of the higher SPL bands in the conduction band for both O_i^{oct} and O_i^{tet} is possibly an artifact of the underestimated band gap typical of GGA/GGA+U calculations.

B. Energetics and transition levels

The GGA+U calculated formation enthalpies of the defects for Cu-rich/O-poor conditions are shown in Fig. 5(a). V_{Cu} again has the lowest formation energy of $\Delta H^f(V_{Cu}, 0)$ =0.92 eV. The formation energy of V_{Cu}^{split} is $\Delta H^f(V_{Cu}^{split}, 0)$ =1.66 eV, which is significantly higher than the energy predicted using GGA. This is in contrast to the previous LDA study of Wright and Nelson[36] and the GGA/GGA+U study of Nolan and Elliott.[37] O_i^{tet} and O_i^{oct} have formation energies of 1.97 and 2.07 eV, respectively. Under Cu-poor/O-rich conditions, the formation energy of the V_{Cu} and V_{Cu}^{split} are lowered to 0.73 and 1.47 eV, with the oxygen interstitial formation energies shifted downwards to 1.59 and 1.69 eV for O_i^{tet} and O_i^{oct}, respectively. Changing to the experimental formation energies of Cu_2O and CuO, we find that only the formation energy of the oxygen interstitials are strongly affected with increases of ~0.2 eV. Again these results clearly show that the defect chemistry of Cu_2O will be dominated by copper vacancies, and as such this change in the formation energy of the oxygen interstitials is irrelevant.

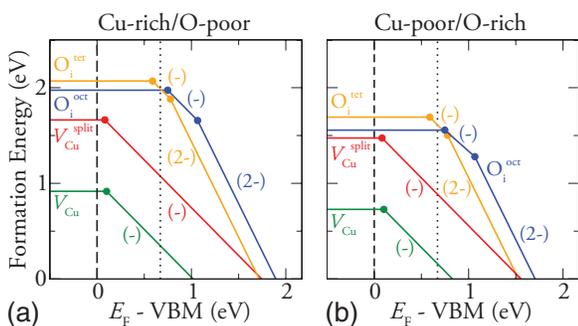TABLE II. GGA and GGA+U calculated acceptor transition levels, $\epsilon_A(q/q')$, for the p-type defects investigated. ΔE is the shift of the GGA+U transition level relative to the GGA transition level; $\Delta E = \epsilon_D^{GGA+U}(q/q') - \epsilon_D^{GGA}(q/q')$.

	V_{Cu}	V_{split}	O_i^{oct}		O_i^{tet}	
	$\epsilon_A(0/-)$	$\epsilon_A(0/-)$	$\epsilon_A(0/-)$	$\epsilon_A(-/-2)$	$\epsilon_A(0/-)$	$\epsilon_A(-/-2)$
GGA	0.01	−0.04	0.16	0.43	0.34	0.65
GGA+U	0.10	0.08	0.59	0.77	0.75	1.06
ΔE	0.09	0.12	0.43	0.34	0.31	0.41

The calculated $\epsilon(0/-)$ transition levels for V_{Cu}^{split} and V_{Cu} are 0.10 and 0.08 eV. Again, these transition levels are not in agreement with the two trap levels reported from DLTS studies.[27] The $\epsilon(0/-)$ transition levels of O_i^{oct} and O_i^{tet} are 0.59 and 0.75 eV, and the $\epsilon(-/-2)$ transition levels are 0.77 and 1.06 eV. We find that the difference in transition levels between GGA and GGA+U is not well represented by a rigid shift, particularly when comparing calculated levels for oxygen interstitials with those for copper vacancies (Table II). The transition levels for the oxygen interstitials are too deep to be associated with the hole traps observed at 0.45 eV in the DLTS studies,[27] at variance with conclusions of Raebiger et al.[38]

VII. DISCUSSION

With both GGA and GGA+U, V_{Cu} is the most energetically favorable p-type defect for Cu_2O under all growth conditions, and is therefore predicted to be the most likely source of hole carriers in Cu_2O. V_{Cu}^{split} is considerably higher in energy with both methods, and O_i^{oct} and O_i^{tet} are unfavored under all conditions and are therefore unlikely to be the source of any conductivity.

The magnitude of the formation energy of the various defects changes dramatically from GGA to GGA+U. Our GGA calculated formation energy for V_{Cu} is 0.41 eV, which is close to the GGA result of Nolan and Elliott of 0.34 eV (Ref. 37) (162 atom cell). The GGA formation energy of the V_{Cu}^{split} was found to be 1.24 eV, which is considerably higher than that of the V_{Cu}. Nolan and Elliott reported that V_{Cu}^{split} was only 0.06 eV less stable than V_{Cu} in a 48 atom cell.[37] They did not, however, report the formation energy for V_{Cu}^{split} in a 162 atom cell, but the recent study conducted by Soon et al. reported that V_{Cu}^{split} is as much as 0.31 eV less stable than V_{Cu} in a 48 atom cell also using GGA.[39] The GGA+U calculated formation energy for V_{Cu} is found to be 0.92 eV, and for V_{Cu}^{split} it is found to be 1.66 eV. Previous GGA+U (U=7 eV) calculations[37] had also found that the energy to form both V_{Cu} and V_{Cu}^{split} *increases* as you move from GGA to GGA+U. The magnitude of both vacancies from our work is less than in that study, although this is probably a consequence of the larger simulation cell used in our work and the differing U values utilized.

Neither GGA or GGA+U give SPL and $\epsilon(0/-)$ transition levels that can be interpreted as being in good agreement with experiment. The polaronic nature of Cu_2O is not correctly described by GGA for any of the p-type defects investigated; all the SPLs indicate semimetallic behavior. Indeed

FIG. 5. Formation energies for intrinsic p-type defects in Cu_2O in (a) Cu-rich/O-poor conditions and (b) Cu-poor/O-rich conditions calculated using GGA+U. The solid dots denote the transition levels $\epsilon(q/q')$. The dashed and the dotted lines indicate the position of the VBM and the CBM, respectively.

TABLE III. Localization of hole spin states on ions neighboring the copper vacancies calculated using GGA and GGA+U. For V_{Cu} this is the total spin on the six copper ions coordinated to the three-coordinate oxygens and for the V_{split} this corresponds to the spin on the tetrahedrally coordinated copper, with the spins on the four oxygens coordinated to this in parentheses.

	GGA	GGA+U
V_{Cu}	0.01	0.03
V_{split}	0.17 (0.02)	0.46 (0.05)

the weak localization effects of V_{Cu} using both GGA and GGA+U are shown in Table III, which lists the spin populations on the nearest neighbor atoms, from which it is clear that V_{Cu} does not represent a localized polaron in either methodology. The calculated transition levels for V_{Cu}^{split} are in the valence band and for V_{Cu} are so shallow as to be thermally ionized at room temperature. This is inconsistent with the deep ionization levels seen experimentally.[26,27,29] The GGA+U description of V_{Cu} is similarly inconsistent with the polaronic nature of Cu$_2$O, predicting a SPL that crosses the Fermi energy at the top of the valence band. GGA+U predicts that V_{Cu}^{split} and both O$_i^{tet}$ and O$_i^{oct}$ have distinct hole SPLs in the band gap. Although this is consistent with the experimentally noted polaronic, activated conduction,[15,16,18,35] the calculated transition levels do not agree with the positions of the deep levels seen in DLTS experiments.[27]

Comparison of the $\epsilon(0/-)$ transition levels calculated using GGA and GGA+U shows that the GGA+U results are not equivalent to the GGA transition levels plus a rigid shift, particularly when comparing oxygen interstitials with copper vacancies. This suggests that caution should be taken when interpreting results obtained from applying compensatory shifts to GGA transition levels in systems where defect states are thought to be polaronic.

A higher value of U might be expected to split off these levels even further from the VBM. As the value of U of 5.2 eV employed here closely reproduces valence band features of Cu$_2$O and CuMO$_2$ (M=Al, Cr),[46,47] it is likely that applying such a correction to the Cu $3d$ states would only be an unphysical attempt to compensate for other shortcomings in the GGA+U description for this system, and would be unjustified. An accurate description of the localized polaronic nature of p-type defects in Cu$_2$O can be achieved by hybrid functionals, which allow a degree of exact exchange to be applied to every species and not just to the Cu d states as for GGA+U. This has been shown to provide an improved description of the mixed Cu d/O p VBM and allowed the elucidation of the deep trap levels seen in DLTS studies.[62]

VIII. CONCLUSION

We have investigated p-type defects in Cu$_2$O using both GGA and GGA+U and found that V_{Cu} is the most stable defect under all conditions with both methods. Neither GGA nor GGA+U can accurately reproduce the polaronic nature of defects of Cu$_2$O, with the SPLs for V_{Cu} delocalized and crossing the Fermi level using both methods, inconsistent with the experimentally known activated hopping mechanism. Calculated transition levels for all the defects investi-

gated cannot reproduce the deep hole trap levels as seen in previous DLTS experiments. While the GGA+U description of the SPLs for V_{Cu}^{split}, O$_i^{tet}$, and O$_i^{oct}$ are improved compared to the GGA descriptions, the calculated transition levels are not in keeping with experimental results. We conclude that both GGA and GGA+U are unsuitable methods for modeling p-type defects in Cu$_2$O.

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