Deep donor state of the copper acceptor as a source of green luminescence in ZnO
J. L. Lyons, A. Alkauskas, A. Janotti, and C. G. Van de Walle

Citation: Appl. Phys. Lett. 111, 042101 (2017); doi: 10.1063/1.4995404
View online: http://dx.doi.org/10.1063/1.4995404
View Table of Contents: http://aip.scitation.org/toc/apl/111/4
Published by the American Institute of Physics
Deep donor state of the copper acceptor as a source of green luminescence in ZnO

J. L. Lyons, A. Alkauskas, A. Janotti, and C. G. Van de Walle

Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375, USA
Center for Physical Sciences and Technology, Vilnius LT-10257, Lithuania
Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716, USA
Materials Department, University of California, Santa Barbara, California 93106-5050, USA

(Received 1 May 2017; accepted 10 July 2017; published online 24 July 2017)

Copper impurities have long been linked with green luminescence (GL) in ZnO. Copper is known to introduce an acceptor level close to the conduction band of ZnO, and the GL has conventionally been attributed to transitions involving an excited state which localizes holes on neighboring oxygen atoms. To date, a theoretical description of the optical properties of such deep centers has been difficult to achieve due to the limitations of functionals in the density functional theory. Here, we employ a screened hybrid density functional to calculate the properties of Cu in ZnO. In agreement with the experiment, we find that CuZn features an acceptor level near the conduction band of ZnO. However, we find that CuZn also gives rise to a deep donor level 0.46 eV above the valence band of ZnO; the calculated optical transitions involving this state agree well with the GL observed in ZnO:Cu. [http://dx.doi.org/10.1063/1.4995404]

The properties of copper impurities in ZnO have been studied extensively since the 1960s.1–10 These investigations have partly been driven by the general interest in acceptors and potential p-type dopants in ZnO. Cu has also been intentionally doped into ZnO to give nonlinear current-voltage characteristics useful for varistors to create highly resistively doped into ZnO to give nonlinear current-voltage

FIG. 1. Local lattice configurations of copper in the (a) CuZn and (b) Cu0 charge states in ZnO. In both cases, the yellow isosurface represents the spin density and is set to 5% of the maximum.
(which partially corrects the band gap) also predicted much deeper Cu\textsubscript{Zn} levels,\textsuperscript{7} although the ultimate value depended on the details of the correction scheme. Another DFT + \( U \) study (based on GGA + \( U \)), in conjunction with PL experiments, identified a Cu\textsuperscript{3+} ion as a final state of the GL,\textsuperscript{22} but did not report transition levels.

In this work, we employ a hybrid functional to study the Cu acceptor in ZnO. Our calculations are based on the generalized Kohn-Sham scheme\textsuperscript{23} with the hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE),\textsuperscript{24,25} as implemented in the Vienna Ab-Initio Simulation Package (VASP),\textsuperscript{26} in which a fraction of exact exchange is mixed with the short-range GGA exchange potential of Perdew, Burke, and Ernzerhof (PBE).\textsuperscript{27} The mixing parameter for the Hartree-Fock potential is set to 0.36, and the screening length is set to the standard 0.2 Å\(^{-1}\), resulting in a band gap of 3.35 eV, which is in good agreement with the experimental value.\textsuperscript{28}

Although a different combination of parameters could in principle correctly describe the bulk band structure, such an exploration of the full parameter space is beyond the scope of this work. HSE has also been demonstrated to produce structural parameters that are also close to the experiment.\textsuperscript{29}

The interactions between the valence electrons and the ionic cores are described using the projector-augmented wave (PAW) method.\textsuperscript{30,31} Cu\textsubscript{Zn} calculations are performed using a 96-atom supercell, a plane-wave basis set with a cutoff of 400 eV, and a \( 2 \times 2 \times 2 \) special \( k \)-point set for integrations over the Brillouin zone. Spin polarization is explicitly included. Symmetry-breaking distortions are introduced, and atomic relaxations are consistently performed using the HSE functional. Structures are considered converged when Hellman-Feynman forces are lower than 0.02 eV/Å.

We calculate formation energies of the impurity in various charges using the well-established formalism described in Ref. 19. The formation energy of copper on the zinc site (Cu\textsubscript{Zn}) in charge state \( q \) is given by

\[
E_f^q(Cu^q_{Zn}) = E_{tot}(Cu^q_{Zn}) - E_{tot}(ZnO) + \mu_{Zn} - \mu_{Cu} + q(E_F + \epsilon_i) + \Delta^q,
\]

(1)

in which \( E_{tot}(Cu^q_{Zn}) \) is the total energy of a supercell containing a single Cu\textsubscript{Zn} \( q \) in charge state \( q \) and \( E_{tot}(ZnO) \) is the total energy of a pristine supercell. Electrons that are added or removed from the supercell are exchanged with the Fermi level \( (E_F) \) of the semiconductor host which is referenced to the VBM \( (\epsilon_i) \), and \( \Delta^q \) corresponds to a correction for the finite size of charged supercells.\textsuperscript{32,33} \( \mu_{Zn} \) and \( \mu_{Cu} \) are referenced to the energy of an atom in their respective bulk metals. Both are treated as variables that must satisfy the stability conditions

\[
\mu_{Zn} + \mu_{\text{O}} = \Delta H_f(ZnO),
\]

(2)

and

\[
\mu_{Cu} + \mu_{\text{O}} = \Delta H_f(CuO),
\]

(3)

for which \( \Delta H_f(ZnO) = -3.66 \text{ eV} \) and \( \Delta H_f(CuO) = -1.63 \text{ eV} \).\textsuperscript{34}

In Fig. 2, we plot the formation energy of Cu\textsubscript{Zn} under two conditions, Zn-rich (at which \( \mu_{Zn} = 0 \text{ eV} \)) and O-rich (at which \( \mu_{O} = 0 \text{ eV} \)). We find that Cu\textsubscript{Zn} in ZnO is most stable under O-rich conditions.

The thermodynamic transition level between charge states \( q \) and \( q' \) of the impurity is then given by the Fermi-level position at which the formation energy of the impurity in charge state \( q \) is equal to that in charge state \( q' \). In the case of Cu\textsubscript{Zn}, the \( (0/-) \) transition level (which corresponds to the ionization energy) is given by\textsuperscript{19}

\[
(0/-) = E_f^q(Cu^q_{Zn}; E_F = 0) - E_f^0(Cu^0_{Zn}).
\]

(4)

where \( E_f^q(Cu^q_{Zn}; E_F = 0) \) is the formation energy of Cu\textsubscript{Zn} when the Fermi level is at the VBM and \( E_f^0(Cu^0_{Zn}) \) is the formation energy of Cu\textsubscript{Zn} (which does not vary with the Fermi level).

This transition level represents a thermal ionization energy and should not be confused with optical transition levels, whose energies can differ considerably from ionization energies. Peak transition energies and peak widths can be estimated from configuration coordinate diagrams (as explained in Ref. 19). We also calculate full luminescence lineshapes including vibronic coupling using the procedure outlined in Ref. 35.

Cu acceptors incorporating on the Zn site have a deficit of one electron relative to Zn. In the negative charge state (i.e., with all levels filled), Cu\textsubscript{Zn} produces levels deep in the band gap which are composed of Cu 3\( d \) states. When an electron is removed from the system to create the neutral charge state, the resulting hole is localized mainly on the Cu impurity (from a projection onto the PAW spheres, we estimate that the unpaired electron has a 95% Cu 3\( d \) character). The nature of this state is also illustrated by the spin density in Fig. 1(a); it is localized mostly onto Cu\textsubscript{Zn}, with the 3\( d \) character, with a small fraction of the spin density occurring on a neighboring O atom. We calculate the \( (0/-) \) transition level to be 3.27 eV above the VBM.

Removal of a second electron leads to the Cu\textsubscript{Zn} charge state, which has a total magnetic moment of 2 (i.e., two unpaired electrons). As can be seen in Fig. 1(b), this state
has a strong O 2p character in addition to Cu 3d (we estimate the character to be 60% Cu 3d and 40% O 2p). The involvement of O-2p states is consistent with the positive charge state being stable only for Fermi levels near the VBM as shown in Fig. 2; we calculate that the (+0/) transition level occurs at 0.46 eV above the VBM. A similar near-VBM deep-donor transition level was previously reported for CuZn in ZnO.7

Various charge states of CuZn exhibit very different local lattice relaxations. For CuZn+, all nearest neighbor O atoms relax outward, one by 6% and the other three by 5% of the bulk bond length. In contrast, for CuZn0, one neighboring O atom relaxes inwards by 2% of the bulk bond length, another moves outward by 5%, and the other two remain almost unchanged. For CuZn–, all neighboring O atoms move inwards, three by 6% of the bulk bond length, and one by 3%. In all cases, the Cu atom remains in the vicinity of the Zn substitutional site.

We now examine optical transitions related to CuZn. The configuration coordinate diagrams shown in Fig. 3 address both recombinations of a hole with the – charge state and of an electron with the + charge state. The large difference in atomic configurations between the three CuZn charge states gives rise to sizeable relaxation energies, causing the peak energies of the optical transitions to be very different from the thermodynamic transition levels (which determine the ZPL) and leading to broad PL bands. For the processes related to the (0–/) level [Fig. 3(a)], the absorption peak (to lift an electron out of the VBM and make the impurity negatively charged) occurs at 3.85 eV, with a relaxation energy of 0.48 eV above the ZPL. A similar near-VBM deep-donor transition level was previously reported for CuZn in ZnO.7

For the emission process (involving the electron on the + charge state), the relaxation energy gives rise to a broader PL signal peaking at 2.54 eV, while the (+0) transition gives rise to a narrower PL signal peaking at 2.39 eV. Since our calculations are based on the effective one-dimensional configuration-coordinate picture,35 they yield the overall shape of the luminescence band but not its detailed fine structure.

The calculated luminescence lineshapes for the optical transitions described in Fig. 3 are shown in Fig. 4. We compare these with the experimental spectra observed in Ref. 36 by normalizing the luminescence intensities. The (+0) optical transition gives rise to a broad PL signal peaking at 2.54 eV, while the (+0) transition gives rise to a narrower PL signal peaking at 2.39 eV. Since our calculations are based on the effective one-dimensional configuration-coordinate picture,35 they yield the overall shape of the luminescence band but not its detailed fine structure.

The calculated vibrational parameters37 for the luminescence lineshapes are listed in Table I. The calculated vibrational frequencies for the (+0) and (+0) transitions are similar and also close to frequencies of the structured GL observed in ZnO (64 meV in Ref. 36). The smaller Huang-Rhys factor of the (+0) transition is consistent with our expectation that this level gives rise to the structured GL observed in ZnO:Cu (since a smaller Huang-Rhys factor leads to more structured lineshapes38). We note that the Huang-Rhys factors of CuZn+ are smaller than those we have previously calculated for other acceptors in ZnO (which have S > 15).35,39

Finally, we note that our proposed mechanism for the Cu-related GL is distinct from that of Dingle.2 The mechanism that we propose is based on the (+0) transition level of CuZn [Fig. 1(b)], which had not been previously considered as a source for the GL. The initial state of this transition features hole localization onto O nearest neighbors, similar to what was proposed in Ref. 2. However, the transition we propose here is based on the CuZn+ charge state, while Dingle focused on an excited state of CuZn0. Our attempts to stabilize such an excited state for CuZn0 were not successful. We also note that CuZn+ was recently proposed to be the final state of the GL in ZnO22 in a combined experimental and theoretical study. Reference 22 did not provide information about transition levels but focused on the doublet structure, i.e., a ZPL

![FIG. 3. Calculated configuration coordinate diagrams for CuZn in ZnO for (a) the recombination of a hole into the (0–/) level and (b) the recombination of an electron into the (+0/) level.](image1)

![FIG. 4. Calculated luminescence lineshapes for the (+0) transition (in red) and the (+0) transition (in blue) for CuZn, compared with the spectra observed (dotted black line) and fitted (solid black line) in Ref. 36.](image2)
splitting of 0.11 meV (which was attributed to isotopic effects by Dingle). Investigating such a fine structure is beyond the scope of our present work.

In conclusion, we have determined the properties of the copper acceptor in ZnO using the HSE hybrid functional. We find that Cu_{Zn} has an acceptor level near the CBM of ZnO, in agreement with experiment. However, we find that Cu_{Zn} also gives rise to a deep donor level 0.46 eV above the ZnO, in agreement with experiment. However, we find that Cu_{Zn} has an acceptor level near the CBM of ZnO, in agreement with experiment. However, we find that Cu_{Zn} also gives rise to a deep donor level 0.46 eV above the VBM. Electron recombination into this level is found to give rise to 2.31 eV green luminescence in ZnO within our 1D configuration-coordinate diagram. Our calculated full luminescence lineshape is in excellent agreement with the experiment.

The work at UCSB was supported by the U. S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) under Award No. DE-SC0010689. A.A. acknowledges support by Marie Sklodowska-Curie Action of the European Union (project NITRIDE-SRH, Grant No. 657054). Computational resources were provided by the Center for Scientific Computing at the California Nanosystems Institute and Materials Research Laboratory (an NSF Materials Research Science and Engineering Center, DMR-1121053) (NSF CNS-0960316) and by the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility under Contract No. DE-AC02-05CH11231. J.L.L. acknowledges support from the Office of Naval Research through the Naval Research Laboratory’s Basic Research Program, and computational support from the DoD Major Shared Resource Center at AFRL.


~\textsuperscript{34}CRC Handbook of Chemistry and Physics, 84th ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 2003).


