Defect energy levels and persistent luminescence in Cu-doped ZnS

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Zinc sulfide (ZnS) based materials are widely used in many applications. Yet, due to a lack of detailed knowledge of defect energy levels, the electrical properties and luminescence mechanisms in the materials still give rise to debate. Here, we report a first-principles study of native point defects and impurities in zincblende ZnS using hybrid density-functional calculations. We find that cation and anion vacancies and antisite defects introduce deep defect levels in the band gap and can act as donors or acceptors depending on the position of the Fermi level. The substitutional impurity CuZn acts as a deep acceptor and thus does not contribute to p-type conductivity. Substitutional impurities AlZn and Cl, on the other hand, are shallow donors. More importantly, we identify the isolated CuZn as a source of the green luminescence observed in ZnS-based phosphors and CuZn–AlZn and CuZn–Cl complexes as sources of blue luminescence. The materials may have both green and blue emissions with the relative intensity dependent on the ratio between the isolated defect and defect complex concentrations, which is also consistent with experimental observations.

I. INTRODUCTION

ZnS has been of great interest for various applications, including display technologies, luminescent devices, and solar cells. ZnS phosphors, for example, have a long history, dating back to the discovery of persistent luminescence in ZnS crystals by Théodore Sidot in 1866. It is now believed that copper impurities in Sidot’s crystals were responsible for the observed phenomenon. Zincblende-based phosphors can emit light in the blue, green, and red spectral regions, depending on the presence of certain native point defects and (intentional or otherwise) impurities. Although the materials have been widely used, the structure of defect centers and the associated luminescence mechanisms are still not well understood.

On the theory side, a number of first-principles studies of native defects and impurities—hereafter commonly referred to as defects—in zincblende (cubic) or wurtzite (hexagonal) ZnS have been reported. However, only limited information on Cu-related defects is available. Moreover, some of these studies are based on density-functional theory (DFT) within the local-density (LDA) or generalized gradient (GGA) approximation and/or the DFT+U extension where U is the on-site Coulomb correction which are known to have limited predictive power. Yet an accurate determination of defect levels in the band gap caused by these defects is crucial to understanding the luminescence of Cu-doped ZnS materials.

Here, we report a first-principles study of defects and doping in zincblende ZnS using a hybrid DFT/Hartree-Fock approach. In addition to native point defects such as cation and anion vacancies and antisites, we consider substitutional Cu, Al, and Cl impurities and their complexes. Copper, aluminum, and chlorine are chosen because they are often present in ZnS phosphors as dopants and/or unintentional impurities. The focus of this work is on determining energy levels in the band-gap region caused by the defects and identifying defect centers in Cu-doped ZnS phosphors that are responsible for the green and blue luminescence observed in experiments.

II. METHODS

Our calculations are based on DFT with the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional as implemented in the Vienna Ab Initio Simulation Package (VASP). The Hartree-Fock mixing parameter and the screening length are set to 0.32 and 10 Å, respectively. The Zn 3d10s2 and S 3s3p4 electrons are treated as valence electrons whereas the inner electrons as core states within the projector augmented wave method. The plane-wave basis-set cutoff is 400 eV and spin polarization is included. In these calculations, the band gap (Eg) of zincblende ZnS is 3.66 eV, a direct gap at Γ, almost identical to the experimental value (3.7 eV). Defects are modeled using a 2×2×2 (64-atom) supercell and a 2×2×2 Monkhorst-Pack k-point mesh for the integrations over the Brillouin zone. In the defect calculations, the lattice constant is fixed to the calculated bulk value (5.42 Å) but all the internal coordinates are relaxed. For comparison, the experimental lattice constant is 5.41 Å.

A general native defect, impurity, or defect complex X in charge state q (with respect to the host lattice) is characterized by its formation energy, defined as:

\[ E^f(X^q) = E_{\text{tot}}(X^q) - E_{\text{tot}}(\text{host}) - \sum_i n_i \mu_i + q(E_v + \mu_e) + \Delta q, \]  

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where $E_{\text{tot}}(X^q)$ and $E_{\text{tot}}(\text{host})$ are the total energies of a supercell containing the defect and the defect-free supercell. $\mu_i$ is the atomic chemical potential, accounting for the species $i$ either added ($n_i > 0$) or removed ($n_i < 0$) from the supercell to form the defect and representing the chemical reservoir with which the species is exchanged. The chemical potentials of Zn and S are referenced to the total energy per atom of bulk Zn and S, respectively, and vary over a range determined by the calculated formation enthalpy of ZnS: $\mu_{\text{Zn}} + \mu_{\text{S}} = \Delta H(\text{ZnS}) = -1.93$ eV; $\mu_{\text{Zn}} = 0$ ($\mu_{\text{S}} = 0$) corresponds to the extreme Zn-rich (S-rich) condition. The chemical potentials of Cu, Al, and Cl are assumed to be limited by the formation of bulk Cu (under the Zn-rich condition) or CuS (under the S-rich condition), Al$_2$ZnS$_4$, and ZnCl$_2$, respectively. $\mu_e$ is the electronic chemical potential, i.e., the Fermi level, which is the energy of the reservoir for electron exchange and, as a convention, referenced to the valence-band maximum (VBM) of the host ($E_v$). Finally, $\Delta^q$ is a correction term to align the electrostatic potentials of the bulk and defect supercells and to account for finite-size effects on the total energies of systems with charged defects.$^{18}$

In the calculation of $\Delta^q$, a total static dielectric constant of 8.18 is used. This dielectric constant is calculated as the sum of the electronic contribution (4.67, obtained in calculations using the HSE functional) and the ionic contribution (3.51, obtained with the Perdew, Burke and Ernzerhof version$^{12}$ of GGA). For comparison, the experimental static dielectric constant is reported to be 8.3.$^4$

From defect formation energies, one can calculate the thermodynamic transition level between charge states $q_1$ and $q_2$ of a defect, $\epsilon(q_1/q_2)$, defined as the Fermi-level position at which the formation energy of the defect in charge state $q_1$ is equal to that in charge state $q_2$, i.e.,$^{17,19}$

$$
\epsilon(q_1/q_2) = \frac{E_f(X^{q_1}) - E_f(X^{q_2})}{q_2 - q_1}.
$$

(2)

This level would be observed in experiments where the defect in the final charge state $q_2$ fully relaxes to its equilibrium configuration after the transition. The optical transition level $E_{\text{opt}}^{q_1/q_2}$ is defined similarly but with the total energy of the final state $q_2$ calculated using the atomic configuration of the initial state $q_1$. Clearly, both the thermodynamic and optical transition levels are independent of the choice of the atomic chemical potentials.

### III. RESULTS AND DISCUSSION

We begin with an examination of native point defects in zincblende ZnS. Figure 1 shows the calculated formation energies of select native defects. In general, these defects are amphoteric, acting as donors or acceptors depending on the position of the Fermi level. The sulfur vacancy, $V_S$, is a deep donor with the transition level from the $-2$ to $0$ charge states, $\epsilon(-2/0)$, at 2.03 eV above the VBM. It can also behave as an acceptor under n-type conditions; the $\epsilon(0/-)$ level is at 0.37 eV below the conduction-band minimum (CBM). In the $V_S^-$ defect configuration, the electron is delocalized over the four nearest Zn neighbors. The zinc vacancy, $V_{\text{Zn}}$, on the other hand, behaves as a deep acceptor; the $\epsilon(+/-0)$ level is at 1.14 eV above the VBM and the $\epsilon(0/+)$ level is at 0.47 eV. The defect can also act as a donor in the range of Fermi-level values closer to the VBM where it can be stable as $V_{\text{Zn}}^+$. The $\epsilon(+/-0)$ level is at 0.33 eV above the VBM. In the $V_{\text{Zn}}^+$ configuration, the electron hole is delocalized over the four nearest S neighbors. Similarly, antisite defects $S_{\text{Zn}}$ and $S_{\text{Zn}}$ behave as deep donors (acceptors) for Fermi-level values closer to the VBM (CBM). $S_{\text{Zn}}$ introduces energy levels at 1.35 eV above the VBM and 1.39 eV below the CBM; $S_{\text{S}}$ has levels at 0.62, 1.01, and 1.46

![FIG. 1. Formation energies of select native defects in ZnS under the extreme (a) Zn-rich and (b) S-rich conditions, plotted as a function of the Fermi level from the VBM to the CBM.](image)

![FIG. 2. Formation energies of select impurities in ZnS under the extreme (a) Zn-rich and (b) S-rich conditions, plotted as a function of the Fermi level from the VBM to the CBM.](image)
eV below the CBM. The energy levels in the band-gap region introduced by the native point defects can act as electron or hole traps and likely play a role in the persistent luminescence observed in ZnS-based materials.

Under both Zn-rich and S-rich conditions, the dominant native defect in ZnS is $V_{\text{Zn}}^2$ under p-type conditions or $Zn_{\text{Zn}}^2$ under n-type conditions. The formation energies of $V_{\text{Zn}}^{2+}$ and $Zn_{\text{Zn}}^{2+}$ are even negative in the range of Fermi-level values near the VBM under the Zn-rich condition, indicating that these defects are strong charge-compensating centers. In that context, the S vacancy, for example, would “pin” the Fermi level at least $\sim$1 eV above the VBM. Under the S-rich condition, the formation energy of $V_{\text{Zn}}^-$ is negative for Fermi-level values near the CBM: the Zn vacancy would thus “pin” the Fermi level at least $\sim$1 eV below the CBM. Given the defect landscape of ZnS, n-type (p-type) doping should be carried out under Zn-rich (S-rich) conditions to avoid charge compensation caused by native defects. In general, our results for zinblende ZnS are similar to those for wurtzite ZnS previously reported by Varley and Lordi.

Next, we examine the effects of impurities, intentionally or otherwise. Figure 2 shows the calculated formation energies of ZnS doped with Cu, Al, or Cl, or co-doped with (Cu,Al) or (Cu,Cl). The substitutional Cu impurity, $\text{Cu}_{\text{Zn}}^0$, is stable as $\text{Cu}_{\text{Zn}}^0$ (i.e., Cu$^{2+}$) under p-type conditions or $\text{Cu}_{\text{Zn}}^-$ (i.e., Cu$^{+}$) under n-type conditions and introduces a deep acceptor $\epsilon(0/-)$ level at 1.22 eV above the VBM. This calculated value is in excellent agreement with the experimental one (1.25 eV) reported in the literature. The result also indicates that Cu$^{2+}$ does not contribute to p-type conductivity, at least at low doping levels. The atomic structure of $\text{Cu}_{\text{Zn}}^0$ is presented in Fig. 2(a). The Cu impurity is tetrahedrally coordinated with sulfur. The Cu–S bond length is 2.333 Å ($\times$4), compared to 2.345 Å of the Zn–S bonds in bulk ZnS. Regarding Al and Cl, they are stable as $\text{Al}_{\text{Zn}}^+$ and $\text{Cl}_{\text{S}}^-$, respectively, over the entire range of Fermi-level values. In this case, the defects donate one electron to the host and become ionized; the electron then transfers to the CBM. $\text{Al}_{\text{Zn}}^+$ and $\text{Cl}_{\text{S}}^-$ are thus shallow donors, which is consistent with experimental observations.

Note that the n-type conductivity is usually observed in as-grown single crystals of ZnS could be due to the presence of unintentional $\text{Al}_{\text{Zn}}^+$ or $\text{Cl}_{\text{S}}^-$ impurities. In the $\text{Al}_{\text{Zn}}^+$ configuration, the Al–S bond length is 2.727 Å ($\times$4), whereas in $\text{Cl}_{\text{S}}^-$ the local lattice environment is slightly more distorted with Cl–Zn bonds of 2.559 Å ($\times$3) and 2.563 Å.

The above impurities, especially those with oppositely charged defect configurations, can form complexes. Explicit calculations are therefore carried out for $\text{Cu}_{\text{Zn}}^-$–$\text{Al}_{\text{Zn}}^+$, $\text{Cu}_{\text{Zn}}^-–\text{Cl}_{\text{S}}^-$, and $\text{Cu}_{\text{Zn}}^0–\text{Cl}_{\text{S}}^-$ under n-type conditions or $\text{Cu}_{\text{Zn}}^0–\text{Al}_{\text{Zn}}^+$ under p-type conditions. The $\epsilon(+/0)$ level is at 0.73 eV above the VBM for $\text{Cu}_{\text{Zn}}^-–\text{Al}_{\text{Zn}}^+$ and 0.66 eV for $\text{Cu}_{\text{Zn}}^-–\text{Cl}_{\text{S}}^-$. The defect level is thus shifted, compared to that in the isolated $\text{Cu}_{\text{Zn}}^-$, due to defect–defect interaction, a phenomenon also observed for defects in other materials. Figures 3(b) and 3(c) show the structure of $\text{Cu}_{\text{Zn}}^0–\text{Al}_{\text{Zn}}^+$ and $\text{Cu}_{\text{Zn}}^0–\text{Cl}_{\text{S}}^-$, respectively. In $\text{Cu}_{\text{Zn}}^-–\text{Al}_{\text{Zn}}^+$, the Cu–S bond lengths are 2.240 Å, 2.284 Å, and 2.376 Å; the Al–S bond lengths are 2.345 Å ($\times$2), 2.322 Å ($\times$2), 2.240 Å, and 2.284 Å. The binding energy is 0.57 eV with respect to isolated $\text{Cu}_{\text{Zn}}^-$ and $\text{Al}_{\text{Zn}}^+$ (i.e., under n-type conditions). In $\text{Cu}_{\text{Zn}}^-–\text{Cl}_{\text{S}}^-$, the Cu–S bond length is 2.528 Å ($\times$3) and the Cl–Zn bond length is 2.471 Å ($\times$3); the Zn–Cl distance is 2.876 Å. The binding energy is 0.77 eV with respect to isolated $\text{Cu}_{\text{Zn}}^-$ and $\text{Cl}_{\text{S}}^-$ (also under n-type conditions). In both cases, the defect centers have lower symmetry than the host lattice. The binding energies are small, which suggests that the concentration of the complexes is likely much smaller than that of their isolated constituents when the material is prepared under thermodynamic equilibrium conditions. The defect complexes are even less stable under p-type conditions: the binding energy of $\text{Cu}_{\text{Zn}}^-–\text{Al}_{\text{Zn}}^+$ is 0.08 eV with respect to isolated $\text{Cu}_{\text{Zn}}^0$ and $\text{Al}_{\text{Zn}}^+$ and that of $\text{Cu}_{\text{Zn}}^-–\text{Cl}_{\text{S}}^-$ is 0.21 eV with respect to isolated $\text{Cu}_{\text{Zn}}^0$ and $\text{Cl}_{\text{S}}^-$.

Given the calculated defect levels, the Cu-related defects can play a role in high-energy luminescent transitions in ZnS. An electron previously excited from the valence band to the conduction band or one at the shallow donor level such as that associated with $\text{Al}_{\text{Zn}}^+$ or $\text{Cl}_{\text{S}}^-$ in n-type ZnS, for example, can recombine with the empty

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**FIG. 3. Structure of Cu-related defects in zincblende ZnS:** (a) $\text{Cu}_{\text{Zn}}^0$, (b) $\text{Cu}_{\text{Zn}}^-–\text{Al}_{\text{Zn}}^+$, i.e., a complex of $\text{Cu}_{\text{Zn}}^-$ and $\text{Al}_{\text{Zn}}^+$, and (c) $\text{Cu}_{\text{Zn}}^-–\text{Cl}_{\text{S}}^-$, i.e., a complex of $\text{Cu}_{\text{Zn}}^-$ and $\text{Cl}_{\text{S}}^-$. Large (gray) spheres are Zn and small (yellow) spheres are S.
defect state of the isolated Cu_{Zn}^{0}, resulting in a Cu_{Zn}^{0} \rightarrow Cu_{Zn}^{+} transition. The corresponding peak emission energy is \( E_g - E_{opt}^{0/0} = 2.28 \text{ eV} \), which is in the green region of the spectrum, with a relaxation energy of 0.16 eV; here, \( E_{opt}^{0/0} \) is given by the formation-energy difference between Cu_{Zn}^{+} and Cu_{Zn}^{0}, both in the lattice configuration of the initial configuration; see also Sec. II. For the Cu_{Zn} –Al_{Zn} and Cu_{Zn} –Cl_{S} complexes, the peak emission energies associated with the transition from the + state to the neutral state is \( E_g - E_{opt}^{+/0} = 2.79 \text{ eV} \) and 2.81 eV with relaxation energies of 0.14 eV and 0.20 eV, respectively. Both the energies are thus in the blue region of the spectrum. The isolated Cu_{Zn} is therefore a source of green luminescence in Cu-doped ZnS phosphors and Cu_{Zn} –Al_{Zn} and Cu_{Zn} –Cl_{S} complexes are sources of green luminescence. As indicated above, the emission in all these cases is assumed to take place from the CBM to the (optical) transition level of the defect centers.

The persistence of the luminescence observed in ZnS-based phosphors\textsuperscript{1} could be due to electron trapping mediated by native defects. An electron excited from the valence band to the conduction band, for example, can be trapped in one of the defect levels \( V_d \) and \( Z_d \) introduce below the CBM (see Fig. 1). The electron can then be released back to the conduction band through some detrapping mechanism (e.g., thermal activation) and participate in the optical transitions discussed above.

Note that in the (Cu,Al) and (Cu,Cl) doping, it is likely that both the isolated defects and defect complexes are present. As a result, the ZnS-based materials can exhibit both green and blue luminescence with different intensities. The concentration ratio between the isolated Cu_{Zn} and the Cu_{Zn} –Al_{Zn} or Cu_{Zn} –Cl_{S} complex expected to depend on the Cu/Al or Cu/Cl ratio in the environment as well as other synthesis conditions. Experimentally, Chen et al.\textsuperscript{22} for example, found that the green (blue) emission is dominant at low (high) Cu concentrations. The observation can be understood as the following: At low Cu doping levels, the probability of Cu being close to the co-dopant (Al or Cl) is low; i.e., Cu is present in the material predominantly as the isolated Cu_{Zn}. The probability of Cu being close to Al or Cl is, however, high at high Cu doping levels; as a result, Cu can be present predominantly in the defect complex form, Cu_{Zn} –Al_{Zn} or Cu_{Zn} –Cl_{S}. It is the defect-defect interaction within the defect complex that causes the shift from green to blue in the luminescence of these doped ZnS materials.

IV. CONCLUSIONS

We have investigated select native point defects and impurities in zincblende ZnS using hybrid density-functional calculations. Cation and anion vacancies and antisite defects are found to introduce deep defect levels in the band-gap region and act as donors or acceptors depending on the position of the Fermi level. The Al and Cl impurities act as shallow donors whereas the Cu-related defects introduce deep defect levels. Most importantly, we identify the isolated Cu_{Zn} as a source of green luminescence in ZnS-type phosphors and Cu_{Zn} –Al_{Zn} and Cu_{Zn} –Cl_{S} complexes are sources of blue luminescence.

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