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Redirecting focus in $CuInSe_2$ research towards selenium-related defects

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Density-functional-theory calculations have often been used to interpret experimental observations of defects in $CuInSe_2$ (CIS). In this work, we bring back under scrutiny conclusions drawn from earlier calculations employing the (semi)local-density approximation. We present hybrid-functional results showing that copper- or indium-related defects such as V_{Cu} or In_{Cu} do not create charge transition levels within the band gap in CIS. Instead, deep levels in CIS can only arise from selenium-related defects, which act as recombination centers in this material.

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I. INTRODUCTION

The electronic properties arising from intrinsic point defects need to be understood when pursuing higher conversion efficiencies for the solar-cell absorber material $CuInSe_2$ (CIS). Besides creating charge carriers through self-doping, the defects also bring about detrimental effects such as charge carrier recombination and Fermi level pinning. A total of twelve intrinsic defects can exist in the CIS chalcopyrite lattice, and they may play a role in these phenomena either on their own or as a cluster of multiple point defects. However, experimental techniques have so far not allowed directly linking particular defects to specific electronic properties of the material.[1,2] Consequently, defect identification in CIS remains at a speculative stage.

In lack of direct evidence, the experimental development of CIS solar cells has relied on trial and error, and conclusions have been drawn from indirect observations which completely depend on interpretation. For instance, regarding self-doping in this material, the observation that Cu-poor material is p type has led to expect that copper vacancies are responsible for p-type conductivity in CIS. Similarly, it has been thought that, since Se-rich CIS is p type whereas Se-poor CIS is n type, selenium vacancies would cause n-type conductivity.[3,4]

Additional help for interpreting experimental results has been sought from theoretical first-principles calculations already for the past 15–20 years. The calculations have been used to study defect formation energies in order to single out energetically most favorable defects, and to obtain charge transition levels that could be compared with experimental ionization levels. Early theoretical studies[5–9] have highlighted the role of several copper- and indium-related defects: V_{Cu} and In_{Cu} as well as some of their complexes have been suggested to have particularly low formation energies among the considered defects, and are predicted to exist in CIS samples in substantial quantities. The charge transition levels corresponding to these defects have been computed and related to experiment, reinforcing the interpretation of V_{Cu} as a p-type acceptor, and bringing forth new candidates for donor-type defects, notably In_{Cu}.[7] It should be noted that all possible point defects have not been systematically studied; even the most thorough and cited report published on the topic[5] ignored selenium-related defects, whose significance, however, has been acknowledged elsewhere.[4]

All along, theoretical calculations have pointed the direction where experimentalists should look, yet the basis of these earlier calculations is not solid, judging by what is known today, and should be brought under critical evaluation. At the time when these studies were conducted, until very recently, state-of-the-art defect calculations were performed with density-functional theory (DFT) and (semi)local-density approximations. The local-density approximation (LDA) inherently underestimates semiconductor band gaps, and in materials with strongly localized Cu d orbitals, such as CIS, it can even lead to a vanishing band gap. Uncertainties related to charge transition level positions due to the band gap underestimation were often tried to be removed by applying *a posteriori* corrections that could, for instance, stretch out the gap up to its experimental value. Their reliability has been questioned since they have not shown consistent improvement over plain LDA results.[10] This is one of the reasons why the speculative assignments of defects to experimentally observed defect levels should be treated with great caution. Indeed, the agreement between theory and experiment for this material has not been satisfactory, and the calculations have been criticized for not reproducing experimental results.[2]

Only recently methods overcoming the band gap problem have become feasible for wider use in defect studies. For instance, the local-density exchange-correlation functional can be replaced by a hybrid functional such as the Heyd-Scuseria-Ernzerhof (HSE) functional.[11] HSE takes part of the exchange energy from a semilocal Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) functional and part from exact exchange, thereby describing localized orbitals more correctly than (semi)local-density functionals.[12] Hybrid functionals have been shown to open up the band gap of CIS,[13–16] and are expected to reliably shed light on the defect structure of CIS.

In this work, we take a fresh look at defects in CIS by employing the range-separated hybrid functional HSE06.[11] We go systematically through the Kohn-Sham band structures of the twelve intrinsic point defects that are feasible in the chalcopyrite lattice as well as some of their complexes. Contrary to common belief, we find that copper- or indium-related defects cannot produce charge transition levels within the CIS band gap. Instead, the experimentally observed ionization levels can only arise from selenium-related defects: selenium antisites, interstitials, or any point defect located on the selenium sublattice. Therefore, particular attention should be paid to selenium-related defects when attempting to reduce charge carrier recombination in CIS solar cells.

II. COMPUTATIONAL DETAILS

The calculations in this work have been performed with the plane-wave code VASP[17,18] using the projector-augmented wave (PAW) method.[19,20] The plane-wave basis set has been truncated with a cutoff energy of 400 eV. The HSE06 functional has been used with a fraction α of 0.25 of exact exchange and the range-separation parameter ω equal to 0.20 1/Å. The defect has been embedded into a supercell consisting of 64 atoms (unless otherwise mentioned), and the system has been allowed to relax until the forces on each atom fell below 0.01 eV/Å. The Brillouin zone has been sampled with $2\times2\times2$ k points.

CIS crystallizes in the chalcopyrite structure, which can be derived from the zinc-blende structure by occupying the cation sites alternatingly with Cu and In atoms.[2] The first-nearest-neighbor shell around each Cu and In atom consists of four Se atoms, while Se is coordinated by two Cu and two In atoms.

In this work, all possible intrinsic defects in the chalcopyrite lattice have been systematically studied in different charge states. These defects include the vacancies (V_{Cu}, V_{In}, V_{Se}), interstitials ($\mathrm{Cu_i}$, $\mathrm{In_i}$, $\mathrm{Se_i}$), and antisites ($\mathrm{Cu_{In}}$, $\mathrm{Cu_{Se}}$, $\mathrm{In_{Cu}}$, $\mathrm{In_{Se}}$, $\mathrm{Se_{Cu}}$, $\mathrm{Se_{In}}$). In addition, two defect complexes (V_{Cu}-V_{Se}, $\mathrm{In_{Cu}}$-$2V_{\mathrm{Cu}}$) have been considered which are likely to exist in CIS according to previous theoretical studies.[5,6]

For each of these defects, the Kohn-Sham band structure has been computed. The band gap regions have been studied attentively to detect the presence of defect-induced single-particle levels. A defect-induced level lying within the Kohn-Sham band gap region is a necessary though not sufficient condition for a transition between two charge states to take place. The quantitative value for a charge transition level must be calculated from total-energy differences. The Kohn-Sham eigenvalues cannot thus be directly compared to experimental spectra, unlike total-energy differences, yet they provide an important qualitative view of the electronic levels. Therefore, the Kohn-Sham levels should be studied to gain an understanding of the possible stable charge states of the defect before proceeding with total-energy calculations[21]—unfortunately, this step is sometimes overlooked, leading to unphysical results.

The analysis of the Kohn-Sham eigenvalues has been supplemented with local densities of states (LDOS) and partial charge densities demonstrating the degree of localization of a suspected defect-induced level. This is particularly important in the case of levels lying in the proximity of the gap edges, whose positioning can be disturbed by inaccurate exchange-correlation functionals (such as LDA) or finite-size effects. If no defect-induced single-particle levels appear in the Kohn-Sham gap or close to it, we can conclude that the defect will be stable in only one charge state, and therefore it will not have transition levels within the gap.

In defects that exist in multiple charge states, the corresponding Kohn-Sham band structures may undergo qualitative changes. The occupation of the states, which depends on the charge state, dictates the atomic relaxation around the defect. Since the atomic structure of a defect is closely related to its electronic structure, strong lattice relaxation can cause the defect-induced single-particle levels to shift. For this reason, the Kohn-Sham band structure should be investigated in several charge states in order to obtain a complete view of the electronic structure of the defect.

As a technical detail of the calculations, it should be estimated to what extent the settings chosen for the hybrid functional could affect the results. In this work, the default values for α and ω derived from theory have been employed, which result in a band gap of 0.86 eV, not fully reproducing the experimental CIS band gap of 1.04 eV.[22] However, for charge transition levels obtained from total-energy differences, it has been shown that changing these parameters within a reasonable range does not affect the results qualitatively.[23] Also, the settings that have been employed in this work give very similar formation energies for the copper vacancy as another study where the parameters were adjusted to reach the experimental band gap.[14] This shows that, at least in the considered range, the outcome does not depend on the detailed values of the parameters.

It should be emphasized that the aim of this work is to describe the fundamental nature of the intrinsic defects in CIS instead of assigning experimentally observed ionization levels to some specific defect structures. Such a type of analysis would ideally require careful consideration of defect energetics, kinetics, and binding, and is beyond the scope of this work.

III. RESULTS AND DISCUSSION

The Kohn-Sham band structures for selected defects are presented in Fig. 1. Regarding the cation defects located on the cation sublattice ($\mathrm{Cu_{In}}$, $\mathrm{In_{Cu}}$, V_{Cu}, V_{In}), it can be clearly seen that none of them yields single-particle levels in or near the band gap. Each of these defects can therefore exist in only one stable charge state corresponding to the fully occupied valence band. The lattice relaxation around each of these defects is isotropic, with the magnitude determined by the size mismatch between Cu and In.

It appears that replacing copper with indium or vice versa, leading to the creation of antisites, does not alter the electronic structure of CIS: the defect always succeeds in recovering the valency of the site that it is occupying. For Cu, the nominal valency is 1, whereas for In, it is 3. As a result, Cu attracts two extra electrons when substituting In (the stable charge state for $\mathrm{Cu_{In}}$ is 2−), and In donates two electrons when replacing Cu (the stable charge state for $\mathrm{In_{Cu}}$ is 2+). Both of them act as compensating defects in the material. The vacancies attract extra electrons, with 1− being the stable charge state for V_{Cu} and 3− for V_{In}, as was already concluded in our previous work.[16]

The cation interstitials (Cu_i and In_i) can occur on several distinct sites in the chalcopyrite lattice. The octahedral

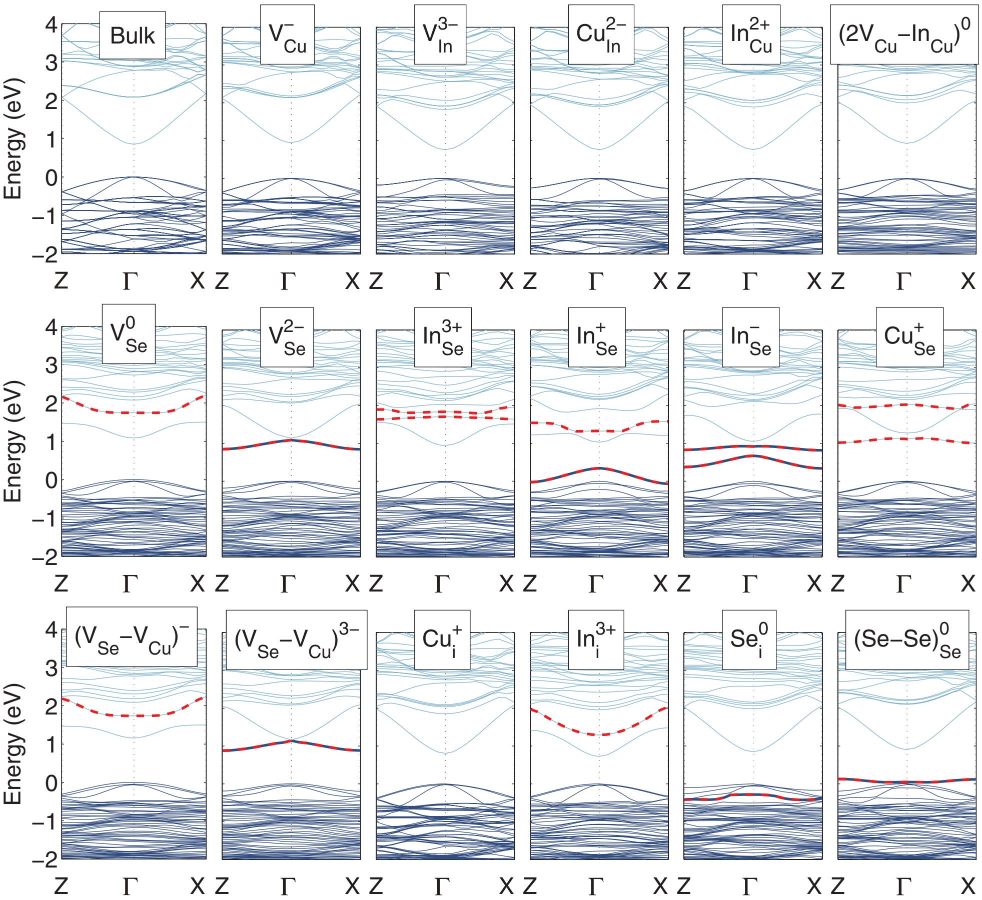


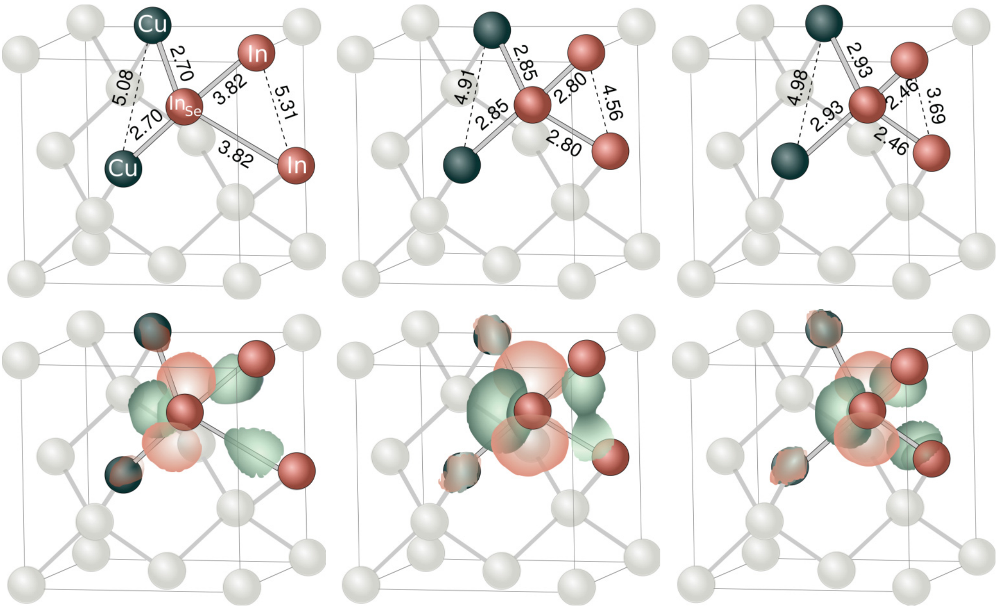
FIG. 1. (Color online) Band structures for bulk CIS and various defects. The occupied levels are drawn in dark blue and the unoccupied levels in light blue. The dashed red lines illustrate the defect-induced levels compared to the bulk band structure in each case.

configuration was found to be energetically most favorable for both interstitials and has thus been considered in the following. Similar to the other cation-type defects, the cation interstitials do not induce defect levels into the band gap according to Fig. 1. However, In_i shows a level lying right above the conduction-band minimum (CBM), which is a localized state according to the partial charge density analysis. In order to make sure that this level truly lies in the CBM and its position is not an artifact of finite-size effects, the calculation was repeated in a larger, 144-atom supercell, with the same qualitative outcome. The cation interstitials act as compensating donors, with Cu_i donating one and In_i three electrons, resulting in stable charge states of Cu_i^{+} and In_i^{3+}.

Unlike in earlier studies,[5–9] we find no defect-induced levels and, consequently, no charge transition levels corresponding to the copper- or indium-related defects. The earlier studies have been conducted within the LDA formalism and, contrary to our work, have required the application of *a posteriori* correction schemes to deal with the band gap underestimation. In these cases, the position of the valence-band maximum (VBM) has been realigned, and transition levels may fall within the gap depending on the amount of downward shift applied to the VBM.[5–9] The transition level positions may also be qualitatively affected by finite-size correction schemes.[16] Since the Kohn-Sham band structures have not been reported in these studies, we cannot be sure whether total energies have also been computed for unphysical charge states (V_{Se} is the only defect for which DOS has been previously presented[6]). If this is the case, then the transition levels, whose existence we were unable to confirm, would arise from (de)occupying extended bulk states near the VBM or CBM instead of defect-induced ones.

Another question is whether the defects under consideration could still be responsible for hydrogenic effective-mass-like states. Such a state is created when a delocalized electron or hole is loosely bound to an ionized defect center due to Coulombic interaction.[24] The nominal charge state of the defect remains the same, but the defect can contribute to conductivity. We want to point out that the question whether a specific defect can create such a state can be neither confirmed nor rejected by the calculations accomplished so far. The reliable theoretical detection of such very delocalized states would require much larger supercells than is currently feasible. Also, the distance of an effective-mass-like state from the VBM or CBM is much smaller than the accuracy of the present calculations. In short, all intrinsic defects remain potential candidates for causing self-doping in CIS based on band structure considerations.

In contrast to cationic defects, selenium-related defects induce single-particle defect levels within the CIS band gap. For the defects located on the selenium sublattice (V_{Se}, Cu_{Se}, In_{Se}), the atoms around the defect are rearranged in



(a) Charge state 3+ (b) Charge state 1+ (c) Charge state 1−

FIG. 2. (Color online) Upper row: Atomic relaxation around the In_{Se} antisite. The interatomic distances around the defect have been labeled on the corresponding bonds (in Å). For comparison, the bond lengths in bulk CIS are 2.45 Å (Cu-Se bond) and 2.61 Å (In-Se bond). Lower row: Partial charge densities around the In_{Se} antisite corresponding to the first (green) and second (pink) defect-induced levels. Only one-eighth of the 64-atom unit cell is shown for clarity.

a nonisotropic way. For V_{Se}, it has been shown previously[6,16] that the two nearest-neighbor In atoms approach each other while the two Cu atoms are pushed apart. This was justified by noting that In-In bonds are energetically preferred over Cu-Cu bonds.[6] While in the case of antisites, the indium atoms are not able to move close enough to each other to form a dimer bond, they are still clearly mutually attracted. For In_{Se}, depicted in Fig. 2, the indium atoms also approach the defect center while the copper atoms move further away when the charge state of the defect becomes more negative. The corresponding partial charge density plots show how the extra electrons stay localized between the defect and the nearest-neighbor In atoms. Each of these defects induces single-particle defect levels into the band gap (see Fig. 1).

When a selenium atom occupies a cation site (Se_{Cu} or Se_{In}), the lattice relaxation around the defect remains isotropic as for the cation-related defects since the surroundings consist of four identical selenium atoms. The selenium atoms stay equally apart and create single-particle levels within the band gap.

A common feature for these selenium-related defects described above is that they can exist in several stable charge states. The addition of electrons is typically accompanied by strong lattice relaxation and single-particle defect levels shifting downwards in the band gap region, as depicted for V_{Se} and In_{Se} in Fig. 1. These defect levels will probably act as recombination centers since they are often located quite deeply in the gap. The levels lying very close to the CBM may also cause donor-type behavior if electrons can be thermally excited to the CBM at room temperature, but this should be investigated more thoroughly with total-energy calculations to find the transition level positions.

A particularly interesting case among the selenium-related defects is the selenium interstitial, which can also exist in a dumbbell configuration $(Se\text{-}Se)_{Se}$. The dumbbell configuration is characterized by two selenium atoms sharing the same Se site as shown in Fig. 3. The selenium interstitial itself creates a defect level to the upper part of the valence band as depicted in Fig. 1. In the dumbbell configuration, this level is shifted above the VBM, thereby introducing a shallow acceptor level in the CIS gap. It remains the topic for a further study whether this dumbbell alone or pairing up with some other defect could be partly responsible for the *p*-type doping in CIS. At least it would agree with the observation of *p*-type material growth under Se-rich conditions.

According to Fig. 1, the band structures of the considered defect complexes seem to retain the characteristics of the

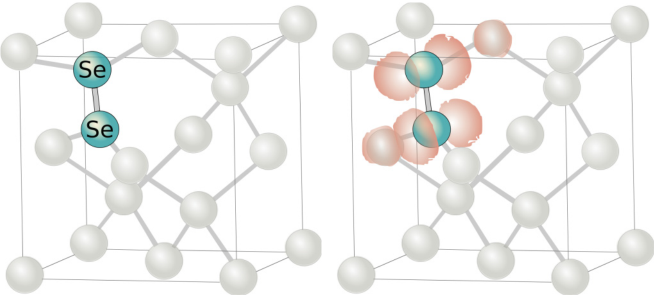


FIG. 3. (Color online) Left: Atomic configuration of the selenium dumbbell $(Se\text{-}Se)_{Se}$. Right: Partial charge density corresponding to the defect-induced level. The unit cell has been rotated 90° around the z axis with respect to Fig. 2 to gain a better view of the partial charge density. Only one-eighth of the 64-atom supercell is shown for clarity.

isolated defects. When a cationic defect (such as V_{Cu} or $\mathrm{In_{Cu}}$) has no single-particle levels within the gap, bringing two or more cationic defects together (such as $2V_{\mathrm{Cu}}$-$\mathrm{In_{Cu}}$) would not affect the electronic structure of the material. On the other hand, if the other one is a selenium-type defect, then the resulting complex would retain the electronic properties of the selenium-type defect, as was also found earlier in the case of the V_{Cu}-V_{Se} complex.[6,8]

IV. CONCLUSIONS

In this work, we stress the importance of selenium-related defects in CIS, which have often been overlooked compared to copper-related ones. Based on reliable calculations employing a hybrid functional, we show that selenium-related and not copper- or indium-related defects can create transition levels within the band gap. Avoiding recombination centers in this material thus means looking out for selenium-related defects.

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