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# Spin orbit coupling effects on predicting defect properties with hybrid functionals: A case study in CdTe

Jie Pan\*, Wyatt K. Metzger, Stephan Lany\*

Materials Science Center, National Renewable Energy Laboratory, Golden, CO  
80401

[Jie.Pan@NREL.gov](mailto:Jie.Pan@NREL.gov), [Stephan.Lany@NREL.gov](mailto:Stephan.Lany@NREL.gov)

## Abstract

Defect formation energies and transition levels are critical in determining doping behavior and recombination in semiconductor applications. Hybrid functionals are often used to overcome the bandgap and delocalization errors of standard density functional theory, and it is tempting to presume that the defect properties are correctly predicted once the hybrid functional mixing parameter reproduces the experimental band gap. However, pronounced spin-orbit coupling (SOC) effects can have an additional important role, this is clearly shown in this work by analyzing SOC effects originating from the Te-*p* orbitals in CdTe. In this work, we therefore use a hybrid functional that reproduces the experimental band gap when SOC is included, requiring a larger mixing parameter  $\alpha = 0.33$  compared to the conventional choice of  $\alpha = 0.25$ . This hybrid functional was then used to predict defect properties, e.g., formation energy, transition level, and defect equilibrium. For defect states that do not directly involve the Te-*p* orbitals, such as the Cd interstitial, we find that the effect of SOC on the defect levels can be captured by simply considering the SOC induced band edge shift. This is not the case for the A center ( $\text{Cl}_{\text{Te}} + \text{V}_{\text{Cd}}$  defect pair), where the localized acceptor state formed by Te-*p* orbitals is more directly affected by the SOC. For this defect, a mixing parameter as large as  $\alpha = 0.40$  is required to reproduce the experimental acceptor level. Regarding the implications for photovoltaics, we suggest that the Cd interstitial, which is the dominant compensating donor, could play an important role as a recombination center. While  $\text{Cd}_i$  is usually thought of as a benign shallow donor, our predicted defect levels in the fully band gap corrected calculations are deep enough to raise a concern, and we propose a new recombination mechanism for electron capture by  $\text{Cd}_i$ .

## 1. Introduction

Defects and dopants have critical impacts on semiconductor material properties and applications. For example in photovoltaics (PV), defect-mediated recombination limits the lifetime of photo-generated minority carriers resulting in decreased open-circuit voltage and efficiency.[1-6] The detrimental or beneficial impacts vary with defect properties such as formation and transition energies.[7-9] Yet, it is often very difficult to measure these properties experimentally even with multiple techniques. Consequently, first principles calculations have played a very important role in calculating defect properties, both

complementing experimental results and serving as a powerful method to scientifically understand, predict, and manipulate defects and material properties.

However, the accurate prediction of defect properties can be challenging and often depends on details in the approach, such as the choice of the functional and the inclusion of spin-orbit coupling (SOC). Standard density functional theory calculations, e.g., with generalized gradient approximation (GGA) [10], often underestimate the band gap [11] and over-delocalize defect states [12-14], which affects the calculated defect properties. For some systems, even when the band gap from DFT-GGA calculations agrees with experiment, the positions of the band edges with respect to the defect transition levels can still be incorrect.[15] Hybrid functionals serve as an alternative to tackle these electronic band structure problems by introducing a certain amount of exact Hartree-Fock (HF) exchange energy into the standard DFT functional to cancel the residual self-interaction error. For semiconductors with heavy elements, e.g., tellurium (Te) and lead (Pb), the inclusion of spin orbit coupling (SOC) becomes important and can significantly influence the band structure and defect properties by either shifting the band edges [15-17] or splitting defect states[18]. In the literature, this brings the calculated results into qualitative agreement with experiments. For example, West et. al. demonstrated that  $\text{Bi}_2\text{Se}_3$  can be predicted as native n-type (instead of native *p*-type without SOC) due to the shift of band edges induced by SOC, and that the  $\text{Bi}_{\text{Se}}$  defect changes from acceptor-type without SOC to donor-type with SOC. [16] Du reported that the combination of both using a hybrid functional and including SOC is necessary to obtain the right edge positions in lead iodide perovskites for a defect picture in agreement with experiments.[15] These examples show that reproducing a realistic host band structure by including SOC and carefully tuning the hybrid functional parameters can be necessary for obtaining reliable defect properties, i.e., formation and transition energies more in alignment with experimental results. It is often tacitly assumed that it is also a sufficient condition, but this is ultimately an open question.

Cadmium telluride (CdTe) is an ideal material system to explore this question. CdTe is a leading thin-film solar absorber material in the PV industry with many advantages, such as an ideal 1.5-eV band gap and high absorption coefficient.[19,20] First Solar has achieved the world-record CdTe solar power conversion efficiency of 22.1%, and this technology is providing electricity at costs competitive with conventional fuels today.[21] However, the CdTe properties still have headroom to further improvement. Polycrystalline CdTe is deposited quickly and followed by  $\text{CdCl}_2$  and Cu exposure to make complete solar cells.[22-26] However, significant self-compensation leads to a limitation of the hole density to about  $10^{14} \text{ cm}^{-3}$ , and recombination losses remain an important problem; both issues limit the performance.[27,28] According to the Shockley-Read-Hall (SRH) theory, deep-level defects can act as non-radiative recombination centers by assisting the coupling of the photo generated carriers[1,2], and thus, limiting the open-circuit voltage and fill-factor.[19] As a result, the accurate determination of defect-levels

with respect to the band edges is very critical for both device modeling and experiments to further improve the performance. Recently, standard hybrid functional calculations without SOC have been employed to predict CdTe bulk and defect properties [19,29-31]. However, strong SOC effects in the Te-*p* shell are known to play an important role for the band structure of tellurides[16] and have been qualitatively discussed for the (0/-) transition level of Cd vacancy in CdTe[32]. As a result, the formation energies of fully ionized defects are expected to change in accordance with the valence band edge shift caused by SOC.[33] In addition, SOC can further split defect states, thereby affecting the transition energies between different charge states.

In this paper, we use CdTe as an example to address coupled effect of the SOC and band-gap corrections via hybrid functionals on the prediction of defect properties. Hybrid functional parameters are chosen to reproduce the experimental CdTe band gap when the SOC is included. We further investigate the SOC effect on predicting the defect formation energy and transition energy with this band-gap corrected hybrid functional. For the effect of SOC on transition energies, we use the Cd interstitial  $Cd_i$  and the A-center  $Cl_{Te}+V_{Cd}$  defect pair as examples of defect states that are indirectly (Cd-s like state) or directly (Te-*p* like state) affected by SOC, respectively. We further simulate the defect equilibrium in intrinsic CdTe and discuss the effect of SOC on net carrier concentrations.

## 2. Methods

The energies and electronic density of states were calculated using the Vienna *ab initio* simulation package (VASP) with the projector-augmented-wave (PAW) implementations for density functional theory (DFT)[34], hybrid functionals[35], and spin-orbit coupling[36]. The bulk/defect supercells were relaxed with a cutoff energy of 330 eV for the plane wave basis sets, a 2x2x2 Gamma k-point mesh. The convergence criteria are total energy difference below  $10^{-4}$  eV per supercell for electronic relaxation and total forces below 0.02 eV/Å on each atom for ionic relaxation. The CdTe crystal has the zinc blende structure (space group:  $F\bar{4}3m$ , No. 216) and a 64-atom simple cubic supercell was constructed for defect calculations. For the exchange and correlation in density functional theory (DFT), we used the generalized-gradient-approximation (GGA) in the revised Perdew-Burke-Ernzerhof form for solids (PBEsol).[37] Hybrid functional calculations were performed using the range separated form of the HSE06 functional.[38] The q-point grid representation of the Fock exchange was uniformly reduced by a factor of 2 (NKRED = 2) to save computational cost. The occupancies in hybrid functional defect calculations with NKRED = 2 were carefully checked to ensure that no partial occupancies occur.

Standard DFT has a notorious problem of underestimating material band gaps. For example, the CdTe band gap from standard DFT is about 0.64 eV, as compared to the experimental room temperature band gap of 1.5 eV.[39] The hybrid functional can alleviate this problem by mixing a certain amount of Hartree-Fock (HF) exchange into the

GGA functional. The standard hybrid functional (HSE06, 25% Fock exchange) gives a band gap value for CdTe of about 1.41 eV (Figure 1a). However, heavy Te atoms in CdTe experience a strong spin-orbit coupling (SOC) effect, which bring the valence band maximum (VBM) up by about 0.33 eV (Fig. 1a). This effect reduces the band gap relative to a HSE06 calculation without SOC, implying that HSE06 significantly underestimates the band gap. In order to have a corrected band-gap close to the experimental value, in this study, we used a modified hybrid functional with 33% Fock exchange. This choice gives about a 1.50 eV band gap including the SOC effects Fig. 1a). In addition, the use of the PBEsol parameterization for the GGA allows us to get a lattice constant of about 6.48 Å. The lattice constant in this functional is very close to the experimental value,[40] and should improve the defect predictions that are sensitive to the lattice parameters, which is especially the case for defects with large relaxations.

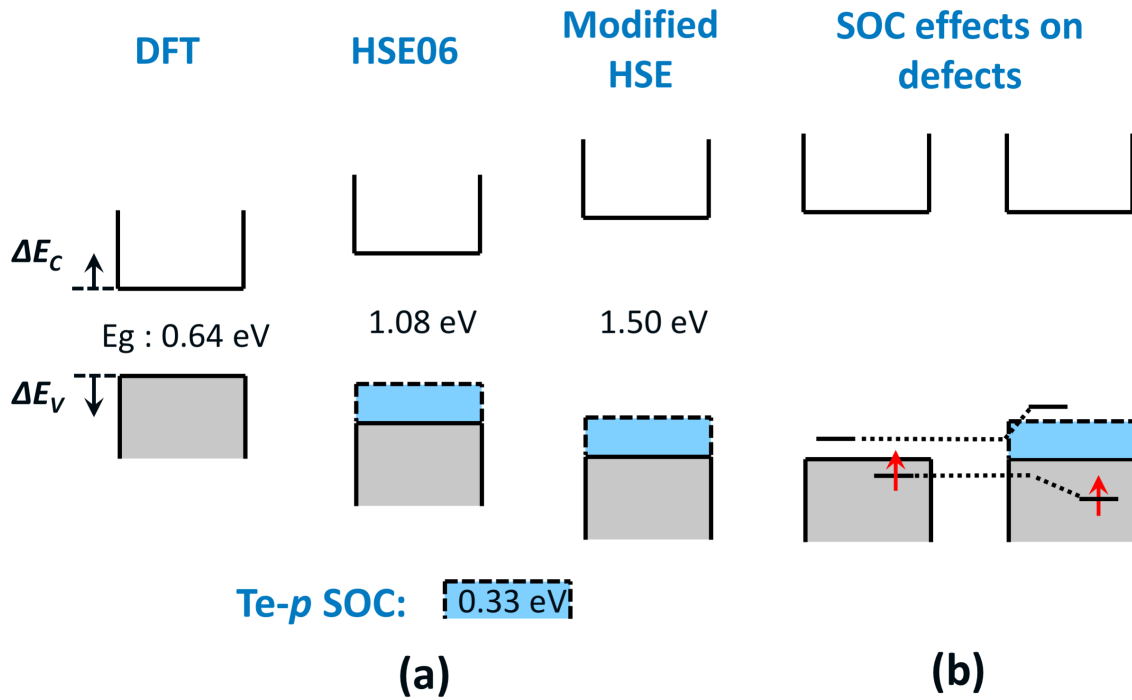


Figure 1: (a) The values of band gap calculated from different calculations: standard DFT, HSE06 with SOC, and modified HSE (33% HF exchange) with SOC; (b) A schematic illustration of the SOC effect on the predicted electronic structure of an open shell defect.

Another problem associated with standard DFT is its failure, even qualitatively, to describe the symmetry broken defect states resulting in partial occupancies instead of the physically correct splitting into fully occupied and empty states.[41] Because of the complex energy surface due to Jahn-Teller distortions [41,42], this additional complexity due to electronic correlations often leads to multiple locally stable configurations for open shell defects. Coupled with the higher computational cost of the hybrid functionals, a complete sampling of the configurations space within hybrid functional calculations becomes very tedious. To overcome this challenge, we employed a GGA+U+V functional

to effectively sample different configurations. Here,  $U$  is the standard DFT+ $U$  potential,[43] and  $V$  is a nonlocal external potential.[44] The  $U/V$  parameters [45] were chosen to approximately correct both the band gap and the non-Koopmans behavior of standard DFT, and to stabilize symmetry broken solutions.[41] This method allows us to obtain a solution with appropriate electronic and atomic symmetries at the cost of a standard DFT calculation. For quantitative energies, we feed the most likely solutions into subsequent HSE calculations, which usually converges quickly from this starting point.

With the corrected bulk properties and efficient defect configuration sampling, the formation energy of each defect is calculated by

$$\Delta H_f(q) = E(q) - E(\text{CdTe}) - \sum n_i(\mu_i^0 + \Delta\mu_i) + q(E_F + E_V), \quad (1)$$

where  $E(q)$  and  $E(\text{CdTe})$  are the ground state energies calculated from DFT for a defect supercell with charge  $q$  and a perfect supercell. Here,  $n_i$  is defined as the difference of the atom numbers between the imperfect and perfect supercells, and  $\mu_i^0$  are the reference energies for the elements in their standard state. For each element  $\Delta\mu_i$  is the chemical potential referenced to the elemental energies, and  $E_F$  is the electronic Fermi level referenced to the bulk VBM ( $E_V$ ). For defect formation energies, potential alignment and image charge corrections have been included as described in Ref. [44]. The potential alignment was also taken into account for single particle energy spectra, i.e., the defect projected density of states (DOS), both for neutral and charged states, to ensure the correct lineup with respect to the host band structure. Additionally, image potential corrections were applied to single-particle energies for charged defect states as described in Ref. [46]. The defect transition energy  $\varepsilon(q/q')$  between charge state  $q$  and  $q'$  can be calculated by

$$\varepsilon(q/q') = [\Delta H_f(q) - \Delta H_f(q')]/(q' - q). \quad (2)$$

To improve the description of the chemical potential ranges, we used the fitted elemental-phase reference energies (FERE)[47]. This approach was designed to improve upon the incomplete error cancellation in DFT when energy differences are taken between different types of matter (insulators, metals, molecules). This approach is also suitable for hybrid functional calculations[33], where the mixing parameter used for the compound (CdTe) phase is not well justified for the elements involved in the studied defects (here, Cd, Te, Cl). To determine FERE energies, we performed a fit for 23 different compounds in the modified HSE functional, based on tabulated experimental enthalpies of formation[48,49]. The resulting FERE energies and enthalpies of formation are given in the Supplemental Material [45], respectively.

### 3. Results and Discussion

#### 3.1 SOC effects on formation energies

The SOC effect influences the band edge energies. For example, the VBM shifts up by about 0.33 eV, and this can affect the formation energies and resulting defect populations. In the case of fully ionized defects that involve only closed shell atomic

orbital configurations (e.g.,  $\text{Te-}p^6$  for  $V_{\text{Cd}}^{2-}$  or  $\text{Cl-}p^6$  for  $\text{Cl}_{\text{Te}}^+$ ), the SOC effects on defect formation energies can be included by a simple VBM shift on top of a non-SOC calculation.[15] This is because the SOC splits the atomic orbital energies such that the average orbital energy is approximately preserved. Hence, for a closed shell orbital occupation, the direct energy contribution due to the splitting is small. The remaining dominant SOC effect is the shift of the band edge energies, which enters the formation energy for charged defects by defining the bounds for  $E_F$  (see eq. (1)). In the case of open shell defect states, e.g.,  $\text{Te-}p^5$  in  $(\text{Cl}_{\text{Te}}\text{-}V_{\text{Cd}})^0$  discussed below, there can be an energy gain associated with the orbital splitting by SOC. Here, it is important to include SOC in the defect supercell calculation for accurate defect calculation of levels. Furthermore, regarding the thermochemical properties, which define the bounds for the chemical potentials, the energy changes due to SOC is approximately a constant energy contribution for each atom[47]. Such atomic energy changes cancel upon taking energy differences that observe the particle conservation, and therefore do not affect the compound formation enthalpies.

Fig. 2 shows the defect formation energies of fully ionized defects in Te-rich and Cd-rich conditions, respectively. In the Te-rich condition ( $\Delta\mu_{\text{Te}} = 0 \text{ eV}$ ), the Cu and Cl chemical potential are chosen as:  $\Delta\mu_{\text{Te}} + \Delta\mu_{\text{Cd}} = \Delta H(\text{CdTe})$  and  $3\Delta\mu_{\text{Cd}} + 2\Delta\mu_{\text{Cl}} + 2\Delta\mu_{\text{O}} = \Delta H(\text{Cd}_3\text{Cl}_2\text{O}_2)$ . In the Cd-rich condition ( $\Delta\mu_{\text{Cd}} = 0 \text{ eV}$ ), the Cu and Cl chemical potential are chosen as:  $\Delta\mu_{\text{Cu}} = 0 \text{ eV}$  (elemental Cu) and  $3\Delta\mu_{\text{Cd}} + 2\Delta\mu_{\text{Cl}} + 2\Delta\mu_{\text{O}} = \Delta H(\text{Cd}_3\text{Cl}_2\text{O}_2)$ . The chemical potential of oxygen ( $\Delta\mu_{\text{O}} = -0.81 \text{ eV}$ ) is the chemical potential of oxygen gas at 450 °C in air (0.2 atm  $p_{\text{O}_2}$ ). These conditions correspond to typical processing protocols for a  $\text{CdCl}_2$  treatment. [50,51] Note that the  $\text{Cd}_3\text{Cl}_2\text{O}_2$  phase imposes a tighter constraint to  $\Delta\mu_{\text{Cl}}$  than  $\text{CdCl}_2$ , thereby supporting the conclusion of Ref. [52] that this ternary phase acts as the major chlorine-containing component under the actual process conditions.

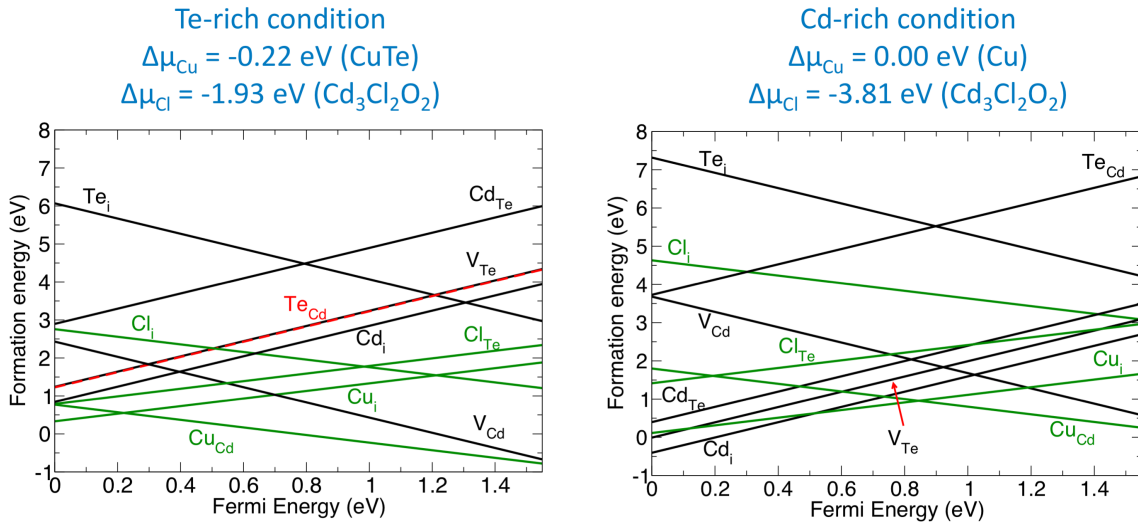


Figure 2: Formation energies of fully ionized defects in CdTe under a Te-rich condition and a Cd-rich condition, calculated using the HSE06 hybrid functional with 33% Hartree-Fock exchange, and including the VBM shift due to SOC.

We now compare the present results using the band gap and SOC corrected functional with previous hybrid functional based calculations[29,31,53] Under the Te-rich condition,  $\text{Cl}_{\text{Te}}^+$  has a lower formation energy than that of  $\text{V}_{\text{Te}}^{2+}$  across the whole band gap region, in agreement with Ref. [31]. However, in Ref. [29], the formation energy of  $\text{Cl}_{\text{Te}}^+$  can be higher than that of  $\text{V}_{\text{Te}}^{2+}$  near the VBM under the same growth condition. This cannot be explained by the choice of  $\Delta\mu_{\text{Cl}}$ , since Ref. [29] used a higher chemical potential value for  $\Delta\mu_{\text{Cl}}$  than that used here. The discrepancy can be attributed to the band edge shift caused by the choice of hybrid functional with a larger HF fraction and the inclusion of SOC. This band edge shift effect is also reflected in the crossing point of  $\text{Cu}_i^+$  and  $\text{Cd}_i^{2+}$ . Under the Cd-rich condition, the crossing point in our calculation is closer to the VBM relative to Ref. [29], in which the crossing point is near the CBM. We also find that the  $\text{Cd}^{2+}$  interstitial is lower in energy than the charged Te vacancy  $\text{V}_{\text{Te}}^{2+}$ , in contrast to Ref. [53], but in agreement with Ref. [31]. Since both defects have the same dependence on chemical potentials and  $E_{\text{F}}$ , the energy ordering discrepancy is not explained by the FERE, band gap, and SOC corrections.

The results demonstrate that the inclusion of the SOC in the hybrid functional calculation can potentially change defect formation energies, and thus their relative populations, importance, doping and recombination properties. For example, for *p*-type CdTe under Te-rich conditions, the majority defects are  $\text{Cu}_i$ ,  $\text{Cu}_{\text{Cd}}$ ,  $\text{Cl}_{\text{Te}}$ , and  $\text{Cd}_i$  with SOC. The  $\text{Te}_{\text{Cd}}$  antisite has been considered an important recombination center in *p*-type CdTe.[54] However, in the present study, the formation energy of  $\text{Te}_{\text{Cd}}^{2+}$  has been raised due to the SOC VBM up-shift. In addition, the  $\text{Te}_{\text{Cd}}^{2+}$  formation energy is always higher than  $\text{Cd}_i$ . In the past,  $\text{Cd}_i$  has often been considered as a benign defect with shallow donor levels. But due to its low formation energy, and the larger band gap in our computational approach, we performed a more detailed study of the non-radiative recombination mechanism for  $\text{Cd}_i$  (see section 3.2.1).

### 3.2 SOC effects on transition levels

The way in which SOC can affect defect states that are not fully ionized depends on the electronic structure of the defect. Generally speaking, the molecular orbitals corresponding to a defect state split due to the crystal-field symmetries and the Coulomb correlation, thereby separating occupied and unoccupied quasi-particle energies.[41] Since SOC causes an additional splitting, it can be expected that the defect transition levels become deeper, as illustrated in Fig. 1b, when viewed relative to a fixed energy reference, such as the average electrostatic potential. On the other hand, the VBM upshift reduces the distance of the unoccupied state from the VBM, which makes acceptor states

more shallow. The final defect level position depends on the balance between these two effects. This balance can have a particularly strong influence on the defect transition for relatively shallow acceptor states close to the VBM, as illustrated in Fig 1b. In the following, we investigate in more detail the transition energies of the  $\text{Cd}_i$  interstitial and the Cl A center[55], a  $V_{\text{Cd}}\text{-Cl}_{\text{Te}}$  defect pair between a Cd vacancy and a substitutional Cl donor. The A center acceptor level has been experimentally established, allowing for a direct comparison with calculated values.

### 3.2.1 Cadmium interstitials

The Cd interstitial ( $\text{Cd}_i$ ) is an important intrinsic defect with low formation energy near the VBM[29,31,53]. As shown in Fig. 3a and Fig. 4, a Cd atom can be located at the interstitial site that is tetrahedrally coordinated by four Te atoms [ $\text{Cd}_i(\text{Te})$ ], or at the Cd coordinated site [ $\text{Cd}_i(\text{Cd})$ ]. Interestingly, the site preference of  $\text{Cd}_i$  depends on the charge state. In the +2 charge state, the  $\text{Cd}_i(\text{Te})$  configuration is lower in energy, but in the neutral state, the  $\text{Cd}_i(\text{Cd})$  structure is energetically favored. Both defect structures produce a state inside the band gap. The  $\text{Cd}_i(\text{Cd})$  creates a deeper donor level with the overall (+2/0) transition at  $E_{\text{CBM}} - 0.45$  eV (Fig. 3d). Thus, here the fully band gap corrected hybrid functional with SOC indicates that Cd interstitials produce a deeper level than found in previous calculations based on DFT or the standard HSE06 functional[29-31,53]. This implies the  $\text{Cd}_i$  defect could act as an electron trap and its role as potential recombination center has been underappreciated.

To test the sensitivity of the defect properties on the details of the hybrid functional and SOC, we show in Fig. 3d the position of the  $\epsilon(+2/0)$  level (average between 1<sup>st</sup> and 2<sup>nd</sup> ionization levels) for  $\text{Cd}_i(\text{Cd})$  defect as a function of the Fock exchange parameter, both with and without SOC. Several observations are notable. First, the transition level stays almost constant on an absolute scale (approximated by using the average electrostatic potential as reference), while the band gap opens more or less symmetrically in the conduction and valence bands. This behavior is often observed for deep levels[56]. Second, the magnitude of the VBM shift due to SOC is not sensitive to the mixing parameter.  $\Delta E_{\text{V}}^{\text{SOC}}$  varies only between 0.316 and 0.355 for  $\alpha = 0.2$  and  $\alpha = 0.5$ , respectively. As expected from the  $l = 0$  angular momentum character, the CBM is virtually unaffected by SOC, with changes less than 0.037 eV. Similarly, the distance of the  $\text{Cd}_i$  level to the conduction band is not affected by the SOC since it also has an  $l = 0$  character. Thus, the deep  $\text{Cd}_i$  state compared to previous calculations is a result only indirectly related to SOC, in that a larger Fock parameter  $\alpha$  is needed to reconcile the experimental band gap when SOC is included. It must be noted, however, that the deep and localized character of  $\text{Cd}_i$  is maintained even for smaller values of  $\alpha$  down to 0.2 (cf. Fig. 3d) and below, implying that its role as a potential recombination center is robust against  $\alpha$  variation.

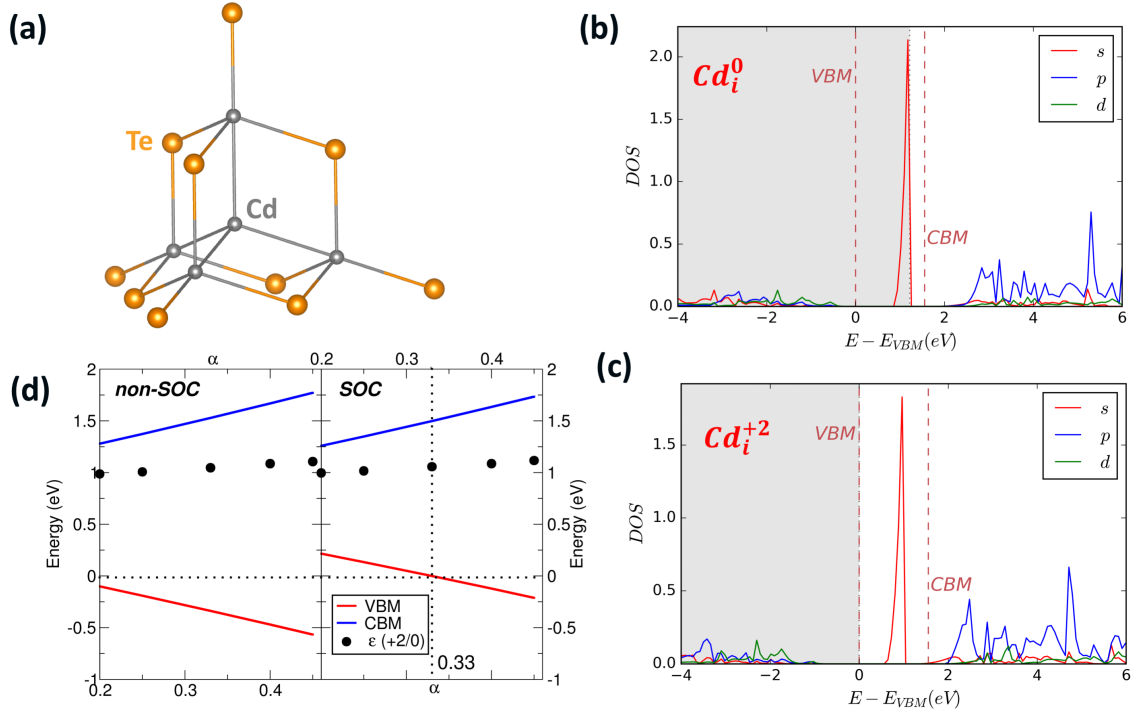
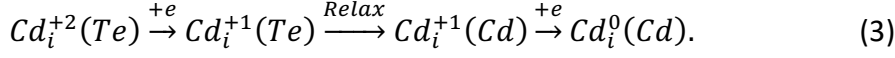


Figure 3 (a) The defect structure of Cd<sub>i</sub> tetrahedrally bonded with 4 nearby Cd ions; (b) defect site projected DOS of Cd<sub>i</sub>(Cd) in the neutral state and (c) in the +2 state. The energy range of occupied states is indicated by the grey shading. The DOS in (b) and (c) were calculated from non-SOC HSE calculations ( $\alpha = 0.33$ ), but the SOC effect on the VBM energy was included. (d) Band edges and  $\epsilon(+2/0)$  transition levels for Cd<sub>i</sub>, determined with and without SOC, as a function of the hybrid functional mixing parameter.

The behavior of a defect as a recombination center depends also on the localization of the defect states. Transition levels in the vicinity of the CBM can indicate either a shallow delocalized effective mass state, or a localized deep level that coincidentally occurs close to the band edge. Our calculated defect DOS, presented in Figs. 3b and 3c, show that Cd<sub>i</sub> clearly produces a localized quasi-particle state inside the gap, separated from the continuum of conduction band states. We now discuss the electron capture mechanism involving this defect state. As shown in Fig. 4, in *p*-type CdTe ( $E_F$  close to VBM), the interstitial Cd prefers to stay at the Te- neighbored site forming Cd<sub>i</sub><sup>+2</sup>(Te), which has its unoccupied defect state right below the CBM[45]. This empty state can capture a free electron which is the minority carrier in *p*-type CdTe and becomes Cd<sub>i</sub><sup>+1</sup>(Te). However, Cd<sub>i</sub><sup>+1</sup>(Te) is thermodynamically unstable and can relax to the more stable Cd<sub>i</sub><sup>+1</sup>(Cd) configuration (black arrow in Fig. 4), which is a spin polarized defect with one occupied state in the middle of the band gap and the other empty state right below the CBM[45]. The unoccupied state can further bind a second free electron, resulting in the neutral Cd<sub>i</sub><sup>0</sup>(Cd) defect. Thus, the capture of two minority carriers can be summarized as a three-step process,



The first capture corresponds to the (+2/+1) transition of  $Cd_i(Te)$  at  $E_{CBM} - 0.21$  eV. The second step is a activated structural relaxation with an energy barrier of  $\Delta E_b = 0.33$  eV, and an associated lifetime of  $10^{-7}$ - $10^{-8}$  s ( $\tau \approx \nu_{ph}^{-1} \exp(\Delta E_b/kT)$ , where  $\nu_{ph}$  is the average phonon frequency, typically  $10^{12}$ - $10^{13}$  s $^{-1}$ )[57]. The third step is the electron capture due to the (+1/0) transition of  $Cd_i(Cd)$  at  $E_{CBM} - 0.24$  eV.

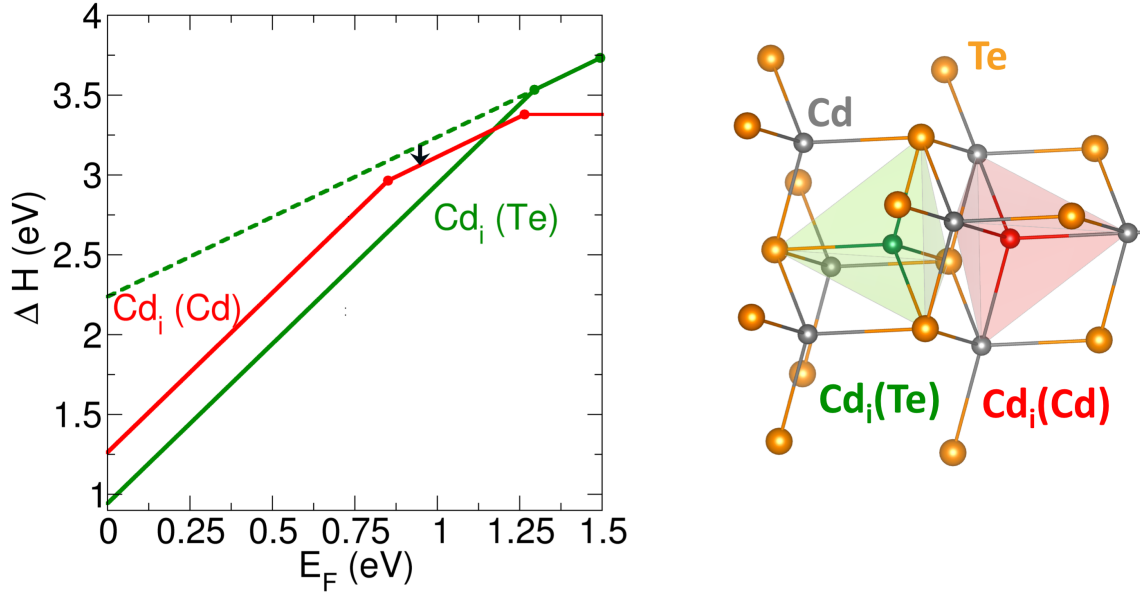


Figure 4: Right: Transition energies  $\varepsilon(+2/+1)$  and  $\varepsilon(+1/0)$  for the two structural configurations of  $Cd_i$  interstitials calculated from non-SOC HSE calculations ( $\alpha = 0.33$ ), but the SOC induced shift of the VBM energy is included ( $\Delta H$  shown for Te-rich condition); Left: Atomic structures of  $Cd_i(Te)$  interstitial surrounded by 4 Te atom and  $Cd_i(Cd)$  interstitial surrounded by 4 Cd atom.

### 3.2.2 The $Cl_{Te}$ - $V_{Cd}$ defect pair (Cl A center)

The Cl A center is an ideal defect for the study of the SOC effect on the transition levels of a shallow acceptor state with a similar atomic orbital character (Te- $p$ ) as the VBM. This defect is considered critical in detector and photovoltaic applications because it offers an explanation for how Cl, which would be a donor on a Te site, contributes to p-type doping. In addition, the acceptor ionization energy, i.e., the  $\varepsilon(0/-1)$  transition level, is experimentally known to be  $120 \pm 3$  meV above the VBM[55]. In the charge neutral  $(Cl_{Te}-V_{Cd})^0$  state, a hole is bound at one of the three Te neighbors surrounding the  $V_{Cd}$  site. Obtaining the correct localization behavior requires using a post-DFT functional that corrects the correlation effects for open-shell defect states[41]. Fig. 5a shows the symmetry-broken atomic structure of a neutral A center with a  $C_{1h}$  symmetry, where the Te atom with the bound hole relaxes much farther away from the  $V_{Cd}$  site than the remaining two Te atoms. The localized hole state is visualized in Fig. 5a by the

magnetization density, i.e., the difference between spin-up and spin-down densities obtained from a non-SOC calculation. The corresponding quasi-particle hole-state is seen as a Te- $p$  like, unoccupied narrow peak in the density of states (Fig. 5b). In the negatively charged  $(\text{Cl}_{\text{Te}}-\text{V}_{\text{Cd}})^{-1}$  state, all valence band derived states are occupied, and the A-center assumes the  $\text{C}_{3v}$  symmetry expected from the atomic lattice decoration.

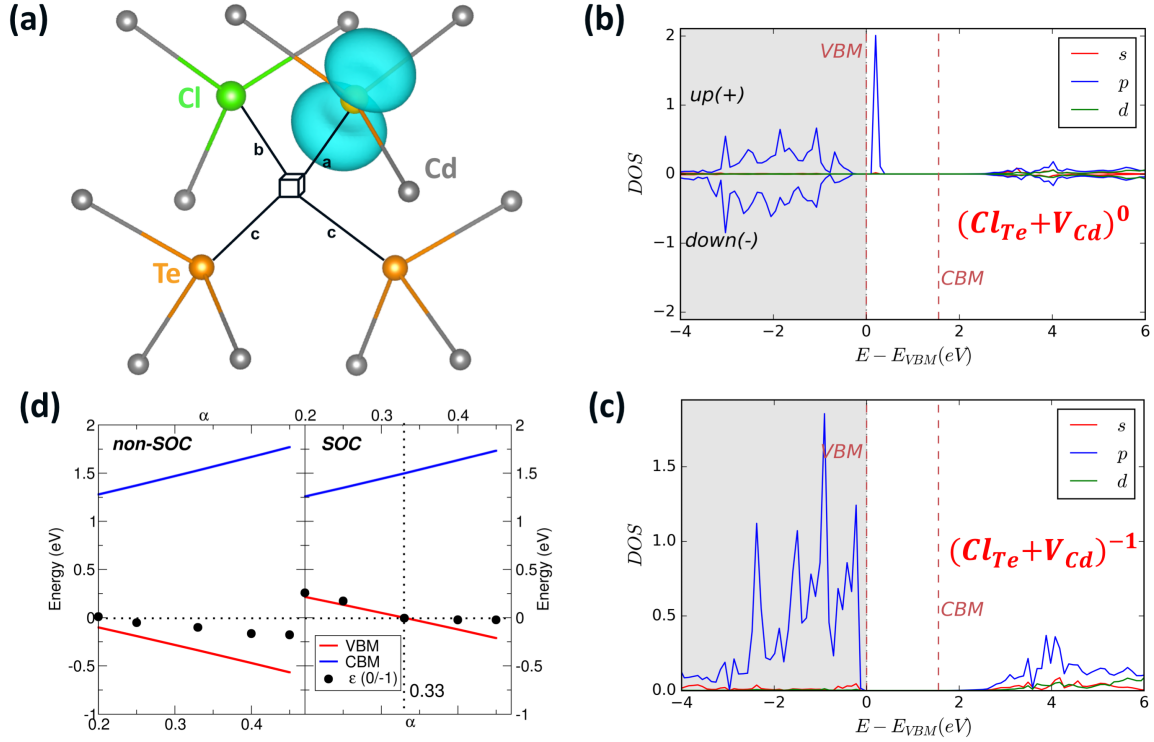


Figure 5: (a) The atomic structure of the charge-neutral A center in  $\text{C}_{1h}$  symmetry (distances from  $\text{V}_{\text{Cd}}$  site:  $a = 2.95 \text{ \AA}$ ,  $b = 3.26 \text{ \AA}$ , and  $c = 2.44 \text{ \AA}$ ), showing also the magnetization density with an isosurface density of  $0.01 \text{ e}/\text{\AA}^3$  (spin-polarized calculation without SOC). (b) Defect site projected DOS on the Te atom with the bound hole in the neutral state and (c) in the -1 charge state of the A center. The DOS in (b) and (c) were calculated from non-SOC HSE calculations ( $\alpha = 0.33$ ), but the SOC effect on the VBM energy was included. (d) Band edges and  $\epsilon(0/-1)$  transition level for  $(\text{Cl}_{\text{Te}}-\text{V}_{\text{Cd}})$ , determined with and without SOC, as a function of the hybrid functional mixing parameter.

The acceptor binding energy, i.e., the  $\epsilon(0/-1)$  transition energy, depends crucially on the hybrid functional parameter  $\alpha$ , controlling the energy splitting between occupied and unoccupied states due to correlation effects[41]. As expected, the acceptor level moves monotonically deeper into the band gap with increasing  $\alpha$ , as shown in Fig. 5(d). At  $\alpha = 0.33$ , the value that reproduces the experimental band gap, the  $\epsilon(0/-1)$  lies at  $0.236 \text{ eV}$  above the VBM (excluding SOC), somewhat deeper than the experimental value of  $0.120 \text{ eV}$ . Unlike the case of the Cd interstitial, where the SOC effect was essentially captured

by adding the SOC induced VBM shift to  $E_v$ , the effect on the A center level is more subtle. At small values of  $\alpha$  (e.g.,  $\alpha = 0.25$ ), the VBM shift is large enough to overcome the localization energy of the acceptor state, so that the hole becomes a delocalized effective mass state. After correction for band-filling effects[58], the  $\varepsilon(0/-1)$  level coincides with the VBM. Only at values of  $\alpha$  larger than 0.33, the localized acceptor level separates again from the valence band, and the further deepens with increasing  $\alpha$  as in case of the non-SOC calculations. It becomes now obvious that the SOC induced shift of the occupied VBM states is significantly larger than that of the unoccupied hole-state of the A center acceptor, even though both are predominantly formed by Te- $p$  states. A value above  $\alpha = 0.4$  is needed to bring the A center acceptor level in agreement with the experimental value of 120 meV. At this large fraction of Fock exchange, however, the band gap is already overestimated ( $E_g = 1.76$  eV), and this value is also much larger than the standard value  $\alpha = 0.25$  of the popular HSE06 functional. Thus, a fully consistent description within the hybrid functional approach remains elusive, but the parameter of  $\alpha = 0.33$  used here for the absolute defect formation energies (see section 3.1) should considerably improve estimates relative to the standard  $\alpha = 0.25$  HSE functional.

### 3.2.3 Carrier concentration

Based on the defect formation energies, we performed thermodynamic simulations[59-61] to calculate the defect and carrier concentrations. Results are shown in Fig. 6 for the intrinsic case without dopants. Both anion and cation defects, such as interstitials, vacancies, and antisites were included in the simulation, however the Te interstitial was excluded because it has a high formation energy across the whole Fermi energy range (see Fig. 2). Both Cd interstitial sites discussed in section 3.2.1 were considered. Intrinsic CdTe can be either  $p$  type or  $n$  type depending on the growth conditions. As shown in Fig. 6, under the Te-rich condition, CdTe is  $p$ -type due to the formation of the  $V_{Cd}$  acceptor, but under the Cd-rich condition, CdTe can be slightly  $n$ -type at elevated temperatures with  $Cd_i(Te)$  as the main donor. The calculated net doping level under the Te-rich condition is about  $10^{14} \text{ cm}^{-3}$  at 330 °C and about  $10^{17} \text{ cm}^{-3}$  at 700 °C. This agrees well with experimentally measured values under Te-rich conditions [39,62]. However, it is one order of magnitude higher (about  $10^{16} \text{ cm}^{-3}$  at 800 K or 523 °C) than the value obtained from defect simulations without the SOC effect included (about  $10^{15} \text{ cm}^{-3}$  at 800 K[19]). In addition, under the Cd-rich condition, the net doping ( $n$ -type) from our calculation is lower than Ref [19] at 800 K. In Ref [19], the major donor under the Cd-rich condition was believed to be  $V_{Te}$ . However, after the inclusion of SOC effect on VBM in our calculation, the major donor is  $Cd_i$  neighbored by four Te atoms (Fig. 6b). This is caused by 1)  $V_{Te}$  in our calculation turns to be a deep level defect[45]; 2) as discussed in section 3.1,  $Cd^{2+}$  interstitial has a lower formation energy value compared with that of  $V_{Te}^{2+}$ . In summary, the inclusion of SOC can change the defect equilibrium and further influence the carrier concentration and net doping levels. Specifically, in the example of CdTe, the inclusion of SOC makes the calculated equilibrated net doping levels at elevated temperatures more aligned with experimentally measured values, such as the net doping in the Te-rich

condition, and shifts the predicted major donor from the previously reported Te vacancy[19] to the Cd interstitial.

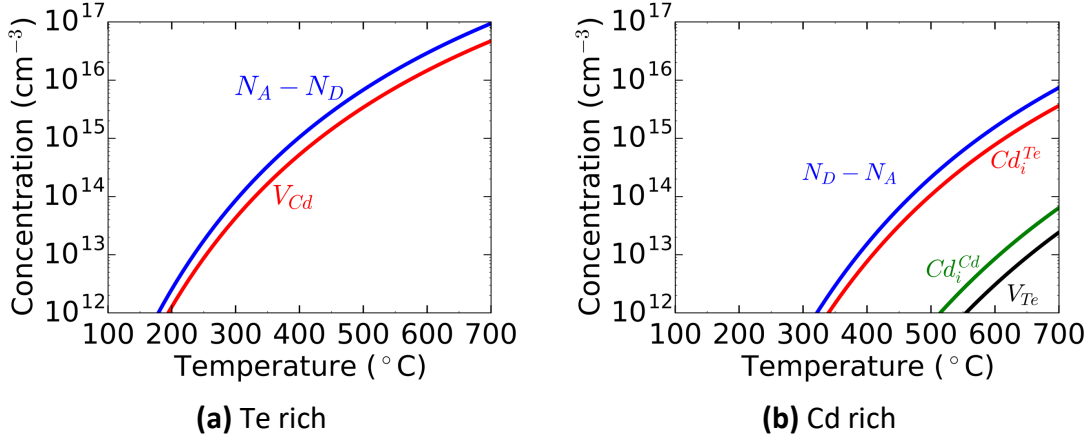


Figure 6: Net doping and major defect concentration as a function of temperature: (a) Te-rich condition ( $\Delta\mu_{Cd} = -1.25$  eV and  $\Delta\mu_{Te} = 0$  eV) and (b) Cd-rich condition ( $\Delta\mu_{Cd} = 0$  eV and  $\Delta\mu_{Te} = -1.25$  eV).

#### 4. Conclusion

The results demonstrate that the inclusion of SOC in band gap corrected hybrid functional calculations has a significant impact on predicted defect properties, populations, doping, and recombination. The standard hybrid functional (HSE06) underestimates the CdTe band gap once SOC is included, and an increase of Fock exchange mixing ( $\alpha = 0.33$ ) is needed to achieve correct values. The PBEsol functional provides an accurate value of lattice constant, which can be important for the calculation of defects with large lattice relaxations. The influence of SOC to the formation energy of closed-shell (fully ionized) defects are dominated by the valence band edge shifts due to SOC (0.33 eV upward shift). Similarly, defect levels such as that of  $Cd_i$  interstitial (Cd-s like) that are not directly affected by SOC can be described by simply adding the band edge shift to a non-SOC calculation. For defect states such as that of the  $Cl_{Te}-V_{Cd}$  pair (Te- $p$  like) that are formed by orbitals subject to SOC, the final transition level depends on the balance between the SOC effects on the band edge and on the defect state. We find here that for the exchange parameter optimized for the band gap, the acceptor state is still too shallow compared to available experimental data.

The predictions for the intrinsic doping and for recombination centers vary also significantly with the SOC inclusion. The formation energy of the  $Te_{Cd}$  recombination site is increased with SOC, lowering its equilibrium concentrations. In our calculations, the dominant donor-type defect is the  $Cd_i$  interstitial defect, which has a somewhat lower formation energy than the  $V_{Te}$  vacancy defect. An important implication for photovoltaics is our finding that the  $Cd_i$  defect forms a localized deep level more than 0.2 eV below the

conduction band and can trap up to two electrons via a phonon-mediated change of the interstitial site. This finding suggests that the impact of  $\text{Cd}_i$  should not be discounted as a benign shallow defect. Overall, our results demonstrate how spin-orbit effects in combination with band gap corrections affect the defect physics of photovoltaic materials with heavy elements such as  $\text{CdTe}$ , and these insights apply also to many other material systems.

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(3) the projected electronic density of states of Cd interstitial neighbored by four Te; (4) the projected electronic density of states of Cd interstitial neighbored by four Cd; (5) the transition level (0/+2) of a Te vacancy.

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