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**Abstract.** The electronic structure and thermodynamic properties of bismuth impurities in cadmium telluride (CdTe) are studied by means density functional theory calculations. The exchange and correlation are treated using the hybrid functional HSE, where the range-separation parameter is tuned to fit the CdTe band gap. The spin-orbit coupling is included in the calculations, showing a strong effect on the Bi-related energy levels. The band diagram and the formation energies are obtained for substitutional and interstitial configurations. It is shown that simple substitutional impurities can generate in-gap bands, which can act as intermediate levels in two-photon absorption and can be appropriate for intermediate-band solar cells.

## 1. Introduction

Cadmium telluride (CdTe) is a semiconductor compound employed as photovoltaic material which is growing rapidly in acceptance, becoming a cheap alternative to the silicon solar cells. CdTe is also widely used for radiation detectors [1]. A recent study [2] has shown a significant increase of the short-circuit current in solar cells doped with Bi. This increase has been attributed to the presence of an intermediate band (IB) that allows the promotion of electrons from the valence band (VB) to the conduction band (CB) by two-step transitions VB to IB to CB, through the absorption of sub-bandgap photons. Previous results had also suggested the existence of an intermediate band in Bi-doped CdTe [3–5]. Seminovski et al [6] have proposed several complex defects, i.e., $2Bi_{Cd}$, $Bi_i–V_{Cd}$, $Bi_{Cd}–O_{Te}$ that can create an IB, but did not find IB associated to simple substitutional defects. Here, it is shown that the simple $Bi_{Cd}$ and $Bi_{Te}$ can create IB. The crucial ingredient is the spin-orbit coupling (SOC).

## 2. Methodology

### 2.1. Electronic structure calculations

Quantum calculations if Bi impurities in supercell models have been performed using density functional theory (DFT). DFT calculations have been done using a plane-wave projector augmented wave [7, 8] scheme, as implemented in the Vienna Ab Initio Simulation Package (VASP) [9]. The band diagrams and total energies have been obtained using the the hybrid functional proposed by Heyd, Scuseria and Ernzerhof (HSE06) [10] with the range separation parameter modified to reproduce the band gap of 1.55 eV given by $G_0W_0$@HSE06 calculation. SOC is included in this framework. This functional will be called $HSE(\omega)+SOC$, with the fitted value $\omega = 0.0811$ Å$^{-1}$. The wavefunctions have been expanded in plane waves with cutoff energy

of 265 eV. This is sufficient to obtain converged forces and total energies using the library of PAW potentials for GW calculations. This PAW library is generally useful for DFT calculations, a fact that we have verified computing the band diagram, lattice parameter and bulk modulus (6.54 Å and 41.05 GPa, respectively). The latter have been obtained by fitting the Birch-Murnaghan equation of state.

In our computational model, the Bi impurities substitute one Cd or Te atom in a 64-atoms supercell (SC64). To sample the reciprocal space, a $\Gamma$-centered $2 \times 2 \times 2$ k-point grids has been used. The atomic positions were relaxed using the generalized gradient approximation (GGA) for the exchange-correlation functional as proposed by Perdew, Burke, and Ernzerhof (PBE) [11].

The calculated CdTe heat of formation, $\Delta H(\mathrm{CdTe})$ is found to be of $-0.78$ eV with PBE and $-1.19$ eV with $\mathrm{HSE}(\omega)+\mathrm{SOC}$. The latter is in good agreement with the updated experimental value $-1.04$ eV [12]. The energy of bulk Cd has been obtained by relaxing the 2-atoms crystallographic unit cell. The Brillouin zone was sampled by a $22 \times 22 \times 10$ k-point grid. The energy of bulk Te has been obtained relaxing the crystallographic 3-atoms unit cell, while the tellurium Brillouin zone was sampled by a $9 \times 9 \times 6$ k-point grid grid.

The formation energy of substitutional bismuth impurities, $\mathrm{Bi_X}$ (X=Cd, Te), has been obtained computing the difference between the total energies of a crystal supercell containing $n$ CdTe units, $E(\mathrm{Cd}_n\mathrm{Te}_n)$, and the energy of the same supercell with a substitution. Therefore, the formation energy of $\mathrm{Bi_{Cd}}$ is

$$\begin{aligned} \Delta H_f(\mathrm{Bi}_{\mathrm{Cd}}^q) \quad = \quad & E(\mathrm{Cd}_{n-1}\mathrm{Te}_n\mathrm{Bi}) - E(\mathrm{Cd}_n\mathrm{Te}_n) + [E(\mathrm{Cd}) + \Delta\mu_{\mathrm{Cd}}] \\ & -[E(\mathrm{Bi}) + \Delta\mu_{\mathrm{Bi}}] + q[E_V + E_F] + \Delta E_{size}. \end{aligned} \qquad (1)$$

To obtain the formation energy of $\mathrm{Bi_{Te}}$, it suffices to exchange Cd with Te in Eq.(1). Here, $E(\mathrm{Cd})$ is the energy of Cd in a reference state, in this case it is the energy per atom of bulk Cd. $\Delta\mu_{\mathrm{Cd}}$ is the chemical potential relative to the reference state, and it depends on the thermodynamic equilibrium conditions. In Cd-rich conditions $\Delta\mu_{\mathrm{Cd}} = 0$, while in Cd-poor conditions $\Delta\mu_{\mathrm{Cd}}$ equals the CdTe heat of formation $\Delta H(\mathrm{CdTe})$ [13]. For a charged vacancy, $q$ is the number of electrons donated to the environment, while $E_V + E_F$ is the electron chemical potential expressed as the sum of the valence band maximum (VBM) $E_V$ and the Fermi level $E_F$ relative to the VBM. $\Delta E_{size}$ includes several size corrections that are explained in [14]. To avoid precipitation of pure Bi or $\mathrm{Bi_2Te_3}$, the chemical potentials must satisfy

$$\Delta\mu_{\mathrm{Bi}} \leq 0, \text{ and } \quad 2\Delta\mu_{\mathrm{Bi}} + 3\Delta\mu_{Te} \leq \Delta H(\mathrm{Bi_2Te_3}), \qquad (2)$$

where $\Delta H(\mathrm{Bi_2Te_3}) = -0.90$ eV is the calculated $\mathrm{Bi_2Te_3}$ heat of formation. The above inequalities imply that in Cd-rich conditions $\Delta\mu_{\mathrm{Bi}} \leq 0$, while in Te-rich condition, $\Delta\mu_{\mathrm{Bi}} \leq -0.45$ eV.

## 3. Electronic structures

In this section we analyze the band structure of substitutional defects $\mathrm{Bi_{Cd}}$ and $\mathrm{Bi_{Te}}$. The band diagrams and density of states (DOS) have been calculated for SC64 models.

*3.1. $Bi_{Cd}$*

$\mathrm{Bi_{Cd}}$ adopts a configuration with $T_d$ symmetry, where the neighboring Te are 3.00 Å far from Bi. Figure 1 shows the band structure calculated for perfect CdTe and for $\mathrm{Bi_{Cd}}$ in the SC64 model. It can be seen that the impurity introduce a band below the CBM. This band is localized, as suggested by its flatness, as well as by comparing the PDOS on the first- and second-neighbors
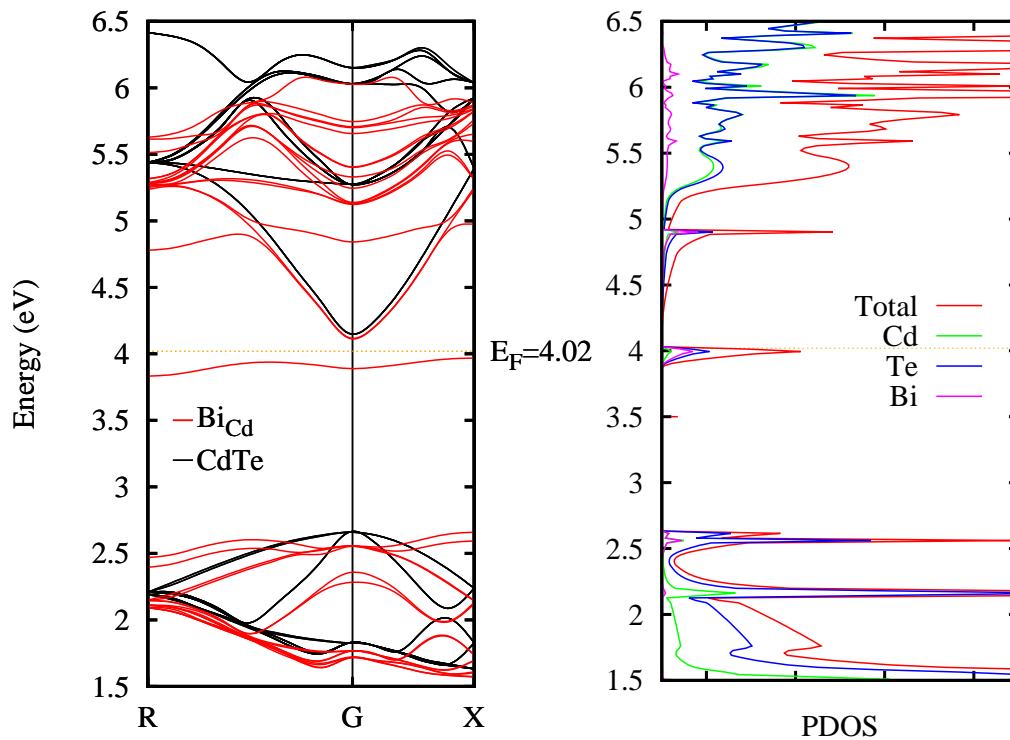
**Figure 1.** (Color online) Band structure of $Bi_{Cd}$ in CdTe performed with a 64-atom supercell. Black lines are the bands for the perfect crystal. Red lines are the bands of the defective supercell in neutral charge state. Dashed lines indicate the Fermi level ($E_F$). The PDOS is shown at the right.

(not shown). This band is non degenerate and it is occupied in the neutral state of the impurity. The center of the IB is 0.105 eV below the CBM. The charge state 1+ is also possible, making $Bi_{Cd}$ a donor impurity. A half-filled IB, as wanted for IB solar cells [15], can be obtained in combination with acceptor impurities or intrinsic defects, e.g., cadmium vacancies.

*3.2. $Bi_{Te}$*

Figure 2 shows the band structure calculations of the perfect CdTe and $Bi_{Te}$ in the SC64 supercell. $Bi_{Te}$ is a deep acceptor with charge states 0 and 1−. In sufficient concentration, as in the SC64 model, $Bi_{Te}$ can create a non-degenerate IB. The center of the IB is 0.80 eV below the CBM. The PDOS shows that the IB has significant contributions from the Te atoms in the supercell. This contribution comes mainly from the second neighbors of Bi (recall that the first neighbors are Cd). The top of the valence band is modified by the presence of Te. The upper part of the valence band in pure CdTe is mainly due to the Te 5p orbitals [16]. Here, $Bi_{Te}$ splits the VBM and causes a complex band structure with some dispersion, formed by Bi and Te orbitals, as it can be appreciated in the DOS. This upper band is occupied, and may act as a hole killer in case of low Bi concentrations.

*3.3. Formation energies*

Figure 3 shows the calculated formation energies using the SC64 model. For $Bi_{Cd}$, only the neutral and 1+ charge states are stable for Fermi level within the CdTe band gap. The transition
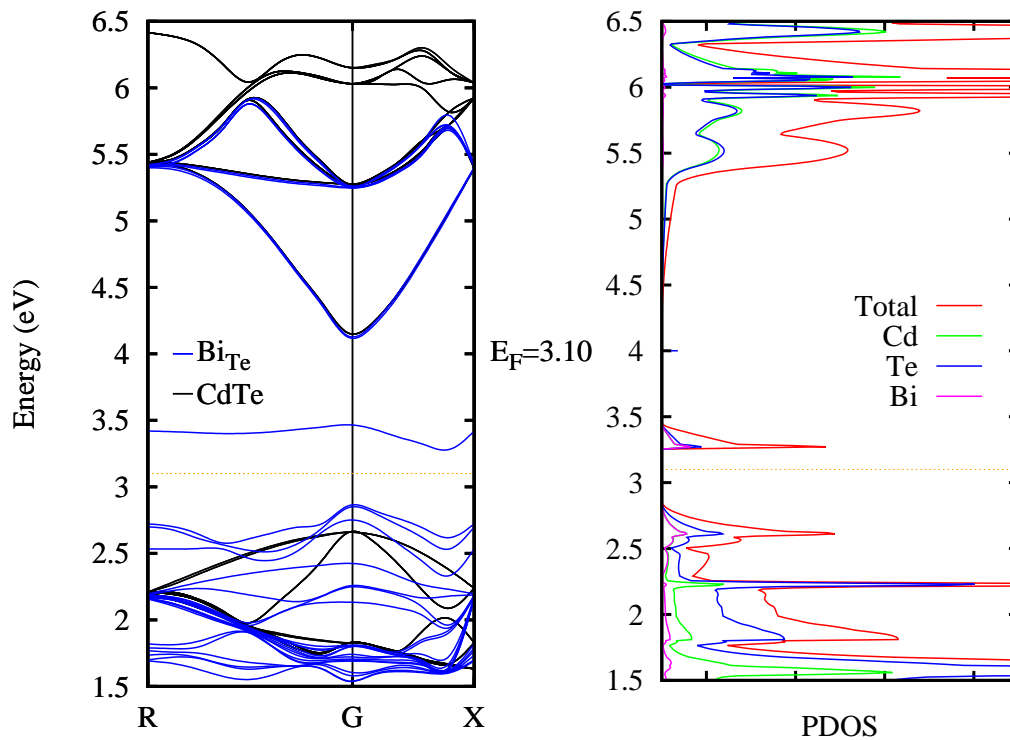
**Figure 2.** (Color online) Band structure of $Bi_{Te}$ in CdTe performed with a 64-atom supercell. Black lines are the bands for the perfect crystal. Blue lines are the bands of the defective supercell in neutral charge state. Dashed lines indicate the Fermi level ($E_F$). The PDOS is shown at the right.

level is $\varepsilon(1+/0) = 1.29$ eV. For $Bi_{Te}$, the 1+, 0 and 1− charge states are stable, with transition levels $\varepsilon(1+/0) = 0.05$ eV and $\varepsilon(0/1-) = 0.84$ eV.

The relative stability of $Bi_{Cd}$ vs $Bi_{Te}$ depends strongly on the relative abundance of Cd and Te. In Cd-rich condition $Bi_{Te}$ has lower formation energy than $Bi_{Cd}$, being most probable in thermodynamic equilibrium. This order is reversed in Te-rich condition. Therefore, the predominant type of substitution can be tuned if the Cd and Te chemical potentials can be controlled. In Te-rich conditions, $Bi_{Cd}$ is favored. $Bi_{Cd}^{1+}$ acts as a deep donor, compensating the Cd vacancies. $Bi_{Te}$ is favored in Cd-rich condition, acting as a deep acceptor. It can also donate electrons for Fermi levels close to the VBM, acting as compensator.

## 4. Conclusions

A modified hybrid functional of the HSE family has been proposed to obtain accurate band structures of CdTe and use it to study defects that have active levels in the gap. This framework has been applied to the study of Bi impurities of CdTe. It is shown that Bi substituting both Cd and Te cause deep levels in the gap and, in sufficient concentrations, can induce an IB. The positioning of the IB in the band gap is accomplished only when the SOC is included in the calculations. These results provide a model that may explain the observed increase of the short-circuit current in Bi-doped CdTe solar cells [2].
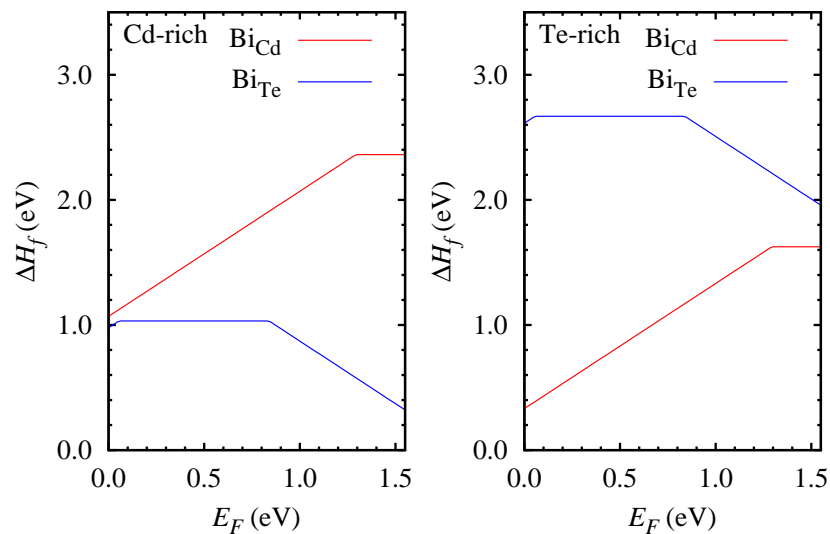
**Figure 3.** (Color online) Formation energies as a function of the Fermi energy for the $Bi_{Cd}$ and $Bi_{Te}$, computed with a 64-atoms supercell (SC64).

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