

Theoretical study of intrinsic defects in CdTe

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Abstract. The quantum states and thermodynamical properties of the Cd and Te vacancies in CdTe are studied by first principles calculations. It is shown that the band structure of a cubic 64-atoms supercell with a Te vacancy is dramatically different from the band structure of the perfect crystal, suggesting that it cannot be used as model to calculate isolated defects. This flaw is solved modeling the Te vacancy within a cubic 216-atoms supercell. However, even with this large supercell, the 2- charge state relaxes to an incorrect distorted structure. This distortion is driven by partial filling of the conduction band induced by the k-point sampling. The correct structures and formation energies are obtained by relaxation with restriction of system symmetry, followed by band-filling correction to the energy, or by using a larger supercell that allows sampling the Brillouin zone with a single k-point.

1. Introduction

Cadmium telluride (CdTe) is a semiconductor crystal employed as photovoltaic material which is growing rapidly in acceptance, becoming a cheap alternative to the silicon solar cells. CdTe has advantages for photovoltaic applications, such as a direct band gap, allowing to absorb solar energy in thin films. Its band gap of 1.5 eV at room temperature is in the range for maximum conversion efficiency of a single absorber solar cell [1]. CdTe is also widely used for radiation detectors [2]. However, the nature of the defects in CdTe thin films has been subject of controversy for long time, and its identification frequently relies on thermodynamics arguments and ab initio calculation of the defects and impurities formation energies. Density functional theory (DFT) is the most popular framework for ab initio calculations.

To explain the computational method, let us define the formation energy of V_{Te} . It can be obtained computing the difference between the total energies of a crystal supercell containing n CdTe units, $E(Cd_n Te_n)$, and the energy of the same supercell with a missing Te, $E(Cd_n Te_{n-1})$, added with the Te chemical potential $E(Te) + \Delta\mu_{Te}$

$$\Delta H_f(V_{Cd}^q) = E(Cd_{n-1} Te_n) + E(Cd) - E(Cd_n Te_n) + \Delta\mu_{Cd} + q[E_V + E_F] + \Delta E_{size} + \Delta E_{q.p.} \quad (1)$$

To obtain the formation energy of the tellurium vacancy, V_{Te} , it suffices to exchange Cd with Te in Eq. (1). Here, $E(Cd)$ is the energy of Cd in a reference state, in this case it is the energy per atom of bulk Cd. $\Delta\mu_{Cd}$ is the chemical potential relative to the reference state, and it depends on the thermodynamic equilibrium conditions. In Cd-rich conditions $\Delta\mu_{Cd} = 0$, while in Cd-poor conditions $\Delta\mu_{Cd}$ equals the CdTe formation energy [3]. For a charged vacancy, q



is the number of electrons donated to the environment, and $E_V + E_F$ 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. ΔE_{size} and $\Delta E_{q.p.}$ are size and gap corrections that are explained in sections 2.2 and 2.3, respectively.

Most calculations of CdTe point defects have been investigated using the 64-atom supercell (SC64) of the perfect crystal [2–8]. This supercell is $2 \times 2 \times 2$ times the 8-atoms conventional cubic unit cell. The SC64 supercell is the standard framework nowadays to model defects in diamond- or zincblende-type semiconductors. It is a popular choice because of its cubic shape, that maximizes the distance between the defect and its periodic images, and allows easy charge corrections. In addition, it is affordable for high level methods beyond DFT. This setup is sufficient to model some defects like V_{Cd} . However, for V_{Te} we will show that the SC64 supercell is too small to obtain a reliable band structure, while thermodynamic calculations are hampered by uncontrollable size effects that are incompatible with the notion of diluted defects. We observe that changes in the conduction band are so dramatic that destroy the reference to apply gap corrections to the formation energy of negatively charged states. We show that this problem is solved using a 216-atom supercell of the perfect crystal (SC216), which is $3 \times 3 \times 3$ times the 8-atom cubic unit cell. In addition, the band filling induced by the use of a k-point grid causes a spurious distortion in the double negatively charged state $2-$. We show that this size effect can be discarded by analyzing the band diagram and applying the band-filling correction. According to our results, a large supercell with only one k-point is enough to avoid this problem. For CdTe, this large supercell can be $4 \times 4 \times 4$ times the cubic unit cell, that contains 512 atoms for the perfect crystal (SC512).

2. Methodology

2.1. Electronic structure calculations

We have performed DFT calculations by using a plane-wave projector augmented wave [9, 10] scheme, as implemented in the Vienna Ab Initio Simulation Package (VASP) [11]. We have used mostly the generalized gradient approximation (GGA) for the exchange-correlation functional as proposed by Perdew, Burke, and Ernzerhof (PBE) [12]. In certain cases, we have also used the hybrid functional proposed by Heyd, Scuseria and Ernzerhof (HSE06) [13]. This functional generally allows one to obtain better band gap energies and structural properties than those obtained with PBE, but at the cost of a great increment in computer time.

We have used a plane-wave cutoff energy of 460 eV for the wavefunctions. To sample the reciprocal space, we have used Γ -centered $3 \times 3 \times 3$ and $2 \times 2 \times 2$ k-point grids for the SC64 and SC216 supercells, respectively. This setup allows convergences of 0.5 meV/atom and 0.4 kbar in total energy and pressure, respectively, as tested for variable cell relaxations of the CdTe zincblende unit cell with $8 \times 8 \times 8$ k-point grid. In fact, a reduced cutoff of 285 eV allows a convergence within 10 meV/atom in total energy and 2 kbar in pressure, but the properties derived from relative energies, e.g., lattice constants and bulk moduli are well converged. The CdTe lattice constant obtained with variable cell relaxation with a cutoff of 285 eV differs by 0.4% from the converged value, but when the energy is fitted with the Birch-Murnaghan equation of state, the difference falls to 0.005 %. The energy difference between the zincblende and wurtzite structures is 3.5 meV/atom considering both cutoffs. The $n \times n \times n$ supercell size is n times the converged theoretical lattice constant of the perfect crystal (6.6212 Å). We have used a cutoff of 285 eV to relax the point defect structures with fixed supercell size, and a cutoff of 460 eV to compute the total energies. The highest precision is needed because the energy error is amplified by the number of atoms in the supercell, e.g., for the neutral Cd vacancy in SC64 supercell, the formation energy computed with both cutoffs differs by 0.03 eV. We have verified that for higher cutoff energy, the forces on the atoms in the relaxed geometry keep below 0.01 eV/Å.

The calculated CdTe heat of formation is found to be of 0.93 eV, in good agreement with the available experimental value of 0.96 eV [2]. The energy of bulk Cd has been obtained by relaxing the 2-atom unit cell of the experimental structure ICSD #52793 available from the MedeA software environment [14]. 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 ICSD #23060. The Brillouin zone was sampled by a $8 \times 8 \times 5$ k-point grid and tested with a $15 \times 15 \times 10$ grid.

2.2. Size corrections

An isolated defect either populates the conduction band minimum (CBM) or create holes at the VBM. However, in a finite supercell, when a k-point mesh is used, the electron or hole created by the point defect fills half a band, considering the spin degeneracy. The single-particle contribution to the total energy is affected by the band dispersion. The correction is to replace the energies of the defect band, either of electrons or holes, by the corresponding band extremum. For donors, the correction can be expressed as [15]

$$\Delta E_{b.f.} = - \sum_{n,k} \Theta(e_{n,k} - e_{min}) w_k \eta_{n,k} (e_{n,k} - e_{min}), \quad (2)$$

where indexes n and k denote the bands and k-points, w_k are the k-point weights, $e_{n,k}$ are the single particle energies with minimum e_{min} , $\eta_{n,k}$ are the occupation numbers, and Θ is the Heaviside function. The correction for acceptors is

$$\Delta E_{b.f.} = \sum_{n,k} \Theta(e_{max} - e_{n,k}) w_k (S - \eta_{n,k}) (e_{max} - e_{n,k}), \quad (3)$$

where $S = 1$ ($S = 2$) stands for spin polarized (unpolarized) calculations. e_{max} is the maximum of the acceptor band.

In VASP calculations, the average of the electrostatic potential is set to zero. Hence, the potential energy reference is undetermined by an additive constant, which is different in supercells containing different number of atoms or different charge. The change has two sources: a) the presence of excess charge, b) the missing or appearance of extra atoms. For charged systems, the additive constant enters in the Hartree term of the total energy per cell:

$$E_H = \int e [n_0(\mathbf{r}) - N(\mathbf{r}) + \Delta n(\mathbf{r})] (v(\mathbf{r}) + \Delta v) d^3 \mathbf{r},$$

where e is the electron charge, $n_0(\mathbf{r})$ is the electron density for a neutral system, $\Delta n(\mathbf{r})$ is the excess electron density. $N(\mathbf{r})$ is the nuclear charge, and Δv is the additive potential implicitly added to make zero the average potential, with respect to the potential of the system without defect and neutral. The contribution of the additive potential to the Hartree energy is equal to

$$\Delta E_H = \int e \Delta n(\mathbf{r}) \Delta v d^3 \mathbf{r} = \left[\int \Delta n(\mathbf{r}) d^3 \mathbf{r} \right] (e \Delta v) = (-q) \Delta V. \quad (4)$$

Here, q is the number of electrons donated $\int \Delta n(\mathbf{r}) d^3 \mathbf{r} / (-e)$, and $\Delta V = e \Delta v$ is the change of electron potential energy. ΔV can be estimated by the core level shifts of atoms far from the defect with respect to the core levels in the calculation with the perfect crystal. The correction to the total energy due to potential alignment (p.a.) is

$$\Delta E_{p.a.} = q \Delta V. \quad (5)$$

Periodic boundary conditions induce an spurious interactions of the charged defect with the periodic replicas. The leading terms can be corrected by the Makov-Payne formula

$$\Delta E_{M-P} = \frac{\alpha_M q^2}{2\epsilon V^{1/3}} + \frac{2\pi q Q}{3\epsilon V} + O(V^{-5/3}),$$

where α_M is a Madelung constant, ϵ is the dielectric constant, V is the supercell volume, and Q is a quadrupole moment. We have used a simplified version due to Lany and Zunger [15]

$$\Delta E_{L-Z} = \frac{2}{3} \frac{\alpha_M q^2}{2\epsilon V^{1/3}}. \quad (6)$$

We have used the static dielectric constant $\epsilon = 12.272$, obtained from density functional perturbation theory calculations and including local field effects [16,17].

In summary, the supercell size corrections are given by the sum of band-filling, potential alignment, and Lany-Zunger corrections

$$\Delta E_{size} = \Delta E_{b.f.} + \Delta E_{p.a.} + \Delta E_{L-Z}. \quad (7)$$

2.3. Gap corrections

Semilocal exchange-correlation functionals (LDA, GGA) cause a severe underestimation of the valence to conduction band gap, and this affects the formation energies. Let us consider the gap error

$$\Delta E_g = E_g^{exp} - E_{gap}^{DFT} = \Delta E_C - \Delta E_V.$$

The above equation established a partition of the gap error in shifts applied to the valence and conduction band.

For shallow acceptors, where active holes occupy perturbed host states, the hole levels undergo the same shift as the valence band edge. This has been verified in quasiparticle calculations. For shallow donors, the active electron levels are perturbed states of the conduction band, undergoing the shift. Including fractional occupations, the shifts of single particle levels and total energies can be expressed as

$$\Delta E_g^{(1)}(q) = \begin{cases} z_e(X, q) \Delta E_C & \text{for donors,} \\ z_h(X, q) (-\Delta E_V) & \text{for acceptors,} \end{cases} \quad (8)$$

where z_e (z_h) is the number of electrons introduced (removed) by the defect near the CBM (VBM).

A second gap correction modifies the reference of the Fermi level

$$\Delta E_g^{(2)}(q) = q \Delta E_V. \quad (9)$$

The total gap correction is

$$\Delta E_{q.p.} = \Delta E_g^{(1)}(q) + \Delta E_g^{(2)}(q). \quad (10)$$

With our computational setup that includes the PBE functional, the VBM and CBM energies are 1.789 and 2.388 eV, respectively. For gap corrections we have used the generalized DFT with the hybrid functional HSE06 [13] including the spin-orbit coupling. The corrected VBM and CBM energies are 1.773 and 2.977 eV, respectively. With this approximation the band gap is 1.204 eV, which is still lower than the experimental value 1.6 eV [18].

3. Results and discussions

3.1. Cadmium vacancy

Figure 1 shows the calculated formation energies of five charge states of V_{Cd} . As can be seen, only the 1- and 2- charge states have the lower formation energies, being stable for the Fermi level within the CdTe band gap. The transition level is $\epsilon(-/2-) = 0.36$ eV. The transition level $\epsilon(0/-) = -0.01$ eV is virtually at the VBM within the error of the calculation. These transition levels are close to the values obtained with the GGA+U^{SIC} approach [8] and with hybrid functional PBE0 [2] and HSE [7]. In the later cases, the transition level $\epsilon(0/-) \sim 0.23$ eV, but this result is affected by the neglect of the spin-orbit interaction, that raises the VBM by ~ 0.3 eV. The neglect of the spin-orbit contribution to the VBM also affects the GGA calculations of Ref. [4].

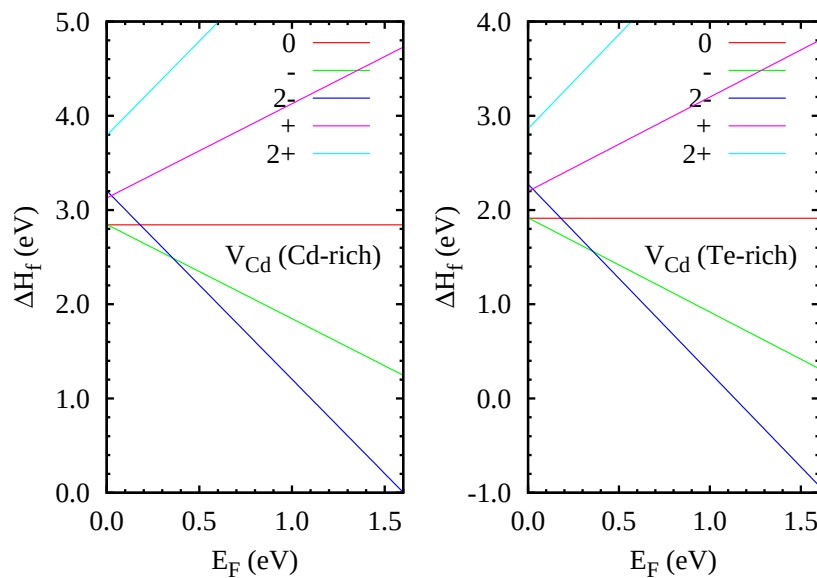


Figure 1. (Color on-line) Formation energies as a function of the Fermi energy for the Cd vacancy computed with a 64-atom supercell (SC64).

The absolute values of the GGA formation energies (present work) are about 0.7 – 1 eV smaller than the values obtained with GGA+U^{SIC} and with PBE0. These differences are related to the different precision of the functionals in the semiconductor CdTe, the metal Cd and the semimetal Te. The formation energy contains the term $E(Cd)$, and let us note that $E(Cd) + E(Te) + \Delta H(CdTe) = E(CdTe)$. The formation energy $\Delta H(CdTe)$ is -1.13 eV and -1.78 eV within PBE0 and GGA+U^{SIC}, respectively. These numbers imply larger values for the sum $E(Cd) + E(Te)$.

From the electronic point of view, V_{Cd} in the neutral state has two holes delocalized in the valence band. Upon charging with two electrons, i.e., the state V_{Cd}^{2-} , the valence band gets fully occupied. In all the charge states considered here the relaxation of the atoms are quite small, consistently with the delocalized character of the holes. These features allow one to calculate the formation energies with the rather small SC64 supercell and to include the size effects as corrections.

3.2. Tellurium vacancy

In this section, we present calculations of V_{Te} with the supercells SC64 and SC216. First, we analyze the band structure of the defective supercells, and show the problems to apply band-filling and gap corrections with the SC64 model.

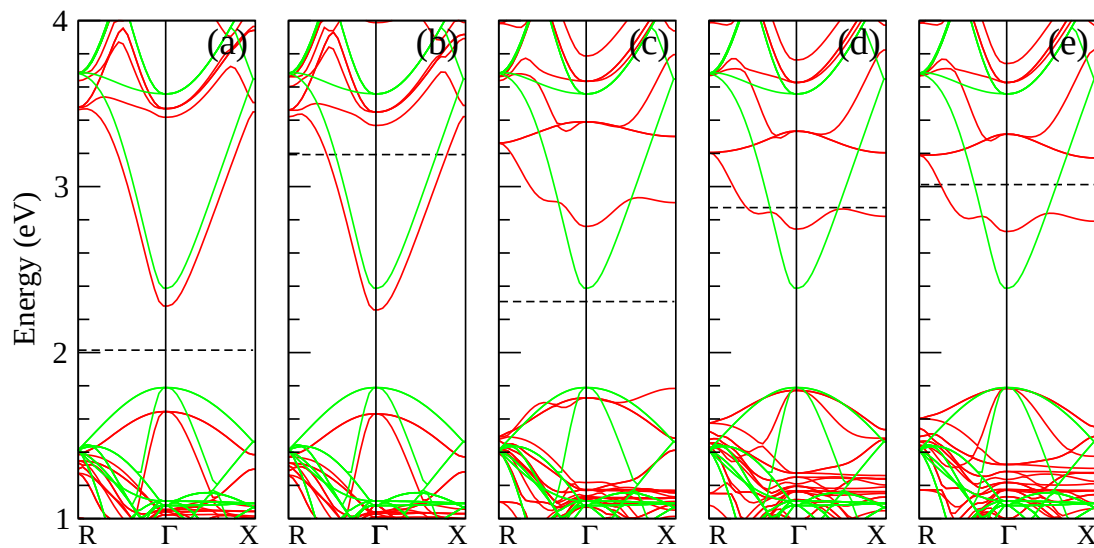


Figure 2. Band structure calculations for the Te vacancy in CdTe performed with a 64-atom supercell. The red lines are the bands of the defective supercell in charge states 2+ (a), 1+ (b), 0 (c), 1- (d), and 2- (d). The green lines are the bands for the perfect crystal. The dashed lines indicate the Fermi levels.

Figure 2 shows the band structure calculations of the perfect CdTe and V_{Te} in the SC64 supercell. The atomic positions were relaxed keeping the T_d symmetry, while distorted configurations will be considered separately using larger supercells. The vacancy in the SC64 supercell is strictly a periodic model of V_{Te} in a concentration of one every 64 atoms or 10^{20} cm^{-3} . Even when the band diagram is not valid in aperiodic situations, it allows a certain order in the visualization of the eigenstates. In Figure 2 we see that for the charge states 0, 1-, and 2-, the conduction band (CB) is dramatically modified with a significant increment of the band gap. This global change produced by the vacancy is incompatible with the notion that an impurity should introduce small perturbations on the crystal band structure. This example shows that band diagrams, which are in principle not adequate to study aperiodic systems, are still useful to uncover flaws in defect models. From the practical side of thermodynamic calculations, the drastic alteration of the conduction band makes impossible to apply gap corrections, resulting in a false stability of the negatively charged states in n-type doping conditions. The only solution to avoid the exaggerated influence of V_{Te} is to explore configurations using a larger supercell.

Figure 3 shows the band diagram of the perfect crystal and the V_{Te} defect in different charge states computed with the SC216 model. The T_d symmetry of the atomic arrangement around the vacancy has been preserved during the relaxation as for SC64. Distorted configurations with lower energy will be studied separately below. For all the charge states considered, the effects of the vacancy are small band shifts and level splits. In addition, one can recognize an empty-defect band over 3.2 eV for $q = 2-, 1-, 0$. As we will see later, the defect band becomes active, driving the so called Jahn-Teller distortions. The origin of the defect band can be understood as follows: Each Te-Cd covalent bond is populated by 0.5 Cd electron and 1.5 Te electron. When V_{Te} is formed, four sp^3 bonding orbitals and six electrons are removed. This process leaves two electrons from the four surrounding Cd 5s orbitals. These orbitals combine to form four defect bands: one mixed with the host valence band (VB) that gets occupied by the electrons left by the Cd broken bonds, and three empty isolated bands ($\sim 3.1 - 3.5 \text{ eV}$). Of these three bands, the lowest two are degenerate. In states 1- and 2-, the defect levels keep empty and the extra

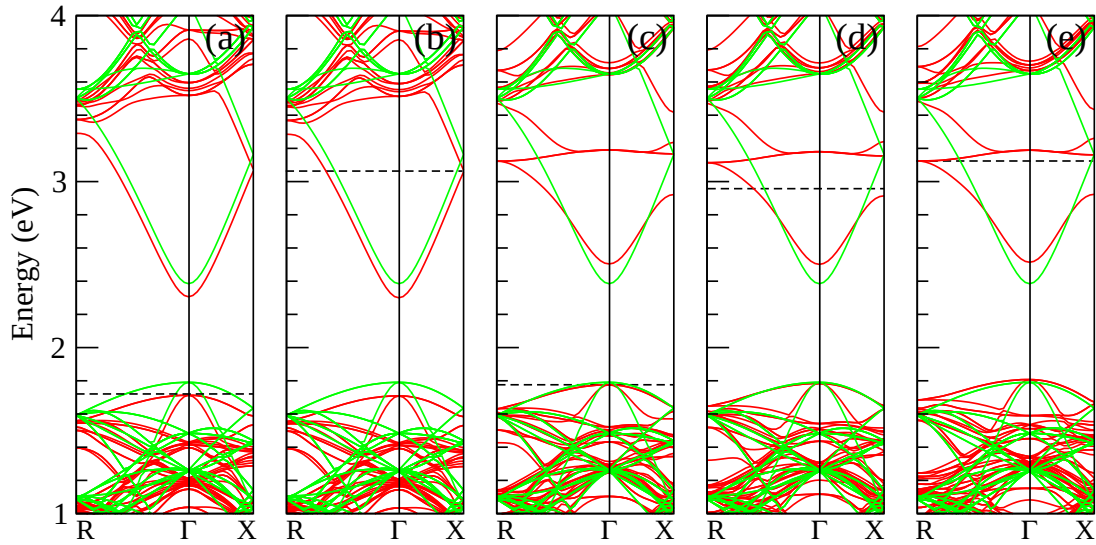


Figure 3. Band structure calculations for the Te vacancy in CdTe performed with a 216-atom supercell. The red lines are the bands of the defective supercell in charge states 2+ (a), 1+ (b), 0 (c), 1- (d), and 2- (e). The green lines are the bands for the perfect crystal. The dashed line indicates the highest occupied level.

electrons occupy perturbed host states [19], that in the supercell calculation appear similar to the CB.

The neutral state shows a similar band structure if the atomic positions keep the T_d symmetry. However, the total energy and the band diagram are modified due to a symmetry breaking (C_{2v} distortion) that lowers the total energy by 0.3 eV. The distortion leads to formation of a Cd_2 dimer with a bond length of 2.86 Å. Figure 4 shows the band diagrams of both symmetric and distorted configurations, and the geometry of the latter. The origin of the distortion is not due to the Jahn-Teller mechanism, because the symmetric state does not present degeneracy. As discussed above for the 2- state, the missing Te atom leaves four broken bonds with 0.5 electron each one. The energy is reduced when two Cd atoms lose 0.5 electrons and move to adopt a quasi-planar bonding structure with their three Te neighbors. The rules of covalent bonding are satisfied if these two Cd atoms distribute their 1.5 electrons in three sp^2 orbitals that make σ bonds with the Te sp^3 orbitals. The other two Cd atoms, which also have $0.5 \times 2 = 1$ electron in dangling bonds, trap the electron released by the first Cd pair, getting closer to form a doubly occupied covalent bond. This bond corresponds to the VB top in Fig. 4(b), where the corresponding charge density (square of the wave function) is shown in Fig. 4.

For the 2- charge state, the total energy is apparently minimized by a D_{2d} distortion leading to the formation of two perpendicular Cd dimers. The band energy is minimized by a downshift of the defect band, that becomes occupied, while the dispersive host-like conduction band gets empty. This mechanism lowers the total energy by 0.6 eV. However, the self-consistent energy must be corrected by subtracting the band filling energy, which is -0.87 eV for the undistorted configuration, but it is negligible for the distorted one. Therefore, the symmetric configuration has lower energy. In order to test this assertion, we have inserted the distorted configuration into a larger supercell composed of $4 \times 4 \times 4$ conventional unit cells, i.e. the SC512 model. Using only the Γ point, the band filling error is null. As expected, the distorted configuration in the SC512 relaxes to the non-distorted structure. Therefore, the distortion around the vacancy for the 2- state is a supercell-size effect driven by the conduction band filling in the SC64 and

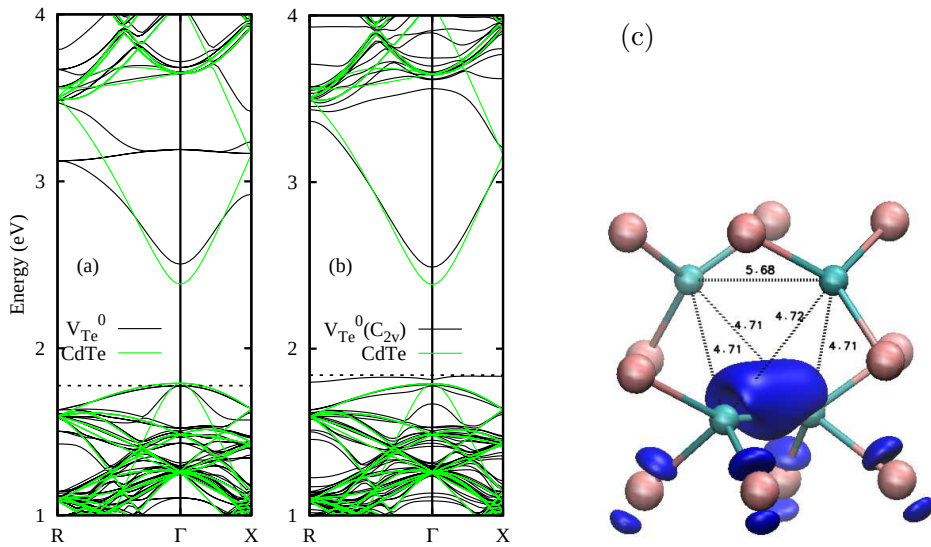


Figure 4. (Color online) Stable geometries and band diagrams for the neutral Te vacancy without (a) and with (b) a C_{2v} distortion, using the SC216 supercell. The solid black (green) lines are the bands of the defective (perfect) supercell, and the dashed lines represent the highest occupied level. (c) Charge density isosurfaces for the valence-band maximum of the distorted Te vacancy in neutral charge state. Pink and cyan balls represent Te and Cd, respectively.

SC216 models.

For the neutral state, there is no need of band filling correction because there is neither hole in the VB nor electron in the CB. Therefore the distorted configuration is more stable. The calculation with the SC512 model confirms this result.

It seems contradictory that for the 1+ state, with one missing electron, the highest occupied level jumps into the CB, and for the 2+ state the highest occupied level returns to the VB. This behavior is due to strong relaxation of the four neighboring Cd atoms into planar configurations CdTe_3 , favoring a sp^2 -like hybridization. Within a sp^2 shell structure, each Cd atom shares its 2 valence electrons with 3×1.5 electrons coming from its three neighboring Te, resulting in 0.5 electron in excess of the sp^2 shell. Adding the four Cd atoms, this sums 2 electrons. The net effect is that two electronic levels are removed (holes). Therefore, the closed-shell structure is recovered in the charge state 2+, while for the state 1+ there is one electron in the CB. For the state 1+, the formation energy must be corrected for the conduction band filling, as well as for the errors in the VB and CB edges, considering $z_e = 1$ and $z_h = 2$ in Eq. 8, respectively.

Figure 5 shows the formation energy plots as function of the Fermi level. For the gap corrections we have approximated the VBM and CBM energies by the values obtained using the HSE06 hybrid functional including the spin-orbit interaction. As this method gives a band gap of 1.2 eV [8], this is the maximum value for the Fermi level in Fig. 5. It can be seen that the stable charge states are the 2+ and the neutral state, with the thermodynamic transition level $\epsilon(2+/0) = 0.69$ eV.

Recent calculations using the HSE06 method [5,6] with the supercell SC64 suggest that V_{Te} is stable only in the state 2+. These authors attribute the high stability of the charged state to the large Cd displacements around the vacancy. We think they may have missed the energy downshift of the neutral state due to C_{2v} distortion. In any case, we consider unreliable the results obtained with the SC64 model.

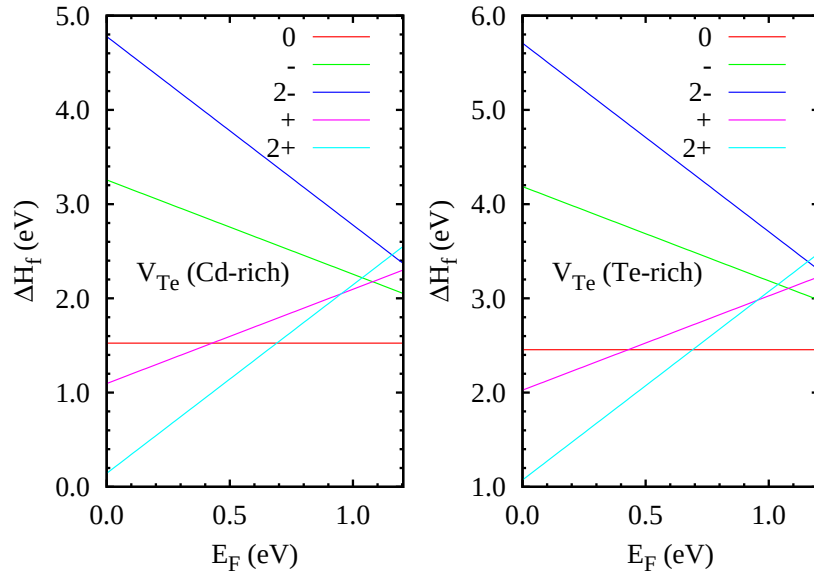


Figure 5. (Color on-line) Formation energies as a function of the Fermi energy for the Te vacancy computed with a 216-atom supercell (SC216).

4. Conclusions

Our results for V_{Cd} , are consistent with the literature [2, 4, 7, 8]. The main difference in our results is the missing of a stable neutral state. We attribute this difference to the location of the VBM, which is upshifted by the inclusion of the spin-orbit interaction.

For V_{Te} , our results challenge the previous studies [2–6], which have been obtained using the SC64 model. On the one hand, we have shown that the band structures of the neutral and negative charge states present unphysical features, such as enlargement of band gap and strong modification of the conduction band dispersion. The study of the band diagram of the supercell calculation is a useful tool to uncover these unphysical states. On the other hand, we have shown that for the charged vacancy V_{Te}^{2-} , the band-filling error associated to the k-point sampling can drive the system to a distorted configuration, as in Ref. [4]. After band-filling corrections are applied, the undistorted configuration has lower energy. Our calculations with the Γ -point sampling using the SC512 model, are free of the band-filling error, confirming that the symmetric configuration has lower energy. For a general case, if calculations with the SC512 model were not affordable, we suggest a careful analysis of the band-filling errors in the distorted and undistorted configurations, provided that optimized undistorted configurations can be obtained. High level calculations like hybrid functionals, Green functions GW, or Quantum Monte Carlo are probably not affordable for such large supercells, and may need to be done for the SC64 model. In these cases, GGA reoptimizations of the distorted structures inserted in a large supercell with a single k-point, are recommended to evaluate the veracity of the distortions.

Acknowledgments

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