Density functional theory study of defects in cadmium telluride: a PBC and QM/MM comparison

M Casanova-Páez\textsuperscript{1,2} and E Menéndez-Proupin\textsuperscript{1}

\textsuperscript{1} Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile
\textsuperscript{2} Departamento de Física, Facultad de Ciencias Físicas y Matemáticas (FCFM), Universidad de Chile, Casilla 487-3, Santiago, Chile

E-mail: marcos.casanova@ug.uchile.cl

Abstract. Ab initio calculations, in the framework of density functional theory (DFT), are employed to determine the formation energies of tellurium vacancy (V\textsubscript{Te}) for different ionized states. We performed a periodic boundary conditions (PBC) calculation, applying quasiparticle corrections and establishing the thermodynamic transition level. In addition, we have also used the quantum mechanics/molecular mechanics (QM/MM) approach in order to check its capability predicting formation energies, finding similar results compared to the previous supercell method.

1. Introduction

It is important for photovoltaic devices to achieve the control over the charge carriers and the management of impurities and native defects. Cadmium telluride (CdTe) is an iconic example of II-VI compound and one of its main uses is as photovoltaic material, gaining fast acceptance due its competitiveness to respect the traditional silicon solar cells, becoming a cheap alternative. CdTe is also widely used as radiation detectors [1]. One advantage of CdTe as photovoltaic material is its direct band gap (1.5 eV at room temperature) which positions it in the range of maximum spectral irradiance and reaching the maximum efficiency for a single absorber solar cell [2]. Defects in CdTe are widely studied through DFT, since they have been subject of controversy for a long time, based on local or semi-local density approximation (LDA or GGA). Furthermore, most native defects in CdTe occur in both their neutral and one or more ionized states [3]. There is no direct evidence of tellurium from experiments, but theoretical calculations predict that this is one of the most important intrinsic donors [1; 4–6].

Point defects formation energies are calculated by taking the difference in total energies of a system with and without the defect of interest. One complication that arises is that isolated point defects energies are desired in most cases, making necessary the use of a big supercell in order to reduce the size effects as much as possible. The formation energy of V\textsubscript{Te} of a crystal containing \( n \) CdTe units is computed as

\[
\Delta H_f(V_{\text{Te}}^q) = E(\text{Cd}_n\text{Te}_{n-1}) + E(\text{Te}) - E(\text{Cd}_n\text{Te}_n) + \Delta \mu_{\text{Te}} + qE_F + \Delta E_{\text{size}} + \Delta E_{\text{q.p}},
\]
where $E(\text{Te})$ is the energy per atom of bulk Te. $E(\text{Te}) + \Delta \mu_{\text{Te}}$ is the chemical potential of the corresponding species, and it depends on the thermodynamic equilibrium conditions. In Te-rich conditions it is set to 0 eV but in Te-poor conditions it equals the CdTe heat of formation [7]. Also, the analogue of the chemical potential for charge is given by the chemical potential of electrons, i.e., the Fermi energy $E_F$. Finally, $\Delta E_{\text{size}}$ and $\Delta E_{\text{q.p}}$ are correction terms that accounts for finite k-point sampling, interaction between supercells, quasiparticle and band-edge corrections. More detailed information about these corrections can be found in Ref. [7].

Most calculations of CdTe defects have been studied using the 64-atoms supercell (SC64) of the perfect crystal [1; 4–6; 8–10]. This supercell is $2 \times 2 \times 2$ times the 8-atoms cubic unit cell. A previous work [7] showed that the SC64 supercell is too small to obtain reliable results for the $V_{\text{Te}}$ band structure, they overcame this problem using a 216-atoms supercell (SC216). In this work we have used a 512-atoms supercell (SC512), which is a $4 \times 4 \times 4$ times the 8-atoms cubic unit cell with only one k-point. On the other hand, we have also performed a calculation using the QM/MM approach. For an embedded cluster calculation, a part of the crystal structure containing the defect and surrounding atoms is chosen. This set of atoms are treated fully quantum-mechanically (QM region). The cluster is embedded in a set of point charges (MM region) to account for long-range electrostatic interactions due to atoms of the crystal lattice outside the cluster region. In addition to point charges, the embedding needs an intermediate region of pseudopotentials which are placed at the first shell of embedding cadmium atoms of a CdTe cluster to minimize non-physical polarization. Within this model, an ion in the intermediate region is treated as a point core and a shell connected by a spring, simulating its dipole polarizability. The positions of the cores and shells in the intermediate region can be optimized with respect to the total energy of the system, in accordance with the relaxed geometric and electronic structure of the inner cluster. Despite the fact that CdTe is not an ionic material, we are assuming that the ions are in the formal oxidation state, i.e. the crystal consists of Te$^{-2}$ and Cd$^{+2}$ ions.

2. Computational details

2.1. Supercell approach

Supercell calculations were performed using the all-electron, full-potential electronic structure code FHI-aims [11]. Our calculations were performed using the generalized gradient approximation (GGA) for the exchange-correlation functional proposed by Perdew, Burke and Ernzerhof (PBE) [12]. We have used the tight basis set for the wavefunctions (which are radial functions proposed by FHI-aims for well converged energies). The lattice constant was obtained through the Birch-Murnaghan equation of state, differing by 2.2 % from its experimental value of 6.48 Å. The SC512 supercell was constructed using 4 times the converged theoretical lattice constant of the 8-atoms cubic unit cell calculated before (6.625 Å). For all the structures, forces were minimized until residuals fell below $10^{-3}$ eVÅ$^{-1}$ per atom.

The heat of formation of CdTe is found to be -0.93 eV, which is in good agreement with respect to its experimental value of -0.96 eV [3]. The energies of the bulk Cd and Te were calculated by relaxing the 2-atoms and 3-atoms unit cells of the experimental structures, respectively. The Brillouin zone was sampled by a $22 \times 22 \times 10$ and $9 \times 9 \times 6$ Monkhorst-Pack k-points grid sampling for Cd and Te, respectively.

2.2. QM/MM approach

The embedded cluster calculation was performed by the computational chemistry code Chemshell [13], which acts as a linker between FHI-aims and GULP [14], an interatomic potential code used in the classical region. FHI-aims performs all the quantum calculations obtaining the interacting forces which goes directly to GULP in order to move the atoms, point charges, etc. Our QM region setup is a Cd$_{32}$ Te$_{43}$ cluster embedded into a MM region.
of about 5000 point charges and 200 cadmium pseudopotentials. The forcefield for classical interactions include the Buckingham and Lennard-Jones potentials and a harmonic-type term for the polarizability. The basis used in the QM region are tight (as explained before), and the lattice parameter used to construct the cluster is the one calculated by the Birch-Murnaghan equation of state (6.625 Å). The norm-conserving pseudopotential was constructed by the FHI98PP pseudopotential program [15] using the procedure of Troullier and Martins.

3. Results
3.1. Tellurium vacancy in SC512 supercell: Geometric and electronic properties
Geometric relaxations are important as they play an important role in formation energies, specially for ionized states. When a Te atom in removed from the CdTe lattice, the arrangement of atoms in the neighborhood of the defect will adjust to lower the energy of the system.

![Figure 1. C₄ᵥ symmetry (left) for neutral and negative charge states, T₉°ut symmetry (middle) for positive charge states and D₂d symmetry (right) for 2- charge state in the QM/MM approach.](image)

The Tₐ symmetry of the atomic arrangement around the vacancy is conserved in the relaxation for both the 1+ and 2+ ionized states. The neighboring cadmium atoms relaxed outward, keeping the symmetry, locating approximately at the center of the triangles formed by the neighboring tellurium atoms. Let us denote this configuration as T₉°ut in order to differentiate it from the configuration with inward relaxation T₉°in and from the absence of relaxation Tₐ⁰deₐ₉. The Cd-Cd distance in this configuration is 5.88 Å. On the other hand, for the neutral and negative states, two of the four Cd atoms get closer inducing a C₂ᵥ distortion. This distortion leads to formation of a Cd₂ dimer with a bond length between 2.86 Å and 2.88 Å, depending of the charge state. It is important to mention that our calculations show that C₂ᵥ symmetry is the most stable structure for the 2⁻ charge state, at difference with previous reports. For example, some groups have found a D₂d symmetry for this charge state [4; 7], which has a higher energy with respect to our structure by 0.4 eV, approximately. We found this symmetry as well in the QM/MM approach and it will be explained in the corresponding section 3.2.

Some advantages of using a 512-atoms supercell is that the band-filling correction is not necessary, since we are using only one k-point in the calculation. On the other hand, the Coulomb interaction between charged defects is reduced as much as possible, reaching its maximum value of 0.17 eV for 2± charge state. For all the ionized states considered here, the effects of the vacancy are small band shifts and splits.

3.1.1. Defect energy states
The defect energy states were found in both the neutral and 1+ charge states. In the neutral state (with C₂ᵥ symmetry) one level is located in the band gap and the other level is in the conduction band (Fig. 2(a) 2(b)). On the other hand, the 1+ state (with T₉°ut symmetry) both levels are located in the conduction band (Fig. 2(c) 2(d)). This can be confirmed through the total density of states (DOS) of the pristine crystal calculation and
Figure 2. Wavefunction isosurface for neutral charge state (top panels) and 1+ state (bottom panels). (a) level in the band gap (b) level in the conduction band (c) and (d) levels in the conduction band, respectively.

the charged states. In addition, we also plotted the wavefunction isosurface onto those states and we checked their energy location.

Figure 3. PBE total DOS (a) in ideal CdTe (b) tellurium vacancy with neutral charge state and (c) tellurium vacancy with single positive charge state through the PBC approach. The vertical dashed line indicates the Fermi level of the ideal CdTe and also the defect levels are shown in red and blue colors.

The total density of states shown in Fig. 3 correspond to the supercell calculation using only the Γ-point and, for this reason, the Van Hove singularity can not be seen. Nevertheless, using a denser K-point mesh will fix this problem.

The value of the wavefunction isosurface was set to $\pm 0.044$ a.u., in both charge states. The location of these defect energy levels are: For neutral charge state, one level is located in the
band gap at -5.15 eV and the other level is in the conduction band at -3.42 eV (red and blue lines in Fig. 3(b)). In the 1+ charge state, these levels are both located in the conduction band at -3.43 eV and -2.94 eV (blue lines in Fig. 3(c)).

3.1.2. Formation energy It is well known that GGA underestimate the band gap of materials, causing errors in the formation energy. To obtain the band edges using semilocal exchange-correlation functionals one needs a subsequent beyond-DFT calculation, like the GW approximation. The corrections to the band edges were reported in Ref. [7]. Fig. 4 shows the formation energies with and without corrections. From here we have that 0 and 2+ states are the only stable states. The quasiparticle corrections have been applied, shifting the VBM by -0.470 eV and the CBM by +0.481 eV [7]. The 1+ state is insensitive to the quasiparticle corrections due a correction cancellation between the modification of the Fermi level and the donor correction. These corrections are not required for the neutral state. As this method gives a band gap of 1.55 eV, this is the maximum value of the Fermi level. The calculated thermodynamic transition level is $\varepsilon(2+/0)=1.17$ eV.

3.2. Tellurium vacancy in the QM/MM approach: Geometric and electronic properties The geometric relaxation was computed by the Chemshell code and the structure was fully relaxed until residual forces fell below $10^{-3}$ eV/Å. In order to take account for the polarization response, we have calculated the static dielectric constant ($\varepsilon_0=11.972$) and the high-frequency dielectric constant ($\varepsilon_{\infty}=8.707$).

All the structures were constrained to relax only in the inner QM region (i.e. the QM boundary layer was fixed during the relaxation) in order to avoid asymmetric movement of ions near
the coupling region. The relaxed structures correspond to the same structure in the supercell approach, except for the 2− ionized state, which presents a $D_{2d}$ distortion (Fig.1), leading to the formation of two perpendicular Cd dimers with bond length of 2.88 Å. This well known size problem is described in Ref. [7]. Bond lengths are almost kept for both approaches, varying between 0.04 Å to 0.09 Å in some cases.

3.2.1. Electronic properties  In the QM/MM approach it is important to recover the electronic properties of the extended periodic material. For this reason, we have calculated the total density of states (DOS) and we compared it with respect to a 64-atoms supercell calculation (Fig.5).

![Figure 5. Comparison of the total density of states (DOS) using pseudopotentials, point charges and polarization response. Even a relatively small embedded Cd$_{32}$Te$_{43}$ cluster recovers important features from the reference bulk calculation (green color).](image)

The HOMO-LUMO gap is overestimated and it is more pronounced in small clusters. As reference, the periodic boundary conditions calculation leads to a gap of 0.57 eV while in the QM/MM approach, using a Cd$_{32}$Te$_{43}$ cluster, the gap reaches up to 2.03 eV. This is known as quantum confinement effect and is qualitatively described in chapter 1 in ref.[16].

3.2.2. Defect energy states  The defect energy states were found for the same charge states that were studied with periodic boundary conditions in section 3.1.1. The neutral charge state (with $C_{2v}$ symmetry) the defect states are located in the band gap and conduction band (Fig. 7(a) and (b)). Meanwhile in 1+ charge state (with $T_{d}^{out}$ symmetry) these levels are both located in the conduction band (Fig. 7(c) and (d)). We confirmed this through the density of states of both charge states and the pristine calculation, as well as plotting the wavefunction isosurface onto

![Figure 6. PBE total DOS (a) in ideal CdTe (b) tellurium vacancy with neutral charge state and (c) tellurium vacancy with single positive charge state through the QM/MM approach. The vertical dashed line indicates the Fermi level of the ideal CdTe and also the defect levels are shown in red and blue colors.](image)
Figure 7. Wavefunction isosurfaces in the QM/MM approach for neutral charge state (top panels) and 1+ state (bottom panels). (a) level in the band gap (b) level in the conduction band (c) and (d) levels in the conduction band, respectively.

those states. The value of the wavefunction was set to ±0.085 a.u. The location of these states are: For neutral, the one in the band gap is located at -6.17 eV and the other is at -4.56 eV, inside the conduction band. In the 1+ charge state, these levels are located in the conduction band at -4.33 eV and -3.76 eV (Fig. 6).

3.2.3. Formation energies Potential alignment was carried out comparing by the density of states (DOS) for all the charge states. They were aligned with respect to deep energy levels (∼−17 eV) of the pristine crystal calculation. Fig. 8 shows this alignment in a simple way.

Figure 8. Diagram of the potential alignment for neutral charge state from QM/MM to PBC approach. The red dashed line is the VBM reference and the blue dashed line is the CBM reference from the PBC approach.
Table 1. Potential alignment for all the charge states (in eV). $\Delta E_v$ and $\Delta E_c$ are the energy differences with respect to the periodic VBM and CBM, respectively.

| Ionized state | 2- | 1- | 0  | 1+ | 2+ |
|--------------|----|----|----|----|----|
| $E_v$        | -3.59 | -5.14 | -6.17 | -7.95 | -8.99 |
| $E_c$        | -2.45 | -3.57 | -4.58 | -5.82 | -6.82 |
| $\Delta V$   | -2.14 | -1.05 | -0.03 | 1.05  | 2.14 |
| $E_{p,a}^v$  | -5.73 | -6.19 | -6.20 | -6.90 | -6.85 |
| $E_{p,a}^c$  | -4.59 | -4.62 | -4.61 | -4.77 | -4.68 |
| $\Delta E_v$ | 0.55  | 1.01 | 1.02 | 1.72 | 1.67 |
| $\Delta E_c$ | -0.02 | 0.02 | 0.01 | 0.17 | 0.08 |

Once again, in Fig. 4 we observe that the 0 and 2+ states are the only stable states found. Compared to the previous periodic boundary approach, all the energies are shifted upwards. However, despite of this shifting, the tendency is kept in both approaches. The calculated thermodynamic transition level in this approach is found to be $\varepsilon(2+/0)=1.18$ eV.

4. Conclusions
In the supercell approach the relaxed structures found have $C_{2v}$ symmetry for the neutral and negatives charge states and $T_{d}^{out}$ symmetry for the positives states. We observe that the first symmetry has a localized state above the VBM that is shifted upward when the symmetry is changed. In addition, our calculations predict that in the 2- charge state, $V_{2-Te}^{2-}$ takes the $C_{2v}$ symmetry, which was not found previously. The thermodynamic transition level found is $\varepsilon(2+/0)=1.17$ eV. Nevertheless, one calculation has predicted a negative formation energy for $V_{2+Te}^{2+}$ in Te-poor conditions (-0.84 eV). Negative formation energies indicate a trend to high defect concentration and this scheme needs to be studied by a different methodology that correct this result [17].

On the other hand, the relaxed structures found in the QM/MM approach are: $D_{2d}$ for the 2− state, $C_{2v}$ for the 1− and neutral state and $T_{d}^{out}$ for positive states. All the ionized states are the same in both approaches but for the 2− state, which presents a different structure due size effects. One crucial step was the potential alignment that was performed by comparing the total density of states of the pristine crystal with respect to the charged ones. Finally, the formation energies are slightly shifted upward compared with the supercell calculations, but the tendency was kept in this approach. Once again, only two states seems to be stables and the thermodynamic transition level found is $\varepsilon(2+/0)=1.18$ eV, just one hundredth of eV above the supercell result.

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