Cl-doping of Te-rich CdTe: Complex formation, self-compensation and self-purification from first principles

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The coexistence in Te-rich CdTe of substitutional Cl-dopants, Cl_{Te}, which act as donors, and Cd vacancies, V_{Cd}^{-1}, which act as electron traps, was studied from first principles utilising the HSE06 hybrid functional. We find Cl_{Te} to preferably bind to V_{Cd}^{-1} and to form an acceptor complex, $(Cl_{Te}–V_{Cd})^{-1}$. The complex has a (0,-1) charge transfer level close to the valence band and shows no trap state (deep level) in the band gap. During the complex formation, the defect state of $V_{Cd^{-1}}$ is annihilated and leaves the Cl-doped CdTe bandgap without any trap states (self-purification). We calculate Cl-doped CdTe to be semi-insulating with a Fermi energy close to midgap. We calculate the formation energy of the complex to be sufficiently low to allow for spontanous defect formation upon Cl-doping (self-compensation). In addition, we quantitatively analyse the geometries, DOS, binding energies and formation energies of the $(Cl_{Te}–V_{Cd})$ complexes. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4928189]

CdTe is used in a vast amount of applications, e.g. photodetectors operating at room temperature and solar cells.[1–3] CdTe grown under Te rich conditions is mostly reported to be *p*-type and has a low resistivity.[4] For room temperature photodetector applications a high resistivity is mandatory. Residual and native defects in Te-rich CdTe are in general electrically active and the high resistivity (i.e low carrier density) required for detector applications is usually achieved by counterdoping with donor (Al, In, Cl, I) impurities. Cl-doped CdTe is frequently applied in this context because it is well known that Cl-doping increases the resistivity of CdTe with eight orders of magnitude.[5–8] Surprisingly, the physics behind this rise in resistivity has up to now been an open question. In this paper we explain the high resistivity of Cl-doped CdTe as a consequence of self-compensation and self-purification.

The Cl-dopant stands out because it gives rise to a resistivity of $\rho > 10^9 \ \Omega \cdot cm$, which is similiar to the resistivity of impurity free, stoichometric CdTe.[5,6] For this reason, the effect of the Cl-doping has been described as *self-purification*,[9] labelling the ability of defected CdTe to rid itself of any defect-levels in its bandgap. In other words, Cl-doped CdTe becomes a semi-insulator without defect levels (or trap states) in the bandgap although it contains defects and impurities. Al-, In- and I-dopants also rise the resistivity of CdTe due to self-compensation, but a) increase less than the Cl-dopant and b) do not show self-purification.[10]

Theory has predicted wide-band gap semiconductors to show *self-compensation, that* is the spontanous formation of (acceptor-type) intrinsic defects to compensate or passivate (donor-type) dopants.[11] It is expected that Cl in CdTe forms a shallow donor (*n*-type CdTe) because Cl has one more electron than Te. Instead, under Te-rich growth conditions, Cl-doping does not create *n*-type CdTe,[12] because the negatively charge Cd vacancy, V_{Cd}^{-1}, traps the free carriers and forms $(Cl_{Te}–V_{Cd})^{-1}$ (*compensation*). Experimentally, it was shown that even for Cl concentrations larger

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than the concentration of intrinsic V_{Cd}^{-1}, Cl-doped CdTe still does not turn *n*-type.[8] This is explained by the spontaneous formation of the $(Cl_{Te}-V_{Cd})^0$ complex, which energetically is more favourable than the creation of a neutral Cl_{Te} (*self-compensation*).

In summary, compensation explains why CdTe containing V_{Cd}^{-1} does not become *n*-type upon Cl-doping, self-compensation explains why CdTe without V_{Cd}^{-1} does not become *n*-type upon Cl-doping, and self-purification explains why CdTe gets rid of any deep levels in the bandgap upon Cl-doping. CdTe shows both self-compensation and self-purification, but not every semiconductor showing self-compensation also shows self-purification.

The complex discussed in this paper, $(Cl_{Te}-V_{Cd})^{-1}$, consists of a pairing of a cation vacancy (V_{Cd}) with a donor impurity (Cl_{Te}) and is often referred to as an A-center. Experimentally, the $(Cl_{Te}-V_{Cd})^{-1}$ complex was identified in 1992 with photoluminescence (PL) and optically detected magnetic resonance techniques (ODMR).[13] The complex was found to be an acceptor with a charge transfer level (0/-1) of 0.12 eV above the valence band and to consist of a Cd vacancy and a Cl-donor on a nearest Te site. The symmetry of the complex was found to be trigonal. Subsequent experiments confirmed these findings.[1,10,14,15]

First principles investigations provide essential complements to experiments, particularly for experimentally challengeing systems. Two recent reviews highlight possibilities and challenges of first-principles calculations of point defects in solids.[16,17] We are aware of three earlier first-principles calculations of the $(Cl_{Te}-V_{Cd})^{-1}$ complex:[18–20] Chang et al.[18] and Zhu et al.[20] both use the Local density approximation (LDA) which we earlier have shown is insufficient to describe especially the properties of the V_{Cd}^{-1}, whereas Biswas et al. neglects the hole polaron solution of the V_{Cd}^{-1}. Throughout this paper we compare our results with these calculations but in principle this is the first time the $(Cl_{Te}-V_{Cd})^{-1}$ complex in CdTe is studied from first-principles with a method that gives the correct bandgap and predicts the properties of the V_{Cd}^{-1} in agreement with experiment.

In the field of CdTe production, the self-compensation and self-purification effects of Cl_{Te} are well known and widely used.[21,22] Despite this, the physics behind these two effects is still unsettled. The main question of this paper is the mechanism of self-compensation and self-purification of CdTe by Cl. We focus on the interaction of Cl_{Te} with the V_{Cd} and do not discuss the interaction of Cl_{Te} with other possible dopants. In this paper we show that the formation of the $(Cl_{Te}-V_{Cd})^{-1}$ complex, the so called A-center, explains both the self-compensation and self-purification of Cl-doped CdTe.

I. CALCULATIONAL DETAILS

Our calculations were performed using the VASP (Vienna Ab-initio Simulation Package) code[23] employing the screened hybrid functional of Heyd, Scuseria and Ernzerhof (HSE06)[24,25] with a screening parameter of 0.2 Å^{-1} and a mixing parameter of 0.25. Using HSE06, the bandgap of CdTe comes out to be 1.53 eV and the lattice constant 6.58 Å. Experimental values are 1.56 eV and 6.48 Å.[26] The electron-ion interactions were described by projector augmented wave (PAW) pseudopotentials. Configurations for valence electrons were -4d^{10}, -5s^2 , -5s^2, -5p^4 and -5s^2, -5p^5 for Cd ,Te and Cl respectively. The valence wave functions were expanded in a plane-wave basis with a cut-off energy of 350 eV. For geometry optimizations, the atoms were relaxed until the Feynman-Hellman forces on each atom reached 0.01 eV/Å. For the k-point sampling of the 128 atoms in the unit cell we used a Gamma-centered 2x2x2 grid with a Gaussian smearing of 0.025 eV. Charged defects were calculated with a charge-compensating background to ensure convergence of the total energy. For supercells with an odd number of electrons, spin-polarized calculations were performed and the spin moment was constrained to 1 μ_B.

The formation energies $\Delta H_f(E_F)$ for the Te-rich conditions were calculated as follows:

$$\Delta H_f(E_F) = \Delta E - \sum_i n_i \mu_i + q(E_{VBM} + \delta_{VBM} + E_F) \tag{1}$$

where ΔE is the energy difference between the total energy of the defect supercell in a charge state q and the corresponding total energy of the neutral defect free system. n_i is the difference

in the number of atoms for the i-th atomic species between the defect-containing and defect-free supercells. μ_i is the chemical potential of the i-th atomic species. For V_{Cd} $\sum_i n_i \mu_i = -\mu_{Cd}$; for Cl_{Te} $\sum_i n_i \mu_i = -\mu_{Te} + \mu_{Cl}$ and for $(V_{Cd} - Cl_{Te})$ $\sum_i n_i \mu_i = -\mu_{Te} + \mu_{Cl} - \mu_{Cd}$. q is the defect charge, E_{VBM} is the valence band maximum of bulk CdTe. E_F is the Fermi level which varies in the energy range between E_{VBM} and conduction band minimum (E_{CBM}). Total energy calculations of charged defects in finite-size supercells include unwanted defect-defect interactions.[27,28] Many of the known correction schemes are either computationally too expensive for HSE06 calculations or not generally reliable to minimize the errors.[27,28] On the other hand, a computationally cheap and reliable correction scheme is "potential alignment",[29,30] where the potential in the defect cell is aligned to that of bulk by δ_{VBM}. For δ_{VBM} we use the difference between the potential of the most unperturbed point in the defect-containing supercell and the same point in the defect-free supercell.[31] For V_{Cd}^{-1} (V_{Cd}^{-2}) $\delta_{VBM} = -0.04$ eV ($\delta_{VBM} = -0.17$ eV) is used.
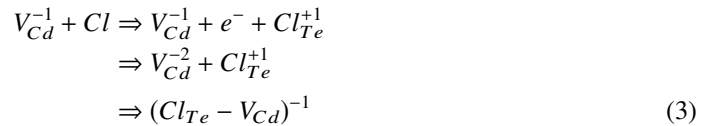
II. RESULTS AND DISCUSSION

A. Complex formation

In the literature, the A-center formation is explained by the formation of a defect complex consisting of Cl_{Te} and V_{Cd}^{-2}.[12] The generally accepted model gives chlorine a similar role as lithium has in Si compensation in the presence of residual acceptors. It is assumed that the doubly charged vacancy, V_{Cd}^{-2}, acts as an acceptor in CdTe and is compensated by Cl_{Te} as follows:[32–34]

$$2V_{Cd}^{-2} + 3Cl \Rightarrow (Cl_{Te} - V_{Cd})^{-1} + (2Cl_{Te} - V_{Cd})^0 + 3e^- \tag{2}$$
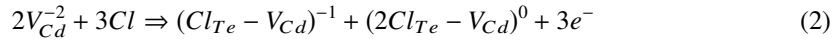
In contrast to our findings, this general model assumes that a) the donated electrons of Cl are not directly participating in the complex formation and b) that V_{Cd}^{-2} acts as electron trap and is mainly responsible for the detector detoriation and finally c) that a tricomplex, $(2Cl^{+1}, V_{Cd}^{-2})^0$ consisting of two Cl ions and one vacancy is stable.

We suggest instead the following compensation reaction which is supported by our calculations:

$$V_{Cd}^{-1} + Cl \Rightarrow V_{Cd}^{-1} + e^- + Cl_{Te}^{+1}$$
$$\Rightarrow V_{Cd}^{-2} + Cl_{Te}^{+1}$$
$$\Rightarrow (Cl_{Te} - V_{Cd})^{-1} \tag{3}$$

Our calculations reveal the following: a) the donated electrons of Cl are directly participating in the complex formation: Te-rich p-type CdTe is dominated by V_{Cd}^{-1}. Cl transfers one electron to V_{Cd}^{-1}, creating a V_{Cd}^{-2} with which Cl_{Te}^{+1} forms the complex (see Eq. (3)); b) V_{Cd}^{-2} does not act as electron trap as our earlier calculations have shown.[35] The presence of V_{Cd}^{-2} in CdTe does not cause p-type doping and is not responsible for the low resistivity of Te-rich CdTe. Only V_{Cd}^{-1} gives rise to an unoccupied defect state (hole polaron) within the bandgap and acts thus as an electron trap during detector operation (see also top panel in Fig.4); c) the tricomplex we believe to be unstable as will be discussed further on.

EPR and ODMR experiments confirmed that the Cl-dopant occupies the Te sublattice.[5,13] A number of experiments confirm the existence of a $(Cl_{Te}\text{-}V_{Cd})^{-1}$ complex.[1,5,10,14,15,36,37] Several theoretical calculations of the $(Cl_{Te}\text{-}V_{Cd})^{-1}$ exist[18–20] but none of those consider the polaronic nature of the V_{Cd}^{-1}.

B. Geometry of the Cl_{Te}–V_{Cd} complex

First, we analyze the geometry of the defect complex (see Fig.1 and Tab. I). The complex (Fig.1(c)) consists of a Cl atom substituted in the Te sublattice, Cl_{Te} (see Fig.1(a)) and a Cd vacancy, V_{Cd} (see Fig.1(b)). We find the complex to be stable in two charge states, neutral and (-1). The neutral complex, $(Cl_{Te}–V_{Cd})^0$, has C_s symmetry whereas the (-1) charged complex,
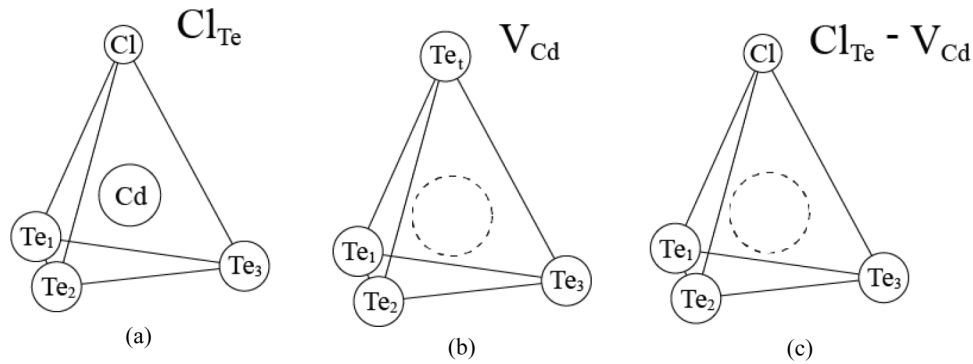
FIG. 1. Schematic geometrical configurations of (a) Cl_{Te}, (b) V_{Cd} and (c) Cl_{Te}–V_{Cd} defects in CdTe. Te_1 - is the Tellurium atom, on which the polaron, if existent, is localised.

$(Cl_{Te}$–$V_{Cd})^{-1}$, has C_{3v} symmetry. This is in agreement with the trigonal symmetry found in experiment.[13] The difference in symmetry between the two charge states of the complex is solely explained by polaron formation: $(Cl_{Te}$–$V_{Cd})^0$ consists of a Cl_{Te}^{+1} defect and a V_{Cd}^{-1} defect. The latter is stabilized by the formation of a hole polaron which is centered on Te_1 in Fig.1.[35] On the other hand, $(Cl_{Te}$–$V_{Cd})^{-1}$ consists of a Cl_{Te}^{+1} defect and a V_{Cd}^{-2} defect. The latter contains no polaron and therefore Te_1, Te_2 and Te_3 are equivalent.

In both the neutral complex, $(Cl_{Te}$–$V_{Cd})^0$, and the (-1) complex, $(Cl_{Te}$–$V_{Cd})^{-1}$, the distance between Cl and the vacancy is elongated by 17 % (from 2.85 to 3.35 Å) compared to the ideal lattice. Compared to V_{Cd}^{-1}, the distance in the neutral complex between the equivalent Te_2 and Te_3 atoms and the vacancy is shortened by 0.9% and the distance between Te_1 and vacancy is shortened by 0.7% (see FIG.1). Compared to V_{Cd}^{-2} the distance in the (-1) complex between the equivalent Te_1, Te_2 and Te_3 atoms and the vacancy is shortened by 1%.

In an earlier work by Chang et al.[38,39] the same two complexes have been calculated using LDA within a 54-atom supercell considering only complexes with C_{3v} symmetry. The Cl-vacancy

TABLE I. Calculated distances in Cl_{Te}, V_{Cd} and Cl_{Te}–V_{Cd} complex in various charge states. Te_1^* indicates the existence of a hole polaron at Te_1. See schematic geometrical configurations of the defects in Fig 1.

Defect	Selected atoms	Distance, Å	Symmetry
V_{Cd}^{-1}	Te_1^*–Te_2	4.37	C_{3v}
	Te_2–Te_3	4.27	
	Te_2–V_{Cd}	2.61	
	Te_1^*–V_{Cd}	2.77	
V_{Cd}^{-2}	Te_1–Te_2	4.21	T_d
	Te_1–V_{Cd}	2.58	
Cl_{Te}^{+1}	Cl–Te_1	4.63	C_{3v}
	Te_1–Te_2	4.67	
	Cl–Cd	2.96	
$(Cl_{Te}$–$V_{Cd})^{-1}$	Te_1–Te_2	4.17	C_{3v}
	Cl–Te_1	4.86	
	Te_1–V_{Cd}	2.57	
	Cl–V_{Cd}	3.36	
$(Cl_{Te}$–$V_{Cd})^0$	Te_1^*–Te_2	4.31	C_s
	Te_2–Te_3	4.21	
	Cl–Te_1^*	5.02	
	Cl–Te_2	4.90	
	Te_1^*–V_{Cd}	2.75	
	Te_2–V_{Cd}	2.58	
	Cl–V_{Cd}	3.35	

distance was found to increase by 20% in agreement with our results. But the Te-Te distances and Te-vacancy distance were shortened by on the order of 10%. This discrepancy may be explained by the level of approximation used by Chang et al., but the principal difference between Chang and our results is due to the non-consideration of the polaronic solution.[38] It is worth mentioning that Chang et al. have compared their LDA results with LDA+spin-orbit results and that they find no difference in the geometry of the two complexes.

In the following we compare the geometries of Cl_{Te}^{+1} between a single Cl_{Te}^{+1} (Fig.1(a)) and the Cl_{Te}^{+1} within the complex (Fig.1(c)). In the Cl_{Te}^{+1} defect, Cl keeps four Cd neighbours at a distance of 2.96 Å. In the complex, the Cl atom moves closer to the 3 nearest Cd atoms reducing the Cd-Cl bond length to 2.76 Å and changing the Cd-Cl-Cd bond angle from 110° to 117°. This structure is approaching the $CdCl_2$ geometry, where each Cl has 3 Cd neighbours at a distance of 2.64 Å and the Cd-Cl-Cd bond angle is 94°.[40] In Fig. 2 we compare a charge density contour of Cl_{Te}^{+1} and $(Cl_{Te}-V_{Cd})^{-1}$. The bond formation between Cl and its Cd neighbours within the complex is clearly visible in Fig.2(b) suggesting bonds between Cl and Cd of both ionic and covalent character as in $CdCl_2$. On the other hand, for Cl_{Te}^{+1}, the charge density contours (Fig.2(a)) suggest Cl to form mainly ionic bonds with Cd.
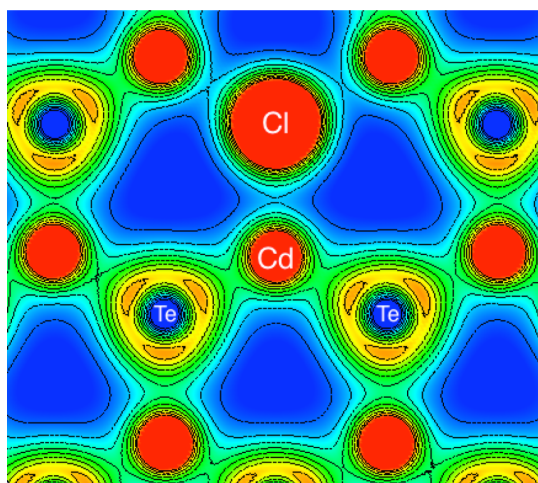
(a)
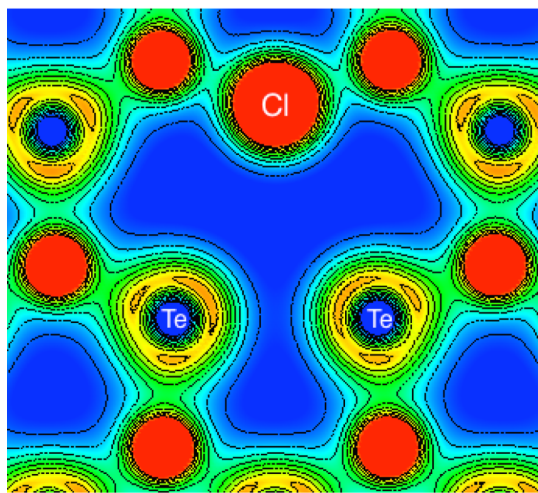
(b)

FIG. 2. Charge density contours through the plane containing the Cl atom of (a) Cl_{Te}^{+1} and (b) $(Cl_{Te}-V_{Cd})^{-1}$.

TABLE II. Hole poltroon states for different defects. $\epsilon_{polaron}$ labels the energy eigenvalue of the hole-polaron state at the Γ-point in [eV] relative to the VBM. ne stands for "non existent" and indicates that no polaron exists for this particular defect. The last column indicates if the defect acts as an electron trap.

Defect	$\epsilon_{polaron}$	electron trap
V_{Cd}^{-1}	0.43	yes
V_{Cd}^{-2}	ne	no
$(Cl_{Te}-V_{Cd})^0$	0.28	yes
$(Cl_{Te}-V_{Cd})^{-1}$	ne	no

We conclude that the complex formation gives rise to an inward movement of $Te_{1,2,3}$ towards the vacancy and the Cl atom moves out towards its 3 Cd neighbours. The creation of a Cd vacancy gives rise to stronger bonds between Cl and its 3 Cd neighbours. In Tab. II we have summarized the energy eigenvalue of the polaronic state at the Γ-point. From Tab. II we see that the energy eigenvalue of the polaronic state in the neutral complex is closer to the VBM than in a single V_{Cd}^{-1} defect. The lower defect level of the complex (Tab. II) is equivalent to less binding of the hole within the complex. Our above analysis of the complex geometry showed that the distance between Cl and the vacancy is independent of the hole existence (see Tab. I). Therefore, we conclude that Cl is not an active part of the Jahn-Teller distortion. The energy gain of the Jahn-Teller distortion is given by the increased coulomb attraction between the hole and the occupied dangling bonds close to it. In the complex, the energy gain is thus only provided by two Te dangling bonds. This leads to a gain in Coulomb attraction that is lower than for V_{Cd}^{-1} where three Te dangling bonds contribute to the Jahn-Teller distortion.

C. Charge transfer levels of the *Cl_Te*–*V_Cd* complex

In Fig. 3 we show the Te-rich formation energies of Cl_{Te}, V_{Cd} and the Cl_{Te}–V_{Cd} complex for different charge states. We calculate the Cl_{Te}–V_{Cd} complex to be stable both for neutral and -1 charge states. The (0/-1) charge transfer level is located at 0.07 eV above the valence band (see Fig.2(a), red lines). Biswas et al.[19] reports this charge transfer level to be about 0.2 eV above the valence band. One difference between Biswas et al. and our work is they do not consider the polaronic nature of the V_{Cd}^{-1}. The experimental value of the (0/-1) charge transfer level is measured at about 0.12 eV above the valence band.[1,10,13,15] Experiment and theory thus agree that the (0/-1) charge transfer level of the Cl_{Te}–V_{Cd} complex is rather close to the valence band.

D. Coulomb binding of the *Cl_Te*–*V_Cd* complex

Next we discuss the binding of the Cl_{Te}–V_{Cd} complex. In Fig.3(b) we show apart from the formation energy of the complex (full line) also the sum of the formation energies of the non-interacting constitutents (dotted line). The complex in its zero charge state, $(Cl_{Te}-V_{Cd})^0$, consists of a Cl_{Te}^{+1} defect and a V_{Cd}^{-1} defect. If we assume a CdTe sample with one Cl_{Te}^{+1} infinitly far away from one other V_{Cd}^{-1} defect, we can calculate this sample's formation energy by adding the formation energies (see Fig.2(a)) of these two (non-interacting) defects and obtain the dotted line in Fig.3(b). The difference between the formation energy of the complex and the sum of the non-interacting constituting defects is identical with the binding energy of the complex. We calculate the binding energy of the $(Cl_{Te}-V_{Cd})^0$ complex to be 0.56 eV, whereas the binding energy of the $(Cl_{Te}-V_{Cd})^{-1}$ is 0.93 eV. In other words, the binding energy between Cl_{Te}^{+1} and V_{Cd}^{-2} is almost twice the binding between Cl_{Te}^{+1} and V_{Cd}^{-1}, which agrees with expectations from the Coulomb interaction between two point charges.

E. Self-compensation

Experimentally, the resistivity of Cl-doped CdTe saturates at about $10^9 \ \Omega \cdot cm$ with the rise of chlorine concentration[7,8] up to the Cl solubility limit. Therefore, it has been suggested, that
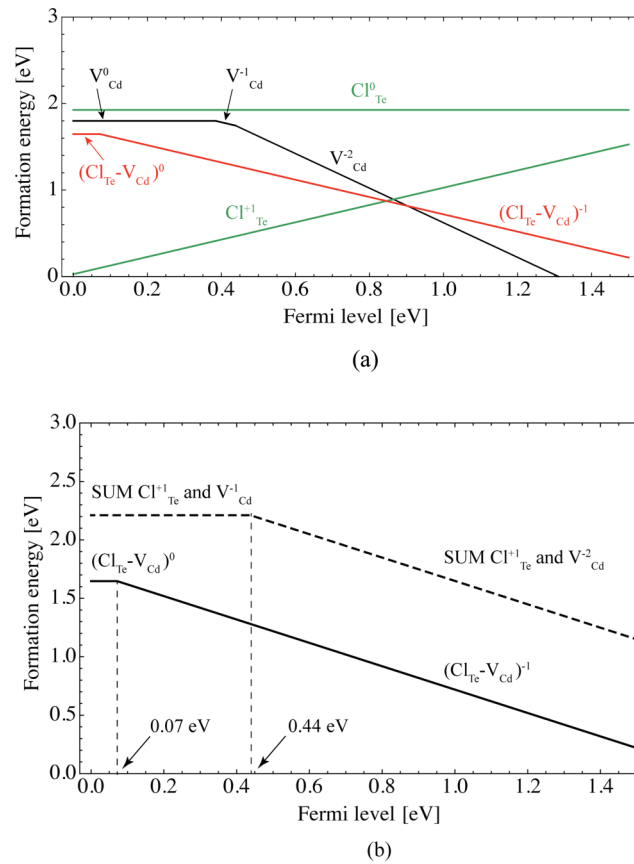
FIG. 3. (a) Formation energies of Cl and V_{Cd} related defects in CdTe and (b) formation energies of the $Cl_{Te}-V_{Cd}$ complex (solid lines) and the sum of the formation energies of the complex constitutents, $V_{Cd}+Cl_{Te}$ (dashed lines).

the addition of Cl exceeding the concentration of already existing Cd vacancies, gives rise to the formation of compensating native defects. We propose the following self-compensation reaction:

$$Cl \Rightarrow (Cl_{Te} - V_{Cd})^0 + Cd(g) + Te(g) \qquad (4)$$
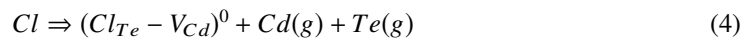
The addition of one Cl atom to CdTe leads to the formation of a complex between a positive charged substitutional Cl ion and a negative charged Cd vacancy. $Cd(g)$ and $Te(g)$ indicate that one Cd and one Te atom are leaving the sample and are in equilibrium with the surrounding gas or form one new CdTe bond.

Self-compensation will happen, if the energy cost of spontaneous defect formation is lower than the energy gain due to the interaction of the defect with the impurity.[11] The formation energies, $E(X)$, where X stands for the involved defects and impurities, have to fulfill the following inequality:

$$E(Cl_{Te}) > E(V_{Cd}^{-1}) + E(Cl_{Te}^{+1}) - \epsilon_{binding}^{complex} \qquad (5)$$

Note, that the formation energy is evaluated under the assumption of chemical equilibrium with in principle the surrounding gas (see Eq.(1)). Therefore the two last terms in Eq.(4) do not enter explicitly in Eq.(5). Further, the right hand side of Eq.(5) is per definition identical to the formation energy of the complex. Then Eq.(5) reads instead:

$$E(Cl_{Te}) > E((V_{Cd} - Cl_{Te})^0) \qquad (6)$$

Under Te-rich conditions, $E(Cl_{Te})$ (horizontal green line in Fig.3(a)) is calculated to be higher than the formation energy of the $(Cl_{Te}-V_{Cd})^0$ complex (red line in Fig.3(a)) independent of the

Fermi level. This confirms that energy is gained after Cl-doping due to the formation of the complex even if the V_{Cd} did not exist prior to Cl-doping.

The fact that Cl_{Te} and the V_{Cd} attract each other allows us to conclude that under Te-rich conditions, a single V_{Cd}^0 or V_{Cd}^{-1} will never coexist with a single Cl-dopant without forming a complex. Moreover, the $(Cl_{Te}-V_{Cd})^0$ will never coexist with a single neutral Cl-dopant. Instead, Cl will transfer an electron to the complex:

$$E(Cl_{Te}^0) + E((Cl_{Te} - V_{Cd})^0) > E(Cl_{Te}^{+1}) + E(Cl_{Te} - V_{Cd})^{-1}) \qquad (7)$$

From Fig.3(a) we determine the left hand side of Eq.(7) to be > 2 eV, while the right hand side is 1.8 eV. In other words, either Cl forms a complex with V_{Cd} or it donates an electron to an already formed neutral complex.

In Eq.(2) a tricomplex was suggested consisting of two Cl ions and one Cd vacancy, $(2Cl_{Te}-V_{Cd})^0$. We have not explicitly calculated this tricomplex, but our calculations let us conclude the following: a) this tricomplex will not act as an electron trap, because neither an unbound Cl_{Te}^{+1} nor a bound Cl_{Te}^{+1} nor the V_{Cd}^{-2} acts as an electron trap; b) the binding energy of this tricomplex should be smaller than for $(Cl_{Te}-V_{Cd})^{-1}$ because of the increased Coulomb repulsion between the two Cl_{Te}^{+1} neighbours in the tricomplex. We therefore do not regard this tricomplex to alter the here presented results and even predict it to be unstable. Moreover, we are not aware of experimental verification of this tricomplex.

F. Self-purification

In the following, we discuss the experimentally observed so called self-purification.[9] We start by analysing the density of states (DOS) of the defect complex shown in Fig.4. In the top panel we show the DOS of V_{Cd}^{-1}, which contains a hole polaron and accordingly acts as electron trap. The signature of the hole polaron is an unoccupied state above the valence band edge in only one spin channel.[35] Self-purification is thus identical to getting rid of the polaronic state thereby opening up the bandgap.
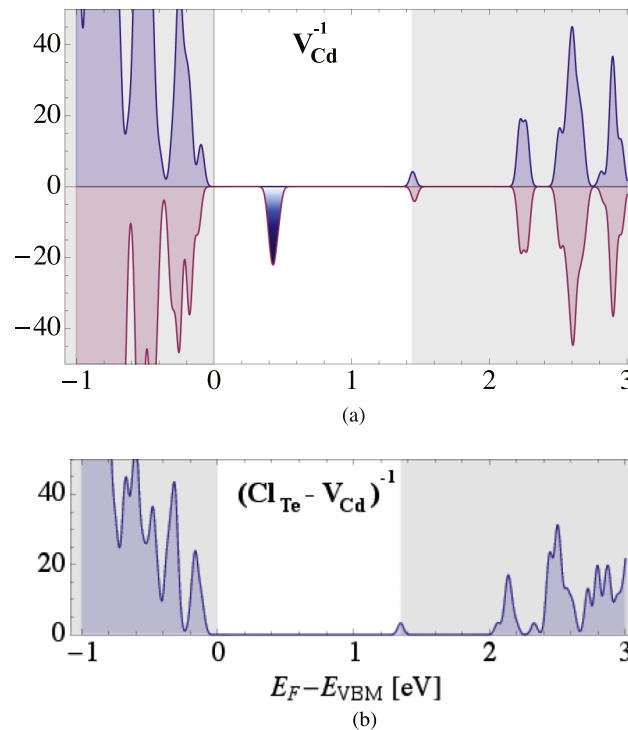

FIG. 4. DOS of the V_{Cd}^{-1} (polaronic state) and $(Cl_{Te}-V_{Cd})^{-1}$ (non-polaronic state) defect complex.

In the bottom panel of Fig.4 we show the DOS of the $(Cl_{Te}-V_{Cd})^{-1}$ complex where the polaronic state has disappeared. Although our supercell contains two nearby defects, V_{Cd}^{-2} and Cl_{Te}^{+1}, the bandgap is completly free of any defect states and looks like the DOS of an ideal CdTe sample. This is called self-purification. An electron photo-excited to the conduction band might get trapped by V_{Cd}^{-1} (see Fig.4, top panel), but not by the $(Cl_{Te}-V_{Cd})^{-1}$ complex (Fig.4, bottom panel). Note: The $(Cl_{Te}-V_{Cd})^{-1}$ complex does not provide any empty state. Therefore it is no electron trap.

The electron counting model[41] based on a simple analysis of the dangling-bond energy levels helps us to understand the existence (absence) of a polaron in the zero-charged (-1 charged) complex (Fig. 5). In the ideal CdTe crystal, for the bond formation, each Te (Cd) donates 6 (2) electrons.
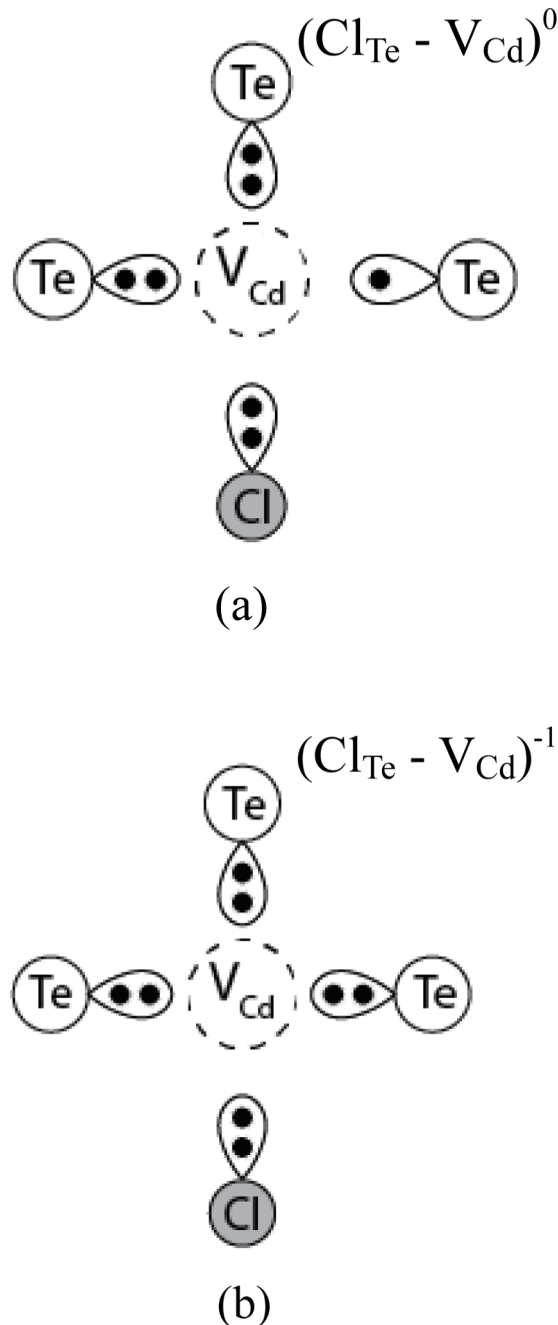

FIG. 5. Electron counting model diagram for the (a) $(Cl_{Te}-V_{Cd})^0$ and (b) $(Cl_{Te}-V_{Cd})^{-1}$ complexes.

Each atom in the CdTe (zinc-blende) structure has 4 neighbours. It means that Te (Cd) donates 3/2 (1/2) of an electron to each neighbour. When we make a zero-charged $Cl_{Te}-V_{Cd}$ complex, we take away one Cd (2 valence electrons) and replace one Te by Cl. It means that 3/2 electrons from each Te form a dangling bond, in total $3 \cdot (3/2) = 9/2$ electrons. In addition we have to consider the Cl atom, which forms bonds by the same principle with the three neighbouring Cd (3/2 electron per each) and thus would form a dangling bond with remaining 7-3(3/2) = 5/2 electrons.

According to Pashley,[41] the lowest-energy structure is obtained by filling all dangling bonds on the anion atom and keeping empty the ones on the cation atom. In our case we have 7 (= 9/2 + 5/2) electrons which have to be distributed among 4 dangling bonds, and we see that we can fully satisfy only 3 bonds, while one has to remain half-occupied (Fig. 5(a)), creating a hole-polaron on the Te_1-site. The hole-polaron creates an extra level in the bandgap of CdTe in only one spin channel (Fig. 4).

The electron counting analysis of the $(Cl_{Te}-V_{Cd})^{-1}$ is basically the same as for $(Cl_{Te}-V_{Cd})^0$, apart from the number of electrons on the Cl site. For the -1 charged complex Cl has 8 electrons instead of 7. As a result, we see that all dangling bonds of $(Cl_{Te}-V_{Cd})^{-1}$ are filled and polaron formation, as well as symmetry breaking, do not lead to an energy gain (Fig. 5(b)).

G. High resistivity

We now make the following two assumptions: 1. We assume CdTe to be intrinsic, so that the Fermi energy (electron chemical potential) is determined by the native defect content. 2. Only Cl_{Te} and V_{Cd} and their complexes are important in determining the Fermi energy. All other native defects can be neglected. This is reasonable because the chlorine concentration range $N_{Cl} = 10^{18} - 10^{19}$ cm^{-3}, for which the resistivity is high, is larger than typical native defect concentrations of 10^{16} cm^{-3}.[8]

A semiconductor remains charge neutral even when it has been doped. The positive charged defect with the highest concentration in Cl-doped CdTe is Cl_{Te}^{+1}. Charge neutrality then demands the existence of one or more defects that provide an equal amount of negative charge. Due to self-compensation the negative charge is solely provided by $(Cl_{Te}-V_{Cd})^{-1}$. This is confirmed by experiments where it is found that the concentration of the complex increases with an increase of the Cl-dopant concentration.[37,42] For the spontaneous formation of the $(Cl_{Te}-V_{Cd})^{-1}$ complex two Cl-dopants are needed (see Eq. (7)):

$$2Cl \Rightarrow Cl_{Te}^{+1} + (Cl_{Te} - V_{Cd})^{-1} \qquad (8)$$
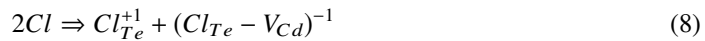
For Cl concentrations above 10^{16} cm^{-3} we thus expect the above self-compensation reaction to be the dominating process. This agrees with experimental findings where not all Cl-dopants are found to be part of the complex.[8,43,44] The charge neutrality condition for Cl-doped CdTe then reads:

$$[(Cl_{Te} - V_{Cd})^{-1}] = [Cl_{Te}^{+1}] \qquad (9)$$

The formation energies of Cl_{Te}^{+1} and $(Cl_{Te}-V_{Cd})^{-1}$ are equal at a Fermi energy of 0.84 eV relative to the VBM (Fig.3(a)). In other words, Cl-doped CdTe will have a Fermi energy of 0.84 eV because for that electron chemical potential the number of holes equals the number of electrons. This explains the semi-insulating behaviour of Cl-doped CdTe.

III. CONCLUSIONS

From first principles we have calculated that Cl_{Te} donates an electron to V_{Cd}^{-1}. They form a complex, $(Cl_{Te}-V_{Cd})^{-1}$, with a binding energy of 0.93 eV and a (0/-1) charge transfer level at 70 meV above the valence band. This complex does not act as electron trap. Instead, the complex formation between Cl_{Te} and V_{Cd}^{-1} annihilates the intrinsic electron trap states of V_{Cd}^{-1} (*self-purification*). When Cl_{Te} has formed a complex with all existing V_{Cd}^{-1}, a further increase of the Cl_{Te} concentration gives rise to spontaneous formation of $(Cl_{Te}-V_{Cd})$ (*self-compensation*). This experimentally known fact is confirmed by our formation energy calculations. We find the bond

distance between Cl_{Te} and its Cd nearest neighbours within the complex to approach the $CdCl_2$ structure. For Cl-doped CdTe with a Cl_{Te} concentration exceeding the intrinsic V_{Cd}^{-1} concentration, we calculate the Fermi level to be midgap, thus explaining the high resistivity of Cl-doped CdTe.

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[1] M. Fiederle, V. Babentsov, J. Franc, and J.-P. Konrath, Cryst. Res. Technol. **38**, 588 (2003).
[2] B. Basol, in *Photovoltaic Specialists Conference, 1990., Conference Record of the Twenty First IEEE*, (1990) Vol. 1, pp. 588–594.
[3] M. F. Lichterman, A. I. Carim, M. T. McDowell, S. Hu, H. B. Gray, B. S. Brunschwig, and N. S. Lewis, Energy Environ. Sci. **7**, 3334 (2014).
[4] P. Fochuk, R. Grill, and O. Panchuk, J. Electron. Mater. **35**, 1354 (2006).
[5] D. M. Hofmann, W. Stadler, P. Christmann, and B. K. Meyer, Nucl. Instr. and Meth. in Phys. Res., A **380**, 117 (1996).
[6] R. Krause-Rehberg, H. S. Leaper, T. Abgarjan, and A. Polity, Appl. Phys. A **66**, 599 (1998).
[7] P. Höschl, R. Grill, J. Franc, P. Moravec, and E. Belas, Mater. Sci. Eng. B **16**, 215 (1993).
[8] V. Popovych, I. Virt, F. Sizov, V. Tetyorkin, Z. Tsybrii, L. Darchuk, O. Parfenjuk, and M. Ilashchuk, J. Crystal Growth **308**, 63 (2007).
[9] Y. Marfaing, Prog. Crystal Growth Charact. **4**, 317 (1981).
[10] T. Schlesinger, J. Toney, H. Yoon, E. Lee, B. Brunett, L. Franks, and R. James, Mater. Sic. Engineering **32**, 103 (2001).
[11] G. Mandel, Phys. Rev. **134**, A1073 (1964).
[12] V. S. Bagaev, Y. V. Klevkov, S. A. Kolosov, V. S. Krivobok, and A. A. Shepel, Phys. Solid State **53**, 1554 (2011).
[13] D. Hofmann, P. Omling, H. Grimmeiss, B. Meyer, K. Benz, and D. Sinerisu, Phys. Rev. B **45**, 6247 (1992).
[14] K. Zanio, Semicond. Semimet. **13**, 129 (1978).
[15] A. Castaldini, A. Cavilling, B. Fraboni, P. Fernandez, and J. Piqueras, Appl. Phys. Lett **69**, 3510 (1996).
[16] S. Zhang, J.Phys.: Condens. Matter **14**, R881 (2002).
[17] C. Freysoldt, B. Grabovski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, Rev. Mod. Phys. **86**, 253 (2014).
[18] Y.-C. Chang, R. B. James, and J. W. Davenport, Phys. Rev. B **73**, 035211 (2006).
[19] K. Biswas and M.-H. Du, New J. Phys. **14**, 063020 (2012).
[20] H. Zhu, M. Gu, L. Huang, J. Wang, and X. Wu, Mater. Chem. Phys. **143**, 637 (2014).
[21] C. Szeles, IEEE Trans. Nucl. Sci. **51**, 1242 (2004).
[22] M. Fiederle, V. Babentsov, J. Franc, A. Fauler, and J.-P. Konrath, Cryst. Res. Technol. **38**, 588 (2003).
[23] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[24] J. Heyd, J. E. Peralta, and G. E. Scuseria, J. Chem. Phys. **123**, 174101 (2005).
[25] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 1219906 (2006).
[26] G. Lutz, *Semiconductor Radiation Detectors. Device Physics* (Springer, 1999).
[27] C. Castleton, A. Höglund, and S. Mirbt, Physical Review B ISSN: 1098-0121 **73**, 035215 (2006) URL http://link.aps.org/doi/10.1103/PhysRevB.73.035215.
[28] H.-P. Komsa, T. T. Rantala, and A. Pasquarello, Physical Review B ISSN: 1098-0121 **86**, 045112 (2012) URL http://link.aps.org/doi/10.1103/PhysRevB.86.045112.
[29] C. G. Van de Walle, Journal of Applied Physics ISSN: 00218979 **95**, 3851 (2004) URL http://link.aip.org/link/?JAP/95/3851/1&Agg=doi.
[30] C. Freysoldt, B. Grabowski, T. Hickel, and J. Neugebauer, Reviews of modern physics **86**, 253 (2014).
[31] A. Höglund, C. W. M. Castleton, and S. Mirbt, Phys. Rev. B **72**, 195213 (2005).
[32] T. Schlesinger and R. James, in *Semiconductors and Semimetals*, edited by R. Willardson, A. Beer, and E. Weber (Academic Press, San Diego, 1995), Vol. 43.
[33] C. Canali, G. Ottaviano, R. Bell, and F. Wald, J. Phys. Chem. Solids **35**, 1405 (1974).
[34] R. Bell, Solid State Comm. **16**, 913 (1975).
[35] A. Lindström, Ph.D. thesis, Uppsala University (2015).
[36] L. Woresch, W. Ossau, F. Fischer, A. Waag, and G. Landwehr, J. Cryst. Growth **161**, 134 (1996).
[37] D. V. Korbutyak, S. G. Krylyuk, P. M. Tkachuk, V. I. Tkachuk, N. D. Korbutjak, and M. D. Raransky, J. Cryst. Growth **197**, 659 (1999).
[38] Y.-C. Chang, R. B. James, and J. W. Davenport, Phys. Rev. B **73**, 035211 (2006).
[39] Y.-C. Chang and R. B. James, Proc. SPIE **3768**, 381 (1999).
[40] D. E. Partin and O'Keeffe, J. Sol. St. Phys. **95**, 176 (1991).
[41] M. D. Pashley, Phys. Rev. B **40**, 10481 (1989).
[42] H. Kauppinen, L. Baroux, K. Saarinen, C. Corbel, and P. Hautojärvi, J. Phys.: Condens. Matter **9**, 5495 (1997).
[43] M. Hage-Ali and P. Siffert, Nucl. Instr. and Meth. in Phys. Res., A **322**, 313 (1992).
[44] W. Stadler, D. Hofmann, A. Alt, T. Muschik, B. Meyer, E. Weigel, G. Müller-Vogt, E. Salk, E. Rupp, and K. Benz, Phys. Rev. B **51**, 10619 (1995).