Hybrid density functional studies of cadmium vacancy in CdTe*

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(Received 9 October 2013; revised manuscript received 14 January 2014; published online 22 May 2014)

The intrinsic defect of cadmium vacancy (V_{Cd}) in cadmium telluride (CdTe) has been studied by first-principles calculations using potentials with both the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) approximation and the generalized gradient approximation of the Perdew–Burke–Ernzerhof form (PBE-GGA). Both results show that the T_d structure of the V_{Cd} defect for different charges is the most stable structure as compared with the distorted C_{3v} structure with one hole localized at one of the four nearest Te atoms. This indicates that the John–Teller distortion (C_{3v}) structure may be unstable in bulk CdTe crystal. The reason likely lies in the delocalized resonance nature of the t_2 state of the V_{Cd} defect. Moreover, the formation energy obtained by the HSE method is about 0.6–0.8 eV larger than that obtained by the PBE method. The transition levels calculated by the PBE method and the HSE method are similar and well consistent with the experimental results.

Keywords: defect levels, semiconductor compound, density functional theory

PACS: 71.15.Mb, 71.55.–i, 71.20.Nr **DOI:** 10.1088/1674-1056/23/7/077103

1. Introduction

CdTe is one of the most promising optoelectronic materials due to its large band gap, high absorption coefficient, and high intrinsic resistivity. A Te rich CdTe single crystal grown by the Bridgeman technique with a high content of defects in the cation site is often obtained due to the large vapor pressure of Cd.[1] Therefore, the most important intrinsic defects in CdTe are cadmium vacancy (V_{Cd}) and tellurium antisite (Te_{Cd}).[2] Between these two defects, V_{Cd} often behaves as a dominant acceptor in the unintentional p-type CdTe and is also considered as an important compensation source in n-type CdTe.[3] Extensive experimental works have been focused on the V_{Cd} defect properties. The ionization levels related to V_{Cd} have been studied by deep level transient spectroscopy (DLTS),[4] photo-induced current transient spectroscopy (PICTS),[4] admittance spectroscopy,[5] Hall measurements,[6] and thermoelectric effect spectroscopy (TEES).[7,8] The obtained levels attributed to V_{Cd} can be summarized into two types. One type is located near the valence band maximum (VBM, E_v), at around E_v + 0.1 eV to E_v + 0.2 eV, while the other type is just below the midgap, at around E_v + 0.4 eV to E_v + 0.5 eV.[4–9] The former type is ascribed to the $\varepsilon(-1/0)$ level of V_{Cd}, which is a relatively narrow level that leads to the p-type nature of the undoped CdTe crystal. The latter type is related to $\varepsilon(-2/-1)$, which may lead to the pinning of the Fermi level near the mid-band gap and thus acts as a major compensation source in n-type CdTe. The local structure properties of V_{Cd}^- were studied by electron paramagnetic resonance (EPR).[10,11] The results implied that the hole in V_{Cd}^- is localized in one of the four nearest Te atoms and, therefore, leads to a John–Teller distortion (C_{3v}) structure.[12,24] However, this John–Teller distortion structure has not been verified by either theoretical investigations or other experiments. A number of first-principles calculations based on the local density approximation (LDA) and the generalized gradient approximation (GGA) for native point defects in CdTe[9,13,14] have been carried out. No John–Teller distortion structure was found.

In fact, the band gaps calculated by either the LDA or the GGA method are significantly smaller than the corresponding experimental values due to a spurious electron self-interaction. To overcome this, the Heyd, Scuseria, and Ernzerhof (HSE) method[15] has been proposed. The HSE method can accurately describe the localized state due to the partial elimination of the self-interaction error of the semilocal functional. To the authors' knowledge, the native defects in CdTe have not been investigated by the HSE method. Therefore, in this paper, we investigate the electronic and the structural properties of V_{Cd} in CdTe by the first-principles calculation using potentials with both the generalized gradient approximation of the Perdew–Burke–Ernzerhof parametrization form (PBE-GGA) and the HSE non-local approximation.[16] The rest of this paper is arranged as follows. In Section 2, we simply introduce the theoretical approach. Section 3 presents the results and discussion. Finally, we summarize the conclusions in Section 4.

*Project supported by the National Natural Science Foundation of China (Grant No. A050506), the Innovation Program of Shanghai Municipal Education Commission, China (Grant No. 12ZZ096), the Shanghai Leading Academic Disciplines, China (Grant No. S30107), and the Science and Technology Commission of Shanghai, China (Grant No. 11530500200).

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2. Theoretical approach

We perform calculations based on the density functional theory as implemented in the code VASP (Vienna *ab initio* simulation package).[17] The valance wave functions are expanded in a plane-wave basis with a cutoff energy of 350 eV. All of the calculations about V_{Cd} are performed using a 64-atom cubic cell. A 2×2×2 grid is used for the k-point sampling of the Brillouin zone. All of the atoms are relaxed to minimize the Feynman–Hellmann forces to below 0.02 eV/Å. The calculations are performed with potentials of both the PBE-GGA form and the HSE hybrid functional form. For the HSE method, two parameters are introduced in the hybrid functionals. A fraction β of the non-local exact exchange is mixed to the GGA exchange. So, the exchange energy is given by

$$E_{\rm x}^{\rm hybrid} = \beta E_{\rm x}^{\rm exact} + (1-\beta)E_{\rm x}^{\rm GGA}. \quad (1)$$

The correlation potential is taken from the GGA absolutely. It turns out that the exact exchange contribution $\beta = 0.25$ is optimal for both lattice constants and the band gap in CdTe. For the other parameter, a screening length of around 0.2 Å^{-1} is adopted.

The formation energy of a point defect strongly depends on the chemical potentials and the Fermi level $E_{\rm F}$. Here, the formation of a V_{Cd} defect requires the removal of one cadmium atom. The formation energy is

$$E^{\rm f}\left(V_{\rm Cd}^{q}\right) = E_{\rm tot}\left(V_{\rm Cd}^{q}\right) - E_{\rm tot}\left({\rm CdTe}\right) + \mu_{\rm Cd} + q(E_{\rm F}+E_{\rm v}), \quad (2)$$

where $E_{\rm tot}(V_{\rm Cd}^{q})$ is the total energy of a supercell containing CdTe in the charge state q, $E_{\rm tot}({\rm CdTe})$ is the total energy of a CdTe perfect crystal in the same supercell, and $\mu_{\rm Cd}$ is the cadmium chemical potential. Expressions similar to Eq. (2) apply to all of the native point defects.

The formation energy also determines the relative stability of various charge states, and thus the ionization level of defects.[18] The transition level $\varepsilon(q/q')$ is defined as the Fermi-level position for which the formation energies of charge states q and q' are equal; that is,

$$\varepsilon(q/q') = \frac{E^{\rm f}({\rm D}^{q};E_{\rm F}=0) - E^{\rm f}({\rm D}^{q'};E_{\rm F}=0)}{q'-q},$$

where $E^{\rm f}({\rm D}^{q};\, E_{\rm F}=0)$ is the formation energy of defect D in the charge state q when the Fermi level is at the valence band maximum ($E_{\rm F}=0$).

For the formation energy of a charged defect, a Makov–Payne correction based on a dipole expansion was suggested.[19] Here, we just adopt the first-order correction.

3. Results and discussion

3.1. Structural parameters and band structure of bulk CdTe

The bulk calculations are performed with a 2-atom primitive cell of zinc blend structure. The Monkhorst–Pack special k-point mesh is $11\times11\times11$. The obtained lattice parameters are listed in Table 1. They are found to be in good agreement with the available experimental and theoretical data. Figure 1 shows the band structure and the total density of state of bulk CdTe. The band structure in Fig. 1(a) shows that CdTe has a direct band gap with the VBM and the conduction band maximum (CBM) at the Γ point. The band gap obtained by the PBE method is only 0.58 eV, which is about 0.90 eV less than the experimental value due to the well-known DFT eigen-value problem. However, the band gap obtained by the HSE method with a 25% HF exchange is about 1.49 eV, which is very close to the experimental value.[20]

Table 1. Lattice parameters a, band gap $E_{\rm g}$, and bulk modulus B_0 for CdTe.

	PBE	HSE	Previous work	Expt.
a/Å	6.63	6.58	6.45[9], 6.63[21]	6.53[22], 6.46–6.48[23]
$E_{\rm g}$/eV	0.58	1.49	0.60[9], 0.62[21]	1.44[22], 1.48[25]
B_0/GPa	34.8	38.7	44[9,25]	42–45[24]

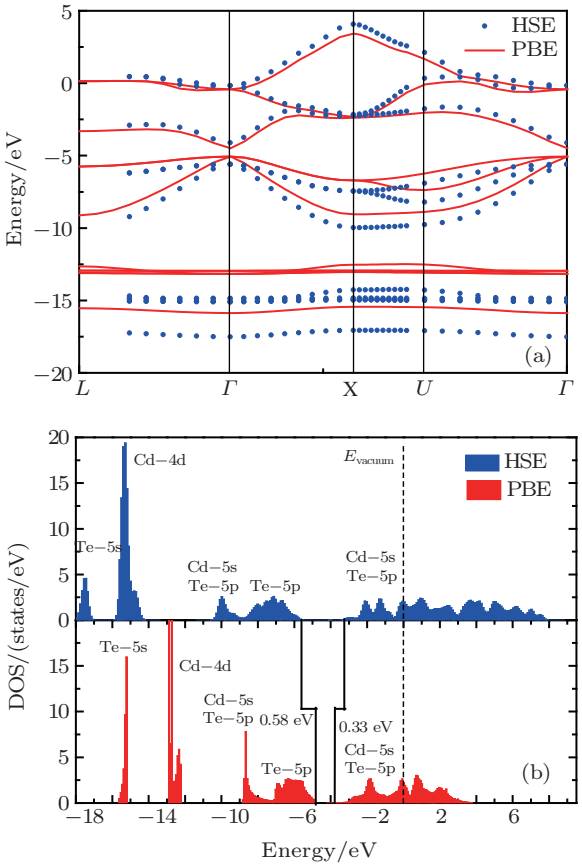


Fig. 1. (color online) Band structure and total density of state for bulk CdTe: (a) band structure, (b) total density of states.

The HSE effects on the electronic structure can be indicated by the alignment of the absolute energy with the vacuum energy level for both the PBE and the HSE results. This can be done by performing the surface calculation with a slab geometry. To position the VBM relative to the vacuum energy level, a common reference energy should be used for both the bulk and the slab calculations. Here, the Cd or Te core potential in the middle of the atom layers of the slab model is aligned with that of the same atom in the bulk calculation. It is worthwhile noticing that a non-polar surface with the same slab geometry (surface orientation and reconstruction) for both PBE and HSE calculations is chosen to minimize the surface orientation and reconstruction effect on the position of the VBM.

The aligned band structures and the total density of states (DOS) are shown in Figs. 1(a) and 1(b), respectively. For the HSE results, the VBM is lowered by 0.58 eV while the CBM is lifted by 0.33 eV, as compared with the results obtained by the PBE method. The lowering of the VBM originates from the reduction of self-interaction of the Te 5p-derived state that composes the highest part of the VBM, since the Fock exchange is totally free from self-interaction. Similarly, all of the corresponding HSE valence bands such as Te 5s, Cd 4d, and Cd 5s derived states are lower than those obtained by the PBE method. The upward shift of the CBM can also be ascribed to the reduced self-interaction of the unoccupied states. In addition, it can be observed that the HSE valence bands are wider after the partial elimination of the self-interaction. Therefore, the band gap obtained by the HSE method is much larger than that obtained by the PBE method.

3.2. Cadmium vacancy: electronic structure and lattice relaxation

V_{Cd} is the most important native defect in CdTe, which often leads to p-type CdTe without intentional doping. The electronic and structure properties of cadmium vacancy can be understood from the molecular-orbital theory. Removing a Cd atom leaves four dangling bonds of the nearest Te atoms, which are directed towards the center of the vacancy. Thus, the molecular orbitals of the vacancy center are linear combinations of these dangling bonds. The respective defect states can result in a single a_1, which lies within the bulk valence band in energy, and a triplet t_2, which is supposed to be located within the energy gap. For the remaining six electrons, after the removal of one Cd, two of the remaining six electrons stay on the a_1 singlet, while the other four are on the t_2 triplet. Thus, a neutral vacancy has two empty states on t_2, resulting in a double acceptor.[12] In the doubly charged state, the t_2 level is fully occupied and the ionic relaxation preserves the T_d point symmetry of the perfect lattice. However, in principle, for the neutral or singly charged vacancies, the t_2 orbital would split into an occupied e level and an unoccupied (V_{Cd}^0) or half occupied (V_{Cd}^-) upper a_1 level accompanied by a symmetry lowering from T_d to C_{3v} or D_{2d} or other lower symmetry. This C_{3v} symmetry (i.e., one Te atom would relax stronger towards the vacancy site than the others) was evidenced from the EPR measurement.[10,11]

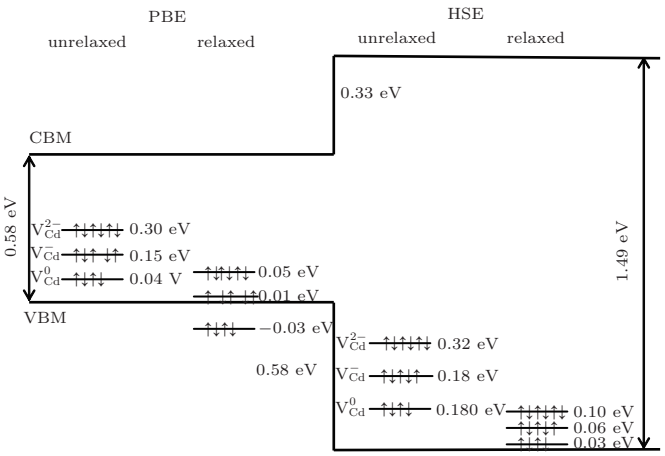


Fig. 2. Schematic energy-level diagram for V_{Cd} within the band gap (not to scale); the values in the gap are relative to the VBM.

Table 2. Structural relaxations around cadmium vacancy in different charge states. For PBE, the bond length is $d_0 = 2.87$ Å; and for HSE, $d_0 = 2.85$ Å; the factor of d_0 less than 1 means inward relaxation. The value in bracket indicates the length of the bond with a localized hole in the C_{3v} structure.

PBE		HSE	
T_d	C_{3v}	T_d	C_{3v}
$0.918d_0$	$0.915d_0$ ($0.901d_0$)	$0.922d_0$	$0.928d_0$ ($0.906d_0$)
$0.910d_0$	$0.915d_0$ ($0.901d_0$)	$0.910d_0$	$0.916d_0$ ($0.900d_0$)
$0.908d_0$	$0.910d_0$	$0.908d_0$	$0.910d_0$

It should be noted that the occurrence of this John–Teller distortion is dependent of the position of the defect-related levels with respect to the valence band of the host crystal, which determines the filling of the t_2 state. Here, the energy position and the occupancy of the t_2 state are closely related to the local structure relaxation of the V_{Cd} defect. For V_{Cd}^{2-}, the total number of bonding electrons trapped around the vacancy is still eight, which is the same as the origin one. So, the nearest four Te atoms tend to relax strongly to the center of the vacancy due to the reduction of the repulsive interaction from the core electron cloud after the removal of the Cd^{2+} ion. Consequently, after relaxation, the t_2 state shifts to a lower energy that is much closer to the valence band maximum, as shown in Fig. 2. After the removal of one or two electrons, the bonds are weakened due to the loss of electrons. The inward relaxation therefore becomes smaller for the cases of V_{Cd}^- and V_{Cd}^0 (see Table 2). This argument also implies that the relaxation energies become smaller, as shown in Fig. 2. After the relaxation, the t_2 state of V_{Cd} in any of the three charge states becomes closer to the VBM, and may merge into the valence

states of the dangling bond and become a delocalized resonance state. Therefore, the John–Teller distortion may not be observed since it should be related to the localized states. We try to optimize the atomic structure using a C_{3v} distorted structure as a starting point. The results in Table 3 show that the C_{3v} structure is almost the same energy as the T_d structure. The difference of the local relaxation structure between the C_{3v} and the T_d structures is very much smaller, about 1%, as shown in Table 2. All of these results are independent of the supercell size, tested by a 216-atom supercell, and the spin state. These results are also in agreement with those of the previous studies.[9]

Table 3. Formation energy of the relaxed structure of cadmium vacancy in different charge states. The John–Teller energies are also indicated. The values in brackets are corrected according to the Makov–Payne (MP) method.

	PBE			HSE		
	T_d (MP)	C_{3v} (MP)	$\Delta E_{\rm JT}$	T_d (MP)	C_{3v} (MP)	$\Delta E_{\rm JT}$
V_{Cd}^{0}	1.524	1.674	–0.150	2.257	2.258	–0.001
V_{Cd}^{-}	1.616 (1.767)	1.730 (1.881)	–0.114	2.331 (2.482)	2.340 (2.491)	–0.009
V_{Cd}^{2-}	1.875 (2.479)	1.913 (2.517)	–0.038	2.519 (3.123)	2.531 (3.135)	–0.012

It is expected that the HSE results may lead to a lower energy for the C_{3v} structure due to the tendency to localize the electron by the exact Fock exchange that is included. However, the results calculated by the HSE method are similar to those by PBE. The energy difference between the C_{3v} and the T_d structures is almost the same for both PBE and HSE methods, likely arising from the merger of the t_2 state into the valence band after relaxation, and thus the small difference between the T_d and the C_{3v} symmetry relaxation structures.

3.3. Formation energies and transition level

The relative stability of the various charge state is determined by the formation energy, as defined in Eq. (1). This formation energy is directly related to the chemical potential of the Cd atom. Here, we only consider the Te-rich condition since this condition most often happens during the growth of a CdTe crystal. The calculated formation energies as a function of the Fermi level for V_{Cd} in CdTe are shown in Fig. 3. The occupation and the position of the t_2 state are essential for a proper description of the formation energy of V_{Cd} in CdTe. After relaxation, the t_2 state changes from within the band gap to the edge of the valence band maximum, leading to lowering of the formation energy. Moreover, stronger relaxation results in much more lowering of the t_2 state, and thus a decrease of the formation energy. Actually, the formation energy differences of V_{Cd}^{0}, V_{Cd}^{-}, and V_{Cd}^{2-} between the relaxed and the unrelaxed structures as calculated by HSE are 0.23 eV, 0.31 eV, and 0.48 eV, respectively.

The formation energies of V_{Cd} in different charge states calculated by HSE are larger than those by PBE. This is a general trend for HSE as compared to the seimilocal functional. It was concluded by Henderson, Paier, and Scuseria that LDA and PBE underestimate the formation energy much more than does HSE, as compared to the DMC results.[26] For instance, LDA, PBE, and HSE underestimate the formation energy of the X, H, T interstitial defect in Si by 1.5 eV, 1.0 eV, and 0.25 eV, respectively.[26] Therefore, HSE can obtain better formation energy than PBE as compared with the DMC results. Here, the formation energies of V_{Cd} calculated by HSE are larger by 0.6–0.8 eV than those by PBE. This may indicate that V_{Cd} is more difficult to form than expected, especially in the heavily doped p-type CdTe. This is the reason why the undoped CdTe generally tends to be lightly p-doped but it is hard

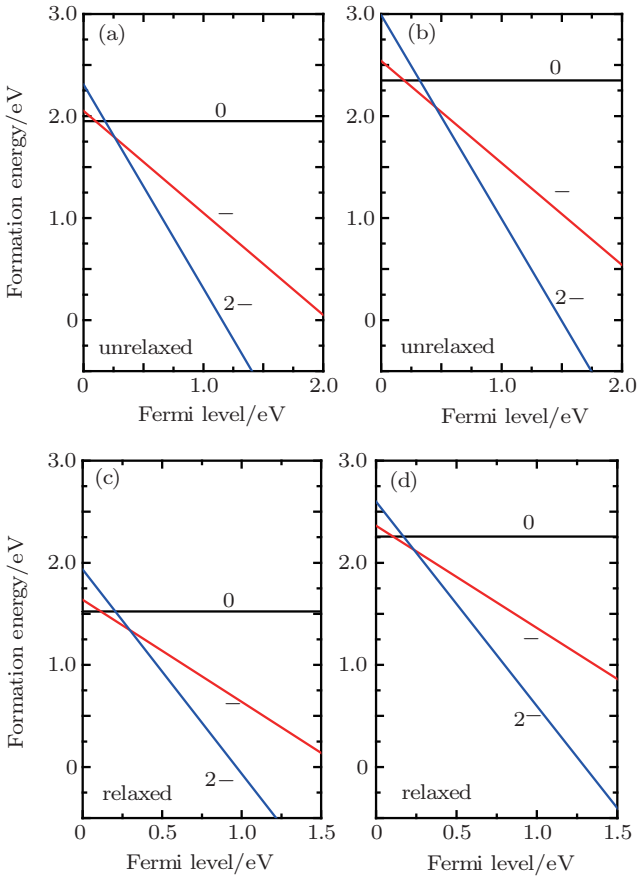


Fig. 3. (color online) Calculated formation energies as a function of the Fermi level for cadmium vacancy in CdTe under Te-rich conditions. Panels (a) and (c) are results calculated by the PBE method; panels (b) and (d) are results calculated by the HSE method. Panels (a) and (b) correspond to the unrelaxed cases; panels (c) and (d) correspond to the fully relaxed cases.

to increase the carrier density higher than 10^{16} cm^{-3}. Since the t_2 level of neutral V_{Cd} has two unoccupied states, it can obtain two extra electrons, leaving to two acceptor levels in the band gap, as shown in Table 4. The $\varepsilon(-1/0)$ level is a shallow level, while $\varepsilon(-2/-1)$ is a much deeper level. This observation is consistent with the previous theoretical results. The convergence is also tested with 96- and 216-atom supercells. The $\varepsilon(-1/0)$ level easily converges, while the $\varepsilon(-2/-1)$ level slowly converges since the spurious electrostatic interaction between the negative charged defect and the positive charged neutralizing background is q^2 dependent. The calculated $\varepsilon(-1/0)$ level agrees well with the experimental result, which is in the range from $E_v + 0.1$ eV to $E_v + 0.2$ eV. However, for the $\varepsilon(-2/-1)$ level, the calculated results deviate strongly from the experimental results. In addition, it is possible that the Makov–Payne correction overestimates the image-charge effects for the doubly charged defect since the correction is based on the simplified point charge model.[27]

Table 4. Transition levels (eV) of cadmium vacancy with reference to the top of the valence band. The values in brackets are corrected according to the Makov–Payne method.

Level	PBE (MP)	HSE (MP)
0/–	0.09 (0.24)	0.07 (0.22)
–/2–	0.26 (0.71)	0.19 (0.64)

Generally, the transition level should be strongly dependent on the band gap calculated. The PBE underestimates the band gap while the HSE method could obtain the result closed to the experimental band gap. However, as shown in Fig. 3 and Table 3, the transition levels calculated by HSE are similar to those of PBE. This may result from the valence band nature of the V_{Cd} defect. It is believed that the defect transition level is less affected by the band gap error for the defect state with the most valence character. As described previously, the t_2 state of the V_{Cd} defect is correlated with the valence state, featuring with the great valence character.

4. Discussion

The cadmium vacancy is one of most important intrinsic defects in CdTe, and is often suggested to be the major source of acceptor in CdTe.[3] Experimentally, Meyer *et al.* identified V_{Cd} by EPR in the early 1990s, which is the most cited work regarding V_{Cd} in CdTe by theoretical researchers.[9,13] The trigonal symmetry was observed by EPR in its singly negative charge state. The explanation for this is that the hole in V_{Cd}^- is localized in one of the four nearest Te atoms, and thus the original T_d symmetry structure should be changed to this John–Teller C_{3v} distortion structure. However, this trigonal structure is still not confirmed by any theoretical calculation despite the fact that a lot of studies have been focused on this point.[9,14] Lany *et al.* found that no single unoccupied band (containing the localized holes) would be separated from the valence band in the case of V_{Cd}^0 and V_{Cd}^- using the linearised augmented plane wave (LAPW) method.[14] Carvalho *et al.* and JAkubas *et al.* reached similar conclusions that a valence-like band defect state leads to the absence of this John–Teller distortion by using the psedopotential methods based on the LDA and the GGA approximations.[9] This trigonal or tetragonal John–Teller distortion could not be found by Chang *et al*. using symmetrized-basis LASTO calculations based on the LDA approximation.[28] It was suggested that this discrepancy between experiment and theory may arise from the limitation of LDA and GGA, which sometimes fails to predict the small polaron formation.[29] HSE can better describe the exact exchange interaction, and thus may lead to the localization of hole and the formation of polaron.[30,31] However, as described previously, HSE still shows that the T_d symmetry structure is the stable structure for CdTe. The failure of prediction of the John–Teller distortion may result from the intrinsic valence-like nature of the V_{Cd} defect state, as evidenced by the position of the defect state close to the VBM and the similarity of the dispersion of the defect state with the top valence band. We also increase the Fock exact exchange ratio to 35% in the hybrid exchange potential of HSE, and the conclusion is still the same. Notably, the previous first-principles calculations by Illgner and Overhof indicated that the isotropic hyperfine interaction of V_{Cd}^- is off by a factor of 6 as compared to the experimental data when the C_{3v} symmetry is deliberately imposed.[32] The defect identification in the EPR experiments is, therefore, doubted according to these results.

5. Conclusion

Both HSE and PBE potentials are used to study the V_{Cd} defect properties in CdTe through the first-principles calculations. Both results show that the John–Teller distortion structure (C_{3v} structure) is unstable in CdTe crystal. The resonance feature of the t_2 state of the Cd vacancy near the valence band maximum may be responsible for the missing of the John–Teller distortion structure. Moreover, a larger formation energy is obtained by the HSE as compared with that obtained from the PBE, and the band gap obtained by the HSE is similar to the available experimental band gap, which is much higher than that obtained from the PBE method. The transition levels calculated by PBE and HSE are almost the same due to the valence band character of the V_{Cd} defect state.

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