***Graphical Abstracts (for review)**

**LDA+ U /GGA+ U calculations of structural and electronic properties of
CdTe:**

Dependence on the effective U parameter

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Abstract

We present a detailed assessment of the structural and electronic properties of CdTe calculated by density functional theory (DFT) with on-site Coulomb self-interaction potentials (LDA+ U /GGA+ U) on the Cd 4*d* band. We systematically calculate the lattice constants, bulk moduli, elastic constants, band structure, and density of states as a function of the U value, and compare the results with those calculated by using standard LDA/GGA and the hybrid functional (HSE06). Our study gives a more accurate account of the strong localization effect of Cd 4*d* electrons onto the overall electronic structure, in particular to the nature of localized Cd 4*d* derived bands and delocalized Te 5*s* derived bands and the coupling between them. We find that the s - d coupling is significant, which is underestimated within conventional DFT calculations (showing a single s -like peak, in disagreement with the experiments). LDA+ U removes this discrepancy by shifting down the Cd-4*d* band closer to the Te-5*s* band, enhancing the s - d coupling, and leading to the appearance of two s -like peaks, which perfectly explains the so-called low intensity “shoulder” on the high-energy side of the Cd-4*d* peak in experimental spectra. Moreover, our results indicate LDA+ U reveals an much more acceptable agreement with experiment at a adequate U than HSE06 does. A well balanced choice of U within LDA+ U scheme is proposed to be at 7 eV.

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I. INTRODUCTION

Cadmium Telluride (CdTe) and its alloys are important materials for optoelectronic applications such as solar cells [1, 2] and X- and γ -ray semiconductor detectors. [3–5] The performance of these materials depends critically on their electrical properties, which are dominated by the formation of defects, including both point and extended defects. Therefore, understanding the formation and effects of defects in CdTe and its alloys has attracted great attention.[6, 7] Calculations within the density-functional theory (DFT) have been proven as a powerful method to understand the structural and electronic properties of semiconductors.

Most DFT calculations use the local density approximation (LDA)[8] or generalized gradient approximation (GGA)[9] as the exchange-correlation functional. However, it is well known that DFT with standard LDA or GGA underestimate the band gap of semiconductor. For CdTe, the calculated band gaps are 0.63/0.58 eV with LDA/GGA, much smaller than the experimental value of ~ 1.5 eV (Ref. [10]). This is largely because standard LDA/GGA overestimates the delocalization of Cd-4*d* electrons, which push up the valence electrons (the Te-5*p* valence band). Moreover, LDA and GGA can sometimes produce qualitatively wrong optical and electronic properties. Some recent publications have shown that standard LDA/GGA calculations produce structural and electronic properties that are inconsistent with experimental data.[11–15] To correctly predict the structural and electronic properties, an improved or modified exchange-correlation functional that describes the strong localization of Cd-4*d* electrons are needed.

Many approaches have been proposed to overcome the deficiency of standard LDA/GGA. To lower the energies of semi-core states, corrections can be made, for instance, by means of self-consistent self-interaction-corrected (SIC) calculations or simplified SIC calculations.[16] Hybrid functional (e.g., B3LYP,[17] PBE0[18] and HSE.[19]), which mix a fraction of nonlocal single-determinant exchange with conventional DFT exchange-correlation functional, have also been developed to improve the calculation of structural, thermodynamic, and bonding properties of solids. [20, 21] The underestimation of band gap can also be solved by appropriately calculating the quasi-particle energies, e.g., the *ab initio* GW method.[22] However, these methods are very computing power intensive. It is currently not practical for studying defects in semiconductor, which usually requires the use of large supercells. LDA+*U*/GGA+*U* is another approach that has been frequently used to correct the calculated band gaps.[23, 24] This approach applies on-site Coulomb self-interaction potentials (*U*) to selected bands. It combines the explicit treatment of

electronic correlation with a Hubbard-like model[25] for a subset of states in the system. Non-integer or double occupations of these states are described by introducing of two parameters: (1) U , which reflects the strength of the on-site Coulomb interaction, and (2) J , which adjusts the strength of the exchange interaction. Typically, for simplicity, Dudarev’s method,[26] within which the two parameter can be combined into a single effective one, $U_{eff} = U - J$, is usually used. This effective parameter U_{eff} is typically referred to as U .

The LDA+ U /GGA+ U approach is much less computationally demanding than the GW and hybrid functional methods. It is rather attractive for studying defects in semiconductors because it can be used to calculate the structural and electronic properties of large supercells. The calculated results depend on the U values. The determination of the optimal U value for each material remains a matter of debate because a U value is often optimal for some calculated properties, but not all of them. From an *ab initio* point of view, it would be desirable to determine U in a self-consistent way. Cococcioni[27–29] proposed a linear response method, which is fully consistent with the definition of the DFT+ U Hamiltonian. An alternative route is to change the U value systematically and compare the calculated results with experimental data. Furthermore, to understand how whether the results calculated by LDA+ U /GGA+ U are meaningful, it is necessary to assess the results by comparing them with those results calculated by other approaches and experimental data.

In this work, we systematically calculate the lattice constants, bulk moduli, elastic constants, band structure, and density of states of CdTe as a function of U , and compare the results with those calculated by using standard LDA/GGA and hybrid functional (HSE06). We find that with appropriate U values, LDA+ U /GGA+ U gives better results on lattice constants, bulk modulus, and elastic constant than standard LAD/GGA or HSE06. For electronic properties, LDA+ U /GGA+ U gives similar results on the conduction and valence bands as HSE06 when $U = 12.5/13.9$ eV, including the bandwidth, dispersion, and band gap. Furthermore, LDA+ U /GGA+ U down shifts the Cd 4d bands and enable strong d - s (Cd-4d and Te-5s) coupling, which cannot be predicted by the standard LDA/GGA or HSE06 calculation. At $U = 7$ eV, the LDA+ U calculation matches well with experimental photoemission spectra. Our assessment reveals that a LDA+ U /GGA+ U calculation predicts well the structural and electronic properties of CdTe. Because of its low demand on computing power, the LDA+ U /GGA+ U approach is an attractive means to study the physics of defects in CdTe and its alloys.

II. COMPUTATIONAL DETAILS

In our study, all the structural optimizations and energy band calculations are performed with the VASP code.[30, 31] The projected augmented wave method (PAW) [32] is employed. The LDA (Ref. 8) and the PBE (Ref. 9) form of the GGA exchange-correlation potentials are used together with their LDA+ U and GGA+ U variants. The Cd (4*d*, 5*s*) and Te (5*s*, 5*p*) are treated as valence states. The energy cutoff is set at 350 eV and an $8 \times 8 \times 8$ k -point grid is used for structural optimizations. All structures are fully relaxed until the force acting on each atom is less than 0.02 eV/Å.

Another functional used in this work is HSE functional, which is derived from PBE0 (Ref. 18) by replacing the long-range part of the exact exchange by a local expression of PBE exchange. We use the default composition of the PBE0 functional, with 25% of the exact exchange, and 75% of the PBE exchange, and 100% of the PBE correlation energy. The screening parameter μ is set to 0.2 Å⁻¹, conforming to the HSE06 functional. The NKRED parameter is set to 2 meaning that a HF kernel is evaluated on a coarser k -point grid.[20]

The structures of different functionals with different U s are obtained by calculating at various constant volumes and making a least squares fit of the energy-volume data to the form proposed by Birch:[33]

$$E(V) = E_0 + \frac{8}{9}B_0V_0 \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 + \frac{9}{16}B_0(B'_0 - 4)V_0 \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2, \quad (1)$$

where E_0 , V_0 , B_0 and B'_0 are, respectively, the equilibrium energy, volume, bulk modulus, and pressure derivative of the bulk modulus. Through fitting the energy-volume data to the equation of (1), we can obtain all the values of the parameters V_0 , E_0 , B_0 and B'_0 .

For a cubic crystal there are only three non-zero independent elastic constants: C_{11} , C_{12} , and C_{44} . All of the rest are either zero or follow from the general condition $C_{ij} = C_{ji}$. In order to calculate the elastic constants C_{ij} , we have employed the following two independent deformations,[34]

$$\begin{aligned} \text{case(i)} : \vec{\epsilon} &= (\delta, -\delta, \delta^2/(1 - \delta^2), 0, 0, 0); \\ \text{case(ii)} : \vec{\epsilon} &= (0, 0, \delta^2/(4 - \delta^2), 0, 0, \delta). \end{aligned} \quad (2)$$

In the above two deformations the unit-cell volume of the crystal has been kept unchanged (i.e., volume-conserving strain tensors), so that there is no pressure or stress term.[35] Application of

these strains change the total energy from its unstrained value to

$$\begin{aligned} \text{case(i)} : E(\delta) &= E(0) + (C_{11} - C_{12})V\delta^2 + O[\delta^4]; \\ \text{case(ii)} : E(\delta) &= E(0) + \frac{1}{2}C_{44}V\delta^2 + O[\delta^4], \end{aligned} \quad (3)$$

where V is the volume of the unit cell and $E(0)$ is the energy of the unstrained lattice at volume V . For each of the above cases we have used seven different values of δ : $\delta = 0, \pm 0.01, \pm 0.02, \pm 0.03$. Combining the equations of (1) and (3) with the well-known relation for a cubic crystal,

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad (4)$$

we can determine the full elastic tensor. B in equation (4) is the bulk modulus as B_0 in equation (1).

III. RESULTS AND DISCUSSION

A. Structural properties

The calculated lattice constant (a_0), bulk modulus (B), the pressure derivative of bulk modulus (B'), and the elastic constants (C_{11} , C_{12} , and C_{44}) for CdTe using standard LDA/GGA, LDA+ U /GGA+ U , and HSE06, are summarized in Table I. For LDA+ U /GGA+ U calculation, a range of U value from 3 eV to 15 eV is used. The experimental values available in literature are also given in Table I.

The calculated a_0 , B , and B' using LDA+ U /GGA+ U depend on the U values. To reveal the dependence, the calculated a_0 and B , as a function of U is shown in Figure 1. The experimental values are indicated by horizontal dashed lines. The values calculated by HSE06 functional are indicated by stars. It is seen that standard LDA, i.e., $U = 0$ eV, underestimates a_0 by about 0.9%. LDA+ U increases the underestimation of a_0 as U increases. At $U = 10$ eV, the underestimation becomes 1.9%. As for bulk modulus and elastic constants, standard LDA overestimate the values with respect to experimental values. LDA+ U reduces the overestimation. Standard GGA overestimate a_0 of CdTe by 2.3% and underestimate B by nearly 20% compared to experimental values. GGA+ U reduces the overestimation. However, the reduction of a_0 becomes significant only when U reaches certain values. The calculated a_0 matches the experimental value when $U \approx 13$ eV. HSE06 overestimates a_0 of CdTe by 1.5% and slightly underestimates the bulk modulus and elastic constants.

It is worth pointing out that the calculated a_0 of CdTe by LDA+ U /GGA+ U decreases monotonically as U increases. However, the calculated B of CdTe shows a different trend. It initially decreases monotonically as U increases. Once the U reaches a critical value (11 eV for LDA+ U and 8 eV for GGA+ U), the calculated B suddenly increases. These behaviors can be understood qualitatively by the effects of U . The calculated a_0 is largely determined by the energy position of outmost valence electrons such Te-5 p electrons in CdTe. However, B is mainly determined by more localized deep core-like electrons, such as Cd-4 d electrons. When a U is applied to Cd-4 d electrons, the Cd-4 d band becomes more localized and is also pushed down in energy. As a consequence, the valence bands are pulled down in energy and lead to decreased a_0 . This is why the calculated a_0 of CdTe decreases monotonically as U increases. When Cd-4 d band is moved down

TABLE I. Lattice constant a_0 (Å), bulk modulus B (GPa), the pressure derivative of bulk modulus B' , and the Elastic constants C_{11} , C_{12} , and C_{44} (GPa) for CdTe obtained after complete structural optimization with HSE06, standard LDA/GGA, and LDA+ U /GGA+ U compared to experiments.

Method	U (eV)	a_0 (Å)	B (GPa)	B'	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
LDA		6.421	45.77	4.80	57.99	39.66	21.70
LDA+ U	3	6.419	45.06	4.35	57.15	39.02	21.42
LDA+ U	5	6.412	44.61	3.86	56.73	38.55	21.25
LDA+ U	7	6.400	43.91	3.14	55.53	38.11	20.79
LDA+ U	10	6.360	40.46	0.99	52.25	34.56	21.87
GGA		6.630	35.02	3.73	45.95	29.55	18.46
GGA+ U	3	6.633	34.52	1.97	45.29	29.14	17.96
GGA+ U	5	6.631	34.06	0.25	44.66	28.75	17.87
GGA+ U	7	6.623	32.97	-2.35	43.39	27.76	18.27
GGA+ U	10	6.593	32.58	-0.14	43.44	27.15	18.41
HSE06		6.579	38.14	7.13	49.40	32.51	19.11
Expt.		6.48 ^a	44.5 ^a , 42 ^b	—	56.2 ^c , 53.5 ^d	39.4 ^c , 36.8 ^d	20.6 ^c , 19.9 ^d

^a Reference 36.

^b Reference 37.

^c Reference 38.

^d Reference 39.

FIG. 1. Dependence of (a) lattice parameter a_0 and (b) bulk modulus B on U of different methods: standard DFT ($U = 0$ eV), LDA+ U (squares), and GGA+ U (circles). The stars correspond to the HSE06 values. The dash lines represent the experimental values, which can be found in Table I.

in energy, the calculated B decreases. However, when U reaches the critical value, Cd-4d band will be moved below the Te-5s band. In this case, the B is mainly determined by Te-5s band. This is responsible for the observed sudden increase of B .

B. Electronic properties

The most important electronic property of semiconductors for optoelectronic applications is the band gap. HSE06 predicts a band gap of 1.53 eV for CdTe, which agrees very well with the experimental value (1.51 eV, Photoluminescence at 300 K).[10] Standard LDA/GGA gives band gap of 0.63/0.58 eV for CdTe, which are significantly lower than the experimental value. As mentioned above, the application of U on Cd-4d band results in lower position in energy for the valence band. Therefore, LDA+ U /GGA+ U leads to an increased band gap as compared to standard LDA/GGA. Figure 2 shows the calculated band gap values of CdTe as a function of the U value by LDA+ U /GGA+ U marked by squares/circles. The star indicates the HSE06 value. The

FIG. 2. Calculated DFT+ U band gap for CdTe as a function of the U parameter of different methods: standard DFT ($U = 0$ eV), LDA+ U (squares), and GGA+ U (circles). The star corresponds to the HSE06 value. The dash line represents the experimental value of 1.51 eV.

dash line represents the experimental value of 1.51 eV. It is seen that the LDA+ U /GGA+ U calculated band gap increases almost linearly with the increasing of the U value, confirming the fact that introducing a Hubbard U correction term substantially improves the accuracy of the calculated band gap. As U value is increasing, Cd-4d bands shift downward with respect to the VBM, which means the p - d coupling between Cd-4d and Te-5p (the bands at VBM) is getting weaker, thus the Cd-4d will not push up Te-5p so high, i.e. the VBM drops down, and the band gap is opened. The LDA+ U /GGA+ U calculated band gap reaches to experimental value at $U = 12.5/13.9$ eV. However, at these U values, LDA+ U /GGA+ U poorly predicts the structural properties.

Therefore LDA+ U /GGA+ U can correctly predict the band gap for CdTe when large U values are used. To understand whether or not the calculations with such large U values correctly predict the band structures, we have compared the calculated band structures to those calculated by HSE06. The band structures calculated by standard LDA, LDA+ U with $U = 7$ and 12.5 eV, and HSE06 are shown in Figure 3. Because GGA+ U gives similar results to LDA+ U , band structures calculated by GGA+ U are not shown. For all band structures, the zero energy is referred to the valence band maximum (VBM). It is seen that the valence and conduction bands are very similar in these band structures calculated by standard LDA, LDA+ U , and HSE06. They have almost the same bandwidth and dispersions. This indicates that LDA+ U predicts not only the band gap, but also the nature of the valence and conduction bands of CdTe, meaning that LDA+ U can appropri-

FIG. 3. Calculated band structures of CdTe (zincblende crystal structure) with (a) LDA, (b)-(c) LDA+ U with U values of 7 and 12.5 eV, and (d) HSE06. The band-gap regions are shaded. Dashed lines indicate doubly degenerate states. The energy zero is set to the VBM.

ately describe the electronic properties derived from valence and conduction bands. However, the band structures shown in Fig. 3, exhibit very different features for Cd-4d and Te-5s bands. The localized degenerate states, marked by dashed lines below the valence bands are the signature of Cd-4d bands. In the standard LDA calculation [Fig. 3(a)], the Cd-4d band is located at about 8 eV below the VBM. The curved state in the Cd-4d band indicates that there is a weak coupling between the Cd-4d and Te-5s bands. The Te-5s band is located far below the energy levels of the Cd-4d states. In LDA+ U calculations [Fig. 3(b) and 3(c)], the Cd-4d band is moved downward. For $U = 7$ eV, the Cd-4d and Te-5s bands are completely mixed, leading to the appearance of two s -like states. When U is increased to 12.5 eV, which correctly predicts the band gap, the Cd-4d band is located below the Te-5s band. In the HSE06 calculation, the Cd-4d and Te-5s bands are very similar to those calculated by standard LDA. The coupling between Cd-4d and Te-5s is very weak.

To understand more about the nature of the hybridization between Cd-4d and Te-5s, we have calculated the l -decomposed density of states (DOS). Figure 4(a) and 4(b) show the calculated l -decomposed DOS by standard LDA and LDA+ U ($U = 7$ eV). These DOS plots correspond the band structures shown in Figs. 3(a) and 3(b). The solid lines are Cd-4d states and the dashed lines are Te-5s states. The zero energies are set at VBM. For clarity, the valence and conduction

FIG. 4. Calculated l -decomposed DOS of CdTe with (a) standard LDA and (b) LDA+ U ($U = 7$ eV). The solid lines are Cd-4d states and the dashed lines are Te-5s states. The DOS are normalized by a factor of $1/(2l + 1)$ and a Gaussian broadening of 0.2 eV is used. The energy zero is set to the VBM.

bands are not shown. It is seen that the standard LDA calculation [Fig. 4(a)] shows three peaks as marked by p_1 , p_2 , and p_3 . The p_1 peak consists of a large Cd-4d component and a small Te-5s component. The p_2 peak is derived from Cd-4d. The p_3 peak is derived mainly from Te-5s, but with a very small Cd-4d contribution. This l -decomposed DOS indicates that there is only a very weak hybridization between the Cd-4d band and Te-5s band in the standard LDA calculation. However, LDA+ U calculation significantly enhances the hybridization between the Cd-4d band and Te-5s bands when $U = 7$ eV. The calculated l -decomposed DOS for $U = 7$ eV [Fig. 4(b)] also shows three peaks. However, the p_2 peak, which is derived from Cd-4d, is shifted down in energy to be close to Te-5s. The p_1 peak is now dominated by Te-5s and the p_3 peak contains large contribution from Cd-4d.

The observed changes of the DOS peaks caused by LDA+ U can be understood qualitatively by the strong s - d coupling[40, 41] that occurs when the Cd-4d band is shifted to be close to the Te-5s band. CdTe possesses the zinc blende structure, which has the T_d point group symmetry. At the Brillouin zone center (Γ point), the Cd-4d band exhibits doubly degenerate e states, which correspond to the Γ_{12d} state in Fig. 3, and triply degenerate t_2 states, which corresponds to the Γ_{15d} in Fig. 3. Due to the different symmetry, these states do not couple with Te-5s state ($V_{sd} = 0$). However at points away from Γ point in the Brillouin zone, the situation may change because

FIG. 5. Calculated DOS of CdTe using the (a) HSE06, (b) standard LDA method, and (c)-(f) LDA+ U with U values of 3, 5, 7, 10, and 12.5 eV. The energy zero is set to the VBM.

the point-group symmetry is reduced. For example, at X point, the t_2 states will split, resulting a state that has the a_1 character. This state has similar symmetry as the Te-5s state and therefore they couple with each other. The p_1 peak in the DOS plot is the antibonding-like states of this coupling, whereas the p_3 peak is the bonding-like state of the coupling. For standard LDA calculation, the Cd-4d band is much higher in energy than the Te-5s band, i.e., the s - d coupling is very weak so that p_1 peak is very close to p_2 peak and the contribution to p_1 peak from Te-5s is very small. As the U value increases, the Cd-4d band is shifted closer to the Te-5s band and the coupling becomes stronger. At $U = 7$ eV, the p_1 peak comes mainly from Te-5s band and the p_3 peak contains a significant Cd-4d component. This three-peak feature explains very well the experimental photoemission spectra of CdTe measured by Löher et al.[14, 15] The experimental spectra indicate that the Cd-4d exhibit two peaks, one at about $E_v - 10.8$ eV and one at $E_v - 11.5$ eV. There is also a low intensity “shoulder” (with binding energies of 9.5–10.0 eV).

To explore how U values may affect the three-peak features, we have calculated l -decomposed DOS as a function of U and compare these values with those calculated by standard LDA and HSE06. The calculated total DOS plots are shown in Figure 5. The three peaks corresponding to

Cd-4*d* and Te-5*s* are marked by p_1 , p_2 , and p_3 . Like the band structures, the valence and conduction bands in these DOS plot are very similar, indicating that LDA+ U gives a good description of the valence and conduction bands. The relative positions for p_1 and p_2 peaks in the DOS curves (a) and (b) are very similar, revealing that the HSE06 calculation also significantly underestimate the coupling between Cd-4*d* and Te-5*s*, though it correctly predicts the band gap of CdTe. This is because the predicted position for Cd-4*d* band is too high in energy. As the U value increases, the p_2 peak moves to lower energy. When the U value becomes too large, Cd-4*d* will be below the Te-5*s* band and the s - d coupling will decrease. At $U = 10$ eV, the p_3 peak becomes unclear. At $U = 12.5$ eV, the Cd-4*d* band is below the Te-5*s* band. The DOS does not match the experimental photoemission data though LDA+ U predicts correctly the band gap at this U value. The calculated peaks with $U \approx 7$ eV match the best with experimental photoemission spectra. However, LDA+ U with this U value does not correctly predict the band gap. A similar evolution is observed for GGA+ U . The calculated DOS matches experimental data with $U \approx 6$ eV.

IV. CONCLUSION

In conclusion, we have calculated the lattice constant, bulk modulus, elastic constants, band structures, and DOS of CdTe using LDA+ U /GGA+ U and have compared the results with those calculated by standard LDA/GGA and hybrid HSE06 functional. We found that LDA+ U /GGA+ U methods can generally improve the prediction of electronic properties of CdTe as compared to standard LDA/GGA, when the appropriate U values are used. However, different properties require different U values to achieve optimal results. It is not possible to extract a universal U value to reproduce all the properties of CdTe. Reproducing the experimental band gap requires a U value of about 12.5 eV for LDA+ U and 13.9 eV for GGA+ U . With these U values, LDA+ U /GGA+ U can also give similar valence and conduction bands of CdTe. However, they cannot correctly describe Cd-4*d* and Te-5*s* states. In addition, very large U values incorrectly describe the structural properties of CdTe. As expected, HSE06 calculation gives excellent prediction band gap, but it does not accurately reproduce the lattice parameter or the electronic structures of Cd-4*d* and Te-5*s* bands. The most interesting thing is, LDA+ U /GGA+ U down shifts the Cd 4*d* bands and correctly describes the strong s - d coupling. Such coupling is much underestimated by the standard LDA/GGA or HSE06 calculation. At $U = 7$ eV, LDA+ U produces a density of states that explains well the so-called low-intensity “shoulder” on the high-energy side of the Cd-4*d* peak

seen in experimental photoemission spectra. Our results suggest that LDA+ U /GGA+ U method is well suited for investigating the structural and electronic properties of CdTe, making it very attractive for calculating the structural and electronic properties of large CdTe systems because of the relatively less computing power demand.

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