

Effects of crystal ordering and composition on properties of $\text{CdS}_x\text{Te}_{1-x}$ alloys: a first-principle insight

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Effects of crystal ordering and composition on the properties of $\text{CdS}_x\text{Te}_{1-x}$ alloys are studied using first-principle calculations. The authors find that the chalcopyrite structure with (201) ordering has the lowest formation energy. (110) Y2 ordering can occur in disordered structure due to the small energy difference. The authors find that the spin-orbit (SO) splitting, band gap and their bowing parameters are significantly dependent on the ordering and composition. For the compound $\text{CdS}_{0.5}\text{Te}_{0.5}$, negative bowing parameter of SO splitting is found in ordered structures, while positive bowing parameter is found in disordered structure. For a given (100) ordering, the bowing parameter of energy gap increases with the decreasing of the bowing parameter of SO splitting.

1. Introduction

Thin film cadmium sulfide/cadmium telluride solar cells have been extensively studied in the last few years due to the ideal band gap and high absorption coefficient of cadmium telluride. High energy conversion efficiencies up to 16%¹ have been achieved. The interdiffusion between the cadmium sulfide window layer and cadmium telluride absorber layer leads to the formation of a mixed $\text{CdS}_x\text{Te}_{1-x}$ interfacial layer. This layer is generally believed to be beneficial to the solar cell performance. Through interfacial layer formation, (a) the large strain energy due to the lattice mismatch (10.7%) between cadmium sulfide and cadmium telluride can be largely relieved; (b) the degree of interdiffusion will certainly shift the electrical junction away from the metallurgical interface and reduce the defect density at the interface² and (c) the adjustable band gap (E_g), with respect to the alloy composition, will result in changes in the open-circuit voltage V_{oc} and thus the efficiency of the solar cell. Unfortunately, despite the significant benefits from $\text{CdS}_x\text{Te}_{1-x}$ alloy, many fundamental properties of this system are not yet understood. These fundamental properties include the following:

- (i) Possible sublattice crystal orderings and their effects on alloy's properties: Theoretical studies on group III–V and II–VI ternary alloys, with larger lattice mismatch,

usually assume a perfectly random structure with no ordering effects.³ However, in experiments, spontaneous ordering has been found in many alloys.⁴ For $\text{CdS}_x\text{Te}_{1-x}$, a short-range ordering has been observed recently by room temperature Raman spectroscopy measurements.⁵ Therefore, it is worthwhile to address the possible crystal orderings and their effects on the properties of this system.

(ii) Sign of the SO splitting (Δ_{SO}) and bowing parameter $b(\Delta_{SO})$: The composition variation of the spin-orbit (SO) splitting can be fitted to the form:

$$1. \quad \Delta_{SO}(x) = \bar{\Delta}_{SO}(x) - x(1-x)b(\Delta_{SO})$$

where, $\bar{\Delta}_{SO}$ is the concentration-weighted average SO splitting. Controversy has existed for a long time on the sign of $b(\Delta_{SO})$. Most of the early experimental studies⁶ reported positive values, for example GaPAs (0.175 eV), InPAs (0.357 eV), GaInP (0.101 eV) and GaInAs (0.144 eV). Later on,^{7,8} some negative values have been reported, for example ZnSeTe (-0.59 eV) and GaInP (-0.05 eV). Therefore, it is interesting to find out the SO splitting and its bowing parameter of $\text{CdS}_x\text{Te}_{1-x}$ alloys.

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(iii) Dependence of band gap and its bowing parameter b on the alloy composition: The optical bowing parameter b of the $\text{CdS}_x\text{Te}_{1-x}$ system, analogous to Equation 1, is given by

$$2. \quad E_g(x) = \bar{E}_g(x) - x(1-x)b$$

For most semiconductor alloys, the bowing parameter is nearly independent of composition x . However, for alloys with large size and chemical disparity between its constituents, the bowing parameter could be strongly composition dependent.⁹ Therefore, it is interesting to see whether the bowing parameter varies with composition in $\text{CdS}_x\text{Te}_{1-x}$ compounds.

In order to answer these questions, the authors have studied, systematically, the electronic structures of $\text{CdS}_x\text{Te}_{1-x}$ compounds using the first-principle method. The authors calculated (a) the crystal orderings and alloy formation energy; (b) valence band splitting, including crystal field (CF) splitting Δ_{CF} and SO splitting Δ_{SO} ; (c) the alloy band gaps and bowing parameters and (d) density of states (DOS). Results are compared with the available experimental data.

2. Method of calculations

The total energy and electronic properties for various crystal orderings and compositions are performed based on the local density approximation (LDA).^{9,10} The cut-off energies and size of k points are tested to ensure that the total energies converge within 0.1 meV/atom. The authors use the Ceperley–Alder exchange correlation potential¹¹ as parameterized by Perdew and Zunger.¹² The Cd d electrons are treated in the same footing as the other valence states. Atomic and volume relaxations are performed for all orderings. The calculated equilibrium lattice constants are 5.77 and 6.42 Å for cadmium sulfide and cadmium telluride, respectively, within 0.7% of the experimental values.¹³

For the fully ordered alloys, at composition $x = 0.5$, the authors use the layered tetragonal $P4m2$ ('CuAu-I like', CA), the chalcopyrite $I\bar{4}2d$ (CH), the layered trigonal $R3m$ ('CuPt like', CP) and the layered orthorhombic $Pnm2_1$ (Y2) structures, ordering along (001), (201), (111) and (110) planes, respectively.^{9,14} At composition $x = 0.25$ and 0.75, the (100) ordering $P43m$ ('Luzonite', LZ) structure is used. For the disordered alloys, the authors use the 'special quasirandom structure' approach¹⁵ to generate base-centered monoclinic SQS8 structures.

3. Results and discussion

The calculated properties of ordered and disordered $\text{CdS}_{0.5}\text{Te}_{0.5}$ are listed in Table 1. The authors find that the formation energy, defined as, $\Delta E = E(x) - \bar{E}(x)$, follows the trend: $\Delta E(\text{CP}) > \Delta E(\text{CA}) > \Delta E(\text{SQS8}) > \Delta E(\text{Y2}) > \Delta E(\text{CH})$, indicating that CH is the ground state structure and contains lower strain energy and Madelung energy. It is noteworthy that the difference of formation

energies between Y2 ordering and disordered SQS8 structures can be as small as 2 meV/atom. This suggests a possible ordered and disordered mixed structure. Indeed, recent Raman spectroscopy measurements⁵ have reported a short-range ordering in random $\text{CdS}_x\text{Te}_{1-x}$ system.

It is known that the CF splitting (Δ_{CF}) and SO splitting (Δ_{SO}) separate the triply degenerate valence band maximum states into a singly and a doubly degenerate states. The authors have extracted Δ_{CF} and Δ_{SO} of all the ordered and disordered structures, as given in Table 1, using the Hopfield quasicubic model.¹⁶ Δ_{CF} is defined to be positive if the doubly degenerate states are above the non-degenerate state. According to the perturbation theory and the folding relations, Δ_{CF} is inversely proportional to the difference of the unperturbed energy levels of the end-point binary constituents before folding into new states of the ordered ternary compounds.¹⁴ On the basis of this theory, the authors can explain the ordering effects on the CF splitting in terms of the energy levels of the binary constituents, as listed in Table 2.¹⁷ From Table 1, the authors find that (a) for the ordered structures, the following relationship holds: $\Delta_{\text{CF}}(\text{CP}) > \Delta_{\text{CF}}(\text{CA}) > \Delta_{\text{CF}}(\text{CH}) > \Delta_{\text{CF}}(\text{Y2})$. This is because the energy difference follows the opposite trend. For example, the energy difference in $\text{CH}(\Gamma_{15v} - W_{3v} = 2 \text{ eV})$ is larger than $\Gamma_{15v} - X_{5v} = 1.68 \text{ eV}$ in CA and $\Gamma_{15v} - L_{3v} = 0.67 \text{ eV}$ in CP ordering. (b) The CF splitting in CH ordering is small and negative due to the fact that the stronger $(\Gamma_{15v} - W_{3v})$ coupling than $(\Gamma_{15v} - X_{5v})$ coupling makes the Γ_{4v} above Γ_{5v} state. (c) Different from CA, CP and CH, the doubly degenerate state in Y2 ordering is further split by a small amount into two non-degenerate states due to the yet lower symmetry.

Earlier perturbation theory¹⁸ treats the SO splitting (Δ_{SO}) as a disorder-induced effect and relates its bowing $b(\Delta_{\text{SO}})$ to the difference in $s-p$ interaction of the alloy constituents. This theory predicts positive $b(\Delta_{\text{SO}})$. In order to explain some experimentally observed negative bowing values,^{7,8} Wei *et al.*¹⁹ propose that the interband $p-p$ coupling enhances Δ_{SO} and dominates the value of $b(\Delta_{\text{SO}})$. From their calculated values, in Table 1, for $\text{CdS}_x\text{Te}_{1-x}$, the authors find that: (a) the SO splitting shows strong ordering dependence. This indicates that the ordering geometry strongly affects the $s-p$ and $p-p$ coupling; (b) ordering structures yield negative $b(\Delta_{\text{SO}})$ and disordered structures yield a positive value. The ordering induced negative $b(\Delta_{\text{SO}})$ are consistent with the results of Wei *et al.*¹⁹ and can be attributed to the intraband $p-p$ coupling. The positive $b(\Delta_{\text{SO}})$ for disordered structure is due to the fact that the disorder effect mixes d state at the top of the valence band with p states and this $p-d$ hybridization reduces Δ_{SO} and (c) largest $b(\Delta_{\text{SO}})$ is found in CP ordering and smallest is found in SQS8 structure. This suggests that the $p-d$ coupling is strongest in SQS8 and weakest in CP ordering.

The calculated results also show that CP ordering has the smallest band gap (0.71 eV). This is due to the fact that the smallest

Structure	$a: \text{\AA}$	η	$\Delta E: \text{eV/atom}$	$\Delta_{\text{cf}}: \text{eV}$	$\Delta_{\text{so}}: \text{eV}$	$b(\Delta_{\text{so}}): \text{eV}$	$E_g: \text{eV}$	$b: \text{eV}$
CA	6.0961	0.996	0.038	0.230	0.566	-0.437	0.189 (1.37)	1.843
CH	6.0893	0.997	0.019	-0.124	0.497	-0.161	0.524 (1.70)	0.506
CP	6.1002	1.002	0.051	0.720	0.678	-0.885	-0.471 (0.71)	4.485
Y2	6.0889	0.995	0.027	-0.422	0.551	-0.377	0.202 (1.38)	1.792
SQS8	6.0914	0.995	0.029	-0.219	0.417	0.161	0.270 (1.45)	1.518

The HSE06 corrected band gaps are given in parenthesis.

Table 1. Calculated properties of $\text{CdS}_{0.5}\text{Te}_{0.5}$ for various structures, including lattice constant, tetragonal distortion parameter, formation energy, crystal field splitting, spin-orbit splitting and its bowing parameter, band gap and optical bowing parameter

	Γ_{15v}	W_{3v}	X_{5v}	L_{3v}
Cadmium sulfide	0.00	-1.95	-1.66	-0.65
Cadmium telluride	0.00	-2.05	-1.70	-0.68

Table 2. Local density approximation calculated valence band energy levels of cadmium sulfide and cadmium telluride, relative to valence band maximum

($\Gamma_{15v} - L_{3v}$) energy difference causes strongest repulsion in its energy levels. This repulsion lowers Γ_{1c} and raises Γ_{15v} states and thus results in smallest band gap. Similarly, CH ordering has the largest band gap relative to other structures. In principle, an ideal solar cell material should have a direct band gap that is equal to the average photon energy in the visible component of the solar spectrum, that is, around 1.3–1.5 eV. Therefore, experimental conditions should be controlled to avoid the formation of CP ordering. According to Equation 2, the optical bowing parameter also shows strong structure dependence, as listed in Table 1.

The authors now look at the composition effects by calculating the properties of $\text{CdS}_x\text{Te}_{1-x}$ at composition 0.25, 0.5 and 0.75. Their calculated lattice constants follow a simple linear function of composition x . The interaction parameter, $\Omega = \Delta E / x(1-x)$, increases with the increasing of tellurium concentration. The SO splitting increases monotonically when anion atomic number increases from sulfur to tellurium. This is because the valence band has large anion p character and the atomic SO splitting of the anion valence p state increases with the atomic number.²⁰ The change in Δ_{so} , however, is not a linear function of the composition. Its bowing parameter, $b(\Delta_{\text{so}})$, as listed in Table 3, shows significant composition dependence. The calculations of band gap E_g show that, initially, adding sulfur into cadmium telluride will actually reduce the band gap. Further increase in sulfur concentration will eventually increase the band gap. This is due to the fact that, at low sulfur concentration, the bowing parameter b is larger than the band gap difference between

Composition	a	Ω	$b(\Delta_{\text{so}})$	b
$x = 0.25$	6.2589	0.140	-0.265	1.291
$x = 0.5$	6.0961	0.152	-0.437	1.843
$x = 0.75$	5.9352	0.163	-0.466	1.819

Table 3. Calculated properties of $\text{CdS}_x\text{Te}_{1-x}$ at various compositions, along (100) ordering, including lattice constant, interaction parameter, bowing parameter of spin-orbit splitting and band gap

cadmium sulfide and cadmium telluride. Results show that b and $b(\Delta_{\text{so}})$ are both strongly composition dependent. The authors find, however, that b increases as $b(\Delta_{\text{so}})$ decreases, unlike the scaling assumption used in the *s-p* model.^{18,21}

The authors now look at the variations of the partial and total DOS of $\text{CdS}_x\text{Te}_{1-x}$ with compositions and orderings. As shown in Figure 1, for pristine cadmium sulfide and cadmium telluride, the top of the valence band is dominated by S 3p and Te 5p states, respectively, and the bottom of the conduction band is mainly derived from Cd 5s state. The DOS of ternary $\text{CdS}_x\text{Te}_{1-x}$ can be seen as the combination of cadmium sulfide and cadmium telluride. With increasing tellurium concentration, the magnitude of tellurium states increases while the magnitude of sulfur states decreases. The authors also find that (*a*) the main Cd 4d peak red shifts from cadmium sulfide to cadmium telluride, implying that *p-d* coupling becomes weaker which explains the increase in SO splitting and the reduction of band gap; (*b*) the valence bandwidth increases with the mixing of cadmium sulfide and cadmium telluride and it reaches maximum at $\text{CdS}_{0.5}\text{Te}_{0.5}$, indicating the formation of $\text{CdS}_x\text{Te}_{1-x}$. This leads to increase in the mobility of holes generated by light irradiation and hence improves the solar cell performance. Calculation of DOS for various orderings (not shown), at a composition of 0.5, show that the CP ordering has the widest valence bandwidth, followed by Y2 and disordered phase. Shifts in Cd 4d state show that the *p-d* coupling is strongest in CH and disordered phase and weakest in CP-ordered phase.

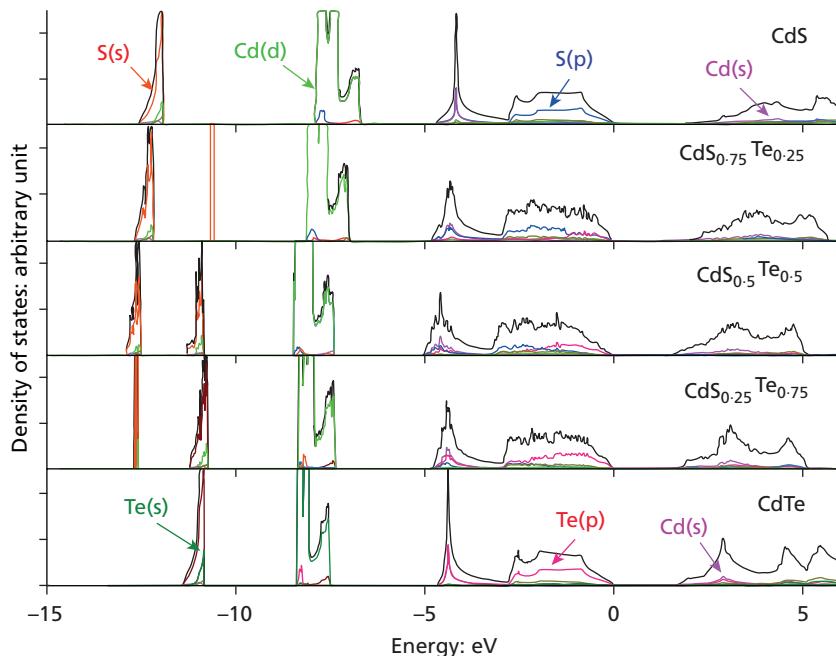


Figure 1. Variation of density of states of $\text{CdS}_x\text{Te}_{1-x}$ with composition and ordering

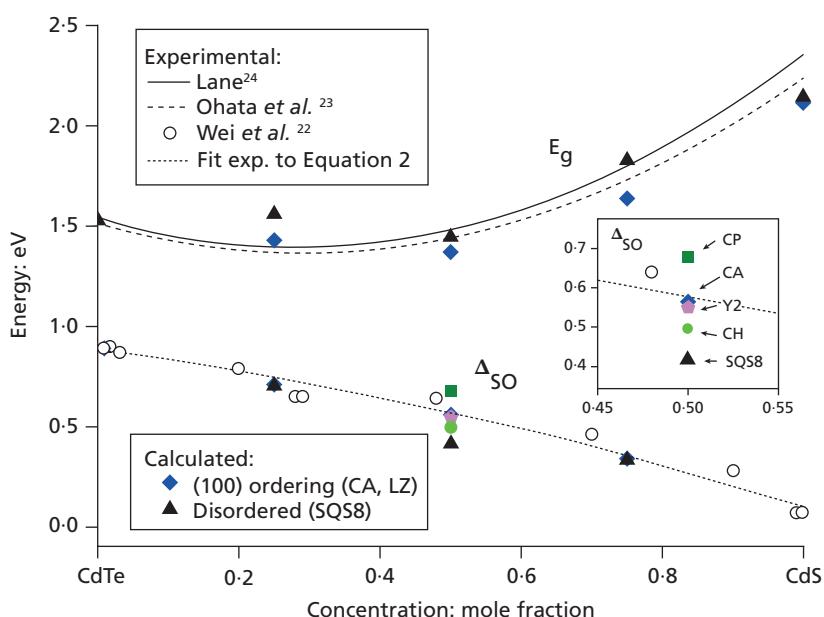


Figure 2. Comparison of calculated spin-orbit splitting and band gap with experimental data

4. Comparison with experiments

The calculated SO splitting and band gaps are compared with the experimental data in Figure 2. Good agreement is found throughout the entire composition range. The only available data²² in the literature on SO splitting was measured at room temperature by

ellipsometry. The authors have fitted the experimental values to Equation 1 and a negative $b(\Delta_{SO})$ (-0.408 eV) is obtained. Therefore, the authors expect that the samples are at least partially ordered. In order to have a direct comparison of the calculated band gaps with experiments,^{23–25} the authors have corrected the LDA results

according to the Heyd–Scuseria–Ernzerhof hybrid functional calculations (HSE06)²⁶ since LDA underestimates the absolute band gaps. The comparison shows that (a) among the ordered structures, (100) ordering (CA and LZ) is the best representation of the random alloy and (b) a small amount of tellurium in cadmium sulfide can drastically reduce its band gap. This is because the impurity limit tellurium substitution on sulfur site leads to a localized isovalent impurity level.³ The experimentally reported optical bowing parameters are in the range of 1.7–1.88 eV,^{23,25} consistent with the calculated disordered and representative (100) ordering results.

5. Conclusions

In conclusion, the authors have investigated the effects of crystal ordering and composition on the properties of $\text{CdS}_{x}\text{Te}_{1-x}$ alloys using the first-principle approach. Good agreement is obtained between calculated results and experimental data. The authors find that (a) CH is the ground state structure. Y2 ordering may occur in disordered structure due to small energy difference, (b) ordering can significantly affect the SO splitting and energy gap, (c) negative bowing parameter of SO splitting is found in ordered structure while positive value is found in disordered structure and (d) the bowing parameters of energy gap and SO splitting are both strongly ordering and composition dependent. However, the bowing parameter of the energy gap increases with the decreasing of the bowing parameter of the SO splitting.

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REFERENCES

1. Aramoto, T.; Kumazawa, S.; Higuchi, H.; Arita, T.; Shibutani, S.; Nishio, T.; Nakajima, J.; Tsuji, M.; Hanafusa, A.; Hibino, T.; Omira, K.; Ohyama, H.; Murozono, M. 16.0% efficient thin-film CdS/CdTe solar cells. *Japanese Journal of Applied Physics* **1997**, *36*, 6304–6305.
2. Wang, D.; Hou, Z.; Bai, Z. Study of interdiffusion reaction at the CdS/CdTe interface. *Journal of Materials Research* **2011**, *26*, 697–705.
3. Wei, S.; Zhang, S. B.; Zunger, A. First-principles calculation of band offsets, optical bowings, and defects in CdS, CdSe, CdTe, and their alloys. *Journal of Applied Physics* **2000**, *87*, 1304–1311.
4. Adachi, S. *Properties of Semiconductor Alloys: Group IV, III-V and II-VI Semiconductors*, London: Wiley, 2009.
5. Fischer, A.; Anthony, L.; Compaan, A. D. Raman analysis of short-range clustering in laser-deposited $\text{CdS}_{x}\text{Te}_{1-x}$ films. *Applied Physics Letters* **1998**, *72*, 2559–2561.
6. Berolo, C.; Wooley, J. C. *Proceedings of the Eleventh International Conference on the Physics of Semiconductors* (Miasek, M. (ed.)). Warsaw: PWN/Polish Scientific, 1972.
7. Lange, H.; Donecker, J.; Friedrich, H. Electroreflectance and wavelength modulation study of the direct and indirect fundamental transition region of $\text{In}_{1-x}\text{Ga}_x\text{P}$. *Physica Status Solidi (B)* **1979**, *73*, 633–639.
8. Ebina, A.; Yamamoto, M.; Takahashi, T. Reflectivity of $\text{ZnSe}_{x}\text{Te}_{1-x}$ single crystals. *Physical Review B* **1972**, *6*, 3786–3791.
9. Chen, D.; Ravindra, N. M. Electronic and optical properties of Cu2ZnGeX4 (X = S, Se and Te) quaternary semiconductors. *Journal of Alloys and Compounds* **2013**, *579*, 468–472.
10. Blochl, P. E. Projector augmented-wave method. *Physical Review B* **1994**, *50*, 17953–17979.
11. Ceperley, D. M.; Alder, B. J. Ground state of the electron gas by a stochastic method. *Physical Review Letters* **1980**, *45*, 566–569.
12. Perdew, J. P.; Zunger, A. Self-interaction correction to density-functional approximations for many-electron systems. *Physical Review B* **1981**, *23*, 5048–5079.
13. Adachi, S. *Handbook on Physical Properties of Semiconductors*. Boston: Kluwer Academic, 2004.
14. Wei, S. H.; Zunger, A. Band gaps and spin-orbit splitting of ordered and disordered $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{GaAs}_x\text{Sb}_{1-x}$ alloys. *Physical Review B* **1989**, *39*, 3279–3304.
15. Wei, S. H.; Ferreira, L. G.; Bernard, J. E.; Zunger, A. Electronic properties of random alloys: special quasirandom structures. *Physical Review B* **1990**, *42*, 9622–9649.
16. Hopfield, J. J. Fine structure in the optical absorption edge of anisotropic crystals. *Journal of Physics and Chemistry of Solids* **1960**, *15*, 97–107.
17. Zakharov, O.; Rubio, A.; Blasé, X.; Cohen, M. L.; Louie, S. G. Quasiparticle band structures of six II-VI compounds: ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe. *Physical Review B* **1994**, *50*, 10780–10787.
18. Chadi, D. J. Spin-orbit splitting in crystalline and compositionally disordered semiconductors. *Physical Review B* **1977**, *16*, 790–796.
19. Wei, S.; Zunger, A. Negative spin-orbit bowing in semiconductor alloys. *Physical Review B* **1989**, *39*, 6279–6282.
20. Carrier, P.; Wei, S. Calculated spin-orbit splitting of all diamondlike and zinc-blende semiconductors: effects of p1/2 local orbitals and chemical trends. *Physical Review B* **2004**, *70*, 035212–0352129.
21. Van Vechten, J. A.; Berolo, O.; Woolley, J. C. Spin-orbit splitting in compositionally disordered semiconductors. *Physical Review Letters* **1972**, *29*, 1400–1403.
22. Wei, K.; Pollak, F. H.; Freeouf, J. L.; Shvydka, D.; Compaan, A. D. Optical properties of $\text{CdTe}_{1-x}\text{S}_x$ ($0 \leq x \leq 1$): experiment and modeling. *Journal of Applied Physics* **1999**, *85*, 7418–7425.

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23. Ohata, K.; Saraie, J.; Tanaka, T. Optical energy gap of the mixed crystal $\text{CdS}_x\text{Te}_{1-x}$. *Japanese Journal of Applied Physics* **1973**, *12*, 1641–1642.
24. Lane, D. W. A review of the optical band gap of thin film $\text{CdS}_x\text{Te}_{1-x}$. *Solar Energy Materials & Solar Cells* **2006**, *90*, 1169–1175.
25. Chen, D.; Ravindra, N. M. Pressure dependence of energy gap of III–V and II–VI ternary semiconductors. *Journal of Materials Science* **2012**, *47*, 5735–5742.
26. Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *Journal of Chemical Physics* **2003**, *118*, 8207–8215.

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