

Bulk vacancies in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ ^{a)}

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We report the first theoretical study of vacancies in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ alloys. The study employs the tight-binding method for obtaining the Hamiltonian. The Slater-Koster Green's function method is used to obtain the electronic states that result from removing a cation or anion from the virtual crystal used to model the alloys. The primary results are that the anion vacancy levels are far into the conduction band and hence are not likely to produce levels in the gap. In contrast, the cation vacancy is found to produce levels near the valence band edge. We find that spatially these states are very localized on the atoms nearest the vacancy.

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I. INTRODUCTION

Vacancies are believed to play a major role in the electronic structure of $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$. For instance, the observed shallow acceptor level in this material is commonly believed to be due to Hg vacancies.¹ As a preliminary to a more extensive study, we have carried out Green's function calculations for the ideal bulk vacancies in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$. Calculations of this type have been carried out extensively for III-V materials^{2,3} where they have been rather successful in obtaining qualitatively the electronic properties not only of the vacancy but of other deep defects as well.

The main question that we are attempting to answer is what is the location and spatial extent of the electronic levels associated with the deep defects in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$. Further we would like to be able to make a comparison between the results in the II-VI's with those for similar defects in the III-V semiconductors.

The primary results of this study are that unlike the anion vacancies in the III-V semiconductors anion vacancies in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ do not produce levels in the band gap. The cation vacancies produce levels in the ideal model that are sufficiently close to the valence band edge so that corrections due to the Coulomb interaction and lattice distortion are likely to produce levels in the gap. Further, the electronic wave functions for these levels are rather strongly localized on the nearest neighbor atoms, leading us to question the validity of an effective mass approach for treating the cation vacancy levels in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$.

II. CALCULATIONAL METHODS

We use the empirical tight binding (ETB) method⁴ to calculate the band structure for CdTe and HgTe. We employ eight orbitals per atom (the usual *s* and *p* orbitals, which are doubled by the spin-orbit interaction). Since there are two atoms per unit cell, we are dealing with a total of sixteen energy bands.

Furthermore we include up to second nearest-neighbor interactions in the tight binding Hamiltonian, so that we have a total of 21 parameters. The parameters for CdTe were obtained by fitting the band structure to the structure given by Chelikowsky and Cohen,⁵ and those for HgTe were ob-

tained by fitting to the results of Chadi *et al.*⁶ The two sets of parameters so obtained are given in Table I. To obtain the band structure for $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ we use the virtual crystal approximation.

Once the band structure is known we proceed to calculate the states associated with (ideal) bulk vacancies. This is done with the Green's function method,⁷⁻⁹ according to which the energy levels of the vacancy states are determined by

$$\det |1 - G^0(E)V| = 0. \quad (1)$$

Here *V* is the defect potential associated with the vacancy and $G^0(E)$ is the ideal crystal Green's function given by

$$G^0(E) = \lim_{\epsilon \rightarrow 0^+} (E - H^0 + i\epsilon)^{-1}, \quad (2)$$

where H^0 is the ideal crystal Hamiltonian. For an ideal vacancy one chooses the potential *V* to be such that it acts only

TABLE I. Tight-binding parameters for CdTe and HgTe in the notation of Ref. 7. The subscripts 0 and 1 designate anion and cation, respectively. Δ is the strength of the spin-orbit interaction.

	CdTe	HgTe
1. $E_{ss}(000)_0$	- 8.905	- 9.056
2. $E_{ss}(000)_1$	1.703	1.159
3. $E_{xx}(000)_0$	0.703	0.225
4. $E_{xx}(000)_1$	3.935	2.470
5. $E_{ss}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	- 0.224	- 0.093
6. $E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{01}$	0.768	1.128
7. $E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})_{10}$	0.973	0.643
8. $E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.459	0.223
9. $E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.125	1.113
10. $E_{xy}(110)_0$	0.001	0.099
11. $E_{xy}(110)_1$	0.142	0.312
12. $E_{xx}(110)_0$	0.087	0.175
13. $E_{xx}(110)_1$	0.140	0.299
14. $E_{xx}(011)_0$	- 0.255	- 0.432
15. $E_{xx}(011)_1$	- 0.046	- 0.103
16. $E_{xx}(110)_0$	0.106	0.098
17. $E_{xx}(110)_1$	0.000	0.000
18. $E_{ss}(110)_0$	- 0.319	- 0.421
19. $E_{ss}(110)_1$	- 0.014	- 0.119
20. Δ_0	0.347	0.284
21. Δ_1	0.013	0.017

on the atom to be removed and is of infinite strength, thereby removing the basis states on the central atom from the problem without altering the rest of the crystal. Furthermore, by symmetry, the orbitals belonging to different rows of various irreducible representations do not mix, so that the problem reduces to solving for the zero's of the diagonal components of the Green's function itself,⁹ i.e.,

$$G_{\alpha\alpha}^0(E) = \lim_{\epsilon \rightarrow 0} \sum_{nk} \frac{\langle \alpha | nk \rangle \langle nk | \alpha \rangle}{E - E_n(k) + i\epsilon} = 0. \quad (3)$$

Here $E_n(k)$ are the eigenvalues of H^0 and $|nk\rangle$ are the corresponding eigenstates. The states $|\alpha\rangle$ are a set of basis states used to expand the Green's function. In the case of the zincblende structure the irreducible representations of interest are Γ_6 , Γ_7 , and Γ_8 .

Once the energy of a bound state (a state occurring in the gap) is known, it is possible to solve for the wave function itself, which is given by⁹

$$\psi_\alpha = \frac{\sum_\beta G_{\alpha\beta}^0(E_b)}{[-G_{\alpha\alpha}^0(E_b)]^{1/2}} |\beta\rangle. \quad (4)$$

Here the prime denotes differentiation with respect to the energy and E_b is the energy of the bound state.

III. RESULTS

The results of the band structure calculations are shown in Figs. 1 and 2, for CdTe and HgTe, respectively. It is clear that the states close to the top of the valence band agree well with the pseudopotential calculations. Similar agreement is obtained for the alloy. For example, for $\text{Cd}_{0.2}\text{Hg}_{0.8}\text{Te}$ we find a band gap of 0.07 eV, which compares well with the experimental value of ~ 0.1 eV. The virtual crystal approxi-

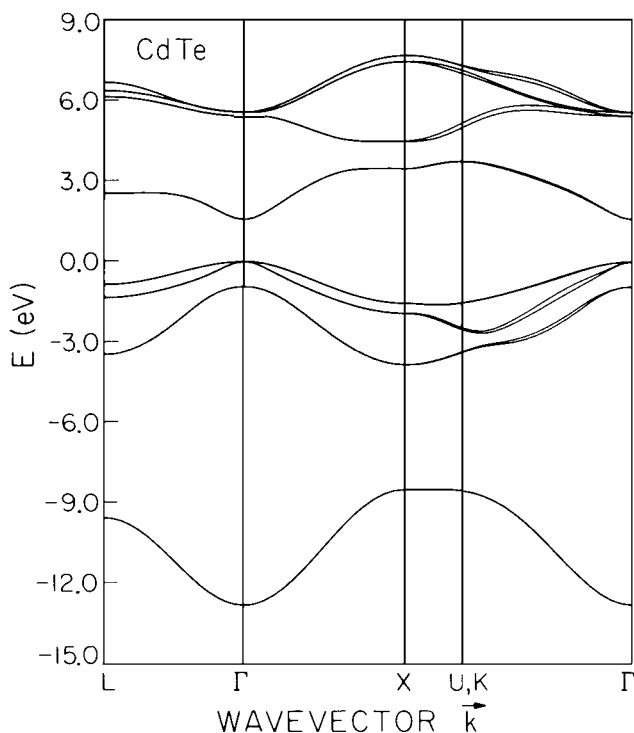


FIG. 1. Band structure of CdTe.

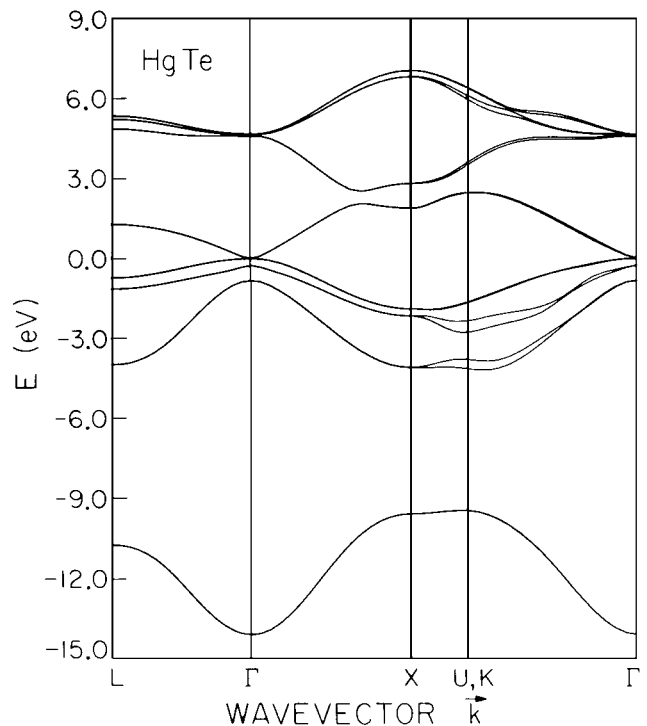


FIG. 2. Band structure of HgTe.

mation leads to an almost linear variation in band gap with composition, with the band gap becoming zero for $x \cong 0.15$, as shown in Fig. 3.

With the band structures obtained with the tight-binding method we next proceed to calculate the ideal crystal Green's function $G_{\alpha\alpha}^0(E)$ and the position of the vacancy levels. The results of these calculations for the vacancy levels as a function of composition are given in Fig. 3. The states associated with anion vacancies are always resonances far up in the conduction band, indicating that anion vacancies are probably not responsible for any states in the gap observed in these materials.

States associated with cation vacancies on the other hand can produce bound states, especially in Cd-rich compounds. We see that for $x \gtrsim 0.7$ an ideal cation vacancy produces both a Γ_7 and a Γ_8 state in the gap, with binding energies $\lesssim 0.065$ eV. For $x \lesssim 0.7$ these states become unbound and give rise to resonances in the valence band. In all cases, these states remain close to the valence band maximum, so that a more realistic defect potential V , corrected for Coulomb interactions and lattice distortion, may well lead to states in the gap for those alloys that have an energy gap. The Γ_6 state associated with a cation vacancy is always a resonance fairly far below the valence band maximum ($E \lesssim -0.34$ eV) and is probably not responsible for any experimentally observed states in the gap.

The situation in these materials differs from that in the III-V materials, where the ideal vacancy calculations always led to bound states fairly far removed from the band edges. In those cases one could first calculate the ideal vacancy states and then apply various improvements on the defect potential with perturbation theory. Due to the proximity of the valence band maximum this will no longer work in the

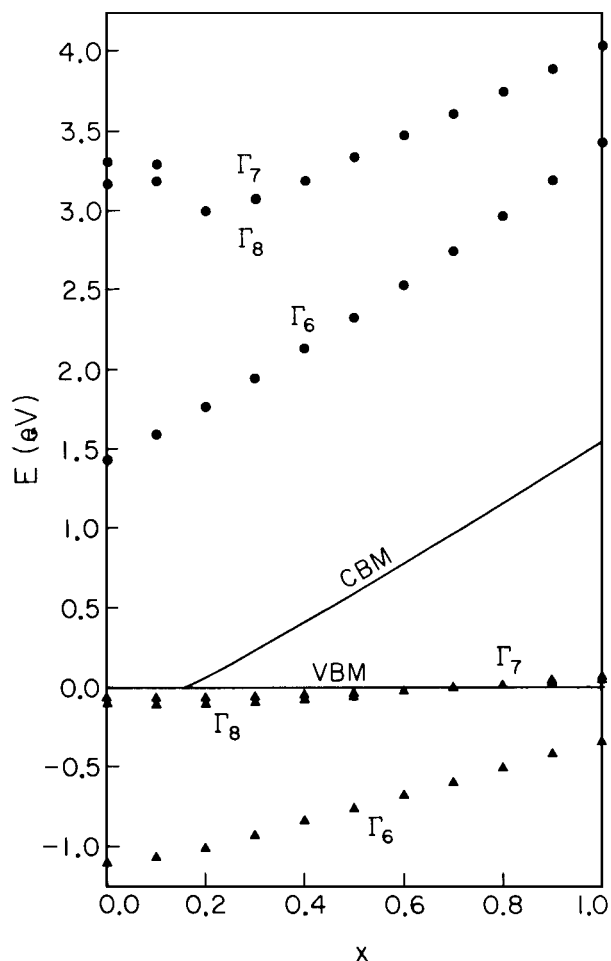


FIG. 3. Band gap variation and energy positions of vacancy states as a function of composition. The anion-vacancy levels are marked by ●; the cation-vacancy levels are marked by ▲.

present case, and improvements on the defect potential will have to be carried through from the start in the Green's function formalism. Such improvements are very important in determining whether these vacancy states can be identified as acceptor levels in these materials.

Another feature of interest for these bound states is the localization of the wave function. Using Eq. (4) we determine that approximately 55% of the wave function is localized on the first nearest neighbors. This result indicates that we are dealing with a very localized wave function, despite the fact that its energy is so close to the valence band maximum. The situation seems to resemble that of the nitrogen trap in $\text{GaAs}_x\text{P}_{1-x}$,¹⁰ which also behaves as a deep trap (localized wave function) despite the fact that the state lies very close to the conduction band minimum. It is clear from these results that the cation vacancy in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ cannot be treated with effective mass theory, as one might hope to do at first glance. Again, future work must be carried out along the line sketched above: One must incorporate a more realistic defect potential V in the Green's function calculations.

Finally we would like to point out that Jahn–Teller distortions may play an important role in these vacancies. Here we consider only the cation vacancy. For the neutral system the cation vacancy states are occupied by six electrons. The cal-

culations for the ideal vacancy show that the Γ_8 level always occurs below the Γ_7 level, so that the Γ_8 level will be completely filled, whereas the Γ_7 level will be empty. Therefore Jahn–Teller distortions that remove the T_d symmetry are not expected to occur, since they do not lead to a lowering of the energy (in first order). On the other hand, the symmetric distortion (where all the first nearest neighbors are allowed to move toward the vacancy position) is expected to occur. Since that would presumably lead to a lowering of the energy, it becomes likely that the Γ_8 level will move into the valence band entirely. This raises the possibility that only the Γ_7 level remains in the fundamental gap, where it then acts as a double acceptor. This would be consistent with the experimental observations. However, when we are dealing with a charged vacancy the Coulomb interaction must be taken into account as well, so that it is clear that a lot more work needs to be done before this can be put on a firm footing. Once again it is clear that these effects cannot be addressed using perturbation theory, because of the proximity of the valence band edge to the state of interest.

IV. SUMMARY

We have shown that ideal cation vacancies in $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ introduce levels very close to the valence band maximum. A more realistic defect potential, which takes into account the relaxation of the first shell of anions surrounding the vacancy, may be capable of determining whether these states can behave as a double acceptor.

Furthermore, we have shown that these states are localized so that they cannot be treated in the effective mass approximation. Again this means that for more realistic calculations one needs to carry out the Green's function calculation with a more realistic defect potential. Calculations along those lines are presently under way.

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