Bond relaxation in $Hg_{1-x}Cd_xTe$ and related alloys

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The local structural properties of $Hg_{1-x}Cd_xTe$, $Hg_{1-x}Zn_xTe$, and $Cd_{1-x}Zn_xTe$ are examined using a self-consistent pseudopotential approach. An accurate description of the limiting crystals is obtained by adding empirical corrections to *ab initio* total energies calculated with the group-II d states included in the cores. Similar calculations for $x = 0.5$ ordered alloys confirm the presence of nearest-neighbor bond-length differences in these systems without violation of Vegard's law. An anomalously large "relaxation" is predicted here for $Hg_{1-x}Cd_xTe$ ($\sim 2\%$ bond-length difference in the alloy compared to only 0.3% between limiting crystals) due to the dominance of chemical effects neglected from simple valence force models. The implications of the present results for alloy mixing energies and possible deviations from randomness are discussed.

I. INTRODUCTION

The local structural poperties of tetrahedrally bonded semiconducting alloys play an important role in determining the electronic,[1,2] thermodynamic,[3–6] and defect properties[7,8] of these materials. Recent extended x-ray absorption fine-structure (EXAFS) measurements[9–11] have demonstrated that in a variety of $A_{1-x}B_xC$ zinc-blende systems, the individual A–C and B–C nearest-neighbor bond lengths do not simply equalize to an average "virtual lattice" value but instead each bond length remains much closer to that of its limiting crystal. The "relaxation" of an A–C bond is conveniently described by the dimensionless parameter

$$\epsilon = (d_{\rm AC}[\text{BC:A}] - d^{\,0}_{\rm BC})/(d^{\,0}_{\rm AC} - d^{\,0}_{\rm BC}),$$

where $d^{\,0}_{\rm AC}$ and $d^{\,0}_{\rm BC}$ are the limiting crystal bond lengths and $d_{\rm AC}[\text{BC:A}]$ is the A–C bond length associated with an isolated A impurity in a BC crystal. Typical values of ϵ measured in EXAFS experiments range from 0.6 to 0.8. An upper bound of $\epsilon = 1$ is predicted by classical valence force (VF) models[3,5] which involve a competition between bond-stretching and bond-bending forces.

In the case of $Hg_{1-x}Cd_xTe$ (MCT), local structural distortions have generally been assumed to be unimportant in view of the excellent agreement between limiting crystal bond lengths ($\Delta d \sim 0.01$ Å). Tight-binding calculations[8] presented at the 1983 MCT Workshop, however, suggested the possibility of an anomalously large relaxation ($\epsilon > 1$) in this system due to an additional chemically induced force omitted from simple VF models. We have recently confirmed this prediction using a more realistic self-consistent pseudopotential total energy minimization procedure.[12] In this paper we present a more detailed account of this work and its implications for other alloy properties (e.g., charge redistribution and mixing energies). Similar calculations are reported for the closely related $Hg_{1-x}Zn_xTe$ and $Cd_{1-x}Zn_xTe$ systems, which have become increasingly important in their own right.

II. THEORETICAL APPROACH

A. Limiting crystals

We begin with a straightforward application of the *ab initio* pseudopotential method[13] to the limiting crystals HgTe, CdTe, and ZnTe. This approach has been extremely successful in describing the structural properties of group IV and III–V crystals and has recently yielded important insight into the effects of bond relaxation in $In_{1-x}Ga_xP$[4] and $In_{1-x}Ga_xAs$.[14] A complicating factor in the case of II–VI's is the presence of shallow group-II d states[15] (> -1 Ry). For computational convenience, we treat these states here as part of the core. We later add empirical corrections to the total energy to compensate for the errors introduced by this assumption.

Ab initio, "norm-conserving" pseudopotentials are generated for Hg^{2+}, Cd^{2+}, Zn^{2+}, and Te^{6+} using a slight modification[16] of the Hamann–Schlüter–Chiang procedure.[17] Relativistic effects, which play an important role in these heavy ions,[18] are included in the scalar approximation of Ref. 19. Total energy calculations are performed within the local density approximation using a plane-wave basis[20] and a Hedin–Lundqvist exchange–correlation potential.[21] Plane waves with energies up to 8 Ry are treated exactly and those between 8 and 12 Ry are treated perturbatively. Brillouin zone integrals are evaluated using two special k points[22] for zinc-blende crystals and the corresponding k point sets for lower symmetry structures.

Total energies are obtained for each crystal at both a series of zinc-blende lattice constants and a series of (111) trigonal distortions. Results in the former case are used to calculate the equilibrium lattice constant (a), bulk modulus (B), and cohesive energy ($E_{\rm coh}$). The latter results are used to calculate the zone-center transverse-optic phonon frequency[23] [$\nu_{\rm TO}(\Gamma)$]. *Ab initio* predictions for these quantities are compared to experiment[24] in the upper part of Table I. The theoretical lattice constant in each case is too small by

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TABLE I. Top: Comparisons of calculated and experimental (Ref. 24) lattice constants a (in Å), bulk moduli B (in kbar), cohesive energies E_{coh} (in eV/cell), and zone-center phonon frequencies $\nu_{TO}(\Gamma)$ (in 10^{12} Hz). Deviations from experiment are listed in parentheses. Bottom: Coefficients (in eV Å^6) of nearest-neighbor (V_1) and cation second-neighbor (V_2)r^{-6} repulsions assumed in modified total energy results.

		ZnTe	CdTe	HgTe
a	*Ab initio*	5.618(-8%)	5.818(-10%)	5.616(-13%)
	modified; expt	6.103	6.482	6.462
B	*Ab initio* (at a_{expt})	273(-46%)	133(-69%)	47(-89%)
	modified	544 ($+7\%$)	412 (-3%)	447($+2\%$)
	expt	509	424	437
E_{coh}	*Ab initio* (at a_{expt})	6.75($+41\%$)	6.77($+54\%$)	7.05($+115\%$)
	modified	4.69(-2%)	4.23(-4%)	3.44(-5%)
	expt	4.80	4.40	3.28
$\nu_{TO}(\Gamma)$	*Ab initio* (at a_{expt})	4.41(-17%)	3.07(-27%)	2.20(-38%)
	modified; expt	5.30	4.20	3.54
V_1		90.530	193.350	230.733
V_2		1074.311	1482.937	2556.274

~10% and the other three quantities are predicted with even less accuracy. By comparison, similar calculations for group IV and III–V crystals[13] typically yield errors of only 1% in a, 5% in B and E_{coh}, and 3% in $\nu_{TO}(\Gamma)$.

We attribute the much larger errors here to an inadequate treatment of the cation d states. The "frozen core" approximation breaks down because the large radii of these states make it impossible to choose fully satisfactory cutoff radii for the d components of the ionic pseudopotentials. In contrast to the present results, *ab initio* calculations for II–VI's which include the d electrons on the same footing as valence s and p electrons yield accuracies comparable to those for group IV and III–V systems.[25–27]

To compensate for the errors inherent in the frozen core approximation, we add empirical repulsive forces to the total energy which we assume to be independent of chemical environment. The particular choice of these interactions is motivated by a desire to provide an accurate description of the limiting crystal properties in Table I with as few empirical parameters as possible. The best compromise we have achieved assumes pairwise repulsions of the form $V_1 r^{-6}$ between nearest neighbors and $V_2 r^{-6}$ between *cation* second neighbors, where r is the separation between atoms. This introduces only two parameters for each crystal which we fit to the experimental lattice constants and $\nu_{TO}(\Gamma)$ values. The resulting V_1 and V_2 parameters are listed at the bottom of Table I. The increase in magnitudes from Zn→Cd→Hg is consistent with a corresponding increase in the d-state radius. The significant improvements achieved in the modified B and E_{coh} values in the upper part of the table support the validity of this approach and give us the confidence to employ the same empirical corrections in the alloy calculations described below.

B. Ordered alloys

A direct extension of this approach to intermediate alloy concentrations is practical only for ordered configurations with small unit cells. Here we consider only the simplest such arrangement: the $A_{0.5}B_{0.5}C$ simple tetragonal structure shown in Fig. 1. We assume that the A and B atoms in this structure occupy alternating (001) planes of an undistorted fcc sublattice. The neglect of an overall tetragonal distortion is consistent with the relatively weak broadening of the cation–cation separation observed in EXAFS measurements on random alloys.[9–11] The C atom location in Fig. 1 is allowed to vary from its ideal tetrahedral position ($u = 0.25$) to accommodate a relaxation of nearest-neighbor bond lengths. The A–C and B–C bond lengths are given by $(u^2 + 0.125)^{1/2} a$ and $[(u - 0.5)^2 + 0.125]^{1/2} a$, respectively, where a is the lattice constant.

The modified total energy is minimized with respect to both u and a for each of the $Hg_{0.5}Cd_{0.5}Te$, $Hg_{0.5}Zn_{0.5}Te$, and $Cd_{0.5}Zn_{0.5}Te$ systems. *Ab initio* calculations are first performed for each system in exact analogy with those of Sec. II A. Empirical corrections are then added by assuming that the A–C, B–C, A–A, and B–B interactions in an $A_{0.5}B_{0.5}C$ alloy are well described by the same V_1 and V_2

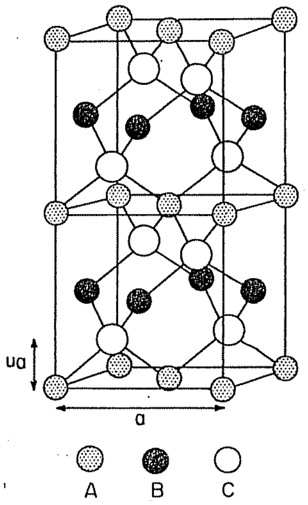

FIG. 1. Simple tetragonal structure assumed for an $A_{0.5}B_{0.5}C$ ordered alloy with lattice constant a. The parameter u is allowed to vary to accommodate a difference in A–C and B–C bond lengths.

parameters as in the limiting crystals. The only complication which arises concerns an A–B interaction, for which there is no crystalline counterpart. Here we assume that the appropriate V_2 parameter for this interaction is given by either an arithmetic or a geometric mean of the corresponding V_2 parameters for the A–A and B–B interactions. The two approximations will be seen in Sec. III B to lead to slightly different alloy mixing energies. The equilibrium bond lengths in the two cases are indistinguishable, however, since the cation–cation interaction plays no role in determining the equilibrium u value for a given lattice constant.

III. RESULTS AND DISCUSSION

A. Alloy structural properties

The calculated equilibrium lattice constants for $Hg_{0.5}Cd_{0.5}Te$, $Hg_{0.5}Zn_{0.5}Te$, and $Cd_{0.5}Zn_{0.5}Te$ are all found to be within 0.5% of the limiting crystal averages. This result is consistent with the nearly linear (Vegard's law) concentration dependencies observed in x-ray lattice constant measurements on $Hg_{1-x}Cd_xTe$,[18] $Hg_{1-x}Zn_xTe$,[28] and $Cd_{1-x}Zn_xTe$.[10]

The predicted nearest-neighbor bond-length behavior is summarized in Fig. 2. The dashed lines represent the average variation $\bar{d}(x)$ expected for both bond types in an undistorted virtual lattice. The relaxed bond lengths calculated for the $x = 0.5$ ordered alloys are denoted by ×'s. In the corresponding random alloys, one expects a distribution of bond lengths due to variations in the local environment. We estimate the mean values in such systems (solid lines in Fig. 2) using a binomial distribution analysis similar to that of Ref. 4. The specific assumptions made are that (1) the A and B atoms in an $A_{1-x}B_xC$ system remain fixed on their fcc lattice sites, (2) the A–C bond length associated with a given nearest-neighbor environment of the C atom varies linearly with the number of B neighbors, (3) the A–C bond associated with a configuration of two A and two B nearest neighbors at $x = 0.5$ has the length $d_{\mathrm{AC}}^{\mathrm{ord}}$ calculated for the corresponding ordered alloy, and (4) the mean A–C bond length $d_{\mathrm{AC}}^{\mathrm{rand}}(x)$ varies linearly with x (as observed in EXAFS experiments). The resulting mean value at $x = 0.5$ is

$$d_{\mathrm{AC}}^{\mathrm{rand}}(0.5) = 3d_{\mathrm{AC}}^{\mathrm{ord}}/4 + \bar{d}(0.5)/4.$$

The smaller relaxation compared to the ordered case is a consequence of the fact that, while the bond lengths relax coherently in the ordered systems, many of the local environments in the random alloys are more highly strained[4] [e.g., the A–C bond length associated with a configuration of four A nearest neighbors in our model is always the virtual lattice value $\bar{d}(x)$].

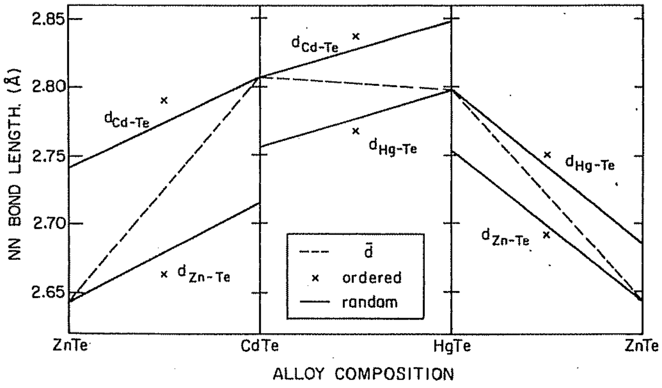

FIG. 2. Calculated nearest-neighbor (NN) bond lengths in ordered and random alloys compared to average behavior ($\bar{d}$) predicted for unrelaxed virtual lattice.

The solid lines in Fig. 2 for $Cd_{1-x}Zn_xTe$ correspond to relaxation parameters of $\epsilon \simeq 0.6$. This is in reasonable agreement with recent EXAFS experiments[10] ($\epsilon \simeq 0.75$) as well as with previous VF[3,5] and tight-binding[5] calculations. The slightly smaller relaxation predicted here may be an artifact of our assumed perfection of the cation sublattice.

Much more unusual behavior is found here for the two Hg-based systems. The anomalously large relaxation predicted for $Hg_{1-x}Cd_xTe$ ($\epsilon \simeq 5.8$) supports the earlier tight-binding analysis of Ref. 8 ($\epsilon \simeq 2$) and is in striking contrast to the predictions of VF models. The Hg–Te and Cd–Te bond lengths are found to differ by ~2% (0.05 Å) in this system, which should be easily resolvable in EXAFS experiments. By contrast, the relaxation predicted here for $Hg_{1-x}Zn_xTe$ ($\epsilon \simeq 0.21$) is much smaller than that in previous VF[3,5] and tight-binding[5] calculations ($\epsilon \geqslant 0.70$). EXAFS results for this system would thus also be of interest.

We attribute the dramatic failure of VF predictions for $Hg_{1-x}Cd_xTe$ and $Hg_{1-x}Zn_xTe$ to the presence of an additional chemically induced force associated with a difference in cation electronegativities. Such a force has been discussed previously in the tight-binding analysis of Refs. 5 and 8 and shown to result from the difference in "metallic coupling" between the alloy and crystalline environments. The metallic coupling is defined as the interaction between a given bonding state and its neighboring antibonding states.[29] The fact that an A–C bonding state is coupled to some B–C antibonding states in an $A_{1-x}B_xC$ alloy produces a change in the effective A–C force constant. Relative to the virtual lattice structure, the presence of this effect generally drives a contraction of the less ionic bond in order to increase charge transfer from the less to the more electronegative cation. In the case of $Hg_{1-x}Cd_xTe$, Hg is more electronegative and the contraction of the Hg–Te bond results in a net Cd→Hg charge transfer, which is energetically favorable. The anomalous behavior in this system results from the unusual situation in which the limiting crystals have roughly the same bond length despite an appreciable difference in ionicities.[30] In systems which are poorly lattice matched (e.g., $Hg_{1-x}Zn_xTe$ and $Cd_{1-x}Zn_xTe$), the consequences of the chemical force are more difficult to predict due to additional complications associated with bond angle changes (e.g., rehybridization). The present calculations, which include these effects automatically, suggest that the chemical force has little effect on the resulting bond lengths in $Cd_{1-x}Zn_xTe$ but is responsible for the much smaller relaxation predicted here for $Hg_{1-x}Zn_xTe$ compared to previous VF estimates.

One final feature of Fig. 2 which is worth noting is the fact that the calculated bond lengths satisfy the transitivity relationship

$$d_{\mathrm{ZnTe}}[\mathrm{CdTe{:}Zn}] + d_{\mathrm{CdTe}}[\mathrm{HgTe{:}Cd}] + d_{\mathrm{HgTe}}[\mathrm{ZnTe{:}Hg}] = d^{0}_{\mathrm{ZnTe}} + d^{0}_{\mathrm{CdTe}} + d^{0}_{\mathrm{HgTe}}$$

to within better than 0.2%. (This is equivalent to saying that the sum of the slopes of the solid lines in Fig. 2 is zero.) We are unable to provide a simple explanation for this behavior at this time but we note that simple VF estimates of impurity bond lengths in a wide variety of zinc-blende systems[3,5] predict a similar relationship to hold in most common anion and common cation systems. Further EXAFS studies would be useful to test for such transitivity experimentally.

B. Alloy mixing energies

We conclude this paper by exploring some of the implications of the above bond-length calculations for the thermodynamic properties of $Hg_{1-x}Cd_xTe$, $Hg_{1-x}Zn_xTe$, and $Cd_{1-x}Zn_xTe$. The discussion is based on the total excess energies ΔE_0 of the $x = 0.5$ ordered alloys relative to their segregated crystals. Srivastava, Martins, and Zunger[4] have recently shown that, contrary to previous expectations, the ΔE_0's associated with various ordered phases of $In_{1-x}Ga_xP$ are actually negative which suggests that such phases may actually represent the stable low-temperature ground states of this system. Here we find a similar result for $Hg_{1-x}Cd_xTe$ but a much smaller tendency towards ordering in the two Zn alloys.

We proceed as in Ref. 4 by considering the formation of a relaxed $x = 0.5$ ordered alloy as a three-step process. In step one, the segregated crystals are appropriately expanded or contracted to the alloy lattice constant $\bar{a}$. This costs a valence distortion (VD) energy ΔE^{VD} which is always positive and is the only contribution considered in simple virtual lattice strain models of alloy mixing energies.[31] Calculated values of ΔE^{VD} in the three systems considered here are listed in the top line of Table II. The negligible distortion energy in $Hg_{0.5}Cd_{0.5}Te$ is a consequence of the excellent lattice match in this system.

In the second step, the ordered alloy is formed with all atoms in their ideal tetrahedral locations ($u = 0.25$). The associated chemical energy contribution ΔE^{CE} results from a slight charge redistribution which occurs at this stage to smooth out any discontinuities in the charge densities at the boundaries of the crystalline unit cells. ΔE^{CE}, in general, can be of either sign. Here we find negative values in each of the three systems in Table II with magnitudes which depend sensitively on the averaging procedure (arithmetic or geometric mean) used to treat the empirical repulsion between cation second neighbors.

In the final step, the individual nearest-neighbor bond lengths in the alloy are allowed to relax to their preferred equilibrium positions. This yields a structural energy contribution ΔE^{S} which is always negative. The magnitudes of ΔE^{S} are generally much larger than the predictions of simple VF models[3,5] since the local distortions in the alloy are accompanied by the additional charge redistribution effects discussed in Sec. III A. The presence of these effects gives rise to a much larger $|\Delta E^{\mathrm{S}}|$ value compared to $|\Delta E^{\mathrm{VD}}|$ in $Hg_{0.5}Cd_{0.5}Te$ but is not sufficient to overcome the valence distortion energies in the Zn alloys.

The total excess energies in Table II are obtained by summing the ΔE^{VD}, ΔE^{CE}, and ΔE^{S} results. Despite the large uncertainties in these numbers, there does seem to be a much larger tendency towards ordering (negative ΔE_0) in the $Hg_{0.5}Cd_{0.5}Te$ system than in the two Zn alloys. Even in $Hg_{0.5}Cd_{0.5}Te$, however, the magnitude of ΔE_0 is probably too small to overcome entropy effects at typical growth temperatures. [It is important to note that, while the smaller ΔE_0 value in $Hg_{0.5}Cd_{0.5}Te$ compared to $Hg_{0.5}Zn_{0.5}Te$ means that the former *ordered* alloy is more "stable" in the technical sense, the present results provide no direct information on individual bond strengths in the two systems. The tight-binding prediction[8] that the weak Hg–Te bond (cf. E_{coh} values in Table I) may be somewhat stronger in $Hg_{1-x}Zn_xTe$ than in $Hg_{1-x}Cd_xTe$ is thus not contradicted by our results.]

The bottom line of Table II lists experimentally determined enthalpies of formation ΔH_D for *disordered* $Cd_{1-x}Zn_xTe$, $Hg_{1-x}Cd_xTe$, and $Hg_{1-x}Zn_xTe$ alloys.[32] Like ΔE_0, ΔH_D is also found to be smallest in magnitude in $Hg_{1-x}Cd_xTe$, although its sign is positive. A possible origin of the positive ΔH_D value in $Hg_{1-x}Cd_xTe$ has recently been proposed in terms of the Coulomb energy associated with charge fluctuations in a disordered ionic system.[33] The present bond-length results suggest an additional contribu-

TABLE II. Contributions to the total excess energies ΔE_0 of the $x = 0.5$ ordered alloys. The valence distortion energies (ΔE^{VD}), chemical energies (ΔE^{CE}), and structural energies (ΔE^{S}) are defined in the text. Results are presented for both the arithmetic mean (a.m.) and geometric mean (g.m.) treatments of the empirical repulsion between unlike cation second neighbors. The final line gives the experimentally determined enthalpies of formation ΔH_D of the corresponding *disordered* alloys. All energies are in eV/(zinc-blende cell).

	$Cd_{0.5}Zn_{0.5}Te$	$Hg_{0.5}Cd_{0.5}Te$	$Hg_{0.5}Zn_{0.5}Te$
ΔE^{VD}	+ 0.075	+ 0.0002	+ 0.071
ΔE^{CE} (a.m.)	− 0.001	− 0.002	− 0.003
(g.m.)	− 0.009	− 0.034	− 0.085
ΔE^{S}	− 0.047	− 0.012	− 0.013
ΔE_0 (a.m.)	+ 0.027	− 0.014	+ 0.055
(g.m.)	+ 0.019	− 0.046	− 0.027
ΔH_D (expt)	+ 0.014	+ 0.007, + 0.015	+ 0.032

tion in terms of the strain associated with different local environments in the disordered alloy. This effect is believed to be the dominant source of the positive ΔH_D values in poorly lattice-matched systems[4] (e.g., $Cd_{1-x}Zn_xTe$ and $Hg_{1-x}Zn_xTe$) but has previously been assumed to be negligible in $Hg_{1-x}Cd_xTe$. The fact that it may not be also suggests that deviations from randomness[4,6] in $Hg_{1-x}Cd_xTe$ may also be larger than expected.

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