

Bond lengths around isovalent impurities and in semiconductor solid solutions

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Using a valence force field, we predict the symmetric lattice distortions around isovalent impurities in 64 semiconductor-impurity systems. For the five systems for which extended x-ray absorption fine-structure (EXAFS) data are available, the results are in excellent agreement with experiment. Our theory also explains quantitatively, without adjustable parameters, the observed bond-length variations in solid solutions $A_{1-x}B_xC$ of semiconductor alloys, as well as their excess enthalpies of mixing.

Nonlinear variations in the band gaps of solid solutions $A_{1-x}B_xC$ of binary AC and BC semiconductors have long been known to be associated with changes in the microscopic atomic structure of the alloy. Early x-ray diffraction experiments on alloys by Huang¹ indicated that, although on the macroscopic length scale (many lattice constants), characteristic of coherent diffraction, the alloy retains the overall space group of the parent materials, the attendant diffuse scattering background suggests that the atomic structure changes on a microscopic scale (a few bond lengths). In the dilute (impurity) limit $AC:B$, it is equally clear that changes in the atomic structure associated with strain fields contribute to electron and hole binding energies to isovalent impurities,² and give rise to numerous strain-split states in the pair spectra.³ Considering the composition (x) dependence of the two bond lengths $R_{AC}(x)$ and $R_{BC}(x)$ in an alloy (Fig. 1), two limiting possibilities were recognized quite early.⁴⁻⁶ First, Bragg's⁴ and Pauling's⁵ notions that atomic radii are approximately conserved quantities (and hence, are transferable) in different chemical environments suggest that $R_{AC}(x)$ and $R_{BC}(x)$ will be composition independent and will equal their ideal values R_{AC}^0 and R_{BC}^0 , respectively, of the pure, end-point materials [denoted as $R_{AC}^p(x)$ and $R_{BC}^p(x)$ in Fig. 1]. Hence, the dimensionless relaxation parameter

$$\epsilon = (R_{BC}[AC:B] - R_{AC}^0) / (R_{BC}^0 - R_{AC}^0), \quad (1)$$

where $R_{BC}[AC:B]$ is the BC bond length around the B im-

purity in the AC host crystal, equals 1 in this limit (complete relaxation), and the alloy is thought of as sustaining two chemically distinct bonds ("bond alternation"). On the other hand, Vegard's⁶ discovery that the alloy lattice constant $a(x)$ equals approximately the concentration-weighted average of the lattice constants a_{AC} and a_{BC} of the end-point materials [$a(x) \approx (1-x)a_{AC} + xa_{BC}$] has led many workers in the field to assume that since the bond length R_{AC}^0 of the pure solid is a simple linear function of its lattice constant (e.g., in zinc-blende systems $R_{AC}^0 = \sqrt{3}a_{AC}/4$), then $R_{AC}(x)$ and $R_{BC}(x)$ in the alloy will also display such a linear averaging $R_{AC}(x) = R_{BC}(x) = \sqrt{3}a(x)/4$. In this limit $\epsilon = 0$ (no relaxation), and the alloy is thought of as sustaining a single (average) chemical bond (i.e., no bond alternation). This is the underlying premise of the virtual crystal approximation (VCA) that has been invoked to explain⁷ optical bowing in terms of the band structure of such an equal-bond-length material. Recent extended x-ray absorption fine-structure (EXAFS) experiments⁸ on $In_{1-x}Ga_xAs$ alloys have indicated that reality [$R_{AC}^{expt.}(x)$ and $R_{BC}^{expt.}(x)$ in Fig. 1] is intermediate between these two limits, but is considerably closer to the Pauling limit ($\epsilon = 1$) than to the VCA limit ($\epsilon = 0$). Zunger and Jaffe⁹ have showed that not only is it possible for the alloy to accommodate bond alternation ($R_{AC} \neq R_{BC}$) while retaining Vegard's rule for $a(x)$, but that, in fact, the very existence of bond alternation (calculated at $x = 0.5$ for many alloys⁹) is responsible for much of the observed optical bowing, in the same way that it leads to band-gap anomalies in ternary ABC_2 semiconductors.¹⁰ In this work we show (i) how the bond lengths $R_{AC}[BC:A]$ and $R_{BC}[AC:B]$ (and hence ϵ) in the dilute limit can be simply predicted for all isovalent impurities (results are given for 64 systems), (ii) that the concentration dependence $R_{AC}(x)$ and $R_{BC}(x)$ in the alloy is, to within a good approximation, merely a linear interpolation between these values and R_{AC}^0 and R_{BC}^0 , respectively, and (iii) that the alloy excess enthalpy of mixing can be calculated with no adjustable parameters from the same theory. Our simple model requires only the knowledge of the lattice constants, bulk moduli, and ionicities of the pure, end-point compounds, and reveals with no adjustable parameters, the chemical regularities in the relaxation and enthalpies of mixing over a large range of materials.

Imagine the process leading to a replacement of an A atom in the AC crystal by an isovalent impurity atom B to take place in two steps. First, compress (or dilate) the AC lattice bonds so that the larger (smaller) BC bond can be inserted, and replace the AC bond charge density by that pertinent to an ideal BC bond, as it occurs in the pure BC crys-

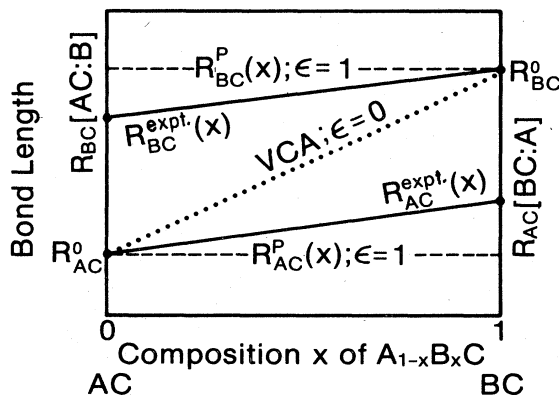


FIG. 1. Schematic variation of the bond lengths $R_{AC}(x)$ and $R_{BC}(x)$ in an $A_{1-x}B_xC$ alloy with composition, depicting the prediction of VCA, Pauling's model [$R_{AC}^p(x)$ and $R_{BC}^p(x)$] and experiment [$R_{AC}^{expt.}(x)$ and $R_{BC}^{expt.}(x)$]. Here, R_{AC}^0 and R_{BC}^0 denote the bond lengths in the pure, end-point compounds.

tal. Hence, rather than assuming that *bond lengths* are transferable, in the manner of Pauling, we assume instead that *bond densities* and their attendant elastic response are transferable (i.e., independent of their environment). Whereas the true charge density $\rho_{BC}[AC:B]$ of the impurity *BC* bond can differ substantially from that of the *AC* host density it replaces, (i.e., $\Delta\rho_1 = \rho_{BC}[AC:B] - \rho_{AC}[AC]$ can be a large perturbation), we expect $\rho_{BC}[AC:B]$ to be closer to the density $\rho_{BC}[BC]$ of the *BC* bond in the *pure BC system* (i.e., $\Delta\rho_2 = \rho_{BC}[AC:B] - \rho_{BC}[BC]$ is a smaller perturbation). Neglecting the small density perturbation $\Delta\rho_2$, the change in elastic deformation energy *U* induced by the insertion process can be modeled by a valence force field (VFF), *generalized to have the appropriate force constants for each kind of bond*, e.g., the VFF of Keating:^{11,12}

$$U = \sum_l \sum_{m=1}^4 \frac{3}{8d^2} \alpha [\bar{r}_m(l,1) \cdot \bar{r}_m(l,1) - d^2]^2 + \sum_l \sum_{s=1}^2 \sum_{m=1}^3 \sum_{n=m+1}^4 \frac{3}{8d^2} \beta \left[\bar{r}_m(l,s) \cdot \bar{r}_n(l,s) + \frac{d^2}{3} \right]^2, \quad (2)$$

where $d = R_{ij}^0$ is the equilibrium interatomic distance, $\bar{r}_m(l,s)$ is the vector connecting atom *s* in unit cell *l* to its *m*th nearest neighbor, and α and β are the bond stretching and the bond-bending force constants, respectively. The first sum in Eq. (2) extends over all nearest-neighbor pairs, whereas the second sum extends over all bond angles around every atom. For this *AC:B* impurity system, we describe the *B-C* bond around the impurity using the parameters α_{BC} , β_{BC} , and d_{BC}^2 taken from the pure *BC* crystal, β' and $d_{AC}d_{BC}$ are used for the *B-A-C* bond bending, and the constants α_{AC} , β_{AC} , and d_{AC}^2 , which are taken from the pure *AC* crystal, are used to describe all other bonds.

In the second step of our insertion process we imagine letting the frozen density $\rho_{BC}[BC]$ relax to its equilibrium value $\rho_{BC}[AC:B]$, equalizing thereby the chemical potential throughout the system. The charge fluctuation $\Delta\rho_2(\bar{r})$ will set up a change in the force acting on the neighboring atoms and will add an "electrochemical" correction $\Delta U(\Delta\rho_2)$ to the deformation energy *U*. Were it not for the existence of a prototypical reference system *BC* to approximate the *BC* bond in an *AC:B* system, we would have been forced to evaluate the additional force due to the *strong perturbation* $\Delta\rho_1(\bar{r})$, a step that must be carried out quantum mechanically,¹³ and which often indicates substantial displacements (e.g., for transition atom impurities in silicon¹³). However, we hypothesize that for *isovalent* impurities the fluctuation $\Delta\rho_2(\bar{r})$ is weak, localized, and screened out effectively (we know from local symmetry and charge conservation that it has at most quadrupolar components). Consequently, the changes in the *relaxation* (i.e., the *derivative* of ΔU) due to this charge displacement are expected to be small and are neglected [however, the electrochemical energy $\Delta U(\Delta\rho_2)$ need not be negligible]. This approximation is motivated by the fact that for completely soluble isovalent alloys treated here even the stronger perturbation $\Delta\rho_1$ does not split impurity states into the gap. When this does occur (e.g., for GaP:*N*, or for nonisovalent impurities¹³), $\Delta\rho_2(\bar{r})$ can be large (or have long tails), and corrections are necessary.

We obtain the force constants¹⁴ α and β from the fitting of the elastic constants¹⁵ method of Martin.¹² These parameters, the input for our model, are depicted in Table I. Using these force constants we minimize the deformation energy *U* with respect to the breathing mode displacements of the first two shells around the impurity. This does not im-

TABLE I. Input quantities for the calculation.

Compound	<i>d</i> (Å)	$\alpha(N/m)$	β/α
C ^a	1.545	129.33	0.655
Si ^a	2.352	48.50	0.285
Ge ^a	2.450	38.67	0.294
α -Sn ^b	2.810	25.45	0.253
SiC ^b	1.888	88.	0.54
AlP ^b	2.367	47.29	0.192
AlAs ^b	2.451	43.05	0.229
AlSb ^a	2.656	35.35	0.192
GaP ^a	2.360	47.32	0.221
GaAs ^a	2.448	41.19	0.217
GaSb ^b	2.640	33.16	0.218
InP ^a	2.541	43.04	0.145
InAs ^a	2.622	35.18	0.156
InSb ^a	2.805	26.61	0.161
ZnS ^a	2.342	44.92	0.107
ZnSe ^a	2.454	35.24	0.120
ZnTe ^a	2.637	31.35	0.142
CdTe ^a	2.806	29.02	0.084
β -HgS ^b	2.534	41.33	0.062
HgSe ^b	2.634	36.35	0.065
HgTe ^b	2.798	27.95	0.092
γ -CuCl ^b	2.341	22.9	0.044
γ -CuBr ^b	2.464	23.1	0.057
γ -CuI ^b	2.617	22.5	0.091

^aReference 12.

^bCalculated as in Ref. 12 from the experimental constants of Ref. 15.

ply that the other shells do not relax, but rather that the "feedback" of their relaxation onto the first shell is neglected. It turns out that the involved algebraic expressions we obtain in minimizing *U* can be subjected to a hierarchy of order approximations, yielding a simple result:

$$\epsilon \approx 1 / \left[1 + \frac{1}{6} \frac{\alpha_{AC}}{\alpha_{BC}} \left(1 + 10 \frac{\beta_{AC}}{\alpha_{AC}} \right) \right]. \quad (3)$$

Predictions of the impurity bond length for 64 systems are given in Table II along with the relaxation parameter ϵ . The Pauling and VCA predictions can be directly obtained from Table I. Notice that when the bond relaxation $\Delta \equiv R_{BC}[AC:B] - R_{AC}^0$ is positive we have an outward relaxation. Experimental results are available for a limited number of systems. For GaAs:In (Ref. 8), InAs:Ga (Ref. 8), CdTe:Mn (Ref. 16), ZnSe:Te (Ref. 8), and ZnTe:Se (Ref. 8), we find a "VCA error" $R^{\text{expt.}} - R^{\text{VCA}}$ of 0.139 Å (5.4%), -0.134 Å (-5.4%), -0.044 Å (-1.6%), 0.142 Å (5.6%), and -0.141 Å (-5.8%), respectively, a "Pauling error" $R^{\text{expt.}} - R^P$ of -0.035 Å (-1.4%), 0.040 Å (1.6%), 0.014 Å (0.5%), -0.042 Å (1.6%), and 0.043 Å (1.7%), whereas the present method produces yet smaller errors of 0.031 Å, -0.007 Å, 0.001 Å, 0.011 Å, and -0.006 Å, respectively, i.e., mostly within the experimental error of 0.01 Å. We hence feel that Eq. (3) can be used as reliable estimates when EXAFS data are unavailable. Since the stretching force constant α scales as $\alpha \approx 4dB/\sqrt{3}$, where *B* is the bulk modulus, and since¹² $B \sim d^{-4}$, we have $\alpha_{AC}/\alpha_{BC} \approx (d_{BC}/d_{AC})^3$, yielding $0.7 \leq \alpha_{AC}/\alpha_{BC} \leq 1.4$ for most semiconductors. Similarly, β/α was found¹² to scale with Phillips's ionicity f_i as $\beta/\alpha \approx 0.3(1 - f_i)$, leading to the approximate relation

$$\epsilon \approx 1 / \left[1 + \left(\frac{d_{BC}}{d_{AC}} \right)^3 \left(\frac{2}{3} - \frac{1}{2} f_i \right) \right]. \quad (4)$$

TABLE II. Predicted impurity BC bond length $R = R_{BC}^{AC:B}$ (in Å) for an isovalent B -atom impurity in an AC host crystal and the relaxation parameter ϵ [Eq. (1)].

System	R (Å)	ϵ	System	R (Å)	ϵ
AlP:In	2.480	0.65	InP:Al	2.414	0.73
GaP:In	2.474	0.63	InP:Ga	2.409	0.73
AlAs:In	2.553	0.60	InAs:Al	2.495	0.74
GaAs:In	2.556	0.62	InAs:Ga	2.495	0.73
AlSb:In	2.746	0.61	InSb:Al	2.693	0.75
GaSb:In	2.739	0.60	InSb:Ga	2.683	0.74
AlP:As	2.422	0.65	AlAs:P	2.395	0.67
AlP:Sb	2.542	0.61	AlSb:P	2.444	0.73
AlAs:Sb	2.574	0.60	AlSb:As	2.510	0.71
GaP:As	2.414	0.62	GaAs:P	2.387	0.68
GaP:Sb	2.519	0.57	GaSb:P	2.436	0.73
GaAs:Sb	2.564	0.60	GaSb:As	2.505	0.70
InP:As	2.595	0.67	InAs:P	2.562	0.74
InP:Sb	2.700	0.60	InSb:P	2.597	0.79
InAs:Sb	2.739	0.64	InSb:As	2.667	0.75
ZnS:Se	2.420	0.70	ZnSe:S	2.367	0.78
ZnS:Te	2.539	0.67	ZnTe:S	2.407	0.78
ZnSe:Te	2.584	0.71	ZnTe:Se	2.502	0.74
β -HgS:Se	2.611	0.76	HgSe:S	2.553	0.80
β -HgS:Te	2.716	0.71	HgTe:S	2.579	0.82
HgSe:Te	2.748	0.74	HgTe:Se	2.665	0.80
ZnS:Hg	2.482	0.73	β -HgS:Zn	2.380	0.80
ZnSe:Hg	2.587	0.74	HgSe:Zn	2.494	0.78
ZnTe:Cd	2.755	0.70	CdTe:Zn	2.674	0.78
ZnTe:Hg	2.748	0.69	HgTe:Zn	2.673	0.78
γ -CuCl:Br	2.440	0.81	γ -CuBr:Cl	2.367	0.79
γ -CuCl:I	2.563	0.80	γ -CuI:Cl	2.407	0.76
γ -CuBr:I	2.585	0.79	γ -CuI:Br	2.500	0.76
C:Si	1.665	0.35	Si:C	2.009	0.74
Si:Ge	2.380	0.58	Ge:Si	2.419	0.63
Si:Sn	2.473	0.53	α -Sn:Si	2.645	0.70
Ge:Sn	2.549	0.55	α -Sn:Ge	2.688	0.67

In agreement with the detailed calculations, we therefore find the following: (i) ϵ is in the range of 0.6–0.8 for most semiconductors, i.e., considerably closer to the Pauling limit ($\epsilon=1$) than to the VCA limit ($\epsilon=0$). Hence, the VCA model and its application to optical bowing appears to be substantially in error. (ii) Ionic host systems and small impurities have larger relaxation parameters than covalent hosts and large impurities. (iii) The relaxation involves a balance between two opposing effects: adding the second neighbor shell to the model *reduces* the relaxation, whereas introducing bond bending ($\beta \neq 0$) *increases* the relaxation. Hence, models that neglect both effects¹⁶ [yielding $\epsilon = 1/(1 + \frac{1}{3}\alpha_{AC}/\alpha_{BC})$, which coincides with our general expression in Eq. (4) for $\beta/\alpha \approx 0.1$] are considerably better (due to cancellation of errors) than those that incorporate only one of them.

There are very few quantum-mechanical calculations of relaxation parameters of isovalent impurities available for comparison. The semiempirical cluster complete neglect of differential overlap (CNDO) calculation of Mainwood¹⁷ for C:Si yields $R = 1.93$ Å (or $\epsilon = 0.52$), compared with our result of $R = 1.66$ Å ($\epsilon = 0.35$). The elastic model of Baldereschi and Hopfield,² where the impurity-host interaction is described by a spring constant and the host crystal is treated as an elastic continuum, gives a much smaller relaxation ($\epsilon \approx 0.4$) for several III-V and II-VI semiconductors.

We next wish to indicate that the variations with composition $R_{AC}(x)$ and $R_{BC}(x)$ in an $A_{1-x}B_xC$ alloy (Fig. 1), can be obtained by a linear interpolation between ($R_{AC}^0, R_{AC}[BC:A]$) and ($R_{BC}^0, R_{BC}[AC:B]$), using the data of Tables I and II. First, note that the experimental data^{8,16} show such an approximate linear relationship to exist. Second, note that linear behavior was obtained in an alloy model,¹⁶ where the A and B atoms are not allowed to displace from their nominal sites on the VCA lattice, but the C atoms are allowed to relax according to the local environment, and the distortion energy U is calculated from a valence force field model with bond stretching forces only [i.e., $\beta=0$ in Eq. (2)]. For the dilute (impurity) limit this assumption corresponds in our model to neglecting simultaneously bond-bending forces and the next-nearest-neighbor relaxation. Assuming a random distribution of A and B atoms, the average value of $R_{AC}(x)$ is linear with a small correction of the order of

$$[R_{AC}(0) - R_{AC}(1)]x(1-x)(\alpha_{AC} - \alpha_{BC})/(\alpha_{AC} + \alpha_{BC}),$$

whereas the variance is

$$\Delta R(x) \approx (\sqrt{3}/4)\sqrt{x(1-x)}|R_{AC}^0 - R_{BC}^0|.$$

For $\text{Ga}_{0.5}\text{In}_{0.5}\text{As}$, this variance is 0.04 Å, which is considerably larger than the experimental⁸ broadening of the interatomic distances of less than 0.01 Å.

Our model for the dilute alloy can be extended to the whole range of composition by assuming that alloy force constants and lattice parameters can be obtained by interpolation of the data of the end-point materials. If we consider each individual A or B atom as an isovalent impurity system

TABLE III. Interaction parameter Ω in kcal/mole of the regular solution model for the excess enthalpy of mixing of an alloy. Our values calculated both with the "full model" (A) and with $\beta=0$ and nearest-neighbor (NN) relaxation only (B) are compared with the indirect estimations from the experimental phase diagrams (Ref. 18) (Exptl.), and with the calculated values of the dielectric two band model of Van Vechten (Ref. 20) (VV), the delta lattice parameter (DLP) of Stringfellow (Ref. 19) and the elastic model of Fedders and Muller (Ref. 21) (FM).

System	Exptl.	Present work		VV	DLP	FM
		A	B			
$\text{Al}_{1-x}\text{Ga}_x\text{As}$	0.0	0.00	0.00	0.11	0.00	0.00
$\text{Al}_{1-x}\text{Ga}_x\text{Sb}$	0.0	0.02	0.02		0.02	0.03
$\text{Ga}_{1-x}\text{In}_x\text{P}$	3.5,3.25	4.56	3.19		3.63	2.94
$\text{Al}_{1-x}\text{In}_x\text{As}$	2.5	3.60	2.46		2.81	2.37
$\text{Ga}_{1-x}\text{In}_x\text{As}$	1.65,3.0,2.0	2.49	3.57	1.25	2.81	2.42
$\text{Al}_{1-x}\text{In}_x\text{Sb}$	0.6	2.06	1.47		1.46	1.45
$\text{Ga}_{1-x}\text{In}_x\text{Sb}$	1.47,1.9	2.53	1.76		1.85	1.83
$\text{GaP}_{1-x}\text{As}_x$	0.4,1.0	1.15	0.73	0.12	0.98	0.66
$\text{GaAs}_{1-x}\text{Sb}_x$	4.5,4.0	4.58	2.94		3.35	2.76
$\text{InP}_{1-x}\text{As}_x$	0.4	0.72	0.55		0.58	0.52
$\text{InAs}_{1-x}\text{Sb}_x$	2.9,2.25	2.89	2.22	6.56	2.29	2.17
$\text{Zn}_{1-x}\text{Cd}_x\text{Te}$	1.34	2.12	1.86		1.97	1.63
$\text{Zn}_{1-x}\text{Hg}_x\text{Te}$	3.0	1.91	1.65		1.81	1.48
$\text{Cd}_{1-x}\text{Hg}_x\text{Te}$	1.4	0.00	0.00		0.00	0.00
$\text{ZnSe}_{1-x}\text{Te}_x$	1.55	2.91	2.40	3.12	3.11	2.12
$\text{HgSe}_{1-x}\text{Te}_x$	0.7	1.80	1.86		1.87	1.64
$\text{Ge}_{1-x}\text{Si}_x$	1.2	1.63	0.89	1.67	1.19	0.89
$\text{Si}_{1-x}\text{Sn}_x$	19.5	27.5	15.7		18.5	17.1
$\text{Ge}_{1-x}\text{Sn}_x$	7.55	15.3	8.73		10.4	9.03

in the average alloy, then the relaxation is still given by Eq. (3) using the alloy averaged values for the host force constants. The alloy bond length is

$$R_{AC}(x) = R_{AC}^0 + x[1 - \epsilon(x)][R_{BC}^0 - R_{AC}^0],$$

which is essentially linear except for the small dependence of ϵ on x .

The contribution of the deformation energy to the excess enthalpy of mixing ΔH_m of the alloys is directly obtained from Eq. (2) since the reference system for the energy is given by the pure AC and BC crystals. Using the regular solution model, $\Delta H_m = x(1-x)\Omega$, we find

$$\Omega = (R_{AC}^0 - R_{BC}^0)^2 \bar{\alpha} \frac{1 + 11.25(1 + 2.2\bar{\beta}/\bar{\alpha})\bar{\beta}/\bar{\alpha}}{1 + \frac{1}{6}(1 + 10\bar{\beta}/\bar{\alpha})}, \quad (5)$$

where the values of $\bar{\alpha}$ and $\bar{\beta}/\bar{\alpha}$ are alloy averaged. The calculated values of Ω are compared in Table III with experiment¹⁸ and with the results of other calculations.¹⁹⁻²¹ The experimental values of Ω are obtained from a fit of the solidus and liquidus curves in the phase diagram of the alloy, and are, therefore, dependent on the thermodynamic model assumed in the fit. We notice that the dielectric two-band model of Van Vechten²⁰ is in poor agreement with experiment, and that the models of Stringfellow¹⁹ and Fedders and Muller²¹ both use an adjustable parameter to fit the experimental data, whereas our model is parameter free. The success of their fit^{19,21} is explained by the dependence of Ω on $(R_{AC}^0 - R_{BC}^0)^2$. This scaling evolves naturally in our model by considering a limiting case. By a cancellation

of errors, the energies calculated with $\beta=0$ and neglecting next-nearest-neighbors relaxation [$\Omega = 1.5\bar{\alpha}(R_{AC}^0 - R_{BC}^0)^2$ in column B] are in good agreement with experiment. Our calculated values, using the full model [Eq. (5), column A] reproduce the experimental trends, suggesting that local elastic deformations, not optical bowing,²⁰ are the primary physical factor deciding ΔH_m . However, the deformation model gives values that are higher than the experimental values, suggesting that the electrochemical factor $\Delta U(\Delta\rho_2)$ (stabilization of the alloy by charge transfer, proportional to the electronegativity difference of the alloyed components), cannot be neglected. A better agreement could be obtained if we used smaller values of β/α , as suggested before.¹⁴

Note added in proof: After the completion of this work we were informed by N. Motta [A. Balzarotti, M. T. Czyzyk, A. Kisiel, N. Motta, M. Podgorny, and M. Zimnal-Starnawska (private communication) for which we are grateful] that they have recently performed EXAFS measurements on $Cd_{1-x}Zn_xTe$, finding $R_{CdTe}[ZnTe: Cd] = 2.75(2)$ Å and $R_{ZnTe}[CdTe: Zn] = 2.68-2.69$ Å (extrapolated), in excellent agreement with our predicted values of Table II (2.755 and 2.674 Å, respectively).

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¹⁴Various authors have noticed [e.g., G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 5662 (1980); R. Alben, D. Weaire, J. E. Smith, Jr., and M. H. Brodsky, *ibid.* **11**, 2271 (1975)] that a range of β/α values can be obtained if one deduces it by emphasizing in the fit certain aspects of the phonon spectra.

Although our expression for ϵ shows little sensitivity to the value of β/α , the enthalpy of mixing is fairly sensitive to this parameter. The scarcity of experimental data for the relaxation and the uncertainty in the experimental values of the enthalpy of mixing do not warrant, in our view, a refinement of β/α at this stage.

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