PHYSICAL REVIEW B VOLUME 40, NUMBER 3 15 JULY 1989-II

First-principles calculation of the formation energies of ordered and disordered phases of AlAs-GaAs

N. E. Christensen
Max-Planck-Institut für Festkörperforschung, Postfach 80 60 65, D-7000 Stuttgart 80, Federal Republic of Germany

S.-H. Wei and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401

(Received 6 April 1989)

The total energy of ordered and disordered phases of AlAs-GaAs systems is expanded in a series of multiatom interaction energies determined from first-principles linear muffin-tin orbital and linear augmented-plane-wave calculations of simple superstructures. These interaction energies are used to discuss the stability of different superlattices and that of the random alloy.

I. INTRODUCTION

Wei and Zunger[1] have shown that the total excess energy per cell $\Delta E(n,\mathbf{G})$ of lattice-matched $(AC)_n(BC)_n$ superlattices with layers repeated along the direction $\mathbf{G}$,

$$\Delta E[n,\mathbf{G}]=E[(AC)_n(BC)_n;\mathbf{G}]-nE[AC]-nE[BC]\ , \tag{1}$$

can be represented with respect to the equilibrium energies of pure AC and BC as a reasonably rapidly convergent series of k-atom m-neighbor interaction energies $J_{k,m}$:

$$\Delta E[n,\mathbf{G}]=\sum_{k}^{K}\sum_{m}^{M}\xi_{k,m}(n,\mathbf{G})J_{k,m}\ . \tag{2}$$

Here, $\xi_{k,m}(n,\mathbf{G})$ are geometric constants representing the occurrence frequency in the superlattice (relative to its constituent binary solids) of k-atom "figures" whose A and B sites are separated by up to the mth nearest neighbor (given in Tables I and II of Ref. 1). The utility of this analysis[1,2] lies in the ability to deduce the set $\{J_{k,m}\}$ by performing directly self-consistent total-energy calculations for N simple periodic structures $\{s\}$ involving AC and BC, and using the inverse form

$$J_{k,m}=\sum_{s=1}^{N}[\xi_{k,m}(s)]^{-1}\Delta E(s) \tag{3}$$

to find N values of $J_{k,m}$. Provided that convergence of Eq. (2) can be demonstrated for this set of N values of $J_{k,m}$, this expansion affords simple calculations of ΔE for more complex structures $\{s'\}$, through calculation of the coefficients $\xi_{k,m}(s')$, rather than by the more laborious direct self-consistent total-energy calculation of $\Delta E(s')$. This procedure was applied[1] to $(\mathrm{AlAs})_n(\mathrm{GaAs})_n$ superlattices using nine $\Delta E(s)$ values calculated by the general potential linear-augmented-plane-wave (LAPW) method[1,3] where it was found that three- and four-body interactions ($k=3$ and 4) are negligible for this system. In this work we show how calculations of $\Delta E(s)$ for simple short-period structures can be used in conjunction with this energy-expansion method to predict the excess energies of longer period $(\mathrm{AlAs})_n(\mathrm{GaAs})_n$ superlattices in different orientations as well as the energy of the random $\mathrm{Al}_{0.5}\mathrm{Ga}_{0.5}\mathrm{As}$ alloy. General conclusions on the relative thermodynamic stabilities of these systems are drawn.

II. APPLICATION TO AlAs-GaAs SYSTEMS

Recently, one of us[4] calculated, using the linear muffin-tin orbital (LMTO) method[3] and atomic-sphere approximation (ASA), the excess energies $\Delta E(n,\mathbf{G})$ of $(\mathrm{AlAs})_n(\mathrm{GaAs})_n$ superlattices for $\mathbf{G}=(001)$, (111), and (110) up to $n\leq 7$ and of other ordered AlAs-GaAs compounds. These calculations afford the use of Eqs. (2) and (3) to deduce the interaction energies underlying the LMTO method. For superlattices for which both LMTO and LAPW calculations exist (Table I) the LMTO method produces systematically higher values[5] of $\Delta E(n,\mathbf{G})$, e.g., $\Delta E[1,(001)]=13.8$ meV/cell in the LAPW calculation (14.9 meV/cell in the pseudopotential calculation[6]) and 32.0 meV/cell in the LMTO calculation, or $\Delta E[2,(001)]=11.8$ meV/cell in the LAPW calculation and 35.2 meV/cell in the LMTO calculation. Pseudopotential[6] calculations also give ΔE values which are smaller than the LMTO results, e.g., $\Delta E[3,(001)]=1.7$ meV/cell [Ref. 6(c)] (compared with 33.3 meV in the LMTO calculation) and $\Delta E[3,(110)]=27.8$ meV/cell [Ref. 6(a)] (compared with 50.4 meV in the LMTO calculation). Nevertheless, the LMTO method was applied to the widest range of superlattices yet, and while it will produce undoubtedly a different set of interaction energies $\{J\}$ than the LAPW method, this set can probably be viewed as *internally consistent*. Comparison between the predictions of these methods will establish which aspects of the relative thermodynamic stability of various orientations of AlAs-GaAs superlattices are robust.

We use Eqs. (1)–(3) to obtain ten interaction parameters from the LMTO calculated energies for ten ordered structures. These are the following. (i) The two endpoint zinc-blende compounds AlAs and GaAs [for which $\Delta E = 0$ by the definition of Eq. (1)]. (ii) For 50%-50% composition we use four (AlGaAs$_2$) structures: the "CuAuI" (denoted CA, with space group $P\bar{4}m2$), chalcopyrite (denoted CH, with space group $I\bar{4}2d$), "CuPt" (denoted CP, space group $R3m$), and the (AlAs)$_2$(GaAs)$_2$ (001) superlattice (denoted $Z2$). (iii) For the 25%-75% (Al$_3$GaAs$_4$) and 75%-25% (AlGa$_3$As$_4$) compositions we use four structures: two "luzonite" (denoted $L1$ and $L3$, for each of the two compositions, respectively; space group $P\bar{4}3m$) and two famatinite (denoted $F1$ and $F3$, space group $I\bar{4}2m$). Table I of Ref. 1 gives the expansion coefficients $\xi_{k,m}(s)$ for these structures and Refs. 7 and 8 give pictures of these crystal structures. Along with these ten structures, we use ten interaction energies $J_{k,m}$. These include the following. (i) Four *pair* ($k=2$) interactions between the first, second, third, and fourth neighbors $J_{2,1}$, $J_{2,2}$, $J_{2,3}$, and $J_{2,4}$, respectively. (ii) Two *three-body* ($k=3$) interactions: $J_{3,1}$ (between first neighbors) and $J_{3,2}$ (where two of the three sites are second neighbors). (iii) Two *four-body* ($k=4$) interactions: $J_{4,1}$ (between first neighbors) and $J_{4,2}$ (where one pair is second neighbor). (iv) The one-site $J_{1,1}$ and the constant term $J_{0,1}$. The first column of Table I gives the LMTO-calculated excess energies for these (and other, see below) structures. Using Eq. (3) with $N=10$, we obtain the values of the ten interaction energies denoted in Table II as "set I."

To assess the importance of the $k>2$ ("many-body") interactions, we have used as "set II" the same ten structures, but retain only the four *pair* interactions $J_{2,m}$ $(1 \le m \le 4)$ in the expansion of Eq. (2), along with $J_{0,1}$ and $J_{1,1}$. (In this fit, the excess energies of Al$_3$GaAs$_4$ and AlGa$_3$As$_4$ are averaged.) A least-squares fit to these six interaction energies produces the values denoted in Table II as "set II." Table I shows the good quality of the fit [root-mean-square (rms) error of 0.7 meV]. Using these four pair-interaction energies, we give also in Table I the

TABLE I. Calculated excess energies ΔE for AlAs-GaAs superstructures. Energies are in meV/(4 atoms), except those for (001), (110), and (111) superlattices which are in meV per cell (4n atoms). For structures and J's used in different sets, see text. The asterisk denotes those values used in the fit, excluding the reference energy $\Delta E = 0$ for GaAs and AlAs; other values are predicted.

		Series expansion to LMTO							
		Set I	Set II	Set III					Direct
	Direct	10 struct.	10 struct.	6 struct.	Direct	Series expansion to LAPW			pseudo-
	LMTO	10 J's	6 J's	6 J's	LAPW	Set I	Set II	Set III	potential[a]
(001)									
$n=1$ (CA)	32.0	32.0*	33.0*	32.0*	13.8	13.8*	13.8*	13.8*	14.9
$n=2$ ($Z2$)	35.2	35.2*	35.2*	35.2*	11.8	11.8*	11.8*	11.8*	
$n=3$	33.3	35.2	35.2	35.2		11.8	11.8	11.8	1.7
$n=5$	30.0	35.2	35.2	35.2		11.8	11.8	11.8	
$n=7$	28.7	35.2	35.2	35.2		11.8	11.8	11.8	
(110)									
$n=1$ (CA)	32.0	32.0*	33.0*	32.0*	13.8	13.8*	13.8*	13.8*	14.9
$n=2$		51.5	50.3	51.0	19.6	19.3	18.9	19.1	
$n=3$	50.4	58.0	52.2	52.5		18.5	17.9	18.2	27.8
$n=4$		58.5	52.1	52.7		18.3	17.7	17.9	
$n=5$	43.0	58.5	52.1	52.7		18.3	17.7	17.9	
$n=7$	45.5	58.5	52.1	52.7		18.3	17.7	17.9	
(111)									
$n=1$ (CP)	25.6	25.6*	25.6*	25.6*	9.8	9.8*	9.8*	9.8*	11.4
$n=2$		31.7	26.8	27.2	7.0	8.8	8.3	8.6	
$n=3$	31.0	31.7	26.8	27.2		8.8	8.3	8.6	15.4
(201)									
$n=2$ (CH)	32.3	32.3*	32.1*	32.3*	13.5	13.5*	13.5*	13.5*	
A_3B and AB_3									
Al$_3$Ga ($L1$)	29.4	29.4*	24.7*	24.0	10.3	10.3*	10.45*	10.3	
AlGa$_3$ ($L3$)	22.9	22.9*	24.7*	24.0	10.6	10.6*	10.45*	10.3	
Al$_3$Ga ($F1$)	25.1	25.1*	24.3*	24.1	10.2	10.2*	10.2*	10.2	
AlGa$_3$ ($F3$)	22.9	22.9*	24.3*	24.1	10.2	10.2*	10.2*	10.2	
Alloy, $x=0.5$		25.7	25.1	25.1		9.75	9.61	9.73	−80[b]
rms of fit		0.0	0.7	0.0		0.0	0.0	0.0	
rms of predictions		1.7	1.8	1.9		0.6	0.3	0.4	

[a] Reference 6.

[b] From average−t-matrix correction to the virtual crystal, Ref. 6(d).

predicted values [from Eq. (2)] of the energies $\Delta E(n,\mathbf{G})$ for structures *not* included in the fit. Comparison with the directly calculated LMTO values shows a rms error for *predicted* structures of 2 meV/(4 atoms). This good predictive power of the pair-interaction model suggests the relative unimportance of three- and four-body terms for this system.

We next examine whether fewer than ten structures can be used to achieve similarly good predictive ability of the energy expansion model. To this end, we have used as "set III" the four 50%-50% structures (CA, CH, CP, and Z2) and pure AlAs and GaAs and the four pair interactions $J_{2,m}$, $1 \leq m \leq 4$. Solving Eq. (3) (exactly) produces the interaction energies denoted in Table II as "set III." The predictive ability of this set for structures not included in this "fit" is demonstrated in Table I, giving a rms error similar to set II [2 meV/(4 atoms)]. We conclude that even set III is adequate for this system.

For comparison, Tables I and II give also the results of sets I, II, and III obtained by using the same procedure, but replacing the LMTO energies by the more accurate LAPW energies.[1,9] To assure an effective cancellation of errors in Eq. (1), one may calculate the total energies of the three systems $(AC)_n(BC)_n$, $(AC)_n(AC)_n$, and $(BC)_n(BC)_n$ in precisely the same crystal structure (i.e., that of the superlattice **k** points). This procedure has been used in the LMTO study of Ref. 4, with a regular mesh of (up to 45) **k** points. The same cancellation of errors may be achieved (more economically) if the total energies of AC and BC are calculated in the two-atom zinc-blende unit cell, whereas that of the $(AC)_n(BC)_n$ superlattice is calculated using the *equivalent set* of **k** points obtained by folding the zinc-blende points into the superlattice Brillouin zone. This procedure has been used in the LAPW study,[1] where the two *special* **k** points were used for the zinc-blende structure, with equivalent **k** points for the superlattices. It was verified that $E[(AC)_n(AC)_n]=nE(AC,\text{zinc-blende})$. Since the LMTO calculations were performed using a large number of **k** points, we have repeated the LAPW calculations reported in Ref. 1 using ten special zinc-blende **k** points. The results are given in Table I. The small change[10] in energies relative to Ref. 1 does not alter our conclusions.

The series-expansion method[1] leads to a number of interesting conclusions.

(i) The dominant interaction in this system is due to first-cation (Ga-Al) nearest neighbors and is *repulsive* ($J_{2,1}<0$). Its value is robust, in the sense that different fitting schemes produce similar values (Table II). The remaining pair interactions are much smaller. Although their values are nonunique (compare different sets in Table II), they combine to produce very similar predictions for the total energies of structures not used in the fit (Table I). Our results conflict with the recent conclusions of Cohen and Schlijper,[11] who found from simplified ASW calculations that ΔE for the CA, $L1$, and $L3$ structures are *negative* [-420, -40, and -260 meV/(4 atoms), denoted in Ref. 11 as -2δ, $-2\delta'$, and $2\delta''$, respectively]. This produces *attractive* pair interactions, in conflict with other calculations.[1,4,6]

(ii) The significance of the signs of $J_{2,m}$ is that they decide, through the generalized face-centered-cubic (fcc) Ising model,[12,13] the type of ground states supported by the system. Use of the LAPW-calculated interaction energies (set I) as input to such a multispin Ising Hamiltonian and its solution[14] through the cluster-variation method[15] show a "ferromagnetic" ground state corresponding to phase separation (into AlAs plus GaAs) at $T=0$ with no stable or metastable ordered compounds. All calculations shown in Table I indeed exhibit $\Delta E>0$, indicating that none of these ordered structures is a thermodynamic ground state. Similarly, the dominance of *repulsive* pair interactions in the LMTO results (Table II) suggests the same type of phase-separated ground state. Since, however, an ordered (CuAuI-like) $AlGaAs_2$ compound *was* observed in molecular-beam-epitaxy (MBE) and metal-organic chemical-vapor-deposition (MOCVD) growth,[16] we must conclude that this is not a consequence of bulk thermodynamics (surface and kinetic effects have been suggested[17] as a likely cause). Our conclusion conflicts

TABLE II. Interaction energies $J_{k,m}$ (in meV) extracted from the total energies of Table I.

	LMTO series expansion			LAPW series expansion		
	Set I 10 struct.[a] 10 J's	Set II 10 struct.[a] 6 J's	Set III 6 struct.[b] 6 J's	Set I	Set II	Set III
$J_{2,1}$	-1.9187	-1.9400	-1.9187	-0.9062	-0.9075	-0.9062
$J_{2,2}$	0.0458	-0.0713	-0.1333	0.0542	0.0481	0.0458
$J_{2,3}$	-0.1844	-0.0613	-0.0406	0.0156	0.0213	0.0219
$J_{2,4}$	-0.0708	0.0100	-0.0260	0.0271	0.0306	0.0292
$J_{0,1}$	12.8250	12.5295	12.5562	4.8750	4.8060	4.8625
$J_{1,1}$	1.6000	0.0	0.0	-0.1500	0.0	0.0
$J_{3,1}$	0.2031			-0.0094		
$J_{4,1}$	-0.2687			-0.0125		
$J_{3,2}$	-0.2687			0.0188		
$J_{4,2}$	0.1437			0.0063		

[a] Ten structures: AC, CH, CA, CP, $L1$, $L3$, $F1$, $F3$, BC, and $Z2$.
[b] Six structures: AC, BC, CH, CA, CP, and $Z2$.

with that of Cohen and Schlijper,[11] who deduced *attractive* pair interactions for AlAs-GaAs, hence predicting stable low-temperature ordering. Their revised calculations[18] suggest, however, that $J<0$, hence that "the ordered superlattice is probably thermodynamically unstable." Note that for *lattice-mismatched* semiconductor pairs (e.g., GaAs-GaSb) metastable long-range ordering *is* predicted by our mode as the dominant *J*'s are attractive.[8,14]

(iii) The fact that the most accurate fit ("set I") produces $J_{2,1}<0$ and $J_{2,2}>0$ suggests an interesting topological property of these structures—they are "spin frustrated"[12,13] in the sense that the atomic arrangements are unable to satisfy simultaneously these two conditions (*A* surrounded by *A* only in the first-neighbor shell, since $J_{2,1}<0$, but by *B* only in the next shell, since $J_{2,2}>0$ and the same for *B*). If both $J_{2,1}$ and $J_{2,2}$ are negative, there is no spin frustration and the system corresponds to a simple ferromagnet.

(iv) Since each $(\mathrm{AlAs})_n(\mathrm{GaAs})_n$ superlattice has $4n$ atoms and two interfaces per unit cell, the total energy *per cell* $\Delta E(n,\mathbf{G})$ can be thought of as twice an effective interface energy *I*. Our calculation shows that this energy tends to saturate to the "bulk" interface energy as a function of the repeat period *n* past a critical value $n_c(\mathbf{G})$: retaining in Eq. (2) up to $(M=4)$th-order pair interactions, this saturation occurs at $n_c=2$ for the (001) and (111) orientations, but at $n_c=4$ for (110) [the small decrease in $\Delta E(n,\mathbf{G})$ *past* these n_c values evident in the LMTO results of Table I testifies to the possible existence of correspondingly small interactions beyond $M=4$]. The saturation of $\Delta E(n,\mathbf{G})$ implies that the excess energy *per atom* $\Delta E(n,\mathbf{G})/4n$ decreases for such lattice-matched systems to zero as $\sim 1/n$ for $n\geq n_c(\mathbf{G})$, a result also deduced from different considerations by Wood *et al.*[19] This scaling relation, implying that such "repelling" superlattices become more stable per atom as the repeat period *n* increases, reflects the finite range of the (net repulsive) interaction across the interface.

(v) The LMTO interfacial energies [half of $\Delta E(n_c,\mathbf{G})$] are $I(001)\simeq 18$ meV, $I(110)\simeq 29$ meV, and $I(111)\simeq 13$ meV, showing the same trends as the LAPW results[1] [$I=5.9$, 9.2, and 4.4 meV for the (001), (110), and (111) orientations, respectively], i.e., that for this lattice-matched system, the (111) interface is the stablest while the (110) is the least stable. This result has been shown[8,19] to reflect the excess electrostatic energies of these interfaces. Also, $\Delta E[n,(110)]$ is nonmonotonic with *n* in both calculations. Results found by Bylander and Kleinman[6] in their pseudopotential calculation also imply this trend. The small increase of $\Delta E[n,(001)]$ for small *n* (relative to $n=1$) found in LMTO calculations is not observed in other calculations.[1,6] A similar increase in $\Delta E[n,(110)]$ *is* common to all calculations. Note that the CuPt structure is predicted to be the stablest monolayer superlattice in this series, as confirmed by a number of calculations[1,4,6] and discussed by Bernard *et al.*[8] (For lattice-mismatched systems, however, the CuPt is the *least stable* in this series.[8,14])

(vi) The pair-interaction energies $J_{2,m}$ can be used to predict the excess energy $\Delta E(R)$ of the 50%-50% random (*R*) alloy, for which $\xi_m(R)$ (per two atoms) are[1] -6, -3, -12, and -6 for $m=1$, 2, 3, and 4, respectively (for disordered but nonrandom alloys, $\xi_{k,m}$ need to be calculated[8,14,15] from the corresponding Ising model). Using the LMTO interaction energies we find for the random alloy $\Delta E(R)=25\pm 1$ meV/(4 atoms) (Table I), corresponding to an "interaction parameter" $\Omega=4\Delta E(R)=50\pm 2$ meV/(2 atoms)$\simeq 1.15$ kcal/(2 atom) mol, compared with 0.45 kcal/mol obtained with LAPW (Ref. 1) and the range 0–1.6 kcal/mol deduced from experiment.[20] The fact that the energy of the random alloy is far less sensitive to the details of the fit (Table I) than the energies of certain superlattices is very encouraging. The finding that $\Delta E(R)>0$ (i.e., the random alloy is unstable thermodynamically towards decomposition at $T=0$ to its binary constituents) contradicts the finding of Shen, Bylander, and Kleinman[6(d)] that $\Delta E(R)$ is negative [-80 meV/(4 atoms)], implying that *the random alloy is the $T=0$ ground state.* The latter result suggests that interactions *beyond* the range included here are both *attractive* and statistically more significant than the shorter-range ($m\leq 4$) interactions. This (in our view, unlikely) situation is certainly not met by any of the superlattice calculations considered here: the expansion of Eq. (2) using up to four neighbor terms suffices to represent the (positive) excess energies at least up to $n=7$ superlattices, and gives a stable fit to the energy of the random alloy.

(vii) The random alloy is predicted by LMTO, pseudopotential,[6] and LAPW (Ref. 1) calculations to be stabler at $T=0$ than any of the monolayer superlattices (Table I). Since the random alloy is stabilized at finite *T* by entropy more than the ordered superlattices are, we expect[1] that the free energy $F(R,T)$ of the random alloy will be lower than that of monolayer superlattices $F(1,G,T)$ at *all* temperatures. By conclusion (iv) above, we see that as the repeat period *n* increases, the $1/n$ scaling of $\Delta E(n,\mathbf{G})$ will eventually make such longer-period superlattices stabler at $T<T_c(n,\mathbf{G})$ than the random alloy, where $T_c(n,\mathbf{G})$ is defined through $F(n,\mathbf{G},T_c)-F(R,T_c)=0$. For example, using the LAPW data we see that while for the monolayer superlattices $\Delta E(1,\mathbf{G})=13.8$, 13.8, and 9.8 meV for the (001), (110), and (111) superlattices, respectively, i.e., *higher* than the random-alloy value of $\Delta E(R)=9.75$ meV/(4 atoms), for $n=2$ we have $\Delta E(2,\mathbf{G})=5.9$, 9.2, and 4.4 meV/(4 atoms), respectively, so that they are now all stabler than the random alloy at $T=0$. Once formed, such superlattices have no thermodynamic incentive to disorder at low *T*. This contradicts the pseudopotential results,[6] which suggest that the random alloy is stabler than *any* $\mathbf{G}=(001)$, (011), or (111) superlattices for *all* repeat period *n* and temperatures *T*.

ACKNOWLEDGMENTS

The work at the Solar Energy Research Institute, Golden, Colorado, has been supported by the Office of Energy Research, Materials Science Division, U.S. Department of Energy under Grant No. DE-AC02-77-CH00178.

[1] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **61**, 1505 (1988).

[2] J. W. D. Connolly and A. Williams, Phys. Rev. B **27**, 5169 (1983); G. P. Srivastava, J. L. Martins, and A. Zunger, *ibid.* **31**, 2561 (1985).

[3] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[4] N. E. Christensen, Solid State Commun. **68**, 959 (1988).

[5] The differences between the "LAPW" and "LMTO" values of ΔE are mainly due to the ASA and muffin-tin (MT) approximations used in the LMTO calculation. The LMTO method, however, can be applied without imposing the ASA and MT restrictions; see, e.g., O. K. Andersen, M. Methfessel, C. O. Rodriguez, P. Blöchl, and H. M. Polatoglou, in *Atomistic Modeling of Materials Beyond Pair Potentials,* edited by D. J. Srolovitz and V. Vitek (Plenum, New York, in press).

[6] (a) D. M. Bylander and L. Kleinman, Phys. Rev. Lett. **60**, 472(E) (1988); (b) Phys. Rev. B **36**, 3229 (1987); (c) Phys. Rev. Lett. **59**, 2091 (1987); (d) Y. T. Shen, D. M. Bylander, and L. Kleinman, Phys. Rev. B **38**, 13 257 (1988).

[7] L. Martins and A. Zunger, J. Mater. Res. **1**, 523 (1986).

[8] J. E. Bernard, L. G. Ferreira, S.-H. Wei, and A. Zunger, Phys. Rev. B **38**, 6338 (1988).

[9] In Table II of Ref. 1, the expansion coefficient $\xi_{2,2}(2,[001])$ was incorrectly written as -16. The correct value should be -8. Consequently, the fitted value of $\Delta E(2,[001])$ in Table II should be 4.0 meV instead of 3.6 meV. The fitted pair interactions $J_{2,m}$ for ten structures should be $J_{2,1}=-0.785$, $J_{2,2}=0.088$, $J_{2,3}=0.036$, and $J_{2,4}=0.120$, instead of $J_{2,1}=-0.758$, $J_{2,2}=0.089$, $J_{2,3}=0.022$, and $J_{2,4}=0.112$ given in Ref. 1. Other results and conclusions are unchanged.

[10] The LAPW energies obtained in Ref. 1 with the equivalent of two zinc-blende **k** points were 11.5, 5.7, 7.5, 3.2, 9.8, 8.7, 8.4, 7.7, and 7.3 meV for the structures CA, $Z2$, CP, $n=2(111)$, CH, $L1$, $L3$, $F1$, and $F3$, respectively. The average ratio of LMTO over LAPW energies for the eight structures for which common values are available in Table I was 3.50 ± 0.64, with the largest deviation for the $Z2$ structure (ratio of 6.07). Using the ten-**k**-point LAPW data the average ratio is 2.50 ± 0.24 and the largest deviation is again for the $Z2$ structure, for which the ratio is 3.00. The ten-**k**-point results hence considerably improve the LAPW-LMTO correlation. Since ΔE for this system is small, even ~ 20 meV errors in LMTO are amplified into a substantial LMTO-to-LAPW energy ratio. For systems with larger ΔE values, a smaller ratio is to be expected.

[11] J. S. Cohen and A. G. Schlijper, Phys. Rev. B **36**, 1526 (1987).

[12] C. Domb, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and M. S. Green (Academic, London, 1974), Vol. 3, p. 357; D. M. Burley, *ibid.* Vol. 2, p. 329.

[13] D. de Fontaine, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 73.

[14] L. G. Ferreira, S.-H. Wei, and A. Zunger, Phys. Rev. B (to be published).

[15] For the method of solution, see A. A. Mbaye, L. G. Ferreira, and A. Zunger, Phys. Rev. Lett. **58**, 49 (1987), and references therein.

[16] T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, Phys. Rev. Lett. **54**, 201 (1985).

[17] J. A. Van Vechten, J. Cryst. Growth **71**, 326 (1985).

[18] Repeating their calculations with different sets of ASW input parameters (sphere radii) produces positive excess energies, in agreement with Ref. 1; see J. S. Cohen and A. G. Schlijper, Phys. Rev. B **38**, 12 694(E) (1988).

[19] D. M. Wood, S.-H. Wei, and A. Zunger, Phys. Rev. B **37**, 1342 (1988); Phys. Rev. Lett. **58**, 1123 (1987).

[20] L. M. Foster, J. E. Scardefield, and J. F. Woods, J. Electrochem. Soc. **119**, 765 (1977); V. T. Bublik and V. N. Liekin, Phys. Status Solidi A **46**, 365 (1978).