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Reply to "Comment on 'Atomic structure and ordering in semiconductor alloys' "

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The claim by Podgórny and Czyżyk (preceding comment) that their simplified empirical alloy model captures the essence of the first-principles model of the present authors is shown to be unfounded.

In a recent article[1] we (Srivastava, Martins, and Zunger; hereafter SMZ) predicted, based on total-energy calculations, the possibility of the existence of ordered semiconductor alloys (e.g., $\mathrm{Ga}_n\mathrm{In}_{4-n}\mathrm{P}_4$ for $n=1$, 2, and 3) despite the long-known fact that the disordered (high-temperature) phase of these alloys has a positive enthalpy of mixing. We have recognized[1] that our local-density-functional calculations overestimated the (negative) formation enthalpies of the ordered phases at low temperatures, and have therefore scaled these values to reproduce the observed high-temperature mixing enthalpy of the disordered phase. In the preceding comment, Podgorny and Czyzyk[2] (PC) "do not share (SMZ's) enthusiasm about the possibility of growing ordered phases." PC have confirmed that use of SMZ's unscaled formation enthalpies of the ordered phases overestimates their stability, while using the scaled values results in good agreement with the observed mixing enthalpy of the disordered phase. Finally, they present a calculation of the phase diagram of pseudobinary semiconductor alloys using the quasichemical approach (QCA), in which no ordered phases exist.

In this reply we note the following: (i) ordered semiconductor alloy phases of precisely the same structures as predicted by SMZ have been recently observed to grow spontaneously[3-5] (even for a perfectly lattice-matched substrate,[3] and for truly continuous rather than layer-by-layer growth[3-5]); (ii) correcting the underestimation of the lattice mismatch (hence, also the underestimation of the positive strain energy) in the underlying local-density pseudopotential formalism of SMZ, we recover the adjusted SMZ values for the formation enthalpies of the ordered phases with no need for empirical adjustments; (iii) physically plausible phase diagrams, including the possibility of stable and metastable long-range ordered phases, are obtained using the cluster variational method (CVM), whereas the quasichemical approach[2] used by PC is, as they state, "not particularly suitable for phase-diagram calculations" and reveals no long-range order.

We first briefly summarize the basic physical model of SMZ on which PC comment. An alloy $A_xB_{1-x}C$ of fourfold-coordinated binary (zinc-blende) components AC and BC can be approximately described[1] by considering the five different nearest-neighbor arrangements ("clusters") A_nB_{4-n} ($n=0$, 1, 2, 3, and 4) around the common atom C. These clusters also occur in periodic ternary crystals $A_nB_{4-x}C_4$ of a particular ordering vector (Landau-Lifshitz structures). SMZ (Ref. 1) have calculated from first principles, using the local-density pseudopotential formalism, the lattice-parameter- (a) dependent excess total energies $\Delta E^{(n)}(a)$ of the five ordered (Landau-Lifshitz) structures $A_nB_{4-n}C_4$ for $AC=\mathrm{GaP}$ and $BC=\mathrm{InP}$. Minimizing the total energy for each unit cell volume a^2c with respect to the cell-internal degrees of freedom (i.e., bond lengths $R_{AC}^{(n)}$ and $R_{BC}^{(n)}$, obtaining thereby a bimodal bond-length distribution), they evaluated at equilibrium (eq) the enthalpies of formation $\Delta H^{(n)} \equiv \Delta E^{(n)}(a_{\mathrm{eq}}^{(n)}, R_{AC}^{(n)}, R_{BC}^{(n)})$ and the equilibrium lattice constants $a_{\mathrm{eq}}^{(n)}$ of these ordered structures. They modeled the high-temperature mixing enthalpy $\Delta H^{(D)}(x)$ of the disordered (D) alloy as

$$\Delta H^{(D)}(x) = \sum_{n=0}^{4} P_R^{(n)}(x) \Delta E^{(n)}(a(x)) , \tag{1}$$

where ${P_R}^{(n)}(x)$ are the random (R) occurrence probabilities (appropriate for high temperatures) of each cluster A_nB_{4-n} at the composition x [where the alloy lattice parameter is $a(x)$]. SMZ pointed out that their $\Delta H^{(n)} = \Delta E_{\mathrm{eq}}^{(n)}$ values appear to be somewhat too negative. They therefore proceeded by scaling down $\Delta H^{(n)}$ (for example, $\Delta H^{(2)}$ was taken as -0.30 kcal/mol) so that the observed $\Delta H^{(D)}(x)$ was reproduced via Eq. (1). Their main prediction was that the inherent instability[6] of the disordered phase towards disproportionation [$\Delta H^{(D)}(x) > 0$, normally taken to suggest that no compounds will exist] was nonetheless consistent with the possibility that ordered phases ($\Delta H^{(n)} < 0$) could exist at lower temperatures and stoichiometric compositions. This is so because the large elastic strain present in the disordered phase (due to its inability to simultaneously accommodate ideal bond configurations for all cluster types), is minimized by the coherent bond arrangement of the ordered stoichiometric phase. Hence, in general, at stoichiometric compositions $X_n = n/4$, one has

$$\Delta H^{(D)}(X_n) > \Delta H^{(n)} \tag{2}$$

(whether scaled or unscaled $\Delta H^{(n)}$ values are used). Subsequent to these predictions, ordered phases $A_nB_{4-n}C_4$ of precisely the same structures as calculated by SMZ were observed experimentally for the first time[3-5] for[3] $AC =$ GaAs, $BC =$ InAs; $AC =$ GaAs, $BC =$ GaSb;[4] and[5] $A =$ Si, $B =$ Ge (see also Ref. 7 for the ordering observed in non-zinc-blende semiconductor alloys).

Using the unscaled $\Delta H^{(n)}$ values of SMZ (instead of those actually used by SMZ), Podgorny and Czyzyk[2] have shown [their Fig. 2(b)] that one gets $0 > \Delta H^{(D)}(x) > \Delta H^{(n)}$, but that $\Delta H^{(D)} < 0$, in conflict with experiment. On this basis they state "We are tempted to contest the value of (the unscaled) $\Delta H^{(2)}$ reported by SMZ." We find this to be a misplaced criticism, since one correctly recovers the experimental $\Delta H^{(D)}(x)$ value (3 ± 1 kcal/mol for $x = \frac{1}{2}$, deduced from the high-temperature solidius-liquidus data) if one uses the scaled theoretical parameters actually employed by SMZ, as demonstrated by SMZ [their Fig. 3(c)] and subsequently by PC [their Figs. 2(a) and 4(c)]. The unscaled SMZ values should not be used.

We have recently found[8] that an empirical fit to the observed $\Delta H^{(D)}(x)$ by scaling $\Delta H^{(n)}$ is no longer needed if one accounts for the fact that the lattice mismatch $\Delta a = a_{\text{InP}} - a_{\text{GaP}}$ in SMZ's first-principles calculation was somewhat too small (Ref. 11 in Ref. 1). Although such an error (~ 0.2 Å), often found in other state-of-the-art local-density calculations, can be tolerated in models of cohesion of pure semiconductors (where one is concerned with the cohesive energy of the order of 5 eV), a similar error in Δa, with its attendant effect on $\Delta H^{(n)}$ can be significant for the weakly bound octet semiconductor alloys (where formation enthalpies $|\Delta H^{(n)}|$ are only of the order of ~ 0.01 eV). Correcting for the underestimation of Δa, we found[8] Δa-corrected $\Delta H^{(n)}$ values of -0.24, -0.29, and -0.24 kcal/mol for $n = 1$, 2, and 3, respectively in $\text{Ga}_n\text{In}_{4-n}\text{P}_4$. In particular, $\Delta H^{(2)} = -0.29$ kcal/mol is remarkably similar to the empirically scaled $\Delta H^{(2)}$ value of -0.30 kcal/mol used by SMZ and explains the success of their values in reproducing the experimental $\Delta H^{(D)}(x)$.

SMZ have demonstrated (see also Ref. 9) that the excess energies $\Delta E^{(n)}(a)$ of ordered phases could be decomposed into a chemical (chem) piece (positive or negative) and into an (always positive) microscopic strain (MS) piece

$$\Delta E^{(n)}(a) = \Delta E^{(n)}_{\text{chem}}(a) + \Delta E^{(n)}_{\text{MS}}(a) \ , \tag{3}$$

where the equilibrium value of $\Delta E^{(n)}(a_{\text{eq}})$ is the formation enthalpy $\Delta H^{(n)}$ of the ordered phase $A_nB_{4-n}C_4$ from $nAC + (4-n)BC$. Ordered phases can become stable[6] ($\Delta H^{(n)} < 0$) when the (generally nonpairwise-additive) chemical interactions (charge transfer, and polarization resulting from anion displacements) outweigh the elastic strain energies.[1] This was subsequently found to be the case also for[10(a)] CdTe-MnTe and[10(b)] Si-C. Instead, PC have replaced the negative $\Delta E^{(n)}_{\text{chem}}$ used by SMZ with positive (and pairwise-additive) energies $n(4-n)w$ (with $w > 0$). Having artificially set all bond angles in the alloy to equal the ideal tetrahedral angles, PC underestimate the true strain energies ΔE_{MS}. They compensate for this by using overly positive chemical energies w. This was done[2] by using the empirical w values determined from the disordered phase (their Ref. 9) which, by Eq. (2) here, is always higher in enthalpy than the ordered phase. Calculating the probabilities $P^{(n)}(x,T)$ by the quasichemical approach with pairwise additive chemical energies (this is a less adequate version of the quasichemical model previously used by Chen and Sher,[11] who retained many-atom interactions), PC show that they could reproduce the results of the scaled SMZ model: in particular the excess free energy of the disordered phase [their Fig. 4(c)] and probabilities [their Fig. 4(a)]. They proceeded to analyze in detail this "surprising"[2] agreement, concluding that their own "primitive empirical ansatz . . . works at least as well as other theories developed until now."[2] Their results are, however, a trivial manifestation of the fact that excess free energies of disordered phases are insensitive to changes (e.g., even by 100%) in $\Delta E^{(n)}_{\text{chem}}$, since they are dominated by elastic energies $\Delta E^{(n)}_{\text{MS}}(a)$. This was amply demonstrated by Martins and Zunger[12] and by Chen and Sher[13] and was further shown in Ref. 8 where virtually the same free energies quoted by PC were independently obtained using negative chemical energies [and nonrandom cluster probabilities $P^{(n)}(x,T)$]. Furthermore, since PC underestimate strain energies but correspondingly overestimate chemical energies (relative to SMZ), agreement with the results of SMZ cannot testify, by itself, to the adequacy of PC's model.

There is, however, another property which *is* sensitive to the sign and magnitude of $\Delta E^{(n)}_{\text{chem}}$: the existence or nonexistence of either stable or metastable ordered phases in the phase diagram. Whereas PC have selected $\Delta E^{(n)}_{\text{chem}} > 0$ since[2] they "do not share their (SMZ's) enthusiasm about the possibility of growing ordered phases," the fact is that such ordered phases were recently grown and observed directly.[3-5] Whereas the observation of spontaneous ordering[3-5] is suggestive of a stable phase, it does not prove that the phase is not metastable. PC's phase diagram does not exhibit either stable or metastable long-range ordered phases (instead, stable mixed phase regions are reported near $x = \frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$), hence their model simply does not explain any of the new experimental observations.[3-5] To check in detail the predictions of SMZ's model, one of the present authors and his co-workers[8] have recently calculated the phase diagram of GaP-InP using the Δa-corrected $\Delta H^{(n)}$ values [which are virtually indistinguishable from SMZ's scaled value; compare Fig. 1(a) in Ref. 8 with Fig. 3(b) of Ref. 1], and using the cluster variation method[14] (CVM), retaining up to four-body interactions [Fig. 1(a)]. These results support SMZ's point: even if $\Delta H^{(D)} > 0$, in agreement with experiment, the calculated phase diagrams (using $\Delta E^{(n)}_{\text{chem}} < 0$) show [Fig. 1(a) here] that stable long-range ordered phases are possible. In contrast, the calculation of PC [their Fig. 3(b)] misses those phases al-

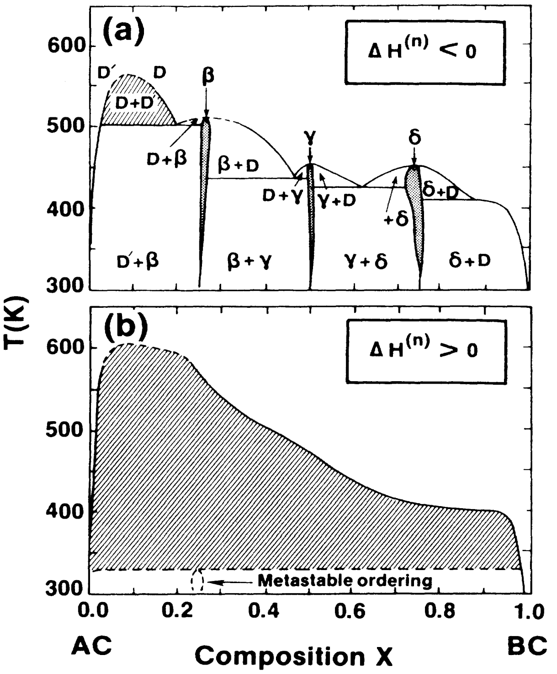

FIG. 1. Calculated phase diagrams for $AC=\mathrm{GaP}$ and $BC=\mathrm{InP}$, using the Cluster Variation Method in the tetrahedron approximation: (a) Using the Δa-corrected enthalpies of formation $\Delta H^{(n)}$, virtually identical (see text) to those used by SMZ in Ref. 1; (b) using positive enthalpies of formation. Dashed areas denote miscibility gaps, where two disordered phases coexist. Shaded areas in (a) denote ordered phases. $\beta=\mathrm{Ga_3InP_4}$, $\gamma=\mathrm{GaInP_2}$, $\delta=\mathrm{GaIn_3P_4}$, and D denotes disordered. (a) is from Ref. 8. Note the metastable ordered phase observed at stoichiometric compositions for $\Delta H^{(n)}>0$.

together. [Note also that our Fig. 1(a) here shows that the ordering temperatures $T_O \simeq 500$ K are indeed lower than conventional growth temperatures by at least 200 K, in agreement with SMZ but in sharp conflict with the statement of PC that our T_O is 1600 K.]

Given the fact that the mixing enthalpy $\Delta H^{(D)}(x)$ is not very sensitive to the details of the cluster energies $\Delta E^{(n)}(a)$ (but rather to the sum of chemical and strain energies), we seek to identify a property (e.g., existence or nonexistence of long-range ordered phases) which can discriminate PC's model (positive chemical energies) from ours (negative chemical energies). To do so we have repeated the calculation of the phase diagram of GaP-InP using $\Delta H^{(n)}>0$ but SMZ's negative chemical energies. We find [Fig. 1(b)] that inside the broad miscibility gap (dashed areas) there exist long-range ordered metastable phases at stoichiometric compositions. We have verified that these phases (having higher free energies than the two-phase mixture, but lower free energy than a single-phase disordered alloy) disappear if $\Delta E^{(n)}_{\mathrm{chem}}>0$. While it still remains to be seen whether the observed long-range ordering[3-5] corresponds to stable [Fig. 1(a)] or metastable [Fig. 1(b)] phases, the fact remains that PC's model shows neither, whereas the present model shows that both are possible (depending on small changes in $\Delta H^{(n)}$ of the order of $\pm|\Delta H^{(n)}|\simeq 0.01$ eV which is also the accuracy limit of our calculation).

Since both PC's modeling of the energetics and the (quasichemical[13]) approach used by them for solving the statistical problem miss the stable ordered phases of Fig. 1(a) as well as the metastable phases of Fig. 1(b), we are inclined to think that their methodology might be too crude for treating the delicate phenomena of ordering and metastability in weakly bound alloys.

In summary, (i) The unscaled $\Delta H^{(n)}$ values of SMZ should not be used. As shown by SMZ, the scaled values produce good agreement with the measured thermodynamic data; PC's results do not alter or add to this conclusion. (ii) The need for scaling $\Delta H^{(n)}$ of SMZ arises mostly from the underestimation of the lattice mismatch Δa (and to a lesser extent by "Brillouin-zone effects"[1] present in ordered crystals but not in isolated clusters). When Δa is fixed no empirical scaling is necessary. (iii) Since the measured excess enthalpy of mixing of lattice-mismatched semiconductor alloys reflects mostly elastic effects, it cannot be used to accurately establish chemical energies. Therefore, chemical energies cannot be reliably extracted from data on the disordered phase, as PC do. (iv) Long-range ordering (stable or long-lived metastable) in semiconductor alloys is indisputably observed. PC's calculation does not show any long-range ordering. Our calculation shows both stable (when $\Delta H^{(n)}<0$) and metastable (when $\Delta H^{(n)}>0$ and elastic energies are large) ordering. We conclude that (v) PC's methodology of selecting chemical energies (rather than calculating them from a microscopic model for, e.g., ordered structures) and using a highly simplified statistical solution does not appear to have the accuracy needed to compute order-disorder phenomena in weakly bound alloys, as evidenced by comparing their phase diagram with our recent results.

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[3] H. Nakayama and M. Fujita, in *Gallium Arsenide and Related Compounds, 1985*, Vol. 79 of *Institute of Physics Conference Series*, edited by M. Fujimoto (Institute of Physics, Bristol and London, 1986), p. 289; T. S. Kuan, T. F. Kuech, W. I. Wang, and E. L. Wilkie, in *Proceedings of the 7th International Conference on Ternary and Multinary Compounds*, edited by S. K. Deb and A. Zunger (Materials Research Society, Pittsburgh, 1987), p. 325, and to be published.

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[6] We use here the terms "stability" ("instability") to imply $\Delta H<0$ ($\Delta H>0$), i.e., whether the alloy has a lower (higher) enthalpy relative to equivalent amounts of its binary constit-

uents. Stability with respect to a two-phase mixture (miscibility gap) depends instead on the composition derivatives of the free energy. This is treated in detail in our phase-diagram calculations (e.g., Ref. 8).

[7] Evidence for spontaneous partial ordering in non-zinc-blende semiconductor alloys was also presented for Cd_3As_2-Zn_3As_2 by G. A. Castellion and L. C. Beegle, J. Phys. Chem. Solids **26**, 767 (1965); for Cd_3P_2-Zn_3P_2 by K. Masumoto, S. Isomura, and K. Sasaki, Phys. Status Solidi A **6**, 515 (1971) and by J. Berak and Z. Pruchnik in Rocz. Chem. **45**, 1425 (1971); and for InAs-CdTe by E. N. Khabarov, Acta Crystallogr. Sect. A **31**, S92 (1975). Here and in Ref. 1 we treat only the simpler, zince-blende-derived structures.

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[12] J. L. Martins and A. Zunger, Phys. Rev. B **30**, 6217 (1984).

[13] A. B. Chen and A. Sher, Phys. Rev. B **32**, 3695 (1985).

[14] The quasichemical approach with pair interactions used by PC is known to drastically overestimate critical temperatures, whereas the Cluster Variation Method with many-body interactions (used here and in Ref. 8) is far closer to the nearly exact results for the three-dimensional Ising model (Monte Carlo or high-temperature expansion); see D. de Fontaine in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 73 and C. M. Van Baal, Physica **64**, 571 (1973). Indeed, as PC stated (Ref. 2), "approximations inherent to the quasichemical approximation make this method not particularly suitable for phase diagram calculations," yet it is this method which forms the sole basis for their discussions in their comment and all of their previous work (Ref. 2 in their comment).