

First-Principles Calculation of Semiconductor-Alloy Phase Diagrams

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Combining first-principles self-consistent local-density total-energy calculations with the cluster variation method, we calculate the phase diagram of a semiconductor alloy. It is demonstrated that inclusion of both elastic and chemical interactions in the total-energy functional leads to new features, including the appearance in the same phase diagram of ordering and phase separation, and strain stabilization of both stable and metastable ordered phases.

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Reaction of a compound A with another B leads in general to the formation of ordered stoichiometric compounds A_nB_m , disordered solid solutions A_xB_{1-x} of composition x , and/or phase separation. Correlating the boundaries of these different regions in the temperature-composition (T, x) plane (or even their existence) with the microscopic properties of the constituents A and B and their interactions has been an ongoing challenge both in metallurgy¹⁻⁴ and in semiconductor physics.⁵⁻⁹ The enormous data base of experimental phase diagrams^{10,11} presents, however, a number of conceptual challenges to contemporary theoretical approaches.⁴⁻⁹ These can be best illustrated by consideration of the physical content of the energies appearing in a general binary phase-diagram problem.

Consider perfectly ordered stoichiometric structures $\{A_nB_m\}$ ($n+m = \text{const}$) formed by distribution of A and B on a fixed lattice. Each structure (n, m) can be characterized by its lattice vectors $\{a\}$ and the excess total energy as a function of $\{a\}$ (measured with respect to equivalent amounts of the constituents at their equilibrium lattice parameters a_A and a_B)

$$\Delta E^{(n)}(a) = E[A_nB_m; \{a\}] - nE[A; a_A] - mE[B; a_B]. \quad (1)$$

The formation enthalpy of each perfectly ordered phase is the equilibrium (eq) value of Eq. (1), i.e., $\Delta H^{(n)} \equiv \Delta E^{(n)}[a_{\text{eq}}^{(n)}]$. If we represent a *substitutionally disordered* (D) phase on a lattice with lattice parameter $a(x)$ as a superposition, with probabilities $P^{(n)}(x, T)$, of all permissible local atomic arrangements^{12,13} exhibited by $\{A_nB_m\}$, the excess free energy of the disordered phase (at zero pressure) is¹³

$$\Delta \mathcal{F}^{(D)}(x, T) = \Delta H^{(D)}(x, T) - T\Delta S^{(D)}(x, T),$$

where $\Delta S^{(D)}$ is the excess configurational entropy [zero if $P^{(n)}(x, T)$ were random], and $\Delta H^{(D)}(x, T)$ is the mixing enthalpy (zero in the absence of interactions), given by

$$\Delta H^{(D)}(x, T) = \sum_n P^{(n)}(x, T) \Delta E^{(n)}[a(x)]. \quad (2)$$

Here, $P^{(n)}(x, T)$ and $\{a(x)\}$ are those that minimize¹³ the alloy free energy $\mathcal{F} = \mathcal{F}_0 + \Delta F^{(D)}$ at each (x, T) and the subscript 0 denotes the ideal value.

One can conceptualize the physical content of the interaction energy curves $\Delta E^{(n)}(a)$ for a perfectly ordered phase A_nB_m by considering its formation from the constituents A and B in two steps.¹⁴ *First*, place $n+m$ A atoms on the sites of A_nB_m at the equilibrium lattice parameters $a_{\text{eq}}^{(n)}$ of A_nB_m (and the same for B atoms). Since the equilibrium volumes of pure A and pure B are now changed, this step involves investment of an elastic energy denoted by $\Delta F[nA, mB, a_{\text{eq}}^{(n)}]$. *Second*, "flip" the necessary number of A atoms in A_nA_m and B atoms in B_nB_m on this fixed, "prepared" lattice to create A_nB_m . (If in addition to A and B there is also a third, common sublattice C , let this sublattice relax to its equilibrium position in $A_nB_mC_{n+m}$). The second step hence involves "spin-flip" substitution (or "chemical") energies $\varepsilon^{(n)}$ associated with interactions between A and B (e.g.,¹⁴ charge transfer, polarization, spin coupling) on a *fixed* A, B lattice.¹⁵ This is the only term considered in conventional coherent lattice models of phase diagrams.^{12,13} The formation enthalpy of the ordered compound is

$$\Delta H^{(n)} \equiv \Delta F[nA, mB, a_{\text{eq}}^{(n)}] + \varepsilon^{(n)}. \quad (3)$$

If there is no lattice mismatch (vanishing $\Delta a = a_A - a_B$), then $\varepsilon^{(n)}$ simply equals $\Delta H^{(n)}$. Using $\Delta E^{(n)}(a) = \varepsilon^{(n)} + [\Delta E^{(n)}(a) - \varepsilon^{(n)}]$ in Eq. (2), we have

$$\Delta \mathcal{F}^{(D)}(x, T) = \sum_n P^{(n)}(x, T) \varepsilon^{(n)} + G[a(x)] - T\Delta S^{(D)}, \quad (4)$$

where $G[a(x)]$ is the average alloy elastic energy.¹⁶ The first two terms of Eq. (4) reflect the dual coordinates used in phenomenological models of solubility,^{2,8} compound stability,^{1,3,17} and mixing enthalpies,³ e.g., the Darken-Gurry² and Miedema³ models.

Equations (3) and (4) can serve to illustrate many of the various approaches adopted in the past to the phase-diagram program. *First*, contemporary models of semiconductor phase diagrams⁵⁻⁹ have generally ignored the n -dependent chemical energies $\varepsilon^{(n)}$, retaining various ap-

proximations to the elastic energy $G[a(x)]$ alone and setting $\Delta S^{(D)}=0$. This description⁵⁻⁷ precludes the existence of any ordered intermediate phases or order-disorder transformations, in agreement with then-available data,⁵ but in apparent conflict with recent observations.¹⁸ *Second*, a large class of models addressing coherent phase diagrams (i.e., on the rigid lattice^{12,13,19} common to A , B , and A_xB_{1-x}) have naturally ignored the elastic energy $G[a(x)]$, tacitly assuming $\Delta a=0$. The application of this general approach to the actual solid solutions has three significant consequences. (i) Tendencies of phase separation [$\varepsilon^{(n)} > 0$] and ordering [$\varepsilon^{(n)} < 0$] in the same phase diagram become mutually exclusive (in conflict with the data^{10,11,18}), unless one introduces a rather artificial *ad hoc* mix of positive and negative $\varepsilon^{(n)}$'s. (ii) In identifying $\varepsilon^{(n)}$ alone with the enthalpy of formation $\Delta H^{(n)}$ of the perfectly ordered phase [Eq. (3)], it became impossible to reconcile the observed order-disorder critical temperatures [decided by the $\varepsilon^{(n)}$'s] with thermodynamic data [e.g., $\Delta H^{(n)}$]. For example, adjusting¹⁹ $\varepsilon^{(2)}$ of the CuAu system to the observed¹⁰ order-disorder critical temperature at $x = \frac{1}{2}$ one obtains $\varepsilon^{(2)} = -5.3$ kcal, in substantial disagreement with $\varepsilon^{(2)} \equiv \Delta H^{(2)} = -2.1$ kcal measured directly.¹⁰ (iii) These approaches require that if $\Delta H^{(D)} > 0$ (as is the case for all isovalent semiconductor alloys^{5,6}) no ordering can exist, and conversely, if ordering exists,¹⁸ one must have $\Delta H^{(D)} < 0$, both in conflict with the data. Recent calculations,⁴ combining statistical methods with the calculation of the electronic pieces of $\varepsilon^{(n)}$, have clearly illustrated this point.

To illustrate the consequences of the interplay between elastic and chemical ordering energies for phase diagrams, we have combined a first-principles calculation^{14,20} of $\Delta E^{(n)}(a)$ for the perfectly ordered structures $\{A_nB_{4-n}C_4\}$ with a cluster-variation method¹³ (CVM) calculation of the probability functions $P^{(n)}(x, T)$ and the many-body (correlated) configurational entropies $\Delta S^{(D)}(x, T)$. We hence treat chemical and elastic effects on the same footing, including both in the internal energy and in the entropy. Using the $\text{In}_x\text{Ga}_{1-x}\text{P}$ semiconductor alloy as an example, we calculate $\Delta E^{(n)}(a)$ of Eq. (1) for the five $\text{In}_n\text{Ga}_{4-n}\text{P}_4$ Landau-Lifshitz fcc structures^{13,14} [corresponding to the ordering vectors¹³ (1,0,0)]. For $n=0$ and $n=4$ we use the $F\bar{4}3m$ zincblende structure (clusters of Ga_4 and In_4 , respectively), for $n=1$ and $n=3$ the $P\bar{4}3m$ luzonite form (Ga_3In and GaIn_3 clusters, respectively), whereas for $n=2$ we use the $P\bar{4}m2$ structure (the Ga_2In_2 cluster). We retain only fourfold coordinated structures which obey the octet rule (i.e., have eight valence electrons per anion-cation pair). $\Delta E^{(n)}(a)$ are calculated self-consistently from first principles in the local-density formalism, with use of the momentum-space pseudopotential total-energy representation and a plane-wave basis set.²⁰ For each n and lattice parameter a we have also optimized the cell-

internal coordinates, i.e., the position of the phosphorus atom inside each tetrahedron; this was essential to obtain minimum-strain ordered structures.¹⁴ The minima of $\Delta E^{(n)}(a)$ give the equilibrium lattice parameters $a_{\text{eq}}^{(n)}$ of the perfectly ordered phases and their enthalpies $\Delta H^{(n)}$. We correct²¹ for our ~ 0.2 -Å underestimation¹⁴ of $\Delta a = a_{\text{InP}} - a_{\text{GaP}}$ (hence, the elastic energies), by using the observed value¹¹ of 0.42 Å. While our CVM calculation does not utilize the separation of variables indicated in Eq. (3) [we use directly $\Delta E^{(n)}(a)$ of Eq. (1)], for purposes of analysis we display this decomposition by calculating separately the elastic energy at equilibrium $\Delta F[nAC, (4-n)BC, a_{\text{eq}}^{(n)}]$ for each ordered structure from an elastic bond-bending and bond-stretching valence-force-field model,¹⁴ and define $\varepsilon^{(n)}$ from Eq. (3) using our $\Delta H^{(n)}$. The resulting $\Delta E^{(n)}(a)$ curves are depicted in Fig. 1(a), and exhibit stable ordered structures [i.e.,²¹ $\Delta H^{(n)} < 0$] with $\varepsilon^{(n)}$ values of -2.57 , -3.58 , and -2.88 kcal/atom-pair, and $\Delta F[a_{\text{eq}}^{(n)}]$ values of 2.33, 3.29, and 2.64 kcal/atom-pair, for $n=1, 2$, and 3, respectively. Elastic energies are clearly nonnegligible even at equilibrium. Furthermore, $\Delta E^{(n)}(a)$ can *change sign* as a function of a , a feature missing from both elastic⁵⁻⁹ and simple Ising^{13,19} models.

From $\{\Delta E^{(n)}(a)\}$ we calculate, using the CVM, the enthalpies and entropies of all ordered and disordered

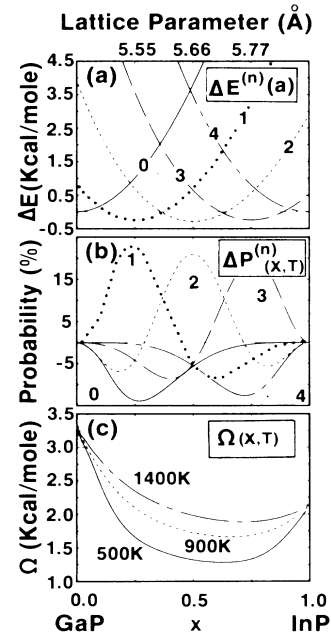


FIG. 1. (a) Excess internal energies [Eq. (1)] of the ordered phases, (b) the difference between actual and random cluster probabilities at $T=600$ K, and (c) the interaction parameter of the disordered alloy. [Thermal expansion, neglected here, removes the degeneracy of the $\Omega(x, T)$ curves at $x=0$ and $x=1$.] One mole is taken here as an atom pair.

phases as functions of x and T , minimizing $\mathcal{F}(x, T)$ with respect to volume to find $a(x, T)$.

The calculated thermodynamic properties [Figs. 1(b) and 1(c)] and phase diagram [Fig. 2(a)] obtained from the data of Fig. 1(a) point to a number of qualitative features. (i) Despite an ever *positive* $\Delta H^{(D)}$ of the disordered phase evident in Fig. 1(c) [a calculated interaction parameter $\Omega(x, T) \equiv \Delta\mathcal{F}^{(D)}(x, T)/x(1-x)$ at $T=1400$ K and $x=0.5$ of 2.0 kcal/mole, compared with the value 3 ± 1 kcal/mole inferred^{5,6} from high-temperature data], ordered phases [shaded areas in Fig. 2(a)] are predicted to be stable at low temperatures [since $\Delta H^{(n)} < 0$] in contradiction with predictions of all elastic models,⁵⁻⁹ but in agreement with recent observations of the A_3BC_4 and AB_3C_4 (in InGaAs^{18a}) and ABC_2 (in GaSbAs^{18b}) ordered phases and with the earlier predictions of Srivastava, Martins, and Zunger.¹⁴ This confirms the conclusions of Ref. 14: Whereas the dominance of chemical interactions over elastic ones can stabilize at $a_{eq}^{(n)}$ some ordered phases [i.e., $\Delta H^{(n)} < 0$] each having a *single* type of local atomic arrangement, the elastic energy $G[a(x)]$ can destabilize the disordered system (which has *several* local atomic arrangements), since at each $a(x)$ one or more of these local arrangements are strained relative to the ideal $a_{eq}^{(n)}$. Consequently, (ii) this elastic energy tends to favor, at each alloy composition x , those local atomic arrangements which are least strained

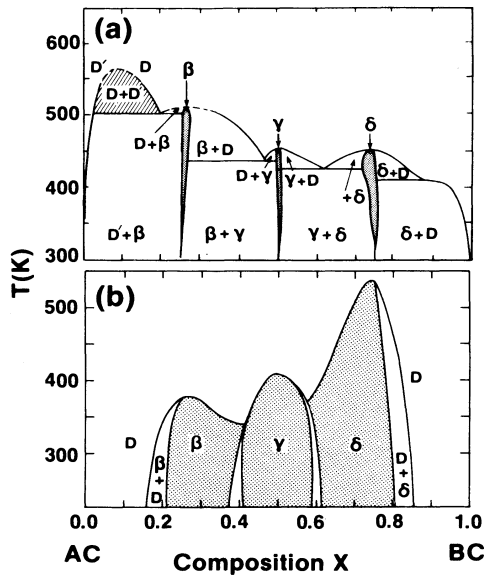


FIG. 2. CVM phase diagrams in the tetrahedron approximation for (a) first-principles (elastic+chemical) energies of Fig. 1(a), and (b) chemical energies only. Shaded areas represent single ordered phases; dashed areas, miscibility gaps of two disordered phases. D , β , γ , and δ denote disordered, A_3BC_4 ($n=1$), ABC_2 ($n=2$), and AB_3C_4 ($n=3$) phases, respectively.

at the corresponding lattice parameter $a(x)$. This is evidenced by the substantial departure from randomness ("clustering") of $P^{(n)}(x, T)$ for the imperfectly disordered phase; e.g., Fig. 1(b) exhibits a $\sim 20\%$ enhancement at $T=600$ K of the $n=1, 2, 3$ species at $x = \frac{1}{4}, \frac{1}{2}$, and $\frac{3}{4}$, respectively. This strain-induced selection of species (not to be confused with $\epsilon^{(n)}$ -induced long-range order) is likely to be quenched in as the sample is cooled, leading to often observed^{5,11} but unexplained growth-temperature-dependent semiconductor alloy properties. This clustering phenomenon might be pertinent to partial order observed in low-temperature-grown samples.¹⁸ (iii) This (x, T) -dependence of $P^{(n)}(x, T)$ introduces similar dependences in $\Delta\mathcal{F}^{(D)}$ through Eq. (4) evident in Fig. 1(c). While absent in all regular solution models,⁵⁻⁸ such hitherto unexplained dependence had to be incorporated phenomenologically in detailed fits to measured phase diagrams.⁹ These models⁹ miss, however, the strong *composition* variation of $\Omega(x, T)$ [Fig. 1(c)], resulting from the different bulk moduli (hence, elastic energy) of the constituents. (iv) Despite the all-attractive ordering energies $\epsilon^{(n)}$, a miscibility gap for disordered phases [dashed area in Fig. 2(a)] can appear in the same phase diagram with ordering (shaded areas), in contradiction with the predictions of simple Ising models with fixed interactions.^{12,13} This often observed phenomenon^{10,18} manifests the system's ability to reduce strain at low temperatures [Fig. 1(c)] through selection of the least strained species [Fig. 1(b)], compared with an entropy-favored (but strained) nearly random distribution $P^{(n)}(x, T)$ at higher temperatures.

To analyze the consequences of models which retain in $\Delta E^{(n)}$ only chemical ordering energies,^{12,13,19} we show in Fig. 2(b) the phase diagram calculated with the same (attractive) $\{\epsilon^{(n)}\}$ of Fig. 2(a), but omitting the elastic energy $G(a)$. Comparison of Figs. 2(a) and 2(b) illustrates the two main effects of elastic energy on systems with attractive chemical interactions. *First*, strain leads to *stabilization of ordered stoichiometric compounds*, as evidence in Fig. 2(a) by narrower single-phase domains (shaded areas) and broader two-phase domains relative to Fig. 2(b). While this principle was recognized long ago in structural chemistry (e.g., Laves phases are stabilized by large mismatch in bond lengths¹⁷), simple alloy models,^{3,5-9} have invariably characterized atomic size mismatch as a universally destabilizing factor. *Second*, the elastic energy is seen to lead to a miscibility gap where two disordered phases exist [D and D' in Fig. 2(a), appearing near the GaP end due to its higher bulk modulus]. This clarifies the known phenomenological correlations⁸ between miscibility temperatures and size-mismatch-induced elastic strain energy.

Since for many compounds there is an effective cancellation between chemical and elastic effects [Eq. (3)] to yield a rather small^{3,10,11} formation enthalpy $\Delta H^{(n)}$ [e.g., in isovalent semiconductors,^{5,6} it can be as small as the

errors in the calculated total energies²¹], it seems sensible to explore the phase diagram as a function of $\Delta H^{(n)}$. Remarkably, we find that for positive but sufficiently small $\Delta H^{(n)}$'s (e.g., below $\Delta F[nA, mB, a_{\text{eq}}^{(n)}]$) there exist low-temperature *metastable ordered phases* $A_n B_{4-n} C_4$ at stoichiometric compositions inside the miscibility gap. While the free energy of those ordered phases is higher than that of the mixture of two disordered phases, it is still *lower* than the energy of the single-phase disordered alloy. Hence if phase separation is kinetically inhibited at low temperatures (e.g., by coherent strain effects⁶ or insufficient diffusivity), these ordered phases would be quenched in. It is a distinct possibility that some of the ordered phases reported to occur inside miscibility gaps at low temperatures¹⁸ indeed correspond to such metastably quenched phases.

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¹*Phase Stability in Metals and Alloys*, edited by P. S. Rudman, J. Stringer, and R. I. Jaffe (McGraw-Hill, New York, 1967).

²L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals* (McGraw-Hill, New York, 1953).

³A. R. Miedema, F. R. de Boer, and P. F. de Chatel, *J. Phys.* **F 3**, 1558 (1973).

⁴C. Sigli, M. Kosugi, and J. M. Sanchez, *Phys. Rev. Lett.* **57**, 253 (1986); D. D. Johnson, D. M. Nicholson, F. J. Pinski, B. L. Gyorffy, and G. M. Stocks, *Phys. Rev. Lett.* **56**, 2088 (1986); J. W. D. Connolly and A. R. Williams, *Phys. Rev. B* **27**, 5169 (1983).

⁵M. B. Panish and M. Ilegems, *Prog. Solid State Chem.* **7**, 39 (1972).

⁶G. B. Stringfellow, *J. Cryst. Growth* **27**, 21 (1974).

⁷P. A. Fedders and M. W. Muller, *J. Phys. Chem. Solids* **45**, 685 (1984).

⁸L. M. Foster, *J. Electrochem. Soc.* **121**, 1662 (1974).

⁹R. F. Brebrick, C. H. Su, and P. K. Liao, in *Deep Levels*,

GaAs, Alloys, Photochemistry, edited by R. K. Willardson and A. C. Beer, *Semiconductors and Semimetals Vol. 19* (Academic, New York, 1983), p. 171.

¹⁰R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelly, *Selected Values of the Thermodynamic Properties of Binary Alloys* (Wiley, New York, 1963).

¹¹*Landolt-Börnstein: Numerical Data and Functional Relationships*, edited by O. Madelung (Springer-Verlag, Berlin, 1982), Vol. 17, Pts. a and b.

¹²D. M. Burley, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1972), p. 329.

¹³D. De Fontaine, in *Configurational Thermodynamics of Solid Solutions*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull, *Solid State Physics Vol. 34* (Academic, New York, 1979), p. 73.

¹⁴G. P. Srivastava, J. L. Martins, and A. Zunger, *Phys. Rev. B* **31**, 2561 (1985).

¹⁵In the terminology of Ref. 14, we have $\varepsilon^{(n)} = \Delta E_{VFF}[a_{\text{eq}}^{(n)}] + \Delta E_{CE}[a_{\text{eq}}^{(n)}] + \Delta E_{\text{pol}}[a_{\text{eq}}^{(n)}]$, $\Delta F[nA, mB, a_{\text{eq}}^{(n)}] = \Delta E_{VD}[a_{\text{eq}}^{(n)}]$. Other decompositions will be discussed elsewhere.

¹⁶If the elastic energy $\Delta E^{(n)}(a) - \varepsilon^{(n)}$ depends linearly on composition n (e.g., like the pure deformation energy $\Delta F[nA, mB, a]$), then $G[a(x)]$ is temperature independent. This is so when the equilibrium volume does not depend on the state of order.

¹⁷E.g., article by O. Kubaschewski in Ref. 1, p. 63, and Fig. 3.

^{18a}H. Nakayama and H. Fujita, in *Gallium Arsenide and Related Compounds—1985*, edited by M. Fujimoto, IOP Conference Proceedings No. 79 (Institute of Physics, Bristol and London, 1986).

^{18b}H. R. Jen, M. J. Cherng, and G. B. Stringfellow, *Appl. Phys. Lett.* **48**, 1603 (1986).

¹⁹R. Kikuchi, J. M. Sanchez, D. De Fontaine, and H. Yamauchi, *Acta Metall.* **28**, 651 (1980).

²⁰J. Ihm, A. Zunger, and M. L. Cohen, *J. Phys. C* **12**, 4409 (1979).

²¹In Ref. 14 the *predicted* Δa was used (underestimating the observed value). This resulted in $\Delta H^{(2)} = -1.48$ kcal/mole. To fit the observed^{5,6} $\Delta H^{(D)} = 0.75 \pm 0.25$ kcal at $x = \frac{1}{2}$, a scaling down of $\Delta H^{(2)}$ was needed.¹⁴ Use here of the observed Δa instead of scaling $\Delta H^{(2)}$ results in $\Delta H^{(n)}$ of -0.24 , -0.29 , and -0.24 kcal/mole for $n = 1, 2$, and 3 , respectively, and $\Delta H^{(D)}(\frac{1}{2}) = +0.5$ kcal/mole at 1400 K [Fig. 1(c)] in good agreement with experiment, and with the empirically scaled results of Ref. 14.