

Molecular simulation study of miscibility in $\text{In}_x\text{Ga}_{1-x}\text{N}$ ternary alloys

Jhumpa Adhikari and David A. Kofke^{a)}

Department of Chemical Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260-4200

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Monte Carlo molecular simulation is applied to calculate miscibility behavior of a valence force-field model of InGaN alloy as a function of temperature. Calculations find that the upper critical solution temperature is 1550 K, in good agreement with previous studies based on regular solution theory. The simulations show that the excess entropy is small, and the excess enthalpy is insensitive to temperature, indicating that the regular-solution treatment is appropriate for this system. © 2004 American Institute of Physics. [DOI: 10.1063/1.1686897]

InGaN alloys exhibit a miscibility gap, meaning that at certain conditions an alloy of a given composition will be thermodynamically more stable if it separates into two coexisting bulk phases, one richer in InN and the other in GaN. This behavior is very important practically. Strategies and protocols for synthesizing the alloy must work with or around the tendency for it to phase separate. Furthermore, the drive to phase separate can manifest itself more subtly in the microstructure of the material, promoting the formation of domains of InN- or GaN-rich regions that can profoundly impact the optical properties. For the epitaxial manufacture of InGaN crystals, surface behavior is most important, but there is nevertheless interest in the thermodynamics of the bulk-phase crystal, as it is simpler to study and not without relevance to the surface behavior.

Although there is clear experimental evidence for phase separation in InGaN,¹ the nature of solid-phase immiscibility makes this phenomenon difficult to characterize quantitatively. Instead, quantitative insight has been obtained through the application of molecular-thermodynamic modeling. The state of the art in modeling bulk-phase $\text{In}_x\text{Ga}_{1-x}\text{N}$ miscibility employs a molecular model to characterize the interactions of the constituent atoms, which is used to determine infinite-dilution, zero-temperature (energy minimized) strain energies for InN in GaN and vice versa. These two strain energies are averaged and the result is input to simple regular-solution treatment to extract the thermodynamic behavior. The seminal work in this direction was performed by Ho and Stringfellow,² who used a valence force-field (VFF) model³ for the interatomic interactions. Their influential study concurred that the alloy has a miscibility gap at normal growth temperatures, and is unstable over the entire range of compositions that are relevant to the manufacture of photonic and electronic devices; in particular they report an upper solution critical temperature (UCST) of 1505 K. A number of other studies have followed this work,^{4,5} and they attempt to improve upon it primarily through application of better models for the interatomic interactions. In almost all cases the

treatment employs regular-solution theory and/or zero-temperature strain energies to extract the miscibility behavior from the molecular model.

Aside from the use of the VFF potential, the Ho–Stringfellow modeling approach contains two key approximations that are largely untested. First is the neglect of the effect of temperature on the infinite-dilution strain energies (or more appropriately, free energies). The temperature dependence of the miscibility gap is of central concern in these calculations, and in the Ho–Stringfellow treatment the only connection between the thermodynamics and the molecular model is made through this strain energy. Consequently, it is reasonable to be concerned about the response of the infinite-dilution free energy to changes in temperature. Second is the use of the regular-solution model to extract the thermodynamic behavior from the molecular model. The regular-solution model is derived by assuming that the system forms a completely random mixture,⁶ with no fluctuations or correlations in the arrangements of the In or Ga atoms. Normally the effect of such correlations would be to lower the critical temperature—a system that is allowed to partially relax via compositional correlations will remain miscible to lower temperatures than one that is forced to choose between perfect homogeneity or phase splitting. Thus we should expect that the Ho–Stringfellow calculation yields only an upper bound to the critical temperature.

Molecular simulation⁷ is the appropriate tool to use to test the approximations in the Ho–Stringfellow treatment. Molecular simulations performed for the VFF model can provide exact data for the thermodynamic behavior exhibited by the model. By comparing these data to the Ho–Stringfellow treatment, based on the same model, we can determine if the strain-energy and regular-solution approximations are valid. What we cannot say in this comparison is whether the VFF model is providing a good description of the interatomic interactions. However, any comparison of simulation data to experiment will provide an unambiguous test of the molecular model because the simulation involves no other uncontrolled source of approximation.

Accordingly, we performed Monte Carlo (MC) molecular simulations⁷ of cubic zincblende $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy using the VFF model^{2,8} as the interaction potential between a ni-

^{a)}Electronic mail: kofke@eng.buffalo.edu

trogen atom and its four indium or gallium neighbors. Although the hexagonal, wurzite structure is more common for this system, we examined the cubic form to adhere better to the Ho–Stringfellow study. They suggest that the difference between the phase behavior of the cubic and hexagonal forms is not expected to be large. In the VFF theory, for a ternary alloy of the type $A_xB_{1-x}C$ like the one considered in this article, the strain energy, E_m , is the sum of two- and three-body contributions which take into consideration the bond stretching and bond bending, respectively,

$$E_m = \frac{3}{8} \sum_{i=1}^4 \alpha_i \frac{(d_i^2 - d_{i0}^2)^2}{d_{i0}^2} + \frac{6}{8} \sum_{i=1}^4 \sum_{j=i+1}^4 \frac{\beta_i + \beta_j}{2} \frac{(\mathbf{d}_i \cdot \mathbf{d}_j + d_{i0}d_{j0}/3)^2}{d_{i0}d_{j0}}, \quad (1)$$

where d_i is the distance between the central atom C and a corner atom A or B in the tetrahedron, d_{i0} is the equilibrium bond length in the binary compound AC or BC (4.52 for GaN Å and 4.98 Å for InN), α is the bond stretching force constant force (81.09 N/m for GaN and 63.5 N/m for InN), and β is the bond bending force constant⁹ (12.16 N/m for GaN and 8.05 N/m for InN. For a perfect, undistorted InN or GaN crystal, $E_m = 0$.

We determined the phase diagram using the transition-matrix Monte Carlo (TMCM) method,¹⁰ which yields the Gibbs free energy as a function of composition, from which a double-tangent construction gives the phase coexistence properties.⁶ All simulations were conducted in a semigrand isobaric–isothermal ensemble¹¹ at a pressure of 1 bar, with temperatures ranging from 500 K to the measured UCST. MC trials were also attempted to exchange the positions of different atoms at fixed composition, thereby permitting fluctuations in compositional ordering. The simulated system comprised 216 particles, where 108 are nitrogen atoms and the rest are either indium or gallium. Finite-size effects were gauged by performing additional simulations for a 512-particle system.

Infinite-dilution free energies can be extracted from the TMCM data, but we found that better results were obtained using a modified version of Bennett’s method.¹² At the lowest temperatures even this approach fails, so we also considered thermodynamic integration to enable us to connect to the 0 K strain energies reported by Ho and Stringfellow. Our calculations provide directly the difference in free energy between an InN crystal having one In replaced by a Ga atom, relative to pure InN; we denote this difference as $\Delta G_{\text{In} \rightarrow \text{Ga}}^\infty$ and we define a similar quantity $\Delta G_{\text{Ga} \rightarrow \text{In}}^\infty$ for the GaN crystal infinitely dilute in InN.

According to regular solution theory,^{6,13} the molar excess Gibbs free energy as a function of temperature T and InN mole fraction x has the form

$$g^E(T, x) \equiv g(T, x) - \{xg_{\text{GaN}}^o + (1-x)g_{\text{InN}}^o + RT[x \ln x + (1-x) \ln(1-x)]\} = \Omega x(1-x), \quad (2)$$

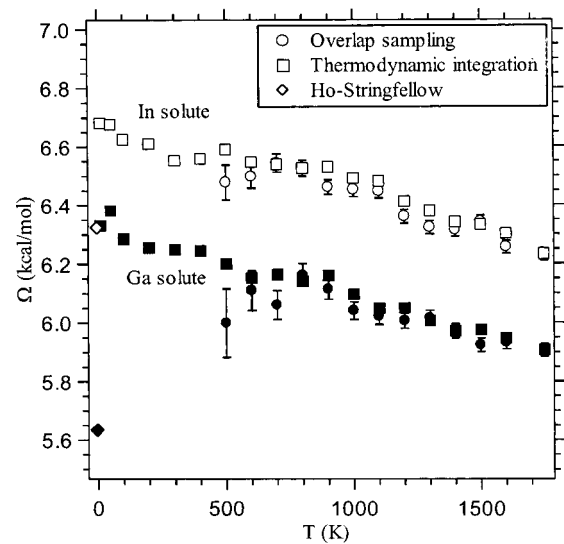


FIG. 1. Temperature dependence of regular solution parameter Ω when evaluated using solution free energies taken for the respective pure phases, as given by Eq. (3). Circles are based on overlap-sampling calculations, and squares are results of thermodynamic integration. Energy-minimized lattice-strain results from Ho and Stringfellow (Ref. 2) are indicated by diamonds at $T=0$. In all cases, open symbols indicate data for GaN with an In solute, and filled symbols are for InN with a Ga solute.

where $g(T, x)$ is the molar Gibbs free energy of the mixture, g_i^o is that of pure species i and R is the gas constant; the first equality defines g^E and the second equality describes the regular-solution model for it. The key quantity characterizing deviation from ideal-mixing behavior is Ω , which regular solution theory prescribes as independent of T and x . Ho and Stringfellow use $\Omega = 5.98$ kcal/mol, obtained by averaging the two infinite-dilution strain energies as described above. The temperature-dependent infinite-dilution free energies provide the necessary information to extend this approach to higher temperature. The appropriate formulas are, for each infinite-dilution limit

$$\Omega = \begin{cases} \Delta G_{\text{In} \rightarrow \text{Ga}}^\infty + (g_{\text{InN}}^o - g_{\text{GaN}}^o) & \text{Ga dilute} \\ \Delta G_{\text{Ga} \rightarrow \text{In}}^\infty + (g_{\text{GaN}}^o - g_{\text{InN}}^o) & \text{In dilute} \end{cases} \quad (3)$$

These expressions are consistent with Ho and Stringfellow’s practice of equating Ω to the infinite-dilution strain energy, as at 0 K the ΔG^∞ terms equal the corresponding strain energies, and the pure-phase free energies vanish because the energy of the perfect (0 K, pure) crystal is zero. Moreover, the pure-phase contributions cancel at all temperatures if the infinite-dilution values are averaged to define Ω .

The values of Ω computed from the simulation data using Eq. (3) are plotted in Fig. 1. We observe some variation of Ω with temperature when computed according to each limit. The change is about 5%–10% over the temperature range considered, but it does not exceed the difference between the two limit values, so we do not consider it to be consequential. It must also be noted that the limiting values obtained upon extrapolation of the data to 0 K differ from the strain-energy Ω reported by Ho and Stringfellow. These values should agree, and despite considerable effort to uncover the cause of this discrepancy we have no explanation for it.

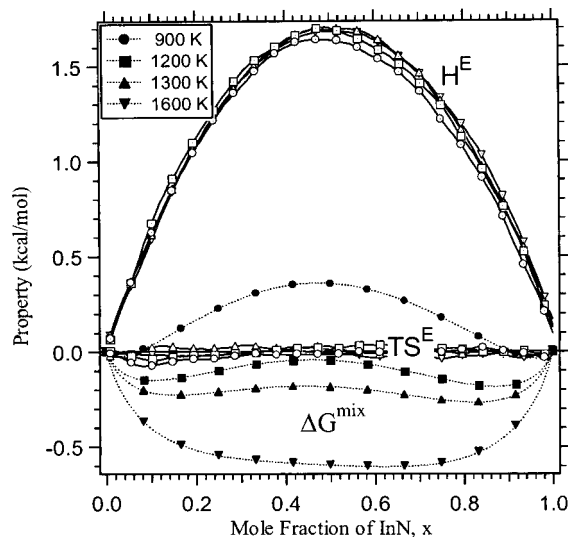


FIG. 2. Gibbs free energy of mixing ΔG^{mix} (broken lines), excess enthalpy H^E , and excess entropy TS^E for the VFF model of InGaN as computed by the full TMMC calculations.

Although the difference is significant, it is no larger than the variation of Ω over the temperature range (in fact the Ho–Stringfellow Ω is not so far off from higher-temperature values here). Our results might be compared also with the data of Takayama *et al.*⁴ (who report $\Omega=6.63$ kcal/mol) and Saito and Arakawa⁵ (reporting 6.36 kcal/mol), but these works each involve a slightly different molecular model, so firm conclusions cannot be drawn from the comparisons.

The excess enthalpy $h^E = [\partial(g^E/T)/\partial(1/T)]_{x,P}$ and entropy $s^E = -(\partial g^E/\partial T)_{x,P}$ provide a direct indication of the validity of regular solution theory. In particular, regular solution theory postulates that the excess entropy is zero. Using the simulation data for g^E we calculated these excess properties, with results presented in Fig. 2. The data strongly support the use of the regular solution model. The excess entropy is negligible, while the excess enthalpy is practically constant with temperature. A negative excess entropy would indicate a “structure-making” effect on mixing, and might be expected to arise from formation of correlated clusters of solute atoms in the mixture, formed to reduce the strain. On the other hand, one could also expect a “structure-breaking” positive excess entropy, which might arise if the atoms exploit the greater disorder of the mixed lattice to move further from their lattice positions. This effect is seen in mixtures of hard spheres.¹⁴ Space constraints prevent a detailed discussion here, but study of the local composition on the lattice does show some evidence for mild nonrandomness in the mixture, which one should expect for such a nonideal system. The near-zero excess entropy thus might be the result of these offsetting influences.

Finally, the miscibility diagram computed from the TMMC simulation data is presented in Fig. 3. The UCST determined from the TMMC simulation data is 1550 K,

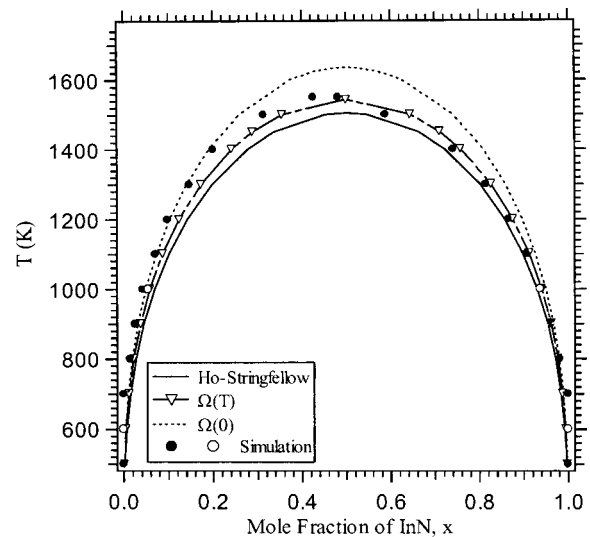


FIG. 3. Miscibility diagram for the InGaN system. Filled and open circles are the results of the full TMMC calculations for 216- and 512-atom systems, respectively. All other lines are based on regular-solution theory. Ho–Stringfellow curve uses a constant $\Omega=5.98$ kcal/mol; $\Omega(T)$ curve calculates a different parameter for each temperature by averaging the values plotted in Fig. 1. $\Omega(0)$ curve uses fixed value (6.5 kcal/mol) of parameter obtained by averaging the $T=0$ values in Fig. 1.

which is very close to the Ho–Stringfellow value of about 1505 K. The simulation data yield a curve that is not perfectly symmetric (in contrast to regular solution theory). One consequence is that the In solubility is somewhat less than given by the Ho–Stringfellow analysis.

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