Miscibility gaps and spinodal decomposition in III/V quaternary alloys of the type $A_xB_yC_{1-x-y}D$ [a]

G. B. Stringfellow

University of Utah, Salt Lake City, Utah 84112

Thermodynamic concepts have been developed for the calculation of solid-phase miscibility gaps and spinodal decomposition in quaternary alloys of the type $A_xB_yC_{1-x-y}D$. These concepts have been applied to the analysis of III/V quaternary alloys using the delta-lattice-parameter (DLP) solution model. In addition, the effects of coherency strain energy have been included in the calculation. Results are presented for the systems $Al_xGa_yIn_{1-x-y}P$, $Al_xGa_yIn_{1-x-y}As$, $InP_xAs_ySb_{1-x-y}$, and $GaP_xAs_ySb_{1-x-y}$. Even though these systems all have miscibility gaps, they are shown to be stable against spinodal decomposition at all temperatures due to the elastic strain energy inherent in coherent decomposition of single crystalline alloys.

PACS numbers: 81.30. — x

INTRODUCTION

Quaternary III/V alloys of the type $A_xB_yC_{1-x-y}D$, where three elements share a single sublattice, are interesting for a number of applications. Stringfellow[1] suggested that the system $Al_xGa_yIn_{1-x-y}P$ might be the optimum system for the production of high-efficiency, visible-light-emitting diodes (LEDs) and short-wavelength injection lasers. This system contains the highest direct band gap (2.2 eV) III/V alloy lattice matched to GaAs. These alloys cannot be grown by LPE[5] (liquid phase epitaxy) because of the extremely large Al distribution coefficient. However, they have been grown by MBE (molecular beam epitaxy)[2] and growth may be possible by OMVPE (organometallic vapor phase epitaxy).[1] A similar system is $Al_xGa_yIn_{1-x-y}As$, which may be useful for tandem (or cascade) solar cells[3] and as a confining layer in multilayer structures used for $Ga_xIn_{1-x}As$ active layer field effect transistors.[4] $Al_xGa_yIn_{1-x-y}As$ alloys are difficult to grow by LPE[5] because of the high Al distribution coefficients, but may be grown by MBE[4] and OMVPE.[6] Alloys of the type $AB_xC_yD_{1-x-y}$ such as $InP_xAs_ySb_{1-x-y}$ (Ref. 7) and $GaP_xAs_ySb_{1-x-y}$ (Ref. 8) are also of interest. The former alloys are interesting for superlattice structures and IR light sources and detectors for the wavelength range 3–4 μ. Some $InP_xAs_ySb_{1-x-y}$ alloys have been grown by OMVPE, although the system is found to have a large miscibility gap.[7]

Many pseudobinary III/V alloys have solid phase miscibility gaps, based on experimental evidence and simple thermodynamic calculations.[9] Such miscibility gaps prevent the equilibrium growth of a range of solid compositions when the critical temperature T_c, above which no immiscibility, exists is higher than the growth temperature. Even for alloys where T_c is less than the growth temperature but greater than 300 K, the miscibility gap could cause problems, since spinodal decomposition and clustering would be expected to occur during high temperature processing or even stimulated by recombination enhanced diffusion[10] during laser or LED device operation.

Recent calculations[9] have shown that quaternary alloys of the type $A_xB_{1-x}C_yD_{1-y}$ have even larger miscibility gaps and higher values of the critical temperature than the bounding pseudobinary systems. One purpose of this paper is to analyze alloys of the type $A_xB_yC_{1-x-y}D$ (or $AB_xC_yD_{1-x-y}$ which is thermodynamically equivalent) to determine whether these alloys are also less stable than the bounding pseudobinary systems.

In addition to considering only chemical driving forces for phase separation, Cahn[11] showed that in metal systems, the coherency strain energy acts to stabilize alloys. Stringfellow[12] extended these calculations to $A_xB_{1-x}C_yD_{1-y}$ quaternary alloys and showed that most III/V pseudobinary and $A_xB_{1-x}C_yD_{1-y}$ quaternary alloys are stabilized against spinodal decomposition by the coherency strain energy at all temperatures. These calculations will also be extended to type $A_xB_yC_{1-x-y}D$ quaternary alloys in the present work.

The purpose of this paper is to develop the thermodynamic concepts necessary to calculate the spinodal and critical temperature for a system of the type $A_xB_yC_{1-x-y}D$ (or $AB_xC_yD_{1-x-y}$) in the conventional way, including only chemical terms, and in addition to include the effects of the coherency strain energy. Results will be presented specifically for the systems $Al_xGa_yIn_{1-x-y}P$, $Al_xGa_yIn_{1-x-y}As$, $GaP_xAs_ySb_{1-x-y}$, and $InP_xAs_ySb_{1-x-y}$.

CALCULATION OF THE SPINODAL NEGLECTING STRAIN ENERGY

The stability criterion for pseudoternary alloys of the type $A_xB_yC_{1-x-y}D$ (or $AB_xC_yD_{1-x-y}$) may be written[12,14]

$$\left(\frac{\partial^2 G}{\partial x^2}\right)_{T,P}\left(\frac{\partial^2 G}{\partial y^2}\right)_{T,P} - \left(\frac{\partial^2 G}{\partial x \partial y}\right)^2_{T,P} \geqslant 0, \qquad (1)$$

where G is the Helmholtz free energy per unit volume, which is taken to be equal to the Gibbs free energy per unit volume for a solid phase at one atmosphere pressure.[13] Thus, G is the product of the Gibbs free energy per mole of the solid G^s and the number of moles per unit volume of the initial, homogeneous solid N_v. The value of G^s is obtained from a simple thermodynamic model of the solid, either the regular solu-

tion model[14] or the DLP (delta-lattice-parameter) model.[15] For the regular solution model,

$$G^s = xy\alpha_1 + x(1 - x - y)\alpha_2 + y(1 - x - y)\alpha_3$$
$$+ RT[x \ln x + y \ln y + (1 - x - y)\ln(1 - x - y)]$$
$$+ xG^0_{AD} + yG^0_{BD} + (1 - x - y)G^0_{CD}, \qquad (2)$$

where α_1, α_2, and α_3 are the interaction parameters for the three pseudobinary systems bounding the pseudoternary solidus plane, α_{AD-BD}, α_{AD-CD}, and α_{BD-CD}, respectively, and G^0_{AD}, G^0_{BD}, and G^0_{CD} are the free energies per mole of the three pure binary compounds. For the DLP model,

$$G^s = -Ka_0^{-2.5} + RT[x \ln x + y \ln y$$
$$+ (1 - x - y)\ln(1 - x - y)], \qquad (3)$$

where K is a constant equal to 1.15×10^7 cal mole^{-1} Å$^{2.5}$. Unfortunately the empirical regular solution interaction parameters are not known for the systems InP$_x$Sb$_{1-x}$ and GaP$_x$Sb$_{1-x}$, so would have to be estimated from the DLP model. For the other systems under consideration, the regular solution model interaction parameters agree with those predicted from the DLP model.[15] The largest deviation is for the GaAs$_y$Sb$_{1-y}$ system where the DLP interaction parameter (3355 cal/mole) is considerably smaller than the 4000 cal/mole obtained from a regular solution model fit to the pseudobinary phase diagram. Thus, the simplest and most consistent approach is to develop the calculation based on the DLP model.

Relation (1) can now be written, using the DLP model,

as

$$\left\{ -M\Delta a_A^2 + RT\left[\frac{(1-y)}{x(1-x-y)}\right]\right\}$$
$$\times\left\{ -M\Delta a_B^2 + RT\left[\frac{(1-x)}{y(1-x-y)}\right]\right\}$$
$$- \left[-M\Delta a_A \Delta a_B + RT/(1-x-y)\right]^2 \geqslant 0, \qquad (4)$$

where $M = 8.75\ Ka_0^{-4.5}$, $\Delta a_A = a_{AD} - a_{CD}$, and $\Delta a_B = a_{BD} - a_{CD}$ where the lattice parameter of the compound ij is denoted a_{ij}. Relation (4) can be manipulated to yield an expression for the spinodal surface,

$$T = (M/R)[x\Delta a_A^2 + y\Delta a_B^2 - (x\Delta a_A + y\Delta a_B)^2]. \qquad (5)$$

This equation can be solved to yield the values of x_c, y_c, and T_c. It can be shown that in all cases, either x_c, y_c, or $(1 - x_c - y_c)$ is equal to zero, i.e., the critical temperature is equal to that for the boundary pseudobinary having the highest value of T_c. This result is strikingly different than that for quaternary alloys of the type $A_x B_{1-x} C_y D_{1-y}$, where T_c often falls near $x_c = y_c = 0.5$ and is substantially higher than T_c for any of the bounding pseudobinary systems. The calculated spinodal isotherms for the systems InP$_x$As$_y$Sb$_{1-x-y}$, Al$_x$Ga$_y$In$_{1-x-y}$P, Al$_x$Ga$_y$In$_{1-x-y}$As, and GaP$_x$As$_y$Sb$_{1-x-y}$ are shown in Figs. 1–4.

For the InP$_x$As$_y$Sb$_{1-x-y}$ system, Fig. 1, $x_c = 0.56$, $y_c = 0$, and $T_c = 1319$ K. The value of x_c is slightly different than that calculated, assuming $\Delta a \ll \bar{a}$ where $\bar{a}$ is the average value of lattice parameter. This approximation yields $x_c = 0.5$ (Refs. 9, 12) and $T_c = 1303$ K. This 1% error is negli-
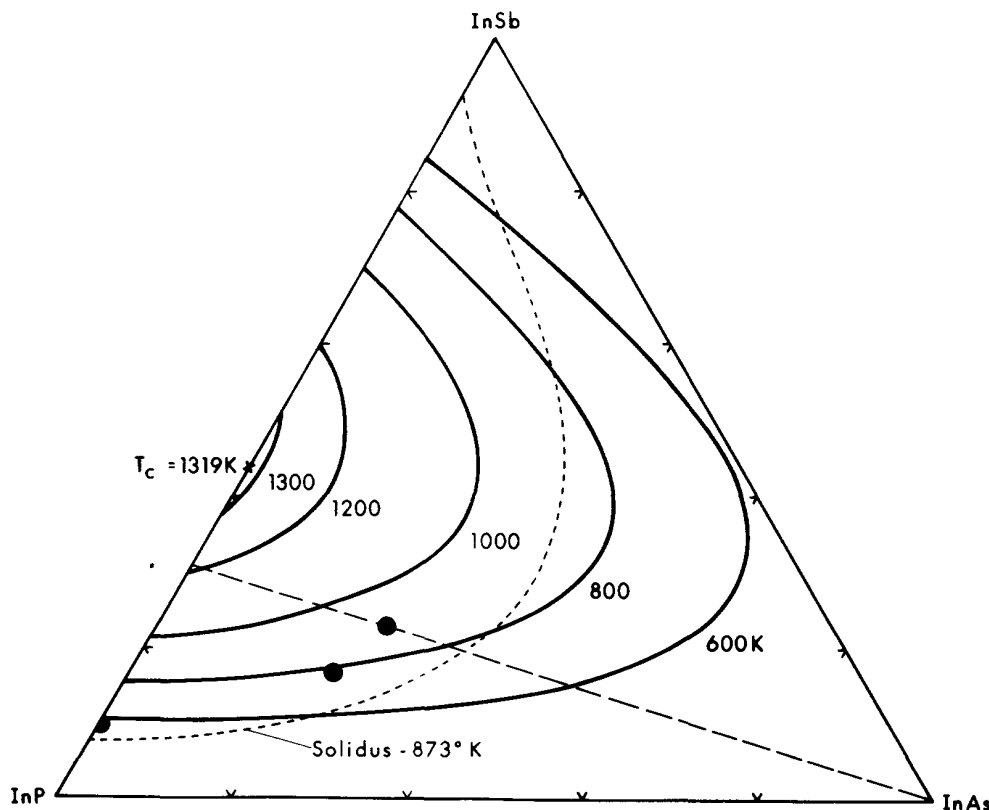

FIG. 1. Calculated spinodal isotherms for the system InP$_x$As$_y$Sb$_{1-x-y}$ neglecting the effects of coherency strain energy. Including the coherency strain energy gives $T_s < 0$ K. The data points are from Fukui and Horikoshi[7] obtained at 600 °C for OMVPE growth on InAs substrates. For comparison, the binodal isotherm calculated for $T = 600$ °C (873 °K) is also plotted.
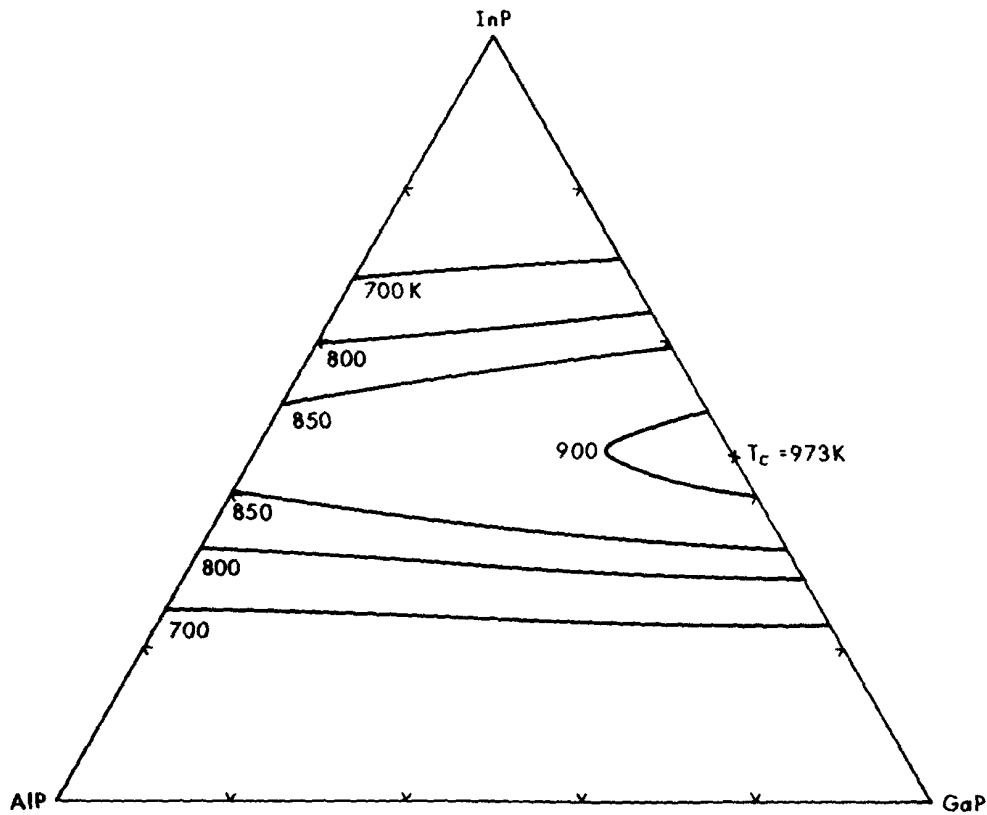
FIG. 2. Calculated spinodal isotherms for the system $Al_xGa_yIn_{1-x-y}P$. The calculation neglects the coherency strain energy. Including this contribution to the free energy gives $T_s < 0$.
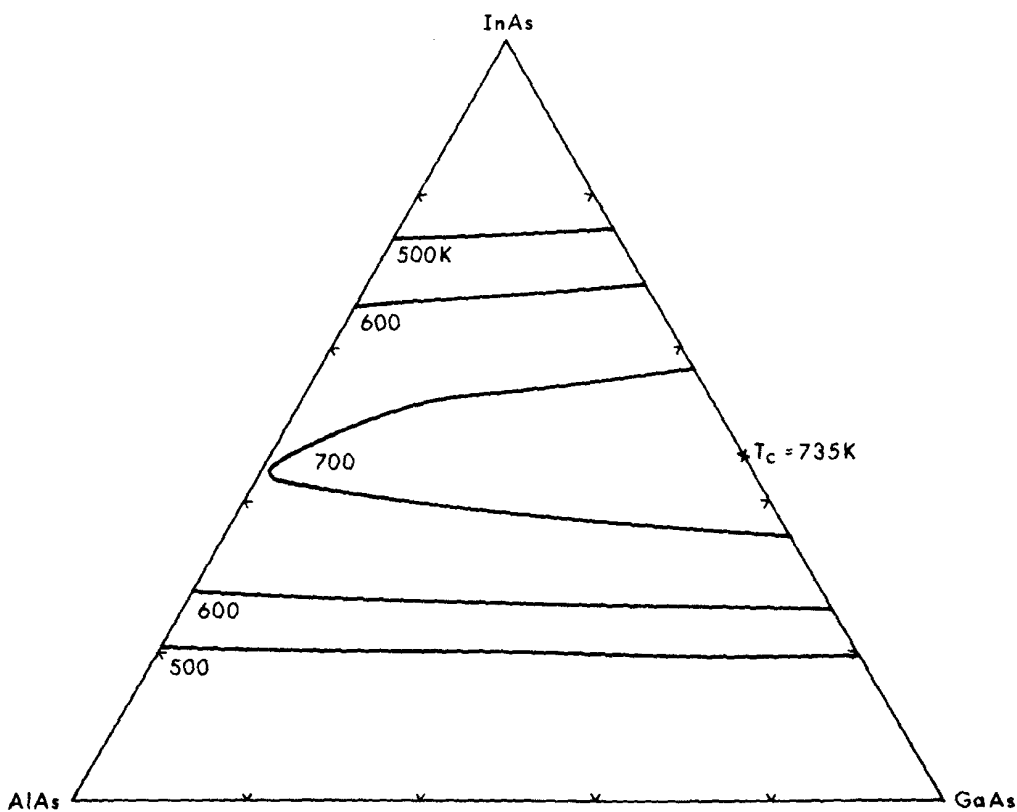

FIG. 3. Calculated spinodal isotherms for the system $Al_xGa_yIn_{1-x-y}As$. The calculation does not include the coherency strain energy. The strain energy would make the solid stable over the entire composition range.
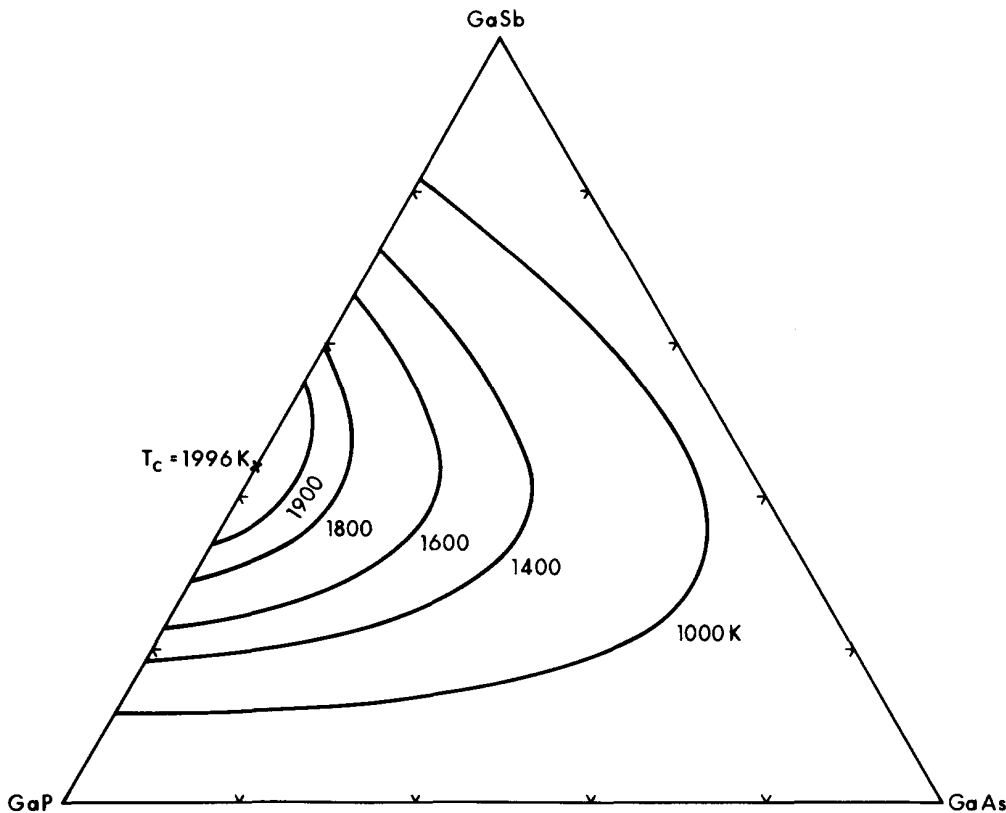
FIG. 4. Calculated spinodal isotherms for the system $GaP_x As_y Sb_{1-x-y}$. The calculation neglects the coherency strain energy $T_s > 0$.

gible relative to the uncertainties in the thermodynamic model.

Three experimental 600 °C data points were reported for the extent of the miscibility gap in $InP_x As_y Sb_{1-x-y}$ by Fukui and Horikoshi[7] obtained from organometallic vapor phase epitaxy growth experiments. These data points are not spinodal points, but represent the extent of the miscibility gap. For comparison, we have calculated the binodal curve (solidus) at 600 °C (873 °K) using the approach described in Ref. 9. One complication in interpreting these data is that for epitaxial layers, the elastic energy due to lattice parameter mismatch is known to stabilize otherwise unstable alloys in systems other than $InP_y As_y Sb_{1-x-y}$.[16,17] This effect would be expected to be most noticeable for the data point at $x = 0.51$ and $y = 0.26$, where the alloy is nearly lattice matched to the InAs substrate. One would expect this factor to produce an "effective miscibility gap" somewhat smaller than the true chemical equilibrium miscibility gap. However, the data do seem to support the general features of the calculated results.

For the $Al_x Ga_y In_{1-x-y}P$ system, $x_c = 0$, $y_c = 0.55$, and $T_c = 913$ K. The approximation $\Delta a \ll \bar{a}$ would yield $y_c = 0.5$ and $T_c = 908$ K, again only slightly in error. For this system, the miscibility gap is largest for the region with $x + y \cong 0.5$. Unfortunately, this is the solid region with lattice parameter equal to that for GaAs, so it is the region of most practical interest. The same is true for the $Al_x Ga_y In_{1-x-y}As$ system, where the alloys with $x + y \cong 0.5$ are lattice matched to the InP substrates com-

monly used. For this system, $T_c = 735$ K, slightly larger than the value of 729 K calculated for $\Delta a \ll \bar{a}$.[12]

For the system $GaP_x As_y Sb_{1-x-y}$, the calculated spinodal isotherms are plotted in Fig. 4. The critical temperature for the quaternary is located on the $GaP_x Sb_{1-x}$ edge of the solid phase field. No data are available for that system, but solidus data are available for the $GaAs_y Sb_{1-y}$ system at lower temperatures, as shown in Fig. 5. The data of Gratton et al.[19] were obtained by equilibration through a liquid phase. The data of Cooper et al.[20] were obtained by OMVPE. The DLP model is known[9,15] to underestimate the solid phase interaction parameter, and hence the critical temperature and the size of the miscibility gap. Thus, the binodal curve plotted in Fig. 5 was calculated assuming the DLP constant K to be 1.37×10^7 cal mole^{-1} Å$^{2.5}$ in accordance with the pseudobinary liquid-solid phase diagram. The calculated binodal curve agrees very well with the Gratton et al. data for the GaSb-rich solids and the OMVPE data for both the GaAs- and GaSb-rich solids. It should be mentioned that these were grown on GaAs and GaSb substrates, respectively.

These data, plus those of Fukui and Horikoshi for the $InP_x Sb_{1-x}$ system show that for large lattice parameter mismatch of the epitaxial layer with the substrate that little if any "lattice latching"[16,17] is observed. The GaAs rich solidus data of Gratton et al. show an unexpectedly low GaAs solubility and practically no temperature dependence. The latter is contrary to the predictions of any simple model for the miscibility gap.
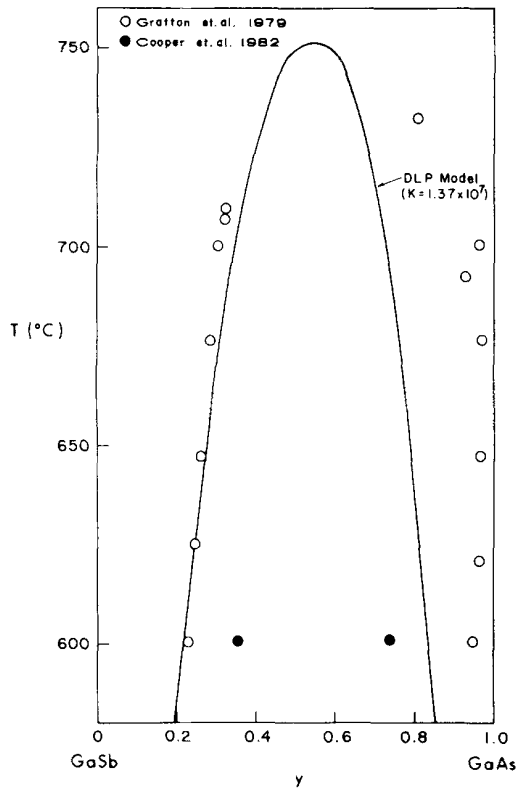
FIG. 5. Solidus for the system $GaAs_y Sb_{1-y}$. The data for Gratton et al.[19] (O) were obtained by equilibration through a liquid phase and the data of Cooper et al. (●) were obtained by OMVPE. The solid line was calculated using the DLP model with $K = 1.37 \times 10^7$ cal mole^{-1} Å$^{2.5}$.

EFFECT OF COHERENCY STRAIN

Cahn[11] showed 20 years ago that for binary metal alloys, the coherency strain energy involved in spinodal decomposition would significantly reduce the critical temperature, written T_s when the strain energy is included. The strain energy clearly acts to stabilize alloys considered unstable from a consideration of only the chemical energy. Stringfellow[12] extended the calculation to pseudobinary and quaternary $A_x B_{1-x} C_y D_{1-y}$ alloys. The coherency strain energy was found to completely stabilize most alloys considered. T_s is less than 0 K for these types of III/V alloys, except those with very large miscibility gaps.

We will use the approach[12,13] of defining a new free energy function containing the effect of coherency strain energy,

$$G'(x,y) = G^s N_v + \frac{\Delta a_A^2 E (x - x_0)^2}{a_0^2 (1-v)} + \frac{\Delta a_B^2 E (y - y_0)^2}{a_0^2 (1-v)}$$
$$+ \frac{2\Delta a_A \Delta a_B (x - x_0)(y - y_0) E}{a_0^2 (1-v)}, \quad (6)$$

where E is Young's modulus and v is Poisson's ratio. x_0 and y_0 are the composition parameters for the homogeneous alloy before spinodal decomposition is allowed to begin. Using this free energy function, the stability criterion can be written

$$\left\{ - (M - S) \Delta a_A^2 + RT \left[\frac{(1-y)}{x(1-x-y)} \right] \right\}$$
$$\times \left\{ - (M - S) \Delta a_B^2 + RT \left[\frac{(1-x)}{y(1-x-y)} \right] \right\}$$
$$- \left[- (M - S) \Delta a_A \Delta a_B + RT/(1-x-y) \right]^2 \geq 0, \quad (7)$$

a duplicate of relation (4) with M replaced by $(M - S)$ where

$$S = 2E/N_v (1 - v) a_0^2. \quad (8)$$

Naturally, this yields an equation similar to Eq. (5) (for the critical temperature) with M replaced by $(M - S)$.

The values of $E/(1-v)$ were obtained from the data of V. V. Voronkov,[18] either directly or by estimation from similar systems. All four quaternary systems considered in this paper are stabilized by the coherency strain energy, i.e., $T_s < 0$ K.

CONCLUSIONS

The thermodynamics of spinodal decomposition in quaternary alloys of the type $A_x B_y C_{1-x-y} D$ have been developed. Based on the DLP model of the free energy of mixing of semiconductor alloys, an analysis has been developed for the calculation of the spinodal surface and the critical temperature for solid quaternary III/V alloys where the mixing is restricted to three elements on a single sublattice. It is found that the critical temperature for such alloys always occurs at the edge of the triangular solid phase field, i.e., for either x_c, y_c, or $1 - x_c - y_c$ equal to zero. Thus, the critical temperature is never higher in the quaternary than for the bounding pseudobinary systems. Solid-solid isotherms are presented for the systems $Al_x Ga_y In_{1-x-y} P$, $Al_x Ga_y In_{1-x-y} As$, $GaP_x As_y Sb_{1-x-y}$, and $InP_x As_y Sb_{1-x-y}$. The calculations agree quite well with experimental data for the systems $InP_x As_y Sb_{1-x-y}$ and $GaAs_y Sb_{1-y}$.

Concepts are also developed for the thermodynamic analysis of spinodal decomposition in these quaternary alloys, including the effect of the coherency strain energy. This addition to the free energy of the inhomogeneous solid is shown to completely stabilize the alloys of interest even at temperatures below room temperature.

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