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The System In-Ga: Thermodynamics and Computed Phase Equilibria

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The accepted solidus [5] on the In-rich side of the In-Ga phase diagram has been shown to be thermodynamically infeasible. A solidus consistent with the liquidus and microcalorimetric heats of solution measurements [6] has been constructed with an analysis utilising a linear programming computer technique. The thermodynamic interaction parameter α [defined by $\alpha_{ij} = \ln \gamma_i/(1 - N_i)^2$] have been determined as functions of temperature and composition for the liquid and In-rich solid solutions. The liquid and solid solutions are found to be not far from regular. The In-rich solvus curve has also been computed.

1. Introduction

This system is of interest principally because it constitutes one binary of the In-Ga-As ternary system, which is of some importance in the semiconductor industry and which has received a great deal of attention in recent years. A review of the literature indicates some inconsistencies and an attempt is being made here to resolve these. The procedure followed was the simultaneous analysis of all available phase equilibria and thermochemical information on the system using a linear programming optimisation technique.

1.1. Phase Diagram

The liquidus has been measured by French, Saunders, and Ingle [1], Denny, Hamilton and Lewis [2], Swirbely and Selis [3] and, most recently, by Predel and Stein [4]. As discussed in Hansen and Anderko [5], the curve of Swirbely and Selis is the most acceptable, particularly in the region $N_{\mathrm{Ga}} < 0.6$. In this region, the curve is almost exactly matched by that of Predel. Consequently it is accepted as quite accurate and used in the analysis. The solidus has been determined by French *et al.* [1] and Swirbely and Selis [3], that of the latter being accepted by Hansen. Using a simple analysis, one can show that, given their liquidus, the solidus is much too flat in the dilute region; i.e., the limiting k_0 (segregation coefficient) value is too high, taking the heat of fusion of In to be 780 cals/mole and assuming that Raoult's Law is obeyed in that region. Given this conclusion, one needs to (i) find a possible explanation for the incorrect solidus determination and (ii) attempt to determine the solidus consistent with the liquidus and available thermodynamic measurements.

1.2. Thermodynamics

Unfortunately, there are no measurements of thermodynamic quantities for the solid solution. Several investigations have been made in the liquid. Bros [6] and Bros, Castanet, and Laffitte [7] measured the integral heat of mixing (ΔH^{M}) quite precisely using a micro calorimeter, and their findings are generally accepted as accurate. Predel and Stein [4] also determined ΔH^{M} values somewhat larger but with enough scatter to justify the use of the Bros data. Macur, Edwards, and Wahlbeck [8] estimated α_{InGa}' [as defined by $\log_{10}\gamma_{\mathrm{In}}/(1 - N_{\mathrm{In}})^2$] at three temperatures and at various compositions. Their findings were, however, considered somewhat unreliable and consequently not used by us.

2. Phase Diagram Analysis

The Swirbely and Selis liquidus was accepted and a systematic attempt was made to find the solidus that matched it and the Bros ΔH^{M} findings. A linear programming optimisation technique (to be described elsewhere [9]) was used to conduct the analysis. The principle is to require the chemical potential of each species to be equal on the ends of a tie-line, i.e.,

$$\mu_i^{\mathrm{L}} = \mu_i^{\mathrm{S}} \qquad i = \mathrm{In, Ga} \qquad (1)$$

$$\mu_i{}^{\beta} = \mu_{i0}{}^{\beta} + RT\,ln(\gamma_i{}^{\beta}\,.\,N_i{}^{\beta}) \quad \beta = \mathrm{L, S} \qquad (2)$$

where $N_i{}^{\mathrm{L}}$ and $N_i{}^{\mathrm{S}}$ represent compositions on either side of the tie-line, $\mu_{i0}{}^{\beta}$ is the standard chemical potential of pure i. $ln\,\gamma_{\mathrm{In}}{}^{\beta}$ is now expressed in terms of an α parameter defined as

$$\alpha^{\beta}_{\mathrm{InGa}} = \frac{ln\,\gamma^{\beta}_{\mathrm{In}}}{(1 - N_{\mathrm{In}}{}^{\beta})^2} \qquad (3)$$

where $\alpha^{\beta}_{ij} = l^{\beta} + a^{\beta}N^{\beta}_{j} + c^{\beta}/T$. And by Gibbs Duhem equation,

$$ln(\gamma^{\beta}_{\mathrm{Ga}}/\gamma^{\beta 0}_{\mathrm{Ga}}) = \alpha^{\beta}_{\mathrm{InGa}}(N^{\beta 2}_{\mathrm{In}} - 1) + \frac{a^{\beta}}{2}\,(N^{\beta}_{\mathrm{Ga}})^2 \qquad (4)$$

where $ln\,\gamma^{\beta 0}_{\mathrm{Ga}} = l^{\beta} + c^{\beta}/T + a^{\beta}/2$.

This 3-parametric representation of α implies that $\Delta\bar{H}_i$ is of the form $B_2R(1 - N_i)^2$ where B_2 is a factor constant with composition and temperature [10]. Such a representation is consistent with the almost symmetric representation of ΔH^{M} versus N found by Bros *et al.* and Predel.

Equations (1) to (4) combine to give two tie-line equations with six unknowns. Sixteen of these are solved simultaneously (with redundancy) using a computerised linear programme having the following features: (1) The excess partial molar entropies and enthalpies are required to remain within reasonable bounds. (2) The heats of solution in the liquid are required to match the results of Bros within set error limits corresponding to the experimental uncertainty. (3) Each tie-line equality – i.e., equation generated by the equality of chemical potentials of the two phases in equilibrium – is permitted a slack variable ϵ^i and the solution minimises $\sum(|\epsilon^i| + |\delta^i|)$, where δ^i is the slack variable in the ΔH^{M} equation. One therefore obtains the closest fit to the tie-line equalities and the thermodynamic constraints. If the positions of the liquidus and solidus (as manifested in the tie-lines) are not thermodynamically consistent with the other constraints, this shows up in the magnitude of the slacks ϵ^i. Furthermore, the α's that represent the solution in such a case will not regenerate the original input solidus and liquidus upon their being fed into another programme that generates phase diagrams. Using this feature we input the Swirbely liquidus and a trial solidus. The α's obtained are used to generate the solidus and liquidus consistent with these α parameters. If the liquidus does not match the experimental one, another solidus is attempted to obtain a different set of α's, and so forth.

First, the Swirbely and Selis solidus (shown in fig. 1 as solid circles and distinguished from the liquidus by virtue of being the lower temperature point of a pair at any given composition)

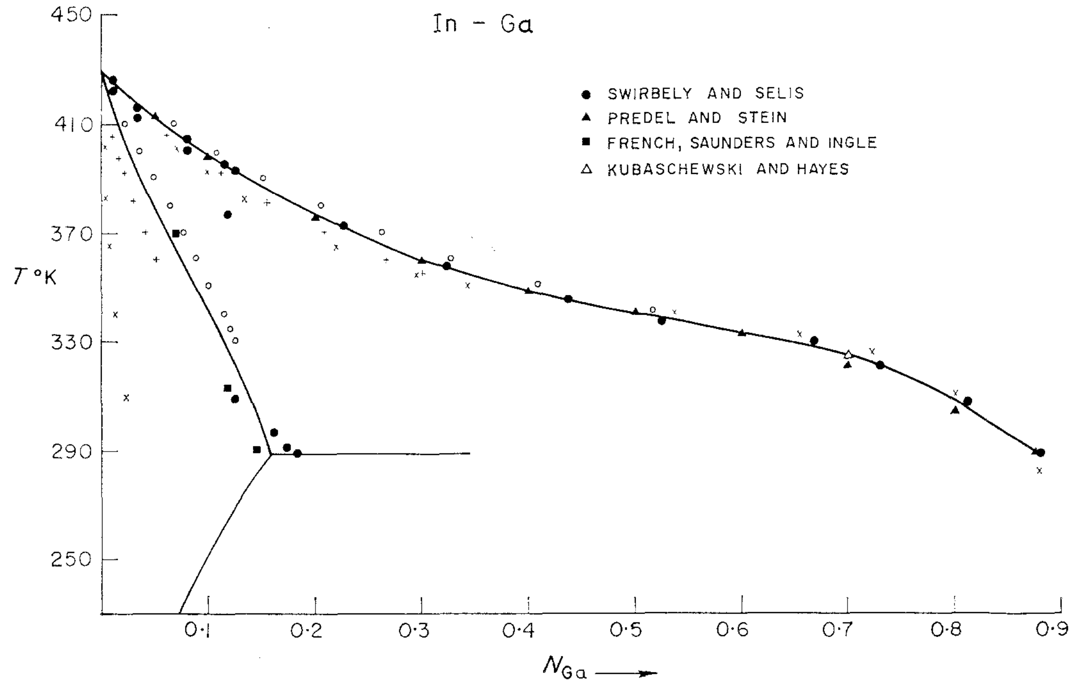

Figure 1 The computed In-Ga phase diagram.

was tried. As expected, the upper part of the solidus showed up as being inconsistent with the lower part. Next, the solidus suggested by Predel [4] based upon the findings of Heubner and Wincierz [11] was used. The solidus and liquidus generated by the α's for that system are shown as (x) in fig. 1. The liquidus is seen to be below the experimental one in the region $N_{Ga} < 0.6$. The limiting liquidus slope is also seen to be very close to that for $k_0 = 0$, which is consistent with the very low solubility assumed in the calculations. Qualitatively, the liquidus is expected to rise if the solid solubility is increased and so various soliduses were attempted, and here we arbitrarily chose to take the maximum solid solubility limit to be (in the absence of any other information) that suggested by Swirbely and Selis. Two of these trials are marked on fig. 1, one of them (o) being a case where we overshot the experimental liquidus. The solid line was generated by the functions

$$\alpha^{L}_{InGa} = -0.258 + 0.497\,N_{Ga} + 513.5/T$$
$$\alpha^{S}_{InGa} = 0.202 + 0.455\,N_{Ga} + 591.0/T$$

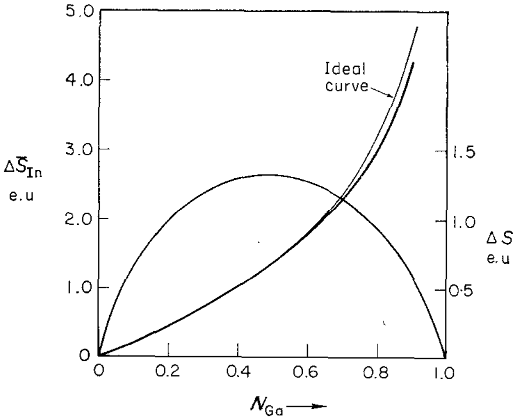

Figure 2 $\Delta\bar{S}_{In}$ and ΔS^{m} in liquid solutions.

In general, it was found that the functions generating higher liquidus curves had higher excess entropy effects (comparatively). The maximum solid solubility point predicted by this is between that of French *et al.* and Swirbely and Selis. Any thermodynamic information concerning the solid would be invaluable in pinning down, beyond doubt, the exact line; this is probably the appropriate one. It predicts $\Delta\bar{H}_{In}{}^{S}$ as being positive whereas most of the steeper soliduses predicted negative values.

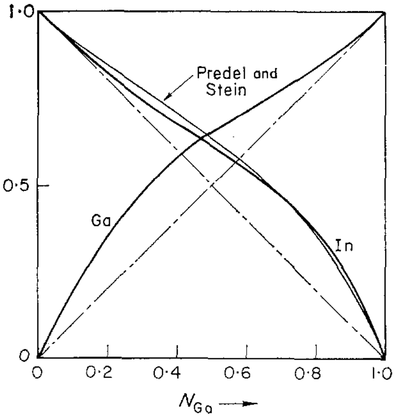

Figure 3 Activities of Ga and In in liquid solutions at 623°K.

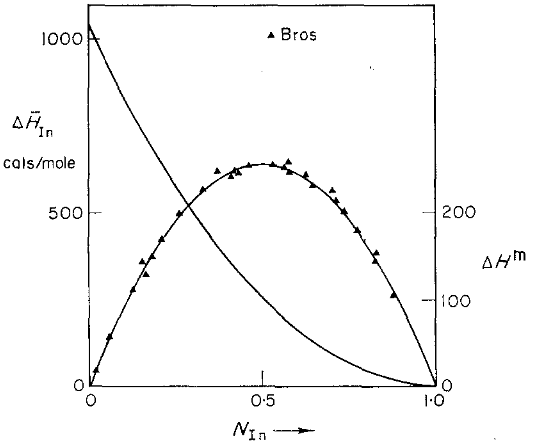

Figure 4 $\Delta\bar{H}_{In}$ and ΔH^{m} in liquid solutions.

The computed phase diagram is drawn in fig. 1. Fig. 2 shows $\Delta\bar{S}_{In}$ and ΔS^{M} in the liquid as functions of N_{Ga}, where $\Delta\bar{S}_{In}$ is the partial molar entropy of In and ΔS^{M} is the integral entropy of mixing. In fig. 3, the liquid activity curves for In and Ga at 623°K are drawn. Fig. 4 shows the $\Delta\bar{H}_{In}$ and ΔH^{M} profiles in the liquid with fig. 5 detailing ΔH^{M} and ΔS^{M} for the In-rich solid solution. Activities in the solid solution are shown in fig. 6 and the solvus curve detail is shown in fig. 7.

Further credibility is lent to the results by an analysis of the solvus curve. The solubility of In in Ga has been reported as being very nearly zero in the solid state. This means that points on the In-rich solvus are in equilibrium with essentially pure Ga. The α^{S}_{InGa} function is used to generate activity versus composition curves at several temperatures. The composition at which the

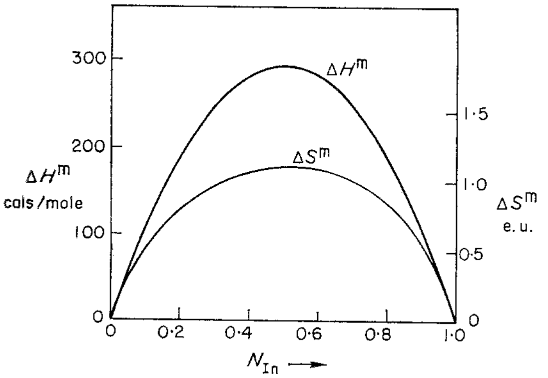

Figure 5 ΔH^m and ΔS^m in In-rich solid solutions

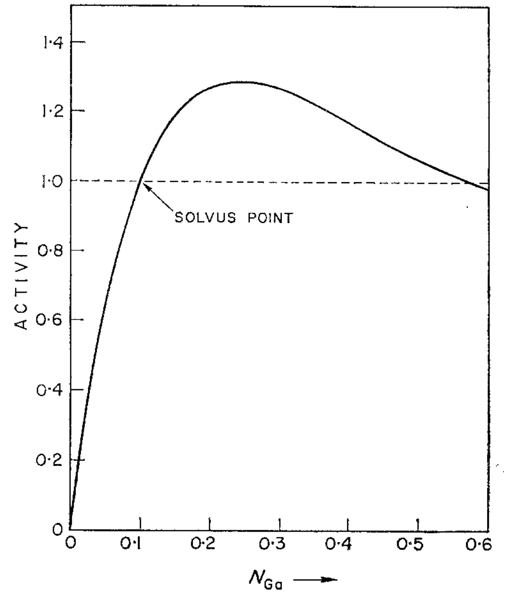

Figure 6 Activities of Ga in In-rich solid solutions at 250° K.

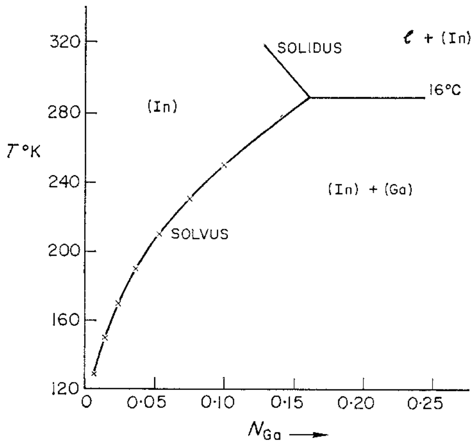

Figure 7 Solvus curve.

activity of Ga is equal to 1.0 is noted at several temperatures. These points are then joined to give our estimate of the solvus (fig. 7), which intersects the computed solidus line at $N_{\mathrm{Ga}} = 0.16$ and 16°C (289°K). This compares very favourably with the experimental eutectic temperature of 15.7°C. In determining the solvus, we drew a smooth curve through the points at 250°K and below. No matter how small the solid solubility of In in Ga, it is certainly going to be the maximum at the eutectic temperature. Swirbely and Selis report a possible maximum of < 0.3 at. % In. At any rate, temperatures within 40°K of the eutectic were avoided as being regions of possible breakdown of the assumption. It must also be added that the points on the solvus could be joined and extrapolated a little differently, giving a corresponding slight shift in the computed eutectic temperature.

3. Discussion

The solidus obtained by us is substantially different from that of Swirbely and Selis. The probable explanation is that they had non-equilibrium effects due to the annealing times being too short. They annealed at "a few degrees below the solidus" (by which one presumes that they could conceivably have started heating in the two-phase region and never, in fact, crossed the phase boundary) for "at least 15 h." The self-diffusion coefficient of In at these temperatures is of the order of 10^{-13} cm^2/sec, which is small enough to warrant much greater annealing times.

The comparison between the computed ΔH^{M} curve in the liquid and the experimental one of Bros [6] is made in fig. 4. The strictly parabolic curve appears to be a satisfactory representation. The points of Bros *et al.* [7] are not drawn since they differ very little from the other work and have a maximum at $N_{\mathrm{In}} = 0.5$ of 265 cals. The error limits are indicated by the scatter and Bros' estimate of $\approx 2.5\%$. The $\Delta \bar{S}_{\mathrm{In}}$ curve drawn in fig. 2 demonstrates the relatively small excess entropy effects in the system, indicating that the system is very nearly regular. The (In) solid solution appears to have small excess entropies as well, with heats of mixing comparable to the liquid, as shown in fig. 5.

A comparison of the excess free energies with those measured experimentally by Macur *et al.* shows that their values are substantially higher. They use the parameter α' already defined and obtain a constant α' of 0.42 ($\pm$ 0.1) at 1269°K in the composition range $N_{\text{In}} < 0.88$. They observe considerable composition dependence thereafter but claim large error limits in this region. As a representative comparison, the computed value of α' at 1269°K and $N_{\text{In}} = 0.5$ is 0.172.

A publication brought to our attention after completion of the above analysis is that of Hayes and Kubaschewski [12], who did a thermodynamic reassessment of the system using a lot of the data already discussed by us. They note, as did we, that the Macur α' parameters are inaccurate. They too choose to use Bros' measurements of ΔH^{M} in preference to those of Predel. In this connection, it must also be added that several investigators, including Stringfellow and Greene [13] and Mabbitt [14], have incorrectly translated Macur's α' values into quasi-chemical interaction parameters Ω, defined as $\Omega_{12} = RT \ln \gamma_1/(1 - N_1)^2$. They make an error in the reading of the definition of the α' parameter used by Macur *et al.* (in terms of $\log_{10}$) and so come up with $\Omega_{\text{InGa}} = 1066$ which is in error by a factor of 2.303. However, as our investigation has pointed out, the actual Macur α's are too big by a factor of about 2.4 at $N_{\text{In}} = 0.5$, and so the value of 1066 cal is fortuitously a reasonable number to represent the quasi-chemical Ω.

The significant aspect of Hayes and Kubaschewski's work with regard to our findings is the one liquidus point measurement they made at 70 at. % Ga in an effort to resolve the discrepancy in that region between the curves of Predel and Stein, Swirbely and Selis, Heubner and Wincierz and Denny *et al.* They used high purity (99.99 %) materials and obtained the point as being 51°C on cooling and 50.9°C on heating, through very careful measurements. Our computed curve goes right through that point.

4. Conclusions

The hitherto accepted solidus of Swirbely and Selis is thermodynamically infeasible. The solidus computed as being consistent with the accepted liquidus and heats of solution measurements is a relatively smooth curve. The computed solvus curve intersects the solidus at 16 at. % Ga and 16°C. One may conclude that in systems such as this, where equilibrium in the solid state is achieved very slowly, it might be more convenient and reliable to calculate the solidus and solvus by procedures such as above, preferably with a knowledge of some of the thermodynamics in the solid phase.

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