# Se–Ga$_{2/3}$Se PHASE EQUILIBRIA: A REGULAR ASSOCIATED SOLUTION MODEL FOR THE Ga–Se LIQUID

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**Abstract**—Se vapor pressures were measured by the dew point method for the binary system Ga$_{1-x}$Se$_x$, $0.60 < x <$ 1.00 (Ga$_2$Se$_3$–Se), between 700 and 1050°C. The Se vapor pressure was found to decrease rapidly near $x = 60$ atomic% Se. The $T$–$X$ and $P$–$X$ liquidus curves are thermodymanically modelled by a regular associated solution model for the liquid phase, with the associate, Ga$_2$Se$_3$. The best fit to the data was obtained with 4000 cal/mole of Ga$_2$Se$_3$ for the regular solution interaction parameter and 0.10 for the degree of dissociation in the stoichiometric liquid ($x = 0.60$).

## INTRODUCTION

The $\gamma$ polymorph of the compound Ga$_2$Se$_3$ crystallizes with the zincblende crystal structure ($F\bar{4}3m$)[1], in which the stoichiometry reflects the normal valence states of Ga ($+3$) and Se ($-2$). Since 1/3 of the cation sites are unoccupied, a more descriptive chemical formula is Ga$_{2/3}$Se. This compound is in a sense an "average" of two other isostructural (and isoelectronic) compounds, GaAs and ZnSe. All three compounds are semiconducting with bandgaps of 1.5, 2.0 and 2.8 eV for GaAs, Ga$_{2/3}$Se and ZnSe, respectively[2, 3]. The vacancies in Ga$_{2/3}$Se influence the semiconducting properties, resulting in only $p$-type conduction with a very low carrier mobility[3]. The broad optical absorption edge[4] resembles that of amorphous As$_2$Se$_3$[5] and suggests that a distribution of electronic states associated with the random distribution of vacancies in Ga$_{2/3}$Se is similar to the band-tails characteristic of disordered solids. Recent extended-X-ray-absorption-fine-structure (EXAFS) measurements[6] on the $\gamma$ phase indicated that, although the lattice has long-range crystalline order with the zincblende structure, there is local relaxation of the Se around the Ga vacancies which results in two Ga–Se distances of 2.33 and 2.44 Å. These values are approximately equal to those obtained by X-ray diffraction for the ordered, monoclinic $\beta$-Ga$_2$Se$_3$ phase[7].

The binary Ga–Se diagram has been determined by several authors[7–9], and the equilibrium between Ga$_{2/3}$Se and Se has been recently reexamined in detail[10, 11]. Ga$_{2/3}$Se melts congruently at 1010°C; the Se-rich liquidus decreases rapidly to approx. 840°C, remains nearly flat at 770°C (75–95 at.% Se), and then decreases rapidly near pure Se. This behavior resembles liquid immiscibility, i.e. the nearly isothermal liquidus has been mistaken for a monotectic reaction[7], but thermal and metallurgical analysis indicated the absence of a monotectic[10], in agreement with Refs.[8, 9, 11].

The properties of molten Ga$_{2/3}$Se indicate that the liquid retains a large fraction of the Ga–Se bonds that characterize the semiconducting solid. First, liquid Ga$_{2/3}$Se is semiconducting[12], whereas GaAs and other III–V semiconductors become metallic upon melting[13]. Second, Ga$_{2/3}$Se expands on melting[10], whereas the III–V semiconductors contract. Finally, Ga$_{2/3}$Se has an entropy of fusion[11, 14] approx. 1/3 that of GaAs, consistent with the view that a large number of Ga–Se bonds remain in the liquid. Although a completely-dissociated liquid adequately describes the III–V binary and ternary phase diagrams[15], we anticipate that the thermochemistry of Ga–Se liquids should resemble the II–VI associated liquids, like Te–ZnTe[16].

## EXPERIMENTAL

Ten-gram samples of the desired stoichiometry were synthesized from high purity elements in a two-furnace arrangement that allowed the Ga to be maintained at 1020°C or higher while the Se temperature (and pressure) was slowly increased. Specimens were loaded into capillary-tip ampoules, shown schematically in Fig. 1, and annealed prior to each vapor pressure measurement to assure equilibrium had been achieved.

Distillation of liquids containing 60–100 at.% Se indicated that the vapor was composed of predominantly Se species. The total Se vapor pressure was determined by a dew point method, i.e., by measuring the condensation temperature ($T_c$) of Se vapor in equilibrium with either a Ga–Se liquid or a mixture of Ga–Se liquid + Ga$_{2/3}$Se solid and referring to the published vapor pressure over pure Se[17] at $T_c$. These conditions were achieved by using a multi-zone furnace; a representative profile, corresponding to a sample temperature, $T_1$, of 900°C and a $T_c$ of 820°C, is shown in Fig. 1. The solid Ga$_{2/3}$Se and Se-rich liquid, or homogeneous Ga–Se liquid, were first equilibrated at the temperature of in-
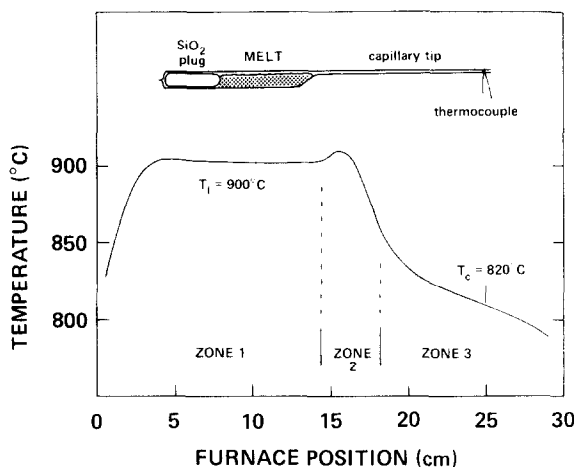
Fig. 1. Schematic of the dew point capillary ampoule and typical 3-zone furnace profile for $T_1 = 900°C$ and $T_c = 820°C$.



Fig. 2. P–T data for the total Se pressure for compositions in atomic% Se: O, 62; △, 65; □, 66.7; ●, 70; ▲, 75; ■, 80; – –, the published total pressure for pure Se.

terest, $T_1$, and then the temperature of the capillary tip was decreased until the first droplet of Se condensed at $T_c$. Condensation of droplets smaller than 1 mg was observed through a microscope mounted above a small slit in the furnace insulation, illuminated from below, while the temperature was measured by the thermocouple in contact with the capillary tip. By reheating the capillary, the condensed Se could be re-evaporated, and after equilibration the experiment could be repeated many times.

The free volumes of the ampoules, minimized by using a capillary tip and a fused silica plug were determined gravimetrically by filling them with water after the pressure measurements. At the highest pressures measured in this study the stoichiometry corrections were less than 0.2 at.% Se, and they have been ignored in the subsequent analysis. The uncertainty of $T_1$ is estimated to be ±2°C arising from the slight thermal gradient at the condensed phase, and ±5°C for $T_2$ based on heating and cooling runs and the fact that the thermocouple is not surrounded by the liquid condensate.

## VAPOR PRESSURE RESULTS

The results of our dew point measurements are shown in Fig. 2. The dashed line at the right side of the figure represents the published total vapor pressure over pure Se[17]. The heavy solid curve represents the liquidus–solidus equilibrium, i.e. solid, nearly stoichiometric, $Ga_{2/3}Se[9, 11]$ and Se-rich liquid in equilibrium with Se vapor. Up to 730°C the total pressure in equilibrium with Se-rich melts is nearly equal to that of pure Se, consistent with the very low solubility of Ga in liquid Se at these temperatures [7–11]. The nearly parallel curves extending above the liquidus curve represent homogeneous liquids in equilibrium with Se vapor, i.e. all of the $Ga_{2/3}Se$ is dissolved. The region labeled "solid solution" pertains to the two-phase equilibrium between solid $Ga_{2/3}Se$ and Se vapor. Since the reported stoichiometry range of solid $Ga_{2/3}Se$ is <0.3 at.% Se [10, 11, 18], and the composition of the solid will depend strongly on the amount of Se in the vapor volume of the ampoule (i.e. change with temperature), no solid-vapor measurements
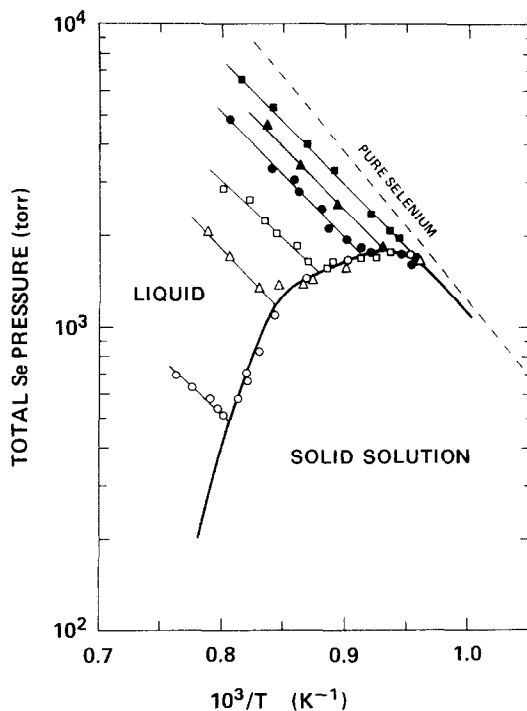
were attempted. The striking feature of the data in Fig. 2 is that the total Se pressure decreases rapidly as the liquidus composition approaches $Ga_{2/3}Se$ (60 at.% Se), even though liquidus temperature is rapidly increasing. This is a general feature of II–VI phase diagrams, except that in those systems the chalcogen vapor pressure decreases rapidly as the liquidus composition approaches 50 at.% chalcogen[19].

The vapor pressure measurements can also be used to examine features of published phase diagrams. There is no indication in the vapor pressure measurements of a monotectic between 75 and 85 at.% Se [7]. Such behavior would require a separate branch of 3-phase equilibrium: two liquids and Se vapor, and none was observed. We therefore conclude that any liquid immiscibility must be within ~15°C of our liquidus curve, the estimated equivalent scatter in our data. In addition, there was no evidence for a peritectic reaction involving a compound of stoichiometry $GaSe_2$ [7], since the 62, 64, and 65 at.% Se samples followed the same liquidus (vapor pressures) as the Se-rich compositions. The Se vapor pressure appears insensitive to whether the solid is the metastable $\alpha$-$Ga_{2/3}Se$ or the equilibrium $\beta$ and $\gamma$ phases. Thus, in the thermodynamic modeling which follows, we assume that there is only a single solid phase in equilibrium with the Se-rich liquid and Se vapor.

## MODELING OF T–X AND P–X LIQUIDUS

Initially we attempted to use the regular associated solution (RAS) model developed by Jordan[16], in which we considered the liquid to be composed of monomeric Ga and Se and associate complex, GaSe. However, this model cannot be used to fit the vapor pressure data

which are seen to decrease markedly when the liquid composition nears a Se to Ga ratio of 3 : 2. This behavior would be expected for a highly associated liquid with the associate being the complex Ga$_2$Se$_3$, instead of GaSe, and would be consistent with the results of Glasov et al.[20], which showed that the fusion of the isovalent compound, Ga$_2$Te$_3$, produced a liquid having definite semiconductor properties. The viscosity also shows a maximum for a Te to Ga ratio of 3 : 2.

The liquidus equation may be written, after Vieland[21]

$$\Delta H^F(T/T^F - 1) = 2RT \ln (a^l_{Ga}/a^{sl}_{Ga}) + 3RT \ln (a^l_{Se}/a^{sl}_{Se}) \tag{1}$$

where $\Delta H^F$ is the enthalpy of fusion, 20,000 cal/mole for Ga$_2$Se$_3$[11, 14], $T^F$ is the temperature of fusion, 1283 K [10], $a^l$ and $a^{sl}$ refer to the activities of Ga and Se in the liquid and in the stoichiometric liquid (Se : Ga = 3 : 2), respectively. $R$ and $T$ have their normal meaning.

The notation for the liquid composition follows Jordan[16]. The liquid consists of $n_A$ moles of Ga, $n_B$ moles of Se, and $n_{A_2B_3}$ moles of Ga$_2$Se$_3$ associate molecules. The overall composition is expressed in terms of $n_1$, the number of moles of Ga both free and in associates, and $n_2$ the total number of Se atoms. Thus

$$n_1 = n_A + 2 n_{A_2B_3}, \tag{2a}$$

and

$$n_2 = n_B + 3 n_{A_2B_3}. \tag{2b}$$

As shown by Prigogine and Defay[22], the chemical potentials,

$$\mu_A = \mu_1, \tag{3a}$$

and

$$\mu_B = \mu_2, \tag{3b}$$

independent of the mode of association.

The concentrations of the various species in the liquid are connected through the mass action expression,

$$K = \frac{a_A^2 a_B^3}{a_{A_2B_3}} \tag{4}$$

where the equilibrium constant, $K$, is taken to be temperature independent in this simple model.

The mole fractions are defined in a natural manner to be,

$$X_A = \frac{n_A}{n_A + n_B + n_{A_2B_3}} \tag{5a}$$

$$X_B = \frac{n_B}{n_A + n_B + n_{A_2B_3}} \tag{5b}$$

and

$$X_1 = \frac{n_1}{n_1 + n_2} = \frac{n_A + 2n_{A_2B_3}}{n_A + n_B + 5n_{A_2B_3}} \tag{6a}$$

$$X_2 = \frac{n_2}{n_1 + n_2} = \frac{n_B + 3n_{A_2B_3}}{n_A + n_B + 5n_{A_2B_3}}. \tag{6b}$$

Algebraic manipulation yields expressions for $X_A$ and $X_B$ in terms of $X_{A_2B_3}$[16]:

$$X_A = X_1 + 2(X_1 - X_2)X_{A_2B_3} \tag{7a}$$

and

$$X_B = X_2 + (X_2 - 3X_1)X_{A_2B_3} \tag{7b}$$

Using the same regular solution approach developed by Jordon we find the following approximate relations for the activity coefficients

$$RT \ln \gamma_A \approx \alpha X_2^2 \tag{8a}$$

$$RT \ln \gamma_B \approx \alpha X_1^2 \tag{8b}$$

where $\alpha$ is the regular solution interaction parameter. Using the Gibbs–Duhem equation, mathematical manipulation yields an explicit expression for the $A_2B_3$ activity coefficient,

$$RT \ln \gamma_{A_2B_3} = 2\alpha[0.9 - 3X_1X_2 - X_2^2/2]. \tag{9}$$

The mass action expression, eqn (4), can now be written in terms of $X_1$, $X_2$, and $X_{A_2B_3}$

$$\ln K - 1.2\,\alpha/RT = \ln \{[X_1 + 2(X_1 - X_2)X_{A_2B_3}]^2 \\ \times [X_2 + (X_2 - 3X_1)X_{A_2B_3}]^3/X_{A_2B_3}\}. \tag{10}$$

Equation (10) can be written in terms of $\beta$, the degree of dissociation for the stoichiometric liquid (Ga$_2$Se$_3$, $X_2 = 0.6$),

$$\ln K - 1.2\,\alpha/RT = \ln [(0.4)^2(0.6)^3\beta^5/(1 - \beta)]. \tag{11}$$

Combining eqns (10) and (11) yields an equation which allows the determination of $X_{A_2B_3}$ for a given value of $\beta$, $X_1$ and $X_2$. The equation cannot be solved analytically so the liquidus and vapor pressure calculations must be performed numerically. Knowing $X_{A_2B_3}$, $X_A$ and $X_B$ are obtained from eqns (7a, b). The activity coefficients are given in terms of $X_1$ and $X_2$, then eqn (1), the liquidus equation, can be solved to give $T$ vs $X_2$. The calculation has two adjustable parameters $\alpha$ and $\beta$. In the following discussion, $X_{Se}$ refers to the total Se fraction in the liquid, $X_2$, not the free Se, $X_B$.

The values of $\alpha$ and $\beta$ were determined by comparing the calculated activities, $a^l_{Se}$, along the liquidus with those obtained from the experimental vapor pressure data. In Fig. 3 the calculated values of $a^l_{Se}(X_{Se}\gamma_{Se})$ vs $X^l_{Se}$ using the Ga$_2$Se$_3$ associate (solid curve) are compared with those obtained from our total vapor pressure data, using
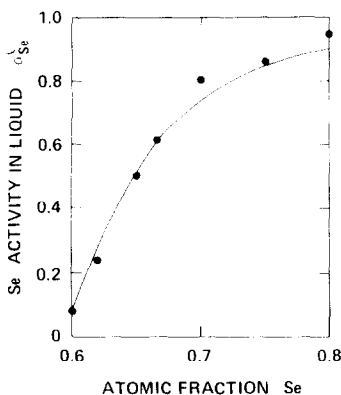
Fig. 3. Comparison of calculated and experimental $a_{Se}^l$ along the $P_{Se_2}$-$X$ liquidus for $Ga_{1-x}Se_x$, for $0.60 < x < 0.80$. The calculated curve is for $Ga_2Se_3$ associates, $\alpha = 4000$ cal/mole and $\beta = 0.10$, and a standard deviation of 0.056.

the published equilibria between $Se_n$ vapor molecules[23], where

$$a_{Se}^l = (P_{Se_2}/P_{Se_2}^0)^{1/2}. \qquad (12)$$

For $\alpha = 4000$ cal/mole and $\beta = 0.10$, the agreement of the calculated $a_{Se}^l$ with experiment is excellent, with a standard deviation of 0.056. The values of $a_{Se}$ for the ($Ga_2Se_3$) RAS model fall rapidly as the liquid approaches the composition $X_{Se} = 0.6$ because most of the Se is bonded in the complex represented by $Ga_2Se_3$, thus dramatically reducing $X_{Se}$, the fraction of free Se in the liquid, and consequently $P_{Se_2}$. On the other hand, for a RAS model which assumes GaSe to be the associate, $P_{Se_2}$ can fall rapidly only near $X_{Se} = 0.5$. The reduction in $a_{Se}$ at the 2:3 stoichiometry has also been observed in the Sb–Se and Bi–Se systems [24], where the compounds $Sb_2Se_3$ and $Bi_2Se_3$ probably retain significant bonding in the liquid.

The liquidus curve was calculated for $\alpha = 4000$ cal/mole and $\beta = 0.10$. In Fig. 4 the results are compared with experimental data[10, 11]. The agreement is fair with a standard deviation between theory and experiment of 41°C, ignoring the data point of $X_{Se} = 0.995$. The calculated liquidus does not show the incipient liquid immiscibility suggested by the data. Using smaller values of $\Delta H^f$ will allow the calculated liquidus to better approximate this feature of the experimental data, but the good agreement between two experimental measurements of $\Delta H^f$, 20 kcal/mole[11] and 21.9 kcal/mole[14], does not warrant adjusting $\Delta H^f$. We point out that the liquidus can be better fit by a RAS model with the GaSe associate, but the corresponding $a_{Se}$ values are not physical, being greater than unity for $X_{Se}$ between 0.6 and 1.0 (and not decreasing rapidly near 0.6, as discussed above). The value of having vapor pressure data, in addition to liquidus data, with which to model the liquid structure cannot be overemphasized. Whereas the success of the $Ga_2Se_3$-associate in modeling the vapor pressure lies in the reduction of the $P_{Se_2}$ at $X_{Se} = 0.6$, accurate modeling of the liquidus behavior probably requires more complex liquid interactions than
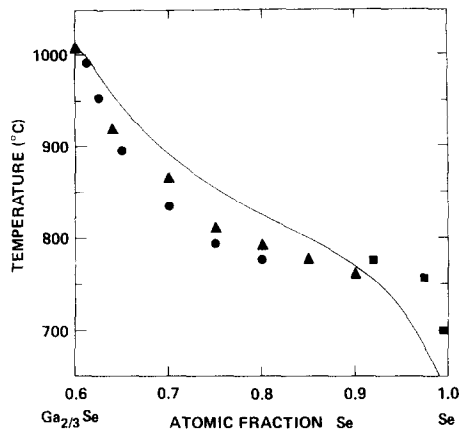


Fig. 4. Comparison of calculated and experimental $T$–$X$ liquidus for $Ga_{1-x}Se_x$, for $0.60 < x < 1.00$; ▲, ■, Ref. 10; ●, Ref. 11. The solid curve is calculated assuming $Ga_2Se_3$ associated with $\alpha = 4000$ cal/mole and $\beta = 0.10$, and the standard deviation is 41°C.

those permitted in the simple RAS model which includes only $Ga_2Se_3$, Ga, and Se as distinct species. In fact, liquid Se is not an atomic liquid, but consists of extended, covalently-bonded, chains and rings[25]. Although experimental data can generally be fit better with the additional adjustable parameters available in more complex models, the physical meaning of those parameters can be quickly obscured.

The values of $\alpha$ and $\beta$ for $Ga_{2/3}Se$ can be compared with those obtained by Jordan[16] for the systems Te–CdTe ($\alpha = 3100$ cal/mole, $\beta = 0.055$) and Te–ZnTe ($\alpha = 900$ cal/mole, $\beta = 0.057$). In these two systems the associate is ZnTe or CdTe, so the comparable associate in the Se–$Ga_{2/3}Se$ system could be regarded as $Ga_{2/3}Se$. We do not suggest that there are fractions of Ga atoms in the liquid, just as there are probably not $Ga_2Se_3$ molecular species in the liquid. An associate with a 2:3 Ga:Se ratio merely accounts for the fact that the structure of the stoichiometric liquid differs little from the hot solid with regard to the amount of free Se it contains. Similarly, molten ZnTe probably does not contain diatomic ZnTe molecules, but more likely contains a covalently-bonded extended, or chain-like, structure[26]. For a $Ga_{2/3}Se$-associate, the values of 1333 cal/mole ($Ga_{2/3}Se$) and 0.036 for $\alpha$ and $\beta$, respectively, are similar to those reported for Te–CdTe and Te–ZnTe. It appears that the Ga vacancies, which distinguish $Ga_{2/3}Se$ from stoichiometric zincblende crystals, such as ZnTe, do not greatly weaken the bonding in the liquid, as reflected by the values of $\alpha$ and $\beta$. In fact, the tendency for covalently-bonded structures to exist in chalcogenide liquids increases from ZnSe to $Ga_{2/3}Se$ to $Ge_{1/2}Se$, which is a good glass-forming liquid and in which all Ge atoms are tetrahedrally bonded to 4 Se, which are in turn two-fold coordinated to Ge[27]. The viscosity of Se–$GeSe_2$ liquids has been successfully modeled with a $GeSe_2$ associate[28]. If the structure of liquid $Ga_{2/3}Se$ is very much like the solid, 1/3 of the Se atoms are 2-coordinated, and the rest are 3-coordinated[6].

In conclusion, the RAS model assuming the associate to be $Ga_2Se_3$, $\alpha = 4000$, and $\beta = 0.10$ gives excellent

agreement with vapor pressure data and fair agreement with the liquidus data for the system Ga$_{1-x}$Se$_x$ with $0.6 < x < 1.0$. The existence of associates in the liquid phase even at the relatively high temperature of fusion of Ga$_{2/3}$Se is amply supported by (1) the rapid decrease of $a_{Se}$ as $x$ approaches 0.6, (2) the shape of the liquidus curve, as discussed by Jordan[16], and (3) the observed nature of molten Ga$_{2/3}$Se, i.e. the semiconducting properties, decreased density relative to the solid, and small entropy of fusion.

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