

Thermodynamic description of the Ga-Yb binary system

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Abstract. Pure gallium metal and many gallium based alloys and intermetallic compounds have extensive technological applications and fundamental interest. Gallium is used as a doping component in electronic devices (as in transistors or photovoltaic cells) [1]. The development of multi-alloy material depends now for most of them on preliminary numerical simulations. Such simulations are only useful when accurate thermodynamic databases are available. Such databases are developed by the CALPHAD (CALculation of PHase Diagram) method on a basis of experimental thermodynamic and phase diagram measurements. The excess term of the Gibbs energy of the liquid phase was assessed with the recent exponential temperature dependence of the interaction energies by Kaptay [2-4] and compared with the Redlich-Kister [5] polynomial equation results. The calculations based on the thermodynamic modelling and optimisation are in good agreement with the phase diagram data available in the literature.

1 Introduction

This study is a part of a thermodynamic investigation of the Ga-R systems (R= La [6], Y [7] and Ce [8]) which is intended to give a better understanding of the constitutional properties and potential technological applications of these alloys. Thermodynamic description is also needed to obtain the thermodynamic parameters via the CALPHAD approach [9]. No thermodynamic description of the Ga-Yb system is available in the literature. In the present work, a thermodynamic optimization for the Ga-Yb binary system is performed based essentially on the experimental phase diagram data.

2 Experimental

A recent assessment of the Ga-Yb system by Palenzona and Cirafici [10] is based on the original references, essentially the works of [11-15]. [11, 12, 14] investigated the Ga-Yb phase diagram by DTA and X-ray analysis. They reported the existence and structure of Ga₄Yb and Ga₂Yb. Ga₄Yb melts peritectically at 785 °C and Ga₂Yb melts congruently at 1120 °C. They also reported the peritectic formation of two other intermediate phases of tentative stoichiometry, GaYb and Ga₃Yb₅, with respective peritectic temperatures of 905 and 680°C. Palenzona and Cirafici [11] investigated the Ga-Yb system by DTA, microscopy, and X-ray diffraction. Pelleg et al. [13], in a careful investigation of the Ga-rich side of the RE-Ga systems, found an additional Ga-rich phase Ga₆RE, common to almost all RE metals, and having the Ga₆Pu-type structure. In the Ga-Yb system, Ga₆Yb is formed by a peritectic reaction at 282 °C. Cirafici and Fornasini [16] investigated the 20 to 32 at.%

Yb region of the Ga-Yb system by X-ray and metallographic methods, see Table 1. As Ga₆Y, Ga₆Yb is a Pauli paramagnet. Two new phases were identified: Ga₈Yb₃_HT=Ga_{0.727}Yb_{0.273}, which exists in a narrow range of temperatures estimated between 830 and 870 °C, and Ga_(3-x)Yb_LT=Ga_{0.737} Yb_{0.263}, which melts peritectically at a temperature of about 740 °C. No thermal analysis data were reported; the characteristic temperatures for these two new phases were determined approximately by examining a high number of alloys in the as-cast and annealed conditions. Ga_(3-x)Yb presents a narrow homogeneity range (~0.025 at.) around 0.263 at. Yb and Ga₈Y₃_HT is not the high temperature polytype of Ga_(3-x)Yb_LT. [16] also confirmed the existence of Ga₄Yb and resolved its crystal structure. [13] confirmed the existence of Ga₂Yb and studied structures of GaYb and GaYb₂. These two phases were found to be isomorphous with the AuCu-I and Co₂Si type, respectively. Besides the above intermediate phases, the liquid, and two terminal solid solutions (Ga) and (βYb then (γYb) with negligible solubility exist.

3 Modeling

3.1 Unary phases

The Gibbs energy function $G_i^\phi(T) = {}^0G_i^\phi - H_i^{SER}$ (298.15K) for the element i (i=Ga,Yb) in the Φ phase (Φ = Liquid, BCC, FCC and ORTHORHOMBIC) is described by an equation of the following form:

$$G_i^\phi(T) = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (1)$$

where: H_i^{SER} (298.15K) is the molar enthalpy of the element i at 298.15K in its standard element reference (SER) state, FCC for Ytterbium and ORTHORHOMBIC for Gallium. In this paper, the Gibbs energy functions are taken from the SGTE compilation of Dinsdale [17].

3.2 Liquid phase

The liquid phase was assessed with the recent exponential temperature dependence of the interaction energies by Kaptay [2-4] and compared with the linear model using the Redlich-Kister [5] polynomial equation results.

The Gibbs energy of one mole of formula unit of phase is expressed as the sum of the reference part ^{ref}G , the ideal part ^{id}G and the excess part ^{xs}G .

$$G_m^\phi(T) = ^{ref}G_m^\phi + ^{id}G_m^\phi + ^{xs}G_m^\phi \quad (2)$$

The excess terms of all the phases were modelled by the Redlich-Kister model [5].

$$^{xs}G_m^\phi(T) = x_i x_j \sum_{\lambda=0}^{\lambda} L_{i,j}^\phi(T) (x_i - x_j)^\lambda \quad (3)$$

where $L_{i,j}^\phi$ is the λ th interaction parameter between the elements Ga and Yb which is evaluated in the presented work according to:

** the linear model of Redlich-Kister of temperature dependence

$$\lambda L_{i,j}^\phi(T) = a_\lambda + b_\lambda T \quad (4)$$

a_λ and b_λ are the coefficients to be optimized, or.

** the Kaptay model of exponential temperature dependence

$$\lambda L_{i,j}^\phi = h^\lambda * \exp\left(-\frac{T * s^\lambda}{h^\lambda}\right) \quad (5)$$

h^λ enthalpy part and s^λ entropy part to be optimized.

In order to avoid the formation of an artificial inverted miscibility gap above the liquidus line as suggested by [18-20], in the case of the linear model, the stability constraint was enforced by requiring that the Gibbs energy of the liquid phase had a positive curvature, i.e.,

$$\frac{\partial^2 G^L}{\partial x_i^2} > 0 \text{ at all compositions and temperatures up to 4000}$$

K.

3.3 Stoichiometric compounds

The Gibbs energy of the stoichiometric compounds

G_m^{GamYbn} is expressed as follows:

$${}^0G_m^{GamYbn} = \frac{m}{m+n} {}^0G_{Ga} + \frac{n}{m+n} {}^0G_{Yb} + a + bT \quad (6)$$

where ${}^0G_{Ga}$ and ${}^0G_{Yb}$ are the Gibbs energy of the pure elements Ga and Yb respectively; a and b are parameters to be determined. The intermediate phases Ga_6Yb , Ga_4Yb , Ga_8Yb_3 (high temperature phase), Ga_2Yb , $GaYb$ and $GaYb_2$ have been treated as stoichiometric compounds while a solution model has been used for the description of the liquid phase and the (Ga) and (Yb) solid solutions. The intermetallic compound $Ga_{(3-x)}Yb$

which has a homogeneity range, was treated as the formula $(Ga,Yb)_{0.263}:(Yb,Ga)_{0.737}$ by a two-sublattice model with a mutual substitution of Ga and Yb on both sublattices.

4 Results

The experimental phase diagram is shown in Fig. 1 and the calculated one in Fig. 2. A very good agreement is noted. The optimized enthalpies of mixing of the liquid phase (at 1750 K) are shown in Fig. 3 as well as the infinite dilution enthalpies $\overline{\Delta H_{Yb}^\infty}$ and $\overline{\Delta H_{Ga}^\infty}$ at 1750 K.

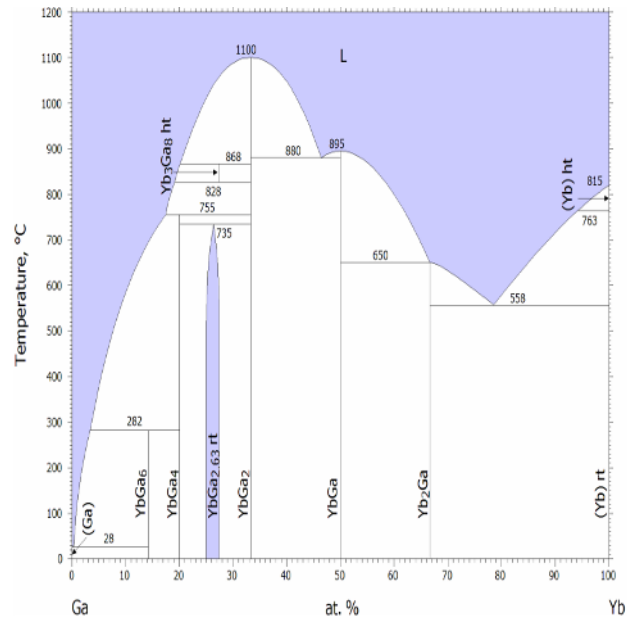


Figure 1. The Ga-Yb phase diagram evaluated by [5].

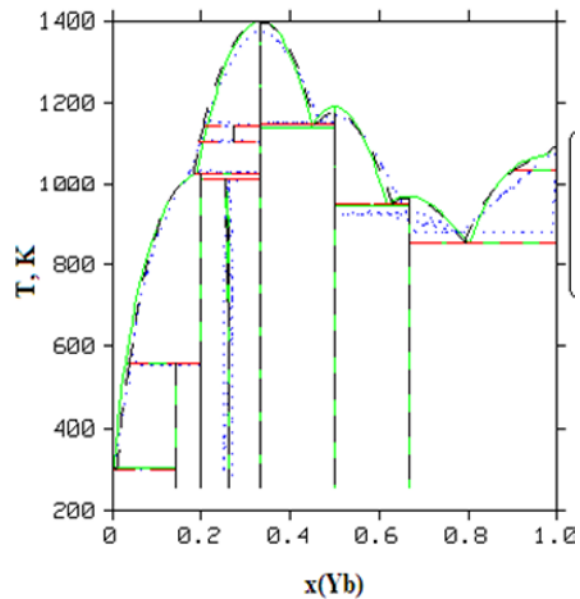


Figure 2. Comparison of the Ga-Yb calculated phase diagram with the experimental data, - - - (Redlich-Kister model), — (Kaptay model, (Experiment, Palenzona et al, [8]).

The optimized enthalpies and entropies of mixing of the liquid phase with the two temperature dependences of the

excess parameters (linear + positive curvature of the liquidus and exponential) are shown in Table 2. A satisfactory agreement is observed between the two models.

The enthalpies of formation of the intermediate phases are shown in Fig. 4. These latter are consistent with the thermodynamic parameters of the terminal solid solutions because when the liquid phase is suspended, the calculated phase diagram shows that they are no more stable at very high temperature [17-19]. For this system, no predictive value for the enthalpies of mixing of the liquid phase and for the enthalpies of formation was calculated by the Miedema model [21].

Table 1. Symbols and crystal structures of the solid phases in the Ga-Yb alloys.

Diagram Symbol	Composition at %Yb	Pearson symbol	Prototype
α (Ga)	0	<i>oC8</i>	α Ga
Ga ₆ Yb	14.3	<i>tP14</i>	Ga ₆ Pu
Ga ₄ Yb	20	<i>mS10</i>	CaGa ₄
Ga _(3-x) Yb	25 to 27.5	<i>hP54.3</i>	Ga _(3-x) Yb
Ga ₈ Yb ₃	27.3	<i>oI22</i>	Eu ₈ Ga ₃
Ga ₂ Yb	33.3	<i>hP6</i>	CaIn ₂
GaYb	50	<i>tP4</i>	AuCu-I
GaYb ₂	66.7	<i>oP12</i>	Co ₂ Si
γ (Yb)	~100	<i>cI2</i>	W
β (Yb)	~100	<i>cF4</i>	Cu
α (Yb)	~100	<i>hP2</i>	Mg

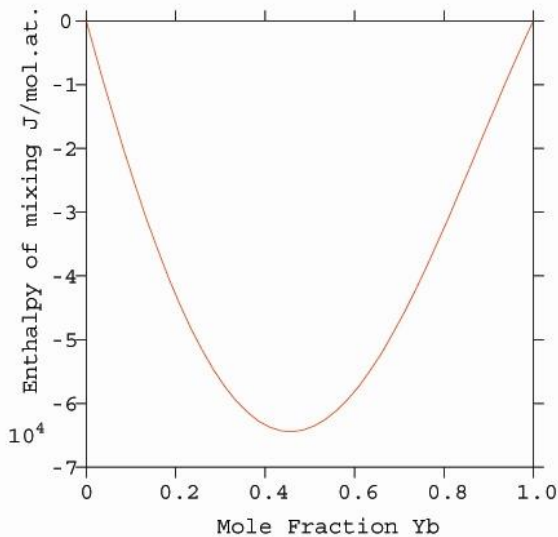


Figure 3. Enthalpy of mixing of the liquid phase at 1750 K. Enthalpy at infinite dilution at 1750 K.

$$\overline{\Delta H_{Yb}^{\infty}} = -387.25 \quad \text{kJ/mol.at}$$

$$\overline{\Delta H_{Ga}^{\infty}} = -348.94 \quad \text{kJ/mol.at}$$

Table 2. Comparison of the excess parameters optimized with the two models of temperature dependence.

Excess parameter	Temperature Dependence	
	Linear	Exponential
$\lambda_{L_{i,j}^{Liq}}$	$\lambda_{L_{i,j}^{\phi}}(T) = a\lambda + b\lambda T$ + $\frac{\partial^2 G^L}{\partial x_i^2} > 0$	$\lambda_{L_{i,j}^{\phi}} = h^{\lambda} * \exp\left(-\frac{T * s^{\lambda}}{h^{\lambda}}\right)$
λ	h^{λ} J/mol.at.// s^{λ} J/mol.at.K	h^{λ} J/mol.at.// s^{λ} J/mol.at.K
0	-258.18 // -47.08	-259.70 // -29.30
1	-119.25 // -76.38	-121.11 // -127.62
2	+54.07 // +6.04	+54.93 // +5.50

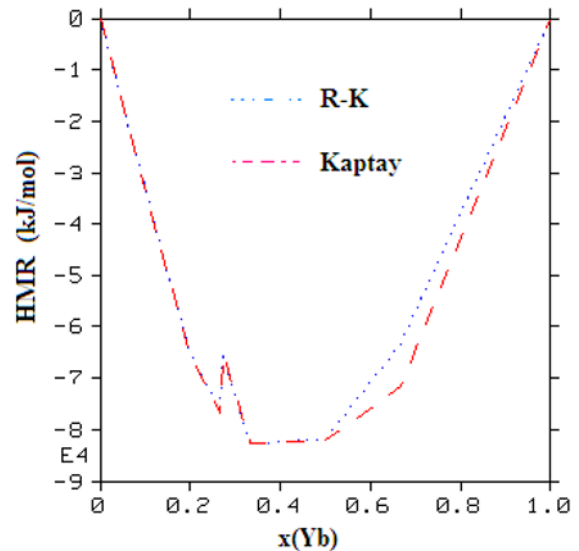


Figure 4. Calculated enthalpies of formation of the intermediate phases. The lower value (- 67 kJ/mol.at.) around $x(\text{Yb}) \sim 0.27$ at. corresponds to the Ga₈Yb₃ HT phase, the temperature range of existence of which is not well known.

5 Conclusion

A consistent set of thermodynamic parameters of the different phases of the Yb-Ga binary system has been optimized. The two temperature dependences (linear or exponential) of the excess parameters of the Gibbs energy of the liquid phase gave account of the same calculated phase diagram. The computed values are in very good agreement with the experimental data. The calculated phase diagram and thermodynamic properties of the Yb-Ga binary system can be used to further understand the thermodynamics of other ternary or quaternary systems such as Yb-Ga-* or *-Ga-Y-*.

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