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Thermodynamic properties of liquid Ga–Li alloys: Experiment vs. modeling

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ABSTRACT

The integral molar enthalpy of mixing was determined by the drop calorimetric method for binary Ga–Li liquid alloys. The measurements were conducted at three temperatures, i.e. 873 K, 992 K and 1039 K, and in the following concentration ranges: $X_{Li} = 0.7030$ to 0.9801, 0.0908 to 0.3748 and 0.4284 to 0.8282, respectively. A strong negative deviation from the ideal solution was observed, with the minimum value equal to −21.2 kJ/mol for $X_{Li} = 0.5421$. The analysis of the experimental data suggests that the integral mixing enthalpy of the Ga–Li liquid solutions is independent of temperature. The values calculated from the Miedema's model are more positive in comparison to the measured ones, and the maximum difference of about 12.5 kJ/mol is observed for the 0.5 mol fraction of Li. By way of applying the calorimetric data from this work and the electromotive force measurements of Wen and Huggins and Yatsenko et al., the Redlich–Kister relation was worked out for the excess Gibbs energy of the liquid Ga–Li liquid solutions. The calculated $Scc(0)$ partial structure factor points to the GaLi associates in liquids.

1. Introduction

Lithium gallium alloys are one of the binary lithium alloys which have been considered to be possible negative electrode materials. For comparison, the theoretical capacity of the $GaLi_2$ phase (around $750\,mAh \cdot g^{-1}$) [1] is about twice as high as the maximum capacity of the graphite which is used in Li-ion batteries [2].

The investigations of the gallium–lithium (Ga–Li) system were initiated by Schneider and Hilmer [3], who measured the enthalpy of fusion of the GaLi phase by the drop calorimetric method. Next, in 1970, Thümmel and Klemm [4] used the thermal analysis (TA) for the investigations of the temperature phase transitions and the molar volume measurements, in order to confirm the found intermetallic phases: GaLi, Ga_2Li and $GaLi_2$ (or Ga_4Li_9). They also proposed, for the first time, the Ga–Li phase diagram with the mentioned phases as well as two eutectic reactions (the proposed concentrations and temperatures were not cited in the original work). They also measured the lattice parameters for the GaLi phase by the X-ray analysis. Using the differential thermal analysis (DTA), Yatsenko et al. [5] studied the Ga–Li system and, beside the phases cited by [4], they found two additional ones: Ga_4Li and Ga_2Li_3. In the same year, Yatsenko et al. [6] conducted Li activity tests in the Ga–Li liquid solutions at $T = 1023$ K, using the electromotive force measurement (EMF) of the concentration cells as well as liquid Li as the reference electrode. The heat of fusion of the GaLi intermetallic phase was determined in 1980 by Buschmanov and Yatsenko [7], who used the differential scanning calorimetric method (DSC). The electrochemical investigations for the Ga–Li liquid and solid solutions were performed by Wen and Huggins [8] between 0.1 and 72 at.% of Li at $T = 688$ K (415 °C), with the use of an (Al) + LiAl two-phase electrode as the reference one. The temperature dependence of the EMF for the two-phase $(Ga)_l + (GaLi)_s$ alloys with the overall composition of 40 at.% Li was determined to be between 653 and 848 K (380 °C to 575 °C). Next to the EMF study, the diffusion chemical coefficient in the GaLi intermetallic phase was measured by [8] at $T = 688$ K (415 °C). Based on the studies mentioned above, in 1991, Sangster and Pelton [9], for the first time, evaluated the Ga–Li phase diagram with the six following intermetallic phases: $Ga_{14}Li_3$, Ga_7Li_2, GaLi, Ga_4Li_5, Ga_2Li_3 and $GaLi_2$ and two eutectics.

With the consideration of the new data from the X-ray diffraction and the DTA study by Tillard-Charbonnel and Belin [10], a new version of the Ga–Li phase diagram was proposed by Okamoto [11], with two new intermetallic phases (Ga_8Li_3, Ga_9Li_5) found by [10].

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In 2003, Yuan et al. [12] conducted a critical evaluation of all the available data for the Ga–Li system and, for the first time, they elaborated a complete set of optimized modeled parameters, which they used for the calculation of the Ga–Li phase diagram. In 2006, Okamoto [13] once again demonstrated the Ga–Li phase diagram, which showed disagreement with the liquidus lines calculated by Yuan et al. [12] and the available literature DTA data. Moreover, the existence of the Ga_8Li_3 phase proposed by [10] should be confirmed.

As the literature data has shown disagreement in respect of the description of the thermodynamics of the Ga–Li liquid phase, and as the change of the enthalpy of mixing ($\Delta_{mix}H$) is an important thermodynamic function, the main aim of this work was to measure $\Delta_{mix}H$ by the drop calorimetric technique and to work out the Redlich–Kister equation describing the excess free enthalpy of the Ga–Li liquid solutions based on the available literature experimental data.

2. Material and methods

2.1. Calorimetric study

Calorimetric measurements were performed with the use of the Setaram MHTC 96 Line evo calorimeter. This calorimeter has a thermopile constructed on 20 thermocouples and a graphite tube resistance furnace operating up to $T = 1723$ K. For heat effects registration and data evaluation the Calisto software was used.

To determine the integral enthalpy of mixing of the liquid Ga–Li alloys, metallic gallium and lithium were used (table 1). All the calorimetric measurements were carried out with the protective atmosphere of high purity argon. For the calorimetric study, tungsten crucibles with a protective alumina tube were used.

Because sapphire (α-Al_2O_3), commonly used for calorimetric calibration, reacts with lithium, it cannot be used in these measurements [14]. Taking this into account, at the beginning of the whole series, the calorimeter was calibrated by means of pieces of gallium or lithium.

In the case of the calibration with the use of lithium, the prepared pieces were closed inside a glove box with high purity argon in a calorimetric antechamber. The antechamber was removed from the glove box and connected to the calorimeter. Before each experimental run and before the dropping of the pieces of Ga or Li samples into the calorimeter, the apparatus was evacuated with a turbo molecular pump several times and then flushed with high purity argon. The calorimetric measurements were carried out at $T = 1039$ K (Series 1), at $T = 992$ K (Series 2), and at $T = 873$ K (Series 3).

2.2. Miedema's model

The Ga–Li system is one of the systems for which there are no known experimental data of the integral molar enthalpy of mixing. To obtain these data, modeling can be applied. One of the semi-empiric models allowing for the estimation of the integral molar enthalpy of mixing in binary systems is the Miedema's model [15,16]. According to this model, the integral molar mixing enthalpy of the Ga–Li liquid alloys can be calculated by way of applying equation (1).

TABLE 1
Materials applied in this study.

Chemical name	Source	Final purity [mass. %]	Purification method	Analysis method
Gallium	Alfa Aesar	99.999	None	Certified purity
Lithium	Alfa Aesar	99.9	None	Certified purity
Argon	Air Products	99.9999	None	Certified purity

$$\Delta_{mix}H = X_{Ga}X_{Li}(c^s_{Ga}\Delta H^0_{Li,Ga} + c^s_{Li}\Delta H^0_{Ga,Li}), \tag{1}$$

where:

X_{Ga}, X_{Li}, are the molar fractions of gallium and lithium, respectively. c^s_{Ga}, c^s_{Li}, $\Delta H^0_{Ga,Li}$ and $\Delta H^0_{Li,Ga}$ are determined with the use of the following equations:

$$c^s_{Ga} = \frac{X_{Ga}V^{2/3}_{Ga}}{X_{Ga}V^{2/3}_{Ga} + X_{Li}V^{2/3}_{Li}}, \tag{2}$$

$$c^s_{Li} = 1 - c^s_{Ga}, \tag{3}$$

$$\Delta H^0_{Ga,Li} = \frac{2V^{2/3}_{Ga}\cdot\left[-P(\Delta\Phi^*)^2 + Q\left(\Delta n^{1/3}_{ws}\right)^2 - R_{(l)}\right]}{\left[(n^{Ga}_{ws})^{-1/3} + (n^{Li}_{ws})^{-1/3}\right]}, \tag{4}$$

$$\Delta H^0_{Li,Ga} = \frac{2V^{2/3}_{Li}\cdot\left[-P(\Delta\Phi^*)^2 + Q\left(\Delta n^{1/3}_{ws}\right)^2 - R_{(l)}\right]}{\left[(n^{Ga}_{ws})^{-1/3} + (n^{Li}_{ws})^{-1/3}\right]}. \tag{5}$$

P, Q, $R_{(l)}$, are the empiric constants determined by Miedema et al. [16], n^{Ga}_{ws}, n^{Li}_{ws} are the densities of the electrons at the Wigner–Seitz cell boundary. More details can be found in our previous work [17].

3. Results and discussion

In the case of the Ga–Li system, the measured enthalpy is the integrated heat flow at a constant pressure, and it follows the following equations:

$$H_{DISS-X} = (\Delta H_{Signal}\cdot K) - (H_X^{T_D\to T_M}\cdot n_X), \tag{6}$$

$$K = \frac{H_X^{T_D\to T_M}\cdot n_X}{\Delta H_{Calibration}}, \tag{7}$$

$$\Delta_{mix}H_m = \frac{\sum H_{DISS-X}}{n_{Ga} + n_{Li}}, \tag{8}$$

where ΔH_{Signal} is the heat effect for each drop of metal (Ga or Li) which equaled the added drop enthalpy, K is the calorimeter constant, T_D and T_M are the drop and calorimeter absolute temperatures, respectively. The $H_X^{T_D\to T_M}$ is the enthalpy change of the pure gallium or lithium which was obtained from Pandat 2014 (Pan_SGTE database based on the original SGTE v4.4 database), n_{Ga} and n_{Li} are the numbers of moles of Ga and Li, respectively. $\Delta H_{Calibration}$ is the heat effect of dropped metal, which was used for calibration. The H_{DISS-X} is the enthalpy of dissolution of pure gallium or lithium.

The enthalpy of the pure metals, the numbers of moles, the mole fraction of pure lithium, the drop enthalpy and the integral molar enthalpy of mixing of the liquid Ga–Li alloys obtained in three separate experimental series at the three following temperatures: 1039 K (Series 1), 992 K (Series 2) and 873 K (Series 3), are given in table 2. The measurements of Li-rich alloys (Series 3) were performed at $T = 873$ K, with the purpose to avoid Li evaporation and to verify the existence of the temperature dependence of the mixing enthalpy. In the temperature range of 873 K to 1039 K, no differences in the value of the molar enthalpy of mixing were