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Calorimetric studies of mixing enthalpy in the liquid system Ga-Li, and Ga-Li-Sn

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ABSTRACT

Partial enthalpies of mixing for the liquid phase of the binary Ga-Li and ternary Ga-Li-Sn systems at a temperature of 1081 K were measured by high-temperature drop calorimetry. The binary system was investigated to a maximum lithium content of $x(\mathrm{Li}) = 0.59$. In the ternary, seven composition sections were investigated: $x(\mathrm{Ga})/(x(\mathrm{Ga}) + x(\mathrm{Sn})) = 0.15, 0.45, 0.70, 0.85$, and $x(\mathrm{Ga})/(x(\mathrm{Ga}) + x(\mathrm{Li})) = 0.80, 0.50, 0.40$. It is shown, that the binary sub-system Ga-Li shows a strong exothermic behavior with a molar liquid mixing enthalpy of $\Delta_{\mathrm{mix}}H = -22.4\ \mathrm{kJ \cdot mol^{-1}}$ at $x(\mathrm{Li}) = 0.58$ (1081 K). In accordance with an even more negative molar mixing enthalpy of $\Delta_{\mathrm{mix}}H = -36.82\ \mathrm{kJ \cdot mol^{-1}}$ at $x(\mathrm{Li}) = 0.7$ (1081 K) in the binary sub-system Li-Sn, the ternary Ga-Li-Sn system is characterized by a strong exothermic behavior. Our experimental values for the binary Ga-Li system agree well with literature data and $\Delta_{\mathrm{mix}}H$ against composition was described by a Redlich-Kister polynomial. It is shown, that for the ternary Ga-Li-Sn system the extrapolation model of Toop is sufficient enough to describe the mixing enthalpy of the liquid phase. Moreover, our experimental ternary data were numerically fitted on the basis of an extended Redlich-Kister-Muggianu model which was designed for the excess energy of the substitutional-regular-solution model.

1. Introduction

The increasing demand of powerful batteries for electro-mobility and load leveling is driving the research into developing new battery technologies [1]. Li-Ion batteries (LIB) which are widely used for hand held devices like cell phones, notebooks and cameras need to be improved mandatorily in terms of higher capacities, energy- and power density as well as higher cyclability. Such improvements are primarily targeting on the increase of charge density i.e., the amount of charge carriers, which can be stored within the individual electrode materials, and the increase of cell voltage. Both together specify the energy a galvanic cell can theoretically supply. Various active materials are under discussion for high-capacity anodes; metals and intermetallics are among them. For instance, the theoretical charge capacity of $C_{\mathrm{th}} = 990\ \mathrm{mAh \cdot g^{-1}}$ for Sn is almost three-times that of carbon-based anodes used today ($C_{\mathrm{th}} = 372\ \mathrm{mAh \cdot g^{-1}}$) [2]. Degradation of such electrodes by significant volume changes during continuous lithiation/delithiation hampers the commercialization of Li-Ion batteries with metallic anode materials, see e.g., Choi et al. [3]. An approach to prevent degradation and enhance cycle life of the battery cell is to embed the active material into an inactive conducting matrix, which is able to buffer the mechanical stress. The matrix should be ductile and/or nano-crystalline or liquid. The matrix material can be introduced by simple mechanical mixing, however better results are obtained by co-precipitation. Co-precipitation can be efficiently realized using intermetallic phases instead of pure metals as anode materials. Alloys, which consist of active and less or inactive metals show co-precipitation on lithiation/delithiation. Wu et al. [4] recently showed, that a “self-healing” fully liquid anode material of eutectic Ga-Sn, inhibits the negative effect of crack formation caused by volume changes. On lithiation, several $\mathrm{Li_xSn_{1\text{-}x}}$ and $\mathrm{Li_xGa_{1\text{-}x}}$ compounds are formed. To fully describe and understand the reactions of Li with Ga-Sn alloys, a self-consistent and reliable thermodynamic description of the ternary Ga-Li-Sn system is necessary. The binary Li-Sn, and Ga-Sn systems are already sufficiently described by CALPHAD-type assessments from Reichmann et al. and Anderson and Ansara [5,6]. The first CALPHAD description of the Ga-Li system by [7] was updated by Azza et al. [8]. However, additional experimental thermodynamic data such as enthalpies of mixing, heat capacities, and enthalpies of formation are still needed for a full self-consistent

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CALPHAD-type assessment of Ga-Li and Ga-Li-Sn. In this work, we study molar enthalpies of mixing for the liquid phase in the Ga-Li and Ga-Li-Sn systems at 1081 K.

2. Literature review

2.1. Ga-Li

Thermodynamic investigations in the Ga-Li system were first performed by Schneider and Hilmer [9] using drop calorimetry to measure heat increments of the compound βLiGa to derive enthalpies and entropies of fusion. Yatsenko et al. [10] obtained thermodynamic data by using Gibbs-Duhem integration of emf data at 1023 K and found a minimum in the integral heat of mixing of -5500 cal·mol^{-1} (-23 kJ·mol^{-1}) at x(Li) = 0.5. Moreover, Bushmanov and Yatsenko [11] investigated the heat of melting for the intermetallic phase βLiGa with differential scanning calorimetry. Using emf measurements at 688 K, Wen and Huggins determined Gibbs energies of mixing in the liquid and Gibbs energies of formation as well as chemical diffusion coefficients of Li in βLiGa compounds. Moreover, they calculated Li activities in solid phases [12]. More recently, Dębski et al. and Terlicka et al. [13,14] measured the mixing enthalpies in the liquid phase between 873 and 1039 K with drop calorimetry. A minimum of $\Delta_{\text{mix}}H = -21.2$ kJ·mol^{-1} at x(Li) = 0.5421 was found observing only a negligible temperature dependence. In an early work of Dębski and Dębski et al. [15,16], the authors presented enthalpies of formation for a series of Ga-Li compounds i.e., Li_2Ga_7, Li_5Ga_9, LiGa, Li_5Ga_4, Li_3Ga_2, and Li_2Ga.

2.2. Ga-Sn

First investigations of the enthalpies of solution of Ga in liquid Sn were performed by Kleppa [17] in 1958 and Cohen et al. in 1961 [18] using drop solution calorimetry. The authors listed partial molar heats of solution for Ga in liquid Sn at temperatures of 513, 573, and 623 K. Pool and Lundin [19] used liquid-metal solution calorimetry at 750 K and calculated the partial molar heats of solution of Ga in liquid Sn. Bros et al. [20] investigated enthalpies of mixing in the whole composition range using a Calvet-type drop-calorimeter. Measurements were performed between 473 and 743 K. Katayama et al. [21] performed emf measurements at 1073 K and obtained partial and integral molar free energies of mixing. More recently, mixing enthalpy data were verified using modified differential scanning calorimetry by Zivkovik et al. [22] and by the same authors by Oelsen calorimetry [23] within the temperature range 350–650 K. Even more recently, Li et al. [24] measured the mixing enthalpy in the range of x(Sn) = 0–0.3 by drop calorimetry.

2.3. Li-Sn

Thermodynamic properties of the Li-Sn system were intensively investigated over the last decades. Wen and Huggins, for instance determined thermochemical properties such as Gibbs free energies of formation within the temperature range 633 to 863 K [25], and also confirmed six intermetallic compounds by coulometric titration and emf measurements. Afterwards, Moser et al. [26] measured mixing enthalpy data by drop calorimetry at temperatures between 691 and 938 K in a composition range of x(Li) = 0.01–0.5 and x(Li) = 0.87–0.99. A minimum mixing enthalpy of $\Delta_{\text{mix}}H = -40$ kJ·mol^{-1} at x(Li) = 0.77 was obtained by interpolation. Based on that, Gasior and Moser [27] performed emf measurements between 777 and 975 K in a composition range of x(Li) = 0.025–0.725 and 0.91–0.954. They assumed that the minimum is caused by ordering phenomena of a Li_4Sn associate in the liquid. Recently, Fürtauer et al. [28] presented mixing enthalpy data gained by drop calorimetry of the liquid phase in a composition range of x(Li) = 0.0077–0.6230 and x(Li) = 0.9203–0.9995 at 773 K as well as in the whole composition range at 1073 K. They found a minimum of $\Delta_{\text{mix}}H = -36.82$ kJ·mol^{-1} at x(Li) = 0.80 with no significant temperature dependence. The first numerical description of the partial limiting enthalpy of mixing of Li in Sn was done by Yassin and Castanet [29], with a small temperature dependence given as $\Delta_{\text{mix}}H_{\text{Li}} = -64 + 0.0079$ T kJ·mol^{-1}.

2.4. Ga-Li-Sn

The ternary system Ga-Li-Sn was first investigated by Blessing [30] who found three intermetallic phases $Li_{10.6}Ga_{1.4}Sn_4$, Li_8Ga_3Sn, and $Li_6Ga_4Sn_2$ with narrow homogeneity ranges based on X-ray diffraction experiments. Crystal structure information is limited to Bravais lattices and lattice parameters. Recently, Blase et al. [31] found five additional intermetallic compounds ($Li_7Ga_7Sn_3$, Li_2Ga_2Sn, $Li_5Ga_5Sn_3$, $Li_3Ga_3Sn_2$, and LiGaSn) doing X-ray diffraction and thermal analysis. All five compounds belong to a quasi-binary section from GaLi to Sn supposed by the authors. A full crystal structure description is available only for LiGaSn and Li_2Ga_2Sn. The crystal systems and lattice parameters are given for $Li_3Ga_3Sn_2$ and $Li_5Ga_5Sn_3$. No crystallographic information is given for $Li_7Ga_7Sn_3$. To the best of our knowledge, no experimental thermodynamic data are available for the ternary Li-Ga-Sn system until now.

3. Materials and methods

Samples were prepared from pure materials: Sn rod, Li rod (in mineral oil), and Ga pellets; see Table 1. Before using Li, the protecting mineral oil was removed in a supersonic bath with n-hexane and further dried under vacuum in a glove box antechamber to remove the residual solvent. The calorimetric measurements were performed with a high-temperature isoperibolic Calvet-type twin micro-calorimeter HT-1000 (Setaram, France). The calorimeter is equipped with two 3D thermopiles with 210 pairs of type S-type thermocouples each allowing for a temperature resolution of about 10^{-3} K. In this arrangement, one chamber contains the sample material while the other acts as a reference and contains an alumina block. The voltage signals of the two thermopiles are connected in compensation circuit to suppress influences from the surrounding. Moreover, the calorimeter is equipped with a self-constructed auto sampler for automated dropping of sample material. The sample crucible is arranged in a protecting quartz tube and the whole measuring setup is made gas-tight to prevent sensitive alloys from oxidation. Measurement parameters and furnace settings are controlled by a user-assembled software structure (LabView) which serves also for data acquisition. The entire apparatus is described in detail by Flandorfer et al. [32].

To determine the partial and integral molar enthalpies of mixing of the liquid binary Ga-Li system, small pieces of Li with a mass of 8–30 mg were dropped from $T_{\text{d}} = 305$ K into liquid Ga-bath (approx. 2 g) placed in a BN-crucible inside the calorimeter at a bath temperature of $T_{\text{c}} = 1081$ K. Partial and integral molar enthalpies of mixing in the liquid ternary Ga-Li-Sn system were investigated by dropping either Li (6–15 mg) from around $T_{\text{d}} = 305$ K into liquid alloys of Ga_xSn_{1-x} or Sn (67–133 mg) into liquid alloys of Li_xGa_{1-x}, each at 1081 K. Seven compositions were investigated in the ternary: x(Ga)/(x(Ga) + x(Sn)) = 0.15, 0.45, 0.70, 0.85, and x(Ga)/(x(Ga) + x(Li)) = 0.80, 0.50, 0.40.; see Fig. 1. The liquid alloys inside the calorimeter were prepared by weighing the pure metals into the individual boron nitride crucibles before introducing them into the calorimeter furnace. The air and moisture sensitive Li and their alloys were prepared in a glovebox and transferred in a protecting container to the calorimeter. A constant Ar gas flow (x(Ar) = 0.99999, additionally purified from oxygen) with a flow rate of 50–70 mL·min^{-1} (0.83–1.17 mL·s^{-1}) was used after flushing the whole system three times. Traces of residual oxygen were gettered by titanium which was situated close to the sample crucible inside the quartz tube. For all measurements, boron nitride crucibles (inner diameter 11 mm, height 70 mm) were used because they are inert against liquid Ga, Li, and Sn up to temperatures of at least 1100 K. Thermal equilibration of the system to obtain a stable baseline before dropping

Table 1
Materials and purity for the experiments.

Chemical name	Source	Initial mole fraction purity	Purification method	Analysis method
Gallium	Alfa Aesar	0.9999999	None	Certified purity
Lithium	Alfa Aesar	0.9998	None	Certified purity
Tin	Alfa Aesar	0.9985	None	Certified purity
Argon		0.99999	Purification	Certified purity

the sample material lasted approx. 16 h. To verify a negligible weight loss caused by evaporation, the total mass of the crucible and samples were weighed before and after measurements. The time interval between each drop of Li or Ga was set to 40 min (2400 s), allowing the heat flow signal to return safely to the baseline, and the data acquisition interval was 0.5 s.

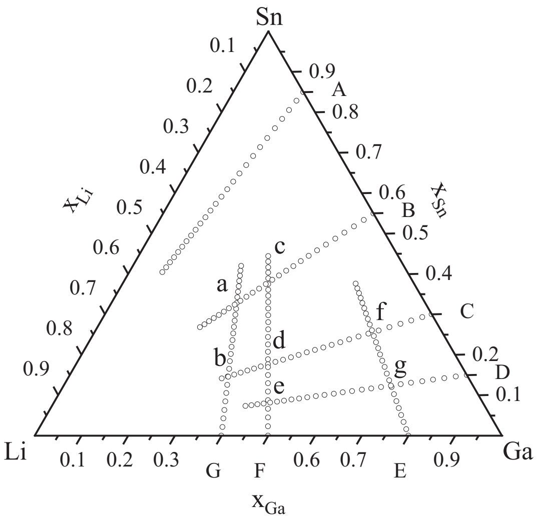

Fig. 1. Measured composition sections A to G in the ternary Ga-Li-Sn system.

For the calibration of the calorimeter, five pieces of NIST SRM 720 (National Institute of Standards and Technology, Gaithersburg, MD) standard sapphire were dropped at the end of each sample series. The measured and integrated voltage signals (*IVS*) from the thermopiles are proportional to the integrated heat flow. The constant *k* (calorimeter constant, see Eq. (1)) is calculated using the molar enthalpy increment of the reference material $\Delta_{Td\rightarrow Tc}H_{ref}$ derived from polynomials (provided by the National Institute of Standards and Technology), their molar amount n_{ref} and the heat signal from the calibration drop *IVS*:

$$k = \frac{\Delta_{Td\rightarrow Tc}H_{ref} \cdot n_{ref}}{IVS} \tag{1}$$

The mean value and standard deviation of the calibration constant is calculated from five calibration drops.

At constant pressure, $\Delta H_{ij,\text{ signal}}$ corresponds to the integrated voltage signal of the sample drop multiplied by *k*. It consists of the molar enthalpy increment of the dropped sample from solid state at T_d and liquid state at T_c, derived from Dinsdale polynomials listed in the SGTE unary database [33] multiplied by n_i and the reaction enthalpy $\Delta H_{ij,\text{reaction}}$ dissolving the sample in the liquid alloy bath (Eq. (2)).

$$\Delta H_{ij,\text{signal}} = n_i \cdot \left[H_{i(l)}, c - H_{i(s)}, d\right] + \Delta H_{ij,\text{reaction}} \tag{2}$$

Table 2
Partial and Integral molar enthalpies of mixing of liquid Ga-Li alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	ΔH_{signal}/J	$u(H_{signal})$/J	x(Li) avg	$\Delta_{mix}\overline{H}$/J·mol^{-1}	$u(\Delta_{mix}\overline{H})$/J·mol^{-1}	x(Li)	$\Delta_{mix}H$/J·mol^{-1}	$u(\Delta_{mix}H)$/J·mol^{-1}
Starting amount: $n_{Ga} = 30.144 \cdot 10^{-3}$ mol $T_d = 305.00$ K $T_c = 1081.25$ K $k = 574.6$ J·(Vs)$^{-1}$								
						0.0000	0	
0.00114681	−32.560	1.309	0.0183	−56,025	1142	0.0366	−2053	42
0.00136868	−37.011	1.324	0.0568	−54,674	967	0.0770	−4259	81
0.00137732	−35.097	1.317	0.0957	−53,114	957	0.1144	−6235	116
0.00141334	−34.957	1.317	0.1320	−52,366	932	0.1497	−8075	149
0.00146809	−35.162	1.317	0.1666	−51,584	898	0.1835	−9805	178
0.00148538	−34.099	1.314	0.1993	−50,589	885	0.2151	−11,382	206
0.00160496	−34.143	1.314	0.2308	−48,906	819	0.2466	−12,888	230
0.00161360	−33.712	1.313	0.2612	−48,525	814	0.2758	−14,269	253
0.00161504	−29.697	1.301	0.2893	−46,021	806	0.3028	−15,455	274
0.00171157	−28.308	1.297	0.3161	−44,172	758	0.3294	−16,549	292
0.00171301	−25.502	1.290	0.3417	−42,520	754	0.3540	−17,502	309
0.00173750	−24.203	1.287	0.3656	−41,562	741	0.3772	−18,366	324
0.00176343	−20.796	1.280	0.3881	−39,425	726	0.3991	−19,106	338
0.00179081	−18.727	1.276	0.4094	−38,090	713	0.4198	−19,760	351
0.00182683	−15.226	1.271	0.4296	−35,967	696	0.4395	−20,311	363
0.00183259	−12.654	1.267	0.4487	−34,537	692	0.4580	−20,780	373
0.00188878	−12.317	1.267	0.4669	−34,154	671	0.4758	−21,219	383
0.00195937	−7.039	1.262	0.4844	−31,225	644	0.4930	−21,549	391
0.00196658	−5.061	1.261	0.5012	−30,206	641	0.5093	−21,826	399
0.00198242	−1.346	1.260	0.5169	−28,312	636	0.5246	−22,029	406
0.00206598	1.027	1.260	0.5321	−27,136	610	0.5396	−22,190	412
0.00209624	4.168	1.260	0.5468	−25,644	602	0.5539	−22,297	417
0.00209912	6.134	1.261	0.5606	−24,710	601	0.5673	−22,370	422
0.00210344	9.584	1.264	0.5737	−23,076	601	0.5800	−22,390	427
0.00215099	12.931	1.268	0.5861	−21,621	590	0.5922	−22,368	431

Standard uncertainties u are: $u(T_d) = u(T_c) = 0.001$ K, $u(n_i) \leq 1 \cdot 10^{-6}$ mol $u(IVF) = 0.00219$ Vs $u(k) = 4.3$ J·(Vs)$^{-1}$.

Table 3
Section A: partial and Integral molar enthalpies of mixing of liquid Ga-Li-Sn alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	ΔH_{signal}/J	u(H_{signal})/J	x(Li) avg	$\Delta_{\text{mix}}\overline{H}$/J·mol^{-1}	u($\Delta_{\text{mix}}\overline{H}$)/J·mol^{-1}	x(Li)	$\Delta_{\text{mix}}H$/J·mol^{-1}	u($\Delta_{\text{mix}}H$)/J·mol^{-1}
Starting amount: $n_{\text{Sn}} = 26.919 \cdot 10^{-3}$ mol $n_{\text{Ga}} = 4.751 \cdot 10^{-3}$ mol $T_{\text{d}} = 305.02$ K $T_{\text{c}} = 1081.29$ K $k = 594.7$ J·(Vs)$^{-1}$								
							499	
0.00082265	−27.303	1.665	0.0127	−60,823	2025	0.0253	−1054	51
0.00093646	−29.887	1.728	0.0390	−59,548	1846	0.0526	−2692	102
0.00094079	−28.132	1.685	0.0656	−57,537	1792	0.0786	−4193	148
0.00104740	−33.201	1.813	0.0922	−59,332	1731	0.1058	−5824	195
0.00114393	−34.860	1.857	0.1198	−58,108	1624	0.1338	−7460	239
0.00116122	−35.254	1.868	0.1471	−57,993	1609	0.1604	−9016	281
0.00121164	−36.608	1.905	0.1735	−57,847	1573	0.1866	−10,535	321
0.00128512	−37.181	1.921	0.1996	−56,565	1495	0.2126	−12,006	359
0.00129232	−39.092	1.975	0.2248	−57,883	1529	0.2371	−13,434	395
0.00132258	−38.473	1.957	0.2489	−56,723	1480	0.2606	−14,771	428
0.00133698	−40.195	2.007	0.2718	−57,697	1501	0.2830	−16,070	461
0.00136868	−40.070	2.003	0.2938	−56,910	1464	0.3046	−17,298	491
0.00141190	−41.916	2.057	0.3150	−57,321	1457	0.3255	−18,501	520
0.00142054	−41.891	2.056	0.3354	−57,123	1448	0.3453	−19,635	547
0.00145800	−41.118	2.033	0.3549	−55,835	1395	0.3644	−20,695	571
0.00147385	−40.676	2.021	0.3736	−55,232	1371	0.3827	−21,687	594
0.00154733	−43.293	2.097	0.3917	−55,613	1356	0.4008	−22,680	617
0.00155453	−41.459	2.043	0.4093	−54,304	1315	0.4179	−23,584	636
0.00156029	−42.603	2.077	0.4260	−54,938	1331	0.4341	−24,458	656
0.00163809	−43.061	2.091	0.4422	−53,921	1276	0.4502	−25,296	673
0.00166258	−42.033	2.060	0.4579	−52,915	1239	0.4656	−26,070	689
0.00174615	−43.560	2.105	0.4733	−52,580	1206	0.4809	−26,829	704
0.00179369	−46.292	2.188	0.4883	−53,442	1220	0.4958	−27,589	718
0.00184267	−45.124	2.152	0.5029	−52,122	1168	0.5101	−28,288	731
0.00191183	−44.957	2.147	0.5172	−51,149	1123	0.5242	−28,945	742

Standard uncertainties u are: u(T_{d}) = u(T_{c}) = 0.001 K, u(n_i) ≤ 1·10^{-6} mol u(*IVF*) = 0.00219 Vs u(k) = 22.6 J·(Vs)$^{-1}$.

Since the molar amount of the dropped material is relatively small (n <<1 mol) compared to the liquid alloy inside the calorimeter bath, the partial enthalpy is approximately considered as:

$$\Delta_{\text{mix}}\overline{H}_{ij} = \frac{\Delta H_{ij,\text{reaction}}}{n_i} \tag{3}$$

The integral molar enthalpy of mixing $\Delta_{mix}H_{ij}$ for the binary Ga-Li and the ternary Ga-Li-Sn is simply calculated by summarizing the enthalpy increments $\Delta H_{ij,\text{ reaction}}$ and dividing by the total molar amount of drop n_i and bath materials n_j (Eq. (3)).

$$\Delta_{\text{mix}}H_{ij} = \frac{H_0 + \sum_{ij}\Delta H_{ij,\text{reaction}}}{n_j + \sum_i n_i} \tag{4}$$

For ternary sections, the integral binary enthalpy H_0 is considered as the starting point.

Contributions and sources of errors include impurities, reactions with the crucible, evaporation, and incomplete reactions together with systematic errors from the construction of the calorimeter, calibration procedure, and signal integration. Errors from weighing and temperature measurements were shown to be insignificant. Nevertheless, the standard deviations were calculated according to the ISO 98-3:2008 norm [34] considering weight error, temperature error and the statistical error of the calibration constant and peak integration.

4. Results and discussion

4.1. The binary Ga-Li system

Enthalpies of mixing in the binary Ga-Li system were measured by dropping Li from ambient temperatures into liquid Ga-bath at a temperature of 1081 K. As the melting point of pure Ga was slightly below the temperature in the environment of the auto sampler, experiments dropping solid Ga into Li-bath were not possible. Throughout the experimental setup, a composition range up to x(Li) = 0.59 was accessible. All data of the measurements are listed in Table 2. The partial molar enthalpies were calculated according to Eq. (3) and the integral molar enthalpies according to Eq. (4). Based on that, the enthalpies of mixing were extrapolated to pure Li ($\Delta_{\text{mix}}H = 0$) using the conventional Redlich-Kister approach (Eq. (5)) [35].

$$\Delta_{\text{mix}}H_{ij} = x_i \cdot x_j \cdot \sum_{\nu=0}^{\nu} L_{\nu}^{ij} \left(x_i - x_j\right)^{\nu} \tag{5}$$

Indices

i and j correspond to Ga and Li with L being the binary interaction parameter and ν its order. A reasonable fit was observed applying two interaction parameters L_{ν}^{ij} without temperature dependence. The corresponding results are listed in Table 3. As it can be seen in Fig. 2,

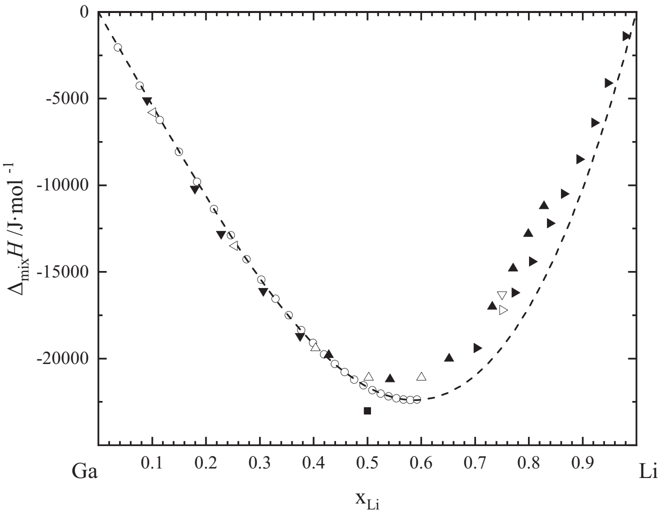

Fig. 2. Integral molar enthalpies of mixing for the binary Ga-Li system. ○ own experiments, ■ 1073 K [36], ▲ 1039 K [13], ► 873 K [13], △ 1044 K [14], ▽ 1018 K [14], ⊲ 993 K [14], ⊳ 891 K [14], - - - - - Redlich-Kister fit of own experimental data; standard state: pure liquid elements.

Table 4
Section B: partial and Integral molar enthalpies of mixing of liquid Ga-Li-Sn alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	$\Delta H_{\mathrm{signal}}$/J	u(H_{signal})/J	x(Li) avg	$\Delta_{\mathrm{mix}}\overline{H}$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}\overline{H}$)/J·mol^{-1}	x(Li)	$\Delta_{\mathrm{mix}}H$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}H$)/J·mol^{-1}
Starting amount: $n_{\mathrm{Sn}} = 917.071\cdot10^{-3}$ mol $n_{\mathrm{Ga}} = 14.001\cdot10^{-3}$ mol $T_{\mathrm{d}} = 304.72$ K $T_{\mathrm{c}} = 1081.24$ K $k = 575.5$ J·(Vs)$^{-1}$								
							910	
0.00091485	−28.365	1.445	0.0143	−58,637	1580	0.0286	−793	45
0.00098401	−25.403	1.411	0.0431	−53,448	1434	0.0576	−2365	87
0.00102147	−28.643	1.449	0.0718	−55,674	1419	0.0859	−3967	127
0.00103155	−28.633	1.449	0.0994	−55,390	1405	0.1128	−5481	164
0.00111223	−31.537	1.485	0.1265	−55,988	1336	0.1401	−7036	200
0.00112808	−31.303	1.482	0.1532	−55,382	1315	0.1662	−8499	234
0.00113384	−31.242	1.482	0.1785	−55,187	1307	0.1908	−9878	266
0.00113961	−30.830	1.476	0.2025	−54,686	1296	0.2141	−11,169	295
0.00115257	−29.913	1.465	0.2252	−53,586	1271	0.2364	−12,371	323
0.00116410	−30.250	1.469	0.2470	−53,618	1262	0.2576	−13,518	349
0.00121020	−33.761	1.515	0.2680	−55,530	1253	0.2785	−14,699	374
0.00123037	−32.873	1.503	0.2885	−54,351	1222	0.2985	−15,800	398
0.00125918	−32.883[a]	1.503	0.3082	−53,748	1194	0.3179	−16,849	420
0.00136292	−36.588	1.555	0.3278	−54,478	1142	0.3377	−17,942	441
0.00137012	−36.276	1.551	0.3471	−54,110	1132	0.3565	−18,968	460
0.00141622	−36.855	1.559	0.3657	−53,657	1101	0.3749	−19,957	478
0.00146809	−35.229	1.536	0.3838	−51,630	1047	0.3928	−20,866	495
0.00148826	−35.604	1.541	0.4014	−51,556	1036	0.4099	−21,733	510
0.00149834	−35.541	1.540	0.4181	−51,353	1028	0.4263	−22,552	524
0.00150411	−34.886	1.531	0.4340	−50,827	1018	0.4418	−23,316	538
0.00152139	−33.774	1.516	0.4492	−49,832	996	0.4566	−24,022	550
0.00155021	−33.240	1.508	0.4638	−49,075	973	0.4710	−24,683	561
0.00159775	−33.717	1.515	0.4780	−48,736	948	0.4850	−25,320	571
0.00163665	−34.397	1.524	0.4918	−48,650	932	0.4986	−25,936	581
0.00172598	−33.878	1.517	0.5054	−47,261	879	0.5122	−26,514	589

Standard uncertainties u are: u(T_{d}) = u(T_{c}) = 0.001 K, u(n_i) ≤ $1\cdot10^{-6}$ mol u(IVF) = 0.00219 Vs u(k) = 14.3 J·(Vs)$^{-1}$.

[a] Unexpected behavior - linear interpolation.

our experimental data fit quite well to the literature data up to x(Li) = 0.5 whereas the empirical fit in the Li rich part deviates slightly from data given by [13,14]. This is, however, also the case at x(Li) = 0.5 to 0.6 where experimental values from our work are available. We observed a minimum of $\Delta_{\mathrm{mix}}H = -22.4$ kJ·mol^{-1} at x(Li) = 0.58 slightly lower and shifted to higher Li content compared to [13,14].

4.2. Measurements and modelling in the ternary Ga-Li-Sn

The experimental results of the seven independent measurements, including composition, starting values, and partial and integral molar enthalpies of mixing, are listed in Tables 3–9. Figs. 3–9 show the integral molar enthalpies of mixing as a function of x(Li) or x(Sn), respectively. It

Table 5
Section C: partial and Integral molar enthalpies of mixing of liquid Ga-Li-Sn alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	$\Delta H_{\mathrm{signal}}$/J	u(H_{signal})/J	x(Li) avg	$\Delta_{\mathrm{mix}}\overline{H}$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}\overline{H}$)/J·mol^{-1}	x(Li)	$\Delta_{\mathrm{mix}}H$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}H$)/J·mol^{-1}
Starting amount: $n_{\mathrm{Sn}} = 9.606\cdot10^{-3}$ mol $n_{\mathrm{Ga}} = 22.394\cdot10^{-3}$ mol $T_d = 306.25$ K $T_{\mathrm{c}} = 1081.39$ K $k = 585.0$ J·(Vs)$^{-1}$								
							731	
0.00078519	−18.089	1.290	0.0120	−50,671	1644	0.0239	−500	39
0.00095952	−25.177	1.297	0.0378	−53,872	1352	0.0517	−2018	77
0.00099121	−25.735	1.297	0.0652	−53,597	1309	0.0788	−3490	112
0.00106613	−24.466	1.296	0.0925	−50,581	1216	0.1062	−4892	145
0.00113672	−29.063	1.301	0.1199	−53,200	1145	0.1337	−6378	175
0.00114249	−28.664	1.301	0.1467	−52,723	1139	0.1597	−7769	204
0.00114393	−27.653	1.299	0.1719	−51,807	1137	0.1842	−9053	232
0.00116122	−27.893	1.300	0.1959	−51,654	1120	0.2077	−10,278	257
0.00118571	−28.636	1.301	0.2190	−51,784	1097	0.2303	−11,462	281
0.00118571	−29.835	1.302	0.2409	−52,795	1099	0.2516	−12,608	304
0.00126783	−29.094	1.301	0.2624	−50,582	1027	0.2731	−13,702	325
0.00130097	−29.214	1.301	0.2836	−50,089	1001	0.2940	−14,746	344
0.00134707	−30.136	1.303	0.3042	−50,005	967	0.3144	−15,764	362
0.00143063	−30.582	1.303	0.3246	−49,010	911	0.3348	−16,752	378
0.00146953	−33.836	1.308	0.3446	−50,658	890	0.3545	−17,757	393
0.00156750	−33.468	1.307	0.3644	−48,985	834	0.3743	−18,715	407
0.00161072	−33.092	1.307	0.3838	−48,178	812	0.3934	−19,614	419
0.00168275	−33.461	1.307	0.4028	−47,518	777	0.4121	−20,477	430
0.00171733	−31.715	1.305	0.4211	−46,101	760	0.4301	−21,260	440
0.00173894	−32.747	1.306	0.4387	−46,465	751	0.4472	−22,018	450
0.00182827	−31.348	1.304	0.4557	−44,780	714	0.4642	−22,714	458
0.00197522	−33.509	1.307	0.4727	−44,598	662	0.4813	−23,415	464
0.00200836	−32.089	1.305	0.4895	−43,611	650	0.4977	−24,052	470
0.00208904	−32.179	1.305	0.5056	−43,037	625	0.5136	−24,655	475
0.00212505	−32.620	1.306	0.5212	−42,984	615	0.5288	−25,228	480

Standard uncertainties u are: u(T_{d}) = u(T_{c}) = 0.001 K, u(n_i) ≤ $1\cdot10^{-6}$ mol u(IVF) = 0.00219 Vs u(k) = 4.4 J·(Vs)$^{-1}$.

Table 6
Section D: partial and Integral molar enthalpies of mixing of liquid Ga-Li-Sn alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	$\Delta H_{\mathrm{signal}}$/J	u(H_{signal})/J	x(Li) avg	$\Delta_{\mathrm{mix}}\overline{H}$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}\overline{H}$)/J·mol^{-1}	x(Li)	$\Delta_{\mathrm{mix}}H$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}H$)/J·mol^{-1}
Starting amount: $n_{\mathrm{Sn}} = 5.254\cdot10^{-3}$ mol $n_{\mathrm{Ga}} = 29.753\cdot10^{-3}$ mol $T_{\mathrm{d}} = 305.23$ K $T_{\mathrm{c}} = 1081.40$ K $k = 562.7$ J·(Vs)$^{-1}$								
							429	
0.00091629	−24.812	1.259	0.0128	−54,715	1374	0.0255	−978	35
0.00100274	−26.554	1.262	0.0387	−54,118	1260	0.0520	−2421	68
0.00104308	−26.867	1.263	0.0650	−53,394	1211	0.0780	−3821	100
0.00106613	−26.626	1.262	0.0906	−52,611	1185	0.1032	−5154	129
0.00114393	−26.793	1.263	0.1160	−51,058	1105	0.1287	−6461	157
0.00114393	−26.674	1.263	0.1408	−50,954	1104	0.1528	−7692	183
0.00115113	−28.353	1.266	0.1643	−52,267	1101	0.1758	−8900	208
0.00118139	−29.436	1.269	0.1870	−52,553	1075	0.1981	−10,082	232
0.00127791	−29.584	1.269	0.2095	−50,787	994	0.2209	−11,239	253
0.00129952	−28.591	1.267	0.2319	−49,638	975	0.2428	−12,319	273
0.00142343	−33.034	1.278	0.2541	−50,844	898	0.2654	−13,469	292
0.00143927	−30.457	1.271	0.2762	−48,798	884	0.2870	−14,505	309
0.00146953	−29.653	1.269	0.2973	−47,815	864	0.3077	−15,473	326
0.00160207	−32.412	1.276	0.3183	−47,868	797	0.3289	−16,468	340
0.00163233	−31.463	1.274	0.3391	−46,911	781	0.3493	−17,392	353
0.00167123	−31.215	1.273	0.3591	−46,314	762	0.3689	−18,263	366
0.00171733	−28.984	1.268	0.3784	−44,513	739	0.3879	−19,051	377
0.00173174	−29.386	1.269	0.3969	−44,605	733	0.4059	−19,802	387
0.00173318	−25.942	1.261	0.4143	−42,604	728	0.4228	−20,454	397
0.00176343	−25.799	1.261	0.4310	−42,266	715	0.4391	−21,070	406
0.00178649	−23.472	1.256	0.4469	−40,775	703	0.4547	−21,618	414
0.00182971	−24.083	1.257	0.4623	−40,799	687	0.4699	−22,150	422
0.00183115	−21.008	1.252	0.4770	−39,109	684	0.4842	−22,607	429
0.00188301	−19.957	1.250	0.4911	−38,235	664	0.4981	−23,029	435
0.00198675	−17.813	1.247	0.5050	−36,602	628	0.5120	−23,405	440

Standard uncertainties u are: u(T_{d}) = u(T_{c}) = 0.001 K, u(n_i) ≤ $1\cdot10^{-6}$ mol u(*IVF*) = 0.00219 Vs u(k) = 5.7 J·(Vs)$^{-1}$.

is worth mentioning that drop no. 13 of section B showed an unexpected behavior, see insert of Fig. 10. The endothermic signal indicates heating and melting of Sn but the exothermic mixing reaction is missing. The tin drop stuck at the border of the crucible opening and did not fall into the liquid bath. To be able to calculate the integral mixing enthalpy, the peak area is interpolated with a linear function as shown in Fig. 10.

To validate the experimental data, the integral enthalpy values at the intersections of the measured concentration sections (see Fig. 1) are compared. Table 10 lists the integral molar enthalpies of mixing at the cross-sections a-g of sections B-G. As can be seen, the various integral enthalpies of mixing at the intersection points fit nicely and the deviations lie between 175 and 500 J·mol^{-1}, well below the overall experimental error of 1 kJ·mol^{-1}.

Table 7
Section E: partial and Integral molar enthalpies of mixing of liquid Ga-Li-Sn alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	$\Delta H_{\mathrm{signal}}$/J	u(H_{signal})/J	x(Sn) avg	$\Delta_{\mathrm{mix}}\overline{H}$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}\overline{H}$)/J·mol^{-1}	x(Sn)	$\Delta_{\mathrm{mix}}H$/J·mol^{-1}	u($\Delta_{\mathrm{mix}}H$)/J·mol^{-1}
Starting amount: $n_{\mathrm{Li}} = 6.879\cdot10^{-3}$ mol $n_{\mathrm{Ga}} = 27.518\cdot10^{-3}$ mol $T_{\mathrm{d}} = 305.89$ K $T_{\mathrm{c}} = 1080.99$ K $k = 591.2$ J·(Vs)$^{-1}$								
							−10,635	
0.00056693	16.432	1.300	0.0081	−277	2293	0.0162	−10,468	37
0.00062834	20.317	1.302	0.0249	3073	2072	0.0336	−10,228	73
0.00064443	19.239	1.301	0.0422	594	2019	0.0508	−10,036	108
0.00068014	20.506	1.302	0.0595	888	1914	0.0683	−9835	141
0.00069649	21.939	1.303	0.0769	2239	1870	0.0855	−9611	173
0.00071595	21.347	1.302	0.0941	556	1819	0.1026	−9421	204
0.00076017	23.005	1.303	0.1113	1002	1715	0.1200	−9219	233
0.00077011	22.982	1.303	0.1285	582	1693	0.1370	−9029	261
0.00078106	22.761	1.303	0.1453	−119	1669	0.1536	−8858	288
0.00078822	23.565	1.304	0.1617	635	1654	0.1697	−8677	314
0.00080170	24.470	1.304	0.1776	1262	1627	0.1855	−8489	339
0.00081518	24.470	1.304	0.1932	757	1600	0.2009	−8314	363
0.00082344	26.040	1.306	0.2084	2362	1585	0.2159	−8113	386
0.00087162	26.630	1.306	0.2236	1291	1498	0.2312	−7930	408
0.00088291	27.676	1.307	0.2386	2086	1480	0.2461	−7736	428
0.00089470	25.926	1.305	0.2533	−284	1459	0.2606	−7593	448
0.00089470	28.194	1.307	0.2675	2251	1461	0.2745	−7407	467
0.00091416	27.732	1.307	0.2814	1075	1429	0.2882	−7247	486
0.00094381	28.423	1.307	0.2951	854	1385	0.3019	−7091	503
0.00094853	28.353	1.307	0.3085	630	1378	0.3151	−6946	519
0.00095569	28.144	1.307	0.3215	188	1368	0.3279	−6812	535
0.00097018	28.370	1.307	0.3341	−19	1347	0.3404	−6686	550
0.00097111	28.622	1.307	0.3464	213	1346	0.3524	−6560	565
0.00098197	28.519	1.307	0.3583	−219	1331	0.3642	−6445	579
0.00102098	29.752	1.308	0.3701	−120	1281	0.3760	−6328	592

Standard uncertainties u are: u(T_{d}) = u(T_{c}) = 0.001 K, u(n_i) ≤ $1\cdot10^{-6}$ mol u(*IVF*) = 0.00219 Vs u(k) = 3.6 J·(Vs)$^{-1}$.

Table 8
Section F: partial and Integral molar enthalpies of mixing of liquid Ga-Li-Sn alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	ΔH_{signal}/J	u(H_{signal})/J	x(Sn) avg	$\Delta_{\text{mix}}\overline{H}$/J·mol^{-1}	u($\Delta_{\text{mix}}\overline{H}$)/J·mol^{-1}	x(Sn)	$\Delta_{\text{mix}}H$/J·mol^{-1}	u($\Delta_{\text{mix}}H$)/J·mol^{-1}
Starting amount: $n_{\text{Li}} = 13.298 \cdot 10^{-3}$ mol $n_{\text{Ga}} = 13.280 \cdot 10^{-3}$ mol $T_{\text{d}} = 305.69$ K $T_{\text{c}} = 1081.06$ K $k = 580.5$ J·(Vs)$^{-1}$								
							−21,646	
0.00062025	0.141	1.273	0.0114	−29,041	2052	0.0228	−21,814	47
0.00062522	2.531	1.273	0.0338	−25,221	2036	0.0448	−21,891	92
0.00063491	6.347	1.273	0.0554	−19,271	2005	0.0661	−21,832	134
0.00067239	8.898	1.273	0.0769	−16,036	1894	0.0876	−21,699	175
0.00070516	11.472	1.274	0.0984	−13,000	1806	0.1092	−21,493	213
0.00070887	12.836	1.274	0.1195	−11,161	1797	0.1299	−21,253	250
0.00072420	14.820	1.274	0.1399	−8804	1760	0.1500	−20,965	285
0.00073077	16.427	1.275	0.1597	−6790	1744	0.1694	−20,641	318
0.00076085	17.925	1.275	0.1791	−5709	1676	0.1887	−20,294	350
0.00076598	18.859	1.275	0.1980	−4647	1665	0.2073	−19,937	380
0.00080389	20.369	1.276	0.2165	−3931	1587	0.2258	−19,562	408
0.00083641	20.637	1.276	0.2350	−4595	1525	0.2442	−19,206	435
0.00088232	22.251	1.276	0.2535	−4050	1446	0.2627	−18,835	459
0.00089546	22.746	1.276	0.2717	−3866	1425	0.2806	−18,472	483
0.00090110	23.812	1.277	0.2892	−2843	1417	0.2977	−18,100	505
0.00091366	24.819	1.277	0.3060	−2104	1398	0.3143	−17,723	526
0.00093084	25.560	1.277	0.3223	−1809	1372	0.3304	−17,350	546
0.00094019	25.679	1.277	0.3381	−1956	1359	0.3459	−16,994	565
0.00094407	25.625	1.277	0.3533	−2125	1353	0.3607	−16,656	583
0.00094676	25.637	1.277	0.3678	−2190	1349	0.3750	−16,334	600
0.00099233	28.074	1.278	0.3821	−978	1288	0.3892	−15,984	615
0.00101162	28.311	1.278	0.3961	−1283	1264	0.4031	−15,650	630
0.00102755	28.843	1.278	0.4098	−1199	1244	0.4166	−15,324	644
0.00111979	31.587	1.280	0.4235	−1061	1143	0.4305	−14,982	656
0.00112206	31.248	1.279	0.4372	−1419	1140	0.4439	−14,663	667

Standard uncertainties u are: u(T_{d}) = u(T_{c}) = 0.001 K, u(n_i) ≤ $1 \cdot 10^{-6}$ mol u(IVF) = 0.00219 Vs u(k) = 2.4 J·(Vs)$^{-1}$.

Integral molar enthalpies of mixing in the ternary are usually described by a Redlich-Kister-Muggianu polynomial (Eq. (6)) [37] which is given in the form of

$$\Delta_{\text{mix}}H^{\text{RKM}} = \sum_i \sum_{j>i} x_i x_j \sum_\nu L_\nu^{ij} \left(x_i - x_j\right)^\nu + x_i x_j x_k \left(x_i M_\nu^{ijk} + x_j M_\nu^{ijk} + x_k M_\nu^{ijk} \right) \qquad (6)$$

where
i,*j* and *k* corresponds to Ga, Li, and Sn respectively, L_ν^{ij} are the binary interaction parameter and M_ν^{ijk} are the ternary interaction parameters. Together with the binary interaction parameters L_ν^{ij} in Table 11 and the experimental data, the ternary interaction parameters *M* were calculated with a least-squares fit based on the empirical Redlich-Kister-Muggianu polynomial in Eq. (6). The fitted M_ν^{ijk}-parameters are as well listed in Table 11 and imply significant ternary interactions. This,

Table 9
Section G: partial and Integral molar enthalpies of mixing of liquid Ga-Li-Sn alloy at 1081 K; standard state: pure liquid elements.

n_i/mol	ΔH_{signal}/J	u(H_{signal})/J	x(Sn) avg	$\Delta_{\text{mix}}\overline{H}$/J·mol^{-1}	u($\Delta_{\text{mix}}\overline{H}$)/J·mol^{-1}	x(Sn)	$\Delta_{\text{mix}}H$/J·mol^{-1}	u($\Delta_{\text{mix}}H$)/J·mol^{-1}
Starting amount: $n_{\text{Li}} = 19.614 \cdot 10^{-3}$ mol $n_{\text{Ga}} = 13.059 \cdot 10^{-3}$ mol $T_{\text{d}} = 306.16$ K $T_{\text{c}} = 1081.28$ K $k = 566.8$ J·(Vs)$^{-1}$								
							−22,380	
0.00071199	−20.375	1.2860	0.0107	−57,879	1806	0.0213	−23,138	39
0.00073650	−12.713	1.2597	0.0319	−46,523	1710	0.0425	−23,642	75
0.00076843	−6.829	1.2476	0.0530	−38,149	1624	0.0635	−23,962	108
0.00080128	−2.245	1.2432	0.0741	−32,063	1552	0.0846	−24,144	141
0.00082680	2.951	1.2436	0.0949	−25,693	1504	0.1053	−24,179	171
0.00083363	6.153	1.2467	0.1153	−21,881	1496	0.1253	−24,128	200
0.00088830	9.425	1.2521	0.1354	−18,651	1410	0.1456	−24,000	228
0.00089192	12.640	1.2595	0.1553	−15,090	1412	0.1651	−23,797	254
0.00090270	14.973	1.2663	0.1745	−12,675	1403	0.1839	−23,546	279
0.00091441	16.715	1.2720	0.1930	−10,982	1391	0.2021	−23,266	304
0.00092082	18.076	1.2769	0.2109	−9631	1387	0.2197	−22,966	327
0.00092511	19.313	1.2817	0.2281	−8385	1385	0.2365	−22,651	349
0.00092823	21.335	1.2901	0.2446	−6277	1390	0.2527	−22,303	371
0.00095434	22.084	1.2934	0.2607	−6121	1355	0.2687	−21,958	391
0.00096445	23.213	1.2986	0.2764	−5193	1346	0.2841	−21,603	411
0.00097439	24.139	1.3030	0.2916	−4489	1337	0.2991	−21,246	430
0.00099318	24.309	1.3039	0.3064	−4786	1313	0.3137	−20,902	448
0.00102173	26.374	1.3144	0.3209	−3449	1286	0.3281	−20,535	465
0.00102224	26.289	1.3140	0.3351	−3545	1285	0.3420	−20,186	481
0.00105610	26.765	1.3165	0.3488	−3918	1247	0.3557	−19,847	497
0.00110201	29.638	1.3326	0.3625	−2367	1209	0.3694	−19,475	511
0.00110766	29.769	1.3334	0.3760	−2386	1204	0.3826	−19,117	525
0.00111667	29.616	1.3325	0.3890	−2740	1193	0.3953	−18,779	539
0.00112779	29.688	1.3329	0.4015	−2938	1182	0.4077	−18,455	552
0.00117025	31.733	1.3453	0.4139	−2145	1150	0.4200	−18,116	564

Standard uncertainties u are: u(T_{d}) = u(T_{c}) = 0.001 K, u(n_i) ≤ $1 \cdot 10^{-6}$ mol u(IVF) = 0.00219 Vs u(k) = 9.2 J·(Vs)$^{-1}$.

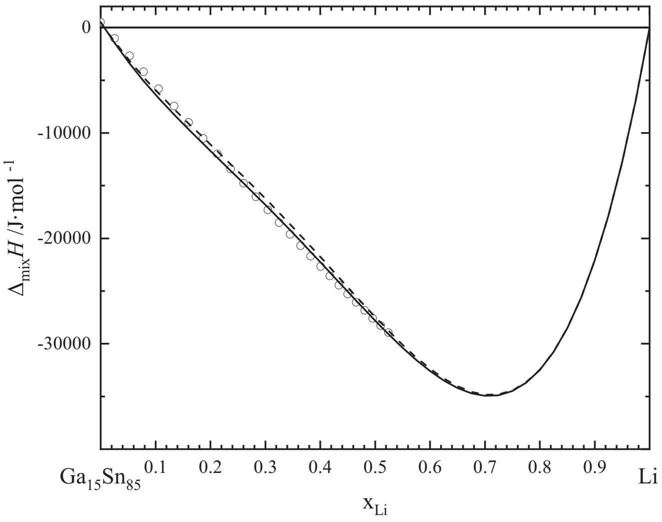

Fig. 3. Integral molar enthalpies of mixing for section A: ○ own experiments,—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

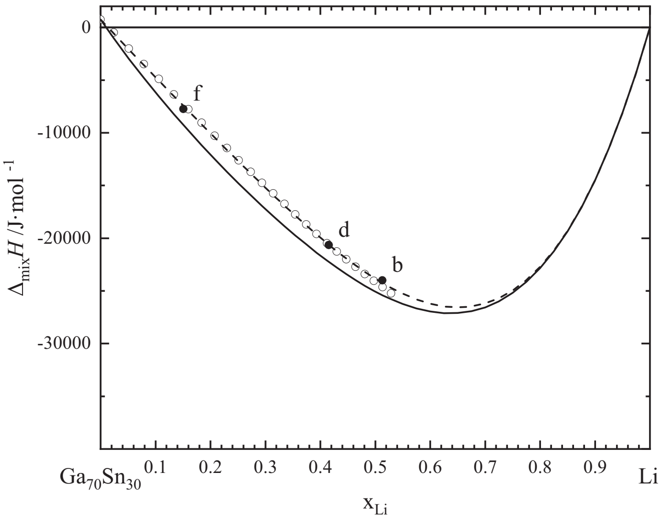

Fig. 5. Integral molar enthalpies of mixing for section C: ○ own experiments, ● intersections,—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

however has to be handled with care since the extrapolation of binary interactions according to the Muggianu model can be insufficient. This is especially the case if the mixing behavior of the three constituent binaries is not congeneric. In the case of Ga-Li-Sn, the Ga-Sn system possesses weak endothermic mixing behavior of the liquid compared to the distinct exothermic behavior of the Ga-Li and Li-Sn system. In such situations the asymmetric extrapolation model of [38], where the last term describes the contribution of the asymmetric system can essentially improve the prediction of the ternary mixing enthalpy. An adapted version of the extrapolation formula according to Toop is presented in Eq. (7), where i,j and k correspond to Ga, Li, and Sn.

$$\Delta_{\mathrm{mix}}H^{\mathrm{Toop}} = \frac{x_i}{1-x_j}\Delta_{\mathrm{mix}}H_{i,j}(x_j,1-x_j) + \frac{x_k}{1-x_j}\Delta_{\mathrm{mix}}H_{j,k}(x_j,1-x_j) + (x_i+x_k)^2\Delta_{\mathrm{mix}}H_{i,k}\left(\frac{x_i}{x_i+x_k},\frac{x_k}{x_i+x_k}\right) \qquad (7)$$

The description of the ternary enthalpies of mixing in Ga-Li-Sn using the asymmetric extrapolation model of Toop is satisfying (see Figs. 3–9) and not far away from Redlich-Kister-Muggianu with ternary interaction. Seemingly, the ternary M_{ν}^{ijk}-parameters (given in Table 11) serve rather for correction of the inappropriate extrapolation model of Muggianu than as a description of real ternary interaction of the three different atoms. This leads to the conclusion that we could not proof significant ternary interactions in the Ga-Li-Sn system. The respective calculated integral molar enthalpies of mixing from Toop and Redlich-Kister-Muggianu are plotted together with the experimental data for each section as shown in Figs. 3–9.

The iso-enthalpy plot across the ternary system calculated with the Redlich-Kister-Muggianu model and Toop model (Fig. 11) shows a minimum in the integral molar enthalpy of mixing in the binary system Li-Sn of $\Delta_{\mathrm{mix}}H = -36.82$ kJ·mol^{-1} at x(Sn) = 0.8. Strongly exothermic behavior is observed in the Li-rich part where also the ternary solid compounds [30,31] are situated. When Li is added to the endothermic Ga-Sn system, generally strong exothermic mixing behavior occurs. Adding Sn to the exothermic Ga-Li system leads to an increase or decrease of the integral mixing enthalpy, depending on the starting point. The same is the case for adding Ga to Li-Sn alloys. The attractive interaction of Li with both Ga and Sn dominates the ternary mixing behavior in Ga-Li-Sn.

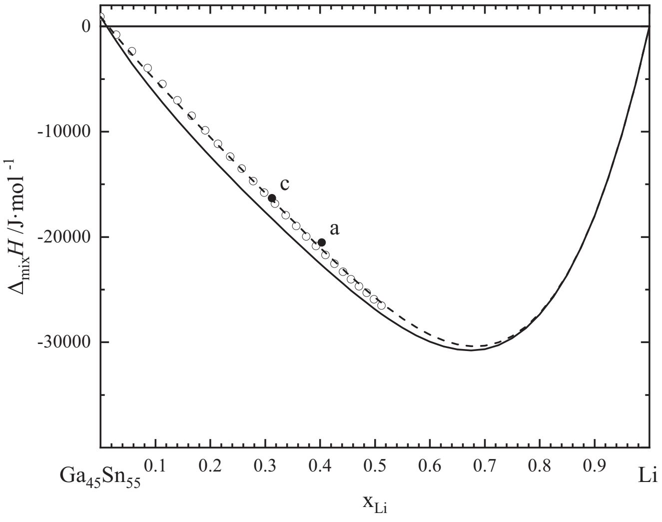

Fig. 4. Integral molar enthalpies of mixing for section B: ○ own experiments, ● intersections,—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

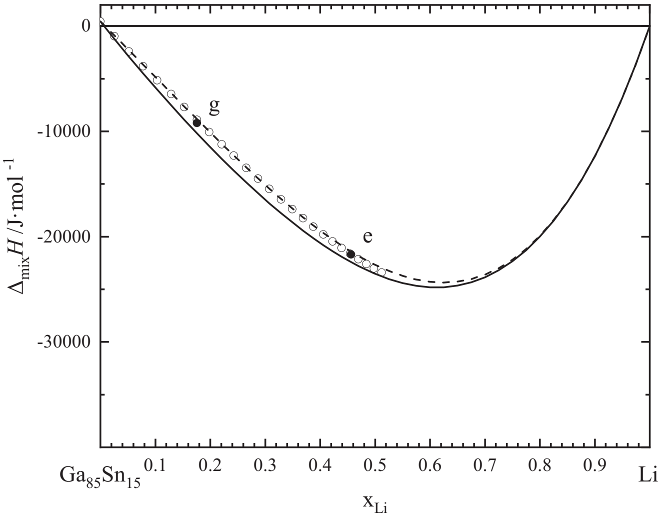

Fig. 6. Integral molar enthalpies of mixing for section D: ○ own experiments, ● intersections,—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

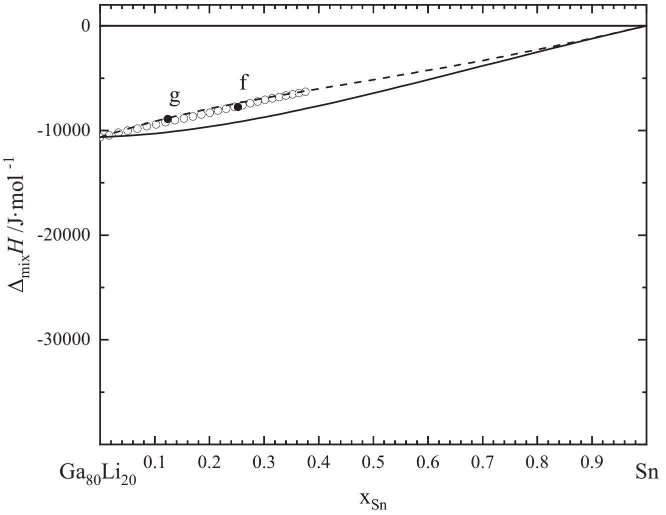

Fig. 7. Integral molar enthalpies of mixing for section E: ○ own experiments, ● intersections,—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

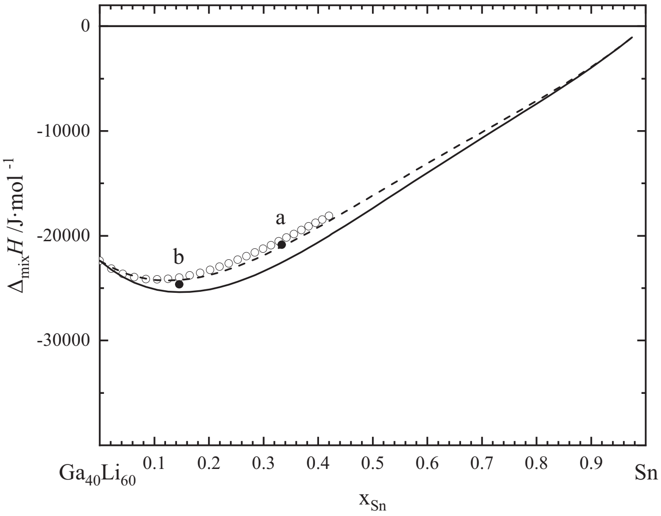

Fig. 9. Integral molar enthalpies of mixing for section G: ○ own experiments, ● intersections,—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

5. Summary

The partial molar enthalpies of mixing were measured at 1081 K along seven composition sections in the liquid ternary system Ga-Li-Sn. Additionally, we measured the mixing enthalpy in the binary Ga-Li system and could confirm most of the literature data.

Experimental integral molar enthalpies of mixing in the ternary liquid phase served as an input to fit ternary interaction parameters according to the Redlich-Kister-Muggianu model. The obtained ternary interaction parameters together with those from the binary systems allowed us to describe the integral mixing enthalpy of the liquid phase over the entire composition range. The two constituent binary systems Ga-Li and Li-Sn with enthalpy minima at approximately -22 kJ·mol^{-1} at x(Li) = 0.5 and -37 kJ·mol^{-1} at x(Li) = 0.8, respectively dominate the mixing behavior in the ternary system. We also observed that the ternary enthalpies of mixing can be well described by extrapolation of the binary enthalpies of mixing based on the asymmetric Toop model. We assume that ternary interactions implied by the Redlich-Kister-Muggianu parameter fit are rather corrections of the inappropriate symmetric Muggianu extrapolation model. Consequently, real ternary interaction of three unlike atoms constellations is considered to be negligible. Nevertheless, the ternary Redlich-Kister-Muggianu polynomial can be used for the description of the ternary integral enthalpies of mixing in Ga-Li-Sn.

The deviation between the experimental and calculated values for all investigations were found to be less than ±2 kJ·mol^{-1} for the Toop model and ±1 kJ·mol^{-1} for the Redlich-Kister-Muggianu fit. Reliability of our measurements was demonstrated by excellent agreement of data at seven intersection points from independent measurements.

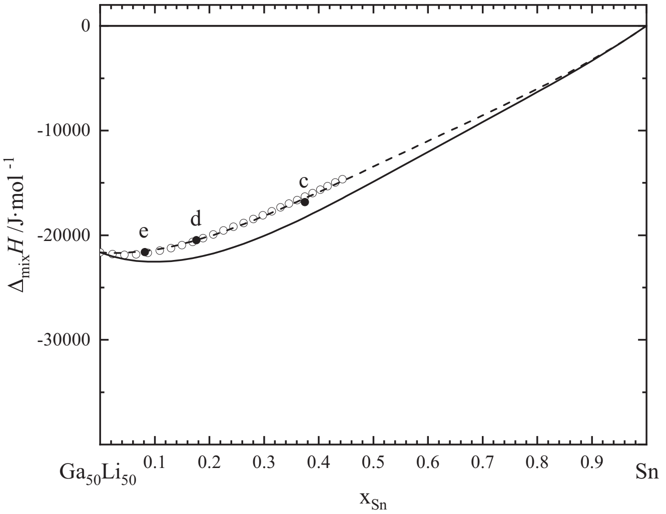

Fig. 8. Integral molar enthalpies of mixing for section F: ○ own experiments, ● intersections,—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

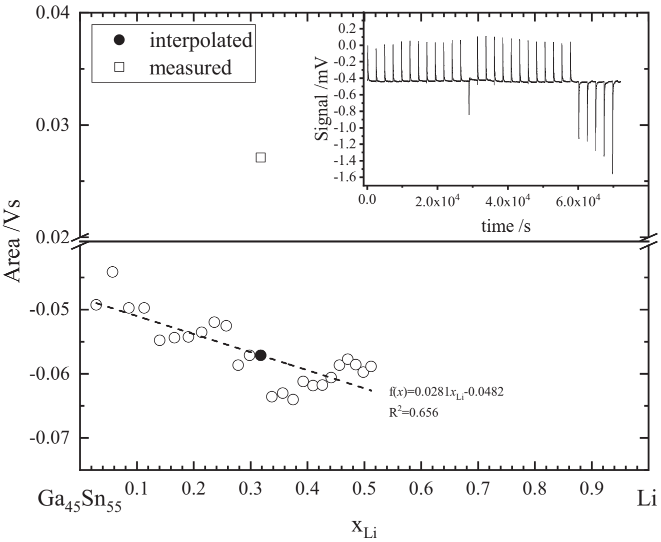

Fig. 10. Interpolated peak area from section B. Drop 13 is calculated by the interpolation of all peak areas to minimize the overall error.

Table 10
Comparison of integral enthalpies of mixing for the ‘cross-sections’ a–g.

Inter-section	Composition			Integral molar enthalpy of mixing ($J \cdot mol^{-1}$)					
				B	C	D	E	F	G
	x(Ga)	x(Li)	x(Sn)	$Ga_{45}Sn_{55}$ + Li	$Ga_{70}Sn_{30}$ + Li	$Ga_{85}Sn_{15}$ + Li	$Ga_{80}Li_{20}$ + Sn	$Ga_{50}Li_{50}$ + Sn	$Ga_{40}Li_{60}$ + Sn
a	0.27	0.40	0.33	−20,866(495)					−20,535(465)
b	0.34	0.51	0.15		−24,655(475)				−24,000(228)
c	0.31	0.31	0.38	−16,849(420)				−16,334(600)	
d	0.41	0.41	0.18		−20,477(430)			−20,294(350)	
e	0.46	0.46	0.08			−21,618(414)		−21,699(175)	
f	0.59	0.15	0.26		−7769(204)		−7593(448)		
g	0.70	0.18	0.12			−8900(208)	−9219(233)		

Table 11
Interaction parameter (Redlich-Kister and Redlich-Kister-Muggianu model parameter) for the liquid of the binary's and ternary Ga-Li-Sn system.

System	Literature	Interaction parameter ($J \cdot mol^{-1}$)
Li-Sn	[28]	$L_0^{Li,\,Sn} = -111{,}137$ $L_1^{Li,\,Sn} = -124{,}601$ $L_2^{Li,\,Sn} = -89{,}726$
Ga-Li	This work	$L_0^{Ga,\,Li} = -86{,}559.52$ $L_1^{Ga,\,Li} = 33{,}479.52$
Ga-Sn	Based on [24]	$L_0^{Ga,\,Sn} = 3636.91$ $L_1^{Ga,\,Sn} = -394.31$
Ga-Li-Sn	This work	$M_0^{Ga,\,Li,\,Sn} = 121{,}494.31$ $M_1^{Ga,\,Li,\,Sn} = 269{,}475.45$ $M_2^{Ga,\,Li,\,Sn} = -55{,}145.96$

Author contributions

J.F. and P.B. prepared and performed the experiments. J.F. analyzed the data. J.F., P.B., H.F, T.R., H.S. discussed the results. J.F. drafted the manuscript. T.R. conceived the idea for the project. Overall scientific support for the work came from H.F.

Declaration of competing interest

None.

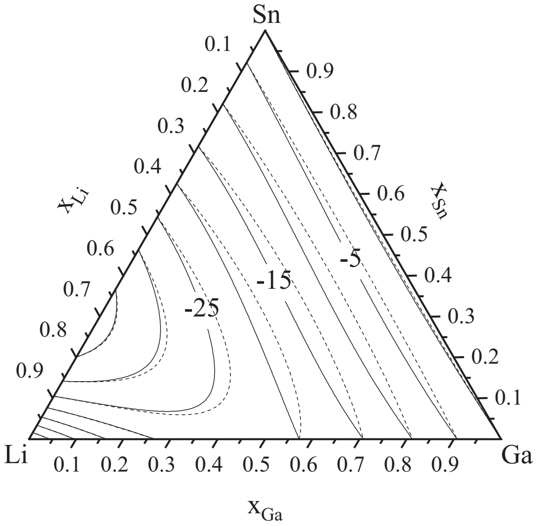

Fig. 11. Iso-enthalpy plot of the integral molar enthalpies of mixing for the Ga-Li-Sn system at 1081 K:—— Toop model, - - - - Redlich-Kister-Muggianu fit; standard state: pure liquid elements.

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