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Calorimetric studies of Cu–Li, Li–Sn, and Cu–Li–Sn

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ABSTRACT

Integral molar enthalpies of mixing were determined by drop calorimetry for Cu–Li–Sn at 1073 K along five sections $x_{\text{Cu}}/x_{\text{Sn}} \approx 1:1$, $x_{\text{Cu}}/x_{\text{Sn}} \approx 2:3$, $x_{\text{Cu}}/x_{\text{Sn}} \approx 1:4$, $x_{\text{Li}}/x_{\text{Sn}} \approx 1:1$, and $x_{\text{Li}}/x_{\text{Sn}} \approx 1:4$. The integral and partial molar mixing enthalpies of Cu–Li and Li–Sn were measured at the same temperature, for Li–Sn in addition at 773 K. All binary data could be described by Redlich–Kister–polynomials. Cu–Li shows an endothermic mixing effect with a maximum in the integral molar mixing enthalpy of $\sim 5300 \text{ J} \cdot \text{mol}^{-1}$ at $x_{\text{Cu}} = 0.5$, Li–Sn an exothermic minimum of $\sim -37,000 \text{ J} \cdot \text{mol}^{-1}$ at $x_{\text{Sn}} \sim 0.2$. For Li–Sn no significant temperature dependence between 773 K and 1073 K could be deduced. Our measured ternary data were fitted on the basis of an extended Redlich–Kister–Muggianu model for substitutional solutions. Additionally, a comparison of these results to the extrapolation model of Chou is given.

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1. Introduction

The generation of basic kinetic and thermodynamic data of material systems, which could be relevant for the design of new lithium ion batteries, is forced by the DFG priority program 1473 “WeNDeLIB”. Within this priority program several joint projects with different experimental and theoretical approaches exist, one of these projects targets on the thermodynamic description of intermetallic anode materials. Such systems, which are able to reversibly uptake lithium, are in discussion as an alternative to the commonly used carbon anodes. Multiphase ternary alloys with selective activity of a certain phase towards lithium exchange promise to overcome the well-known problem of electrode destruction due to large volume changes in the cycling process. The idea is to have a phase with a high lithium activity with the ability to release lithium ions during discharging. Additionally, during discharging a second phase, which acts as a stabilizing matrix, should be formed. This stabilizing phase buffers the destructive volume changes. One promising candidate is the system Cu–Li–Sn, where $\text{Li}_{17}\text{Sn}_4$ should be the active phase and copper or Cu–Sn-phases form the stabilizing matrix. The challenging experimental handling of lithium and its alloys caused a scarce knowledge of the thermodynamics of these systems, especially of the ternaries. In the scope of a tailored design of new materials for lithium ion batteries, these thermodynamic data are indispensable. Thermodynamic data, e.g. molar enthalpies of mixing, are necessary to model ternary and higher ordered phase diagrams with

the CALPHAD method and to predict phase relations and thermodynamic properties. This work provides thermodynamic data of the liquid range, which is another important puzzle piece to fully understand the Cu–Li–Sn phase diagram.

2. Literature review

2.1. Cu–Sn

The determination of thermodynamic data like molar enthalpies of mixing and formation for the Cu–Sn system has started in the middle of the 20th century by several authors [1–5]. A critical assessment of thermodynamic data of the Cu–Sn system was first published by Hultgren *et al.* [6]. Further calorimetric measurements on liquid alloys were done by Itagaki and Yazawa [7], Yazawa *et al.* [8], Pool *et al.* [9] and Lee *et al.* [10]. The integral molar mixing enthalpies in these works have been measured in the temperature range from 723 K to 1523 K covering the whole composition range. Overall, the curves are S-shaped with a minimum at $x_{\text{Cu}} \approx 0.75$, which corresponds to the most stable intermetallic phase Cu_3Sn . Some authors report a slightly positive value at the tin-rich side [4], whereas others find continuous exothermic integral molar mixing enthalpies [7]. No temperature dependence can be determined from a comparison of these works, because the data show no significant tendency. In 2008 Flandorfer *et al.* [11] systematically investigated the integral molar mixing enthalpies of the Cu–Sn liquid alloys between 773 K and 1523 K and found significant changes in the integral molar mixing enthalpy values between 773 K and 973 K, but they could indicate smaller temperature dependence at higher temperatures. Yassin and Cas-

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tanet [12] compared the limiting partial molar enthalpies of mixing of copper in tin at different temperatures in their compilation and found a clear temperature dependence ($\Delta_{\text{mix}}\overline{H}_{\text{Cu}}^{\infty}/10^3 \text{ J} \cdot \text{mol}^{-1} = -13.31 + 0.021 \cdot T/\text{K} - 6.3 \cdot 10^{-6} \cdot T^2/\text{K}^2$). Below approximately 823 K the limiting partial molar enthalpies are negatively, at higher temperatures they become positive. This trend was also found by Flandorfer *et al.* [11], nevertheless the values start to become positive from 773 K. Critical assessments of the phase diagram based on experimental data and thermodynamic calculations were done by Saunders and Miodownik [13], Shim *et al.* [14] and recently by Li *et al.* [15].

2.2. Cu–Li

This system is one of the less investigated binary systems concerning thermodynamic properties. Nevertheless, DTA, XRD, and other methods have been applied to determine the phase diagram. Noteworthy are the works of Pastorello *et al.* [16] and Klemm and Volavšek [17], who investigated the liquidus by thermal analysis and found the homogeneity range of fcc-(Cu) and bcc-(Li). Pelton [18] assessed the available data to the hitherto known eutectic Cu–Li phase diagram. The first work regarding the thermodynamic data was published by Mikhailovskaya and Sudavtseva [19]. They have measured integral and partial molar mixing enthalpies with a mixing calorimeter at $x_{\text{Li}} < 0.3$ and a temperature of 1373 K. They also calculated activities, entropy and Gibbs energy data deduced from the phase diagram [18]. Gasior *et al.* [20] performed DTA and EMF-measurements in the temperature range between 633 K and 923 K.

2.3. Li–Sn

Wen and Huggins [21] have investigated this system by means of coulometric titration and EMF-measurements in the temperature range of 633 K to 863 K. They confirmed the existence of six intermetallic phases and were able to determine various thermo-

TABLE 1

Binary and ternary interaction parameters in Cu–Li–Sn (1073 K).

System	Reference	${}^{\nu}L_{ij}^H/\text{J} \cdot \text{mol}^{-1}$	or	${}^{\nu}M_{ij}^H/\text{J} \cdot \text{mol}^{-1}$
Cu–Sn	[11]	${}^0L = -10232$	${}^1L = -22098$	${}^2L = -13216$
Cu–Li	This work	${}^0L = 21165$	${}^1L = -1681$	
Li–Sn	This work	${}^0L = -111137$	${}^1L = -124601$	${}^2L = -89726$
Cu–Li–Sn	This work	${}^0M = -388766$	${}^1M = -501989$	${}^2M = 134799$

${}^{\nu}L_{ij}^H$ or ${}^{\nu}M_{ij}^H$, binary or ternary interaction parameters.

ν , order.

i, j, elements in binary system.

chemical properties. Later on, Moser *et al.* [22] also performed EMF-measurements on this system, and in addition drop calorimetry at temperatures between 691 K and 938 K, in a composition range of $x_{\text{Li}} = 0.01$ to 0.5 and 0.87 to 0.99. Results were integral molar mixing enthalpies, which showed a triangular shaped $\Delta_{\text{mix}}H$ -curve with an extrapolated minimum of $-40,000 \text{ J} \cdot \text{mol}^{-1}$ at $x_{\text{Li}} = 0.77$. According to earlier results from EMF-measurements this integral molar mixing enthalpy minimum can be understood as an ordering phenomenon in the liquid, which supports the theory of associates of Li_4Sn in the melt. In 1999 Gasior and Moser [23] finalized their EMF-measurements at temperatures between 777 K and 975 K and compositions of $x_{\text{Li}} = 0.025$ to 0.725 and 0.91 to 0.954. In this extensive work they published partial and integral thermodynamic properties, which supported the associate theory. Two years later Yassin and Castanet [24] compiled the partial molar limiting enthalpies of mixing of alkali metals in tin and described a slight temperature dependence for the partial molar limiting enthalpy of lithium in tin ($(\Delta_{\text{mix}}\overline{H}_{\text{Li}}^{\infty}/10^3 \text{ J} \cdot \text{mol}^{-1} = -64 + 0.0079 \cdot T/\text{K})$). Available assessments, which incorporate thermodynamic as well as crystallographic data, are from Sangster and Bale [25] in 1998, Yin *et al.* [26] in 2005 and Du *et al.* [27] in 2006. The later assessments done by Yin *et al.* [26] and Du *et al.* [27] summarize the available thermodynamic data, fit the thermodynamic properties and optimize the Li–Sn phase diagram with the CALPHAD approach.

TABLE 2

Partial and integral molar enthalpies of mixing of liquid Cu–Li alloys at 1073 K; standard states: pure liquid metals.

Dropped mole $n_{\text{Cu}}/10^{-3} \text{ mol}$	Drop enthalpy $\Delta H_{\text{signal}}/\text{J}$	Partial molar enthalpy		Integral molar enthalpy	
		x_{Cu}^a	$\Delta_{\text{mix}}\overline{H}_{\text{Cu}}/\text{J} \cdot \text{mol}^{-1}$	x_{Cu}^b	$\Delta_{\text{mix}}H/\text{J} \cdot \text{mol}^{-1}$
0.4709	20,763	0.0043	23,124 ± 458	0.0086	199 ± 4
0.5173	22,534	0.0132	22,588 ± 452	0.0179	408 ± 8
0.5343	22,843	0.0226	21,779 ± 444	0.0273	613 ± 12
0.5626	23,644	0.0321	21,056 ± 436	0.0370	817 ± 17
0.5993	24,554	0.0421	20,002 ± 426	0.0471	1019 ± 21
0.6317	25,494	0.0524	19,381 ± 419	0.0576	1220 ± 25
0.6621	26,551	0.0629	19,131 ± 416	0.0683	1424 ± 30
0.6948	27,296	0.0738	18,311 ± 408	0.0793	1623 ± 34
0.7190	28,020	0.0848	17,998 ± 405	0.0904	1820 ± 39
0.7517	28,790	0.0960	17,330 ± 398	0.1017	2013 ± 43
0.7984	30,488	0.1075	17,213 ± 397	0.1134	2212 ± 48
0.8229	31,602	0.1193	17,430 ± 399	0.1252	2413 ± 52
0.8478	32,076	0.1311	16,864 ± 393	0.1370	2608 ± 57
0.8909	33,371	0.1430	16,486 ± 389	0.1490	2802 ± 62
0.9247	33,883	0.1551	15,668 ± 381	0.1612	2986 ± 66
0.9534	35,120	0.1673	15,864 ± 383	0.1734	3173 ± 71
0.9800	35,111	0.1794	14,854 ± 372	0.1855	3345 ± 75
1.0182	35,823	0.1916	14,209 ± 365	0.1978	3508 ± 80
1.0414	36,356	0.2039	13,939 ± 363	0.2099	3666 ± 84
1.0708	36,841	0.2160	13,431 ± 357	0.2221	3816 ± 88
1.1006	37,054	0.2281	12,693 ± 350	0.2341	3954 ± 92
1.1487	38,406	0.2403	12,460 ± 347	0.2464	4090 ± 96
1.1753	38,869	0.2524	12,098 ± 343	0.2585	4219 ± 100
1.2077	39,784	0.2645	11,969 ± 342	0.2705	4344 ± 104
1.2366	41,009	0.2765	12,191 ± 344	0.2824	4473 ± 108

^a Average of x_{Cu} before and after the drop.

^b Per mole of binary mixture.

2.4. Cu–Li–Sn

For the ternary system Cu–Li–Sn, to our best knowledge, no thermodynamic description based on experimental data exists. Also no phase diagram or any isothermal section is available, nevertheless two ternary phases have been reported: the phase Li_2CuSn which is fcc [28–30] and the phase Cu_2LiSn which is hexagonal [31]. Some experiments considering lithiation of Cu_6Sn_5 and its cycling behaviour in lithium ion batteries have been applied recently [32–40]. However, no information about phase equilibria is given.

3. Experimental

The calorimetric measurements were performed in a Calvet-type twin calorimeter with two thermopiles with more than 200 thermocouples each. ΔT -values down to 10^{-5} K to 10^{-4} K could be detected. To enable isoperibolic environment a wire wound resistance furnace was used. Drops were performed using an automated device with a capacity of 30 drops. This device and all measuring facilities are controlled by an user-assembled software in LabVIEW, and the obtained data were evaluated by using HiQ program (for more details see [41]). To prevent oxidation all measurements were carried out under Ar flow ($x_{\text{Ar}} = 0.99999$, flow rate = $30 \text{ ml} \cdot \text{min}^{-1}$, usage of an additional gas purification unit), traces of oxygen were gettered by small slices of titanium next to the crucible. The crucibles (inner diameter 9 mm, length 80 mm) were made of molybdenum for lithium-rich alloys and boron nitride for lithium-poor alloys. Molybdenum is inert against liquid lithium [42], but boron nitride reacts with lithium at higher temperatures (~ 1100 K). Vice versa, boron nitride is inert against liquid tin, but with molybdenum, tin could form intermetallic phases [43]. The boron nitride crucibles were stored in methanol for some days to esterify the boric acid at the surface to volatile methyl esters, which were evaporated in vacuum at 1173 K. Samples were prepared from tin rods (Alfa Aesar, $x_{\text{Sn}} = 0.999985$), lithium wire (Alfa Aesar, $x_{\text{Li}} = 0.998$, stored in mineral oil) and copper wire (Goodfellow, $x_{\text{Cu}} = 0.9998$). The lithium wire was cleaned in a supersonic bath in *n*-hexane and the solvent removed under vacuum in the glove box antechamber. The copper wire was treated under H_2 -flow at 473 K for 5 h to remove oxide layers. Calibration was done by dropping five pieces of the pure element into the bath

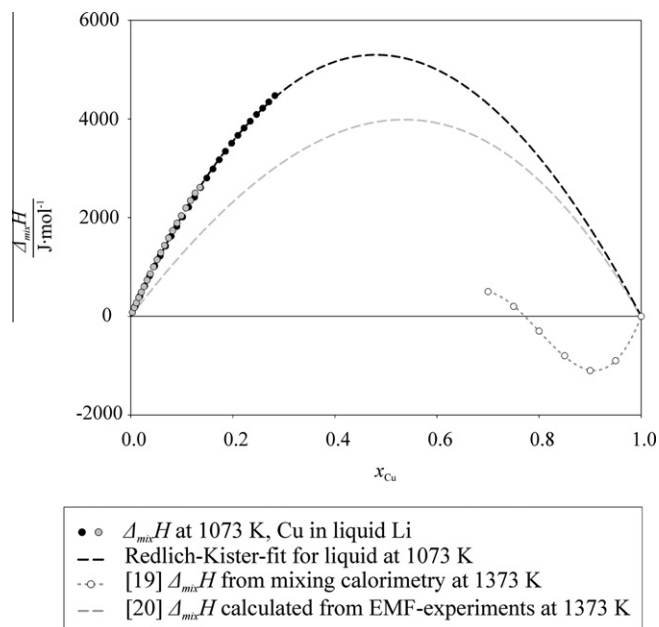


FIGURE 1. Integral molar enthalpies of mixing of liquid Cu–Li alloys at 1073 K; comparison with literature values.

of the same element at the start of each measurement. In addition to the calibration with the pure elements also dropping of pieces of NIST standard sapphire was applied. For determining the binary integral and partial molar mixing enthalpies, copper or tin were dropped in liquid lithium and lithium was dropped in liquid tin. The maximum measurement temperature of 1073 K corresponds to the limit of safe handling of liquid lithium. Furthermore, at higher temperatures the lithium melt crept out of the crucible and reacted with the quartz glass wall of our outer tube.

The intervals between the drops were usually 40 min, heat flow acquisition was 0.5 s. The signals obtained from the thermocouples were recorded, integrated and quantified applying the calorimeter constant, which was determined by the first five calibration drops. To validate the measurements each run was repeated at least one time. The measured enthalpy $\Delta H_{\text{ij};\text{signal}}$ is the integrated heat flow at constant pressure and follows this equation:

TABLE 3

Limiting partial molar enthalpies in Cu–Li and Li–Sn, comparison of measured and literature data.

System	T/K		Run no.			Literature, at T/K			
			1	2	3	[19] 1373	[20] ^a 1373		
Cu–Li	1073	$\Delta_{\text{mix}}\bar{H}_{\text{Cu}}^{\infty}/\text{J} \cdot \text{mol}^{-1}$	23,200 (±400)	24,300 (±200)			13,500		
Cu–Li		$\Delta_{\text{mix}}\bar{H}_{\text{Li}}^{\infty}/\text{J} \cdot \text{mol}^{-1}$				–30,900	18,500		
Li–Sn	773	$\Delta_{\text{mix}}\bar{H}_{\text{Sn}}^{\infty}/\text{J} \cdot \text{mol}^{-1}$	–163,100 (±1100)	–172,200 (±2700)		[21] ^a 688	[22] 807	[23] ^a	[24] ^a 773
Li–Sn	773	$\Delta_{\text{mix}}\bar{H}_{\text{Li}}^{\infty}/\text{J} \cdot \text{mol}^{-1}$	–57,900 (±800)	–57,800 (±700)		–55,500	–57,400	–56,500	–57,900
Li–Sn	1073	$\Delta_{\text{mix}}\bar{H}_{\text{Sn}}^{\infty}/\text{J} \cdot \text{mol}^{-1}$	–170,200 (±1400)	–168,600 (±4100)		[22] 938	[24] ^a 1073		
Li–Sn	1073	$\Delta_{\text{mix}}\bar{H}_{\text{Li}}^{\infty}/\text{J} \cdot \text{mol}^{-1}$	–59,400 (±400)	–56,800 (±300)	–58,600 (±400)	–56,700	–55,500		

$\Delta_{\text{mix}}\bar{H}_i^{\infty}$, limiting partial molar enthalpy.

^a Calculated.

TABLE 4
Partial and integral molar enthalpies of mixing of liquid Li–Sn alloys at 1073 K; standard states: pure liquid metals.

A: Li in liquid Sn					
Dropped mole	Drop enthalpy	Partial molar enthalpy		Integral molar enthalpy	
$n_{\text{Li}}/10^{-3}$ mol	$\Delta H_{\text{signal}}/\text{J}$	x_{Li}^a	$\Delta_{\text{mix}}\bar{H}_{\text{Li}}/\text{J} \cdot \text{mol}^{-1}$	x_{Li}^b	$\Delta_{\text{mix}}H/\text{J} \cdot \text{mol}^{-1}$
Starting amount: $n_{\text{Sn}} = 19.2055 \cdot 10^{-3}$ mol, calibration: 5 pieces Sn, calibration constant $k = (0.56048 \pm 0.0040) \text{J} \cdot (\mu\text{V} \cdot \text{s})^{-1}$					
0.3256	-11,578	0.0083	-60,939 ± 254	0.0167	-1016 ± 4
0.3688	-12,468	0.0258	-59,184 ± 242	0.0349	-2094 ± 9
0.4250	-14,240	0.0450	-58,886 ± 240	0.0551	-3282 ± 13
0.4913	-15,746	0.0662	-57,431 ± 229	0.0774	-4560 ± 19
0.6109	-20,134	0.0905	-58,340 ± 236	0.1037	-6093 ± 25
0.6454	-20,212	0.1168	-56,696 ± 224	0.1299	-7572 ± 31
0.7535	-23,242	0.1443	-56,225 ± 221	0.1586	-9179 ± 37
0.8284	-27,165	0.1733	-58,172 ± 234	0.1881	-10,894 ± 44
0.8558	-25,650	0.2023	-55,353 ± 214	0.2164	-12,447 ± 50
0.9408	-29,308	0.2309	-56,534 ± 223	0.2454	-14,076 ± 56
0.9840	-29,576	0.2594	-55,437 ± 215	0.2735	-15,616 ± 62
1.0647	-31,703	0.2875	-55,158 ± 213	0.3016	-17,147 ± 68
1.1482	-35,602	0.3156	-56,386 ± 222	0.3296	-18,720 ± 74
1.2577	-38,134	0.3437	-55,700 ± 217	0.3578	-20,275 ± 80
1.3269	-40,114	0.3714	-55,612 ± 216	0.3851	-21,776 ± 86
1.3802	-41,241	0.3981	-55,261 ± 214	0.4111	-23,193 ± 91
1.4249	-41,710	0.4234	-54,654 ± 209	0.4358	-24,510 ± 96
1.5099	-43,965	0.4477	-54,499 ± 208	0.4597	-25,784 ± 101
1.6251	-46,986	0.4715	-54,293 ± 207	0.4833	-27,030 ± 106
1.6727	-47,799	0.4945	-53,957 ± 204	0.5056	-28,190 ± 110
1.7505	-50,261	0.5162	-54,093 ± 205	0.5269	-29,307 ± 114
1.8182	-49,586	0.5370	-52,653 ± 195	0.5472	-30,308 ± 117
1.8744	-48,911	0.5568	-51,475 ± 187	0.5664	-31,203 ± 120
1.9378	-49,175	0.5754	-50,758 ± 181	0.5845	-32,023 ± 123
2.0141	-49,755	0.5932	-50,084 ± 177	0.6019	-32,777 ± 125
B: Sn in liquid Li					
Dropped mole	Drop enthalpy	Partial molar enthalpy		Integral molar enthalpy	
$n_{\text{Sn}}/10^{-3}$ mol	$\Delta H_{\text{signal}}/\text{J}$	x_{Sn}^a	$\Delta_{\text{mix}}\bar{H}_{\text{Sn}}/\text{J} \cdot \text{mol}^{-1}$	x_{Sn}^b	$\Delta_{\text{mix}}H/\text{J} \cdot \text{mol}^{-1}$
Starting amount: $n_{\text{Li}} = 28.2874 \cdot 10^{-3}$ mol, calibration: 5 pieces Li, calibration constant $k = (0.64430 \pm 0.0168) \text{J} \cdot (\mu\text{V} \cdot \text{s})^{-1}$					
0.8476	-130,494	0.0145	-183,228 ± 4025	0.0291	-5330 ± 117
0.8778	-140,136	0.0433	-188,916 ± 4174	0.0575	-10,700 ± 236
0.9260	-154,635	0.0716	-196,260 ± 4366	0.0857	-16,254 ± 359
0.9671	-168,763	0.0996	-203,778 ± 4562	0.1134	-21,937 ± 487
2.0686	-380,843	0.1404	-213,376 ± 4813	0.1674	-33,594 ± 750
1.0982	-120,392	0.1804	-138,899 ± 2866	0.1935	-36,891 ± 816
2.3200	-33,766	0.2185	-43,822 ± 380	0.2435	-37,321 ± 789
1.2179	-12,091	0.2554	-39,196 ± 260	0.2674	-37,380 ± 773
1.2674	-2548	0.2790	-31,279 ± 53	0.2906	-37,186 ± 750
1.3092	6985	0.3019	-23,932 ± 139	0.3132	-36,765 ± 722
1.3458	14,436	0.3241	-18,542 ± 280	0.3349	-36,188 ± 690
1.3900	21,541	0.3455	-13,771 ± 405	0.3560	-35,479 ± 655
1.4303	27,439	0.3661	-10,084 ± 502	0.3763	-34,678 ± 619
1.4728	32,727	0.3861	-7048 ± 581	0.3959	-33,809 ± 581
1.5011	37,382	0.4053	-4366 ± 651	0.4147	-32,894 ± 543
1.5579	40,971	0.4238	-2970 ± 688	0.4329	-31,960 ± 504
1.5628	44,193	0.4416	-991 ± 739	0.4502	-31,019 ± 466
1.6465	48,418	0.4587	139 ± 769	0.4672	-30,053 ± 428
1.6929	50,830	0.4755	758 ± 785	0.4837	-29,101 ± 391
1.7374	54,300	0.4916	1985 ± 817	0.4996	-28,145 ± 354
1.7470	55,722	0.5071	2628 ± 834	0.5146	-27,223 ± 318
1.8094	58,645	0.5219	3143 ± 847	0.5292	-26,308 ± 283
1.8587	61,125	0.5362	3617 ± 860	0.5433	-25,410 ± 249

^a Average of x_i before and after the drop.

^b Per mole of binary mixture.

$$\Delta H_{\text{ij};\text{signal}} = n_i \cdot [H_{i(\text{l}),\text{FT}} - H_{i(\text{s}),\text{DT}}] + \Delta H_{\text{ij};\text{reaction}} \quad (1)$$

The number of moles of dropped element i is n_i , the furnace temperature is FT and the drop temperature is DT. The furnace temperatures as well as the drop temperatures were recorded for each drop. For the calculation the mean values over all drops were taken because the scattering of the temperature values was low enough to not influence the accuracy of the method. The values for the term $H_{i(\text{l}),\text{FT}} - H_{i(\text{s}),\text{DT}}$ were calculated using the polynomials for pure elements in the SGTE unary database [44]. The rather small masses

which were added allow the consideration for the partial molar enthalpy of mixing:

$$\Delta_{\text{mix}}\bar{H}_{\text{ij}} \approx \frac{\Delta H_{\text{ij};\text{reaction}}}{n_i} \quad (2)$$

The integral molar enthalpy of mixing was calculated by summing the respective reaction enthalpies and division by the total molar amount of substance, where n_j stands for the molar amount of substance which was already present in the crucible:

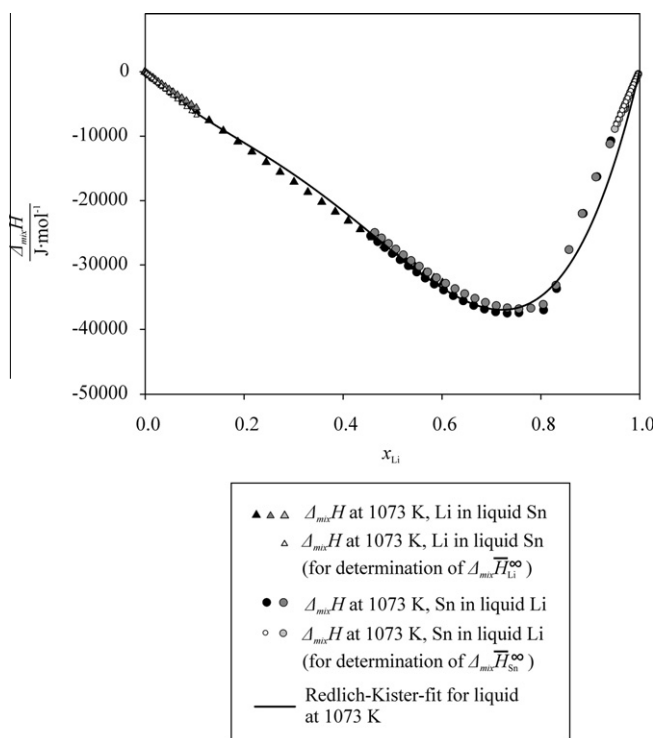


FIGURE 2. Integral molar enthalpies of mixing of liquid Li-Sn alloys at 1073 K.

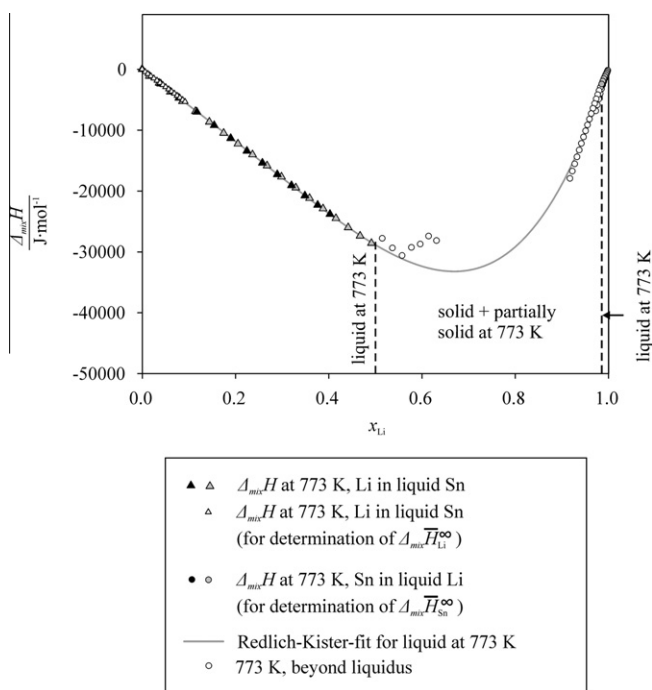


FIGURE 3. Integral molar enthalpies of mixing of liquid Li-Sn alloys at 773 K.

$$\Delta_{\text{mix}}H_{ij} = \frac{\sum_{i,j} \Delta H_{ij;\text{reaction}}}{n_j + \sum_i n_i} \quad (3)$$

The respective binary starting value for the sections in the ternary system was calculated from the information listed in table 1. Random errors as well as systematic errors of calorimetry depend on the construction of the calorimeter, calibration procedure, signal

integration and “chemical errors”, e.g. incomplete reactions, impurities, reactions between the liquid metal and the crucible or evaporation of lithium and reaction of the vapour with the quartz glass wall. Considering many calibration measurements done by dropping NIST standard sapphire, the standard deviation can be estimated to be less than $\pm 1\%$ for the HT-1000. The systematic errors are mainly caused by parasitic heat flows, base line problems at signal integration and mixing problems. One can estimate that the overall error is $\pm 250 \text{ J} \cdot \text{mol}^{-1}$.

4. Results and discussion

4.1. The binary systems Cu-Li and Li-Sn

Due to the lack of information in the binary Cu-Li system, calorimetric studies were necessary. As mentioned in chapter 3 our experiments had to be restricted to 1073 K because lithium and lithium-rich alloys crept out of the crucible at higher temperatures. Thus only the lithium-rich side, where solid copper was dropped into liquid lithium, could be examined. Although the integral molar enthalpy of mixing is endothermic (see table 2 and figure 1) the copper pieces dissolved easily at 1073 K in lithium. Based on our data of two runs until $x_{\text{Cu}} \sim 0.28$ we extrapolated the integral molar enthalpies of mixing to $x_{\text{Cu}} = 1$ ($\Delta_{\text{mix}}H = 0$) with a Redlich-Kister-fit using two interaction parameters [45]:

$$\Delta_{\text{mix}}H_{ij} = x_i \cdot x_j \cdot \sum_{\nu} {}^{\nu}L_{ij}^H (x_i - x_j)^{\nu} \quad (4)$$

Variables i and j are the binary elements, L is the binary interaction parameter and ν its order. The parameters 0L and 1L for Cu-Li are given in table 1. Our data are quite satisfying matching to the data of Gasior *et al.* [20], where integral molar mixing enthalpy values have been derived from EMF-measurements. At estimated $x_{\text{Cu}} = 0.5$ there is an endothermic maximum of $\sim 5300 \text{ J} \cdot \text{mol}^{-1}$. Data from Mikhailovskaya and Sudavtseva [19] at the copper-rich side show, however, quite different behaviour. They are slightly exothermic at the copper-rich side and become slightly endothermic at $x_{\text{Li}} = 0.23$. It has to be pointed out here that there is obviously a mismatch of measured partial and calculated integral molar enthalpy values in this report. Generally, endothermic behaviour which maximum values significantly higher than $1000 \text{ J} \cdot \text{mol}^{-1}$ to $2000 \text{ J} \cdot \text{mol}^{-1}$ indicates the occurrence of a miscibility gap in the liquid mixture. This assumption is supported by thermodynamic calculations of Pelton [18], who supposed such a miscibility gap with a maximum at $x_{\text{Li}} \sim 0.4$. In order to determine the limiting partial molar enthalpy of copper in liquid lithium ($\Delta_{\text{mix}}\bar{H}_{\text{Cu}}^{\infty}$), we performed two measurements with all drops within $x_{\text{Cu}} = 0$ to 0.05. The obtained values of the partial molar enthalpy of mixing have been extrapolated to pure lithium applying a linear regression. This leads to a highly symmetric mixing curve with endothermic maxima at $23,200 \text{ J} \cdot \text{mol}^{-1}$ and $24,300 \text{ J} \cdot \text{mol}^{-1}$ (see table 3). The choice of a first-order extrapolation is supported by Gasior’s calculations from EMF-values [20], which show a very similar tendency to our data, but, nevertheless, with significantly less endothermic values. In addition, no stable intermetallic compounds with a stoichiometry apart from 1:1 are known to this day, therefore no asymmetry in the integral molar mixing enthalpies should be assumed.

Measurements in the Li-Sn system at 773 K were mainly dedicated to the validation of our calorimetric method for lithium-containing systems, as most literature data was available around this temperature. Furthermore, no calorimetric determination of $\Delta_{\text{mix}}H$ over the entire concentration range was hitherto published. Thus we did further measurements at 1073 K, slightly above the maximum liquidus temperature in this system. Our measured integral molar enthalpy values from the tin- and the lithium-rich side coincided very well (see also table 4 and figure 2). The data were again

TABLE 5
Partial and integral molar enthalpies of mixing of liquid Li–Sn alloys at 773 K; standard states: pure liquid metals.

A: Li in liquid Sn					
Dropped mole	Drop enthalpy	Partial molar enthalpy		Integral molar enthalpy	
$n_{\text{Li}}/10^{-3}$ mol	$\Delta H_{\text{signal}}/\text{J}$	x_{Li}^a	$\Delta_{\text{mix}}\bar{H}_{\text{Li}}/\text{J} \cdot \text{mol}^{-1}$	x_{Li}^b	$\Delta_{\text{mix}}H/\text{J} \cdot \text{mol}^{-1}$
Starting amount: $n_{\text{Sn}} = 16.8847 \cdot 10^{-3}$ mol, calibration: 5 pieces Sn, calibration constant $k = (0.46792 \pm 0.0057)\text{J} \cdot (\mu\text{V} \cdot \text{s})^{-1}$					
0.2651	-14,777	0.0077	-72,564 ± 678	0.0155	-1122 ± 10
0.3760	-13,977	0.0260	-53,992 ± 452	0.0366	-2256 ± 20
0.4481	-19,607	0.0486	-60,580 ± 532	0.0606	-3710 ± 33
0.5143	-21,885	0.0737	-59,373 ± 517	0.0867	-5258 ± 46
0.5806	-24,864	0.1006	-59,647 ± 521	0.1145	-6914 ± 61
0.6627	-27,856	0.1294	-58,855 ± 511	0.1443	-8659 ± 76
0.7362	-31,359	0.1597	-59,418 ± 518	0.1751	-10,485 ± 92
0.7881	-32,648	0.1904	-58,250 ± 504	0.2056	-12,256 ± 107
0.8716	-35,190	0.2213	-57,195 ± 491	0.2369	-14,026 ± 122
0.9393	-39,206	0.2525	-58,560 ± 507	0.2680	-15,839 ± 138
1.0200	-43,151	0.2835	-59,125 ± 514	0.2990	-17,673 ± 154
1.1036	-46,197	0.3144	-58,682 ± 509	0.3297	-19,469 ± 169
1.1598	-48,637	0.3445	-58,759 ± 510	0.3592	-21,198 ± 184
1.2477	-52,358	0.3737	-58,787 ± 510	0.3882	-22,898 ± 199
1.3024	-54,054	0.4020	-58,325 ± 505	0.4158	-24,494 ± 213
1.3687	-56,302	0.4290	-57,958 ± 500	0.4422	-26,008 ± 226
1.4436	-57,078	0.4549	-56,361 ± 481	0.4676	-27,389 ± 237
1.5243	-55,867	0.4798	-53,474 ± 446	0.4920	-28,585 ± 247
1.5891	8857	0.5036	-11,249 ± 68	0.5152	-27,794 ± 233
1.6424	-75,724	0.5261	-62,927 ± 561	0.5370	-29,377 ± 247
1.7101	-68,630	0.5474	-56,953 ± 488	0.5577	-30,612 ± 258
1.8095	28,000	0.5677	-1349 ± 188	0.5778	-29,288 ± 238
1.8715	-399	0.5872	-17,035 ± 3	0.5966	-28,740 ± 227
1.9478	34,401	0.6056	839 ± 215	0.6146	-27,425 ± 208
2.0098	-54,946	0.6230	-44,161 ± 332	0.6315	-28,159 ± 213
B: Sn in liquid Li					
Dropped mole	Drop enthalpy	Partial molar enthalpy		Integral molar enthalpy	
$n_{\text{Sn}}/10^{-3}$ mol	$\Delta H_{\text{signal}}/\text{J}$	x_{Sn}^a	$\Delta_{\text{mix}}\bar{H}_{\text{Sn}}/\text{J} \cdot \text{mol}^{-1}$	x_{Sn}^b	$\Delta_{\text{mix}}H/\text{J} \cdot \text{mol}^{-1}$
Starting amount: $n_{\text{Li}} = 79.8948 \cdot 10^{-3}$ mol, calibration: 5 pieces Li, calibration constant $k = (0.44009 \pm 0.0035)\text{J} \cdot (\mu\text{V} \cdot \text{s})^{-1}$					
0.0836	-12,187	0.0005	-166,064 ± 1164	0.0010	-174 ± 1
0.1013	-14,213	0.0017	-160,562 ± 1120	0.0023	-376 ± 3
0.1209	-17,031	0.0031	-161,082 ± 1124	0.0038	-619 ± 4
0.1315	-19,127	0.0046	-165,738 ± 1162	0.0054	-889 ± 6
0.1517	-21,819	0.0064	-164,103 ± 1149	0.0073	-1196 ± 8
0.1698	-24,380	0.0084	-163,851 ± 1147	0.0094	-1539 ± 11
0.1853	-29,547	0.0105	-179,660 ± 1273	0.0117	-1947 ± 14
0.2037	-35,023	0.0129	-192,031 ± 1373	0.0142	-2425 ± 17
0.2210	-39,343	0.0155	-198,148 ± 1422	0.0168	-2957 ± 21
0.2316	-41,064	0.0182	-197,431 ± 1416	0.0196	-3509 ± 25
0.2528	-49,782	0.0212	-216,908 ± 1572	0.0227	-4169 ± 30
0.2674	-52,712	0.0243	-217,154 ± 1574	0.0259	-4864 ± 35
0.2860	-57,918	0.0275	-222,543 ± 1617	0.0292	-5620 ± 40
0.3044	-60,017	0.0310	-217,164 ± 1574	0.0328	-6399 ± 46
0.3221	-67,882	0.0347	-230,724 ± 1683	0.0366	-7270 ± 52
0.3361	-70,680	0.0385	-230,230 ± 1679	0.0405	-8170 ± 59
0.3569	-75,234	0.0425	-230,775 ± 1683	0.0446	-9120 ± 66
0.3661	-77,203	0.0466	-230,860 ± 1684	0.0487	-10,086 ± 73
0.3868	-80,975	0.0509	-229,312 ± 1672	0.0531	-11,091 ± 80
0.4064	-85,745	0.0554	-230,952 ± 1685	0.0576	-12,145 ± 88
0.4202	-88,539	0.0599	-230,656 ± 1682	0.0623	-13,223 ± 96
0.4401	-92,875	0.0647	-231,002 ± 1685	0.0671	-14,341 ± 104
0.4570	-96,418	0.0696	-230,944 ± 1685	0.0720	-15,491 ± 112
0.4726	-10,0081	0.0746	-231,718 ± 1691	0.0771	-16,671 ± 121
0.4878	-10,2871	0.0797	-230,846 ± 1684	0.0823	-17,871 ± 130

Beyond the liquidus.

^a Average of x_i before and after the drop.

^b Per mole of binary mixture.

fitted for each temperature with a Redlich–Kister–polynomial [45], values for ⁰L, ¹L, and ²L are listed in table 1. Graphs are shown in figure 2 for 1073 K and figure 3 for 773 K. At 773 K there are no experimental data available between $x_{\text{Li}} = 0.5$ and 0.98, because the obtained alloys were already partially or completely solid (see table 5 and figure 3). The fit of the data at 1073 K is based on experimental data over the entire concentration range. Our experimental data from both temperatures together with the liter-

ature data from EMF- and calorimetric measurements at various temperatures [21,22] have been as well fitted and are shown figure 4. In all cases the integral molar enthalpy of mixing is purely exothermic. The resulting curve which fits all values shows a minimum of $\sim 37,000\text{J} \cdot \text{mol}^{-1}$ at $x_{\text{Sn}} = 0.20$ (see figure 4). Whereas this curve corresponds very well to that evaluated from our data at 1073 K, the fitted curve for 773 K features a minimum at $-33,000\text{J} \cdot \text{mol}^{-1}$ and $x_{\text{Sn}} = 0.33$. We believe that this is rather

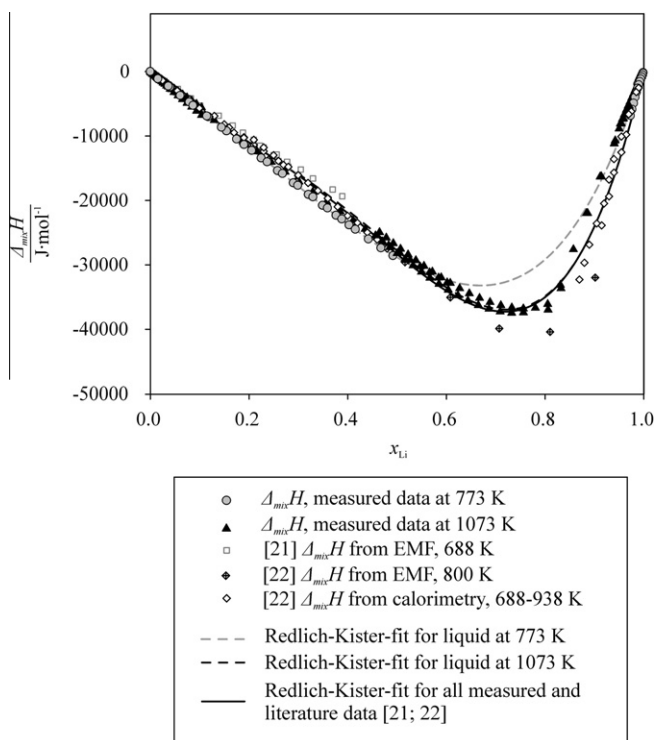


FIGURE 4. Integral molar enthalpies of mixing of liquid Li–Sn alloys at 773 K and 1073 K; comparison with literature values.

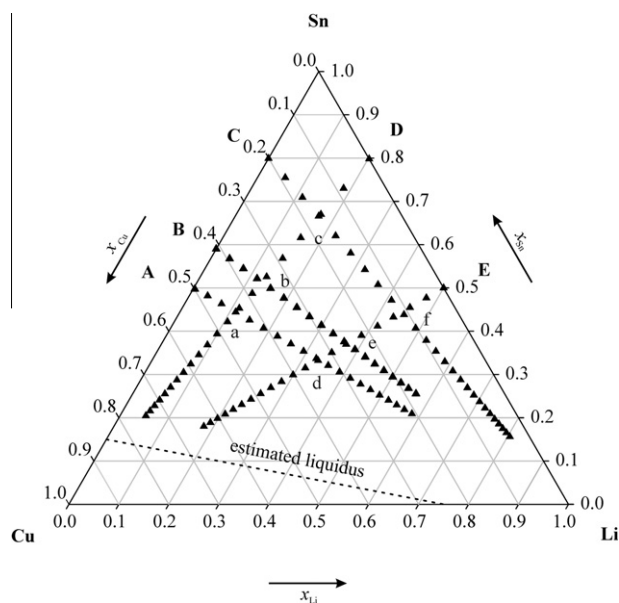


FIGURE 5. Measured sections (A, B, C, D, E) and alloy compositions in the ternary Cu–Li–Sn system at 1073 K.

caused by the lack of experimental data in this region than by temperature dependence. In the latter case values at lower temperature should be more exothermic. The pronounced minimum of the integral molar enthalpy of mixing at about Li_4Sn is related to the two most stable intermetallic compounds Li_7Sn_2 [25] and $\text{Li}_{17}\text{Sn}_4$ [46], which melt congruently. This indicates the formation of an associate “ Li_4Sn ”, which is already present in the melt close to the liquidus temperature. The associate can be interpreted by an interaction based on the electronic configuration of the two

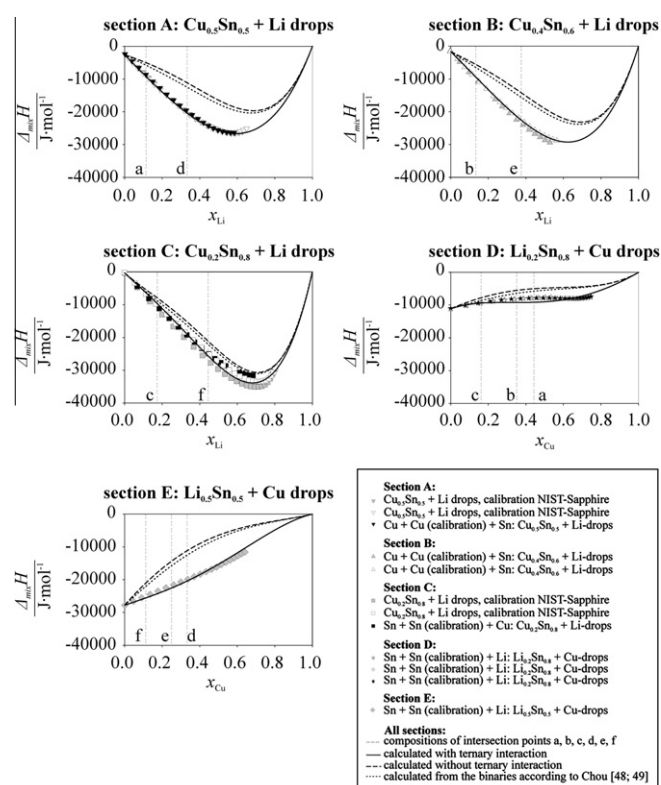


FIGURE 6. Integral molar enthalpies of mixing of liquid Cu–Li–Sn alloys at 1073 K for the sections: (A) $\text{Cu}_{0.5}\text{Sn}_{0.5} + \text{Li-drops}$; (B) $\text{Cu}_{0.4}\text{Sn}_{0.6} + \text{Li-drops}$; (C) $\text{Cu}_{0.2}\text{Sn}_{0.8} + \text{Li-drops}$; (D) $\text{Li}_{0.2}\text{Sn}_{0.8} + \text{Cu-drops}$; (E) $\text{Li}_{0.5}\text{Sn}_{0.5} + \text{Cu-drops}$; standard states: pure liquid metals. Comparison between fit with ternary interactions, fit without ternary interactions and extrapolation from binary data [48,49].

elements. The highly electropositive lithium has a strong tendency to provide one electron per atom ($[\text{He}] 2s^1$), which could be accepted by the remaining free 5p orbitals of tin ($[\text{Kr}] 4d^{10}5s^25p^2$). In the same way as described for Cu–Li, we have determined the limiting partial molar enthalpies from both sides of the binary system at 773 K and 1073 K (see table 3). Values of lithium in tin ($\Delta_{\text{mix}}\overline{H}_{\text{Li}}^\infty$) were found to be between $-56,800 \text{ J} \cdot \text{mol}^{-1}$ and $-59,400 \text{ J} \cdot \text{mol}^{-1}$, which is supported by literature data [21–24], whereas for tin in lithium ($\Delta_{\text{mix}}\overline{H}_{\text{Sn}}^\infty$) it was found to be between $-163,100 \text{ J} \cdot \text{mol}^{-1}$ and $-172,200 \text{ J} \cdot \text{mol}^{-1}$. No literature data was available for $\Delta_{\text{mix}}\overline{H}_{\text{Sn}}^\infty$. No significant temperature dependence could be observed.

4.2. Measurements and modelling in the ternary system Cu–Li–Sn

Lithium was dropped at 1073 K to liquid mixtures with ratios of $x_{\text{Cu}}/x_{\text{Sn}} \approx 1:1$, $x_{\text{Cu}}/x_{\text{Sn}} \approx 2:3$, and $x_{\text{Cu}}/x_{\text{Sn}} \approx 1:4$, as well as copper was dropped to mixtures of $x_{\text{Li}}/x_{\text{Sn}} \approx 1:1$ and $x_{\text{Li}}/x_{\text{Sn}} \approx 1:4$, according to the compositions which are shown in figure 5. The measured integral and partial molar enthalpies of mixing are listed in table 6. Plots of the integral molar enthalpies versus concentration of lithium or copper, respectively, are shown in figure 6. Most experiments have been carried out several times to assure reproducibility. The integral molar enthalpy values at all intersection points have been compared (see table 7), the maximum errors are between $\sim 300 \text{ J} \cdot \text{mol}^{-1}$ and $\sim 1250 \text{ J} \cdot \text{mol}^{-1}$, what is satisfying regarding the method and the kind of materials used.

The integral molar enthalpies of mixing in the ternary system were described with a least square fit, according to a Redlich–Kister–Muggianu-polynomial

TABLE 6
 Partial and integral molar enthalpies of mixing of liquid Cu–Li–Sn alloys at 1073 K; standard states: pure liquid metals.

Dropped mole	Drop enthalpy	Partial molar enthalpy		Integral molar enthalpy	
$n_i/10^{-3}$ mol	$\Delta H_{\text{signal}}/\text{J}$	x_i^a	$\Delta_{\text{mix}}\bar{H}/\text{J} \cdot \text{mol}^{-1}$	x_i^b	$\Delta_{\text{mix}}H/\text{J} \cdot \text{mol}^{-1}$
<i>Section A: $x_{\text{Cu}}/x_{\text{Sn}} \approx 1:1$; $i = \text{Li}$; starting amounts: $n_{\text{Cu}} = 7.9212 \cdot 10^{-3}$ mol; $n_{\text{Sn}} = 7.8768 \cdot 10^{-3}$ mol, calibration: 5 pieces of NIST-sapphire, calibration constant $k = (1.2364 \pm 0.0272)\text{J} \cdot (\mu\text{V} \cdot \text{s})^{-1}$</i>					
0.0000		0.0000		0.0000	–2577
0.2953	–12,205	0.0092	–66,515 ± 910	0.0184	–3750 ± 17
0.3991	–15,628	0.0302	–64,350 ± 862	0.0421	–5217 ± 37
0.4682	–18,114	0.0553	–63,875 ± 852	0.0686	–6836 ± 60
0.5115	–18,044	0.0822	–60,469 ± 777	0.0958	–8406 ± 81
0.5748	–19,458	0.1102	–59,037 ± 745	0.1246	–10,019 ± 102
0.6584	–22,593	0.1400	–59,504 ± 755	0.1554	–11,760 ± 125
0.7492	–23,356	0.1717	–56,365 ± 686	0.1880	–13,478 ± 146
0.7665	–21,602	0.2033	–53,373 ± 620	0.2187	–14,990 ± 164
0.8860	–26,976	0.2351	–55,635 ± 670	0.2515	–16,697 ± 186
0.9566	–26,353	0.2678	–52,737 ± 606	0.2840	–18,259 ± 204
1.0373	–27,459	0.3001	–51,660 ± 583	0.3161	–19,759 ± 221
1.1151	–25,769	0.3319	–48,298 ± 509	0.3476	–21,073 ± 234
1.1699	–24,262	0.3627	–45,929 ± 457	0.3777	–22,219 ± 244
1.2030	–22,020	0.3918	–43,493 ± 403	0.4058	–23,181 ± 252
1.2952	–21,685	0.4196	–41,932 ± 369	0.4334	–24,052 ± 257
1.3600	–18,755	0.4466	–38,979 ± 304	0.4598	–24,746 ± 259
1.4450	–17,743	0.4725	–37,468 ± 270	0.4852	–25,345 ± 260
1.4839	–15,426	0.4971	–35,584 ± 229	0.5090	–25,818 ± 258
1.6179	–12,806	0.5207	–33,104 ± 174	0.5325	–26,166 ± 254
1.6554	–8819	0.5434	–30,516 ± 117	0.5543	–26,370 ± 248
1.7548	–4099	0.5648	–27,525 ± 51	0.5753	–26,424 ± 239
1.8167	1571	0.5852	–24,324 ± 19	0.5951	–26,326 ± 227
1.8571	5796	0.6043	–22,068 ± 69	0.6135	–26,133 ± 213
1.9579	14,022	0.6223	–18,027 ± 158	0.6312	–25,762 ± 196
2.0112	20,855	0.6394	–14,820 ± 228	0.6477	–25,272 ± 177
<i>Section B: $x_{\text{Cu}}/x_{\text{Sn}} \approx 2:3$; $i = \text{Li}$; starting amounts: $n_{\text{Cu}} = 7.5713 \cdot 10^{-3}$ mol; $n_{\text{Sn}} = 10.8901 \cdot 10^{-3}$ mol, starting alloy made from dropping Sn in Cu; calibration: 5 pieces Cu, calibration constant $k = (0.8934 \pm 0.0147)\text{J} \cdot (\mu\text{V} \cdot \text{s})^{-1}$</i>					
0.0000		0.0000		0.0000	–1618
0.7276	–27,306	0.0190	–62,861 ± 616	0.0379	–3940 ± 23
0.8140	–31,736	0.0575	–64,318 ± 640	0.0771	–6397 ± 48
0.8817	–31,264	0.0965	–60,788 ± 582	0.1160	–8693 ± 71
0.9437	–32,647	0.1351	–59,927 ± 568	0.1542	–10,908 ± 93
1.0243	–33,987	0.1732	–58,509 ± 545	0.1922	–13,042 ± 113
1.0877	–38,198	0.2105	–60,447 ± 577	0.2289	–15,196 ± 134
1.1713	–36,427	0.2468	–56,430 ± 511	0.2648	–17,119 ± 151
1.2088	–35,395	0.2817	–54,612 ± 481	0.2986	–18,841 ± 167
1.3125	–37,116	0.3153	–53,610 ± 464	0.3319	–20,492 ± 181
1.3615	–36,309	0.3476	–52,000 ± 438	0.3633	–21,972 ± 193
1.4594	–36,445	0.3785	–50,302 ± 410	0.3938	–23,329 ± 203
1.5358	–38,013	0.4083	–50,082 ± 407	0.4229	–24,614 ± 213
1.5833	–34,829	0.4365	–47,328 ± 361	0.4501	–25,685 ± 220
1.6611	–33,335	0.4631	–45,398 ± 330	0.4760	–26,614 ± 225
1.7548	–30,275	0.4885	–42,583 ± 283	0.5009	–27,372 ± 228
1.8196	–28,228	0.5126	–40,844 ± 255	0.5243	–28,004 ± 229
1.8484	–25,064	0.5351	–38,890 ± 223	0.5459	–28,499 ± 229
1.9867	–23,403	0.5565	–37,110 ± 193	0.5671	–28,900 ± 227
<i>Section C: $x_{\text{Cu}}/x_{\text{Sn}} \approx 1:4$; $i = \text{Li}$; starting amounts: $n_{\text{Cu}} = 1.6002 \cdot 10^{-3}$ mol; $n_{\text{Sn}} = 6.3727 \cdot 10^{-3}$ mol, calibration: 5 pieces of NIST-sapphire, calibration constant $k = (0.6523 \pm 0.0049)\text{J} \cdot (\mu\text{V} \cdot \text{s})^{-1}$</i>					
0.0000		0.0000		0.0000	–280
0.4697	–16,767	0.0278	–16,767 ± 271	0.0556	–3654 ± 15
0.5446	–17,187	0.0842	–17,187 ± 239	0.1129	–6873 ± 29
0.5849	–18,316	0.1400	–18,316 ± 237	0.1671	–9907 ± 41
0.6973	–22,344	0.1953	–22,344 ± 243	0.2236	–13,123 ± 55

0.7103	-22,180	0.2487	-22,180 ± 237	0.2739	-15,925 ± 67
0.7693	-23,855	0.2976	-23,855 ± 235	0.3214	-18,564 ± 78
0.8054	-24,003	0.3432	-24,003 ± 226	0.3649	-20,903 ± 87
0.9581	-27,015	0.3874	-27,015 ± 214	0.4100	-23,208 ± 96
1.0287	-27,994	0.4308	-27,994 ± 206	0.4517	-25,275 ± 104
1.1094	-29,437	0.4711	-29,437 ± 201	0.4906	-27,152 ± 111
1.1655	-28,330	0.5082	-28,330 ± 184	0.5259	-28,703 ± 116
1.2102	-27,545	0.5418	-27,545 ± 172	0.5577	-29,997 ± 120
1.3082	-27,066	0.5727	-27,066 ± 157	0.5876	-31,073 ± 122
1.3413	-24,990	0.6010	-24,990 ± 141	0.6144	-31,902 ± 124
1.4825	-24,271	0.6273	-24,271 ± 124	0.6402	-32,550 ± 124
1.5012	-21,950	0.6516	-21,950 ± 111	0.6630	-33,013 ± 123
1.5963	-20,274	0.6737	-20,274 ± 96	0.6843	-33,323 ± 121
1.6467	-18,137	0.6940	-18,137 ± 83	0.7036	-33,501 ± 119
1.7577	-15,471	0.7127	-15,471 ± 67	0.7218	-33,533 ± 116
1.8239	-13,375	0.7301	-13,375 ± 56	0.7385	-33,474 ± 112
1.8917	-6487	0.7461	-6487 ± 26	0.7537	-33,192 ± 107
1.9738	3026	0.7608	3026 ± 12	0.7679	-32,646 ± 100
2.0156	17,570	0.7743	17,570 ± 66	0.7808	-31,751 ± 91
2.1611	28,626	0.7869	28,626 ± 100	0.7931	-30,641 ± 80
2.2072	38,862	0.7987	38,862 ± 133	0.8043	-29,393 ± 69

Section D: $x_{Li}/x_{Sn} \approx 1:4$; $i = Cu$; starting amounts: $n_{Li} = 3.0269 \cdot 10^{-3}$ mol; $n_{Sn} = 12.0795 \cdot 10^{-3}$ mol, starting alloy made from dropping Li in Sn, calibration: 5 pieces of Sn, calibration constant $k = (0.7834 \pm 0.0027) J \cdot (\mu V \cdot s)^{-1}$

0.0000		0.0000		0.0000	-11,006
1.2644	43,171	0.0386	248 ± 116	0.0772	-10,137 ± 9
1.3169	43,050	0.1116	-1206 ± 111	0.1459	-9472 ± 17
1.4439	45,717	0.1782	-2234 ± 108	0.2104	-8926 ± 23
1.5464	48,188	0.2399	-2734 ± 106	0.2694	-8463 ± 30
1.6243	46,888	0.2960	-5029 ± 98	0.3226	-8212 ± 35
1.7292	48,241	0.3470	-5999 ± 95	0.3714	-8053 ± 39
1.8275	50,044	0.3936	-6512 ± 93	0.4158	-7944 ± 43
1.9228	51,516	0.4360	-7104 ± 91	0.4562	-7886 ± 46
1.9834	51,792	0.4744	-7783 ± 89	0.4925	-7879 ± 49
2.0895	54,042	0.5091	-8032 ± 88	0.5258	-7889 ± 51
2.1442	54,949	0.5407	-8269 ± 87	0.5557	-7913 ± 54
2.2464	56,918	0.5694	-8559 ± 86	0.5832	-7953 ± 56
2.3173	57,863	0.5957	-8926 ± 85	0.6083	-8012 ± 57
2.3726	60,934	0.6196	-8214 ± 87	0.6310	-8023 ± 59
2.4413	62,437	0.6414	-8321 ± 87	0.6517	-8040 ± 61
2.5132	66,124	0.6613	-7585 ± 89	0.6708	-8015 ± 62
2.5773	69,533	0.6796	-6917 ± 92	0.6883	-7957 ± 64
2.6678	73,454	0.6964	-6363 ± 94	0.7046	-7874 ± 65
2.7556	78,629	0.7121	-5362 ± 97	0.7197	-7745 ± 67
2.8442	82,386	0.7267	-4930 ± 98	0.7337	-7604 ± 69
2.9341	88,256	0.7403	-3817 ± 116	0.7468	-7418 ± 9

Section E: $x_{Li}/x_{Sn} \approx 1:1$; $i = Cu$; starting amounts: $n_{Li} = 8.6616 \cdot 10^{-3}$ mol; $n_{Sn} = 8.6560 \cdot 10^{-3}$ mol, starting alloy made from dropping Li in Sn, calibration: 5 pieces of Sn, calibration constant $k = (0.5944 \pm 0.0032) J \cdot (\mu V \cdot s)^{-1}$

0.0000		0.0000		0.0000	-27,794
0.8344	26,253	0.0230	-2428 ± 169	0.0460	-26,628 ± 8
0.8771	26,726	0.0680	-3419 ± 164	0.0899	-25,559 ± 15
0.9703	29,099	0.1120	-3902 ± 161	0.1341	-24,508 ± 22
1.0236	30,438	0.1552	-4155 ± 160	0.1763	-23,517 ± 29
1.1607	34,291	0.1978	-4347 ± 159	0.2194	-22,514 ± 36
1.2203	35,711	0.2397	-4626 ± 157	0.2601	-21,581 ± 42
1.2772	37,121	0.2792	-4827 ± 156	0.2983	-20,714 ± 48
1.3640	39,735	0.3167	-4761 ± 157	0.3351	-19,879 ± 54
1.4049	41,363	0.3521	-4450 ± 158	0.3691	-19,089 ± 59
1.4926	44,352	0.3854	-4176 ± 160	0.4017	-18,320 ± 64
1.5719	47,377	0.4171	-3752 ± 162	0.4325	-17,570 ± 69

(continued on next page)

TABLE 6 (continued)

Dropped mole $n_i/10^{-3}$ mol	Drop enthalpy $\Delta H_{\text{signal}}/J$		Partial molar enthalpy x_i^a		Integral molar enthalpy x_i^b	
1.6144	49,679	-3120 ± 166	0.4467	$-16,843 \pm 74$	0.4610	$-16,130 \pm 79$
1.7203	53,488	$-2,799 \pm 167$	0.4747	$-16,344 \pm 174$	0.4884	$-15,405 \pm 83$
1.7802	57,425	$-1,411 \pm 175$	0.5012	-898 ± 177	0.5140	$-14,693 \pm 88$
1.9103	62,046	-458 ± 180	0.5263	-247 ± 181	0.5387	$-14,012 \pm 93$
1.9504	64,351	-90 ± 182	0.5501	-400 ± 180	0.5615	$-13,348 \pm 97$
2.0330	67,970		0.5722		0.5829	$-12,711 \pm 101$
2.1217	71,384		0.5931		0.6032	$-12,102 \pm 105$
2.2138	74,828		0.6128		0.6224	$-11,562 \pm 108$
2.2200	74,350		0.6311		0.6398	

^a Average of x_i before and after the drop.

^b Per mole of binary mixture.

$$\begin{aligned} \Delta_{\text{mix}} H_{ijk} = & x_i \cdot x_j \cdot \sum_v L_{ij}^H (x_i - x_j)^v + x_j \cdot x_k \cdot \sum_v L_{jk}^H (x_j - x_k)^v \\ & + x_k \cdot x_i \cdot \sum_v L_{ki}^H (x_k - x_i)^v + x_i \cdot x_j \cdot x_k \cdot ({}^{(0)}M_{i,j,k}^H \cdot x_i \\ & + {}^{(1)}M_{i,j,k}^H \cdot x_j + {}^{(2)}M_{i,j,k}^H \cdot x_k) \end{aligned} \quad (5)$$

In this equation the variables i, j, k are copper, lithium and tin and v -values are 0, 1 or 2. The L -values are the binary interaction parameters for the Redlich–Kister–polynomials, the M -values describe the ternary interactions. The resulting ternary M -values are listed in table 1 together with the binary L -values applied. For Cu–Sn literature values were taken from Flandorfer *et al.* [11]. Based on this equation the integral molar enthalpies of mixing were calculated for the whole ternary composition range. Calculated integral molar enthalpy curves for all sections have been added to the plots, shown in figure 6. Isoenthalpy curves across the whole ternary composition range are plotted in a Gibbs triangle in figure 7. The values in the plot refer to the solid lines. It is noteworthy to say that the values outside of the fully liquid range at 1073 K, which is shown as a shaded field, have to be considered as integral molar enthalpies of the metastable liquid phase. The liquidus limit was estimated from the constituent binary phase diagrams [18,47]. In addition the integral molar enthalpies of mixing were calculated without ternary interaction parameters (equation (5) without ternary interaction term) along the sections A–E. Generally, the values are significantly less exothermic compared to the calculation with ternary interaction parameters (see figure 6). The negative contribution of the ternary interaction term indicates additional ternary interaction of copper, lithium and tin. In order to check, whether an alternative extrapolation model is able to describe our experimental results, the approach of Chou's model [48,49] was applied. This model describes the integral molar enthalpy of mixing as follows:

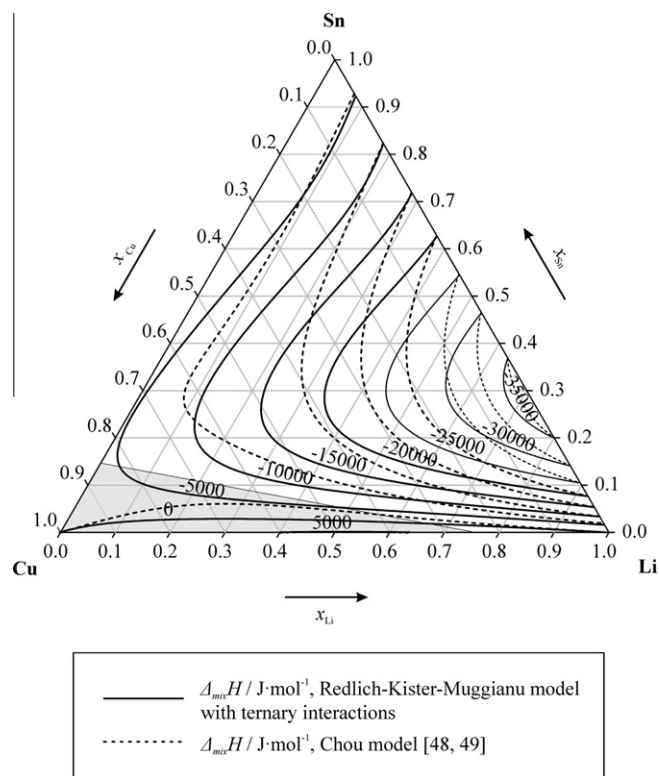


FIGURE 7. Isoenthalpy curves of liquid Cu–Li–Sn alloys at 1073 K; standard states: pure liquid metals; metastable liquid region is indicated by shadowed field.

TABLE 7

Experimental values of the integral molar enthalpy of mixing at the intersection points a, b, c, d, e, and f.

Intersection	Composition			Integral molar enthalpy of mixing $\Delta_{\text{mix}}H/J \cdot \text{mol}^{-1}$				
	x_{Cu}	x_{Li}	x_{Sn}	A Cu _{0,5} Sn _{0,5} + Li	B Cu _{0,4} Sn _{0,6} + Li	C Cu _{0,2} Sn _{0,8} + Li	D Li _{0,2} Sn _{0,8} + Cu	E Li _{0,5} Sn _{0,5} + Cu
a	0.443	0.114	0.443	–8800			–7900	
b	0.351	0.133	0.516		–9350		–8100	
c	0.161	0.173	0.666			–10,300	–9300	
d	0.333	0.334	0.333	–20,200				–19,900
e	0.250	0.375	0.375		–22,800			–21,800
f	0.112	0.444	0.444			–24,700		–24,800

TABLE 8

Similarity coefficients and deviation sum of squares for Chou's model [48,49] applied on Cu–Li–Sn.

Deviation sum of squares	$n_{\text{I}}/J^2 \cdot \text{mol}^{-2} = 39,312,253$		$n_{\text{II}}/J^2 \cdot \text{mol}^{-2} = 785,249,940$		$n_{\text{III}}/J^2 \cdot \text{mol}^{-2} = 471,413,453$	
Interaction of	Cu–Li	Cu–Sn	Li–Cu	Li–Sn	Sn–Cu	Sn–Li
			$\eta_{\text{II}} > \eta_{\text{III}} \gg \eta_{\text{I}}$			
Similarity coeff.	$\zeta_{\text{CuLi}} = 0.0477$		$\zeta_{\text{LiSn}} = 0.6247$		$\zeta_{\text{SnCu}} = 0.9230$	

$$\Delta_{\text{mix}}H_{\text{ijk}} = x_{\text{i}} \cdot x_{\text{j}} \cdot \sum_{\text{v}}^{\text{v}} L_{\text{ij}}^{\text{H}}(x_{\text{i}} - x_{\text{j}})^{\text{v}} + x_{\text{j}} \cdot x_{\text{k}} \cdot \sum_{\text{v}}^{\text{v}} L_{\text{jk}}^{\text{H}}(x_{\text{j}} - x_{\text{k}})^{\text{v}} + x_{\text{k}} \cdot x_{\text{i}} \cdot \sum_{\text{v}}^{\text{v}} L_{\text{ki}}^{\text{H}}(x_{\text{k}} - x_{\text{i}})^{\text{v}} + x_{\text{i}} \cdot x_{\text{j}} \cdot x_{\text{k}} \cdot f \quad (6)$$

The factor f represents the ternary interaction coefficient and can be expressed as

$$f = (2 \cdot \zeta_{\text{ij}} - 1) \cdot [(2L_{\text{ij}}^{\text{H}} \cdot (2 \cdot \zeta_{\text{ij}} - 1) \cdot x_{\text{k}} + 2 \cdot (x_{\text{i}} - x_{\text{j}})) + 1L_{\text{ij}}^{\text{H}}] + (2 \cdot \zeta_{\text{jk}} - 1) \cdot [(2L_{\text{jk}}^{\text{H}} \cdot (2 \cdot \zeta_{\text{jk}} - 1) \cdot x_{\text{i}} + 2 \cdot (x_{\text{j}} - x_{\text{k}})) + 1L_{\text{jk}}^{\text{H}}] + (2 \cdot \zeta_{\text{ki}} - 1) \cdot [(2L_{\text{ki}}^{\text{H}} \cdot (2 \cdot \zeta_{\text{ki}} - 1) \cdot x_{\text{j}} + 2 \cdot (x_{\text{k}} - x_{\text{i}})) + 1L_{\text{ki}}^{\text{H}}] \quad (7)$$

The factors ζ_{ij} , ζ_{jk} , and ζ_{ki} are similarity coefficients of i, j, and k and are a relation of the “deviation sums of squares” η_{I} , η_{II} , and η_{III} :

$$\zeta_{\text{ij}} = \frac{\eta_{\text{I}}}{\eta_{\text{I}} + \eta_{\text{II}}}; \quad \zeta_{\text{jk}} = \frac{\eta_{\text{II}}}{\eta_{\text{II}} + \eta_{\text{III}}} \quad \text{and} \quad \zeta_{\text{ki}} = \frac{\eta_{\text{III}}}{\eta_{\text{III}} + \eta_{\text{I}}} \quad (8)$$

η_{I} , η_{II} , and η_{III} are integral values of the square of the difference between the binary integral molar enthalpies of mixing as follows:

$$\eta_{\text{I}} = \int_0^1 (\Delta_{\text{mix}}H_{\text{ij}} - \Delta_{\text{mix}}H_{\text{ik}})^2 dX_{\text{i}}; \quad \eta_{\text{II}} = \int_0^1 (\Delta_{\text{mix}}H_{\text{ji}} - \Delta_{\text{mix}}H_{\text{jk}})^2 dX_{\text{j}}; \quad \eta_{\text{III}} = \int_0^1 (\Delta_{\text{mix}}H_{\text{ki}} - \Delta_{\text{mix}}H_{\text{kj}})^2 dX_{\text{k}} \quad (9)$$

In our case i, j, and k are copper, lithium, and tin, respectively. Capital X is the binary concentration of copper, lithium or tin, lower-case x is the concentration in the ternary system. The similarity coefficients and the deviation sums of squares for Cu–Li, Sn–Cu, and Li–Sn are listed in table 8.

From the resulting ζ -values we can conclude that the integral molar mixing enthalpies of Cu–Li and Cu–Sn are more similar to each other than to Li–Sn, respectively. According to the shape of the curves this is obvious because Cu–Li shows relatively low endothermic, Cu–Sn low exothermic values, whereas Li–Sn has a pronounced exothermic behaviour. As we can see in figure 6, Chou's model, however, is not able to describe our experimental data better than the Muggianu model without ternary interaction parameters. For all sections, the two models result in very similar values. Considering that Chou's model would provide the best extrapolation from the asymmetric binaries, we can conclude that

additional ternary interactions exist in this system. Figure 7 shows a comparison between fitted experimental data and those ones calculated with the Chou-model in an isoenthalpy plot. For Cu–Sn an associate “Cu₂Sn” was postulated in Flandorfer *et al.* [11], and we have indications for the occurrence of an associate “Li₄Sn” in Li–Sn. Regarding the isoenthalpy plot in figure 7 one can see an exothermic integral molar enthalpy of mixing valley which connects those two associates. Compared to the extrapolation data the valley according to the experimental results is shifted towards more exothermic values and slightly lower tin content. The assumption of an additional ternary interaction between the two associates is supported by the formation of two ternary intermetallic compounds along this valley, Cu₂LiSn and CuLi₂Sn [28–31].

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References

- [1] M. Kawakami, Sci. Rep. Tohoku Imp. Univ. 19 (1930) 521.
- [2] L.B. Ticknor, M.B. Bever, Trans. Am. Inst. Min. Metall. Eng. 194 (1952) 941–945.
- [3] J.B. Cohen, J.S.L. Leach, M.B. Bever, Trans. Am. Inst. Min. Metall. Eng. 200 (1954) 1257–1258.
- [4] O.J. Kleppa, J. Phys. Chem. 60 (1956) 842–846.
- [5] O.J. Kleppa, J. Phys. Chem. 60 (1956) 852–858.
- [6] R.R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley, Selected values of the thermodynamic properties of the elements, American Society for Metals, Metals Park, Ohio, 1973.
- [7] K. Itagaki, A. Yazawa, Trans. Jpn. Inst. Met. 16 (1975) 679–686.
- [8] A. Yazawa, K. Itagaki, T. Azakami, Trans. Jpn. Inst. Met. 16 (1975) 687–695.
- [9] M.J. Pool, B. Predel, E. Schultheiss, Thermochim. Acta 28 (1979) 349–358.
- [10] J.J. Lee, B.J. Kim, W.S. Min, J. Alloys Compd. 202 (1993) 237–242.
- [11] H. Flandorfer, C. Luef, U. Saeed, J. Non-Cryst. Solids 354 (2008) 2953–2972.
- [12] A. Yassin, R. Castanet, J. Alloys Compd. 307 (2000) 191–198.
- [13] N. Saunders, A.P. Miodownik, Bull. Alloy Phase Diagrams 11 (1990) 278–287.
- [14] J.H. Shim, C.S. Oh, B.J. Lee, D.N. Lee, Z. Metallkd. 87 (1996) 205–212.
- [15] D. Li, P. Franke, S. Fürtauer, D. Cupid, H. Flandorfer, Intermetallics 34 (2013) 148–158.
- [16] S. Pastorello, W. Klemm, B. Volavsek, Gazz. Chim. Ital. 60 (1930) 988–992.
- [17] W. Klemm, B. Volavšek, Z. Anorg. Allg. Chem. 296 (1958) 184–187.
- [18] A.D. Pelton, Bull. Alloy Phase Diagrams 7 (1986) 142–144.
- [19] M.V. Mikhailovskaya, V.S. Sudavtseva, Ukr. Khim. Zh. 55 (1989) 1106–1108.
- [20] W. Gasior, B. Onderka, Z. Moser, A. Debski, T. Gancarz, CALPHAD – Comput. Coupl. Phase Diagrams Thermochem. 33 (2009) 215–220.

- [21] C.J. Wen, R.A. Huggins, *J. Electrochem. Soc.* 128 (1981) 1181–1187.
- [22] Z. Moser, W. Gasior, F. Sommer, G. Schwitzgebel, B. Predel, *Metall. Trans. B* 17 (1986) 791–796.
- [23] W. Gasior, Z. Moser, *Arch. Metall.* 44 (1999) 83–92.
- [24] A. Yassin, R. Castanet, *J. Alloys Compd.* 314 (2001) 160–166.
- [25] J. Sangster, C.W. Bale, *J. Phase Equilib.* 19 (1998) 70–75.
- [26] F. Yin, X. Su, Z. Li, J. Wang, *J. Alloys Compd.* 393 (2005) 105–108.
- [27] Z.M. Du, Z.Q. Jiang, C.P. Guo, *Z. Metallkd.* 97 (2006) 10–16.
- [28] H.U. Schuster, *Die Naturwiss.* 53 (1966) 360–361.
- [29] H. Pauly, A. Weiss, H. Witte, *Z. Metallkd.* 59 (1968) 47–58.
- [30] H.U. Schuster, D. Thiedemann, H. Schönemann, *Z. Anorg. Allg. Chem.* 370 (1969) 160–170.
- [31] P.I. Kripyakevich, G.I. Oleksiv, *Dopov. Akad. Nauk Ukr. RSR A* (1970) 63–65.
- [32] K.D. Kepler, J.T. Vaughey, M.M. Thackeray, *Electrochem. Solid State Lett.* 2 (1999) 307–309.
- [33] G.X. Wang, L. Sun, D.H. Bradhurst, S.X. Dou, H.K. Liu, *J. Alloys Compd.* 299 (2000) L12–L15.
- [34] S. Sharma, L. Fransson, E. Sjostedt, L. Nordstrom, B. Johansson, K. Edstrom, *J. Electrochem. Soc.* 150 (2003) A330–A334.
- [35] W. Choi, J.Y. Lee, H.S. Lim, *Electrochem. Commun.* 6 (2004) 816–820.
- [36] H.C. Shin, M.L. Liu, *Adv. Funct. Mater.* 15 (2005) 582–586.
- [37] A.H. Reshak, D.A.O. Ortiz, *J. Phys. Chem. B* 113 (2009) 13208–13215.
- [38] S. Zhang, Y. Xing, T. Jiang, Z. Du, F. Li, L. He, W. Liu, *J. Power Sources* 196 (2011) 6915–6919.
- [39] A. Jansen, J. Clevenger, A. Baebler, J. Vaughey, *J. Alloys Compd.* (2011) 4457–4461.
- [40] Y.S. Lin, J.G. Duh, H.S. Sheu, *J. Alloys Compd.* 509 (2011) 123–127.
- [41] H. Flandorfer, F. Gehringer, E. Hayer, *Thermochim. Acta* 382 (2002) 77–87.
- [42] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak (Eds.), *Li–Mo (Lithium–Molybdenum)*, The Materials Information Society, Ohio, 1990.
- [43] L. Brewer, R.H. Lamoreaux (Eds.), *Mo–Sn (Molybdenum–Tin)*, The Materials Information Society, Ohio, 1990.
- [44] A.T. Dinsdale, *CALPHAD – Comput. Coupl. Phase Diagrams Thermochem.* (1991) 317–425.
- [45] O. Redlich, A.T. Kister, *Ind. Eng. Chem.* 40 (1948) 345–348.
- [46] C. Lupu, J.G. Mao, *Inorg. Chem.* 42 (2003) 3765–3771.
- [47] S. Fürtauer, D. Li, D. Cupid, H. Flandorfer, *Intermetallics* 34 (2013) 142–147.
- [48] K.C. Chou, *CALPHAD – Comput. Coupl. Phase Diagrams Thermochem.* 19 (1995) 315–325.
- [49] K.C. Chou, W.C. Li, F.S. Li, M.H. He, *CALPHAD – Comput. Coupl. Phase Diagrams Thermochem.* 20 (1996) 395–406.

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