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Calorimetric measurement of liquid aluminium–lithium–zinc alloys

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Abstract

The enthalpy of mixing of liquid Al–Li–Zn ternary alloys was measured in the 729–955 K range using a high temperature mixing calorimeter. An association model is used to calculate the thermodynamic mixing functions of the ternary alloys on the basis of the enthalpy of mixing of the base binary systems. The calculated enthalpy of mixing shows in the region around the ternary ρ-phase lower negative values than the measured ones. The existence of ternary phases and the possibility to obtain metastable quasicrystals by rapid solidification show that these deviations are caused by additional ternary interactions. These ternary interactions are correlated with a value of 1.8 of the mean number of conduction electrons per atom. © 1997 Elsevier Science B.V.

Keywords: Association model; Enthalpy of mixing

1. Introduction

The phase equilibria of the ternary Al–Li–Zn system are partially established in the concentration triangle Al–LiAl–Zn [1] but thermodynamic data of the liquid alloys are not available. The Al–Li–X alloys are of great importance in the light metal industry because they have low specific weight and are currently being developed for the aerospace industry. Thermodynamic studies are necessary to provide a database which permits the calculation of multicomponent phase equilibria for the development and utilization of these light alloys. Recently, metastable quasicrystals are found to be formed in certain concentration ranges of Al–Li–Zn alloys by rapid solidification from the liquid state [2] or as grain boundary precipitation by a solid-state transformation [3]. The formation of the quasicrystalline phase seems to be closely related to the structure of the equilibrium phases, since it is observed that most of the quasicrystalline phases are formed in composition ranges where equilibrium crystalline phases occur [4]. The quasicrystalline phase is generally regarded as a new solid-phase intermediate between crystals and glasses [5]. In many alloy systems with compound forming tendency, a chemical short-range order (CSRO) is present in the liquid state. This CSRO is closely connected with the possibility to quench alloy melts into the vitreous state [6,7]. Thermodynamic properties of the liquid phase should therefore be helpful in understanding the energetics of alloy formation and tendencies of the Al–Li–Zn alloys to form quasicrystals. Among the thermodynamic properties, the dependence on concentration and temperature of the enthalpy of mixing ΔH yield direct evidence for CSRO in the liquid state, because ΔH values are

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directly influenced by structural peculiarities caused by changes of the interatomic interactions on alloy formation. In addition, they are directly accessible by measurements. In this paper, the results of calorimetric measurements of the enthalpy of mixing of liquid Al–Li–Zn alloys are presented and discussed in comparison with calculated values determined by using an association model [8,9].

2. Experimental

The measurements are performed with a high-temperature mixing calorimeter using the isoperibolic procedure. The experimental arrangement and the procedure for the determination of ΔH of liquid ternary alloys have been described previously [10]. Here only some important details are specified. Aluminium (purity 99.9%), lithium (purity 99.9%) and zinc (purity 99.999%) are used to prepare the alloy samples for these measurements. The samples for charging have a rod-shaped geometry with a diameter of 3.0 mm. Experimental studies of lithium alloys are extremely difficult due to their high reactivity with oxygen, nitrogen and moisture. The lithium samples are prepared and stored in an argon glove-box. At the beginning of each series of measurements, the liquid bath substance was kept at a constant temperature. The bath substance for the measurements of ternary liquid alloys is a binary alloy belonging to one of the three bordering systems. The binary bath substances are prepared by melting them under an argon atmosphere. During a series of measurements solid samples of the respective third pure component are successively added through a charging tube into the alumina reaction crucible containing the liquid binary bath substance at a temperature lower than the room temperature. In the case of measurements with lithium containing binary bath material, the bath substance is made by adding lithium to the pure second component in the calorimeter before adding the third one. The temperature change due to the addition of a component sample or calibration sample is detected by a Ni–NiCr thermopile situated below the reaction crucible. The thermopile consists of 63 thermocouples. The resulting heat effect is $\Delta Q(x_C)$. The calorimeter is calibrated by dropping 6 to 9 inert molybdenum samples in between addition of the component samples during measurements. The calibration is based on the known enthalpy data of molybdenum at each measurement temperature referred to 298 K [11]. The standard deviation of the calibration of each single series is in the order of ±3%. A stirrer with a molybdenum blade guarantees a good mixing of the components. The experiments are performed under pure argon gas at atmospheric pressure.

3. Results

The values $\Delta Q(x_C)$ of liquid Al–Li–Zn alloys were determined for four sections with constant concentration ratios of two components ($Al_{0.25}Zn_{0.75}$–Li, $Al_{0.50}Zn_{0.50}$–Li, $Al_{0.70}Zn_{0.30}$–Li and $Al_{0.75}Li_{0.25}$–Zn) at different temperatures and are given in Tables 1–4. Alloys with high lithium content react with the alumina reaction crucible and measurements in concentration ranges with high lithium content were not performed. The high vapour pressure of zinc allows only low measurement temperature and restricts the concentration ranges for measurements. The enthalpy of the added pure components in the liquid or undercooled liquid state at each measurement temperature, which has to be substracted from $\Delta Q(x_c)$ to obtain $\delta\Delta H(x_c)$, is calculated using the data given by Dinsdale [11]. The ΔH values of the ternary liquid alloys can be obtained by adding the ΔH value of the binary bordering systems:

$$\begin{aligned}\Delta H(x_A/x_B &= \text{const.}, x_C)\\ &= (1-x_C)\Delta H(x_A/x_B = \text{const.})\\ &\quad + \sum_i \delta\Delta H_i(x_C)_{(x_A/x_B=\text{const.})}\end{aligned} \quad (1)$$

The resulting concentration dependences of ΔH of each concentration section are shown in Figs. 1–4. The experimental data of a single series are self-consistent and show only small scatter. The data and the intersection points coincide within the experimental accuracy of ±5% (see Figs. 3 and 4).

4. Discussion

It has been shown from many results of thermodynamic and structure-sensitive physical properties of

Table 1
Enthalpy of mixing of liquid $(Al_{0.25}Zn_{0.75})_{1-x}$–$Li_x$ alloys at different temperatures

Measured				Calculated		
starting amounts		added amounts	heat effect	mole fraction	enthalpy of mixing	
n_{Al}/(mol)	n_{Zn}/(mol)	Δn_{Li}/(mol)	ΔQ/(J)	Li/(at.%)	$\sum \delta \Delta H_i$/(kJ mol^{-1})	ΔH/(kJ mol^{-1})
$T = 729$ K						
0.0684	0.2052	—	—	—	—	2.0
		0.0061	−274.7	2.2	−1.32	0.6
		0.0078	−129.1	4.9	−2.15	−0.25
		0.0132	−478.7	9.0	−4.32	−2.5
		0.0140	−438.3	13.1	−6.20	−4.5
		0.0147	−148.6	17.0	−7.06	−5.4
$T = 750$ K						
0.1268	0.3805	—	—	—	—	2.0
		0.0072	−281.0	1.4	−0.77	1.2
		0.0147	−513.5	4.1	−2.16	−0.25
		0.0156	−555.7	6.9	−3.58	−1.7
		0.0162	−460.5	9.6	−4.76	−2.95
		0.0168	−534.1	12.2	−6.01	−4.25
		0.0166	−470.0	14.7	−7.08	−5.4
		0.0158	−679.3	16.9	−8.42	−6.8
		0.0186	−822.7	19.3	−9.95	−8.3
$T = 791$ K						
0.0699	0.2097	—	—	—	—	2.0
		0.0053	−200.4	1.9	−1.02	0.9
		0.0056	−180.1	3.8	−1.96	−0.03
		0.0064	−223.7	5.8	−3.04	−1.15
		0.0086	−270.9	8.5	−4.32	−2.5
		0.0093	−301.4	11.2	−5.66	−3.9
		0.0099	−478.9	13.9	−7.48	−5.8

alloy systems with a compound-forming tendency that CSRO occurs in the liquid state [9]. ΔH for liquid Al–Li and Li–Zn alloys exhibit negative values. For Li–Zn alloys a strong asymmetric dependence on concentration exists, which is an additional evidence of the presence of CSRO. The thermodynamic properties (ΔH, activity) of these two liquid alloys can be described by an association model for Zn–Li [12] and an ideal association model for Al–Li [13] assuming associates with Li_1Zn_2 and Al_1Li_1 stoichiometry respectively. These stoichiometries correspond to the composition of congruently melting intermetallic phases. The associates are in steady dynamic equilibrium with the non-associated atoms, which is governed by the law of mass action. Lifetime and spatial arrangement of the atoms of the associate do not enter in this model. ΔH for Al–Zn alloys show a demixing tendency with small positive values and follows a simple regular solution behaviour [14]. The model parameters determined from the available experimental data of the liquid binary alloys are given in Table 5. If no additional ternary association reaction occurs, the enthalpy and entropy of mixing ΔS of Al–Li–Zn alloys are given by the following expressions:

$$\begin{aligned}\Delta H = {} & C_{Li_1,Zn_1}\frac{n_{Li_1}n_{Zn_1}}{n} + C_{Li_1,Li_1Zn_2}\frac{n_{Li_1}n_{Li_1Zn_2}}{n} \\ & + C_{Zn_1,Li_1Zn_2}\frac{n_{Zn_1}n_{Li_1Zn_2}}{n} + C_{Al_1,Zn_1}\frac{n_{Al_1}n_{Zn_1}}{n} \\ & + n_{Li_1Zn_2}\Delta H^0_{Li_1Zn_2} + n_{Al_1Li_1}\Delta H^0_{Al_1Li_1} \qquad (2)\end{aligned}$$

$$\begin{aligned}\Delta S = {} & -R(n_{Al_1}\ln x_{Al_1} + n_{Li_1}\ln x_{Li_1} + n_{Zn_1}\ln x_{Zn_1} \\ & + n_{Al_1Li_1}\ln x_{Al_1Li_1} + n_{Li_1Zn_2}\ln x_{Li_1Zn_2}) \\ & + n_{Al_1Li_1}\Delta S^0_{Al_1Li_1} + n_{Zn_1Li_2}\Delta S^0_{Zn_1Li_2} \qquad (3)\end{aligned}$$

Table 2
Enthalpy of mixing of liquid $(\mathrm{Al}_{0.50}\mathrm{Zn}_{0.50})_{1-x}$–$\mathrm{Li}_x$ alloys at different temperatures

Measured					Calculated		
starting amounts			added amounts	heat effect	mole fraction		enthalpy of mixing
n_{Al}/(mol)	n_{Zn}/(mol)	n_{Li}/(mol)	Δn_{Li}/(mol)	ΔQ/(J)	Li/(at.%)	$\sum \delta \Delta H_i$/(kJ mol^{-1})	ΔH/(kJ mol^{-1})
$T = 827$ K							
0.1270	0.1270	—	—	—	—	—	2.6
			0.0038	−137.6	1.5	−0.80	1.7
			0.0083	−241.0	4.6	−2.25	0.2
			0.0084	−228.8	7.5	−3.57	−1.2
			0.0093	−232.6	10.5	−4.87	−2.6
			0.0086	−185.5	13.1	−5.90	−3.7
			0.0085	−181.5	15.6	−6.86	−4.7
			0.0082	−175.8	17.8	−7.72	−5.6
			0.0131	−286.6	21.2	−9.03	−7.0
			0.0145	−215.9	24.6	−10.07	−8.1
0.1087	0.1087	—	—	—	—	—	2.6
		0.0030		−96.3	1.4	−0.6	1.85
			0.0027	−79.3	2.5	−1.25	1.35
			0.0034	−95.9	4.0	−1.93	0.5
			0.0033	−35.2	5.4	−2.31	0.1
			0.0036	−105.7	6.8	−3.01	−0.6
			0.0039	−86.7	8.3	−3.62	−1.3
			0.0096	−217.3	11.9	−5.07	−2.8
			0.0105	−129.8	15.5	−6.11	−3.9
$T = 951$ K							
0.1420	0.1420	0.0710	—	—	—	−8.50	−6.4
			0.0083	−92.5	21.8	−9.25	−7.2
			0.0198	−181.7	25.9	−10.81	−8.9
			0.0210	−180.9	29.7	−12.27	−10.5
			0.0179	−94.0	32.7	−13.26	−11.5
			0.0189	−67.3	35.6	−14.14	−12.5
			0.0207	−53.2	38.5	−14.98	−13.4
			0.0223	35.6	41.3	−15.61	−14.1
			0.0220	106.4	43.8	−16.04	−14.6

where $n_i (i = \mathrm{Al}_1, \mathrm{Li}_1, \mathrm{Zn}_1)$ are the number of moles of free atoms in equilibrium with $n_{\mathrm{Al}_1\mathrm{Li}_1}$, $n_{\mathrm{Li}_1\mathrm{Zn}_2}$ moles of associates. x_{Al_1}, x_{Li_1}, x_{Zn_1}, $x_{\mathrm{Al}_1\mathrm{Li}_1}$ and $x_{\mathrm{Li}_1\mathrm{Zn}_2}$ are the mole fractions of the respective species in 1 mol of a ternary alloy. ΔH_i^0 and ΔS_i^0 $(i = \mathrm{Al}_1\mathrm{Li}_1, \mathrm{Li}_1\mathrm{Zn}_2)$ refer to the enthalpy and entropy of formation of the two associates. $C_{i,j}$ represents an interaction parameter between the assumed species i and j. The equilibrium values of $n_{\mathrm{Al}_1\mathrm{Li}_1}$ and $n_{\mathrm{Li}_1\mathrm{Zn}_2}$ are determined by two laws of mass action:

$$\exp\left(\frac{-(\Delta H^0_{\mathrm{Al}_1\mathrm{Li}_1} - T\Delta S^0_{\mathrm{Al}_1\mathrm{Li}_1})}{RT}\right) = \frac{x_{\mathrm{Al}_1\mathrm{Li}_1}\gamma_{\mathrm{Al}_1\mathrm{Li}_1}}{(x_{\mathrm{Al}_1}\gamma_{\mathrm{Al}_1})(x_{\mathrm{Li}_1}\gamma_{\mathrm{Li}_1})} \tag{4}$$

$$\exp\left(\frac{-(\Delta H^0_{\mathrm{Li}_1\mathrm{Zn}_2} - T\Delta S^0_{\mathrm{Li}_1\mathrm{Zn}_2})}{RT}\right) = \frac{x_{\mathrm{Li}_1\mathrm{Zn}_2}\gamma_{\mathrm{Li}_1\mathrm{Zn}_2}}{(x_{\mathrm{Li}_1}\gamma_{\mathrm{Li}_1})(x_{\mathrm{Zn}_1}\gamma_{\mathrm{Zn}_1})^2} \tag{5}$$

Here γ_i is the activity coefficient of the respective species. The nonlinear Eqs. (2)–(5) are solved simultaneously by an iterative process. The calculated values for the enthalpy, entropy and Gibbs energy of mixing are given in Figs. 1–4. For the section $\mathrm{Al}_{0.25}\mathrm{Zn}_{0.75}$–Li the agreement between the measured and calculated values lies within the experimental error (see Fig. 1). For other concentration sections the experimental ΔH values exhibit more negative values compared with the calculated ones (see

Table 3
Enthalpy of mixing of liquid $(Al_{0.70}Zn_{0.30})_{1-x}$–$Li_x$ alloys at 883 K

Measured				Calculated		
starting amounts		added amounts	heat effect	mole fraction		enthalpy of mixing
n_{Al}/(mol)	n_{Zn}/(mol)	Δn_{Li}/(mol)	ΔQ/(J)	Li/(at.%)	$\sum \delta \Delta H_i$/(kJ mol^{-1})	ΔH/(kJ mol^{-1})
0.3289	0.1409	—	—	—	—	2.2
		0.0069	−318.8	1.4	−0.96	1.2
		0.0130	−356.3	4.1	−2.18	−0.1
		0.0146	−289.1	6.8	−3.27	−1.2
		0.0174	−299.5	9.9	−4.39	−2.4
		0.0190	−299.8	13.1	−5.49	−3.6
		0.0192	−278.8	16.1	−6.48	−4.7
		0.0240	−371.9	19.5	−7.67	−5.9
		0.0178	−275.9	21.9	−8.49	−6.8
0.1780	0.0763	—	—	—	—	2.2
		0.0042	−77.0	1.6	−0.61	1.5
		0.0078	−155.4	4.5	−1.76	0.3
		0.0091	−157.9	7.7	−2.94	−0.9
		0.0094	−151.7	10.7	−4.02	−2.1
		0.0094	−137.0	13.6	−5.00	−3.1
		0.0101	−137.8	16.4	−5.94	−4.1
		0.0106	−152.9	19.2	−6.89	−5.1
		0.0110	−146.5	22.0	−7.78	−6.1
		0.0122	−126.1	24.8	−8.59	−7.0
		0.0128	−166.0	27.5	−9.47	−7.9
		0.0110	−163.4	29.7	−10.24	−8.7

Table 4
Enthalpy of mixing of liquid $(Al_{0.75}Li_{0.25})_{1-x}$–$Zn_x$ alloys at 995 K

Measured				Calculated		
starting amounts		added amounts	heat effect	mole fraction		enthalpy of mixing
n_{Al}/(mol)	n_{Li}/(mol)	Δn_{Zn}/(mol)	ΔQ/(J)	Zn/(at.%)	$\sum \delta \Delta H_i$/(kJ mol^{-1})	ΔH/(kJ mol^{-1})
0.3376	0.1126	—	—	—	—	−6.15
		0.0096	250.5	2.1	−0.01	−6.0
		0.0182	474.3	5.8	−0.015	−5.8
		0.0177	464.3	9.2	−0.02	−5.6
		0.0192	508.1	12.6	−0.01	−5.4
		0.0276	726.9	17.0	−0.01	−5.1
		0.0289	763.1	21.2	−0.01	−4.9
		0.0382	988.1	26.2	−0.04	−4.6
		0.0384	974.4	30.5	−0.10	−4.4
0.1984	0.0661	-	-	-	-	−6.15
		0.0091	220.6	3.3	−0.07	−6.0
		0.0091	226.84	6.4	−0.11	−5.9
		0.0100	260.1	9.6	−0.12	−5.7
		0.0103	261.8	12.7	−0.15	−5.5
		0.0108	288.5	15.7	−0.14	−5.3
		0.0103	268.2	18.4	−0.14	−5.2
		0.0108	286.5	21.0	−0.13	−5.0
		0.0114	315.8	23.6	−0.08	−4.8
		0.0114	314.5	26.0	−0.03	−4.6

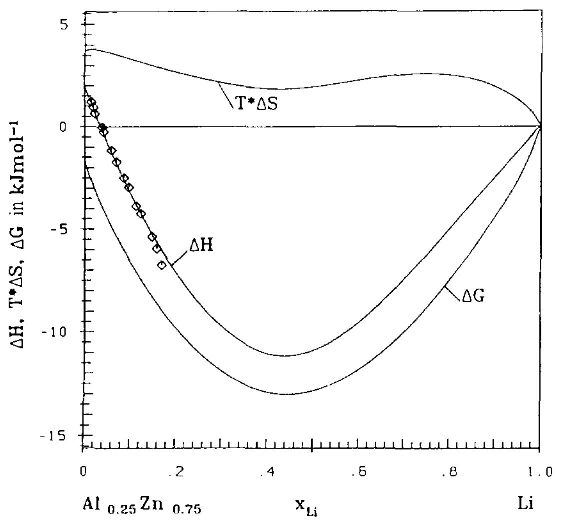

Fig. 1. Enthalpy, entropy and Gibbs energy of mixing of $(Al_{0.25}Zn_{0.75})_{1-x}Li_x$ ternary liquid and undercooled liquid alloys at 791 K calculated using the association model. (◇ – experimental results for the enthalpy of mixing at different temperatures).

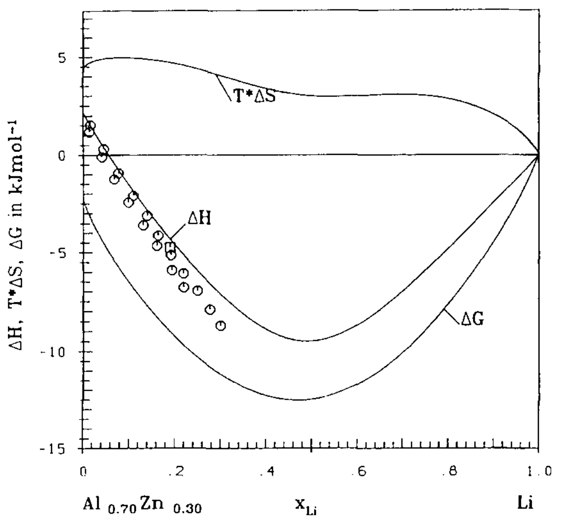

Fig. 3. Enthalpy, entropy and Gibbs energy of mixing of $(Al_{0.70}Zn_{0.30})_{1-x}Li_x$ ternary liquid and undercooled liquid alloys at 883 K calculated using the association model. (○ – experimental results for the enthalpy of mixing at 883 K; ☐ – from a different section).

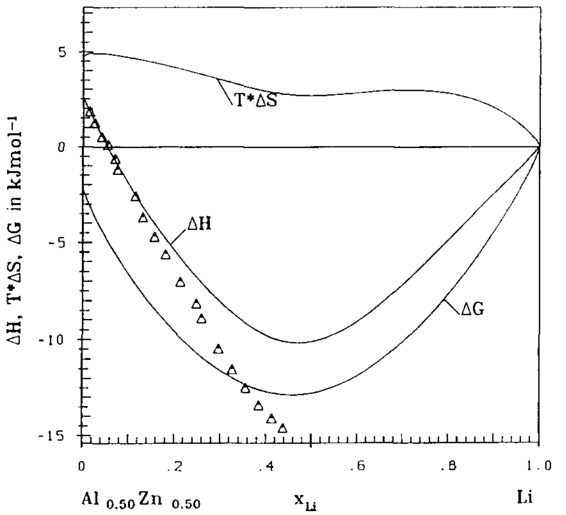

Fig. 2. Enthalpy, entropy and Gibbs energy of mixing of $(Al_{0.50}Zn_{0.50})_{1-x}Li_x$ ternary liquid and undercooled liquid alloys at 827 K calculated using the association model. (△ – experimental results for the enthalpy of mixing at different temperatures).

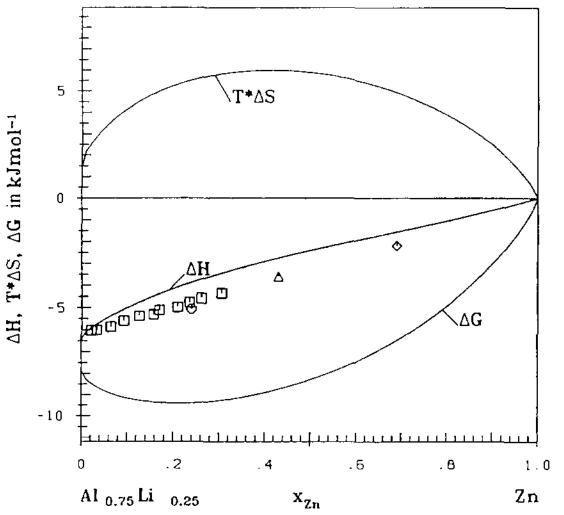

Fig. 4. Enthalpy, entropy and Gibbs energy of mixing of $(Al_{0.75}Li_{0.25})_{1-x}Zn_x$ ternary liquid and undercooled liquid alloys at 955 K calculated using the association model. (☐ – experimental results for the enthalpy of mixing at 955 K; (○, △, ◇ – from different sections).

Figs. 2–4). These deviations could be caused by a negative contribution to the enthalpy of mixing due to the presence of additional ternary interactions or additional ternary associates in the melt which have not been taken into account in the model calculation. The presence of additional ternary interaction in the liquid state is supported by the existence of three ternary intermetallic phases in this

Table 5
Association model parameters of the binary systems

System	Associate	$\Delta H_{A_iB_j}$/ (kJ mol^{-1})	$\Delta S_{A_iB_j}$/ (kJ mol^{-1} K^{-1})	C_{A_1,B_1} / (kJ mol^{-1})	C_{A_1,A_iB_j}/ (kJ mol^{-1})	C_{B_1,A_iB_j}/ (kJ mol^{-1})	Reference
Al–Li	Al_1Li_1	−30.60	−0.0166	—	—	—	[13]
Li–Zn	Li_1Zn_2	−47.30	−0.0395	−18.50	−26.90	−18.30	[12]
Al–Zn	—	—	—	10.28	—	—	[14]

system, which are designated as $\tau(Li_3ZnAl_5)$, $\rho(Li_{26}Al_6(Zn_{1-x}Al_x)_{49})$, and $\gamma(LiZn_3Al)$ [1]. The quasicrystalline phases are formed by rapid solidification or as grain boundary precipitates by a solid-state reaction in the ρ-phase region. The ρ-phase has a high solubility of zinc (16.7–43.3 at.% Zn at 32 at.% Li) and is formed through a peritectic reaction at higher temperature than the τ and γ phases. The difference between measured and calculated values of ΔH is shown in Fig. 5 together with the position of the ternary intermetallic phases. Fig. 5 shows that the deviation amounts to -3.5 kJ mol^{-1} in the concentration region where the ρ-phase exists, which points to additional ternary interactions in this concentration region. In the region of the ternary τ- and γ-phase the deviation is small in comparison to that in the ρ-phase region. This indicates that the ternary interactions in these regions are relatively weak and the influence of the ternary ρ-phase is predominant for liquid Al–Li–Zn alloys.

The high values of additional ternary interactions are found for ternary alloys with 1.8 conducting electrons per atom (the mean number $\bar{z}$) Fig. 5. It is well known that the existence of Hume–Rothery phases can be correlated to $\bar{z}$. At special $\bar{z}$ values certain crystalline intermetallic phases exist. The stability of Hume-Rothery phases can be explained as a band-structure effect. Similar concepts can be used for the amorphous state and for the liquid phase. Comprehensive reviews of this topic are given by Häussler [15,16]. For $\bar{z} = 1.8$ the positions of the ions match in a disordered system the minima of the effective pair potentials. The density of states of alloys with $\bar{z} = 1.8$ exhibits a pseudogap at the Fermi energy. This special influence of conduction electrons on ionic structure results in a negative contribution of the band-structure energy to the total energy. This effect is already present in the binary liquid Li–Zn alloy where the most negative $\Delta H(x)$-values are given near $x_{Zn} = 0.2$ with $\bar{z} = 1.8$. The $\Delta H(x)$-values of the liquid ternary Al–Li–Zn alloys point to an increasing influence of the electron-structure effect along $\bar{z} = 1.8$.

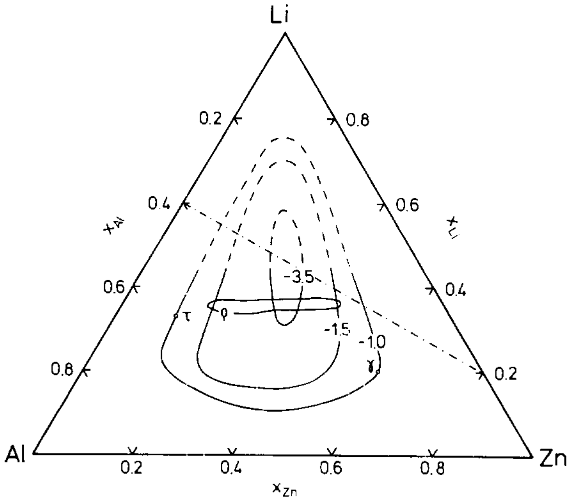

Fig. 5. Difference (in kJ mol^{-1}) between the experimental and the calculated enthalpy of mixing og Al-Li-Zn ternary liquid and undercooled liquid alloys at 955 K using the association model (———, from measurements; - - - - -, extrapolated). The positions o ternary phases τ, ρ and γ and of $\bar{z}$ (- · · · · · -) are indicated

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