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Thermodynamic study of liquid lithium–lead alloys using the EMF method

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Abstract

Liquid Li–Pb alloys were investigated by the electromotive force (emf) method at Li concentrations of $0.025 \leqslant X_{\mathrm{Li}} \leqslant 0.965$ mole fraction and at temperatures from 775 to 975 K. The experiments were conducted at constant temperature, and the Li concentration was changed by the coulometric-titration technique. The two-phase Li–Bi alloys and liquid lithium were used as the reference electrodes. The dependence of emfs on temperature for each investigated alloy was linear, and from the linear equations ($E = a + bT$), partial Li excess Gibbs energies, partial enthalpies and entropies of lithium were calculated, and compared with previously published data. The excess stability function ES and the concentration–concentration partial structure factor $S_{\mathrm{cc}}(0)$ were calculated and discussed in relation to the neutron diffraction data and other properties. A change in the type of chemical bonding near the composition Li_4Pb is indicated. This study was initiated since Pb–17Li eutectic alloy has been proposed as a breeder blanket fluid for fusion reactors. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thermodynamic studies on Li alloys were initiated at the Institute of Metallurgy and Materials Science of the Polish Academy of Sciences in 1972, after Smith and Moser [1] had published an evaluation of binary Li alloys. The electromotive force (emf) and calorimetric measurements were undertaken in co-operation with foreign laboratories and the following binary alloys Li–Sn [2,3], A1–Li [4], Li–Zn [5,6], In–Li [7], Li–T1 [8], Bi–Li [9], Li–Mg [10] and ternary alloys Al–Li–Mg [11,12] and Al–Li–Cu [13] have been investigated and the data used in phase diagram calculations. In 1996, density and chemical diffusion studies on constituent binaries [14–17] and on ternary Al–Li–Mg alloys were started based on the galvanostatic technique.

The main aim of this work is to report the complete partial thermodynamic functions of the liquid Li–Pb alloys by the emf method of concentration cells, to compare them with previously published data, to use our experimental data for calculation of the Bhatia–Thornton $S_{\mathrm{cc}}(0)$ structure factor [18] and to compare it with data obtained directly from neutron diffraction studies.

Experimental thermodynamic measurements of liquid Li–Bi, Li–Pb and Li–Sn systems were reported by Gąsior [19,20]. Lithium activities of the Li–Pb alloys of this study were obtained in the entire range of concentrations, including the eutectic composition which is being considered for a blanket material for controlled nuclear fusion [21]. The main interest is the behaviour of Pb–17Li alloy with various stainless steels, Li_2O and Al_2O_3, and the interaction of oxygen and its possible influence on compatibility between these materials [22]. In parallel, the structural and physical properties were studied, and there were shown anomalies at a similar concentration (about 20 at.% Pb), indicating the strong tendency for heterocoordination of nearest neighbours with strong chemical short range order (CSRO) and with a maximum near the composition Li_4Pb, where the transfer of electrons from Li to Pb is expected to form non-metallic ions species.

The phase diagram reported in the binary alloys phase diagrams [23] was updated by Okamota [24] using

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data of Hubberstey et al. [25] who reinvestigated the eutectic reaction on the Pb-rich side (84.3 ± 0.2 at.% Pb) and found good agreement with the previously reported value of 83 at.% Pb at the eutectic temperature of 508 K.

Emf measurements have been made on liquid alloys in the Li–Pb system by Demidov et al. [26] in the temperature range 783–843 K and in the composition range $0.03 \leqslant X_{\mathrm{Li}} \leqslant 0593$, by Yatsenko et al. [27] in the composition range $0.038 \leqslant X_{\mathrm{Li}} \leqslant 0.908$, the thermodynamic functions being reported at 1073 K, by Saboungi et al. [28] in the ranges $0.002 \leqslant X_{\mathrm{Li}} \leqslant 0.0693$ and $0.831 \leqslant X_{\mathrm{Li}} \leqslant 0.949$ between 770 and 932 K, and by Becker et al. [29] between 780 and 900 K with molar fractions of Li smaller than 0.74. The vapour pressure of Li over liquid and solid alloys of Li–Pb has been measured by Neubert [30] in the mole fraction range $0.05 \leqslant X_{\mathrm{Li}} \leqslant 0.95$ at temperatures between 700 and 900 K using Knudsen-effusion mass spectrometry. Veleckis [31] measured the lithium activity in the two-phase fields $\beta + \mathrm{Li_7Pb_2}$, $\mathrm{Li_7Pb_2} + \mathrm{Li_3Pb}$ and $\mathrm{Li_3Pb_3} + \mathrm{Li_8Pb_3}$ of the Li–Pb system by the hydrogen titration method.

The integral enthalpy of mixing of the Li–Pb liquid alloys at 1000 K was measured by Predel and Oehme [32] in the entire concentration range and the heat capacity measurements of liquid Li–Pb alloys were conducted by Sommer [33] and by Saar et al. [34].

2. Experimental

Liquid Li–Pb alloys were investigated by means of three types of concentration cells:

$$\mathrm{Li}_{(1)} \mid \mathrm{LiCl\text{–}LiF_{eut}} \mid (\mathrm{Li,\ Pb})_{(1)},$$

$$775\ \mathrm{K} \leqslant T \leqslant 915\ \mathrm{K}, \quad 0.876 \leqslant X_{\mathrm{Li}} \leqslant 0.965, \qquad \mathrm{(I)}$$

$$RT \ln a_{\mathrm{Li}} = -nFE,$$

$$\mathrm{Li_3Bi}_{(s)} + (\mathrm{Li_3Bi, Bi})_{(1)} \mid \mathrm{LiCl\text{–}LiF_{eut}} \mid (\mathrm{Li,\ Pb})_{(1)},$$

$$775\ \mathrm{K} \leqslant T \leqslant 975\ \mathrm{K}, \quad 0.025 \leqslant X_{\mathrm{Li}} \leqslant 0.750, \qquad \mathrm{(II)}$$

$$RT \ln a_{\mathrm{Li}} = -nF(E + E_{\mathrm{ref}}),$$

$$\mathrm{Li}_{(1)} \mid \mathrm{LiCl\text{–}LiF_{eut}} \mid \mathrm{Li_3Bi}_{(s)} + (\mathrm{Li_3Bi, Bi})_{(1)},$$

$$773\ \mathrm{K} \leqslant \mathrm{T} \leqslant 990\ \mathrm{K}, \quad X_{\mathrm{Li}} = 0.6, \qquad \mathrm{(III)}$$

$$RT \ln a_{\mathrm{Li}} = -nFE_{\mathrm{ref}},$$

where R denotes the gas constant, T the temperature in K, a_{Li} the activity of Li, E the measured emf value, n valency for Li = 1 and F the Faraday's constant. In cell II, E_{ref} expressed as a function of temperature is obtained from cell III by the following equation:

$$E_{\mathrm{ref}} = -1683.2 - 0.903T + 465.66 \ln(T), \qquad (1)$$

which is in good agreement with the values obtained by Saboungi et al. [28] and by Foster et al. [35]. The use of the two-phase (Bi–Li) reference electrode remarkably diminishes the dissolution of Li in the electrolyte and limits the change of concentration of the Li–Pb alloys used in emf measurements.

The lithium used in the experiments was of 99.5% purity and Pb of 99.995%. Lead was pre-melted in a hydrogen atmosphere to remove traces of the absorbed oxygen. Cells were set up in a glove-box with circulating argon of high purity. The amount of oxygen and water were lower than 1 ppm. Nitrogen, which was not monitored, was absorbed using Ti-sponge. The coulometric-titration method was used to change the composition of

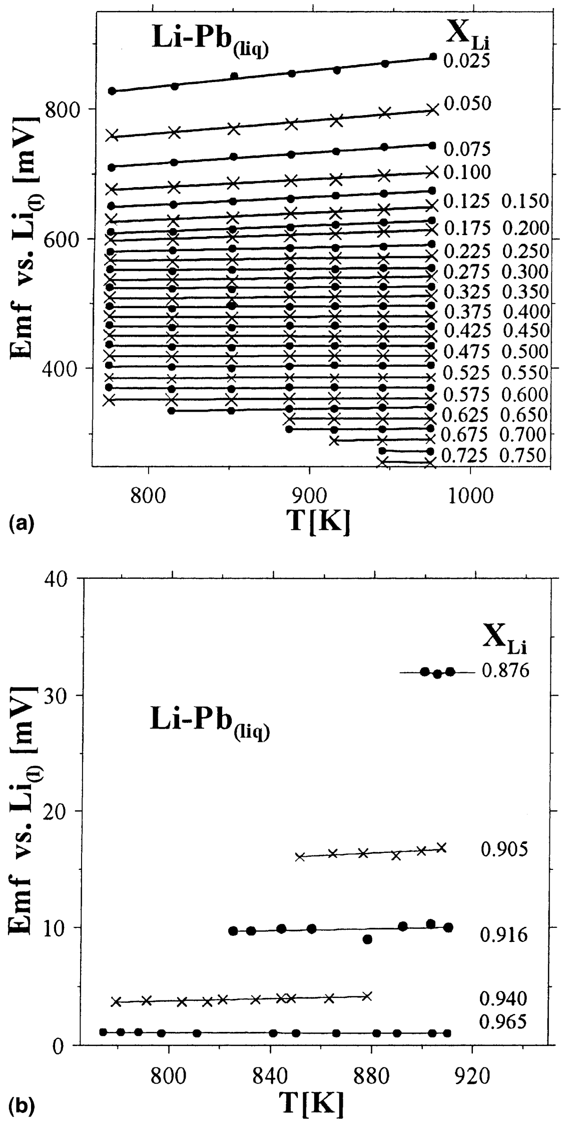

Fig. 1. The temperature dependencies of the electromotive forces versus $\mathrm{Li}_{(1)}$ of the Li–Pb liquid alloys; (a) for X_{Li} from 0.025 to 0.75 and (b) for very concentrated in lithium alloys (X_{Li} = 0.862– 0.962).

the alloys and the details of the construction of the cell are reported in [29].

3. Results

The emf versus $T(K)$ is linear (Figs. 1(a) and 1(b)) for all investigated Li–Pb alloys in cells I and III and therefore the equations ($E = a + bT$) are presented in Table 1 from which are calculated the partial excess Gibbs energy of lithium ($\bar{G}^E_{\mathrm{Li}} = -\mathrm{nFE} - RT\ln(X_{\mathrm{Li}})$), partial enthalpy ($\bar{H}_{\mathrm{Li}} = -nFa$) and partial excess entropy ($\bar{S}^E_{\mathrm{Li}} = -nFb - R\ln(X_{\mathrm{Li}})$).

The errors in the a and b parameters and of the calculated thermodynamic functions (Table 1) were estimated using the variation analysis presented in [36]. The pronounced errors of $\bar{H}_{\mathrm{Li}}$ and$\bar{S}^E_{\mathrm{Li}}$ for the X_{Li} from 0.7 to 0.876 are connected with the low temperature range measurement and the limited data points (2 to 4). At lithium mole fractions of 0.725 and 0.750, linear equations are composed only from two points. Generally, the estimated errors of $\bar{G}^E_{\mathrm{Li}}$ and $\bar{H}_{\mathrm{Li}}$ are lower than 7%, but, in the case of excess Li, entropy the errors are higher.

To determine the partial thermodynamic functions of Pb and the integral function of the LI–Pb system, Pelton–Flengas [37] polynomials were used, being one of the possible solutions of the Gibbs–Duhem equation. To apply this method, with the linear equations of emfs versus temperature (Table 1), the excess Gibbs energies of lithium were calculated at 773–973 K and were used for presenting the polynomials describing the dependence of $\bar{G}^E_{\mathrm{Li}}$ on temperature and concentration. It has been confirmed that, similar to the work of Saboungi et al. [28], the polynomial description of experimental excess Gibbs energies of Li requires two separate concentration ranges for lower and higher Li contents,

Table 1
Temperature dependence of emfs vs. $\mathrm{Li}_{(1)}$, partial excess Gibbs energies at 800 K, partial enthalpies and partial excess entropies of lithium with the estimated errors

X_{Li}	$E = a + bT$ (mV)	$\bar{G}^E_{\mathrm{Li}}$ (kJ mol^{-1})	$\bar{H}_{\mathrm{Li}}$ (kJ mol^{-1})	$\bar{S}^E_{\mathrm{Li}}$ (J K^{-1} mol^{-1})
0.025	= 628 + 0.257T	−56.1 ± 0.8	−60.7 ± 3.6	−5.9 ± 4.1
0.050	= 595 + 0.208T	−53.7 ± 0.9	−57.4 ± 3.8	−4.8 ± 4.3
0.075	= 579 + 0.171T	−52.0 ± 0.5	−55.9 ± 2.1	−5.0 ± 2.4
0.100	= 573 + 0.132T	−50.4 ± 0.4	−55.4 ± 1.9	−6.4 ± 2.1
0.125	= 554 + 0.123T	−49.3 ± 0.4	−53.5 ± 1.5	−5.4 ± 1.7
0.150	= 536 + 0.116T	−48.2 ± 0.8	−51.8 ± 3.5	−4.5 ± 4.0
0.175	= 533 + 0.097T	−47.5 ± 0.5	−51.5 ± 2.0	−5.1 ± 2.2
0.200	= 531 + 0.084T	−47.3 ± 0.4	−51.3 ± 1.8	−5.2 ± 2.0
0.225	= 539 + 0.053T	−46.4 ± 0.3	−52.1 ± 1.4	−7.3 ± 1.5
0.250	= 541 + 0.032T	−45.7 ± 0.5	−52.3 ± 2.1	−8.5 ± 2.4
0.275	= 537 + 0.018T	−44.9 ± 0.4	−51.9 ± 1.8	−9.0 ± 2.1
0.300	= 516 + 0.026T	−44.0 ± 0.5	−49.8 ± 2.1	−7.5 ± 2.4
0.325	= 513 + 0.014T	−43.3 ± 0.4	−49.5 ± 1.9	−8.0 ± 2.1
0.350	= 493 + 0.019T	−42.3 ± 0.5	−47.6 ± 2.1	−6.9 ± 2.4
0.375	= 485 + 0.012T	−41.4 ± 0.4	−46.9 ± 1.9	−7.0 ± 2.2
0.400	= 475 + 0.005T	−40.4 ± 0.5	−45.9 ± 2.0	−7.1 ± 2.3
0.425	= 464 + 0.001T	−39.4 ± 0.5	−44.8 ± 2.1	−7.0 ± 2.4
0.450	= 450 − 0.001T	−38.3 ± 0.4	−43.5 ± 1.9	−6.7 ± 2.1
0.475	= 434 + 0.000T	−37.2 ± 0.5	−41.2 ± 2.2	−6.2 ± 2.5
0.500	= 412 + 0.008T	−35.9 ± 0.5	−39.8 ± 1.9	−5.0 ± 2.2
0.525	= 396 + 0.009T	−34.7 ± 0.6	−38.2 ± 2.5	−4.5 ± 2.8
0.550	= 382 + 0.004T	−33.3 ± 0.3	−36.9 ± 1.0	−4.6 ± 1.1
0.575	= 366 + 0.004T	−32.1 ± 0.4	−35.4 ± 1.8	−4.2 ± 2.0
0.600	= 342 + 0.013T	−30.7 ± 0.2	−33.0 ± 0.7	−3.0 ± 0.8
0.625	= 309 + 0.012T	−29.2 ± 0.4	−29.8 ± 1.7	−0.9 ± 1.9
0.650	= 297 + 0.027T	−28.0 ± 0.8	−28.7 ± 4.0	−1.0 ± 4.4
0.675	= 294 + 0.014T	−26.9 ± 0.8	−28.4 ± 4.5	−1.9 ± 4.8
0.700	= 259 + 0.033T	−25.2 ± 4.2	−25.0 ± 22	0.3 ± 24
0.725	= 242 + 0.033T	−23.7	−23.3	0.5
0.750	= 225 + 0.033T	−22.3	−21.7	0.8
0.876	= 32 + 0.000T	−2.2 ± 3.7	−3.1 ± 27	−1.1 ± 28
0.905	= 7 + 0.011T	−0.8 ± 0.3	−0.7 ± 1.0	0.2 ± 1.1
0.916	= 6 + 0.004T	−0.3 ± 0.1	−0.6 ± 0.9	−0.4 ± 1.1
0.940	= 0.5 + 0.005T	0.1 ± 0.1	0.1 ± 0.1	0.0 ± 0.1
0.965	= 20.001T	0.1 ± 0.1	−0.2 ± 0.1	−0.4 ± 0.0

with the standard deviations equal to 0.3 and 0.6 kJ mol^{-1}. Attemps to use only one polynomial with a standard deviation lower than 1 kJ mol^{-1} (almost all errors of $\bar{G}^E_{\mathrm{Li}}$ are lower than 1 kJ/mol) caused the activity of Li in Li–Pb alloys to become higher than 1 for higher concentrations ($X_{\mathrm{Li}} > 0.9$). Thus, the polynomials describing partial and integral excess Gibbs energies at two concentration ranges are of the following forms:

$0.025 \leqslant X_{\mathrm{Li}} \leqslant 0.8$,

$$\begin{aligned}\bar{G}^E_{\mathrm{Li}} = {} & (-1388 + 0.0422T)X^2_{\mathrm{Pb}} + (7164 - 0.416T)X^3_{\mathrm{Pb}} \\ & + (-17357 + 0.0030T)X^4_{\mathrm{Pb}} + 22011X^5_{\mathrm{Pb}} \\ & - 14014X^6_{\mathrm{Pb}} + 3524X^7_{\mathrm{Pb}} \quad [\mathrm{kJ/mol}], \end{aligned} \tag{2}$$

$$\begin{aligned}\bar{G}^E_{\mathrm{Pb}} = {} & (-305 + 0.0224T) + (2776 - 0.0844T)X_{\mathrm{Pb}} \\ & + (-12134 + 0.1046T)X^2_{\mathrm{Pb}} + (30307 - 0.0456T)X^3_{\mathrm{Pb}} \\ & + (-44871 + 0.0030T)X^4_{\mathrm{Pb}} + 38828X^5_{\mathrm{Pb}} - 18125X^6_{\mathrm{Pb}} \\ & + 3524X^7_{\mathrm{Pb}} \quad [\mathrm{kJ/mol}], \end{aligned} \tag{3}$$

$$\begin{aligned}G^E = {} & (-305 + 0.0224T)X_{\mathrm{Pb}} + (1338 - 0.0422T)X^2_{\mathrm{Pb}} \\ & + (-3582 + 0.0208T)X^3_{\mathrm{Pb}} + (5786 - 0.0010T)X^4_{\mathrm{Pb}} \\ & - 5503X^5_{\mathrm{Pb}} + 2803X^6_{\mathrm{Pb}} - 587X^7_{\mathrm{Pb}} \quad [\mathrm{kJ/mol}]. \end{aligned} \tag{4}$$

$0.8 \leqslant X_{\mathrm{Li}} \leqslant 1$,

$$\begin{aligned}\bar{G}^E_{\mathrm{Li}} = {} & (242 + 0.0422T)X^2_{\mathrm{Pb}} + (-4913 - 0.0416T)X^3_{\mathrm{Pb}} \\ & + (6146 + 0.0030T)X^4_{\mathrm{Pb}} \quad [\mathrm{kJ/mol}], \end{aligned} \tag{5}$$

$$\begin{aligned}\bar{G}^E_{\mathrm{Pb}} = {} & (-165 + 0.0224T) + (-484 - 0.0844T)X_{\mathrm{Pb}} \\ & + (7611 + 0.1046T)X^2_{\mathrm{Pb}} + (-13108 - 0.0456T)X^3_{\mathrm{Pb}} \\ & + (6146 + 0.0030T)X^4_{\mathrm{Pb}} \quad [\mathrm{kJ/mol}], \end{aligned} \tag{6}$$

$$\begin{aligned}G^E = {} & (-165 + 0.0224T)X_{\mathrm{Pb}} + (-242 - 0.0422T)X^2_{\mathrm{Pb}} \\ & + (2456 + 0.0208T)X^3_{\mathrm{Pb}} \\ & + (-2049 - 0.0010T)X^4_{\mathrm{Pb}} \quad [\mathrm{kJ/mol}]. \end{aligned} \tag{7}$$

Describing experimental data of the excess Gibbs energies of Li by means of Eqs. (2) and (5), special attention was given to obtain enthalpies of mixing close to those obtained by Predel and Oehme [32] from calorimetric measurements.

The results of $\bar{G}^E_{\mathrm{Li}}$ and G^E at 800 K are graphically presented in Fig. 2 and compared with date from literature. Experimental data of $\bar{G}^E_{\mathrm{Li}}$ and those calculated from Eqs. (2) and (5) are very close to the results of Demidov et al. [26] and Neubert [30] at Li concentrations higher than 0.15 molar fractions and slightly lower than the data of Saboungi et al. [28] and Yatsenko and Saltykova [27]. Results of Becker et al. [29] are the highest within all the published information. For dilute solutions the data from this study are lower than other results and at $X_{\mathrm{Li}} = 0$ the different approaches 10 kJ/mol. There is general agreement in values of the integral excess Gibbs energies, except for the results of Neubert [30] from vapour pressure studies, and the calculated minimum is about −25 kJ/mol and is situated in the region where in the phase diagram of the Li–Pb system intermetallic phases with the highest melting points are present. This is in agreement with the anomalies of electrical and magnetic properties as noted previously.

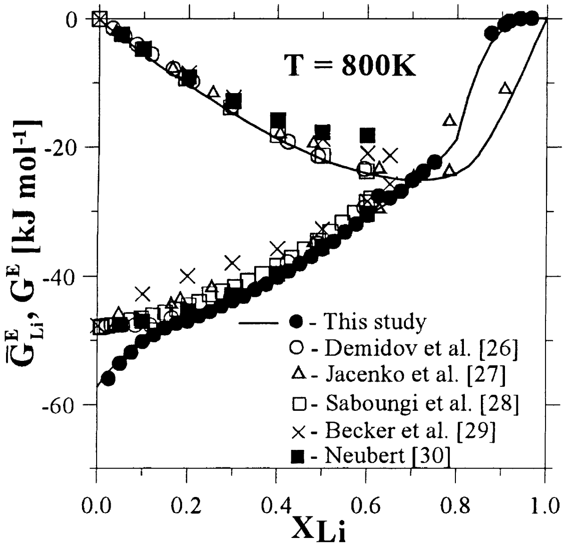

Fig. 2. The partial excess Gibbs energy of Li and integral excess Gibbs energy of the Li–Pb liquid alloys at 800 K from this study and from the literature data.

The partial enthaply of Li and the integral enthalpy of mixing of the liquid Li–Pb alloys are plotted in Fig. 3 and particularly the data of partial enthalpies from various sources are scattered. The limiting values of $\bar{H}_{\mathrm{Li}}$ from this study, equal to about −60 kJ/mol, is in good agreement with the data of Neubert [30] (about −57 kJ/mol), but it differs by more than 10 kJ/mol in comparison with the results of Yatsenko et al. [27], Becker et al. [29] and of Demidov et al. [26]. At higher concentrations of Li better agreement is generally observed between values of partial enthalpy when comparing them with [26,27]. Data of Becker et al. [29] and Neubert [30] are more negative especially in the central range of Li concentrations.

Data of integral enthalpy of mixing of this study, represented in Fig. 3 by the solid line, are similar to other references except higher differences noted for [30] and [27]. Good agreement is observed with calorimetric results of Predel et al. [32], with the minimum in integral enthalpy of mixing which is situated close to the concentration of $\mathrm{Li_4Pb}$ suggested as the most stable compound.

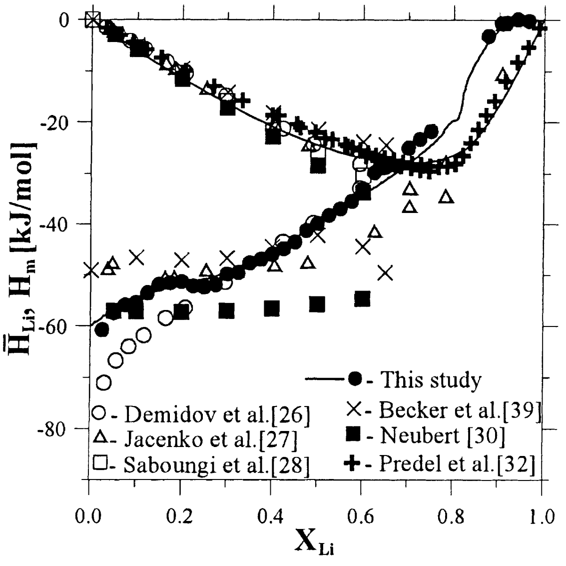

Fig. 3. The partial enthalpy of Li and the integral enthalpy of mixing for the Li–Pb liquid alloys from this study and from the literature data.

The excess entropies obtained in this study are presented in Fig. 4 and compared with the results of others. The observed values of $\bar{S}^E_{Li}$ for $X_{Li} = 0$ change from negative values close to 0 [26,27,29] to about −10 J/mol K [28,30]. Data obtained in this work (calculated from Eq. (2)) from dilute solutions to about 0.5 molar fraction of Li amount to about −5 J/K mol. The most negative values of excess entropy of Li were measured by Neubert [30] and, generally speaking, there are pronounced discrepancies between data of $\bar{S}^E_{Li}$, slightly smaller are noted for integral excess entropy.

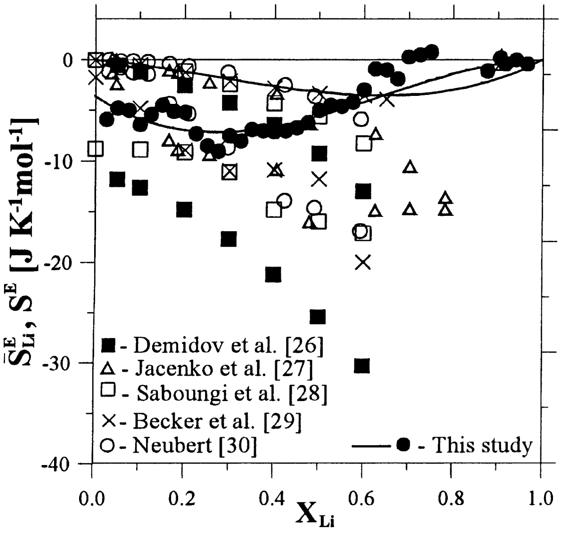

Fig. 4. The partial excess entropy of Li and integral excess entropy for the Li–Pb liquid alloys from this study compared with the data of the other authors.

4. Discussion

High-temperature experimental thermodynamic studies of Li alloys are very difficult. This is due partly to the extreme reactivity of these alloys. Setting up of emf cells in the glove-box, even at low content of oxygen and moisture, is still affected by the possibility of formation of the nitrides. In addition, the electrode samples are small and therefore very sensitive to the change of composition. This is especially important in the case of liquid Li–Pb alloys having components with very different electronegativities which, after alloying, exhibit a change from metallic behaviour to at least partly ionic. The effect is most evident near the concentration of Li_4Pb and, close to this composition in the liquid, clusters or associates are present which are connected also with the presence of compounds with the highest melting points in the phase diagram of the Li–Pb system. Due to the pronounced difference in the eletronegativity there are also high measured emf values in these liquid alloys influencing the transport of Li through the electrolyte from the reference electrode to the alloy electrode, changing the composition of the investigated alloy. The use of the two-phase electrode $Li_3Bi_{(s)} + LiBi_{(l)}$ diminishes the flow rate of Li through electrolyte but does not eliminate this factor.

Considering the many different sources of factors influencing the measurements, the scatter in the data of this study as seen in Figs. 2–4 seem to be justified, and results from the emf technique are more accurate than those from the vapour pressure method.

There is one characteristic feature in the emf versus temperature relation-namely linear dependence, which according to the deviations from ideal behaviour, the existence of associates in liquid alloys connected with intermetallic phases should be expected to be curvilinear and simultaneously the integral enthalpy of mixing should be temperature dependent. Predel et al. [32] reported enthalpies of mixing only at one temperature, leaving the problem open, which however, became more evident in view of the excess heat capacities measured by two different techniques by Sommer [33] and by Saar et al. [34]. Results of [33] for concentrations close to $Li_4Pb(Li_7Pb_2)$, exceeding 15 JK^{-1} mol^{-1} at temperatures 1004–1110 K, and [34] amounting to about 25 JK^{-1} mol^{-1} at temperatures T_L and 1100 K and close to the Li_4Pb composition clearly indicate the temperature dependence of the integral enthalpy of mixing.

The complicated character of liquid Li–Pb alloys is also evident from Darken's excess stability function Es [38], connected with the Bhatia–Thornton partial structure factor [18] through the following relations in which γ denotes the activity coefficient of Li obtained in this study

$$\mathrm{ES} = \frac{RT}{(1-X_{\mathrm{Li}})}\frac{\mathrm{d}\ln\gamma_{\mathrm{Li}}}{\mathrm{d}X_{\mathrm{Li}}} \qquad T = \mathrm{const}, \tag{8}$$

$$S_{\mathrm{cc}}(0) = \frac{RT^{*}X_{\mathrm{Li}}(1-X_{\mathrm{Li}})}{RT - ES^{*}X_{\mathrm{Li}}(1-X_{\mathrm{Li}})} \qquad T = \mathrm{const}. \tag{9}$$

The calculated ES and the parameter $S_{\mathrm{cc}}(0)$ are presented in Fig. 5(a) and 5(b) as solid lines. The dotted lines indicate the discontinuity of both functions as two polynomials were used for describing the temperature-concentration dependence of the excess Gibbs energy of lithium. According to the suggestions of the authors [38] and [18,39], the ES maximum and $S_{\mathrm{cc}}(0)$ minimum are located at or near the concentration where the associates are present. In Fig. 5(b) $S_{\mathrm{cc}}(0)$ values, calculated from the neutron diffraction measurements of Ruppersberg et al. [40], are also presented, and the agreement with calculations based on experimental data of this study is evidence of mutual consistency.

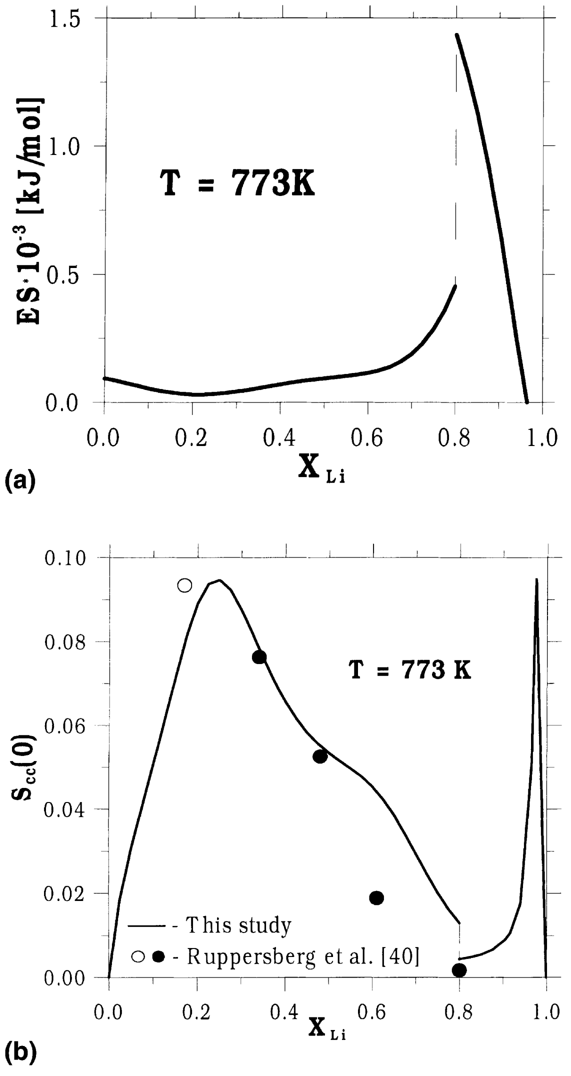

Fig. 5. The excess stability function (Fig. 5a) and the $S_{\mathrm{cc}}(0)$ partial structure factor (Fig. 5b) calculatted at 773 K from the data of this study and from the neutron diffraction measurements [40].

5. Conclusions

The experimental results of this study are in general agreement with the other published data mainly for the excess Gibbs energies of Li, exhibiting, however, greater discrepancies for partial enthalpies and partial excess entropies of lithium. It should be noted that calculations of the latter two partial functions from slopes of emf versus T (K) are always charged with errors since the separation of Gibbs energy into enthalpy and entropy terms is based only on directly measured activities. To get a better description of the thermodynamic properties of the liquid Li–Pb alloys, it seems necessary to take into account the temperature dependence of the integral enthalpy proved by the excess heat capacity data. The resulting thermodynamic description should be verified by phase diagram calculations of the Li–Pb system.

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