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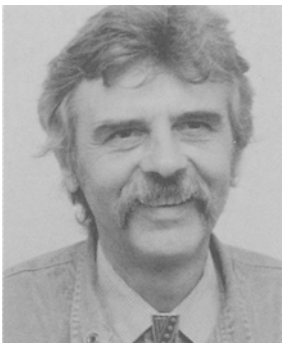

PREDICTING OF THE THERMODYNAMIC PROPERTIES FOR THE TERNARY SYSTEM Pb-Bi-Mg

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Abstract

R-function method for predicting the ternary thermodynamic properties from its binary ones was applied to the ternary system Pb–Bi–Mg. Activities, activity coefficients, partial and integral molar quantities for Pb, Bi and Mg for the quasibinary sections Pb–X (X = B, C, D, E, F) in the investigated ternary system Pb–Bi–Mg calculated by means of *R*-function method are given in this paper. Also, it was determined that results obtained by *R*-function method reach a good agreement with the experimental results obtained by Oelsen calorimetry.

Keywords: Pb–Bi–Mg system, thermodynamic parameters

Introduction

Many formulae for predicting ternary thermodynamic properties from binary ones has been reported by several investigators, such as Kohler, Muggianu [1], Colinet [2], Toop [3], Hillert [4] and Chou [5–7]. These methods are specially useful in cases of experimental difficulties, such as: elevated temperatures, corrosive atmosphere, etc.

Investigated ternary system Pb–Bi–Mg is of the practical interest for the extractive metallurgy of lead [8]. During the refinement of lead from bismuth by magnesium, many processes in the ternary system Pb–Bi–Mg are occurring. In spite of the great importance of the thermodynamic determination of this sys-

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tem, there are just a few articles dealing with thermodynamic behaviour of the ternary system Pb–Bi–Mg [9–11]. The presence of magnesium, which oxidize easily, makes experimental measuring difficult (especially in the magnesium corner of the investigated system). That was the main reason for thermodynamic prediction applying.

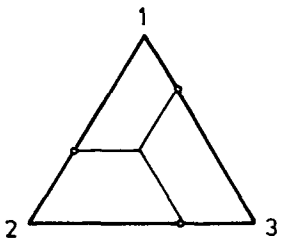

Fig. 1 The geometric representation of the *R*-function method

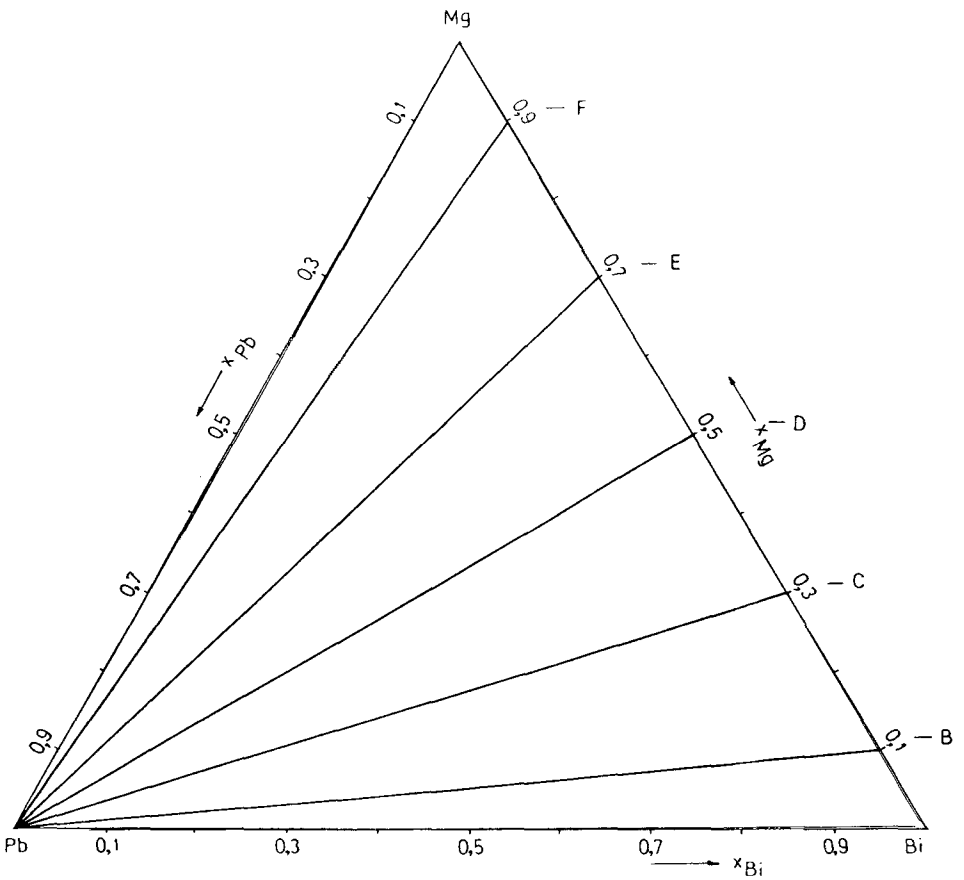

Fig. 2 Ternary system Pb–Bi–Mg

Table 1 Composition of the chosen alloys

	Molar content														
Section	B			C			D			E			F		
N°	Pb	Bi	Mg	Pb	Bi	Mg	Pb	Bi	Mg	Pb	Bi	Mg	Pb	Bi	Mg
1	0.9	0.09	0.01	0.9	0.07	0.03	0.9	0.05	0.05	0.9	0.03	0.07	0.9	0.01	0.09
2	0.8	0.18	0.02	0.8	0.14	0.06	0.8	0.10	0.10	0.8	0.06	0.14	0.8	0.02	0.18
3	0.7	0.27	0.03	0.7	0.21	0.09	0.7	0.15	0.15	0.7	0.09	0.21	0.7	0.03	0.27
4	0.6	0.36	0.04	0.6	0.28	0.12	0.6	0.20	0.20	0.6	0.12	0.28	0.6	0.04	0.36
5	0.5	0.45	0.05	0.5	0.35	0.15	0.5	0.25	0.25	0.5	0.15	0.35	0.5	0.05	0.45
6	0.4	0.54	0.06	0.4	0.42	0.18	0.4	0.30	0.30	0.4	0.18	0.42	0.4	0.06	0.54
7	0.3	0.63	0.07	0.3	0.49	0.21	0.3	0.35	0.35	0.3	0.21	0.49	0.3	0.07	0.63
8	0.2	0.72	0.08	0.2	0.56	0.24	0.2	0.40	0.40	0.2	0.24	0.56	0.2	0.08	0.72
9	0.1	0.81	0.09	0.1	0.63	0.27	0.1	0.45	0.45	0.1	0.27	0.63	0.1	0.09	0.81

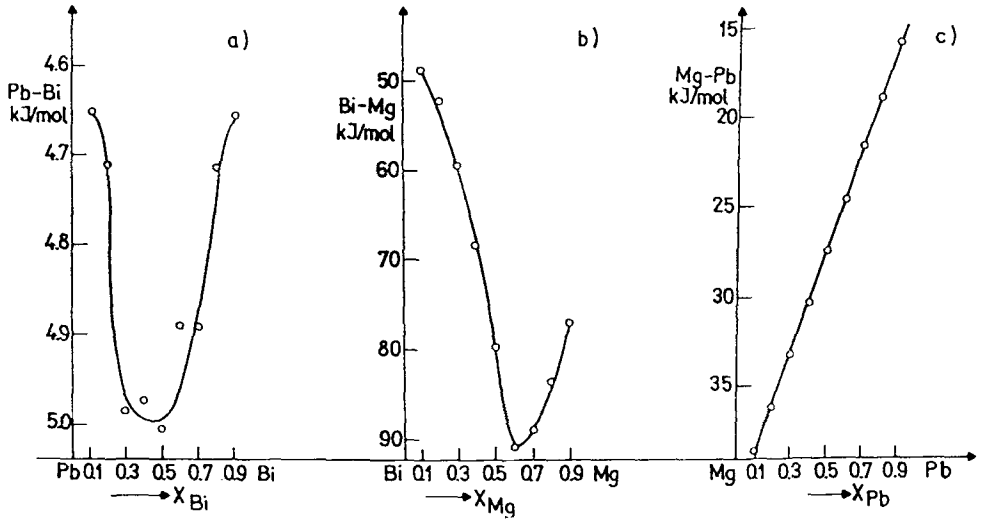

Fig. 3 The plot of α function *vs.* mole fraction at 973 K (A - system Pb–Bi, B - system Bi–Mg, C - system Mg–Pb)

Table 2 Polynominal coefficients of α function for Pb–Bi, Bi–Mg and Mg–Pb binary systems at 973K /J·mol^{-1}

System	a_o	a_1	a_2	a_3
Pb–Bi	–4330	–3278	4838	–1742
Bi–Mg	–50604	58166	–401304	340639
Mg–Pb	–41789	29147	0	0

In this paper, *R*-function method for predicting thermodynamic properties from binary ones, proposed by Chou [5–7], was used for the thermodynamic investigation of the ternary system Pb–Bi–Mg. This method was chosen for its simplicity as compared with other methods of predicting.

According to Chou [5–7], the ternary molar excess free energy, ΔG^{xs} can be expressed by the following equation

$$\Delta G^{xs} = x_2\Delta G^{xs}_{12} / (1-x_1) + x_3\Delta G^{xs}_{23} / (1-x_2) + x_1\Delta G^{xs}_{31} / (1-x_3) \qquad (1)$$

where ΔG^{xs}_{12} , ΔG^{xs}_{23} , ΔG^{xs}_{31} indicate the binary molar excess free energies for the 1–2, 2–3, 3–1 binary systems respectively. The geometric representation is shown in the Fig. 1.

Equation (1) can be rewritten in the following form in terms of α function

$$\Delta G^{xs} = x_1x_2\alpha_{12} + x_2x_3\alpha_{23} + x_3x_1\alpha_{31} \qquad (2)$$

Table 3 Results of the thermodynamic predicting by *R*-function method in the ternary system Pb–Bi–Mg

Section	Thermodynamic quantities													
	G_{Bi}^{xs} /	G_{Mg}^{xs} /	G_{Pb}^{xs} /	γBi	γMg	γPb	a_{Bi}	a_{Mg}	a_{Pb}	G_{Bi}^{M} /	G_{Mg}^{M} /	G_{Pb}^{M} /	ΔG^{xs} /	ΔG^{M} /
	J·mol^{-1}									J·mol^{-1}			J·mol^{-1}	J·mol^{-1}
B1	–4674	–17891	48	0.561	0.109	1.006	0.051	0.001	0.905	–24153	–55144	–805	–557	–3449
B2	–4696	–22314	163	0.559	0.634	1.02	0.101	0.001	0.816	–18568	–53960	–1643	–1162	–5730
B3	–4487	–25983	311	0.574	0.040	1.04	0.155	0.001	0.727	–15078	–54349	–2574	–1773	–7504
B4	–4125	–28952	473	0.601	0.028	1.06	0.216	0.001	0.636	–12389	–54991	–3660	–2360	–8856
B5	–3684	–31252	647	0.634	0.021	1.083	0.285	0.001	0.542	–10143	–55486	–4960	–2897	–9819
B6	–3231	–32869	877	0.671	0.017	1.114	0.362	0.001	0.446	–8216	–55628	–6535	–3366	–10388
B7	–2844	–33679	1311	0.704	0.016	1.176	0.443	0.001	0.353	–6581	–55189	–8429	–3756	–10538
B8	–2638	–33163	2483	0.722	0.017	1.359	0.519	0.001	0.272	–5296	–53593	–10537	–4056	–10208
B9	–2894	–28889	6844	0.699	0.028	2.33	0.566	0.003	0.233	–4589	–48368	–11783	–4260	–9256

Table 3 Continued

Section	Thermodynamic quantities														
	G^{xs}_{Bi} /	G^{xs}_{Mg} /	G^{xs}_{Pb} /	γBi	γMg	γPb	a_{Bi}	a_{Mg}	a_{Pb}	G^{M}_{Bi} /	G^{M}_{Mg} /	G^{M}_{Pb} /	ΔG^{xs} /	ΔG^{M} /
	J·mol^{-1}									J·mol^{-1}			J·mol^{-1}	J·mol^{-1}
C1	–5273	–16597	64	0.521	0.129	1.008	0.036	0.004	0.907	–26785	–44963	–788	–809	–3933
C2	–5864	–19579	220	0.484	0.089	1.028	0.058	0.005	0.822	–21769	–42339	–1586	–1820	–6857
C3	–6240	–21764	427	0.462	0.068	1.054	0.097	0.006	0.738	–18865	–41243	–2458	–2970	–9394
C4	–6536	–23277	682	0.446	0.056	1.088	0.125	0.007	0.653	–16834	–40429	–3450	–4214	–11635
C5	–6896	–24170	1036	0.426	0.050	1.137	0.149	0.008	0.568	–15389	–39517	–4572	–5521	–13599
C6	–7482	–24376	1643	0.397	0.049	1.225	0.167	0.009	0.490	–14500	–38248	–5770	–6873	–15283
C7	–8497	–23604	2866	0.349	0.054	1.425	0.171	0.011	0.428	–14268	–36229	–6873	–8261	–16661
C8	–10224	–21085	5530	0.283	0.074	1.981	0.158	0.018	0.396	–14914	–32630	–7489	–9680	–17681
C9	–13119	–14906	11585	0.198	0.158	4.187	0.124	0.043	0.419	–16856	–25498	–7042	–11131	–18208

Table 3 Continued

Section	Thermodynamic quantities													
	G^{xs}_{Bi} /	G^{xs}_{Mg} /	G^{xs}_{Pb} /	γBi	γMg	γPb	a_{Bi}	a_{Mg}	a_{Pb}	G^{M}_{Bi} /	G^{M}_{Mg} /	G^{M}_{Pb} /	ΔG^{xs} /	ΔG^{M} /
	J·mol^{-1}									J·mol^{-1}			J·mol^{-1}	J·mol^{-1}
D1	−5856	−15389	43	0.485	0.149	1.005	0.024	0.007	0.905	−30090	−39623	−809	−1023	−4214
D2	−7082	−17194	121	0.417	0.119	1.015	0.042	0.012	0.812	−25709	−35821	−1685	−2331	−7501
D3	−8329	−18322	196	0.357	0.104	1.025	0.054	0.016	0.717	−23676	−33669	−2689	−3861	−10484
D4	−9884	−18924	295	0.295	0.096	1.037	0.059	0.019	0.622	−22904	−31943	−3838	−55855	−13272
D5	−12005	−19005	515	0.227	0.095	1.066	0.057	0.024	0.533	−23219	−30240	−5092	−7500	−15911
D6	−14929	−18511	1047	0.158	0.101	1.138	0.047	0.030	0.455	−24668	−28251	−6366	−9613	−18422
D7	−1886	−17086	2206	0.097	0.121	1.313	0.034	0.042	0.394	−27378	−25579	−7534	−11929	−20795
D8	−24119	−14216	4499	0.051	0.172	1.744	0.020	0.069	0.349	−31531	−21625	−8521	−14434	−22968
D9	−30911	−9010	8735	0.022	0.328	2.944	0.009	0.148	0.294	−37370	−15470	−9892	−17091	−24767

Table 3 Continued

Section	Thermodynamic quantities													
	G^{xs}_{Bi} /	G^{xs}_{Mg} /	G^{xs}_{Pb} /	γBi	γMg	γPb	a_{Bi}	a_{Mg}	a_{Pb}	G^{M}_{Bi} /	G^{M}_{Mg} /	G^{M}_{Pb} /	ΔG^{xs} /	ΔG^{M} /
	J·mol^{-1}									J·mol^{-1}			J·mol^{-1}	J·mol^{-1}
E1	–6439	–14243	–12	0.451	0.172	0.998	0.014	0.012	0.899	–34805	–35755	–865	–1201	–4325
E2	–8452	–15000	–116	0.352	0.157	0.986	0.021	0.021	0.789	–31211	–30905	–1921	–2700	–7737
E3	–11026	–15189	–359	0.256	0.153	0.957	0.023	0.032	0.669	–30505	–27814	–3244	–4433	–10857
E4	–14637	–14942	–728	0.164	0.158	0.914	0.019	0.044	0.548	–31789	–25239	–4860	–6377	–13798
E5	–19582	–14269	–1174	0.089	0.171	0.865	0.013	0.059	0.432	–34929	–22762	–6782	–8519	–16597
E6	–25985	–13086	–1637	0.040	0.198	0.817	0.007	0.083	0.327	–39856	–20104	–9049	–10828	–19237
E7	–33797	–11241	–2072	0.015	0.249	0.774	0.003	0.122	0.232	–46422	–17011	–11811	–13227	–21627
E8	–42806	–8549	–2487	0.005	0.348	0.735	0.001	0.194	0.147	–54351	–13239	–15507	–15558	–23560
E9	–52642	–4839	–2988	0.001	0.549	0.691	0.0004	0.346	0.069	–63233	–8577	–21615	–17651	–24638

Table 3 Continued

Section	Thermodynamic quantities													
	G^{xs}_{Bi} /	G^{xs}_{Mg} /	G^{xs}_{Pb} /	γBi	γMg	γPb	a_{Bi}	a_{Mg}	a_{Pb}	G^{M}_{Bi} /	G^{M}_{Mg} /	G^{M}_{Pb} /	ΔG^{xs} /	ΔG^{M} /
	J·mol^{-1}									J·mol^{-1}			J·mol^{-1}	J·mol^{-1}
F1	–7035	–13141	–100	0.419	0.197	0.988	0.0004	0.018	0.889	–44289	–32620	–952	–1343	–4236
F2	–10057	–12881	–493	0.288	0.203	0.941	0.006	0.037	0.753	–41703	–26753	–2298	–2914	–7488
F3	–14504	–12078	–1291	0.166	0.225	0.852	0.005	0.061	0.597	–42870	–22670	–4177	–4600	–10331
F4	–20955	–10871	–2586	0.075	0.261	0.726	0.003	0.094	0.436	–46994	–19136	–6718	–6303	–12799
F5	–29459	–9344	–4475	0.026	0.315	0.575	0.001	0.142	0.288	–53693	–15804	–10082	–7915	–14837
F7	–50179	–5585	–10643	0.002	0.501	0.268	0.0001	0.316	0.080	–71691	–9323	–20383	–10224	–17007
F8	–59849	–3529	–15423	0.0006	0.646	0.149	0	0.465	0.029	–80281	–6186	–28443	–10413	–16565
F9	–66483	–1570	–21866	0.0003	0.824	0.067	0	0.667	0.007	–85962	–3275	–40492	–9442	–14438

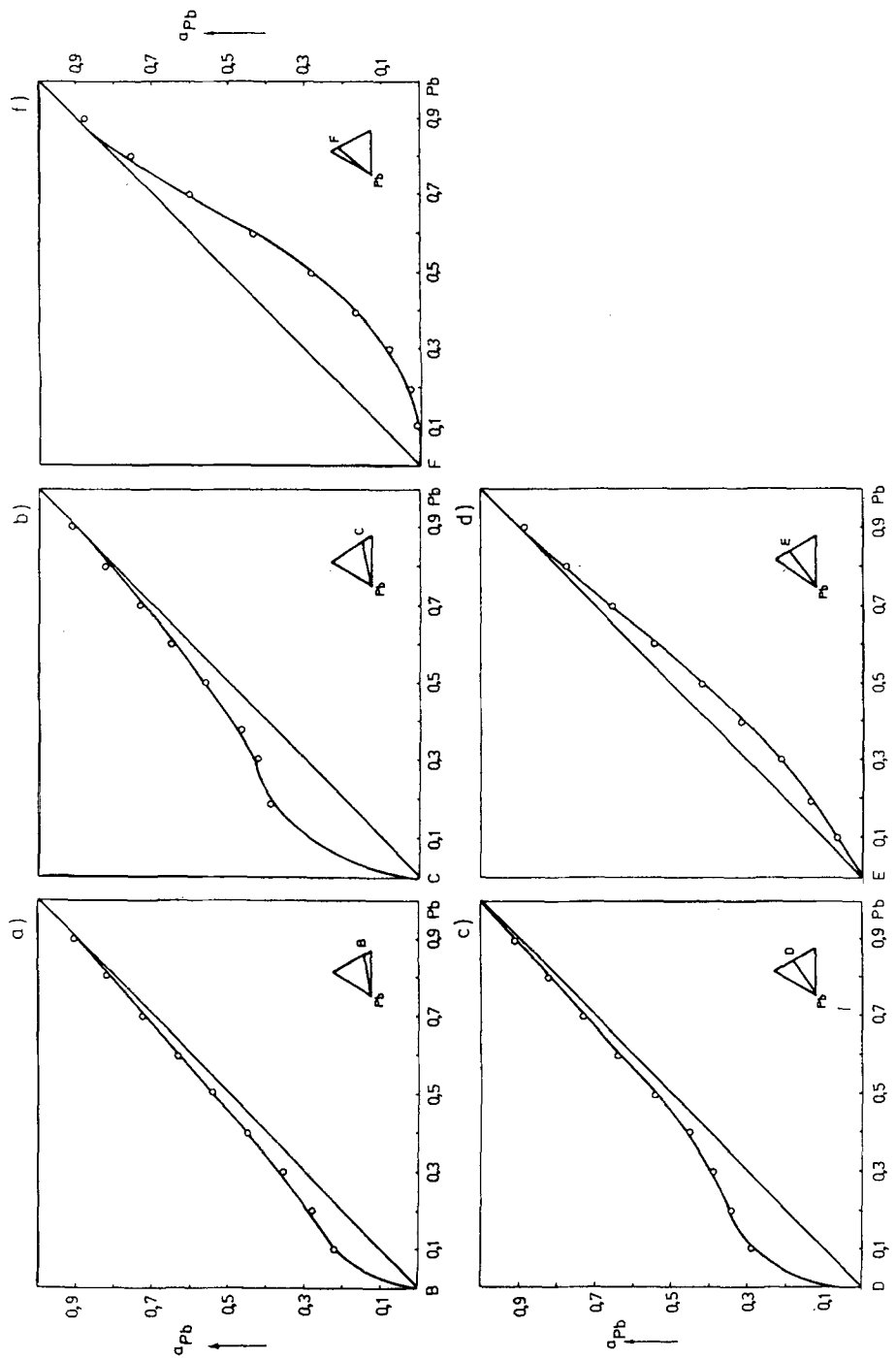

Fig. 4 Activity curves for Pb *vs.* mole fraction at 973 K (a - Pb-B, b - Pb-C, c - Pb-D, d - Pd-E, e - Pb-F)

where

$$\alpha_{12} = \Delta G_{12}^{xs} / x_1(1 - x_1)$$

$$\alpha_{23} = \Delta G_{23}^{xs} / x_2(1 - x_2)$$

$$\alpha_{31} = \Delta G_{31}^{xs} / x_3(1 - x_3) \quad (3)$$

R-function is defined as [5–7]

$$R = \Delta G^{xs} / (1 - x_1) = x_1(1 - y)\alpha_{12} + (1 - x_1)y(1 - y)\alpha_{23} + x_1 y \alpha_{31} \quad (4)$$

where

$$y = x_3 / (1 - x_1) \quad (5)$$

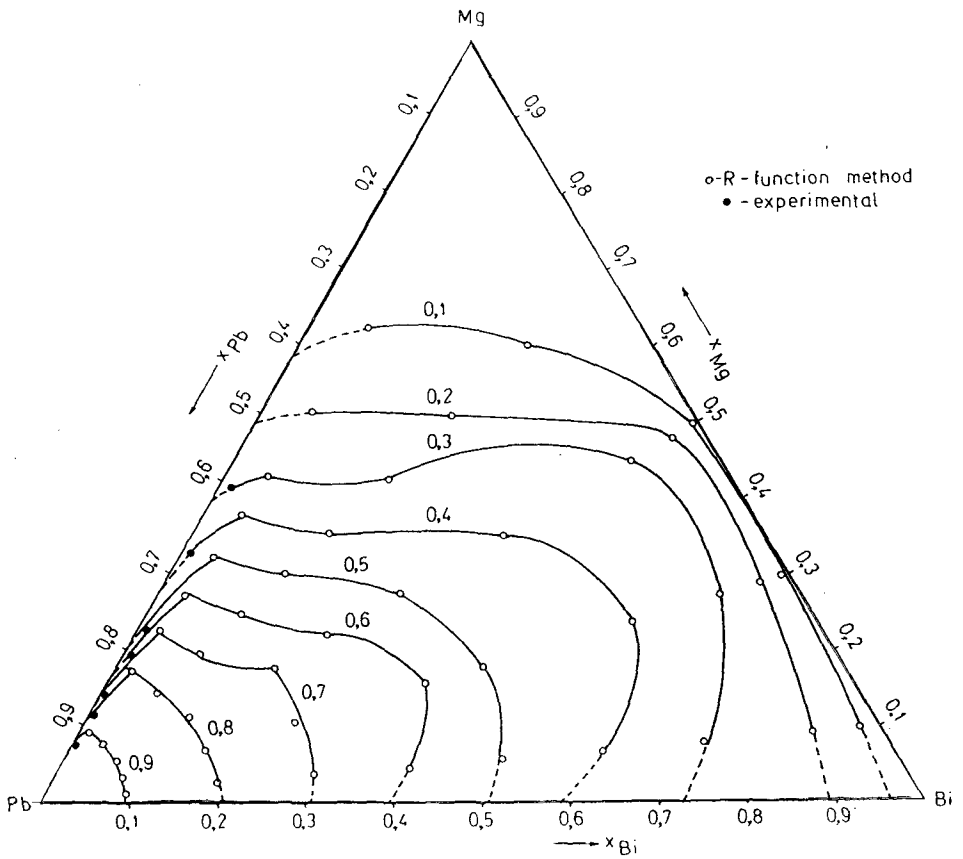

Fig. 5 Isoactivity curves for Pb in the ternary system Pb–Bi–Mg at 973 K

Substituting α function expressions fitted by third degree polynom

$$\alpha = a_o + a_1 x + a_2 x^2 + a_3 x^3 \quad (6)$$

into Eq. (4) will obtain the value of R-function. The excess partial molar free energies G_1^{xs}, G_2^{xs}, G_3^{xs} can be calculated then

$$G_1^{xs} = (1 - x_1)(\sigma R / \sigma x_1)y$$

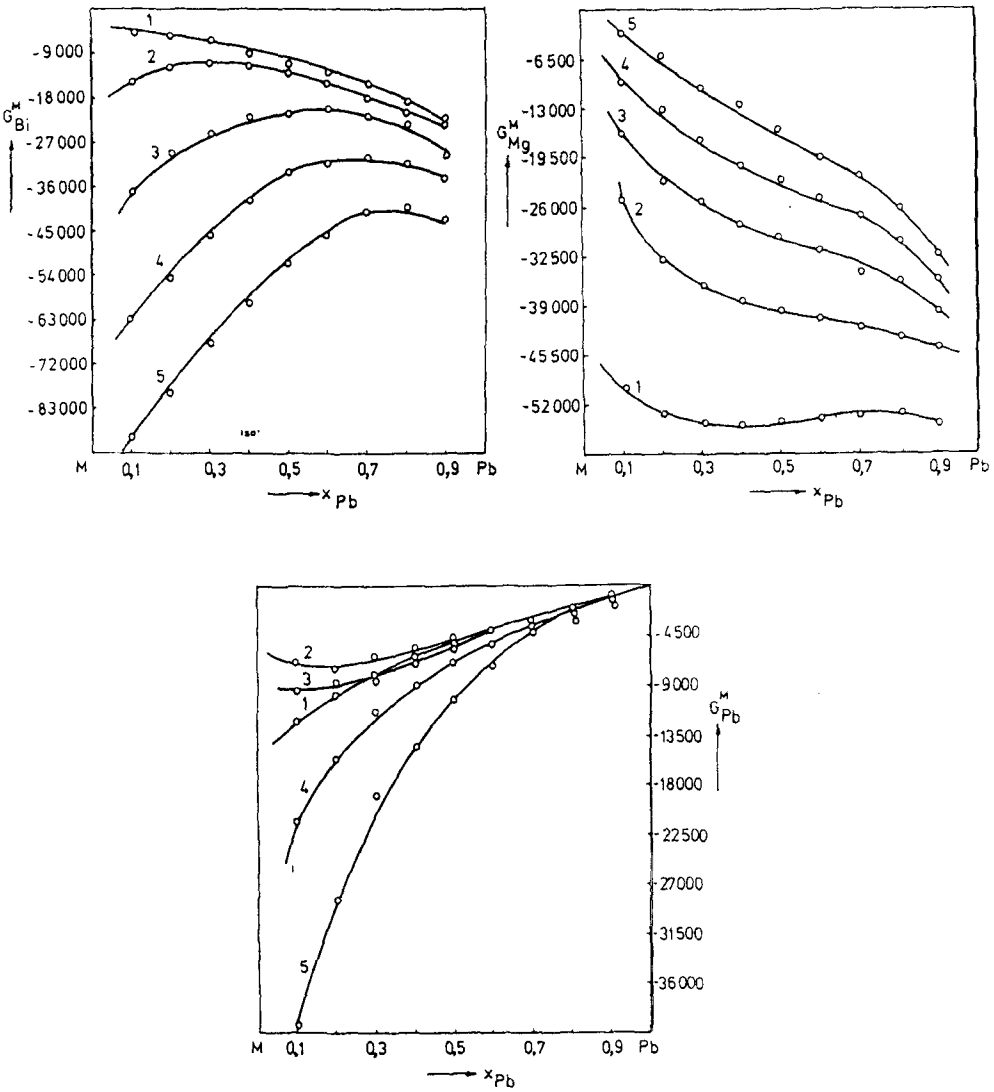

Fig. 6 G^M_{Pb}, G^M_{Bi}, G^M_{Mg} *vs.* molar content at 973 K (J/mol) (1- Pb-B; 2- Pb-C; 3- Pb-D; 4- Pb-E; 5- Pb-F)

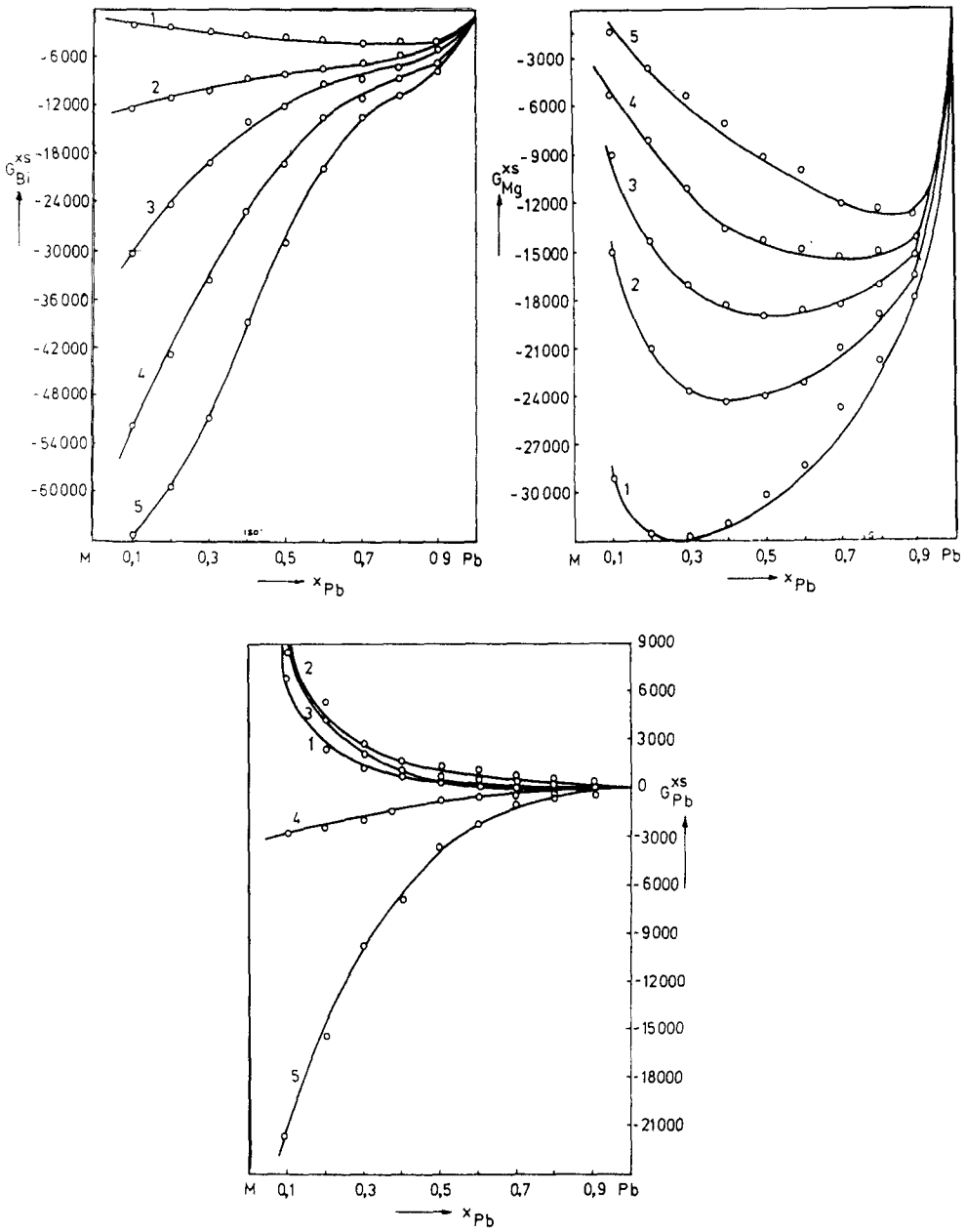

Fig. 7 G^{xs}_{Pb}, G^{xs}_{Bi}, G^{xs}_{Mg} *vs.* molar content at 973 K (J/mol) (1- Pb-B; 2- Pb-C; 3- Pb-D; 4- Pb-E; 5- Pb-F)

$$G_2^{xs} = (\sigma(R / y) / \sigma(1 - y))_{x_i} - x_1 G_1^{xs} / (1 - x_1)$$

$$G_3^{xs} = (\sigma(R / (1 - y)) / \sigma(1 / (1 - y)))_{x_i} - x_1 G_1^{xs} / (1 - x_1) \quad (7)$$

Results and discussion

In intention to cover the whole concentration area of the ternary system Pb–Bi–Mg, five quasibinary sections, Pb–X (X = B, C, D, E, F), were investigated and that is presented in the Fig. 2.

Composition of the chosen alloys in the investigated quasibinary sections is given in the Table 1.

The excess free energies of three binary systems Pb–Bi, Bi–Mg and Mg–Pb are taken from Hultgren *et al.* [12]. The plots of α function of three binary systems *vs.* mole fraction x at the temperature 973 K are shown in Fig. 3.

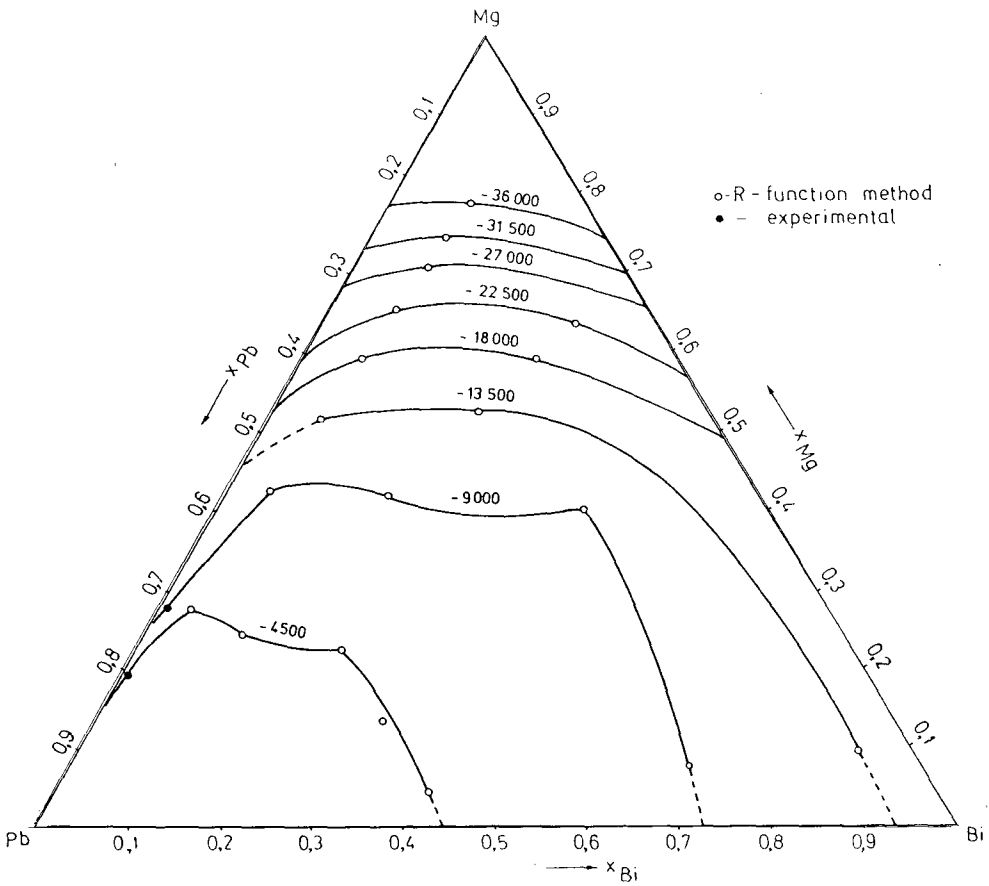

Fig. 8 G_{Pb}^{M} in the ternary system Pb–Bi–Mg at 973 K (J/mol)

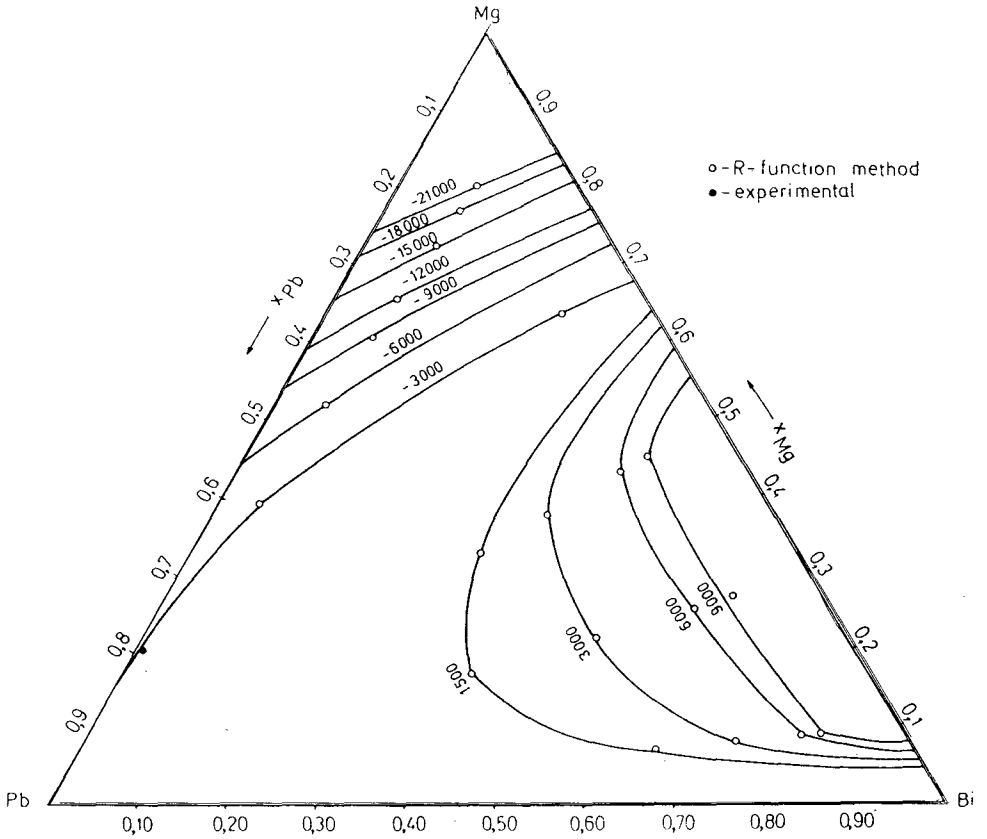

Fig. 9 G^{xs}_{Pb} in the ternary system Pb-Bi-Mg at 973 K (J/mol)

α functions have been fitted by third degree polynom and the fitting coefficients are listed in the Table 2.

Results of activities, activity coefficients and other partial and integral molar quantities for Pb, Bi and Mg for the investigated quasibinary sections Pb–X (X = B, C, D, E, F) in the ternary system Pb–Bi–Mg predicted by means of R-function method are given in the following Table 3.

Activity curves for Pb at 973 K for all investigated sections in the ternary system Pb–Bi–Mg are given in the Fig. 4. Sections Pb-B, Pb-C and Pb-D show positive deviation from Raoult law, and the other sections Pb-E and Pb-F show negative deviation.

Isoactivity curves for Pb in the ternary system Pb–Bi–Mg at 973 K are shown in Fig. 5. Experimental values of lead activity at the same temperature obtained by Oelsen calorimetry [11] are also presented in the Fig. 5 and show

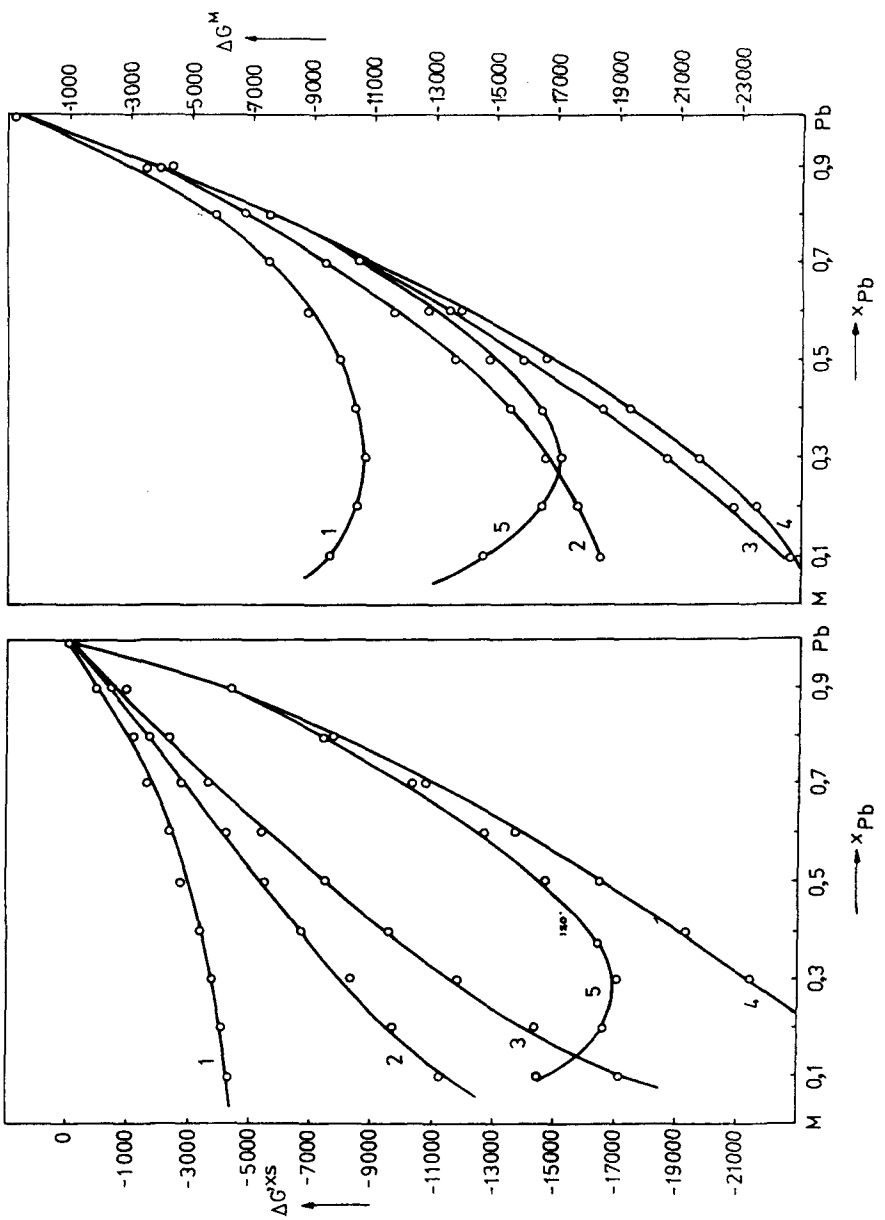

Fig. 10 ΔG^{M} and ΔG^{xs} *vs.* molar content at 973 K (J/mol)

a good agreement with the predicted values calculated by means of *R*-function method.

Dependence of the partial molar free energies of mixing for Pb, Bi and Mg *vs.* molar content at 973 K for all investigated quasibinary sections is presented in the Fig. 6. Partial molar excess free energies curves for Pb, Bi and Mg *vs.* molar content under the same conditions are given in the Fig. 7.

Values of partial molar free energy of mixing and partial molar excess free energy for lead in the ternary system Pb–Bi–Mg at 973 K are given in the Figs 8 and 9, respectively. Experimental values for G^{M}_{Pb} and G^{xs}_{Pb} obtained by Oelsen calorimetry [11] are presented at the same figure and show a good agreement with the calculated values.

The ternary molar excess free energy and ternary molar free energy of mixing *vs.* molar content for the ternary system Pb–Bi–Mg at 973 K are also presented (Fig. 10).

Figures 4 and 9 confirm the fact that quasibinary sections Pb-B, Pb-C and Pb-D shows positive deviation from Raoult law, which can be also concluded by positive values of $G^{x}_{Pb}s$ and $\gamma_{Pb}>1$ (Table 3). That points out on lead dividing from the solution in this part of the ternary system Pb–Bi–Mg. Thermodynamic behaviour of lead in the other sections can be determined in the same way. Figures 4 and 9 show negative deviation from Raoult law for quasibinary sections Pb-E and Pb-F, as well as negative values of G^{Pb}_{xs} and $\gamma<1$ (Table 3). That points out on a good miscibility between components in this part of the ternary system Pb–Bi–Mg.

Also, results obtained by *R*-function method predicting reach a good agreement with the experimentally ones, which illustrates that calculated values are good consistent.

* * *

The above study has originated in the former cooperation within the Pentagonal states and is now continued under separate projects of Serbia and the Czech Republic (No 210128 supported by Academy of Sciences).

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Zusammenfassung — Am ternären System Pb–Bi–Mg wurde die *R*-Funktionsmethode zur Abschätzung der ternären thermodynamischen Eigenschaften anhand der binären angewendet. Vorliegend werden für die quasibinären Abschnitte Pb–X (X= B, C, D, E, F) des untersuchten ternären Systemes Pb–Bi–Mg die mittels der *R*-Funktionsmethode berechneten Aktivitäten, Aktivitätskoeffizienten, partiellen und integralen molaren Größen von Pb, Bi und Mg angegeben. Außerdem wurde ermittelt, daß die mittels der *R*-Funktionsmethode erhaltenen Resultate in guter Übereinstimmung mit den experimentellen Ergebnissen nach der Oelsen-Kalorimetrie stehen.