

CHEMICAL THERMODYNAMICS
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Thermodynamic Properties of Liquid Copper–Lanthanum Alloys¹

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Abstract—Mixing enthalpies of alloys in the Cu–La system are measured using isoperibolic calorimetry method over the ranges $0 < x_{\text{La}} < 0.185$ at 1400–1430 K and $0.659 < x_{\text{La}} < 1$ at 1370 K. They have moderate exothermic values over the whole concentration range and agree with literature data. Activities of the components, enthalpies and entropies of formation of intermetallics in this system, and its phase diagram are optimized using an ideal associated solution (IAS) model, and agree with most literature data. The updated thermodynamic properties can be used in further investigation of multicomponent systems based on the binary Cu–La.

Keywords: copper, lanthanum, calorimetry, thermodynamic modeling, enthalpies, activities, phase diagram

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Alloys of La with 3d-metals are used as hydrogen storage materials, magnetic materials and amorphous alloys. The alloys of Cu–La system are part of the superconductive materials in the quaternary systems Cu–La–Ba–O and Cu–La–Sr–O. To improve the techniques of obtaining these materials, it is necessary to know their physicochemical properties, among which the most fundamental are the thermodynamic properties of liquid alloys and intermetallics.

Thermochemical properties of alloys in the Cu–La system have been studied before by calorimetry method [1–3]. The authors [1] measured the enthalpies of mixing (ΔH) of the melts over the whole range of concentrations at 1373 K, and calculated the partial enthalpies of the components at infinite dilution ($\overline{\Delta H}_i^\infty$). Anomalous exothermic heat effects of mixing were observed at low lanthanum concentrations, due to reaction of lanthanum with oxygen impurities dissolved in liquid copper. ΔH and $\overline{\Delta H}_i$ of these liquid alloys have been measured in [2] for $0 < x_{\text{La}} < 0.14$ at 1526 K. Unfortunately, the polynomial dependences of these functions on concentration contradict to the figure in the same article, which indicates a change of $\overline{\Delta H}_{\text{La}}$ from -72 kJ/mol at $x_{\text{La}} = 0$ to -49 kJ/mol at $x_{\text{La}} = 0.1$. At almost similar temperature (1523 K), partial and integral enthalpies of mixing of the liquid Cu–La alloys have been measured in [3]. Initial data in that work were $\overline{\Delta H}_i$, where the ΔH values were calculated from.

So far, partial enthalpies of mixing of copper $\overline{\Delta H}_{\text{Cu}}$ in the range $0.5 < x_{\text{La}} < 1$ have only been determined in [3]. On the other hand, the data [3] are characterized by a sharp decrease of exothermic effects of mixing of lanthanum in copper-rich alloys, in the range $0 < x_{\text{Cu}} < 0.1$. The data [1] report much more exothermic effects of mixing in this range than [2, 3].

The activities of components of the liquid alloys in the Cu–La system have been determined using effusion method in [4, 5] at 1549 and 1623 K, respectively. It can be seen that the data of those works do not agree, especially in the composition range $0 < x_{\text{La}} < 0.5$, where the actual experimental study was performed in [4].

The phase diagram of the Cu–La system has been studied in several works: Cirafici [6] has found the compounds LaCu_6 , LaCu_5 , LaCu_2 , and LaCu ; Meyer-Liautaud [7] also observed the incongruently melting phases LaCu_4 and LaCu_{-13} (the latter is only stable over a narrow range of temperatures between ~ 800 – 850 and 873°C).

The enthalpies of formation of intermetallics in the Cu–La system have been determined by Watanabe [1], Pasturel [8], Meyer-Liautaud [9], and Sommer [10]. Enthalpies and heat capacities of solid and liquid alloys in the temperature range 850–1300 K, as well as the enthalpies of fusion of the solid phases in the Cu–La system have been measured by Qi [11]. The excess heat capacities of the liquid alloys are positive, i.e., the exothermic heat effects of formation of alloys from pure liquid components decrease with temperature. This feature is typical for most binary metallic

¹ The article was translated by the authors.

systems [12], and may indicate the presence of clusters (associates) of dissimilar atoms in the melt, which gradually decompose at increasing temperature, with the properties of the solution tending to ideal.

Thermodynamic modeling of the Cu–La system has been conducted by Du [13]. It should be noted that those authors obtained quite adequate description of the properties of this system. However, they did not account for some literature data [2, 3, 5, 14], so the difference from modeled [13] and experimental [2, 3] $\overline{\Delta H}_i$ reaches 30 kJ/mol, which exceeds the allowed errors. Noteworthy, the authors [13] included two modifications of the LaCu₆ compound in their model, though none of the previous experimental works had given any indication for that. Probably, the authors [13] could not describe both the steep liquidus (corresponding to small heat of formation and possible instability of the phase at low temperature) and the experimental data for the enthalpy of formation of LaCu₆ (indicating large exothermic effect) within one phase.

Our current investigation of thermodynamic properties of the ternary Cu–In–La system requires reliable experimental data for all its binary boundary systems. Therefore, our present task is to determine the thermochemical properties of the liquid Cu–La alloys over a wide range of concentrations by calorimetry method, at lower temperatures (1370–1430 K) than it has been done in [3], as well as to create a thermodynamic model which would describe our and literature experimental data, including the phase diagram.

EXPERIMENTAL

The experimental technique has been described previously in [15]. The experiments were conducted in molybdenum crucibles for the whole studied range of concentration. Two series of experiments have been performed from Cu side, and one series from La side (Table 1). The initial weight of pure metal in the crucible at the beginning of each series was 1.5–1.8 g, and the samples dropped into the crucible ranged from 0.012 to 0.046 g. The calorimeter was calibrated at the beginning of the series with the solvent metal (i.e. the same as in the crucible). The difference between the enthalpy of liquid metal at the temperature of experiment and solid at the room temperature (298 K) was calculated according to [16]. The calibration was then repeated periodically (altering 3–4 calibrating samples with 10–20 main samples), using either the same metal-solvent, which still had small partial enthalpies of mixing that could be calculated from Gibbs–Duhem equation, or molybdenum. The repeated calibrations allowed us to trace the change of the heat exchange coefficient of the calorimeter (i.e., its apparent heat capacity) which gradually increased 1.2–1.4 times during the whole series, due to increasing mass of the alloy in the crucible. Each experimental series was fin-

ished with adding several dozens of indium samples, which allowed us to determine the enthalpies of mixing of the ternary Cu–In–La alloys (to be published elsewhere).

Partial enthalpies of mixing of the components ($\overline{\Delta H}_i$) were calculated using the equation

$$\overline{\Delta H}_i = -\Delta H_{298}^{T_0}(i) + \frac{k}{n_i} \int_{\tau_0}^{\tau_\infty} (T - T_0) dt,$$

where k is the heat exchange coefficient of the calorimeter, determined from calibration with the component A as

$$k = \Delta H_{298}^{T_0}(A) n_A \int_{\tau_0}^{\tau_\infty} (T - T_0) dt,$$

where $\Delta H_{298}^{T_0}(i)$ is the enthalpy difference between the liquid metal i at experimental temperature and solid at 298 K [16]; n_i is molar quantity of metal in the sample; $\int_{\tau_0}^{\tau_\infty} (T - T_0) dt$ is the area under the peak of the thermal curve (τ_0 , τ_∞ are the start and finish times of the heat effect recording; T is temperature; T_0 is the equilibrium temperature; t is time).

Integral enthalpies of mixing of the liquid alloy were calculated using the equation

$$\Delta H^{n+1} = \Delta H^n + \left(\overline{\Delta H}_i^{n+1} - \Delta H^n \right) \times \left(x_i^{n+1} - x_i^n \right) / \left(1 - x_i^n \right),$$

which is valid provided the change in concentration of the component i from x_i^n to x_i^{n+1} at adding the $(n+1)$ th sample is small.

The results obtained are presented in Fig. 1 together with the existing literature data. It is clear from Fig. 1 that our present and literature [1, 2] values of ΔH agree with each other. The $\overline{\Delta H}_{La}^\infty$ from [1] is more exothermic than our data and [2, 3], which may be explained by oxygen dissolved initially in copper. The model [13] does not describe this value well, overestimating its absolute value by 30 kJ/mol in comparison to our present data and [2, 3]. Our values of $\overline{\Delta H}_{Cu}$ agree with the results [1, 3], despite the differences in the experimental temperatures. Therefore, the thermochemical properties of the Cu–La system can be considered reliable.

RESULTS AND DISCUSSION

The ideal associated solution (IAS) model has been already used before in the work [14] to calculate the thermodynamic properties of the Cu–La liquid alloys. However, those authors did not account for the results

Table 1. Experimental values of the partial and integral enthalpies of mixing of liquid alloys in the Cu–La system (kJ/mol)

x_{La}	$-\Delta\bar{H}_{La}$	$-\Delta H$	x_{La}	$-\Delta\bar{H}_{La}$	$-\Delta H$	x_{La}	$-\Delta\bar{H}_{Cu}$	$-\Delta H$
Series 1 1400 K			Series 1 1420 K			Series 3 1370 K		
0.0031	78.2	0.24	0.1319	33.8	9.02	0.9850	33.3	0.50
0.0061	71.6	0.46	0.1367	34.0	9.16	0.9700	28.7	0.93
	1420 K		0.1424	35.5	9.33	0.9544	27.3	1.36
0.0095	84.6	0.75	0.1480	40.2	9.54	0.9391	31.5	1.84
0.0129	80.1	1.02	0.1531	25.0	9.63	0.9242	29.2	2.27
0.0166	77.0	1.30		Series 2		0.9096	34.5	2.78
0.0202	86.6	1.61		1430 K		0.8953	22.2	3.09
0.0240	74.4	1.90	0.0879	74.2	6.75	0.8811	28.7	3.49
0.0279	81.0	2.22	0.0908	61.2	6.93	0.8670	30.7	3.93
0.0318	78.8	2.52	0.0939	80.0	7.17	0.8532	26.5	4.29
0.0357	72.3	2.80	0.0969	62.0	7.36	0.8394	32.2	4.74
0.0385	81.8	3.03	0.1000	57.2	7.53	0.8355	28.0	4.84
0.0422	82.4	3.34	0.1032	70.3	7.75	0.8226	29.1	5.22
0.0460	78.8	3.63	0.1065	57.0	7.93	0.8096	30.0	5.61
0.0498	82.1	3.95	0.1099	61.0	8.14	0.7970	29.1	5.98
0.0536	81.8	4.26	0.1134	76.5	8.40	0.7844	31.7	6.38
0.0574	78.9	4.56	0.1170	68.3	8.65	0.7722	31.8	6.78
0.0613	75.4	4.85	0.1206	71.2	8.91	0.7603	26.1	7.08
0.0653	74.9	5.15	0.1244	59.1	9.12	0.7485	22.8	7.32
0.0696	75.5	5.47	0.1287	62.0	9.38	0.7370	23.0	7.56
0.0738	75.9	5.79	0.1324	56.7	9.58	0.7258	19.3	7.74
0.0755	82.3	5.94	0.1361	56.6	9.78	0.7149	19.7	7.92
0.0797	78.3	6.26	0.1401	45.1	9.94	0.7038	26.0	8.20
0.0839	51.5	6.47	0.1441	46.1	10.11	0.6925	29.7	8.55
0.0882	67.9	6.76	0.1481	47.9	10.29	0.6812	28.2	8.87
0.0931	65.1	7.07	0.1522	50.6	10.48	0.6701	22.0	9.08
0.0975	54.7	7.30	0.1565	48.5	10.68	0.6590	19.2	9.25
0.1020	63.8	7.58	0.1609	52.6	10.90			
0.1071	55.9	7.86		1420 K				
0.1073	67.1	7.87	0.1650	41.0	11.04			
0.1120	53.6	8.11	0.1738	39.7	11.34			
0.1167	59.1	8.38	0.1791	25.5	11.44			
0.1216	58.7	8.66	0.1852	32.2	11.59			
0.1270	44.8	8.88						

of other works, where the activities of the components [4, 5] and the phase diagram [6, 7, 11] were studied. Therefore, the entropies of formation of the associates, optimized in [14], are not reliable enough, since these temperature-dependent contributions to Gibbs energy of the melt cannot be accurately derived from the enthal-

pies of mixing at a single temperature alone. We are trying to correct these drawbacks in the present study.

Using IAS model and all the thermodynamic properties of the phases in the Cu–La presently available, we have calculated the activities of the components and the molar fractions of the associates (Fig. 2). For

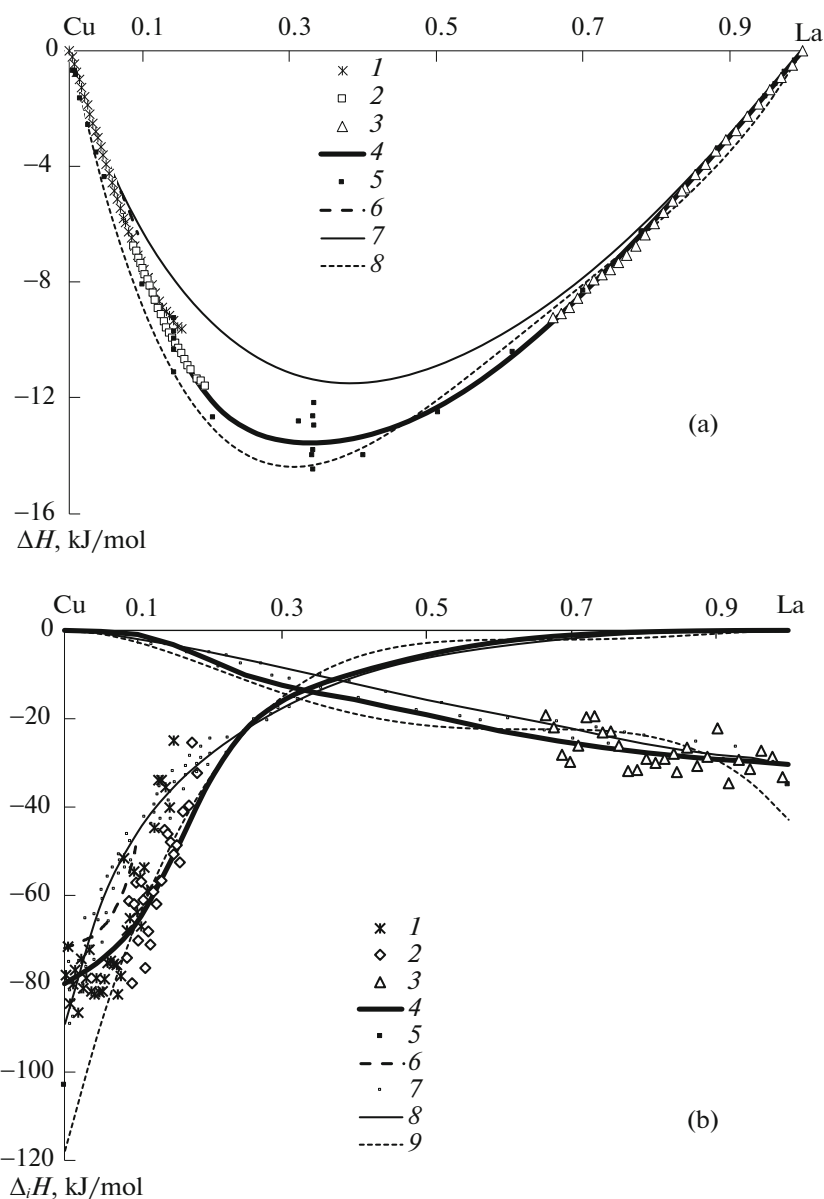


Fig. 1. Integral enthalpies of mixing (a) and partial enthalpies of mixing of the components (b) of the Cu–La liquid alloys: our experimental results at 1400–1420 (1), 1430 (2), and 1370 K (3); smoothed using IAS model, 1400 K (4). Literature data: experimental [1] ((5) only $\overline{\Delta H}_i^\infty$), [2] (6), [3] ((7) points, (8) polynomial curve); CALPHAD-model [13], 1373 K ((a) 8, (b) 9).

this purpose, we selected four associates: CuLa, Cu₂La, Cu₄La, Cu₆La. They all correspond to intermetallics in the solid alloys, though only two of them (Cu₂La and Cu₆La) melt congruently.

According to our calculations, the maximum molar fraction corresponds to the LaCu associate. The calculated activities of the components of the Cu–La liquid alloys agree relatively well with the experimentally determined [4, 5]. In the range $0 < x_{La} < 0.3$, where the results [4, 5] differ significantly, our model gives preference to the data [5]. Unlike the model [13], our calculated activities of lanthanum do not show positive

deviations in the range $0.55 < x_{La} < 1$. There is a sharp decrease on the isotherms of copper activity (a_{Cu}), determined in [5], at $x_{La} \approx 0.5$. We think that this feature is due to experimental errors. If this compositional dependence of a_{Cu} would be true, it will also cause an inflection on the lanthanum activity isotherm, as they are linked by Gibbs–Duhem equation. Moreover, the incongruent melting of LaCu intermetallic at quite low temperature (798 K) is not consistent with sharp change in copper activity at the same compositions.

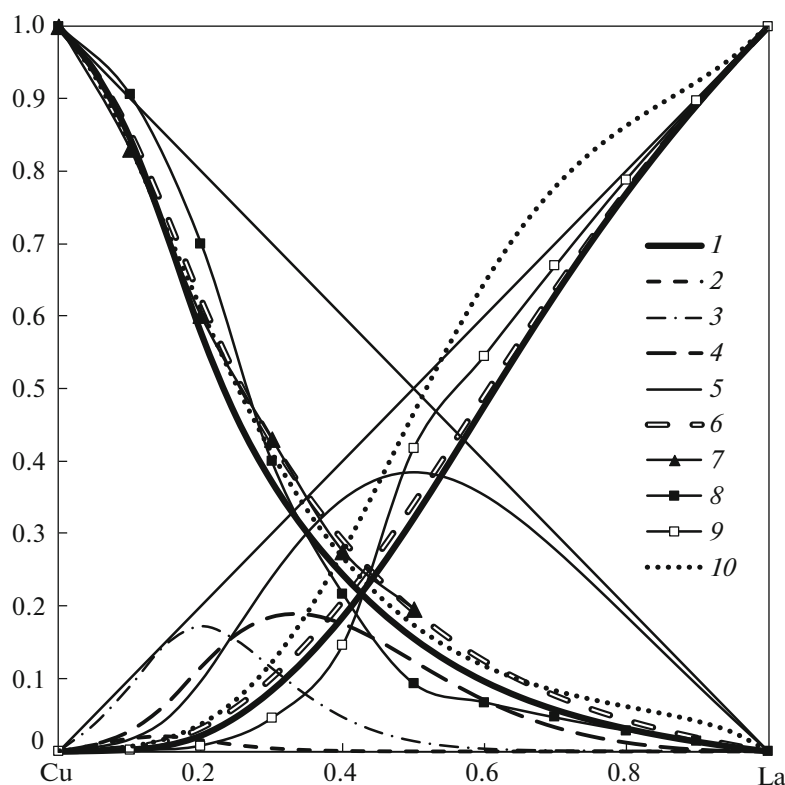


Fig. 2. Activities of the components (a_i , (1)) and molar fractions of the associates (x_i : (2) LaCu_6 , (3) LaCu_4 , (4) LaCu_2 , (5) LaCu) in the Cu–La liquid alloys at 1400 K, and a_i (6) at 1623 K (IAS model). Literature data, effusion method [4], 1549 K: (7) a_{Cu} ; [5] 1623 K: (8) a_{Cu} , (9) a_{La} . CALPHAD assessment: (10) a_i [13], 1623 K.

The enthalpies of formation ($\Delta_f H$) of the intermetallics and the associates, obtained experimentally in [1, 8–10] and assessed by CALPHAD technique in

[13], are presented in Fig. 3 and Table 2. It is obvious that all these results agree well with each other. This confirms the reliability of both our and [13] calcula-

Table 2. Enthalpies (kJ/mol) of formation and fusion, and entropies (J/(mol K)) of formation of the compounds in the Cu–La system, according to experimental and calculated data

x_{La}	0.075	0.143	0.143	0.167	0.2	0.333	0.5
$-\Delta_f H^{\text{sol}}$	LaCu_{13}	αLaCu_6	βLaCu_6	LaCu_5	LaCu_4	LaCu_2	LaCu
Experiment:							
[1]		9.9 ± 1.8				16.2 ± 1.6	
[8]				12.6			
[9]		11.3 ± 0.7		12.4 ± 1.0	13.2 ± 0.9	17.7 ± 1.5	15.8 ± 2.2
[10]		12.9 ± 1.2				15.1 ± 2.6	
$\Delta_{\text{melt}} H$:							
[1]		12.3				15.1	
[10]		11.4 ± 0.8				13.5 ± 0.9	
[11]		13.2 ± 0.5				12.1 ± 0.6	
Model [13]:							
$-\Delta_f H^{\text{sol}}$	1.8	9.3	8.6	10.8	13.3	16.1	16.2
$-\Delta_f S^{\text{sol}}$	-3.2	0.0	-1.4	0.0	1.5	1.2	5.4
Present work:							
$-\Delta_f H^{\text{sol}}$	—	—	5.4	11.6	12.6	16.6	17.0
$-\Delta_f S^{\text{sol}}$	—	—	-3.7	1.3	1.4	1.7	6.0
$-\Delta_f H^{\text{liq}}$	—	—	13.0	—	17.6	17.3	17.1
$-\Delta_f S^{\text{liq}}$	—	—	5.8	—	5.5	4.7	3.8

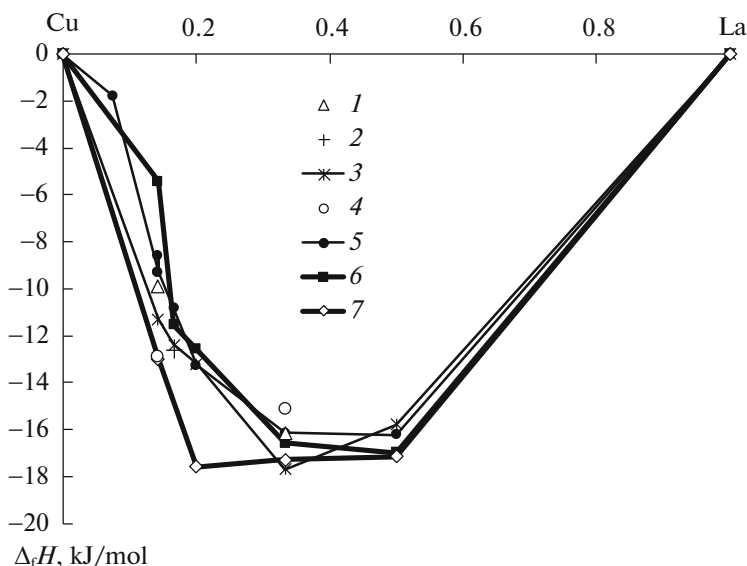


Fig. 3. Enthalpies of formation of the intermetallics and the associates in the Cu–La system, determined experimentally (1) [1], (2) [8], (3) [9], (4) [10], assessed with CALPHAD method (5) [13] and calculated by us using IAS model ((6) intermetallics in the solid alloys, (7) associates in the liquid alloys).

tions of $\Delta_f H$ of the lanthanum cuprides. The compound LaCu_{13} (having very narrow temperature range of stability) is not described with our model. Only the high-temperature modification (β) of the two (α and βLaCu_6) is considered in our present model, since it is involved in equilibrium with the melt.

The entropies of formation of the associates and the intermetallic in the Cu–La system, calculated using CALPHAD method [13] and by us using IAS

model, are presented in the Fig. 4 and Table 2. It is obvious that they show good correlation, with an exception for $\Delta_f S^{\text{sol}}(\text{LaCu}_6)$. This difference may become possible to review after experimental proofs of existence or absence of two modifications of the LaCu_6 compound.

The optimized thermodynamic properties of the liquid alloys in the Cu–La system are presented in Table 3. The errors of the integral and partial enthalp-

Table 3. Partial and integral enthalpies, excess Gibbs energies (kJ/mol) and entropies (J/(mol K)) of mixing of the Cu–La liquid alloys according to optimized IAS model at 1400 K

x_{La}	$-\Delta H$	$-\Delta \bar{H}_{\text{Cu}}$	$-\Delta \bar{H}_{\text{La}}$	$-\Delta G^{\text{ex}}$	$-\Delta S^{\text{ex}}$
0	0	0	80.1 ± 9.1	0	0
0.1	7.5 ± 0.9	0.9 ± 0.1	66.2 ± 7.5	4.9	1.8
0.2	12.3 ± 1.4	6.7 ± 0.8	34.4 ± 3.9	8.2	2.9
0.3	13.5 ± 1.6	12.4 ± 1.5	16.1 ± 1.8	9.6	2.8
0.4	13.3 ± 1.6	15.7 ± 1.8	9.7 ± 1.1	9.9	2.5
0.5	12.3 ± 1.4	19.1 ± 2.3	5.6 ± 0.6	9.4	2.1
0.6	10.6 ± 1.2	22.7 ± 2.7	2.6 ± 0.3	8.2	1.7
0.7	8.4 ± 1.0	25.5 ± 3.0	1.1 ± 0.1	6.6	1.3
0.8	5.8 ± 0.7	27.6 ± 3.2	0.35 ± 0.04	4.7	0.8
0.9	3.0 ± 0.3	29.1 ± 3.4	0.07 ± 0.01	2.4	0.4
1	0	30.4 ± 3.6	0	0	0

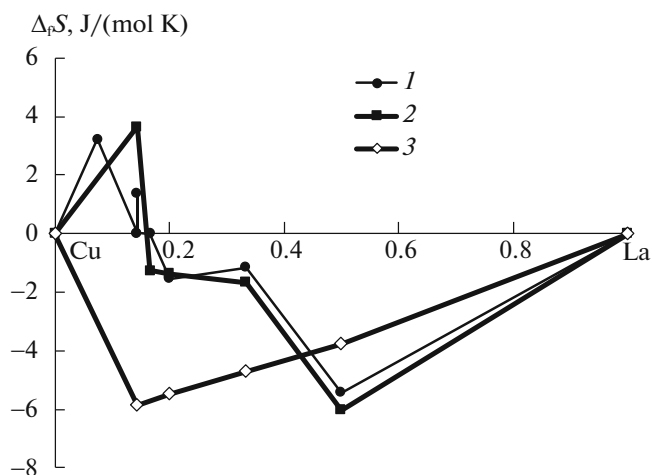


Fig. 4. Entropies of formation of the associates and the solid compounds in the Cu–La system, calculated with CALPHAD method (1) [13] and by us using IAS model ((2) intermetallics in solid alloys, and (3) associates in the liquid).

ies of mixing are evaluated from the scatter of experimental points relatively to smoothing curves of IAS model. The relative errors of each function are consid-

ered constant within the whole range of concentrations.

Using our own and literature data for thermodynamic properties of phases in the Cu–La system, we calculated its liquidus coordinates using IAS model (Fig. 5).

It is clear that our data somewhat deviate from the experimental. In particular, the eutectics between Cu and LaCu_6 , and between LaCu and La, according to our calculations, correspond to x_{La} , equal to 0.11 and 0.69, respectively. If further investigations are going to be done, they will definitely clarify this. At the present moment we believe that there are no principal inconsistencies between different results for liquidus of this phase diagram.

To sum up, the enthalpies of mixing of liquid alloys in the Cu–La system are moderate exothermic values over the whole range of concentrations, and this agrees with the literature data. The activities of the components, Gibbs free energies and entropies of mixing of alloys in this system, as well as its phase diagram, are all in agreement with the majority of data from literature. Optimized thermodynamic model of alloys in the Cu–La system valid in a wide range of concentrations

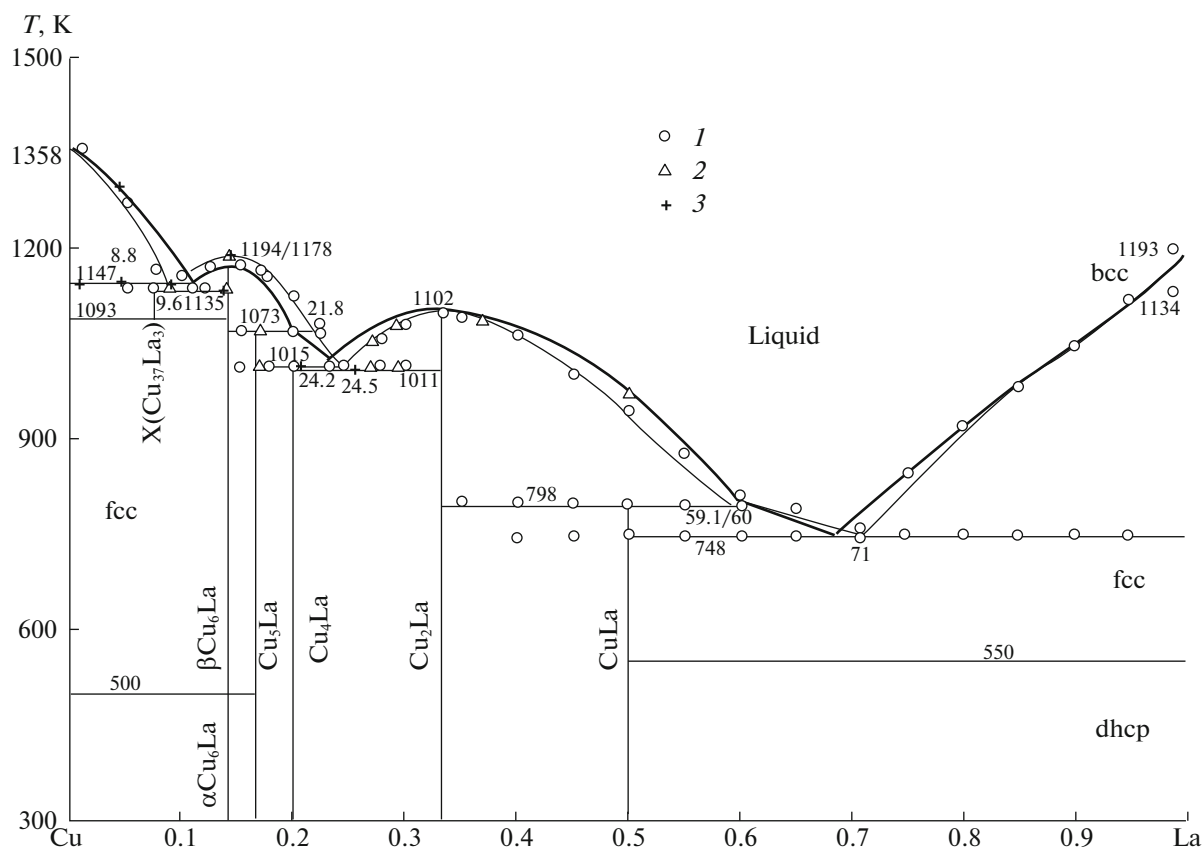


Fig. 5. Phase diagram of the Cu–La (liquidus calculated by us using IAS model is shown as a bold curve), compared to the data from literature: experimental ((1) [6], (2) [7], and (3) [11]) and modeled [13] (thin lines).

and temperatures is mostly confirming the results of experimental studies and the earlier modeling [13].

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