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# Thermodynamic Properties of Alloys of the Binary In–Yb System[1]

**M. A. Shevchenko, M. I. Ivanov, V. V. Berezutski, and V. S. Sudavtsova**

*Frantsevitch Institute for Problems of Materials Science, ul. Krzhizhanovskogo 3, Kyiv, 03142 Ukraine*
*e-mail: sud@ipms.kiev.ua, maximshevch@ukr.net*

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**Abstract**—The thermochemical properties of melts of the binary In–Yb system were studied by the calorimetry method at 1160–1380 K over the whole concentration interval. It was shown that significant negative heat effects of mixing are characteristic features for these melts. Using the ideal associated solution (IAS) model, the activities of components, Gibbs energies and the entropies of mixing in the alloys, and the phase diagram of this system were calculated. They agree with the data from literature.

*Keywords:* In–Yb binary system, thermochemical properties of alloys.

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Alloys of the rare-earth metals with *p*-elements of the third group are promising as superconductors, catalysts and promoters, as well as cathode materials with various emission properties [1, 2]. However, there are only few works in the literature devoted to investigation of thermodynamic properties of indium-lanthanide alloys. Even those which were conducted, are related mostly to the alloys containing 75% indium or more. This is caused by poor accessibility of the components in pure state, and by instability of their alloys in air.

Nevertheless, in the rest, these alloys are quite easy objects to investigate, since they are mostly low-melting, non-volatile, and not interacting with refractory crucible materials. This allows us to conduct investigation of thermodynamic properties of the In–Ln melts using calorimetry method over wide concentration ranges. Our research group has already done it successfully for the Eu–In [3] and the Ce–In systems. The present work is devoted to the In–Yb liquid alloys. Studying wide range of such systems, including the Gd–In and the In–La, will give an opportunity to determine the regularities of interaction between the components of the In–Ln systems.

The phase diagram of the In–Yb system was investigated by McMasters et al. [4] using differential thermal analysis, metallography and X-ray diffraction methods. Fields of solid solutions, containing up to 1 at % In, were found for two ytterbium modifications (β- and γ-Yb). Five intermetallics were identified: $YbIn_3$, $YbIn_2$, YbIn, $Yb_2In$, and $Yb_5In_2$. Two of them melt congruently ($YbIn_2$, YbIn), and two else decompose by peritectic reactions ($YbIn_3$, $Yb_2In$). For the last intermetallic, the authors [4] proposed stoichiometry $Yb_5In_2$ and peritectic melting. However, later in the work [5] the crystal structure and composition of this compound were updated—$Yb_8In_3$. A review [6] gave the phase diagram of the In–Yb system which includes this modification. Shifting of the composition from 71.4 to 72.7 at % Yb makes peritectic melting type of the $Yb_8In_3$ compound questionable—instead, congruent melting becomes possible. Unfortunately, in both the handbook [7] and the CALPHAD thermodynamic assessment [8] this updating of stoichiometry was missed, and an old variant was used—$Yb_5In_2$.

The solubility of Yb in liquid In (which is equivalent to a part of the liquidus curve for the $YbIn_3$—melt equilibrium) was investigated by high-temperature filtration method [9]. It was described by an equation $\log x_{Yb} = -0.183 - 1110 / T$, $500\text{ K} < T < 800\text{ K}$ [10]. The enthalpy of formation of the $YbIn_3$ compound was measured using dynamic differential calorimetry [11]: $\Delta_f H^0_{YbIn_3} = -39.7$ kJ/mol. Thermodynamic properties of other phases have never been investigated.

Systematic analysis of the phase diagrams of the indium–lanthanide systems [12, 13] and thermodynamic properties of the $LnIn_3$ compounds [14] shows no distinct differences for ytterbium interacting with indium, compared to other lanthanides, at least for $x_{Ln} < 0.5$.

So, there are no experimental data for the thermochemical properties of liquid alloys over the whole concentration range of the In–Yb system, and for the intermetallics rich in ytterbium; thus, they would be interesting to study. The purpose of the present work is measuring the mixing enthalpies of the In–Yb melts using isoperibolic calorimetry, and creating the ther-

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[1] The article was translated by the authors.

**Table 1.** Experimental values of partial and integral mixing enthalpies of the In–Yb melts (kJ/mol)

| $x_{\mathrm{Yb}}$ | $-\Delta\bar{H}_{\mathrm{Yb}}$ | $-\Delta H$ | $x_{\mathrm{Yb}}$ | $-\Delta\bar{H}_{\mathrm{Yb}}$ | $-\Delta H$ | $x_{\mathrm{Yb}}$ | $-\Delta\bar{H}_{\mathrm{In}}$ | $-\Delta H$ |
|---|---|---|---|---|---|---|---|---|
| | Series 1 | | | 1380 K | | | Series 2 | |
| | 1310 K | | 0.1785 | 99.1 | 19.38 | | 1160 K | |
| 0.0076 | 118.2 | 0.90 | 0.1856 | 97.6 | 20.05 | 0.9824 | 93.7 | 1.65 |
| 0.0151 | 113.8 | 1.76 | 0.1925 | 97.6 | 20.71 | 0.9635 | 99.2 | 3.52 |
| 0.0226 | 108.5 | 2.57 | 0.1994 | 97.1 | 21.36 | 0.9458 | 99.4 | 5.28 |
| 0.0300 | 121.1 | 3.46 | 0.2065 | 92.3 | 21.99 | 0.9276 | 92.0 | 6.95 |
| 0.0372 | 115.8 | 4.30 | 0.2135 | 88.3 | 22.58 | 0.9085 | 87.0 | 8.60 |
| 0.0446 | 115.9 | 5.15 | 0.2210 | 96.6 | 23.28 | 0.8898 | 95.5 | 10.39 |
| 0.0520 | 114.6 | 6.00 | 0.2279 | 93.8 | 23.91 | 0.8724 | 93.6 | 12.02 |
| 0.0593 | 107.8 | 6.78 | 0.2352 | 87.4 | 24.51 | 0.8552 | 87.2 | 13.50 |
| 0.0666 | 112.0 | 7.60 | 0.2412 | 93.1 | 25.05 | 0.8320 | 98.4 | 15.80 |
| 0.0738 | 108.0 | 8.38 | 0.2482 | 89.8 | 25.65 | 0.8067 | 84.5 | 17.90 |
| 0.0811 | 110.0 | 9.18 | 0.2552 | 85.4 | 26.20 | 0.7892 | 88.6 | 19.43 |
| 0.0883 | 113.5 | 9.99 | 0.2620 | 85.4 | 26.75 | 0.7718 | 80.9 | 20.78 |
| 0.0954 | 112.3 | 10.79 | 0.2689 | 84.1 | 27.28 | 0.7545 | 93.5 | 22.42 |
| 0.1029 | 108.8 | 11.61 | 0.2756 | 90.0 | 27.86 | 0.7388 | 84.4 | 23.71 |
| 0.1103 | 111.6 | 12.43 | 0.2711* | 88.5 | | 0.7157 | 85.3 | 25.63 |
| 0.1180 | 107.2 | 13.25 | 0.2776 | 86.2 | 28.01 | 0.7006 | 92.2 | 27.04 |
| 0.1207* | 105.3 | 13.54 | 0.2841 | 84.9 | 28.53 | | (start of the heterogeneous field) | |
| 0.1280 | 106.3 | 14.30 | 0.2905 | 80.8 | 28.99 | 0.6860 | 99.5 | 28.54** |
| 0.1351 | 105.5 | 15.04 | 0.2968 | 82.5 | 29.47 | 0.6720 | 101.0 | 30.02 |
| 0.1422 | 103.2 | 15.77 | 0.3031 | 80.5 | 29.93 | 0.6586 | 109.5 | 31.61 |
| 0.1495 | 101.2 | 16.50 | 0.3094 | 79.1 | 30.37 | 0.6451 | 102.2 | 33.06 |
| 0.1567 | 104.7 | 17.25 | 0.3155 | 80.4 | 30.81 | | 1200 K | |
| 0.1641 | 101.4 | 17.98 | 0.3216 | 74.2 | 31.20 | 0.6288 | 134.1 | 35.61 |
| 0.1714 | 99.2 | 18.69 | 0.3275 | 73.5 | 31.57 | 0.6168 | 124.7 | 37.30 |
| | | | 0.3339 | 73.2 | 31.96 | 0.6051 | 139.1 | 39.24 |
| | | | 0.3403 | 70.7 | 32.33 | 0.5936 | 145.7 | 41.25 |
| | | | 0.3442 | 70.4 | 32.56 | 0.5823 | 155.3 | 43.43 |
| | | | 0.3498 | 69.3 | 32.87 | 0.5713 | 152.1 | 45.49 |
| | | | 0.3555 | 68.4 | 33.19 | 0.5607 | 171.2 | 47.82 |
| | | | 0.3613 | 67.5 | 33.49 | 0.5501 | 157.8 | 49.89 |
| | | | 0.3669 | 65.9 | 33.78 | 0.5399 | 173.1 | 52.19 |
| | | | 0.3725 | 62.0 | 34.03 | 0.5297 | 151.5 | 54.05 |
| | | | 0.3779 | 63.5 | 34.28 | 0.5184 | 164.6 | 56.41 |
| | | | 0.3834 | 65.5 | 34.56 | 0.5089 | 107.3 | 57.35 |
| | | | 0.3889 | 60.6 | 34.79 | 0.4996 | 6.9 | 56.43 |
| | | | 0.3943 | 61.2 | 35.02 | 0.4906 | −11.0 | 55.22 |
| | | | 0.3997 | 56.3 | 35.21 | 0.4819 | −8.3 | 54.10 |
| | | | 0.4050 | 53.3 | 35.37 | 0.4735 | −4.2 | 53.08 |
| | | | 0.4102 | 56.2 | 35.55 | 0.4652 | 2.3 | 52.19 |
| | | | 0.4153 | 55.4 | 35.73 | 0.4571 | 2.3 | 51.32 |
| | | | 0.4204 | 53.1 | 35.88 | 0.4492 | −0.7 | 50.42 |
| | | | 0.4255 | 51.6 | 36.01 | 0.4415 | 4.4 | 49.63 |
| | | | 0.4305 | 50.8 | 36.14 | 0.4340 | 10.4 | 48.97 |
| | | | 0.4356 | 49.9 | 36.27 | 0.4268 | 9.4 | 48.31 |
| | | | 0.4409 | 49.6 | 36.39 | 0.4199 | 7.4 | 47.65 |
| | | | 0.4461 | 48.9 | 36.51 | 0.4129 | 8.3 | 46.99 |
| | | | 0.4513 | 48.2 | 36.62 | 0.4061 | 7.4 | 46.34 |

* Before these experimental points, several calibrating samples were dropped into crucible, that shifted the composition towards lower concentration of the second component.

** The enthalpies of formation of the heterogeneous alloy are presented relatively to pure liquid components; note that incomplete achievement of equilibrium phase composition in the alloy was possible.

**Table 2.** Partial and integral enthalpies of mixing of the In–Yb melts at 1160 and 1350 K, kJ/mol

| $x_{\mathrm{Yb}}$ | $-\Delta H^{1160}$ | $-\Delta\overline{H}^{1160}_{\mathrm{In}}$ | $-\Delta\overline{H}^{1160}_{\mathrm{Yb}}$ | $-\Delta H^{1350}$ | $-\Delta\overline{H}^{1350}_{\mathrm{In}}$ | $-\Delta\overline{H}^{1350}_{\mathrm{Yb}}$ |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 117.1 ± 4.4 | 0 | 0 | 113.0 ± 4.2 |
| 0.1 | 11.5 ± 0.3 | 0.3 ± 0.0 | 113.0 ± 4.2 | 11.1 ± 0.3 | 0.3 ± 0.0 | 108.3 ± 4.0 |
| 0.2 | 22.3 ± 0.6 | 2.3 ± 0.1 | 102.6 ± 3.8 | 21.4 ± 0.6 | 2.3 ± 0.1 | 98.0 ± 3.7 |
| 0.3 | 31.2 ± 0.8 | 9.0 ± 0.5 | 83.0 ± 3.1 | 29.9 ± 0.8 | 8.8 ± 0.5 | 79.0 ± 2.9 |
| 0.4 | 37.1 ± 1.0 | 20.0 ± 1.1 | 62.7 ± 2.3 | 35.2 ± 0.9 | 21.4 ± 1.1 | 56.0 ± 2.1 |
| 0.5 | 39.1 ± 1.0 | 44.7 ± 2.4 | 33.5 ± 1.2 | 36.5 ± 1.0 | 42.2 ± 2.2 | 30.8 ± 1.1 |
| 0.6 | 34.9 ± 0.9 | 72.9 ± 3.9 | 9.6 ± 0.4 | 33.0 ± 0.9 | 65.3 ± 3.5 | 11.6 ± 0.4 |
| 0.7 | 27.3 ± 0.7 | 85.3 ± 4.5 | 2.5 ± 0.1 | 26.3 ± 0.7 | 79.9 ± 4.2 | 3.3 ± 0.1 |
| 0.8 | 18.6 ± 0.5 | 90.6 ± 4.8 | 0.6 ± 0.0 | 18.0 ± 0.5 | 87.1 ± 4.6 | 0.8 ± 0.0 |
| 0.9 | 9.4 ± 0.3 | 93.3 ± 5.0 | 0.1 ± 0.0 | 9.2 ± 0.2 | 90.6 ± 4.8 | 0.1 ± 0.0 |
| 1 | 0 | 94.8 ± 5.0 | 0 | 0 | 92.6 ± 4.9 | 0 |

modynamic model to describe our and literature experimental data, including the phase diagram.

## EXPERIMENTAL PART

We have described the experimental technique before in [15]. The experiments were conducted in molybdenum crucibles over the whole concentration range. Owing to the temperatures chosen as low as possible to keep away from formation of the In–Yb intermetallics, we managed to avoid the vaporization of the components (Yb being the most important), and from the interaction of melts with the crucible material.

We conducted one series of experiments for each side of the system—from In and Yb (Table 1). Starting masses of pure indium and ytterbium in the crucible were 1.3 g; the samples of mass 0.015–0.04 g were dropped into the crucible. The calorimeter was calibrated at the beginning of the experimental series with the samples of the same metal as was in the crucible. The enthalpy change between the solid metal at room temperature (298 K) and the liquid at the experimental temperature was calculated accordingly to [16]. Then, the calibration was periodically repeated (alternating 3–4 samples for calibration with 15–30 major samples of the second component). Either molybdenum or the same first component was used for that, since the partial enthalpies of the latter are small values and may be calculated using the Gibbs-Duhem equation. These repeated calibrations allowed us to control the change of the heat exchange coefficient of the calorimeter (i.e. its apparent heat capacity), which increased smoothly 1.2–1.5 times during the whole series, due to increasing mass of the alloy in the crucible.

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

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

where $k$ is the heat exchange coefficient of the calorimeter, determined using calibration component $A$ as:

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

$\Delta H_{298}^{T_0}(i)$ is the enthalpy change between the solid metal $i$ at room temperature and the liquid at the temperature of the experiment, from [16]; $n_i$ is the molar quantity of metal in the sample; $\int_{\tau_0}^{\tau_\infty}(T - T_0)dt$ is the area under the peak on a thermal curve ($\tau_0$, $\tau_\infty$ are the start and the end times of the heat effect recording, respectively, $T$ is the temperature, $T_0$ is the equilibrium temperature, $t$ is time).

Integral mixing enthalpies of the melt were calculated through the equation

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

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

The obtained experimental points were approximated with smooth concentration dependences accordingly to the ideal associated solution (IAS) model, which is described below in detail. Partial and integral mixing enthalpies of melts of the In–Yb system at 1160–1380 K are presented in Fig. 1, and their values at rounded concentrations with errors (smoothed using IAS model, at 1160 and 1350 K)—in

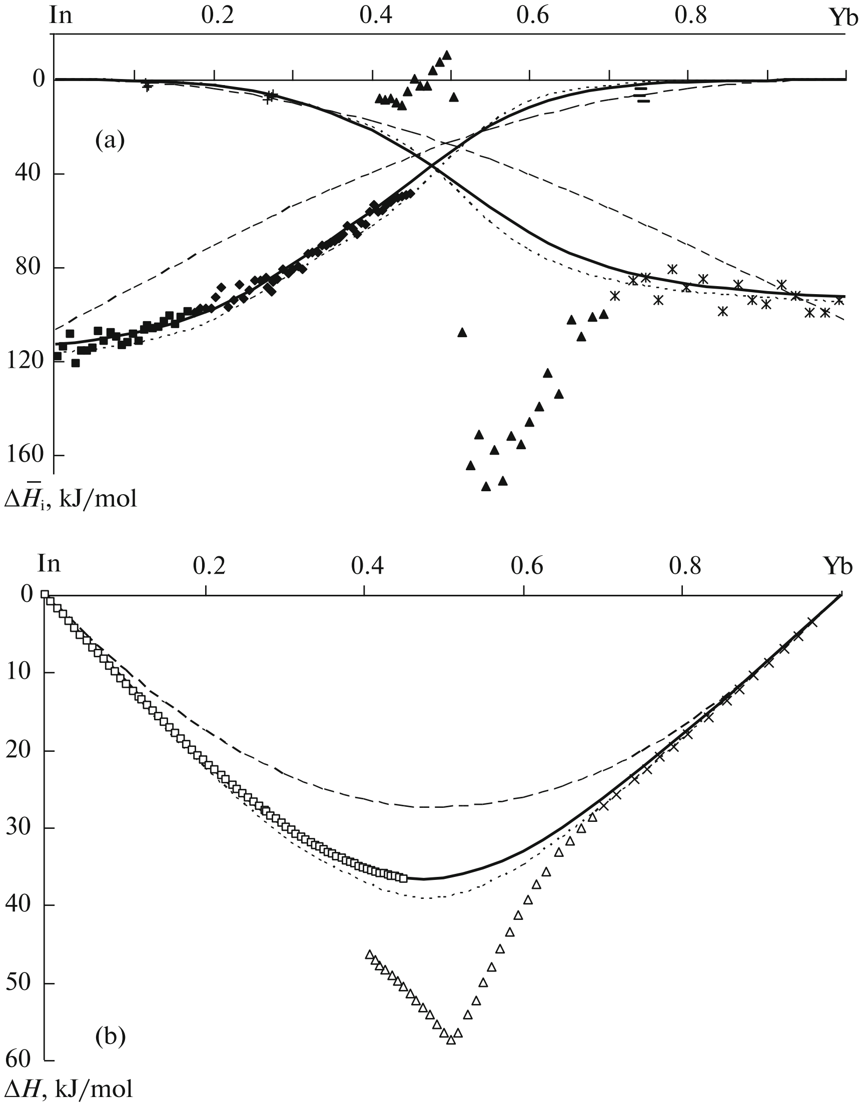

**Fig. 1.** Partial (a) and integral (b) mixing enthalpies of melts of the In–Yb system: investigated by us experimentally (series 1: (■) $\Delta\overline{H}_{\mathrm{Yb}}$, 1310 K; (◆) $\Delta\overline{H}_{\mathrm{Yb}}$, 1380 K; (+) $\Delta\overline{H}_{\mathrm{In}}$, 1310–1380 K (calibration); (□) $\Delta H$, 1310–1380 K; series 2: (*) $\Delta\overline{H}_{\mathrm{In}}$; (–) $\Delta\overline{H}_{\mathrm{Yb}}$ (calibration); (×) $\Delta H$—1160 K; heterogeneous field: (▲) $\Delta\overline{H}_{\mathrm{In}}$, (△) $\Delta H$—1160–1200 K); approximated using IAS model (—— 1350 K, ------ 1160 K); and from literature (— — assessment [8], not dependent on temperature).

Table 2. The errors were evaluated as the mean square deviations of the experimental points from the smooth curves. Each function $\Delta H$, $\Delta\overline{H}_{\mathrm{Yb}}$, $\Delta\overline{H}_{\mathrm{In}}$ was assumed to have errors proportional to its absolute value.

Since the calculation of the thermodynamic properties using IAS model requires special software and is not always available, it is desirable to provide a simpler description of the concentration dependences of the thermodynamic properties. However, such expression is less accurate to describe the experimental data, and it is valid over a limited temperature range only. The obtained set of the partial and integral enthalpies of mixing was approximated with polynomial dependences (kJ/mol):

$$\Delta\overline{H}_{\mathrm{Yb}}^{1160} = (1 - x_{\mathrm{Yb}})^2(-117.1 - 124.4x_{\mathrm{Yb}} - 1305.1x_{\mathrm{Yb}}^2 + 4574.3x_{\mathrm{Yb}}^3 - 3120.6x_{\mathrm{Yb}}^4),$$

$$\Delta\overline{H}_{\mathrm{In}}^{1160} = x_{\mathrm{Yb}}^2(-54.9 + 745.6x_{\mathrm{Yb}} - 4735.8x_{\mathrm{Yb}}^2 + 7070.8x_{\mathrm{Yb}}^3 - 3120.6x_{\mathrm{Yb}}^4),$$

$$\Delta H^{1160} = x_{\mathrm{Yb}}(1 - x_{\mathrm{Yb}})(-117.1 - 62.2x_{\mathrm{Yb}} - 435.0x_{\mathrm{Yb}}^2 + 1143.6x_{\mathrm{Yb}}^3 - 624.1x_{\mathrm{Yb}}^4),$$

$$\Delta\overline{H}_{\mathrm{Yb}}^{1350} = (1 - x_{\mathrm{Yb}})^2(-113.0 - 161.8x_{\mathrm{Yb}} - 772.8x_{\mathrm{Yb}}^2 + 3261.7x_{\mathrm{Yb}}^3 - 2282.8x_{\mathrm{Yb}}^4),$$

**Table 3.** Enthalpies (kJ/mol at.) and entropies (J/(mol K)) of formation of the associates (liq) and intermetallics (sol) in the In–Yb system at 298 K

| Composition | $x_{\rm Yb}$ | $-\Delta_{\rm f}H^{\rm liq}$ | $-\Delta_{\rm f}S^{\rm liq}$ | $-\Delta_{\rm f}H^{\rm sol}$ | $-\Delta_{\rm f}S^{\rm sol}$ |
|---|---|---|---|---|---|
| $\rm YbIn_3$ | 0.25 | 32.6 | 15.2 | 39.7 | 16.2 |
| $\rm YbIn_2$ | 0.333 | 37.3 | 15.5 | 45.4 | 15.3 |
| YbIn | 0.5 | 43.6 | 16.3 | 49.0 | 15.0 |
| $\rm Yb_2In$ | 0.667 | 35.5 | 17.4 | 35.9 | 10.8 |
| $\rm Yb_8In_3$ | 0.727 | | | 31.1 | 9.5 |

$$\Delta\overline{H}_{\rm In}^{1350} = x_{\rm Yb}^2(-32.1 + 353.39x_{\rm Yb} - 3219x_{\rm Yb}^2 + 5087.9x_{\rm Yb}^3 - 2282.8x_{\rm Yb}^4),$$

$$\Delta H^{1350} = x_{\rm Yb}(1 - x_{\rm Yb})(-113.0 - 80.9x_{\rm Yb} - 257.6x_{\rm Yb}^2 + 815.4x_{\rm Yb}^3 - 456.6x_{\rm Yb}^4).$$

Integral excess entropies, evaluated from the IAS model (see below), were approximated with the dependences (J/(mol K)):

$$\Delta S^{\rm ex,1160} = x_{\rm Yb}(1 - x_{\rm Yb})(-42.6 - 14.3x_{\rm Yb} - 356.1x_{\rm Yb}^2 + 803x_{\rm Yb}^3 - 424.8x_{\rm Yb}^4);$$

$$\Delta S^{\rm ex,1350} = x_{\rm Yb}(1 - x_{\rm Yb})(-39.4 - 29.1x_{\rm Yb} - 215.2x_{\rm Yb}^2 + 542.4x_{\rm Yb}^3 - 291.7x_{\rm Yb}^4).$$

## DISCUSSION OF THE RESULTS

The obtained data, together with those from literature, were treated by means of the software complex developed by us, based on the model of ideal associated solutions (IAS). The same method has been used before to treat the results of calorimetrical investigation of liquid alloys simultaneously with the literature data from phase equilibria and thermodynamic properties of many metallic systems with strong interaction between the components [17–19]. The correctness of this method has been shown in the work [20]. Apparently, this model is only unsuitable for description of thermodynamic properties of liquid metallic alloys with positive enthalpies of mixing.

All available experimental data, supplemented by a list of compounds in the solid alloys (accordingly to the phase diagram) and assumed associates in the liquid alloys, were inserted into the created program. Arbitrary starting values of enthalpies ($\Delta_{\rm f}H^{\rm sol}$, $\Delta_{\rm f}H^{\rm liq}$) and entropies ($\Delta_{\rm f}S^{\rm sol}$, $\Delta_{\rm f}S^{\rm liq}$) of formation were set for these compounds in the solid alloys and the associates; then they served as variable parameters during the optimization. In the case of correct list of the associates and non-contradictory literature data, some combination of values of these parameters gives satisfactory agreement with all those experimental data for the alloys.

The equilibrium concentrations of the associates in the melt at given composition and temperature correspond to a minimum of the function

$$\Delta G = RT\left(a_{\rm A}\ln a_{\rm A} + a_{\rm B}\ln a_{\rm B} + \sum_{n=1}^{N} x_n \times\left(\frac{\Delta G_n}{RT} + \ln x_n\right)\right)\Bigg/\left(1 + \sum_{n=1}^{N}(i_n + j_n - 1)x_n\right),$$

where $\Delta G_n = \Delta_{\rm f}H_n^{\rm liq} - T\Delta_{\rm f}S_n^{\rm liq}$; $a_{\rm A} = x_{\rm A_1}$ and $a_{\rm B} = x_{\rm B_1}$ are the molar fractions of the monomers, which are similar to the activities of the components due to IAS model principles; $x_n$ are the molar fractions of the associates. The normalizing conditions are

$$a_{\rm A} + a_{\rm B} + \sum_{n=1}^{N} x_n = 1,$$

$$1 - x_{\rm A} = x_{\rm B} = \left(a_{\rm B} + \sum_{n=1}^{N} x_n j_n\right)\Bigg/\left(a_{\rm A} + a_{\rm B} + \sum_{n=1}^{N} x_n(i_n + j_n)\right),$$

where $x_{\rm A}$, $x_{\rm B}$ are the total molar fractions of the components in the melt.

As soon as the minimum of $\Delta G$ and the corresponding values of $a_{\rm A}$, $a_{\rm B}$, and $x_n$ $(n = 1\ldots N)$ are found, we can calculate other thermodynamic functions, for example

$$\Delta H = \left(\sum_{n=1}^{N}\Delta_{\rm f}H_n\cdot x_n\right)\Bigg/\left(1 + \sum_{n=1}^{N}(i_n + j_n - 1)x_n\right).$$

We used the programs developed in our laboratory to calculate the thermodynamic properties from the given $\Delta_{\rm f}H_n^{\rm liq}$ and $\Delta_{\rm f}S_n^{\rm liq}$ parameters, as well as to optimize these parameters in order to achieve the best approximation of the thermodynamic properties to the experimental data.

To describe the thermodynamic properties of the In–Yb system, we chose a model accounting for formation of 4 associates: $\rm YbIn_3$, $\rm YbIn_2$, YbIn, $\rm Yb_2In$. All of them have rather simple composition (no more than 4 atoms), and correspond to the compounds existing in the solid alloys. The obtained parameters of the IAS model for the In–Yb system are presented in Table 3.

Most solid phases were treated as stoichiometric, and only for the β-Yb, γ-Yb, and YbIn phases homogeneity ranges were described by introducing the con-

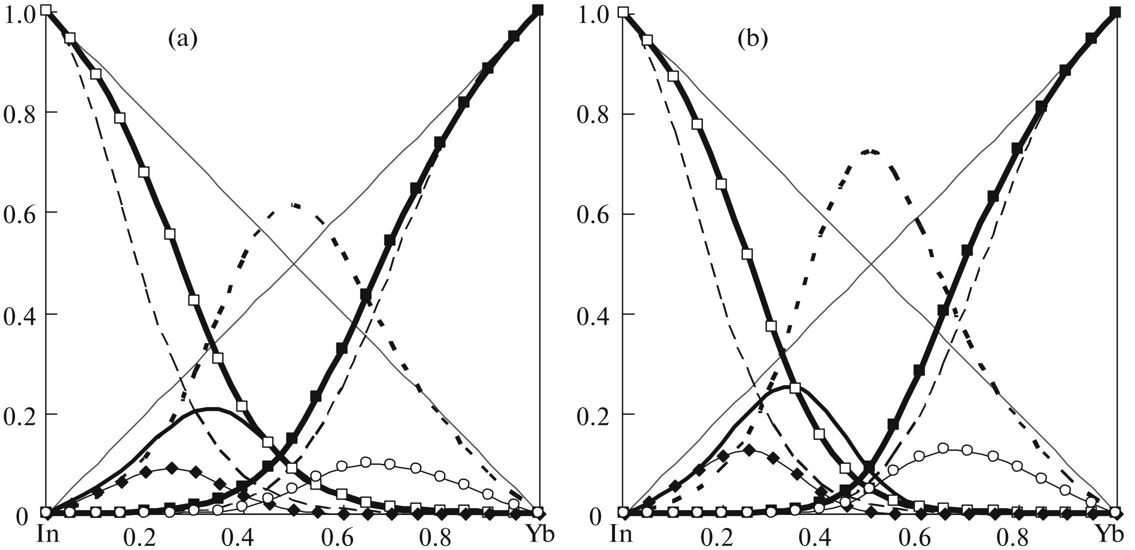

**Fig. 2.** Activities of the pure components ($a_i$: —□— In, —■— Yb) and molar fractions of the associates ($x_i$: —◆— $YbIn_3$, —— $YbIn_2$, - - - YbIn, —○— $Yb_2In$) in the In–Yb melts (including undercooled) at (a) 1350 and (b) 1160 K, according to the obtained IAS model; — — assessed $a_i$ from [8].

centration dependences of the Gibbs energies of formation (kJ/mol, $x \equiv x_{Yb}$):

$$\begin{aligned} G_{(\gamma-\mathrm{Yb})} &= (1-x)G_{\mathrm{In}}^{T} + xG_{\mathrm{Yb}}^{T} \\ &+ RT\left(x\ln x + (1-x)\ln(1-x)\right) \\ &+ (-114 + 0.035T)(1-x) + 2000(1-x)^{2}, \end{aligned}$$

$$\begin{aligned} G_{(\beta-\mathrm{Yb})} &= (1-x)G_{\mathrm{In}}^{T} + xG_{\mathrm{Yb}}^{T} \\ &+ RT\left(x\ln x + (1-x)\ln(1-x)\right) \\ &+ (-114 + 0.035T)(1-x) + 2200(1-x)^{2}, \end{aligned}$$

$$G_{\mathrm{YbIn}} = \begin{cases} (1-x)G_{\mathrm{In}}^{T} + xG_{\mathrm{Yb}}^{T} - 49 + 0.015T; \\ x < 1/2, \\ (1-x)G_{\mathrm{In}}^{T} + xG_{\mathrm{Yb}}^{T} - 49 + 0.015T \\ + (27.5 - 0.0127T)(x - 1/2) \\ + 720(x - 1/2)^{2}; \quad x > 1/2. \end{cases}$$

The enthalpies and entropies of formation of all associates and intermetallics were assumed independent on temperature.

It is evident from Fig. 1 that the IAS model effectively describes the experimental values of partial and integral enthalpies of mixing, including their temperature dependences. Our results are also quite close to the assessment [8], particularly in the fields of dilute solutions from both sides ($0 < x_{Yb} < 0.1$ and $0.9 < x_{Yb} < 1$). However, in the middle range of concentrations, the integral enthalpies of mixing obtained by us demonstrate more pronounced and sharp minimum than those predicted in [8]. This is explained with taking account for association of the components, which is especially intensive at equiatomic composition (the YbIn associate).

The calculated activities of components (Fig. 2) show significant negative deviations from the Raoult's law, which become even stronger at low temperatures. As well as the mixing enthalpies of the melts, they are characterized by slightly asymmetric shape, with the minima of $\Delta H$ and $\Delta G$ shifted towards indium. According to the IAS model, the greatest concentrations are observed for the simplest associate, YbIn.

According to IAS model, the temperature dependences of partial mixing enthalpies, Gibbs energies and entropies of the components of the In–Yb liquid alloys at infinite dilution (Fig. 3) is characterized by slow tendency to ideality at higher temperatures, which is in agreement with the general regularities [21].

The Gibbs energies of mixing of the In–Yb melts are less negative, and the entropies of mixing are more negative values, than those assessed in [8] (Fig. 4). The enthalpy of formation of the $YbIn_3$ compound agrees with the values given in [8, 11] (Fig. 5).

The calculated liquidus and solidus curves (or polylines) of the phase diagram (Fig. 6, Table 4) agree well with given in literature [4, 8] over the most part of concentration range. The substitution [4, 8] of the $Yb_5In_2$ compound towards the updated [5, 6] formula $Yb_8In_3$ changed its melting type from peritectic to congruent. However, this had almost no effect on the reproduction of experimental temperatures of invariant reactions.The homogeneity ranges of solid phases are also well described by our model. The liquidus

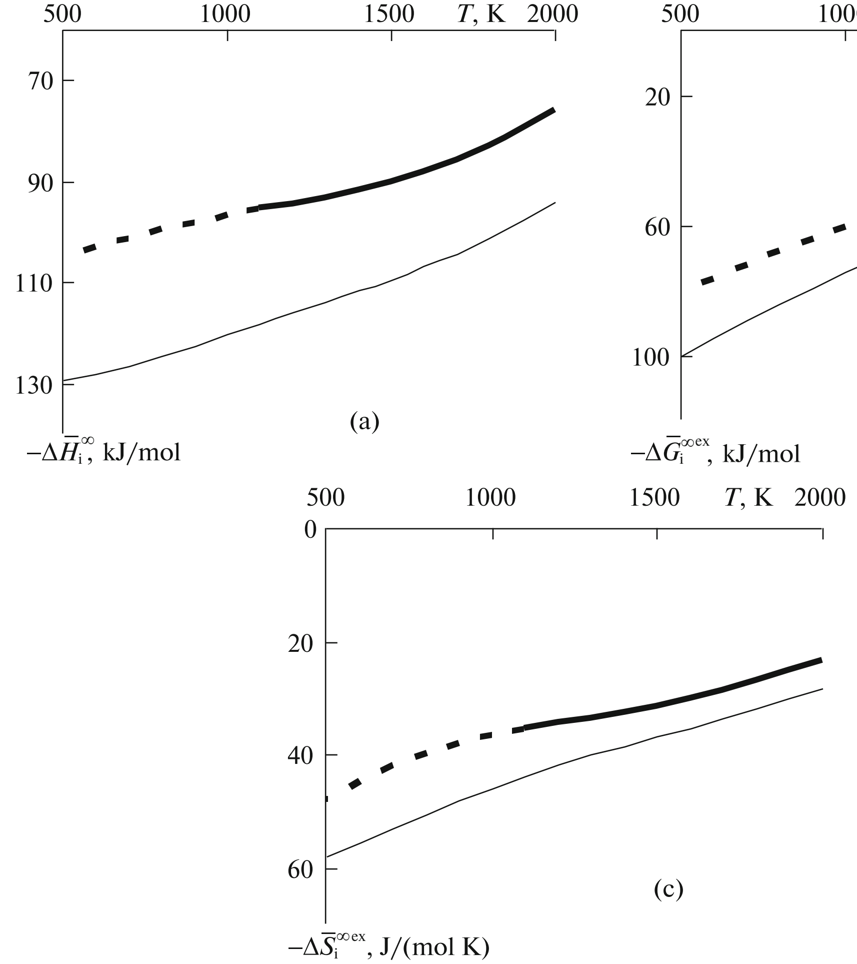

**Fig. 3.** Dependences of partial enthalpies (a), excess Gibbs energies (b), and excess entropies (c) of the components of the In–Yb melts at infinite dilution (▬▬ In in Yb, —— Yb in In, ▪ ▪ ▪ In in undercooled Yb) on temperature, according to the IAS model.

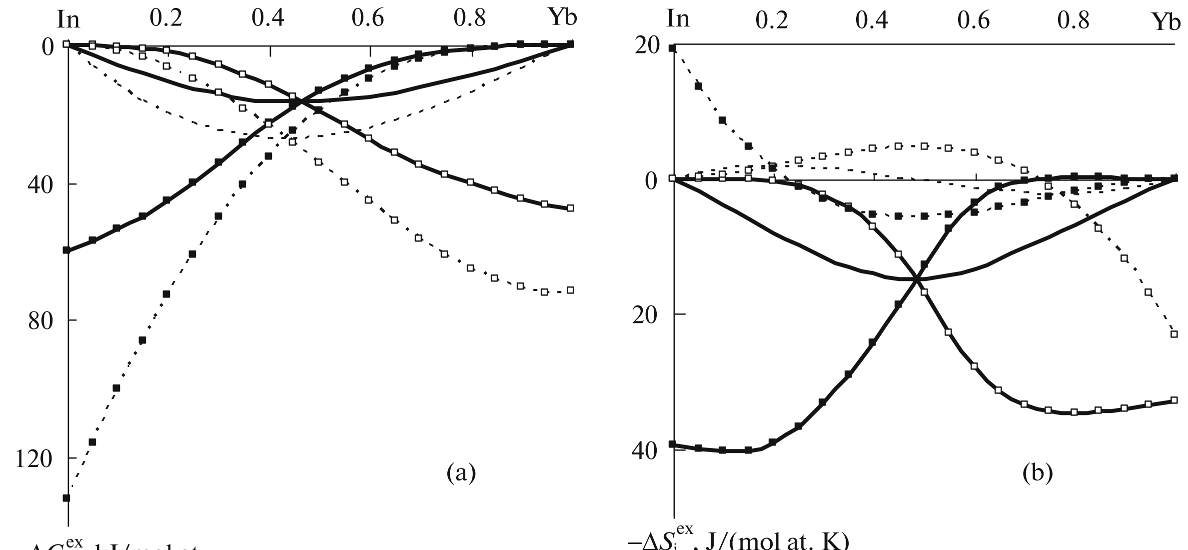

**Fig. 4.** Partial and integral mixing Gibbs energies (a) and entropies (b) of the In–Yb melts at 1350 K, calculated using the IAS model (—— $\Delta G^{ex}$, $\Delta S^{ex}$, —□— $\Delta\overline{G}^{ex}_{In}$, $\Delta\overline{S}^{ex}_{In}$, (—■— $\Delta\overline{G}^{ex}_{Yb}$, $\Delta\overline{S}^{ex}_{Yb}$); assessment [8] (----- $\Delta G^{ex}$, $\Delta S^{ex}$, --□-- $\Delta\overline{G}^{ex}_{In}$, $\Delta\overline{S}^{ex}_{In}$, --■-- $\Delta\overline{G}^{ex}_{Yb}$, $\Delta\overline{S}^{ex}_{Yb}$).

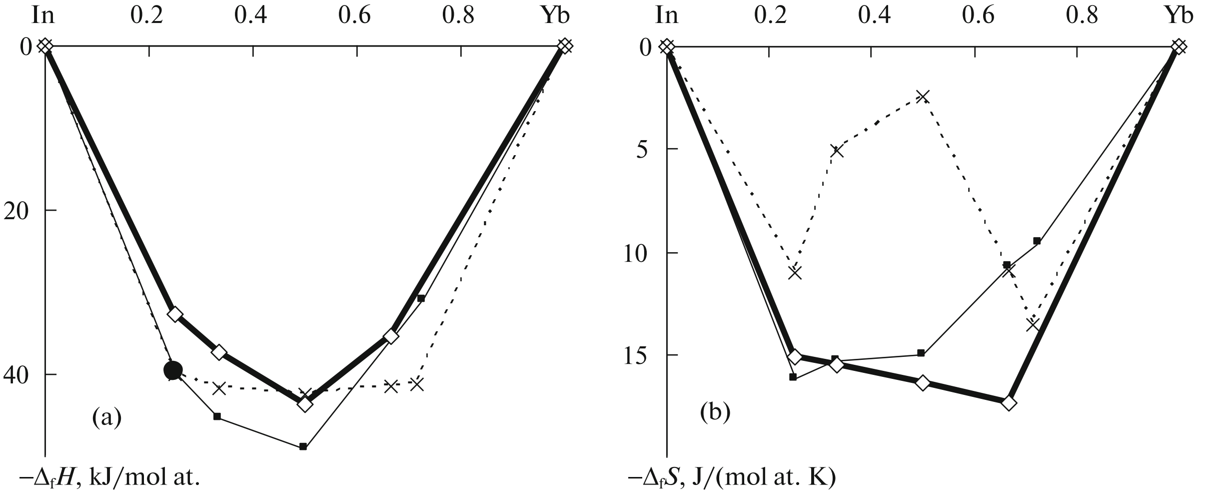

**Fig. 5.** Enthalpies (a) and entropies (b) of formation of the associates in the melts (▬◇▬) and intermetallics (—■—) in the In–Yb system, according to our optimized thermodynamic model, and data from literature: ● [11], calorimetry; - -×- - [8], CALPHAD assessment.

**Table 4.** Invariant liquidus points of the phase diagram of the In–Yb system (IAS = ideal associated solution model)

| Reaction | $x_{\mathrm{Yb}}^{\mathrm{liq}}$, at % | $x_{\mathrm{Yb}}^{\mathrm{sol_1}}$, at % | $x_{\mathrm{Yb}}^{\mathrm{sol_2}}$, at % | $T$, K | Reaction type | Reference or model |
|---|---|---|---|---|---|---|
| Liq = In + $\mathrm{YbIn_3}$ | <1 | 0 | 25 | 427 | Eutectic | [4] |
| | 0.03 | ″ | ″ | 429 | | [8] |
| | 0.015 | ″ | ″ | 429.7 | | IAS |
| Liq + $\mathrm{YbIn_2}$ = $\mathrm{YbIn_3}$ | 13.5 | 25 | 33.3 | 903 | Peritectic | [4] |
| | 16.7 | ″ | ″ | 903 | | [8] |
| | 14.8 | ″ | ″ | 903 | | IAS |
| Liq = $\mathrm{YbIn_2}$ | 33.3 | 33.3 | | 1163 | Congruent | [4] |
| | ″ | ″ | | 1158 | | [8] |
| | ″ | ″ | | 1158 | | IAS |
| Liq = $\mathrm{YbIn_2}$ + YbIn | 37 | 33.3 | 50 | 1148 | Eutectic | [4] |
| | 36.7 | ″ | ″ | 1153 | | [8] |
| | 36.1 | ″ | ″ | 1152 | | IAS |
| Liq = YbIn | 50 | 50 | | 1340 | Congruent | [4] |
| | ″ | ″ | | 1339 | | [8] |
| | 50.1 | 50.1 | | 1341 | | IAS |
| Liq + YbIn = $\mathrm{Yb_2In}$ | 72 | 53 | 66.7 | 1093 | Peritectic | [4] |
| | 69.9 | 52.3 | ″ | 1093 | | [8] |
| | 70.0 | 52.9 | ″ | 1093 | | IAS |
| Liq + $\mathrm{Yb_2In}$ = $\mathrm{Yb_5In_2}$ | 75 | 66.7 | 71.4 | 1083 | Peritectic | [4] |
| Liq + $\mathrm{Yb_2In}$ = $\mathrm{Yb_8In_3}$ | 75 | ″ | 72.7 | 1083 | | [6] |
| Liq + $\mathrm{Yb_2In}$ = $\mathrm{Yb_5In_2}$ | 71.7 | ″ | 71.4 | 1083 | | [8] |
| Liq = $\mathrm{Yb_2In}$ + $\mathrm{Yb_8In_3}$ | 72.2 | 66.7 | 72.7 | 1081.5 | Eutectic | IAS |
| Liq = $\mathrm{Yb_8In_3}$ | 72.7 | 72.7 | | 1081.6 | Congruent | IAS |
| Liq = $\mathrm{Yb_5In_2}$ + (β-Yb) | 88.5 | 71.4 | 99 | 963 | Eutectic | [4] |
| Liq = $\mathrm{Yb_8In_3}$ + (β-Yb) | 88.5 | 72.7 | 99 | 963 | | [6] |
| Liq = $\mathrm{Yb_5In_2}$ + (β-Yb) | 90 | 71.4 | 98.6 | 963 | | [8] |
| Liq = $\mathrm{Yb_8In_3}$ + (β-Yb) | 88.7 | 72.7 | 99.3 | 964 | | IAS |
| (γ-Yb) = Liq + (β-Yb) | 95 | 98 | 98.5 | 1023 | Catatectic | [4] |
| | 94 | 99 | 99.2 | 1023 | | [8] |
| | 93.2 | 99.3 | 99.4 | 1023 | | IAS |

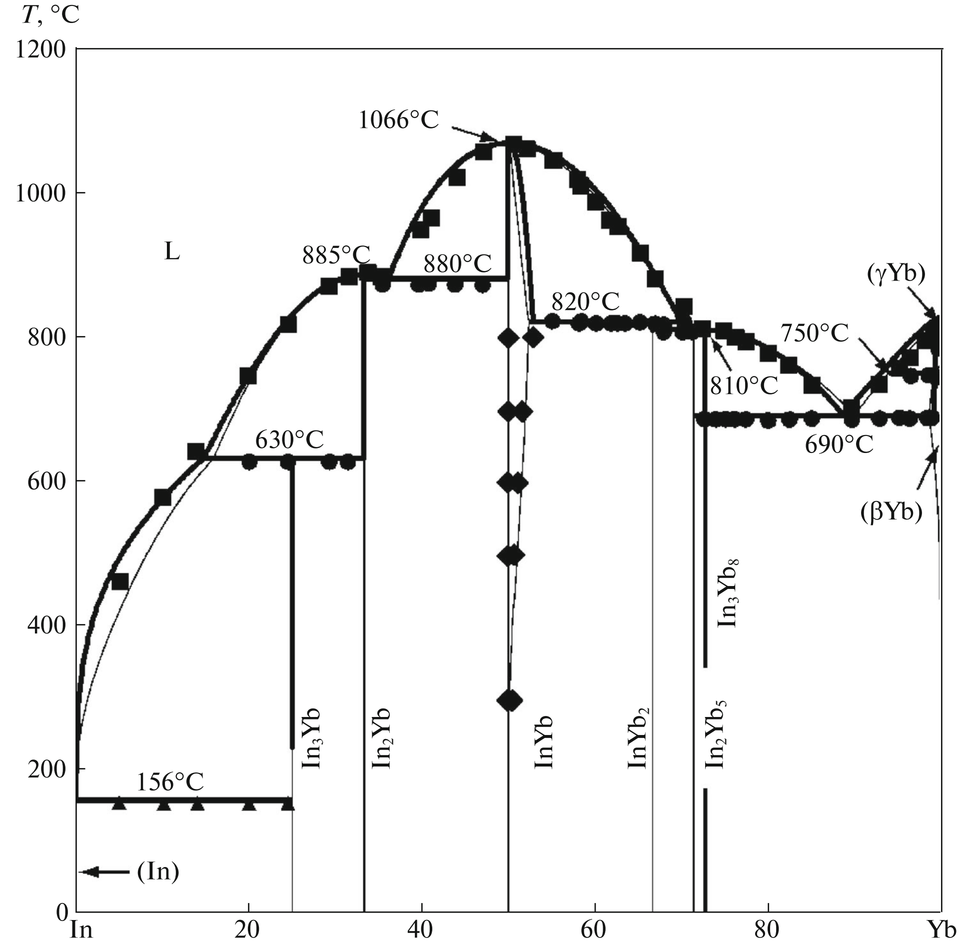

**Fig. 6.** Modeled phase diagram of the In–Yb system (liquidus and solidus are bold curves/polylines) compared to the data from literature—experimental ([4]: ●—thermal effects at heating and cooling, ▲—at heating, ■—liquidus, ◆—results of X-ray diffraction analysis), and the CALPHAD assessment [8] (thin curves).

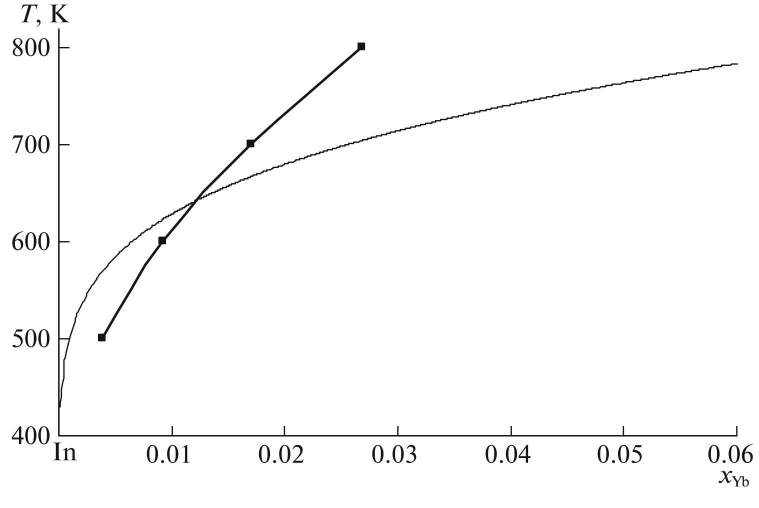

**Fig. 7.** Liquidus curve (the melt–YbIn$_3$ equilibrium) for alloys rich in indium, according to our calculation (——) and the data [9] (–▪–).

curve over the range $0 < x_{Yb} < 0.06$, $500 K < T < 800 K$ agrees with the data [9] around the middle of that temperature range, but goes less steeply (Fig. 7).

To sum up, the enthalpies of mixing of the In–Yb liquid alloys are great negative values over the whole range of concentrations. The activities of the components, the Gibbs energies and entropies of mixing of the alloys of this system, and its phase diagram, all calculated using the IAS model, agree with most literature data. The optimized thermodynamic model of the In–Yb alloys over the wide ranges of temperature and concentration predominantly confirms the results of earlier modeling [8]; however, its reliability has been additionally trusted with the new experimental data.

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