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Thermodynamic properties of liquid germanium–yttrium alloys

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Abstract

Partial enthalpy of mixing of yttrium ($\Delta_{\text{mix}}\bar{H}_{\text{Y}}$) in the Ge–Y system was measured at 1770 K using a new high-temperature mixing calorimeter. Literature data on the enthalpies of mixing in the Ge–Y system and results of present examination were compared and discussed. Temperature dependence of $\Delta_{\text{mix}}\bar{H}_{\text{Y}}$ was estimated based on comparative analysis of the enthalpies of mixing, and corresponding heat capacity change at alloy formation was evaluated. Polynomial equations approximating thermodynamic functions ($\Delta_{\text{mix}}\bar{H}_{\text{Y}}$, $\Delta_{\text{mix}}H$, $\Delta_{\text{mix}}\bar{C}_{p,\text{Y}}$, and $\Delta_{\text{mix}}C_p$) versus yttrium mole fraction were determined. Some trends observed in the thermodynamic properties of the Ge–Y alloys were described.

Keywords: Ge–Y; Calorimetry; Thermodynamics; Mixing enthalpy; Liquid alloys

1. Introduction

Magnetic refrigeration, operating with solid magnetic materials as the cooling agents, makes freezing considerably more effective and environmentally safer compared to conventional vapor-cycle refrigeration, because no chlorofluorcarbones destroying ozonosphere are used. The principle of magnetic refrigeration is based on application of magnetocaloric effect (MCE), i.e. the ability of magnetic materials to change their entropy or temperature in the isothermal or adiabatic magnetising-demagnetising cycles, respectively [1]. The MCE can be increased considerably when it is coupled to a phase transition accompanied by the change of the magnetic properties of a material. In this case, significant contribution into the entropy change is achieved by the field-induced transformation [1]. Large MCE's have been reported recently, in particular for $\text{MnFeP}_{0.45}\text{As}_{0.55}$ [2], $\text{LaFe}_{11.7}\text{Si}_{1.3}$ [3] and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [4,5] alloys. The $\text{Y}_5\text{Si}_x\text{Ge}_{4-x}$ ($x = 3.5$–4) alloys with the monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$-type structure were reported in [6]. Consequently, the temperature of the giant MCE in the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ can be tuned through a partial substitution of the Gd by a nonmagnetic Y [6,7].

Therefore, the examination of quaternary Gd–Ge–Si–Y alloys as well as of the corresponding ternary and binary systems are of special interest for creation of new alloys with the MCE. Previously, the Gd–Si system was studied by calorimetry [8]. In the present work, we continue the examination of the binary boundaries of the Gd–Ge–Si–Y system and represent analysis of enthalpies of mixing in the Ge–Y alloys.

Phase diagram of the Ge–Y system is characterized by several refractory intermetallics. The germanides Y_5Ge_3, Y_5Ge_4 melt congruently at 2238 K and 2218 K, while the $\text{Y}_{11}\text{Ge}_{10}$ and YGe melt incongruently at 2173 K and 2003 K, respectively [9,10]. The refractory yttrium germanides make the liquid alloys examination too complicated for $0.4 < x_{\text{Y}} < 0.8$. Thus, a number of thermodynamic examinations have been performed by high temperature calorimetry only for $0.0 < x_{\text{Y}} < 0.46$ [11–14] and for $0.8 < x_{\text{Y}} < 1.0$ [12–14]. The data comparison is shown on Figs. 1 and 2. Nikolaenko and co-authors have measured the $\Delta_{\text{mix}}\bar{H}_{\text{Y}}$ for $0.0 < x_{\text{Y}} < 0.235$ at 1523 K [11] and for $0.0 < x_{\text{Y}} < 0.423$ at 1900 K [12,13]. The $\Delta_{\text{mix}}\bar{H}_{\text{Ge}}$ was also measured in

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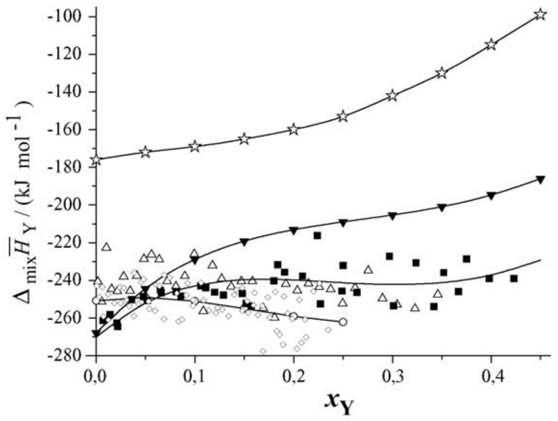

Fig. 1. Plot of partial enthalpy of mixing of yttrium against mole fraction of yttrium; literature data: (◊) data of [11] at 1523 K; (–○–) smoothed data of [11]; (–▼–) smoothed data of [12] at 1900 K; (■) data of [13] at 1900 K; (—) smoothed data of [13]; (–☆–) smoothed data of [14] at 1920 K; (△) our experimental data at 1770 K.

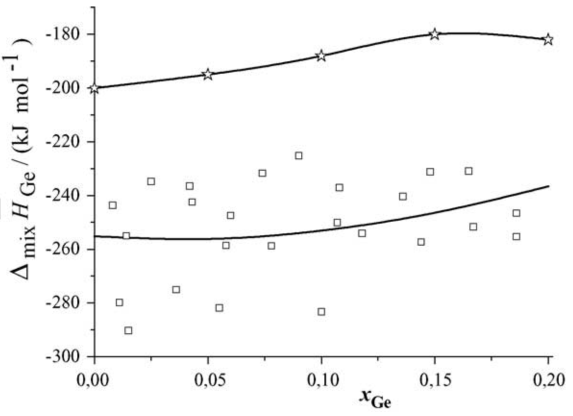

Fig. 2. Plot of partial enthalpy of mixing of germanium against mole fraction of germanium: (□) data of [12,13] at 1900 K; (—) smoothed data of [12,13]; (–☆–) smoothed data of [14] at 1920 K.

[12,13] for $0.0 < x_{Ge} < 0.186$ at 1900 K. Esin et al. have measured the $\Delta_{mix}\overline{H}_Y$ for $0.0 < x_Y < 0.46$ and the $\Delta_{mix}\overline{H}_{Ge}$ for $0.0 < x_{Ge} < 0.2$ at 1920 K [14]. The data of [14] are significantly less negative than those of [11–13]. Moreover, the $\Delta_{mix}\overline{H}_Y$ data reported in [12] and [13] for $T = 1900$ K are different. The present examination has been performed to critically analyze the literature data on the enthalpies of mixing and to determine temperature dependence of the $\Delta_{mix}H$.

2. Experimental

2.1. Materials

The germanium, yttrium and tungsten, which was used as a reference material, are applied in calorimetric studies. The germanium (Alfa-Aesar, 99.9999%), yttrium distillate (Dahuachem, 99.97%) and reference material, i.e. tungsten (Alfa-Aesar, 99.96%) were used for the experiments. High-purity argon (NII KM Ltd., Russia, Moscow, 99.997 vol.%) was used as inert atmosphere in the calorimeter's internal volume.

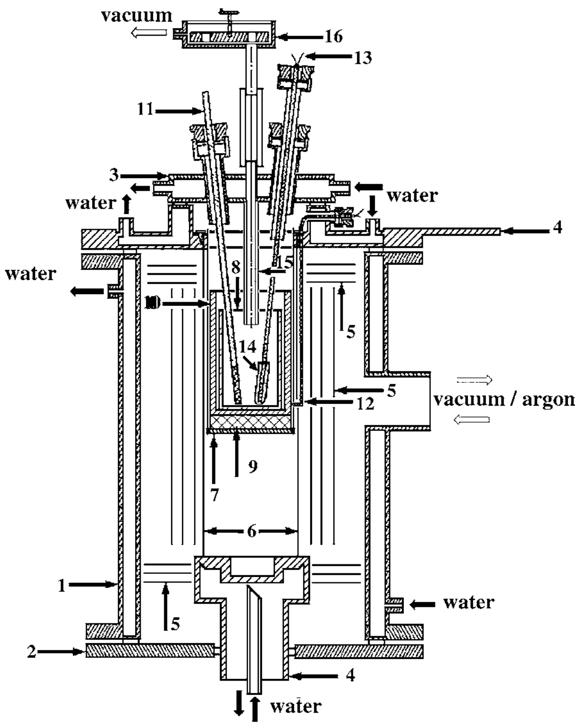

Fig. 3. The schematic of the calorimeter's principal part: (1) water-cooled jacket, (2) lower cover, (3) upper water-cooled cover, (4) water-cooled current leads, (5) reflecting shields, (6) tungsten heater, (7) niobium hanger, (8) alumina crucible, (9) boron–aluminum nitride gasket, (10) molybdenum block, (11) stirrer, (12) controlling W–Re 5/20 type thermocouple, (13) measuring W–Re 5/20 type thermocouple, (14) zirconia protector, (15) alumina tube, (16) revolving container.

2.2. Apparatus

The apparatus construction is similar to the high-temperature mixing calorimeter for determination of the enthalpies of mixing at temperatures up to 1900 K briefly discussed in [15]. The schematic of the calorimeter's principal part is drawn in Fig. 3.

The calorimeter is based on a vacuum resistant furnace providing 5–10 kW output powered through a reducing transformer (OSU-40/0.5 of Elecar Ltd., Russia). The transformer primary coil voltage is applied through thyristor converter (RNTO-190-250 of Electroproject Ltd., Russia). High temperature in the calorimeter is maintained by a cylindrical tungsten heater (6) constructed of Ø = 2 mm rods. The heater ($h = 310$ mm, Ø = 90 mm) is mounted on a copper water-cooled current leads (4). The block of coaxial molybdenum shields (5), made of 0.5 mm foil, surrounds the heater to minimize radiative heat losses. A massive molybdenum crucible-like block (10) hangs in the central part of the heater. High thermal conductivity and mass of the block smooth-out temperature fluctuations, in that way a volume of isotropic thermal field is formed in the central part of the massive block. An alumina crucible with alloy under examination (8) is placed in the volume mentioned. The alumina crucible is lined with Y_2O_3 to prevent chemical reactions of the alloy with the crucible material. A stirrer (11) and measuring thermocouple (13) of W-Re 5/20 type covered by zirconia protector (14) are inserted into the calorimetric crucible. Controlling thermocouple of W-Re 5/20 type (12) is situated into a closed aperture of the massive block. The cold ends of the thermocouples (12) and (13) are thermostated at 273 K. Samples are dropped into the liquid bath from a revolving container (16) through the alumina tube (15). The stirrer (11), thermocouple (13) and alumina tube (15) are fixed on the upper water-cooled cover (3).

Constructional materials and substances under study react actively with air oxygen at high temperatures. Thus, it is necessary to protect the calorimetric room with vacuum before measurements. Vacuumization is performed using a vacuum line of an oil-diffusion pump (N-05(2) of Promtekhservis Ltd., Russia) and a mechanical vacuum pump (2NVR-5DM of "NPO Technocom", Yekaterinburg, Russia). The vacuum is monitored by vacuum ionization thermocouple gage (VIT-3, "Automatika", Smolensk, Russia). Residual pressure in the calorimeter under vacuumization is less then 0.005 Pa. The high-purity argon fill the calorimetric room at temperature 50–100 K below the initial component melting to prevent evaporation from the crucible.

The temperature is monitored by PID-controller. The PID-controller compares a signal from the thermocouple (12) with the predetermined one and generates an electric signal. This signal transforms to a leading signal for the thyristor converter. The thyristor converter, in turn, operates with current of the reducing transformer primary coil. The temperature drift during operation is not more than 0.5 K.

The pure samples dropping into the calorimetric bath and subsequent dissolution of components lead to fluctuation in temperature of the melt. The difference in signals between thermocouples (12) and (13), which corresponds to the temperature fluctuation in the crucible, is registered by KEITHLEY multimeter and stored in a PC in the form of e.m.f. versus time dependences using a specially developed software.

2.3. Measurements technique and data treatment

The temperature of calorimetric bath was 1770 K and the samples in the revolving container were stored at $T = 298$ K. The measurements were performed under argon at atmospheric pressure. Dropping of germanium samples into the molten germanium performed a first calorimeter calibration. After that weighted samples of Y were dropped up to yttrium mole fraction (x_Y) in the binary alloy being 0.35. After the mixing experiment, the W samples were added into the melt for final calorimeter calibration. The absence of interaction between tungsten and the melt was controlled by mass analysis after the ingots were cooled and cut.

The heat-exchange coefficient of the calorimeter was calculated using the formula

$$k_i = \Delta H_{298}^{\mathrm{T}} \frac{n_i}{S_i}, \tag{1}$$

where $\Delta H_{298}^{\mathrm{T}}$ is the standard enthalpy of component heating from 298.15 K up to the experimental temperature [16], i is the dropped sample number, n_i is the mole quantity of the dropped sample, S_i is the area of heat-exchange peak on the e.m.f. versus time curve. The k_i values were treated by the least square regression (l.s.r.) using a linear model

$$k = a + bm_{\mathrm{alloy}}, \tag{2}$$

where m_{alloy} is the current alloy mass in the crucible, a and b are the l.s.r. coefficients. The partial enthalpy of mixing was calculated from the experimental heat-exchange curves by the formula

$$\Delta_{\mathrm{mix}} \bar{H}_{\mathrm{Y}} = -\Delta H_{298}^{\mathrm{T}} + k \frac{S_i}{n_i}. \tag{3}$$

The values of the $\Delta_{\mathrm{mix}} \bar{H}_{\mathrm{Y}}$ were assigned to the middle point of the composition range before and after sample addition. The experimental partial enthalpy of mixing was expressed via an alpha function

$$\alpha_{\mathrm{Y}} = \frac{\Delta_{\mathrm{mix}} \bar{H}_{\mathrm{Y}}}{(1 - x_{\mathrm{Y}})^2}, \tag{4}$$

The alpha function, in turn, was smoothed using l.s.r. for the polynomial equation:

$$\alpha_{\mathrm{Y}} = \sum_{j=0}^{l} Q_j x_{\mathrm{Y}}^j, \tag{5}$$

where Q_i are the polynomial coefficients and l is the polynomial order determined by the Fisher's exact test.

The concentration dependence of $\Delta_{\mathrm{mix}} \bar{H}_{\mathrm{Y}}$ can be then represented via equation

$$\Delta_{\mathrm{mix}} \bar{H}_{\mathrm{Y}} = (1 - x_{\mathrm{Y}})^2 \sum_{j=0}^{l} Q_j x_{\mathrm{Y}}^j. \tag{6}$$

Calculation of the integral enthalpy of mixing was performed by the Darken's method

$$\Delta_{\mathrm{mix}} H = (1 - x_{\mathrm{Y}}) \int_0^{x_{\mathrm{Y}}} \alpha_{\mathrm{Y}} \, \mathrm{d}x_{\mathrm{Y}}. \tag{7}$$

After substitution of Eq. (5) into Eq. (7) and integration, one gets

$$\Delta_{\mathrm{mix}} H = x_{\mathrm{Y}}(1 - x_{\mathrm{Y}}) \sum_{j=0}^{l} (j+1)^{-1} Q_j x_{\mathrm{Y}}^j. \tag{8}$$

The deviations of integral enthalpy of mixing were determined as proposed in [17].

$$\sigma(\Delta_{\mathrm{mix}}H) = (1 - x_{\mathrm{Y}})\left(x_{\mathrm{Y}}\int_0^{x_{\mathrm{Y}}} D(\alpha_{\mathrm{Y}})\,\mathrm{d}x_{\mathrm{Y}}\right)^{1/2}, \tag{9}$$

where $D(\alpha_{\mathrm{Y}})$ is dispersion of the alpha function. Confidence intervals were calculated from deviations of appropriate functions as $t\sigma$, where t is the Student's coefficient for a 0.95 confidence level, which is equal to 2.

Extrapolation of the $\Delta_{\mathrm{mix}}H$ determined for two distinct concentration regions into the area of undercooled liquid alloys was preformed by statistical treatment of ζ-function ($\zeta = \Delta_{\mathrm{mix}}H/(x_{\mathrm{Y}}x_{\mathrm{Ge}})$) via polynomial model

$$\zeta = \sum_{j=0}^{l} Q'_j x_{\mathrm{Y}}^j. \tag{10}$$

3. Results and discussion

The results of our calorimetric measurements are listed in Table 1. The experimental $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ data scatter is shown on the Fig. 1 as open triangles. As one can see, our data at 1770 K are somewhat less negative than the $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ values measured at 1523 K [11]. On the other hand, our data are in a good agreement with $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ measured in [13] at 1900 K and more negative than the data of [12] at 1900 K. It should be noted, that the data reported in [12,13] refer to the same experiment. But, the coefficients in the Eq. (2) were defined more precisely in [13]. It should be mentioned that the data reported in [14] are too positive in comparison with the whole set [11–13].

With respect to the analyzed data, the $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ becomes less negative with temperature increase from $T = 1523$ K to 1770 K and remains practically unchanged with subsequent temperature increase up to 1900 K [13]. This fact can be explained as follows. A short-range ordering of chemical compound-type remains in liquid phase at melting of intermetallides. This leads to significant negative $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ values. The short-range ordering is destructed at subsequent heating of the melt. Consequently, the solution tends to be more ideal and $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ values decreases by absolute value. At further heating, when the short-range ordering is destructed, the temperature dependence of $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ becomes weaker.

Referring to the temperature dependence of $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ in the interval of 1523–1770 K, one can estimate heat capacity change at yttrium dissolution in the Ge–Y alloy ($\Delta_{\mathrm{mix}}\bar{C}_{p,\mathrm{Y}}$) at average temperature of 1646 K:

$$\Delta_{\mathrm{mix}}\bar{C}_{p,\mathrm{Y}} = \frac{\mathrm{d}\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}}{\mathrm{d}T} \approx \frac{\Delta\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}}{\Delta T}. \tag{11}$$

Table 1
Results of calorimetric study of the Ge–Y system

Added substance	Added amount (m_i) (g)	S_i (arb. units)	x_{Y}	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ (kJ mol^{-1})
Ge	0.2142	0.03655		
	0.1498	0.02406		
	0.1957	0.03186		
	0.1125	0.01820		
	0.2219	0.03697		
	0.1536	0.02542		
	0.2451	0.04002		
	0.1774	0.02996		
Y	0.0155	−0.00490	0.0017	−240.68
	0.0203	−0.00679	0.0056	−251.37
	0.0241	−0.00686	0.0104	−222.69
	0.0264	−0.00851	0.0158	−244.62
	0.0285	−0.00927	0.0216	−245.74
	0.0309	−0.00960	0.0278	−237.89
	0.0331	−0.01078	0.0344	−245.55
	0.0348	−0.01078	0.0413	−237.52
	0.0371	−0.01096	0.0485	−228.55
	0.0399	−0.01160	0.0561	−226.31
	0.0405	−0.01197	0.0639	−228.88
	0.0445	−0.01404	0.0720	−240.46
	0.0484	−0.01556	0.0807	−243.14
	0.0517	−0.01609	0.0899	−237.66
	0.0528	−0.01533	0.0993	−225.95
	0.0527	−0.01818	0.1086	−256.29
	0.0550	−0.01658	0.1179	−232.01
	0.0551	−0.01729	0.1272	−239.05
	0.0598	−0.01924	0.1367	−243.23
	0.0676	−0.02143	0.1470	−240.54
	0.0732	−0.02320	0.1581	−240.44
	0.0740	−0.02536	0.1694	−254.77
	0.0772	−0.02716	0.1807	−259.66
	0.0810	−0.02593	0.1922	−241.93
	0.0818	−0.02669	0.2037	−245.29
	0.0844	−0.02697	0.2151	−241.67
	0.0791	−0.02559	0.2260	−243.60
	0.0983	−0.03203	0.2375	−244.69
	0.0943	−0.03197	0.2496	−252.20
	0.1130	−0.03672	0.2622	−244.05
	0.1154	−0.03556	0.2756	−234.77
	0.1379	−0.04621	0.2899	−249.53
	0.1370	−0.04680	0.3048	−252.97
	0.2132	−0.07369	0.3229	−255.01
	0.2598	−0.08641	0.3459	−247.51
W	0.4293	0.01554		
	0.5147	0.01810		
	0.6381	0.02311		
	0.4972	0.01719		

The starting mass of the initial component in the crucible is 2.2483 g, the coefficients of Eq. (2) are $a = 6.45676$, $b = -0.03432$.

The $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ measured in the present work at 1770 K can be expressed as follows (in kJ mol^{-1})

$$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}} = (1 - x_{\mathrm{Y}})^2(-241.14 - 347.19x_{\mathrm{Y}} - 1816.62x_{\mathrm{Y}}^2), \tag{12}$$

Table 2
The enthalpies of mixing at 1770 K and 1523 K [11], and heat capacity change at alloy formation at 1646 K

x_{Y}	Presented data at 1770 K			Ref. [11] at 1523 K			Heat capacity change at alloy formation at 1646 K		
	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}} \pm 2\sigma$ (kJ mol^{-1})	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Ge}}$ (kJ mol^{-1})	$\Delta_{\mathrm{mix}}H \pm 2\sigma$ (kJ mol^{-1})	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}} \pm 2\sigma$ (kJ mol^{-1})	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Ge}}$ (kJ mol^{-1})	$\Delta_{\mathrm{mix}}H \pm 2\sigma$ (kJ mol^{-1})	$\Delta_{\mathrm{mix}}\bar{C}_{p,\mathrm{Y}}$ (J mol^{-1} K^{-1})	$\Delta_{\mathrm{mix}}\bar{C}_{p,\mathrm{Ge}}$ (J mol^{-1} K^{-1})	$\Delta_{\mathrm{mix}}C_p$ (J mol^{-1} K^{-1})
0.00	−241.1 ± 8.7	0.0	0.0	−250.0 ± 8.1	0.0	0.0	35.99	0.0	0.0
0.05	−237.4 ± 4.5	−0.072	−11.94 ± 0.34	−248.4 ± 3.6	−0.021	−12.44 ± 0.30	44.40	−0.21	2.02
0.10	−238.2 ± 3.9	0.007	−23.81 ± 0.58	−250.6 ± 3.6	0.18	−24.90 ± 0.52	50.54	−0.70	4.43
0.15	−241.4 ± 4.0	0.48	−35.80 ± 0.79	−254.9 ± 3.0	0.79	−37.56 ± 0.69	54.62	−1.27	7.11
0.20	−245.3 ± 3.5	1.30	−48.01 ± 0.98	−259.3 ± 3.3	1.73	−50.48 ± 0.86	56.83	−1.73	9.98
0.25	−248.3 ± 3.1	2.18	−60.45 ± 1.13						
0.30	−249.3 ± 3.8	2.53	−73.02 ± 1.32						
0.35	−247.2 ± 5.7	1.50	−85.56 ± 1.72						

correspondingly,

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Y}}(1 - x_{\mathrm{Y}})(-241.14 - 173.60x_{\mathrm{Y}} - 605.54x_{\mathrm{Y}}^2). \tag{13}$$

The $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ data, which are reported in [11] at 1523 K, can be represented through the alpha function by a third order polynomial dependence with the third term equal to $-1816.62x_{\mathrm{Y}}^2$ (in kJ mol^{-1}):

$$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}} = (1 - x_{\mathrm{Y}})^2(-250.03 - 412.41x_{\mathrm{Y}} - 1816.62x_{\mathrm{Y}}^2). \tag{14}$$

The corresponding $\Delta_{\mathrm{mix}}H$ function can be derived by the following equation (in kJ mol^{-1})

$$\Delta_{\mathrm{mix}}H = x_{\mathrm{Y}}(1 - x_{\mathrm{Y}})(-250.03 - 206.21x_{\mathrm{Y}} - 605.54x_{\mathrm{Y}}^2). \tag{15}$$

By substitution of Eqs. (12) and (14) into Eq. (11), the following expressions can be derived (in J mol^{-1} K^{-1})

$$\Delta_{\mathrm{mix}}\bar{C}_{p,\mathrm{Y}} = (1 - x_{\mathrm{Y}})^2(35.99 + 264.05x_{\mathrm{Y}}), \tag{16}$$

$$\Delta_{\mathrm{mix}}C_p = x_{\mathrm{Y}}(1 - x_{\mathrm{Y}})(35.99 + 132.02x_{\mathrm{Y}}). \tag{17}$$

The partial and integral enthalpies of mixing with confidence intervals and calculated heat capacity change at alloy formation calculated by Eqs. (12–17) are listed in Table 2.

Since, the $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ is practically constant in the temperature interval from 1770 K to 1900 K, it is reasonable to treat our data and data of [13] together and to extrapolate the enthalpies of mixing on the whole concentration range. The following equations have been derived (in kJ mol^{-1})

$$\begin{aligned}\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}} = (1 - x_{\mathrm{Y}})^2(&-246.22 - 1122.34x_{\mathrm{Y}} + 16659.12x_{\mathrm{Y}}^2 \\ &- 129161.4x_{\mathrm{Y}}^3 + 358577.55x_{\mathrm{Y}}^4 - 399868.92x_{\mathrm{Y}}^5 \\ &+ 155561.42x_{\mathrm{Y}}^6),\end{aligned} \tag{18}$$

$$\begin{aligned}\Delta_{\mathrm{mix}}H = x_{\mathrm{Y}}(1 - x_{\mathrm{Y}})(&-246.22 - 561.17x_{\mathrm{Y}} + 5553.04x_{\mathrm{Y}}^2 \\ &- 32290.35x_{\mathrm{Y}}^3 + 71715.51x_{\mathrm{Y}}^4 - 66644.82x_{\mathrm{Y}}^5 \\ &+ 22223.06x_{\mathrm{Y}}^6).\end{aligned} \tag{19}$$

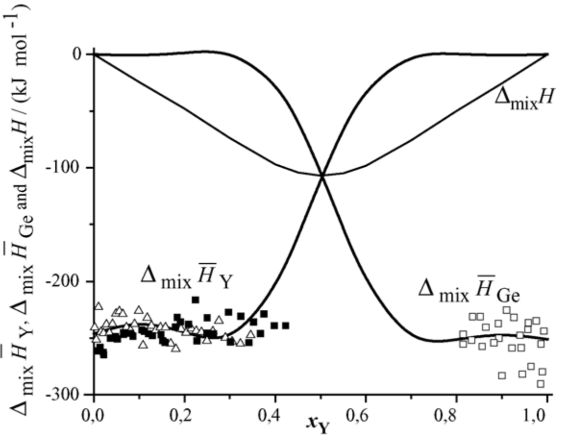

Fig. 4. Plot of partial and integral enthalpies of mixing in liquid Ge–Y alloys: (△) present work, experimental data on $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ at 1770 K; (■) data on $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ at 1900 K [13]; (□) data on $\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Ge}}$ at 1900 K [12,13]; lines are results of joint treatment of data from [13] and this work.

The results of common treatment of data from [13] and this work are shown on Fig. 4. The smoothed values of the enthalpies of mixing calculated using Eqs. (17) and (18) with their confidence intervals are listed in Table 3.

The standard enthalpies of formation of yttrium germanides ($\Delta_{\mathrm{f}}H$) were measured by e.m.f. [18], calorimetry

Table 3
The enthalpies of mixing at temperatures from 1770 K to 1900 K determined by treating the data of the present study and Ref. [13] together, evaluated through the ζ-function (in kJ mol^{-1})

x_{Y}	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}} \pm 2\sigma$	$\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Ge}}$	$\Delta_{\mathrm{mix}}H \pm 2\sigma$	ζ
0.0	−246.2 ± 8.5	0.0	0.0	−246.2
0.1	−234.1 ± 3.5	−1.2	−24.5 ± 0.6	−272.6
0.2	−244.4 ± 3.4	1.1	−48.0 ± 0.9	−299.8
0.3	−257.1 ± 2.7	4.8	−73.8 ± 1.2	−351.5
0.4	−206.6 ± 4.4	−24.0	−97.0 ± 1.7	−404.3
0.5	−110.5 ± 6.6	−103.5	−107.0 ± 2.9	−428.0
0.6	−29.7	−201.3	−98.3	−409.7
0.7	1.7	−256.8	−75.9	−361.2
0.8	0.4	−251.1 ± 11.8	−49.9 ± 2.1	−311.7
0.9	−1.1	−245.5 ± 6.9	−25.5 ± 1.0	−283.3
1.0	0.0	−251.0 ± 15.2	0.0	−251.0

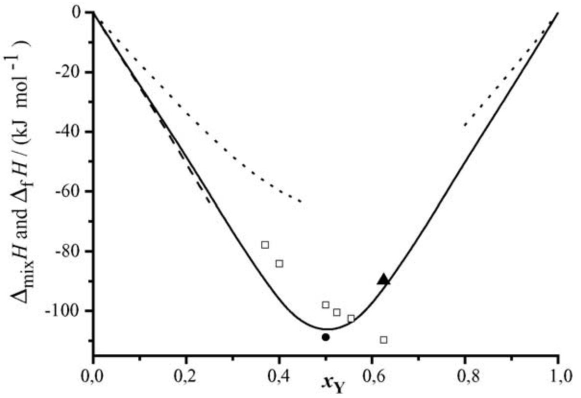

Fig. 5. Plot of integral enthalpy of mixing in the liquid Ge–Y alloys vs. mole fraction of yttrium; (—) common treatment of data from [13] and this work; (- - -) smoothed data of [11]; (· · ·) smoothed data of [14]; and enthalpies of formation of yttrium germanides: (☐) e.m.f. data of [18]; (▲) calorimetric datum of [19]; (●) calculated by Miedema's method [20].

[19] and calculated by Miedema's method [20]. The $\Delta_f H$ values are compared with the $\Delta_{mix}H$ of the liquid Ge–Y alloys on Fig. 5. The $\Delta_f H$ data are in a good agreement with the results of joint treatment, while they are significantly more negative than the data of [14]. This fact serves as an additional confirmation that the data of Ref. [14] are out of range.

Observed significant negative $\Delta_{mix}H$ values close to $\Delta_f H$ testify that strong inter-component interaction in the yttrium germanides remains at melting. This interaction can lead to formation of Y_xGe_{1-x} binary associates, which stoichiometry corresponds to the solid yttrium germanides.

4. Conclusions

In this work, the $\Delta_{mix}\bar{H}_Y$ values were measured in the Ge–Y system by mixing calorimetry at 1770 K. Our data were compared with those found in literature, and heat capacity change during alloy formation was estimated. Present results on $\Delta_{mix}\bar{H}_Y$ were combined with critically selected literature values of the $\Delta_{mix}\bar{H}_Y$ and $\Delta_{mix}\bar{H}_{Ge}$ and respective ζ-function was extrapolated onto the region of undercooled liquid alloys. Significant negative $\Delta_{mix}H$ values close to $\Delta_f H$ ones can lead to suggestion that Y_xGe_{1-x} binary associates with the yttrium germanides stoichiometry form in the melt.

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