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Calorimetric study of enthalpies of mixing in liquid gallium–germanium–yttrium alloys

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Abstract

The yttrium partial enthalpies of mixing ($\Delta_{\text{mix}}\bar{H}_{\text{Y}}$) and the integral enthalpies of mixing ($\Delta_{\text{mix}}H$) of liquid Ga–Ge–Y alloys have been determined by high-temperature mixing calorimetry for five sections with constant ratios of Ga and Ge at 1760 K. Plots of concentration dependence of $\Delta_{\text{mix}}\bar{H}_{\text{Y}}/(1-x_{\text{Y}})^2$ show sharp inflections, which correspond to transition of the liquid alloys into heterogeneous state and can be used for determination of liquidus surface. Furthermore, the $\Delta_{\text{mix}}H$ has been estimated in the ternary system using seven geometric models and the Bonnier model has been chosen as the most adequate one. The differences between the experimental and model integral enthalpies of mixing have been described by polynomial concentration dependence. The possible contribution of binary and ternary intermetallide compounds into the thermodynamics of the liquid Ga–Ge–Y alloys has been considered.

Keywords: Calorimetry; Enthalpy of mixing; Thermodynamics; Liquid alloys; Gallium–germanium–yttrium

1. Introduction

Multicomponent alloys of gallium and germanium with rare-earths are of high actuality due to possible application in production of novel magnetic materials. Molten gallium has been used as a solvent for the synthesis of rare-earth (RE) intermetallides containing germanium and transition metals, e.g. $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Ge}_x$ [1], $\text{RE}_3\text{Ga}_9\text{Ge}$ [2], REMGa_3Ge (M = Co, Ni) [3], $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ [3], REGaGe [4], and $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ [5]. Substitution of magnetic elements (i.e. rare-earth or transition metals) by non-magnetic dilutor such as yttrium, results in a change of magnetic properties of the compounds. Consequently, the Ga–Ge–Y is of considerable interest as a boundary ternary system of the quaternary Ga–Ge–Y–TR ones (TR is rare-earth or transition metal). No systematic examinations on the thermodynamic properties of the Ga–Ge–Y system have been reported in the literature.

Crystal structures of intermetallide compounds, which are formed in the Ga–Ge–Y system, have been examined by X-ray powder diffraction using Rietveld refinement [6,7]. The isothermal sections have been studied at two temperatures: firstly at 1073 K in the region from 33.3 to 100 at.% Y [6] and later at 873 K in the region up to 37 at.% Y [7]. Four rare-earth intermetallide compounds have been found in the system at 1073 K [6], namely $\text{YGe}_{0.6}\text{Ga}_{1.4}$ (**I**), $\text{Y(Ge}_x\text{Ga}_{1-x})_{1.8}$ $(0.2222 < x < 0.3889)$ (**II**), $\text{Y(Ge}_x\text{Ga}_{1-x})_{1.7}$ $(0.5882 < x < 0.7647)$ (**III**) and $\text{Y}_2\text{(Ge}_x\text{Ga}_{1-x})_3$ $(0.5667 < x < 0.7667)$ (**IV**). Besides, continuous series of solid solution $\text{YGa}_x\text{Ge}_{1-x}$ $(0 < x < 1)$ (**V**) form on the YGa–YGe section at 1073 K [6]. At least eight ternary compounds are registered in the system at 873 K, i.e. (**I**), (**III**), $\text{Y}_2\text{Ge}_{6.66}\text{Ga}_{0.34}$ (**VI**), $\text{Y(Ge}_x\text{Ga}_{1-x})_{3.34}$ $(0.7425 < x < 0.8713)$ (**VII**), $\text{Y}_2\text{(Ge}_x$

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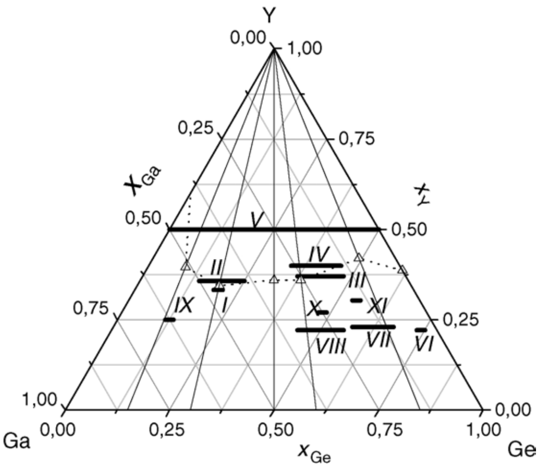

Fig. 1. Plot of intermetallides compositions in the Ga–Ge–Y system. (**I**) $YGe_{0.6}Ga_{1.4}$, (**II**) $Y(Ge_xGa_{1-x})_{1.8}$ ($0.2222 < x < 0.3889$), (**III**) $Y(Ge_xGa_{1-x})_{1.7}$ ($0.5882 < x < 0.7647$), (**IV**) $Y_2(Ge_xGa_{1-x})_3$ ($0.5667 < x < 0.7667$), (**V**) YGa_xGe_{1-x} ($0 < x < 1$), (**VI**) $Y_2Ge_{6.66}Ga_{0.34}$, (**VII**) $Y(Ge_xGa_{1-x})_{3.34}$ ($0.7425 < x < 0.8713$), (**VIII**) $Y_2(Ge_xGa_{1-x})_7$ ($0.5714 < x < 0.7143$), (**IX**) $YGe_{0.5}Ga_{2.5}$, (**X**) $YGe_{1.78}Ga_{0.92}$ and (**XI**) $YGe_{1.8}Ga_{0.5}$. Compounds (**I**)–(**V**) have been found at 1073 K [6], compounds (**I**), (**III**) and (**VI**)–(**XI**) have been determined at 873 K [7]. Dotted line bounds the region of liquid alloys examined by calorimetry in the present study. Triangles denote the concentrations corresponding to the transition into a two-phase region. Lines connecting the Y-corner of the Gibbs triangle and the Ga–Ge boundary denote the studied sections.

$Ga_{1-x})_7$ ($0.5714 < x < 0.7143$) (**VIII**), $YGe_{0.5}Ga_{2.5}$ (**IX**), $YGe_{1.78}Ga_{0.92}$ (**X**) and $YGe_{1.8}Ga_{0.5}$ (**XI**) [7]. Fig. 1 demonstrates concentration regions of the intermetallide compounds existence reported in [6,7].

However, for assessment of the phase equilibria it is necessary to know the thermodynamic properties of the system in particular in the liquid state. Therefore, the present work is directed on calorimetric measurements of the enthalpies of mixing in the liquid Ga–Ge–Y alloys.

2. Experimental

2.1. Materials

Gallium (Alfa, 99.9999%), germanium (Alfa, 99.9999%), yttrium distillate (Dahuachem, 99.97%) and tungsten (Alfa, 99.96%) were used for the calorimetric experiments. High-purity argon (99.997 vol.%) was utilized for filling of the calorimeter's internal volume to prevent the alloys chemical reactions with air constituents.

2.2. Calorimetric procedure and data treatment

The heats of mixing have been measured using a high-temperature mixing calorimeter [8] at 1760 K. The mixing experiments have been performed under the argon at atmospheric pressure. The measurements have been done along five sections of the Ga–Ge–Y system with Ga–Ge basis. The molar ratios of x_{Ga}:x_{Ge} are 0.15:0.85, 0.4:0.6, 0.5:0.5, 0.7:0.3 and 0.85:0.15 for $0.0 < x_Y < 0.65$. The calorimetric measurements routine has been previously reported in [9]. The initial calorimetric data are listed in Tables 1–5.

The heat-exchange coefficient of the calorimeter is calculated by the formula

$$k_i = \Delta H^T_{298} n_i / S_i, \tag{1}$$

where ΔH^T_{298} is the enthalpy of 1 mol of reference component (Ge or W) heating from $T = 298$ K up to experimental temperature [10], i is the dropped sample number, n_i is the mole quantity of the dropped sample, and S_i is the area of heat-exchange peak. The k_i values are treated by the least square regression (l.s.r.) for the linear model

$$k = a + b m_{\text{alloy}}, \tag{2}$$

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

$$\Delta_{\text{mix}}\bar{H}_Y = -\Delta H^T_{298} + k_i S_i / n_i, \tag{3}$$

where ΔH^T_{298} is the standard enthalpy of Y [10]. The values of the $\Delta_{\text{mix}}\bar{H}_Y$ are assigned to the middle point of the composition range before and after sample addition. The experimental partial enthalpy of mixing is expressed via an alpha function

$$\alpha_Y = \Delta_{\text{mix}}\bar{H}_Y / (1 - x_Y)^2. \tag{4}$$

The alpha function is smoothed using l.s.r. for the polynomial model. Respectively, concentration dependence of the $\Delta_{\text{mix}}\bar{H}_Y$ is represented via the equation

$$\Delta_{\text{mix}}\bar{H}_Y = (1 - x_Y)^2 \sum_{j=0}^{l} Q_j x_Y^j, \tag{5}$$

where Q_i are the polynomial coefficients and l is the polynomial degree determined by the Fisher's exact test [11]. The Darken's integration of Eq. (5) leads to

$$\Delta_{\text{mix}}H = (1 - x_Y)\left[\Delta_{\text{mix}}H^\circ + \sum_{j=0}^{l}(j+1)^{-1} Q_j x_Y^{j+1}\right], \tag{6}$$

where $\Delta_{\text{mix}}H^\circ$ is the integral enthalpy of mixing in the binary Ga–Ge alloy. The deviations of integral enthalpies of mixing have been determined as proposed in [9]

$$\sigma(\Delta_{\text{mix}}H) = (1 - x_Y) \times \left\{ D(\Delta_{\text{mix}}H^\circ) + x_Y \int_0^{x_Y} D(\alpha_Y)\,\mathrm{d}x_Y \right\}^{1/2}, \tag{7}$$

Table 1
Results of calorimetric study of x_{Ga}:x_{Ge} = 0.15:0.85 section of the Ga–Ge–Y system

Added substance (A)	Run 1: m_0 = 1.0923 g, a = 10.27400, b = 0.0[a]				Run 2: m_0 = 0.4761 g; a = 10.94372, b = 0.0			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})
Ge	0.0886	0.00858			0.0453	0.00468		
	0.0753	0.00746			0.0547	0.00473		
	0.0832	0.00851			0.0872	0.00768		
	0.0841	0.00794			0.0891	0.00809		
	0.1564	0.01799			0.0498	0.00562		
	0.0893	0.00830			0.0628	0.00619		
	0.0754	0.00848			0.0636	0.00675		
	0.0878	0.00921			0.1826	0.01550		
Ga	0.0693	0.00475	0.0193	4.78	0.0514	0.00227	0.0235	−10.64
	0.1073	0.00524	0.0653	−9.36	0.0549	0.00331	0.0688	1.64
	0.1340	0.00615	0.1216	−11.44	0.0820	0.00423	0.1213	−4.98
Y	0.0063	−0.00117	0.0012	−231.86	0.0087	−0.00184	0.0027	−267.84
	0.0106	−0.00248	0.0044	−276.47	0.0111	−0.00218	0.0088	−253.51
	0.0097	−0.00204	0.0082	−254.99	0.0135	−0.00240	0.0163	−235.26
	0.0113	−0.00250	0.0121	−264.92	0.0138	−0.00226	0.0245	−221.71
	0.0104	−0.00207	0.0161	−244.67	0.0143	−0.00297	0.0328	−264.52
	0.0132	−0.00252	0.0204	−237.10	0.0154	−0.00254	0.0414	−222.73
	0.0117	−0.00216	0.0249	−231.02	0.0195	−0.00377	0.0513	−250.44
	0.0134	−0.00281	0.0294	−253.78	0.0201	−0.00428	0.0623	−269.59
	0.0131	−0.00252	0.0341	−238.43	0.0246	−0.00388	0.0744	−215.85
	0.0148	−0.00268	0.0390	−227.91	0.0240	−0.00460	0.0872	−248.87
	0.0162	−0.00346	0.0444	−257.77	0.0247	−0.00380	0.0997	−212.31
	0.0181	−0.00394	0.0503	−261.19	0.0237	−0.00405	0.1118	−228.65
	0.0196	−0.00430	0.0567	−262.81	0.0311	−0.00532	0.1251	−229.01
	0.0204	−0.00429	0.0634	−254.64	0.0297	−0.00515	0.1394	−231.39
	0.0245	−0.00551	0.0708	−268.01	0.0327	−0.00552	0.1536	−226.82
	0.0280	−0.00531	0.0793	−235.77	0.0314	−0.00536	0.1677	−228.53
	0.0286	−0.00631	0.0883	−264.07	0.0387	−0.00698	0.1826	−238.00
	0.0310	−0.00608	0.0976	−241.69	0.0355	−0.00597	0.1978	−226.16
	0.0312	−0.00650	0.1070	−252.75	0.0411	−0.00735	0.2129	−236.58
	0.0392	−0.00764	0.1176	−240.46	0.0390	−0.00707	0.2281	−238.87
	0.0427	−0.00898	0.1295	−254.54	0.0443	−0.00795	0.2433	−237.05
	0.0551	−0.01107	0.1433	−246.02	0.0442	−0.00778	0.2588	−233.81
	0.0570	−0.01233	0.1586	−260.10	0.0511	−0.00917	0.2748	−237.17
	0.0608	−0.01163	0.1741	−237.23	0.0510	−0.00969	0.2912	−247.39
	0.0495	−0.01112	0.1881	−267.72	0.0573	−0.00941	0.3078	−222.24
	0.0613	−0.01459	0.2017	−279.94	0.0557	–	0.3243	–
	0.0662	−0.01557	0.2168	−277.29	0.0563	−0.01042	0.3399	−242.53
	0.0762	−0.01597	0.2330	−253.88	0.0603	−0.00923	0.3554	−211.36
	0.0724	−0.01515	0.2492	−253.60	0.0605	−0.00994	0.3707	−222.43
	0.0798	−0.01643	0.2651	−250.54	0.0612	−0.01053	0.3854	−229.87
	0.0781	−0.01630	0.2809	−253.14	0.0602	−0.00554	0.3994	−152.05
	0.0869	−0.01822	0.2967	−253.97	0.0661	−0.00696	0.4133	−164.88
	0.0834	−0.02070	0.3123	−289.27	0.0644	−0.01314	0.4270	−261.03
	0.0878	−0.01672	0.3273	−236.40	0.0684	−0.01322	0.4403	−250.50
					0.0644	−0.01193	0.4530	−242.72
					0.0680	−0.0179	0.4651	−318.57
					0.0670	−0.01697	0.4769	−309.00
					0.0706	−0.02358	0.4884	−387.50
					0.0708	−0.02223	0.4997	−367.98
					0.0771	−0.00860	0.5110	−171.10
					0.0877	−0.00208	0.5230	−85.60
					0.0945	−0.01689	0.5356	−236.39
					0.0915	0.01075	0.5478	51.78
					0.0949	0.00849	0.5594	24.53

[a] Here and hereafter the m_0 is the starting mass of Ge in the crucible, a and b are the l.s.r. coefficients of Eq. (2).

Table 2
Results of calorimetric study of x_{Ga}:x_{Ge} = 0.4:0.6 section of the Ga–Ge–Y system

Added substance (A)	Run 1: m_0 = 1.0114 g, a = 11.16332, b = −0.18982				Run 2: m_0 = 0.8521 g, a = 10.65293, b = 0.0			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})
Ge	0.0489	0.00421			0.0538	0.00545		
	0.0632	0.00550			0.0604	0.00572		
	0.1068	0.01186			0.1311	0.01154		
	0.0602	0.00536			0.0579	0.00531		
	0.0788	0.00717			0.0951	0.00971		
	0.0501	0.00536			0.0749	0.00744		
	0.0437	0.00467			0.0765	0.00770		
	0.0544	0.00528			0.1262	0.01393		
Ga	0.2676	0.01335	0.0841	−6.68	0.0688	0.00357	0.0229	−5.76
	0.2831	0.01658	0.2192	−0.36	0.1147	0.00648	0.0792	−2.40
	0.2976	0.01749	0.3243	−0.43	0.1283	0.00687	0.1444	−4.55
	0.1234	0.00672	0.3844	−3.77	0.2075	0.01338	0.2207	3.55
					0.2252	0.01160	0.3010	−6.07
					0.2339	0.01159	0.3699	−7.53
Y	0.0155	−0.00246	0.0025	−213.13	0.0119	−0.00208	0.0019	−227.82
	0.0164	−0.00279	0.0076	−224.35	0.0139	−0.00226	0.0060	−216.51
	0.0203	−0.00304	0.0134	−204.62	0.0172	−0.00279	0.0109	−216.08
	0.0233	−0.00408	0.0202	−228.89	0.0207	−0.00348	0.0168	−221.73
	0.0222	−0.00393	0.0272	−230.65	0.0203	−0.00360	0.0231	−230.66
	0.0319	−0.00535	0.0354	−221.49	0.0232	−0.00406	0.0297	−228.38
	0.0367	−0.00641	0.0456	−228.03	0.0222	−0.00386	0.0365	−227.27
	0.0348	−0.00644	0.0560	−237.88	0.0252	−0.00459	0.0436	−235.02
	0.0426	−0.00816	0.0670	−243.72	0.0229	−0.00430	0.0506	−240.56
	0.0527	−0.00976	0.0802	−237.67	0.0252	−0.00506	0.0575	−252.57
	0.0574	−0.01092	0.0950	−242.15	0.0322	−0.00560	0.0656	−227.28
	0.0579	−0.01030	0.1100	−230.37	0.0371	−0.00757	0.0752	−255.71
	0.0566	−0.01109	0.1244	−247.14	0.0411	−0.00843	0.0858	−256.79
	0.0710	−0.01427	0.1399	−251.73	0.0428	−0.00818	0.0969	−243.57
	0.0638	−0.01322	0.1557	−257.42	0.0424	−0.00775	0.1079	−235.54
	0.0743	−0.01490	0.1713	−250.88	0.0433	−0.00807	0.1187	−238.99
	0.0701	−0.01385	0.1870	−247.79	0.0478	−0.00979	0.1299	−256.55
	0.0868	−0.01661	0.2034	−241.68	0.0507	−0.00980	0.1417	−245.51
	0.0777	−0.01431	0.2199	−234.69	0.0523	−0.01021	0.1537	−247.42
	0.0939	−0.01757	0.2364	−237.17	0.0555	−0.01041	0.1659	−240.17
	0.0886	−0.01578	0.2532	−228.45	0.0555	−0.01024	0.1781	−237.32
	0.1023	−0.01769	0.2700	−223.39				
	0.0976	−0.01645	0.2868	−219.02				
	0.1107	−0.01960	0.3035	−226.63				
	0.1038	−0.01643	0.3199	−208.88				
	0.1129	−0.01985	0.3357	−224.83				
	0.1144	−0.01597	0.3515	−191.08				
	0.1196	−0.01069	0.3670	−144.66				
	0.1099	−0.00625	0.3815	−114.65				
	0.1221	−0.00488	0.3955	−99.06				
	0.1120	−0.00160	0.4090	−75.58				
	0.1293	0.01148	0.4223	18.37				
	0.1214	0.00640	0.4355	−14.58				
	0.1332	0.00554	0.4483	−24.78				
	0.1271	0.00961	0.4608	5.86				
	0.1433	0.01135	0.4732	8.94				
	0.1332	0.01136	0.4853	14.27				
	0.1517	0.01085	0.4972	1.70				
	0.1393	0.01200	0.5088	14.63				
	0.1577	0.01102	0.5201	−0.13				
	0.1479	0.01337	0.5312	17.92				
	0.1607	0.01420	0.5419	15.89				
	0.1503	0.01217	0.5522	9.12				

Table 2 (*Continued*)

Added substance (A)	Run 1: $m_0 = 1.0114$ g, $a = 11.16332$, $b = -0.18982$			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\bar{H}_A$ (kJ mol^{-1})
Y	0.1689	0.01623	0.5623	22.23
	0.1722	0.01591	0.5726	18.71
	0.1786	0.01502	0.5827	11.14
	0.1784	0.01527	0.5925	12.23
	0.1884	0.01752	0.6021	18.37
	0.1965	0.01843	0.6117	18.77
	0.2209	0.01875	0.6216	10.71
	0.2053	0.01878	0.6312	16.09
	0.2389	0.02285	0.6407	19.29
	0.2294	0.02152	0.6502	17.35
W	0.5634	0.01083		
	0.4338	0.01116		
	0.2504	0.00637		
	0.2528	–		

where $D(\Delta_{mix}H^\circ)$ and $D(\alpha_Y)$ are the dispersions of the $\Delta_{mix}H^\circ$ and α_Y-functions, respectively. Confidence intervals have been calculated from deviations of appropriate functions as $tD^{1/2}$, where t is the Student's coefficient for a 0.05 significance level, which is equal to 2. The confidence intervals in the initial Ga–Ge system have been assumed as 10%. This approach is acceptable because the enthalpies of mixing in the Ga–Ge system are considerably less than those in the Ga–Ge–Y system.

The interpolation method discussed in [9] have been used for the presentation of ternary alloys thermodynamics. Corresponding to the method, the calculation of integral enthalpy of mixing in the ternary system is performed by one of geometric models. The differences ($\Delta\Delta_{mix}H$) between the experimental ($\Delta_{mix}H_{exp}$) and model ($\Delta_{mix}H_{model}$) integral enthalpies of mixing have been described by polynomial concentration dependence using l.s.r. analysis. The integral enthalpy of mixing in the ternary system is represented as a sum of $\Delta_{mix}H_{model}$ and the polynomial dependence of $\Delta\Delta_{mix}H$. The choice of the geometric model is performed using certain parameters: the minimal average value of the $\Delta\Delta_{mix}H$, the minimal scattering of the $\Delta\Delta_{mix}H$ and the minimal deviation of the $\Delta_{mix}H_{model}$ with respect to $\Delta_{mix}H_{exp}$, which is the χ-parameter

$$\chi\,(\%) = \langle|(\Delta_{mix}H_{model} - \Delta_{mix}H_{exp})/\Delta_{mix}H_{exp}|\rangle \times 100. \tag{8}$$

The $\Delta_{mix}H$ data for the boundary basis Ga–Ge systems, which is necessary for calculation of $\Delta_{mix}H$ by Eq. (6) and for the interpolation of $\Delta_{mix}H$ in the ternary system, have been taken from [12]. The equation reported in [12] is result of common treatment of data [13,14] (in kJ mol^{-1})

$$\Delta_{mix}H_{Ga\text{–}Ge} = x_{Ge}(1 - x_{Ge})(-2.805 + 3.69x_{Ge} - 14.25x_{Ge}^2 + 20.23x_{Ge}^3 - 9.9x_{Ge}^4). \tag{9}$$

The equations describing the integral enthalpy of mixing in the boundary binary Ga–Y and Ge–Y systems have been taken from [15,16], respectively (in kJ mol^{-1})

$$\begin{aligned}\Delta_{mix}H_{Ga\text{–}Y} = x_Y(1 - x_Y)(&-189.76 - 200.79x_Y \\ &+ 338.89x_Y^2 - 5916.63x_Y^3 + 17768.71x_Y^4 \\ &-13665.14x_Y^5),\end{aligned} \tag{10}$$

$$\begin{aligned}\Delta_{mix}H_{Ge\text{–}Y} = x_Y(1 - x_Y)(&-246.22 - 561.17x_Y \\ &+ 5553.04x_Y^2 - 32290.35x_Y^3 + 71715.51x_Y^4 \\ &- 66644.82x_Y^5 + 22223.06x_Y^6).\end{aligned} \tag{11}$$

3. Results and discussion

The partial enthalpies of mixing of gallium, which have been estimated at $Ga_{0.15}Ge_{0.85}$, $Ga_{0.4}Ge_{0.6}$, $Ga_{0.5}Ge_{0.5}$, $Ga_{0.7}Ge_{0.3}$ and $Ga_{0.85}Ge_{0.15}$ initial binary alloys preparation, are represented in Fig. 2. Fig. 2 shows a satisfactory agreement between obtained partial enthalpies of mixing and literature data [12]. It should be noticed, that partial enthalpies of mixing are calculated precisely by Eq. (3) only in the case, when added component amount is not more than 1 mol% from the alloy quantity. But the amounts of the Ga samples added to prepare the binary Ga_xGe_{1-x} alloys have been significantly more than 1 mol%. This leads to considerable scattering of the data plotted in Fig. 2, which is not peculiar for the ternary alloys.

The α_Y-functions are shown in Fig. 3(a)–(e). The α_Y-functions for the mixtures with x_{Ga}:x_{Ge} = 0.15:0.85 and 0.5:0.5 sharply decrease at x_Y = 0.42 and 0.36, correspondingly (Fig. 3(a) and (c)). As yttrium mole fraction increases further, sharp increasing of the α_Y-functions up to zero is

Table 3
Results of calorimetric study of $x_{Ga}:x_{Ge} = 0.5:0.5$ section of the Ga–Ge–Y system

Added substance (A)	Run 1: $m_0 = 0.4704$ g, $a = 12.82579$, $b = 0.00$				Run 2: $m_0 = 0.4698$ g, $a = 11.2278$, $b = 0.0$			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})
Ge	0.0387	0.00342			0.0325	0.00323		
	0.0514	0.00395			0.0433	0.00370		
	0.0741	0.00571			0.0610	0.00575		
	0.0422	0.00308			0.0692	0.00678		
	0.0558	0.00484			0.0441	0.00388		
	0.0339	0.00268			0.0292	0.00286		
	0.0896	0.00772			0.0658	0.00551		
	0.0493	0.00432			0.0630	0.00639		
Ga	0.1739	0.00812	0.0909	−2.60	0.1435	0.00664	0.0784	−8.12
	0.2093	0.00989	0.2426	−2.07	0.2331	0.01265	0.2357	−1.86
	0.2043	0.00864	0.3582	−6.50	0.2526	0.01297	0.3736	−4.14
	0.2821	0.01356	0.4559	−1.34	0.2140	0.01209	0.4661	−0.11
Y	0.0151	−0.00189	0.0034	−205.16	0.0082	−0.00109	0.0019	−195.36
	0.0154	−0.00185	0.0102	−199.49	0.0131	−0.00219	0.0068	−229.51
	0.0156	−0.00221	0.0170	−224.27	0.0137	−0.00206	0.0129	−212.56
	0.0168	−0.00237	0.0240	−223.17	0.0156	−0.00247	0.0195	−220.88
	0.0170	−0.00212	0.0312	−204.64	0.0186	−0.00268	0.0271	−206.48
	0.0178	−0.00271	0.0385	−236.24	0.0222	−0.00352	0.0360	−220.84
	0.0190	−0.00272	0.0461	−225.69	0.0213	−0.00379	0.0453	−240.10
	0.0204	−0.00279	0.0541	−218.63	0.0244	−0.00404	0.0549	−227.60
	0.0252	−0.00361	0.0632	−225.86	0.0243	−0.00418	0.0649	−234.26
	0.0280	−0.00417	0.0736	−232.29	0.0315	−0.00528	0.0761	−229.93
	0.0317	−0.00520	0.0851	−249.63	0.0302	−0.00522	0.0882	−235.06
	0.0382	−0.00581	0.0981	−236.09	0.0370	−0.00633	0.1010	−233.24
	0.0377	−0.00596	0.1118	−242.90	0.0398	−0.00701	0.1152	−238.21
	0.0406	−0.00590	0.1255	−228.10	0.0429	−0.00774	0.1300	−242.52
	0.0384	−0.00592	0.1389	−238.27	0.0421	−0.00725	0.1447	−234.44
	0.0468	−0.00738	0.1529	−242.30	0.0439	−0.00760	0.1591	−235.32
	0.0451	−0.00704	0.1675	−240.61	0.0458	−0.00735	0.1736	−222.62
					0.0966	−0.01559	0.1956	−223.59
					0.0502	−0.00844	0.2171	−230.44
					0.0527	−0.00887	0.2315	−230.51
					0.0580	−0.00965	0.2464	−228.61
					0.0587	−0.00945	0.2615	−223.23
					0.0596	−0.00889	0.2762	−211.48
					0.0628	−0.00844	0.2908	−196.63
					0.0593	−0.00739	0.3048	−186.95
					0.0642	−0.00925	0.3184	−206.27
					0.0614	−0.00769	0.3317	−187.57
					0.0663	−0.00897	0.3447	−197.60
					0.0645	−0.00742	0.3575	−177.31
					0.0736	−0.01279	0.3705	−235.92
					0.0705	−0.00391	0.3835	−117.89
					0.0775	0.00151	0.3963	−43.08
					0.0707	0.00262	0.4086	−25.49
					0.0837	0.00584	0.4209	7.11

observed. The functions behavior can be explained as follows. At transition into heterogeneous area, the weighed samples of Y are dissolved in the melt with simultaneous crystallization of rare-earth intermetallide compound. The crystallization is accompanied by a significant heat evolution and leads to sharp decrease of the α_Y-function. Subsequent increasing of the x_Y results in essential slowing down of the Y weighed samples dissolution due to kinetic difficulties and in increasing of the α_Y-function up to zero. The α_Y-functions of the mixtures with $x_{Ga}:x_{Ge} = 0.4:0.6$, 0.7:0.3 and 0.85:0.15 (Fig. 3(b), (d) and (e)) do not decrease at transition into the heterogeneous area due to the crystallization, but increase sharply at $x_Y = 0.36$, 0.345 and 0.395, respectively, because of the cessation in the Y dissolution.

Table 4
Results of calorimetric study of x_{Ga}:x_{Ge} = 0.7:0.3 section of the Ga–Ge–Y system

Added substance (A)	Run 1: m_0 = 0.4898 g, a = 9.86342, b = 0.00				Run 2: m_0 = 0.3314 g, a = 10.64834, b = −0.12505			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\overline{H}_A$ (kJ mol^{-1})
Ge	0.0351	0.00341			0.0253	0.00257		
	0.039	0.00400			0.0835	0.00748		
	0.0954	0.01090			0.0639	0.00551		
	0.0495	0.00478			0.0262	0.00274		
	0.0982	0.01129			0.0762	0.00704		
	0.0816	0.01046			0.0459	0.00499		
	0.0902	0.00881			0.0920	0.00799		
	0.1104	0.01146			0.0890	0.01240		
Ga	0.2452	0.00972	0.1049	−17.07	0.2684	0.01512	0.1436	−3.06
	0.3469	0.01672	0.2858	−11.19	0.2517	0.01763	0.3300	6.84
	0.3434	0.02189	0.4220	−0.50	0.3007	0.02055	0.4558	5.42
	0.4461	0.02528	0.5255	−5.36	0.3135	0.02640	0.5498	16.74
	0.5342	0.03330	0.6118	−1.47	0.3379	0.01764	0.6195	−6.62
	0.5252	0.03572	0.6756	2.44	0.3955	0.02755	0.6760	5.75
Y	0.0268	−0.00458	0.0030	−212.35	0.0150	−0.00206	0.0022	−188.16
	0.0282	−0.00502	0.0091	−218.51	0.0180	−0.00263	0.0070	−196.14
	0.0311	−0.00559	0.0156	−220.14	0.0384	−0.00634	0.0151	−213.79
	0.0289	−0.00518	0.0221	−219.56	0.0210	−0.00354	0.0235	−216.86
	0.0329	−0.00569	0.0287	−214.29	0.0307	−0.00481	0.0307	−205.89
	0.0307	−0.00551	0.0354	−219.98	0.0299	−0.00483	0.0390	−210.31
	0.0347	−0.00597	0.0422	−213.38	0.0348	−0.00600	0.0477	−220.22
	0.0435	−0.00784	0.0502	−220.49	0.0326	−0.00528	0.0566	−210.58
	0.0471	−0.00897	0.0593	−229.52	0.0384	−0.00651	0.0658	−217.41
	0.0483	−0.00896	0.0687	−225.18	0.0388	−0.00647	0.0756	−214.86
					0.0441	−0.00744	0.0859	−216.54
					0.0407	−0.00691	0.0962	−217.31
					0.0461	−0.00730	0.1065	−206.81
					0.0427	−0.00747	0.1168	−222.04
					0.0500	−0.00897	0.1273	−225.96
					0.0459	−0.00789	0.1379	−219.00
					0.0524	−0.00926	0.1485	−223.28
					0.0599	−0.01005	0.1603	−215.09
					0.0645	−0.01060	0.1730	−211.77
					0.0659	−0.01142	0.1859	−219.76
					0.0719	−0.01222	0.1991	−216.61
					0.0738	−0.01165	0.2126	−205.59
					0.0792	−0.01359	0.2263	−217.81
					0.1506	−0.02087	0.2460	−187.72
					0.0827	−0.01217	0.2650	−195.32
					0.0787	−0.01240	0.2776	−204.52
					0.0871	−0.00955	0.2901	−161.24
					0.0819	−0.00944	0.3024	−166.25
					0.0917	−0.01379	0.3146	−197.67
					0.0897	−0.01228	0.3269	−185.46
					0.1016	−0.01129	0.3394	−162.19
					0.0922	0.00519	0.3516	−12.11
					0.1175	0.00479	0.3643	−26.08
					0.1148	0.00846	0.3778	3.30
					0.1296	0.00713	0.3914	−13.43
					0.1221	0.00883	0.4048	1.86
					0.1251	0.00915	0.4174	2.52
					0.1226	0.00875	0.4295	0.82
					0.1381	0.00885	0.4417	−5.75
					0.1320	0.01191	0.4538	17.28
					0.1455	0.01151	0.4657	7.34
					0.1371	0.01417	0.4773	28.56
					0.1583	0.01570	0.4889	24.74
					0.1508	0.01421	0.5005	20.19

Table 4 (*Continued*)

Added substance (A)	Run 2: $m_0 = 0.3314$ g, $a = 10.64834$, $b = -0.12505$			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\bar{H}_A$ (kJ·mol^{-1})
Y	0.1759	0.01841	0.5122	29.18
	0.1880	0.01613	0.5246	12.48
	0.1954	0.02173	0.5370	34.42
	0.1990	0.01916	0.5491	21.22
	0.2066	0.02073	0.5609	24.52
	0.2438	0.02550	0.5733	27.89
	0.3052	0.03075	0.5875	24.26
	0.3087	0.03596	0.6023	37.40
W	0.4257	–		
	0.4755	0.01186		
	0.2664	0.00561		
	0.4531	–		

The inflection points of the α_Y-functions can refer to the liquidus surface at the appropriate temperature (Fig. 1). The inflection points are in a well agreement with compositions of the ternary intermetallides reported in [6]. The inflection point on the section $x_{Ga}:x_{Ge} = 0.15:0.85$ can correspond to transition into the two-phase region in which the liquid alloy and solid intermetallide coexist. The solid intermetallide, which is in the equilibria with the liquid, can be (**IV**) or (**V**) compound with the close probability. The inflection point found on the section $x_{Ga}:x_{Ge} = 0.4:0.6$ most likely corresponds to transition into the two-phase region of liquid with (**IV**) or with less probability into that of liquid with (**III**). In the second case the temperature of melting (T_m) of (**III**) should be close to the temperature of our experiment (1760 K), because the concentration corresponding to the inflection point is close to the intermetallide stoichiom-

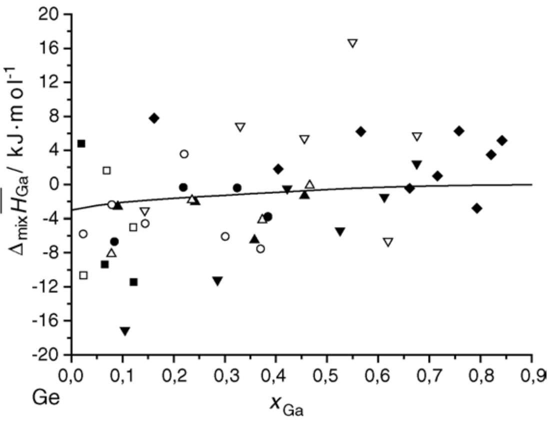

Fig. 2. Partial enthalpy of mixing of gallium ($\Delta_{mix}\bar{H}_{Ga}$) in the liquid Ga–Ge alloys against mole fraction of gallium. Solid and open symbols are experimental data of runs 1 and 2, respectively, measured at the initial Ge_xGa_{1-x} alloys preparation for the sections: (■, □) $Ga_{0.15}Ge_{0.85}$–Y; (●, ○) $Ga_{0.4}Ge_{0.6}$–Y; (▲, △) $Ga_{0.5}Ge_{0.5}$–Y; (▼, ▽) $Ga_{0.7}Ge_{0.3}$–Y; (♦) $Ga_{0.85}Ge_{0.15}$–Y. Solid line is data of [12] (common treatment of data of [13,14]).

Table 5
Results of calorimetric study of $x_{Ga}:x_{Ge} = 0.85:0.15$ section of the Ga–Ge–Y system

Added substance (A)	$m_0 = 0.3019$ g, $a = 12.43074$, $b = 0.00729$			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{mix}\bar{H}_A$ (kJ mol^{-1})
Ge	0.0213	0.00161		
	0.0237	0.00206		
	0.0208	0.00192		
	0.0767	0.00601		
	0.0731	0.00638		
	0.0592	0.00477		
	0.0447	0.00398		
	0.0509	0.00433		
Ga	0.2495	0.01499	0.1619	7.78
	0.3790	0.02016	0.4047	1.81
	0.4273	0.02489	0.5660	6.21
	0.4099	0.02072	0.6613	−0.47
	0.3276	0.01710	0.7162	0.98
	0.4651	0.02711	0.7583	6.28
	0.4367	0.02088	0.7932	−2.81
	0.5211	0.02869	0.8207	3.49
	0.4429	0.02523	0.8419	5.16
Y	0.0231	−0.00259	0.0021	−186.96
	0.0245	−0.00320	0.0064	−207.32
	0.0280	−0.00319	0.0111	−188.90
	0.0330	−0.00422	0.0165	−204.37
	0.0379	−0.00394	0.0227	−177.64
	0.0397	−0.00475	0.0294	−195.15
	0.0401	−0.00536	0.0362	−210.55
	0.0456	−0.00589	0.0434	−205.55
	0.0536	−0.00676	0.0516	−202.32
	0.0536	−0.00714	0.0603	−210.09
	0.0645	−0.00823	0.0697	−203.86
	0.0663	−0.00903	0.0799	−213.49
	0.0701	−0.00870	0.0903	−200.00
	0.0831	−0.01077	0.1017	−206.12
	0.0378	−0.00500	0.1105	−209.27
	0.0897	−0.01185	0.1196	−208.95
	0.0913	−0.01073	0.1322	−192.82
	0.0936	−0.01228	0.1447	−207.90
	0.0984	−0.01263	0.1573	−204.78

Table 5 (*Continued*)

Added substance (A)	$m_0 = 0.3019$ g, $a = 12.43074$, $b = 0.00729$			
	Added amount, m_i (g)	Area, S_i (a.u.)	Mole fraction, x_A	Partial enthalpy, $\Delta_{\text{mix}}\bar{H}_A$ (kJ mol^{-1})
	0.1026	−0.01461	0.1701	−220.43
	0.1129	−0.01458	0.1834	−205.68
	0.1285	−0.01543	0.1978	−195.67
	0.1270	−0.01528	0.2125	−195.90
	0.1345	−0.01621	0.2270	−196.18
	0.1389	−0.01547	0.2416	−186.01
	0.1591	−0.01616	0.2569	−175.19
	0.1660	−0.01773	0.2729	−181.01
	0.1716	−0.01932	0.2888	−187.43
	0.1723	−0.01706	0.3043	−172.40
	0.1731	−0.01341	0.3192	−148.46
	0.1779	−0.01338	0.3337	−145.97
	0.1809	−0.01243	0.3479	−138.77
	0.1885	−0.01290	0.3619	−138.47
	0.1834	−0.00871	0.3754	−115.22
	0.1931	−0.00857	0.3885	−111.79
	0.1876	0.00787	0.4012	−15.92
	0.2065	0.00690	0.4138	−25.40
	0.1949	0.00613	0.4261	−27.58
	0.2171	0.01011	0.4382	−10.78
	0.2022	0.01112	0.4500	−1.42
	0.2241	0.00856	0.4615	−20.08
	0.2011	0.01443	0.4725	17.21
	0.2381	0.00863	0.4834	−22.21
	0.2114	0.01421	0.4941	12.22
	0.2486	0.01451	0.5046	2.37
	0.2267	0.01755	0.5150	23.57
	0.2597	0.01926	0.5252	19.96
	0.2429	0.01806	0.5353	20.17
	0.3086	0.02089	0.5459	12.80
	0.2972	0.02321	0.5570	24.39
	0.3692	0.02664	0.5686	17.77
W	0.3784	0.00648		
	0.2315	0.00434		
	0.2286	0.00378		
	0.4492			

etry. The transition into the two-phase region, where the liquid with (**II**) or (**IV**), or less probably with (**III**) coexist, is observed on the section x_{Ga}:x_{Ge} = 0.5:0.5 at x_{Y} = 0.36. The inflection point registered on the section x_{Ga}:x_{Ge} = 0.7:0.3 is close to stoichiometry of (**II**). This observation can be evidence that the T_{m} of (**II**) is near 1760 K. The inflection point on the section x_{Ga}:x_{Ge} = 0.85:0.15 more likely corresponds to transition into the two-phase region of liquid with (**V**) than into that of liquid with (**II**). The enthalpy data measured after the inflections were omitted from subsequent calculations.

The Q_j coefficients, which approximate the enthalpies ($\Delta_{\text{mix}}\bar{H}_{\text{Y}}$ and $\Delta_{\text{mix}}H$) for the sections studied, are listed in Table 6. The enthalpies of mixing ($\Delta_{\text{mix}}\bar{H}_{\text{Y}}$ and $\Delta_{\text{mix}}H$) calculated by Eqs. (5) and (6) with confidence intervals are listed in Table 7. As it can be seen from Fig. 4, the integral enthalpies of mixing measured for the sections of the Ga–Ge–Y system agree well with the data for the boundary Ga–Y and Ge–Y systems. The $\Delta_{\text{mix}}H$ function becomes more negative as at x_{Y} increasing as well as at x_{Ga}:x_{Ge} ratio decreasing.

The differences between $\Delta_{\text{mix}}H_{\text{exp}}$ and $\Delta_{\text{mix}}H_{\text{model}}$ estimated by seven geometric models [17–22] are shown in Table 8. The $\Delta_{\text{mix}}H$ values estimated by the Bonnier model [17] are the best when compared with the experimental data. The model is characterized by the least scattering of $\Delta\Delta_{\text{mix}}H$ term and the least χ-parameter among the entire models used. Consequently, the Bonnier model has been chosen and $\Delta_{\text{mix}}H$ has been interpolated by the equation

$$\begin{aligned}\Delta_{\text{mix}}H &= x_{\text{Ga}}/(1-x_{\text{Y}})\Delta_{\text{mix}}H_{\text{Ga–Y}}(x_{\text{Y}})\\ &\quad + x_{\text{Ge}}/(1-x_{\text{Y}})\Delta_{\text{mix}}H_{\text{Ge–Y}}(x_{\text{Y}})\\ &\quad + (1-x_{\text{Y}})\Delta_{\text{mix}}H_{\text{Ga–Ge}}\{x_{\text{Ge}}/(1-x_{\text{Y}})\}\\ &\quad + \Delta\Delta_{\text{mix}}H, \end{aligned} \tag{12}$$

where $\Delta_{\text{mix}}H_{\text{Ga–Y}}(x_{\text{Y}})$ and $\Delta_{\text{mix}}H_{\text{Ge–Y}}(x_{\text{Y}})$ functions are taken from Eqs. (10) and (11), respectively, $\Delta_{\text{mix}}H_{\text{Ga–Ge}}\{x_{\text{Ge}}/(1-x_{\text{Y}})\}$ term is determined by the following equation (in kJ mol^{-1}):

$$\begin{aligned}&\Delta_{\text{mix}}H_{\text{Ga–Ge}}\{x_{\text{Ge}}/(1-x_{\text{Y}})\}\\ &\quad = x_{\text{Ge}}/(1-x_{\text{Y}})[1-\{x_{\text{Ge}}/(1-x_{\text{Y}})\}]\\ &\qquad \times[-2.805+3.69\{x_{\text{Ge}}/(1-x_{\text{Y}})\}\\ &\qquad -14.25\{x_{\text{Ge}}/(1-x_{\text{Y}})\}^2+20.23\{x_{\text{Ge}}/(1-x_{\text{Y}})\}^3\\ &\qquad -9.9\{x_{\text{Ge}}/(1-x_{\text{Y}})\}^4]. \end{aligned} \tag{13}$$

The contribution of $\Delta\Delta_{\text{mix}}H$ term in Eq. (12), which may be partially attributed to the ternary interactions, is derived by the formula (in kJ mol^{-1})

$$\begin{aligned}\Delta\Delta_{\text{mix}}H &= x_{\text{Y}}x_{\text{Ga}}(1-x_{\text{Ga}}-x_{\text{Y}})(53.23-1944x_{\text{Y}}\\ &\quad +34.15x_{\text{Ga}}+3257x_{\text{Y}}^2-111.31x_{\text{Ga}}^2\\ &\quad +1412x_{\text{Y}}x_{\text{Ga}}). \end{aligned} \tag{14}$$

Table 6
Evaluated Q_j coefficients for Eqs. (5) and (6) in kJ mol^{-1}, which approximate the $\Delta_{\text{mix}}\bar{H}_{\text{Y}}$ and $\Delta_{\text{mix}}H$ for sections of the Ga–Ge–Y system

Section, x_{Ga}:x_{Ge}	Q_0	Q_1	Q_2	Q_3
0.15:0.85	−247.92	−428.15	−1307.00	
0.4:0.6	−216.36	−897.44	419.66	
0.5:0.5	−206.89	−928.62	779.37	
0.7:0.3	−205.83	−728.06	559.84	
0.85:0.15	−195.81	−449.79	−2035.07	6436.27

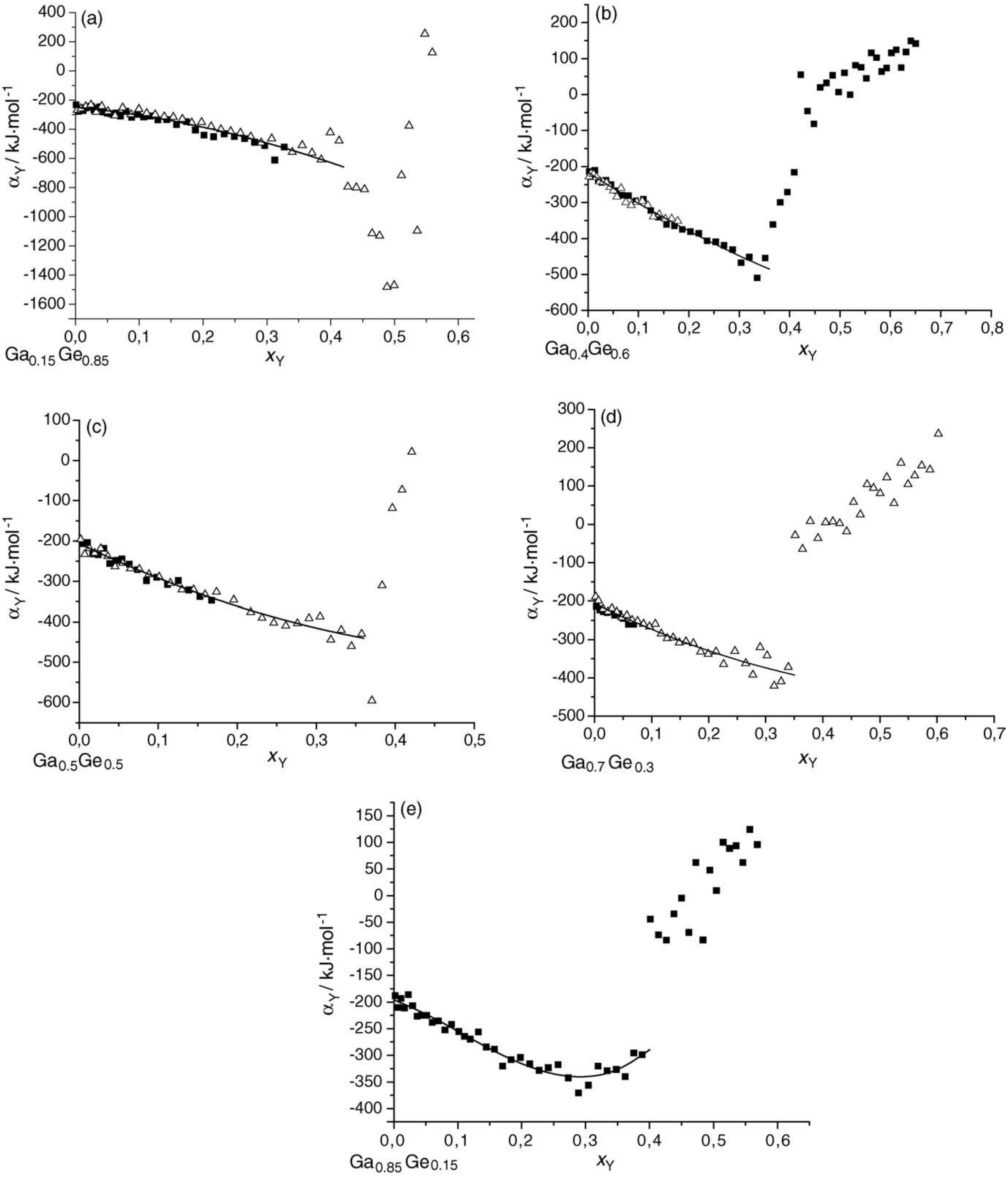

Fig. 3. Plot of alpha function of yttrium vs. mole fraction of yttrium for sections (a–e) of the ternary Ga–Ge–Y system at 1760 K; (■) and (△) data of runs 1 and 2, respectively; (—) smoothed data of runs 1 and 2.

Table 7
The partial and the integral enthalpies of mixing in liquid Ga–Ge–Y alloy

x_{Y}	$x_{Ga}:x_{Ge}$				
	0.15:0.85	0.4:0.6	0.5:0.5	0.7:0.3	0.85:0.15
	$\Delta_{mix}\bar{H}_{Y}$ (kJ mol^{-1})				
0.0	−247.92 ± 14.25	−216.36 ± 7.08	−206.89 ± 7.73	−205.83 ± 7.97	−195.81 ± 12.10
0.05	−246.02 ± 7.68	−234.82 ± 3.66	−226.86 ± 3.97	−217.35 ± 5.67	−200.88 ± 5.66
0.10	−246.08 ± 6.86	−244.55 ± 3.51	−236.49 ± 3.77	−221.16 ± 4.27	−206.31 ± 5.86
0.15	−246.77 ± 7.19	−246.76 ± 3.75	−237.45 ± 4.08	−218.51 ± 3.85	−207.60 ± 4.94
0.20	−246.93 ± 6.59	−242.60 ± 3.45	−231.32 ± 3.76	−210.59 ± 4.10	−202.03 ± 4.35
0.25	−245.61 ± 5.56	−233.15 ± 3.15	−219.56 ± 3.23	−198.48 ± 4.57	−188.37 ± 4.50
0.30	−242.06 ± 5.63	−219.43 ± 3.75	−203.51 ± 3.46	−183.19 ± 4.98	−166.66 ± 4.03
0.35	−235.71 ± 7.56	−202.40 ± 5.23	−184.39 ± 4.76	−165.65 ± 5.22	−137.98 ± 3.65
0.40	−226.19 ± 10.36				−104.19 ± 7.04
	$\Delta_{mix}H$ (kJ mol^{-1})				
0.0	−0.345 ± 0.035	−0.632 ± 0.063	−0.653 ± 0.065	−0.528 ± 0.053	−0.320 ± 0.032
0.05	−12.66 ± 0.56	−11.93 ± 0.28	−11.52 ± 0.31	−11.12 ± 0.34	−10.21 ± 0.46
0.10	−24.94 ± 0.97	−23.95 ± 0.48	−23.15 ± 0.52	−22.11 ± 0.60	−20.40 ± 0.80
0.15	−37.25 ± 1.35	−36.30 ± 0.68	−35.07 ± 0.74	−33.12 ± 0.81	−30.79 ± 1.08
0.20	−49.58 ± 1.68	−48.59 ± 0.85	−46.82 ± 0.93	−43.81 ± 1.01	−41.06 ± 1.30
0.25	−61.88 ± 1.95	−60.44 ± 1.01	−58.00 ± 1.08	−53.87 ± 1.25	−50.73 ± 1.52
0.30	−74.03 ± 2.22	−71.50 ± 1.21	−68.25 ± 1.26	−63.00 ± 1.53	−59.21 ± 1.71
0.35	−85.81 ± 2.67	−81.46 ± 1.58	−77.22 ± 1.56	−70.95 ± 1.84	−65.87 ± 1.86
0.40	−96.99 ± 3.51				−70.11 ± 2.43

Table 8
Comparison of $\Delta_{mix}H$ estimated by geometric models with experimental data for the liquid Ga–Ge–Y alloys under study

Geometric model	$\Delta\Delta_{mix}H$ (kJ mol^{-1}) = $\Delta_{mix}H_{exp} - \Delta_{mix}H_{model}$				χ (%)
	$\Delta\Delta_{mix}H_{min}$	$\Delta\Delta_{mix}H_{max}$	$\langle\Delta\Delta_{mix}H\rangle$[a]	$\langle\lvert\Delta\Delta_{mix}H\rvert\rangle$[b]	
Bonnier[c]	−4.4320	1.6678	−1.6627	1.8115	3.6524
Toop[c]	−4.5505	1.5910	−1.7373	1.8747	3.7864
Hillert 1[c]	−4.5520	1.5968	−1.7377	1.8748	3.7863
Hillert 2[c]	−4.5510	1.5910	−1.7391	1.8755	3.7882
Kohler	−2.7043	6.4768	1.7614	2.2307	5.2735
Right-hand Colinet	−5.4180	8.2970	1.9959	3.4199	9.3752
Muggianu	−0.6060	8.3061	3.8344	3.8701	11.8273

[a] $\langle\Delta\Delta_{mix}H\rangle$ is the arithmetic mean of $\Delta\Delta_{mix}H$.

[b] $\langle\lvert\Delta\Delta_{mix}H\rvert\rangle$ is the arithmetic mean of absolute value of $\Delta\Delta_{mix}H$.

[c] Boundary Ga–Ge system was used as a basis for calculation by the models.

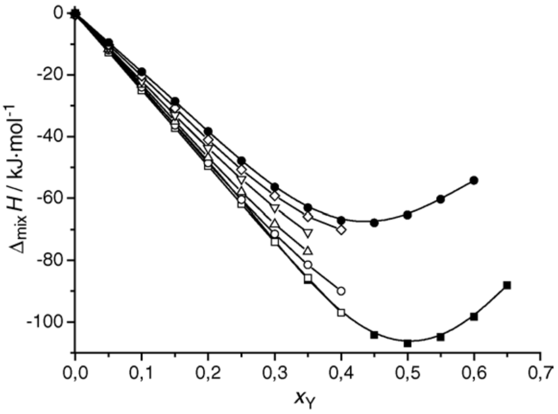

Fig. 4. Integral enthalpy of mixing in the liquid Ga–Ge–Y alloys against mole fraction of yttrium for sections: (□) $Ga_{0.15}Ge_{0.85}$–Y; (◯) $Ga_{0.4}Ge_{0.6}$–Y; (△) $Ga_{0.5}Ge_{0.5}$–Y; (▽) $Ga_{0.7}Ge_{0.3}$–Y; (◊) $Ga_{0.85}Ge_{0.15}$–Y; and literature data on the binary boundary systems: (●) Ga–Y [15]; (■) Ge–Y [16].

Fig. 5(a) demonstrates that the $\Delta_{mix}H$ values calculated from the Bonnier model are in well agreement with experimental data. As one can see from Fig. 5(a), the extreme $\Delta_{mix}H$ values are observed near the YGa–YGe section. This evidences that the YGa and YGe intermetallide compounds have large effect on the liquid phase thermodynamics with possible formation of corresponding binary clusters in the melt. The other intermetallide compounds, which can pay the essential contribution into the thermodynamics of liquid ternary alloys, are Ga_2Y, (**II**), (**III**) and (**IV**).

The difference between experimental and calculated $\Delta_{mix}H$ possesses values from −4.5 to 3 kJ mol^{-1} in the concentration region studied (Fig. 5(b)). The significant area of negative $\Delta\Delta_{mix}H$ values can be an evidence of ternary clusters presence in the liquid. As ternary intermetallides (**X**) and (**XI**) exist at concentrations close to extreme of the $\Delta\Delta_{mix}H$ function, so the most reliable composition of the ternary clusters in the melts are $YGe_{1.78}Ga_{0.92}$ or $YGe_{1.8}Ga_{0.5}$. If such clusters really exist in the liquid, in that case the intermetal-

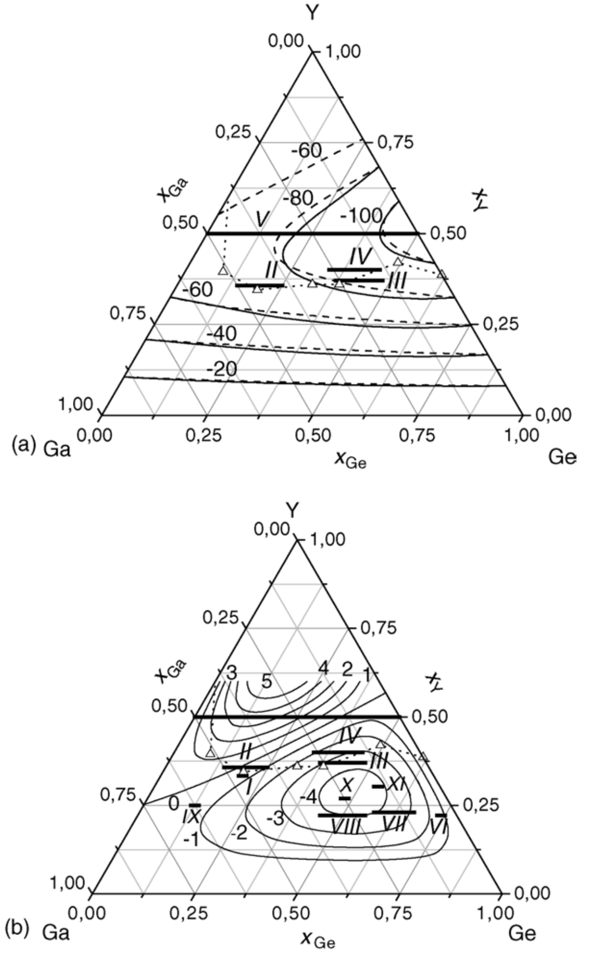

Fig. 5. (a) Projection of the integral enthalpy of mixing isolines on the Gibbs triangle for Ga–Ge–Y system at 1760 K (in kJ mol^{-1}): (—) experimental data; (- - -) data calculated by the Bonnier model [17]. (b) The contribution of the term $\Delta\Delta_{\mathrm{mix}}H$ in Eq. (12) (in kJ mol^{-1}). Solid lines numbered (**I**–**XI**) are denoted to the intermetallide compounds as in Fig. 1. Dotted line bounds the region of liquid alloys examined by calorimetry in the present study. The extrapolation of the $\Delta_{\mathrm{mix}}H$ and $\Delta\Delta_{\mathrm{mix}}H$ functions is performed by the method reported in [9] (see Eqs. (12) and (14)). The area of extrapolation is situated above the dot line. Triangles denote the concentrations corresponding to the transition into a two-phase region.

lide compounds (**X**) and/or (**XI**) can melt congruently. The other possible compositions of the ternary clusters are isostoichiometric to (**III**), (**IV**), (**VII**) or (**VIII**).

4. Conclusions

The yttrium is mixed with the Ga–Ge–Y alloys with a significant heat evolution. The enthalpies of mixing ($\Delta_{\mathrm{mix}}\bar{H}_{\mathrm{Y}}$ and $\Delta_{\mathrm{mix}}H$) become more negative from section with x_{Ga}:x_{Ge} = 0.85:0.15 to one with x_{Ga}:x_{Ge} = 0.15:0.85. The extreme of $\Delta_{\mathrm{mix}}H$ is observed in the boundary binary Ge–Y system (−107 kJ mol^{-1}). The maximal inter-component interaction lies near the YGa–YGe section, which testifies about significant contribution of binary YGa and YGe intermetallides into the thermodynamics of the ternary liquid alloys. The minimal contribution into the thermodynamics of the liquid is paid by the boundary Ga–Ge system, which does not form intermetallide compounds and is characterized by the phase diagram of simple eutectic type. The difference between experimental and calculated by the Bonnier model integral enthalpies of mixing possesses values from −4.5 to 3 kJ mol^{-1} in the concentration region studied. The location of negative extreme of the $\Delta\Delta_{\mathrm{mix}}H$ function can be indirect evidence of existence of ternary $\mathrm{YGe_{1.78}Ga_{0.92}}$ or $\mathrm{YGe_{1.8}Ga_{0.5}}$ clusters in the melt.

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