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The excess enthalpies of liquid Bi–Sb–Se alloys

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Abstract

The excess enthalpies of liquid alloys in the ternary system Bi–Sb–Se were determined at 873 K in a heat flow calorimeter for five sections $Bi_ySb_{1-y}Se$ with $y = 0.2$, 0.4, 0.5, 0.6 and 0.8 and for the section $Bi_{0.5}Sb_{0.5}$–Se at 773 K. The enthalpy surface in the ternary system is determined by a valley of exothermic minima stretching from 2 : 3 compositions Bi_2Se_3 to Sb_2Se_3 in the liquid binaries. The excess enthalpies in the binary systems were adapted with the association model using the Lukas program. Ternary interactions were taken into account for the analytical description of the ternary system. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Liquid alloys; Enthalpies of mixing; High temperature calorimetry; Bi–Sb–Se system

1. Introduction

Thermodynamic excess functions of liquid mixtures provide informations about interactions in the liquid state. For this reason the excess enthalpies of liquid alloys in systems with tellurium were measured in previous investigations [1–8]. In this paper we report the excess enthalpies in the ternary system Bi–Sb–Se. The excess enthalpies in a system with chalcogen as one component are nearly triangular shaped functions of the concentration. Sommer [9,10] presented a thermodynamic formalism, which allows to fit the experimental data in such systems.

2. Experimental

The measurements were performed with the aid of a high temperature heat flow calorimeter [11], using the isoperibolic procedure. The experimental arrangement and the procedure for the determination of H^E have been described previously [1–4]. Bi (Alfa, 99.999%), Sb (Preussag, 99.999%) and Se (Heraeus, 99.999%) were used for the experiments. The Bi_ySb_{1-y} alloys were prepared by melting Bi and Sb in the wanted composition in silica tubes which were evacuated and then sealed.

The measurements started on the metal rich side of the sections Bi_ySb_{1-y}–Se with binary Bi_ySb_{1-y} alloys, which were brought into the calorimeter tube and heated to the temperature of the measurement. Small amounts of pure Se were consecutively added from ambient temperature ($T = 298$ K) after temperature equilibration of the calorimeter. On the selenium rich part of the system small amounts of Bi_ySb_{1-y} were successively added to liquid selenium. The temperature of the measurements was 873 K and in addition 773 K for the section $Bi_{0.5}Sb_{0.5}$–Se. The enthalpy increments $H(T = 298\text{ K})$ of Bi_ySb_{1-y} and Se were needed to calculate the excess enthalpies of

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Table 1
Coefficients of the fitting of the binary systems Bi–Se, Sb–Se and Bi–Sb

	System (*i*,*j*)		
	Bi–Se (2,3)	Sb–Se (2,3)	Bi–Sb (0,0)
$\Delta H^0_{\mathrm{A}_i\mathrm{B}_j}$ (kJ mol^{-1})	−139.5	−165.2	–
$\Delta S^0_{\mathrm{A}_i\mathrm{B}_j}$ (J K^{-1} mol^{-1})	−98.9	−128.9	–
$C^H_{\mathrm{A,B}}$(kJ mol^{-1})	–	–	2.3
$C^S_{\mathrm{A,B}}$(J K^{-1}mol^{-1})	–	–	1.6
$C^H_{\mathrm{A,A}_i\mathrm{B}_j}$(kJ mol^{-1})	53.7	−17.4	–
$C^S_{\mathrm{A,A}_i\mathrm{B}_j}$(J K^{-1}mol^{-1})	84.8	−37.7	–
$C^H_{\mathrm{B,A}_i\mathrm{B}_j}$(kJ mol^{-1})	−25.8	28.4	–
$C^S_{\mathrm{B,A}_i\mathrm{B}_j}$(J K^{-1}mol^{-1})	−43.5	28.8	–

the ternary alloys. These data were determined in separate experiments by dropping $\mathrm{Bi}_y\mathrm{Sb}_{1-y}$ or Se in liquid $\mathrm{Bi}_y\mathrm{Sb}_{1-y}$, or Se, respectively, at the temperature of the measurements. The calibration of the calorimeter was carried out after each measurement by dropping pieces of tin into a second tube, which ends in the liquid alloy. The enthalpy increments $H(T=298\ \mathrm{K})$ of tin were taken from Barin [12]. The reproducibility of the heat effects was better than ±7%. All experiments were carried out under dry argon gas at atmospheric pressure.

3. Analytical descriptions

3.1. Binary systems

The calculation of the thermodynamic functions was carried out by means of the software 'BINGSS' and 'BINFKT' developed by Lukas et al. [13–15]. The thermodynamic functions of the liquid binary selenium alloys were described using the association model of Sommer [9,10]. These systems contain the associates $\mathrm{Bi_2Se_3}$ or $\mathrm{Sb_2Se_3}$in the melt. The thermodynamic functions of the limiting Bi–Sb system were expressed by a Redlich–Kister formalism. The resulting coefficients which were fitted to the experimental data by a least squares method are given in Table 1.

Table 2
Ternary interaction parameters of the association model of the system Bi–Sb–Se

Bi–Sb–Se	kJ mol^{-1}
$C^H_{\mathrm{Bi,\,Sb_2Se_3}}$	17.0
$C^H_{\mathrm{Sb,\,Bi_2Se_3}}$	29.7
$C^H_{\mathrm{Bi_2Se_3,\,Sb_2Se_3}}$	8.0

The SGTE description of the temperature dependence of the Gibbs energy function for the elements Bi and Sb was taken from [16] and [17] for Se.

3.2. Ternary system

For the analytical description of the ternary system Bi–Sb–Se the association model was used with additional parameters for interactions between the associates $\mathrm{Bi_2Se_3}$, $\mathrm{Sb_2Se_3}$ and the pure components. The procedure is analogous to the calculation of the ternary excess enthalpies in the Ge–Sn–Te system reported by Schlieper et al. [18]. The parameters of the system Bi–Sb–Se obtained by a numerical optimisation are given in Table 2. The determination of the ternary excess enthalpies from these parameters is presented in Eq. (1).

$$\begin{gathered}H^{\mathrm{E}}_{\mathrm{Bi-Sb-Se}} = n_{\mathrm{Bi}}\cdot n_{\mathrm{Sb}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Bi,Sb}}\\ +n_{\mathrm{Bi_2Se_3}}\cdot\Delta H^{\mathrm{o}}_{\mathrm{Bi_2Se_3}} + n_{\mathrm{Bi}}\cdot n_{\mathrm{Bi_2Se_3}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Bi,Bi_2}\mathit{Se}_2} + n_{\mathrm{Se}}\cdot n_{\mathrm{Bi_2Se_3}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Se,Bi_2Se_3}}+\\ +n_{\mathrm{Sb_2Se_3}}\cdot\Delta H^{\mathrm{o}}_{\mathrm{Sb_2Se_3}} + n_{\mathrm{Sb}}\cdot n_{\mathrm{Sb_2Se_3}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Sb,Sb_2Se_3}} + n_{\mathrm{Se}}\cdot n_{\mathrm{Sb_2Se_3}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Se,Sb_2Se_3}}\\ +n_{\mathrm{Sb}}\cdot n_{\mathrm{Bi_2Se_3}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Sb,Bi_2Se_3}} + n_{\mathrm{Bi}}\cdot n_{\mathrm{Sb_2Se_3}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Bi,Sb_2Se_3}} + n_{\mathrm{Bi_2Se_3}}\cdot n_{\mathrm{Sb_2Se_3}}n^{-1}\cdot C^{\mathrm{H}}_{\mathrm{Bi_2Se_3,Sb_2Se_3}}.\end{gathered} \tag{1}$$

4. Binary systems

4.1. The Bi–Se system

A critical analysis and matching of data was given by Chizhevskaya et al. [19]. The system is characterized by several intermediate phases which are derived from the rock-salt structure of BiSe by bond breaking processes due to additional selenium. Only one of the phases melts congruently: Bi_2Se_3. The excess enthalpies of the melt have been determined calorimetrically by Maekawa et al. [20]. Predel et al. [21,22] calculated activities from vapour pressure experiments. The thermodynamic functions of the melt were calculated from these literature data with the assumption of Bi_2Se_3 associates in the liquid. An exothermic minimum is found near the composition Bi_2Se_3 at -24.0 kJ mol^{-1} ($T = 873$ K).

4.2. The Sb–Se system

The system is characterized by the congruently melting compound Sb_2Se_3 ($T_m = 881$ K) and a miscibility gap at the selenium rich side. The system was assessed by Ghosh [23]. The excess enthalpies were measured by Maekawa et al. [20]. Chemical potentials were determined by Predel et al. [21,22] . A minimum of the exothermic enthalpies is found near the composition Sb_2Se_3 with –29.0 kJ mol^{-1} at 873 K. The coefficients of the optimisation of Ghosh for the description of the liquid phase could not be used because the formalism is different in our software. Therefore thermodynamic functions of the melt were recalculated with the assumption of Sb_2Se_3 associates in the liquid.

4.3. The Bi–Sb system

This phase diagram is characterized by complete solubility of the components in solid and liquid state. Thermodynamic data for the binary system were evaluated critically and a consistent coefficient set for the description of the thermodynamic properties was presented by Feutelais et al. [24]. The enthalpy of mixing of the melt deviates positively from ideality with a maximum of about 0.6 kJ mol^{-1}. For an adaption to our software, the liquid phase was reoptimized by Römermann [25]. Experimental thermodynamic data were given by Wittig and Müller [26], Yazawa et al. [27], Savitskii et al. [28], and Kawakami [29].

4.4. The ternary system Bi–Sb–Se

The section Bi_2Se_3–Sb_2Se_3 of the system was investigated by Kuznetsov et al. [30]. Recently Bi–Sb–Se thin films have been subject of several physicochemical and physical investigations because of their optomagnetical and electro-optical properties [31,32].

5. Results and discussion

The heat effects ΔQ of the mixing were determined for five sections with constant concentration ratio of two components ($y_{Bi}/y_{Sb} = 0.2, 0.4, 0.5, 0.6$ and 0.8) at 873 K and for one section with $y_{Bi}/y_{Sb} = 0.5$ at 773 K. The experimental enthalpies H^E_{exp} of the reaction

$$(1-x)Bi_ySb_{1-y}(l) + xSe(l) \rightarrow Bi_{y(1-x)}Sb_{(1-y)(1-x)}Se_x(l), \qquad (2)$$

and the ternary excess enthalpies H^E of the reaction

$$(1-x)(y)Bi(l) + (1-x)Sb(l) + xSe(l) \rightarrow Bi_{y(1-x)}Sb_{(1-x)(1-y)}Se_x(l), \qquad (3)$$

are presented in Table 3 and representatively for two sections in Figs. 1 and 2.

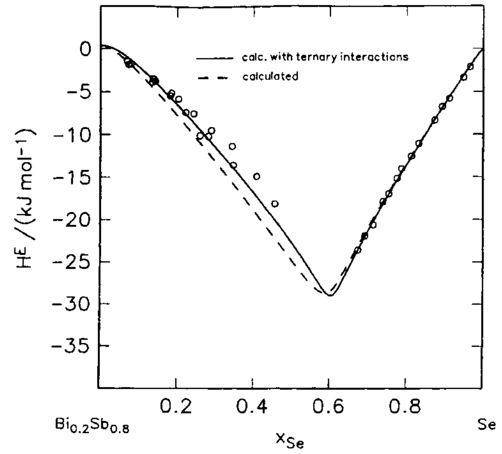

Fig. 1. Measured and calculated excess enthalpies of the ternary system Bi–Sb–Se at $T = 873$ K for the sections $Bi_ySb_{1-y}Se$ with $y = 0.2$ and 0.8. Symbols represent the measurements.

Table 3

Heat effects ΔQ, H^{E}_{exp} experimental excess enthalpies according to the reaction $(1-x)\ \mathrm{Bi}_y\mathrm{Sb}_{1-y}(\mathrm{l}) + x\ \mathrm{Se}(\mathrm{l}) \rightarrow \mathrm{Bi}_{y(1-x)}\mathrm{Sb}_{(1-y)(1-x)}\mathrm{Se}_x(\mathrm{l})$ and ternary excess enthalpies H^{E} according to the reaction $(1-x)\ (y)\ \mathrm{Bi}(\mathrm{l}) + (1-x)\ (1-y)\ \mathrm{Sb}(\mathrm{l}) + x\ \mathrm{Se}(\mathrm{l}) \rightarrow \mathrm{Bi}_{y(1-x)}\mathrm{Sb}_{(1-x)(1-y)}\mathrm{Se}_x(\mathrm{l})$ in the Bi–Sb–Se system at 873 K of the sections $\mathrm{Bi}_y\mathrm{Sb}_{1-y}$–Se and at 773 K of the section $\mathrm{Bi}_{0.5}\mathrm{Sb}_{0.5}$–Se

Starting amount $n_{\mathrm{Bi}_y\mathrm{Sb}_{1-y}}$ (mol)	Added amount n_{Se} (mol)	Mole fraction x_{Se}	Heat effect ΔQ (J)	Experimental excess enthalpy H^{E}_{exp} (J mol^{-1})	Ternary excess enthalpy H^{E} (J mol^{-1})
$\mathrm{Bi}_{0.2}\mathrm{Sb}_{0.8}$–Se					
0.009339	0.000694	0.069	−4.1	−1866	−1529
	0.000760	0.135	−6.6	−3821	−3509
	0.001529	0.242	−23.6	−7865	−7592
	0.001873	0.342	−28.7	−11622	−11384
	0.001541	0.407	−41.2	−15160	−14946
	0.001426	0.456	−46.4	−18349	−18153
0.010057	0.000728	0.068	−3.7	−1757	−1421
	0.000876	0.138	−7.6	−3853	−3541
	0.000666	0.184	−8.5	−5467	−5172
	0.001633	0.280	−44.7	−10486	−10225
	0.001406	0.345	−36.8	−13841	−13605
0.010057	0.000785	0.072	−7.2	−2190	−1855
	0.000752	0.133	−9.3	−4210	−3897
	0.000668	0.180	−8.3	−5805	−5508
	0.000644	0.221	−15.1	−7732	−7450
	0.000642	0.258	−27.6	−10394	−10126
0.010057	0.000853	0.078	−5.3	−2128	−1795
	0.000799	0.141	−7.7	−4073	−3763
	0.000901	0.202	−10.9	−6149	−5861
	0.001507	0.288	−29.3	−9809	−9552
$\mathrm{Bi}_{0.4}\mathrm{Sb}_{0.6}$–Se					
0.008940	0.001663	0.157	−12.0	−4429	−3972
	0.001436	0.257	−28.5	−8778	−8376
	0.001423	0.336	−36.0	−12742	−12382
	0.001408	0.399	−25.5	−15239	−14914
	0.001553	0.456	−53.3	−19032	−18737
	0.001411	0.499	−56.1	−22333	−22061
0.008940	0.000794	0.082	−5.5	−2279	−1782
	0.000770	0.149	−6.9	−4304	−3844
	0.000572	0.193	−6.2	−5729	−5292
	0.000067	0.198	−9.3	−6654	−6220
	0.000797	0.251	−14.0	−8789	−8384
	0.001611	0.340	−37.5	−13008	−12651
	0.001390	0.402	−39.3	−16381	−16057
	0.001648	0.461	−55.8	−20204	−19912
$\mathrm{Bi}_{0.5}\mathrm{Sb}_{0.5}$–Se, $T = 773$ K					
0.008464	0.000705	0.077	−8.3	−2329	−1808
	0.000670	0.140	−9.1	−4352	−3867
	0.000602	0.189	−10.4	−6166	−5709
	0.000769	0.245	−14.7	−8323	−7897
	0.000693	0.289	−21.0	−10675	−10274
	0.000557	0.321	−28.5	−13313	−12929

Table 3 (*Continued*)

Starting amount $n_{\mathrm{Bi}_y\mathrm{Sb}_{1-y}}$ (mol)	Added amount n_{Se} (mol)	Mole fraction x_{Se}	Heat effect ΔQ (J)	Experimental excess enthalpy $H^{\mathrm{E}}_{\mathrm{exp}}$ (J mol^{-1})	Ternary excess enthalpy H^{E} (J mol^{-1})
0.008464	0.000647	0.071	−8.3	−2224	−1700
	0.000721	0.139	−14.9	−4936	−4450
	0.000581	0.187	−21.3	−7739	−7281
	0.000694	0.238	−19.2	−10143	−9713
	0.000769	0.287	−24.4	−12741	−12339
	0.000566	0.320	−39.1	−16143	−15759
0.008464	0.000736	0.080	−8.5	−2400	−1881
	0.000868	0.159	−13.5	−5132	−4657
	0.000637	0.209	−12.3	−7076	−6630
	0.000756	0.261	−16.7	−9287	−8870
$\mathrm{Bi}_{0.5}\mathrm{Sb}_{0.5}$–Se					
0.008464	0.000689	0.075	−5.7	−2208	−1686
	0.000761	0.146	−11.5	−4811	−4329
	0.000672	0.200	−8.5	−6638	−6187
	0.000793	0.256	−12.8	−8767	−8347
	0.000676	0.298	−12.5	−10492	−10096
0.008464	0.000714	0.078	−4.3	−2103	−1582
	0.000662	0.140	−5.9	−3976	−3491
	0.000724	0.199	−9.6	−6056	−5604
	0.000736	0.251	−12.5	−8138	−7715
	0.000679	0.293	−13.4	−9983	−9584
0.008464	0.000890	0.095	−4.3	−2455	−1944
	0.000745	0.162	−7.5	−4564	−4091
	0.000751	0.220	−9.2	−6547	−6107
	0.000779	0.272	−14.1	−8728	−8317
	0.000851	0.322	−16.7	−10903	−10521
	0.000625	0.354	−15.6	−12577	−12212
	0.000579	0.381	−16.0	−14106	−13757
	0.000831	0.417	−24.4	−16184	−15855
	0.000723	0.445	−22.7	−17903	−17590
	0.000799	0.472	−27.6	−19776	−19478
$\mathrm{Bi}_{0.6}\mathrm{Sb}_{0.4}$–Se					
0.008041	0.000728	0.083	−6.0	−2418	−1922
	0.000850	0.164	−8.6	−4941	−4489
	0.000826	0.230	−10.7	−7225	−6808
	0.000681	0.277	−11.0	−9049	−8658
	0.000642	0.317	−12.1	−10717	−10347
	0.000735	0.357	−17.7	−12729	−12381
	0.000740	0.393	−16.2	−14409	−14081
	0.000694	0.423	−17.6	−15990	−15677
	0.000736	0.452	−21.3	−17687	−17391
	0.000817	0.481	−29.6	−19764	−19483
0.008041	0.000680	0.078	−4.7	−2159	−1660
	0.000717	0.148	−5.9	−4200	−3738
	0.000686	0.206	−8.3	−6151	−5721
	0.000064	0.211	−9.6	−7189	−6762
	0.000670	0.259	−11.8	−9120	−8719

Table 3 (*Continued*)

Starting amount $n_{\mathrm{Bi}_y\mathrm{Sb}_{1-y}}$ (mol)	Added amount n_{Se} (mol)	Mole fraction x_{Se}	Heat effect ΔQ (J)	Experimental excess enthalpy $H^{\mathrm{E}}_{\mathrm{exp}}$ (J mol^{-1})	Ternary excess enthalpy H^{E} (J mol^{-1})
$\mathrm{Bi}_{0.8}\mathrm{Sb}_{0.2}$–Se					
0.007311	0.000798	0.098	−5.7	−2767	−2441
	0.000721	0.172	−6.7	−5011	−4712
	0.000782	0.239	−9.6	−7313	−7038
	0.000703	0.291	−10.8	−9294	−9038
	0.000854	0.345	−15.8	−11601	−11365
	0.000718	0.385	−16.4	−13553	−13331
0.007311	0.000685	0.086	−5.8	−2530	−2200
	0.000836	0.172	−7.6	−5134	−4836
	0.000811	0.242	−11.8	−7688	−7414
	0.000693	0.293	−10.3	−9573	−9318
	0.000803	0.344	−17.2	−11946	−11709
	0.000728	0.384	−15.5	−13805	−13582
	0.000699	0.418	−17.7	−15617	−15407

Starting amount n_{Se} (mol)	Added amount $n_{\mathrm{Bi}_y\mathrm{Sb}_{1-y}}$ (mol)	Mole fraction x_{Se}	Heat effect ΔQ (J)	Experimental excess enthalpy $H^{\mathrm{E}}_{\mathrm{exp}}$ (J mol^{-1})	Ternary excess enthalpy H^{E} (J mol^{-1})
Se—$\mathrm{Bi}_{0.2}\mathrm{Sb}_{0.8}$					
0.016653	0.000918	0.948	−28.3	−3402	−3383
	0.000705	0.911	−23.0	−5851	−5819
	0.0008	0.873	−26.4	−8425	−8379
	0.001431	0.812	−49.3	−12629	−12561
	0.000968	0.775	−36.3	−15295	−15214
	0.000625	0.754	−28.8	−17133	−17044
	0.001211	0.714	−64.2	−20776	−20672
0.015186	0.000552	0.965	−14.8	−2142	−2134
	0.001286	0.892	−38.4	−6822	−6796
	0.001249	0.831	−44.3	−11118	−11077
	0.001014	0.787	−34.1	−14105	−14052
	0.001269	0.739	−54.7	−18010	−17946
	0.001386	0.692	−65.7	−22029	−21953
	0.000586	0.674	−30.5	−23702	−23622
Se–$\mathrm{Bi}_{0.4}\mathrm{Sb}_{0.6}$					
0.012708	0.000904	0.934	−23.4	−3890	−3854
	0.000928	0.874	−26.0	−7521	−7452
	0.001052	0.815	−32.8	−11325	−11225
	0.000913	0.770	−35.8	−14678	−14553
	0.000937	0.729	−38.4	−17848	−17701
Se–$\mathrm{Bi}_{0.5}\mathrm{Sb}_{0.5}$, $T = 773$ K					
0.017791	0.000932	0.950	−44.4	−3829	−3801
	0.000889	0.907	−55.3	−7800	−7748
	0.000376	0.890	−24.8	−9445	−9383
	0.000484	0.869	−30.6	−11410	−11336
	0.001489	0.810	−112.7	−17753	−17646
0.017593	0.000290	0.984	−14.8	−1573	−1564
	0.000672	0.948	−35.5	−5091	−5061

Table 3 (*Continued*)

Starting amount $n_{Bi_ySb_{1-y}}$ (mol)	Added amount n_{Se} (mol)	Mole fraction x_{Se}	Heat effect ΔQ (J)	Experimental excess enthalpy H^E_{exp} (J mol^{-1})	Ternary excess enthalpy H^E (J mol^{-1})
	0.000654	0.916	−35.2	−8307	−8260
	0.000605	0.888	−34.4	−11187	−11124
	0.000854	0.851	−55.1	−15283	−15199
	0.000206	0.843	−14.0	−16255	−16167
Se–$Bi_{0.5}Sb_{0.5}$					
0.0016568	0.000738	0.957	−17.5	−2340	−2316
	0.001023	0.904	−26.9	−5414	−5360
	0.001225	0.847	−35.6	−8847	−8761
	0.001399	0.791	−46.8	−12569	−12451
	0.000958	0.756	−38.2	−15123	−14985
	0.001721	0.701	−80.3	−19685	−19516
	0.000888	0.676	−55.2	−22351	−22168
0.016482	0.000687	0.960	−19.5	−2382	−2360
	0.000830	0.916	−21.0	−4876	−4829
Se–$Bi_{0.6}Sb_{0.}$					
0.0016554	0.001078	0.939	−29.3	−3772	−3738
	0.001232	0.878	−48.3	−8342	−8274
	0.000975	0.834	−30.9	−11186	−11093
	0.001218	0.786	−43.8	−14617	−14497
	0.000574	0.765	−26.1	−16351	−16219
	0.001202	0.725	−90.0	−21249	−21095
	0.000386	0.713	−45.0	−23406	−23245
Se–$Bi_{0.8}Sb_{0.2}$					
0.016636	0.000550	0.968	−12.5	−1708	−1697
	0.000614	0.935	−16.7	−3643	−3619
	0.000488	0.910	−12.4	−5040	−5007
	0.000841	0.870	−23.1	−7372	−7325
	0.001033	0.825	−38.9	−10490	−10427
	0.000382	0.810	−14.1	−11548	−11480
	0.000986	0.773	−54.3	−14944	−14862
	0.000652	0.750	−63.4	−18263	−18173

A projection of the isoenthalpics on the Gibbs triangle is given in Fig. 3. The exothermic values increase smoothly from through of minima along Sb_2Se_3–Bi_2Se_3 to the corners of the ternary system.

Ternary interaction parameters were at first not used in the calculation of the ternary data from H^E data of the constituent binaries. However, the enthalpy curves of the ternary mixtures were not well reproduced (Figs. 1 and 2). The systems contains binary associates which are in equilibrium with constituent non-associated atoms and with each other. Therefore these interactions had to be considered. The best fit of the system was obtained, when the interactions $Bi_2Se_3 \leftrightarrow Sb$, $Sb_2Se_3 \leftrightarrow Bi$ and $Bi_2Se_3 \leftrightarrow Sb_2Se_3$ were assumed. The excess enthalpies decrease slightly with increasing temperature (−28 to −26 kJ mol^{-1}). The effect is due to the dissociation of the associates with increasing temperatures.

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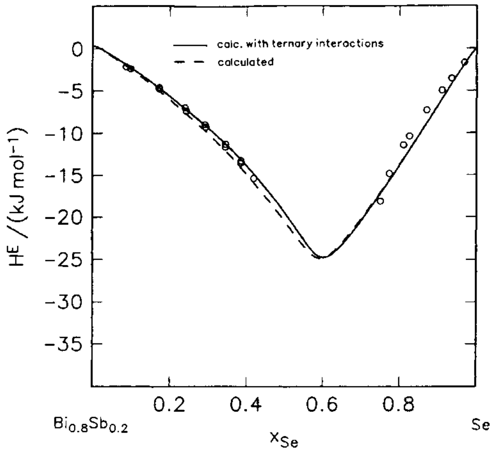

Fig. 2. Measured and calculated excess enthalpies of the ternary system Bi–Sb–Se at $T = 873$ K for the sections $Bi_ySb_{1-y}Se$ with $y = 0.2$ and 0.8. Symbols represent the measurements.

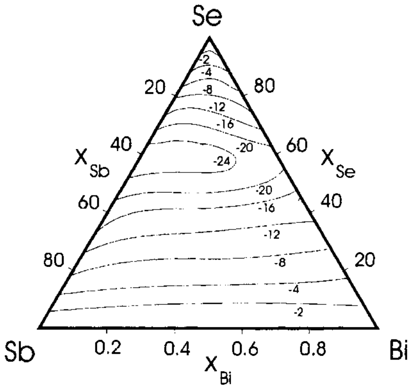

Fig. 3. Projection of the isoenthalpics on the Gibbs triangle in the Bi–Sb–Se system at $T = 873$ K in kJ mol^{-1}.

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