

## **COMPARATIVE THERMODYNAMIC ANALYSIS OF Ga–GeSb<sub>0.855</sub> SECTION IN THE TERNARY SYSTEM Ga–Ge–Sb**

*A. Kostov<sup>1</sup>, D. Ivković<sup>2</sup> and M. Ivković<sup>2</sup>*

<sup>1</sup>Copper Institute Bor, Department of Metallurgy, Zeleni bulevar 35, 19210 Bor

<sup>2</sup>University of Belgrade, Technical Faculty, VJ 12, 19210 Bor, Yugoslavia

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### **Abstract**

Thermodynamic investigations of Ga–GeSb<sub>0.855</sub> section in the ternary system Ga–Ge–Sb, which is of a practical importance in electric-industry, are presented in this paper. Results of a comparative thermodynamic analysis at 1273 K obtained by Olsen calorimetry and predicting methods – general solution model and Hajra's method are also given.

**Keywords:** calorimetry, Ga–Ge–Sb alloys, predicting methods, ternary systems, thermodynamics

### **Introduction**

It is well known that gallium and germanium, as well as ternary systems based on these metals, possess special semiconducting characteristics, necessary for further progress in electronics. These materials are specially used in the optical and electronic devices: for transistors, optical cables, semiconductors, integrated circuits, etc.

One of these Ga–Ge based systems is the ternary system Ga–Ge–Sb, which is of a practical interest in semiconducting industry. As this system has not been investigated from the thermodynamic point of view up to now, there is no thermodynamic data for the ternary system Ga–Ge–Sb.

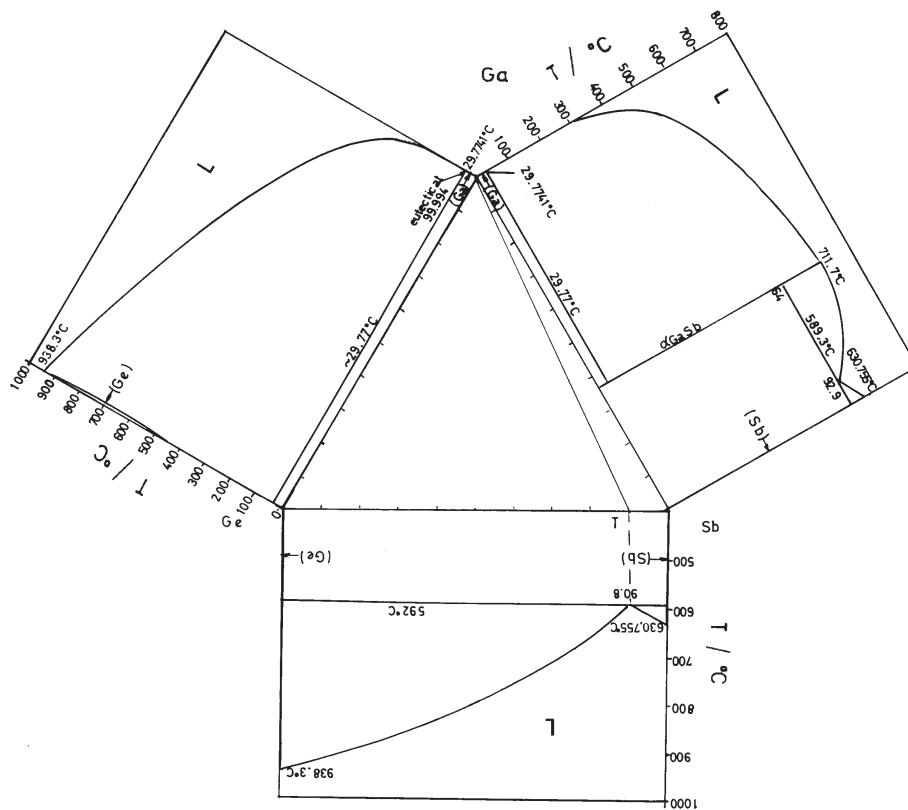
Works in this area include only the determination of the thermodynamic characteristics in the constituent binary systems. So, Ansara, Bros and Gambino [1] gave expressions for the determination of the heat of mixing and the heat of formation for binary system Ga–Ge. Eslami, Muggianu, Gambino and Bros [2] also determined the enthalpies of formation of liquid Ga–Ge alloys between 713 and 1230 K with a Calvet-type high temperature calorimeter by direct reaction calorimetry. Fornaris, Muggianu, Gambino and Bros [3] gave the equation for excess molar free energy of formation at 1240 K for Ga–Ge system, while Franceschi, Fornaris, Gambino and Bros [4] gave equations for the enthalpy of formation of Ga–Ge liquid alloys and the excess entropy of mixing.

As far as Ge–Sb system is concerned, Predel and Stein [5] determined enthalpy of mixing of liquid alloy Ge–Sb at 1273 K directly by a high-temperature calorimeter, and Chevalier [6] determined enthalpy of mixing by the use of TERMODATA software.

Ga–Sb binary system is mostly investigated among all constitutional binaries in the Ga–Ge–Sb ternary system [7–9], and the best review of thermodynamic data for Ga–Sb is given in Hultgren book [10]. Thermodynamic investigations of Ga–Sb binary system are also done in favour of thermodynamic analysis some ternary systems such as: Ga–Sb–Cu [11], Ga–Sb–S [12, 13] and Ga–Sb–Te [14].

Considering the fact that there are no thermodynamic data for the ternary system Ga–Ge–Sb and the existing literature data are mostly related to the thermodynamic properties of constitutional binary systems, there is a need for more complete thermodynamic determination of this ternary system.

For this reason, thermodynamic investigations of the Ga–GeSb<sub>0.855</sub> section in the ternary system Ga–Ge–Sb, are presented in this paper based on the results of the compar-



**Fig.1** Ternary system Ga–Ge–Sb and the investigated Ga–GeSb<sub>0.855</sub> section with the phase diagrams of the binary systems

ative thermodynamic analysis obtained by experimental method of Oelsen calorimetry [15–17] and predicting methods according to Chou [18–20] and Hajra [21, 22].

The ternary system Ga–Ge–Sb and the investigated Ga–GeSb<sub>0.855</sub> section with the phase diagrams of the constitutional binary systems Ga–Ge, Ge–Sb and Ga–Sb are presented in Fig. 1.

## Experimental

All experimental investigations were carried out with pure germanium, gallium and antimony of p.a. grade.

Oelsen calorimetry was used for the experimental thermodynamic investigation of the Ga–GeSb<sub>0.855</sub> section in the ternary system Ga–Ge–Sb. Descriptions of this experimental technique were reported in [15–17].

Six samples with determined composition and constant volume of 1 cm<sup>3</sup> for the Ga–GeSb<sub>0.855</sub> section of the ternary system Ga–Ge–Sb were chosen for experimental investigation. Their composition is given in Table 1.

**Table 1** Composition of the investigated samples

N <sup>o</sup>	Composition/mass%			Molar content			Mass/g			$\Sigma m/g$
	Ga	Ge	Sb	$x_{Ga}$	$x_{Ge}$	$x_{Sb}$	Ga	Ge	Sb	
T0	0	9.2	90.8	0	0.145	0.855	0.0000	0.6513	5.8621	6.5134
T1	13.24	8.48	78.28	0.2	0.123	0.677	0.8515	0.5452	5.0330	6.4297
T2	28.84	7.19	63.97	0.4	0.092	0.508	1.8246	0.4549	4.0464	6.3259
T3	47.79	5.06	47.15	0.6	0.061	0.339	2.9691	0.3143	2.9294	6.2128
T4	70.96	2.86	26.18	0.8	0.031	0.169	4.3101	0.1739	1.5899	6.0739
T5	100	0	0	1	0	0	5.9100	0	0	5.9100

The water equivalent was determined by a standard method using dissolved Na<sub>2</sub>CO<sub>3</sub> and it has a value of 3453 J K<sup>-1</sup> for the used Oelsen's calorimeter.

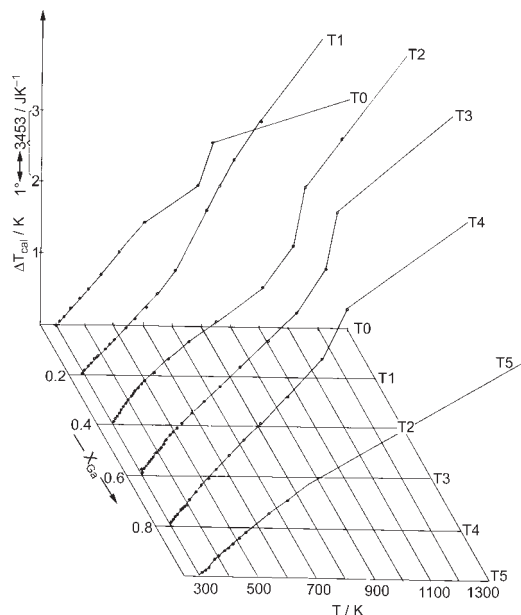
## Results and discussion

### *Thermodynamic analysis by Oelsen calorimetry*

Based on the cooling curves obtained by rapid cooling of the investigated samples in Oelsen's calorimeter, the space diagram dependence of the temperature change of the calorimeter upon molar content and temperature is obtained and shown in Fig. 2.

According to the temperature change of the calorimeter read from the space diagram, the enthalpy diagrams shown in Fig. 3 for the temperature interval 350–1300 K for the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb was constructed.

In Oelsen's thermodynamic analysis [15–17] thermodynamic properties are determined by so-called Oelsen's integral, which enable calculating partial molar Gibbs energy of mixing from directly measured values of enthalpies, and activities of the



**Fig. 2** The space diagram: the temperature change of the calorimetric vs. molar content and temperature for the Ga-GeSb<sub>0.855</sub> section in ternary system Ga-Ge-Sb

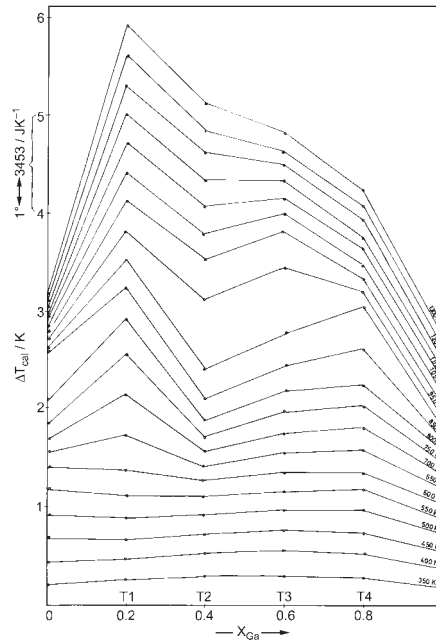
components of the system as well. Therefore, the basic equation used in Oelsen thermodynamic analysis is:

$$-\frac{G_i^M}{T} = \int_{1/T_0}^{1/T} H_{x,T} d\left(\frac{1}{T}\right) = -R \ln a_i \quad (1)$$

where  $G_i^M$  is the partial Gibbs energy for component  $i$ ,  $T_0$  is the starting temperature,  $T$  the final temperature,  $H_{x,T}$  the enthalpy value measured in the Oelsen's calorimeter for the temperature change from  $T_0$  to  $T$ ,  $R$  the gas constant and  $a_i$  the activity of the component  $i$ .

According to the Oelsen's thermodynamic analysis [15–17], the next step is graphic planimetry, as shown in Fig. 4 for sample T3, which enables further quantitative thermodynamic analysis.

The construction of the tangent for the determination of  $-R \ln a_i$  at 1273 K is shown in Fig. 5. The results of the Oelsen's quantitative thermodynamic analysis, which include values for activities, activity coefficients, partial molar Gibbs energy of mixing and partial molar Gibbs excess energy for gallium at 1273 K, for investigated Ga-GeSb<sub>0.855</sub> section of the ternary system Ga-Ge-Sb are given in Table 2.



**Fig. 3** The enthalpy isotherm diagram for the temperature interval 350–1300 K for the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb

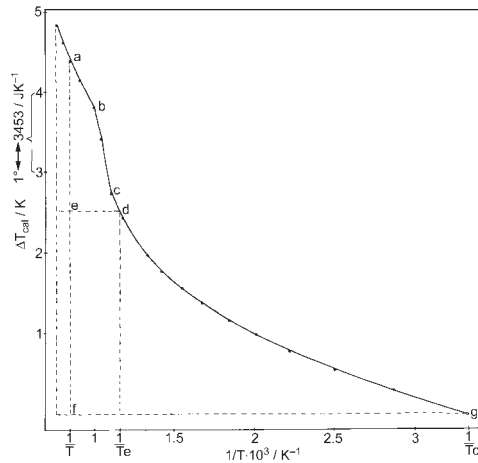
**Table 2** Results of the Olsen's quantitative thermodynamic analysis for the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb at 1273 K

N <sup>o</sup>	a <sub>Ga</sub>	γ <sub>Ga</sub>	$G_{\text{Ga}}^{\text{xs}} = RT \ln \gamma_{\text{Ga}}$ $G_{\text{Ga}}^{\text{xs}} = RT \ln a_{\text{Ga}}$	
			J mol <sup>-1</sup>	
T0	0	–	–	–
T1	0.1198	0.5990	–5424	–22458
T2	0.2721	0.6802	–4079	–13776
T3	0.4989	0.8315	–1953	–7359
T4	0.7666	0.9582	–452	–2813
T5	1	1	0	0

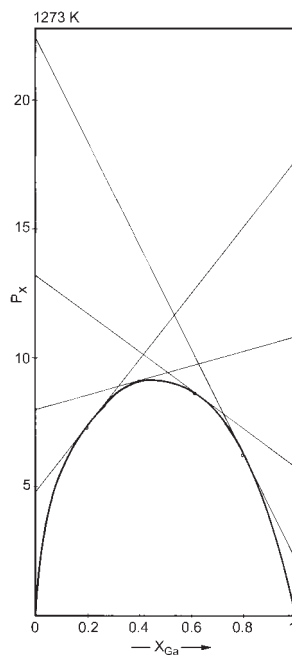
#### *Predicting thermodynamic properties by Chou's general solution model*

The Chou's general solution model for predicting thermodynamic properties of a multi-component system from binaries [18–20] has been used to predict thermodynamic properties of the investigated Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb.

The method provided recently by Chou [18–20] has been proved to be the most reasonable one in all aspects among other geometrical models. This model cannot only generalize various kinds of situations, break down the boundary between sym-



**Fig. 4** Graphic planimetry (for sample T3)



**Fig. 5** The construction of the tangent for determination of  $-R\ln a_{\text{Ga}}$

metrical and asymmetrical systems, but also can thoroughly rule out any human interference in the calculation process [23]. The accuracy of this model has already been proved theoretically and the accuracy of calculation has also been shown in some practical examples [18–20, 23]. Therefore, this model is applied for calculating the thermodynamic properties of the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb.

When the Chou's model is applied to the Ga–Ge–Sb system, first of all, it is necessary to calculate the similarity coefficients for three binaries that are defined as [19]:

$$\xi_{i(j)}^{(k)} = \frac{\eta(ij, ik)}{\eta(ij, ik) + \eta(ji, jk)}, \quad (2)$$

$(i, j, k=1, 2, 3, i \neq j \neq k)$

where  $\eta(ij, ik)$  is a function related to the excess Gibbs free energy of 'ij' and 'ik' two binaries:

$$\eta(ij, ik) = \int_{x_i=0}^{x_i=1} (\Delta G_{ij}^{xs} - \Delta G_{ik}^{xs})^2 dx_i, \quad (3)$$

$$X_i = X_{i(j)} = X_{i(ik)}, \quad (i, j, k=1, 2, 3, i \neq j \neq k)$$

and called as 'the deviation sum of squares'. Thus, the selected binary compositions  $X_{i(j)}$  can be calculated in terms of the ternary composition  $x_i$ :

$$X_{i(j)} = x_i + x_k \xi_{i(j)}^{(k)} \quad (4)$$

and the total excess Gibbs free energy of mixing will be

$$\Delta G^{xs} = W_{12} \Delta G_{12}^{xs} + W_{23} \Delta G_{23}^{xs} + W_{31} \Delta G_{31}^{xs} \quad (5)$$

where the probability weight  $W_{ij}$  is defined as

$$W_{ij} = \frac{x_i x_j}{X_{i(j)} X_{j(i)}} \quad (6)$$

Therefore, when the three binary excess Gibbs energies of mixing are known, according to the above equations, one may calculate the ternary Gibbs energy of mixing. If the binary excess Gibbs energy of mixing is given in terms of regular solution parameters, the above calculation can be simplified to:

$$\begin{aligned} \Delta G^{xs} = & x_1 x_2 (A_{12}^0 + A_{12}^1 (x_1 - x_2) + A_{12}^2 (x_1 - x_2)^2) + \\ & + x_2 x_3 (A_{23}^0 + A_{23}^1 (x_2 - x_3) + A_{23}^2 (x_2 - x_3)^2) + \\ & + x_3 x_1 (A_{31}^0 + A_{31}^1 (x_3 - x_1) + A_{31}^2 (x_3 - x_1)^2) + f x_1 x_2 x_3 \end{aligned} \quad (7)$$

where  $A_{ij}^0$ ,  $A_{ij}^1$ ,  $A_{ij}^2$  parameters for binary system 'ij' are independent of composition, only relying on temperature, which have been used in the regular type equation:

$$\Delta G_{ij}^{xs} = X_i X_j [A_{ij}^0 + A_{ij}^1 (X_i - X_j) + A_{ij}^2 (X_i - X_j)^2 + \dots + A_{ij}^n (X_i - X_j)^n] \quad (8)$$

where  $X_i$  and  $X_j$  indicate the mole fraction of component 'i' and 'j' in 'ij' binary system.

The function  $f$  is the ternary interaction coefficient expressed by [19]:

$$\begin{aligned}
 f = & (2\xi_{12} - 1)[A_{12}^2((2\xi_{12} - 1)x_3 + 2(x_1 - x_2)) + A_{12}^1] + \\
 & + (2\xi_{23} - 1)[A_{23}^2((2\xi_{23} - 1)x_1 + 2(x_2 - x_3)) + A_{23}^1] + \\
 & + (2\xi_{31} - 1)[A_{31}^2((2\xi_{31} - 1)x_2 + 2(x_3 - x_1)) + A_{31}^1]
 \end{aligned}
 \tag{9}$$

The thermodynamic calculations in the investigated ternary system Ga–Ge–Sb were carried out along the Ga–GeSb<sub>0.855</sub> section. The excess Gibbs energies of the three binary systems Ga–Ge, Ge–Sb and Sb–Ga are taken from [3, 5, 8], respectively. Binary regular-solution parameters for the binary systems Ga–Ge, Ge–Sb and Sb–Ga at temperature 1273 K, used for applying the general solution model were fitted according to Eq. (8). The values for these parameters are shown in Table 3.

**Table 3** Binary regular-solution parameters for Ga–Ge, Ge–Sb and Sb–Ga binaries at 1273 K (Ga–Ge–Sb is set in 1–2–3 order)

Parameter	Ga–Ge	Ge–Sb	Sb–Ga
$A_{ij}^0$	–4777.1	–12960.275	–13137.225
$A_{ij}^1$	1593.9	2145.55	3339.45
$A_{ij}^2$	1150.7	–10431.275	2208.975

Based on the presented starting data, the calculation according to predicting method of Chou was done for the investigated Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb at temperature 1273 K. The ternary interaction coefficient  $f$  is calculated according to Eq. (9). Also, ternary integral excess Gibbs energy and the other thermodynamic properties – activities, activity coefficients, and partial molar quantities for gallium, germanium and antimony are calculated. These results are given in Table 4.

#### *Predicting of thermodynamic properties by Hajra's method*

Hajra's method [21, 22] has been used to predict thermodynamic properties of the investigated Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb.

Hajra's method for predicting the thermodynamic properties of ternary systems is based on the knowledge of the infinite dilution constants and interaction parameters for the constitutive binary systems [21, 22]. Although these parameters are originally intended to be useful in the interpretation of properties for dilute solutions, by this method the approach is extended to the concentrated solutions [22].

Hajra developed a ternary function based on the Maclaurin infinite series and subjected to different boundary conditions, which presents the summary of these series. It is thermodynamically consistent and capable of interpreting properties of the ternary systems [22].

According to Hajra [21, 22] integral molar Gibbs excess energy for a ternary system,  $\Delta G_{123}^{xs}$ , could be presented in a following functional form:



$$\begin{aligned}
\frac{\Delta G_{123}^{xs}}{RT} = & x_1 x_2 (a_1 x_1 + a_2 x_2 + x_1 x_2 (a_3 x_1 + a_4 x_2)) + \\
& + x_1 x_3 (a_5 x_1 + a_6 x_3 + x_1 x_3 (a_7 x_1 + a_8 x_3)) + \\
& + x_2 x_3 (a_9 x_2 + a_{10} x_3 + x_2 x_3 (a_{11} x_2 + a_{12} x_3)) + \\
& + x_1 x_2 x_3 (a_{13} x_1 + a_{14} x_2 + a_{15} x_3)
\end{aligned} \tag{10}$$

where  $x_1, x_2, x_3$  are molar contents for three system components, and  $a_1$  through  $a_{15}$  are the empirical constants, which may be expressed by infinite dilution constants,  $\gamma_{i(j)}^0$  and interaction parameters,  $\epsilon_{i(j)}^i$ , as follows:

$$\begin{aligned}
a_1 &= \ln \gamma_{2(1)}^0 \\
a_2 &= \ln \gamma_{1(2)}^0 \\
a_3 &= \frac{1}{2} \epsilon_{2(1)}^2 + 2 \ln \gamma_{2(1)}^0 - \ln \gamma_{1(2)}^0 \\
a_4 &= \frac{1}{2} \epsilon_{1(2)}^1 + 2 \ln \gamma_{1(2)}^0 - \ln \gamma_{2(1)}^0 \\
a_5 &= \ln \gamma_{3(1)}^0 \\
a_6 &= \ln \gamma_{1(3)}^0 \\
a_7 &= \frac{1}{2} \epsilon_{3(1)}^3 + 2 \ln \gamma_{3(1)}^0 - \ln \gamma_{1(3)}^0 \\
a_8 &= \frac{1}{2} \epsilon_{1(3)}^1 + 2 \ln \gamma_{1(3)}^0 - \ln \gamma_{3(1)}^0 \\
a_9 &= \ln \gamma_{3(2)}^0 \\
a_{10} &= \ln \gamma_{2(3)}^0 \\
a_{11} &= \frac{1}{2} \epsilon_{3(2)}^3 + 2 \ln \gamma_{3(2)}^0 - \ln \gamma_{2(3)}^0 \\
a_{12} &= \frac{1}{2} \epsilon_{2(3)}^2 + 2 \ln \gamma_{2(3)}^0 - \ln \gamma_{3(2)}^0 \\
a_{13} &= \epsilon_{2(1)}^3 + 2 \ln \gamma_{2(1)}^0 - \ln \gamma_{3(1)}^0 \\
a_{14} &= \epsilon_{3(2)}^1 + 2 \ln \gamma_{1(2)}^0 + 2 \ln \gamma_{3(2)}^0 \\
a_{15} &= \epsilon_{1(3)}^2 + 2 \ln \gamma_{1(3)}^0 + 2 \ln \gamma_{2(3)}^0 + \frac{1}{2} \epsilon_{1(3)}^1 + 2 \ln \gamma_{1(3)}^0 - \ln \gamma_{3(1)}^0
\end{aligned} \tag{11}$$

It should be noted that constants  $a_1$  through  $a_{12}$  match exactly as corresponding binary functions, while the constants pertaining to specific ternary interaction ( $a_{13}$ – $a_{15}$ ) differ due to the truncational effects. Namely, in case of binary system ( $x_1, x_2$ ) Hajra's model can describe as four-parameters function [21, 22]:

**Table 4** Ternary interaction coefficient  $f$  and thermodynamic properties of the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb at 1273 K obtained by Chou’s general solution model

N°	$f$ J mol <sup>-1</sup>	$a_{\text{Ga}}$	$\gamma_{\text{Ga}}$	$G_{\text{Ga}}^{\text{xs}}/ G_{\text{Ga}}^{\text{M}}/$		$a_{\text{Ge}}$	$\gamma_{\text{Ge}}$	$G_{\text{Ge}}^{\text{xs}}/ G_{\text{Ge}}^{\text{M}}/$		$a_{\text{Sb}}$	$\gamma_{\text{Sb}}$	$G_{\text{Sb}}^{\text{xs}}/ G_{\text{Sb}}^{\text{M}}/ \Delta G^{\text{xs}}/ \Delta G^{\text{M}}/$			
				J mol <sup>-1</sup>				J mol <sup>-1</sup>				J mol <sup>-1</sup>			
T0	8405	0	0.703	-3721		0.635	4.379	15632	-4805	0.710	0.831	-1957	-3615	593	-3788
T1	5540	0.119	0.599	-5424	-22457	0.588	4.785	16571	-5608	0.561	0.829	-1983	-6112	-389	-9319
T2	2934	0.272	0.680	-4072	-13770	0.116	1.263	2475	-22778	0.381	0.751	-3026	-10194	-2939	-12782
T3	327	0.498	0.831	-1957	-7364	6E-3	0.106	-23679	-53280	0.203	0.600	-5399	-16848	-4449	-13380
T4	-2308	0.766	0.958	-449	-2811	2E-4	0.006	-53548	-90313	0.067	0.398	-9745	-28561	-3666	-9875
T5	4915	1	1	0	0	0				0				0	0

$$\frac{\Delta G^{xs}}{RT} = x_1(1-x_1)[a_1 + a_2x_2 + x_2(1-x_2)(a_3 + a_4x_2)] \quad (12)$$

where is:

$$\begin{aligned} a_1 &= \ln\gamma_2^0 \\ a_2 &= \ln\gamma_1^0 - \ln\gamma_2^0 \\ a_3 &= \frac{1}{2}\epsilon_2^2 - \ln\gamma_1^0 + 2\ln\gamma_2^0 \\ a_4 &= \frac{1}{2}(\epsilon_1^1 - \epsilon_2^2) + 3(\ln\gamma_1^0 - \ln\gamma_2^0) \end{aligned} \quad (13)$$

Therefore, the first step in Hajra's method is to obtain the infinite dilution constants and interaction parameters for the constitutive three binary systems Ga–Ge, Ge–Sb and Sb–Ga at the investigated temperature 1273 K according to Eqs (12) and (13), and then to determine the infinite dilution constants and interaction parameters for the ternary system Ga–Ge–Sb, according to Eq. (11).

Obtained values of these parameters for binary systems Ga–Ge, Ge–Sb and Sb–Ga and ternary system Ga–Ge–Sb at 1273 K are shown in Table 5.

**Table 5** Values of the infinite dilution constants and interaction parameters for binary systems Ga–Ge, Ge–Sb and Sb–Ga, and ternary system Ga–Ge–Sb at 1273 K

Systems			
Ga–Ge	Ge–Sb	Sb–Ga	Ga–Ge–Sb
$\gamma_{\text{Ge(Ga)}}^0 = 0.825$	$\gamma_{\text{Sb(Ge)}}^0 = 0.134$	$\gamma_{\text{Ga(Sb)}}^0 = 0.488$	$\epsilon_{\text{Ge(Ga)}}^{\text{Sb}} = 2.708$
$\gamma_{\text{Ga(Ge)}}^0 = 0.611$	$\gamma_{\text{Ge(Sb)}}^0 = 0.090$	$\gamma_{\text{Sb(Ga)}}^0 = 0.260$	$\epsilon_{\text{Sb(Ge)}}^{\text{Ga}} = 3.574$
$\epsilon_{\text{Ga(Ge)}}^{\text{Ga}} = 0.719$	$\epsilon_{\text{Sb(Ge)}}^{\text{Sb}} = 11.089$	$\epsilon_{\text{Ga(Sb)}}^{\text{Ga}} = -1.498$	$\epsilon_{\text{Ga(Sb)}}^{\text{Ge}} = 8.369$
$\epsilon_{\text{Ge(Ga)}}^{\text{Ge}} = -1.088$	$\epsilon_{\text{Ge(Sb)}}^{\text{Ge}} = 13.521$	$\epsilon_{\text{Sb(Ga)}}^{\text{Sb}} = 2.288$	

By substituting these obtained values into Eq. (10), the integral molar excess Gibbs energy for ternary system Ga–Ge–Sb at 1273 K is calculated, and afterwards, remaining thermodynamic properties for all three components of the investigated system were also calculated and given in Table 6.

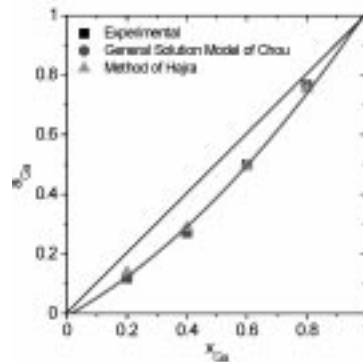
#### *Comparative thermodynamic analysis of the obtained results at 1273 K*

According to the above presented results, the values of the thermodynamic properties for all three components in this ternary system are obtained by predicting methods of Chou and Hajra, while the experimental Oelsen's calorimetry method gave only the values for one component – gallium.

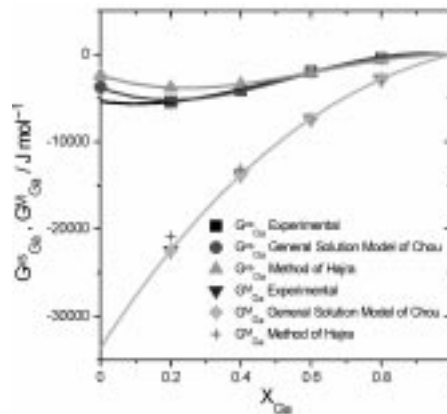
For this reason, comparative analysis is done for thermodynamic properties of gallium, which are obtained by the following methods: experimental use of Oelsen's calorimetry, and predicting methods according to Chou and Hajra, at the investigated temperature 1273 K in the Ga–GeSb<sub>0.855</sub> section of the ternary system Ga–Ge–Sb.

**Table 6** Thermodynamic properties of the Ga–GeSb<sub>0.855</sub> section in the ternary system Ga–Ge–Sb at 1273 K obtained by Hajra’s method

N <sup>o</sup>	$a_{\text{Ga}}$	$\gamma_{\text{Ga}}$	$G_{\text{Ga}}^{\text{xs}}/ G_{\text{Ga}}^{\text{M}}/$		$a_{\text{Ge}}$	$\gamma_{\text{Ge}}$	$G_{\text{Ge}}^{\text{xs}}/ G_{\text{Ge}}^{\text{M}}/$		$a_{\text{Sb}}$	$\gamma_{\text{Sb}}$	$G_{\text{Sb}}^{\text{xs}}/ G_{\text{Sb}}^{\text{M}}/ \Delta G^{\text{xs}}/ \Delta G^{\text{M}}/$			
			J mol <sup>-1</sup>				J mol <sup>-1</sup>				J mol <sup>-1</sup>			
T0	0	0.798	-2381		0.173	1.197	1903	-18534	0.678	0.793	-2449	-4107	-1818	-6199
T1	0.139	0.697	-3806	-20840	0.225	1.832	6410	-15769	0.559	0.825	-2026	-6154	-1344	-10274
T2	0.289	0.724	-3416	-13114	0.114	1.248	2346	-22906	0.406	0.800	-2353	-9521	-2345	-12190
T3	0.493	0.822	-2072	-7478	0.015	0.249	-14678	-44279	0.226	0.668	-4264	-15712	-3584	-12515
T4	0.753	0.941	-634	-2996	5E-4	0.015	-44303	-81069	0.074	0.441	-8650	-27467	-3343	-9552
T5	1	1	0	0	0				0				0	0



**Fig. 6** Activity vs. molar content of gallium of the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb at 1273 K obtained by experimental Oelsen’s calorimetry, and predicting methods of Chou and Hajra



**Fig. 7** Partial molar excess Gibbs energy and partial molar Gibbs energy of mixing vs. molar content of gallium of the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb at 1273 K obtained by experimental Oelsen’s calorimetry, and predicting methods of Chou and Hajra

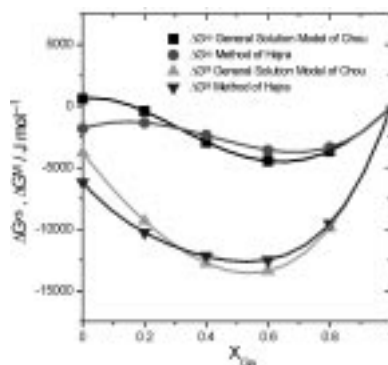
Dependence of gallium activity upon molar content obtained by different methods in ternary system Ga–Ge–Sb for Ga–GeSb<sub>0.855</sub> section at 1273 K is shown in Fig. 6.

Dependence of partial molar excess Gibbs energy and partial molar Gibbs energy of mixing for gallium obtained by experimental and predicting methods upon molar content at 1273 K are given in Fig. 7.

Dependence of integral molar excess Gibbs energy and integral molar Gibbs energy of mixing for ternary system upon molar content obtained by predicting method of Chou and Hajra at 1273 K are given in Fig. 8.

Considering the results shown, the following observations can be made:

- Results obtained by predicting methods of Chou and Hajra show good agreement with results obtained by experimental Oelsen calorimetry.
- Better agreement was noticed between experimental results and results obtained by Chou's method, than one obtained by Hajra's method application.
- Obtained negative deviation of  $a_{\text{Ga}}$  from Raoult's law indicates good miscibility in the investigated system. Also, a negative deviation from Raoult's law is noticed for antimony, while germanium showed a positive deviation from Raoult's law. This indicates better miscibility between gallium and antimony than germanium; i.e. antimony is more dissolved into gallium than germanium into gallium (Fig. 1).
- The dependence of  $\Delta G^{\text{XS}}$  and  $\Delta G^{\text{M}}$  upon molar content shows minimum at  $x_{\text{Ga}} \approx 0.6$  which pointed out the possible existence of the eutectic in Ga–GeSb<sub>0.855</sub> section of this ternary system. (This statement has to be proved by further phase equilibrium investigations.)



**Fig. 8** Integral excess Gibbs energy and integral Gibbs energy of mixing vs. molar content of gallium of the Ga–GeSb<sub>0.855</sub> section in ternary system Ga–Ge–Sb at 1273 K obtained by predicting methods of Chou and Hajra

It should also be stressed that, these observations confirm the conclusions about the thermodynamic behavior of investigated Ga–GeSb<sub>0.855</sub> section in the ternary system Ga–Ge–Sb with respect to Raoult's law. Namely, it is noticed that negativity of the partial molar excess Gibbs energy and partial molar Gibbs energy of mixing for gallium decreases with increasing of molar content. If the negativity more increase, there will be a stronger interaction between components, considering the compound formed between gallium and antimony.

The obtained and shown thermodynamic data describe the investigated Ga–GeSb<sub>0.855</sub> section of the ternary system Ga–Ge–Sb completely thermodynamically at the investigated temperature of 1273 K. At the same time, those thermodynamic data present a contribution to a better knowledge of this section in ternary system Ga–Ge–Sb, and also present the starting base for all further thermodynamic research.

## References

- 1 I. Ansara, J. P. Bros and M. Gambino, CALPHAD, 3 (1979) 225.
- 2 H. Eslami, Y. M. Muggianu, M. Gambino, J. P. Bros and P. Leydet, J. Less-Common Metals, 64 (1979) 31.
- 3 M. Fornaris, Y. M. Muggianu, M. Gambino and J. P. Bros, Z. Naturforsch., 35a (1980) 1256.
- 4 J. Franceschi, M. Fornaris, M. Gambino and J. P. Bros, Canadian Metallurgical Quarterly, 21 (1982) 273.
- 5 B. Predel and D. W. Stein, Z. Metallkd., 61 (1970) 909.
- 6 P. Y. Chevalier, Thermochem. Acta, 155 (1989) 227.
- 7 I. Katayama, J. Nakayama, T. Nakai and Z. Kozuka, Transaction of the Japan Institute of Metals, 28 (1987) 129.
- 8 I. Katayama, T. Ikura, K. Maki and T. Iida, Materials Transactions, JIM, 36 (1995) 41.
- 9 J. Šesták, V. Šestáková, . ivković and D. ivković, Pure and Appl. Chem., 67 (1995) 1885.
- 10 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. Kelley, The Selected Values of the Thermodynamic Properties of Binary Alloys, ASM, Metals Park, OH, 1973.
- 11 J. Šesták, B. Stepanek, H. Yokokawa and V. Šestáková, J. Thermal Anal., 43 (1995) 389.
- 12 J. Šesták, B. Stepanek, J. Leitner and H. Yokokawa, Thermochem. Acta, 245 (1994) 189.
- 13 G. Moiseev and J. Šesták, J. Thermal Anal., 43 (1995) 539.
- 14 B. Stepanek, V. Šestáková, J. Šesták and J. Leitner, Semicond. Sci. Tech., 9 (1994) 341.
- 15 W. Oelsen, Arch. Eisenhnettenwes, 26 (1955) 519.
- 16 W. Oelsen, E. Schurmann and H. J. Weight, Arch. Eisenhnettenwes, 27 (1956) 487.
- 17 W. Oelsen, F. Bieret and G. Schwabe, Arch. Eisenhnettenwes, 27 (1956) 607.
- 18 K. C. Chou, W. C. Li, F. Li and M. He, Calphad, 20 (1996) 395.
- 19 K. C. Chou and S. K. Wei, Metall. Metallurgical and Materials Transactions B, 28B, (1997) 439.
- 20 K. C. Chou, Y. Liu, J. Zhang, F. Li, S. Wei, S. Chen, F. Zhang and Y. A. Chang, Calphad XXVII, Beijing, China, 1998 p. 6.
- 21 S. R. Reddy and J. P. Hajra, Materials Science and Engineering, B20 (1993) 308.
- 22 J. P. Hajra, Metallurgical Transactions B, 22B, 10 (1991) 583.
- 23 D. ivković, . ivković and Y. H. Liu, J. Alloys and Compounds, 265 (1998) 176.