

## The excess enthalpies of liquid Ga–Sb–Te alloys<sup>1</sup>

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### Abstract

The excess enthalpies of liquid alloys in the ternary system Ga–Sb–Te were determined at 1173 K in a heat-flow calorimeter for five sections  $\text{Ga}_y\text{Sb}_{1-y}\text{Te}$  with  $y = 0.2, 0.4, 0.5, 0.6$  and  $0.8$ . and for the section  $\text{Ga}_{0.4}\text{Sb}_{0.6}\text{Te}$  at 1073 K. The enthalpy surface in the ternary system is determined by a valley of exothermic minima stretching from a minimum at composition  $\text{Ga}_2\text{Te}_3$  to one at composition  $\text{Sb}_2\text{Te}_3$  in the 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. © 1998 Elsevier Science B.V.

*Keywords:* Enthalpies of mixing; Ga–Sb–Te system; High-temperature calorimetry

### 1. Introduction

Thermodynamic excess functions of liquid mixtures provide information 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]. The excess enthalpies in metal–tellurium systems vary in many cases as nearly triangular shaped functions of the concentration. The exothermic minima of these curves were found close to the composition of congruently melting compounds. Wagner [9] assumed associates in the melt to explain this behaviour. Based on this hypothesis, Sommer [10] presented a thermodynamic formalism, which allows to fit the experimental data in such

systems. These optimized data sets can be used to calculate the phase diagrams of multicomponent systems of technical relevance.

Within the systematic investigation of systems with chalcogen as constituent component, we have measured the excess enthalpies of liquid Ga–Sb–Te alloys.

### 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 [1–8]. In this paper only some relevant details are given. Ga (Alfa, 99.999%), Sb (Preussag, 99.999%) and Te (Fluka, 99.999%) were used. The binary alloys were prepared by melting Ga and Sb in evacuated and sealed silica tubes.

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The measurements started on the metal-rich side of the sections  $\text{Ga}_y\text{Sb}_{1-y}\text{-Te}$  with binary  $\text{Ga}_y\text{Sb}_{1-y}$  alloys, which were brought into the calorimeter tube and heated to the temperature of the measurement. Small amounts of pure Te were consecutively added from ambient temperature ( $T = 298\text{ K}$ ) after temperature equilibration. On the tellurium-rich part of the system, small amounts of  $\text{Ga}_y\text{Sb}_{1-y}$  were successively added to liquid tellurium. The temperature of the measurements was  $1173\text{ K}$  and, in addition,  $1073\text{ K}$  for the section  $\text{Ga}_{0.4}\text{Sb}_{0.6}\text{-Te}$ . The enthalpy increments  $H(T) - H(298.15\text{ K})$  of  $\text{Ga}_y\text{Sb}_{1-y}$  and Te which were needed to calculate  $H^E$  of the ternary alloys were determined in separate experiments by dropping  $\text{Ga}_y\text{Sb}_{1-y}$  or Te in liquid  $\text{Ga}_y\text{Sb}_{1-y}$ , and Te, 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 was located in the liquid alloy. The enthalpy increments  $H(T - 298\text{ K})$  of tin were taken from Barin [12]. The reproducibility of the heat effects was better than  $\pm 5\%$ . All experiments were carried out under dry argon gas at atmospheric pressure.

### 3. Binary systems

#### 3.1. The Ga–Te system

Four intermediate compounds were observed in the system Ga–Te: GaTe and  $\text{Ga}_2\text{Te}_3$  melt congruently at  $1108$  and  $1071\text{ K}$ .  $\text{Ga}_3\text{Te}_4$  decomposes in a peritectic reaction at  $1049\text{ K}$  and the high-temperature phase  $\text{Ga}_2\text{Te}_5$  is formed in an eutectoid reaction at  $680\text{ K}$  with peritectic decomposition at  $757\text{ K}$ . The thermodynamic properties of the melt have been studied calorimetrically by Irle et al. [4], Castanet and Bergman [13], Said and Castanet [14], Glazov et al. [15], Alfer et al. [16], using emf measurements by Katayama et al. [17] and Srikanth and Jacob [18]. Predel et al. [19] gained activities from vapour pressures, Takeda et al. [20] determined  $c_p$  values. The system was optimized by Irle et al. [4] and Oh and Lee [21]. In the calculation of Irle, ten coefficients were used for the description of the liquid phase. These coefficients could not be used in our work because of the deviating formalism in our software. Therefore thermodynamic functions of the melt were optimized,

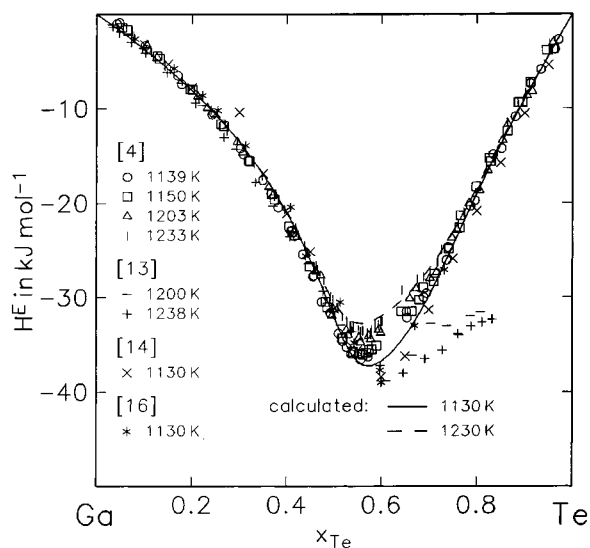


Fig. 1. Calculated and experimental excess enthalpies of liquid Ga–Te alloys.

using literature data with the assumption of  $\text{Ga}_2\text{Te}_3$  associates in the liquid. Additional phase equilibrium data were used to describe the miscibility gap in the range 8–28 mol% [22]. The exothermic minimum is found near the composition  $\text{Ga}_2\text{Te}_3$  at  $-39.5\text{ kJ mol}^{-1}$  ( $T = 1173\text{ K}$ ). The fitted data of  $H^E$  are given in Fig. 1.

#### 3.2. The Sb–Te system

The system is characterized by the congruently melting compound  $\text{Sb}_2\text{Te}_3$  ( $T_m = 891\text{ K}$ ) with a narrow homogeneity range. Between Sb and  $\text{Sb}_2\text{Te}_3$  two phases,  $\gamma$  and  $\delta$ , with broad homogeneity ranges were observed. The  $\gamma$ -phase decomposes peritectically at  $831\text{ K}$ . The  $\delta$ -phase exists between 16 and 38 mol% Te with a minimum melting point at  $818\text{ K}$ . The phase diagram was optimized by Ghosh et al. [23,24]. The excess enthalpies were measured by Maekawa et al. [25] and Feutelais et al. [26]. Chemical potentials were determined by Bolte [27], Feutelais et al. [28] and Onderka et al. [29].  $H^E$  values at  $1173\text{ K}$  and the coefficients for an analytical description were given by Schlieper [30]. The minimum of the exothermic enthalpy values is found near the composition  $\text{Sb}_2\text{Te}_3$  with  $-7.4\text{ kJ mol}^{-1}$  at  $1173\text{ K}$ .  $H^E$  data and the calculated curves are given in Fig. 2.

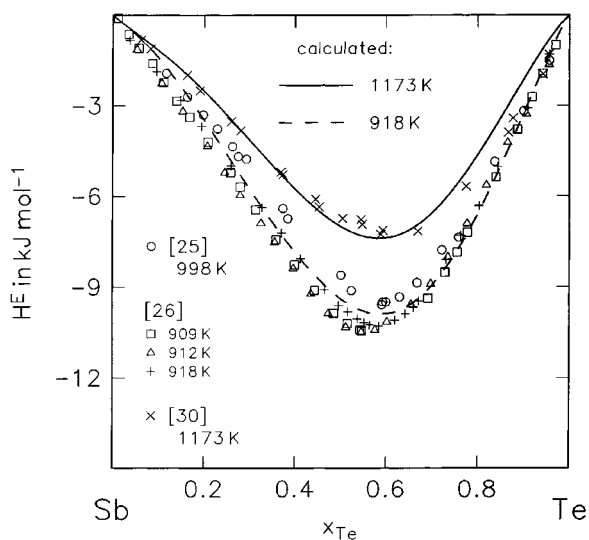


Fig. 2. Calculated and experimental excess enthalpies of liquid Sb–Te alloys.

### 3.3. The Ga–Sb system

This system contains a congruently melting compound, GaSb, and two eutectic reactions in the Ga–GaSb and GaSb–Sb part of the phase diagram. The eutectic in the Ga–GaSb region is degenerated. The other is found at 862.5 K and 8.9 mol% Sb. The mutual solid solubilities of Ga and Sb are negligible. The phase diagram was assessed by Ngai et al. [31]. Excess enthalpies and activities of the melt were measured by several authors. Hsi-Hsing et al. [32] and Bergman et al. [33] calculated the activities of Ga from vapour pressure measurements. Gerasimenko et al. [34], Danilin and Yatsenko [35], Pong [36], Anderson et al. [37] and Katayama et al. [17] derived the activities of Ga by emf experiments. Yazawa et al. [38], Predel and Stein [39] and Gambino and Bros [40] measured enthalpies of mixing in liquid Ga–Sb alloys. The thermodynamic functions of the melt were optimized with the assumption of GaSb associates. Some data were discarded in the optimization because the data were either not available [35] or did not agree with other data [36]. The excess enthalpies used for the calculation of  $H^E$  in the ternary system according to the reaction (2) are weakly exothermic with a minimum of about  $-1.0 \text{ kJ mol}^{-1}$  at the composition GaSb

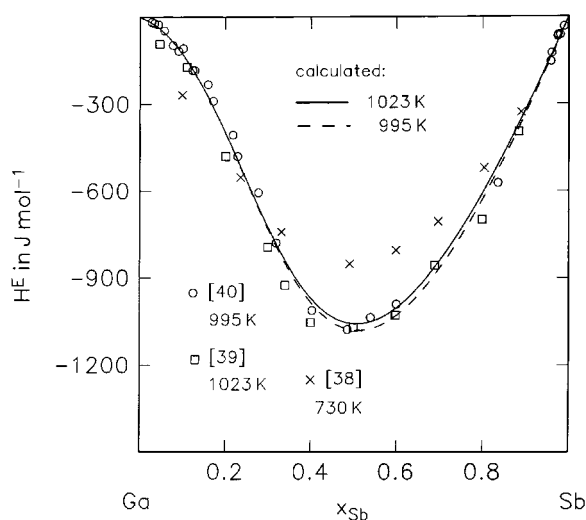


Fig. 3. Calculated and experimental excess enthalpies of liquid Ga–Sb alloys.

at  $T = 1173 \text{ K}$ . Experimental and calculated data for  $H^E$  are given in Fig. 3.

## 4. The ternary system Ga–Sb–Te

The system was investigated with DTA and X-ray methods by Mirgaslovskaja and Komova [41], Dashowsky et al. [42] and by Rustamov and Geidrova [43]. The latter gave a projection of the liquidus surface. Recently, Katayama et al. [44] performed emf measurements in the entire composition range.

## 5. Analytical descriptions

### 5.1. Binary systems

These systems contain the associates  $\text{Ga}_2\text{Te}_3$ ,  $\text{Sb}_2\text{Te}_3$  and GaSb in the melts. The thermodynamic functions of the limiting binaries were calculated according to the association model given by Sommer [10] with additional temperature dependent parameters. This correction was necessary for the analytical description of the binary systems which contain chalcogens. The equations are given in a preceding paper [45]. The determination of the coefficients in these equations and the calculation of the thermody-

Table 1  
Coefficients of the association model of the binary systems Ga–Te, Sb–Te and Ga–Sb

| System<br><i>i,j</i>   | Ga–Te<br>2,3 | Sb–Te<br>2,3 | Ga–Sb<br>1,1 |
|--|--------------|--------------|--------------|
| $\Delta H_{A_i B_j}^0$ [kJ mol <sup>-1</sup> ]               | -293.4       | -60.9        | -10.8        |
| $\Delta S_{A_i B_j}^0$ [JK <sup>-1</sup> mol <sup>-1</sup> ] | -175.1       | -51.3        | -14.6        |
| $C_{A_i B_j}^H$ [kJ mol <sup>-1</sup> ]                      | —            | -12.0        | —            |
| $C_{A_i B_j}^S$ [JK <sup>-1</sup> mol <sup>-1</sup> ]        | —            | —            | —            |
| $C_{A_i A_i B_j}^H$ [kJ mol <sup>-1</sup> ]                  | 188.6        | -30.8        | 10.2         |
| $C_{A_i A_i B_j}^S$ [JK <sup>-1</sup> mol <sup>-1</sup> ]    | 228.1        | —            | 20.9         |
| $C_{B_i A_i B_j}^H$ [kJ mol <sup>-1</sup> ]                  | 119.4        | -33.0        | -5.9         |
| $C_{B_i A_i B_j}^S$ [JK <sup>-1</sup> mol <sup>-1</sup> ]    | 119.9        | —            | -13.5        |

dynamic functions were performed with the programs BINGSS and BINFKT developed by Lukas et al. [46–48]. The coefficients are given in Table 1.

### 5.2. Ternary system

For the analytical description of the ternary system Ga–Sb–Te, the association model was used with additional parameters for interactions between associates and pure components, as well as those between associates [45]. From the coefficients of the limiting binaries GaSb and taking into account the ternary interactions, the excess enthalpies were determined from Eq. (1):

$$\begin{aligned}
 H_{\text{Ga-Sb-Te}}^E = & n_{\text{GaSb}} H_{\text{GaSb}}^0 \\
 & + \frac{n_{\text{Ga}} n_{\text{GaSb}}}{n} C_{\text{Ga, GaSb}}^H \\
 & + \frac{n_{\text{Sb}} n_{\text{GaSb}}}{n} C_{\text{Sb, GaSb}}^H \\
 & + \frac{n_{\text{Ga}_2\text{Te}_3} n_{\text{Te}}}{n} C_{\text{Ga}_2\text{Te}_3, \text{Te}}^H \\
 & + n_{\text{Ga}_2\text{Te}_3} H_{\text{Ga}_2\text{Te}_3}^0 \\
 & + \frac{n_{\text{Ga}_2\text{Te}_3} n_{\text{Ga}}}{n} C_{\text{Ga, Ga}_2\text{Te}_3}^H \\
 & + n_{\text{Sb}_2\text{Te}_3} H_{\text{Sb}_2\text{Te}_3}^0 + \frac{n_{\text{Sb}} n_{\text{Te}}}{n} C_{\text{Sb, Te}}^H \\
 & + \frac{n_{\text{Sb}_2\text{Te}_3} n_{\text{Sb}}}{n} C_{\text{Sb}_2\text{Te}_3, \text{Sb}}^H \\
 & + \frac{n_{\text{Sb}_2\text{Te}_3} n_{\text{Te}}}{n} C_{\text{Sb}_2\text{Te}_3, \text{Te}}^H \\
 & + \frac{n_{\text{Sb}} n_{\text{Ga}_2\text{Te}_3}}{n} C_{\text{Sb, Ga}_2\text{Te}_3}^H \\
 & + \frac{n_{\text{Ga}} n_{\text{Sb}_2\text{Te}_3}}{n} C_{\text{Ga, Sb}_2\text{Te}_3}^H \\
 & + \frac{n_{\text{Sb}_2\text{Te}_3} n_{\text{Ga}_2\text{Te}_3}}{n} C_{\text{Sb}_2\text{Te}_3, \text{Ga}_2\text{Te}_3}^H \quad (1)
 \end{aligned}$$

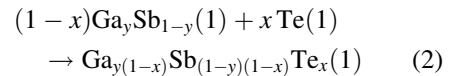
Table 2  
Ternary interaction parameters of the association model of the system Ga–Sb–Te

| Ga–Sb–Te   | kJ mol <sup>-1</sup> |
|--|----------------------|
| $C_{\text{Ga, Sb}_2\text{Te}_3}^H$                     | 84.7                 |
| $C_{\text{Sb, Ga}_2\text{Te}_3}^H$                     | -122.6               |
| $C_{\text{Ga}_2\text{Te}_3, \text{Sb}_2\text{Te}_3}^H$ | 42.3                 |

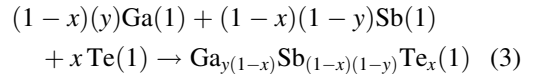
The coefficients of the last three terms were fitted by a numerical optimisation procedure using the least squares method [30] and are given in Table 2.

## 6. Results and discussion

The heat effect,  $\Delta Q$ , of the mixing was determined for five sections with constant concentration ratio of two components ( $y_{\text{Ga}}/y_{\text{Ga}} + y_{\text{Sb}} = 0.2, 0.4, 0.5, 0.6$  and 0.8) at 1173 K and for one section with  $y_{\text{Ga}}/y_{\text{Ga}} + y_{\text{Sb}} = 0.4$  at 1073 K. The experimental enthalpies,  $H_{\text{exp}}^E$ , of the reaction



and the ternary excess enthalpies,  $H^E$ , of the reaction



are presented in Table 3 and Fig. 4 (for one section).

A projection of the isoenthalpic lines is given in Fig. 5. It shows that the exothermic values decrease smoothly from the maximum at  $\text{Ga}_2\text{Te}_3$  to the corners of the ternary system.

Ternary interaction parameters were at first not used in the calculation of ternary data from  $H^E$  data of the constituent binaries. However, the enthalpy curves of the ternary mixtures could not be reproduced (Fig. 4). The Ga–Sb–Te system contains binary associates which are in equilibrium with constituent non-associated atoms. Therefore ternary interaction had to be considered. The best fit over the whole system was obtained by assuming the ternary interactions  $\text{Ga}_2\text{Te}_3 \leftrightarrow \text{Sb}, \text{Sb}_2\text{Te}_3 \leftrightarrow \text{Ga}$  and  $\text{Ga}_2\text{Te}_3 \leftrightarrow \text{Sb}_2\text{Te}_3$ . The excess enthalpies decrease slightly with increasing temperature. The effect is due to a lower associate concentration at higher temperatures.

Table 3

Heat effects  $\Delta Q$ , experimental excess enthalpies according to the reaction  $(1-x)\text{Ga}_y\text{Sb}_{1-y}(1) + x\text{Te}(1) \rightarrow \text{Ga}_{y(1-x)}\text{Sb}_{(1-y)(1-x)}\text{Te}_x(1)$  and ternary excess enthalpies according to the reaction  $(1-x)(y)\text{Ga}(1) + (1-x)(1-y)\text{Sb}(1) + x\text{Te}(1) \rightarrow \text{Ga}_{y(1-x)}\text{Sb}_{(1-x)(1-y)}\text{Te}_x(1)$  in the Ga–Sb–Te system at 1173 K of the sections  $\text{Ga}_y\text{Sb}_{1-y}$ –Te and at 1073 K of the section  $\text{Ga}_{0.4}\text{Sb}_{0.6}$ –Te

| Starting amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Added amount<br>$n_{\text{Te}}$ (mol)                  | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
|---|--|----------------------------------|-------------------------------|---|---|
| <b>Ga<sub>0.2</sub>Sb<sub>0.8</sub>–Te</b>                |  |                                  |                               |   |   |
| 0.021492  | 0.000661   | 0.030                            | 13.3                          | –721  | –1105   |
|   | 0.001300   | 0.084                            | 27.7                          | –1958   | –2321   |
|   | 0.002082   | 0.158                            | 47.4                          | –3558   | –3891   |
|   | 0.002992   | 0.247                            | 63.3                          | –5618   | –5916   |
|   | 0.004045   | 0.340                            | 97.3                          | –7438   | –7699   |
|   | 0.003855   | 0.410                            | 95.9                          | –8711   | –8945   |
|   | 0.003658   | 0.464                            | 103.3                         | –9385   | –9598   |
| 0.017205  | 0.000864   | 0.048                            | 18.9                          | –1071   | –1448   |
|   | 0.001357   | 0.114                            | 29.2                          | –2590   | –2941   |
|   | 0.002319   | 0.209                            | 57.6                          | –4393   | –4707   |
|   | 0.003066   | 0.306                            | 77.0                          | –6227   | –6501   |
|   | 0.004176   | 0.406                            | 110.0                         | –7923   | –8158   |
|   | 0.004404   | 0.485                            | 131.6                         | –8786   | –8990   |
|   | 0.004684   | 0.548                            | 161.2                         | –8926   | –9105   |
| Starting amount<br>$n_{\text{Te}}$ (mol)                  | Added amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| <b>Te–Ga<sub>0.2</sub>Sb<sub>0.8</sub></b>                |  |                                  |                               |   |   |
| 0.015543  | 0.004563   | 0.937                            | 2.0                           | –2777   | –2802   |
|   | 0.004608   | 0.874                            | 13.3                          | –4926   | –4976   |
|   | 0.003634   | 0.790                            | 30.8                          | –7264   | –7347   |
|   | 0.002481   | 0.702                            | 51.6                          | –9244   | –9362   |
|   | 0.003634   | 0.603                            | 123.4                         | –9602   | –9760   |
|   | 0.004608   | 0.511                            | 203.1                         | –8401   | –8594   |
| 0.0014609   | 0.000693   | 0.995                            | –5.0                          | –2397   | –2415   |
|   | 0.001118   | 0.890                            | 8.9                           | –4807   | –4851   |
|   | 0.001645   | 0.809                            | 21.9                          | –7323   | –7399   |
|   | 0.002582   | 0.708                            | 52.1                          | –9605   | –9721   |
|   | 0.003832   | 0.597                            | 130.5                         | –9929   | –10089  |
|   | 0.004253   | 0.508                            | 190.9                         | –8587   | –8781   |
| Starting amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Added amount<br>$n_{\text{Te}}$ (mol)                  | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| <b>Ga<sub>0.4</sub>Sb<sub>0.6</sub>–Te</b>                |  |                                  |                               |   |   |
| 0.011842  | 0.000905   | 0.071                            | 14.4                          | –2017   | –2804   |
|   | 0.001345   | 0.160                            | 11.2                          | –5261   | –5973   |
|   | 0.001506   | 0.241                            | 21.5                          | –7653   | –8297   |
|   | 0.001716   | 0.316                            | 24.8                          | –9856   | –10435  |
|   | 0.002850   | 0.413                            | 42.9                          | –12605  | –13102  |
|   | 0.003559   | 0.501                            | 64.6                          | –14643  | –15066  |
|   | 0.016006   | 0.000831                         | 0.049                         | 8.0   | –1713   |
| 0.001053  |  | 0.105                            | 16.1                          | –3323   | –4081   |

Table 3  
(Continued)

|   | 0.001364   | 0.169                            | 14.4                          | –5481   | –6185   |
|---|--|----------------------------------|-------------------------------|---|---|
|   | 0.002219   | 0.255                            | 5.9                           | –9221   | –9852   |
|   | 0.003031   | 0.347                            | 50.4                          | –11507  | –12061  |
|   | 0.004019   | 0.439                            | 82.7                          | –13235  | –13711  |
|   | 0.004549   | 0.517                            | 109.0                         | –14256  | –14666  |
| Starting amount<br>$n_{\text{Te}}$ (mol)                  | Added amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| Te–Ga <sub>0.4</sub> Sb <sub>0.6</sub>                    |  |                                  |                               |   |   |
| 0.012249  | 0.001212   | 0.910                            | 3.5                           | –4730   | –4806   |
|   | 0.001422   | 0.823                            | 16.3                          | –8485   | –8635   |
|   | 0.002316   | 0.712                            | 19.5                          | –13679  | –13922  |
|   | 0.002929   | 0.609                            | 82.7                          | –15653  | –15989  |
| 0.0011651   | 0.000757   | 0.939                            | –8.0                          | –4043   | –4094   |
|   | 0.001608   | 0.831                            | 13.6                          | –8974   | –9117   |
|   | 0.001872   | 0.733                            | 20.1                          | –13188  | –13414  |
|   | 0.002396   | 0.637                            | 49.6                          | –16019  | –16326  |
|   | 0.002519   | 0.560                            | 96.2                          | –16172  | –16545  |
|   | 0.002739   | 0.495                            | 135.2                         | –15003  | –15431  |
| 0.010938  | 0.000720   | 0.938                            | –4.8                          | –3840   | –3893   |
|   | 0.001256   | 0.847                            | 7.1                           | –8314   | –8444   |
|   | 0.001915   | 0.738                            | 19.1                          | –13113  | –13336  |
|   | 0.002406   | 0.635                            | 53.3                          | –15933  | –16242  |
|   | 0.003137   | 0.537                            | 129.3                         | –15673  | –13066  |
|   | 0.003527   | 0.458                            | 192.2                         | –13507  | –13967  |
| Starting amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Added amount<br>$n_{\text{Te}}$ (mol)                  | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| Ga <sub>0.4</sub> Sb <sub>0.6</sub> –Te, $T = 1073$ K     |  |                                  |                               |   |   |
| 0.016955  | 0.000754   | 0.043                            | 7.3                           | –1392   | –2256   |
|   | 0.001244   | 0.105                            | 11.5                          | –3481   | –4287   |
|   | 0.001393   | 0.167                            | 9.6                           | –5678   | –6429   |
|   | 0.002069   | 0.244                            | 12.9                          | –8495   | –9177   |
|   | 0.002998   | 0.333                            | 8.7                           | –12144  | –12756  |
|   | 0.003618   | 0.416                            | 21.5                          | –1586   | –15713  |
|   | 0.003969   | 0.486                            | 39.0                          | –17279  | –17743  |
|   | 0.001563   | 0.509                            | 22.0                          | –17780  | –18222  |
|   | 0.1012722  | 0.000876                         | 0.064                         | 1.7   | –2611   |
| 0.001314  |  | 0.147                            | 10.3                          | –5426   | –6195   |
| 0.001609  | 0.001609   | 0.230                            | 10.2                          | –8414   | –9108   |
|   | 0.002151   | 0.319                            | –42.1                         | –14588  | –15203  |
| Starting amount<br>$n_{\text{Te}}$ (mol)                  | Added amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| Te–Ga <sub>0.4</sub> Sb <sub>0.6</sub> , $T = 1073$ K     |  |                                  |                               |   |   |
| 0.009339  | 0.000968   | 0.906                            | 1.6                           | –4985   | –5069   |
|   | 0.001615   | 0.783                            | 2.7                           | –11505  | –11700  |

Table 3  
(Continued)

|   | 0.002267   | 0.658                            | 12.3                          | –17549  | –17857  |
|---|--|----------------------------------|-------------------------------|---|---|
|   | 0.002691   | 0.553                            | 83.0                          | –18562  | –18964  |
|   | 0.004512   | 0.437                            | 212.5                         | –16261  | –16769  |
| 0.0014609   | 0.000693   | 0.995                            | –5.0                          | –2397   | –2415   |
|   | 0.001118   | 0.890                            | 8.9                           | –4807   | –4851   |
|   | 0.001645   | 0.809                            | 21.9                          | –7323   | –7399   |
|   | 0.002582   | 0.708                            | 52.1                          | –9605   | –9721   |
|   | 0.003832   | 0.597                            | 130.5                         | –9929   | –10089  |
|   | 0.004253   | 0.508                            | 190.9                         | –8587   | –8781   |
| Starting amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Added amount<br>$n_{\text{Te}}$ (mol)                  | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| $\text{Ga}_{0.5}\text{Sb}_{0.5}\text{-Te}$                |  |                                  |                               |   |   |
| 0.022757  | 0.000880   | 0.037                            | –0.8                          | –1685   | –2578   |
|   | 0.001248   | 0.086                            | 14.3                          | –3249   | –4097   |
|   | 0.002647   | 0.173                            | 24.1                          | –6326   | –7092   |
|   | 0.002499   | 0.242                            | 20.4                          | –8810   | –9513   |
|   | 0.004966   | 0.350                            | 52.3                          | –12358  | –12961  |
|   | 0.004255   | 0.420                            | 48.8                          | –14581  | –15119  |
| 0.0171434   | 0.000758   | 0.042                            | –0.6                          | –1911   | –2799   |
|   | 0.001154   | 0.100                            | 4.8                           | –4232   | –5067   |
|   | 0.001705   | 0.174                            | 10.4                          | –7025   | –7791   |
|   | 0.001939   | 0.245                            | 17.2                          | –9456   | –10156  |
|   | 0.002187   | 0.311                            | 14.9                          | –11922  | –12561  |
|   | 0.002821   | 0.381                            | 0.8                           | –15194  | –15768  |
|   | 0.004024   | 0.460                            | 53.8                          | –17193  | –17694  |
| Starting amount<br>$n_{\text{Te}}$ (mol)                  | Added amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| $\text{Te-Ga}_{0.5}\text{Sb}_{0.5}$                       |  |                                  |                               |   |   |
| 0.013871  | 0.001057   | 0.929                            | 4.7                           | –4106   | –4171   |
|   | 0.001324   | 0.854                            | 8.0                           | –8357   | –8493   |
|   | 0.002214   | 0.751                            | 15.6                          | –13993  | –14223  |
|   | 0.003260   | 0.638                            | 67.6                          | –18143  | –18478  |
|   | 0.004076   | 0.538                            | 182.2                         | –18073  | –18502  |
|   | 0.005686   | 0.441                            | 353.7                         | –14843  | –15362  |
| 0.013803  | 0.001330   | 0.912                            | 1.7                           | –5372   | –5454   |
|   | 0.001488   | 0.830                            | 3.9                           | –10243  | –10401  |
|   | 0.001920   | 0.744                            | 17.1                          | –14721  | –14958  |
|   | 0.002965   | 0.642                            | 51.9                          | –18879  | –19211  |
| Starting amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Added amount<br>$n_{\text{Te}}$ (mol)                  | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>-1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>-1</sup> ) |
| $\text{Ga}_{0.6}\text{Sb}_{0.4}\text{-Te}$                |  |                                  |                               |   |   |
| 0.017401  | 0.000744   | 0.041                            | 3.7                           | –1611   | –2481   |
|   | 0.001173   | 0.099                            | –35.8                         | –6060   | –6878   |
|   | 0.001493   | 0.164                            | 3.8                           | –8623   | –9381   |
|   | 0.002126   | 0.241                            | 4.5                           | –11736  | –12424  |

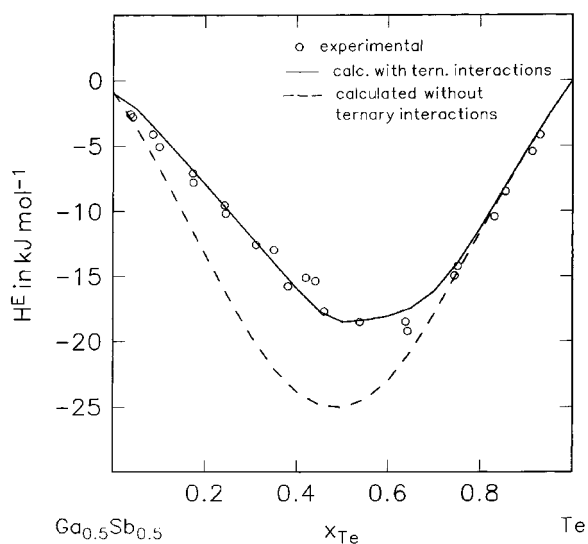
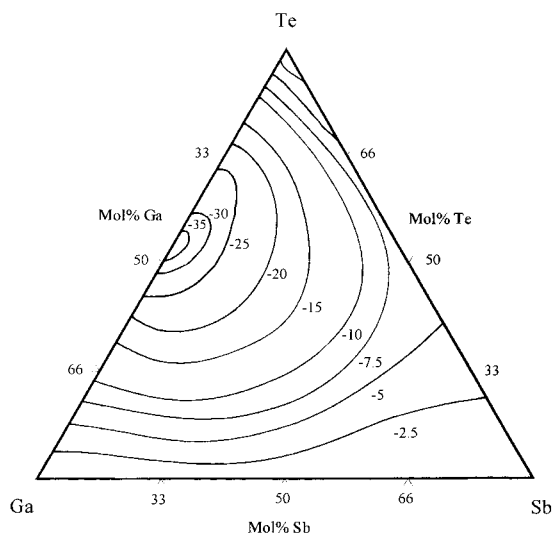
Table 3  
(Continued)

|   |  |                                  |                               |   |   |
|---|--|----------------------------------|-------------------------------|---|---|
|   | 0.002703   | 0.321                            | 1.6                           | –15109  | –15725  |
|   | 0.003396   | 0.401                            | 5.4                           | –18343  | –18887  |
|   | 0.004250   | 0.477                            | 22.7                          | –20980  | –21455  |
|   | 0.002875   | 0.519                            | 31.6                          | –21962  | –22399  |
| 0.014540  | 0.000643   | 0.042                            | 2.8                           | –1696   | –2565   |
|   | 0.001070   | 0.105                            | 8.6                           | –3976   | –4787   |
|   | 0.001702   | 0.190                            | 10.8                          | –7200   | –7935   |
|   | 0.001886   | 0.267                            | 11.8                          | –10185  | –10850  |
|   | 0.003086   | 0.366                            | 15.5                          | –14109  | –14684  |
|   | 0.002766   | 0.434                            | 16.9                          | –16708  | –17221  |
|   | 0.004073   | 0.512                            | 58.8                          | –18514  | –18957  |
| 0.016081  | 0.000628   | 0.038                            | 0.8                           | –1621   | –748  |
|   | 0.001006   | 0.092                            | 4.7                           | –3785   | –2961   |
|   | 0.001798   | 0.176                            | –12.4                         | –8159   | –7411   |
|   | 0.001524   | 0.236                            | 6.2                           | –10483  | –9790   |
|   | 0.002973   | 0.330                            | 7.5                           | –14364  | –13756  |
|   | 0.002841   | 0.401                            | –20.8                         | –18308  | –17765  |
|   | 0.003092   | 0.463                            | 18.2                          | –20389  | –19902  |
| Starting amount<br>$n_{\text{Te}}$ (mol)                  | Added amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>–1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>–1</sup> ) |
| <hr/>   |  |                                  |                               |   |   |
| Te–Ga <sub>0.6</sub> Sb <sub>0.4</sub>                    |  |                                  |                               |   |   |
| 0.011635  | 0.001105   | 0.913                            | –18.2                         | –6023   | –6102   |
|   | 0.001914   | 0.794                            | –19.4                         | –13487  | –13674  |
|   | 0.002408   | 0.682                            | –8.7                          | –19574  | –19862  |
|   | 0.002618   | 0.591                            | 44.7                          | –21749  | –22120  |
|   | 0.002981   | 0.513                            | 120.0                         | –20568  | –21009  |
|   | 0.004537   | 0.428                            | 241.0                         | –17120  | –17639  |
| 0.011353  | 0.001305   | 0.897                            | –14.4                         | –9900   | –6694   |
|   | 0.001008   | 0.785                            | –17.1                         | –13584  | –13779  |
|   | 0.002682   | 0.662                            | –1.1                          | –19814  | –20120  |
|   | 0.003500   | 0.550                            | 114.1                         | –19916  | –20324  |
| Starting amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Added amount<br>$n_{\text{Te}}$ (mol)                  | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ (J mol <sup>–1</sup> ) | Ternary excess<br>enthalpy $H^E$ (J mol <sup>–1</sup> ) |
| <hr/>   |  |                                  |                               |   |   |
| Ga <sub>0.8</sub> Sb <sub>0.2</sub> –Te                   |  |                                  |                               |   |   |
| 0.023693  | 0.001009   | 0.041                            | 10.5                          | –1385   | –1950   |
|   | 0.001184   | 0.085                            | 6.1                           | –3113   | –3653   |
|   | 0.001529   | 0.136                            | 7.2                           | –5148   | –5658   |
|   | 0.002435   | 0.206                            | 0.7                           | –8321   | –8789   |
|   | 0.002859   | 0.276                            | –10.9                         | –11801  | –12228  |
|   | 0.003363   | 0.343                            | –25.4                         | –15539  | –15925  |
|   | 0.004802   | 0.420                            | –77.1                         | –20809  | –21151  |
|   | 0.004600   | 0.479                            | –81.5                         | –25981  | –25288  |
| 0.016947  | 0.000674   | 0.038                            | 3.3                           | –1508   | –2075   |
|   | 0.001383   | 0.108                            | 9.6                           | –4118   | –4644   |
|   | 0.001469   | 0.172                            | 4.3                           | –6791   | –7279   |
|   | 0.002294   | 0.256                            | –2.5                          | –10686  | –11125  |



Table 3  
(Continued)

| Starting amount<br>$n_{\text{Te}}$ (mol)   | Added amount<br>$n_{\text{Ga}_y\text{Sb}_{1-y}}$ (mol) | Mole fraction<br>$x_{\text{Te}}$ | Heat effect<br>$\Delta Q$ (J) | Experimental excess<br>enthalpy $H_{\text{exp}}^E$ ( $\text{J mol}^{-1}$ ) | Ternary excess<br>enthalpy $H^E$ ( $\text{J mol}^{-1}$ ) |
|--|--|----------------------------------|-------------------------------|--|--|
|  | 0.003134   | 0.346                            | -14.6                         | -15322   | -15708   |
|  | 0.004434   | 0.441                            | -40.5                         | -20899   | -21228   |
|  | 0.004504   | 0.514                            | -6.8                          | -24125   | -2411  |
| <b>Te–Ga<sub>0.8</sub>Sb<sub>0.2</sub></b> |  |                                  |                               |  |  |
| 0.011456                                   | 0.001231   | 0.903                            | -36.2                         | -6620  | -6677  |
|  | 0.001780   | 0.792                            | -53.2                         | -14261   | -14383   |
|  | 0.002629   | 0.670                            | -97.6                         | -23756   | -23950   |
|  | 0.003577   | 0.554                            | 23.2                          | -25244   | -25507   |
| 0.014434                                   | 0.001106   | 0.929                            | -53.8                         | -6225  | -6183  |
|  | 0.002090   | 0.819                            | -17.2                         | -14131   | -14024   |
|  | 0.001939   | 0.738                            | -84.3                         | -20891   | -20736   |
|  | 0.002907   | 0.624                            | -68.9                         | -26281   | -26070   |
|  | 0.003233   | 0.561                            | -50.4                         | -25902   | -25643   |

Fig. 4. Ga<sub>0.5</sub>Sb<sub>0.5</sub>–Te section ( $T = 1173$  K).Fig. 5. Projection of the isenthalpic lines on the Gibbs triangle in the Ga–Sb–Te system at  $T = 1173$  K in  $\text{kJ mol}^{-1}$ .

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