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Antimony activities in the ternary NiAs-phase of the In–Ni–Sb system

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Abstract

Antimony vapor pressures were determined in the ternary In–Ni–Sb system along, an isopleth with $x_{In}/x_{Ni}=1/9$, using an isopiestic method. The measurements were made between 980 and 1350 K, covering a composition range 43–48 at% Sb, with a few samples at higher antimony contents. Thermodynamic activities and partial molar enthalpies of antimony were derived for the ternary ζ-phase which crystallizes in an NiAs-type structure. The composition dependence of the activities is given for a temperature of 1173 K, and isoactivity curves are constructed for the same temperature. The variation of the antimony activity along the $\zeta/(\zeta+L)$ phase boundary is estimated. © 1998 Elsevier Science B.V.

Keywords: In–Ni–Sb: Antimony vapor pressures; In–Ni–Sb system; In–Ni–Sb: Ternary NiAs-phase; In–Ni–Sb: Thermodynamic properties; Isopiestic method

1. Introduction

A prerequisite for the construction of integrated circuits based on compound semiconductors is the formation of stable metal contacts. For this reason, the problem of suitable contact materials has been investigated extensively over the last two decades from different points of view (see for e.g. [1–4]). To understand the possible reaction sequence between the contacting metal and the compound semiconductor under consideration, a thorough knowledge of the corresponding ternary phase diagram is very important. Furthermore, any thermodynamic information on these ternary systems will be helpful for the estimation of the stability of the compounds formed at the contact site.

We have recently embarked on a study of ternary systems, involving one of the transition metals, Ni, Pd, or Pt (as possible contact materials), and one of the two compound semiconductors, GaSb or InSb. Besides an experimental investigation of the phase equilibria it was our additional goal to attempt a calculation of the corresponding phase diagrams supporting the experimental results and extending the information into temperature and composition ranges where experiments are difficult. Again values of partial or integral thermodynamic data for ternary alloys will be extremely valuable for this purpose.

In the In–Ni–Sb system it was discovered that the two NiAs-(B8-)type phases $Ni_{1\pm x}Sb$ and ζ-$InNi_2$ form a continuous solid solution (in the following designated as ζ-phase), at least in the temperature range where the latter one is stable [5]. Since Sb has a considerably higher vapor pressure than both In and Ni, it was decided to employ a well-established iso-

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piestic method [6–8] for the determination of Sb activities in this solid solution. Originally it was planned to study an isopleth with $x_{In}/x_{Ni}=1/2$; however, preliminary experiments showed that the Sb vapor pressures were far too low. Therefore, a section closer to the Ni–Sb binary system, i.e. with $x_{In}/x_{Ni}=1/9$ was selected for the isopiestic experiments; Sb vapor pressures were obtained in the composition range between 43 and 48 at% Sb which covers part of the ζ-phase and part of the $(\zeta+L)$ two-phase region.

2. Experimental procedure

Starting material for all isopiestic experiments was a master alloy with a composition $In_{0.06}Ni_{0.54}Sb_{0.40}$, i.e. well within the solid solution of the ζ-phase. It was prepared from Sb lumps (99.99%, ASARCO, South Plainfield, NJ), Ni foil (99.99%, Advent, Halesworth, England), and In shot (99.99%, Alfa-Ventron, Karlsruhe, F.R.G.). Weighed amounts of the pure elements were melted in an evacuated quartz tube and annealed at 900°C for one week. Since the weight loss during the preparation of the alloy was <0.05%, its final composition was assumed to be identical with the nominal one.

The alloy was finely powdered and re-annealed at 900°C for a period of six weeks. After that the powder was characterized by X-ray diffraction (Debye–Scherrer method, double radius camera, CuK_α-radiation) and was found to be single phase with the expected hexagonal NiAs structure. The corresponding lattice parameters were determined to be $a=4.0037(6)$ and $c=5.159(2)$ Å.

The experimental details of the employed isopiestic method have been described earlier [6–8]. Specially devised small quartz crucibles – as described by Ipser and Komarek [7] – were used to contain the individual samples. All quartz parts were cleaned with an acid mixture (5% HF, 30% HNO_3, rest water) before rinsing with distilled water and drying. The completely assembled isopiestic apparatus was degassed by heating overnight at 1000°C under a vacuum of ca. 10^{-1} Pa.

The reservoir was filled with ca. 40 g of pure Sb, and an amount of ca. 150 mg of the previously prepared master alloy was weighed into each crucible with an accuracy of ±0.05 mg. An average of 15 such sample crucibles were arranged in the isopiestic reaction tube. The fully assembled apparatus was evacuated to 10^{-1} Pa, flushed several times with purified Ar, and finally sealed under vacuum. It was placed into the temperature gradient of a two-zone furnace and heated for periods of 7 to 16 days. The temperatures of the individual samples and of the Sb reservoir were measured periodically by raising a calibrated Pt/Pt10%–Rh-thermocouple in a thermocouple well. All experiments were terminated by quenching the reaction tube in water. The compositions of the samples after equilibration were calculated from their mass increase which was attributed to the uptake of Sb.

3. Experimental results

Six successful isopiestic experiments were carried out in the ternary In–Ni–Sb system along the isopleth with $x_{In}/x_{Ni}=1/9$; reservoir temperatures were between 918 and 1009 K and sample temperatures between ca. 980 and 1350 K. All experimental results together with the experimental conditions are listed in Table 1. The so-called equilibrium curves (sample temperatures vs. sample composition) are shown in Fig. 1; for the evaluation of the data, the two runs, Nos. 3 and 4 with reservoir temperatures of 956 and 958 K, respectively, were treated as one single experiment with an average reservoir temperature of 957 K.

Unfortunately, the phase boundary of the ζ-phase is rather difficult to recognize in Fig. 1; this is due to the fact that the equilibrium curves are not horizontal in the two-phase field (as they would have to be in binary systems) due to the additional degree of freedom in a ternary system. The steep slope of these curves in the two-phase field is apparently an indication that the tie lines connecting ζ and liquid phase must intersect the line of constant ratio $x_{In}/x_{Ni}=1/9$ at a rather large angle. This can be visualized from the following consideration: If the tie lines would lie exactly in the isopleth, the equilibrium curves would have to be horizontal in the two-phase field, and no samples would be expected in the corresponding composition range. The larger the angle between the tie lines and the investigated section, the steeper will be the slope of the equilibrium curves.

Table 1
Experimental isopiestic results in the ternary In–Ni–Sb system; standard state: Sb(l)

Sample No.	Sb (at%)	T (K)	ln a_{Sb} (T_{S})	$\Delta\overline{H}_{\mathrm{Sb}}$ (kJ mol^{-1})	ln a_{Sb} (1173 K)
Run 1: T_{R}=1009 K, 7 days					
1 [a]	47.36	1099	−0.286		
2 [a]	47.17	1112	−0.331		
3 [a]	47.03	1126	−0.380		
4 [a]	46.95	1144	−0.446		
5 [a]	46.66	1164	−0.522		
6	46.29	1194	−0.644	−5.3	−0.653
7	45.98	1228	−0.794	−11.3	−0.846
8	45.66	1257	−0.933	−17.5	−1.053
9	45.36	1284	−1.069	−23.5	−1.277
10	45.27	1302	−1.163	−25.4	−1.420
11	44.89	1317	−1.242	−32.7	−1.609
12	44.77	1329	−1.305	−35.1	−1.727
13	44.62	1341	−1.369	−38.1	−1.858
14	44.46	1349	−1.411	−41.3	−1.964
Run 2: T_{R}=996 K, 7 days					
1 [a]	77.36	1030	−0.105		
2 [a]	63.88	1037	−0.128		
3 [a]	56.42	1044	−0.151		
4 [a]	47.91	1054	−0.185		
5 [a]	47.46	1072	−0.245		
6 [a]	47.15	1096	−0.327		
7 [a]	46.82	1128	−0.442		
8 [a]	46.46	1164	−0.581		
9	46.15	1200	−0.734	−7.9	−0.752
10	45.82	1233	−0.888	−14.5	−0.960
11	45.48	1260	−1.022	−21.2	−1.172
12	45.24	1281	−1.132	−25.8	−1.355
13	45.30	1299	−1.227	−24.7	−1.472
Run 3: T_{R}=958 K, 16 days					
1 [a]	47.38	1024	−0.233		
2 [a]	47.19	1058	−0.352		
3 [a]	46.84	1084	−0.446		
4 [a]	46.48	1121	−0.587		
5	46.14	1161	−0.757	−8.0	−0.748
6	45.85	1199	−0.937	−13.8	−0.968
7	45.52	1231	−1.103	−20.3	−1.201
8	45.26	1257	−1.245	−25.5	−1.419
9	44.98	1275	−1.346	−30.9	−1.599
10	44.79	1289	−1.425	−34.8	−1.746
11	44.61	1299	−1.481	−38.3	−1.862
12	44.42	1307	−1.527	−42.0	−1.968
13	44.37	1310	−1.544	−43.0	−2.005
Run 4: T_{R} =956 K, 8 days					
1 [a]	47.50	1025	−0.245		
2 [a]	47.28	1051	−0.335		
3 [a]	46.94	1076	−0.425		
4 [a]	46.58	1113	−0.565		
5	46.23	1152	−0.728	−6.4	−0.716

Table 1 (*continued*)

Sample No.	Sb (at%)	T (K)	ln a_{Sb} (T_S)	$\Delta\overline{H}_{Sb}$ (kJ mol^{-1})	ln a_{Sb} (1173 K)
6	45.93	1193	−0.919	−12.2	−0.940
7	45.59	1227	−1.094	−18.9	−1.179
8	45.29	1252	−1.231	−24.9	−1.411
9	45.03	1272	−1.343	−30.0	−1.582
10	44.80	1287	−1.427	−34.6	−1.742
11	44.62	1298	−1.490	−38.1	−1.866
Run 5: T_R=941 K, 7 days					
1 [a]	47.44	1019	−0.287		
2 [a]	47.22	1041	−0.365		
3 [a]	47.13	1060	−0.433		
4 [a]	46.80	1074	−0.485		
5 [a]	46.63	1090	−0.546		
6	46.41	1112	−0.634	−2.7	−0.619
7	46.11	1141	−0.758	−8.7	−0.733
8	45.76	1179	−0.938	−15.7	−0.946
9	45.38	1221	−1.159	−23.0	−1.252
10	45.08	1254	−1.345	−29.0	−1.537
11	44.64	1280	−1.495	−37.6	−1.817
12	44.24	1303	−1.628	−45.6	−2.094
13	43.90	1321	−1.731	−52.8	−2.338
14	43.57	1334	−1.806	−57.3	−2.515
15	43.32	1344	−1.862	−59.5	−2.638
Run 6: T_R=918 K, 14 days					
1 [a]	47.54	982	−0.254		
2 [a]	47.15	997	−0.308		
3 [a]	47.04	1017	−0.380		
4 [a]	46.81	1041	−0.469		
5 [a]	46.55	1070	−0.580		
6	46.16	1108	−0.737	−7.8	−0.690
7	45.89	1150	−0.932	−13.1	−0.905
8	45.49	1192	−1.153	−21.0	−1.187
9	45.05	1231	−1.377	−29.5	−1.519
10	44.77	1262	−1.561	−35.1	−1.815
11	44.37	1286	−1.705	−43.0	−2.092
12	43.96	1304	−1.811	−51.9	−2.345
13	43.57	1319	−1.899	−57.3	−2.550
14	43.31	1329	−1.957	−59.5	−2.674
15	43.16	1335	−1.992	−60.2	−2.741

[a] Sample in two-phase field (ζ+L).

On the other hand, samples in the ζ-phase and those in the (ζ+L) two-phase field could be distinguished from their optical appearance, at least under a microscope, and from that the position of the phase boundary could be fixed at ca. 46.4 at% Sb, as it is shown in Fig. 1. This is in very good agreement with the results of the phase diagram investigation [5]. In run 2 there are three samples at low temperatures (below 1050 K) with rather high Sb contents (56.42 to 77.36 at% Sb; cf. Table 1). This drastic flattening of the equilibrium curve could be caused by a turning of the tie lines in the two-phase field (ζ+L). However, this effect will be difficult to separate from any other effects on the slope of the equilibrium curves described, for example the variation of the phase boundaries with temperature.

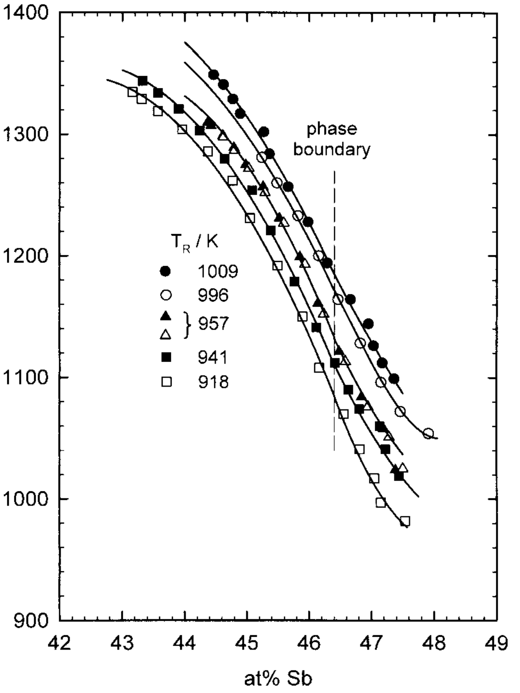

Fig. 1. Sample temperature vs. sample composition for six isopiestic experiments in the ternary In–Ni–Sb system along an isopleth with x_{In}/x_{Ni}=1/9.

For the evaluation of the experimental data it was assumed that the vapor pressures of In and Ni are negligible, and that the total vapor pressure in the system is therefore determined by the temperature of the Sb reservoir. Following the detailed discussion by Leubolt et al. [9], the total Sb vapor pressure in the system is given by

$$p_{\mathrm{total}} = p_{\mathrm{Sb_4}} + p_{\mathrm{Sb_2}} \tag{1}$$

and the activity of any sample at the sample temperature T_S is expressed on the basis of the main species Sb_4 as

$$a_{\mathrm{Sb}}(T_{\mathrm{s}}) = \left(\frac{p_{\mathrm{Sb_4}}(T_{\mathrm{s}})}{p^0_{\mathrm{Sb_4}}(T_{\mathrm{s}})}\right)^{1/4}. \tag{2}$$

The equilibrium between the two species Sb_2 and Sb_4 in the gas phase is governed by the corresponding dissociation constant

$$K = \frac{p^2_{\mathrm{Sb_2}}}{p_{\mathrm{Sb_4}}}. \tag{3}$$

Since the total vapor pressure in the system is fixed by the reservoir temperature, the vapor pressure of Sb_4 over the samples can be calculated from Eqs. (1) and (3) as a function of temperature:

$$p_{\mathrm{Sb_4}}(T) = \frac{K(T) + 2p_{\mathrm{total}} - \sqrt{K(T)^2 + 4K(T)p_{\mathrm{total}}}}{2}. \tag{4}$$

The dissociation constant K at any temperature T is

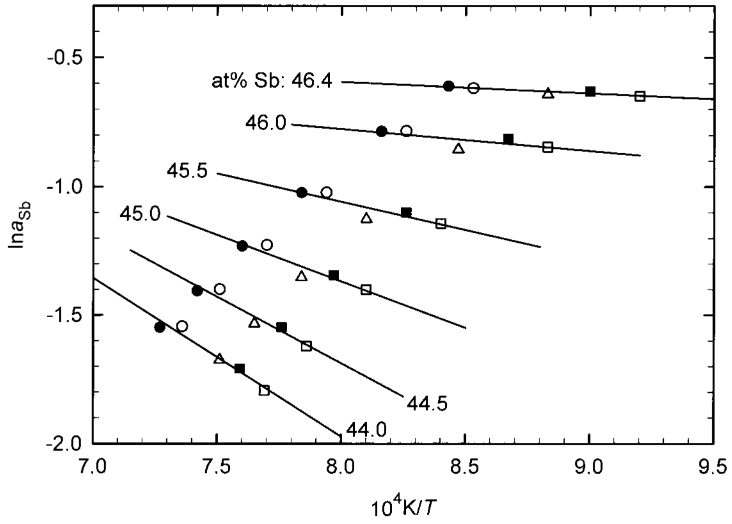

Fig. 2. Antimony activity as a function of reciprocal temperature for selected compositions in the ζ-phase. Symbols are the same as in Fig. 1.

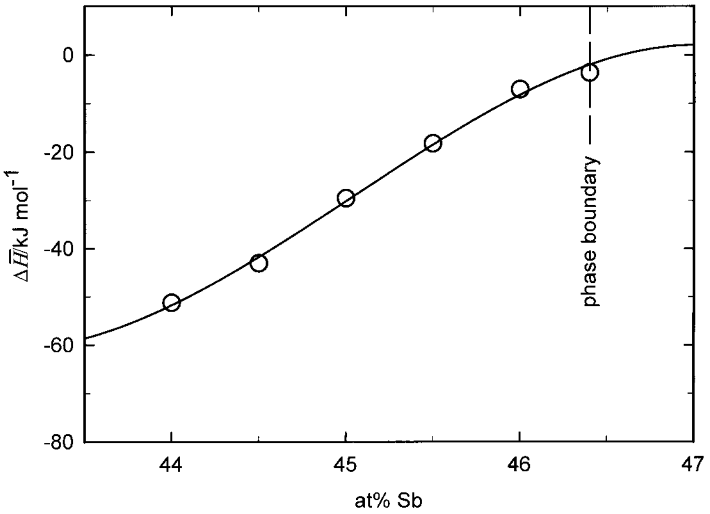

Fig. 3. Partial molar enthalpy of antimony in the ζ-phase as a function of composition with experimental data points derived from Fig. 2. Standard state: Sb(l).

obtained by Eq. (3) using tabulated values of the partial pressure for Sb_2 and Sb_4 over pure antimony [10].

Natural logarithms of the Sb activities for all samples at the individual sample temperatures were calculated by means of Eq. (2), and they are given in Table 1. Partial molar enthalpies of mixing for Sb were obtained from the temperature dependence of the activities according to the following equation:

$$\frac{\partial \ln a_{Sb}}{\partial(1/T)} = \frac{\Delta\overline{H}_{Sb}}{R}. \tag{5}$$

Values of $\ln a_{Sb}$ were plotted as a function of the reciprocal temperature at regular composition intervals, and straight lines with a slope of $\Delta\overline{H}_{Sb}/R$ were obtained by linear regression. This is shown in Fig. 2 for some selected compositions in the ζ-phase. The values of the partial molar enthalpy of Sb are plotted as a function of composition in Fig. 3. Partial enthalpies from this curve were used to convert the Sb activities to a common temperature of 1173 K. Values of $\ln a_{Sb}$ at this temperature are included in Table 1 together with the corresponding $\Delta\overline{H}_{Sb}$ values. They are also plotted in Fig. 4.

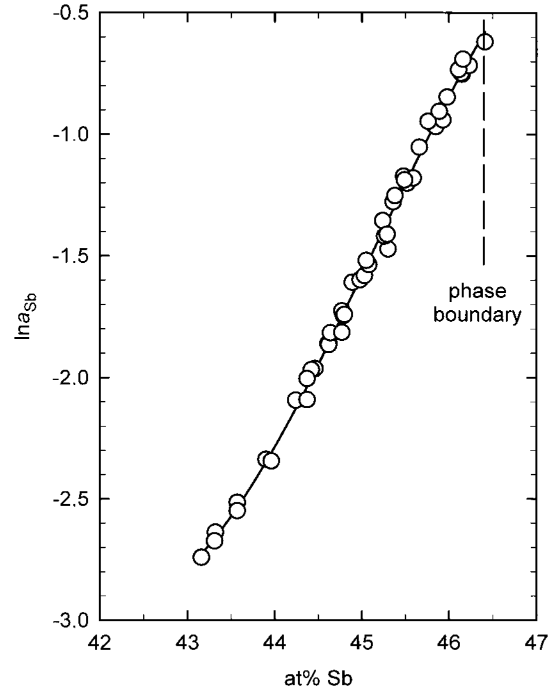

Fig. 4. Activity of antimony as function of composition in the ζ-phase at 1173 K. Standard state: Sb(l).

4. Discussion

No data could be found in the literature dealing with the thermodynamics of ternary In–Ni–Sb alloys. However, it may be quite interesting to compare Sb activities in the ternary ζ-phase with corresponding experimental values for the NiAs-phase in the limiting binary Ni–Sb system. Leubolt et al. reported partial thermodynamic properties of Sb for $Ni_{1\pm x}Sb$, also derived from isopiestic measurements [9]. Taking activity values for 1173 K from Ref. [9] and comparing them with those of the present study yields iso-activity curves which are shown in Fig. 5. For the construction of this diagram it was assumed that these iso-activity curves are linear in the composition range under consideration. The phase boundaries of the

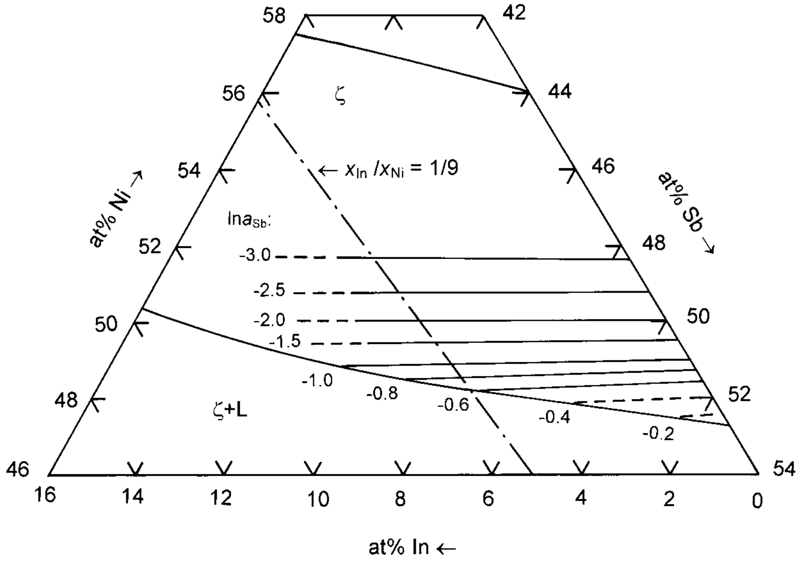

Fig. 5. Iso-activity curves for 1173 K in the indium-poor composition range of the ζ-phase. Standard state: Sb(l). Phase boundaries are from Ref. [5].

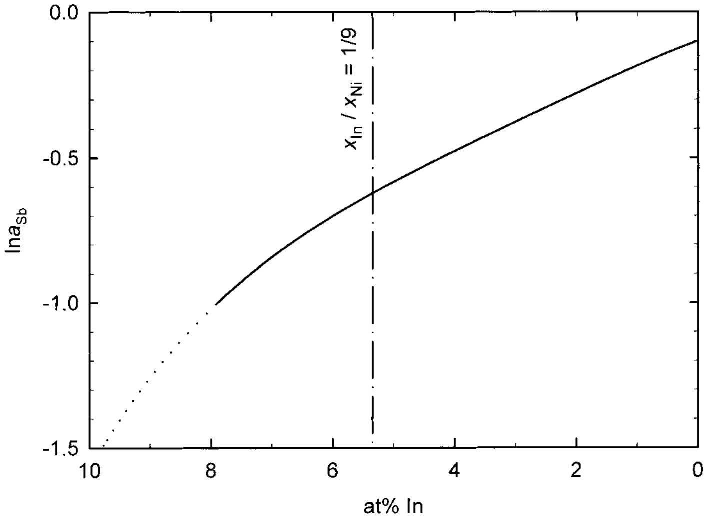

Fig. 6. Variation of the antimony activity with composition along the $\zeta/(\zeta+L)$ phase boundary. Standard state: Sb(l).

ζ-phase were taken from Richter and Ipser [5] and combined with the extension of the binary $Ni_{1\pm x}Sb$-phase at the same temperature (44.0 to 52.7 at% Sb) reported by Leubolt et al. [11]. For simplicity, the $\zeta/(\zeta+L)$ phase boundary is shown to be linear in the range 0–5.4 at% In (where it intersects the investigated isopleth).

On the basis of Fig. 5 it is also possible to estimate the variation of the Sb activity along the corresponding phase boundary. This is shown in Fig. 6. A similar comparison for the partial molar enthalpy of Sb shows a value of $\Delta\overline{H}_{Sb} = -4$ kJ mol^{-1} at the Sb-rich end of the binary $Ni_{1\pm x}Sb$-phase [9], whereas a value of ca. -2 kJ mol^{-1} can be read from Fig. 3 for the corresponding limit of the ternary ζ-phase in the investigated isopleth; apparently, the partial enthalpy of Sb remains nearly constant along the $\zeta/(\zeta+L)$ phase boundary at 1173 K. Unfortunately, since all phase boundaries probably change considerably with temperature, it is almost impossible to utilize these $\Delta\overline{H}_{Sb}$ values for a conversion of the Sb-activities for all the samples in the $(\zeta+L)$ two-phase field (obtained for the corresponding sample temperatures; cf. Table 1) to one common temperature.

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