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Measurement of Thermodynamic Properties of Al–Sb System by Calorimeters†

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The free energy, heat and entropy of mixing in a liquid Al–Sb alloy were derived by combining heat contents of the alloy with the heat and entropy of formation of the equiatomic compound of AlSb at a reference temperature. The heat contents of the alloy were measured using a drop calorimeter in a temperature range from 800 to 1450 K and in a concentration range of N_{Sb} from 0.05 to 0.95. The heat and entropy of formation of AlSb were determined respectively from the heat of solution measurements at 773 K using a twin solution calorimeter and from the heat capacity measurements in a temperature range from 4 to 300 K using an adiabatic calorimeter.

The obtained thermodynamic and phase diagram data for the Al–Sb system were analyzed using a Redlich-Kister polynomial equation and the optimized parameters were derived as a function of alloy composition and temperature.

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I. Introduction

High temperature thermodynamic properties of the Al–Sb system provide an important basis for processing semiconducting materials. However, only a few data exist for the mixing properties of the liquid alloys. Predel and Schallner(1) and Glazov *et al.*(2) conducted e.m.f. measurements and Girard *et al.*(3) determined the heat of mixing.

Based on a thermodynamic analysis method which was originally developed by Oelsen(4), the thermodynamic integral molar quantities are obtainable by combining the heat content of the alloy with the heat and entropy of formation of the equiatomic compound AlSb at a reference temperature. In the present study, this method was applied to the Al–Sb system whose thermodynamic quantities are not necessarily easy to determine by means of the conventional methods at high temperatures.

Three kinds of calorimetric experiments were carried out in this study for applying the thermodynamic analysis method. The heat contents of the alloy were determined by using a drop calorimeter in a temperature range from 800 to 1450 K in a concentration range of N_{Sb} from 0.05 to 0.95. The entropy of formation of AlSb was determined from the heat capacity measurements in a temperature range from 4 to 300 K by using an adiabatic calorimeter while the heat of formation of AlSb was obtained from the heat of dissolution measurements at 773 K by using a Calvet-type twin solution calorimeter. The phase diagram of the Al–Sb system was also determined from the heat content-temperature-composition relationships.

The obtained thermodynamic and phase diagram data for the Al–Sb system were analyzed based on a Redlich-Kister polynomial equation(5) and the optimized parameters were derived as a function of alloy composition and temperature.

II. Theory of the Thermodynamic Analysis Method

The thermodynamic analysis method is described in detail by Oelsen(4) and its principle is summarized as follows:
The heat content, J_T, is defined as

$$J_T = H_T - H_\theta \tag{1}$$

where H_T and H_θ are the enthalpies of a specimen at T K and a specified reference temperature, θ K, respectively. On the basis of the second law of the thermodynamics, we can obtain the following equation:

$$T\int_{1/\theta}^{1/T} J_T \mathrm{d}(1/T) + H_\theta - TS_\theta = H_T - TS_T \tag{2}$$

where S_T and S_θ are the entropies of the specimen at T K and θ K, respectively. By applying eq. (2) to the pure components A, B and a mixture with the mole fraction x of the component A, the Gibbs energy of mixing, $\Delta G_{x,T}^{\mathrm{mix}}$, at T K is given by eq. (3)

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$$\Delta G^{\mathrm{mix}}_{x,T}=T\left[\int_{1/\theta}^{1/T} J_{x,T}\mathrm{d}(1/T)-x\int_{1/\theta}^{1/T} J_{\mathrm{A},T}\mathrm{d}(1/T)-(1-x)\int_{1/\theta}^{1/T} J_{\mathrm{B},T}\mathrm{d}(1/T)\right]+\Delta H^{\mathrm{mix}}_{x,\theta}-T\Delta S^{\mathrm{mix}}_{x,\theta} \tag{3}$$

here $\Delta H^{\mathrm{mix}}_{x,\theta}$ and $\Delta S^{\mathrm{mix}}_{x,\theta}$ are the heat and entropy of mixing at θ K, respectively. The heat and entropy of mixing at T K can be derived by the following equations:

$$\Delta H^{\mathrm{mix}}_{x,T}=\Delta H^{\mathrm{mix}}_{x,\theta}+J_{x,T}-xJ_{\mathrm{A},T}-(1-x)J_{\mathrm{B},T} \tag{4}$$

$$\Delta S^{\mathrm{mix}}_{x,T}=\Delta S^{\mathrm{mix}}_{x,\theta}+1/T[J_{x,T}-xJ_{\mathrm{A},T}-(1-x)J_{\mathrm{B},T}]-\left[\int_{1/\theta}^{1/T} J_{x,T}\mathrm{d}(1/T)-x\int_{1/\theta}^{1/T} J_{\mathrm{A},T}\mathrm{d}(1/T)-(1-x)\int_{1/\theta}^{1/T} J_{\mathrm{B},T}\mathrm{d}(1/T)\right] \tag{5}$$

The phase diagram of the Al–Sb system[6] forms a stoichiometric compound at $x_{\mathrm{Sb}}=0.5$ and has no primary solid solution. Therefore the terms $\Delta H^{\mathrm{mix}}_{x,\theta}$ and $\Delta S^{\mathrm{mix}}_{x,\theta}$ in eqs. (3), (4) and (5) are given by eq. (6) or eq. (7), provided that a temperature below the eutectic is adopted as the reference, θ K.

$$\Delta H^{\mathrm{mix}}_{x,\theta}=(\Delta H_{\mathrm{f},\theta}/2)\times x_{\mathrm{Sb}}$$

and

$$\Delta S^{\mathrm{mix}}_{x,\theta}=(\Delta S_{\mathrm{f},\theta}/2)\times x_{\mathrm{Sb}};\quad (0\leqq N_{\mathrm{Sb}}\leqq 0.5) \tag{6}$$

$$\Delta H^{\mathrm{mix}}_{x,\theta}=(\Delta H_{\mathrm{f},\theta}/2)\times(1-x_{\mathrm{Sb}})$$

and

$$\Delta S^{\mathrm{mix}}_{x,\theta}=(\Delta S_{\mathrm{f},\theta}/2)\times(1-x_{\mathrm{Sb}});\quad (0.5\leqq N_{\mathrm{Sb}}\leqq 1.0) \tag{7}$$

where $\Delta H_{\mathrm{f},\theta}$ and $\Delta S_{\mathrm{f},\theta}$ are the heat and entropy of formation of AlSb at θ K.

Thus we can derive the integral molar quantities of the liquid Al–Sb alloy from the heat content for the Al–Sb system and the heat and the entropy of formation of the AlSb compound.

III. Experimental Procedure

The purity of the AlSb compound obtained from Cerac Incorporation had over 99.99 mass% and those of aluminum and antimony were more than 99.999 mass%. Gallium metal used as a solvent and α-aluminum oxide used for the calibration in the measurements of heat of formation were 99.99 mass%.

1. Heat of formation of AlSb

A Calvet-type twin calorimeter was used to determine the heat of formation. The details of the calorimeter and the experimental procedure have been described in a previous paper[7]. Gallium metal was used as the solvent instead of tin metal. Calibration was made by a drop method using solid α-$\mathrm{Al_2O_3}$ as a standard whose enthalpy value was taken from a table by Knacke *et al.*[8]. The AlSb sample of 0.03 ~ 0.22 g was vacuum-sealed into a thin breakable Pyrex glass ampoule with a thickness 0.4 mm and an outer diameter 13 mm. In the experiments for the mechanical mixture, the Al and Sb metals were vacuum-sealed into the two glass ampoules independently. The ampoule was held at 773 K in the calorimeter cell with the gallium solvent (50 g). After thermal equilibrium was attained in the calorimeter, the dissolution experiment was initiated by breaking the ampoule with an alumina manipulation rod. The heat of formation of the AlSb compound was derived by the difference between the heats of dissolution of the compound and the mechanical mixture.

2. Entropy of AlSb

The entropy of AlSb was determined from the heat capacity measurements. Two adiabatic calorimeters were used, one with a Ge resistance thermometer for a temperature range from 4 to 40 K, and the other with a Pt resistor for a temperature range from 40 to 300 K. The construction of these calorimeters and of the external parts of the cryostat were similar except for the diameter of a copper lead wire for a heating element. The experimental arrangement employed is shown in Fig. 1. The addenda consists of two thin copper plates (99.999 mass%) coated with gold (thickness 0.3 mm, diameter 20 mm), on which a calibrated Ge or Pt resistor purchased from Lake Shore Cryotronic Inc. and a heater (1001.7 Ω) are attached. The addenda was suspended in a frame via Nylon threads. Copper wires with a 0.08 mm diameter and a 1.6 m long were used as an electrical lead to the thermometer and the heater inside cell for the temperature range from 4 to 40 K while copper wires of 0.2 mm diameter and 1.6 m long were used for the temperature range from 40 to 300 K. The leads were led through two thermal anchors outside the cell to reduce the large heating effect.

The sample was set on the addenda using 0.05 g of Apiezon-N grease as a thermal bond. The cell was first pumped to $5.3\cdot 10^{-4}\sim 8.0\cdot 10^{-4}$ Pa at room temperature. After the system was precooled to a liquid nitrogen temperature, the cell was put into liquid helium or liquid

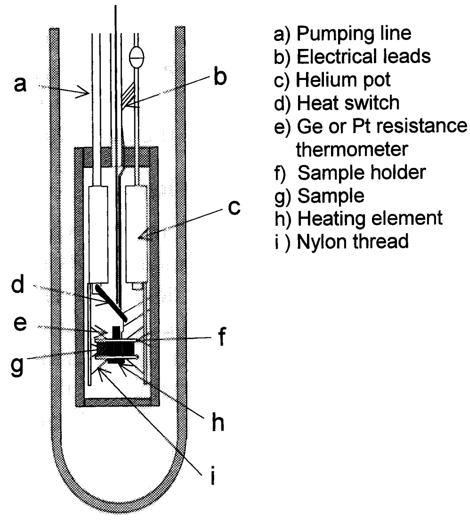

Fig. 1 Schematic diagram of the adiabatic calorimeter cell.

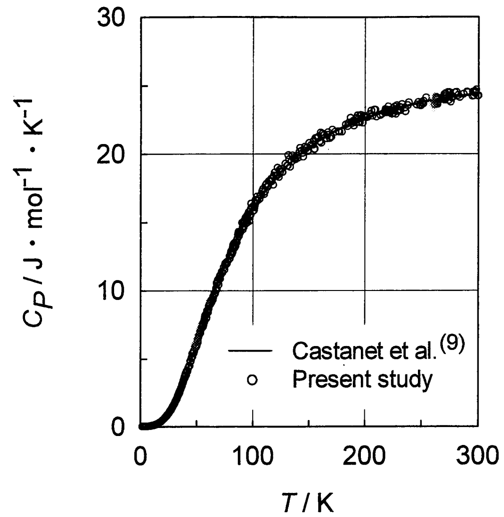

Fig. 2 Heat capacity of Cu as a function of temperature.

nitrogen.

A conventional heat-pulse method was used for determining the heat capacities. The voltage across the resistance thermometer was measured continuously with a digital voltage meter, and was recorded on a personal computer through a GP-IB interface. The heater voltage and current were measured by a digital voltmeter and were controlled in a given time interval ranging from 20 to 30 s. The time was measured by a frequency counter. The temperature drift was recorded for a few minutes before and after the providing the heat pulse.

The heat capacity per mole of compound, C_P, is given by the following equations:

$$C_P=(Q/\Delta T-C_{P,\mathrm{ad.}})/m \tag{8}$$

$$Q=RI^2t \tag{9}$$

where Q is the provided heat which was defined by a resistance of the heater, R, a heater current, I, and the providing time, t; ΔT the temperature increase due to the sample assembly; $C_{P,\mathrm{ad.}}$ the heat capacity of the addenda and m the number of moles of the sample.

The accuracy of the experimental arrangement and procedure was tested by performing the measurements for 6.64 g poly-crystal copper (99.999 mass%) in a temperature range from 4 to 300 K. As shown in Fig. 2, the results agree within ±5% with the literature values⁽⁹⁾.

3. Heat content of Al-Sb alloys

A drop calorimeter was used as the experimental apparatus for the heat content measurements for the Al-Sb alloys, details of which are described in a separate paper⁽¹⁰⁾. The sample of about 6 g was kept in a boron nitride (BN) crucible with an inner diameter of 14 mm and a height of 10 mm, which was vacuum-sealed into a silica ampoule with a weight of 2.5 g. This assembly was held at a specified temperature T in a Pt crucible. After thermal equilibrium had been reached, the assembly was dropped into the calorimeter. The experiments were conducted for 18 samples having different mole fractions of Sb ($0.05 \leqq N_{\mathrm{Sb}} \leqq 0.95$) in the temperature range from 800 to 1450 K.

After completing the experiments, the specimens were analyzed by X-ray diffraction and the stable phase combinations at ambient temperature, which are reported in the literature⁽⁶⁾, were confirmed.

IV. Results and Discussion

1. Heat of formation of AlSb

The heats of dissolution of the AlSb compound and the mechanical mixture of AlSb are shown in Fig. 3, in relation to the concentration of AlSb in the liquid Ga alloy. The heat of formation, ΔH_f, which is given by the difference in the heat of dissolution between the compound and the mechanical mixture, is constant against the composition within the experimental error in the measured concentration range, and the averaged value of ΔH_f at 773 K is given in Table 1. The standard heat of formation, $\Delta H^\circ_{\mathrm{f},298.15}$, was calculated from the following equation:

$$\Delta H^\circ_{\mathrm{f},298.15}=\Delta H_{\mathrm{f},T}-\int_{298.15}^{T}\Delta C_P \mathrm{d}T \tag{10}$$

From a combination of the heat of formation at 773 K obtained in present work with the heat capacity data of the AlSb compound⁽¹¹⁾ and the elements⁽⁸⁾, the standard heat of formation at 298.15 K was derived as shown in Table 1. The value determined in this study is 6.6 kJ/mol lower than that obtained by Martosudirdjo and Pratt with a precipitation calorimetry⁽¹²⁾.

2. Entropy of formation of AlSb

The experimental values for the heat capacity, C_P, of the AlSb compound is shown in Fig. 4 with the reported

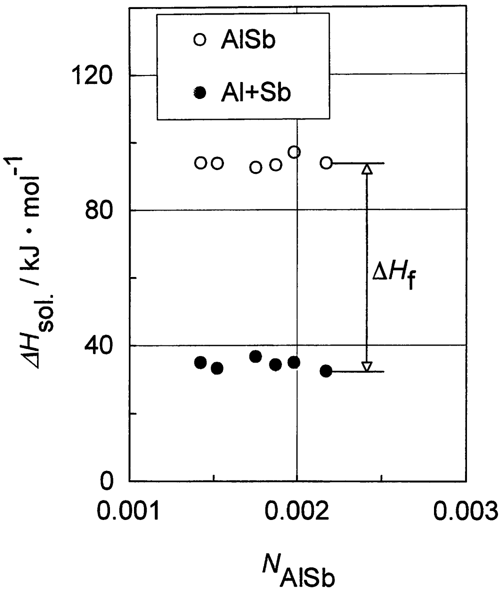

Fig. 3 Heats dissolution for the AlSb compound and for equivalent amounts of (Al+Sb) in Ga at 773 K.

Table 1 Heat of formation and standard entropy of the AlSb compound.

	Themodynamic quantities	Experimental method	Reference
$\Delta H_{f,773}$(kJ·mol^{-1})	−59.6±0.6	Ga solution calorimetry	Present study
$\Delta H_{f,298.15}$(kJ·mol^{-1})	−50.6±0.8 −57.2±0.6	Precipitation calorimetry Ga solution calorimetry	Martosudirdjo and Pratt(12) Present study
$S^{\circ}_{298.15}$(J·mol^{-1}·K^{-1})	64.2 63.9	Adiabatic calorimetry Adiabatic calorimetry	Piesbergen(13) Present study

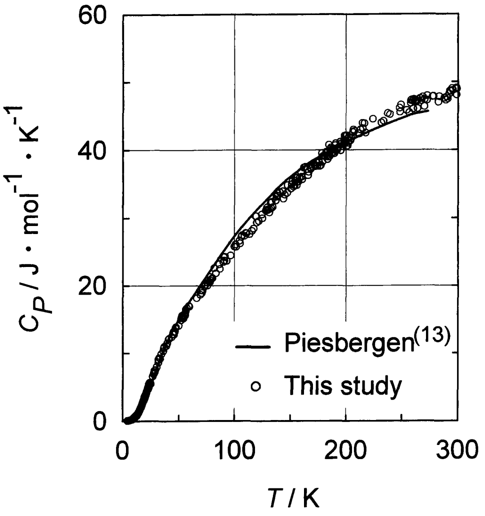

Fig. 4 Heat capacity of the AlSb compound as a function of temperature.

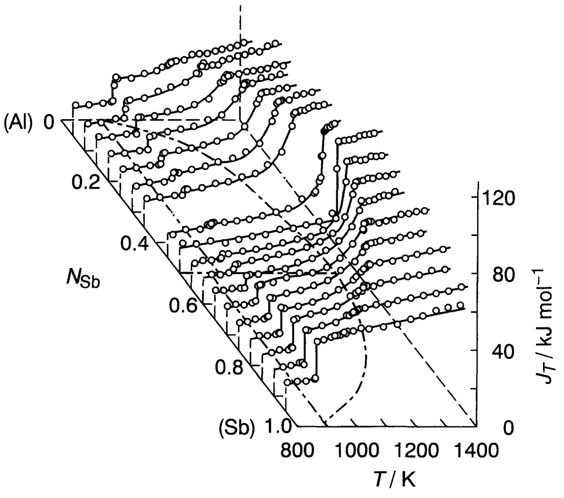

Fig. 5 Heat contents, J_T, of the Al-Sb system.

values by Piesbergen(13). The present results agree well with the reported ones at temperature below 50 K, and in temperature ranges from 50 to 190 K and from 190 K to 300 K, they are 4% lower and 2% higher than the reported ones(13), respectively. Based on the obtained heat capacity data, the standard entropy of the AlSb compound was derived by the following equation:

$$S^{\circ}_{298.15}=\int_{0}^{298.15}(C_P/T)\mathrm{d}T \tag{11}$$

and the result is shown in Table 1, which is 0.3 J/mol/K lower than the value by Piesbergen obtained with the similar calorimetry(13).

3. Heat content of AlSb

The enthalpy increments for the Al-Sb system, J_T, which was defined in eq. (1), with a reference temperature of 298.15 K, is illustrated in a three dimensional plot in Fig. 5. The deflection points in the J_T vs. T curves correspond to the temperature of phase changes and the phase diagram can be obtained by projecting the J_T points to the T vs. N_{Sb} plane. The obtained phase diagram is shown in Fig. 6 with the previous reported values(1)(14)-(17).

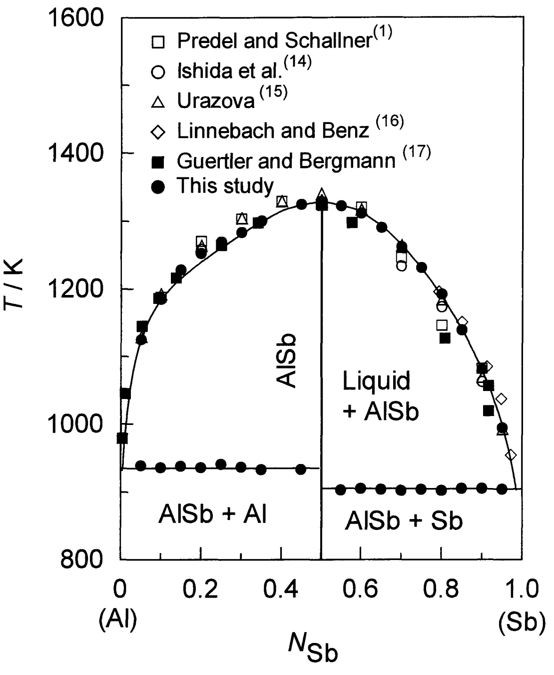

Fig. 6 Phase diagram of the Al-Sb system.

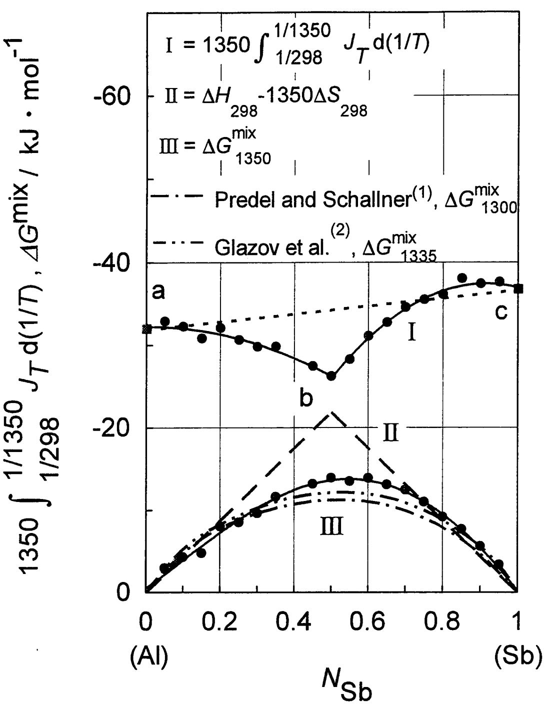

Fig. 7 $T\int_{1/\theta}^{1/T} J_T\mathrm{d}(1/T)$ plots and free energy of mixing in the Al-Sb melts (1350 K).

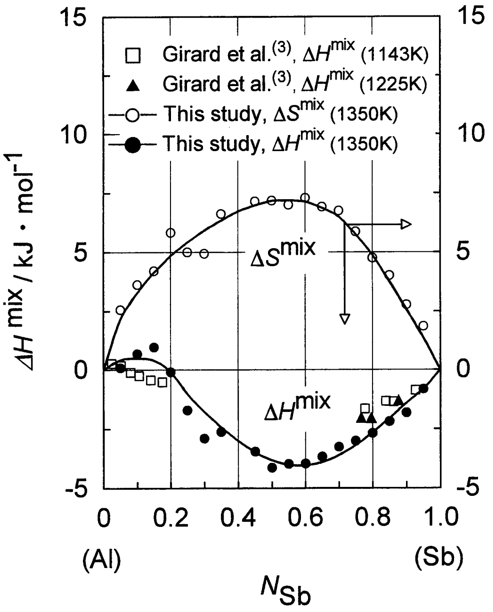

Fig. 8 Heat and entropy of mixing in the Al-Sb binary melts.

4. Thermodynamic quantities

On the basis of eq. (3) the integral free energy of formation can be derived through the integration of J_T over $1/T$. The reference temperature θ was 298.15 K. In Fig. 7 the values for $T[\int_{1/\theta}^{1/T} J_T\mathrm{d}(1/T)]$ and for $\Delta G^{\mathrm{mix}}_{1350}$ at 1350 K are plotted. The standard states are liquid Al and Sb. The term, $\Delta H^{\circ}_{\mathrm{f},298.15} - 1350\Delta S^{\circ}_{\mathrm{f},298.15}$, of eq. (3) was calculated from the heat of formation and entropy of AlSb at 298.15 K determined in the present study. ΔG^{mix} values obtained by Predel and Schallner(1) and Glazov *et al.*(2) using fused salt electrolytes are also shown in Fig. 7 for comparison. The present results are about 1 ~ 2 kJ/mol lower than these values.

The heat and entropy of mixing of the liquid Al-Sb binary system were derived at 1350 K on the basis of eqs. (4) and (5) and are shown in Fig. 8 with the heat of mixing values at 1143 and 1225 K reported by Girard *et al.*(3) Both results agree fairly well within the limit of experimental accuracy.

V. Thermodynamic Evaluation

The phase diagram and thermodynamic data obtained in the present study were analyzed using a Redlich-Kister polynomial equation for the excess integral free energy of mixing, ΔG^{ex}, as expressed in eq. (12), and the coefficients, $A^{(v)}$, $B^{(v)}$ and $C^{(v)}$ for the vth order in the polynomial equation were determined.

$$\Delta G^{\mathrm{ex}} = x_{\mathrm{Al}}x_{\mathrm{Sb}}\sum_{v=0}^{n}(x_{\mathrm{Al}} - x_{\mathrm{Sb}})^{v}L^{(v)}_{\mathrm{AlSb}}(T) \qquad (12)$$

Table 2 Coefficients of the Redlich-Kister polynomial for the excess Gibbs energy of the liquid Al-Sb system.

$L^{(v)}=A^{(v)}-B^{(v)}T+C^{(v)}T(1-\ln T)$(J/mol)			
	$A^{(v)}$	$B^{(v)}$	$C^{(v)}$
$v=0$	−7267.7	45.063	−5.311
$v=1$	−84580.7	−476.224	65.306
$v=2$	−23452.1	−174.094	23.751
$v=3$	41556.7	127.766	−14.779

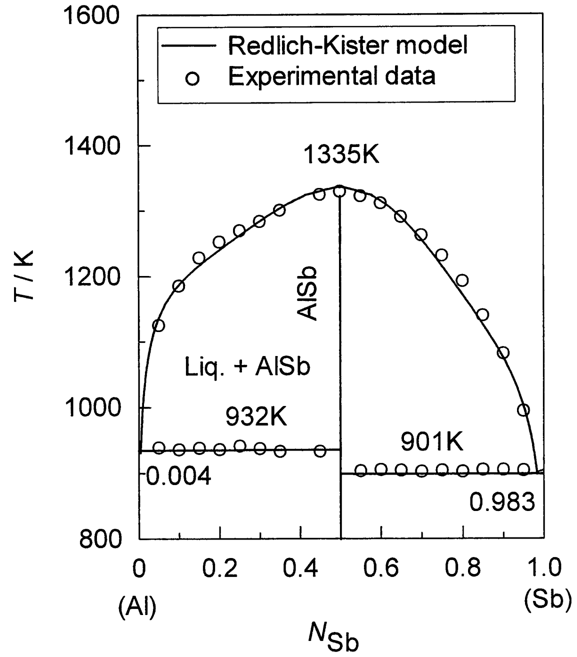

Fig. 9 Comparison between the calculated and experimental Al-Sb phase diagram.

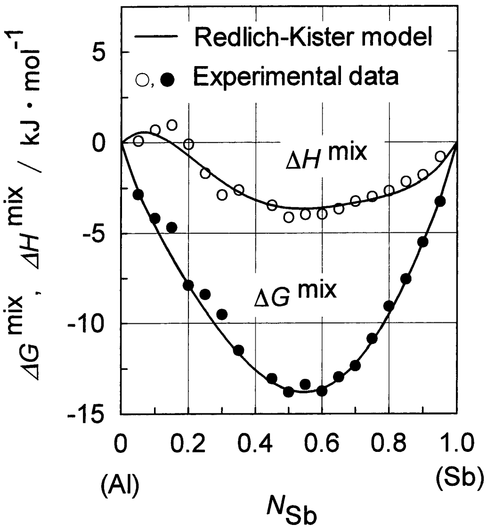

Fig. 10 Free energy and heat of mixing in the Al-Sb melts at 1350 K; comparison between the calculated and experimental values.

$$L^{(v)}_{\rm AlSb}(T)=A^{(v)}_{\rm AlSb}-B^{(v)}_{\rm AlSb}T+C^{(v)}_{\rm AlSb}T(1-\ln T) \qquad (13)$$

Here $x_{\rm Al}$ and $x_{\rm Sb}$ are the mole fractions and $L^{(v)}_{\rm AlSb}(T)$ is a non-liner function of temperature, relating to the heat and entropy of mixing.

$\Delta G^{\rm ex}$ coefficients for the liquid Al-Sb system are listed in Table 2. The phase diagram calculated with a set of evaluated coefficients is shown in Fig. 9. The evaluated liquidus lines and eutectic temperatures for Al and Sb sides are in good agreement with the experimental data. The evaluated and measured values of the free energy and heat of mixing at 1350 K, are shown in Fig. 10 for comparison. A satisfactory agreement is found between the two results.

VI. Summary

The heat of formation of the AlSb compound was determined at 773 K by a Calvet-type twin solution calorimetry using liquid gallium as the calorimetric solvent. The standard entropy of the AlSb compound at 298.15 K was determined from the heat capacity measurements carried out over a temperature range of 4 to 300 K using an adiabatic calorimeter. The heat contents of the binary Al-Sb system were determined by a drop calorimeter in a concentration range from $N_{\rm Sb}=0.05$ to 0.95 and in a temperature range of 800 to 1450 K. Based on the thermodynamic analysis method, the integral molar thermodynamic quantities of the liquid Al-Sb system were obtained by combining the entropy and heat of formation of the AlSb compound and the heat contents of the binary Al-Sb system. The obtained thermodynamic and phase diagram data for the Al-Sb system were analyzed using a Redlich-Kister polynomial equation and the optimized parameters were derived as a function of alloy composition and temperature.

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