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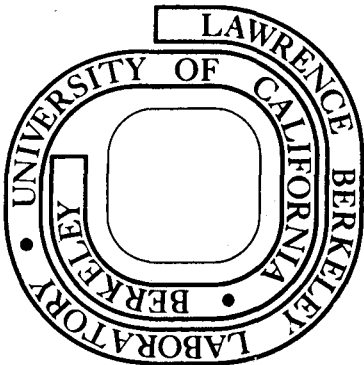
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Solid-State Electrochemical Study of  
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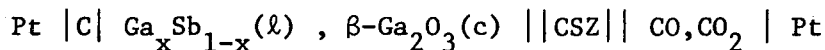
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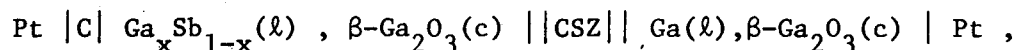
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## Abstract

Component activities in Ga-Sb liquid alloys were measured in the high temperature galvanic cells



and



with calcia-stabilized zirconia (CSZ) as the solid electrolyte and a CO + CO<sub>2</sub> gaseous mixture or a gallium-gallium sesquioxide coexistence electrode as the reference electrode. The Ga-Sb liquid alloys show a negative deviation from idealities with moderate deviations of component activities from Raoult's law. Liquidus temperatures derived from the experimental data are in excellent agreement with the experimentally measured values. Using the results of this study in conjunction with previously reported calorimetric data the degree of short range ordering in the liquid alloy was determined.

## INTRODUCTION

Gallium and antimony combine to form a single intermetallic compound, gallium antimonide (GaSb) with the sphalerite structure. This compound is of current practical interest for its semiconducting properties, especially in application to Gunn effect diodes.<sup>(1)</sup>

The thermodynamics of the gallium - antimony system at and above the melting temperature of GaSb,  $T_m$ , has received considerable attention. Much recent consideration has been given to solution models for the prediction of thermodynamic data from liquidus temperatures. Such indirect methods, however, are sensitive to errors in available liquidus data. For example, the melting point of GaSb as determined by different studies is presented in table 1. The melting point as measured by different investigators shows marked differences though the generally accepted value is 985 K.<sup>(17,18)</sup> Compiled also in table 1 is a list of the experimentally determined enthalpy of fusion of GaSb,  $\Delta H_f^C(\text{GaSb})$ , and the corresponding entropy of fusion of GaSb,  $\Delta S_f^C(\text{GaSb})$ , calculated assuming that the melting temperature is 985 K. As can be seen, the large range of  $2.0 \text{ kcal}_{th} \text{ g}\cdot\text{atom}^{-1}$  exists for the reported  $\Delta H_f^C(\text{GaSb})$ .

The Ga-Sb phase diagram has been determined by a number of investigators,<sup>(4,5,19)</sup> all in generally excellent agreement, though shifted somewhat below the accepted melting temperature.

Enthalpy of mixing data for liquid alloys have been measured by Predel and Stein<sup>(20)</sup>, Yazawa, Kawashima and Itagaki<sup>(21)</sup> and Gambino and Bros<sup>(34)</sup> who found a maximum in this quantity of -258, -204, and -260  $\text{cal}_{th} \text{ g}\cdot\text{atom}^{-1}$ ,

Table 1. Comparison of the melting temperature and the enthalpy and entropy of fusion of GaSb, as reported by different investigators, based on a melting temperature for  $\beta\text{-Ga}_2\text{O}_3$  of 985 K.\*

$T_m(\text{GaSb})$ °K	$\frac{\Delta H_f^C(\text{GaSb})}{\text{kcal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$	$\frac{\Delta S_f^C(\text{GaSb})}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}\text{K}^{-1}}$	Reference
975			2,3
979			4
982			5
985			6,7,8
993			9
998			10
	7.78 ( $\pm 0.1$ )	7.90 ( $\pm 0.11$ )	6
	7.9	8.0	11
	6.0 ( $\pm 0.5$ )	6.1	12
	7.3 ( $\pm 0.3$ )	7.4	13
	7.5 ( $\pm 0.3$ )	7.6	14
	8.0 ( $\pm 0.8$ )	8.1	15
	7.0 ( $\pm 0.3$ )	7.1	16
	7.2 ( $\pm 0.3$ )	7.3	34

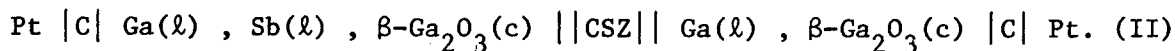
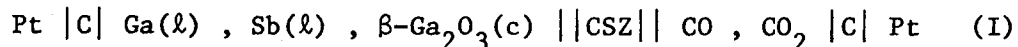
\*  $\text{cal}_{\text{th}} = 4.184 \text{ J}$

respectively, at an equimolar composition. Activities in the liquid phase have been measured with electrochemical techniques.<sup>(22-24)</sup> All of the reported results show extremely large negative deviation from ideality. Small negative deviations were found by Yazawa, Kawashima and Itagaki<sup>(21)</sup> when they applied a strictly regular solution model to their heat of mixing data, while Predel and Stein<sup>(20)</sup> calculated moderate positive deviations near the melting temperature of GaSb. On the other hand, vapor pressure studies<sup>(25,35)</sup> have shown a moderately negative derivation from ideality. Thus, the thermodynamic properties of the Ga-Sb system at and above the melting temperature of GaSb are not well defined.

In this study, gallium activities in the liquid phase of the Ga-Sb system were directly determined with a high temperature galvanic cell employing a calcia-stabilized zirconia solid electrolyte and using both a CO-CO<sub>2</sub> gaseous mixture and a gallium-gallium oxide mixture as the reference electrode.

#### THEORY

The activity of gallium in Ga-Sb liquid alloys can be measured electrochemically in high temperature galvanic cells. The cells utilized in this study can be represented schematically by



At thermodynamic equilibrium the electrochemical potential of oxygen is equilibrated by the passage of oxygen anions through the calcia-stabilized zirconia (CSZ) solid electrolyte, and a Nernst voltage is established with a magnitude given by

$$E = (RT/4F) \ln \{a(O_2; \text{ref})/a(O_2; \text{Ga-Sb})\} . \quad (1)$$

Here  $a(O_2; \text{ref})$  is the oxygen activity in the reference electrode which is a gaseous mixture in cell (I) and a metal-metal oxide coexistence electrode in cell (II).

In the gaseous reference electrode, the oxygen activity is established by the reaction,



for which the Gibbs energy of reaction can be represented by

$$\Delta G(2)/\text{cal}_{\text{th}} \text{mol}^{-1} = -68270 - 0.18(T/K) \ln (T/K) - 0.34 \times 10^{-3} (T/K)^2 + 0.87 \times 10^5 / (T/K) + 23.28(T/K) \quad (3)$$

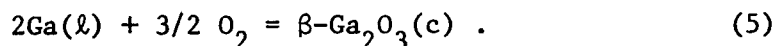
based on the experimental data of Wicks and Block.<sup>(26)</sup> The oxygen activity in the gaseous reference electrode is then given by

$$a(O_2; \text{ref}) = \left[ \frac{p(\text{CO}_2)}{p(\text{CO})} \right]^2 \exp \{2\Delta G(2)/RT\} \quad (4)$$

where the ratio of  $\text{CO}_2$  and  $\text{CO}$  partial pressures can be controlled experimentally.



In the metal-metal oxide coexistence electrode, the oxygen activity is established by the  $\beta\text{-Ga}_2\text{O}_3$  formation reaction,



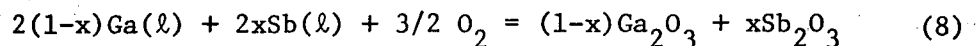
The standard Gibbs energy of formation of  $\beta\text{-Ga}_2\text{O}_3$ ,  $\Delta G(5)$ , has been previously studied by the authors,<sup>(27)</sup> and can be represented by the expression

$$\Delta G(5)/\text{cal}_{\text{th}} \text{mol}^{-1} = -265830 + 83.45(T/K) . \quad (6)$$

The oxygen activity in the gallium-gallium oxide coexistence electrode of cell (II) is then

$$a(\text{O}_2; \text{ref}) = \exp \{2\Delta G(5)/3RT\} . \quad (7)$$

In the working electrode which contains the Ga-Sb liquid alloy, the oxygen activity is established by the reaction



where it can be shown that the magnitude of  $x$  is negligible, since  $\beta\text{-Ga}_2\text{O}_3$  has a significantly larger Gibbs energy of formation than does  $\text{Sb}_2\text{O}_3$ . Thus, the Gibbs energy of reaction (8) is essentially the same as that of reaction (5).

The oxygen activity in the working electrode can now be derived for both experimental cells by utilizing the above results. For cell (I) the activity of oxygen is given by reaction (5), where the gallium activity is now a function of composition. Thus,

$$a(O_2; \text{Ga-Sb}) = [a(\text{Ga}; \text{Ga-Sb})]^{-4/3} \exp \{2\Delta G(5)/3RT\} \quad (9)$$

The gallium activity in the working electrode in cell (I) can be found by substituting equations (1) and (4) into equation (9):

$$a(\text{Ga}; \text{Ga-Sb}) = \left[ \frac{p(\text{CO}_2)}{p(\text{CO})} \right]^{-3/2} \exp \left\{ \frac{3FE}{RT} - \frac{3\Delta G(2)}{2RT} + \frac{\Delta G(5)}{2RT} \right\} \quad (10)$$

For cell (II) which contains the coexistence electrode, the gallium activity is found by substituting equations (1) and (7) into equation (9):

$$a(\text{Ga}; \text{Ga-Sb}) = \exp \left\{ - \frac{3FE}{RT} \right\} \quad (11)$$

Once the activity of gallium has been obtained experimentally, the activity of antimony can be found by graphically integrating the Gibbs-Duhem equation.

The partial molar enthalpy of Ga and Sb can be calculated from the relations

$$\Delta \bar{H}_{\text{Ga}} = -RT^2 \frac{d \ln a(\text{Ga}; \text{Ga-Sb})}{dT} \quad (12)$$

$$\Delta \bar{H}_{\text{Sb}} = - \int \frac{x_{\text{Ga}}}{x_{\text{Sb}}} d\Delta \bar{H}_{\text{Ga}} \quad (13)$$

Similarly, the partial molar entropies can be determined from

$$\Delta \bar{S}_{\text{Ga}} = \frac{d \ln a(\text{Ga}; \text{Ga-Sb})}{dT} \quad (14)$$

$$\Delta \bar{S}_{\text{Sb}} = \Delta \bar{H}_{\text{Sb}}/T - R \ln a_{\text{Sb}} \quad (15)$$

## EXPERIMENTAL

Materials

The alloy coexistence electrodes used in this study were prepared from high purity materials. Semiconductor-grade elemental gallium and antimony were obtained from Cominco American. Powdered  $\text{Ga}_2\text{O}_3$  of 99.999% purity was obtained from Alfa Products. The materials were allowed to contact only high-purity alumina during the mixing process. High purity graphite was used in the preparation of the containers for the alloy coexistence electrode. Calcia-stabilized zirconia tubes having a nominal composition of  $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$  were obtained from Zircoa Corporation of America, Solon, Ohio. The high temperature part of the experimental cell housing was constructed entirely of high purity recrystallized alumina. The electrode assembly was contained within a split tube of 99.99 tantalum which acted as a support and as an oxygen getter.

Apparatus

The basic experimental cell consisted of a 2 inch-diameter closed-end alumina tube 18 inch in length secured by a Viton O-ring to the brass cell head. This envelope contained three electrode designs as shown in figure 1. In each case the three working alloy electrodes were constructed by placing a small amount of  $\beta\text{-Ga}_2\text{O}_3(\text{c})$  upon the desired alloy within a graphite closed crucible in contact with a 0.250 inch diameter CSZ tube containing the reference electrode. The two alternate metal reference electrode designs are shown in figures 1a and 1b. The  $\text{CO}+\text{CO}_2$  gaseous reference electrode is depicted in figure 1c and consisted of a platinum paste contact between a platinum

wire and the electrolyte. Cell design 1b had the advantage of completely isolating the two electrodes. Three 1/8 inch bored-through cajon connectors (for thermocouples and lead wires) were placed on the cell head symmetrically around a 1/4 inch central cajon fitting through which the calcia-stabilized zirconia tube passed. The thermocouples used were type K (.020 inch Pt, Pt 10% Rh) which were calibrated in separate experiments within the cell against an NBS-traceable calibrated thermocouple.

In this investigation argon gas was used as the inert gas blanket. High purity, tank argon was further purified by passing it through a column of Linde 4A molecular sieve at the temperature of the dry ice-acetone equilibrium to remove the majority of water vapor present, then over hot Ti sponge at 1100 K.

The cell was heated with a Marshall resistance heated furnace (20 inches in length with a 2 1/2 inch bore). Excellent temperature control was furnished by an integrating, triac-controlled regulating power supply designed and built at Lawrence Berkeley Laboratory.

Cell emfs were measured with a Keithley 640 electrometer accompanied with an adaptor input head. A guarded cable connected the cell to the electrometer input head where connection was made to a triaxial connector.

Data acquisition was automated with an Intel 8008-based microcomputer. The system had the capability of setting the cell operation temperature and monitoring cell emfs and thermocouple outputs on a predetermined time base, thus allowing continuous cell operation. The precision of recorded data was 0.01%.

## PROCEDURE

The general experimental procedure was to assemble the desired electrode arrangement and connect it to the peripheral apparatus. The cell was then successively evacuated (approximately  $10^{-5}$  torr) and filled with argon, and the process repeated three times. The absence of leaks was checked by sealing the cell under vacuum or under an excess pressure and monitoring the cell pressure. With the use of a ramp set-point controller, the cell temperature was then raised to the highest operating temperature at a rate of  $100 \text{ K hr}^{-1}$  in order to prevent thermal shock to the electrolyte. At this point the control was switched to the Intel 8008-based microcomputer and a control program initiated. The cell emf was monitored automatically as the microcomputer reset the temperature in increments of  $\sim 20^\circ\text{C}$  over a fixed range after complete equilibrium had been reached at each temperature. At least two cycles of the temperature range of interest were completed in order to reveal any hysteresis effects in the measurement. After completion of each run the temperature was slowly lowered at  $100 \text{ K hr}^{-1}$  and the cell disassembled. The electrode material was then examined by x-ray diffraction analysis to confirm the absence of side reaction products.

## RESULTS

The activity of Ga in the liquid alloys of Ga-Sb was measured electrochemically in two solid-state galvanic cells which can be represented schematically as shown by reactions (I) and (II). At equilibrium, the electrochemical potential of oxygen is equal in

both electrodes and is related to the cell emf by equation (1).

A linear least squares analysis was applied to the measured equilibrium cell potentials and corresponding temperatures, the results of which are listed in table 2. Listed in table 3 is the activity of gallium calculated from equations (10) or (11). The activity of Sb was found by graphical integration of the Gibbs-Duhem equation. The relative partial molar enthalpy of Ga was then calculated from equation (12). Then, the relative partial molar enthalpy of Sb was obtained by graphical integration with equation (13).

The results for  $\Delta\bar{H}_{\text{Ga}}$  using the gas reference electrode exhibited a systematic concentration dependence similar to that expected while the data obtained using the metal reference electrode showed much scatter. Thus in calculating  $\Delta\bar{H}_{\text{Sb}}$  only the results with the gas reference electrode were used.

The relative partial molar entropy of Ga was then determined from equation (14), and the relative partial molar entropy of Sb calculated from equation (15). The resulting values of  $\Delta\bar{S}_{\text{Ga}}$  and  $\Delta\bar{S}_{\text{Sb}}$  are also listed in table 3 along with the integral values of the enthalpy, entropy and Gibbs energy of mixing. In the above calculations, a temperature of 1003 K was used.

Figure 2 shows the gallium and antimony activities as a function of the gallium mole fraction,  $x_{\text{Ga}}$ , obtained from this study. For comparison, the emf results of Danilin and Yatsenko,<sup>(23)</sup> obtained at 988 K, and those of Gerasimenko, et al.<sup>(24)</sup> at a temperature of 1023 K. Neither of these investigators reported an emf temperature

Table 2. Emf as a function of temperature, in the form  $E/mV = a - b(T/K)$ , of the experimental cells. Temperature range is 920 to 1100 K.

<u>Reference Electrode</u>	<u><math>x_{Ga}</math></u>	<u>a</u>	<u><math>b \times 10^3</math></u>
CO, CO <sub>2</sub>	0.0390	415.71 ± 2.41	-131.16 ± 2.36
CO, CO <sub>2</sub>	0.293	434.33 ± 0.86	- 75.57 ± 0.83
CO, CO <sub>2</sub>	0.500	440.12 ± 1.51	- 58.64 ± 1.45
CO, CO <sub>2</sub>	0.639	441.48 ± 1.26	- 48.60 ± 1.22
CO, CO <sub>2</sub>	0.833	449.74 ± 0.44	- 48.03 ± 0.41
Ga(l), β-Ga <sub>2</sub> O <sub>3</sub>	0.242	5.97 ± 2.88	+ 44.2 ± 2.9
Ga(l), β-Ga <sub>2</sub> O <sub>3</sub>	0.388	1.86 ± 0.99	+ 36.5 ± 0.9
Ga(l), β-Ga <sub>2</sub> O <sub>3</sub>	0.500	4.73 ± 0.94	+ 24.4 ± 0.9
Ga(l), β-Ga <sub>2</sub> O <sub>3</sub>	0.687	-7.71 ± 0.68	+ 22.4 ± 0.6
Ga(l), β-Ga <sub>2</sub> O <sub>3</sub>	0.896	23.28 ± 1.13	- 18.7 ± 1.1
Ga(l), β-Ga <sub>2</sub> O <sub>3</sub>	0.956	-18.22 ± 1.56	+ 21.7 ± 1.7

Table 3. Summary of thermodynamic data for Ga-Sb alloys derived from emf measurements at 1003°K ( $\text{cal}_{\text{th}}=4.184\text{J}$ )

$x_{\text{Ga}}$	$a_{\text{Ga}}$	$a_{\text{Sb}}$	$\frac{\Delta\bar{H}_{\text{Ga}}}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$	$\frac{\Delta\bar{H}_{\text{Sb}}}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$	$\frac{\Delta H^{\text{M}}}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$	$\frac{\Delta\bar{S}_{\text{Ga}}}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$	$\frac{\Delta\bar{S}_{\text{Sb}}}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$	$\frac{\Delta S^{\text{M}}}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$	$\frac{\Delta G^{\text{M}}}{\text{cal}_{\text{th}}\text{g}\cdot\text{atom}^{-1}}$
0.039	0.0124	0.955	-2788	-10	-118	5.944	0.082	.31	-429
0.293	0.164	0.613	-1499	-240	-609	2.098	.733	1.133	-1745
0.500	0.362	0.370	-1099	-490	-795	0.924	1.487	1.205	-2003
0.639	0.539	0.218	-1005	-790	-927	.226	2.239	0.953	-1883
0.833	0.732	0.075	-433	-2310	-746	.188	2.844	0.632	-1380
0.242	0.174	0.700	-413	-180	-236	3.063	.529	1.143	-1382
0.388	0.263	0.492	-135	-380	-285	2.520	1.031	1.608	-1898
0.500	0.364	0.370	-327	-490	-409	1.682	1.487	1.585	-1998
0.687	0.599	0.178	+529	-960	+63	1.546	2.473	1.836	-1779
0.896	0.856	0.045	-1606	-2990	-1750	-1.292	3.181	-.827	-921
0.956	0.884	0.018	+1280	-4470	+1027	1.521	3.527	1.609	-587



derivative. Also shown are the calculated activities of Yazawa et al.<sup>(21)</sup> determined by applying a regular solution model to their heat of mixing data at a temperature of 1003 K. Not depicted are recent results by Pong,<sup>(22)</sup> determined also with a solid oxygen-conducting electrolyte and with a  $\text{Ga}(l)\text{-Ga}_2\text{O}_3(c)$  reference electrode. Pong found that the activity versus composition curve had the same general shape as that obtained in this study but shifted somewhat to more negative values. The calorimetry study at  $x_{\text{Ga}} = 0.5$  by Predel and Stein<sup>(20)</sup> gave a value of  $-258 \text{ cal g}\cdot\text{atom}^{-1}$  for  $\Delta H^M$ . The calculated activities of Predel and Stein<sup>(20)</sup> show a positive deviation from ideality while the vapor pressure studies of Hsi-Hsiung et al.<sup>(25)</sup> agree very closely with those of this study. Also not shown are the mass spectrometer results of Bergman et al.<sup>(35)</sup> whose results agree closely with this study. The large negative deviations found in the other two emf studies whose results are shown in figure 2 might have arisen from problems in the experimental galvanic cell used. Both studies used a chloride electrolyte and assumed a value of 3 for the number of equivalents in the Nernst equation whereas gallium has known valences of both + 3 and + 1 and therefore the value of  $n$  is indeterminate. A value for  $n$  less than 3 would raise the measured activities, but the general shape of the activity curve would still differ from that found in this study.

Figure 3 shows the Gibbs energy of mixing of the elements in the Ga-Sb liquid alloys, as determined in this study. The value for the enthalpy and entropy changes upon mixing calculated from the temperature dependence of the cell voltages and listed in table 3 are not shown as they exhibited much scatter. Also shown in figure 3 is the enthalpy of mixing determined calorimetrically by Predel and

Stein<sup>(20)</sup> and Yazawa et al.<sup>(21)</sup> Combining the primary experimental results of this work (component activities) with the primary results of the calorimetric studies (enthalpies of mixing) should produce a reliable entropy of mixing. These results are also shown in figure 3 along with the entropy change for ideal mixing. This method gives a significant positive excess entropy of mixing.

The experimental data for the liquidus temperature of the Ga-Sb system as well as direct determinations from other sources can be checked for consistency with the following two expressions for the liquidus temperature derived elsewhere<sup>(28)</sup>

$$T_{\ell} = \frac{2\Delta H_f^c(\text{GaSb}) + \Delta \bar{H}_{\text{Ga}}(x) + \Delta \bar{H}_{\text{Sb}}(x)}{2\Delta S_f^c(\text{GaSb}) + R \ln \{a_{\text{Ga}}^s(T_m) a_{\text{Sb}}^s(T_m)\} + \Delta \bar{S}_{\text{Ga}}(x) + \Delta \bar{S}_{\text{Sb}}(x)} \quad (16)$$

and

$$T_{\ell} = \frac{2\Delta H_f^o(\text{GaSb}) - \Delta \bar{H}_{\text{Ga}}(x) - \Delta \bar{H}_{\text{Sb}}(x)}{2\Delta S_f^o(\text{GaSb}) - \Delta \bar{S}_{\text{Ga}}(x) - \Delta \bar{S}_{\text{Sb}}(x)} \quad (17)$$

where  $\Delta H_f^o(\text{GaSb})$  and  $\Delta S_f^o(\text{GaSb})$  are the standard enthalpy and entropy of forming solid GaSb from the pure liquid elements,  $T_{\ell}$  is the liquidus temperature,  $a_{\text{Ga}}^s(T_m)$  and  $a_{\text{Sb}}^s(T_m)$  are the activities of gallium and antimony in solid GaSb at the melting temperature and all other terms are as previously defined. All quantities in equations (16) and (17) are expressed on a g-atom basis. In the derivation of these equations GaSb(c) is considered an equimolar line compound, and the temperature dependence of the partial molar quantities and formation enthalpy and entropy is neglected. The liquidus temperature for the Sb-rich region then becomes

$$T_{\ell} = \frac{\Delta H_f^c(\text{Sb}) + \Delta \bar{H}_{\text{Sb}}(x)}{\Delta S_f^c(\text{Sb}) + \Delta \bar{S}_{\text{Sb}}(x)} \quad (18)$$

Tables 4 and 5 show the liquidus temperature calculated from either equation (16), (17) or (18) for the eleven alloy compositions studied here. In these calculations the partial molar enthalpies of Predel and Stein<sup>(20)</sup> were used while partial molar entropies were obtained from our experimental results via equations (14) and (15). The fusion data listed in table 1 was used in equation (16).

Table 4. Comparison of liquidus temperatures, (T/K) in the Ga-Sb system.

Method	$x_{\text{Ga}}$										Reference Source Data for $\Delta H_f^c(\text{GaSb})/\Delta H_f^o(\text{GaSb})$
	.293	.500	.639	.833	.242	.388	.500	.687	.896	.956	
	gas reference electrode				metal electrode						
Equation (16)	948.8	984.6	968.0	889.2	972.2	980.1	985.2	955.9	847.4	772.4	6
Equation (16)	951.9	987.3	970.9	892.8	975.1	982.9	988.0	959.0	851.3	776.7	11
Equation (16)	936.9	983.2	961.6	862.4	967.1	977.4	984.1	946.1	811.4	723.8	12
Equation (16)	948.0	986.2	968.5	884.8	973.1	981.5	987.0	955.6	840.6	762.3	13
Equation (16)	949.4	986.6	969.4	887.6	973.8	982.0	987.3	956.8	844.3	767.3	14
Equation (16)	952.5	987.5	971.3	894.1	975.5	983.1	988.1	959.5	852.9	778.9	15
Equation (16)	945.8	985.7	967.2	880.3	971.9	980.7	986.4	953.8	834.7	754.4	16
Equation (17)	970.2	1006.5	989.7	901.9	994.1	1002.0	1007.1	977.4	866.6	790.0	30
Equation (17)	974.0	1008.7	992.6	908.4	996.9	1004.4	1009.3	980.9	874.4	800.0	29
Ideal	962.3	985.0	975.1	917.4	948.1	978.7	985.0	966.7	876.2	804.6	6
Experimental	952.1	982.4	968.8	894.3	930.3	974.2	982.4	957.4	852.0	-	5

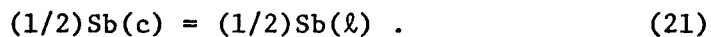
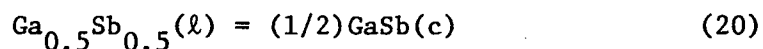
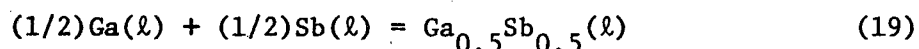
Table 5. Comparison of liquidus temperatures (T/K) of an antimony-rich Ga-Sb alloy.

$x_{\text{Ga}}$	$T_{\ell}$ , Equation (18)	$T_{\ell}$ , Ideal	$T_{\ell}$ , Experimental
0.039	888.6	890.6	890.7

The Gibbs energy of formation of GaSb has been previously measured with emf methods by two other investigators.<sup>(29,30)</sup> In order to use their results in equation (17), the enthalpy and entropy change for melting Sb had to be introduced. An enthalpy of fusion value of  $4750 \text{ cal}_{\text{th}} \text{ mol}^{-1}$  and a melting temperature of 904 K was selected from Hultgren et al.<sup>(17)</sup> Listed also in table 4 for comparison is the liquidus temperature as determined by Maglione and Potier.<sup>(5)</sup> Table 5 shows the liquidus temperature calculated for an antimony-rich Ga-Sb liquid alloy. The accepted temperature is in excellent agreement with the temperature derived from our experimental value.

Based on the results shown in table 4, several conclusions can be made. The accepted liquidus temperatures in the Ga-Sb system are very well predicted by our activity data and the enthalpy data of Predel and Stein,<sup>(20)</sup> along with accepted value for the heat of fusion. The results obtained here show that value of  $\Delta H_f^c(\text{GaSb})$  obtained by Schottky and Bever<sup>(12)</sup> is probably too low. The results of this study are consistent with other literature data, although the measured activity for the alloy  $x_{\text{Ga}} = 0.242$  appears to be a few percent high. Figure 4 shows the liquidus temperatures calculated with equation (16) and  $\Delta H_f^c(\text{GaSb})$  given by Lichter and Sommelet.<sup>(6)</sup> Also shown for comparison are the liquidus temperatures calculated using the electromotive force activity measurement of Danilin and Yatsenko<sup>(23)</sup> and of Gerasimenko et al.<sup>(24)</sup> As can be seen application of equation (16) to these two studies produces liquidus temperatures that are lower than the experimental temperature in Ga rich solutions.

When calculation of  $T_\ell$  is performed with the literature data for the GaSb formation reaction the liquidus temperatures predicted are much too high, however. Similar calculations employing equation (17) were performed with the literature electrochemical studies of Danilin and Yatsenko<sup>(23)</sup> and Gerasimenko et al.<sup>(24)</sup> These results are shown in figure 5. It can be seen that the calculated liquidus temperatures are considerably lower than the experimental temperatures. Owing to the good consistency found with equation (16), the probable cause of this error is in the values assigned in previous studies to the enthalpy and entropy of the GaSb formation reaction. A new expression for the Gibbs energy of formation of solid GaSb can be derived utilizing the results of this study. Consider the following reaction scheme:



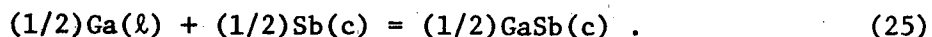
The Gibbs energy of reaction for the above reactions can be approximated by

$$\Delta G^\circ(19) = \Delta H^M - \Delta S^M(T/K) \quad (22)$$

$$\Delta G^\circ(20) = -\Delta H_f^C(\text{GaSb})\{1 - (T/K)/T_m(\text{GaSb})\} \quad (23)$$

$$\Delta G^\circ(21) = (1/2)\Delta H_f^C(\text{Sb})\{1 - (T/K)/T_m(\text{Sb})\} \quad (24)$$

The overall reaction is the formation reaction given by



The corresponding Gibbs energy of formation is

$$\Delta G_f^{\circ}(\text{GaSb}, c, T) = \Delta H_f^{\circ}(\text{GaSb}, c, T) - \Delta S_f^{\circ}(\text{GaSb}, c, T) (T/K) \quad (26)$$

where

$$\Delta H_f^{\circ}(\text{GaSb}, c, T) = \Delta H^M + (1/2)\Delta H_f^c(\text{Sb}) - \Delta H_f^c(\text{GaSb}) \quad (27)$$

and

$$\Delta S_f^{\circ}(\text{GaSb}, c, T) = \Delta S^M + (1/2)\Delta H_f^c(\text{Sb})/T_m(\text{Sb}) - \Delta H_f^c(\text{GaSb})/T_m(\text{GaSb}). \quad (28)$$

In the above equations all quantities are on a g·atom basis. Using the accepted literature values of  $\Delta H_f^c(\text{GaSb}) = 7780 \text{ cal}\cdot\text{g}\cdot\text{atom}^{-1}$ ,  $T_m(\text{GaSb}) = 985 \text{ K}$ ,  $\Delta H_f^c(\text{Sb}) = 4750 \text{ cal}\cdot\text{g}\cdot\text{atom}^{-1}$ ,  $T_m(\text{Sb}) = 904 \text{ K}$  and the  $\Delta H^M$  as given by Predel and Stein<sup>(20)</sup> along with the Gibbs energy of mixing of this work produces the following expression

$$\Delta G_f^{\circ}(\text{GaSb}, c, T) = -5660 + 3.536 (T/K) . \quad (29)$$

Figure 6 graphically depicts the liquidus temperatures calculated using equation (17) in conjunction with equation (29). Shown are the liquidus temperature calculated using our activity measurements and the molten salt galvanic cell activities of Danilin and Yatsenko<sup>(23)</sup> and Gerasimenko et al.<sup>(24)</sup> It can be seen that equation (29) produces excellent agreement between the experimental and calculated liquidus temperature when used with the results of this study while the results of Danilin and Yatsenko<sup>(23)</sup> and Gerasimenko et al.<sup>(24)</sup> shows poor agreement. This can be partially explained since the derivation of equation (29) constrains the calculated  $T_m(\text{GaSb})$  to the experimental



value. This suggests that a similar procedure be applied to the activity measurements of Danilin and Yatsenko<sup>(23)</sup> and Gerasimenko et al.<sup>(24)</sup> Performing such calculations yields liquidus temperatures in Ga rich solutions which are lower than the experimental temperatures. Furthermore, calculation of  $\Delta G_f^0(\text{GaSb}, c, 985 \text{ K})$  employing the activity data of Danilin and Yatsenko<sup>(23)</sup> and Gerasimenko et al.<sup>(24)</sup> produces the values  $-3280$  and  $-3680 \text{ cal g}\cdot\text{atom}^{-1}$ , respectively, while equation (29) gives a value of  $-2180 \text{ cal g}\cdot\text{atom}^{-1}$ . These results can be compared to the primary experimental results of Sirota et al.<sup>(29)</sup> and Abbasov et al.<sup>(30)</sup> that yield  $\Delta G_f^0(\text{GaSb}, c, 985)$  values of  $-2375$  and  $-2350 \text{ cal g}\cdot\text{atom}^{-1}$ , respectively. Thus  $\Delta G_f^0(\text{GaSb}, c, T)$  as given by equation (29) exhibits good agreement when compared to the measured electromotive force  $\Delta G_f^0(\text{GaSb}, c, T)$ , the reported liquidus temperatures and the activity measurements of this study.

A pair potential analysis was applied to these results. This analysis indicated a preference for Ga-Sb pairing which is consistent with the negative total enthalpy for the alloy. The pairing, though not extensive because of the small values of  $\Delta H^M$ , would produce a negative contribution to the excess entropy. This contribution is probably offset by a positive excess volume (as has been found for the related In-Sb<sup>(31)</sup> system and in other metallic solutions) and by possible changes in excitation of internal degrees of freedom resulting from the pairing, which contribute to the positive excess entropy observed.

In order to quantify these observations a short-range order parameter,  $\alpha$ , was calculated based on a lattice theory discussed by

Averbach. (32) This parameter is defined as

$$\alpha = 1 - P_{\text{GaSb}} / \{ZN_o x_{\text{Ga}} x_{\text{Sb}}\} \quad (30)$$

where  $P_{\text{Ga-Sb}}$  is the number of Ga-Sb pairs in the liquid solution,  $Z$  is the number of nearest neighbors,  $N_o$  is the number of lattice sites and  $x$  is the mole fraction of gallium or antimony. Through statistical methods Averbach shows that the excess entropy can be approximated by

$$S^E \approx |\alpha| kN_o [x_{\text{Ga}} \ln x_{\text{Ga}} + x_{\text{Sb}} \ln x_{\text{Sb}}] - \frac{\partial}{\partial T} [ZN_o x_{\text{Ga}} x_{\text{Sb}} (1-\alpha)g(T)] \quad (31)$$

and the enthalpy of mixing by

$$\Delta H^M = ZN_o x_{\text{Ga}} x_{\text{Sb}} (1-\alpha) [\mu + j(x)] \quad (32)$$

where  $k$  is the Boltzman constant. The quantities  $\mu + j(x)$  and  $g(T)$  are defined in terms of the quasichemical interchange energy,  $\Omega$ , and given by

$$\Omega = ZN_o [\mu + j(x) + g(T)] \quad (33)$$

thus allowing the interchange energy to have a composition and temperature dependence. The authors are aware that the quasichemical solution theory is not directly applicable here because a positive excess entropy cannot be predicted, but the theory gives some insight

into the relative amount of ordering in this system. Finally,  $\alpha$  can be expanded in terms of the mole fraction and the interchange energy, and truncated after the first terms to give

$$\alpha \approx \frac{2x_{\text{Ga}}x_{\text{Sb}}[\mu + j(x) + g(T)]}{kT} . \quad (34)$$

If the excess entropy and enthalpy are known, then equations (31), (32) and (34) can be solved simultaneously for  $\alpha$ . The temperature dependence of  $g(T)$  was assumed to be linear and given by

$$g(T) = \bar{g}T . \quad (35)$$

Figure 7 shows the calculated short-range order parameter,  $\alpha$ , as a function of the gallium mole fraction. Listed in table 6 is the calculated value of  $\alpha$ , the terms  $N_0[\mu + j(x)]$  and  $N_0[\bar{g}]$  and the reduced interaction energy,  $\Omega/ZRT$ , for the eleven compositions studied. In these calculations the heat of mixing of Predel and Stein<sup>(20)</sup> was used with the excess entropy obtained using our Gibbs energy data. A value of 6 was used for  $Z$  which is substantiated by x-ray measurements on In-Sb<sup>(33)</sup> which showed that the number of nearest neighbors was 5.7. The temperature of calculation was 1003 K.

The values of  $\alpha$  listed can be used to predict values of  $\Delta H^M$ ,  $\Delta S^E$  when used in equations (31) and (32). It is observed that the effect of a temperature dependent term  $g(t)$  is nearly twice or more that of the term  $[\mu + j(x)]$ , therefore the degree of Ga-Sb pairing is much greater than would be predicted by using the heat of mixing data alone.

Table 6. Short-range order parameter and quasichemical interchange energies. ( $\text{cal}_{\text{th}} = 4.184 \text{ J}$ )

$x_{\text{Ga}}$	$\alpha$	$\frac{N_{\text{O}} [\mu+j(x)]}{\text{cal}_{\text{th}} \text{g} \cdot \text{atom}^{-1}}$	$\frac{N_{\text{O}} [\bar{g}]}{\text{cal}_{\text{th}} \text{g} \cdot \text{atom}^{-1} \text{K}^{-1}}$	$\Omega/ZRT$
0.039	-0.0165	-149.0	-.297	-.220
0.293	-0.0985	-145.8	-.327	-.238
0.500	-0.1169	-152.8	-.313	-.234
0.639	-0.1095	-151.1	-.321	-.237
0.833	-0.0908	- 96.7	-.552	-.326
0.242	-0.0529	-156.2	-.131	-.144
0.388	-0.1062	-152.3	-.292	-.223
0.500	-0.1161	-152.9	-.309	-.232
0.687	-0.1000	-141.6	-.321	-.233
0.897	-0.0476	- 67.2	-.445	-.258
0.956	-0.0408	- 79.9	-.833	-.459

## CONCLUSION

Previous studies on the Ga-Sb system have concluded that the liquid alloys are either ideal<sup>(12,5)</sup> or regular<sup>(20,21)</sup> solutions, while Gibbs energy determinations have indicated that the solutions are highly non-ideal, showing strong negative deviations from ideality. The results of this study have shown the Ga-Sb system to deviate negatively, but moderately so, from Raoult's law with a significantly positive excess entropy of mixing. Other thermodynamic data for the Ga-Sb system were examined and found to give good consistency with the experimental results obtained in this study, with the exception that the reported values for the enthalpy and entropy of the GaSb(c) formation reaction did not conform with the other data.

## ACKNOWLEDGEMENT

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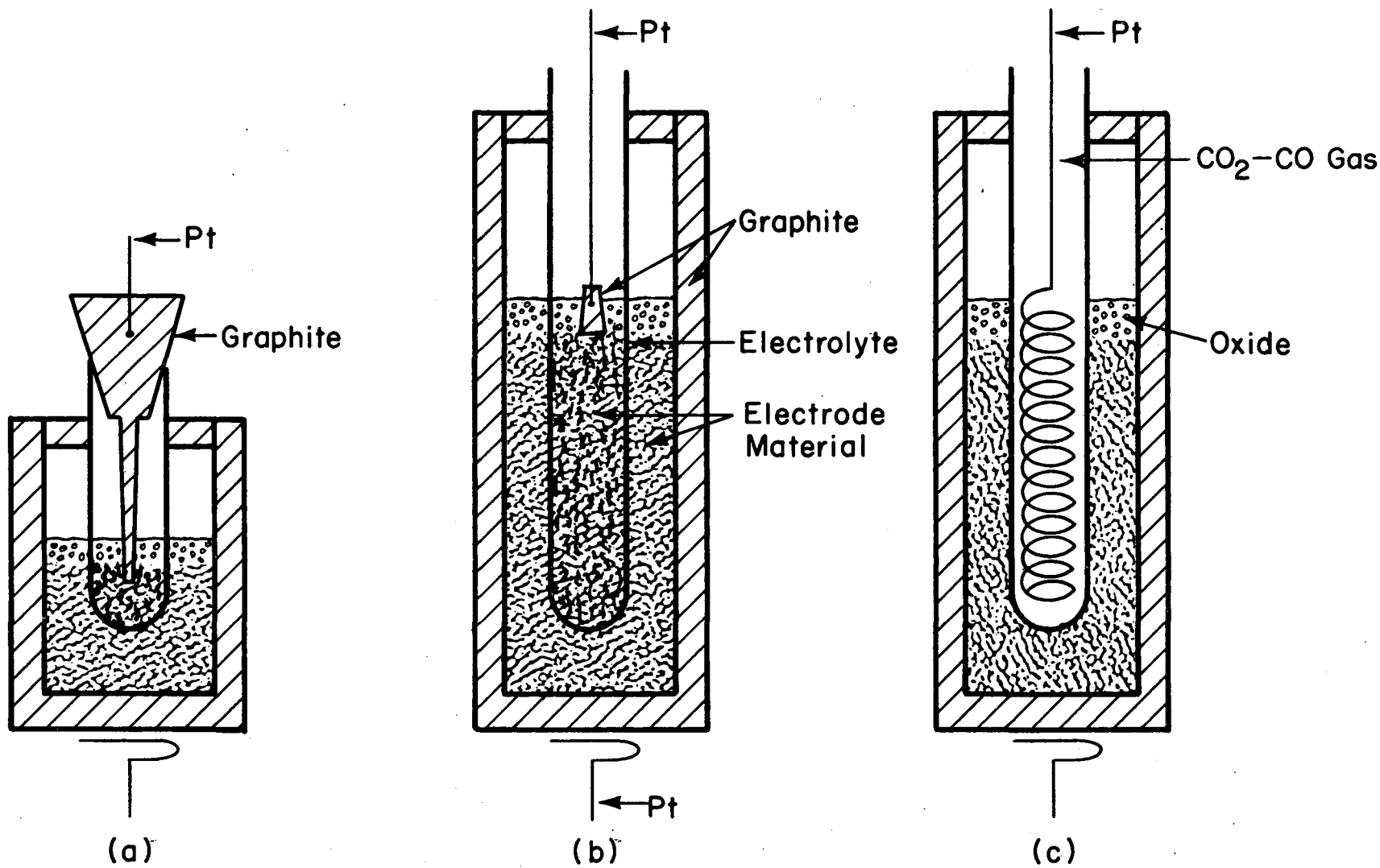
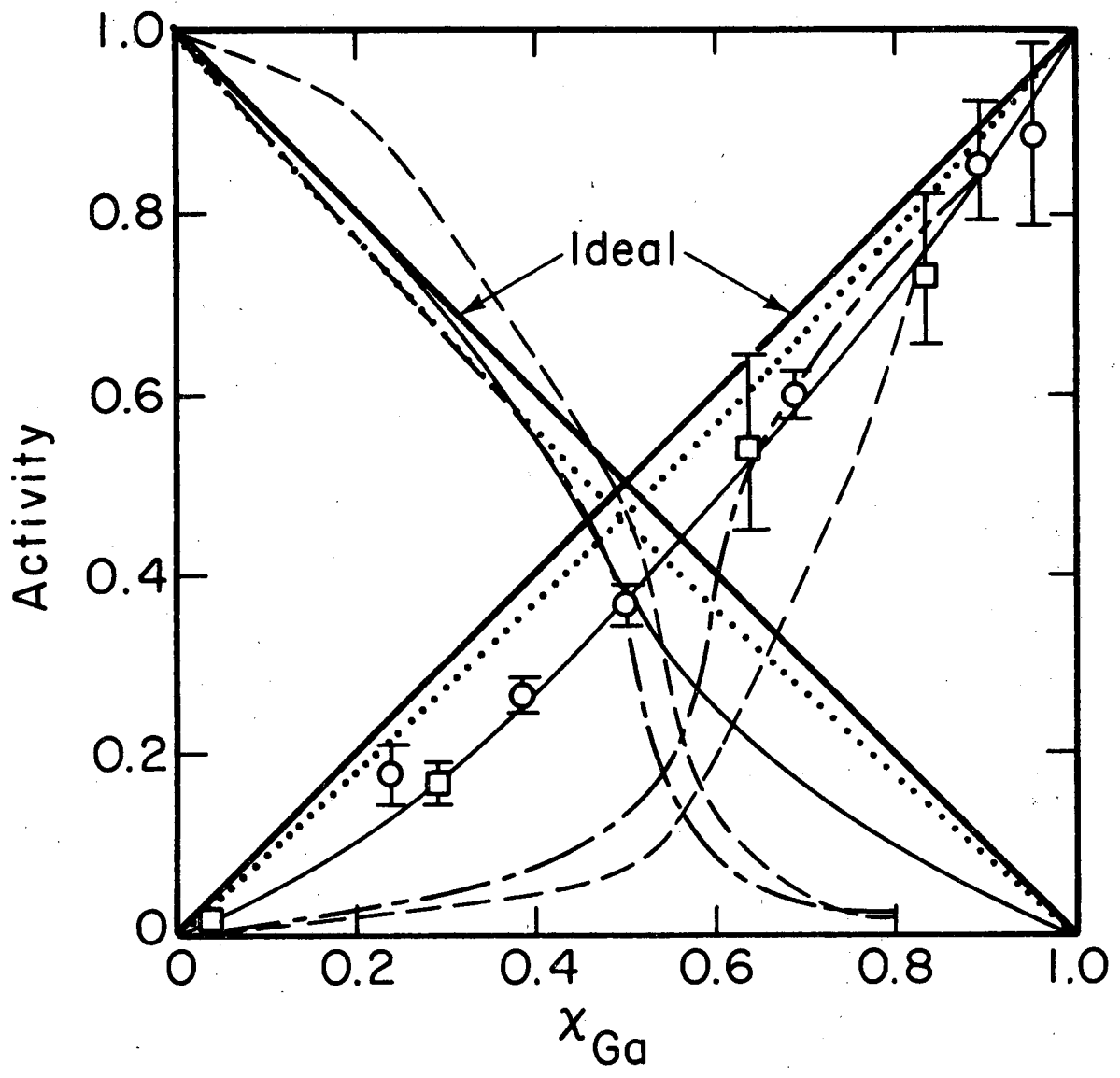


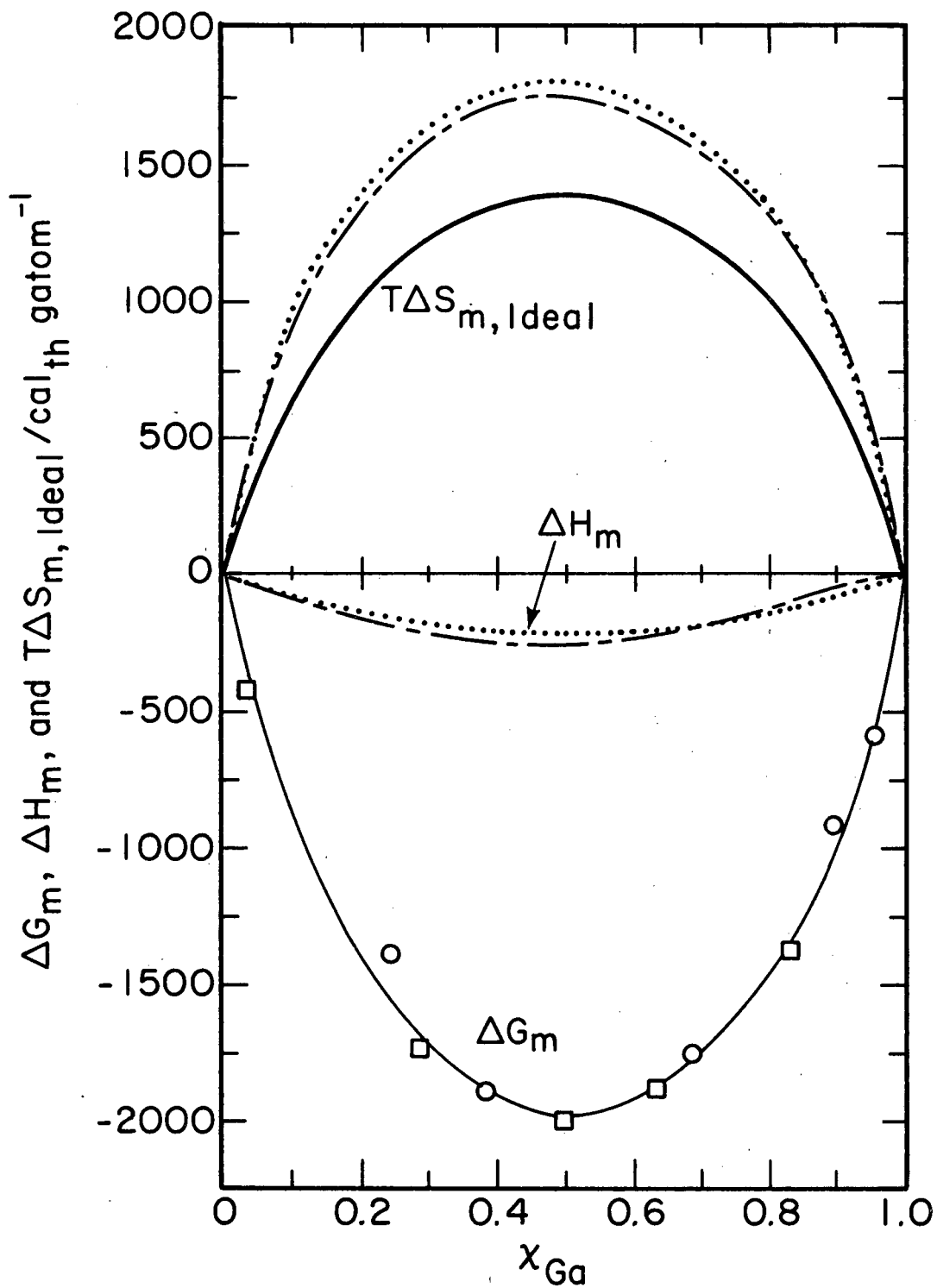
Fig. 1

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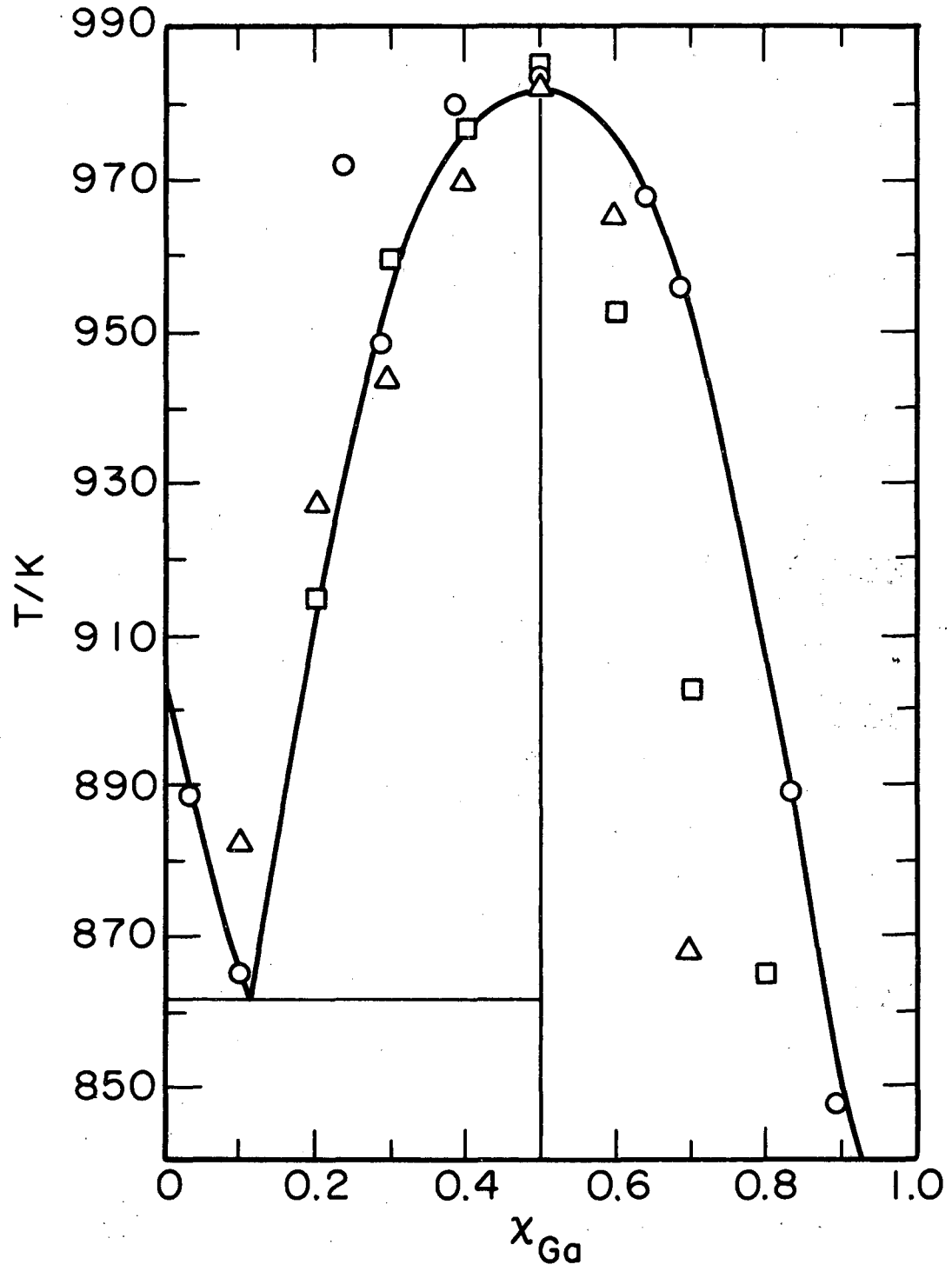
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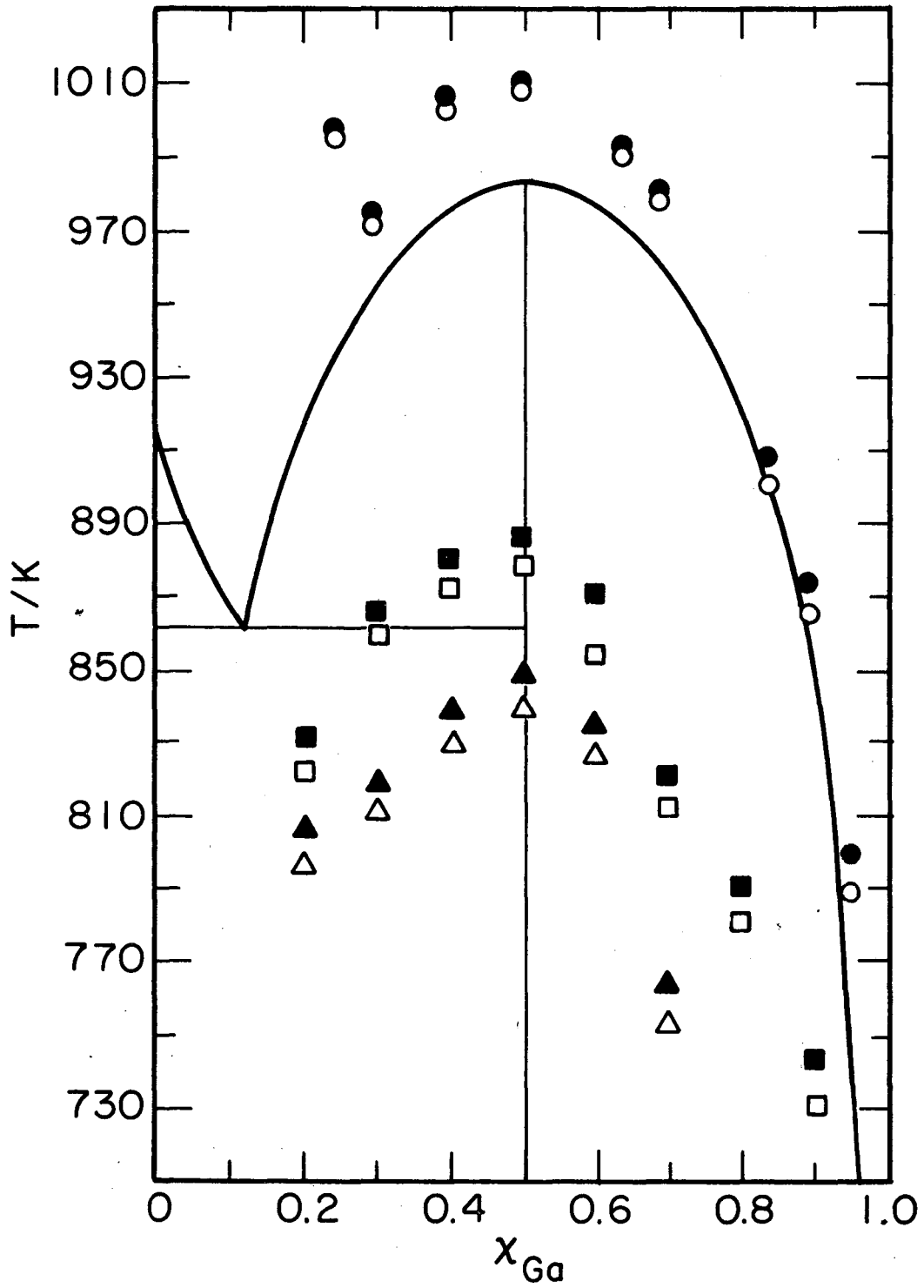
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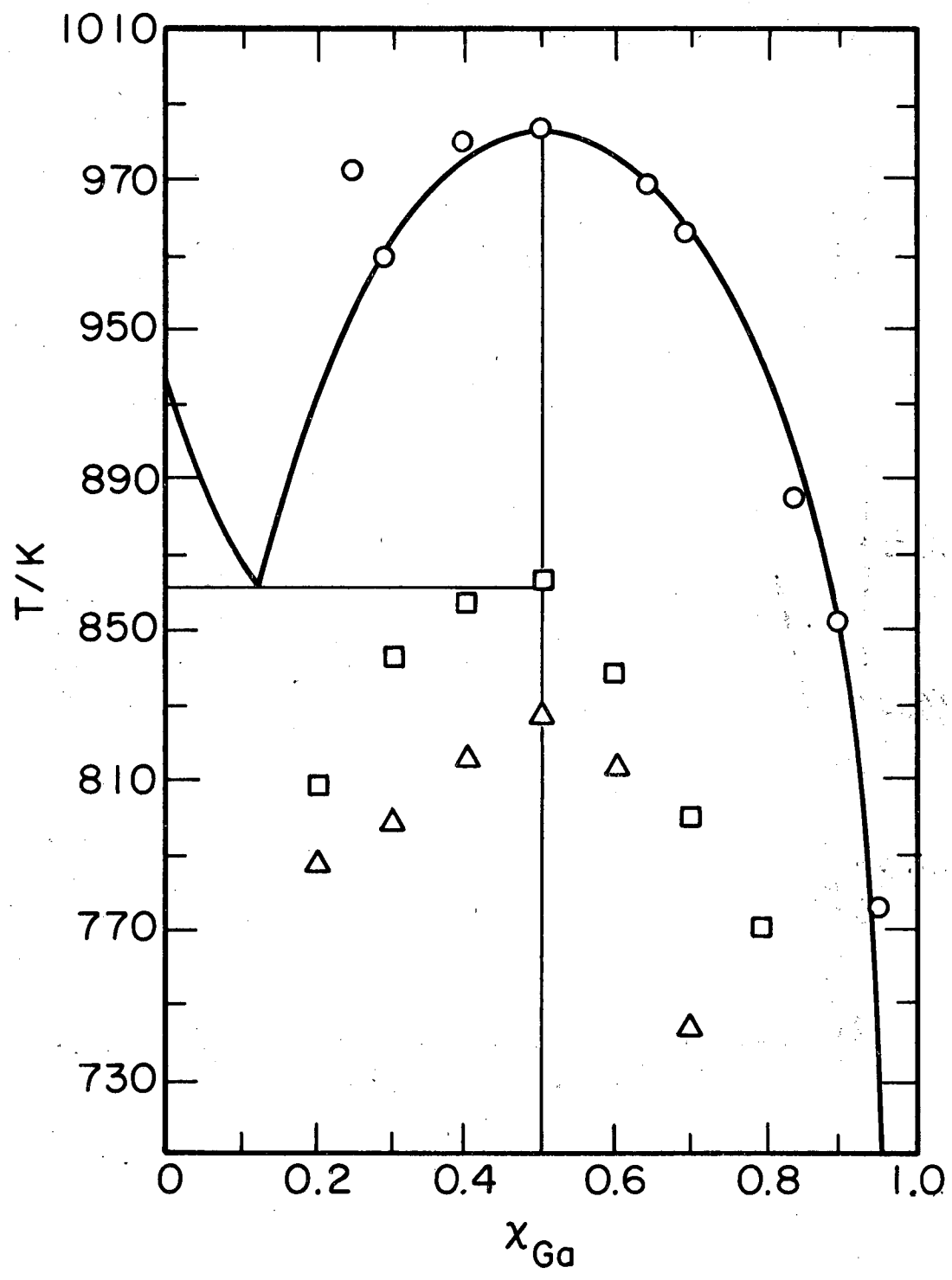
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Fig. 4



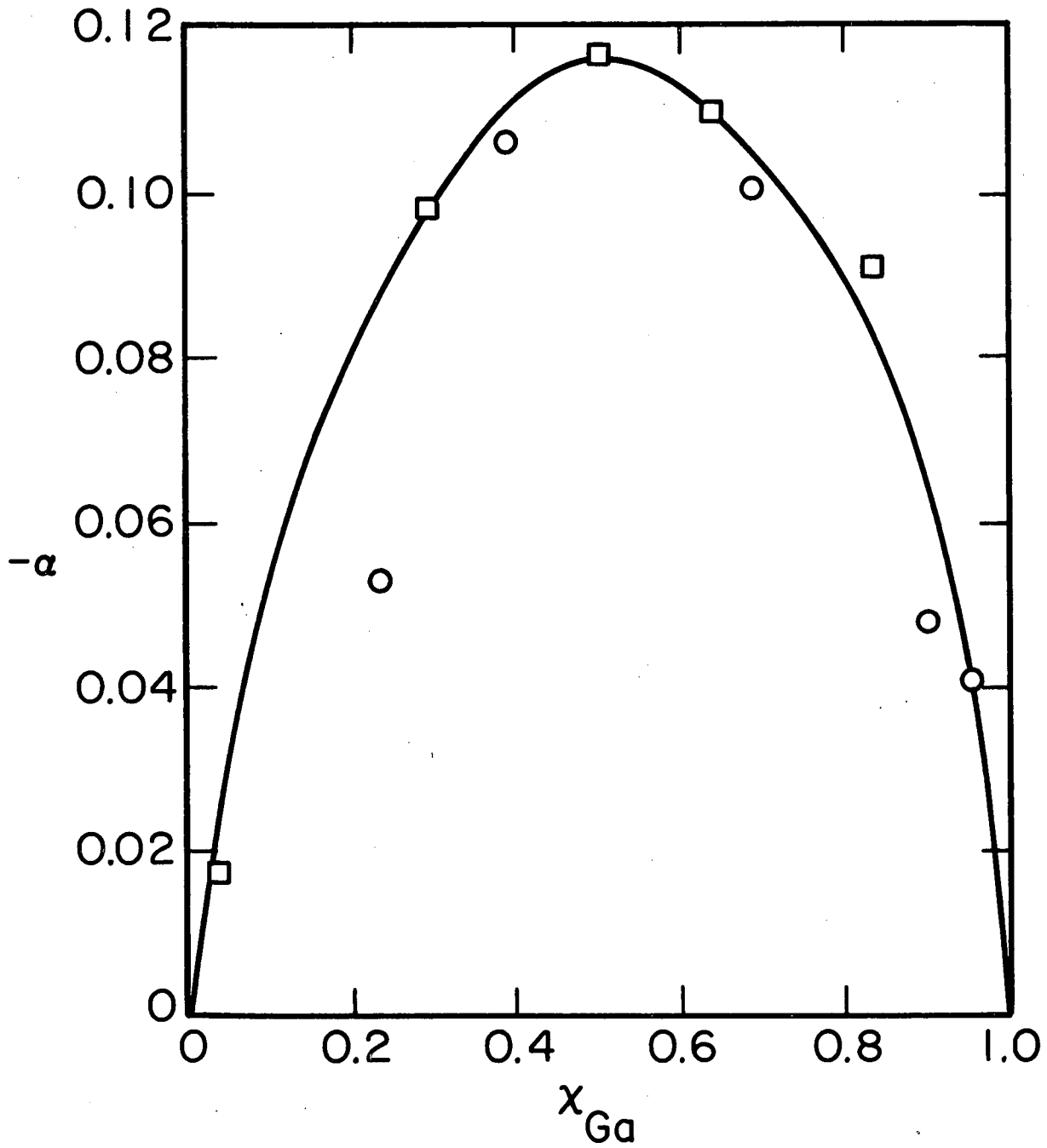
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Fig. 5



XBL 7711-10645

Fig. 6



XBL 775-8835

Fig. 7



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