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The liquid Cd–Ga–Sn: enthalpy of formation

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Abstract

Using a high temperature calorimeter, the enthalpy of formation of the liquid ternary Cd–Ga–Sn system has been determined at 740 K. The enthalpy of formation is positive over the entire concentration range and can be represented by the following modified Muggianu's relation:

$$\begin{aligned}\Delta_{\text{mix}}H_{\text{m}} = {} & \frac{4x_{\text{B}}x_{\text{C}}}{(2x_{\text{B}}+x_{\text{C}})(2x_{\text{C}}+x_{\text{A}})}\,[\Delta_{\text{mix}}H_{\text{m(BC)}}]_{x\text{B(BC)}=x\text{B}+x\text{A}/2} \\ & + \frac{4x_{\text{A}}x_{\text{C}}}{(2x_{\text{A}}+x_{\text{B}})(2x_{\text{C}}+x_{\text{B}})}\,[\Delta_{\text{mix}}H_{\text{m(AC)}}]_{x\text{A(AC)}=x\text{A}+x\text{B}/2} \\ & + \frac{4x_{\text{A}}x_{\text{B}}}{(2x_{\text{A}}+x_{\text{C}})(2x_{\text{B}}+x_{\text{C}})}\,[\Delta_{\text{mix}}H_{\text{m(AB)}}]_{x\text{A(AB)}=x\text{A}+x\text{C}/2}+x_{\text{A}}x_{\text{B}}x_{\text{C}}(ax_{\text{A}}+bx_{\text{B}}+cx_{\text{C}})\end{aligned}$$

where x_{A} and $x_{\text{A(AB)}}$ are the molar fractions of A in the ternary A–B–C and binary A–B alloys respectively, $x_{\text{A}}=x_{\text{Cd}}$, $x_{\text{B}}=x_{\text{Ga}}$, $x_{\text{C}}=x_{\text{Sn}}$, $a=-4.50(8)$ kJ mol^{-1}, $b=+11.67(9)$ kJ mol^{-1}, $c=-4.59(3)$ kJ mol^{-1} and using the binary data already published.

1. Introduction

In the course of a systematic thermodynamic investigation of alloys exhibiting a liquid miscibility gap, thermodynamic measurements have been performed on the Cd–Ga–Sn system. In the same way as for the Al–Bi–Ga system, the aim of this work is (i) to determine the localization of the miscibility gap using several techniques (calorimetry, differential thermal analysis, $C_p=f(T)$ measurements etc.) and (ii) to make a comparison between experimental and calculated equilibrium temperatures [1]. Moreover the influence of the addition of the third metal (here tin) on the miscibility gap will be studied.

According to available compilations [2, 3], the equilibrium phase diagram, enthalpy and free energy of formation of the Cd–Ga–Sn system are unknown. In the present paper the heat of mixing data will be reported and a relation will be proposed for the enthalpy of formation of the Cd–Ga–Sn liquid alloy over the entire concentration range.

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2. Bibliographic survey

For the limiting binary systems, the main information concerning the phase diagram and the enthalpy of formation are reported in the following section. These data are essential to choose the best experimental procedure and to predict ternary enthalpy data.

2.1. Cd–Ga system

2.1.1. Phase diagram

A small miscibility gap has been found. According to Heumann *et al.* [4] and Atamanova *et al.* [5], the coordinates of monotectic and critical points are $T_m = 555$ K with $x_{Ga} = 0.227$ and $T_c = 568$ K with $x_{Ga} = 0.506$ respectively. The conjugate point of the monotectic is at $x_{Ga} = 0.725$. The eutectic temperature is very close to the melting point of pure gallium ($T_e = 302.53$ K at $x_{Ga} = 0.99$). The solid solubility of cadmium in gallium is negligible; that of gallium in cadmium is less than 1 at.%. All these data were obtained by Moser and co-workers [6].

2.1.2. Enthalpy of mixing

The enthalpy of formation of liquid Cd–Ga alloys, using direct calorimetry, was determined by Kleppa [7] at 623 K for the molar fraction range $0.02 < x_{Ga} < 0.89$ and by Moser *et al.* [8] between 602 and 696 K for the molar fraction range $0.014 < x_{Cd} < 0.97$. A temperature dependence has been noticed; the mean value of ΔC_p between 609 and 695 K is about 5.7 J K^{-1} mol^{-1}. In 1981, Vecher *et al.* [9] published new results on the enthalpies of formation of Cd–Ga and Cd–Ga–In liquid alloys at 630 K. Their values of binary enthalpies, which were very similar to Kleppa's results (a difference of about 60 J mol^{-1} at $x_{Cd} = 0.5$) have been used for this study:

$$\begin{aligned}\Delta_{mix}H_{m\,(Cd+Ga)(l)} &= x_{Ga}(1 - x_{Ga})(15.0(39) - 17.4(91)x_{Ga} \\ &= 16.4(05)x_{Ga}{}^{2} - 0.02_{1}x_{Ga}{}^{3})\ \text{kJ mol}^{-1} \qquad (1)\end{aligned}$$

and the values of the limiting molar partial enthalpies are respectively

$$\Delta H_{m^{\infty}\ Ga(l)\ in\ Cd(l)} = +13.9(3)\ \text{kJ mol}^{-1}$$

$$\Delta H_{m^{\infty}\ Cd(l)\ in\ Ga(l)} = +15.0(4)\ \text{kJ mol}^{-1}$$

2.2. Cd–Sn system

2.2.1. Phase diagram

The liquidus temperatures obtained by several workers are in good agreement. The Cd–Sn phase diagram shows a eutectic point ($x_{Sn} = 0.6655$ at $T = 449$ K) and an intermediate solid phase (β) of simple hexagonal A3 structure. The coordinates of the peritectic and eutectic points found by various researchers differ significantly and are close to $T = 496$ K with $x_{Sn} = 0.99$ and $T = 406$ K with $x_{Sn} = 0.947$. The maximum solubility of tin in cadmium is $x_{Sn} = 0.0024$ at 449 K. Dutkiewicz *et al.* [10] have used $x_{Cd} = 0.0063$ at 496 K for the solubility of cadmium in tin.

2.2.2. Enthalpy of mixing

The following equation was obtained from the results compiled by Hultgren *et al.* [11] and obtained by Kleppa [12] using direct calorimetry between 623 and 723 K and by Elliott [13] at 773 K using potentiometric measurements (these two sets of data are in good agreement; calorimetric data previously published by Kawakami [14] are lower than those of Kleppa):

$$\Delta_{\text{mix}}H_{\text{m (Cd+Sn)(l)}}=x_{\text{Sn}}(1-x_{\text{Sn}})(9.8(62)-7.5(27)x_{\text{Sn}}$$
$$+4.4(35)x_{\text{Sn}^2}+0.02(4)x_{\text{Sn}^3})\ \text{kJ mol}^{-1} \qquad (2)$$

with the following limiting molar partial enthalpies:

$$\Delta H_{\text{m}^\infty\ \text{Cd(l) in Sn(l)}}=+6.7(9)\ \text{kJ mol}^{-1}$$

$$\Delta H_{\text{m}^\infty\ \text{Sn(l) in Cd(l)}}=+9.8(6)\ \text{kJ mol}^{-1}$$

By means of isoperibolic solution calorimetry, Boom [15] found $\Delta H_{\text{m}^\infty\ \text{Cd(l) in Sn(l)}}=+7.28\pm0.11\ \text{kJ mol}^{-1}$.

2.3. Ga–Sn system

2.3.1. Phase diagram

The liquidus exhibits a eutectic point near pure gallium ($T_{\text{E}}=293.6$ K at $x_{\text{Ga}}=0.915$) [16]. At the eutectic temperature, the solid solubilities are as follows: in gallium, $x_{\text{Sn}}=0.017$ [17] and, in tin, $x_{\text{Ga}}=0.071$ [16].

2.3.2. Enthalpy of mixing

Between 400 and 700 K, the heat of formation of liquid Ga–Sn alloys was measured by direct calorimetry by Predel [18] and Bros *et al.* [19]. The enthalpy of mixing, which is positive and not temperature dependent, can be represented by

$$\Delta_{\text{mix}}H_{\text{m (Ga+Sn)(l)}}=x_{\text{Sn}}(1-x_{\text{Sn}})(3.80(5)$$
$$-0.82(4)x_{\text{Sn}}+0.29(8)x_{\text{Sn}}^2-0.009x_{\text{Sn}}^3\ \text{kJ mol}^{-1} \qquad (3)$$

and the values of the limiting partial enthalpies are

$$\Delta H_{\text{m}^\infty\ \text{Ga(l) in Sn(l)}}=+3.2(8)\ \text{kJ mol}^{-1}$$

$$\Delta H_{\text{m}^\infty\ \text{Sn(l) in Ga(l)}}=+3.8(1)\ \text{kJ mol}^{-1}$$

Boom's [15] value is $\Delta H_{\text{m}^\infty\ \text{Ga(l) in Sn(l)}}=+2.82\ \text{kJ mol}^{-1}$ at 600 K.

Figure 1 shows the three limiting phase diagrams and the six sections along which the calorimetric experiments were performed.

3. Experimental procedure

High purity (99.999 at.%) metals were employed in this study. Cadmium and tin were rinsed with acetone p.a., dried and cut in small pieces. The

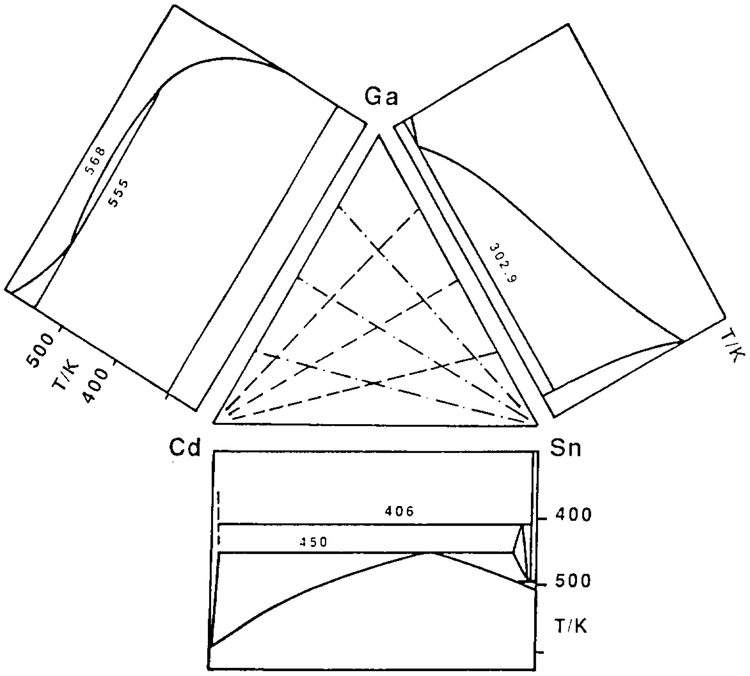

Fig. 1. The limiting binary systems and the six sections along which the calorimetric experiments were performed at 740 K.

gallium was melted in a warm (35 °C) dilute solution of hydrochloric acid (5%) in water, separated in small droplets and dried after rinsing with cold water.

A Calvet high temperature calorimeter, equipped with an automatized sample charger was employed. The experiments were carried out in high purity argon. Argon U (Air Liquid Company) was further purified by passing over a titanium sponge (1100 K) to getter the remaining oxygen. Calibration was accomplished by dropping small pieces of α-Al_2O_3 (samples from National Institute of Standards and Technology) from room temperature into the experimental crucible at the end of each measurements series.

The alloys were formed by multiple successive additions of cadmium (or tin) to the liquid Ga–Sn (or Ga–Cd) liquid bath contained in a graphite crucible of about 50 mm height and 8 mm inside diameter. This graphite crucible is located in the gas-tight silica cell. A complete description of this device has been published previously [20].

The standard deviation of the enthalpies were found to be about 20 or 40 J mol^{-1} for two independent series at the same binary molar fraction. Errors were estimated to be of the same order of magnitude (2–3%) as the difference found for the calibration drops. However, if we take into account the uncertainty in the enthalpy of formation of the limiting alloys, the final accuracy of the enthalpy of formation of Cd–Ga–Sn is about ±4%. The experimental temperature (740 ± 1 K) was determined with a Pt–(Pt–10wt.% Rh) thermocouple.

4. Results and discussion

To obtain the enthalpy of formation of the Cd–Ga–Sn liquid alloys (at T_e), two types of experiment were performed either by additions (at T_0 (room temperature)) of solid cadmium or of solid tin corresponding to

$$\mathrm{Ga}_{x'}\mathrm{Sn}_{1-x'}(\mathrm{l}, T_e) + \mathrm{Cd}(\mathrm{s}, T_0) \longrightarrow \mathrm{Cd}_x\mathrm{Ga}_y\mathrm{Sn}_z(\mathrm{l}, T_e)$$

$$\mathrm{Ga}_{x'}\mathrm{Cd}_{1-x'}(\mathrm{l}, T_e) + \mathrm{Sn}(\mathrm{s}, T_0) \longrightarrow \mathrm{Cd}_x\mathrm{Ga}_y\mathrm{Sn}_z(\mathrm{l}, T_e)$$

$T_e = 740$ K and x' and x, y, z are the binary and ternary molar fractions respectively.

$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/3$ with $0 < x_{\mathrm{Cd}} < 0.51$

$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/1$ with $0 < x_{\mathrm{Cd}} < 0.60$

$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 3/1$ with $0 < x_{\mathrm{Cd}} < 0.60$

and

$x_{\mathrm{Cd}}/x_{\mathrm{Ga}} = 1/3$ with $0 < x_{\mathrm{Sn}} < 0.62$

$x_{\mathrm{Cd}}/x_{\mathrm{Ga}} = 1/1$ with $0 < x_{\mathrm{Sn}} < 0.58$

$x_{\mathrm{Cd}}/x_{\mathrm{Ga}} = 3/1$ with $0 < x_{\mathrm{Sn}} < 0.58$

Along each quasi-binary section, at least two experiments have been performed.

The resulting integral enthalpies are collected in Tables 1 and 2. The values of the molar heat capacity and enthalpy of the melting of tin and cadmium published by Hultgren *et al.* [21] were used to transform our results to the liquid state.

Table 3 in which the enthalpies of formation at the intersection points A, ..., I are given allow us to criticize the reproducibility of these experiments. As we can see, for the same ternary alloy the discrepancy between the enthalpy obtained by dropping cadmium or tin is less than 4%.

Moreover, from the calorimetric results, the limiting molar partial enthalpies of dissolution of cadmium and tin have been deduced (Table 4). Obviously, these data obtained by interpolation of our experimental results are less precise than integral molar enthalpies (about 10%). Nevertheless we can note that the enthalpies of dissolution of tin (or cadmium) in Ga–liquid alloys with increasing molar fraction of cadmium (or tin) change very regularly (Table 4).

To predict the enthalpy of formation, we have used the geometric considerations proposed by Kohler [22] and Muggianu *et al.* [23] and a model developed by Hoch and Arpshofen [24] and Hoch [25].

The relations proposed by Kohler and Muggianu *et al.* are:

TABLE 1

Experimental values of the enthalpy of formation of the Cd–Ga–Sn liquid alloys (at 740 K) obtained by additions of cadmium to liquid binary Ga–Sn alloys ($x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/3$, 1/1 and 3/1) and referred to the liquid state

$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/3$		$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 1/1$		$x_{\mathrm{Ga}}/x_{\mathrm{Sn}} = 3/1$	
x_{Cd}	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ (J mol^{-1})	x_{Cd}	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ (J mol^{-1})	x_{Cd}	$\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ (J mol^{-1})
0.0000	629	0.0000	867	0.0000	678
0.0330	796	0.0427	1198	0.0520	1100
0.0344	813	0.0711	1332	0.0561	1233
0.0867	1098	0.0904	1450	0.1074	1561
0.0916	1125	0.0934	1557	0.1168	1678
0.1372	1347	0.1419	1701	0.1368	1746
0.1966	1621	0.1512	1746	0.1977	2040
0.2435	1774	0.2012	1874	0.2060	2184
0.2484	1742	0.2058	2081	0.2230	2174
0.2938	1864	0.2104	2008	0.2645	2337
0.3074	1963	0.2517	2151	0.2764	2395
0.3280	1938	0.2593	2198	0.3200	2560
0.3570	1999	0.2872	2283	0.3369	2595
0.3680	2094	0.2964	2428	0.3455	2597
0.3842	2062	0.3091	2315	0.3704	2730
0.4115	2128	0.3095	2421	0.3895	2705
0.4196	2101	0.3480	2530	0.4147	2743
0.4625	2176	0.3809	2485	0.4244	2775
0.5043	2182	0.3845	2537	0.4397	2805
1.0000	0	0.3882	2584	0.4817	2802
		0.4447	2546	0.5263	2778
		0.4457	2618	0.5642	2739
		0.4984	2559	0.5979	2700
		0.5032	2642	1.0000	0
		0.5438	2655		
		0.5975	2576		
		1.0000	0		

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}} = (x_{\mathrm{A}}+x_{\mathrm{B}})^2[\Delta_{\mathrm{mix}}H_{\mathrm{m(AB)}}]x_{\mathrm{A}}/x_{\mathrm{B}} + (x_{\mathrm{A}}+x_{\mathrm{C}})^2[\Delta_{\mathrm{mix}}H_{\mathrm{m(AC)}}]\frac{x_{\mathrm{A}}}{x_{\mathrm{C}}} + (x_{\mathrm{B}}+x_{\mathrm{C}})^2[\Delta_{\mathrm{mix}}H_{\mathrm{m(BC)}}]x_{\mathrm{B}}/x_{\mathrm{C}}$$

$$\begin{aligned}\Delta_{\mathrm{mix}}H_{\mathrm{m}} = {} & \frac{4x_{\mathrm{B}}x_{\mathrm{C}}}{(2x_{\mathrm{B}}+x_{\mathrm{A}})(2x_{\mathrm{C}}+x_{\mathrm{A}})}[\Delta_{\mathrm{mix}}H_{\mathrm{m(BC)}}]_{x\mathrm{B(BC)}=x\mathrm{B}+x\mathrm{A}/2} \\ & + \frac{4x_{\mathrm{A}}x_{\mathrm{C}}}{(2x_{\mathrm{A}}+x_{\mathrm{B}})(2x_{\mathrm{C}}+x_{\mathrm{B}})}[\Delta_{\mathrm{mix}}H_{\mathrm{m(AC)}}]_{x\mathrm{A(AC)}=x\mathrm{A}+x\mathrm{B}/2} \\ & + \frac{4x_{\mathrm{A}}x_{\mathrm{B}}}{(2x_{\mathrm{A}}+x_{\mathrm{C}})(2x_{\mathrm{B}}+x_{\mathrm{C}})}[\Delta_{\mathrm{mix}}H_{\mathrm{m(AB)}}]_{x\mathrm{A(AB)}=x\mathrm{A}+x\mathrm{C}/2}\end{aligned}$$

TABLE 2

Experimental values of the enthalpy of formation of the Cd–Ga–Sn liquid alloys (at 740 K) obtained by additions of tin to liquid binary Cd–Ga alloys ($x_{Cd}/x_{Ga}=1/3$, 1/1 and 3/1) and referred to the liquid state

$x_{Cd}/x_{Ga}=1/3$		$x_{Cd}/x_{Ga}=1/1$		$x_{Cd}/x_{Ga}=3/1$	
x_{Sn}	$\Delta_{mix}H_m$ (J mol^{-1})	x_{Sn}	$\Delta_{mix}H_m$ (J mol^{-1})	x_{Sn}	$\Delta_{mix}H_m$ (J mol^{-1})
0.0000	2089	0.0000	2598	0.0000	2192
0.0598	2159	0.0529	2604	0.0570	2366
0.0624	2185	0.0649	2598	0.0574	2429
0.0732	2212	0.0824	2619	0.0789	2397
0.1060	2270	0.0997	2626	0.0859	2438
0.1187	2169	0.1066	2576	0.1043	2457
0.1287	2130	0.1175	2531	0.1266	2464
0.1481	2201	0.1608	2526	0.1758	2443
0.1916	2138	0.1678	2494	0.2038	2421
0.2047	2115	0.1722	2543	0.2282	2390
0.2082	2232	0.1765	2561	0.2619	2382
0.2124	2162	0.2101	2472	0.2734	2377
0.2344	2121	0.2305	2441	0.2820	2355
0.2591	2097	0.2343	2435	0.3272	2294
0.2709	2035	0.2542	2397	0.3390	2309
0.2858	2064	0.2724	2415	0.3419	2231
0.2915	2095	0.2962	2295	0.3541	2257
0.3061	2026	0.3017	2309	0.3809	2181
0.3392	1969	0.3102	2296	0.3965	2231
0.3640	1950	0.3299	2291	0.3987	2192
0.3655	1908	0.3385	2211	0.4293	2113
0.3711	1974	0.3460	2227	0.4347	2067
0.3995	1845	0.3759	2209	0.4527	2056
0.4043	1929	0.3812	2138	0.4578	2109
0.4256	1844	0.3906	2152	0.4699	2007
0.4374	1791	0.4126	2117	0.4907	1956
0.4461	1862	0.4304	2035	0.5069	1950
0.4504	1794	0.4656	1968	0.5199	1896
0.4782	1672	0.5121	1876	0.5412	1852
0.4823	1706	0.5432	1756	0.5530	1823
0.4968	1726	0.5758	1644	0.5620	1793
0.5002	1691			0.5825	1732
0.5135	1573				
0.5248	1637				
0.5276	1626				
0.5278	1626				
0.5343	1569				
0.5592	1587				
0.5678	1507				
0.5881	1449				
0.5901	1432				
0.6199	1340				

TABLE 3

Experimental values of the enthalpy of mixing at the intersection points (A, ..., I)

Points	Sections	Coordinates	$\Delta_{\text{mix}}H_{\text{m}}$ (J mol^{-1})	Δ (%)
A	$x_{Cd}/x_{Ga}=1/3$ $x_{Ga}/x_{Sn}=1/3$	$x_{Cd}=0.0769$ $x_{Ga}=0.2308$ $x_{Sn}=0.6923$	1117 1115	0.01
B	$x_{Cd}/x_{Ga}=1/1$ $x_{Ga}/x_{Sn}=1/3$	$x_{Cd}=0.20$ $x_{Ga}=0.20$ $x_{Sn}=0.60$	1570 1596	0.8
C	$x_{Cd}/x_{Ga}=3/1$ $x_{Ga}/x_{Sn}=1/3$	$x_{Cd}=0.4286$ $x_{Ga}=0.1428$ $x_{Sn}=0.4286$	2132 2135	0.07
D	$x_{Cd}/x_{Ga}=1/3$ $x_{Ga}/x_{Sn}=1/1$	$x_{Cd}=0.1428$ $x_{Ga}=0.4286$ $x_{Sn}=0.4286$	1839 1718	0.03
E	$x_{Cd}/x_{Ga}=1/1$ $x_{Ga}/x_{Sn}=1/1$	$x_{Cd}=0.33$ $x_{Ga}=0.33$ $x_{Sn}=0.33$	2270 2432	3.4
F	$x_{Cd}/x_{Ga}=1/1$ $x_{Ga}/x_{Sn}=1/1$	$x_{Cd}=0.60$ $x_{Ga}=0.20$ $x_{Sn}=0.20$	2428 2528	2.0
G	$x_{Cd}/x_{Ga}=1/3$ $x_{Ga}/x_{Sn}=3/1$	$x_{Cd}=0.20$ $x_{Ga}=0.60$ $x_{Sn}=0.20$	2153 2148	0.12
H	$x_{Cd}/x_{Ga}=1/1$ $x_{Ga}/x_{Sn}=3/1$	$x_{Cd}=0.4286$ $x_{Ga}=0.4286$ $x_{Sn}=0.1428$	2544 2775	4.3
I	$x_{Cd}/x_{Ga}=3/1$ $x_{Ga}/x_{Sn}=3/1$	$x_{Cd}=0.6923$ $x_{Ga}=0.2308$ $x_{Sn}=0.0769$	2356 2428	3.0

TABLE 4

Limiting molar partial enthalpies of cadmium and tin in binary and ternary alloys

$\Delta H_{\text{m}\infty\text{Sn}}$ (J mol^{-1})	Alloy	$\Delta H_{\text{m}\infty\text{Cd}}$ (J mol^{-1})	Alloy
3200[a]	Ga	6600[b]	Sn
5100	Cd–Ga ($x_{Cd}/x_{Ga}=1/3$)	7900	Ga–Sn ($x_{Ga}/x_{Sn}=1/3$)
5600	Cd–Ga ($x_{Cd}/x_{Ga}=1/1$)	9700	Ga–Sn ($x_{Ga}/x_{Sn}=1/1$)
7200	Cd–Ga ($x_{Cd}/x_{Ga}=3/1$)	10800	Ga–Sn ($x_{Ga}/x_{Sn}=3/1$)
9400[b]	Cd	12900[b]	Ga

[a] From ref. 19.
[b] From ref. 11.

TABLE 5

Parameters obtained from the enthalpy data of the limiting binary systems and used in the Hoch–Arpshofen calculation

System	$n(x)$	W (kK)	W (J mol)	$\pm$ (kK)
Ga–Sn	2(Ga)	0.2097	1743.6	0.0024
Ga–Cd	2(Ga)	0.6693	5564.0	0.0000
Sn–Cd	3(Cd)	0.2031	1688.4	0.0027

The Hoch–Arpshofen model was derived originally by looking at associates in the solution and at the strength of the bond between atoms A and B which depends on the presence of the other atoms in the associate. This model was applied to binary, ternary and larger metallic systems [26, 27].

For a binary system AB, the enthalpy of mixing is represented by the following relation:

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}}=Wnx(1-x^{n-1})$$

where W is the interaction parameter, n is an integer (2, 3, 4, ...) and x is the molar fraction of the component so that the extremum of $\Delta_{\mathrm{mix}}H_{\mathrm{m}}$ is at $x>0.5$. The value of n is chosen such that W, determined from thermodynamic data, is independent of composition. From each experimental point, one value is obtained; all these can be averaged and a standard deviation obtained.

For a multicomponent system, the enthalpy of mixing is calculated from the enthalpy of binary systems using the general relation with $x=x_i$, $y=x_j$, in the multicomponent system

$$\Delta_{\mathrm{mix}}H_{\mathrm{m}}=\sum_{ij}W_{ij}n_{ij}x[1-(1-y)^{n_{ij}-1}]$$

In Table 5 are collected the values of W and of n derived from experimental binary enthalpy data given by eqns. (1)–(3). For example the notation 2 (Ga) (Ga–Cd system) indicates that, in this system, $n=2$ and x is the molar fraction of gallium to which the average value of W is equal to 0.6693 kK; the corresponding standard deviation is indicated in the column headed $\pm$.

In Figs. 2 and 3 the experimental and calculated values are reported. The discrepancies between the calculated enthalpies are small and of the same order of magnitude as the experimental error. Nevertheless the relation of Muggianu *et al.* has been retained and a correction term $x_{\mathrm{A}}x_{\mathrm{B}}x_{\mathrm{C}}$ $(ax_{\mathrm{A}}+bx_{\mathrm{B}}+cx_{\mathrm{C}})$ has been introduced. The values of the coefficients a, b and c are respectively $-4.50(8)$ kJ mol^{-1}, $+11.67(9)$ kJ mol^{-1} and $-4.59(3)$ kJ mol^{-1} with $x_{\mathrm{A}}=x_{\mathrm{Cd}}$, $x_{\mathrm{B}}=x_{\mathrm{Ga}}$, $x_{\mathrm{C}}=x_{\mathrm{Sn}}$.

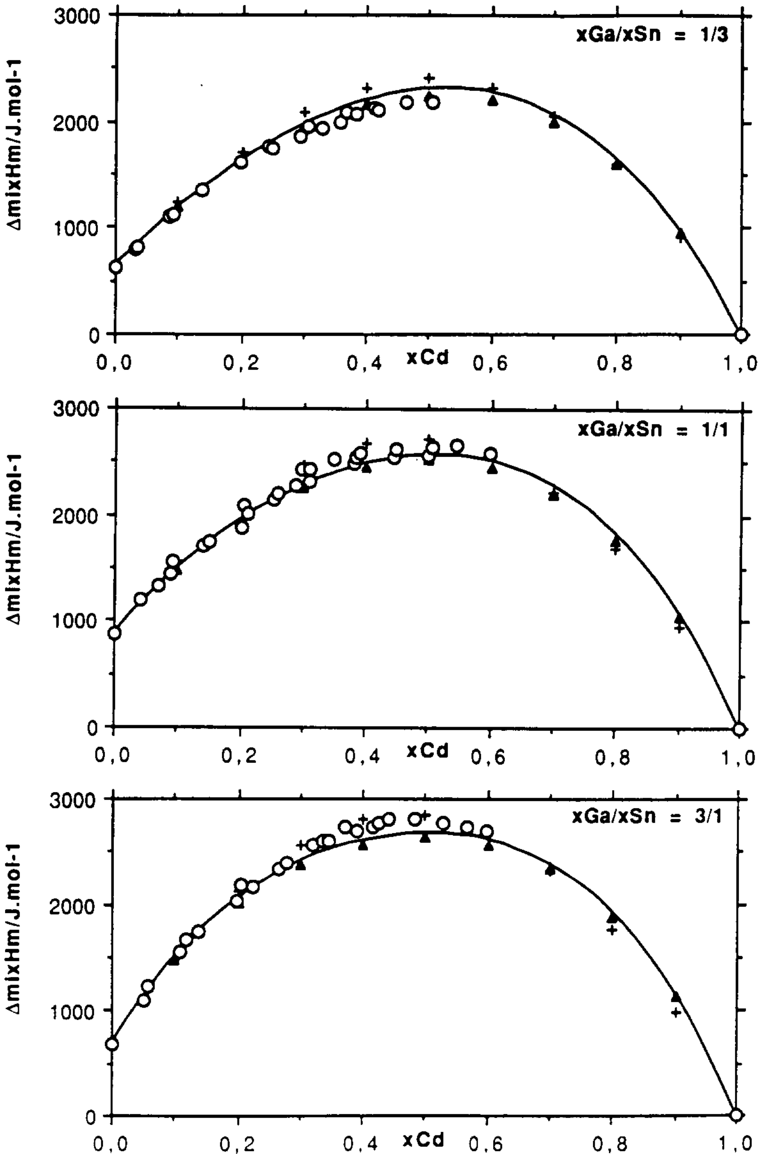

Fig. 2. Enthalpies of formation of Cd–Ga–Sn liquid alloys obtained by additions of solid cadmium to liquid Ga–Sn alloys at 740 K with $x_{Ga}/x_{Sn} = 1/3$, 1/1 and 3/1: ○, experimental results; ——, from the relation of Kohler; ▲, from the relation of Muggianu *et al.*; +, from the Hoch–Arpshofen model.

5. Conclusion

The enthalpy of formation of the Cd–Ga–Sn liquid alloy has been measured by direct high temperature calorimetry and calculated from the corresponding enthalpy of formation of Cd–Ga, Cd–Sn and Ga–Sn systems already published

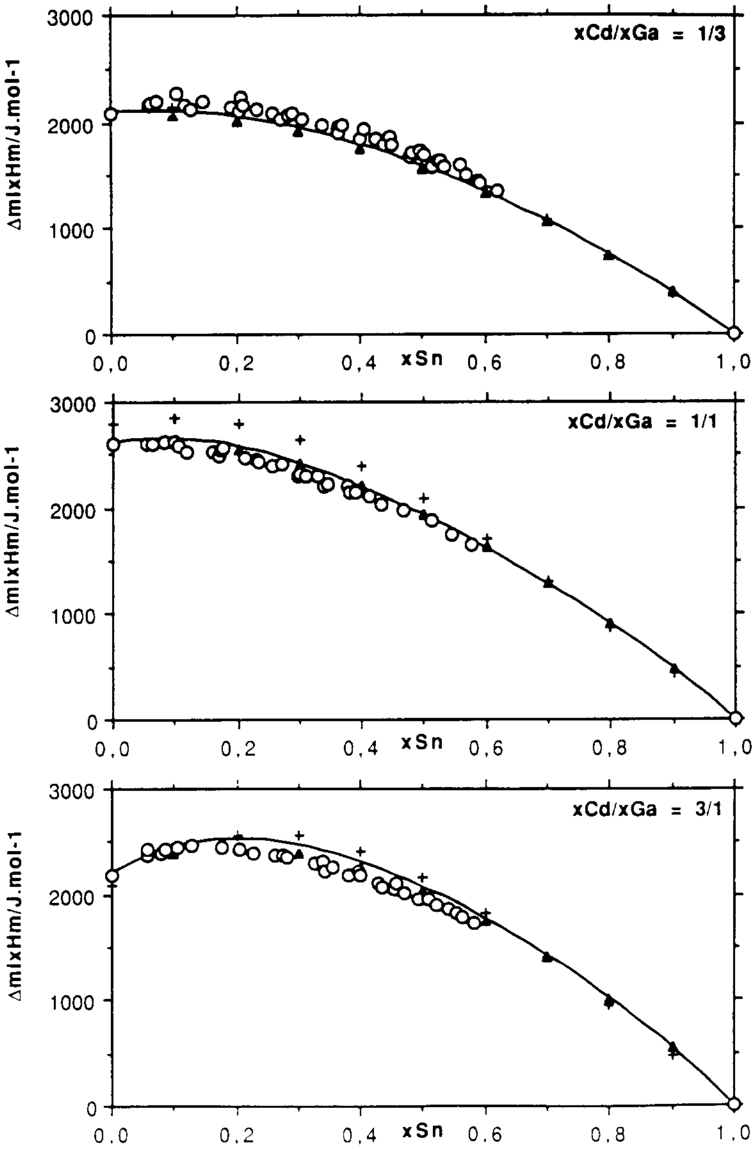

Fig. 3. Enthalpies of formation of Cd–Ga–Sn liquid alloys obtained by additions of solid tin to liquid Ga–Cd alloys at 740 K with $x_{\mathrm{Cd}}/x_{\mathrm{Ga}} = 1/3$, 1/1 and 3/1: ○, experimental results; ——, from the relation of Kohler; ▲, from the relation of Muggianu *et al.*; +, from the Hoch–Arpshofen model.

using the Hoch–Arpshofen model and two polynomial relations (due to Kohler and Muggianu *et al.*). The discrepancy between the calculated and experimental values is of the same order of magnitude as the experimental error. So, to represent the mixing enthalpy of Cd–Ga–Sn liquid alloy, over the entire molar fraction range, the relation of Muggianu *et al.* with a ternary interaction term has been retained.

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