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New experimental results and improvment of the modelization of the (Ga,Mg) system

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Abstract

Differential enthalpic analysis gave solidus and liquidus lines of the diagram. MgGa melts congruently; Mg_2Ga is a stoichiometric compound; $MgGa_2$ melts incongruently. The melting enthalpies of all the compounds were measured. A new numerical optimization of the thermodynamic properties was established using the NANCYUN program (Legendre polynomials), with all the known data. A consistent set of values in agreement with all the data (except one) is presented.

1. Introduction

The (Ga, Mg) system has been widely studied in recent years. An assessment with numerical adjustments [1] was recently published and some of us added [2] another numerical optimization. The results describing the excess Gibbs energy of the liquid phase were convergent. Since publishing these works, we have obtained new experimental data [3] and another study [4] has been published. Therefore, a recalculation was undertaken using the NANCYUN program of optimization.

2. New experimental data

2.1. *Differential enthalpic analysis (DEA)*

2.1.1. *Experimental details*

A Calvet calorimeter (Setaram, 800 °C) was used with increasing or decreasing temperatures. Pieces of magnesium and gallium were weighted and put in a silica tube which was sealed under vacuum with a small free space to avoid distillation of magnesium. Samples were heated and the reaction took place in the liquid state.

In the calorimeter, the alloy was put in an alumina crucible, around a tube of alumina with four holes. Two of these holes admitted a flow of

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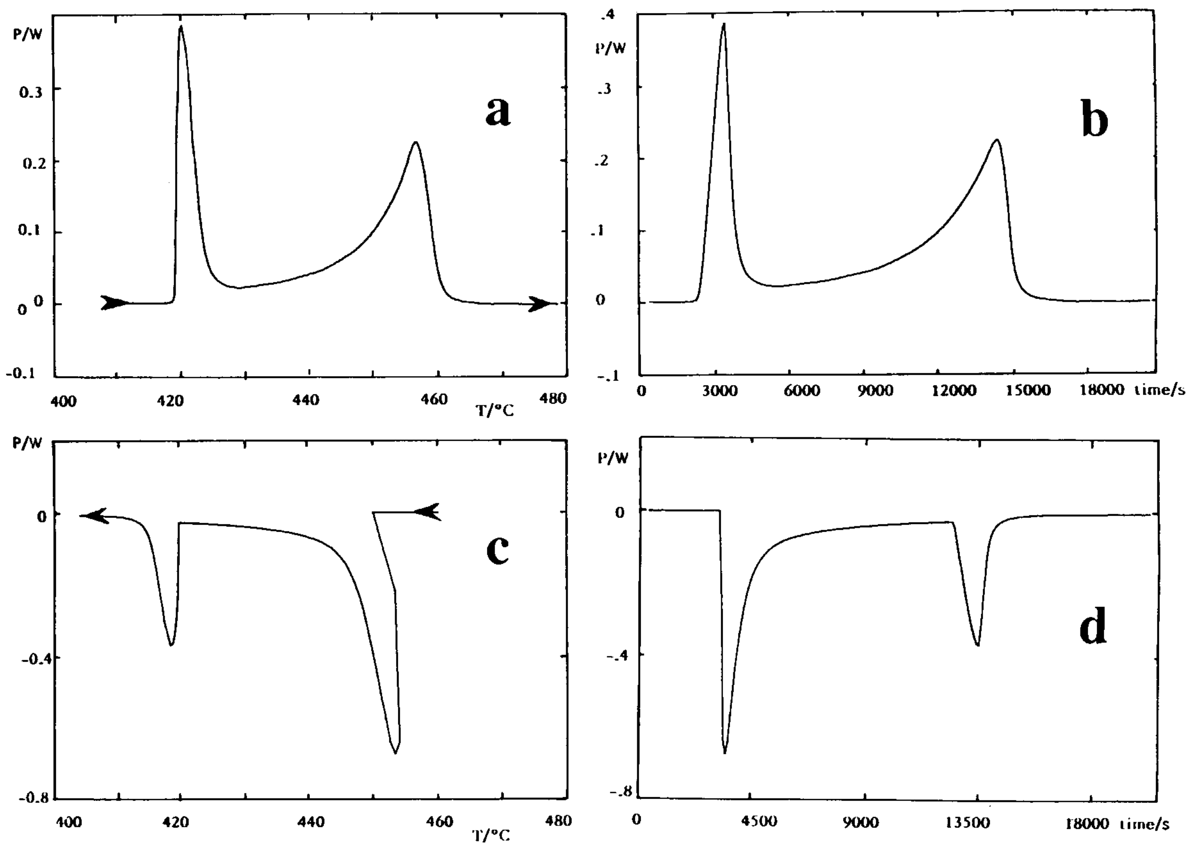

Fig. 1. Typical DEA of $Mg_{0.72}Ga_{0.28}$, rate of temperature variation 10 K h^{-1}: (a) power *vs.* temperature, increasing temperature; (b) power *vs.* time, increasing temperature; (c) power *vs.* temperature, decreasing temperature; (d) power *vs.* time, decreasing temperature.

purified argon (Air Liquid, argon "u", dioxygen partial pressure less than 0.5 Pa). This stirred the liquid alloys after melting and produced homogeneization of the bath with a better curve of solidification.

A chromel–alumel thermocouple (not protected) entered by the two other holes; it gave a temperature very close to the temperature of the bath. In ideal conditions, when increasing the temperature, an invariant point is characterized by a constant value of temperature with an increasing value of calorimeter heat flow. We therefore registered the heat flow as a function of time or as a function of the sample temperature. Figure 1 is a typical example of this method. The first graph gave us a good value of the transformation temperature; the second graph allowed us to obtain the enthalpy of the transformation.

The enthalpic calibration of the calorimeter used the Joule effect during a cycle of temperature variation referred to a blank evolution. Melting points of pure lead and aluminium permitted the temperature calibration of the thermocouple.

The accuracy of this method for determination of the temperature of an invariant step in the diagram is less than 1 K and the accuracy for the melting enthalpy between two temperatures (solidus–liquidus) is of the order of 1%.

2.1.2. *Solidus and liquidus lines*

A choice of various sample compositions allowed us to obtain all the invariant lines of the diagram. Table 1 shows the information we obtained for the solidus and liquidus temperatures. For the three alloys of composition 50, 36 and 34 at.% Ga, an invariant point appeared at 366 ± 1 °C. We tried to determine the type of melting of the MgGa compound.

2.1.3. *Melting of MgGa*

Figure 2 shows the DEA melting and solidification curves for the equiatomic composition. When the temperature is increased, the power–time curve presents a peak. The slope increases at half of the height. This is more noticeable on the power–temperature curve: the first step appears at

TABLE 1

Some experimental points of the (Ga, Mg) diagram and melting functions

x_{Ga}	Liquidus (°C)	Solidus (°C)	Melting enthalpy (J (mol at)$^{-1}$)	T_{melt} (K)	Melting entropy (J K^{-1} (mol at)$^{-1}$)
0.28	460	420	8830	734	12.0
0.32	459	445	8658		
0.34	440	366	8742	723	12.0
0.36	423	365	7923		
0.50	369	367	8046	642	12.5
0.66	310	283	8000	(≈560)	14.3
0.715	270	203	7912	(≈520)	15.2

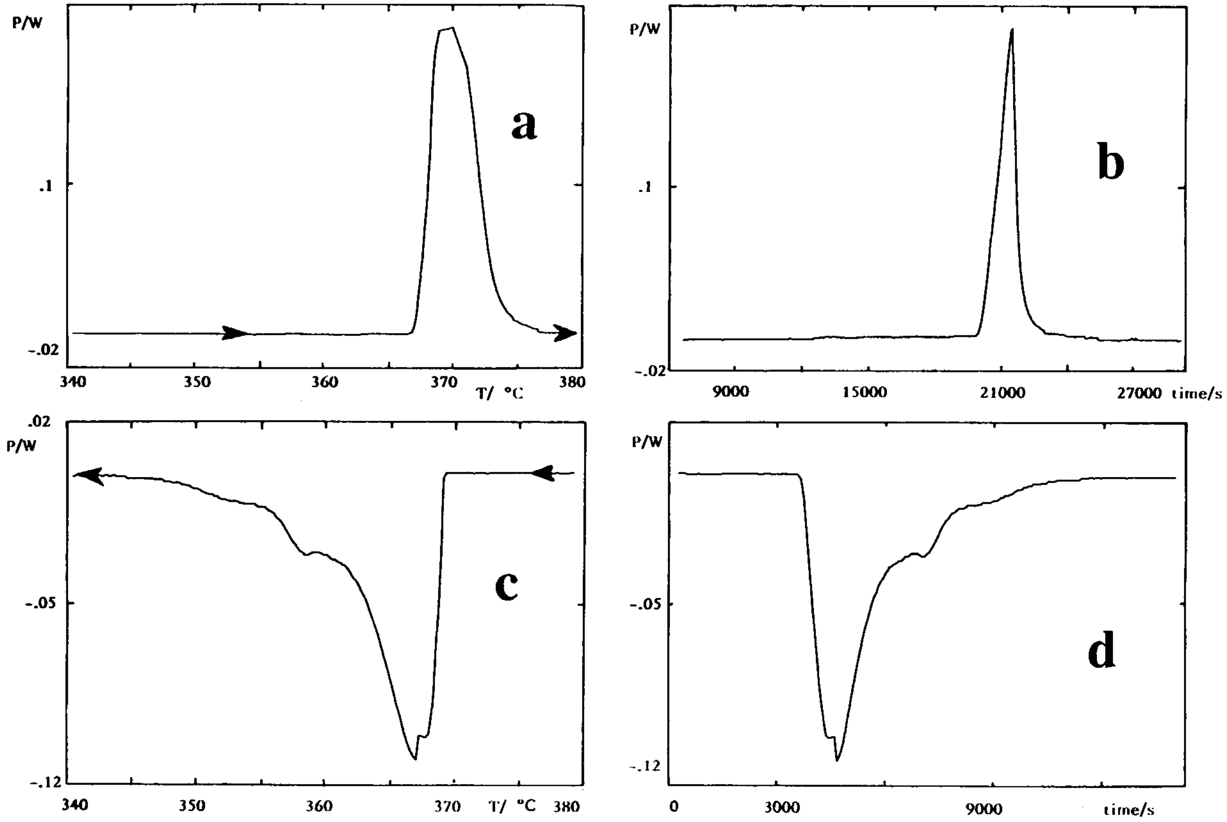

Fig. 2. DEA of the $Mg_{0.50}Ga_{0.50}$ alloy, rate of temperature variation 10 K h^{-1}: (a) power *vs.* temperature, increasing temperature; (b) power *vs.* time, increasing temperature; (c) power *vs.* temperature, decreasing temperature; (d) power *vs.* time, decreasing temperature.

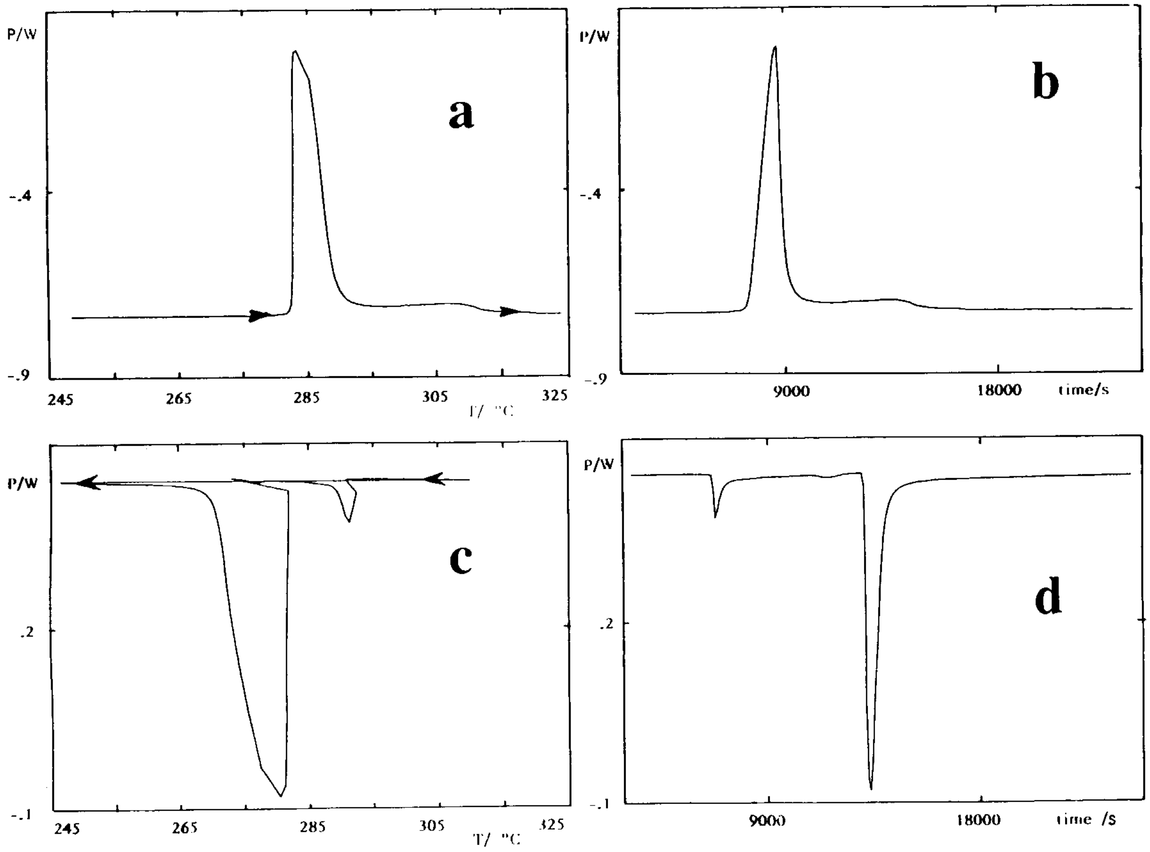

Fig. 3. DEA of the $Mg_{0.34}Ga_{0.66}$ alloy, rate of temperature variation 10 K h^{-1}: (a) power *vs.* temperature, increasing temperature; (b) power *vs.* time, increasing temperature; (c) power *vs.* temperature, decreasing temperature; (d) power *vs.* time, decreasing temperature.

367 °C, the second step at 368 °C. When the temperature is decreased, a large invariant peak appears at 369 °C and a small peak at 367 °C. The second peak corresponds to the previous plateau which ties the two Mg_2Ga and MgGa compounds. The enthalpy of the second transformation is very small in comparison with the first transformation at 369 °C. This is proof that the MgGa compound melts congruently.

This result is consistent with the recent publication of Feschotte and Yvon [4].

2.1.4. *Melting of $MgGa_2$*

Figure 3 shows the melting and solidification curves for the composition $Mg_{0.34}Ga_{0.66}$. The principal peak is situated at 283 ± 0.5 °C, the temperature also obtained by melting or by crystallization: it represents the invariant equilibrium between MgGa, $MgGa_2$ and liquid. The second transformation is very weak during heating (from 283 to 310 °C) and does not correspond to any invariant point. The same transformation appears as a peak with supercooling (below 275 °C) in a decreasing temperature experiment. This is interpreted as the progressive fusion of the MgGa phase formed. So we observe a large melting effect followed by a small enthalpic effect. We deduce from this experiment that the $MgGa_2$ compound melts incongruently.

2.1.5. *The Mg_2Ga phase*

According to the initial study by Weckerle [5], a variation in the gallium content between 31 and 37 at.% Ga appeared in the monophasic Mg_2Ga compound. No recent experimental work has confirmed this observation. Our DEA curves in the vicinity of the Mg_2Ga compound exhibit two types of behaviour on either side of the stoichiometric composition $x_{Ga} = 0.33$.

For higher gallium contents ($x_{Ga} = 0.34$ and $x_{Ga} = 0.36$), the heating curve exhibits a real invariant temperature in the vicinity of 366 °C, followed by a simple weak peak up to the liquidus temperature.

For a lower gallium content ($x_{Ga} = 0.32$), the 366 °C invariant temperature disappears whereas the DEA curve becomes very complex between 420 °C and the liquidus line with an invariant transformation situated at 445 °C. This curve can be interpreted by considering a non-equilibrium initial state with the remaining quantity of the magnesium phase mixed with Mg_2Ga and Mg_5Ga_2. However, X-ray patterns have not proved this interpretation.

Table 2 gives a comparison of the present results with the experimental compositions and temperatures for the three-phase equilibria and some two-phase equilibria given in refs. 2 and 4.

2.2. *Melting enthalpies*

The DEA curves allowed us to determine the enthalpy of melting of the five intermetallic compounds. The peak was integrated between the solidus and liquidus lines, and for the compounds which melted congruently or incongruently. These values gave the melting enthalpies if the heat capacities of the solid and liquid phases did not vary over the temperature range.

TABLE 2

Experimental compositions and temperatures of some equilibria

Equilibrium	Nayeb-Hashemi and Clark [1]		Feschotte and Yvon [4]		Present work	
	x_{Ga} (liquid)	T (K)	x_{Ga} (liquid)	T (K)	x_{Ga} (liquid)	T (K)
(Mg) + Mg_5Ga_2 + liquid	0.19	696	0.195	698		693
Mg_5Ga_2 + liquid	0.286	729	0.286	743		> 733
Mg_5Ga_2 + Mg_2Ga + liquid	0.333	714	0.34	723		718
Mg_2Ga + MgGa + liquid	0.5	646	0.46	638		639
MgGa + liquid	0.5	646	0.5	643	0.50	642
MgGa + liquid					0.66	583
MgGa + $MgGa_2$ + liquid	0.667	558	0.667	556	≈ 0.69	556
$MgGa_2$ + liquid					0.714	541
$MgGa_2$ + Mg_2Ga_5 + liquid	0.86	476	0.85	475		476
Mg_2Ga_5 + liquid + (Ga)	0.999	302.75				

Experimental values are reported in Table 1. The experimental error is less than 100 J $(\text{mol at})^{-1}$.

The melting entropies are estimated from the measured enthalpies and from the most probable temperature of fusion when the compound melts incongruently.

3. The computer calculation

3.1. The computer program NANCYUN

Knowledge of the thermochemical properties of a multicomponent system is complete when the experimental determination of the thermodynamic functions is sufficient to obtain an analytical representation which permits calculation of the phase diagram with a good degree of accuracy.

The computer program NANCYUN uses many types of thermodynamic information: partial or integral formation enthalpies, Gibbs energies and entropies of phases, melting entropies and coordinates of points of the experimental phase diagram of a binary system. Each of these data is introduced in the program as an equation relative to adjustable coefficients describing the Gibbs energy of a phase. When the set of experimental data is consistent, the computer program gives an analytical representation of the system. However, it is impossible to choose a set of weighting factors which permits the calculation of both the phase diagram and the thermodynamic functions with sufficient coherency.

3.2. Primary information

The primary information used in the study of the (Ga, Mg) system is as follows:

H^{melt} and T^{melt} of gallium and magnesium [6];

experimental phase diagram after Nayeb-Hashemi and Clark [1], Feschotte and Yvon [4] and our determinations (Mg_2Ga is supposed to be stoichiometric);

nine enthalpies and entropies of formation of the liquid phase for $x_{\text{Ga}}=0.1$ to $x_{\text{Ga}}=0.9$ obtained simultaneously from seven magnesium partial excess Gibbs energies [7] at $T=770$ K and $T=900$ K from $x_{\text{Ga}}=0.3$ to $x_{\text{Ga}}=0.9$ and from nine enthalpies of formation of the liquid after Moser *et al.* [7];

melting entropies of the five compounds [3].

All this information gives 48 equations and the six phases are represented by 22 unknown parameters:

five formation enthalpies and entropies of the intermetallic compounds

$$G^{\text{form}}=H^{\text{form}}-TS^{\text{form}}$$

twelve adjustable coefficients to represent the excess Gibbs energy of the liquid

$$G^{\text{E}}=x(1-x)\sum(a_i+b_iT)L_i(x) \text{ for } i=0 \text{ to } 4$$

where $x=x_{\text{Ga}}$ and $L_i(x)$ is the Legendre polynomial of order i which is defined by

TABLE 3

Primary information

Diagram

Equilibrium	Composition of liquid x_{Ga}	Temperature (K)	Weighting factor
α-Mg($x_{Ga}=0.035$)–liquid–Mg_5Ga_2	0.19	693	12
Mg_5Ga_2–liquid–Mg_2Ga	0.335	718	8
Mg_2Ga–liquid–MgGa	0.45	639	4
MgGa–liquid–$MgGa_2$	0.69	556	12
$MgGa_2$–liquid–Mg_2Ga_5	0.84	476	17
Mg_2Ga_5–liquid–Ga	0.999	303	1
α-Mg($x_{Ga}=0.005$)–liquid	0.06	873	5
α-Mg($x_{Ga}=0.020$)–liquid	0.15	773	5
Mg_5Ga_2–liquid	0.27	733	1
Mg_5Ga_2–liquid	0.32	732	1
Mg_2Ga_3–liquid	0.38	696	2
MgGa–liquid	0.500	642	75
MgGa–liquid	0.66	583	0
$MgGa_2$–liquid	0.715	541	0

Compounds

	Mg_5Ga_2	Mg_2Ga	MgGa	$MgGa_2$	Mg_2Ga_5
$\Delta_{melt}S$ (J K^{-1} (mol at)$^{-1}$) [3]	12.0	12.0	12.5	14.3	15.2
Weighting factor	1000	1000	2000	1000	1000

Liquid phase referred to solid states

x_{Ga}	$\Delta_{form}H$ (J (mol at)$^{-1}$)	Weighting factor	$\Delta_{form}S$ (J K^{-1} (mol at)$^{-1}$)	Weighting factor
0.1	4268	10	11.71	10000
0.2	470	10	12.96	10000
0.3	−2311	10	14.11	10000
0.4	−3951	10	15.26	10000
0.5	−4401	10	16.46	10000
0.6	−3723	15	17.68	15000
0.7	−2097	15	18.84	15000
0.8	201	15	19.71	15000
0.9	2853	15	19.89	15000

$$iL_i(x)=(2i-1)L_{i-1}(x)-(i-1)L_{i-2}(x)$$

$$L_0(x)=1,\ L_1(x)=2x-1$$

two adjustable coefficients to represent the excess Gibbs energy of the primary magnesium solution

$G^E = x(1-x)(a+bT)$

The set of equations contains four more equations which constrain the third derivative *vs.* x of the Gibbs energy to be zero in the vicinity of $x_{Ga}=0$ and $x_{Ga}=1$, in order to satisfy the experimental observations of Darken [8]. The primary information is collected in Table 3.

3.3. *Analysis of the calculation's results*

3.3.1. *Stoichiometric compounds*

In the better optimization, the computed values (Table 4) of melting entropies of Mg_5Ga_2, Mg_2Ga and Mg_2Ga_5 are close to the experimental values (less than 0.3 J K^{-1}). Those of the two other compounds present a light discrepancy: +0.8 J K^{-1} for MgGa, −0.7 J K^{-1} for $MgGa_2$.

Values of the formation enthalpies of the five compounds are similar to the calculated values presented by Moser *et al.* [7]. The excess formation entropies of the three compounds richer in magnesium are satisfactory, but the difference between computed (this work) and calculated [7] values of the two other compounds reaches 2 J K^{-1} (Table 5). The results can be summarized as follows.

For Mg_5Ga_2 there is confirmation of the congruent temperature of fusion at $T=736$ K.

Mg_2Ga presents an incongruent decomposition with a peritectic equilibrium at $T=714$ K and x_{Ga}(liquid) = 0.35.

For $MgGa_2$ the melting point is a little higher ($T=555.5$ K) than the temperature of the invariant equilibrium MgGa–liquid–$MgGa_2$ ($T=555$ K). The composition of the liquid at this temperature, $x_{Ga}=0.656$, indicates an eutectic point.

Mg_2Ga_5 presents a peritectic decomposition at $T=472$ K.

3.3.2. *The liquid phase*

The thermodynamic description of the excess Gibbs energy of the liquid phase which gives the best agreement with all the experimental data, used in the computation, is given by the polynomial expansion:

TABLE 4

Thermodynamic determination of the five compounds

Compound	$\Delta_{form}H$ (J (mol at)$^{-1}$)	$\Delta_{form}S$ (J K^{-1} mol at)$^{-1}$)	$\Delta_{melt}S$ (J K^{-1} (mol at)$^{-1}$)	T_{melt} (K)
Mg_5Ga_2	−10853	1.92	12.01	736.0
Mg_2Ga	−11377	2.73	11.70	716.5
MgGa	−13128	2.78	13.64	642.7
$MgGa_2$	−10337	4.75	13.76	555.5
Mg_2Ga_5	−9674	3.61	15.40	511.8

The thermodynamic functions are relative to one mole of atoms and referred to solid magnesium and solid gallium.

TABLE 5

Comparison between calculated results (present work) and experimental data and previous calculated results [7] of the partial mixing Gibbs energy ΔG_{Mg}

T (K)	x_{Ga}	ΔG_{Mg} (kJ (mol at)$^{-1}$)	
		Experimental [7]	Calculated (present work)
770	0.3	−5.0	−5.6
770	0.5	−14.7	−14.3
770	0.7	−26.5	−26.3
770	0.9	−41.2	−41.0
900	0.3	−5.6	−5.7
900	0.5	−14.7	−14.4
900	0.7	−26.6	−26.5
900	0.9	−42.6	−42.7

Liquid phase, referenced to liquid pure metals.

	Compound	Excess entropy of formation $\Delta_f^E S$ (J K^{-1} (mol at)$^{-1}$)	
		Calculated [7]	Calculated (present work)
1/7	Mg_5Ga_2	−3.4	−3.1
1/3	Mg_2Ga	−3.0	−2.6
1/2	MgGa	−3.0	−3.0
1/3	$MgGa_2$	−2.7	−0.6
1/7	Mg_2Ga_5	−2.9	−1.4

Solid phases, referenced to solid pure metals.

	Compound	Enthalpy of formation $\Delta_f H$ (kJ (mol at)$^{-1}$)	
		Calculated [7]	Calculated (present work)
1/7	Mg_5Ga_2	−10.9	−10.9
1/3	Mg_2Ga	−11.7	−11.4
1/2	MgGa	−13.0	−13.1
1/3	$MgGa_2$	−11.4	−10.3
1/7	Mg_2Ga_5	−9.9	−9.7

Solid phases, referenced to solid pure metals.

$$G^E = x(1-x)\Sigma(a_i + b_i T)L_i(x)$$

where the adjustable coefficients are

$a_0 = -43898$ $b_0 = 11.97$
$a_1 = 9054$ $b_1 = -7.35$
$a_2 = 4841$ $b_2 = -3.17$
$a_3 = -431$ $b_3 = 0.35$
$a_4 = -528$ $b_4 = 0.35$

The comparison between the experimental values of the partial magnesium mixing Gibbs energy taken from Moser *et al.* [7] and the calculated values of the same function at $T=770$ and 900 K (Table 5) indicated a deviation less than 1000 J (at $T=900$ K and $x_{\mathrm{Ga}}=0.8$).

Figure 4 shows the mixing Gibbs energy, the mixing enthalpy and the mixing entropy at $T=900$ K referred to gallium and magnesium in the liquid state.

3.3.3. *The α-Mg primary solid solution*

The excess Gibbs energy is given by $G^{\mathrm{E}}=x(1-x)(-24562+2.40T)$.

3.3.4. *The phase diagram*

The computed phase diagram (Fig. 5) is close to the experimental data. The experimental points are satisfied with good accuracy ($\Delta T=\pm 4$ K except at the liquidus point ($T=583$ K, $x_{\mathrm{Ga}}=0.667$)).

4. Conclusion

Many runs were executed, using the program NANCYUN, to obtain good agreement between all the available data. In no case was complete coherency

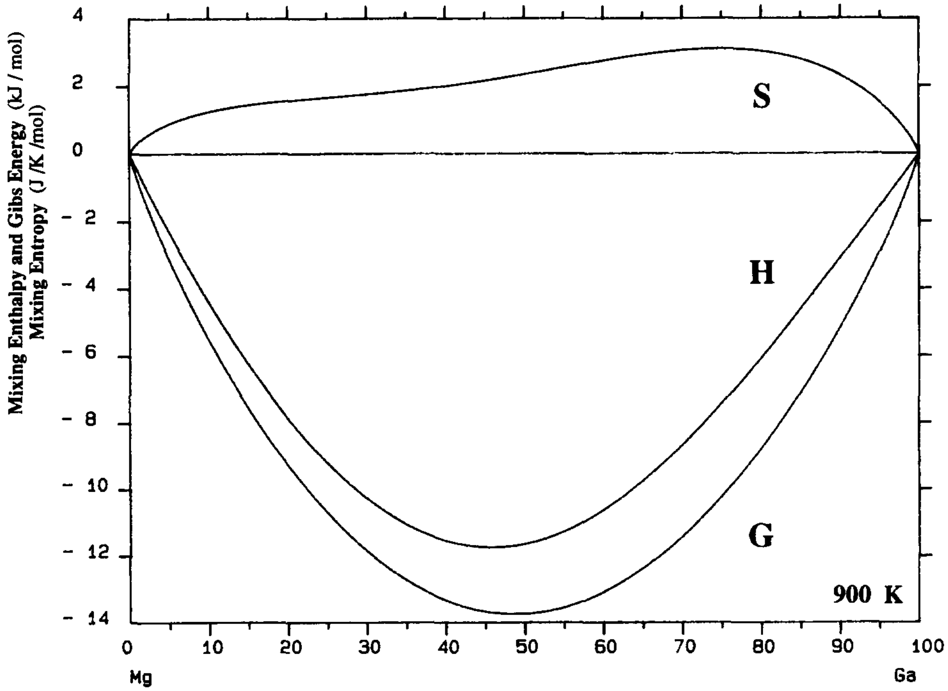

Fig. 4. Mixing functions of the liquid (Ga,Mg): Gibbs energy at $T=900$ K, enthalpy and entropy.

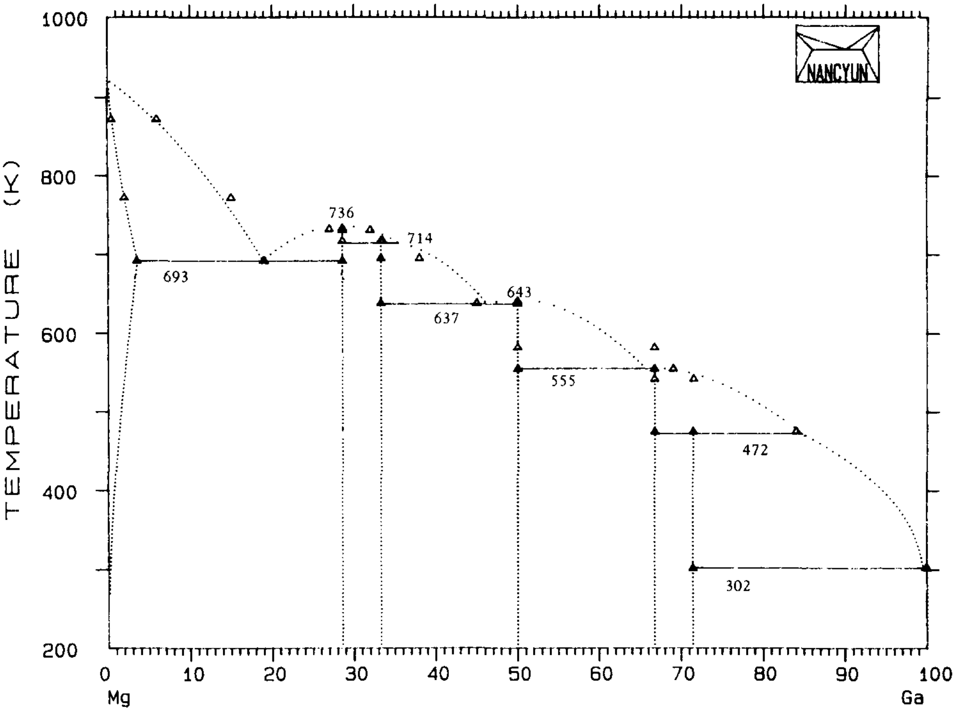

Fig. 5. Computed (Ga, Mg) phase diagram.

observed. In particular, it was impossible to obtain both a good value of the melting entropy of MgGa and a point of the liquidus satisfying the observation reported in Fig. 3, in which one can see that the liquid phase is probably in equilibrium with the MgGa compound at $x_{Ga}=0.667$ and $T=583$ K. To obtain such a peritectic situation for $MgGa_2$ it was necessary to sacrifice the good restitution of the magnesium partial Gibbs energy of the liquid.

In the computation presented here, we have not taken into account the litigious point of the liquidus, and so we obtain a convenient representation of the (Mg, Ga) system.

Reasons for the difficulty of verifying the self-consistency of all the data in this system can be found either in the experiments (error on alloy composition for instance), or in the mathematical formalism: the formation enthalpy and entropy of the phases do not vary with temperature. As the calculation results vary broadly with slight modifications in the primary data, it is possible that the second reason may be of great importance.

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