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Thermodynamic activity measurements of the liquid Cu–Gd alloy by high temperature mass spectrometry

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Abstract

The thermodynamic activity of Cu in the Cu–Gd liquid alloy has been measured by the multiple effusive cell-mass spectrometry method for $x_{Gd} = 0.276–0.844$ (atomic composition) in the 1282 K–1644 K temperature range.

The activity of Gd has been calculated from the integration of the Gibbs–Duhem equation. From the expression of the molar excess Gibbs energy of the liquid system, vs. temperature and composition, we show that the liquid alloy presents a strong negative deviation from the ideal behaviour and specify some points of the phase diagram especially on the Cu-rich liquidus curve. Our values of the Gibbs energies of formation of the intermetallic compounds CuGd and Cu_2Gd, $\Delta G_f^0(CuGd) = 42.2 \pm 2$ kJ mol^{-1} at 1073 K and $\Delta G_f^0(Cu_2Gd) = 68 \pm 4$ kJ mol^{-1} at 1113 K, are in good agreement with the literature.

Keywords: Liquid Cu–Gd alloy; Multiple effusive cell–mass spectrometry; Thermodynamics

1. Introduction

The knowledge of accurate thermodynamic properties such as vapour pressure and Gibbs energies of formation of the compounds are directly necessary to understand the electron beam evaporation (physical vapour deposition for example) behaviour of the liquid alloys. Furthermore, many thermodynamical or physical properties of the metallic alloys can be deduced through simple models from the thermodynamic activity of each component in a given phase. For instance, in the case of the liquid phase, physical data such as density [1], surface tension [2] and viscosity can be deduced from activity measurements and are obviously necessary to model the molten alloy and the evaporation efficiency.

Few thermodynamic data concerning the Cu–Gd binary alloy are available in the literature. Some of the thermodynamic properties of the Cu–Gd system have already been investigated and particularly the phase boundaries and the enthalpy of formation and Gibbs energy of some intermetallic compounds. In 1988, Subramanian and Laughlin estimated the value of the Gibbs energy of mixing of the liquid phase and the Gibbs energy of formation of the intermetallic compounds from the liquidus curves [3]. However, some experimental studies have been performed on the Cu-Gd liquid alloy, especially in order to measure the heat of formation of intermetallic compounds by solution calorimetry in liquid tin at 1100 K (Sommer et al., in 1986 [4]), the mixing enthalpy of liquid alloys at 1629 K by calorimetry (Vitusevich and Ivaňov, in 1987 [5]) and by isothermal calorimetry for temperatures ranging from 1706 K to 1855 K and a gadolinium content up to 10 at.% (Sudavtsova et al., in 1987 [6]).

Since there has been no measurement of the activities in the liquid phase, we have undertaken this high temperature investigation using a multiple Knudsen cell coupled to a quadrupole mass spectrometer.

2. Experimental method

Multiple Knudsen cell mass spectrometry is a standard method for studying chemical equilibria at high temperature [7,8]. Our apparatus has already been described by Gardie et al. in the framework of a thermodynamic study of the U–Fe and U–Ga alloys [9]. In our experimental conditions, on the one hand, the gaseous phase is in equilibrium with the condensed phase and on the other hand the vapour phase can be considered as ideal. The thermodynamic activity a_i of

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the component i in the mixture can also be defined as the ratio of the partial vapour pressure P_i^m of component i in the mixture to the vapour pressure P_i^0 of the pure element, at the same temperature. The mass spectrometer measures the ionic intensity of component i which yields the partial pressure $P_i = I_i T / S_i$. The sensitivity S_i relative to component i remains constant during the experiment. Consequently, the activity equals the ratio of the ionic current of i above the mixture and above the pure element: $a_i = P_i^m / P_i^0 = I_i^m / I_i^0$.

Natural copper and gadolinium consist in respectively two isotopes, ^{63}Cu (69.09%) and ^{65}Cu (30.91%), and seven isotopes, ^{152}Gd (0.2%), ^{154}Gd (2.15%), ^{155}Gd (14.73%), ^{156}Gd (20.47%), ^{157}Gd (15.68%), ^{158}Gd (24.87%) and ^{160}Gd (21.9%). In our measurements, the main mass peaks were used, i.e. ^{63}Cu and ^{158}Gd.

The samples were prepared from oxygen-free high conductivity copper and Johnson Matthey's gadolinium. The purities of those metals are respectively 99.99% and 99.9%. The solubility of Gd in W is 0.013 at.% W at 1313 °C [10]. The crucibles are made out of Y_2O_{3-x} for the copper and of W for the alloys.

Since the gadolinium vapour pressure is much less than that of copper (at $T = 1443$ K, $P^0_{(\mathrm{Cu})} = 0.302$ Pa and $P^0_{(\mathrm{Gd})} = 0.001$ Pa [11]), we have only measured the activity of Cu.

3. Experimental results

The heats of vaporization of pure copper and gadolinium at 298 K were calculated using the second law method [12] and the enthalpy functions given by Pankratz [13]. Our values, $\Delta H_{v,298} = 322.3 \pm 2.7$ kJ mol^{-1} for Cu and $\Delta H_{v,298} = 362.2 \pm 5.9$ kJ mol^{-1} for Gd, are lower than the mean values proposed by Hultgren et al. but are in good agreement with some data of this compilation [14]. This can be taken as an indication that reliable results can be obtained under experimental conditions that involve sufficient alignment of the vapour beam along the collimation axis of the mass spectrometer and homogeneous temperature in the crucibles, leading to satisfactory reproducibility of the measurements.

The thermodynamic activity of Cu in the Cu–Gd liquid alloy has been investigated for a gadolinium content x_{Gd} ranging from 0.276 to 0.844 (atomic composition), and for a temperature range from 1282 K to 1644 K, which corresponds to the pure liquid region (Fig. 1). No boundary of the phase diagram has been crossed and no points of this diagram could be determined directly.

For temperatures higher than the Cu melting point ($T_{\mathrm{m(Cu)}} = 1357.6$ K), the measured activities are naturally referred to liquid copper whereas, for $T < 1357.6$ K, the experimental reference is the solid cop-

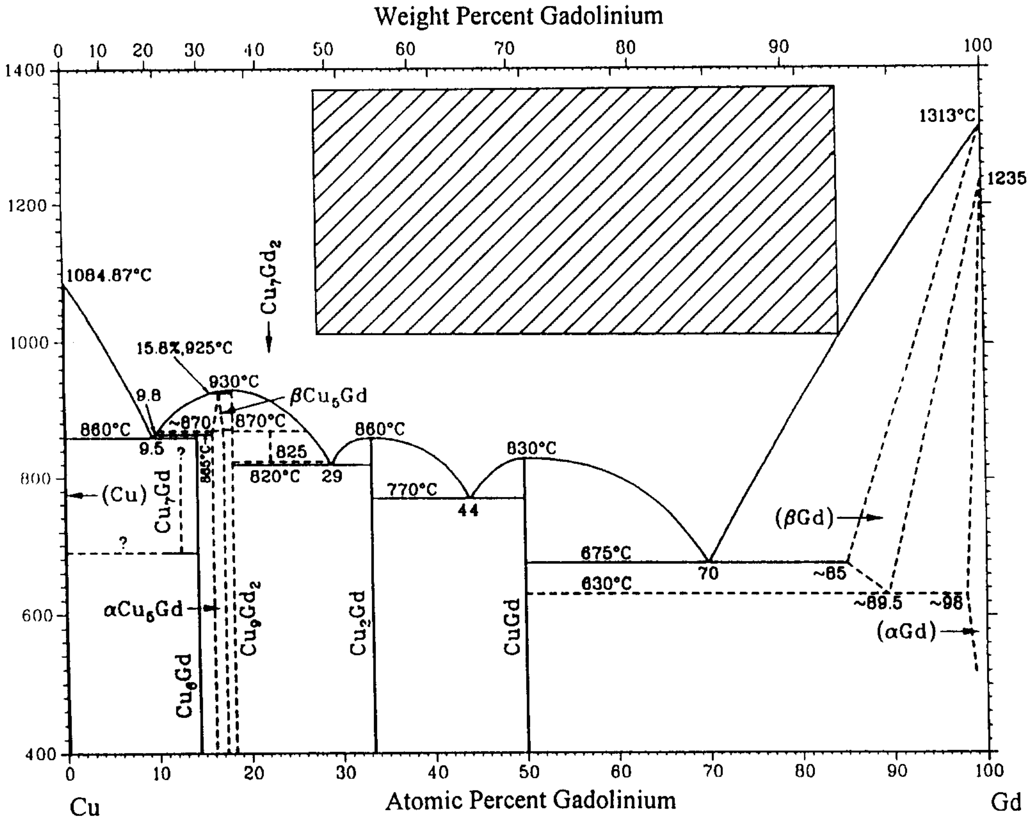

Fig. 1. Phase diagram of Cu–Gd [3]: ▨, studied region.

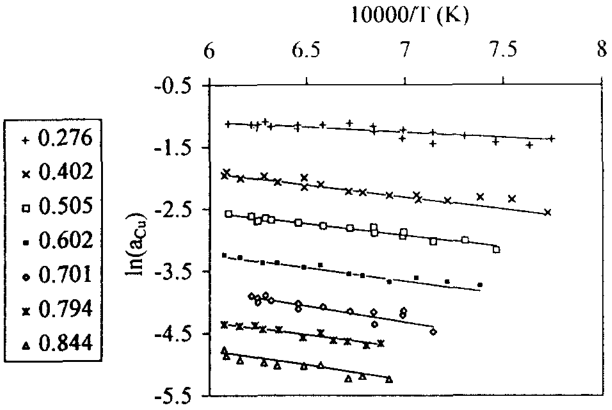

Fig. 2. Natural logarithm of the copper activity (experimental data) referred to the pure liquid copper in the Cu–Gd alloy vs. temperature.

Table 1
$\ln(a_{\mathrm{Cu}}) = f(10^4/T)$.

x_{Gd}	$\ln(a_{\mathrm{Cu}}) = A \pm \delta A + (B \pm \delta B)/T$
0.276	$-(0.086 \pm 0.032) - (1680 \pm 50)/T$
0.402	$(0.412 \pm 0.014) - (3892 \pm 22)/T$
0.505	$-(0.330 \pm 0.011) - (3707 \pm 18)/T$
0.602	$-(0.705 \pm 0.010) - (4224 \pm 160/T$
0.701	$-(0.745 \pm 0.007) - (5106 \pm 10)/T$
0.794	$-(1.822 \pm 0.004) - (4158 \pm 12)/T$
0.844	$-(1.915 \pm 0.004) - (4768 \pm 6)/T$

per. It is more convenient to refer a liquid alloy to liquid elements (for example to compare with Raoult's law: $a_i = x_i$). The way to change the reference is given in Ref. [9]:

$$\ln\frac{a^{\mathrm{s}}_{\mathrm{Cu}}}{a^{\mathrm{l}}_{\mathrm{Cu}}} = \frac{\Delta H^{0}_{\mathrm{m(Cu)}}}{RT}\,\frac{T_{\mathrm{m(Cu)}} - T}{T_{\mathrm{m(Cu)}}} \qquad (1)$$

where $\Delta H^{0}_{\mathrm{m(Cu)}}$ denotes the melting enthalpy ($\Delta H^{0}_{\mathrm{m(Cu)}} = 13.0416\ \mathrm{kJ\ mol^{-1}}$).

Experimental $\ln(a_{\mathrm{Cu}})$ data referred to pure liquid Cu are presented in Fig. 2 vs. $10^4/T$ (T in kelvins). For each composition, a linear mean square fit is expressed as $\ln(a_{\mathrm{Cu}}) = A \pm \delta A + (B \pm \delta B)/T$ (Table 1). The errors on the coefficients A and B are calculated taking into account the accuracies of the ionic intensities at a given temperature [15].

4. Analysis and discussion

4.1. Molar excess functions of liquid Cu, Gd and alloy

From these experimental results, the gadolinium activity in each alloy can then be calculated through an integration of the Gibbs-Duhem relation: $\Sigma\, x_i\ \mathrm{d}\ln a_i = 0$. To compute the gadolinium activity, we take up a Margules' polynomial development for the partial molar excess Gibbs energy.

In order to determine a general expression for the partial molar excess Gibbs energies, we use the well-known α_i function [16]:

$$\alpha_i = \frac{\Delta G_i^{\mathrm{xs}}}{(1 - x_i)^2} = \frac{RT\ln(\gamma_i)}{(1 - x_i)^2}$$

$\gamma_i = a_i/x_i$ being the activity coefficient, which we try to fit with a polynomial of the minimum degree.

In the case of Cu, it is sufficiently accurate to use a linear fit (Fig. 3):

$$\alpha_{\mathrm{Cu}} = A(T) + B(T)(1 - x_{\mathrm{Cu}}) \qquad (2)$$

The coefficients A and B that we compute that way are linear vs. temperature in a large temperature range which allows us to extrapolate at higher temperature. Then Gibbs–Duhem's equation yields

$$\alpha_{\mathrm{Gd}} = C(T) + D(T)(1 - x_{\mathrm{Gd}}) \qquad (3)$$

where

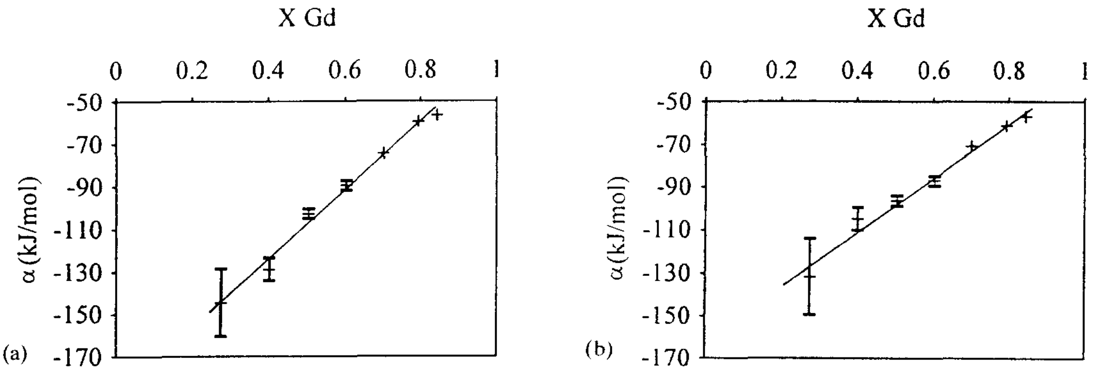

Fig. 3. $\alpha_{\mathrm{Cu}} = f(x_{\mathrm{Gd}})$: +, our measurements at (a) $T = 1500$ K and (b) $T = 2000$ K.

$$C(T) = A(T) + (3/2)B(T)$$
$$D(T) = -B(T)$$

From Eqs. (2) and (3), we can deduce the molar excess Gibbs energy of the (Cu, Gd) liquid alloy referred to the liquid elements (in joules per mole):

$$\Delta G^{\mathrm{xs}}(L) = x_{\mathrm{Cu}}x_{\mathrm{Gd}}\,[E(T) + F(T)(x_{\mathrm{Cu}} - x_{\mathrm{Gd}})] \qquad (4)$$

where

$$E(T) = A(T) + (3/4)B(T)$$
$$F(T) = -B(T)/4$$

The values of the partial molar excess Gibbs energy parameters are listed in Table 2.

Fig. 4 shows the copper activity referred to liquid Cu (experimental data and values deduced from Eq. (2)) and the activity of gadolinium referred to liquid Gd deduced from relation (3). If we compare these results with those calculated from Subramanian and Laughlin's model [3], we note that both sets of values relative to Cu are roughly in agreement with each other but larger discrepancies can be noticed in the case of Gd. This difference stems from two major grounds.

- The data in Ref. [3] are estimated (i) from two experimental liquidus data at the eutectic points (9.5 at.% Gd, 860 °C and 70 at.% Gd, 675 °C), (ii) using a simple subregular model for the liquid phase and (iii) disregarding the large solubility of Cu in solid Gd.
- Our a_{Gd} values are deduced from an integration of Gibbs–Duhem's equation in the Gd-rich region where no measurement was performed. A way to overcome this difficulty would be a direct measurement of a_{Gd}. In that case, however, the two following experimental problems must be taken into account: the gadolinium vapour pressure is much less than that of copper (cf. Section 2), and pure liquid gadolinium strongly wets the crucible (W) or reacts with the cell material (Mo). Consequently, the temperature must on the one hand exceed the threshold for measuring the Gd ionic intensity (about 1230 °C in the case of pure gadolinium) and, on the other hand, be cold enough to avoid Gd overflow in the reference cell and a quick Gd enrichment in the alloy sample.

The activity of Cu and Gd presents a strong negative deviation from Raoult's law ($a_i = x_i$) which corresponds to a strong attraction of the components in liquid phase.

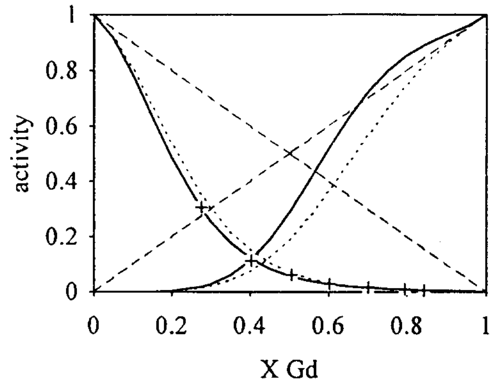

Fig. 4. +, experimental activity of Cu referred to liquid Cu; ——, Margules fit for Cu and Gd; ---, activity of Cu and Gd deduced from G(L) expression [3]; – – –, Raoult's law at $T = 1500$ K.

Using the $\Delta G_i^{\mathrm{xs}}(x, T)$ expressions, we can estimate the excess entropy $\Delta S^{\mathrm{xs}} = -(\partial\,\Delta G^{\mathrm{xs}}/\partial T)_{\mathrm{p}}$, and then the enthalpy $\Delta H^{\mathrm{xs}} = \Delta G^{\mathrm{xs}} + T\,\Delta S^{\mathrm{xs}}$ (ΔH in joules per mole, ΔS in joules per mole per kelvin) referred to the liquid state

$$\Delta S^{\mathrm{xs}}_{\mathrm{Cu}} = -54.132x^2_{\mathrm{Gd}} + 68.94x^3_{\mathrm{Gd}}$$
$$\Delta S^{\mathrm{xs}}_{\mathrm{Gd}} = 49.278(1 - x_{\mathrm{Gd}})^2 - 68.94(1 - x_{\mathrm{Gd}})^3$$
$$\Delta S^{\mathrm{xs}}(\mathrm{L}) = x_{\mathrm{Gd}}(1 - x_{\mathrm{Gd}})[-54.132 + 34.47(1 + x_{\mathrm{Gd}})]$$

(L denotes "liquid"),

$$\Delta H^{\mathrm{xs}}_{\mathrm{Cu}} = -269\,915x^2_{\mathrm{Gd}} + 264\,596x^3_{\mathrm{Gd}}$$
$$\Delta H^{\mathrm{xs}}_{\mathrm{Gd}} = 126\,979(1 - x_{\mathrm{Gd}})^2 - 264\,596(1 - x_{\mathrm{Gd}})^3$$
$$\Delta H^{\mathrm{xs}}(\mathrm{L}) = x_{\mathrm{Gd}}(1 - x_{\mathrm{Gd}})[-269\,915 + 132\,298(1 + x_{\mathrm{Gd}})] \qquad (5)$$

4.2. Chemical short-range order

If we plot $\Delta H^{\mathrm{xs}}(\mathrm{L})$ vs. x_{Gd} (Fig. 5) we notice that there is a minimum in $\Delta H^{\mathrm{xs}}(\mathrm{L})$ at a value of $x_{\mathrm{Gd}} = 0.340$ which corresponds to the composition of the intermetallic compound $\mathrm{Cu_2Gd}$. Sommer et al.'s and Vitusevich and Ivanov's results respectively exhibit a minimum at $x_{\mathrm{Gd}} = 0.33$ [4] and at $x_{\mathrm{Gd}} = 0.40$ [5] (this value is calculated from the expression of the enthalpy of mixing). Following Sommer et al. [4], "the concentration dependences for the enthalpy of mixing of the liquid alloys $\Delta H(x_{\mathrm{Gd}})$ indicate the existence of a chemical short-range order (CSRO) in the liquid state with a maximum at ~33% at. Gd which can be

Table 2
Partial molar excess Gibbs energy parameters (in joules per mole) of the (Cu, Gd) alloy referred to liquid elements

$A(T) = -269\,915 + 54.132T$	$C(T) = 126\,979 - 49.278T$	$E(T) = -71\,468 + 2.427T$
$B(T) = 264\,596 - 68.94T$	$D(T) = -264\,596 + 68.94T$	$F(T) = -66\,149 + 17.235T$

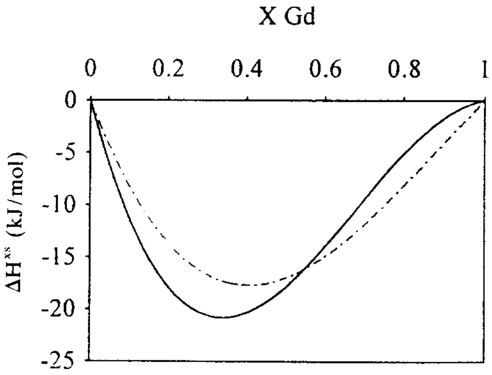

Fig. 5. Excess enthalpy in liquid alloy at $T = 1629$ K: ——, our values; - - -, from Vitusevich and Ivanov [5].

described in terms of thermodynamic models for $\Delta H(x, T)$ as a formation of associates with a stoichiometry of A_2B" [17,18]. For Vitusevich et al. [5], the minimal value of the enthalpy of mixing of the liquid alloy correlates with the existence of many intermetallic compounds and especially in the copper-rich range. In our mind, CSRO takes place in the liquid copper-rich region and more particularly in the concentration range between CuGd and Cu_9Gd_2. The minimum of ΔH^{xs} indicates that this CSRO is located near the composition of Cu_2Gd.

A way to study this CSRO more precisely is to use the association model in order to describe the concentration dependence of the excess enthalpy ΔH^{xs} of the liquid alloy taking into account two association equilibria: CuGd and Cu_2Gd, or Cu_2Gd and Cu_9Gd_2 [17,18]. In both cases, it seems unreasonable to fit with the five parameters C^{reg}, ΔH_{CuGd}, ΔH_{Cu_2Gd}, ΔS_{CuGd}, ΔS_{Cu_2Gd} or C^{reg}, ΔH_{Cu_2Gd}, $\Delta H_{Cu_9Gd_2}$, ΔS_{Cu_2Gd}, $\Delta S_{Cu_9Gd_2}$ [18] (interaction parameter between Cu and Gd free atoms in the liquid, enthalpies and entropies of formation of the associates), since Eq. (5), which depends only on two parameters, suits our experiments fairly well. Another way would be to determine the partial structure factors by X-ray and neutron diffraction measurements [19].

4.3. Liquidus curve in the Cu-rich region

Using the activity values referred to solid copper (Eq. (1)), we can determine the liquidus curve in the Cu-rich region by computing, for a given temperature, the composition x_{Gd} such that a^s_{Cu} equals unity. We disregard the solubility of Gd in solid Cu (during an experimental investigation of the Cu–Gd system by X-ray diffraction analysis, Carnasciali and Cirafici did not detect any significant solubility of Gd in solid Cu [20]). The agreement is quite good with the most recent phase diagram found in the literature [3] up to $x_{Gd} = 0.058$, $T = 1223$ K. Our extrapolated value $x_{Gd} = 0.081$ for the eutectic concentration at 1133 K (Fig. 6) is slightly less than that of the phase diagram, $x_{Gd} = 0.095$, at the same temperature.

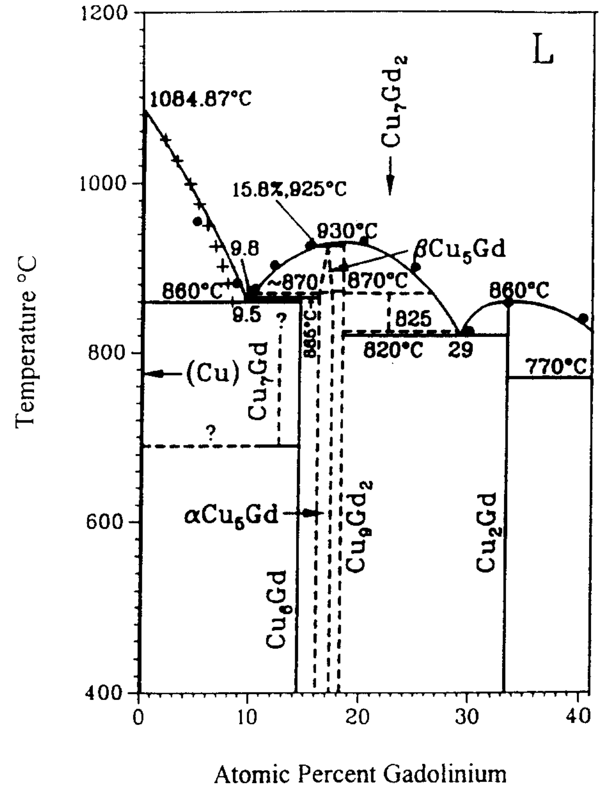

Fig. 6. Comparison of the liquidus line in Cu-rich region: +, computed in this work; ●, from Carnasciali and Cirafici [20].

4.4. Gibbs energy of formation of CuGd and Cu_2Gd

The expressions for ΔG^{xs}_{Cu} and ΔG^{xs}_{Gd} also yield some thermodynamic properties of the compounds. Using relations (2) and (3), the boundaries of the phase diagram and the properties of pure Cu and Gd, we deduced the free enthalpy of formation of both intermetallic compounds CuGd and Cu_2Gd.

The free enthalpy of formation of CuGd corresponds to the reaction

$$Cu_{(s)} + Gd_{(s)} \rightleftharpoons CuGd_{(s)} \qquad (6)$$

On the liquidus curve, as $948\,K < T < 1103\,K$ and $0.5 < x_{Gd} < 0.7$ the following equilibrium takes place:

$$Cu_{(l)} + Gd_{(l)} \rightleftharpoons CuGd_{(s)} \qquad (7)$$

with the following Gibbs energy: $\Delta G = RT \ln(a_{Cu(l)} + a_{Gd(l)})$.

In order to calculate the free enthalpy of the equilibrium (6), we need the melting Gibbs energy of pure Cu and Gd, and we write $\Delta G_f(CuGd) = \Delta G + \Delta G_{m(Cu)} + \Delta G_{m(Gd)}$.

The solid reference for Gd is the β phase. The same

Table 3
Comparison of our ΔG_f^0(CuGd) data with the literature

T (K)	ΔG_f^0(CuGd) (kJ mol^{-1}), solid reference (this work)	ΔG_f^0(CuGd) (kJ mol^{-1}), liquid reference (this work)	ΔG_f^0(CuGd) (kJ mol^{-1}), liquid reference [3]
1103	-41.61 ± 4.84	-47.11 ± 5.18	-48.52
1073	-42.18 ± 1.98	-48.16 ± 2.26	-49.32
1033	-42.38 ± 2.12	-49.00 ± 2.45	-50.37
1013	-42.22 ± 2.11	-49.16 ± 2.46	-50.90
948	-41.28 ± 0.02	-49.31 ± 0.03	-52.62

Table 4
Comparison of our ΔG_f^0(Cu_2Gd) data with the literature

T (K)	ΔG_f^0(Cu_2Gd) (kJ mol^{-1}), solid reference (this work)	ΔG_f^0(Cu_2Gd) (kJ mol^{-1}), liquid reference (this work)	ΔG_f^0(Cu_2Gd) (kJ mol^{-1}), liquid reference [3]
1113	-67.99 ± 4.08	-75.37 ± 4.52	-71.90
1093	-67.83 ± 4.07	-76.03 ± 4.56	-71.99
1073	-67.97 ± 4.08	-76.27 ± 4.58	-72.07
1053	-67.69 ± 4.06	-76.91 ± 4.61	-72.16

calculations for Cu_2Gd yield $\Delta G_f(\mathrm{CuGd}) = 42.2 \pm 2$ kJ mol^{-1} at 1073 K and $\Delta G_f(\mathrm{Cu_2Gd}) = 68 \pm 4$ kJ mol^{-1} at 1113 K. The Gibbs energy data in the literature [3] are referred to the liquid pure elements (Eq. (7)). Our values of the free enthalpies of formation are compared in Tables 3 and 4 with those evaluated by Subramanian and Laughlin [3]. The results are very close to each other.

Let us compare the free enthalpies $\Delta G_f^0(\mathrm{CuGd}) = -21.09 \pm 1.00$ kJ mol^{-1} and $\Delta G_f^0(\mathrm{Cu_2Gd}) = -22.66 \pm 1.36$ kJ mol^{-1} of formation of CuGd and of Cu_2Gd, referred to 1 mol of reactants: we notice that both error bars overlap which unhappily does not throw light on the existence of the minimum in the $\Delta H^{xs}(x_{Gd})$ curve at $x_{Gd} = 0.340$.

5. Conclusion

The thermodynamic activity of Cu in the Cu–Gd alloy, in the temperature and composition ranges $T =$ 1282 K–1644 K and $x_{Gd} = 0.276$–0.844, has been measured by a multiple Knudsen effusion cell-mass spectrometry method.

From the $\ln(a_{Cu}) = f(10^4/T)$ linear fits, we express the partial molar excess Gibbs energies of Cu and Gd referred to the pure liquid elements with a polynomial fit of the third degree; therefore we use the Gibbs–Duhem equation.

In this way we do the following.

- We show that the liquid alloy exhibits a strong negative deviation from Raoult's law, which characterizes the strong attraction between the two components; it is correlated with the existence and the stability of many intermetallic compounds.
- We calculate the Cu-rich liquidus boundary between $x_{Gd} = 0$ and $x_{Gd} = 0.081$ and the value of the eutectic composition.
- We determine the free enthalpies of formation of CuGd between 948 K and 1103 K and of Cu_2Gd between 1043 K and 1133 K.

All these results stem from our high temperature measurements in the liquid phase. However, it must be noticed that they fairly agree as well with previous calculations (activities and Gibbs energies of formation of the compounds), than with experimental results (ΔH^{xs} and CSRO) at lower temperature. With such experimental data, a thermodynamic optimization using a computer code such as THERMO CALC can be performed. Finally, we hope that direct a_{Gd} measurements will be possible using another cell material in order to keep the liquid Gd in the cell and a mass spectrometer with a better sensitivity to detect lower intensities.

We are now working on the electron beam evaporation of the Cu–Gd alloy. The thermodynamic activities of Cu and Gd are very useful in that framework. For instance, we can deduce the value of the source temperature and the vapour composition from source flow measurements, using our activity results. Therefore, we must extrapolate our activity measurements at higher temperature $T > 2000$ °C. All our thermodynamic functions depend on two independent parameters $A(T)$ and $B(T)$ which exhibit a perfect linear behaviour vs. temperature in a large temperature range. These parameters are directly calculated from the experimental results (Eq. (2)), which allows us to extrapolate confidently at higher temperature.

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