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Thermochemistry of binary liquid alloys of silver with rare earth metals*

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Abstract

The heats of mixing of binary liquid alloys of silver with barium and lanthanoid metals (La, Ce, Sm, Eu, Gd, Dy and Yb) were determined by isoperibolic calorimetry. The experimental data show the exothermic effects of alloy formation, thus confirming the strong interactions of the components in Ag–Ln melts which increase from divalent (Ba, Eu, Yb) to trivalent metals, and from light to heavy rare earths.

The results are discussed on the basis of the effective valence model of rare earths. The associated solution model calculations and characteristic dependence of the entropy of mixing show that these alloys have a short-range order in liquid state.

1. Introduction

In an earlier paper [1] the results of vapor pressure measurements of thermodynamic activities in liquid binary alloys of silver with the lanthanoid metals (Ln) were presented. The thermodynamic behavior of Ag–Ln melts indicates the strong interactions between the alloy components and the existence of a chemical short-range ordering (CSRO) in liquid state. Calorimetric data of the mixing enthalpies of liquid Ag–La and Ag–Gd systems [2] are rather scarce and need correction, especially in the lanthanoid-rich concentration range. This paper deals with the results of calorimetric measurements of the mixing enthalpies of binary liquid alloys of silver with barium and lanthanoid metals: La, Ce, Sm, Eu, Gd, Dy and Yb.

2. Experimental details

The SETARAM high temperature calorimeter provided with a voltage stabilizer working up to 1800 K was used for measuring the enthalpies of

*In memory of Professor G. M. Lukashenko who was the initiator of the present investigation.

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mixing of Ag–Ln liquid alloys. The apparatus was applied as a drop calorimeter with constant temperature. The heats of formation may be measured by successive introductions of metal samples (Ag, Ln) placed at standard temperature (298 K) into the metal bath (a liquid metal or an alloy). The mass of the metal in the calorimetric bath was 3–7 g. Temperature measurements were carried out with thermocouples (PtRh6–PtPh30). To obtain the partial molar enthalpies of mixing the metal samples' mass (approximately 0.02–0.08 g) was controlled so that the concentration changes in the bath did not exceed 1.5 at.%. The samples were prepared from silver (99.995% purity), barium (99.6% purity) and lanthanoid elements (La and Ce, 99.86%; Sm, 99.88%; Eu and Yb, 99.83%; Gd, 99.96%; Dy, 99.93% purity) obtained from Giredmet. Molybdenum crucibles with an internal diameter of 5 mm were used as metal solvent containers (molybdenum does not react with any component of the Ag–Ln melts) and placed into standard SETARAM crucibles. The experiments were carried out in purified argon under pressure (5×10^3 Pa).

The experimental method is based on the measurement of the temperature difference (ΔT) between the sample and reference specimen (crucible contained Al_2O_3) plotted as a function of time (t), the heat effects being calculated from ΔT *vs.* t curve by integration [3]. The heat effect of the dissolution of the solid sample in the bath is proportional to the square (ΔF) of the figure surrounding the ΔT *vs.* t curve and base line ($\Delta T = 0$). The general thermal effect may be written using two terms: heating of 1 mol of metal drop from 298 K up to the temperature of the bath (ΔH^T_{298}, see Table 1) and molar heat of mixing (ΔH_i). This results in (for exothermic effect):

$$k(x) \cdot \Delta F_i = \frac{k(x)}{n_i} \int_0^t \Delta T(t)\, \mathrm{d}t = -(\Delta H^T_{i,298} + \Delta \bar{H}_i) \tag{1}$$

TABLE 1

Standard values of enthalpy of heating, ΔH^T_{298}, according to ref. 4 for silver, barium and lanthanoid metals

System (Ag–Ln)	Temperature of experiments (K)	ΔH^T_{298} (J mol^{-1})	
		Ag	Ln
Ag–Ba	1483	45970	45490
Ag–La	1500	46480	47500
Ag–Ce	1500	46480	49800
Ag–Sm	1506	46670	64040
Ag–Eu	1487	46090	49930
Ag–Gd	1623	50240	56870
Ag–Dy	1690	52290	63170
Ag–Yb	1463	45350	47400

where $k(x)$ is the thermal equivalent of calorimeter, n_i is the molar number of the i component, t is the temperature relaxation time and x_i is the mole fraction of the i component.

The initial value of $k(0)$ when the drop metal referred to as 1 is the same as that in the bath one may calculate from eqn. (1) putting $\Delta H^T_{i,298}=0$ (for endothermic effect minus in (1) annuls):

$$k(0)\Delta F_1=\Delta H^T_{1,298}$$

Using the Gibbs–Duhen equations one obtains the system of eqns. (2)–(5) for calculating the concentration dependence of partial molar enthalpies for both components, and the integral value of the enthalpy of mixing [3, 5]:

$$k(x_2)\ \Delta F_1=-\Delta H^T_{1,298}-\Delta\bar{H}_1 \tag{2}$$

$$k(x_2)\ \Delta F_2=-\Delta H^T_{2,298}-\Delta\bar{H}_2 \tag{3}$$

$$\Delta H=x_1\ \Delta\bar{H}_1+x_2\ \Delta\bar{H}_2 \tag{4}$$

$$k(x_2)=\frac{-\Delta H^T_{1,298}}{x_1\Delta F_1+x_2\Delta F_2}\exp\int_0^{x_2}\frac{(\Delta F_1-\Delta F_2)}{x_1\Delta F_1+x_2\Delta F_2}\,\mathrm{d}x_2 \tag{5}$$

where

$$\Delta F_i=\frac{1}{n_i}\int_0^t\Delta T(t)\ \mathrm{d}t\ (i=1,2)$$

To calculate the integral in eqn. (5) one obtains the concentration dependence of $\Delta F_i(x_2)$ using the series of interpolation spline functions [6]. The calculated values of enthalpies were being transformed in the polynomial series expansion using α-functions, defined as follows [7]:

$$\alpha_i=\Delta\bar{H}_i(1-x_i)^{-2}$$

$$\alpha=\Delta H_i\ x_i^{-1}(1-x_i)^{-1}$$

for a statistical treatment and estimation of the error bars

$$\delta\Delta\bar{H}_i=\delta\alpha_i(1-x_i)^2 \qquad \delta\Delta H=\delta\alpha\ x(1-x)$$

with mean square analysis [8]. The ultimate objective of this procedure is to determine the partial and integral enthalpies of mixing using smoothed α-function expansions according to the relationships

$$\Delta\bar{H}_1=\alpha_1(1-x_1)^2$$

$$\Delta\bar{H}_2=-x_1x_2\alpha_1+\int_0^x\alpha_1(x_1)\ \mathrm{d}x_1$$

$$\Delta H=x_2\int_0^{x_1}\alpha_1(x_1)\ \mathrm{d}x_1$$

In special cases the least-squares analysis was applied directly to the experimentally obtained ΔH and $\Delta \tilde{H}_i$ data points [6] due to their simplicity as well as when α-functions did not require adequate representation in dilute concentration regions.

3. Experimental results

3.1. Enthalpies of mixing for Ag–Ba, Ag–Sm, Ag–Eu and Ag–Yb liquid alloys

Experimental data of the heat of mixing are obtained at 41 at.% (Ag–Ba and Ag–Sm systems), 40 at.% (Ag–Eu system) and 30 at.% (Ag–Yb system). The sample weight loss control shows that at higher concentrations of rare earth metals further measurements are incorrect due to the high evaporation rate of liquid metals at experimental temperatures (see Table 1). The concentration dependence of the heat of mixing for liquid Ag–Ba and Ag–Sm alloys may be represented by the following equations ($x = x_{Ln}$):

The Ag–Ba system

$$\Delta \tilde{H}_{Ba} = -(1-x)^2(67.3 + 420.9x - 4502.1x^2 + 15\,416x^3 - 17\,793.6x^4)$$

$$\Delta \tilde{H}_{Ag} = -x^2(-284.4 + 4528.1x - 19\,386.2x^2 + 33210.2x^3 - 17793.6x^4)$$

$$\Delta H = -x(1-x)(67.3 + 69.3x - 412.9x^2 + 532.5x^3)$$

The Ag–Sm system

$$\Delta \tilde{H}_{Sm} = -(1-x)^2(93.2 + 237.5x - 1196.9x^2 + 792.8x^3)$$

$$\Delta \tilde{H}_{Ag} = -X^2(47.1 + 1184.4x + 2044.8x^2 + 792.8x^3)$$

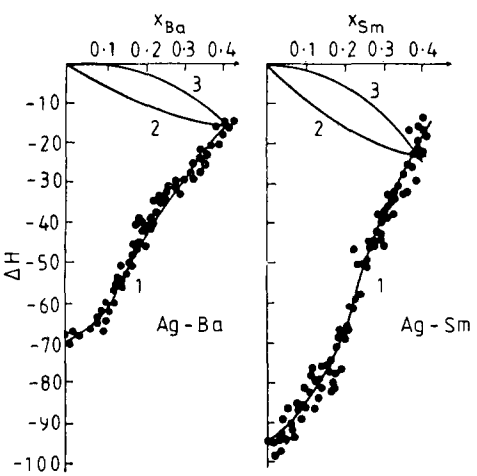


Fig. 1. Concentration dependence of enthalpies of mixing of Ag–Ba and Ag–Sm liquid alloys, kJ mol^{-1}: (1) $\Delta \tilde{H}_{Ba(Sm)}$; (2) ΔH; (3) $\Delta \tilde{H}_{Ag}$.

$$\Delta H = -x(1-x)(93.6+96.8x-250.0x^2-55.1x^3)$$

For dilute solutions in the composition range $0 < x_{Sm} < 0.05$ the linear interpolation is needed;

$$\Delta\bar{H}_{Sm} = -97.9+123.9\ x_{Sm}$$

Concentration dependence of the enthalpies of mixing for Ag–Ba and Ag–Sm liquid alloys are shown in Fig. 1.

The experimental data for Ag–Eu and Ag–Yb systems were treated with α_i polynomials.

The Ag–Eu system

$$\alpha_{Eu} = -73.5-291.5x+7538.2x^2-63308.4x^3+210736.5x^4-231584.5x^5$$

The Ag–Yb system

$$\alpha_{Yb} = -88.0+163.4x-1398.8x^2+2915.0x^3$$

Enthalpies of mixing of liquid Ag–Eu and Ag–Yb alloys calculated with α_i functions expansions are listed in Tables 2 and 3.

3.2. Enthalpies of mixing for Ag–La, Ag–Ce, Ag–Gd and Ag–Dy liquid alloys

Enthalpies of mixing for binary liquid alloys of silver with lanthanum, cerium and gadolinium were determined within a large concentration range, including the lanthanoid-rich part. Either silver or rare earth metals were used as a metal solute in a calorimetric bath. α-Functions were obtained for each component.

3.2.1. The Ag–La system

$$\alpha_{La} = -98.5-376.9x+3569.9x^2-7702.0x^3+6144.7x^4-1433.0x^5$$
$$x = x_{La} \qquad 0 < x_{La} < 0.8$$
$$\alpha_{Ag} = -60.3+5.1x-719.5x^2+2317.5x^3-231.1x^4-13787.0x^5$$
$$x = x_{Ag} \qquad 0 < x_{Ag} < 0.6$$

TABLE 2

Enthalpies of mixing of binary Ag–Eu liquid alloys at 1487 K

X_{Eu}	$-\Delta\bar{H}_{Ag}$ (kJ mol^{-1})	$-\Delta\bar{H}_{Eu}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})
0	0	73.5±5.1	0
0.05	0.20±0.01	68.7±4.1	3.6±0.2
0.10	1.00±0.04	58.5±3.1	6.8±0.3
0.15	1.8±0.1	52.6±2.9	9.5±0.5
0.20	2.9±0.1	47.6±2.3	11.9±0.6
0.25	5.6±0.2	38.4±2.2	13.8±0.7
0.30	11.2±0.3	23.9±1.9	15.0±0.8
0.35	18.2±0.6	9.2±2.0	15.0±1.1
0.40	20.6±1.2	5.0±2.7	14.3±1.8

TABLE 3

Enthalpies of mixing of binary Ag–Yb liquid alloys at 1463 K

X_{Yb}	$-\Delta\bar{H}_{Ag}$ (kJ mol^{-1})	$-\Delta\bar{H}_{Yb}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})
0	0	88.0±2.5	0
0.03	0.12±0.02	79.3±2.0	2.50±0.07
0.06	0.40±0.03	73.0±3.0	4.80±0.11
0.09	0.76±0.09	68.4±3.6	6.87±0.24
0.12	1.18±0.14	65.7±3.9	8.86±0.36
0.15	1.70±0.16	61.5±3.9	10.7±0.5
0.18	2.35±0.18	58.5±3.9	12.4±0.6
0.21	3.17±0.21	55.2±3.7	14.1±0.7
0.24	4.24±0.27	51.5±3.5	15.6±0.8
0.27	5.70±0.36	47.2±3.3	16.9±0.9

3.2.2. The Ag–Gd system

$\alpha_{Gd} = -100.5 + 34.1x + 102.5x^2 \qquad x = x_{Gd} \qquad 0 < x_{Gd} < 1$

$\alpha_{Ag} = -54.7 - 99.1x - 397.4x^2 + 1133.4x^3 - 969.7x^4$

$x = x_{Ag} \qquad 0 < x_{Ag} < 0.62.$

Calculated values of the enthalpies of mixing are listed in Tables 4 and 5.

3.2.3. The Ag–Ce system

Direct statistical treatment of $\Delta\bar{H}_{Ce}$ and ΔH data points leads to the following equations ($x = x_{Ce}$)

$$\Delta\bar{H}_{Ce} = -(1-x)^2(90.5 + 703.6x - 7043.3x^2 + 19336.8x^3 - 21549.7x^4 + 8526.7x^5)$$

$$\Delta H = -x(1-x)(90.5 + 236.9x - 1359.1x^2 + 2031.1x^3 - 974.3x^4)$$

For a dilute solution by analogy with the Ag–Sm system the concentration dependence of $\Delta\bar{H}_{Ce}$ may be presented by the equation:

$$\Delta\bar{H}_{Ce} = -97.6 + 37.6\, x_{Ce}$$

The $\Delta\bar{H}_{Ag}$ values were obtained from the relationship:

$$\Delta H = x_{Ag}\Delta\bar{H}_{Ag} + x_{Ce}\Delta\bar{H}_{Ce}$$

The partial and integral enthalpies of mixing in the Ag–Ce system are listed in Table 4.

3.2.4. The Ag–Dy system

The only dilute solution in the composition range less than $x_{Dy} = 0.05$ has been studied. The limiting value of the partial molar enthalpy of dysprosium is determined:

$$\Delta\bar{H}^0_{Dy} = -105.8 \pm 1.9 \text{ kJ mol}^{-1}$$

TABLE 4

Values of experimental heats of mixing for Ag–La and Ag–Ce liquid alloys at 1500 K

X_{Ag}	Ag–La			Ag–Ce		
	$-\Delta\bar{H}_{Ag}$ (kJ mol^{-1})	$-\Delta\bar{H}_{La}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta\bar{H}_{Ag}$ (kJ mol^{-1})	$-\Delta\bar{H}_{Ce}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})
0	60.3±0.5	0	0	44.3±3.3	0	0
0.1	52.0±1.1	0.4±0.6	5.6±0.6	46.0±2.7	0.1±0.6	4.7±0.3
0.2	46.5±1.6	1.2±1.1	10.4±0.9	43.0±2.5	0.5±1.0	9.0±0.7
0.3	41.2±1.8	2.7±1.4	14.3±1.1	35.3±1.9	2.0±1.3	12.0±0.7
0.4	36.8±1.7	4.1±2.9	17.2±1.9	29.8±1.9	3.7±1.8	14.1±0.8
0.5	33.0±1.5	5.0±4.9	19.0±2.6	26.5±1.7	4.5±2.1	15.5±0.8
0.6	26.0±1.5	10.5±6.6	19.8±2.7	25.3±1.4	6.5±2.9	17.8±0.8
0.7	16.0±1.5	26.9±7.0	19.3±2.7	18.6±1.1	17.0±3.4	18.3±0.7
0.8	7.1±1.4	53.3±6.1	16.3±1.7	8.3±0.9	45.9±4.3	15.8±0.5
0.9	1.1±1.0	86.5±3.4	9.7±1.0	1.1±0.9	85.7±6.2	9.6±0.3
1.0	0	98.5±3.0	0	0	97.6±4.5	0

TABLE 5

Enthalpies of mixing of binary Ag–Gd liquid alloys at 1623 K

X_{Ag}	$-\Delta\bar{H}_{Gd}$ (kJ mol^{-1})	$-\Delta\bar{H}_{Ag}$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})
0	0	54.7±0.9	0
0.1	0.01±0.20	54.3±0.9	5.5±0.1
0.2	0.30±0.26	53.1±1.1	10.9±0.3
0.3	2.2±0.5	47.8±1.2	15.8±0.4
0.4	6.6±0.8	39.7±1.5	19.8±0.8
0.5	14.0±1.4	30.6±1.2	22.3±0.8
0.6	24.5±2.2	22.1±0.7	23.1±1.0
0.7	39.7±3.4	10.7±1.0	19.4±1.2
0.8	57.3±1.9	4.8±0.8	15.3±0.7
0.9	77.8±2.6	1.2±0.3	8.9±0.4
1.0	100.5±4.0	0	0

TABLE 6

Extreme values of the enthalpies of mixing of liquid Ag–Ln alloys in comparison with those in ref. 18

System	$-\Delta\bar{H}^0_{Ln}$ (kJ mol^{-1})	$-\Delta\bar{H}^0_{Ag}$ (kJ mol^{-1})	$-\Delta H_{min}$ (kJ mol^{-1})
Ag–Ba	67.3±2.6(180.6)	– (75.3)	15.2±0.6
Ag–La	98.5±3.0(134.9)	60.3±0.5(79.8)	19.8±2.7
Ag–Ce	97.6±4.5(132.9)	44.3±3.3(80.9)	18.3±0.7
Ag–Sm	97.9±2.9(129.0)	– (82.6)	22.0±0.4
Ag–Eu	73.5±5.1(155.8)	– (78.0)	15.0±1.0
Ag–Gd	100.5±4.0(128.5)	54.7±0.9(82.6)	23.1±1.0
Ag–Dy	105.8±1.9(125.6)	– (83.3)	–
Ag–Yb	88.0±2.5(151.0)	– (83.7)	–

Miedema's model calculations are enclosed in parentheses.

4. Discussion

The results of calorimetric measurements of enthalpies of mixing of silver with barium and lanthanoid metals show high exothermic effects which are in agreement with thermodynamic activity data published earlier [1]. Phase diagrams of Ag–Ln systems also show that the minimal value of ΔH of liquid alloy correlates with the existence of intermetallic compounds, including congruently melting AgLn and Ag_3Ln [8]. The analysis of integral enthalpies of mixing proves an apparent trend to more exothermic values on moving from barium and light lanthanoids to heavy ones (Table 6). This being in agreement with the effective valency lanthanoid metal theory. This theory has been successfully applied to explain the Gibbs energy variation through the lanthanoid row [1]. According to the general conclusions of ref. 10 we have assumed that the alloy formation energy was due to partial

hybridization of lanthanoid f bands with the sd valence electrons while the free electrons transferred from lanthanoid to silver. The extreme values of ΔH correlate with the effective quantity of bonding electrons per lanthanoid atom and follow the same variation as that shown for ΔG^{ex} in ref. 1 (see Fig. 2). It may be noted that $\Delta\bar{H}^0_{Ln}$ absolute values also indicate the linear increase with atomic mass number of rare earth metals (Fig. 3), while the low values for Ba, Eu and Yb are related to their divalency in alloys with silver. Europium and ytterbium can actually be considered members of the 'baride' series of elements, having very similar optical properties [11]. Enthalpy data in Ag–Ce and Ag–Sm melts approach the same values, being found for other trivalent rare earth metal alloys with silver. Similar results for enthalpies have been obtained for liquid Cu–Ln alloys [12–14]. Thermodynamic data for alloys of gadolinium with gold recently obtained by the authors of ref.

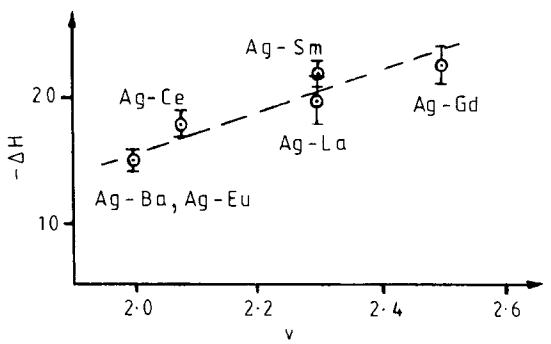


Fig. 2. Correlation of ΔH_{min} with the effective valency (v) of rare earth metals.

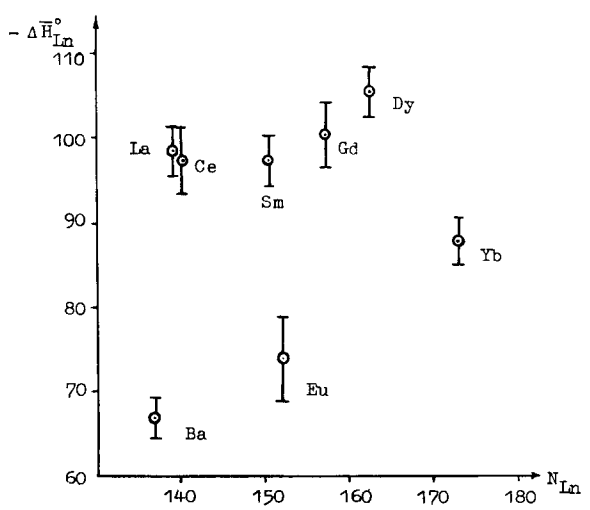


Fig. 3. Variation of $\Delta\bar{H}^0_{Ln}$ values (kJ mol^{-1}) through lanthanoid row for divalent (lower points) and trivalent (upper points) (N_{Ln} is the atom mass number).

15 indicate a stronger interaction of alloy components in Au–Ln melts. The increase in absolute values of ΔH in the row Cu → Ag → Au (Fig. 4) corresponds to great electron affinity with gold.

A characteristic feature of liquid Ag–Ln alloys is the CSRO at concentration ratios 1:1 and 3:1 which is due to associate formation of the unlike atoms. The model calculations in ref. 11 also provide proof of the existence of CSRO in Ag–Ln melts. The concentration dependence of the partial molar entropy of mixing in the Ag–Ce system is characterized by a sharp bend, corresponding to the Ag_3Ce associate formation. The integral values of entropy are negative between two domains of CSRO (Fig. 5). So the behavior of Ag–Ln melts confirms the general conception of AgLn and Ag_3Ln associates formation in the liquid state, which gives the opportunity of calculating ΔH by the ideal association model [16]:

$$\Delta H = \Sigma\, h_i \xi(x_i) \qquad (i = 1,2)$$

where $\xi(x_i)$ is the concentration dependence of the associate mole fraction and h_i is the molar enthalpy of formation of i-type associate. According to the method of calculation described earlier [16, 17] we estimated that $h_{AgCe} = -35$ kJ mol^{-1} and $h_{Ag_3Ce} = -26$ kJ mol^{-1}. The calculations show satisfactory agreement with the experimental data (Fig. 6). However, the model gives poor agreement with experiments in the lanthanoid-rich concentration range where the associate formation has not been taken into account.

It is of current interest to compare the enthalpy values obtained experimentally with the values calculated according to Miedema's model [18].

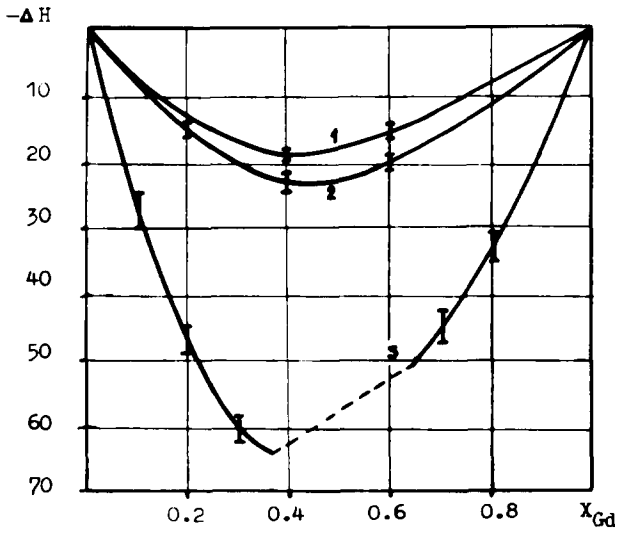
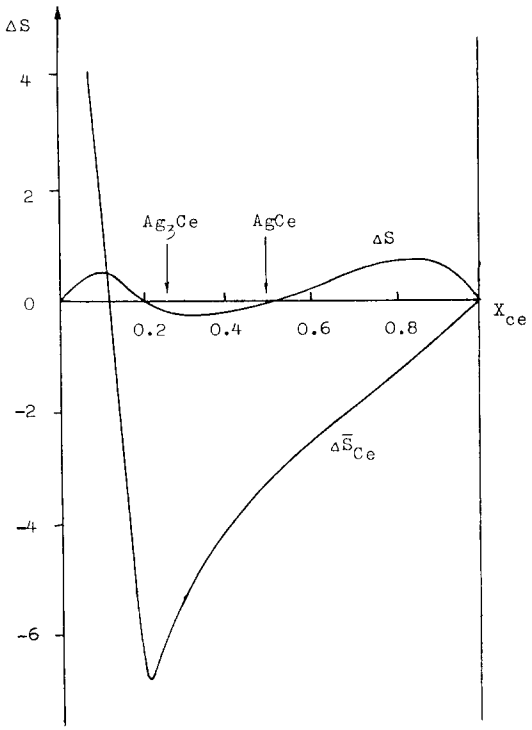


Fig. 4. Enthalpies of formation of liquid alloys of gadolinium with noble metals, kJ mol^{-1}: (1) Cu–Gd at 1629 K, [13]; (2) Ag–Gd at 1623 K, present work; (3) Au–Gd at 1630 K, [15]. The dashed line corresponds to phase field [liquid + $AuGd_{(s)}$].



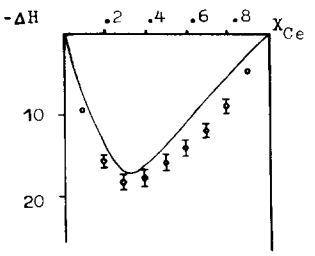


Fig. 5. Entropies of mixing (J mol^{-1} K^{-1}) of Ag–Ce liquid alloys, calculated using Gibbs energies data from ref. 1 at 1363 K.

Fig. 6. Comparison of experimental (points) and calculated values (curve) for the integral heat of mixing of Ag–Ce liquid alloys (kJ mol^{-1}).

As may be seen from Table 6, the calculations do not agree with the experimental results; additionally they do not confirm the regularities obtained for enthalpy variations through the lanthanoid row mentioned above. Such a discrepancy can be the result of disregarding the subtle distinctions in electronic structure of rare earths as well as incorrect estimation of size-mismatch energy which evidently gives a positive contribution to the heat of mixing of several liquid alloys (the Ag–Ba system).

Thus, only direct calorimetric study can offer information about the heats of formation of Ag–Ln alloys. In spite of lack of data for alloys of silver with Sc, Y, Pr, Nd and several heavy lanthanoids, the thermochemical data available allow us to predict the values of enthalpies through the lanthanoid row and to estimate the CSRO in liquid state. In addition the glass-forming ability of several Ag–Ln alloys showing deep eutectics (for example, the Ag–Yb system [19]) is greatly influenced by the CSRO in liquid state. Further investigations of gold–lanthanoid alloys, which remain largely unexplored, would be particularly interesting. A complete set of data for Cu–Ln, Ag–Ln and Au–Ln systems should be useful for obtaining general

information about the thermodynamic properties of liquid alloys of lanthanoids with noble metals.

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