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Thermochemistry of some binary alloys of copper with the lanthanide metals by high-temperature direct synthesis calorimetry

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Abstract

The standard enthalpies of formation of some lanthanide–copper compounds have been measured by high-temperature direct synthesis calorimetry at 1373 ± 2 K. The following results (in kJ/mol of atoms) are reported:

2:1 composition: $Cu_2Tb(-24.7 \pm 1.9)$; $Cu_2Dy(-24.4 \pm 2.3)$; $Cu_2Ho(-25.0 \pm 2.3)$; $Cu_2Er(-27.0 \pm 1.6)$; $Cu_2Tm(-23.4 \pm 2.0)$.
5:1 composition: $Cu_5Tb(-18.4 \pm 2.0)$; $Cu_5Dy(-15.7 \pm 2.2)$; $Cu_5Ho(-17.3 \pm 2.1)$; $Cu_5Er(-18.4 \pm 2.0)$; $Cu_5Tm(-18.9 \pm 2.4)$; Cu_5Lu (-18.8 ± 1.9).

The results are compared with values available in the literature, with the predictions on the basis of the semi-empirical model of Miedema and coworkers and with the values predicted by Gschneider for lanthanide alloys. The results for the Cu alloys are also compared with the recently reported enthalpies of formation of the Ag–LA and Au–LA systems by the present authors.

Keywords: Copper; Lanthanide; Enthalpy; Thermodynamics

1. Introduction

Over a period of a number of years a systematic study of the thermochemistry of the alloys of the noble metals with transition metals and with the lanthanide elements has been pursued in this laboratory [1–12]. Several investigations of the alloys of gold, silver and copper with transition metals and with some of the lanthanide elements were reported by Fitzner and Kleppa [7–9]. Recently, we reported our own study of alloys of the noble metals with transition metals and of the alloys of gold and silver with the lanthanide elements [10–12].

In the present work, we are extending these investigations to the alloys of copper with the lanthanide elements. This will allow us to explore possible systematic trends in these systems and to compare the trends in the noble metal–lanthanide metal alloys.

All the intermetallic compounds were studied by direct synthesis calorimetry using a high-temperature microcalorimeter which can be operated continuously at temperatures up to 1200 °C.

In the present communication, we report new thermochemical data for some intermetallic compounds in the binary systems Cu–Tb, Cu–Dy, Cu–Ho, Cu–Er, Cu–Tm, and Cu–Lu. The phase diagrams of most of these systems are available in the published literature [13]. Some of the X-ray diffraction patterns of the alloy structures are listed in the ASTM powder diffraction file. For those which are not listed, we generated the patterns from available unit cell parameters and atomic coordinates [14].

We found that thermochemical information on these systems is very scarce. However, we found some information on three systems (Cu–Gd, Cu–Dy, Cu–Er) obtained by tin solution calorimetry by Sommer et al. [15].

We will compare all our results with predicted values based on the semi-empirical model of Miedema and coworkers [16].

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Our thermochemical measurements provide a systematic picture of the enthalpies of formation of the Cu–lanthanide alloys in their dependence on the atomic number of the lanthanide element. This allows us to compare our new enthalpy values with the corresponding relative molar volumes and reduced temperatures as suggested by Gschneider [17,18].

Finally, we will compare our results with the enthalpies of formation of the corresponding Ag–LA and Au–LA systems.

2. Experimental

The experiments were carried out at 1373 ± 2 K in a single unit differential calorimeter which has been described in an earlier communication from this laboratory [19]. All the experiments were performed under a protective atmosphere of argon gas, which was purified by passing it over titanium chips at 900 °C. A boron nitride crucible was used to contain most of the samples. All the metals were purchased from Johnson Matthey/Aesar (Ward Hill, MA, USA). All the lanthanide elements were in ingot form, the purities listed as 99.9%. The copper powder was also 99.9% pure and had a 100 mesh particle size. In order to avoid surface oxidation effects, we reduced the copper powder prior to the experiments under a stream of hydrogen gas at approximately 700 °C. The powders from the lanthanide metals were filed from the ingots immediately prior to the experiments. The two components were carefully mixed in the appropriate molar ratio. Then small pellets were prepared, weighed and and then dropped from room temperature into the calorimeter.

In a subsequent set of experiments, the pellets of the reaction products were dropped into the calorimeter to measure their heat contents. Between the two sets of experiments, the samples were kept in a vacuum desiccator to prevent reaction with oxygen and moisture.

Calibration of the calorimeter was achieved by dropping weighed segments of high-purity, 2 mm o.d. copper wire into the calorimeter at 1373 ± 2 K. The enthalpy of pure copper at this temperature 43.184 kJ/mol of atoms, was obtained from Hultgren et al. [20]. The calibrations were reproducible to within ±1.5%.

The reacted samples were examined by X-ray diffraction to assess their structure and to ascertain the absence of unreacted metals. We attempted to prepare a total of 15 compounds. We summarize our findings for all these compounds in Table 1. All the phase diagrams for the considered systems are available in the literature [13]. The X-ray diffraction patterns of most of the Cu–LA alloys are listed in the ASTM powder diffraction file. Where the diffraction patterns were not available we generated them from published unit cell parameters and atomic coordinates [14]. We generated the X-ray diffraction patterns (Table 1) for six compounds not covered by the ASTM file. For three other compounds, we compared our generated patterns with the ASTM patterns.

The CuLA alloys of the early lanthanide elements are very low-melting peritectic compounds which we did not study. The alloys from Sm to Lu all melt congruently [13]. All these phases are listed as having cubic structures of the CsCl type [14]. We generated the X-ray diffraction pattern of CuEr. The other patterns were all listed in the ASTM powder diffraction file. Our X-ray diffraction patterns showed that while the predominant phase in most compounds was CuLA, we also observed a substantial amount of unreacted lanthanide metal as well as a minor amount of the Cu_2LA composition. The presence of unreacted metal was also confirmed by SEM for CuEr where we had enough sample for the processing of the sample by this technique. All the reactions were checked for interaction of the compound with the crucible. Our X-ray diffraction patterns showed the same phases in samples reacted both in BN and in BeO crucibles. We also observed large exothermic baseline shifts in these reactions. This indicates that these reactions may be proceeding continuously without being completed within about 1 h.

Table 1
Summary of physical characteristics of compounds

Compound	m.p.	Structure	Comment
CuTb	900 (c)	ASTM	Incomplete reaction
CuDy	955 (c)	ASTM	Incomplete reaction
CuEr	1055 (c)	G	Incomplete reaction
CuTm	1100 (c)	ASTM	Incomplete reaction
Cu_2Tb	870 (c)	G	Excellent match
Cu_2Dy	890 (c)	ASTM	Very good
Cu_2Ho	915 (c)	ASTM	Excellent match
Cu_2Er	935 (c)	ASTM	Very good
Cu_2Tm	960 (c)	G	<5% CuTm
Cu_5Tb	895 (p)	ASTM, G	Cubic and hexagonal
Cu_5Dy	965 (p)	G	Cubic and hexagonal
Cu_5Ho	970 (p)	ASTM, G	Cubic and hexagonal
Cu_5Er	1005 (p)	G	Cubic and hexagonal
Cu_5Tm	1020 (p)	ASTM, G	Cubic and hexagonal
Cu_5Lu	995 (p)	G	Cubic and hexagonal

G, generated pattern; c, congruently melting; p, peritectically melting.

The alloys of the 2:1 molecular composition all melt congruently [13]. The alloys of this composition of Cu with the early lanthanide metals and with Lu were studied in this laboratory by Fitzner and Kleppa [9]. From Tb to Tm these phases form in the orthorhombic $CeCu_2$ type structure. The X-ray diffraction patterns were available in the ASTM powder diffraction file for Cu_2Dy and Cu_2Er. We generated the patterns of Cu_2Tb and Cu_2Tm. The X-ray diffraction patterns of our products matched well with the ASTM patterns. We found no unreacted elements or significant amounts of secondary phases. We did notice one small unidentified peak in the patterns of Cu_2Dy and Cu_2Er. However, the published pattern showed six unidentified reflections in Cu_2Er [21]. Our Cu_2Tm product showed a minor amount of CuTm (<5%).

The highest melting compounds in the copper lanthanide phase diagrams are rich in copper [13]. From La to Nd, the predominant structure is the 6:1 molecular composition. These phases melt congruently [13]. From Sm to Lu, the

Table 2
Summary of the enthalpies of formation data for the copper–lanthanide element alloys

Compound	$\Delta H(1)$	$\Delta H(2)$	ΔH_f°
Cu_2Tb	$20.6 \pm 1.1(6)$	$45.3 \pm 1.5(5)$	-24.7 ± 1.9
Cu_2Dy	$20.1 \pm 1.5(7)$	$44.5 \pm 1.7(5)$	-24.4 ± 2.3
Cu_2Ho	$18.4 \pm 1.4(6)$	$43.4 \pm 1.8(5)$	-25.0 ± 2.3
Cu_2Er	$17.9 \pm 1.3(6)$	$44.9 \pm 0.9(5)$	-27.0 ± 1.6
Cu_2Tm	$18.8 \pm 0.4(5)$	$42.2 \pm 2.0(5)$	-23.4 ± 2.0
Cu_5Tb	$25.9 \pm 1.4(7)$	$44.3 \pm 1.4(5)$	-18.4 ± 2.0
Cu_5Dy	$26.9 \pm 1.6(6)$	$42.6 \pm 1.5(6)$	-15.7 ± 2.2
Cu_5Ho	$25.1 \pm 1.6(7)$	$42.4 \pm 1.3(5)$	-17.3 ± 2.1
Cu_5Er	$24.7 \pm 1.4(7)$	$43.1 \pm 1.4(5)$	-18.4 ± 2.0
Cu_5Tm	$22.7 \pm 1.7(7)$	$41.6 \pm 1.7(5)$	-18.9 ± 2.4
Cu_5Lu	$23.1 \pm 1.5(6)$	$41.9 \pm 1.2(5)$	-18.8 ± 1.9

Data in kJ/mol of atoms.

formation of Cu_5LA, Cu_9LA_2 and Cu_7LA alloy compounds are reported [13]. However, structural information is available only for the Cu_5LA phases for most of these compounds [14]. The phases with the 5:1 molecular composition melt peritectically [13]. These phases form either in the cubic, $AuBe_5$ type structure or in the hexagonal, $CaCu_5$ modification [22]. The X-ray diffraction patterns of the hexagonal modification of Cu_5Tb, Cu_5Ho and Cu_5Tm are listed in the ASTM powder diffraction file. We generated the patterns of the cubic modification from available unit cell parameters and atomic coordinates [14]. We found that the predominant modification in our products was the cubic form. However, we noticed a small amount of the hexagonal modification in all our samples. We found no unreacted elements or other secondary phases within the limits of the sensitivity of the diffractometer.

3. Discussion

The standard enthalpies of formation of the Cu–LA compounds determined in this study were obtained as a difference between the results of two sets of measurements. In the first set, the following reaction takes place in the calorimeter:

$$LA\,(s,\ 298\,K) + mCu\,(s,\ 298\,K) = LACu_m\,(s\text{ or }l,\ 1373\,K) \tag{1}$$

Here m represents the molar ratio of Cu/LA, LA the lanthanide elements, while s the solid and l the liquid. The reacted pellets were reused in a subsequent set of measurements to determine their heat contents:

$$LACu_m\,(s,\ 298\,K)\ =\ LACu_m\,(s\text{ or }l,\ 1373\,K) \tag{2}$$

The standard enthalpy of formation of the solid compound is then given by:

$$\Delta H_f^\circ = \Delta H(1) - \Delta H(2) \tag{3}$$

Here $\Delta H(1)$ and $\Delta H(2)$ are the enthalpy changes per mole of atoms in the compounds associated with Eqs. (1 and 2).

The experimental results are summarized in Table 2. The heat effects associated with the reactions in Eqs. (1 and 2) are given in kilojoules per mole of atoms as the averages of 5–7 consecutive measurements with the appropriate standard deviations. The last column shows the standard enthalpy of formation of the considered phases. The standard deviations in this column also reflect the small contributions from the uncertainties in the calibrations. As Tables 1 and 2 show, we report no new values for the 1:1 molecular composition. These compounds all showed a significant degree of incomplete reaction and more than one phase present. The heat contents of the Cu_2LA compounds were measured in BeO crucibles. All the measurements on the Cu_5LA compounds were performed in BeO crucibles since these compounds all showed some reaction with the BN crucible.

In Table 3, we compare our results with reported enthalpies of formation in the published literature and with the predicted values from the semi-empirical model of Miedema and coworkers [16]. The enthalpies of formation in the literature were all measured by tin solution calorimetry at 1100 K by Sommer et al. [15]. In general, our values tend to be slightly more exothermic than the enthalpies reported by Sommer.

Table 3
Comparison of the standard enthalpies of formation with values in the literature and with predicted values from Miedema and coworkers [16]

Compound	ΔH_f° This work	ΔH_f° Literature	Method	ΔH_f° Predicted
Cu_2Tb	-24.7 ± 1.9	–	–	−32
Cu_2Dy	-24.4 ± 2.3	-16.4 ± 1.3	Soln. calor. (Sn, 1100 K) (15)	−32
Cu_2Ho	-25.0 ± 2.3	–	–	−31
Cu_2Er	-27.0 ± 1.6	-17.2 ± 1.2	Soln. calor. (Sn, 1100 K) (15)	−33
Cu_2Tm	-23.4 ± 2.0	–	–	−32
Cu_5Tb	-18.4 ± 2.0	–	–	−19
Cu_5Dy	-15.7 ± 2.2	(-12.7 ± 1.1) Cu_9Dy_2	Soln. Calor. (Sn, 1100 K) (15)	−19
Cu_5Ho	-17.3 ± 2.1	–	–	−18
Cu_5Er	-18.4 ± 2.0	-10.7 ± 2.3	Soln. Calor. (Sn, 1100 K) (15)	−19
Cu_5Tm	-18.9 ± 2.4	–	–	−19
Cu_5Lu	-18.8 ± 1.9	–	–	−19

Data in kJ/mol of atoms.

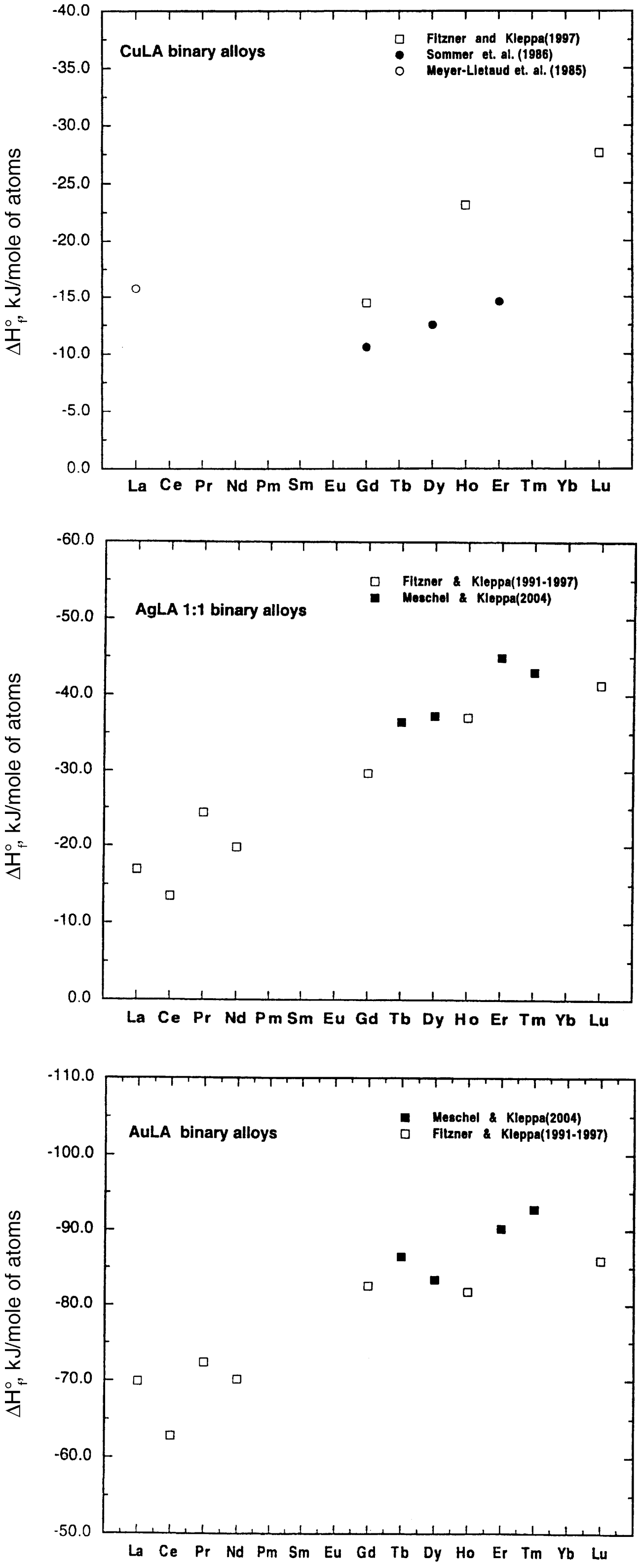

Fig. 1. Comparison of the enthalpies of formation of the Cu–, Ag–, and Au–LA alloys of the 1:1 molecular composition.

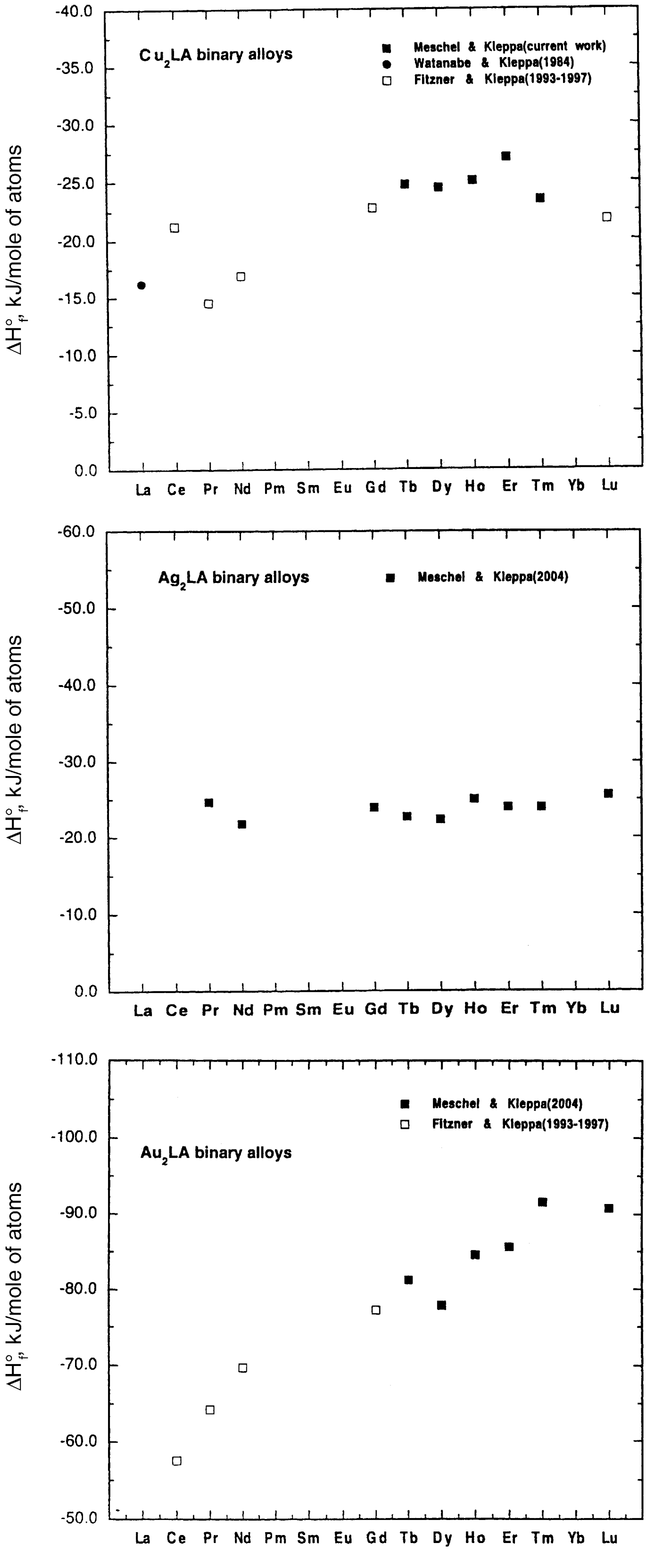

Fig. 2. Comparison of the enthalpies of formation of the Cu–, Ag–, and Au–LA alloys of the 2:1 molecular composition.

The predicted values are nearly constant and slightly more exothermic than our measurements.

In Fig. 1, we plot the enthalpies of formation of the 1:1 molecular composition for Cu, Ag and Au alloys against the atomic numbers of the lanthanide elements. For the Cu compounds, we are plotting calorimetric measurements by Fitzner and Kleppa [9], by Sommer et al. [15], and by Meyer-Liautaud et al. [23]. We report no new data for Cu compounds of this molecular composition, because we found that our products were not completely reacted. For some of the Ag and Au compounds, we are citing measurements by Fitzner and Kleppa [7,8] and new data by the present authors [11,12]. As the graphs show, all three patterns are quite similar. All three show an increase of the magnitude of the enthalpies of formation with increasing atomic number. As one might anticipate, the magnitude of the enthalpies of formation is most exothermic for the Au compounds and least exothermic for the Cu compounds. The change in the enthalpies of formation from La to Lu, are quite similar for the alloys of Ag and Au, but considerably smaller for the Cu compounds.

In Fig. 2, we plot the enthalpies of formation of the 2:1 compounds for the Cu, Ag and Au alloys against the atomic number of the lanthanide elements. We cite previous measurements from this laboratory by Watanabe and Kleppa [3], by Fitzner and Kleppa [7–9], and recent work by the present authors [11,12]. These patterns are quite different from one another. For the Cu compounds, the pattern shows a small increase in magnitude with the atomic numbers. However, this increase is considerably smaller in magnitude than what earlier authors found for the 1:1 composition. For the Ag_2LA compounds, the pattern is nearly constant with respect to the atomic number. On the other hand, the pattern for the Au_2LA composition shows a strong increase in magnitude of the enthalpy of formation with increasing atomic number. This is similar to the pattern for the corresponding compounds of the 1:1 composition. The magnitudes of the enthalpies of formation are roughly comparable for Cu and Ag compounds, but are significantly more exothermic for the Au compounds. In this group of compounds, we observe significant differences between the behavior of the Cu, Ag and Au alloys. We also observe differences between the patterns of the 1:1 and the 2:1 molecular composition.

In Fig. 3, we plot the enthalpies of formation of the copper-rich Cu_6LA, Cu_9Gd_2 and Cu_5LA compounds against the atomic number of the lanthanide elements. We cannot compare these values with data for Ag and Au alloys because these metals do not form compounds of similar stoichiometry [13]. For the early lanthanide elements, we cite the measurements of Watanabe and Kleppa [3] and of Fitzner and Kleppa [8,9]. Note, that we have no values for Pm, Sm, Eu and Yb. The enthalpies of formation of the plotted compounds show a slight increase in magnitude with respect to the atomic number. We note that the enthalpies of formation, as one would expect, are less exothermic than those of the 1:2 compounds. If we assume that the enthalpies of formation vary roughly with composition as the product of the mole fractions of the components, we may estimate the expected value for the 1:5 stoichiometry from our values for the 1:2 molecular composition. On the basis of this rough estimate, we would expect an average value of about −15 kJ/mol of atoms for the 1:5 molecular composition. This agrees reasonably well with our measured values.

In Fig. 4, we plot the reduced temperature of the compounds of three different molecular compositions against the atomic number of the lanthanide elements as suggested by Gschneider [17,18]. The 1:6 molecular composition forms

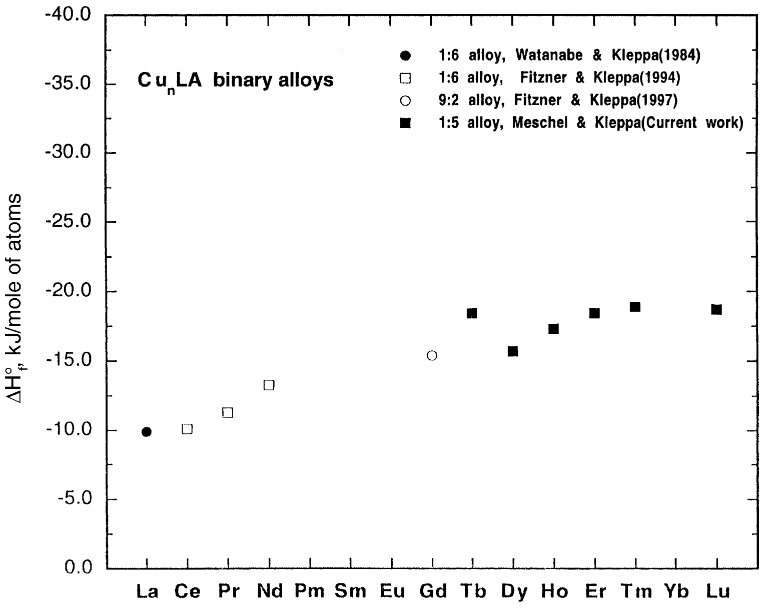

Fig. 3. Enthalpies of formation of the Cu–LA alloys of 1:5 and 1:6 molecular compositions.

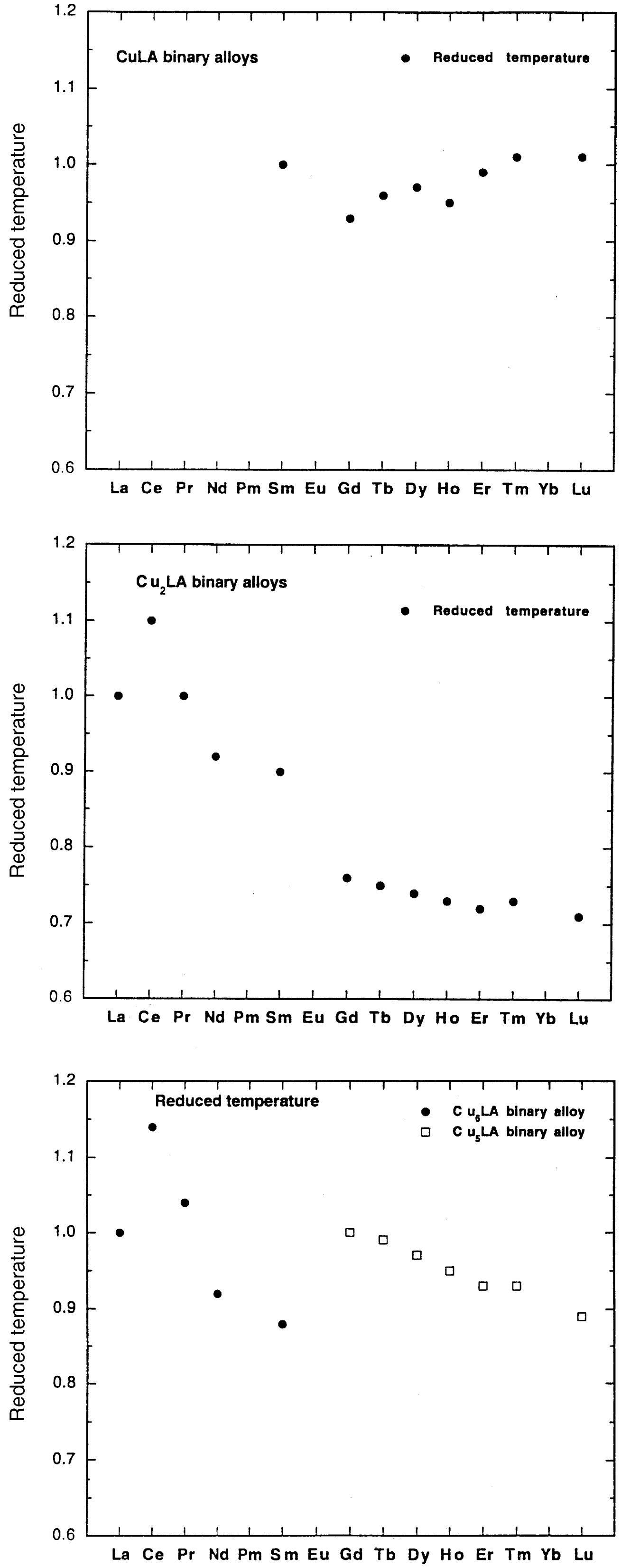

Fig. 4. Comparison of the reduced temperatures of the Cu–LA alloys of 1:1, 1:2, 1:5, and 1:6 molecular compositions.

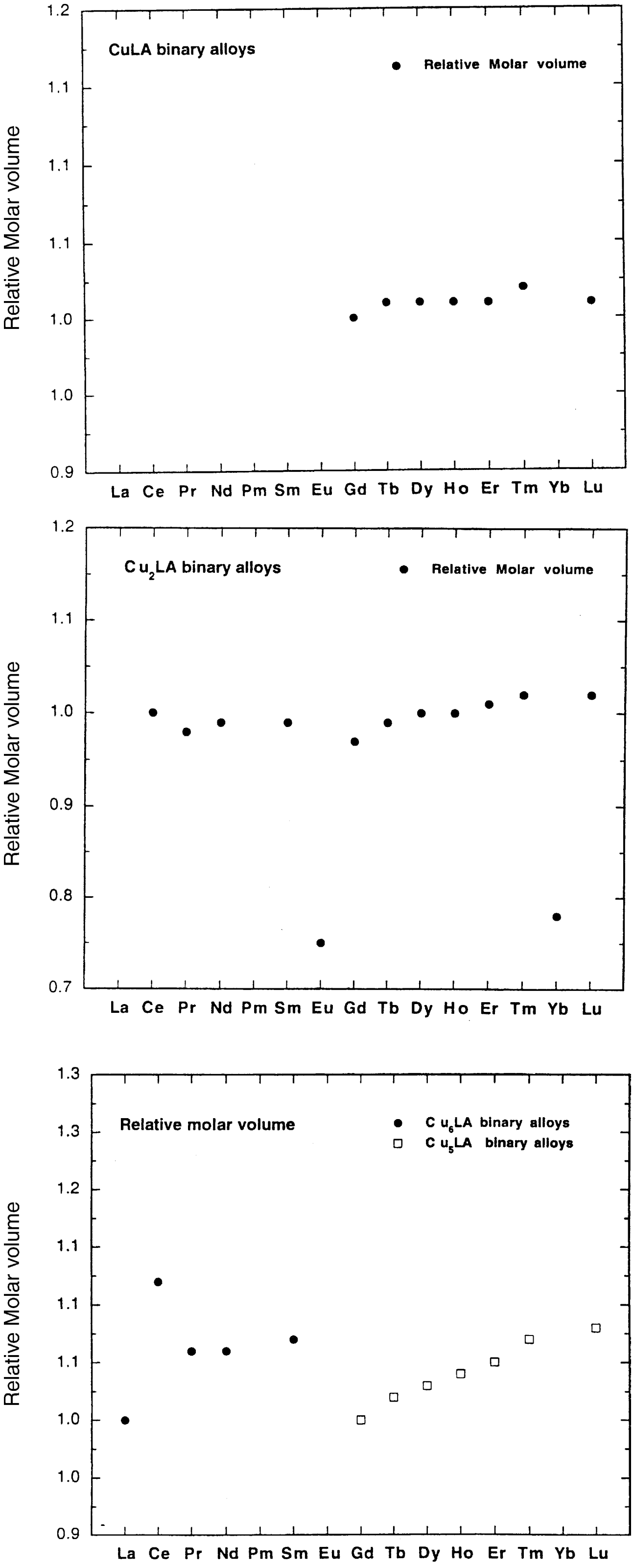

Fig. 5. Comparison of the relative molar volume ratios of the Cu–LA alloys of the 1:1, 1:2, 1:5, and 1:6 molecular compositions.

from La to Sm. From Gd to Lu, the predominant molecular ratio is 1:5; for Gd, the 2:9 molecular ratio has also been observed [13].

The plot for the 1:1 molecular composition shows relatively little change with atomic number. The plots for the 1:2, 1:6 and 1:5 molecular compositions show a significant decrease in the magnitude of the reduced temperature with increasing atomic number.

We did not observe any decrease in magnitude of the enthalpies of formation with respect to atomic number in our measurements. We also did not observe any correlation with the reduced temperature in our earlier study of Ag–LA and Au–LA alloys [11,12].

In Fig. 5, we plot the relative molar volume ratios against the atomic number of the lanthanide elements as also suggested by Gschneider [17,18]. For the CuLA molecular composition, we plotted the relative molar volumes of the CsCl modification (Gd to Lu). Our reference point is CuGd. Note that we have no values for Yb. The compounds from La to Sm have different structures, therefore, we did not include these in the graph. For the Cu_2LA molecular composition, we plotted the relative molar volumes of the orthorhombic Cu_2Ce type modifications. Cu_2La forms in the AlB_2 structure. For this reason, we did not include its value in the graph. Our reference point is Cu_2Ce. Note that we have no value for Pm. For the 1:6 and 1:5 compounds, we plotted the relative molar volumes in two groups. From La to Sm, we plotted the relative molar volumes for the predominant 1:6 molecular ratio. Our reference point is La. Note that we have no values for Pm and Eu. From Gd to Lu, the predominant composition is the 1:5 molecular ratio. Our reference point is Gd. Note that we have no value for Yb.

As Fig. 5 shows the relative molar volumes for the CuLA, and Cu_2LA compositions are nearly constant with the exception of the values for Cu_2Eu and Cu_2Yb. The third pattern is not as clear as the previous two. Here we see some trend of increase in the molar volumes with increasing atomic number. When we compare the patterns of the relative molar volumes with our enthalpies of formation, we see that Gschneider's prediction of the correlation of the enthalpies of formation with the relative molar volume ratios agrees only for the Cu_2LA molecular composition. This is similar to our findings in the Ag–LA systems.

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