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Thermochemistry of binary liquid alloys of copper with barium and lanthanide metals (europium, dysprosium and ytterbium)

N. I. Usenko, M. I. Ivanov and V. M. Petiuh
Institute for Problems of Material Science, Ukrainian Academy of Sciences, 252180 Kiev (Ukraine)

V. T. Witusiewicz
Institute for Foundry Problems, Ukrainian Academy of Sciences, 252180 Kiev (Ukraine)

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Abstract

The heats of mixing of binary liquid alloys of copper with barium, europium and ytterbium in the copper-rich concentration region and the heats of mixing in the Cu–Dy system over the total composition range were measured by isoperibolic calorimetry. The heats of formation increase with increasing atomic number, *i.e.* in agreement with previous investigations for other Cu–Ln melts. The component interaction energy is found to increase along the row Ba, Eu, Yb, Dy. An apparent variation in the partial mixing enthalpies with atomic size factor which contributes positively to the alloy formation energy is observed. Model calculations of integral enthalpy for the Cu–Ba system based on the atomic size difference factor allow one to estimate the mixing enthalpy in the total concentration region.

1. Introduction

In recent years the heats of mixing of binary liquid alloys of copper with rare earth metals (lanthanides (Ln)) which are the subject of practical interest have been measured in detail. The first results obtained by Watanabe and Kleppa [1] for some liquid Cu–Ln alloys in the copper-rich composition range showed strong exothermic effects of alloy formation. As a result of the investigation of Cu–Gd melts over the total concentration region [2] and the extensive experimental series of Turchanin and Nikolaenko [3] the principal thermodynamic properties of liquid Cu–Ln alloys were established. Data on mixing enthalpies show a strong chemical interaction between components in alloy melts. These systems also possess a chemical short-range order (CSRO) which is due to the formation of unlike-atom associates in a liquid [4].

Nevertheless, among the liquid Cu–Ln alloys the Cu–Eu, Cu–Dy and Cu–Yb systems are as yet unexplored and the fact that these data are missing means that we cannot estimate the thermodynamic behaviour of Cu–Ln melts through the lanthanide row. In the present paper the results of a calorimetric study of binary liquid alloys of copper with europium, dysprosium, ytterbium and barium (the data for the Cu–Ba system differ from those for other Cu–Ln alloys [3] and should be confirmed) are presented.

2. Experimental details

A Setaram high temperature calorimeter was used to measure the enthalpies of mixing in the Cu–Ba and Cu–Eu systems [5]. The experimental studies on Cu–Dy and Cu–Yb alloys were carried out in a twin-solution calorimeter operating up to temperatures of 1900 K. The general principles of these types of calorimeter have been described earlier [6]. A schematic diagram of the calorimeter set-up is shown in Fig. 1. The massive molybdenum block 1 with two crucibles – the melt container 2 and the reference crucible 3 – is placed in the constant-temperature zone of the furnace 4 with a coaxial molybdenum heater. The temperature of the block is maintained constant to within ± 0.5 K automatically.

The samples of alloy components or of reference substances taken at standard temperature (298 K) were dropped into the calorimetric bath from the revolving container 5 through the ceramic tube 6. The temperature change in the crucible 2 with respect to the reference crucible and the corresponding time required to establish this temperature difference ΔT, due to the mixing of the components, were measured with the differential thermocouple 7a, 7b. The area under the ΔT *vs.* time curve is proportional to the thermal effect.

The experiments were carried out in purified helium at a pressure of 5×10^3 Pa. The purities of the metals

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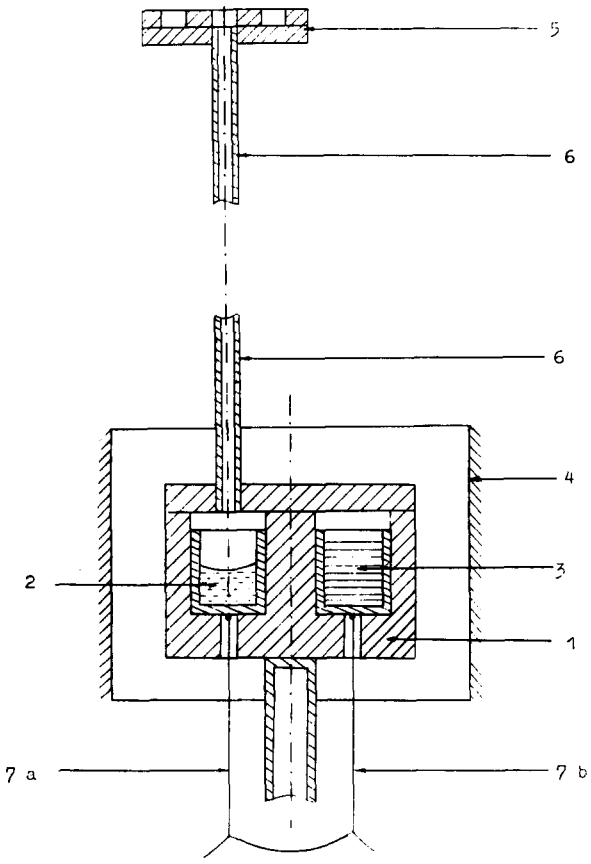

Fig. 1. Schematic diagram of the calorimeter cell: 1, molybdenum block; 2, melt container; 3, reference crucible; 4, molybdenum heater; 5, revolving sample container; 6, ceramic dropping tube; 7, W-(W–Re) differential thermocouple.

TABLE 1. Comparison of experimental values of partial enthalpies of mixing for twin-calorimeter testing with those of alloys for which reliable thermochemical data exist

A–B system	$\Delta\bar{H}^0_B$ (kJ mol^{-1})	
	Our data	Reference data
Cu–Ge	−60.4±5.4 (1473 K)	−55.4±10.2 (1460 K) [9]
Cu–Gd	−109.2±4.0 (1473 K)	−100.0±6.5 (1629 K) [2]
		−103.1±4.1 (1523 K) [3]
Al–Gd	−178.4±5.0 (1593 K)	−174.0±2.5 (1125 K) [10]

were 99.995% for copper, 99.6% for barium, 99.83% for europium and ytterbium, and 99.93% for dysprosium. The metals were obtained from Giredmet (Moscow).

The initial mass of the metal bath was 1 g. The masses of samples were measured to within 0.002–0.02 g and variation in the alloy concentration was less than 1 at.%; therefore we can determine the partial molar enthalpies with sufficient accuracy.

The thermal effect of the process was calculated from the ΔT *vs.* time curve by integration. It is composed of two terms: the enthalpy $\Delta H_{298}{}^T$ for heating 1 mol of metal dropped into the bath from 298 K to the temperature of bath [7] and the partial molar heats $\Delta\bar{H}_i$ of mixing. The resulting equation for the exothermic effect is

$$\frac{k}{n}\int \Delta T(t)\,\mathrm{d}t = -(\Delta H_{i,298}{}^T + \Delta\bar{H}_i) \qquad (1)$$

where k is the thermal equivalent of the calorimeter, n is the molar number of component i and t is the temperature relaxation time.

To determine k at the beginning of each experimental series, metal samples were dropped into a bath of the same pure metal, and reference molybdenum (purity, 99.99%) samples were dropped in at the end of each experiment. In these cases, $\Delta\bar{H}_i$ in eqn. (1) is equal to zero, and one can obtain the value of k.

The sum of the experimental $\Delta\bar{H}_i$ data points are presented as a polynomial series using α functions ($\alpha_i = \Delta\bar{H}_i(1-x)^{-2}$, $\alpha = \Delta H x^{-1}(1-x)^{-1}$) and statistically treated by a least-squares analysis using Forsythe orthogonal polynomials. The program written by Nikolaenko [8] calculates the integral and both partial enthalpies in each system with a confidence interval equal to twice the standard deviation ($\pm 2\sigma$) of the approximate function.

In order to test our calorimeter we determined partial molar enthalpies for some systems, which had previously been investigated. The results of tests are given in Table 1.

3. Experimental results

Experimental data on the heats of mixing for binary liquid alloys were obtained up to 25 at.% Ba for the Cu–Ba system, up to 35 at.% Eu for the Cu–Eu system and up to 40 at.% Yb for the Cu–Yb system. Mass loss control tests showed that further measurements at higher lanthanide metal concentrations were incorrect because of evaporation of the barium or lanthanide at the temperature of the experiments: 1500 K (Cu–Ba), 1480 K (Cu–Eu) and 1453 (Cu–Yb). The Cu–Dy system was investigated at 1690 K over the total composition region. The concentration dependence of the heats of mixing may be presented as an α polynomial series by the following equations (x is the molar fraction of barium or lanthanide). For the Cu–Ba system,

$$\alpha_{Ba} = 15.17 - 53.70x$$

For the Cu–Eu system,

$$\alpha_{Eu} = -34.60 + 79.33x + 251.25x^2$$

For the Cu–Yb system,

$$\alpha_{Yb} = -66.47 + 47.91x + 989.35x^2 - 2122.17x^3$$

For the Cu–Dy system,

$$\alpha = -114.1 - 128.7x + 957.3x^2 + 1834.7x^3 + 1554.1x^4 - 495.8x^5$$

For the Cu–Dy system the two branches of the integral α function obtained for both the copper- and the dysprosium-rich composition region were joined together and treated to obtain the general dependence over the total composition region.

The values of partial and integral mixing enthalpies for liquid Cu–Ba, Cu–Eu, Cu–Yb and Cu–Dy alloys are listed in Tables 2, 3, 4 and 5 respectively. The concentration dependences of the mixing enthalpies are shown in Figs. 2, 3 and 4 for Cu–Eu, Cu–Yb and Cu–Dy systems respectively.

TABLE 2. Enthalpies of mixing of binary Cu–Ba liquid alloys at 1500 K

x_{Ba}	$\Delta H \pm 2\sigma$ (kJ mol^{-1})	$\Delta\bar{H}_{Ba} \pm 2\sigma$ (kJ mol^{-1})	$\Delta\bar{H}_{Cu} \pm 2\sigma$ (kJ mol^{-1})
0	0	15.2±1.9	0
0.05	0.65±0.1	11.3±1.2	0.1±0.01
0.10	1.1±0.1	7.9±0.8	0.4±0.02
0.15	1.4±0.2	5.1±0.9	0.8±0.1
0.20	1.6±0.3	2.8±1.1	1.3±0.2
0.25	1.6±0.5	1.0±1.4	1.8±0.2

TABLE 3. Enthalpies of mixing of Cu–Eu liquid alloys at 1480 K

x_{Eu}	$-\Delta H \pm 2\sigma$ (kJ mol^{-1})	$-\Delta\bar{H}_{Eu} \pm 2\sigma$ (kJ mol^{-1})	$-\Delta\bar{H}_{Cu} \pm 2\sigma$ (kJ mol^{-1})
0	0	34.6±3.9	0
0.05	1.5±0.1	27.1±1.9	0.2±0.01
0.10	2.7±0.1	19.6±1.2	0.8±0.01
0.15	3.4±0.2	12.3±1.2	1.8±0.05
0.20	3.7±0.3	5.6±1.1	3.3±0.1
0.25	3.6±0.4	−0.5±1.1	5.0±0.1
0.30	3.2±0.7	−5.8±1.6	7.0±0.3
0.35	2.4±1.0	−10.1±2.4	9.1±0.7

TABLE 4. Enthalpies of mixing of Cu–Yb liquid alloys at 1453 K

x_{Yb}	$-\Delta H \pm 2\sigma$ (kJ mol^{-1})	$-\Delta\bar{H}_{Yb} \pm 2\sigma$ (kJ mol^{-1})	$-\Delta\bar{H}_{Cu} \pm 2\sigma$ (kJ mol^{-1})
0	0	66.5±3.2	0
0.05	3.1±0.1	55.8±1.6	0.3±0.01
0.10	5.5±0.2	43.7±1.6	1.3±0.05
0.15	7.3±0.2	31.9±1.4	3.0±0.1
0.20	8.4±0.4	21.9±1.5	5.1±0.1
0.25	9.0±0.5	14.5±1.6	7.2±0.2
0.30	9.2±0.6	10.0±1.4	8.9±0.3
0.35	9.2±1.1	8.2±2.0	9.7±0.6
0.40	9.1±2.7	8.1±4.0	9.3±1.2

TABLE 5. Enthalpies of mixing of Cu–Dy liquid alloys at 1690 K

x_{Dy}	$-\Delta H \pm 2\sigma$ (kJ mol^{-1})	$-\Delta\bar{H}_{Dy} \pm 2\sigma$ (kJ mol^{-1})	$-\Delta\bar{H}_{Cu} \pm 2\sigma$ (kJ mol^{-1})
0	0	114.1±7.1	0
0.10	10.7±0.3	95.3±2.7	1.3±0.05
0.20	18.2±0.5	62.7±2.0	7.1±0.1
0.30	22.0±0.7	36.9±2.0	15.6±0.5
0.40	22.8±0.9	21.1±1.4	23.9±0.6
0.50	21.7±1.0	12.4±1.0	31.0±1.0
0.60	19.2±0.9	7.0±0.6	37.5±1.4
0.70	15.7±0.8	3.5±0.4	44.1±1.9
0.80	11.1±0.8	1.3±0.2	50.7±3.1
0.90	5.9±0.4	0.3±0.05	56.1±3.8
1.00	0	0	61.8±5.2

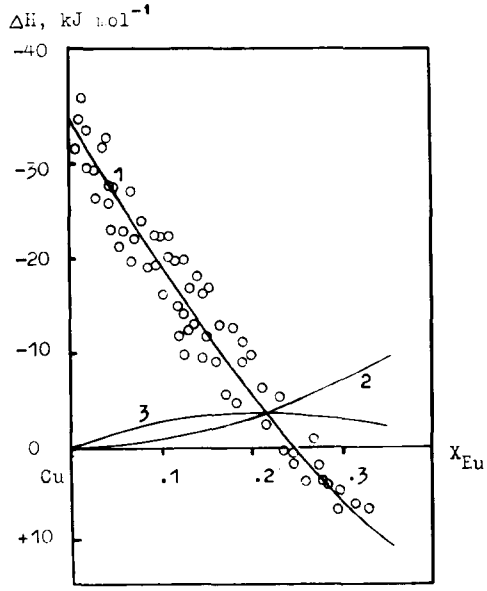

Fig. 2. Experimental data for $\Delta\bar{H}_{Eu}$ and concentration dependence of the mixing enthalpies for Cu–Eu liquid alloys at 1480 K: curve 1, $\Delta\bar{H}_{Eu}$; curve 2, $\Delta\bar{H}_{Cu}$; curve 3, ΔH.

4. Discussion and model analysis of results

The results of calorimetric measurements for Cu–Ln liquid alloys show different values for the mixing enthalpies (positive in the Cu–Ba system, variable sign in the Cu–Eu system and negative in the Cu–Dy and Cu–Yb systems) and reflect the individualities of the component interaction itself, being in agreement with previous investigations [1–3]. The ΔH minima are located in the copper-rich region and correlate with the existence of intermetallic compounds, including congruently melting compounds. A special type of com-

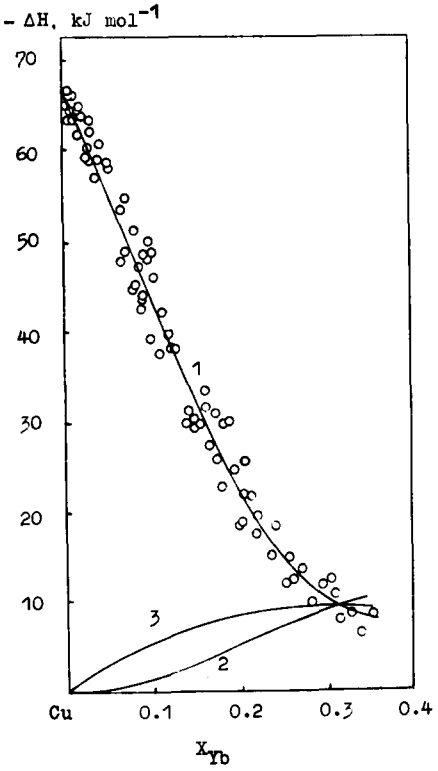

Fig. 3. Experimental data for ΔH_{Yb} and concentration dependence of the mixing enthalpies for Cu–Yb liquid alloys at 1453 K: curve 1, $\Delta\bar{H}_{Yb}$; curve 2, $\Delta\bar{H}_{Cu}$; curve 3, ΔH.

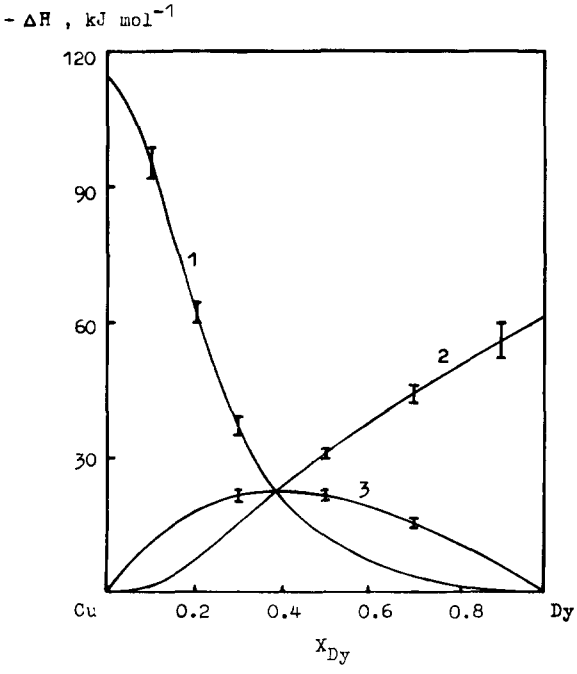

Fig. 4. Concentration dependence of the mixing enthalpies for Cu–Dy liquid alloys at 1690 K: curve 1, $\Delta\bar{H}_{Dy}$; curve 2, $\Delta\bar{H}_{Cu}$; curve 3, ΔH. Only approximate functions are shown.

ponent interaction takes place in the Cu–Ba system for which stable compounds do not exist [11]. For Cu–Eu and Cu–Yb liquid alloys the minimum ΔH correspond to the compounds Cu_5Eu and Cu_5Yb, while for the Cu–Dy system the minimum ΔH (at $x_{Dy}=0.4$) is located within a range of three stable compounds: Cu_5Dy, Cu_2Dy and CuDy [12].

This reveals the tendency to the formation of unlike-atom associates in liquid alloys, the CSRO being conditioned by ordered solid phases. Such a hypothesis was confirmed recently after association solution model calculations of the concentration fluctuation function $S_{CC}(0)$ and activities in Cu–Y, Cu–La and Cu–Lu melts were carried out assuming two types of complex: CuLn and Cu_2Ln [4].

Our experimental results on $\Delta\bar{H}^0_{Ln}$ are also in agreement with the general trend to more exothermic values on going from barium and light lanthanides to heavy lanthanides [3]. In Fig. 5 the absolute values of $\Delta\bar{H}^0_{Ln}$ demonstrate the smooth increase with increasing atomic number of lanthanide metal both for the lanthanide series and for the barium (barium, europium and ytterbium) series. Recently analogous trends have been well established for two series of Ag–La liquid alloys [5]. The explanation of this dependence was given using the effective valency of lanthanide metal which increases through the lanthanide row. Another explanation for the $\Delta\bar{H}^0_{Ln}$ increase based on the analysis of electronic density of states at the Fermi level for liquid trivalent lanthanides and barium was given in ref. 3. It should be noted that the available Fermi level data for divalent and trivalent lanthanides owing to the electrical resistivity measurements [13, 14] show that a Fermi level difference between copper and lanthanide metals arises through the lanthanide row both for the trivalent series (from lanthanum to lutetium) and for the divalent series (from europium to ytterbium). Our experimental results

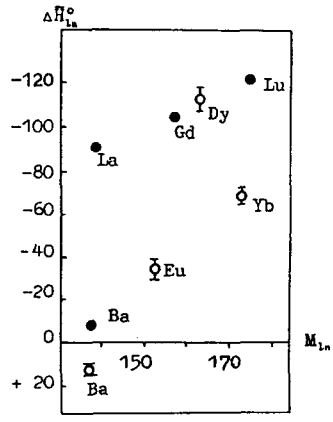

Fig. 5. Variation in $\Delta\bar{H}_{Ln}{}^0$ *vs.* atomic mass number (M_{Ln}) of lanthanides for several liquid Cu–Ln alloys for divalent (lower row of points) and trivalent (upper row of points) lanthanide series: ●, data taken from ref. 3; ◇, results of present work.

on the enthalpies of mixing are in agreement with the peculiarities mentioned above.

According to previous data [5] we may safely consider europium and ytterbium to be divalent in alloys with noble metals and they may be treated as group IIA metals. Indeed the Miedema model parameters determined for europium and ytterbium are very similar to those obtained for calcium and strontium [15]. The mixing enthalpies in the Cu–Sr system recently determined ($\Delta H_{min} = -4.9 \pm 0.1$ kJ mol^{-1} [16]) approach those obtained in the Cu–Eu system (Table 3).

In Table 6 a comparison is made between experimental values for partial enthalpies of mixing and the values calculated from Miedema's model [15]. As was shown for Ag–Ln alloys [5] the size mismatch energy gives a positive contribution to the heats of mixing. The absolute values for the enthalpies calculated from model for Cu–Ln melts remain quite high, and agreement is obtained only for the Cu–Dy system. Analysing Miedema's equation for enthalpy calculation we may finally establish that this model is incapable of estimating the positive contribution to ΔH. The influence due to the Wigner–Seitz cell distortion when a liquid alloy is formed must be displayed more dramatically.

Figure 6 demonstrates the linear correlation between $\Delta\bar{H}^0_{Ln}$ and the atomic volume ratio (V_{Ln}/V_{Cu}). The atomic volume data were taken from ref. 15. We consider the atomic volume to be the principal factor which determines the total alloy formation effect. It is of interest to compare our results with those in ref. 17, where curves of ΔH_{max} *vs.* atomic volume difference factor are presented for several alloys, demonstrating the endothermic effects of alloy formation (see Fig. 16 in ref. 17). Regardless of some scatter in data points the maximum ΔH for Cu–Ba melts agrees with the dependence obtained for several intra-alkaline metal alloys having almost zero electronegativity differences $\Delta\phi$. This behaviour of the Cu–Ba system appears to be doubtful as $\Delta\phi$ for the Cu–Ba couple is equal to 1.0 eV on the Pauling scale [18]. The only realistic explanation for this is due to the Wigner–Seitz cell distortion which accompanies alloy formation and makes it impossible to display an attractive force. We consider

TABLE 6. Comparison of experimental values and values calculated by Miedema's model for the heats of mixing where europium and ytterbium are considered to be divalent metals

Cu–Ln system	$\Delta\bar{H}^0_{Ln}$ (kJ mol^{-1})		$\Delta\bar{H}^0_{Cu}$ (kJ mol^{-1})	
	Experimental	Model	Experimental	Model
Cu–Ba	$+15.2 \pm 1.9$	-64.3		
Cu–Eu	-34.6 ± 3.9	-67.7		
Cu–Dy	-114.1 ± 7.1	-110.9	-61.8 ± 5.2	-57.6
Cu–Yb	-66.5 ± 3.2	-77.5		

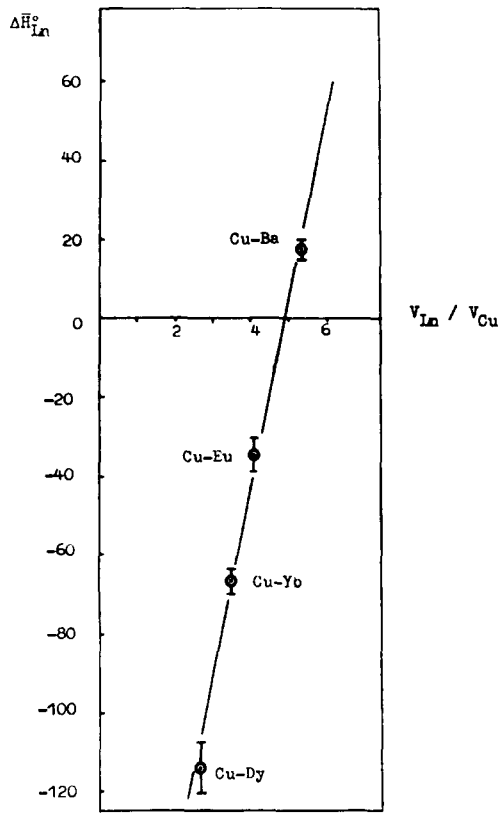

Fig. 6. Correlation of $\Delta\bar{H}_{Ln}{}^0$ for liquid Cu–Ln alloys with atomic volume ratio of components.

that the positive term of the mixing enthalpy almost cancels the negative contribution to ΔH. Thus we may safely calculate the concentration dependence in the Cu–Ba system using some regular solution models which take into account mainly the atomic volume differences of components in the binary mixture.

Earlier Lück and Predel [19] successfully applied a modified regular solution model in which the molar fractions x_i were replaced by the atomic surface area concentrations $x_{s,i}$ ($x_{s,i} = x_i r_i^2 / \sum_i x_i r_i^2$, where r_i is the atomic radius of pure component i to describe the mixing enthalpies in systems with appreciable difference in the atomic sizes. The integral enthalpy of mixing results in the following expression:

$$\Delta H = C^{reg} \frac{x_1 x_2}{[x_1(r_1/r_2) + x_2(r_2/r_1)]^2} \qquad (2)$$

We have attempted to describe the integral mixing enthalpy in the Cu–Ba system by this formula. Figure 7(a) shows that the experimental data are well represented by the curve for which $C^{reg} = 6.2$ kJ mol^{-1}.

Another model applied to systems with a large atomic size difference is the well-known Flory model [20]. Assuming that the term which is not an explicit function of T in the Flory expression for ΔG^{mix} is the enthalpy of mixing, we obtain the following expression for ΔH:

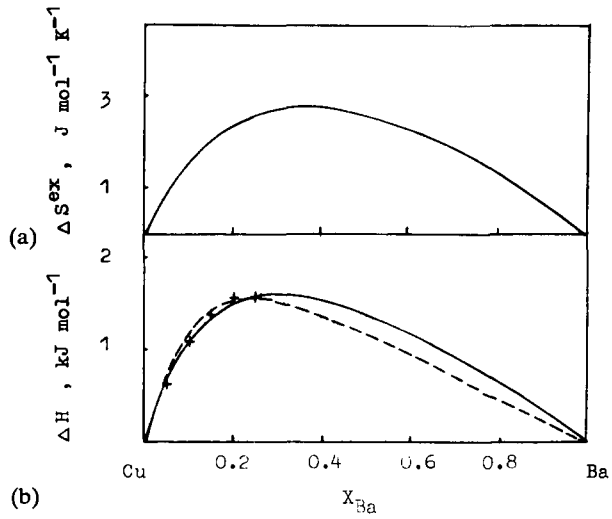

Fig. 7. (a) Integral excess entropies and (b) enthalpies for liquid Cu–Ba alloys: +, experimental data for ΔH; – – –, values calculated from eqn. (2); ——, values calculated from eqn. (3).

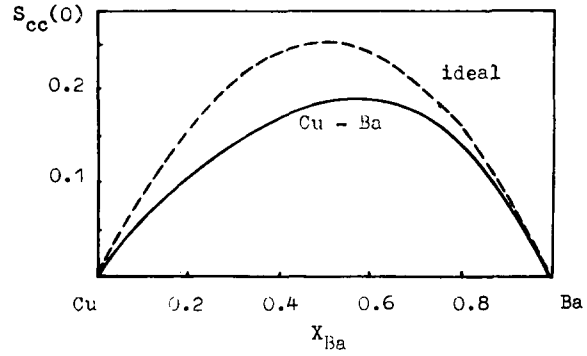

Fig. 8. Correlation fluctuation function $S_{CC}(0)$ for Cu–Ba melts and for an ideal solution.

$$\Delta H = \frac{W x_1(1-x_1)}{1-\beta x_1} \tag{3}$$

where W is the interchange energy, x_1 is the molar fraction of the first component, $\beta=(r-1)/r$ and r is the component volume ratio v_2/v_1.

It was found that our experimental data can be well represented by eqn. (3) with $W=3.3$ kJ mol^{-1}, $\Delta\bar{H}^0_{Ba}$ obtained by differentiation of (3) being in agreement ($\Delta\bar{H}^0_{Ba}=W/(1-\beta)=17.3$ kJ mol^{-1}) with the experimental value within error limits.

The values of ΔS^{ex} and ΔG in the Cu–Ba system apparently can also be satisfactorily described by the Flory model. The excess Flory entropy of mixing is given in Fig. 7(b). The maximum ΔS^{ex} is in agreement with the values for other copper systems given in ref. 21, where Predel and Sandig have considered the influence of the size factor d ($=2(v_1-v_2)/(v_1+v_2)$) on the maximum positive values of ΔS^{ex} for some copper alloys.

By considering that the thermodynamic properties of the Cu–Ba system are well represented by the Flory model, we have also calculated the concentration fluctuation function $S_{CC}(0)$ introduced by Bhatia and Thornton [22]. Following ref. 20, $S_{CC}(0)$ is given in the following form in this case:

$$S_{CC}(0) = \frac{x_1(1-x_1)}{1-x_1(1-x_1)f(x_1)} \tag{4}$$

$$f(x_1) = \frac{x_1+[(2/\beta^3)(1-\beta)\omega-(1/\beta)]}{[(1/\beta)-x_1]^3} \tag{5}$$

where $\omega=W/RT$.

The results of the $S_{CC}(0)$ calculation for the Cu–Ba system ($\beta=0.81$; $\omega=0.26$) are given in Fig. 8, which shows that $S_{CC}(0)$ is less than the values for an ideal solution.

Finally, the data on the mixing enthalpies obtained in present investigation complete the series of experimental studies on Cu–Ln liquid alloys. Despite the progress in theoretical calculations, direct calorimetric measurements are the most reliable source of thermochemical information on rare earth alloys. However, in the case of limited applicability of traditional methods the combination of experiments and model simulations appears to be most acceptable. Such a combination allows one to forecast the thermochemical properties of alloys over the total concentration region.

References

1 I. S. Watanabe and O. J. Kleppa, *Metall. Trans. B, 15* (1985) 357.
2 V. T. Witusiewicz and M. I. Ivanov, *Rep. Acad. Sci. Ukr. B,* (11) (1987) 30.
3 M. A. Turchanin and I. V. Nikolaenko, *Russ. High Temp. Phys., 27* (1989) 1090.
4 V. V. Berezutski, M. I. Ivanov and G. M. Lukashenko, *Proc. Conf. on the Physical Chemistry of the Alloy Industry, Alma-Ata, 1990,* 1990, pp. 23–24.
5 M. I. Ivanov and V. T. Witusiewicz, *J. Alloys Comp., 186* (1992) 255.
6 B. Predel, I. Arpshofen and M. J. Pool, *Thermochim. Acta, 22* (1978) 211.
7 R. Hultgren, P. D. Desai, T. D. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman, *Selected Values of the Thermodynamic Properties of the Elements,* American Society for Metals, Metals Park, OH, 1973.
8 I. V. Nikolaenko and G. I. Batalin, *Theor. Exp. Chem. (Kiev), 23* (1987) 198.
9 I. V. Nikolaenko, M. A. Turchanin, G. I. Batalin and E. A. Beloborodova, *Ukr. Chem. J., 53* (1987) 795.
10 F. Sommer and M. Keita, *J. Less-Common Met., 136* (1987) 95.
11 D. J. Chakrabarti and D. E. Laughlin, *Bull. Alloy Phase Diagr., 5* (1984) 564.

12 P. R. Subramanian and D. E. Laughlin, *Bull. Alloy Phase Diagr., 9* (1988) 331, 342, 398.
13 B. Delley, H. Beck, D. Trautmann and F. Rösel, *J. Phys. F, 9* (1979) 505.
14 B. Delley and H. Beck, *J. Phys. F, 9* (1979) 517.
15 A. K. Niessen, F. R. de Boer, R. Boom, P. F. de Châtel, W. C. M. Mattens and A. R. Miedema, *CALPHAD, 7* (1983) 51.
16 M. V. Michailovskaya and V. S. Sudavtsova, *Metally (Rep. Sov. Acad. Sci.),* (6) (1991) 32.
17 F. Sommer, *Acta Metall., 21* (1973) 1289.
18 M. Clyde Day, Jr., and J. Selbin, *Theoretical Inorganic Chemistry,* Reinhold, New York, 1969.
19 R. Lück and B. Predel. *Z. Metallkd., 76* (1985) 684.
20 A. B. Bhatia and N. H. March, *J. Phys. F, 5* (1975) 1100.
21 B. Predel and H. Sandig, *Z. Metallkd., 60* (1969) 209.
22 A. B. Bhatia and D. E. Thornton, *Phys. Rev. B, 2* (1970) 3004.