

M. Ivanov et al.: Enthalpies of mixing in binary Cu–Eu and ternary Al–Cu–Eu liquid alloys

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## Enthalpies of mixing in binary Cu–Eu and ternary Al–Cu–Eu liquid alloys

The enthalpies of mixing in liquid alloys of the binary Cu–Eu and ternary Al–Cu–Eu systems were determined over a wide range of compositions by means of isoperibolic calorimetry in the temperature range 1300–1450 K. The enthalpies of mixing in the Cu–Eu system demonstrate small exothermic effects ( $\Delta H_{\min} = -4.1 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$  at  $x_{\text{Cu}} = 0.70$ ). The measurements for the liquid ternary Al–Cu–Eu alloys were performed along five sections ( $x_{\text{Cu}}/x_{\text{Eu}} = 0.70/0.30$ ;  $0.50/0.50$  and  $0.27/0.73$  for  $x_{\text{Al}}$  changed from 0 up to 0.30 and  $x_{\text{Al}}/x_{\text{Eu}} = 0.20/0.80$  and  $0.47/0.53$  for  $x_{\text{Cu}}$  changed from 0 up to 0.30). The enthalpies of mixing in the ternary system were found to be exothermic and increasing in absolute values from the Al corner towards the  $\text{Al}_{0.40}\text{Cu}_{0.60}\text{–Al}_{0.60}\text{Eu}_{0.40}$  section and from the constituent binary Cu–Eu system towards the same section. The minimum value of the integral enthalpy of mixing is expected in the vicinity of the  $\text{Al}_{0.6}\text{Eu}_{0.4}$  composition of the binary constituent Al–Eu system (about  $-23.00 \text{ kJ} \cdot \text{mol}^{-1}$ ).

**Keywords:** Aluminium; Copper; Europium; Calorimetry; Enthalpy of mixing

### 1. Introduction

The thermodynamic properties of liquid aluminium alloys with transition and the rare-earth metals are being studied quite intensively, since the data on the thermodynamics of liquid phase are important for thermodynamic description of phase diagrams of the corresponding systems. Information on phase diagrams is important both for materials science re-

search and for monitoring and controlling the processes of manufacturing and production of these alloys. Additives of lanthanides, including europium, to aluminium and its alloys with copper and other transition metals improve the mechanical properties of the materials, contribute to improvement of electrical and to the appearance of interesting magnetic properties [1–3]. At the same time, liquid alloys containing europium remain the least studied among lanthanide alloys and require further systematic investigation. In this work, the enthalpies of mixing of liquid alloys of the Cu–Eu binary system and the Al–Cu–Eu ternary system are studied.

The first experimental results on the determination of the enthalpies of mixing ( $\Delta H$ ) in the Cu–Eu melts were obtained by means of high temperature calorimetry at 1480 K only in the range of compositions rich in copper ( $x_{\text{Cu}} < 0.35$ ) and showed small exothermic effects with a tendency to change the sign of the partial enthalpy of mixing of europium ( $\Delta \bar{H}_{\text{Eu}}$ ) with further increasing of Eu concentration [4]. In an earlier paper Zhang et al. [5] assessed the Cu–Eu and Cu–Yb binary systems with the CALPHAD method using among others the mixing enthalpy data from the Ref. [4]. Calculated integral enthalpies of mixing at 1480 K [5] are in good agreement with the basic data of paper [4]. However, the general view of the integral enthalpy curve given in [5] indicates unusual concentration dependence of unknown partial enthalpy  $\Delta \bar{H}_{\text{Cu}}$ , the latter still remains unexplored and should be studied calorimetrically.

The enthalpies of mixing in liquid alloys of the binary Al–Eu system were recently measured calorimetrically at 1573 K over the entire composition range [6]. The results of these measurements indicate rather significant exothermic values with a minimum of the integral enthalpy of

$-23 \text{ kJ} \cdot \text{mol}^{-1}$  at  $x_{\text{Eu}} = 0.4$ , which, according to the authors, may be connected with the existence of short-range order in the melt due to unlike atoms associates formation. The resulting interpolating equation for the integral enthalpy of mixing ( $\text{kJ} \cdot \text{mol}^{-1}$ ) at 1573 K was represented in [6] as follows ( $x = x_{\text{Eu}}$ ):

$$\Delta H = 224.21x^5 - 601.18x^4 + 489.52x^3 - 15.66x^2 - 96.88x.$$

Moreover, the enthalpies of formation of solid phases in the Al–Eu system also indicate large exothermic effects of alloy formation. Thus, for the  $\text{Al}_2\text{Eu}$  compound (the most stable one in the Al–Eu system) the formation enthalpy has been reported to be  $-36.0 \text{ kJ} \cdot \text{mol}^{-1}$  [7].

A great number of research works are devoted to the study of the thermodynamic properties of liquid alloys of the Al–Cu system [8–10]. According to the latest and the most complete thermodynamic assessment of the binary Al–Cu system [11] the integral enthalpy of mixing in this system ( $\text{kJ} \cdot \text{mol}^{-1}$ ) can be computed neglecting its temperature dependence according to this expression from Ref. [10] ( $x = x_{\text{Al}}$ ):

$$\Delta H = x \cdot (1 - x) \cdot (-75.6 - 63.8x + 231.8x^2 - 130.6x^3).$$

Thereby, significant negative values of the enthalpy of mixing are observed for Al–Cu melts. The extreme  $\Delta H$  value is  $-17.4 \text{ kJ} \cdot \text{mol}^{-1}$  at  $x_{\text{Al}} = 0.4$ .

The phase diagrams of all three constituent binary systems are characterised by the existence of a great number of intermetallic compounds [12], which indicates a significant chemical interaction of the components. As to the ternary Al–Cu–Eu system, its phase diagram and thermodynamic properties of corresponding alloys have not been studied before.

The aim of the present investigation is to determine calorimetrically the enthalpies of mixing of liquid alloys of the ternary Al–Cu–Eu system. As the first step, we performed calorimetric determination of the enthalpies of mixing in the constituent binary Cu–Eu system over the entire composition range both for alloys with a high copper content and for those with a high europium content. Evidently, the existence of a large number of binary compounds in the Cu–Eu phase diagram is somewhat inconsistent with positive  $\Delta \bar{H}_{\text{Eu}}$  values obtained at  $x_{\text{Eu}} > 0.3$  in the previous study [4]. Therefore, it was decided to study the enthalpies of mixing in the Cu–Eu system within the whole composition range. We performed the measurements for the europium-rich liquid alloys for the first time and have checked the results obtained previously for the copper-rich liquid alloys.

## 2. Experimental procedure

The enthalpies of mixing for the Cu–Eu and Al–Cu–Eu liquid alloys were determined by means of isoperibolic calorimetry. The experiments were carried out in a high temperature solution calorimeter in purified helium atmosphere under a pressure of  $2 \cdot 10^5 \text{ Pa}$  in the temperature interval from 1300 to 1450 K. The apparatus and experimental technique were similar to those employed in the previous investigations [4, 13]. The purity of elements used in the experiments was 99.83% for Eu, 99.99% for Cu and Al, 99.96% for Mo (calibrating material). Molybdenum cruci-

bles were used as melt containers in the experiments from the side of pure europium, otherwise alumina crucibles lined with yttrium oxide and thermally treated at 1500 K were used. Europium was mechanically treated just before experiments and stored in petroleum ether to prevent oxidation; europium samples were prepared in a glove box filled with purified helium. The partial enthalpies of mixing of the components were studied at rather low temperature (1313 K) for europium-rich alloys to prevent strong evaporation of Eu from its melts. This lanthanide metal is characterised by high vapour pressure (about  $10^3 \text{ Pa}$  at 1300 K and  $10^4 \text{ Pa}$  at 1450 K) according to the reference data [14, 15]. For the alloys with the mole fraction of europium  $x_{\text{Eu}} < 0.5$  the experimental values of the enthalpies of mixing were obtained at 1400–1450 K. The registered weight loss was observed only for the europium rich melts and was about 5% of total mass of an alloy. Therefore, it has been attributed to europium (the only volatile component in the Cu–Eu and Al–Cu–Eu melts) and taken into account while computing alloy compositions.

The partial heats of mixing were measured in the process of successive introduction of metal samples (Eu, Cu and Al) taken at 298 K (masses within 0.01–0.03 g) into the calorimetric bath (a liquid metal or an alloy, placed in an alumina or molybdenum crucible). The initial mass of a metal in the bath was in the range from 1.5 to 3 g. The change in the alloy concentration after each addition was less than 1.5 at.%. Consequently, we can determine the partial molar enthalpies with sufficient accuracy.

The experimental method is based on the measurement of the temperature difference  $\Delta T$  (temperature measurements were carried out with WRe5/WRe20 thermocouples) between the sample and the reference specimen (a crucible contained W), plotted as a function of temperature relaxation time ( $t$ ).

The resulting heat balance is:

$$k \int \Delta T(t) dT = \Delta H_{i,298}^T + \Delta \bar{H}_i \quad (1)$$

where  $k$  is the molar thermal equivalent of the calorimeter,  $\Delta H_{i,298}^T$  is the enthalpy change for a sample heated (per 1 mole of a metal dropped into the bath) from 298 K to the temperature of liquid bath, taken from Ref. [16],  $\Delta \bar{H}_i$  is the unknown partial molar enthalpy of mixing of component  $i$ . The standard values of  $\Delta H_{i,298}^T$  for the metals used in the experiments always contained a contribution from the enthalpy of fusion of a component even when its melting temperature was higher than that of the experimental procedure. Liquid components have been taken as the reference state.

The thermal equivalent of the calorimeter was determined in calibrating droppings at the beginning and at the end of each experimental series by using the same component as that in the bath and molybdenum, respectively. We assumed that there was a linear composition dependence for the  $k$  in all experimental series.

The set of the experimental data points for each component, computed from Eq. (1), was treated statistically (in the form of a partial  $\alpha$ -function defined as  $\alpha_i = \Delta \bar{H}_i (1 - x_i)^{-2}$ ) by a least-squares analysis using Forsythe orthogonal polynomials and applying the  $F$ -test for a correct choice of polynomial degree [17]. The  $\alpha_i$  function of the component  $i$  was

represented as a polynomial series with polynomial coefficients  $q_j$  as follows:

$$\alpha_i = q_0 + q_1x_i + q_2x_i^2 + \dots + q_jx_i^j + \dots \quad (2)$$

For the binary Cu–Eu system the calculation procedure based on the Darken method [18] of integration of the Gibbs–Duhem equation gives the smoothed values of both the partial enthalpies of mixing of the components and the integral enthalpy of mixing (which is computed as  $\Delta H = (1 - x_i) \cdot \int_{x_i=0}^{x_i} \alpha_i dx_i$ ) with confidence intervals equal to twice the standard deviation of the corresponding approximating function.

For the ternary Al–Cu–Eu system the partial molar enthalpies  $\Delta \bar{H}_{Al}$  were measured along three sections of the concentration triangle with a constant molar fraction ratio  $x_{Cu}/x_{Eu}$  for the other two components. Also the partial molar enthalpies  $\Delta \bar{H}_{Cu}$  were measured along two sections with a constant  $x_{Al}/x_{Eu}$  ratio. To obtain the partial molar enthalpies of the components in the ternary system small samples of aluminium or copper were introduced into a calorimetric bath containing binary melt of a selected component ratio.

For the ternary system the Darken method of integration of the Gibbs–Duhem equation gives the following expression for the integral enthalpy of mixing:

$$\Delta H = (1 - x_3) \cdot \left( \int_{x_3=0}^{x_3} \alpha_3 dx_3 + \Delta H_{x_3=0} \right)_{x_1/x_2} \quad (3)$$

where  $\Delta H_{x_3=0}$  is the integral molar enthalpy of mixing of binary  $Me_1$ – $Me_2$  liquid alloy (with selected constant  $x_1/x_2$  ratio of the molar fractions of the first and second component).

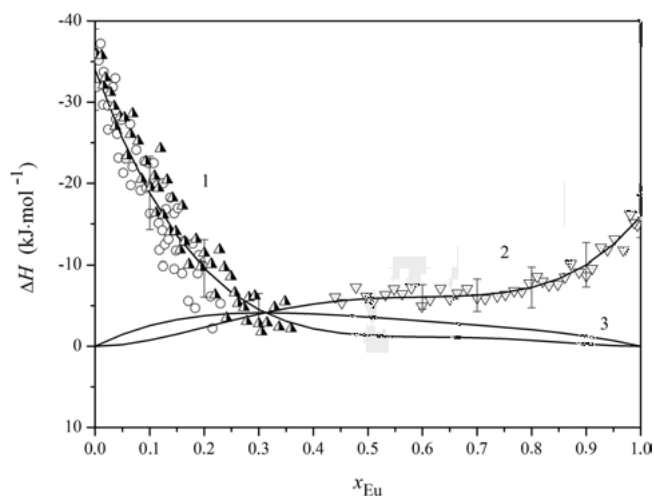


Fig. 1. Enthalpies of mixing in the Cu–Eu liquid alloys at 1300–1400 K: full curves – calculated self-consistent values (1 –  $\Delta \bar{H}_{Eu}$ ; 2 –  $\Delta \bar{H}_{Cu}$ ; 3 –  $\Delta H$ ); triangles and circles – experimental data points of the present investigation and from Ref. [4], correspondingly.

### 3. Experimental results

#### 3.1. The Cu–Eu system

The enthalpies of mixing for the liquid Cu–Eu alloys were measured within the whole concentration interval at 1313 K (for the Eu-rich composition region) and at 1400 K (for the Cu-rich one). The experimental data and computed smoothing curves are given in Fig. 1. In addition, the experimental data points for this system are listed in Appendix A (Table A1). In order to obtain a coherent expression for the enthalpies of mixing across the whole composition region the two branches of the integral  $\alpha$ -function ( $\alpha = \Delta H \cdot x^{-1}(1 - x)^{-1}$ ) computed from both the sides of pure components were treated simultaneously producing the smoothed  $\Delta H$  curve. It should be mentioned that in performing the procedure of statistical treatment we used not only the present study experimental  $\Delta \bar{H}_{Eu}$  data points, but also the data of the previous paper [4] excluding the last ten experimental data points demonstrating small endothermic values of  $\Delta \bar{H}_{Eu}$ . The endothermic  $\Delta \bar{H}_{Eu}$  does not correlate with the Cu–Eu phase diagram and with the present data for  $\Delta \bar{H}_{Cu}$  and cannot be regarded as reliable. Perhaps the positive data points for  $\Delta \bar{H}_{Eu}$  were due to certain experimental difficulties at the end of the experimental series for melts with high europium content.

Finally, the resulting interpolating equation for the integral enthalpy of mixing ( $\text{kJ} \cdot \text{mol}^{-1}$ ) for the Cu–Eu liquid alloys at 1300–1400 K can be represented as follows ( $x = x_{Cu}$ ):

$$\Delta H = x \cdot (1 - x) \cdot (-15.9 + 24.1x - 42.2x^2)$$

The partial and integral enthalpies of mixing for the Cu–Eu liquid alloys with corresponding confidence intervals are listed in Table 1. The integral enthalpy of mixing is slightly negative within the whole concentration region and reaches the minimum  $\Delta H_{\min} = -4.1 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$  at around  $x_{Cu} = 0.7$ .

#### 3.2. The Al–Cu–Eu ternary system

The partial enthalpies of mixing of aluminium in the liquid Al–Cu–Eu alloys were measured along three sections with fixed concentration ratios  $x_{Cu}/x_{Eu}$  of 0.27/0.73, 0.50/0.50, and 0.70/0.30 up to an aluminium content of about  $x_{Al} = 0.3$  at 1313 K (the first section) and 1400 K (the other

Table 1. Mixing enthalpies of the Cu–Eu liquid alloys at 1313–1400 K ( $\text{kJ} \cdot \text{mol}^{-1}$ ) computed from smoothed  $\alpha$ -function.

$x_{Cu}$	$\Delta H$	$\Delta \bar{H}_{Cu}$	$\Delta \bar{H}_{Eu}$
0	0	$-15.9 \pm 1.5$	0
0.1	$-1.3 \pm 0.1$	$-10.0 \pm 0.6$	$-0.3 \pm 0.04$
0.2	$-2.0 \pm 0.2$	$-7.2 \pm 0.5$	$-0.7 \pm 0.1$
0.3	$-2.6 \pm 0.2$	$-6.3 \pm 0.4$	$-1.0 \pm 0.1$
0.4	$-3.1 \pm 0.2$	$-6.1 \pm 0.3$	$-1.2 \pm 0.1$
0.5	$-3.6 \pm 0.3$	$-5.9 \pm 0.3$	$-1.3 \pm 0.3$
0.6	$-4.0 \pm 0.5$	$-5.2 \pm 0.3$	$-2.2 \pm 0.8$
0.7	$-4.1 \pm 0.5$	$-4.0 \pm 0.3$	$-4.5 \pm 0.9$
0.8	$-3.9 \pm 0.2$	$-2.3 \pm 0.03$	$-9.6 \pm 0.9$
0.9	$-2.6 \pm 0.1$	-0.8	$-18.8 \pm 1.0$
1.0	0	0	$-34.0 \pm 2.7$

two sections). The partial enthalpies of mixing of copper in the liquid Al–Cu–Eu alloys were measured along two sections with fixed concentration ratios  $x_{\text{Al}}/x_{\text{Eu}}$  of 0.20/0.80 and 0.47/0.53 up to a copper content of about  $x_{\text{Cu}} = 0.3$  at 1400 and 1450 K, correspondingly. The experimental data points of  $\Delta\bar{H}_{\text{Al}}$  and  $\Delta\bar{H}_{\text{Cu}}$  with the smoothing curves for all studied sections are shown in Fig. 2 and Fig. 3, respectively. The experimental data points are also listed in Appendix A (Tables A2 and A3). The partial enthalpies of

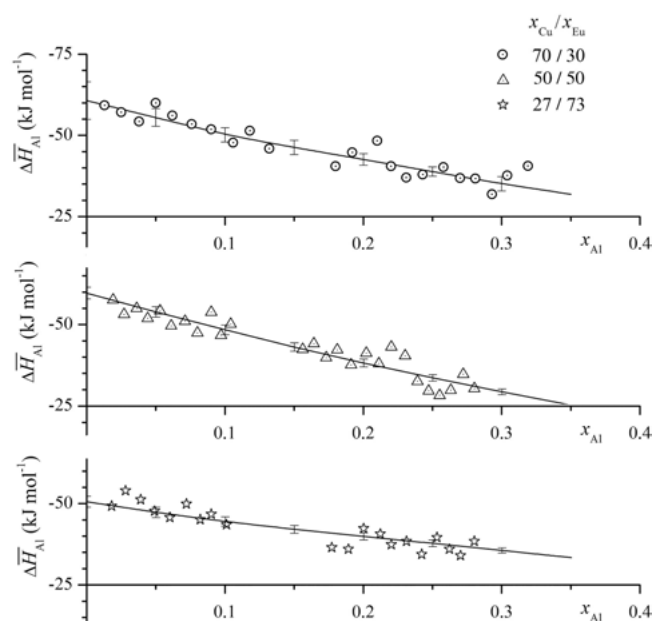


Fig. 2. Experimental data points and approximating functions for the partial mixing enthalpies of Al at 1313–1400 K along the studied composition sections with constant  $x_{\text{Cu}}/x_{\text{Eu}}$  ratio.

mixing at infinite dilution  $\Delta\bar{H}_{\text{Al}}^{\infty}$  for all studied sections demonstrate the same order of magnitude and vary from  $-60.7 \pm 5.8 \text{ kJ} \cdot \text{mol}^{-1}$  for the section with  $x_{\text{Cu}}/x_{\text{Eu}} = 0.70/0.30$  to  $-50.6 \pm 1.7 \text{ kJ} \cdot \text{mol}^{-1}$  for that with  $x_{\text{Cu}}/x_{\text{Eu}} = 0.27/0.73$ . The partial enthalpies of mixing  $\Delta\bar{H}_{\text{Cu}}$  measured for two studied sections with  $x_{\text{Al}}/x_{\text{Eu}} = 0.47/0.53$  and 0.20/0.80 are also of the same order of magnitude, but they are less exothermic than those of Al and reach zero at  $x_{\text{Cu}} \approx 0.3$ . The smoothed values of the partial enthalpies of aluminium and copper and the integral enthalpy of mixing for the liquid Al–Cu–Eu alloys with corresponding confidence intervals are listed in Table 2. The integral enthalpies of mixing computed along the investigated sections are repre-

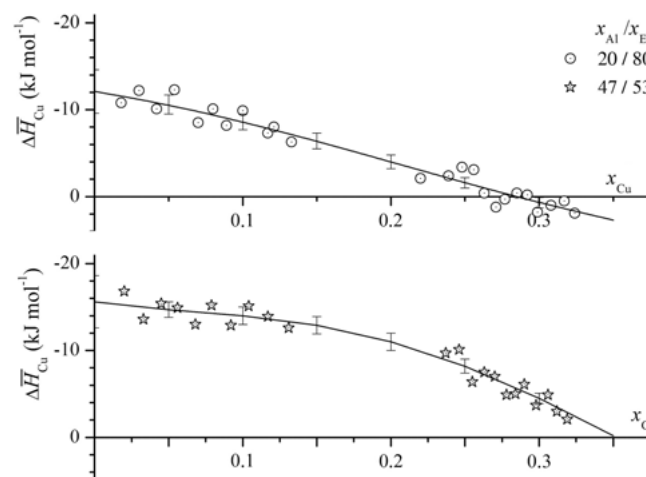


Fig. 3. Experimental data points and approximating functions for the partial mixing enthalpies of Cu at 1400–1450 K along the studied composition sections with constant  $x_{\text{Al}}/x_{\text{Eu}}$  ratio.

Table 2. The enthalpies of mixing (partial for Al, partial for Cu and integral for the Al–Cu–Eu liquid alloys) at 1300–1450 K ( $\text{kJ} \cdot \text{mol}^{-1}$ ).

$x_{\text{Al}}$	$\Delta\bar{H}_{\text{Al}}$ for section with $x_{\text{Cu}}/x_{\text{Eu}}$			$x_{\text{Cu}}$	$\Delta\bar{H}_{\text{Cu}}$ for section $x_{\text{Al}}/x_{\text{Eu}}$	
	0.27/0.73	0.50/0.50	0.70/0.30		0.20/0.80	0.47/0.53
	$T = 1313 \text{ K}$	$T = 1400 \text{ K}$	$T = 1400 \text{ K}$		$T = 1400 \text{ K}$	$T = 1450 \text{ K}$
0	$-50.6 \pm 1.7$	$-59.7 \pm 1.8$	$-60.7 \pm 5.8$	0	$-12.1 \pm 2.5$	$-15.6 \pm 3.0$
0.05	$-47.3 \pm 1.6$	$-53.9 \pm 1.6$	$-55.4 \pm 2.7$	0.05	$-10.6 \pm 1.1$	$-14.7 \pm 0.9$
0.10	$-44.5 \pm 1.4$	$-48.4 \pm 1.5$	$-50.6 \pm 2.2$	0.10	$-8.6 \pm 0.9$	$-14.0 \pm 1.0$
0.15	$-42.1 \pm 1.2$	$-43.1 \pm 1.3$	$-46.3 \pm 2.2$	0.15	$-6.4 \pm 0.9$	$-12.9 \pm 1.0$
0.20	$-39.9 \pm 1.1$	$-38.2 \pm 1.2$	$-42.4 \pm 1.8$	0.20	$-4.0 \pm 0.8$	$-11.0 \pm 1.0$
0.25	$-37.8 \pm 1.0$	$-33.6 \pm 1.0$	$-38.7 \pm 1.4$	0.25	$-1.6 \pm 0.6$	$-8.2 \pm 0.8$
0.30	$-35.6 \pm 0.8$	$-29.3 \pm 0.9$	$-35.2 \pm 2.2$	0.30	$0.7 \pm 0.6$	$-4.5 \pm 0.6$
$x_{\text{Al}}$	$-\Delta H$ for section with $x_{\text{Cu}}/x_{\text{Eu}}$			$x_{\text{Cu}}$	$-\Delta H$ for section $x_{\text{Al}}/x_{\text{Eu}}$	
	0.27/0.73	0.50/0.50	0.70/0.30		0.20/0.80	0.47/0.53
	0	$-2.5 \pm 0.7$	$-3.6 \pm 1.2$		$-4.1 \pm 0.7$	0
0.05	$-4.8 \pm 0.7$	$-6.3 \pm 1.2$	$-6.8 \pm 0.8$	0.05	$-10.0 \pm 0.8$	$-20.6 \pm 2.1$
0.10	$-6.9 \pm 0.8$	$-8.6 \pm 1.2$	$-9.3 \pm 0.9$	0.10	$-10.0 \pm 0.8$	$-20.3 \pm 2.1$
0.15	$-9.0 \pm 0.8$	$-10.7 \pm 1.2$	$-11.4 \pm 1.0$	0.15	$-9.9 \pm 0.8$	$-19.9 \pm 2.1$
0.20	$-10.8 \pm 0.8$	$-12.4 \pm 1.3$	$-13.4 \pm 1.0$	0.20	$-9.6 \pm 0.8$	$-19.5 \pm 2.1$
0.25	$-12.6 \pm 0.8$	$-13.9 \pm 1.3$	$-15.1 \pm 1.0$	0.25	$-9.2 \pm 0.8$	$-18.8 \pm 2.0$
0.30	$-14.2 \pm 0.9$	$-15.1 \pm 1.3$	$-16.5 \pm 1.5$	0.30	$-8.6 \pm 0.8$	$-18.0 \pm 1.9$

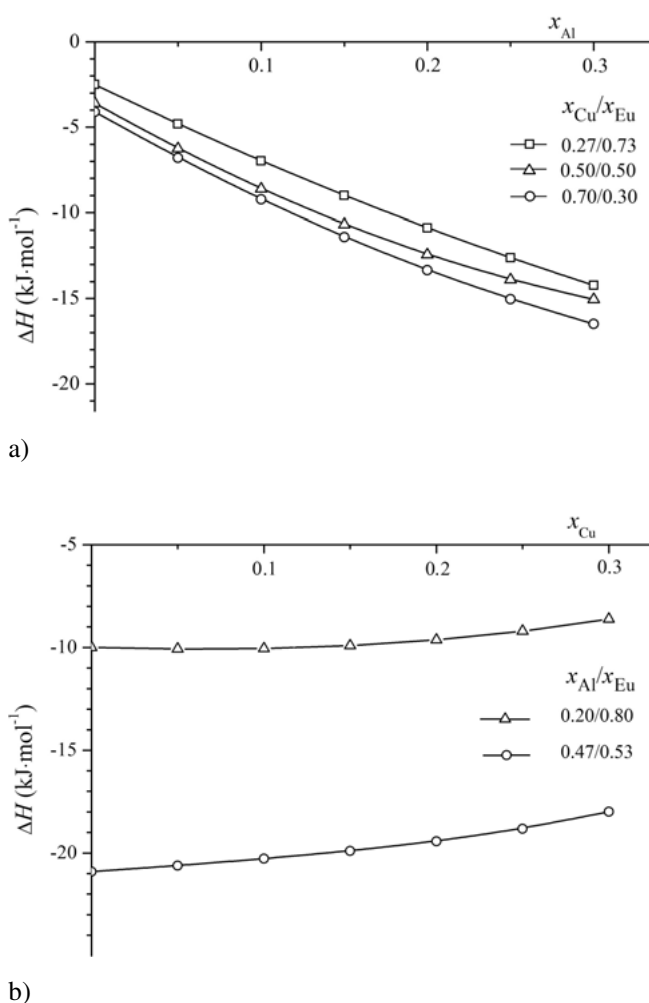


Fig. 4. Integral enthalpies of mixing in the Al–Cu–Eu liquid system at 1300–1450 K along the studied composition sections with constant: (a)  $x_{\text{Cu}}/x_{\text{Eu}}$ , and (b)  $x_{\text{Al}}/x_{\text{Eu}}$  ratio.

sented in Fig. 4. The approximating polynomials of the integral enthalpies of mixing along the investigated sections are listed in Table 3.

We also described our experimental data on the integral enthalpies by a least squares fit to the Redlich–Kister–Muggianu polynomial [19] which is given by the following equation:

$$\begin{aligned} \Delta H(x_{\text{Al}}, x_{\text{Cu}}, x_{\text{Eu}}) = & x_{\text{Al}}x_{\text{Cu}} \sum_{i=0}^n {}^iL_{\text{Al–Cu}}(x_{\text{Al}} - x_{\text{Cu}})^i \\ & + x_{\text{Cu}}x_{\text{Eu}} \sum_{i=0}^n {}^iL_{\text{Cu–Eu}}(x_{\text{Cu}} - x_{\text{Eu}})^i \\ & + x_{\text{Al}}x_{\text{Eu}} \sum_{i=0}^n {}^iL_{\text{Al–Eu}}(x_{\text{Al}} - x_{\text{Eu}})^i \\ & + x_{\text{Al}}x_{\text{Cu}}x_{\text{Eu}}(x_{\text{Al}} {}^0L_{\text{Al–Cu–Eu}} \\ & + x_{\text{Cu}} {}^1L_{\text{Al–Cu–Eu}} + x_{\text{Eu}} {}^2L_{\text{Al–Cu–Eu}}) \quad (4) \end{aligned}$$

where  ${}^iL_{\text{Al–Cu}}$ ,  ${}^iL_{\text{Cu–Eu}}$  and  ${}^iL_{\text{Al–Eu}}$  are the coefficients of the Redlich–Kister polynomial for the constituent binary systems,  $n$  is the power of this polynomial,  ${}^0L_{\text{Al–Cu–Eu}}$ ,  ${}^1L_{\text{Al–Cu–Eu}}$  and  ${}^2L_{\text{Al–Cu–Eu}}$  are the ternary interaction parameters. The Redlich–Kister parameters for the binary systems were obtained by conversion of corresponding polynomial power series given in Section 1 into the Redlich–Kister polynomials. The complete set of binary parameters is listed in Table 4.

The calculation of the mixing enthalpies in the Al–Cu–Eu ternary system using the regular Redlich–Kister–Muggianu model without taking into account a specific ternary term (the last line in Eq. (4)) showed that the experimental enthalpies of mixing are less exothermic than the calculated ones. Systematic deviations of the calculated integral enthalpies towards the more negative values were observed for all investigated sections. Evidently there is a specific endothermic “ternary contribution” to the energy of formation of ternary alloys in this system. The ternary parameters obtained as a result of least square fitting procedure are given in Table 4.

Table 3. The approximating polynomials of the integral enthalpies of mixing  $\Delta H$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) for corresponding composition sections in the Al–Cu–Eu ternary system.

Section $x_{\text{Cu}}/x_{\text{Eu}}$	Polynomial
0.27/0.73	$\Delta H = (1 - x_{\text{Al}})(-2.5 - 50.6x_{\text{Al}} - 13.9x_{\text{Al}}^2 - 51.2x_{\text{Al}}^3)$
0.50/0.50	$\Delta H = (1 - x_{\text{Al}})(-3.6 - 59.7x_{\text{Al}})$
0.70/0.30	$\Delta H = (1 - x_{\text{Al}})(-4.1 - 60.7x_{\text{Al}} - 4.3x_{\text{Al}}^2 - 31.9x_{\text{Al}}^3)$
Section $x_{\text{Al}}/x_{\text{Eu}}$	Polynomial
0.20/0.80	$\Delta H = (1 - x_{\text{Cu}})(-20.9 - 15.6x_{\text{Cu}} - 2.0x_{\text{Cu}}^2 - 75.0x_{\text{Cu}}^3 + 257.6x_{\text{Cu}}^4)$
0.47/0.53	$\Delta H = (1 - x_{\text{Cu}})(-10.0 - 12.1x_{\text{Cu}} - 0.7x_{\text{Cu}}^2 + 51.2x_{\text{Cu}}^3)$

The integral enthalpies calculated using these ternary interaction parameters agree well with the experimental results within the experimental error limits for all studied sections, consequently we can consider that the Redlich–Kister–Muggianu expression with given ternary interaction parameters is appropriate for calculation of the enthalpies of mixing in the Al–Cu–Eu ternary system across the whole composition triangle. The iso-enthalpy contours calculated using the Redlich–Kister–Muggianu expression with increments of  $2 \text{ kJ} \cdot \text{mol}^{-1}$  are plotted in Fig. 5. The present study experimentally determined integral enthalpies are also given in Fig. 5 for the aim of comparison.

Table 4. The binary and ternary interaction parameters for the integral enthalpy of mixing  $\Delta H$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) in liquid alloys of the Al–Cu–Eu system at 1300–1450 K.

System	Interaction parameter
Al–Cu	${}^0L_{\text{Al–Cu}} = -65.9$
	${}^1L_{\text{Al–Cu}} = 35.0$
	${}^2L_{\text{Al–Cu}} = 9.0$
	${}^3L_{\text{Al–Cu}} = -16.3$
Cu–Eu	${}^0L_{\text{Cu–Eu}} = -14.4$
	${}^1L_{\text{Cu–Eu}} = -9.0$
	${}^2L_{\text{Cu–Eu}} = -10.5$
	${}^3L_{\text{Cu–Eu}} = -10.5$
Al–Eu	${}^0L_{\text{Al–Eu}} = -87.0$
	${}^1L_{\text{Al–Eu}} = -46.5$
	${}^2L_{\text{Al–Eu}} = 10.8$
	${}^3L_{\text{Al–Eu}} = 23.8$
Al–Cu–Eu	${}^0L_{\text{Al–Cu–Eu}} = -66.1$
	${}^1L_{\text{Al–Cu–Eu}} = 116.9$
	${}^2L_{\text{Al–Cu–Eu}} = 39.3$

#### 4. Discussion

The enthalpies of mixing in the Cu–Eu liquid alloys show exothermic effects, being not very large in magnitude. The obtained enthalpy data correlate with the phase diagram of the Cu–Eu system [12], which indicates the existence of four intermetallic compounds, including congruently melting phase  $\text{Cu}_5\text{Eu}$ . This compound is also the most stable in the Cu–Eu system and seems to be responsible for strong asymmetry of the concentration dependence of the enthalpies of mixing (Fig. 1). The concentration dependence of the enthalpies of mixing in the liquid Cu–Eu alloys is quite interesting. The integral enthalpy is extremely asymmetric and exhibits a flattened minimum ( $\Delta H_{\text{min}} = -4.1 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$  at  $x_{\text{Cu}} = 0.70$ ). The exothermic partial enthalpies of copper and europium decrease markedly in the region of dilute solutions, then variation of both the curves vs. composition is quite small, being near equal to zero (for  $\Delta \bar{H}_{\text{Eu}}$ ) or demonstrating small constant values across a large concentration interval ( $\Delta \bar{H}_{\text{Cu}}$ ) (Fig. 1).

The exothermic effects of alloy formation in the liquid Cu–Eu alloys may be traditionally explained by a transfer of Eu valence electrons to more electronegative Cu. For this system electronegativity difference  $\Delta\chi$  of the components is 0.7 in Allred–Rochow scale (Ref. [20]) being favourable for large exothermic effect. However, the Cu–Eu binary system is characterised by extremely large size mismatch of the components  $\Delta\phi$  which can be estimated as follows:  $\Delta\phi = \frac{R_{\text{Eu}} - R_{\text{Cu}}}{R_{\text{Eu}} + R_{\text{Cu}}} \cdot 100 \%$  (where  $R$  is the metallic radius of the corresponding atom taken from Ref. [21] or estimated from the crystal structure data [22]). Size mismatch  $\Delta\phi$  is equal to 22% for the Cu–Eu binary system. Such a big size difference completely compensates for the influence of favourable electronegativity factor, and the observed exothermic effects are quite small.

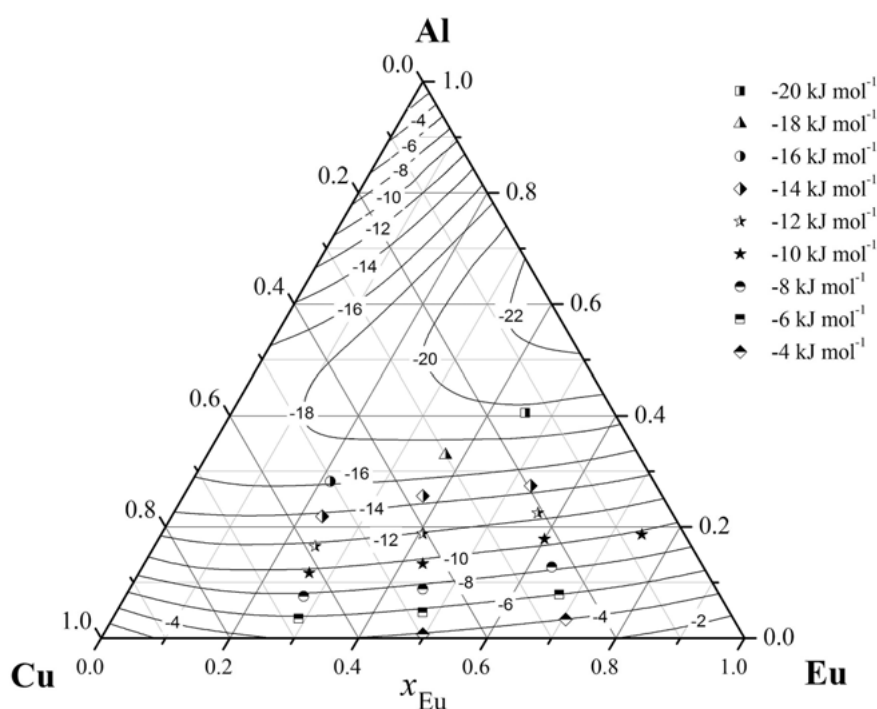


Fig. 5. Integral enthalpy of mixing isolines in the ternary Al–Cu–Eu liquid phase at 1300–1450 K calculated using the Redlich–Kister–Muggianu formula: the experimentally obtained values along the studied composition sections are represented by the corresponding symbols.

It should be also noted that the enthalpies of mixing in the Cu–Eu system are much more endothermic than the enthalpies of mixing of copper with lanthanides such as La or Lu [23–25] which are thoroughly trivalent in their liquid alloys with transition metals. It can be reasonably suggested that europium is divalent in its melts with copper just like with other transition metals as was observed in some previous studies, for example in Ref. [26].

As for the other two constituent binary systems, they demonstrate more exothermic effects of alloy formation mainly since despite less electronegativity difference of components ( $\Delta\chi_{\text{Al–Eu}} = 0.46$ ,  $\Delta\chi_{\text{Al–Cu}} = 0.28$ ) they remain quite significant. At the same time, the size mismatch is less ( $\Delta\varphi_{\text{Al–Eu}} = 16\%$ ;  $\Delta\varphi_{\text{Al–Cu}} = 5.5\%$ ) than in the Cu–Eu system. As a result, the Al–Cu and Al–Eu constituent systems mainly determine the significant component interaction in the Al–Cu–Eu ternary system. The shape of the enthalpy isolines on the concentration triangle demonstrates a gable hill with a gentle slope extending from  $-23 \text{ kJ} \cdot \text{mol}^{-1}$  in the Al–Eu system at  $x_{\text{Al}} = 0.6$  to  $-17 \text{ kJ} \cdot \text{mol}^{-1}$  in the Al–Cu system at  $x_{\text{Al}} = 0.4$ . The exothermic effects of mixing are reduced to zero towards the aluminium corner of the triangle and almost zero towards the Cu–Eu side. The persistence of a positive ternary term found in the studied system apparently indicates a negative effect of the size mismatch between copper and europium atoms on the energy of alloy formation in the Al–Cu–Eu ternary system. Addition of the third component (Eu to the Al–Cu binary system or Cu to the Al–Eu one) destroys the short-range order existing in both these binary alloys and reduces the efficiency of the interaction of the components.

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## Appendix A

Table A1 Experimental data points of the partial enthalpies of mixing of the components in the Cu–Eu system ( $\text{kJ} \cdot \text{mol}^{-1}$ ).

$x_{\text{Eu}}$	$\Delta\bar{H}_{\text{Eu}}$ present work	$x_{\text{Eu}}$	$\Delta\bar{H}_{\text{Eu}}$ from Ref. [4]	$x_{\text{Cu}}$	$\Delta\bar{H}_{\text{Cu}}$
0.003	-35.9	0.003	-31.9	0.006	-14.8
0.012	-35.7	0.007	-35.1	0.012	-15.1
0.015	-32.1	0.010	-37.2	0.019	-16.1
0.019	-33.0	0.015	-29.7	0.032	-11.8
0.028	-31.2	0.016	-33.7	0.048	-13.1
0.035	-29.5	0.024	-29.6	0.061	-11.8
0.037	-27.0	0.025	-26.6	0.073	-12.1
0.046	-28.2	0.033	-31.9	0.089	-9.6
0.054	-28.1	0.037	-32.9	0.104	-8.7
0.059	-23.4	0.039	-27.9	0.113	-9.1
0.065	-26.0	0.041	-26.1	0.126	-10.1
0.069	-28.6	0.043	-23.1	0.139	-8.5
0.079	-25.2	0.049	-27.8	0.152	-7.7
0.085	-20.5	0.052	-21.3	0.168	-7.5
0.093	-22.7	0.057	-23.0	0.180	-8.0
0.102	-19.5	0.065	-27.3	0.190	-8.6
0.109	-20.9	0.066	-19.8	0.204	-7.8
0.112	-16.4	0.069	-22.0	0.218	-6.8
0.116	-19.4	0.076	-24.1	0.232	-6.8
0.12	-24.3	0.084	-19.1	0.248	-6.4
0.125	-16.1	0.091	-22.7	0.263	-6.2
0.132	-20.4	0.094	-19.4	0.285	-5.9
0.137	-14.0	0.099	-22.5	0.298	-6.0
0.142	-18.2	0.101	-16.3	0.318	-7.1
0.148	-14.1	0.107	-20.3	0.336	-6.6
0.156	-11.8	0.108	-22.5	0.350	-5.8
0.16	-17.2	0.114	-19.8	0.367	-7.1
0.164	-12.8	0.117	-15.1	0.386	-5.8
0.172	-10.0	0.118	-11.8	0.401	-4.9
0.185	-13.1	0.124	-14.2	0.420	-7.2
0.194	-9.8	0.125	-20.0	0.437	-6.5
0.2	-11.4	0.126	-9.8	0.452	-7.1
0.213	-10.1	0.128	-12.5	0.468	-6.4
0.22	-6.4	0.130	-16.8	0.490	-5.5
0.228	-11.8	0.135	-13.1	0.503	-6.2
0.237	-9.7	0.138	-18.2	0.522	-7.3
0.241	-3.5	0.145	-16.3	0.548	-5.4
0.249	-8.6	0.146	-9.5	0.560	-6.1
0.256	-6.6	0.148	-11.7		
0.262	-5.3	0.152	-16.9		
0.273	-4.8	0.160	-9.0		
0.278	-3.1	0.163	-12.9		
0.282	-6.0	0.171	-5.6		
0.3	-2.8	0.179	-12.6		
0.293	-6.2	0.184	-4.7		
0.305	-1.8	0.188	-9.0		
0.315	-2.9	0.190	-11.1		
0.329	-4.8	0.198	-9.8		
0.337	-2.4	0.212	-6.1		
0.348	-5.5	0.215	-2.2		
0.359	-2.2	0.230	-5.3		
		0.270	-0.8		



Table A2 Experimental data points of the partial enthalpy of aluminium  $\Delta\bar{H}_{Al}$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) in the Al–Cu–Eu ternary system.

Experimental $\Delta\bar{H}_{Al}$ points for section with $x_{Cu}/x_{Eu}$					
0.27/0.73		0.50/0.50		0.70/0.30	
$x_{Al}$	$\Delta\bar{H}_{Al}$	$x_{Al}$	$\Delta\bar{H}_{Al}$	$x_{Al}$	$\Delta\bar{H}_{Al}$
0.018	–49.3	0.019	–57.6	0.013	–59.2
0.028	–54.0	0.027	–53.1	0.025	–57.1
0.039	–51.3	0.036	–55.0	0.038	–54.3
0.049	–47.7	0.044	–51.9	0.050	–60.0
0.060	–45.8	0.053	–54.2	0.062	–56.1
0.072	–50.0	0.061	–49.6	0.076	–53.5
0.082	–45.1	0.071	–51.0	0.090	–51.9
0.090	–46.8	0.080	–47.4	0.106	–47.7
0.101	–43.5	0.090	–53.8	0.118	–51.4
–	–	0.097	–46.8	0.132	–46.0
0.177	–36.5	0.104	–50.2	–	–
0.189	–37.0	–	–	0.180	–40.5
0.200	–42.4	0.156	–42.4	0.192	–44.7
0.212	–40.7	0.164	–44.1	0.210	–48.4
0.220	–37.4	0.173	–39.8	0.220	–40.6
0.231	–38.5	0.181	–42.2	0.231	–37.0
0.242	–34.4	0.191	–37.6	0.243	–37.9
0.253	–39.6	0.202	–41.2	0.258	–40.2
0.262	–36.0	0.211	–38.0	0.270	–36.9
0.270	–34.0	0.220	–43.1	0.281	–36.7
0.280	–38.4	0.230	–40.4	0.293	–31.9
		0.239	–32.5	0.304	–37.6
		0.247	–29.6	0.319	–40.6
		0.255	–28.2		
		0.263	–29.8		
		0.272	–34.8		
		0.280	–30.4		

Table A3 Experimental data points of the partial enthalpy of copper  $\Delta\bar{H}_{\text{Cu}}$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) in the Al–Cu–Eu system.

Experimental $\Delta\bar{H}_{\text{Cu}}$ points for section with $x_{\text{Al}}/x_{\text{Eu}}$			
0.20/0.80		0.47/0.53	
$x_{\text{Cu}}$	$\Delta\bar{H}_{\text{Cu}}$	$x_{\text{Cu}}$	$\Delta\bar{H}_{\text{Cu}}$
0.018	–10.8	0.020	–16.8
0.030	–12.2	0.033	–13.6
0.042	–10.1	0.045	–15.4
0.054	–12.3	0.056	–14.9
0.070	–8.5	0.068	–13.0
0.080	–10.1	0.079	–15.2
0.089	–8.2	0.092	–12.9
0.100	–9.9	0.104	–15.1
0.117	–7.3	0.117	–13.9
0.121	–8.0	0.131	–12.6
0.133	–6.3	–	–
–	–	0.237	–9.7
0.220	–2.1	0.246	–10.1
0.239	–2.4	0.255	–6.4
0.248	–3.4	0.263	–7.5
0.256	–3.1	0.270	–7.0
0.263	–0.4	0.278	–4.9
0.271	1.2	0.284	–5.0
0.277	0.3	0.290	–6.1
0.285	–0.4	0.298	–3.7
0.292	–0.2	0.306	–4.9
0.299	1.8	0.312	–3.0
0.308	1.0	0.319	–2.1
0.317	0.5		
0.324	1.9		