The ternary system Eu–Cu–Ge at 400°C

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The isothermal section at 400°C of the phase diagram of the system Eu–Cu–Ge was built based on X-ray diffraction and microstructure analysis. The compound $EuCu_2Ge_2$ ($CeAl_2Ga_2$-type structure) was confirmed and its homogeneity region was determined: $EuCu_{2.5-1.65}Ge_{1.5-2.35}$. In addition, three other ternary compounds were found: $EuCuGe$ (HoNiGa-type structure), $EuCu_{0.8-0.5}Ge_{1.2-1.5}$ (AlB_2-type structure), and ~Eu_2Cu_2Ge (unknown structure). The effective valence of Eu in $EuCu_{0.8}Ge_{1.2}$ was found to be 2+. The existence of a binary homogeneity range $Eu_{1-x}Cu_{5+2x}$ was confirmed by complete structure refinements.

Phase diagram / Crystal structure / Effective valence

1. Introduction

The results presented in this paper are part of a systematic investigation of Eu–*T*–Ge systems, where *T* is a transition element. The peculiar properties of europium distinguish this element from the other rare-earth metals. A more thorough knowledge about the interaction of europium with other elements, the conditions under which compounds form, and the crystal structures and properties of these, will make it possible to deduce relations between the properties of compounds and their structure.

The binary systems that delimit the ternary system Eu–Cu–Ge have been studied in the whole concentration range and the corresponding phase diagrams constructed [1]. Four binary compounds exist in the system Eu–Cu [2]. The compound $EuCu_5$ melts congruently at 847°C, whereas $EuCu_2$, EuCu, and Eu_2Cu form *via* peritectic reactions at 597, 537, and 442°C, respectively. In [3] it was noted that the binary compound $EuCu_5$ has a certain homogeneity range. Five binary compounds were found during an investigation of the binary system Eu–Ge [4]. The compounds $EuGe_2$, EuGe, and Eu_3Ge melt congruently at 1030, 1220, and 1215°C, respectively, Eu_3Ge_5 forms peritectically at 1011°C, and Eu_2Ge_3 *via* a peritectoid reaction at 916°C. The compound Eu_3Ge_5 exists only in a limited temperature range (755-1011°C). Two more compounds, Eu_5Ge_3 and Eu_2Ge, have been reported in the same system [5]. The binary system Cu–Ge is characterized by the formation of four phases. Differently from the compounds in the systems Eu–Cu and Eu–Ge (with the exception of $EuCu_5$), the copper germanides have

significant homogeneity ranges (up to 6 at.%). According to the generally accepted phase diagram, the high-temperature phase of approximate composition Cu_3Ge (ε) melts congruently at 747°C and transforms near 650°C, whereas the room-temperature phase of similar composition (ε₁) forms *via* a peritectoid reaction at 636°C. The phases $Cu_{0.85}Ge_{0.15}$ (ζ) and $Cu_{2.5}Ge$ (ε₂) form *via* peritectic reactions at 824 and 698°C, respectively. The latter exists in a limited temperature range (614-698°C).

In this work we present the results of an investigation of the ternary system Eu–Cu–Ge at 400°C. The compound $EuCu_2Ge_2$ was firstly reported in [6]. Its crystal structure belongs to the structure type $CeAl_2Ga_2$.

2. Experimental

The samples were synthesized from high-purity metals (Eu ≥ 98.8 wt.%, Cu ≥ 99.99 wt.%, and Ge ≥ 99.999 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using Ti as a getter and a tungsten electrode. To achieve high efficiency of the interaction between the components, the samples were melted twice. The alloys were then annealed at 400°C in evacuated quartz ampoules for three weeks, and subsequently quenched in cold water.

Phase analysis of 138 samples was performed by X-ray powder diffraction (RKD-57.3, Cr *K* radiation; DRON-2.0, Fe *K*α radiation). The lattice parameters were refined from diffractometer data (DRON-2.0, Fe *K*α radiation; DRON-3.0, Cu *K*α radiation) and

complete crystal structure refinements (diffractometer HZG-4a, Cu *K*α radiation; program DBWS-9807 [7]) were carried out for selected samples. The microstructures were studied visually using a Neophot-30 microscope.

The effective valence of europium was determined by L_{III}-absorption spectroscopy at room temperature.

3. Results and discussion

The crystal structure of the compound $EuCu_5$ was refined from X-ray powder diffraction data of the alloys $Eu_{16.6}Cu_{83.4}$ and $Eu_{18}Cu_{82}$. Experimental details and crystallographic data for this compound, which is best described by the formula $Eu_{1-x}Cu_{5+2x}$ (x = 0-0.07), are given in Table 1, and the atom coordinates, site occupancies and isotropic displacement parameters are listed in Tables 2 and 3. For the stoichiometric composition $EuCu_5$, the structure (space group *P6/mmm*) is described by three fully occupied atom sites (structure type $CaCu_5$ [8]), whereas for the Cu-rich composition $Eu_{0.93(1)}Cu_{5.14(1)}$, vacancies on the Eu site are compensated for by an additional, partly occupied Cu site (structure type $TbCu_7$ [9]). Within the homogeneity region, when the Cu content is increased, Eu atoms are partly (up to 7 %) replaced by Cu-Cu dumb-bells in statistical disorder.

According to the isothermal section of the phase diagram at 400°C, the system Eu–Cu–Ge contains four ternary compounds (Fig. 1, Table 4). The binary compounds of the systems Eu–Cu and Eu–Ge dissolve not more than 5 at.% of the third component. The isothermal section exhibits 17 single-phase, 35 two-phase, and 19 three-phase regions.

The previously reported compound $EuCu_2Ge_2$ [6] with tetragonal $CeAl_2Ga_2$-type structure [12] was confirmed and its homogeneity region determined (Fig. 2). A relatively large region of variable copper and germanium content (from 30 to 47 at.% Ge, *i.e.* 17 at.%) was observed along the isoconcentrate at 20 at.% Eu: $EuCu_{2.5-1.65}Ge_{1.5-2.35}$. The replacement of Cu atoms by Ge atoms is accompanied by an increase of the cell parameter *c*, whereas the cell parameter *a* increases up to the stoichiometric composition $EuCu_2Ge_2$ and then decreases. Atom coordinates and isotropic displacement parameters for this compound at the composition $EuCu_{1.75}Ge_{2.25}$ are presented in Table 5.

The new compound EuCuGe is characterized by a point composition. A complete structure determination showed that the crystal structure belongs to the orthorhombic HoNiGa type [13], which is a branch of the TiNiSi type [14]. The atom coordinates and isotropic displacement parameters for EuCuGe are given in Table 6.

Table 1 Experimental details and crystallographic data for the compound $Eu_{1-x}Cu_{5+2x}$.

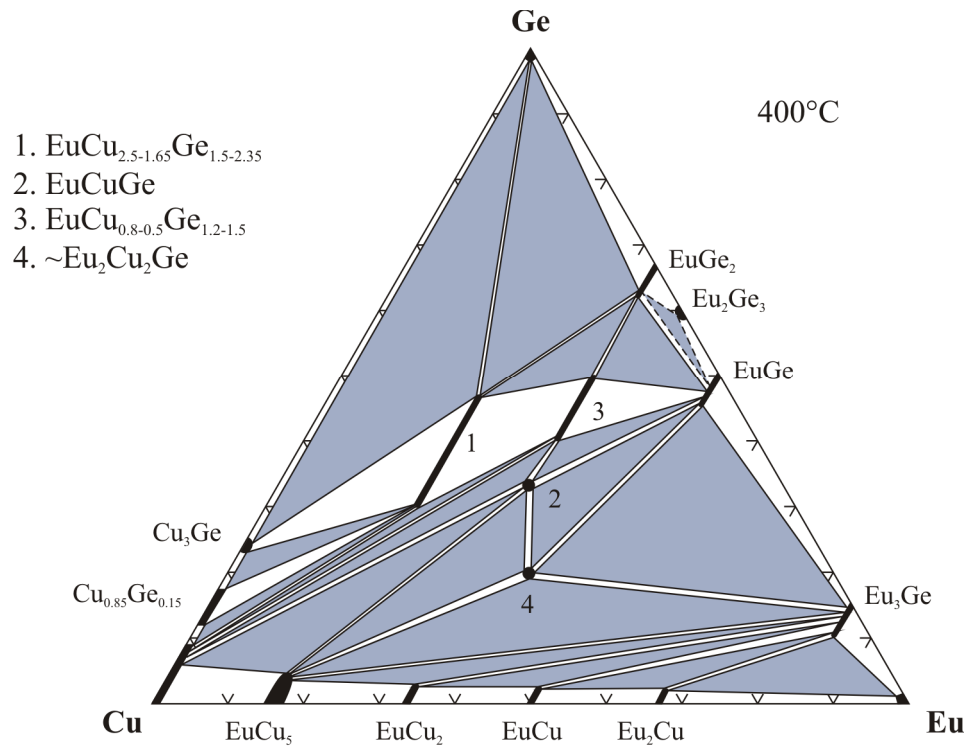| Alloy	$Eu_{18}Cu_{82}$	$Eu_{16.6}Cu_{83.4}$
Main phase (content, wt.%)	$EuCu_5$ (100)	$Eu_{0.93(1)}Cu_{5.14(1)}$ (82(2))
Structure type	$CaCu_5$	$TbCu_7$
Pearson symbol	*hP*6	*hP*8
Space group	*P6/mmm*	*P6/mmm*
Unit-cell parameters *a*, *c*, nm	0.51557(1), 0.40959(1)	0.51460(1), 0.41024(1)
Cell volume *V*, nm^3	0.094289(5)	0.094081(5)
Formula units per cell *Z*	1	1
Density D_X, g cm^{-3}	8.274	8.263
FWHM parameters *U*, *V*, *W*	0.028(5), -0.023(6), 0.014(2)	0.020(6), 0.003(7), 0.010(2)
Mixing parameter *η*	0.94(2)	0.94(1)
Asymmetry parameter C_M	-0.014(1)	-0.018(9)
Texture parameter *G* [direction]	0.992(5) [110]	0.957(6) [110]
Number of reflections	35	35
Number of refined parameters	12	16
Reliability factors R_p, R_{wp}, R_B	0.0303, 0.0387, 0.0685	0.0170, 0.0233, 0.0826
Goodness of fit *S*	0.32	0.45
Additional phase (content, wt.%)	–	Cu (18(2))

Table 2 Atom coordinates, site occupancies and isotropic displacement parameters for $EuCu_5$: structure type $CaCu_5$, *hP*6, *P6/mmm*, *a* = 0.51557(1), *c* = 0.40959(1) nm.

Site	Wyckoff position	*x*	*y*	*z*	Occupancy	$B_{iso} \cdot 10^2$, nm^2
Eu	1*a*	0	0	0	1	0.65(9)
Cu1	3*g*	½	0	½	1	0.75(8)
Cu2	2*c*	⅓	⅔	0	1	

Table 3 Atom coordinates, site occupancies and isotropic displacement parameters for $Eu_{0.93(1)}Cu_{5.14(1)}$: structure type $TbCu_7$, *hP8*, *P6/mmm*, $a = 0.51460(1)$, $c = 0.41024(1)$ nm.

Site	Wyckoff position	x	y	z	Occupancy	$B_{iso} \cdot 10^2$, nm^2
Eu	1*a*	0	0	0	0.934(12)	0.54(9)
Cu1	3*g*	½	0	½	1	
Cu2	2*e*	0	0	0.298(15)	0.066(6)	0.80(8)
Cu3	2*c*	⅓	⅔	0	1	

1. $EuCu_{2.5-1.65}Ge_{1.5-2.35}$
2. $EuCuGe$
3. $EuCu_{0.8-0.5}Ge_{1.2-1.5}$
4. $\sim Eu_2Cu_2Ge$

Fig. 1 Isothermal section of the phase diagram of the Eu–Cu–Ge system at 400°C.

**Table 4** Crystallographic data for the ternary compounds in the Eu–Cu–Ge system [10,11].

No.	Compound	Structure type	Pearson symbol	Space group	a, nm	b, nm	c, nm	V, nm^3
1	$EuCu_{2.5-1.65}Ge_{1.5-2.35}$	$CeAl_2Ga_2$	*tI*10	*I4/mmm*	0.4187(4)-0.4212(2)	–	1.0116(1)-1.0336(3)	0.1773(4)-0.1834(3)
2	$EuCuGe$	HoNiGa	*oP*12	*Pnma*	0.7342(3)	0.4372(2)	0.7550(3)	0.2423(4)
3	$EuCu_{0.8-0.5}Ge_{1.2-1.5}$	AlB_2	*hP*3	*P6/mmm*	0.4217(4)-0.4218(3)	–	0.4432(4)-0.4460(4)	0.0683(2)-0.0687(2)
4	$\sim Eu_2Cu_2Ge$	…	…	…	…	…	…	…

Table 5 Atom coordinates and isotropic displacement parameters for $EuCu_{1.75}Ge_{2.25}$: structure type $CeAl_2Ga_2$, *tI*10, *I4/mmm*, $a = 0.4214(2)$, $c = 1.0296(3)$ nm; $R_B = 0.0977$.

Site	Wyckoff position	x	y	Z	$B_{iso} \cdot 10^2$, nm^2
Eu	2*a*	0	0	0	1.0(3)
$Cu_{0.875}Ge_{0.125}$	4*e*	0	0	0.3785(14)	1.1(5)
Ge	4*d*	0	½	¼	

Table 6 Atom coordinates and isotropic displacement parameters for EuCuGe: structure type HoNiGa, *oP*12, *Pnma*, $a = 0.7342(3)$, $b = 0.4372(2)$, $c = 0.7550(3)$ nm, $R_B = 0.134$.

Site	Wyckoff position	x	y	z	$B_{iso} \cdot 10^2$, nm^2
Eu	4*c*	0.0004(3)	¼	0.7078(2)	1.2(1)
Cu	4*c*	0.2892(2)	¼	0.4084(1)	1.2(1)
Ge	4*c*	0.1914(1)	¼	0.0754(2)	1.0(1)
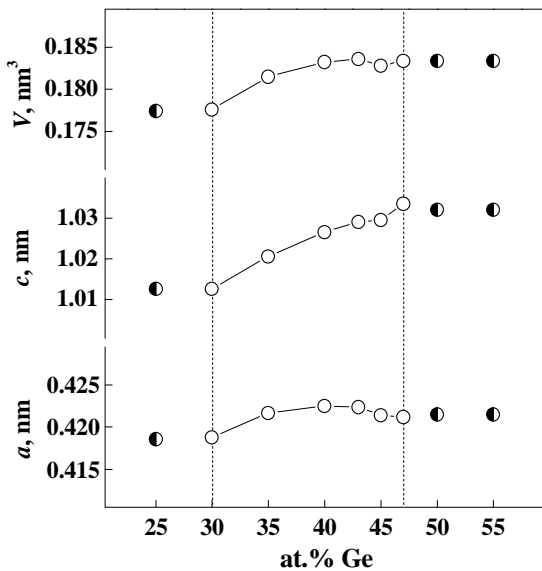
Fig. 2 Cell parameters within the homogeneity region of the compound EuCu$_{2.5-1.65}$Ge$_{1.5-2.35}$.
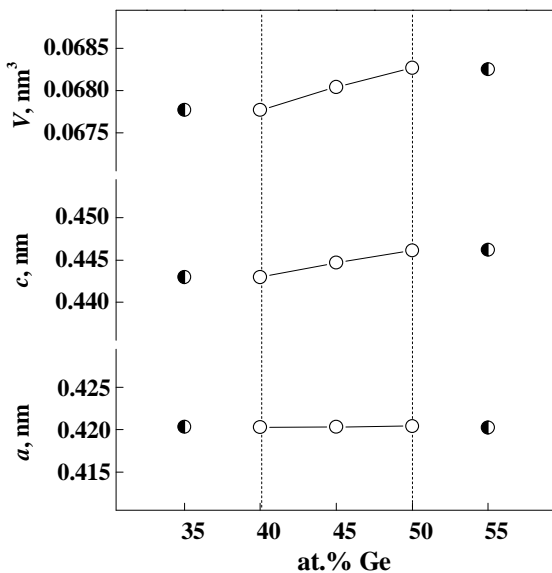
Fig. 3 Cell parameters within the homogeneity region of the compound EuCu$_{0.8-0.5}$Ge$_{1.2-1.5}$.

The third ternary compound, EuCu$_{0.8-0.5}$Ge$_{1.2-1.5}$, is characterized by a variable content of copper and germanium (from 40 to 50 at.% Ge) along the isoconcentrate at 33.3 at.% Eu. Its crystal structure

belongs to the hexagonal AlB$_2$ type [15]; the absence of superstructure reflections indicates that the Cu and Ge atoms form a statistical mixture over the whole homogeneity range. The cell parameter *c* increases with increasing Ge content, whereas the parameter *a* remains practically constant (Fig. 3).

The effective valence of europium in EuCu$_{0.8}$Ge$_{1.2}$ was determined by X-ray L_{III}-absorption spectroscopy. The spectrum, shown in Fig. 4, is characterized by a maximum, the position of which indicates that Eu has a stable valence of 2+. Eu has been shown to be divalent also in EuCu$_2$Ge$_2$ [6].
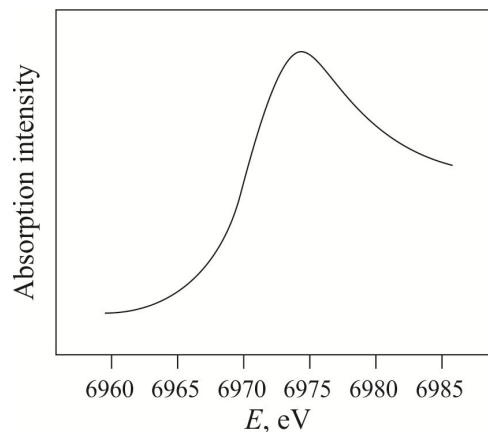
Fig. 4 X-ray L_{III}-absorption spectrum of europium in EuCu$_{0.8}$Ge$_{1.2}$.
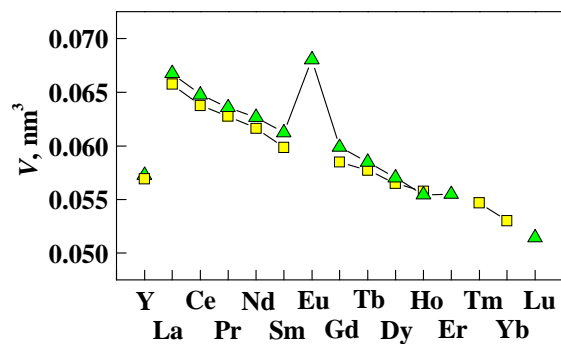
Fig. 5 Cell volume of EuCu$_{0.65}$Ge$_{1.35}$ with AlB$_2$-type structure, compared with the cell volumes of rare-earth copper germanides *R*CuGe (squares) and *R*Cu$_{0.67}$Ge$_{1.33}$ (triangles) with AlB$_2$-type or related structures.

The system Eu–Cu–Ge differs from the ternary systems of copper and germanium with other rare-earth metals, by the number of compounds, and by their crystal structures. A complete row of isostructural compounds is only known for the composition RCu_2Ge_2. Table 7 shows the structure types reported for the different $RCuGe$ compounds. Rieger & Parthé [16] prepared the compositions $RCuGe$ and $RCu_{0.67}Ge_{1.33}$ and identified the structure type AlB_2 for both compositions for all the investigated rare earths (Eu was not studied), except Er and Lu, where an AlB_2-type structure was only observed for the latter composition. They concluded on the existence of extended homogeneity ranges. Iandelli [17] synthesized all the equiatomic compounds (except EuCuGe) for another comparative study. He confirmed the small unit cell for R = La-Gd, but observed a doubling of the cell parameter c for R = Tb-Lu and Y. To the latter, he tentatively assigned the structure type $CaIn_2$ [18], which is a deformation derivative of AlB_2, assuming statistic disorder of the Cu and Ge atoms. Doubling of the parameter c was later confirmed for R = Tb-Er and Yb, and also observed for a single crystal of GdCuGe (whereas the powder pattern showed no superstructure reflections) [19] and for CeCuGe [20]. Complete refinements led in most cases to the structure type LiGaGe [21], an ordered substitution derivative of AlB_2 and $CaIn_2$ with puckered GaGe layers, and more precisely to its branch NdPtSb [22]. For CeCuGe no significant deviation from planarity of the CuGe layers was observed, and the structure was refined according to the structure type BeZrSi [23]. During an investigation of the isothermal section of the Tm–Cu–Ge system at 600°C, Fedyna *et al.* [24] found that the compound with $CaIn_2$-type structure was located off the 1:1:1 composition, and had the formula $TmCu_{1.24}Ge_{0.76}$. Konyk *et al.* [25] observed two distinct compounds with related structures in the Er–Cu–Ge system at 600°C: ErCuGe with $CaIn_2$-type structure (LiGaGe or NdPtSb type according to [26]) and $ErCu_{0.67}Ge_{1.33}$ with AlB_2-type structure.

Within the row of $RCuGe$ compounds, crystallizing with AlB_2-type or related structures, the volume of the AlB_2-type (sub)cell decreases with increasing atomic number of the rare-earth metal [16,17,26]. For the AlB_2-type europium compound investigated here, an anomaly is observed, confirming the lower valence of europium (Fig. 5). The value of the cell volume used on the figure was taken for $EuCu_{0.65}Ge_{1.35}$. This composition, assuming Eu^{2+}, is approximately isoelectronic with $R^{3+}CuGe$. It may be mentioned that also the structure type HoNiGa, observed at the equiatomic composition, can be derived from the AlB_2 type by substitution and deformation [27]. The volume per formula unit for EuCuGe, 0.0606 nm³, falls approximately on the line formed by the other $RCuGe$ compounds.

Table 7 Structure types of ternary compounds with equiatomic composition in the systems R–Cu–Ge (R = rare-earth element) [5].

R	Structure type (space group)
Y	$CaIn_2$ ($P6_3/mmc$), AlB_2 ($P6/mmm$)
La	AlB_2 ($P6/mmm$)
Ce	BeZrSi ($P6_3/mmc$), AlB_2 ($P6/mmm$)
Pr	AlB_2 ($P6/mmm$)
Nd	AlB_2 ($P6/mmm$)
Sm	AlB_2 ($P6/mmm$)
Eu	HoNiGa ($Pnma$)
Gd	NdPtSb ($P6_3mc$), AlB_2 ($P6/mmm$)
Tb	NdPtSb ($P6_3mc$), $CaIn_2$ ($P6_3/mmc$), AlB_2 ($P6/mmm$)
Dy	NdPtSb ($P6_3mc$), $CaIn_2$ ($P6_3/mmc$), AlB_2 ($P6/mmm$)
Ho	NdPtSb ($P6_3mc$), $CaIn_2$ ($P6_3/mmc$), AlB_2 ($P6/mmm$)
Er	NdPtSb ($P6_3mc$), $CaIn_2$ ($P6_3/mmc$)
Tm	$CaIn_2$[a] ($P6_3/mmc$), AlB_2 ($P6/mmm$)
Yb	NdPtSb ($P6_3mc$), $CaIn_2$ ($P6_3/mmc$)
Lu	$CaIn_2$ ($P6_3/mmc$)

[a] refined composition $TmCu_{1.24}Ge_{0.76}$.

Conclusions

Four ternary compounds form in the system Eu–Cu–Ge at 400°C. Two of these, $EuCu_{2.5-1.65}Ge_{1.5-2.35}$ and $EuCu_{0.8-0.5}Ge_{1.2-1.5}$, have significant homogeneity ranges (17 and 10 at.% Cu/Ge, respectively), whereas the two other compounds, EuCuGe and $\sim Eu_2Cu_2Ge$, exhibit point compositions. The binary compounds dissolve up to 5 at.% of the third element. The effective valence of Eu in $EuCu_{0.8}Ge_{1.2}$ was found to be 2+. The difference in valence of Eu probably explains why the system Eu–Cu–Ge differs from the corresponding systems with other rare earths.

Acknowledgement

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