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The ternary Eu-Cu-Si system at 400°C

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Based on X-ray diffraction and microstructure analysis the isothermal section at 400°C of the phase diagram of the system Eu-Cu-Si was built. The compound $EuCu_2Si_2$ ($CeAl_2Ga_2$ structure type) was confirmed and its homogeneity region was determined ($EuCu_{2.25-1.50}Si_{1.75-2.50}$). The compound $EuCu_{0.80-0.20}Si_{1.20-1.80}$ (AlB_2 structure type) is also characterized by a variable content of copper and silicon. In addition, four new compounds with unknown structure were found in this system. The effective valence of europium was studied.

Isothermal section / Crystal structure / Effective valence

1. Introduction

The results presented in this paper are part of a systematic investigation of Eu-*M*-Si (where *M* is a transition element) systems. The peculiar properties of europium distinguish this element from the other rare-earth metals. The investigation of the interaction of europium with other elements, the conditions under which compounds are formed and the crystal structures and properties of these, makes it possible to establish relations between the properties of the compounds and their electronic structure.

The binary systems bordering the ternary system Eu-Cu-Si are well established. Phase diagrams have been constructed for Eu-Cu [1] and Cu-Si [2]; five compounds have been reported in the system Eu-Si [3-6].

Three ternary compounds were previously known in the Eu-Cu-Si system: $EuCu_2Si_2$ [7] and $EuCu_{0.5}Si_{1.5}$ [8] crystallizing with the structure types $CeAl_2Ga_2$ and AlB_2, respectively, and $EuCu_{1.6}Si_{1.4}$ with unknown structure [7].

2. Experimental

The samples were prepared by arc melting under argon on a water-cooled copper hearth. The starting materials were the elements: europium 98.8%, copper 99.99%, and silicon 99.9999%. The alloys were annealed for 2 weeks in evacuated quartz ampoules at 400°C, and subsequently quenched into water.

Phase analysis by X-ray powder diffraction was performed for 160 samples (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 a few complete crystal structure determinations were carried out (diffractometer HZG-4a, Cu *K*α radiation; program DBWS-9807 [9]). 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 system Eu-Cu-Si is characterized by the formation of six ternary compounds and a relatively extended solid solution based on the binary phase $EuCu_{5-x}$ (Fig. 1, Table 1).

According to the isothermal section of the phase diagram of the Eu-Cu-Si system at 400°C the binary compounds of the boundary systems Cu-Si, Eu-Si, and Eu-Cu dissolve not more than 5 at.% of the third component. The only exception is $EuCu_{5-x}$ with $CaCu_5$-type structure (space group *P*6/*mmm*), which dissolves 8 at.% silicon along the isoconcentrate 16.7 at.% europium. In addition, it was found that the binary phase $EuCu_{5-x}$ is characterized by a variable content of copper, ranging from 80 to 83.3 at.% (Figs. 2 and 3).

In addition to the already known europium silicides $EuSi_2$ (α-$ThSi_2$ type, space group $I4_1/amd$) and EuSi (Table 2), two new binary compounds with approximate compositions Eu_7Si_3 and Eu_4Si (unknown structures) were found in the system Eu-Si [3]. It should be noted that the binary compound Eu_2Si [5,6] with $PbCl_2$ structure type (space group *Pnma*) was not observed in this study.

Table 1 Crystallographic data of the ternary compounds in the Eu-Cu-Si system.

No.	Compound	Structure type	Space group	Cell parameters, nm		
				a	*b*	*c*
1	~$Eu_8Cu_{77}Si_{15}$	…	…	…	…	…
2	~$Eu_7Cu_{68}Si_{25}$	…	…	…	…	…
3	$EuCu_{2.25\text{-}1.50}Si_{1.75\text{-}2.50}$	$CeAl_2Ga_2$	*I*4/*mmm*	0.4047(2)-0.4132(2)	–	0.9913(6)-0.9971(5)
4	EuCuSi	…	…	…	…	…
5	$EuCu_{0.80\text{-}0.20}Si_{1.20\text{-}1.80}$	AlB_2	*P*6/*mmm*	0.4107(1)-0.4051(1)	–	0.4447(1)-0.4489(1)
6	~$Eu_{40}Cu_{40}Si_{20}$	…	…	…	…	…

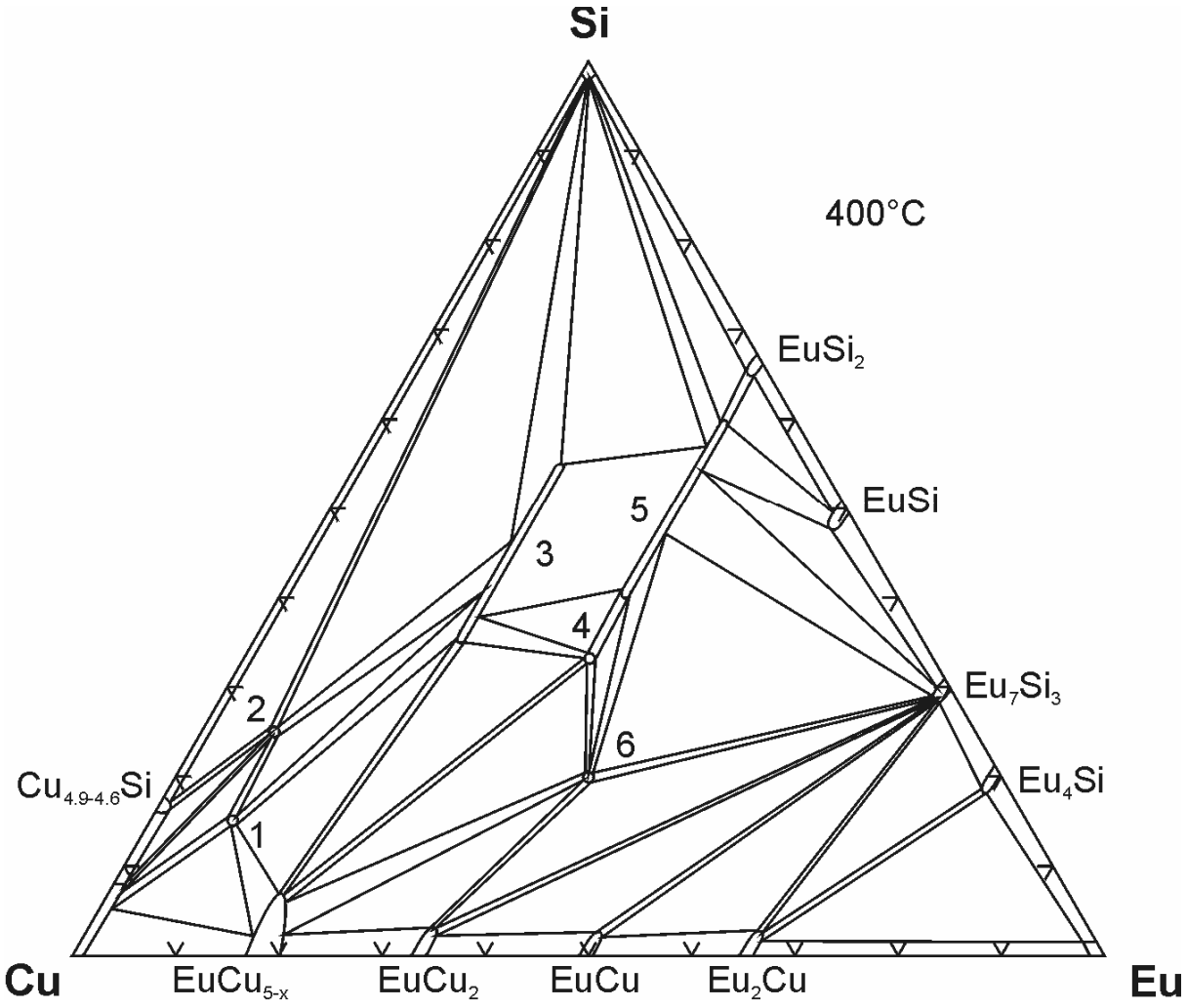

Fig. 1 Isothermal section of the phase diagram of the Eu-Cu-Si system at 400°C.

Table 2 Crystallographic data of the compound EuSi.

Structure type		CrB
Space group		*Cmcm*
Cell parameters	*a*, nm	0.46958(3)
	b, nm	1.11242(5)
	c, nm	0.39799(2)
Cell volume *V*, nm^3		0.20790(2)
Formula units per cell *Z*		4
Density D_x, g cm^{-3}		5.754
Texture parameter *G* [direction]		0.831(4) [0 1 0]
Peak shape parameters *U*, *V*, *W*		0.043(8), -0.026(9), 0.019(2)
Mixing parameter η		0.89(3)
Asymmetry parameter C_M		-0.109(14)
Number of reflections		273
Number of refined parameters		15
Reliability factors	R_p	0.0149
	R_{wp}	0.0192
Goodness of fit *S*		0.36

Atomic parameters

Atom	Wyckoff	*x*	*y*	*z*	B_{iso}, nm^2
Eu	4*c*	0	0.3600(2)	1/4	0.0076(5)
Si	4*c*	0	0.0649(8)	1/4	0.008(2)

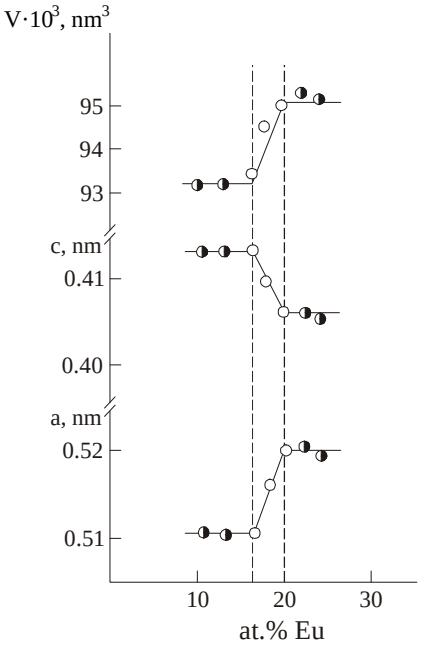

Fig. 2 Cell parameters within the homogeneity range of the binary phase $EuCu_{5-x}$.

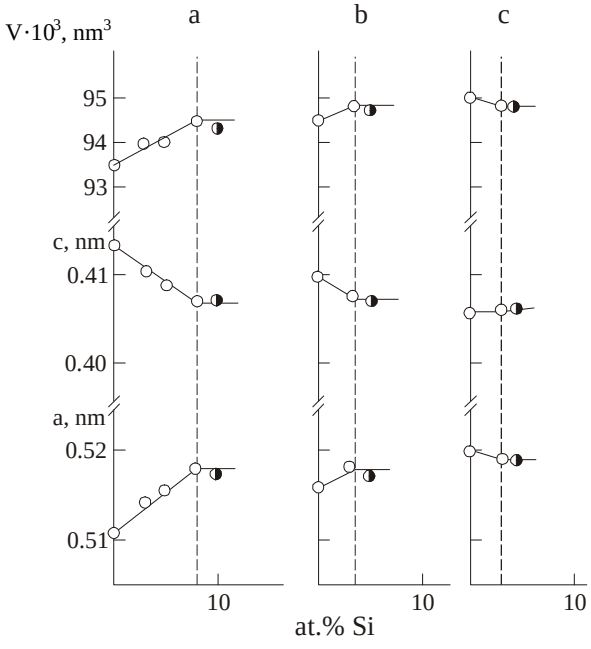

Fig. 3 Cell parameters of the solid solution of Si in $EuCu_{5-x}$: a – 16.7 at.% Eu; b – 18 at.% Eu; c – 20 at.% Eu.

The previously reported compound $EuCu_2Si_2$ [7] with $CeAl_2Ga_2$-type structure was confirmed and its homogeneity region was determined (Fig. 4). The compound $EuCu_{0.80-0.20}Si_{1.20-1.80}$ is characterized by a variable content of copper and silicon along the isoconcentrate 33.3 at.% Eu [10-12] (Fig. 5). The compound $EuCu_{1.6}Si_{1.4}$ [7] was not observed at 400ºC.

The effective valence of europium in alloys of composition $EuCuSi_3$, $EuCu_{1.50}Si_{2.50}$, and $EuCu_{2.25}Si_{1.75}$ was determined by X-ray L_{III}-absorption spectroscopy [13,14].

The spectra of $EuCu_{2.25}Si_{1.75}$ are characterized by two maxima (Fig. 6). Taking into account information obtained by ^{151}Eu Mössbauer spectroscopy on

$EuCu_2Si_2$ [15,16], which showed the presence of interconfiguration fluctuation in the 4*f*-configuration of europium with the frequency 10^{13} Hz, one may conclude that Eu in $EuCu_{2.25}Si_{1.75}$ is present in a status of dynamic intermediate valence, with the effective valence 2.6. The correlation between the ratio of intensities $I(Eu^{3+})/I(Eu^{2+})$ and the effective valence of europium in $EuCu_{2.25\text{-}1.50}Si_{1.75\text{-}2.50}$ decreases with increasing silicon content (Fig. 7).

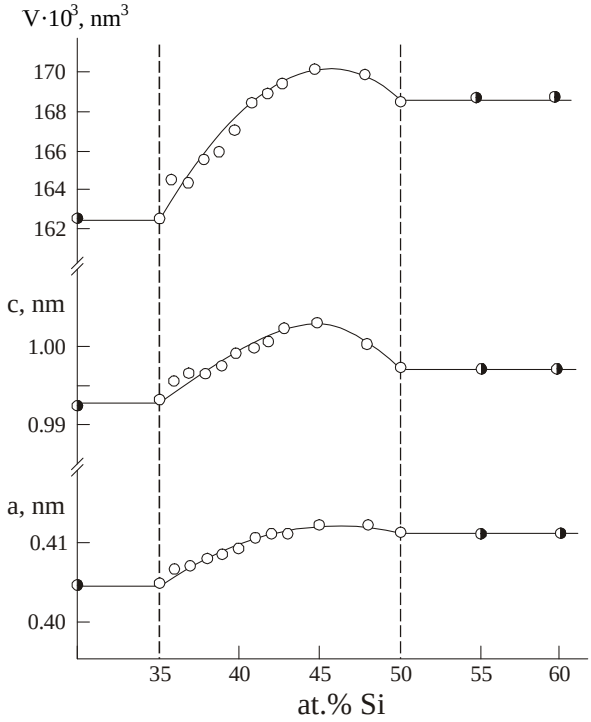

Fig. 4 Cell parameters within the homogeneity region of $EuCu_{2.25\text{-}1.50}Si_{1.75\text{-}2.50}$.

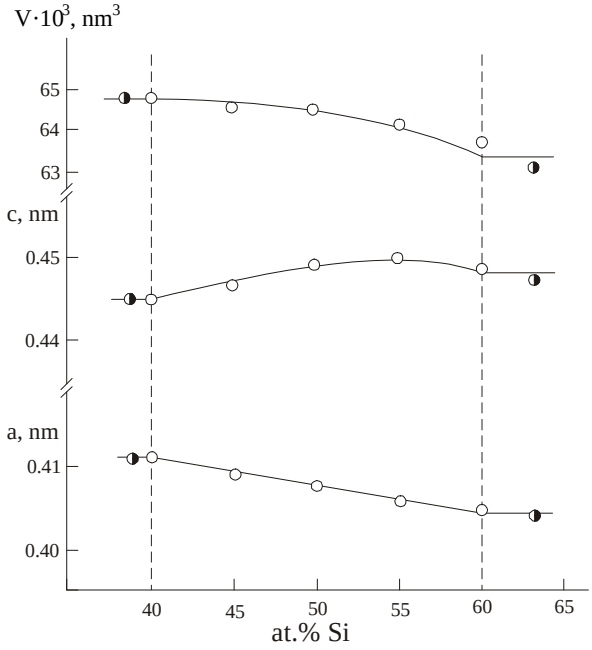

Fig. 5 Cell parameters within the homogeneity region of $EuCu_{0.80\text{-}0.20}Si_{1.20\text{-}1.80}$.

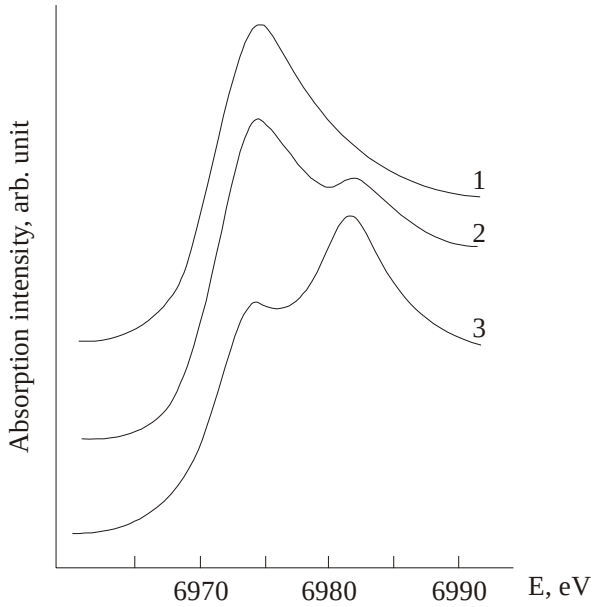

Fig. 6 X-ray L_{III}-absorption spectra of europium in the samples: 1 – $EuCuSi_3$; 2 – $EuCu_{1.50}Si_{2.50}$; 3 – $EuCu_{2.25}Si_{1.75}$.

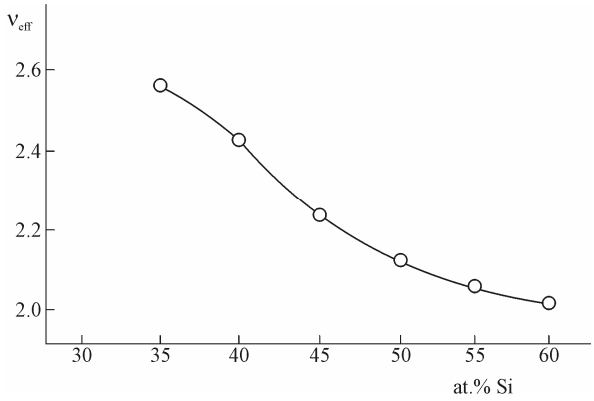

Fig. 7 Effective valence (v_{eff}) of europium in samples with 20 at.% Eu.

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