

## The $RECu_{1-x}Ga_xIn$ ( $RE = La, Ce$ ) systems at 870 K

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The interaction between the components in the  $RECu_{1-x}Ga_xIn$  ( $RE = La, Ce$ ) systems at 870 K was investigated by X-ray diffraction and local EDX-analysis in the full concentration range. The solubility ranges of the solid solutions, the crystal structures of the phases and the changes of the unit-cell parameters were determined:  $LaCu_{1.00-0.80}Ga_{0.0-0.20}In$  (ZrNiAl-type structure):  $a = 755.0-52.0(1)$ ,  $c = 428.0-430.4(1)$  pm;  $CeCu_{1.00-0.80}Ga_{0.0-0.20}In$  (ZrNiAl-type structure):  $a = 749.2-744.4(1)$ ,  $c = 424.5-431.1(1)$  pm;  $LaCu_{0.50-0.25}Ga_{0.50-0.75}In$  ( $CaIn_2$ -type structure):  $a = 473.2(1)-479.5(1)$ ,  $c = 783.2(2)-792.7(2)$  pm;  $CeCu_{0.70-0.25}Ga_{0.30-0.75}In$  ( $CaIn_2$ -type structure):  $a = 472.0(1)-478.1(1)$ ,  $c = 766.5(2)-784.7(2)$  pm. The crystal structure of the  $LaCu_{0.40}Ga_{0.60}In$  compound was investigated by single-crystal X-ray diffraction (Mo  $K\alpha$ -radiation):  $CaIn_2$ -type structure,  $P6_3/mmc$ ,  $hP6$ ,  $a = 473.6(1)$ ,  $c = 786.6(2)$  pm,  $R_1 = 0.0390$  for 107  $F^2$  values and 7 variables.

Indide / Solid solution / Powder diffraction / Single crystal / Crystal structure

### 1. Introduction

The  $LaCuIn$  [1] and  $CeCuIn$  [2] compounds crystallize in the ZrNiAl-type structure. Besides these compounds at 870 K  $RE(Cu,In)_2$  phases with  $AlB_2$ -type structure have been observed [3]. In the Ce–Cu–In system at higher temperatures a compound with  $CaIn_2$ -type structure was reported [4]. All the mentioned structures are related to the  $AlB_2$ -type structure [5]. Electronic structures and physical properties of these compounds have repeatedly been reported [6-14]. Since the structural characteristics of the ternary compounds have been deeply studied, recently research of four-component systems has been conducted to investigate the substitutional effect on the structure and properties of the phases. During the mutual substitution of  $p$ -element atoms in the  $CeNiAl_{1-x}Ga_x$  [15],  $CeNiIn_{1-x}M_x$  ( $M = Al, Ga$ ) [16] systems, the formation of continuous series of solid solutions with ZrNiAl-type structure was observed, while in the  $CeNiIn_{1-x}M_x$  ( $M = Ge, Sb$ ) [17] systems limited solubility based on the equiatomic compounds with different types of crystal structure was observed. A progressive shift from the intermediate-valence to a localized  $4f$ -state with increasing content of germanium is evident from the results of the substitution of Ge atoms for Rh atoms in the  $CeRhIn$  compound [18]. Gnida *et al.* [19] observed systematic changes in the temperature- and field-dependent electrical transport in the  $CePd_{1-x}Ge_xIn$  system. In alloys of the  $CeAu_{1-x}Ni_xIn$  system, the electrical

transport is influenced by the Kondo effect, which, for  $x \leq 0.4$ , transformed from incoherent to coherent scattering with decreasing temperature, while, for larger values of  $x$ , single-ion character in the entire investigated temperature range was exhibited [20]. Replacement of the  $d$ -element (Cu) by a  $p$ -element (Ga) in the mentioned boundary systems can be favorable for the formation of solid solutions or new quaternary compounds, like in the  $R_2Ni_{2-x}Ge_xIn$  systems [21].

### 2. Experimental details

The investigation of the  $LaCu_{1-x}Ga_xIn$  and  $CeCu_{1-x}Ga_xIn$  ( $0 \leq x < 1$ ) systems was made on the basis of 8 and 12 samples, respectively. The samples were synthesized by arc-melting pure elements (all with stated purities better than 99.8%) under argon gas. The surface of lanthanum and cerium was mechanically cleaned before weighing. The alloys were remelted twice and annealed in evacuated quartz ampoules in an electric muffle furnace SNOL with an automatic temperature control of  $\pm 2$  K for a month at a temperature of 870 K to ensure homogeneity. All the samples were stable at room temperature.

Phase analysis was made by X-ray powder diffraction using DRON-2.0M (Fe  $K\alpha$ -radiation) and Guinier patterns (image plate system Fujifilm BAS-1800, Cu  $K\alpha$ -radiation,  $\alpha$ -quartz:  $a = 491.30$ ,  $c = 540.46$  pm as internal standard). Some samples

were additionally examined by means of energy-dispersive X-ray analysis (scanning electron microscope Leica 420i and REMMA-102-02). The phase analysis was made using Powder Cell [22] and STOE WinXPOW [23] programs. The structure refinement on powder data (Stoe Stadi P (Cu  $K\alpha_1$ -radiation)) was made using the FullProf program [24]. Refinement of the mixed Cu/Ga position was impossible by X-ray diffraction due to insufficient electron difference, therefore the refinement was conducted with occupancies fixed on the basis of EDX-analysis data and the initial composition.

Single crystals were grown using a special heat treatment. Arc-melted samples of  $LaCu_{0.40}Ga_{0.60}In$  and  $LaCu_{0.25}Ga_{0.75}In$  (about 1 g) were put into small tantalum containers that were sealed in evacuated silica tubes as an oxidation protection. The ampoules were first heated to 1270 K at a speed of 5°/h and held at that temperature for 120 h. Then the furnace was turned off to cool the samples to room temperature. After cooling, the samples could easily be separated from the tantalum container. No reaction of the container material was evident. The brittle samples of both compounds were stable in air over weeks in powdered as well as in bulk form. The irregularly shaped single crystals exhibited metallic luster.

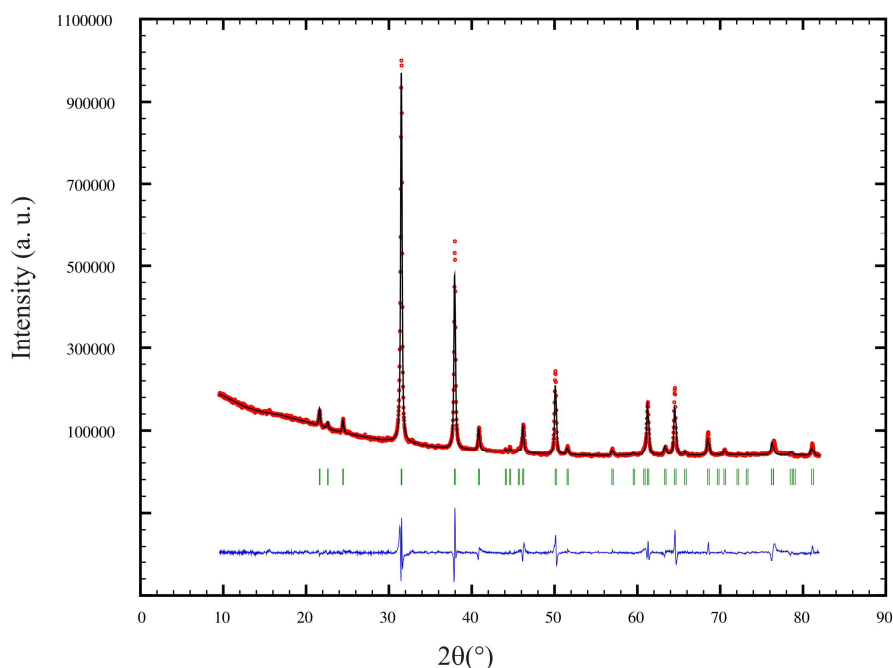
Irregularly shaped crystal fragments with conchoidal fracture were selected from both samples and investigated with a Buerger precession camera (white Mo-radiation, Fujifilm imaging plate) in order to check the quality for intensity data collection. Intensity data were collected at room temperature using a Stoe IPDS II image plate diffractometer with

graphite monochromatized Mo  $K\alpha$ -radiation (71.073 pm). Numerical absorption corrections (based on symmetry-equivalent reflections after optimization of the crystal shape) were applied to the data sets. The crystal structure was refined using the SHELXL-97 program [25] (full-matrix least-squares on  $F^2$ ) with anisotropic displacement parameters for all of the atoms.

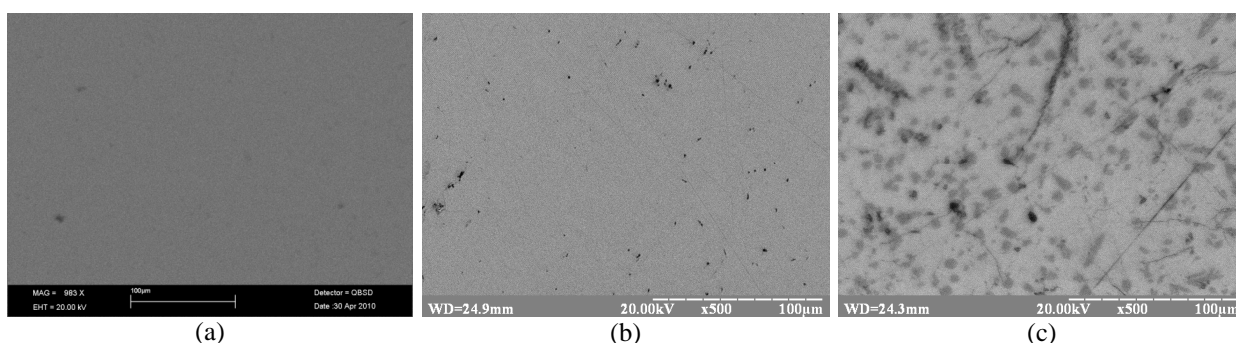
### 3. Results and discussion

The phase analysis of the  $LaCu_{1-x}Ga_xIn$  system at 870 K revealed a substitutional solid solution  $LaCu_{1.0-0.8}Ga_{0.0-0.2}In$  with the same structure as the initial compound  $LaCuIn$  (ZrNiAl-type structure, space group  $P-62m$ ):  $a = 755.0-752.0(1)$ ,  $c = 428.0-430.4(1)$  pm. The samples with low contents of Ga contained small amounts of the additional phases  $LaCu_2In$  (MnCu<sub>2</sub>Al-type structure) and  $LaCu_{0.5}In_{1.5}$  (AlB<sub>2</sub>-type structure), which correlates with the results of investigations of the La–Cu–In system [26]. Higher contents of gallium provided the formation of the new phase  $LaCu_{0.5-0.25}Ga_{0.5-0.75}In$  with CaIn<sub>2</sub>-type structure [27] (space group  $P6_3/mmc$ ,  $a = 473.2(1)-479.5(1)$ ,  $c = 783.2(2)-792.7(2)$  pm). Samples with yet higher gallium contents contained the  $La(Cu,Ga,In)_2$  phases with CaIn<sub>2</sub>-type structure and  $La(Ga,In)_2$  with AlB<sub>2</sub>-type structure.

The diffractogram of the  $LaCu_{0.5}Ga_{0.5}In$  sample is presented in Fig. 1. Scanning electron micrographs of polished samples of the  $LaCu_{1-x}Ga_xIn$  system are shown in Fig. 2.



**Fig. 1** Observed, calculated and difference X-ray patterns of  $LaCu_{0.5}Ga_{0.5}In$ , crystallizing with the CaIn<sub>2</sub> structure (Guinier pattern, Cu  $K\alpha$ -radiation).



**Fig. 2** Scanning electron micrographs of polished samples of the  $LaCu_{1-x}Ga_xIn$  system: (a)  $LaCu_{0.9}Ga_{0.1}In$  (gray phase  $La_{0.34}Cu_{0.28}Ga_{0.4}In_{0.34}$ , black points are surface defects); (b)  $LaCu_{0.5}Ga_{0.5}In$  (gray phase  $La_{0.32}Cu_{0.16}Ga_{0.19}In_{0.33}$ , black points are surface defects); (c)  $LaCu_{0.25}Ga_{0.75}In$  (light gray phase  $La_{0.33}Cu_{0.10}Ga_{0.23}In_{0.34}$ , dark phase  $La_{0.33}Ga_{0.62}In_{0.05}$ , black points are surface defects).

**Table 1** Crystallographic data and structure refinement of  $LaCu_{0.4}Ga_{0.6}In$ ;  $CaIn_2$ -type structure, space group  $P6_3/mmc$ ,  $Z = 2$ .

Empirical formula	$LaCu_{0.4}Ga_{0.6}In$
Formula weight, $g\ mol^{-1}$	641.96
Unit-cell parameters (powder data), pm	$a = 473.6(1)$ $c = 786.6(2)$
Cell volume, $nm^3$	0.1528(1)
Calculated density, $g\ cm^{-3}$	6.977
Crystal size, $\mu m^3$	$30 \times 5 \times 5$
Transmission ratio (min / max)	0.2402 / 0.8334
Detector distance, mm	60
Exposure time, min	10
$\omega$ -range / step width, deg	0-180 / 1.0
Radiation / wavelength, pm	Mo $K\alpha$ / 71.073 pm
Absorption coefficient, $mm^{-1}$	28.878
$F(000)$ , e	272
$\theta$ range for data collection, deg	4.97-30.85
$hkl$ range	$\pm 6, \pm 6, \pm 10$
Total # reflections	1348
Independent reflections / $R_{int}$	107 / 0.0607
Reflections with $I \geq 2\sigma(I)$ / $R_\sigma$	94 / 0.0271
Data / parameters	107 / 7
Goodness-of-fit on $F^2$	1.243
$R1$ / $wR2$ for $I > 2\sigma(I)$	0.0390 / 0.0703
$R1$ / $wR2$ (all data)	0.0471 / 0.0720
Extinction coefficient	0.018(3)
Highest / lowest $\Delta\rho$ , $e\ \text{\AA}^{-3}$	1.82 / -1.89

The results of the phase analysis agree with the single-crystal refinement on data from the  $LaCu_{0.40}Ga_{0.60}In$  sample (STOE IPDS II, Mo  $K\alpha$  radiation). The crystal structure was solved revealing a  $CaIn_2$ -type structure using SHELXL-97 program [25] (full-matrix least-squares on  $F^2$ ). The EDX analysis of the single crystal (Zeiss EVO MA10): 34(2) at.% La; 12(2) at.% Cu; 19(2) at.% Ga; 35(2) at.% In correlates with the initial composition of the sample  $LaCu_{0.40}Ga_{0.60}In$ . The composition of the statistic mixture was fixed according to the EDX-analysis. Possible ordering of the Cu, Ga and In atoms in the crystal structure of the new compound was

tested. We tried to lower the symmetry from  $P6_3/mmc$  (structure type  $CaIn_2$ ) to  $P-6m2$  (structure type  $ScAuSi$ ), but the refinement was not improved. Crystallographic data and details of the structure refinement for  $LaCu_{0.40}Ga_{0.60}In$  are presented in Table 1, atomic positions and isotropic displacement parameters, and interatomic distances in Tables 2 and 3, respectively.

In the  $CeCu_{1-x}Ga_xIn$  system at 870 K a solid solution on the basis of the  $CeCuIn$  compound ( $ZrNiAl$ -type structure, space group  $P-62m$ ) is formed:  $CeCu_{1-0.8}Ga_{0.2}In$   $a = 749.2 - 44.4(1)$ ,  $c = 424.5 - 431.1(1)$  pm. Some samples from this range contained small amounts of  $CeCu_2In$  ( $MnCu_2Al$ -type

structure). Increasing of the Ga content caused a transition from the phase with ZrNiAl-type structure to the phase  $CeCu_{0.70-0.25}Ga_{0.30-0.75}In$  ( $CaIn_2$ -type structure, space group  $P6_3/mmc$ ):  $a = 472.0(1)–478.1(1)$ ,  $c = 766.5(2)–784.7(2)$  pm. Samples with higher Ga contents showed three phases in equilibria:  $Ce(Cu,Ga,In)_2$  with  $CaIn_2$ -type structure,  $Ce(Ga,In)_2$  with  $AlB_2$ -type structure and  $Ce(In,Cu,Ga)_2$  with  $KHg_2$ -type structure. Scanning electron micrographs

of polished samples of the  $CeCu_{1-x}Ga_xIn$  system are presented in Fig. 3.

The crystal structure of the  $CeCu_{0.5}Ga_{0.5}In$  compound was refined by powder diffraction (Fig. 4, Tables 4, 5) using the  $CaIn_2$ -type structure model [22] ( $P6_3/mmc$ ,  $a = 470.7(1)$ ,  $c = 767.1(1)$  pm,  $R_B = 0.0849$ ) with fixed occupancy of the  $4f$  position ( $M = 0.5 In + 0.25 Ga + 0.25 Cu$ ) according to the results of the EDX-analysis (34% Ce, 17% Cu, 16% Ga, and 33% In).

**Table 2** Atomic positions and anisotropic displacement parameters ( $pm^2$ ) of  $LaCu_{0.4}Ga_{0.6}In$  ( $CaIn_2$ -type structure, space group  $P6_3/mmc$ ,  $Z = 2$ ). The equivalent isotropic displacement parameter  $U_{eq}$  is defined as  $U_{eq} = 1/3 (U_{11} + U_{22} + U_{33})$ ;  $U_{23} = U_{13} = 0$ . Standard deviations are given in parentheses.

Atom	Wyckoff site	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{eq}$
La	$2b$	0	0	$1/4$	228(6)	228(6)	137(8)	114(3)	198(5)
$M^a$	$4f$	$1/3$	$2/3$	0.0285(2)	155(6)	150(6)	340(11)	78(3)	217(6)

<sup>a</sup>This site is occupied by 50% In, 30% Ga and 20% Cu.

**Table 3** Interatomic distances (pm) within the first coordination spheres for  $LaCu_{0.4}Ga_{0.6}In$ ; the standard deviations are equal to or smaller than 0.2 pm. The  $M$  site is occupied by 50% In, 30% Ga and 20% Cu.

$LaCu_{0.4}Ga_{0.6}In$							
La:	6	$M$	324.21	$M$ :	3	$M$	277.09
	2	$M$	350.30		3	La	324.21
	4	$M$	350.40		1	$M$	348.50
	2	La	393.30		1	La	350.30
					2	La	350.40

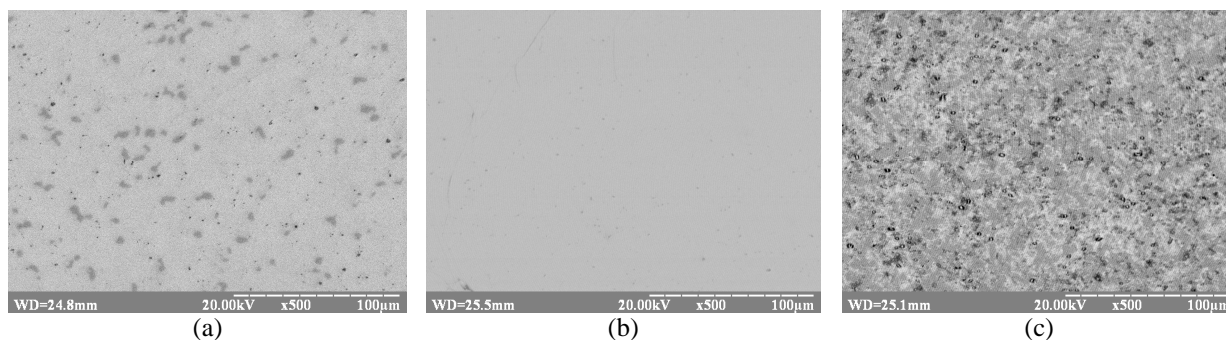
**Table 4** Crystallographic data and structure refinement of  $CeCu_{0.5}Ga_{0.5}In$ ;  $CaIn_2$ -type structure, space group  $P6_3/mmc$ ,  $Z = 2$ .

Empirical formula	$CeCu_{0.5}Ga_{0.5}In$
Unit-cell parameters, pm	$a = 470.7(1)$ $c = 767.1(1)$
Cell volume, $nm^3$	0.1472(1)
Calculated density, $g\ cm^{-3}$	7.261
Preferred orientation parameter [direction]	0.104(10) [100]
Radiation / wavelength, pm	Cu $K\alpha_1$ / 154.060 pm
$2\theta$ range, deg	6.00–110.49
Step size, deg	0.015
Profile parameters $U, V, W$	-0.005(2), 0.026(1), 0.004(1)
Asymmetry parameter $C_M$	0.049(7)
Number of reflections	53
$R_B / R_F$	0.0849 / 0.0789
$R_p / R_{wp}$	0.0733 / 0.0922
Number of refined parameters	13

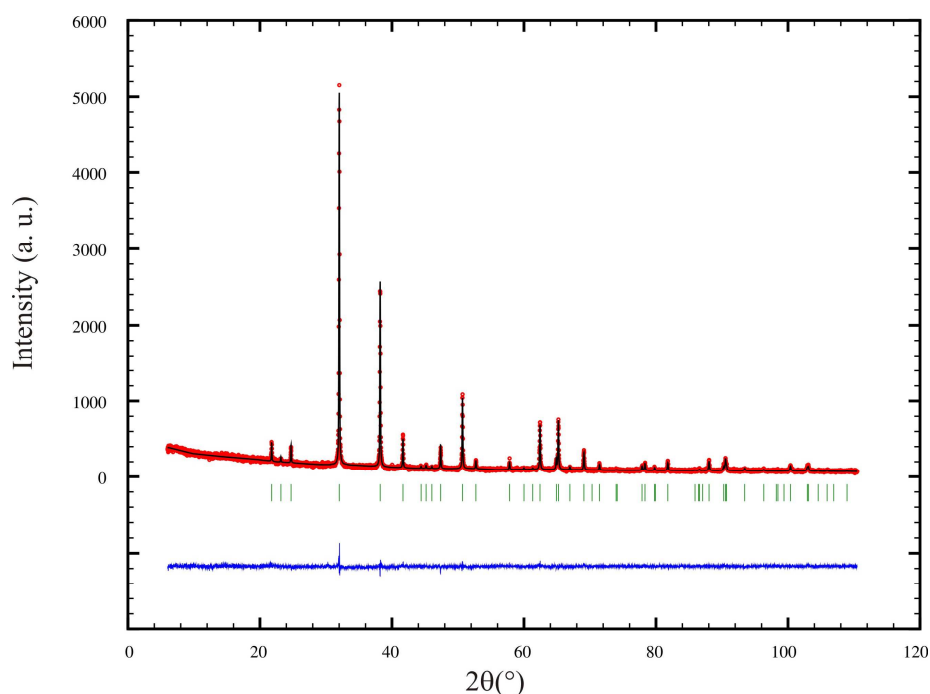
**Table 5** Atomic positions and isotropic displacement parameters ( $pm^2$ ) of  $CeCu_{0.5}Ga_{0.5}In$  ( $CaIn_2$ -type structure, space group  $P6_3/mmc$ ,  $Z = 2$ ).

Atom	Wyckoff site	$x$	$y$	$z$	$U_{iso}, pm^2$
Ce	$2b$	0	0	$1/4$	83(6)
$M^a$	$4f$	$1/3$	$2/3$	0.0341(3)	140(7)

<sup>a</sup>This site is occupied by 50% In, 25% Ga and 25% Cu.



**Fig. 3** Scanning electron micrographs of polished samples of the  $CeCu_{1-x}Ga_xIn$  system: (a)  $CeCu_{0.85}Ga_{0.15}In$  (light phase  $Ce_{0.35}Cu_{0.25}Ga_{0.07}In_{0.33}$ , gray phase  $Ce_{0.29}Cu_{0.47}Ga_{0.18}In_{0.26}$ ); (b)  $CeCu_{0.5}Ga_{0.5}In$  ( $Ce_{0.34}Cu_{0.17}Ga_{0.16}In_{0.33}$ ); (c)  $CeCu_{0.1}Ga_{0.9}In$  (light phase  $Ce_{0.34}Cu_{0.05}Ga_{0.17}In_{0.44}$ , gray phase  $Ce_{0.34}Ga_{0.56}In_{0.10}$ , dark phase  $Ce_{0.30}Ga_{0.08}In_{0.62}$ ).



**Fig. 4** Observed, calculated, and difference X-ray patterns of the  $CeCu_{0.5}Ga_{0.5}In$  alloy (Cu  $K\alpha_1$  radiation).

The  $RECu_{1-x}Ga_xIn$  ( $RE = La, Ce$ ) systems revealed complicated interactions between the elements. In the range of low gallium contents (up to 6.7 at.%) we observed solid solutions  $RECu_{1.0-0.8}Ga_{0-0.2}In$  with ZrNiAl-type structures. Increasing of the Ga content causes the formation of new phases with  $CaIn_2$ -type structures. The unit-cell parameters of the phases with the ZrNiAl and  $CaIn_2$  structure types depend on the size and concentration of the Cu and Ga atoms [28]. The phase analysis of the samples with  $x > 0.7$  correlates with the results of the interaction of the components in the ternary systems  $RE-Cu-In$  [26,29] and  $RE-Cu-Ga$  [30,31] in the area of equiatomic content. In the quasi-ternary systems  $LaGa_2-LaCu_2-LaIn_2$  and  $CeGa_2-CeCu_2-CeIn_2$ , the phases  $La(Cu,Ga,In)_2$  and

$Ce(Cu,Ga,In)_2$  with  $CaIn_2$ -type structures are probably formed as a result of a redistribution of atoms between ZrNiAl-,  $AlB_2$ - and  $KHg_2$ -type structures (Fig. 5), which are related to each other [32].

In the compounds with ZrNiAl-type structures the Cu atoms occupy Wyckoff positions 1a and 2d. The Cu atoms in 1a center trigonal prisms of In atoms, and those in 2d trigonal prisms of RE atoms. The replacement of Cu atoms by Ga atoms probably occurs in position 1a, which leads to a slight decrease of the parameter  $a$  and an increase of the parameter  $c$  within the solid solutions  $RECu_{1.0-0.8}Ga_{0-0.2}In$ . Reducing the Cu content leads to a transformation of the ZrNiAl-type structure to a  $CaIn_2$ -type structure. This change is probably due to the increase of number of valence electrons per atom, as well as the  $r_R/r_M$  ratio

in these phases. The cell parameter ratios ( $c/a$ ), ratios of the atomic radii ( $r_R/r_M$ ), and electron concentrations ( $e/atom$ ) of the compounds in the quasi-ternary systems  $LaGa_2-LaCu_2-LaIn_2$  and  $CeGa_2-CeCu_2-CeIn_2$  are given in Table 6.

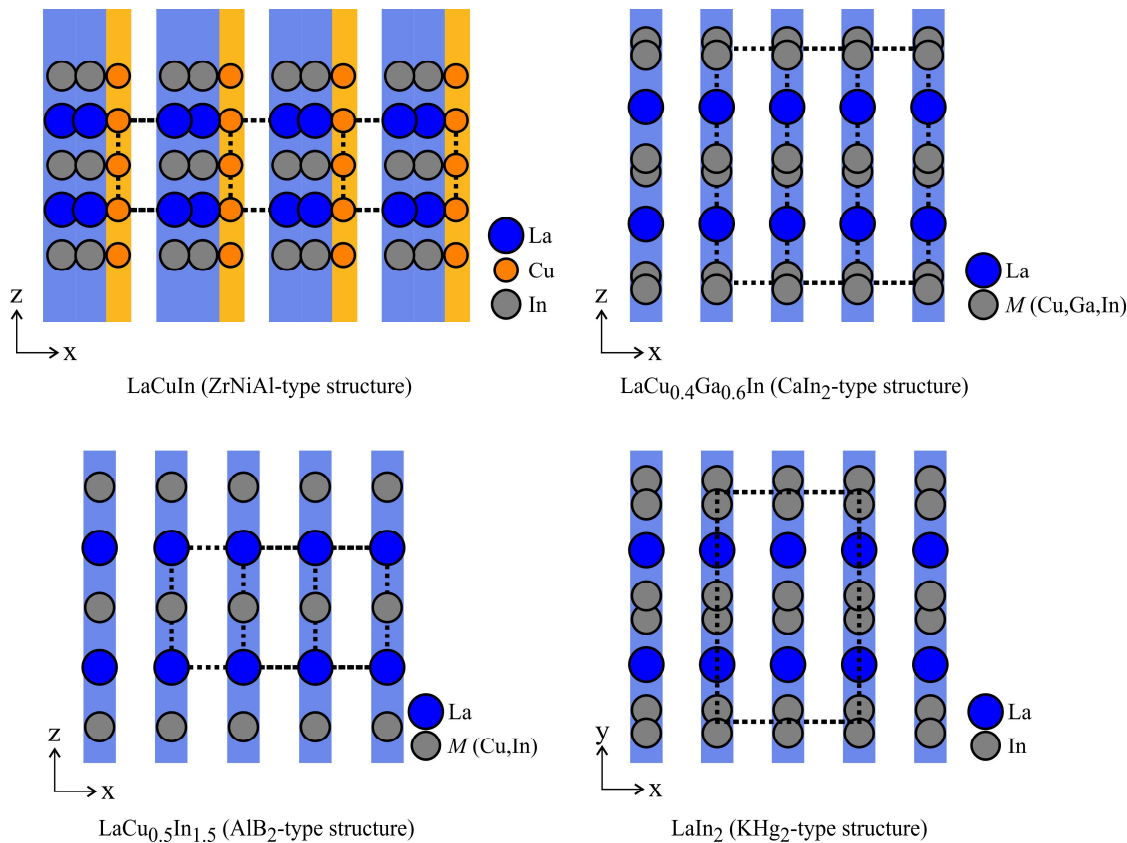
The Cu/Ga ratio influences directly on the formation of different types of structure derived from the  $AlB_2$  structure type and correlates with the results reported by Dwight [35]. A more radical situation occurs in the  $LaCu_2-LaSi_2$  system, where substitution of Si for Cu changes the structure from a hexagonal ZrBeSi-type structure (space group  $P6_3/mmc$ ) for  $LaCuSi$  through an  $AlB_2$ -type structure (space group

$P6/mmm$ ) to a tetragonal  $\alpha-ThSi_2$ -type structure (space group  $I4_1/amd$ ) for  $LaSi_2$  [36].

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**Fig. 5** Layers of atoms in the structures of  $LaCuIn$ ,  $LaCu_{0.5}In_{1.5}$ ,  $LaCu_{0.4}Ga_{0.6}In$  and  $LaIn_2$ .

**Table 6** Cell parameter ratios ( $c/a$ ), ratios between the atomic radii ( $r_R/r_M$ ) and electron concentrations ( $e/atom$ ) of selected compositions in the quasi-ternary systems  $LaGa_2-LaCu_2-LaIn_2$  and  $CeGa_2-CeCu_2-CeIn_2$ .

Compound	$LaCuIn$ [1] (ZrNiAl-type structure, $P-62m$ , 189)	$LaCu_{0.5}In_{1.5}$ [3] ( $AlB_2$ -type structure, $P6/mmm$ , 191)	$LaCu_{0.4}Ga_{0.6}In$ ( $CaIn_2$ -type structure, $P6_3/mmc$ , 194)	$LaIn_2$ [33] ( $KHg_2$ -type structure, $Imma$ , 74)
$c/a$	0.567	0.835	1.661	1.910
$r_R/r_M$ [28]	0.646	0.610	0.654	0.577
$e/atom$	2.67	2.83	2.87	3
Compound	$CeCuIn$ (ZrNiAl) [2]	$CeCu_{0.5}In_{1.5}$ ( $AlB_2$ ) [3]	$CeCu_{0.5}Ga_{0.5}In$ ( $CaIn_2$ )	$CeIn_2$ ( $KHg_2$ ) [34]
$c/a$	0.567	0.809	1.630	1.903
$r_R/r_M$ [28]	0.628	0.593	0.635	0.561
$e/atom$	2.67	2.83	2.83	3

## References

- [1] A.E. Dwight, *Proc. Rare Earth Res. Conf., 12th*, Colorado, 1976, Vol. 1, pp. 480-489.
- [2] A. Szytuła, D. Kaczorowski, M. Kalychak, B. Penc, Yu. Tyvanchuk, A. Winiarski, *J. Phys. Chem. Solids* 69 (2008) 2416-2419.
- [3] V.M. Baranyak, O.V. Dmytrakh, Y.M. Kalychak, P.Y. Zavalii, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 24 (1988) 873-874.
- [4] Y.B. Tyvanchuk, A. Szytuła, A. Zarzycki, U.C. Rodewald, Y.M. Kalychak, R. Pöttgen, *J. Solid State Chem.* 181 (2008) 3223-3228.
- [5] R.-D. Hoffmann, R. Pöttgen, *Z. Kristallogr.* 216 (2001) 127-145.
- [6] A. Szytuła, Yu. Tyvanchuk, T. Jaworska-Gołąb, A. Zarzycki, Y.M. Kalychak, L. Gondek, N. Stüsser, *Chem. Met. Alloys* 1 (2008) 97-101.
- [7] J.L. Bobet, M. Pasturel, B. Chevalier, *Intermetallics* 14 (2006) 544-550.
- [8] A. Szytuła, B. Penc, *Acta Phys. Pol. A* 111(4) (2007) 475-486.
- [9] D.P. Rojas, J.I. Espeso, J.M. Rodriguez Fernandez, J.C. Gomez Sal, *Phys. B (Amsterdam)* 378/380 (2006) 847-848.
- [10] Q. Hu, Z. Xianyu, M. Qui, X. Yan, Z. Cheng, Q. Zhao, W. Sun, *J. Magn. Magn. Mater.* 140-144 (1995) 1225-1226.
- [11] H. Nakotte, E. Brück, K. Prokeš, F.R. de Boer, *IEEE Trans. Magn.* 30(2) (1994) 1202-1204.
- [12] H. Nakotte, K. Prokeš, F.R. de Boer, *IEEE Trans. Magn.* 30(2) (1994) 1205-1207.
- [13] Ya.M. Kalychak, V.I. Zaremba, R. Pöttgen, M. Lukachuk, R.-D. In: K.A. Gschneidner, Jr., J.-C. Bünzli, V.K. Pecharsky (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 34, Elsevier, Amsterdam, 2005, pp. 1-133.
- [14] S. Gupta, K.G. Suresh, *J. Alloys Compd.* 618 (2015) 562-606.
- [15] Yu.N. Grin, K. Hiebl, P. Rogl, *J. Less-Comm. Met.* 110 (1985) 299-305.
- [16] N. Zaremba, G. Nychyporuk, Yu. Schepilov, O. Panakhyd, I. Muts, V. Hlukhyy, V. Pavlyuk, *Ukr. Khim. Zh.* 84(12) (2018) 76-84 (in Ukrainian).
- [17] N. Zaremba, G. Nychyporuk, Yu. Schepilov, R. Serkiz, V. Hlukhyy, V. Pavlyuk, *Visn. Lviv. Univ., Ser. Khim.* 60(1) (2019) 82-90 (in Ukrainian).
- [18] P. Wisniewski, V.I. Zaremba, A. Ślebarski, D. Kaczorowski, *Intermetallics* 56 (2015) 101-106.
- [19] D. Gnida, N. Dominyuk, V. Zaremba, D. Kaczorowski, *J. Alloys Compd.* 622 (2015) 681-686.
- [20] B. Penc, A. Winiarski, A. Szytuła, D. Kaczorowski, *J. Alloys Compd.* 569 (2013) 22-28.
- [21] N. Chumalo, G.P. Nychyporuk, V.V. Pavlyuk, R. Pöttgen, D. Kaczorowski, V.I. Zaremba, *J. Solid St. Chem.* 183 (2010) 2963-2967.
- [22] W. Kraus, G. Nolze *Powder Cell for Windows*. Berlin, 1999.
- [23] STOE WinXPOW, Version 1.2, STOE & CIE GmbH. Darmstadt, 2001.
- [24] J. Rodriguez-Carvajal, *Commission on Powder Diffraction, IUCr Newsletter* 26 (2001) 12.
- [25] G.M. Sheldrick, *SHELX-97. Program for Crystal Structures Refinement*, University of Göttingen, Germany, 1997.
- [26] O.V. Dmytrakh, Ya.M. Kalychak, *Izv. Akad. Nauk SSSR, Met.* 6 (1990) 197-199.
- [27] A. Iandelli, *Z. Anorg. Allg. Chem.* 330 (1964) 221-232.
- [28] J. Emsley, *The Elements*, Oxford University Press, Oxford, U.K., 1999.
- [29] V.M. Baranyak, Ya.M. Kalychak, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 27(6) (1991) 1235-1238.
- [30] I.P. Shevchenko, V.Ya. Markiv, P.P. Kuzmenko, *Visnyk Kiiv. Univ., Ser. Fiz.* 28 (1987) 7-16.
- [31] O. Mykhalichko, R. Gladyshevskii, *Coll. Abstr. XVIII Int. Sem. Phys. Chem. Solids.*, Lviv, 2012, p. 46.
- [32] R.-D. Hoffmann, R. Pöttgen, *Z. Kristallogr.* 216 (2001) 127-145.
- [33] O.D. McMasters, K.A. Gschneidner Jr., *J. Less-Common Met.* 38 (1974) 137-148.
- [34] S. Delfino, A. Saccone, R. Ferro, *Z. Metallkd.* 71 (1980) 165-171.
- [35] A.E. Dwight, In: G.J. McCarthy (Ed.), *The Rare Earths in Modern Science and Technology*, Springer, 1980, Vol. 2, pp. 39-44.
- [36] M. Fedyna, A. Fedorchuk, L. Fedyna, *Visn. Lviv. Univ. Ser. Khim.* 54(1) (2013) 37-44 (in Ukrainian).