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V.Ya. Gvozdetskyi, R.E. Gladyshevskii, N.V. German

Multicomponent Phases with $CeAl_2Ga_2$- and $Y_{0.5}Co_3Ge_3$-Type Structures in the Gd–Ca–Fe–Co–Ge System

Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine, e-mail: volodymyr.gvozdetskyi@gmail.com

New quinary phases with the $CeAl_2Ga_2$ (*tI*10, *I*4/*mmm*) and $Y_{0.5}Co_3Ge_3$ (*hP*8-2, *P*6/*mmm*) structure types were found at 500 ºC in the Gd–Ca–Fe–Co–Ge system based on X-ray powder diffraction data. They are $Gd_{1-x}Ca_xFe_{2-y}Co_yGe_2$ (x = 0.085(7)-0.551(6), y = 0.25-0.75, a = 3.99468(6)-4.00003(8), c = 10.1279(2)-10.3981(5) Å) and $Ca_{0.5-x}Gd_xFe_{3-y}Co_yGe_3$ (x = 0.031(1)-0.314(8), y = 0.75-2.25, a = 5.1081(1)-5.1218(1), c = 3.9751(1)-4.0451(2) Å). The *c*-parameter of the tetragonal $CeAl_2Ga_2$-type (122) phase cell depends much more on the Fe/Co and Gd/Ca ratios, than the *a*-parameter (which remains nearly the same). The volume of the 122 cell increases with increasing Fe and Ca content. The *c*-parameter of the hexagonal cell of the $Y_{0.5}Co_3Ge_3$-type (0.533) phase also depends more strongly on the Fe/Co content than the *a*-parameter, but Gd/Ca substitutions have little effect on the cell parameters. The following new quaternary and ternary phases were also discovered: $GdFe_{2-y}Co_yGe_2$ (y = 0.5-1.5, a = 3.99419(5)-3.99750(7), c = 10.3271(2)-10.1173(3) Å) with $CeAl_2Ga_2$-type structure and $Gd_{0.5}Fe_{3-y}Co_yGe_3$ (y = 0.75-1.5, a = 5.1247(8)-5.1225(7), c = 4.052(1)-4.010(1) Å), $Ca_{0.5}Fe_{3-y}Co_yGe_3$ (y = 0.75-2.25, a = 5.1153(2)-5.1066(2), c = 4.0451(2)-3.9839(3) Å), $Ca_{0.5}Fe_3Ge_3$ (a = 5.10167(9), c = 4.06565(7) Å), and $Ca_{0.5}Co_3Ge_3$ (a = 5.0899(2), c = 3.9199(1) Å) with $Y_{0.5}Co_3Ge_3$-type structure. The latter two phases, together with the already known compounds $Gd_{0.5}Fe_3Ge_3$ and $Gd_{0.5}Co_3Ge_3$, are the parent compounds for the probably complete solid solution $Ca_{0.5-x}Gd_xFe_{3-y}Co_yGe_3$, just as the corresponding ternary compounds (except in the Ca–Fe–Ge system) with $CeAl_2Ga_2$-type structures open access to the $Gd_{1-x}Ca_xFe_{2-y}Co_yGe_2$ solid solution.

Keywords: Gd–Ca–Fe–Co–Ge system, intermetallics, solid solution, crystal structure.

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Introduction

The discovery of superconductivity in $Ba_{0.6}K_{0.4}Fe_2As_2$ [1] has drawn the attention to compounds crystallizing with the $CeAl_2Ga_2$ (122) structure type (Pearson symbol *tI*10, space group *I*4/*mmm*) [1]. Some 700 compounds with 122-type structure are known in different *R*–*T*–*X* (*A* = alkaline-earth, rare-earth metal, *T* = transition metal, *X* = element of the main group) systems [2], leading to a large number of substitution possibilities.

No compounds were previously known in the quinary Gd–Ca–Fe–Co–Ge system. Concerning the ternary boundary systems Gd–Fe–Ge, Gd–Co–Ge, Ca–Co–Ge, and Fe–Co–Ge, 20 phases have been reported [2]: $Gd_{0.5}Fe_3Ge_3$ ($Y_{0.5}Co_3Ge_3$-type structure), $GdFe_2Ge_2$ ($CeAl_2Ga_2$-type structure), $GdFe_{0.52}Ge_2$ ($CeNiSi_2$-type structure), $Gd_{117}Fe_{52}Ge_{112}$ ($Tb_{117}Fe_{52}Ge_{112}$-type structure), $Gd_{0.5}Co_3Ge_3$ ($Y_{0.5}Co_3Ge_3$-type structure), $Gd_3Co_4Ge_{13}$ ($Yb_3Rh_4Sn_{13}$-type structure), $Gd_2Co_3Ge_5$ ($Lu_2Co_3Si_5$-type structure), $GdCo_2Ge_2$ ($CeAl_2Ga_2$-type structure), Gd_2CoGe_6 (Ce_2CuGe_6-type structure), $GdCo_{0.8}Ge_2$ ($CeNiSi_2$-type structure), $Gd_3Co_2Ge_4$ ($Tb_3Co_2Ge_4$-type structure), GdCoGe (TiNiSi-type structure), Gd_2CoGe_2 (Sc_2CoSi_2-type structure), $CaCo_2Ge_2$ ($CeAl_2Ga_2$-type structure), $CoFe_2Ge$ and Co_2FeGe (both Cu_2MnAl-type structure), CoFeGe (BeZrSi-type structure), $(Co_{0.4}Fe_{0.6})Ge_2$ ($CuAl_2$-type structure), $(Co_{0.9}Fe_{0.9})Ge$ ($Co_{1.75}Ge$-type structure), and $(Co_{1.5}Fe_{1.5})Ge$ (BiF_3-type structure). The latter four phases could be solid solutions based on Fe–Ge binaries.

The aim of this work was to search for new multicomponent phases based on Gd, Ca, Fe, Co, and Ge, that adopt the $CeAl_2Ga_2$ (122) structure type.

I. Experiment

Starting materials for the synthesis were ingots of gadolinium, calcium, iron, cobalt, and germanium with purities better than 99.85 %. Quinary alloys with a mass of 0.5 g were synthesized in an arc furnace with a copper water-cooled hearth, using a tungsten electrode under argon atmosphere. The alloys were homogenized in evacuated quartz ampoules at 500ºC for 1440 h in a Vulcan A-550 furnace with an automatic temperature control of ± 1 - 2 °C. The annealed alloys were quenched in cold water without breaking the ampoules. X-ray phase and structural analyses were performed using diffraction data obtained from DRON-2.0M and DRON-4.07 powder diffractometers (Fe *K*α radiation). For the indexation of the experimental diffraction patterns, theoretical patterns were calculated using the program POWDER CELL-2.4 [3] and the databases TYPIX [4] and PEARSON'S CRYSTAL DATA [2]. Crystal structure refinements by the Rietveld method were performed using the FullProf program [5].

II. Results

At the first stage of the investigation, the crystal structures of the five-component phases $Gd_{1-x}Ca_xFeCoGe_2$ and $Ca_{0.5-y}Gd_yFe_{1.5}Co_{1.5}Ge_3$ were refined [6] on X-ray powder diffraction data (Figs 1 and 2) from an alloy of composition $Gd_{1.5}Ca_{0.5}FeCoGe_2$ (homogenized at 500ºC for two months). The unit-cell parameters of the phase $Gd_{1-x}Ca_xFeCoGe_2$ (structure type $CeAl_2Ga_2$ (122), *tI*10, *I*4/*mmm*, *a* = 4.00126(9), *c* = 10.1922(3) Å, *x* = 0.152(8)) are of the same magnitude as those of the isotypic ternary compounds $GdFe_2Ge_2$ (*a* = 3.9867, *c* = 10.4798 Å) [7,8] and $GdCo_2Ge_2$ (*a* = 3.996, *c* = 10.066 Å) [8]. Refinement of the structure of the phase $Ca_{0.5-x}Gd_xFe_{1.5}Co_{1.5}Ge_3$ (structure type $Y_{0.5}Co_3Ge_3$ (0.533), *hP*8-2, *P*6/*mmm*, *a* = 5.1154(2), *c* = 4.0142(3) Å, *x* = 0.045(6)) showed mixed occupation Ca/Gd of site 1*a* (45.5/4.5 %), while a refinement on diffraction data from an as-cast alloy revealed occupation of site 1*a* by Ca

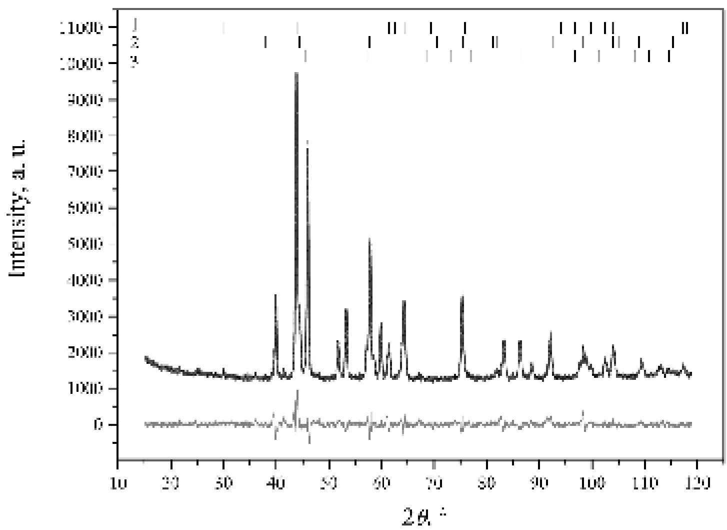

Fig. 1. XRD pattern (Fe *K*α radiation) of an alloy of composition $Gd_{1.5}Ca_{0.5}FeCoGe_2$, homogenized at 500ºC, which contains the following phases: 1 – $Gd_{0.849(8)}Ca_{0.151(8)}FeCoGe_2$ ($CeAl_2Ga_2$, *I*4/*mmm*), 2 – $Ca_{0.455(6)}Gd_{0.045(6)}Fe_{1.5}Co_{1.5}Ge_3$ ($Y_{0.5}Co_3Ge_3$, *P*6/*mmm*), 3 – FeCoGe (ZrBeSi, $P6_3/mmc$)

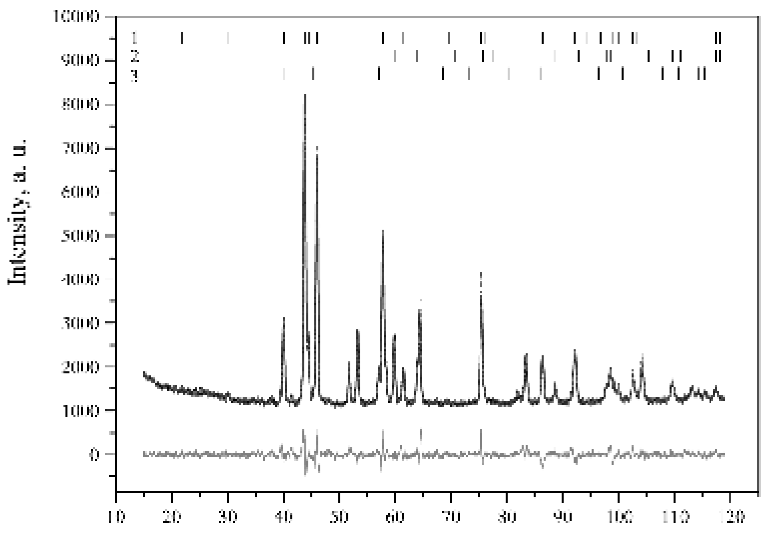

Fig. 2. XRD pattern (Fe *K*α radiation) of an as-cast alloy of composition $Gd_{1.5}Ca_{0.5}FeCoGe_2$, which contains the following phases: 1 – $Gd_{0.897(9)}Ca_{0.103(9)}FeCoGe_2$ ($CeAl_2Ga_2$, *I*4/*mmm*), 2 – $Ca_{0.5}Fe_{1.5}Co_{1.5}Ge_3$ ($Y_{0.5}Co_3Ge_3$, *P*6/*mmm*), 3 – FeCoGe (ZrBeSi, $P6_3/mmc$)

Table 1

Crystallographic parameters of the $Gd_{1-x}Ca_xFeCoGe_2$ and $Ca_{0.5-x}Gd_xFe_{1.5}Co_{1.5}Ge_3$ phases (homogenized alloy)

$Gd_{1-x}Ca_xFeCoGe_2$ (x = 0.151(8)), structure type $CeAl_2Ga_2$, space group $I4/mmm$, a = 4.00126(9), c = 10.1922(3) Å, R_B = 0.0467						
Site	Wyckoff position	x	y	z	Occupation	B_{iso}, Å^2
Gd/Ca	2*a*	0	0	0	0.849(8)/0.151(8)	0.47(5)
Fe/Co	4*d*	0	½	¼	0.5/0.5	0.51(5)
Ge	4*e*	0	0	0.3715(1)	1	0.49(5)
$Ca_{0.5-x}Gd_xFe_{1.5}Co_{1.5}Ge_3$ (x = 0.045(6)), structure type $Y_{0.5}Co_3Ge_3$, space group $P6/mmm$, a = 5.1154(2), c = 4.0142(3) Å, R_B = 0.0933						
Site	Wyckoff position	x	y	z	Occupation	B_{iso}, Å^2
Ca/Gd	1*a*	0	0	0	0.455(6)/0.045(6)	0.47(5)
Fe/Co	3*g*	½	0	½	0.5/0.5	0.51(5)
Ge1	2*c*	⅓	⅔	0	1	0.49(5)
Ge2	2*e*	0	0	0.290(1)	0.5	0.49(5)

Table 2

Crystallographic parameters of the $Gd_{1-x}Ca_xFeCoGe_2$ and $Ca_{0.5-x}Gd_xFe_{1.5}Co_{1.5}Ge_3$ phases (as-cast alloy)

$Gd_{1-x}Ca_xFeCoGe_2$ (x = 0.103(9)), structure type $CeAl_2Ga_2$, space group $I4/mmm$, a = 4.00120(8), c = 10.1872(3) Å, R_B = 0.0498						
Site	Wyckoff position	x	y	z	Occupation	B_{iso}, Å^2
Gd/Ca	2*a*	0	0	0	0.897(9)/0.103(9)	0.34(5)
Fe/Co	4*d*	0	½	¼	0.5/0.5	0.53(5)
Ge	4*e*	0	0	0.3722(1)	1	0.52(4)
$Ca_{0.5-x}Gd_xFe_{1.5}Co_{1.5}Ge_3$ (x = 0, structure type $Y_{0.5}Co_3Ge_3$, space group $P6/mmm$, a = 5.1153(2), c = 4.0120(2) Å, R_B = 0.0846						
Site	Wyckoff position	x	y	z	Occupation	B_{iso}, Å^2
Ca/Gd	1*a*	0	0	0	0.5/0	0.34(5)
Fe/Co	3*g*	½	0	½	0.5/0.5	0.53(5)
Ge1	2*c*	⅓	⅔	0	1	0.52(4)
Ge2	2*e*	0	0	0.293(1)	0.5	0.52(4)

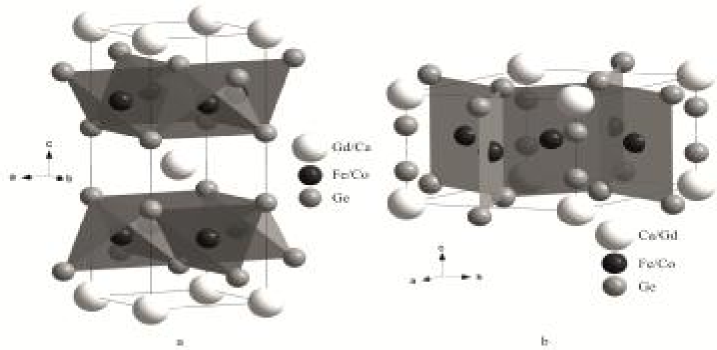

Fig. 3. Crystal structure of the phases (a) $Gd_{1-x}Ca_xFeCoGe_2$ ($CeAl_2Ga_2$, $I4/mmm$) and (b) $Ca_{0.5-x}Gd_xFe_{1.5}Co_{1.5}Ge_3$ ($Y_{0.5}Co_3Ge_3$, $P6/mmm$)

atoms alone – composition $Ca_{0.5}Fe_{1.5}Co_{1.5}Ge_3$ (a = 5.1153(2), c = 4.0120(2) Å). Because of the closeness of the atomic scattering factors of Fe and Co, their content ratio cannot be accurately refined from X-ray diffraction data and was constrained in this and the following refinements to its value in the nominal composition of the alloy. Relevant crystallographic parameters of the refined structures are listed in Table 1 and Table 2. Models of the 122 and 0.533 structures are presented in Fig. 3.

The result, indicating the coexistence of two phases (122 and 0.533) in the alloy with 122 overall composition, motivated more detailed investigations, and additional alloys were synthesized with the compositions given in Table 3.

The diffraction patterns of all of the samples contained 122 and 0.533 phases and small amounts (less than 5 %) of additional ternary and binary phases (among

Table 3

Crystallographic parameters of the $Gd_{1-x}Ca_xFe_{2-y}Co_yGe_2$ and $Ca_{0.5-x}Gd_xFe_{3-y}Co_yGe_3$ phases

Phase 122	Cell parameters, Å		Volume, Å^3	Phase 0.533	Cell parameters, Å		Volume, Å^3
	a	*c*			*a*	*c*	
Nominal composition of the alloy: $Gd_{0.25}Ca_{0.75}Fe_{0.5}Co_{1.5}Ge_2$, refined composition: $Gd_{0.27}Ca_{0.35}Fe_{0.50}Co_{1.50}Ge_2$, molar ratio 122/0.533 = 0.53/0.47							
$Gd_{0.610(7)}Ca_{0.390(7)}\times$ $\times Fe_{0.5}Co_{1.5}Ge_2$	3.99608(8)	10.2034(3)	162.93(1)	$Ca_{0.469(3)}Gd_{0.031(3)}\times$ $\times Fe_{0.75}Co_{2.25}Ge_3$	5.1081(1)	3.9751(1)	89.825(6)
Nominal composition of the alloy: $Gd_{0.5}Ca_{0.5}Fe_{0.5}Co_{1.5}Ge_2$, refined composition: $Gd_{0.55}Ca_{0.25}Fe_{0.50}Co_{1.50}Ge_2$, molar ratio 122/0.533 = 0.78/0.22							
$Gd_{0.793(8)}Ca_{0.207(8)}\times$ $\times Fe_{0.5}Co_{1.5}Ge_2$	3.99644(7)	10.1526(3)	162.15(1)	$Ca_{0.5}Fe_{0.75}Co_{2.25}Ge_3$	5.1066(2)	3.9839(3)	89.97(1)
Nominal composition of the alloy: $Gd_{0.75}Ca_{0.25}Fe_{0.5}Co_{1.5}Ge_2$, refined composition: $Gd_{0.71}Ca_{0.14}Fe_{0.50}Co_{1.50}Ge_2$, molar ratio 122/0.533 = 0.83/0.17							
$Gd_{0.910(7)}Ca_{0.090(7)}\times$ $\times Fe_{0.5}Co_{1.5}Ge_2$	3.99682(6)	10.1279(2)	161.789(8)	$Ca_{0.457(3)}Gd_{0.043(3)}\times$ $\times Fe_{0.75}Co_{2.25}Ge_3$	5.1106(2)	3.9869(3)	90.18(1)
Nominal composition of the alloy: $Gd_{0.25}Ca_{0.75}Fe_1Co_1Ge_2$, refined composition: $Gd_{0.29}Ca_{0.36}Fe_{1.00}Co_{1.00}Ge_2$, molar ratio 122/0.533 = 0.52/0.48							
$Gd_{0.558(7)}Ca_{0.442(7)}\times$ $\times Fe_1Co_1Ge_2$	4.00003(8)	10.2518(3)	164.03(1)	$Ca_{0.450(3)}Gd_{0.050(3)}\times$ $\times Fe_{1.5}Co_{1.5}Ge_3$	5.1150(1)	4.0079(1)	90.811(6)
Nominal composition of the alloy: $Gd_{0.5}Ca_{0.5}Fe_1Co_1Ge_2$, refined composition: $Gd_{0.51}Ca_{0.17}Fe_{1.00}Co_{1.00}Ge_2$, molar ratio 122/0.533 = 0.61/0.39							
$Gd_{0.884(6)}Ca_{0.116(6)}\times$ $\times Fe_1Co_1Ge_2$	3.99949(6)	10.1922(2)	163.03(1)	$Ca_{0.319(4)}Gd_{0.181(4)}\times$ $\times Fe_{1.5}Co_{1.5}Ge_3$	5.1162(1)	4.0105(1)	90.913(6)
Nominal composition of the alloy: $Gd_{0.75}Ca_{0.25}Fe_{1.5}Co_{1.5}Ge_2$, refined composition: $Gd_{0.66}Ca_{0.14}Fe_{1.00}Co_{1.00}Ge_2$, molar ratio 122/0.533 = 0.78/0.22							
$Gd_{0.915(7)}Ca_{0.085(7)}\times$ $\times Fe_1Co_1Ge_2$	3.99903(6)	10.1915(2)	162.985(8)	$Ca_{0.186(8)}Gd_{0.314(8)}\times$ $\times Fe_{1.5}Co_{1.5}Ge_3$	5.1190(2)	4.0168(3)	91.16(1)
Nominal composition of the alloy: $Gd_{0.25}Ca_{0.75}Fe_{1.5}Co_{0.5}Ge_2$, refined composition: $Gd_{0.24}Ca_{0.45}Fe_{1.50}Co_{0.50}Ge_2$, molar ratio 122/0.533 = 0.63/0.37							
$Gd_{0.449(6)}Ca_{0.551(6)}\times$ $\times Fe_{1.5}Co_{0.5}Ge_2$	3.9976(1)	10.3981(5)	166.17(2)	$Ca_{0.5}Fe_{2.25}Co_{0.75}Ge_3$	5.1135(2)	4.0451(2)	91.60(1)
Nominal composition of the alloy: $Gd_{0.5}Ca_{0.5}Fe_{1.5}Co_{0.5}Ge_2$, refined composition: $Gd_{0.51}Ca_{0.17}Fe_{1.50}Co_{0.50}Ge_2$, molar ratio 122/0.533 = 0.62/0.38							
$Gd_{0.882(6)}Ca_{0.118(6)}\times$ $\times Fe_{1.5}Co_{0.5}Ge_2$	3.99612(6)	10.3272(2)	164.915(8)	$Ca_{0.325(4)}Gd_{0.175(4)}\times$ $\times Fe_{2.25}Co_{0.75}Ge_3$	5.1189(1)	4.0410(1)	91.70(1)
Nominal composition of the alloy: $Gd_{0.75}Ca_{0.25}Fe_{1.5}Co_{0.5}Ge_2$, refined composition: $Gd_{0.63}Ca_{0.12}Fe_{1.50}Co_{0.50}Ge_2$, molar ratio 122/0.533 = 0.71/0.29							
$Gd_{0.909(7)}Ca_{0.091(7)}\times$ $\times Fe_{1.5}Co_{0.5}Ge_2$	3.99468(6)	10.3249(2)	164.759(8)	$Ca_{0.263(8)}Gd_{0.237(8)}\times$ $\times Fe_{2.25}Co_{0.75}Ge_3$	5.1218(1)	4.0436(3)	91.86(1)

them $(Co,Fe)_2Ge$ (structure type $Co_{1.75}Ge$, ***hP***6, ***P***6_3/***mmc***), Ca_7Ge ($CuPt_7$, ***cF***32, ***Fm***-3***m***), $GdGe_{1.5}$ (AlB_2, ***hP***3, ***P***6/***mmm***), *etc.*).

The calculation of the composition of the alloys for each case is shown in Table 3.

III. Discussion

The refinements carried out on the samples listed in Table 3, showed that the alloy compositions are located in a concentration region between the 122 and 0.533 phases (Fig. 4), obviously because of losses of Ca during arc-melting (unfortunately the weight losses were always in the range 3-5 %).

Considering the values of the cell parameters of the 122 and 0.533 phases (see Table 3), the following conclusions can be drawn: the *c*-parameter of the tetragonal 122 cell depends more on the Fe/Co and Gd/Ca ratios than the ***a***-parameter (the latter remaining nearly the same). The volume of the 122 cell increases with increasing Fe and Ca content. The ***c***-parameter of the hexagonal 0.533 cell is also more dependent on the Fe/Co content than the ***a***-parameter, but Gd/Ca substitutions have no strong effect on the cell parameters. Contrary to what was observed for the 122 phase, the cell volume of the 0.533 phase increases with decreasing Ca content. The results are shown in Figs 5 and 6, which also take into consideration information (Table 4) about quaternary and ternary phases obtained for other alloys: $GdFe_{1.5}Co_{0.5}Ge_2$ (122 phase), $GdFeCoGe_2$ (122), $GdFe_{0.5}Co_{1.5}Ge_2$ (122), $CaCo_2Ge_2$ (122), $Gd_{0.5}Fe_{2.25}Co_{0.75}Ge_3$ (0.533), $Gd_{0.5}Fe_{1.5}Co_{1.5}Ge_3$ (0.533), $Ca_{0.5}Co_3Ge_3$ (0.533) [9], $Ca_{0.5}Fe_3Ge_3$ (0.533), and from [7,8] – $GdFe_2Ge_2$ (122), $Gd_{0.5}Fe_3Ge_3$ (0.533), and $GdCo_2Ge_2$ (122), and $Gd_{0.5}Co_3Ge_3$ (0.533) from [10].

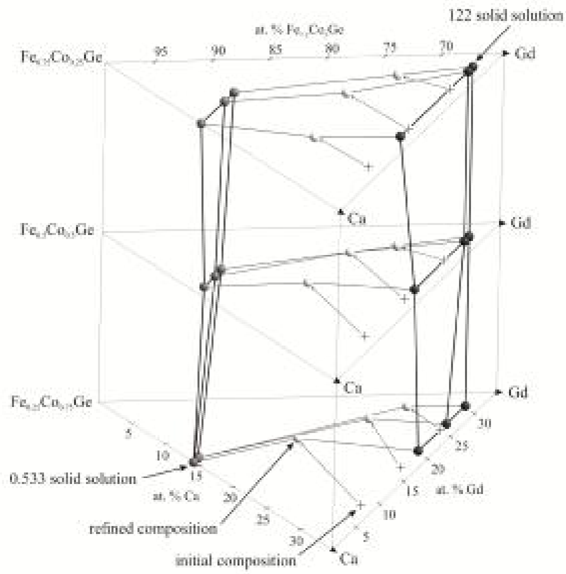

Fig. 4. 122 and 0.533 solid solutions in the quinary Gd–Ca–Fe–Co–Ge system.

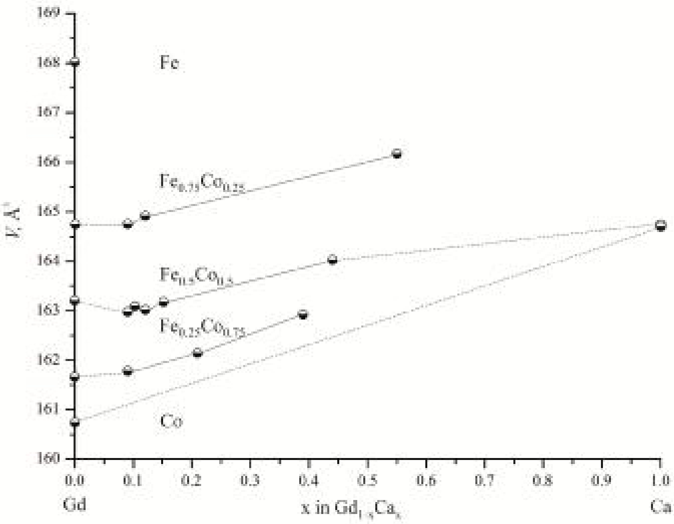

Fig. 5. Cell volume *versus* $Gd_{1-x}Ca_x$ composition of the 122 solid solution in the quinary Gd–Ca–Fe–Co–Ge system.

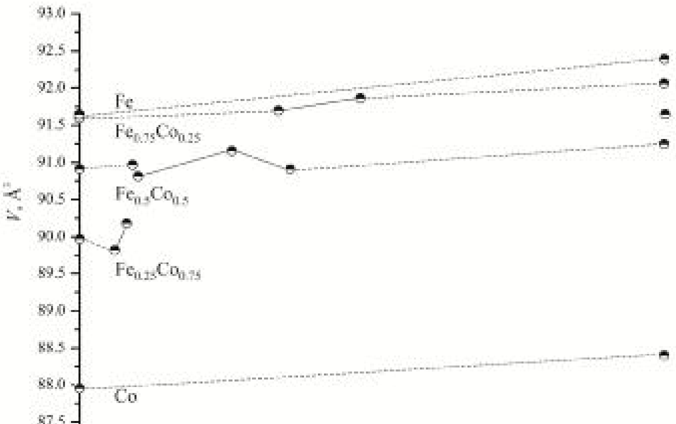

Fig. 6. Cell volume *versus* $Ca_{0.5-x}Gd_x$ composition of the 0.533 solid solution in the quinary Gd–Ca–Fe–Co–Ge system.

Table 4

Crystallographic parameters of quaternary and ternary 122 and 0.533 phases in the Gd–Fe–Co–Ge, Gd–{Fe,Co}–Ge and Ca–{Fe,Co}–Ge systems

Phase 122	Cell parameters, Å		Volume, Å^3	Reference
	a	*c*		
$GdFe_2Ge_2$	3.9867 3.989	10.4798 10.485	166.56 166.84	[7] [8]
$GdFe_{1.5}Co_{0.5}Ge_2$	3.99419(5)	10.3271(2)	164.754(7)	this work
$GdFeCoGe_2$	3.99915(7)	10.2055(2)	163.218(9)	this work
$GdFe_{0.5}Co_{1.5}Ge_2$	3.99750(7)	10.1173(3)	161.67(6)	this work
$GdCo_2Ge_2$	3.996	10.066	160.73	[8]
$CaCo_2Ge_2$	4.0011(8) 3.9900	10.291(4) 10.298	164.7(1) 163.95	this work [9]
Phase 0.533	Cell parameters, Å		Volume, Å^3	Reference
	a	*c*		
$Gd_{0.5}Fe_3Ge_3$	5.1176	4.0714	92.49	[9]
$Gd_{0.5}Fe_{2.25}Co_{0.75}Ge_3$	5.1225(7)	4.052(1)	92.08(5)	this work
$Gd_{0.5}Fe_{1.5}Co_{1.5}Ge_3$	5.1247(8)	4.010(1)	91.25(5)	this work
$Gd_{0.5}Co_3Ge_3$	5.096	3.931	88.41	[10]
$Ca_{0.5}Fe_3Ge_3$	5.10167(9)	4.06565(7)	91.641(5)	this work
$Ca_{0.5}Co_3Ge_3$	5.0899(2)	3.9199(1)	87.948(9)	this work

Conclusions

The new quinary phases $Gd_{1-x}Ca_xFe_{2-y}Co_yGe_2$ (x = 0.085(7)-0.551(6), y = 0.25-0.75, a = 3.99468(6)-4.00003(8), c = 10.1279(2)-10.3981(5) Å), with $CeAl_2Ga_2$-type structure (*tI*10, *I*4/*mmm*), and $Ca_{0.5-x}Gd_xFe_{3-y}Co_yGe_3$ (x = 0.031(1)-0.314(8), y = 0.75-2.25, a = 5.1081(1)-5.1218(1), c = 3.9751(1)-4.0451(2) Å), with $Y_{0.5}Co_3Ge_3$-type structure (*hP*8-2, *P*6/*mmm*), were found at 500ºC in the Gd–Ca–Fe–Co–Ge system. The regions of solid solutions indicated above were deduced from structural refinements of various samples, however, the existence of complete solid solutions based on the ternary compounds cannot be ruled out. The new quaternary 122 phase $GdFe_{2-y}Co_yGe_2$ (y = 0.5-1.5, a = 3.99419(5)-3.99750(7), c = 10.3271(2)-10.1173(3) Å) and the 0.533 phases $Gd_{0.5}Fe_{3-y}Co_yGe_3$ (y = 0.75-1.5, a = 5.1247(8)-5.1225(7), c = 4.052(1)-4.010(1) Å), $Ca_{0.5}Fe_{3-y}Co_yGe_3$ (y = 0.75-2.25, a = 5.1135(2)-5.1066(2), c = 4.0451(2)-3.9839(3) Å), $Ca_{0.5}Fe_3Ge_3$ (a = 5.10167(9), c = 4.06565(7) Å), and $Ca_{0.5}Co_3Ge_3$ (a = 5.0899(2), c = 3.9199(1) Å), were also found during the investigation. The observations raise the question concerning the possible existence of complete multicomponent solid solutions $Gd_{1-x}Ca_xFe_{2-y}Co_yGe_2$ and $Ca_{0.5-x}Gd_xFe_{3-y}Co_yGe_3$ between the boundary ternary compounds.

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Gvozdetskyi V.Ya. – post-graduate student at the Department of Inorganic Chemistry;
Gladyshevskii R.E. – Corresponding Member of the National Academy of Sciences of Ukraine,
Director of the Department of Inorganic Chemistry;
German N.V. – Director of the Laboratory of Inorganic Chemistry and X-Ray Structure Analysis, Department of Inorganic Chemistry.

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В.Я. Гвоздецький, Р.Є. Гладишевський, Н.В. Герман

Багатокомпонентні фази зі структурами типів $CeAl_2Ga_2$ та $Y_{0,5}Co_3Ge_3$ у системі Gd–Ca–Fe–Co–Ge

Кафедра неорганічної хімії, Львівський національний університет імені Івана Франка, вул. Кирила і Мефодія 6, 79005 Львів, volodymyr.gvozdetskyi@gmail.com

За результатами ренгенофазового та рентгеноструктурного аналізу у системах Gd–Ca–Fe–Co–Ge при 500ºC знайдено нові п'ятикомпонентні фази зі структурами типів $CeAl_2Ga_2$ (*tI*10, *I*4/*mmm*) та $Y_{0,5}Co_3Ge_3$ (*hP*8-2, *P*6/*mmm*): $Gd_{1-x}Ca_xFe_{2-y}Co_yGe_2$ (x = 0.085(7)-0.551(6), y = 0.25-0.75, a = 3.99468(6)-4.00003(8), c = 10.1279(2)-10.3981(5) Å) та $Ca_{0.5-x}Gd_xFe_{3-y}Co_yGe_3$ (x = 0.031(1)-0.314(8), y = 0.75-2.25, a = 5.1081(1)-5.1218(1), c = 3.9751(1)-4.0451(2) Å). Параметр c тетрагональної комірки структури типу $CeAl_2Ga_2$ (122) більшою мірою залежить від співвідношення Fe/Co та Gd/Ca, ніж параметр a (залишається майже однаковим). Таким чином, із збільшенням вмісту Fe та Ca, об'єм комірки закономірно збільшується. Параметр c гексагональної комірки структури типу $Y_{0,5}Co_3Ge_3$ (0.533) також більшою мірою залежить від співвідношення Fe/Co, ніж параметр a, проте заміщення Gd/Ca майже не впливає на значення параметрів комірки. Нові тетрарні та тернарні фази були також знайдені: $GdFe_{2-y}Co_yGe_2$ (y = 0,5-1,5, a = 3,99419(5)-3,99750(7), c = 10,3271(2)-10,1173(3) Å) зі структурою типу $CeAl_2Ga_2$ та $Gd_{0,5}Fe_{3-y}Co_yGe_3$ (y = 0,75-1,5, a = 5,1247(8)-5,1225(7), c = 4,052(1)-4,010(1) Å), $Ca_{0,5}Fe_{3-y}Co_yGe_3$ (y = 0,75-2,25, a = 5,1153(2)-5,1066(2), c = 4,0451(2)-3,9839(3) Å), $Ca_{0,5}Fe_3Ge_3$ (a = 5,10167(9), c = 4,06565(7) Å) та $Ca_{0,5}Co_3Ge_3$ (a = 5,0899(2), c = 3,9199(1) Å) зі структурою типу $Y_{0,5}Co_3Ge_3$. Останні дві фази разом із раніше відомими сполуками $Gd_{0,5}Fe_3Ge_3$ та $Gd_{0,5}Co_3Ge_3$ є граничними складами із можливого неперервного твердого розчину $Ca_{0,5-x}Gd_xFe_{3-y}Co_yGe_3$, як і відповідні тернарні сполуки (окрім системи Ca–Fe–Ge) зі структурою типу $CeAl_2Ga_2$ є граничними складами розчину $Gd_{1-x}Ca_xFe_{2-y}Co_yGe_2$.

Ключові слова: система Gd–Ca–Fe–Co–Ge, інтерметаліди, твердий розчин, кристалічна структура.