Multicomponent Phases with CeAl\textsubscript{2}Ga\textsubscript{2} and Y\textsubscript{0.5}Co\textsubscript{3}Ge\textsubscript{3}-Type Structures in the Gd–Ca–Fe–Co–Ge System

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New quinary phases with the CeAl\textsubscript{2}Ga\textsubscript{2} (t110, I4/mmm) and Y\textsubscript{0.5}Co\textsubscript{3}Ge\textsubscript{3} (hP8-2, P6\textbar mmm) structure types were found at 500 °C in the Gd–Ca–Fe–Co–Ge system based on X-ray powder diffraction data. They are Gd\textsubscript{1-x}Ca\textsubscript{x}Fe\textsubscript{2}Co\textsubscript{3}Ge\textsubscript{3} (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\textsubscript{4-x}Gd\textsubscript{x}Fe\textsubscript{2}Co\textsubscript{3}Ge\textsubscript{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\textsubscript{2}Ga\textsubscript{2} (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\textsubscript{0.5}Co\textsubscript{3}Ge\textsubscript{3} 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: (0.533) phase also depends more strongly on the Fe/Co content than the c-parameter.

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

Introduction

The discovery of superconductivity in Ba\textsubscript{0.8}K\textsubscript{0.2}Fe\textsubscript{2}As\textsubscript{2} [1] has drawn the attention to compounds crystallizing with the CeAl\textsubscript{2}Ga\textsubscript{2} (122) structure type (Pearson symbol t110, space group I4/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\textsubscript{0.5}Fe\textsubscript{0.5}Ge\textsubscript{3} (Y\textsubscript{0.5}Co\textsubscript{3}Ge\textsubscript{3}-type structure), GdFe\textsubscript{2}Ga\textsubscript{2} (CeAl\textsubscript{2}Ga\textsubscript{2}-type structure), GdFe\textsubscript{0.5}Ge\textsubscript{2} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), Gd\textsubscript{11}Fe\textsubscript{12}Ge\textsubscript{112} (TB\textsubscript{11}Fe\textsubscript{12}Ge\textsubscript{112}-type structure), Gd\textsubscript{2}CoGe\textsubscript{3} (Y\textsubscript{0.5}Co\textsubscript{3}Ge\textsubscript{3}-type structure), Gd\textsubscript{3}Co\textsubscript{2}Ge\textsubscript{5} (YbRh\textsubscript{0.5}Si\textsubscript{1.5}-type structure), Gd\textsubscript{3}Co\textsubscript{2}Ge\textsubscript{5} (Lu\textsubscript{0.5}Si\textsubscript{1.5}-type structure), GdCo\textsubscript{3}Ge\textsubscript{2} (CeAl\textsubscript{2}Ga\textsubscript{2}-type structure), GdCoGe\textsubscript{2} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), GdCo\textsubscript{3}Ge\textsubscript{2} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), GdCoGe\textsubscript{2} (TiNiSi-type structure), GdCoGe\textsubscript{2} (ScCoSi\textsubscript{2}-type structure), CaCoGe\textsubscript{2} (CeAl\textsubscript{2}Ga\textsubscript{2}-type structure), CoFe\textsubscript{2}Ge\textsubscript{3} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), CoFe\textsubscript{2}Ge\textsubscript{3} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), CoFe\textsubscript{2}Ge\textsubscript{3} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), CoFe\textsubscript{2}Ge\textsubscript{3} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), CoFe\textsubscript{2}Ge\textsubscript{3} (CeNi\textsubscript{2}Si\textsubscript{2}-type structure), and CoFe\textsubscript{2}Ge\textsubscript{3} (CeNi\textsubscript{2}Si\textsubscript{2}-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\textsubscript{2}Ga\textsubscript{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 500°C 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 Kα radiation). For the indexing 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 Gd₁ₓCa₁₋ₓFe₃Co₃Ge₃ and Gd₀.₅ₓCa₀.₅ₓFe₃Co₃Ge₃ were refined [6] on X-ray powder diffraction data (Figs 1 and 2) from an alloy of composition Gd₁.₅ₓCa₀.₅ₓFe₃Co₃Ge₃ (homogenized at 500°C for two months). The unit-cell parameters of the phase Gd₁ₓCa₁₋ₓFe₃Co₃Ge₃ (structure type CeAl₂Ga₂ (122), tI10, I₄/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 GdFe₂Ge₂ (a = 3.9867, c = 10.4798 Å) [7,8] and GdCo₂Ge₂ (a = 3.996, c = 10.066 Å) [8]. Refinement of the structure of the phase Ca₀.₅ₓGd₃₋ₓCo₃₅Ge₃ (structure type Y₀.₅ₓCo₃₅Ge₃ (0.533), hP6-2, P6/mmm, a = 5.1154(2), c = 4.0142(3) Å, x = 0.045(6)) showed mixed occupation Ca/Gd of site 1α (45.5/4.5 %), while a refinement on diffraction data from an as-cast alloy revealed occupation of site 1α by Ca.

**Fig. 1.** XRD pattern (Fe Kα radiation) of an alloy of composition Gd₁.₅ₓCa₀.₅ₓFe₃Co₃Ge₃, homogenized at 500°C, which contains the following phases: 1 – Gd₀.₈₄₉(8)Ca₀.₁₅₁(8)Fe₃Co₃₅Ge₃ (CeAl₂Ga₂, I₄/mmm), 2 – Gd₀.₄₅₅(6)Ca₀.₅₄₅(6)Fe₃Co₃₅Ge₃ (Y₀.₅ₓCo₃₅Ge₃, P6/mmm), 3 – FeCoGe (ZrBeSi, P6₃/mmc)

**Fig. 2.** XRD pattern (Fe Kα radiation) of an as-cast alloy of composition Gd₁.₅ₓCa₀.₅ₓFe₃Co₃Ge₃, which contains the following phases: 1 – Gd₀.₈₉₇(9)Ca₀.₁₀₃(9)Fe₃Co₃₅Ge₃ (CeAl₂Ga₂, I₄/mmm), 2 – Gd₀.₅ₓFe₃Co₃₅Ge₃ (Y₀.₅ₓCo₃₅Ge₃, P6/mmm), 3 – FeCoGe (ZrBeSi, P6₃/mmc)
atoms alone – composition C_{0.5}Fe_{1.5}Co_{3}Ge_{3} (a = 5.1153(2), c = 4.0126(9) 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 Figs. 3.

Table 1

Crystallographic parameters of the Gd_{1-x}Ca_{x}FeCoGe_{3} and Ca_{0.5-x}Gd_{x}Fe_{1.5}Co_{3}Ge_{3} phases (homogenized alloy)

| Site  | Wyckoff | x   | y   | z   | Occupation | \( B_{iso} \), Å² |
|-------|----------|-----|-----|-----|------------|-------------------|
| Gd/Ca | 2a       | 0   | 0   | 0   | 0.849(8)/0.151(8) | 0.47(5)          |
| Fe/Co | 4d       | 0   | ½   | ¼   | 0.5/0.5    | 0.51(5)          |
| Ge    | 4e       | 0   | 0   | 0.3715(1) | 1        | 0.49(5)          |

C_{0.5-x}Gd_{x}Fe_{1.5}Co_{3}Ge_{3} (x = 0.045(6)), structure type Y_{0.5}Co_{0.5}Ge_{3}, space group P6/mmm, 

\[ a = 5.1154(2), \ c = 4.0142(3) \text{ Å}, \ R_{B} = 0.0933 \]

| Site  | Wyckoff | x   | y   | z   | Occupation | \( B_{iso} \), Å² |
|-------|----------|-----|-----|-----|------------|-------------------|
| Ca/Gd | 1a       | 0   | 0   | 0   | 0.455(6)/0.045(6) | 0.47(5)          |
| Fe/Co | 3g       | ½   | 0   | ½   | 0.5/0.5    | 0.51(5)          |
| Ge1   | 2c       | ½   | ¼   | 0   | 1        | 0.49(5)          |
| Ge2   | 2e       | 0   | 0   | 0.290(1) | 0.5        | 0.49(5)          |

Table 2

Crystallographic parameters of the Gd_{1-x}Ca_{x}FeCoGe_{3} and Ca_{0.5-x}Gd_{x}Fe_{1.5}Co_{3}Ge_{3} phases (as-cast alloy)

| Site  | Wyckoff | x   | y   | z   | Occupation | \( B_{iso} \), Å² |
|-------|----------|-----|-----|-----|------------|-------------------|
| Gd/Ca | 2a       | 0   | 0   | 0   | 0.897(9)/0.103(9) | 0.34(5)          |
| Fe/Co | 4d       | 0   | ½   | ¼   | 0.5/0.5    | 0.53(5)          |
| Ge    | 4e       | 0   | 0   | 0.3722(1) | 1        | 0.52(4)          |

C_{0.5-x}Gd_{x}Fe_{1.5}Co_{3}Ge_{3} (x = 0), structure type Y_{0.5}Co_{0.5}Ge_{3}, space group P6/mmm, 

\[ a = 5.1153(2), \ c = 4.0120(2) \text{ Å}, \ R_{B} = 0.0846 \]

| Site  | Wyckoff | x   | y   | z   | Occupation | \( B_{iso} \), Å² |
|-------|----------|-----|-----|-----|------------|-------------------|
| Ca/Gd | 1a       | 0   | 0   | 0   | 0.5/0     | 0.34(5)          |
| Fe/Co | 3g       | ½   | 0   | ½   | 0.5/0.5   | 0.53(5)          |
| Ge1   | 2c       | ½   | ½   | 0   | 1        | 0.52(4)          |
| Ge2   | 2e       | 0   | 0   | 0.293(1) | 0.5        | 0.52(4)          |

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 106
In the range 3-5 %).

Contrary to what was observed for the 122 phase, the cell volume of the 0.533 phase increases with decreasing Ca content. Substitutions have no strong effect on the cell parameters. 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 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 and molar ratio 122/0.533 = 0.53/0.47 than the 122 cell.

### Table 3

| Phase 122 | Cell parameters, Å | Volume, Å³ | Phase 0.533 | Cell parameters, Å | Volume, Å³ |
|-----------|---------------------|------------|-------------|---------------------|------------|
| Gd0.4327Ca0.3037 – Fe0.207Gd2 | 3.9986(8) | 10.2034(3) | 162.93(1) | Ca0.469(3)Gd0.011(3) | 5.1081(1) |
| Gd0.5917Ca0.3907 × Fe0.109Gd2 | 3.9988(6) | 10.1279(2) | 161.789(8) | Ca0.457(3)Fe0.043(3) | 5.1106(2) |
| Gd0.5587Ca0.4427 × Fe0.056Gd2 | 4.0003(8) | 10.2518(3) | 164.03(1) | Ca0.450(3)Gd0.050(3) | 5.1150(1) |
| Gd0.5883Ca0.1167 × Fe0.384Gd2 | 3.9949(6) | 10.1922(2) | 163.03(1) | Ca0.311Gd0.184(4) | 5.1162(1) |
| Gd0.4917Ca0.0857 × Fe0.514Gd2 | 3.9903(6) | 10.1915(2) | 162.985(8) | Ca0.186Gd0.314(8) | 5.1190(2) |
| Gd0.4416Ca0.5511 × Fe0.448Gd2 | 3.9976(1) | 10.3981(5) | 166.17(2) | Ca0.32Gd0.68Ca0.707Gd5 | 5.1135(2) |
| Gd0.3826Ca0.1860 × Fe0.814Gd2 | 3.9961(2) | 10.3272(2) | 164.915(8) | Ca0.325Gd0.178(4) | 5.1189(1) |
| Gd0.9097Ca0.0917 × Fe0.9083Gd2 | 3.9946(8) | 10.3249(2) | 164.759(8) | Ca0.268Gd0.237(8) | 5.1218(1) |

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 and molar ratio 122/0.533 = 0.53/0.47 than the 122 cell.

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: GdFe2Ca0.5Gd2 (122 phase), GdFeCoGe2 (122), GdFeCoGe2 (122), CaCoGe2 (122), Gd3Fe2Ca0.5Gd1 (0.533), GdFeCoGe2 (0.533), CaCoGe2 (0.533) [9], Ca3FeGe3 (0.533), and from [7,8] – GdFe2Ge2 (122), Gd3Fe2Ge2 (0.533), and GdCoGe2 (122), and Gd3Ca2Ge3 (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.
Conclusions

The new quinary phases Gd\(_{1-x}\)Ca\(_x\)Fe\(_2\)Co\(_3\)Ge\(_3\) (\(x = 0.085(7)-0.551(6)\)), y = 0.25-0.75, \(a = 3.99468\) (6)-4.00003 (8), \(c = 10.1279\) (2)-10.3981 (5) Å, with CeAl\(_2\)-type structure (\(I\overline{1}0.4\overline{1}4\overline{1}\overline{4}mmm\)), and Ca\(_{0.5}\)Gd\(_{1.5}\)Fe\(_2\)Co\(_3\)Ge\(_3\) (\(x = 0.031(1)-0.314(8)\)), 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\(_{2}\)-type structure (\(hP8-2\). P\(_6/\overline{mmm}\)), were found at 500°C in the Gd–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\(_2\)Co\(_3\)Ge\(_3\) (\(y = 0.5-1.5, a = 3.9949\) (5)-3.99750 (7), \(c = 10.3271\) (2)-10.1173 (3) Å) and the 0.533 phases Gd\(_{0.5}\)Fe\(_3\)Co\(_3\)Ge\(_3\) (\(y = 0.75-1.5, a = 5.1247\) (8)-5.1225 (7), \(c = 4.052(1)-4.010(1)\) Å), Ca\(_{0.5}\)Fe\(_2\)Co\(_3\)Ge\(_3\) (\(y = 0.75-2.25\), \(a = 5.1135\) (2)-5.1066 (2), \(c = 4.0452\) (1)-3.9839 (3) Å), Ca\(_{0.5}\)Fe\(_3\)Co\(_3\)Ge\(_3\) (\(a = 5.10167\) (9), \(c = 4.0656\) (7) Å), and Ca\(_{0.5}\)Co\(_{3}\)Ge\(_3\) (\(a = 5.0899\) (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\(_{0.5}\)Fe\(_2\)Co\(_3\)Ge\(_3\) and Ca\(_{0.5}\)Co\(_{3}\)Ge\(_3\) between the boundary ternary compounds.

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Багатокомпонентні фази зі структурами типів CeAl₂Ga₂ та Y₀.₅Co₃Ge₃ у системі Gd–Ca–Fe–Co–Ge

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За результатами рентгеновського та рентгеноструктурного аналізу у системах Gd–Ca–Fe–Co–Ge при 500°C знайдено нові п’ятикомпонентні фази зі структурами типів CeAl₂Ga₂ (hP8-2, P6/mmm) та Y₀.₅Co₃Ge₃ (hP8-2, P6/mmm): GdₓCaₓFe₂ₐₓCo₃Ge₃ (x = 0.085(7)-0.551(6), y = 0.25-0.75, a = 3.99468(6)-4.00030(8), c = 10.1279(2)-10.3981(5) Å) та CaₓGdₓFe₃ₐₓCo₃Ge₃ (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 CeAl₂Ga₂ (122) більшою мірою залежить від співвідношення Fe/Co та Gd/Ca, ніж параметр a (залежить майже однаковим). Таким чином, з збільшенням вмісту Fe та Ca, об’єм комірки закономірно збільшується. Параметр c гексагональної комірки структури типу Y₀.₅Co₃Ge₃ (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 тетрахні та тетрані фази були також знайдені: GdₓFeₓCoₓGe₃ (y = 0.5-1.5, a = 3.99419(5)-3.99750(7), c = 10.3271(2)-10.1173(3) Å) зі структурою типу CeAl₁₅Ga₁₅ та GdₓFeₓCoₓGe₃ (y = 0.75-1.5, a = 5.1247(8)-5.1225(7), c = 4.052(1)-4.010(1) Å), CaₓₐₓFe₉ₐₓCo₉ₐₓGe₉ₐₓ (y = 0.75-2.25, a = 5.1153(2)-5.1066(2), c = 4.0451(2)-3.9839(3) Å), CoₓₐₓFe₉ₐₓGe₉ₐₓ (a = 5.10167(9), c = 4.06565(7) Å) та CaₓₐₓCo₉ₐₓGe₉ₐₓ (a = 5.0899(2), c = 3.9199(1) Å) зі структурою типу Y₀.₅Co₃Ge₃. Останні дві фази разом із раніше відомими сполуки GdₓₐₓFe₉ₐₓ та GdₓₐₓCo₉ₐₓ є гранчичними складами із можливого неперервного твердого розчину CaₓₐₓGdₓₐₓFe₉ₐₓCo₉ₐₓ, як і відповідні тетрані сполуки (окрім систем Ca–Fe–Ge) зі структурою типу CeAl₂Ga₂ є гранчастими складами розчину GdₓₐₓCaₓₐₓFe₉ₐₓCo₉ₐₓ.

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