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Synthesis and Crystal Structure of New Ce–Ru–Ga Ternary Intermetallic Phases with Known Structure Types

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Abstract—Five new intermetallic phase of known structure types have been identified in a systematic study of the Ce–Ru–Ga system: $CeRu_{0.90}Ga_{1.10}$ ($MgZn_2$ structure, sp. gr. $P6_3/mmc$, a = 5.44503(5) Å, c = 8.67188(13) Å, very narrow homogeneity range), $Ce_7Ru_6Ga_7$ ($Pr_7Co_6Al_7$ structure, constant composition, sp. gr. $P4/mbm$, a = 13.61910(17) Å, c = 4.34957(5) Å), $Ce_6Ru_{0.18}Ga_{2.82}$ (K_2UF_6-derived structure, sp. gr. $P\bar{6}2m$, a = 8.09628(19) Å, c = 4.38470(13) Å), $Ce_{23}Ru_{10}Ga$ ($Pr_{23}Ir_7Mg_4$ structure, sp. gr. $P6_3mc$, a = 9.867(6) Å, c = 22.153(14) Å) and $Ce_{26}(Ru_{0.59}Ga_{0.41})_{17}$ ($Sm_{26}(Co_{0.65}Ga_{0.35})_{17}$ structure, sp. gr. $P4/mbm$, a = 11.9529(4) Å, c = 15.0135(10) Å). In the structures of $Ce_7Ru_6Ga_7$, $Ce_{23}Ru_{10}Ga$, and $Ce_{26}(Ru_{0.59}Ga_{0.41})_{17}$, some of the Ce atoms form very short Ce–Ru bonds (2.525(3), 2.549(5), and 2.506(2) Å, respectively), which is attributable to their intermediate valence state.

Keywords: cerium, ruthenium, gallium, X-ray diffraction, microstructure

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INTRODUCTION

Intermetallic cerium compounds have been the subject of intense research because they have anomalous low-temperature magnetic and electrical properties due to strongly correlated electron behavior [1–3]. Among ternary compounds containing both cerium and ruthenium, a group of compounds having anomalously short cerium–ruthenium bond distances, shorter than the sum of the covalent radii of cerium and ruthenium (2.89 Å) [4], has been the subject of particularly intensive research effort.

In previous work [5–7], systematic studies of the cerium-rich corner of the Ce–Ru–Ga ternary phase diagram allowed compounds with the compositions $Ce_5Ru_3Ga_2$, $Ce_9Ru_4Ga_5$, and $Ce_4Ru_3Ga_3$ to be identified for the first time. All of these compounds have reduced Ce–Ru bond distances (down to 2.75 Å), and in low-temperature magnetic measurements the cerium atoms in them exhibit valence fluctuations [8].

In this paper, we report a study of the same phase region in the system in question, where we identified and then synthesized another three compounds, $Ce_{23}Ru_{7+x}Ga_{4-x}$, $Ce_6Ru_{1-x}Ga_{2+x}$, and $Ce_{26}(Ru_xGa_{1-x})_{17}$, which have the $Pr_{23}Ir_7Mg_4$, K_2UF_6, and $Sm_{26}(Co_xGa_{1-x})_{17}$ structures, respectively [9–11]. In addition, two intermetallic phases, $Ce_7Ru_6Ga_7$ and $CeRu_{0.90}Ga_{1.10}$, with the $Pr_7Co_6Al_7$ and $MgZn_2$ structures, respectively [12, 13], were identified around the equiatomic composition.

EXPERIMENTAL

Ternary intermetallic compounds were synthesized by reacting stoichiometric ratios of elemental Ce (99.9 wt % Ce), Ru (99.97 wt % Ru), and Ga (99.99 wt % Ga) in an electric arc furnace with a water-cooled copper hearth under an inert atmosphere (extrapure-grade Ar). To remove trace amounts of gases, zirconium was used as a getter. Because of the large difference in melting point between the constituent elements, weighed amounts of samples were melted several times until the reaction reached completion, and the samples were overturned and broken between the melting steps. Next, the resultant melted samples were sealed in an ampule under vacuum and annealed in an electric furnace at a temperature in the range 540–600°C for 720 h to ensure equilibration. After the annealing, the ampules and samples were quenched in ice water.

The samples thus prepared were characterized by X-ray microanalysis. Their phase composition and structure were determined by X-ray diffraction.

X-ray microanalysis was carried out on a LEO EVO 50XPV scanning electron microscope equipped with an Oxford Instruments INCA Energy 450 energy dispersive X-ray spectrometer system (accelerating volt-

Table 1. Structure refinement parameters derived from X-ray powder diffraction data for $CeRu_{0.90}Ga_{1.10}$, $Ce_7Ru_6Ga_7$, and $Ce_6Ru_{0.18}Ga_{2.82}$

Formula	$CeRu_{0.90}Ga_{1.10}$	$Ce_7Ru_6Ga_7$	$Ce_6Ru_{0.18}Ga_{2.82}$
Composition (X-ray microanalysis data)	$Ce_{33.7}Ru_{30.8}Ga_{35.5}$	$Ce_{35.6}Ru_{30.8}Ga_{33.6}$	$Ce_{65.1}Ru_{5.5}Ga_{29.4}$
Symmetry	Hexagonal	Tetragonal	Hexagonal
a, Å	5.44503(5)	13.61910(17)	8.09628(19)
c, Å	8.67188(13)	4.34957(5)	4.38470(13)
V, Å^3	222.661(4)	806.758(18)	248.909(11)
Sp. gr.	$P6_3/mmc$	$P4/mbm$	$P\bar{6}2m$
Z	4	2	1
D_{calc}, g/cm^3	9.181	8.543	7.042
2θ, deg	10–90.09	5–95.09	10–93.19
Reflections	58	263	68
Refinement parameters	19	41	17
η (pseudo-Voigt)	0.67(3)	0.86(3)	1.03(3)
Half-width parameters (U, V, W)	−0.004(16) 0.09(2) −0.004(3)	0.30(3) 0.03(2) 0.024(3)	−0.11(3) 0.29(2) −0.022(4)
Agreement factors for the Rietveld refinement			
R_p/R_{wp}	0.032/0.041	0.020/0.027	0.016/0.020
R_{exp}	0.031	0.015	0.016
χ^2	1.71	3.46	1.64
R_B/R_F	0.071/0.103	0.054/0.034	0.134/0.148

age, 20 kV; probe current, 300 pA). As a reference, we used a ternary intermetallic phase of constant composition: $Ce_5Ru_3Ga_2$. The constituent elements were determined with an accuracy of 1.5 at %.

The phase composition of the samples was determined on a STOE STADI P automatic diffractometer in transmission geometry ($CuK_{\alpha 1}$ radiation, Ge(111) monochromator, linear position-sensitive detector) in the angular range from 2θ = 5°–10° to 90.09°–95.09° with a scan step of 0.01° and a counting time of 10 s per data point. The X-ray diffraction patterns were analyzed using WinXPOW software [14]. For lack of single crystals of satisfactory quality, the structures of the new compounds were refined by the Rietveld method using an experimental X-ray powder diffraction pattern and a known structural model for an analogue or a model derived from experimental X-ray diffraction data for a crystal of comparatively low quality. In our calculations, we used the FullProf [15] and WinPLOTR [16] programs. The background was fitted with a sixth degree Chebyshev polynomial and the peak profile function was modeled using the pseudo-Voigt function. Atomic displacement parameters were refined by least squares fitting in an isotropic approximation. In this way, we determined the structure of the new intermetallic compounds $CeRu_{0.90}Ga_{1.10}$, $Ce_7Ru_6Ga_7$, and $Ce_6Ru_{0.18}Ga_{2.82}$ (Table 1, Figs. 1–3).

Crystals for X-ray structure analysis were isolated from broken samples and mounted on a Bruker APEX-II automatic diffractometer equipped with a CCD detector (MoK_α radiation, graphite monochromator). Crystal structures were determined by direct methods (SHELXS97) and refined by least squares fitting in an anisotropic approximation (SHELXL97) [17]. Absorption correction was made using SADABS [18] or MULTISCAN [19]. The structures were imaged using the DIAMOND 3 program [20]. The crystal structures of $Ce_{23}Ru_{7+x}Ga_{4-x}$ ($x = 3$) and $Ce_{26}(Ru_xGa_{1-x})_{17}$ ($x = 0.59$) were determined using single-crystal data. Note that the intensity data for $Ce_{23}Ru_{7+x}Ga_{4-x}$ ($x = 3$) were collected using a centrosymmetric twin with domains in the ratio 0.72(7) : 0.28(7).

The X-ray structure analysis results are summarized in Table 2, and projections of the crystal structures of $Ce_{23}Ru_{7+x}Ga_{4-x}$ ($x = 3$) and $Ce_{26}(Ru_xGa_{1-x})_{17}$ ($x = 0.59$)

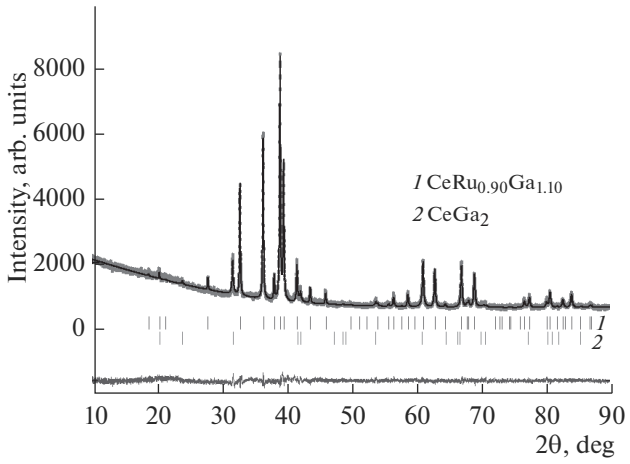

Fig. 1. Structure refinement for $CeRu_{0.90}Ga_{1.10}$ by the Rietveld method using X-ray powder diffraction data.

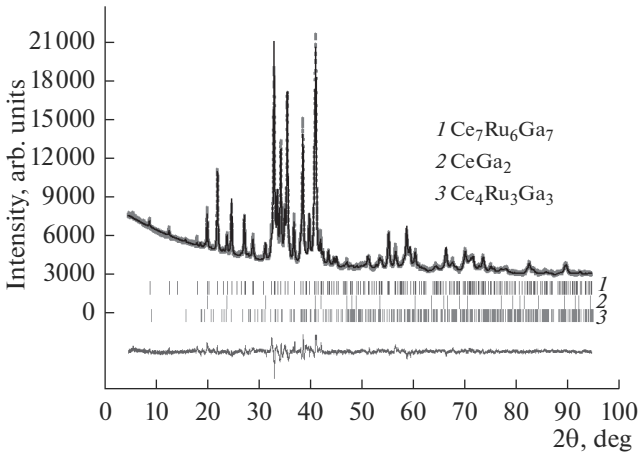

Fig. 2. Structure refinement for $Ce_7Ru_6Ga_7$ by the Rietveld method using X-ray powder diffraction data.

are shown in Figs. 4 and 5. The structural datasets were deposited through the joint CCDC/FIZ Karlsruhe online deposition service: deposition numbers CCDC-1879675 for $CeRu_{0.90}Ga_{1.10}$, CCDC-1879677 for $Ce_7Ru_6Ga_7$, CCDC-1879676 for $Ce_6Ru_{0.18}Ga_{2.82}$, CCDC-1879678 for $Ce_{23}Ru_{10}Ga$, and CCDC-1879679 for $Ce_{26}Ru_{10}Ga_7$

RESULTS AND DISCUSSION

We did not detect a compound with the composition CeRuGa in a region around the equiatomic composition in the Ce–Ru–Ga ternary system, but near it there are the intermetallic compounds $CeRu_{0.90}Ga_{1.10}$ and $Ce_7Ru_6Ga_7$. In the cerium-rich part, we identified three compounds of variable composition, $Ce_6Ru_{1-x}Ga_{2+x}$, $Ce_{23+y}Ru_{7+x}Ga_{4-x-y}$, and $Ce_{26}(Ru_xGa_{1-x})_{17}$, with different extents of their homogeneity range. All of the synthesized intermetallic phases have known structure types or are derivatives of known structure types. The compositions of the compounds were confirmed by X-ray microanalysis (Tables 1, 2). The microstructures of the samples are illustrated in Figs. 6–10.

$CeRu_xGa_{2-x}$, an intermetallic phase of variable composition with the $MgZn_2$ structure, exists in a narrow homogeneity range, $0.88 < x < 0.97$, whose extent does not exceed 3 at %. The cerium atoms in its structure occupy the magnesium site, and the ruthenium and gallium atoms jointly occupy the zinc site. On the whole, the structure can be thought of as a sequence of layers perpendicular to the [001] direction: planar Kagomé layers [21] formed by Ru1/Ga1 atoms and nonplanar layers formed by cerium and Ru2/Ga2 atoms (Fig. 11). The Ce–Ru–Al system contains a similar phase of variable composition with the $MgZn_2$ structure, $CeRu_xAl_{2-x}$, but is has a broader homogeneity range: $0.39 < x < 0.89$ [22].

The ternary compound $Ce_7Ru_6Ga_7$ has constant composition and the $Pr_7Co_6Al_7$ structure. The structure of the new compounds was refined by the Rietveld method using X-ray diffraction data obtained for a powder sample (Fig. 2). The sample contained up to 8 wt % $Ce_4Ru_3Ga_4$ and 1 wt % $CeGa_2$ as impurity phases. The $CeGa_2$ phase is not seen in the micrograph in Fig. 7 because of its low content in the sample. The cerium atoms in its crystal structure occupy three crystallographically inequivalent sites, as do the gallium atoms, and the ruthenium atoms occupy two inequivalent sites (Fig. 12). The nearest neighbor environment of the Ru1 and Ru2 atoms consists of ten and nine atoms, respectively. Each Ru2 atom is coordinated by a tricapped trigonal prism, with one cap formed by a neighboring Ru2 atom. The capping atoms are 2.765(4) Å apart. Neighboring Ru2 polyhedra share a face, and the Ru2 atoms cap a neighboring

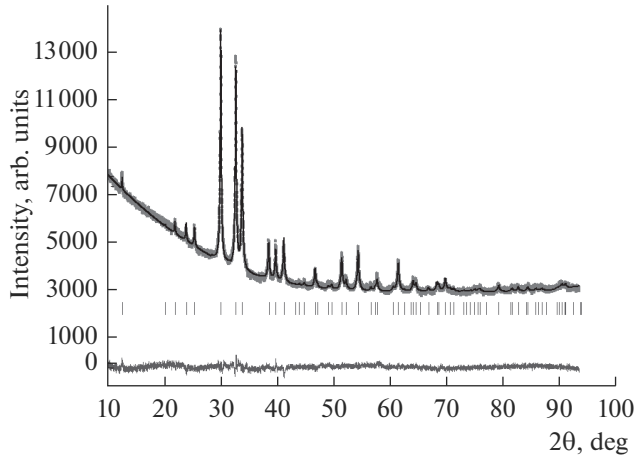

Fig. 3. Structure refinement for $Ce_6Ru_{1-x}Ga_{2+x}$ by the Rietveld method using X-ray powder diffraction data.

Table 2. Main single-crystal structure refinement results for $Ce_{23}Ru_{7+x}Ga_{4-x}$ ($x = 3$) and $Ce_{26}(Ru_xGa_{1-x})_{17}$ ($x = 0.59$)

Formula	$Ce_{23}Ru_{10}Ga$	$Ce_{26}Ru_{10}Ga_7$
Composition (X-ray microanalysis data)	$Ce_{68.2}Ru_{28.2}Ga_{3.6}$	$Ce_{60.9}Ru_{23.1}Ga_{16.0}$
Symmetry	Hexagonal	Tetragonal
a, Å	9.867(6)	11.9529(4)
c, Å	22.153(14)	15.0135(10)
V, Å^3	1868(3)	2145.0(2)
Sp. gr.	$P6_3mc$	$P4/mbm$
Z	2	2
D_{calc}, g/cm^3	7.651	7.961
μ, mm^{-1}	31.941	34.611
$F(000)$	3610	4330
Crystal dimensions, mm	0.12 × 0.1 × 0.06	0.08 × 0.04 × 0.02
θ_{min}–θ_{max}, deg	2.383-30.749	2.410-33.141
Index ranges	$-14 \le h \le 14$ $-12 \le k \le 14$ $-31 \le l \le 31$	$-18 \le h \le 18$ $-18 \le k \le 18$ $-20 \le l \le 23$
Absorption correction	Semiempirical, from equivalents	
Max, min transmission	0.0998, 0.0322	0.0309, 0.0028
Refinement procedure	Least squares fitting to the F^2 data	
Measured reflections	22721	26543
Independent reflections with $I > 2\sigma(I)$, R_{int}	2230, 0.1223	2238, 0.0584
Refinement parameters	77	87
GoF	0.979	1.269
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0431, 0.0962	0.0376, 0.1012
$R1$, $wR2$ (all reflections)	0.0720, 0.1100	0.0415, 0.1032
$\Delta\rho_{max} - \Delta\rho_{min}$, e/Å^3	2.012, −1.813	3.427, −3.749

polyhedron. The Ce3 atoms form anomalously short Ce3–Ru2 bonds, 2.525(3) Å, which is considerably shorter than the sum of the covalent radii of cerium and ruthenium. The other crystallographically inequivalent cerium atoms in the structure under consideration do not form anomalous bonds with the transition metal atoms. In the structure of the $Pr_7Co_6Al_7$ prototype, the Pr–Co bond distance is reduced to 2.591 Å, which is also smaller than the sum of the corresponding covalent radii (2.81 Å), but to a lesser extent than in $Ce_7Ru_6Ga_7$.

The crystal structure of the $Ce_6Ru_{1-x}Ga_{2+x}$ gallide can be thought of as resulting from site exchange in the K_2UF_6 structure: the cerium atoms reside on the fluorine site and the ruthenium and gallium atoms occupy the uranium and potassium sites, respectively. Note that the ruthenium site is occupied by ruthenium and gallium atoms at random, in the ratio 0.18 : 0.82. The nearest neighbor environment of the gallium and ruthenium atoms is formed by six cerium atoms in the form of corner-sharing trigonal prisms (Fig. 13). A similar structural basis was reported for a number of equiatomic intermetallic compounds with the ZrNiAl structure, including CePdMg [23] and CeRhIn [24]. The $Ce_6Ru_{1-x}Ga_{2+x}$ compound has a narrow homogeneity range: $0.18 < x < 0.52$.

The intermetallic phase $Ce_{23}Ru_7Ga_4$ crystallizes in the $Pr_{23}Ir_7Mg_4$ structure. Known isostructural compounds with various combinations of a rare-earth element, noble metal, and p-block element were described in the literature as compounds of constant composition. The $Ce_{23}Ru_7Ga_4$ gallide has a homogeneity region that extends along both a line of constant mole fraction of cerium and that of constant mole fraction of ruthenium: $Ce_{23+y}Ru_{7+x}Ga_{4-x-y}$ ($0 < x < 3.00$,

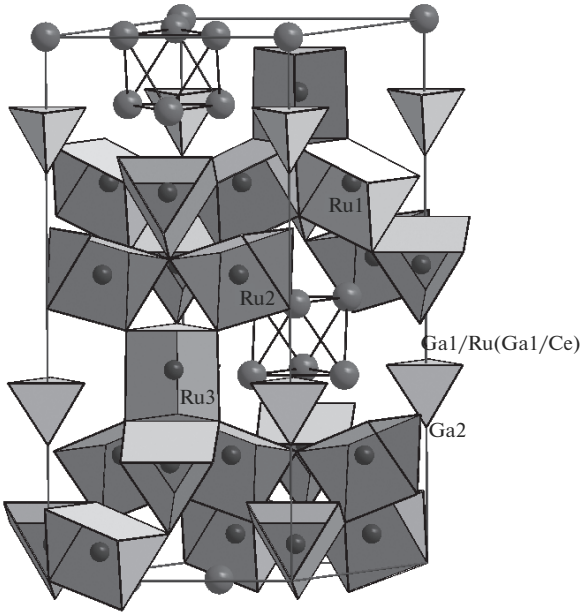

Fig. 4. Crystal structure of $Ce_{23+y}Ru_{7+x}Ga_{4-x-y}$.

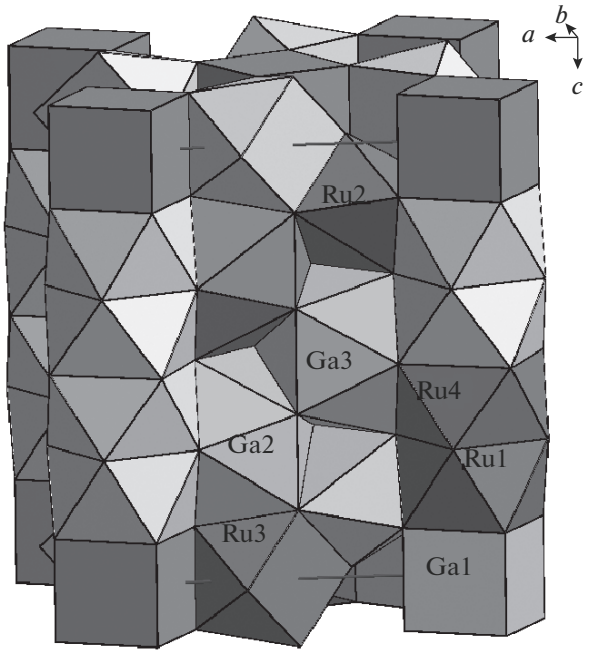

Fig. 5. Crystal structure of $Ce_{26}(Ru_xGa_{1-x})_{17}$.

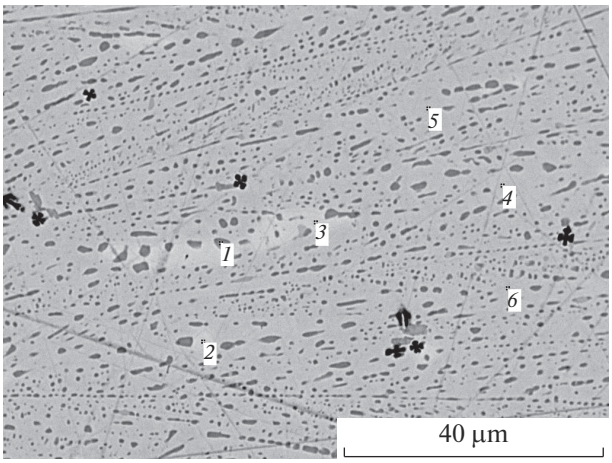

Fig. 6. Microstructure of $CeRu_xGa_{2-x}$: $Ce_{33.7}Ru_{30.8}Ga_{35.5}$, gray areas; $Ce_{33.5}Ga_{66.5}$ ($CeGa_2$), black areas.

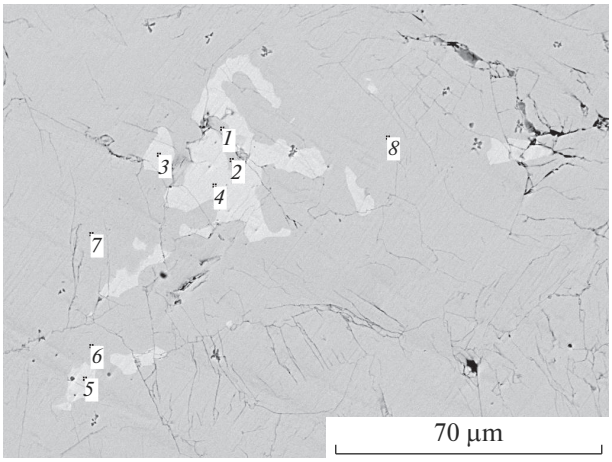

Fig. 7. Microstructure of $Ce_7Ru_6Ga_7$: $Ce_{35.6}Ru_{30.8}Ga_{33.6}$, gray areas; $Ce_{41.0}Ru_{31.9}Ga_{27.1}$ ($Ce_4Ru_3Ga_3$), white areas.

$0 < y < 0.97$). Cerium substitutes for gallium atoms in a very narrow composition range, within 3 at %. The degree of ruthenium substitution for gallium is up to 8 at %. An aluminide similar in composition and structure also has a homogeneity range, but along a line of constant mole fraction of cerium: $Ce_{23}Ru_{7+x}Al_{4-x}$ ($0 < x < 2.97$) [25]. In the structure of $Ce_{23}Ru_7Ga_4$, each ruthenium atom is coordinated by six cerium atoms in the form of a trigonal prism, like in the structure of the binary intermetallic phase Ce_7Ru_3, and the gallium atoms form Ga_4 clusters in the form of hollow tetrahedra (Fig. 4). On the whole, the structure of the compound can be thought of as a sequence of Ce_7Ru_3 groups and layers of Ga_4 tetrahedra, trigonal prisms with ruthenium in their center, and Ce_6 hollow octahedra perpendicular to the *c* axis. The composition of the single crystal studied here is $Ce_{23}Ru_{10}Ga$. Three gallium atoms in each tetrahedron are replaced by ruthenium atoms (one crystallographically inequivalent gallium site). A characteristic feature of this structure is the presence of short Ce–Ru bond distances: 2.549(5) and 2.659(14) Å. Reduced Ce–Ru bond dis-

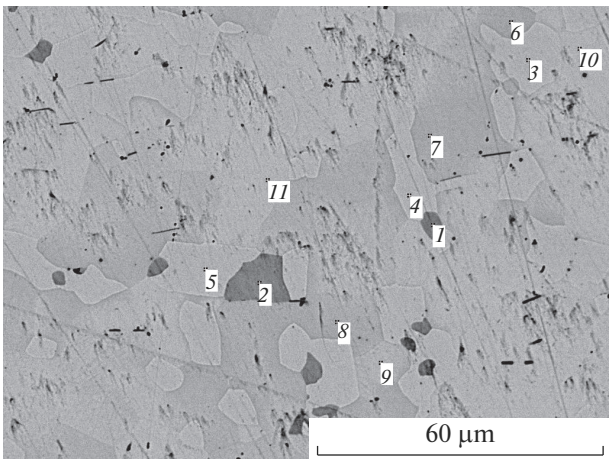

Fig. 8. Microstructure of $Ce_6Ru_{1-x}Ga_{2+x}$: $Ce_{65.1}Ru_{5.5}Ga_{29.4}$, dark gray areas; $Ce_{57.0}Ga_{43.0}$ ($Ce_{4.7}Ga_{3.3}$), black areas; $Ce_{60.0}Ru_{14.6}Ga_{25.4}$ ($Ce_{26}(Ru_xGa_{1-x})_{17}$), light gray areas.

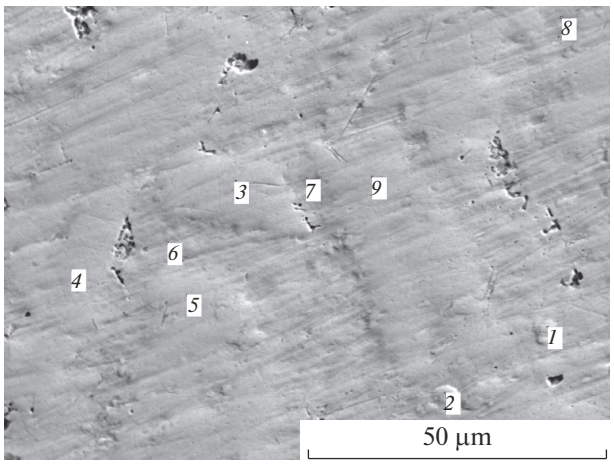

Fig. 9. Microstructure of $Ce_{23+y}Ru_{7+x}Ga_{4-x-y}$: $Ce_{68.2}Ru_{28.2}Ga_{3.6}$.

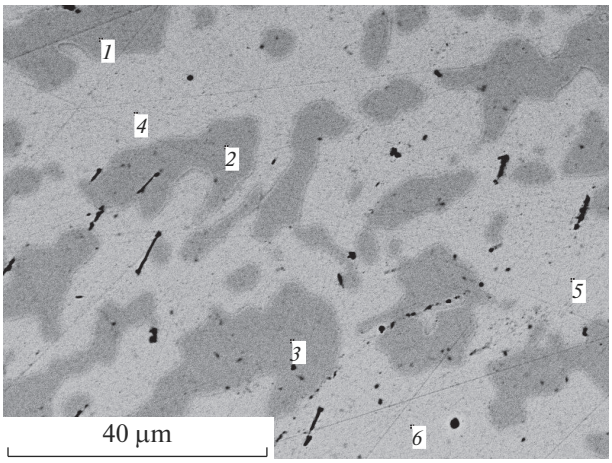

Fig. 10. Microstructure of $Ce_{26}(Ru_xGa_{1-x})_{17}$: $Ce_{48.9}Ru_{30.9}Ga_{20.2}$ ($Ce_5Ru_3Ga_2$), black areas; $Ce_{60.9}Ru_{23.1}Ga_{16.0}$, gray areas.

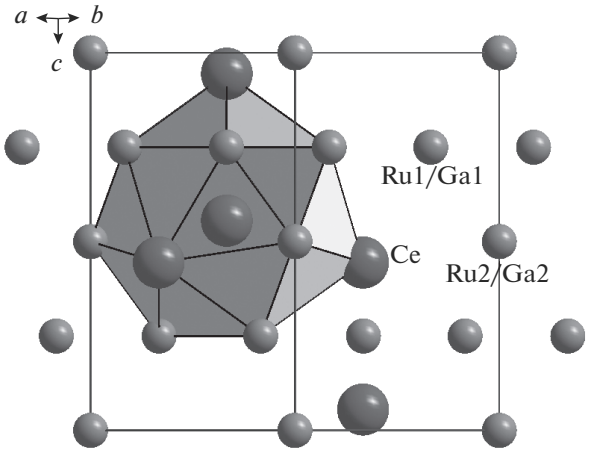

Fig. 11. Crystal structure of $CeRu_{0.90}Ga_{1.10}$ projected along [110].

tances are also observed in isostructural compounds containing Mg or Cd instead of Ga, $Ce_{23}Ru_7Mg_4$ and $Ce_{23}Ru_7Cd_4$, which have variable valence at low temperatures [26, 27].

The existence of the $Ce_{26}(Ru_xGa_{1-x})_{17}$ compound was first reported by Myakush et al. [28], who presented its tetragonal cell parameters (a = 11.597(3) Å, c = 15.563(5) Å, sp. gr. $P4/mbm$, Z = 2, x = 0.63) refined using X-ray powder diffraction data and a structural model for the $Sm_{26}(Co_{0.65}Ga_{0.35})_{17}$ prototype. According to the structure analysis results obtained in this study for a $Ce_{26}(Ru_xGa_{1-x})_{17}$ single crystal (Fig. 5), this compound has the $Sm_{26}(Co_{0.65}Ga_{0.35})_{17}$ structure. The composition of the single crystal was $Ce_{26}(Ru_{0.59}Ga_{0.41})_{17}$. The homogeneity range of the compound is $0.35 < x < 0.65$. In its structure, the cerium atoms occupy six crystallographically inequivalent sites, and the other seven sites are occupied by the ruthenium and gallium atoms. Three of them are fully occupied by the gallium atoms, and the other four, by the Ru atoms. All four ruthenium sites are disordered. The nearest neighbor environment of the ruthenium atoms has the form of an antiprism of cerium atoms. The Ce–Ru bond distances include reduced ones, Ce5–Ru2, which are shorter than the sum of the corresponding covalent radii (2.89 Å): 2.506(2) Å.

All of the previously studied compounds with anomalously short Ce–Ru bond distances exhibited cerium valence fluctuations [1–9]. Note that it is the cerium atoms forming short bonds with the transition metal atoms which are in a mixed valence state:

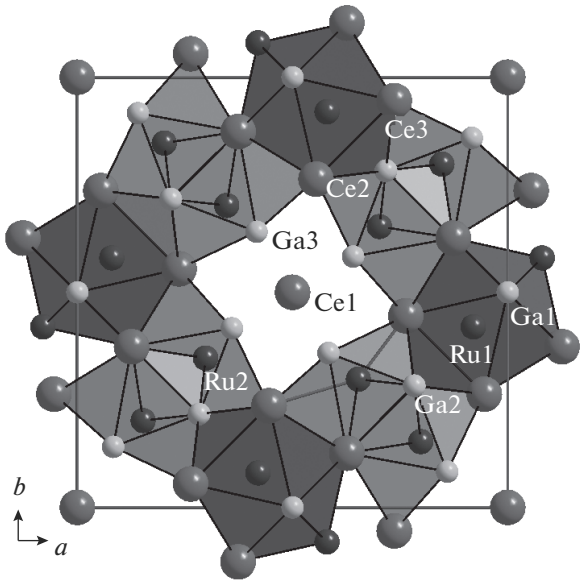

Fig. 12. Crystal structure of $Ce_7Ru_6Ga_7$ projected along [001].

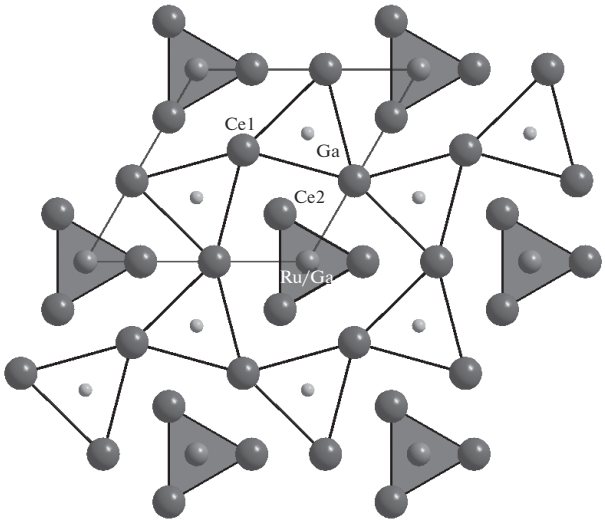

Fig. 13. Crystal structure of $Ce_6Ru_{1-x}Ga_{2+x}$ projected along [001].

Ce^{3+}/Ce^{4+}. Of the five compounds under consideration, three have short cerium–ruthenium bond distances: $Ce_{23}Ru_{10}Ga$, $Ce_{26}(Ru_{0.59}Ga_{0.41})_{17}$, and $Ce_7Ru_6Ga_7$. The most promising of them for low-temperature magnetic and electrical transport measurements is $Ce_7Ru_6Ga_7$, a compound of constant composition, but it is difficult to prepare in single-phase form, suitable for property measurements, because the Ce–Ru–Ga system contains a number of compounds with similar compositions: $Ce_4Ru_3Ga_3$ [7], $CeRu_{0.97}Ga_{1.06}$, $CeRu_{2-x}Ga_x$ [29], and $Ce_2Ru_2Ga_3$ [30].

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REFERENCES

1. Parks, R.D., *Valence Instabilities and Related Narrow-Band Phenomena,* New York: Plenum, 1977.
2. Suski, W., Intermediate valence state of cerium in intermetallics, *J. Magn.,* 1999, vol. 4, no. 3, pp. 102–106.
3. Hermes, W., Matar, S.F., and Pöttgen, R., Unusually short Ce–Ru distances in CeRuAl and related compounds, *Z. Naturforsch., B: Chem. Sci.,* 2009, vol. 64, pp. 901–908.
4. Emsley, J., *The Elements,* Oxford: Clarendon, 1991, 2nd ed.
5. Murashova, E., Tursina, A., Kurenbaeva, Z., Shablinskaya, K., Seropegin, Y., and Kaczorowski, D., New compounds $RE_5Ru_3Ga_2$ (*RE* = La, Ce, Pr, Dy): synthesis, crystal structures, magnetic, electric and thermodynamic properties, *17th Int. Conf. on Solid Compounds of Transition Elements (SCTE2010),* Annecy, 2010, p. 70.
6. Shablinskaya, K., Murashova, E., Tursina, A., Kurenbaeva, Zh., Yaroslavtsev, A., and Seropegin, Y., Intermetallics $La_9Ru_4In_5$ and $Ce_9Ru_4Ga_5$ with new types of structures. Synthesis, crystal structures, physical properties, *Intermetallics,* 2012, vol. 23, pp. 106–110. https://doi.org/10.1016/j.intermet.2011.12.024
7. Shablinskaya, K., Murashova, E., Kurenbaeva, Zh., Yaroslavtsev, A., Seropegin, Y., and Kaczorowski, D., Intermetallic compounds $Ce_4Ru_3Ga_3$ and $La_3Ru_2Ga_2$ with crystal structures of new types, *J. Alloys Compd.,* 2013, vol. 575, pp. 183–189. https://doi.org/10.1016/j.jallcom.2013.04.021
8. Kaczorowski, D., Murashova, E., and Kurenbaeva, Z., Antiferromagnetic ordering in an intermediate valence compound $Ce_9Ru_4Ga_5$, *J. Alloys Compd.,* 2013, vol. 557, pp. 23–26. https://doi.org/10.1016/j.jallcom.2012.11.205
9. Rodewald, U.Ch., Tuncel, S., Chevalier, B., and Pöttgen, R., Rare earth metal-rich magnesium compounds RE_4IrMg (RE = Y, La, Pr, Nd, Sm, Gd, Tb, Dy) and $RE_{23}Ir_7Mg_4$ (RE = La, Ce, Pr, Nd), *Z. Anorg. Allg. Chem.,* 2008, vol. 634, pp. 1011–1016. https://doi.org/10.1002/zaac.200700552
10. Brunton, G., Refinement of the crystal structure of β_1-K_2UF_6, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.,* 1969, vol. 25, pp. 2163–2164.
11. Yarmolyuk, Ya.P., Grin', Yu.N., and Olesh, O.M., Crystal structure of $R_{26}Ga_xCo_{(17-x)}$ (R = La, Ce, Pr, Nd, Sm) and $R_{26}Ga_xNi_{(17-x)}$ (R = Ce, Pr, Nd, Sm)

compounds, *Kristallografiya,* 1980, vol. 25, pp. 248–253.

12. Yarmolyuk, Ya.P., Zarechnyuk, O.S., Akselrud, L.G., Rykhal, R.M., and Rozhdestvenskaya, I.V., Crystal structure of $Pr_7Co_6Al_7$, a new compound of the $R_7Co_6Al_7$ (R = Pr, Nd, Sm) family, *Kristallografiya,* 1986, vol. 31, pp. 392–393.
13. Edwards, A.R., The lattice dimensions of the AB_2 Laves phases, *Metall. Trans. B,* 1972, vol. 3, no. 6, pp. 1365–1372.
14. *Stoe WinXPOW, version 2.21*, Darmstadt: Stoe & Cie GmbH, 2007.
15. Rodriguez-Carvajal, J., Recent Developments of the Program FULLPROF, Commission on Powder Diffraction (*Int. Union of Crystallography*), 2001, vol. 26, pp. 12–19.
16. Roisnel, T. and Rodriguez-Carvajal, J., 2000WinPLOTR: a Windows tool for powder diffraction patterns analysis. *Materials Science Forum (EPDIC 7)*, Barcelona, 2000, p. 118.
17. Sheldrick, G.M., A short history of SHELX, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.,* 2008, vol. 64, pp. 112–122. https://doi.org/10.1107/S0108767307043930
18. Sheldrick, G.M., *SADABS – Bruker Nonius Area Detector Scaling and Absorption Correction,* Göttingen: Univ. of Göttingen, 2004.
19. Blessing, R.H., *An empirical correction for absorption anisotropy, Acta Crystallogr., Sect. A: Fundam. Crystallogr.,* 1995, vol. 51, pp. 33–38. https://doi.org/10.1107/S0108767394005726
20. Bergerhoff, G., *DIAMOND. Visual Crystal Structure Information System*, Bonn: Univ. of Bonn, 1996.
21. Pati, S.K. and Rao, C.N.R., Kagome network compounds and their novel magnetic properties, *Chem. Commun.,* 2008, vol. 37, pp. 4683–4693.
22. Mishra, T., Hoffmann, R.-D., Schwickert, C., and Pöttgen, R., Structure refinement and magnetic properties of Ce_2RuAl_3 and a group–subgroup scheme for $Ce_5Ru_3Al_2$, *Z. Naturforsch., B: Chem. Sci.,* 2011, vol. 66, pp. 771–776.
23. Gibson, B.J., Das, A., Kremer, R.K., Hoffmann, R.D., and Pöttgen, r., Synthesis, structure, and magnetic properties of LaTMg and CeTMg (T = Pd, Pt, Au), *J. Phys.: Condens. Matter,* 2002, vol. 14, pp. 5173–5186.
24. Rossi, D., Mazzone, D., Marazza, R., and Ferro, R., A contribution to the crystallochemistry of ternary rare earth intermetallic phases, *Z. Anorg. Allg. Chem.,* 1983, vol. 507, pp. 235–240. https://doi.org/10.1002/zaac.19835071230
25. Marushina, E., Murashova, E., Kurenbaeva, Zh., and Gribanov, A., The crystal chemistry of Ce-rich compounds Ce_4RuAl and $Ce_{23}Ru_{7+x}Al_{4-x}$ ($0 < x < 2.97$, *J. Alloys Compd.,* 2018, vol. 764, pp. 929–936. https://doi.org/10.1016/j.jallcom.2018.06.145
26. Linsinger, S., Eul, M., Hermes, W., Hoffmann, R.-D., and Pöttgen, R., Intermediate-valent $Ce_{23}Ru_7Mg_4$ and $RE_{23}Ru_7Mg_4$ (*RE* = La, Pr, Nd) with $Pr_{23}Ir_7Mg_4$-type structure, *Z. Naturforsch., B: Chem. Sci.,* 2009, vol. 64, pp. 1345–1352.
27. Tappe, F., Hermes, W., Eul, M., and Pöttgen, R., Mixed cerium valence and unusual Ce–Ru bonding in $Ce_{23}Ru_7Cd_4$, *Intermetallics,* 2009, vol. 17, pp. 1035–1040. https://doi.org/10.1016/j.intermet.2009.05.002
28. Myakush, O., Fedorchuk, A., and Zelinskii, A., Crystal structure of $R_{26}(Ru_xGa_{1-x})_{17}$ (R = Ce, Gd, Y, Tb, Dy, Ho, Er, Tm, Lu) and $HoRu_{0.6}Ga_{0.4}$, *Inorg. Mater.,* 1998, vol. 34, no. 6, pp. 562–565.
29. Kim, Y.G. and Lee, J.Y., Hydrogen-induced transformation to an amorphous state in the Laves phases $Ce(Ru,M)_2$ (M = Fe, Co, Ni), *J. Alloys Compd.,* 1993, vol. 191, pp. 243–249.
30. Murashova, E., Shablinskaya, K., Kurenbaeva, Zh., Yaroslavtsev, A., Menushenkov, A., Chernikov, R., Grishina, O., Nesterenko, S., Seropegin, Y., and Kaczorowski, D., Synthesis, crystal structure and physical properties of $Ce_2Ru_2Ga_3$, *Intermetallics,* 2013, vol. 38, pp. 23–29. https://doi.org/10.1016/j.intermet.2013.02.002

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