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Synthesis, crystal structure and physical properties of Ce₂Ru₂Ga₃

Elena Murashova ^{a, *}, Ksenia Shablinskaya ^a, Zhanaphija Kurenbaeva ^a, Alexander Yaroslavtsev ^b, Alexey Menushenkov ^b, Roman Chernikov ^c, Olga Grishina ^b, Sergey Nesterenko ^a, Yurii Seropegin ^a, Dariusz Kaczorowski ^d

^a Department of Chemistry, Moscow State University, Leninskie Gory 1, 119991 Moscow, Russia

^b National Research Nuclear University "MEPhI", 115409 Moscow, Russia

^c HASYLAB, DESY, D-22607 Hamburg, Germany

^d Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wrocław, Poland

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1. Introduction

ABSTRACT

The novel compound Ce₂Ru₂Ga₃ was synthesized by arc-melting the elemental constituents in argon atmosphere followed by long-term annealing at 873 K. It forms in an orthorhombic system, with a crystal structure of new type (space group *P*2₁2₁2₁, *Z* = 4, *oP*28) and the lattice parameters: *a* = 4.488(2) Å, *b* = 6.912(4) Å, *c* = 17.092(9) Å. The gallide is structurally related to intermetallics crystallizing with the NdRh₂Sn₄-type structure or its derivatives. It represents an unique family of materials with abnormally short Ce–Ru distances, which usually exhibit some instability of the valence state of cerium atoms. Based on the low-temperature magnetic and electrical transport data, as well as the X-ray absorption data, Ce₂Ru₂Ga₃ has been characterised as another intermediate valence system.

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Our previous studies on cerium-rich region of the Ce-Ru-Ga system have revealed the formation of ternary compounds Ce5Ru₃Ga₂ [1], Ce₉Ru₄Ga₅ [2], and Ce₄Ru₃Ga₃ [3]. The crystal structures of these phases are characterized by the interatomic Ce-Ru distances of 2.40(4), 2.3664(8), and 2.7167(17) Å, respectively, which are considerably shorter than the sum of the covalent radii of cerium and ruthenium atoms (2.89 Å) [4]. The shortening of these distances was related to an intermediate valence state of some of the crystallographically independent cerium atoms, which was confirmed in XANES and magnetic susceptibility measurements [1–3]. For a few other ternary compounds obtained in the Ce–Ru– Ga system, i.e., CeRu₂Ga₈ [5], Ce₂Ru₃Ga₅ [6], Ce₂Ru₃Ga₉ [7], and $Ce_{26}(Ru_{1-x}Ga_x)_{17}$ [8], the Ce–Ru distances lie in the range 2.963– 3.398 Å, which is typical of metallic bonds. It is remarkable that most of the known ternary compounds with short Ce-Ru distances are formed in the Ce-rich region of the Ce–Ru–X systems (X = In [9], Al [10], Ga [2], Sn [11], Cd [12], Mg [13]), but Ce₂Ru₂In₃ [14], CeRu_{0.88}In₂ [15], Ce₁₆Ru₈In₃₇ [16], Ce₂RuZn₄ [17] and CeRu₂Mg₅ [18] were found in regions with relatively low cerium content. In this paper we report on the existence of another ternary compound which is formed in the gallium-rich region of the Ce–Ru–Ga phase diagram, namely, Ce₂Ru₂Ga₃. It is interesting that this new gallide also contains unusually short Ce–Ru distances and exhibits strong instability of the valence state of cerium atoms.

2. Experimental

Polycrystalline samples of Ce₂Ru₂Ga₃ were synthesized by arcmelting metallic cerium (99.8 wt.%), ruthenium (99.99 wt.%), and gallium (99.999 wt.%) in argon atmosphere of $0.7 \cdot 10^5$ Pa on a water cooled copper base, performed using an MAM-1 laboratory arc furnace (Bühler) with a tungsten electrode. The samples were turned over and remelted several times to ensure homogeneity. Subsequently, the ingots were sealed in evacuated quartz ampoules and annealed at 873 K for 30 days. Then, the ampoules were quenched in room-temperature water.

The sample composition was checked by energy-dispersive X-ray spectroscopy (EDXS) carried out using a Carl Zeiss LEO EVO 50XVP electron microscope equipped with an Oxford Instruments EDX INCA Energy 450 analyser. Powder X-ray diffraction (PXRD)



^{*} Corresponding author. Tel.: +7 495 9394354; fax: +7 495 9390171. *E-mail address:* murashovaev@rambler.ru (E. Murashova).

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data were collected with an STOE STADI P transmission diffractometer equipped with a linear Position Sensitive Detector (monochromated CuK_{α1} radiation; $10^{\circ} < 2\theta < 90^{\circ}$). The X-ray data processing and refinements of the lattice parameters were made using the WinXPow program package [19]. The atomic coordinates were fitted with the program MRIA [20] using a split-type pseudo-Voigt peak profile function [21]. The anisotropic line-broadening was taken into account by using six variables [22], and symmetrized harmonic expansion up to the fourth order [23,24] was used for correcting the texture effect (see Fig. 1a).

The differential thermal analysis (DTA) was performed in the temperature range 298–1270 K in high-purity helium atmosphere using an NETZSCH STA 449 F1 analyser. A sample of $Ce_2Ru_2Ga_3$ (15.4 mg) was heated at $\frac{1}{4}$ rate of 20 °C/min. The results indicated that the compound melts incongruently at 1241(1) K (Fig. 1).

Ten small "single crystals" were mechanically separated from an annealed button of the initial composition of Ce_{28,57}Ru_{28,57}Ga_{42,8} and tested for X-ray data collection on a four-circle diffractometer. Though none of those samples was found of high quality, the best one was used for the structure determination. The X-ray diffraction experiment was performed on a Bruker APEX-II diffraction system equipped with a CCD detector (MoK $_{\alpha}$ radiation, graphite monochromator). The normal indexing program failed, and the split reflection profiles combined with nice profiles and reflections being very close to one another indicated that the studied sample was a non-merohedral twin. Several orientation matrices were found by the CELL_NOW program [25], but the first domain was much bigger than the others comprising about 60% of all the reflections. Integration with the orientation matrix of the first domain was made using the program SAINT [26]. All the following steps of the structure solution procedure were carried out as for a single crystal. The data were corrected semi-empirically for absorption using the SADABS program [27]. The obtained experimental data showed a primitive orthorhombic cell and systematic extinctions characteristic of the noncentrosymmetric space group $P2_12_12_1$. The selected space group was corroborated in the course of the structure refinement and checked by the program PLATON [28]. The experimental details are summarized in Table 1.

The crystal structure refinements were performed using the SHELX-97 program package [29]. The structure was solved by a combination of direct methods and the difference Fourier syntheses. For the refinement, a full-matrix least-squares program was used with the atomic scattering factors corrected for anomalous dispersion as provided by the utilized program. The applied weighting scheme was $\omega = 1/[\sigma^2(F_0^2) + (0.1000P)^2]$, where $P = (F_0^2 + 2F_c^2)/3$. The displacement parameters of all the atoms were refined by anisotropic approximation. To determine the absolute structure, the Flack parameter was refined by means of TWIN command [29]. The obtained value was 0.42(11), which indicated twinning by inversion. In turn, the ratio of enantiomorphic domains was refined to be 0.42(11):0.58(11).

The atomic coordinates and displacement parameters are listed in Table 2. Selected interatomic distances are given in Table 3. Further details on the crystal structure investigation and the results are given in Supporting information. They can also be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany quoting the depository number CSD-425075.

Magnetic measurements were performed in the temperature range of 1.72–400 K and in external fields up to 5 T using a Quantum Design MPMS-5 SQUID magnetometer. The electrical resistivity was measured over the temperature interval of 4.2–300 K employing the standard dc four-probe technique implemented in a home-made setup.



Fig. 1. (a) The final Rietveld plot for the title compound. The experimental diffraction profile is indicated by black dots. The calculated diffraction profile is shown as a red solid line, the difference profile is shown as the bottom blue solid line and the vertical green bars correspond to positions of the Bragg peaks; (b) A DTA heating (dark blue) and cooling (green) thermograms of Ce₂Ru₂Ga₃ compound. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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Fable 1 Single crystal data and structural refinement for $Ce_2Ru_2Ga_3$.			
Empirical formula	Ce ₂ Ru ₂ Ga ₃		
Molar mass, g/mol	691.54		
Type of structure, Pearson symbol	Ce ₂ Ru ₂ Ga ₃ , oP28		
Space group, Z	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (<i>N</i> ^o 19), 4		
Unit cell dimensions, Å			
а	4.488(2)		
b	6.912(4)		
С	17.092(9)		
<i>V</i> , Å ³	530.2(5)		
Calculated density, g/cm ³	8.7		
Т, К	173(2)		
Crystal size, mm	$0.04\times0.07\times0.09$		
Radiation, λ, Å	ΜοΚ _{α,} 0.71073		
Absorption coefficient, mm ⁻¹	37.2		
$ heta$ range, $^\circ$	2.38, 24.96		
Range in <i>hkl</i>	$-5 \div 5; -8 \div 8; -20 \div 20$		
Total no, reflections	4019		
Independent reflections (R _{int})	938 (0.077)		
Reflections with $I > 2\sigma(I)$ (R σ)	656 (0.068)		
Refined parameters no	65		
Goodness-of-fit on F ²	1.004		
Final <i>R</i> indices $[I > 2\sigma(I)]$ R1	0.054		
wR2	0.134		
R indices (all data) R1	0.091		
wR2	0.161		
Flack parameter	0.42(11)		
Largest diff. peak and hole, e/Å ³	3.847/-2.319		

The valence state of cerium in Ce₂Ru₂Ga₃ was studied by means of XANES spectroscopy. The X-ray absorption spectra were collected in the temperature range of 23-300 K at A1 beamline of the DORIS III positron storage ring at DESY/HASYLAB (Hamburg, Germany) in the transition mode above the L_3 -Ce absorption edge (5723 eV). Energy resolution of the double-crystal Si (111) monochromator (detuned to reject 50% of the incident signal in order to minimize harmonic contamination) with a 0.3 mm slit at 6 keV was about 1.0 eV. Low-temperature measurements were carried out using a liquid helium continuous flow cryostat with temperature control of ± 1 K at 300 K and ± 0.1 K at 23 K.

3. Results and discussion

3.1. Crystal structure

The EDXS study of the prepared sample of Ce₂Ru₂Ga₃ revealed a single phase with the composition Ce (28.3 \pm 0.6 at.%):Ru $(28.4 \pm 0.6 \text{ at.}\%)$:Ga $(42.3 \pm 0.6 \text{ at.}\%)$. According to the X-ray powder diffraction data, the compound crystallizes with the orthorhombic system and the unit cell parameters: a = 4.4856(1), b = 6.9251(2), and c = 17.0817(5) Å. The derived lattice parameters and the distribution of diffraction intensities indicate a close resemblance with Ce₂Ru₂In₃ (cf. Fig. 2), however, the latter compound forms in the space group Pnma, whereas Ce₂Ru₂Ga₃ crystallizes in its subgroup $(P2_12_12_1)$ (Table 4). Actually, the new gallide sets a new structural

Table 2
Atomic coordinates and displacement parameters in the structure of Ce ₂ Ru ₂ Ga ₃ .

Atom	Multiplicity, Wyckoff letter	x/a	y/b	z/c	U _{eq} , Å ²
Ce1	4a	0.3048(5)	0.2940(3)	0.42433(11)	0.0125(5)
Ce2	4a	0.6972(5)	0.3009(3)	0.14520(11)	0.0130(5)
Ru1	4a	0.1945(9)	0.5015(4)	0.03282(19)	0.0136(7)
Ru2	4a	0.3121(8)	0.3045(6)	0.28201(18)	0.0217(8)
Ga1	4a	0.1912(12)	0.1158(6)	0.0318(2)	0.0127(9)
Ga2	4a	0.1891(13)	0.0013(6)	0.1926(3)	0.0175(10)
Ga3	4a	0.1932(13)	0.6089(6)	0.1857(2)	0.0146(10)

able	3		

(1) 6 Sel

Atom1	Atom2	Distance
Ce1	Ru1	2.332(4)
	Ru2	2.434(4)
	Ru1	3.105(4)
	Rul	3.110(4)
	Ga3	3.189(6)
	Gal	3 235(5)
	Gal	3.260(5)
	Ga2	3.311(6)
	Ga2	3.348(6)
	Ga1	3.376(5)
	2Ce1	3.478(3)
	Ce2	3.609(4)
C-2	Ce2	3.700(4)
Cez	Ruz	2.908(4)
	Ga2	3 134(5)
	Ga2	3.140(5)
	Ga3	3.157(5)
	Ga3	3.182(6)
	Ga2	3.185(6)
	Ga1	3.211(5)
	Ga3	3.218(5)
	Ga1	3.248(6)
	RUI But	3.255(4)
	Ce1	3.271(4) 3.609(4)
	Ru2	3 617(4)
	Ru2	3.650(5)
	Ru1	3.692(4)
	Ru2	3.697(5)
	Ce1	3.700(4)
Ru1	Ce1	2.332(4)
	Ga1	2.617(7)
	Gal	2.642(7)
	Gai Ca?	2.000(3)
	Ce1	3.105(4)
	Ce1	3.110(4)
	Ce2	3.255(4)
	Ce2	3.692(4)
Ru2	Ce1	2.434(4)
	Ga2	2.652(6)
	Ga2	2.655(7)
	Ga3	2.657(7)
	642	2.004(7) 2.697(7)
	Ga3	2.724(6)
	Ce2	2.908(4)
	Ce2	3.617(4)
Ga1	Ru1	2.617(7)
	Ru1	2.642(7)
	Ru1	2.666(5)
	Ga2	2.861(6)
	Ce2	3.079(5)
		3.106(3)
	Ce1	3.235(5)
	Ce2	3.248(6)
	Ce1	3.260(5)
	Ce1	3.376(5)
Ga2	Ru2	2.652(6)
	Ru2	2.655(7)
	Ru2	2.664(7)
	Gad	2.715(6)
	Gab Gal	2.790(b) 2.861(6)
	Ce2	2.001(0)
	Ce2	3.140(5)
	Ce2	3.185(6)
	Ce1	3.311(6)
	Ce1	3.348(6)
	Ga3	3.545(6)

(continued on next page)

Table 3 (continued)

Atom1	Atom2	Distance
Ga3	Ru2	2.657(7)
	Ru2	2.697(7)
	Ga2	2.715(6)
	Ru1	2.717(5)
	Ru2	2.724(6)
	Ga2	2.796(6)
	Ce2	3.157(5)
	Ce2	3.182(6)
	Ce1	3.189(6)
	Ce1	3.202(5)
	Ce2	3.218(5)
	Ga2	3.545(6)

type that can be considered as a site-exchange variant of the NdRh₂Sn₄-type unit cell [30]. The compound belongs thus to the structural family of Ce₂Ru₂In₃ and Ce₃Ru₂In₂ [14], which also crystallize as the derivatives of the NdRh₂Sn₄-type structure (see Fig. 2). Another group of intermetallics which represent the same family are those with the overall composition *RET*₂X₄, i.e. CeT₂In₄ (T = Pd, Pt) [31], *RE*Rh₂Sn₄ (*RE* = La–Sm) [30], and *RE*Au₂In₄ (*RE* = La, Ce, Pr, Nd) [32].

In the framework structure of Ce₂Ru₂Ga₃, there can be distinguished networks perpendicular to the [100] direction (Fig. 2a). Within a single network, Ce, Ru and Ga atoms form five-membered and eight-membered cycles, and the adjacent networks are shifted with respect to one another. The Ru1–Ga1, Ru2–Ga2, Ru2–Ga3, and Ga2–Ga3 distances between the layers are in the range of 2.617(7)–2.796(6) Å (Table 3). In contrast to the structure of Ce₂Ru₂In₃, which is built of flat networks, the structure of Ce₂R-u₂Ga₃ consists of corrugated networks (Fig. 2b).

Fig. 3 shows the coordination polyhedra of all the independent atoms in the unit cell of $Ce_2Ru_2Ga_3$. The Ce1 atom is located inside a tricapped tetragonal prism [Ru₄Ga₇] (Fig. 3a). Its coordination number (CN) is 11. In the first coordination shell one finds 7 gallium atoms (Ce1–Ga: 3.189(6)–3.376(5) Å) and 4 ruthenium atoms (Ce1–Ru: 2.332(4)–3.110(4) Å). Two ruthenium caps form the shortest contacts with the central Ce1 atom (Ce1–Ru1: 2.332(4) Å

Table 4

Unit cell parameters and cell volumes of ternary intermetallics belonging to the structural family NdRh₂Sn₄.

	Compound	Space	a, Å	b, Å	<i>c</i> , Å	<i>V</i> , Å ³	Ref.
		group					
	Ce ₂ Ru ₂ Ga ₃	P212121	4.488(2)	6.912(4)	17.092(9)	530.2(5)	This
			4.4856(1)	6.9251(2)	17.0817(5)	530.61(4) ^a	paper
	Ce ₂ Ru ₂ In ₃	Pnma	17.7054(4)	4.7144(1)	7.4072(1)	618.28(4)	[14]
	Ce ₃ Ru ₂ In ₂	Pnma	17.394(2)	4.9073(6)	7.669(1)	654.6(2)	[14]
	CePd ₂ In ₄	Pnma	18.449(3)	4.5647(6)	7.4145(15)	624.4(2)	[31]
	CePt ₂ In ₄	Pnma	18.460(4)	4.5299(13)	7.2670(16)	607.7(3)	[31]
	CeAu ₂ In ₄	Pnma	18.514(3)	4.6624(8)	7.389(1)	637.8(2)	[32]
	CeRh ₂ Sn ₄	Pnma	18.591(6)	4.494(4)	7.252(4)	606(1)	[30]
_	NdRh ₂ Sn ₄	Pnma	18.535(3)	4.463(1)	7.229(1)	598.0(3)	[30]
	-						

^a PXRD data.

and Ce1–Ru2: 2.434(4) Å). The four Ce atoms in the second coordination shell are located at much longer distances (from 3.478(3) to 3.700(4) Å). The other Ce atom (Ce2) is located at the center of a voluminous void (see Fig. 3b) and it is surrounded by 18 atoms at the interatomic distances of 2.908(4)-3.700(4) Å. The nearest neighbors of the Ce2 atom are nine Ga atoms and three Ru atoms (CN = 12). The two Ce atoms and four Ru atoms at the distances of 3.609(4)-3.700(4) Å form the second coordination sphere of the Ce2 atom. The coordination polyhedron of Ce2 can be described as a distorted tetracapped tetragonal prism [Ru₃Ga₉]. Based on the structural features one may speculate that the Ce1 and Ce2 atoms differ in their valence states. It may be expected that Ce2 is trivalent, whereas the valence state of Ce1 is intermediate between three and four.

The Ru1 and Ru2 polyhedra are tricapped trigonal prisms formed by $[Ce_5Ga_4]$ (Fig. 3c) and $[Ce_3Ga_6]$ (Fig. 3d), respectively. Each ruthenium atom is shifted from the center of its prism towards the Ce1 atom that caps a lateral face. The corresponding Ru1–Ce1 and Ru2–Ce1 contacts are the shortest in the structure (Table 3). The polyhedra of the Ga1, Ga2 and Ga3 atoms are distorted tetracapped tetragonal prisms formed by $[Ce_6Ru_3Ga_3]$ (Fig. 3e), $[Ce_5Ru_3Ga_4]$ (Fig. 3f), $[Ce_5Ru_4Ga_3]$ and (Fig. 3g), respectively.

In the crystal structure of the NdRh₂Sn₄ prototype, the threedimensional $[Rh_2Sn_4]_{3\infty}$ framework includes only the Rh and Sn



Fig. 2. Projections of the structures $Ce_2Ru_2Ga_3$ along [100] (a) and [010] (b) directions; $Ce_2Ru_2In_3$ along [010] (c) and [001] (d) directions; $Ce_3Ru_2In_2$ (e) and $NdRh_2Sn_4$ (f) along [010] direction. The corrugate layers in the structure $Ce_2Ru_2Ga_3$ are formed by five-membered and eight-membered cycles of Ce, Ru and Ga atoms: light blue – at x = 0.18-0.32, dark – at x = 0.68-0.82. The analogous flat layers in the $Ce_2Ru_2In_3$, $Ce_3Ru_2In_2$ and $NdRh_2Sn_4$ structures: light blue – at x = 1/4, dark – at x = 3/4. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Coordination polyhedra of all independent atoms in the Ce₂Ru₂Ga₃ structure.

atoms. The Nd atoms are located in voluminous voids of the framework (Fig. 2f). The interatomic Rh–Sn distances (2.679(1)-2.923(2) Å) are close to the sum of the covalent radii of Rh (1.25 Å)and Sn (1.41 Å), and the Sn–Sn distances (3.019(3)-3.630(2) Å) are comparable with the double atomic radius of Sn (1.58 Å).

In the Ce–Ru–X (X = In, Ga, Sn) systems, no ternaries exist at 873 K with the composition CeRu₂X₄. Instead, a few ternary compounds form with different compositions, namely Ce₂Ru₂Ga₃, Ce₂Ru₂In₃, and Ce₃Ru₂In₂, with their crystal structures being very closely related to that of NdRh₂Sn₄. In the unit cells of Ce₂Ru₂Ga₃ and Ce₂Ru₂In₃ (Fig. 2c and d), one of the four Sn sites of the NdRh₂Sn₄-type structure is occupied by a Ce atom. In turn, in the crystal structure of Ce₃Ru₂In₂ (Fig. 2e), two of the three crystallographically independent cerium atoms occupy two Sn positions in the unit cell of NdRh₂Sn₄. In consequence, for all these compounds, the Ce-Ru interatomic distances inside the relevant Ce polyhedra are considerably shorter than the sum of the covalent radii of the Ce and Ru atoms (2.89 Å). In the case of Ce₃Ru₂In₂, the Ce-Ru contacts are as small as 2.2345(9) and 2.2811(9) Å [14], while those found in Ce₂Ru₂In₃ are only 2.3225(8) and 2.3681(8) Å [14]. For both compounds, the short Ce-Ru contacts are oriented along the largest lattice parameter, and hence it is smaller (by about 1 Å) than the corresponding unit cell parameter of the closely related CeT₂X₄ (T = Pd, Pt, Au; X = In, Sn) phases (see Table 4).

The anomalous shortening of the interatomic Ce–Ru distances in the structures of Ce₂Ru₂In₃ and Ce₃Ru₂In₂ was tentatively attributed to intermediate valence state of the cerium atoms [14], yet this presumption has not been experimentally verified yet. Therefore, it seemed highly interesting to examine the physical properties of Ce₂Ru₂Ga₃, which also exhibits the presence of unusually short Ce–Ru contacts.

3.2. Physical properties

The magnetic properties of $Ce_2Ru_2Ga_3$ are presented in Fig. 4. The inverse magnetic susceptibility is a strongly non-monotonic function of temperature with a high-temperature range, where $\chi^{-1}(T)$ follows a Curie–Weiss law (depicted by the solid line), a narrow minimum near $T_{min} = 150$ K, and rapid drop below about 50 K. The Curie–Weiss parameters derived from the experimental data above 250 K are $\mu_{eff} = 2.58(4) \mu_B$ and $\theta_p = -473$ K. Whereas the effective magnetic moment μ_{eff} is nearly equal to the theoretical prediction (within the Russell–Saunders coupling scenario) of 2.54 μ_B for a free trivalent cerium ion, the huge magnitude of the negative paramagnetic Curie temperature θ_p suggests immense hybridization between the cerium 4f shell and the electronic states of ligands. Clearly, the overall observed behaviour of $\chi^{-1}(T)$ cannot be rationalized neither in terms of purely trivalent nor exclusively intermediate-valent cerium ions. However, it can be easily explained with the presence in the crystal lattice of the compound of Ce ions with different valence states. As discussed above, such a scenario could indeed be anticipated from the fact that the



Fig. 4. Temperature dependence of the inverse molar magnetic susceptibility of Ce₂Ru₂Ga₃. The solid straight line emphasises a Curie–Weiss behaviour. Inset: magnetic field variation of the magnetization taken at 1.71 K with increasing (open symbols) and decreasing (full symbols) magnetic field strength.

interatomic Ce-Ru distances in Ce₂Ru₂Ga₃ are so much different for Ce2 and Ce1, that these ions are likely nominally trivalent- and intermediate-valent, respectively. If so, then the strong temperature dependence of the magnetic susceptibility seen at the lowest temperatures should be attributed to the contribution due to the Ce2 ions. Consequently, the magnetization isotherm measured at 1.71 K (see the inset to Fig. 4) primarily probes the electronic ground state of the Ce2 sublattice. In turn, the shape of $\gamma^{-1}(T)$ at higher temperatures is probably governed mainly by the variation of the effective valence of the Ce1 ions, which systematically decreases towards 3+ along with the temperature-induced valence fluctuations between the $4f^0$ ground level and the $4f^1$ excited state. In terms of the Interconfiguration Valence Fluctuation model, developed by Sales and Wohlleben [33], the energetic separation of the two configurations in Ce1 is of the order of about 750 K, as can be roughly deduced from the observation of nearly the 4f¹ characteristics in $\chi^{-1}(T)$ above 250 K. In turn, the characteristic temperature T_{sf} of the Ce1 sublattice, related to spin fluctuations, can be estimated to be about 230 K, if the simplistic relationship $T_{sf} = 3/2$ T_{min} [34] is applied.

The hypothesis on the different valence states of the Ce2 and Ce1 atoms in Ce₂Ru₂Ga₃ finds a support in the temperature dependence of the electrical resistivity of the compound, displayed in Fig. 5. On increasing the temperature from 4.2 K, the resistivity first varies in a metallic manner, typical for intermediate valence systems at low temperatures [35,36] as well as for intermetallics based on stable Ce³⁺ ions. In contrast, above about 150 K, i.e., the temperature where $\gamma^{-1}(T)$ forms a minimum, the $\rho(T)$ variation exhibits a negative temperature coefficient. The latter feature likely signals spin-flip Kondo scattering on the cerium magnetic moments. Though no clear logarithmic dependence can be recognized in the experimental data, one should take into account that in this temperature region, important contributions to the electrical resistivity arise also from scattering on phonons, crystal field excitations, and possibly also local spin fluctuations with their own, sometimes fairly complex, temperature dependencies.

Fig. 6 shows the experimental L_3 -Ce XANES spectra of Ce₂Ru₂Ga₃. The splitting of absorption peaks points to the existence of different valence states of cerium atoms in the compound. Two maxima corresponding to different valence contributions are resolved partially. In the insets to Fig. 6, it is shown that the amplitude of a peak corresponding to the Ce⁴⁺ state slightly increases with temperature while the Ce³⁺ component weakens. Such a transfer of intensity between contributions also confirms the intermediate valence state of Ce atoms and, moreover,



Fig. 5. Temperature dependence of the electrical resistivity of Ce₂Ru₂Ga₃ compound.



Fig. 6. XANES spectra of $Ce_2Ru_2Ga_3$ compound at various temperatures in the range 23–300 K. The changes of Ce^{3+} and Ce^{4+} contributions are shown in insets. The components of fitting function for the spectrum at 23 K are shown also.

demonstrates a small decrease of average valence of Ce atoms upon heating from 23 K up to room temperature. The extraction of the Ce atom valence from the experimental spectra was performed by fitting the complicated absorption spectra to the combinations of Lorentzian, Gaussian and arctangent curves with constrained widths and energy positions (Fig. 6) [37]. Note that the best convergence was achieved when the Ce⁴⁺ component in the fitting function was split by ~2.9 eV into two contributions. This can be due to the crystal field splitting of the cerium $2p^54f^{0}5d^*$ final state, which takes place in various Ce-containing compounds, e.g. in CeO₂ [38]. The average valence of Ce atoms in Ce₂Ru₂Ga₃ compound decreases almost linearly from ~3.17 at 23 K to ~3.14 at 300 K (Fig. 7). This small change might be related to the lattice expansion accompanied by the subsequent elongation of the Ce–Ru interatomic bond on heating.



Fig. 7. The temperature dependence of the average Ce valence obtained from XANES. The value of standard deviation for all points is equal to 0.005.

4. Conclusion

The compound Ce₂Ru₂Ga₃ is a new representative of the structural family that includes Ce₂Ru₂In₃, Ce₃Ru₂In₂, CeT₂In₄ (T = Pd, Pt), *RE*Rh₂Sn₄ (*RE* = La–Sm), and *RE*Au₂In₄ (*RE* = La, Ce, Pr, Nd). All these ternaries form with the NdRh₂Sn₄-type crystal structure or its derivatives. The unit cell of Ce₂Ru₂Ga₃ can be considered as a distorted site-exchange variant of the parent structure. A striking feature of Ce₂Ru₂Ga₃ is the formation of unusually short Ce–Ru interatomic distances, caused by the intermediate valence state of the involved Ce atoms. Previously, similarly short Ce–Ru contacts were observed e.g. for Ce₂Ru₂In₃ and Ce₃Ru₂In₂ [14].

The temperature dependencies of magnetic susceptibility and electrical resistivity of Ce₂Ru₂Ga₃ confirm the hypothesis about different valence states of Ce1 and Ce2 atoms. The experimental data can be consistently interpreted in terms of the presence of a sublattice with stable Ce³⁺ ions and another sublattice, containing cerium ions in the 4f⁰ ground configuration and the shift of the effective valence to 3+ with increasing temperature. This assumption was confirmed by the quantitative analysis of the average valence state of Ce ions and its temperature-induced changes, which was performed with the use of temperature-dependent X-ray absorption (XANES) spectroscopy at cerium L_3 -edge.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.intermet.2013.02.002.

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