Crystal structure and unstable valence in a novel intermetallic phase Ce$_2$Ru$_2$Al

E.V. Marushina a, D. Kaczorowski b, E.V. Murashova a, Zh.M. Kurenbaeva a, A.V. Gribanov a,*,

a Department of Chemistry, Moscow State University, GSP-1, Moscow 119991, Russia
b Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wroclaw, Poland

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New ternary intermetallic compound Ce$_2$Ru$_2$Al was prepared in polycrystalline form, and its crystal structure was determined from both powder and single crystal X-ray diffraction data. The aluminide was found to crystallize with an orthorhombic structure (space group Cmce) with the lattice parameters: $a = 5.8914(4)$ Å, $b = 9.3663(6)$ Å, and $c = 6.9551(4)$ Å. The derived unit cell is an ordered variant of the binary La$_2$Ni$_3$ type, where one of two Ni sites is fully occupied with Ru atoms, while another one accommodates Al atoms. The structure of Ce$_2$Ru$_2$Al can be regarded as a sequence of atomic layers normal to $b$-axis. The remarkable structural feature is a short distance between Ce and Ru atoms equal to 2.7816(4) Å. Magnetic measurements revealed that Ce ions in Ce$_2$Ru$_2$Al possess unstable 4f shell that leads to intermediate valence behavior of the compound. Similar valence instability was observed before for other Ce intermetallics with short Ce–Ru bonds.

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1. Introduction

In recent decades, cerium ternaries forming in systems Ce-T-X (T = d-electron transition metal, X = p-element of 13–15 groups) have been intensively investigated due to wide variety in their chemical compositions and specific crystal structures, peculiarities in their crystal chemistry, and their intriguing physical properties, mostly governed by hybridization between conduction electrons and cerium 4f electrons. Amidst such compounds, those with T = Ru often exhibit a unique structural feature of extremely short Ce–Ru distances (from -2.75 Å down to -2.40 Å, and even to 2.2345 Å in Ce$_2$RuIn$_2$ [1]), which are much less than the sum of metallic radii $R_m$(Ce) + $R_m$(Ru) = 1.83 Å + 1.34 Å = 3.17 Å [2], and even less than the sum of covalent radii $R_c$(Ce) + $R_c$(Ru) = 1.65 Å + 1.24 Å = 2.89 Å [2]. The occurrence of these extremely short Ce–Ru contacts is usually associated with intermediate valence state of Ce ions [3,4].

To date, in the system Ce–Ru–X there have been ten ternary intermetallic phases identified: Ce$_2$Ru$_4$Al$_2$ [5], Ce$_2$Ru$_2$Al$_5$ [6], CeRu$_2$Al$_8$ [7], CeRu$_3$3.5Al$_{10.5}$ (x = 0.17) [8], Ce$_2$Ru$_3$Al$_5$ [9], Ce$_2$RuAl$_2$ [10], Ce$_1$Ru$_2$Al$_6$ [11], Ce$_2$RuAl$_2$ [12,13], Ce$_2$Ru$_3$Al$_5$ [14], and CeRuAl$_2$ [15]. A few of them are characterized by short Ce–Ru distances (2.4404 Å in Ce$_1$Ru$_2$Al$_6$ [11], 2.4821 Å in Ce$_2$Ru$_2$Al$_5$ [14], 2.5299 Å in Ce$_2$Ru$_3$Al$_5$ [10], 2.803 Å in CeRuAl$_2$ [15]). Remarkably, all these materials form in the Ce-rich corner of the ternary phase diagram. In the present work, we established the formation of another compound from this region, namely Ce$_2$Ru$_2$Al. The new aluminide was found to crystallize with its own crystal structure that comprises abnormally short interatomic Ce–Ru distance of 2.7816 Å. Alike the other Ce–Ru–X materials showing this structural feature, the magnetic behavior in Ce$_2$Ru$_2$Al was found to be driven by unstable 4f electronic configuration of the Ce ions.

2. Experimental details

2.1. Synthesis

Polycrystalline sample of Ce$_2$Ru$_2$Al was prepared by arc-melting the elemental constituents (purities: cerium 99.85 mass %, ruthenium 99.99 mass %, aluminum 99.999 mass %) taken in the molten ratio Ce:Ru:Al = 2:2:1. The synthesis was performed under purified argon atmosphere using zirconium as a getter. To promote homogeneity, the ingot was remelted several times. Subsequently, the alloy was annealed in an evacuated quartz ampoule at 823 K for 30
days, and then quenched in cold water. The total mass loss after the preparation was less than 0.2%.

2.2. Sample characterization

The prepared material was examined by energy-dispersive X-ray (EDX) spectroscopy on a Carl Zeiss LEO EVO 50XVP scanning electron microscope. The accuracy in determining the chemical composition was 0.8 at.% for Ce and Ru atoms, and 1.5 at.% for Al atoms.

Differential thermal analysis (DTA) was performed in the temperature interval from 298 K to 1150 K (heating/cooling rate 20 K/min, sample mass 20 mg) using a Netzsch STA449 F1 apparatus equipped with a Platinum RT analyzer.

2.3. Single crystal X-ray diffraction

Small single crystals of Ce2Ru2Al, suitable for crystal structure study, were extracted from the melted ingot by mechanical fragmentation. The X-ray intensity data were collected at room temperature on a Bruker APEX-II four-circle diffractometer equipped with a CCD detector (MoKα radiation, graphite monochromator). The crystal structure determination was carried out by direct methods employing the program SHELXS-97 [16]. The subsequent refinements were made using the program SHELXL-97 [16]. For graphical presentation of the crystal structure the program DIAMOND 3.2k [17] was used.

2.4. Powder X-ray diffraction

The polycrystalline sample of Ce2Ru2Al was examined by powder X-ray diffraction performed at room temperature on a STOE STADI P transmission diffractometer (CuKα1-radiation, Graphite monochromator). 20 range 10°–90° with 0.01° step, counting time 10 s per point. The X-ray pattern was evaluated by Rietveld method implemented in the program FULLPROF [18,19].

Magnetic measurements

Magnetic measurements were performed on polycrystalline sample of Ce2Ru2Al in the temperature range 1.72–400 K and in external fields up to 5 T using a Quantum Design MPMS-5 SQUID magnetometer.

3. Results and discussion

The EDX analysis of the prepared alloy yielded the matrix composition 40.5 at.% Ce, 40.6 at.% Ru, and 18.9 at.% Al that was identified as the compound Ce2Ru2Al. Additionally, a small amount (below 2 mass %) of secondary phase RuAl phase was detected. From the DTA measurement, the melting temperature of Ce2Ru2Al was determined to be 1062(1) K with no phase transition before this point.

The single crystal X-ray diffraction studies revealed that Ce2Ru2Al crystallizes with an orthorhombic base-centered crystal structure, space group Cmce, Z = 4 (Pearson symbol oC20), with the lattice parameters: a = 5.8914(4) Å, b = 9.9603(6) Å, and c = 6.9551(4) Å. The powder X-ray diffraction data corroborated this finding (see Fig. 1). The details on the single-crystal and powder X-ray data collections and the structure refinements are gathered in Table 1. The refined atomic coordinates and the atomic displacement parameters are given in Table 2, while the main interatomic distances are listed in Table 3. The crystal structure of Ce2Ru2Al in a three-dimensional view along the a axis is shown in Fig. 2.

Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Empirical formula</th>
<th>Molar mass (g/mol)</th>
<th>Structure type, Pearson symbol</th>
<th>Crystal system</th>
<th>Space group, Z</th>
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</thead>
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<tr>
<td>Ce2Ru2Al</td>
<td>Ce2Ru2Al</td>
<td>509.36</td>
<td>Ce2Ru2Al, oC20</td>
<td>Orthorhombic</td>
<td>Cmce (No. 64), 4</td>
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Table 2

<table>
<thead>
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<th>Wyckoff symbol</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
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<td>0.3398(3)</td>
<td>0.0813(3)</td>
<td>0.02706(11)</td>
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<td>8e</td>
<td>1/4</td>
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<td>0.14(5)</td>
<td>0.03223(15)</td>
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<td>0</td>
<td>0</td>
<td>0.0212(5)</td>
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</table>
The coordination polyhedra of all the atoms are presented in Fig. 3. Ce atoms are located in a 13-vertex polyhedron Ce[Ce₃Ru₆Al₄]. The coordination polyhedron of Ru is a tetragonal antiprism consisting of six Ce atoms and two Al atoms with two Ru atoms capping the bases of the prism, Ru[Ce₆Ru₂Al₂]. The coordination polyhedron of Al is a distorted icosahedron built of eight Ce atoms and four Ru atoms, Al[Ce₈Ru₄].

The novel compound Ce₂Ru₂Al crystallizes with the structure of a new type that can be regarded as an ordered derivative of the binary La₂Ni₃ type. In the latter structure, La atoms are located in the 8f Wyckoff position and Ni atoms have two positions 8e and 4a.

In Ce₂Ru₂Al, the Ce atoms replace the La atoms, the site 8e is fully occupied by the Ru atoms, while the 4a site is fully filled with the Al atoms.

A characteristic feature of the crystal structure of Ce₂Ru₂Al is the presence of zigzag-like layers of the Ce atoms perpendicular to the b-axis, which alternate along this direction with non-planar Ru₂Al layers. Each Ru₂Al layer is shifted by half the c-parameter with respect to the closest Ru₂Al layer (see Fig. 2). A similar set of two different zigzag-like sheets is observed in V₂Sn₂Ga [20]. In the latter compound, however, the V₂Ga layer has a form of pentagons built of V atoms and centered with Ga atom, while the Sn atoms layer consists of twice the number of the Ce atoms in Ce₂Ru₂Al. As a result, both zig-zag sheets are notably thicker than those in Ce₂Ru₂Al, and consequently the lattice parameter b of V₂Sn₂Ga is doubled with respect to that in the aluminide.

As can be inferred from Table 3, the Ce–Ru distances in the unit cell of Ce₂Ru₂Al are 2.7816(4) Å and 2.9195(6) Å. These values are close to the sum of the respective covalent radii (2.89 Å), and are similar to those reported before for Ce₅Ru₃Al₂ [10], CeRuAl [15], Ce₆RuAl [13], Ce₂RuAl [14] and Ce₁₁Ru₂Al₆ [11]. Remarkably, most of these phases are intermediate valence systems, as concluded from their magnetic susceptibility and electrical resistivity data (see eg., Refs. [10,13]).

The temperature variation of the inverse magnetic susceptibility of Ce₂Ru₂Al is shown in Fig. 4. The overall shape of this curve is typical for intermediate valence systems [21]. In the entire temperature range, the molar susceptibility is small, and above about 100 K it is weakly temperature dependent. Above ca. 200 K, χₘ decreases with increasing temperature, and above room temperature, χₘ(T) shows a tendency to saturate. By analogy to other Ce- and Ru-bearing intermetallics, one may expect the presence of a broad minimum in χₘ(T) above 400 K that would define the characteristic energy scale of valence fluctuations [21] in Ce₂Ru₂Al. For the gallides Ce₂Ru₂Ga₃ [22] and Ce₄Ru₂Ga₃ [23] such a minimum in χₘ(T) was observed near 150 K and 250 K, respectively, but for Ce₉Ru₄Ga₅ [24] and the aluminides Ce₅Ru₃Al₂ [10] and Ce₂RuAl [14] its position was also estimated above 400 K. Remarkably, in all these materials, the Ce ions occupy more than one crystallographic site and some of them exhibit a stable trivalent state that accompanies the valence fluctuations in a different Ce ions sublattice. This may lead to the appearance of long-range magnetic ordering at low temperatures [14,23,24]. In the case of Ce₂Ru₂Al, there is only one position of the Ce ions in the unit cell, and hence the intermediate valence is homogeneous. As can be inferred from the low-temperature χₘ(T) and ξ(H) data (see the insets in Fig. 4), this compound remains paramagnetic down to the terminal temperature in our study (1.72 K). A Curie-like tail in the magnetic susceptibility probably arises because of magnetic impurities (e.g. cerium oxides) present in small amount in the sample investigated, which was not detected in the X-ray diffraction and EDX

### Table 3

<table>
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<tr>
<th>Atom 1</th>
<th>Atom 2</th>
<th>d, Å</th>
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<tbody>
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</tr>
<tr>
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<td>2.9195(6)</td>
</tr>
<tr>
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</table>

![Fig. 2](image-url) The crystal structure of Ce₂Ru₂Al in a three-dimensional view along the a axis.

![Fig. 3](image-url) Coordination polyhedra of the atoms in the unit cell of Ce₂Ru₂Al.
measurements.

4. Conclusions

Ce$_2$Ru$_2$Al is a novel ternary phase in the Ce–Ru–Al system. The compound crystallizes with its own crystal structure that is an ordered derivative of the La$_2$Ni$_3$ type. Alike in a few other Ru-bearing cerium intermetallics, the Ce–Ru interatomic distances in Ce$_2$Ru$_2$Al are short, and this feature is accompanied by the instability of the 4f electronic configuration of the Ce ion that brings about the intermediate valence character of the magnetic behavior.

Acknowledgment

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References


