Crystal growth and structure determination of the novel tetragonal compound Ce$_2$RhGa$_{12}$

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Single crystals of Ce$_2$RhGa$_{12}$ have been synthesized using Ga flux and their structure was determined by single-crystal X-ray diffraction. Ce$_2$RhGa$_{12}$ crystallizes in the tetragonal space group *P4/nbm* (No. 125), and is isostructural to Ce$_2$PdGa$_{12}$, with *Z* = 2 and lattice parameters *a* = 6.0405 Å and *c* = 15.706 Å. Data were collected at the Swiss Norwegian Beam Line at the European Synchrotron Facility, Grenoble, France. Laue diffraction was carried out to confirm the quality of the single crystal and showed well-defined spots and tetragonal symmetry.

Cerium / Rhodium / Gallium / Intermetallic compound / Crystal structure

Introduction

Ternary intermetallic compounds, *Ln-T-X*, consisting of a lanthanide (*Ln*), transition metal (*T*), and a *p*-group metal (*X*) exhibit fascinating physical properties. Rare earth (*RE*) based intermetallic compounds have remarkably diverse crystal structures, magnetic and electronic properties [1-4]. Ce-based intermetallic compounds often show a variety of unusual behaviors in consequence of the competition between the tendency toward magnetic order of the *f*-electrons *via* hybridization pathways with the conduction electrons (Rudermann-Kittel-Kausya-Yoshida (RKKY) interaction) and the screening of magnetic moments (Kondo effect), which in turn produces large effective electron masses, described by the term heavy fermion. Because the effective mass is proportional to the electronic specific heat, unusually large values of electronic specific heat (*γ* typically > 400 mJ/mol K^2) can be observed in heavy fermion compounds. The structures and properties of Ce$_2$PdGa$_{12}$ and CePdGa$_6$ [5] have been reported. Some heavy fermion compounds such as CeCu$_2$Si$_2$ [6] and Ce*T*In$_5$ are superconducting [7].

CeCu$_2$Si$_2$ crystallizes in a tetragonal, ThCr$_2$Si$_2$-type structure and can be described as formed by alternate CuSi and Ce layers [6]. Layered materials occupy a special place when it comes to exploring new heavy fermions and superconducting state and intensifying our understanding of the role of structural dimensionality. The highest *T*$_c$ reported for the superconducting layered material CeCoIn$_5$ is 2.3 K. Ce$_2$RhGa$_{12}$ is isostructural to Ce$_2$PdGa$_{12}$, in which the tetragonal structure is composed of CeGa and PdGa$_{8/2}$ layers, similar to those found in CePdGa$_6$ [8]. This bilayer structure favors magnetic ordering. CePdGa$_6$, which is another layered heavy fermion compound, with a specific heat coefficient *γ* of 300 mJ/mol-Ce K^2, orders antiferromagnetically at *T*$_N$ = 5.5 K. Various other Cu-containing compounds, such as CeCu$_4$Al, CeCu$_3$Al$_2$, and CeCu$_4$Ga, also show heavy fermion behavior [9-11]. Expecting a similar outcome, the substitution of Rh for Pd offered an opportunity to study the intermetallic compound Ce$_2$RhGa$_{12}$, which is similar to the layered Ce$_2$PdGa$_{12}$. We suppose that the title compound may exhibit similar physical properties.

The principal focus of this work is the growth of single crystals and X-ray diffraction studies of the novel intermetallic compound Ce$_2$RhGa$_{12}$.

Crystal growth

Single crystals of Ce_2RhGa_{12} were grown from a Ga-rich flux, starting from an initial composition of Ce, Rh and Ga in the ratio 3:2:21. All the starting materials were of high purity. Ga-rich self-flux is ideal because of its low melting temperature and also it introduces no new elements into the melt. The constituent elements were placed in an alumina crucible and sealed in a quartz ampoule under vacuum. The ampoule was then heated up to 1500°C over a period of 24 h and held at this temperature for some time for proper homogenization. The furnace was cooled very fast down to 750°C to avoid unwanted phase formation. From 750°C to 500°C the furnace was cooled very slowly, at a rate of 1°C/h. Then it was cooled rapidly to room temperature. The crystals were separated by centrifuging the melt in an evacuated glass tube at 300°C and then by treating them in hot water. The resulting as-grown crystals were of the size $10 \times 0.5 \times 0.5$ mm^3, as shown in Fig. 1. EDAX analyses revealed the presence of all three elements in ratios consistent with the stoichiometry. An energy-dispersive spectroscopy (EDS) analysis performed on visibly clean surfaces of the samples gave an atomic composition close to 2:1:12. The crystals were then oriented along the principal crystallographic directions, namely [100] and [001], by means of the Laue back reflection method using a Mo source. The X-ray Laue analysis confirmed the good quality of the single crystals by exhibiting distinct spots and four-fold symmetry. The crystals were then cut again along both the *a*- and *c*-directions, using a spark erosion cutting machine, for magnetic and other physical property measurements. Transport and magnetic measurements are in progress.

Single crystal X-ray diffraction

A single crystal of Ce_2RhGa_{12} was glued on a glass fiber and transferred to the cold stream of a nitrogen cryojet (T = 200 K). The crystal was twinned with two major domains tilted by about 3 degrees along the *b*-axis. Only one domain was used for the integration. Data were collected at the Swiss Norwegian Beam Line at the European Synchrotron Facility, Grenoble, France. The crystallographic parameters and details of the refinement are given in Table 1. Selected interatomic distances are listed in Table 2. Atomic positions and displacement parameters are given in Tables 3 and 4.

Results and discussion

The structure is isomorphous to Ce_2MGa_{12} (*M* = Ni, Cu [12], Pd [5]). It crystallizes in the tetragonal space group *P4/nbm*. Along the *c*-axis slabs of edge-sharing rectangular $RhGa_8$ prisms alternate with Ga-rich areas, in which Ce atoms occupy cavities surrounded by Ga atoms (Fig. 2). The Rh atoms are coordinated by 8 Ga atoms, with distances 2.525(1) and 2.528(1) Å. These Rh-Ga bond distances are close to the expected interatomic distance of 2.50 Å based on the sum of the covalent radii of Rh (1.25 Å) and Ga (1.25 Å) [13], but are slightly higher than the values reported for the binary compounds Rh_4Ga_{21} and Rh_3Ga_{16} (2.4-2.47 Å) [14]. A similar situation is reported for the Pd-Ga distances in Ce_2PdGa_{12} [5], which is isostructural to Ce_2RhGa_{12}.

In the cavities formed by Ga atoms, each Ce atom is surrounded by 14 Ga. The Ce-centered rectangular prism formed by Ga2 and Ga3 atoms is capped by two Ga1 atoms and four Ga4 atoms (Fig. 3). The experimental values of the Ce-Ga distances range from 3.1580(9) to 3.3853(11) Å (see Table 2).
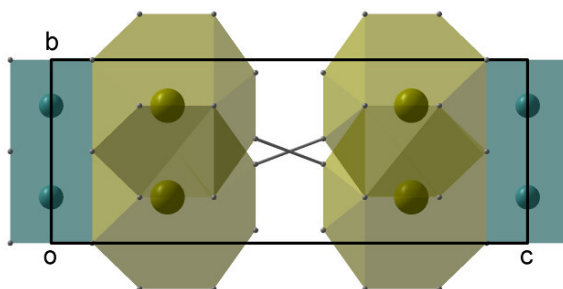

Fig. 1 As-grown single crystals of Ce_2RhGa_{12}.

Fig. 2 View of the structure perpendicular to the *a*-axis. The $RhGa_8$ polyhedra are depicted in blue, while the cavities containing the Ce atom are in gold. The shortest Ga1-Ga1 distances between the cavities are also shown.

Table 1 Crystallographic data and details of the data collection for Ce$_2$RhGa$_{12}$.

Formula	Ce$_2$RhGa$_{12}$
Formula weight	1219.79
Temperature (K)	200
Crystal system	tetragonal
Space group	*P4/nbm*
a, c (Å)	6.0405(17), 15.706(7)
Volume (Å^3)	573.1(3)
Z	2
D$_X$ (mg mm^{-3})	7.069
μ (mm^{-1})	36.781
F(000)	1066
Crystal dimensions (mm^3)	10×0.5×0.5
Theta range for data collection (°)	2.55 to 54.74
Index ranges	-7 ≤ *h* ≤ 7, -7 ≤ *k* ≤ 7, -20 ≤ *l* ≤ 20
Reflections collected	3988
Independent reflections	391 [R$_{int}$ = 0.1091]
Data / restraints / parameters	391 / 0 / 25
Goodness-of-fit on *F*^{2}	1.069
Final R indexes [*I* > 2σ(*I*)]	R$_1$ = 0.0348, wR$_2$ = 0.0927
Final R indexes [all data]	R$_1$ = 0.0378, wR$_2$ = 0.0949
Largest difference peak / hole (e Å^{-3})	2.505 / -3.183

Table 2 Selected interatomic distances for Ce$_2$RhGa$_{12}$ (Å).

Ce-Ga3	3.1580(9)	(×4)
Ce-Ga4	3.2756(13)	(×2)
Ce-Ga4	3.2777(13)	(×2)
Ce-Ga1	3.2846(16)	(×2)
Ce-Ga2	3.3853(11)	(×4)
Ga2-Ga3	2.452(2)	(×1)
Rh-Ga4	2.5251(10)	(×4)
Rh-Ga4	2.5278(10)	(×4)

Table 3 Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for Ce$_2$RhGa$_{12}$. *U*$_{eq}$ is defined as 1/3 of the trace of the orthogonalized *U*$_{ij}$ tensor.

Atom	*x*	*y*	*z*	*U*$_{eq}$
Ce	7500	2500	7558.4(4)	5.7(3)
Ga1	5696.9(10)	4303.1(10)	5711.3(6)	15.1(3)
Ga2	2500	2500	6584.7(9)	8.9(4)
Ga3	2500	2500	8145.7(8)	6.4(4)
Ga4	9998.1(8)	4998.1(8)	9140.6(6)	6.6(3)
Rh	7500	2500	10000	6.0(3)

Table 4 Anisotropic displacement parameters (Å^2×10^3) for Ce$_2$RhGa$_{12}$. The anisotropic displacement factor exponent takes the form: -2π^2[*h*^{2}**a***^{2}*U*$_{11}$+...+2*hk***a***×**b***U$_{12}$].

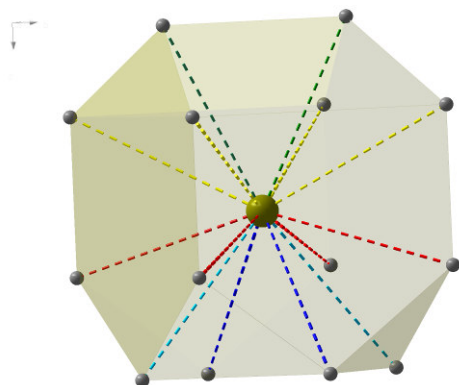| Atom	*U*$_{11}$	*U*$_{22}$	*U*$_{33}$	*U*$_{23}$	*U*$_{13}$	*U*$_{12}$
Ce	5.1(4)	5.1(4)	7.0(4)	0	0	0.17(15)
Ga1	17.8(4)	17.8(4)	9.9(5)	3.3(3)	-3.3(3)	-7.2(3)
Ga2	9.8(5)	9.8(5)	6.9(7)	0	0	0
Ga3	6.3(5)	6.3(5)	6.5(7)	0	0	0
Ga4	6.5(4)	6.5(4)	6.8(5)	0.05(18)	0.05(18)	-0.6(3)
Rh	5.8(4)	5.8(4)	6.3(6)	0	0	0

Fig. 3 The Ce-centered cavity. Equivalent Ce-Ga distances have the same color.
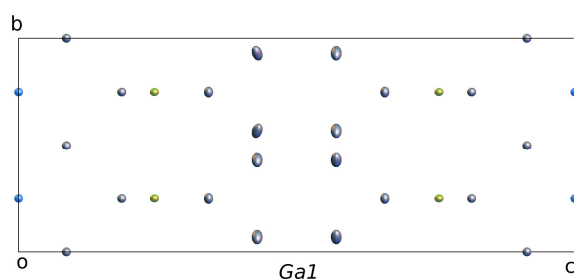

Fig. 4 Representation of the structure with the atoms shown as displacement ellipsoids, revealing the elongated ellipsoids of Ga1.

These are too long to be considered for bonding when compared to the expected interatomic distance of 2.90 Å, determined by the sum of the Ce (1.65 Å) and Ga (1.25 Å) covalent radii [5]. Thus, the Ce-Ga distances may represent weak bonding interactions, as in Ce$_2$PdGa$_{12}$. The Ce-Ga interatomic distances are also in good agreement with other binary and ternary Ce-Ga compounds of various compositions [5,12,15-17].

Between the Ce-centered cavities, segments are found that contain only Ga atoms. In these regions the shortest Ga1-Ga1 distances are 2.532(2) Å, which is close to the bonding distance of 2.5 Å obtained by summing the Ga covalent radii and in agreement with the distances found in the isostructural Ce$_2$PdGa$_{12}$ analog.

As shown in Fig. 4, the anisotropic displacement ellipsoid of one of the Ga atoms (Ga1) is elongated, indicating possible disorder. This is discussed by Cho *et al.* [12], who found the same behavior in La$_2$NiGa$_{12}$ and Ce$_2$NiGa$_{12}$ and attributed it to possible statistical disorder. However, our data, collected on a twinned crystal, do not allow drawing any conclusions on this subject.

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