

Structural Chemistry and Magnetic Properties of Ternary Germanides $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$

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New compounds $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$ as part of an extended solid-solution range of $\text{Ce}_3\text{Rh}_{4-x}\text{Ir}_x\text{Ge}_4$ have been synthesized by the arc melting technique starting from the pure elements. The crystal structures of $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$ have been refined from single crystal counter data. Both compounds were found to be isotypic with the $\text{U}_3\text{Ni}_4\text{Si}_4$ -type (space group $\text{Immm}-D_{2h}^{14}$, No. 71; $Z = 2$). The following lattice parameters were obtained: $a = 0.40915(5)$, $b = 0.42400(19)$, $c = 2.50673(82)$ nm for $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $a = 0.40839(7)$, $b = 0.42437(6)$, $c = 2.50403(39)$ nm for isotypic $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$. For 721 (495) reflections ($|F_o| > 3\sigma$) the obtained reliability factors $R = \sum |\Delta F| / \sum F_o$ were $R = 0.08$ for $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $R = 0.07$ for $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$. According to the topochemical description $2\text{Ce}(\text{Rh}_{0.5}\text{Ge}_{0.5})_2 + \text{CeRh}_2\text{Ge}_2 = \text{Ce}_3\text{Rh}_4\text{Ge}_4$ the structure type of $\text{U}_3\text{Ni}_4\text{Si}_4$ is a combination of structural units of the AlB_2 -type and of the BaAl_4 -type (ThCr_2Si_2 -type) with a complete statistical distribution of the Rh and Ir atoms. Both compounds, $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$, have been investigated at low temperatures by means of dc electrical resistivity and magnetic susceptibility measurements. No magnetic ordering has been detected above 2 K. © 1990 Academic Press, Inc.

1. Introduction

Recently we reported on the structural chemistry and the magnetic and electrical as well as thermochemical properties of the equiatomic compounds CeMGe , with $M = \text{Rh}$ or Ir (1). Investigation of the complete solid-solution $\text{CeRh}_{1-x}\text{Ir}_x\text{Ge}$ revealed an interesting valence transition of cerium around $x = 0.25$ (2). When preparing larger quantities of these materials (ca. 10 g) by arc melting, a few well-crystallized platelets of a secondary impurity phase were found in the vaults of the reguli of the CeRhGe - and the $\text{CeRh}_{0.75}\text{Ir}_{0.25}\text{Ge}$ -alloys. Structural analysis in combination with a magnetochemical characterization of these new phases finally became the subject of the present paper.

2. Experimental

Alloys with a nominal composition $\text{Ce}_3\text{Rh}_{4-x}\text{Ir}_x\text{Ge}_4$, $x = 0, 1, 2, 4$, each weighing ca. 1 g, were prepared by arc melting the elements together on a water-cooled copper hearth, using a nonconsumable tungsten electrode in a protective Ti/Zr-gettered high purity argon atmosphere. 3N-Ce (Auer Remy, Hamburg, FRG) and 5N-Ge (Alfa Ventron, Karlsruhe, FRG) were in the form of ingots, whereas Rh, Ir (99.9% purity, Johnson & Matthey, UK) were in powder form, which prior to melting was compacted into small tablets. Weight losses were checked to be less than 1 wt%. A part of each alloy was wrapped in Mo-foil, sealed in evacuated silica tubes, annealed at 1000°C

for 300 hr, and quenched in water. From X-ray powder analysis, sample preparation and heat treatment proved sufficient to obtain homogeneous products. Precise lattice parameters and standard deviations were obtained by a least-squares refinement of room temperature Guinier–Huber X-ray powder data, using monochromatized $\text{Cu-K}\alpha_1$ -radiation with an internal standard of 99.9999% pure Ge ($a_{\text{Ge}} = 0.5657906$ nm).

Single crystals of $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$ were in the form of thin platelets and were obtained as secondary phases crystallizing in the vaults of arc-melted 10-g alloys with nominal compositions CeRhGe and $\text{CeRh}_{0.75}\text{Ir}_{0.25}\text{Ge}$, respectively. X-ray intensity data were collected on an automatic STOE four circle diffractometer in one hemisphere of the reciprocal space out to a limit of $\sin \theta/\lambda = 8 \text{ nm}^{-1}$ using monochromatized $\text{MoK}\alpha$ radiation. Sets of 834 (598)

symmetry-independent reflections were obtained for $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$ respectively by averaging symmetry-equivalent reflections out of a total number of 2988 (1488) recorded intensities; all observed intensities ($721(495)$ for $|F_o| > 3\sigma(F_o)$) were used in the structure refinement. An empirical absorption correction was applied using ψ -scans of three independent reflections.

Magnetization measurements were carried out between 2 and 300 K using both a Faraday microbalance and a SQUID magnetometer. Electrical resistivity was determined by means of a conventional four-probe dc technique.

3. Structure Determination

Laue and Weissenberg photographs of the two crystal specimens (axes [001] and [100]) were essentially consistent in displaying iso-

TABLE I
CRYSTALLOGRAPHIC DATA FOR $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ AND $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$ ($\text{U}_3\text{Ni}_4\text{Si}_4$ -TYPE) SPACE GROUP Imm-D_{2h}^{25} ,
No. 71; $Z = 2$

Atom	Site	x	y	z	Occ.	U_{11}	U_{22}	U_{33}
$\text{Ce}_3\text{Rh}_4\text{Ge}_4^a$								
Ce1	2a	0	0	0	1.0	2.10(5)	1.74(5)	2.92(8)
Ce2	4j	$\frac{1}{2}$	0	0.3545(0)	1.0	2.17(4)	1.95(4)	1.64(5)
Rh1	4j	$\frac{1}{2}$	0	0.0992(1)	0.98(1)	7.90(14)	1.86(6)	1.52(7)
Rh2	4i	0	0	0.2506(1)	1.0	1.95(5)	1.64(4)	1.57(6)
Ge1	4j	$\frac{1}{2}$	0	0.1969(1)	1.0	2.18(7)	1.72(6)	1.42(8)
Ge2	4i	0	0	0.4501(1)	1.0	2.78(8)	1.72(6)	1.50(8)
$\text{Ce}_3\text{Rh}_3\text{IrGe}_4^b$								
Ce1	2a	0	0	0	1.0	1.71(9)	1.45(8)	4.62(17)
Ce2	4j	$\frac{1}{2}$	0	0.3540(1)	1.0	1.87(6)	1.56(6)	1.89(8)
Rh1	4j	$\frac{1}{2}$	0	0.0984(1)	$\left\{ \begin{array}{l} 0.71(2) \\ 0.29(2) \end{array} \right.$	9.36(27)	1.44(7)	1.66(9)
Ir1								
Rh2	4i	0	0	0.2504(1)	$\left\{ \begin{array}{l} 0.74(1) \\ 0.26(1) \end{array} \right.$	1.62(6)	1.23(5)	1.70(7)
Ir2								
Ge1	4j	$\frac{1}{2}$	0	0.1967(1)	1.0	1.72(11)	1.25(9)	1.81(13)
Ge2	4i	0	0	0.4499(1)	1.0	2.60(14)	1.41(10)	1.77(14)

Note. The standard deviations are given in parentheses. The expression for the anisotropic thermal factors is $T = \exp(2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2})10^{-2})$, by symmetry $U_{12} = U_{13} = U_{23} = 0$.

$a = 0.40915(5)$, $b = 0.42400(19)$, $c = 2.50673(82)$ nm, $V = 0.435 \text{ nm}^3$, $\rho_x = 8.52 \text{ Mg m}^{-3}$, $\mu = 34.3 \text{ mm}^{-1}$. $R = 0.085$, $R_w = 0.079$; isotropic secondary extinction $g = 3.0(3) \times 10^{-6}$.

$b = 0.40839(7)$, $b = 0.42437(6)$, $c = 2.50403(39)$ nm; $V = 0.434 \text{ nm}^3$, $\rho_x = 9.20 \text{ Mg m}^{-3}$, $\mu = 47.3 \text{ mm}^{-1}$. $R = 0.069$, $R_w = 0.068$; isotropic secondary extinction $g = 2.9(2) \times 10^{-6}$.

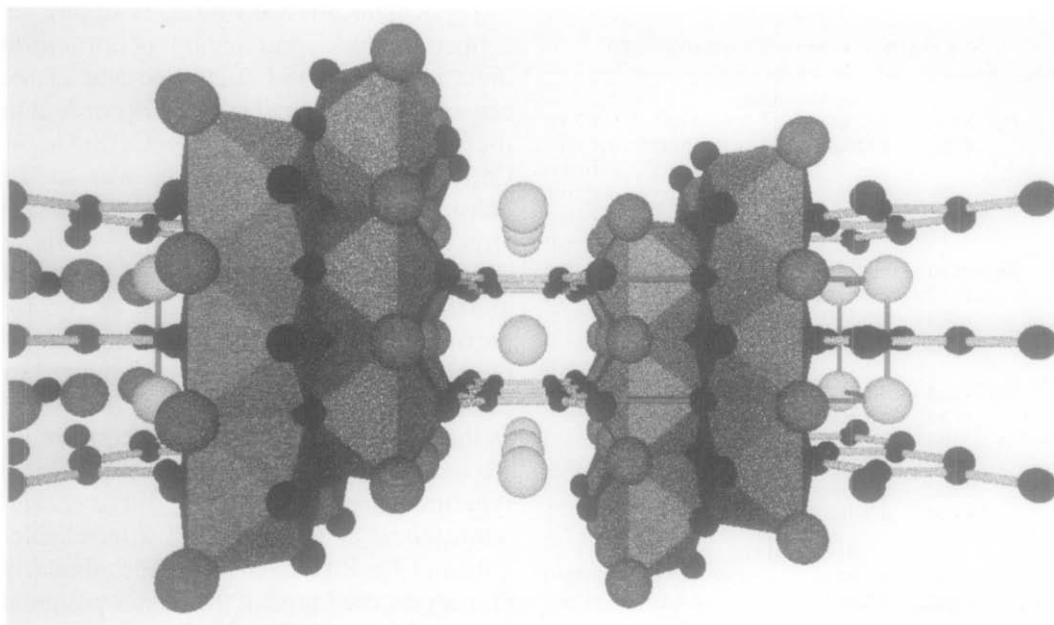


FIG. 1. The crystal structure of $Ce_3Rh_4Ge_4$ in three-dimensional view as seen along a central row of Ce1-atoms parallel [010]. Large atoms are Ce-atoms, medium-sized spheres are Rh-atoms, and small spheres are Ge-atoms (Ge1-atoms are at the centers of the vertical columns of tetrakaidekahedra). The AlB_2 -type layers of (Rh1, Ge2)-atoms are outlined, whereas the tetrakaidekahedral coordination around Ge1-atoms results in vertical columns of (Ce2, Rh2)-atoms edge connected along a puckered Rh2-layer.

typic behavior and revealed an orthorhombic lattice geometry without any superstructure reflections (Table I); the existence of a center of symmetry was indicated from statistical tests. The only observed systematic extinctions were those of a body-centered Bravais lattice compatible with $Immm$ as the centrosymmetric and $Imm2$, $I2_12_12_1$, or $I222$ as the noncentrosymmetric types of space groups. Unit cell dimensions and crystal symmetry indicated a close resemblance to the $La_3Rh_4Ge_4$ -phase (3) with the $U_3Ni_4Si_4$ -type of structure (4). Using the atomic positions of $La_3Rh_4Ge_4$ as starting parameters (3), the crystal structures of $Ce_3Rh_4Ge_4$ and $Ce_3Rh_3IrGe_4$ were both successfully refined employing the STRUCSY full matrix least-squares program system (STOE & CIE, Darmstadt, FRG). The weights used were based upon counting statistics $w_i = 1/(\sigma F_i)^2$, and structure factors were furthermore corrected for isotropic

secondary extinction; different weighting schemes were of no significant influence on the R -values obtained. Similarly, the refinement of the metal atom occupancies did not result in a significant deviation from full occupation. The distribution of Rh and Ir atoms was found to be completely random with no indication of ordering or of preferred arrangement. The final R -values calculated for anisotropic thermal parameters were $R = 0.08$ ($Ce_3Rh_4Ge_4$) and $R = 0.07$ ($Ce_3Rh_3IrGe_4$) respectively, thereby confirming the isotypism with the $U_3Ni_4Si_4$ -type structure. A final electron density difference map was featureless. Positional and thermal parameters are listed in Table I; interatomic distances are shown in Table II and merely reflect the sum of the atom radii. A listing of $|F_o|$ and $|F_c|$ data is available on request.

From the final refinement of the occupancies of the Rh/Ir-sites there is some indication of a composition slightly richer in Ir

TABLE II
INTERATOMIC DISTANCES UP TO 0.4 nm

(A) $Ce_3Rh_4Ge_4$			
Ce1-4 Rh1	0.3226(1)	Ce2-4 Rh1	0.3172(0)
-8 Ge2	0.3206(0)	-2 Rh2	0.3318(1)
		-2 Rh2	0.3389(1)
		-4 Ge1	0.3221(0)
		-1 Ge1	0.3960(2)
		-2 Ge2	0.3158(1)
Rh1-2 Ce1	0.3226(1)	Rh2-2 Ce2	0.3318(1)
-4 Ce2	0.3172(0)	-2 Ce2	0.3389(1)
-1 Ge1	0.2457(2)	-4 Rh2	0.2951(0)
-2 Ge2	0.2458(1)	-2 Ge1	0.2453(1)
		-2 Ge1	0.2499(1)
Ge1-4 Ce2	0.3221(0)	Ge2-4 Ce1	0.3206(0)
-1 Ce2	0.3960(2)	-2 Ce2	0.3158(1)
-1 Rh1	0.2457(2)	-2 Rh1	0.2458(1)
-2 Rh2	0.2453(1)	-1 Ge2	0.2510(4)
-2 Rh2	0.2499(1)		
-4 Ge1	0.3978(2)		
(B) $Ce_3Rh_3IrGe_4$			
Ce1-4 Rh1	0.3212(1)	Ce2-4 Rh1	0.3184(1)
-8 Ge2	0.3208(1)	-4 Rh2	0.3312(2)
		-2 Rh2	0.3375(2)
		-4 Ge1	0.3214(1)
		-2 Ge2	0.3164(2)
Rh1/Ir1-2 Ce1	0.3212(1)	Rh2/Ir2-2 Ce2	0.3312(2)
-4 Ce2	0.3184(1)	-2 Ce2	0.3375(2)
-2 Ge2	0.2446(2)	-4 Rh2	0.2951(0)
-1 Ge1	0.2468(4)	-2 Ge1	0.2505(2)
		-2 Ge1	0.2455(2)
Ge1-4 Ce2	0.3214(1)	Ge2-4 Ce1	0.3208(1)
-1 Ce2	0.3953(3)	-2 Ce2	0.3164(2)
-1 Rh1	0.2468(4)	-2 Rh1	0.2446(2)
-2 Rh2	0.2455(2)	-1 Ge2	0.2516(6)
-2 Rh2	0.2505(2)		

($Ce_3Rh_{2.92}Ir_{1.08}Ge_4$) than the nominal $Ce_3Rh_3IrGe_4$. Figure 1 is a representation of the crystal structure of $Ce_3Rh_4Ge_4$ in three-dimensional view.

4. Structural Chemistry

$Ce_3Rh_4Ge_4$ and $Ce_3Rh_3IrGe_4$ are new representatives of the $U_3Ni_4Si_4$ -type structure (4), which in the course of this investigation was found to be unstable for hypothetical " $Ce_3Ir_4Ge_4$ " despite only marginal differences between the Rh and the Ir atoms in size and electrochemical factor, suggesting thermodynamic instability due to the Ir-rich equilibrium phases.

Topochemically $Ce_3Rh_4Ge_4$ is simply described by the combination of structural units of the ordered AlB_2 -type and of the ordered $BaAl_4$ -type ($ThCr_2Si_2$) according to the relation $2Ce(Rh_{0.5}Ge_{0.5})_2 + CeRh_2Ge_2 = Ce_3Rh_4Ge_4$. The $U_3Ni_4Si_4$ -type was earlier considered (5) as one of the members of a structural series, $RE_{n+m}T_{2n}M_{4m}$, where n and m stand for the numbers of the AlB_2 - and the $BaAl_4$ -units (see also Fig. 1). A comparison of rare earth and alkaline earth compounds with $RE(A)_3T_4M_4$ stoichiometry has been given by Parthé and Chabot (6). As far as the interatomic distances are concerned, we note that the Rh(Ir)-atoms in the AlB_2 -type units are surrounded by three germanium atoms at the center of a tetraikaidkahedral $|Ce_6Rh|Ge_3$ -coordination; similarly Ge1-atoms are found at the center points of tetraikaidkahedra $|Ce_4Rh_2Ge|Rh_3$ (see also Fig. 1). The Rh(Ir)-atoms in the $BaAl_4$ -slabs are, however, tetrahedrally coordinated by four Ge-atoms. The tetrahedral coordination of the transition metal by metametals is furthermore a common feature of $Ce_3Rh_2^{[6,p]}Rh_2^{[4,r]}Ge_2^{[6,p]}Ge_2$ and the $TiNiSi$ - or the $CeCu_2$ -type phase $CeRh^{[4,r]}Ge$ or $Pr(Pt_{0.5}Ge_{0.5})_2$.

5. Magnetic and Electrical Properties

Below 300 K, the magnetic susceptibility χ_m of the new germanides follows a non-Curie-Weiss behavior and was analyzed by using the expression (Fig. 2)

$$\chi_m = \chi_0 + C_m / (T - \theta_p),$$

where χ_0 is the temperature-independent susceptibility arising from Pauli paramagnetism of the conduction electrons, the orbital and the diamagnetic term; C_m is the Curie constant per formula unit; and θ_p is the paramagnetic Curie temperature. The values of χ_0 , C_m , and θ_p , listed in Table III, were refined between 130 and 300 K by a least-squares method. It is noted that the effective moment per cerium atom decreases with the

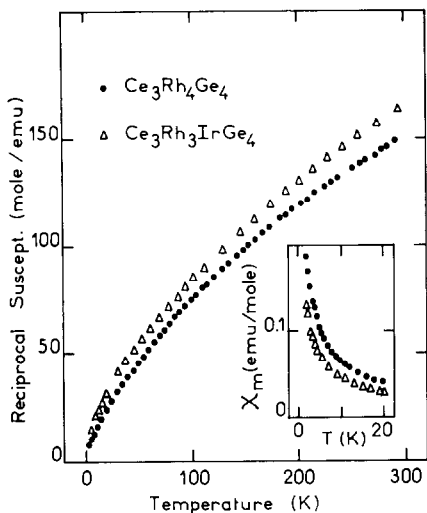


FIG. 2. Temperature dependence of the reciprocal susceptibility χ_m^{-1} of $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$. (Inset: $\chi_m = f(T)$ for $2 \leq T \leq 20$ K.)

substitution of rhodium by iridium and is much smaller than the free Ce^{3+} -ion value ($2.54 \mu_B$). The non-Curie-Weiss behavior of χ_m can be due to the existence of a large crystal field splitting as, for instance, in CeRh_3B_2 (7). No anomaly indicative of magnetic ordering occurs in the susceptibility of these germanides down to 2 K (Fig. 2).

The temperature dependence of the reduced electrical resistance of $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$ is given in Fig. 3. As the temperature is lowered below 270 K, $R(T)/R(270 \text{ K})$ increases slightly and goes through a broad maximum around 100 and 80 K for $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$, respectively. This temperature behavior of $R(T)$ can be

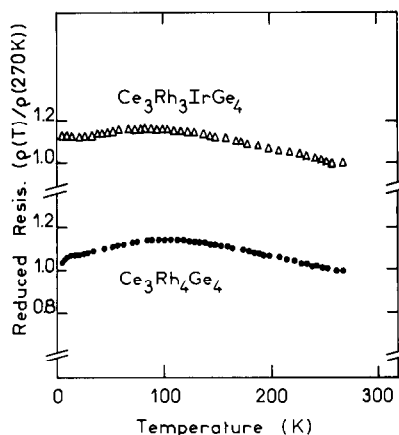


FIG. 3. Temperature dependence of the reduced electrical resistance of $\text{Ce}_3\text{Rh}_4\text{Ge}_4$ and $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$.

ascribed to the effects of crystalline electric fields on the Ce^{3+} -ion. Another maximum near 10 K is observed only for $\text{Ce}_3\text{Rh}_4\text{Ge}_4$; however, as no anomaly occurs in the magnetic susceptibility curve at this temperature, the possibility of a magnetic phase transition must be excluded.

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TABLE III
MAGNETIC DATA OF THE TERNARY GERMANIDES
 CeRh_4Ge_4 AND $\text{Ce}_3\text{Rh}_3\text{IrGe}_4$

Phase	C_m (emu/mole)	μ_{eff} (μ_B/Ce)	θ_p (K)	χ_0 (emu/mole)
$\text{Ce}_3\text{Rh}_4\text{Ge}_4$	2.21	2.43	-90	0.88×10^{-3}
$\text{Ce}_3\text{Rh}_3\text{IrGe}_4$	1.61	2.07	-64	1.56×10^{-3}

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