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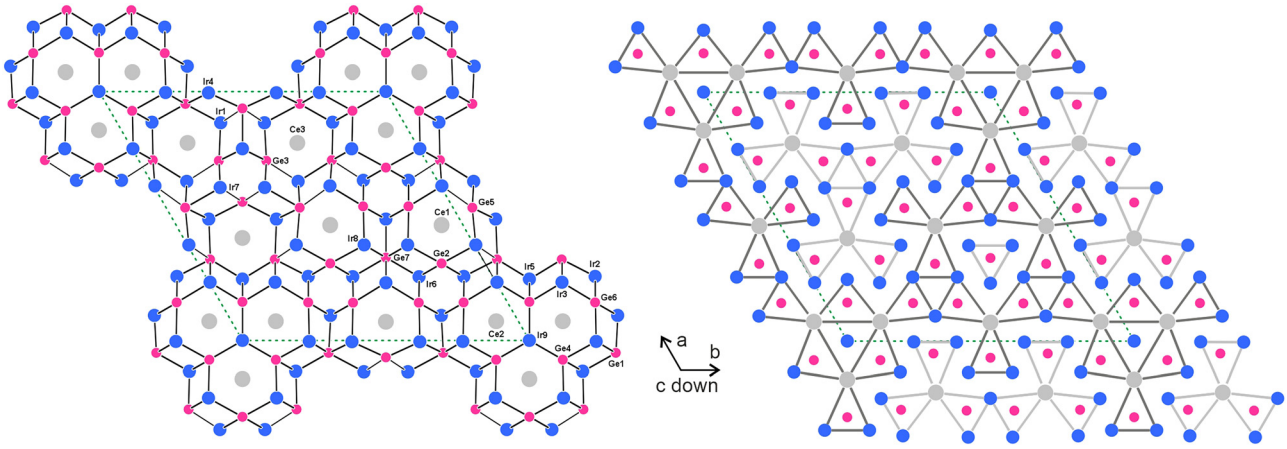
Crystal structure of $Ce_9Ir_{37}Ge_{25}$



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Abstract

$Ce_9Ir_{37}Ge_{25}$, hexagonal, $P\bar{6}m2$ (no. 187), a = 18.3707(16) Å, c = 3.9695(4) Å, and V = 1160.16(18) Å^3, Z = 1, $R_{gt}(F)$ = 0.0315, $wR_{ref}(F^2)$ = 0.0799, T = 293 K.

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Table 1 contains the crystallographic data. The list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

The Figure shows a view of the $Ce_9Ir_{37}Ge_{25}$ structure along the c axis (left). Cerium, iridium and germanium atoms are drawn as medium grey, blue and magenta circles, respectively. The three-dimensional $[Ir_{37}Ge_{25}]$ network is emphasized. The right-hand drawing shows the condensation pattern of the germanium-centered trigonal prisms. The prismatic units drawn in dark (z = 1/2) and light grey (z = 0) are shifted by c/2 with respect to each other.

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Table 1: Data collection and handling.

Crystal:	Needle
Size:	0.4 × 0.2 × 0.1 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	130.1 mm^{-1}
Diffractometer, scan mode:	IPDS Stoe, φ and ω scans
θ_{max}, completeness:	31.5°, 99 %
N $(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23242, 1559, 0.181
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 380
$N(param)_{refined}$:	72
Programs:	Stoe,[1] Superflip[3,4]

1 Source of material

Single crystals of the title compound $Ce_9Ir_{37}Ge_{25}$ were obtained with the bismuth flux technique.[2] Starting materials were cerium pieces (Johnson-Matthey, 99.9 %), iridium powder (Agosi, 99.9 %) and germanium chips (Chempur, 99.9 %). Cerium pieces, iridium powder (cold-pressed to a pellet) and pieces of the germanium chips were weighed in 1:4:3 atomic ratio and arc-melted under purified argon (titanium sponge at T = 873 K, silica gel and molecular sieves). The button was re-melted three times to ensure homogeneity. 500 mg of the product were mixed with 3 g of bismuth (drops, ABCR, 99.9 %) as flux agent and then crushed to a coarse powder in a steel mortar. The reaction mixture was sealed in an evacuated, graphitized (thermal decomposition of acetone) silica ampoule, placed in a muffle furnace and heated to 1300 K at a rate of 500 K h^{-1}. The temperature was kept for 10 days. Then the sample was cooled to room

temperature by switching off the furnace. The bismuth matrix was dissolved in a 1:1 mixture of glacial acetic acid and hydrogen peroxide (35 %) and the product crystals were rinsed with demineralized water. $Ce_9Ir_{37}Ge_{25}$ is air and moisture stable and crystallizes in the form of needles with an aspect ratio of ~5.

2 Experimental details

Needle-shaped $Ce_9Ir_{37}Ge_{25}$ crystals were selected from the flux growth product and glued to quartz fibres using beeswax. The quality of several crystals was tested on a Buerger camera (equipped with a Fujifilm image plate detection system) through Laue photographs. Single crystal X-ray diffraction was performed at room temperature on a Stoe StadiVari diffractometer (Mo microfocus source and a Pilatus detection system). The Gaussian-shaped profile of the microfocus X-ray source of the StadiVari diffractometer required scaling along with a careful numerical absorption correction. The starting atomic parameters were obtained with the charge-flipping algorithm[3] implemented in Superflip[4] and the structure was refined on F^2 with the Jana2020 software package[5] with anisotropic displacement parameters for the cerium and iridium sites and isotropic displacement parameters for the germanium sites. Refinement of the occupancy parameters in separate series of least-squares cycles revealed full occupancy for all sites, confirming the ideal composition $Ce_9Ir_{37}Ge_{25}$ (12.7:52.1:35.2). This is in agreement with an EDX analyses (Zeiss EVO® MA10 scanning electron microscope, CeO_2, Ir and Ge as standards) of the studied crystal: 13 ± 2 at% Ce: 54 ± 2 at% Ir: 33 ± 2 at% Ge. The $Ce_9Ir_{37}Ge_{25}$ structure was refined as an inversion twin with a domain ratio of 0.54(7):0.46. $Yb_9Ir_{37}Ge_{25}$ (a = 18.2528(8) Å, c = 3.9085(2) Å, V = 1127.7 Å^3) is isotypic with $Ce_9Ir_{37}Ge_{25}$.

3 Discussion

$Ce_9Ir_{37}Ge_{25}$ crystallizes with a new structure type, space group $P\bar{6}m2$, Pearson code $hP71$ and Wyckoff sequence $m^3l^3k^5j^6da$.

The iridium and germanium atoms form a three-dimensional $[Ir_{37}Ge_{25}]$ polyanionic network (see Figure, left) in which the three crystallographically independent cerium atoms fill hexagonal prismatic voids. Within the polyanion, the iridium atoms are coordinated to 3–5 germanium atoms with Ir–Ge distances ranging from 239 to 262 pm, comparable to the sum of the covalent radii[6] of 248 pm for Ir + Ge. Similar ranges of Ir–Ge distances were observed for TiNiSi-type CeIrGe (256–275 pm)[7] and $CaBe_2Ge_2$-type $CeIr_2Ge_2$ (244–250 pm).[8] This is indicative of substantial covalent Ir–Ge bonding in $Ce_9Ir_{37}Ge_{25}$.

The $Ce_9Ir_{37}Ge_{25}$ structure contains nine crystallographically independent iridium sites. The Ir9 site is located within a $Ce2_6$ trigonal prism which is capped on the rectangular faces by three Ge4 atoms. Thus, the Ir9 atoms have no iridium neighbors. As expected for an iridium-rich compound, the iridium atoms Ir1–Ir8 in $Ce_9Ir_{37}Ge_{25}$ have between 4 and 6 nearest iridium neighbors at Ir–Ir distances ranging from 275 to 294 pm, comparable to *fcc* iridium (12 × 272 pm Ir–Ir[9]). Similar ranges of Ir–Ir distances have been observed in several iridium-rich phosphides with similar crystal chemistry, e.g., $Lu_3Ir_7P_5$ (271–301 pm Ir–Ir)[10] or $La_5Ir_{19}P_{12}$ (282–296 pm Ir–Ir).[11]

The three crystallographically independent cerium atoms have a hexa-capped hexagonal prismatic coordination. The latter is similar for $Ce1@Ir_{12}Ge_6$ and $Ce3@Ir_{12}Ge_6$. The Ce2 atoms form the trimeric unit around the origin (see Figure). They have two Ce2 neighbors in their coordination shell capping two of the rectangular faces, i. e., $Ce2@Ir_{10}Ge_6Ce_2$. The Ce2 atoms are just closing the coordination shell. There are no bonding Ce–Ce interactions. The shortest Ce–Ce distances correspond to the lattice parameter c (397 pm) and the Ce2–Ce2 distances (427 pm) around the origin are even longer.

The germanium atoms in the $Ce_9Ir_{37}Ge_{25}$ structure all have trigonal prismatic coordination by rare earth and/or iridium atoms. These trigonal prisms are condensed via common edges in *ab* direction forming propeller-like motifs. Prisms drawn in light and dark grey color are shifted by half the translation period c with respect to each other. This way one achieves the capping of the rectangular sides of the trigonal prisms, leading to coordination number 9. The description of the $Ce_9Ir_{37}Ge_{25}$ structure with condensed trigonal prisms is a purely geometrical one, however, it is extremely helpful to classify it within the large family of metal-rich structures. These propeller-like units of trigonal prisms occur in a large number of silicide and phosphide structures.[12,13]

The consequent tri-capped trigonal prismatic coordination of the germanium atoms avoids direct Ge–Ge contacts. The shortest Ge–Ge distances (Ge2–Ge6 of 287 pm, Ge2–Ge2 of 290 pm and Ge3–Ge3 of 304 pm) are significantly longer than the Ge–Ge single bond distance of 245 pm in the element.[9] The Ge2–Ge6 and Ge3–Ge3 distances occur within the triple units of condensed trigonal prisms, which form the empty Ir_6 prisms. This is a kind of geometrical constraint. The same holds true for the Ge2–Ge2 distances.

According to the Pauling electronegativities (Ce: 1.12, Ir: 2.20, Ge: 2.01),[6] the cerium atoms as the less electronegative ones in the $Ce_9Ir_{37}Ge_{25}$ structure essentially have transferred their valence electrons, enabling formation of the covalently bonded $[Ir_{37}Ge_{25}]$ network. In a first approximation, the electron counting can be written as $(Ce_3)^{\delta+}[Ir_{37}Ge_{25}]^{\delta-}$.

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