TaRhGe with TiNiSi-type Structure

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The new germanide TaRhGe was prepared from the elements by arc-melting and subsequent annealing at 1020 K for 10 days. TaRhGe crystallizes with the TiNiSi-type structure, space group *Pnma*, $Z = 4$, *oP*12, $a = 640.2(2)$, $b = 383.2(2)$, $c = 741.7(2)$ pm, $wR2 = 0.0550$, 432 F^2 values, 20 parameters. The structure consists of a three-dimensional [RhGe] network of distorted $RhGe_{4/4}$ tetrahedra with Rh–Ge distances ranging from 244 to 250 pm. The tantalum atoms are coordinated within this network by two folded and mutually tilted Rh_3Ge_3 hexagons. TaRhGe is Pauli-paramagnetic and shows no superconducting transition down to 3 K.

Key words: Tantalum, Germanide, Crystal Structure, Pauli Paramagnetism

Introduction

Equiatomic transition metal (*T*) silicides and germanides *TT′*Si and *TT′*Ge have intensively been studied in the last thirty years since several of these compounds show superconductivity with transition temperatures up to 10 K. Overviews are given in [1 – 4, and references cited therein]. Most of the *TT′*Si and *TT′*Ge compounds crystallize with the orthorhombic TiNiSi-type structure [5]. Herein we present TaRhGe, a new member of this structural family.

Crystals of TaRhGe were first obtained as a by-product during attempts to synthesize lithium-rhodium-germanides and europium-rhodium-germanides in sealed tantalum tubes. Although tantalum tubes are widely used as an inert container material [6], especially for rhodium-containing samples, we repeatedly observed attack of the tubes. After structure analyses of the by-product we synthesized TaRhGe in bulk amounts. The single crystal structure refinement and the magnetic properties of TaRhGe are reported herein.

Experimental Section

Synthesis

Starting materials for the synthesis of TaRhGe were tantalum powder (H. C. Starck), rhodium powder (Heraeus, *ca.* 200 mesh), and germanium lumps (Wacker), all with stated purities better than 99.9 %. Stoichiometric amounts of the three elements were ground and mixed in an agate mortar. The mixture was cold-pressed into a pellet (∅ 6 mm) and subsequently arc-melted [7] under an argon atmosphere of *ca.* 700 mbar. The argon was purified over titanium sponge (870 K), silica gel and molecular sieves. The molten button was remelted three times upside and downside to ensure homogeneity. After the arc-melting the sample was not single-phase. The product button was ground once again, cold-pressed to a pellet and put into a glassy carbon crucible, which was then enclosed in an evacuated silica tube for oxidation protection. The sample was heated to 1020 K for 10 d, resulting in X-ray-pure TaRhGe. Large needle-shaped single crystals exhibit metallic lustre, while the ground powder is dark grey. TaRhGe is stable in air.

EDX data

The TaRhGe single crystal investigated on the diffractometer was analyzed using a LEICA 420 I scanning electron microscope with elemental Ta, Rh, and Ge as standards. No impurity elements heavier than sodium (detection limit of the instrument) were observed. The Ta : Rh : Ge ratio determined semiquantitatively by EDX was in good agreement with the equiatomic composition. A scanning electron micrograph of a selected crystal is shown in Fig. 1.

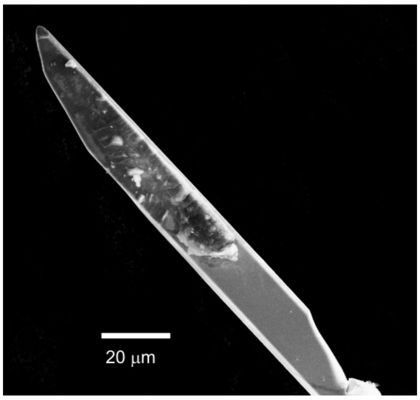

Fig. 1. SEM image of a selected TaRhGe single crystal.

X-Ray powder and single crystal diffraction

The polycrystalline TaRhGe sample was characterized by a Guinier pattern (imaging plate detector, Fujifilm BAS-

Table 1. Crystal data and structure refinement for TaRhGe.

Empirical formula	TaRhGe
Formula weight, g mol^{-1}	356.45
Space group	*Pnma*
Lattice parameters (powder data)	
a, pm	640.2(2)
b, pm	383.2(2)
c, pm	741.7(2)
Cell volume V, nm^3	0.1820
Formula units per cell Z	4
Crystal size, μm^3	$18 \times 18 \times 120$
Calculated density, g cm^{-3}	13.01
$F(000)$, e	600
Radiation; λ, pm	MoK_α; 71.073
Detector distance, mm	60
Exposure time, min	5
ω range; increment, deg	0 – 180, 1.0
Integration parameters A, B, EMS	14.0, 4.0, 0.026
Absorption coefficient μ, mm^{-1}	84.8
Transmission ratio (max / min)	0.166 / 0.079
θ range for data collection, deg	4 – 35
Range in *hkl*	±10, ±6, ±11
Total no. of reflections	2499
Independent reflections / R_int	432 / 0.0706
Reflections with $I \geq 2\,\sigma(I)$ / R_sigma	329 / 0.0605
Data / parameters	432 / 20
Final $R1$ / $wR2$ indices [$I \geq 2\sigma(I)$]	0.0270 / 0.0531
$R1$ / $wR2$ indices (all data)	0.0419 / 0.0550
Goodness-of-fit on F^2	0.916
Extinction coefficient	0.0166(9)
Largest diff. peak / hole, e Å^{-3}	3.76 / −3.98

1800) with Cu$K_{\alpha1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. The correct indexing was ensured through an intensity calculation [8], taking the positions obtained from the structure refinement. The lattice parameters (Table 1) were refined by least-squares calculations. The powder data are in good agreement with those determined from single crystal data (a = 641.0(1), b = 383.21(8), c = 740.6(1) pm).

Needle-shaped single crystals of TaRhGe were isolated from the annealed pellet by mechanical fragmentation, glued to quartz fibres using bees wax and then investigated *via* Laue photographs on a Buerger camera (white Mo radiation) in order to check their quality. Intensity data of a suitable crystal were collected with graphite-monochromatized MoK_α radiation on an IPDS-II diffractometer in oscillation mode. A numerical absorption correction was applied to the data set. All relevant crystallographic data for the data collection and evaluation are listed in Table 1.

Structure refinement

Isotypy of TaRhGe with the orthorhombic TiNiSi type was already evident from the Guinier powder pattern. In parallel, examination of the data set showed a primitive orthorhombic lattice, and the systematic extinctions were compatible with space group *Pnma*, similar to our previous work on TaIrSi [4] and NbPdSi [9]. The atomic parameters of TaIrSi [4] were taken as starting values, and the structure was refined using SHELXL-97 [10] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. As a check for the correct composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within one standard deviation. In the final cycles the ideal occupancy parameters were assumed again. The final difference Fourier synthesis was flat (Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3. Further details on the structure refinement are available.

Table 2. Atomic coordinates and isotropic displacement parameters (pm^2) for TaRhGe. U_eq is defined as one third of the trace of the orthogonalized U_ij tensor.

Atom	W.-position	x	y	z	U_eq
Ta	4c	0.97234(7)	1/4	0.67848(8)	18(2)
Rh	4c	0.35549(15)	1/4	0.43716(16)	12(3)
Ge	4c	0.74013(19)	1/4	0.3765(2)	18(3)

Table 3. Interatomic distances (pm) for TaRhGe (calculated with the powder lattice parameters; standard deviations are all equal or smaller than 0.2 pm). All distances of the first coordination spheres are listed.

Ta:	1	Ge	268.8	Rh:	2	Ge	244.0
	2	Ge	268.8		1	Ge	244.1
	2	Ge	277.1		1	Ge	250.3
	2	Rh	292.7		2	Rh	282.2
	1	Rh	294.7		2	Ta	292.7
	2	Rh	296.8		1	Ta	294.7
	1	Rh	303.7		2	Ta	296.8
	2	Ta	328.7		1	Ta	303.7
	2	Ta	337.2	Ge:	2	Rh	244.0
					1	Rh	244.1
					1	Rh	250.3
					2	Ta	268.8
					1	Ta	268.8
					2	Ta	277.1

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421092.

Magnetic susceptibility measurements

34.096 mg of the TaRhGe sample were packed in kapton foil and attached to the sample holder rod of a VSM for measuring the magnetic properties in a Quantum Design Physical-Property-Measurement-System in the temperature range 3 – 300 K with magnetic flux densities up to 10 kOe.

Discussion

Crystal chemistry

The germanide TaRhGe crystallizes with the orthorhombic TiNiSi-type structure. A view of the structure approximately along the crystallographic *y* axis is presented in Fig. 2. Chemically closely related and isotructural compounds are TaRhSi [3] and NbRhGe [1]. Also $TaRh_2$ (a = 545.4, b = 402.7, c = 817.9 pm [11]) is isopointal with TaRhGe. If each other rhodium position in $TaRh_2$ is replaced by germanium we obtain the equiatomic compound. The differences in the chemical potential of rhodium and germanium leads to substantial differences in chemical bonding which is directly expressed in the course of the lattice parameters (a = 640.2(2), b = 383.2(2), c = 741.7(2) pm for TaRhGe).

The shortest distances in TaRhGe occur between the rhodium and germanium atoms (244 – 250 pm). These distances compare well with the sum of the covalent radii of 247 pm [12]. We can therefore assume substantial covalent Rh–Ge bonding within the three-dimensional [RhGe] network. This change from Rh–Rh bonding in $TaRh_2$ to Rh–Ge bonding in TaRhGe requires geometrical constraints for the distorted $RhGe_{4/4}$ tetrahedra and thus enforces strong shifts in the lattice parameters, although the cell volumes of both phases are almost equal.

Due to the strong tilting of the Rh_3Ge_3 hexagons Rh–Ge interlayer bonding occurs, leading to Rh_2Ge_2 rhombs in which the more electronegative germanium atoms take the position with maximum distance. This bonding pattern is observed in all transition metal compounds with TiNiSi structure [13]. In contrast, the rhodium atoms move towards each other to reach Rh–Rh distances of 282 pm, only slightly longer than in *fcc* rhodium (269 pm) [14]. Therefore at least weak Rh–Rh interactions can be assumed.

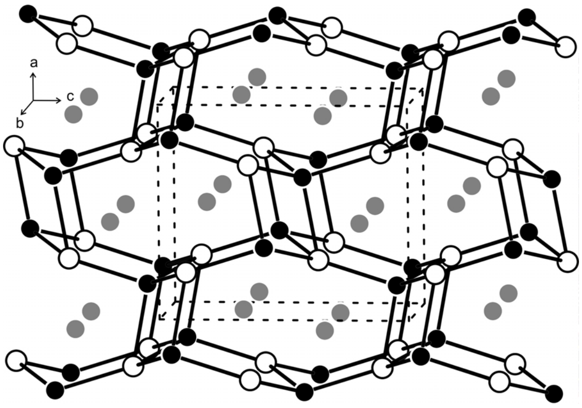

Fig. 2. View of the TaRhGe structure approximately along the crystallographic *y* axis. Tantalum, rhodium, and germanium atoms are drawn as medium grey, black filled, and open circles, respectively. The three-dimensional [RhGe] network is emphasized.

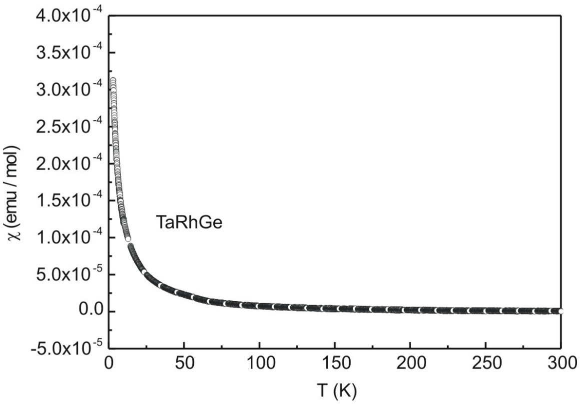

Fig. 3. Temperature dependence of the magnetic susceptibility of TaRhGe measured at an applied field of 10 kOe.

The Ta–Ge (269 – 277 pm) and Ta–Rh (293 – 304 pm) distances are all longer than the sums of the covalent radii of 256 pm for Ta + Ge and 259 pm for Ta + Rh [12]. The tantalum atoms have four close tantalum neighbors at 329 and 337 pm. In comparison with *bcc* tantalum (8 × 286 and 6 × 330 pm) [14], these Ta–Ta distances compare well with the second coordination sphere in the element, implying weak Ta–Ta bonding.

Magnetic data

The temperature dependence of the magetic susceptibility of TaRhGe measured at a magnetic flux density of 10 kOe is presented in Fig. 3. Down to about 100 K the susceptibility is almost independent of temperature with a value of 1.2×10^{-6} emu mol^{-1} at r. t., classifying TaRhGe as a Pauli paramagnet, similar to TaIrSi, NbIrSi [4], NbPtSi, NbRhSi, and TaRhSi [3]. The slight increase of the susceptibility below 100 K can be attributed to trace amounts of paramagnetic impurities (Curie tail). Measurement of the susceptibility at a much lower external field of 100 Oe gave no hint for superconductivity down to 3 K.

Acknowledgements

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