Platinum-Germanium Ordering in the Germanides *RE*PtGe with the Heavy Rare Earth Elements

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The equiatomic germanides *RE*PtGe with the heavy rare earth elements (*RE*) have been reinvestigated with respect to platinum-germanium ordering. The compounds were prepared by arc-melting of the elements followed by annealing for two weeks at 1070 K. The *RE*PtGe germanides crystallize with the TiNiSi-type structure, space group *Pnma*. The structures of ErPtGe (a = 692.01(5), b = 432.03(4), c = 753.19(5) pm, $wR2$ = 0.0523, 435 F^2, 20 variables) and the new germanide LuPtGe (a = 683.1(1), b = 429.2(1), c = 750.3(1) pm, $wR2$ = 0.0696, 358 F^2, 20 variables) have been refined from single crystal diffractometer data. These structures exhibit three-dimensional [PtGe] networks with strong Pt–Ge intra- (251 – 255 pm in LuPtGe) and weaker interlayer (272 pm in LuPtGe) interactions. The crystal chemical peculiarities of the whole *RE*PtGe series are briefly discussed.

Key words: Intermetallics, Rare Earth, Germanides

Introduction

The equiatomic rare earth (*RE*) based germanides *RE*PtGe [1 – 25] are known for all rare earth elements, however, they crystallize with different structure types. LaPtGe [1] adopts the tetragonal LaPtSi-type structure, a ternary ordered version of α-$ThSi_2$. The platinum atoms in LaPtGe have slightly distorted trigonal-planar germanium coordination. LaPtGe becomes superconducting below 3.4 K [2]. $PtGe_{3/3}$ units also occur in the structure of EuPtGe [10, 13] with LaIrSi-type structure (an ordering variant of $SrSi_2$). Due to the stability of the oxidation state +II of the europium atoms, EuPtGe has the largest volume per formula unit in the *RE*PtGe series.

Based on X-ray powder data, Hovestreydt *et al.* [1] ascribed the *RE*PtGe germanides with *RE* = Sc, Y, Sm, Gd–Tm to the TiNiSi-type structure, while the KHg_2 type with a statistical distribution of platinum and germanium was reported for CePtGe, PrPtGe and NdPtGe. Later on, Hovestreydt predicted the TiNiSi type for the germanides YbPtGe and LuPtGe, based on a three-dimensional structure-stability diagram [4]. Recent single crystal studies indeed revealed the TiNiSi type for YbPtGe [25]. Reinvestigation of the CePtGe PrPtGe, and NdPtGe structures, however, showed ordering of the platinum and germanium atoms within a YPdSi-type superstructure [18]. SmPtGe is dimorphic with a YPdSi-type low- and a TiNiSi-type high-temperature modification.

The *RE*PtGe germanides with the heavier rare earth elements have repeatedly been studied with respect to their magnetic properties and their magnetic structures [11, 12, 15 – 17, 20, 21]. However, all these studies were performed on polycrystalline samples *via* powder diffraction. In the course of our systematic studies on AlB_2-related superstructures [26] and in order to complete the crystal chemical studies on the *RE*PtGe germanides we became interested in the precise platinum-germanium ordering in the remaining phases with the smaller rare earth elements including scandium and yttrium. Herein we report on single crystal data of ErPtGe and the new germanide LuPtGe.

Experimental Section

Synthesis

Starting materials for the synthesis of ErPtGe and LuPtGe were ingots of erbium and lutetium (Johnson Matthey and smart elements), platinum powder (Heraeus, *ca.* 200 mesh), and germanium lumps (Wacker), all with stated purities better than 99.9 %. Pieces of erbium and lutetium were first arc-melted [27] to small buttons under an argon atmosphere. The argon was purified before with molecular sieves, sil-

Table 1. Lattice parameters of the ternary germanides *RE*PtGe with the smaller rare earth elements.

Compound	*a* (pm)	*b* (pm)	*c* (pm)	*V* (nm^3)	Reference
ScPtGe	658.5(1)	421.5(1)	741.4(1)	0.2058	[1]
YPtGe	698.6(1)	433.8(1)	755.7(2)	0.2290	[1]
GdPtGe	707.1(1)	437.0(1)	757.1(3)	0.2339	[1]
TbPtGe	702.0(1)	435.4(1)	756.4(2)	0.2312	[1]
TbPtGe	697.8(2)	432.5(1)	754.6(2)	0.2277	[21]
DyPtGe	698.3(2)	434.0(1)	755.4(3)	0.2289	[1]
DyPtGe	699.8(11)	435.9(6)	755.7(11)	0.2305	[21]
HoPtGe	694.9(1)	432.8(1)	753.5(1)	0.2266	[1]
HoPtGe	695.1(3)	432.5(4)	752.9(5)	0.2263	[15]
ErPtGe	692.01(5)	432.03(4)	753.19(5)	0.2252	This work
ErPtGe	691.7(1)	431.9(1)	752.7(1)	0.2249	[1]
ErPtGe	691.1(5)	432.7(3)	753.0(6)	0.2251	[17]
TmPtGe	688.0(1)	430.6(1)	751.7(1)	0.2227	[1]
YbPtGe	686.32(9)	430.47(9)	751.02(8)	0.2219	[25]
YbPtGe	689.7	432.5	754.2	0.2250	[11]
YbPtGe	689.7(2)	432.5(1)	754.2(2)	0.2250	[19]
LuPtGe	683.1(1)	429.2(1)	750.3(2)	0.2200	This work

ica gel, and titanium sponge (900 K). Subsequently the erbium (lutetium) buttons, cold-pressed pellets (∅ 6 mm) of platinum powder and pieces of the germanium lumps were weighed in the ideal 1 : 1 : 1 atomic ratios and reacted in the same arc-melting furnace. The product pellets were remelted three times to ensure homogeneity. The total weight losses after the various meltings were smaller than 0.5 %. The buttons were subsequently sealed in evacuated silica ampoules and annealed at 1070 K for two weeks in muffle furnaces. Polycrystalline and powdered ErPtGe and LuPtGe are stable in air over years.

EDX data

Semiquantitative EDX analyses on the ErPtGe and LuPtGe crystals investigated on the diffractometers were carried out by use of a Leica 420i scanning electron microscope with ErF_3, LuF_3, platinum, and germanium as standards. The experimentally observed compositions were close to the ideal one. No impurity elements heavier than sodium (detection limit of the instrument) were found.

X-Ray diffraction

ErPtGe and LuPtGe were characterized by Guinier diagrams (imaging plate detector, Fujifilm BAS-1800 readout system) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30 and c = 540.46 pm) as internal standard. The lattice parameters (Table 1) were refined by a least-squares routine. Accurate indexing was ensured through intensity calculations [28] taking the atomic positions from the structure refinements.

Small single crystals of ErPtGe and LuPtGe were selected from the crushed annealed samples. Their quality was checked by Laue photographs on a Buerger camera (white Mo radiation). Intensity data of the LuPtGe crystal were collected at r. t. by use of a four-circle diffractometer (CAD4) with graphite-monochromatized MoK_α radiation and a scintillation counter with pulse height discrimination.

Table 2. Crystal data and structure refinement for TiNiSi-type ErPtGe and LuPtGe, space group *Pnma*, Z = 4.

Compound	ErPtGe	LuPtGe
Lattice parameters	Table 1	Table 1
Molar mass, g mol^{-1}	434.94	442.65
Calculated density, g cm^{-3}	12.83	13.37
Absorption coefficient, mm^{-1}	111.7	121.1
Detector distance, mm	80	–
Exposure time, min	20	–
ω range; increment, deg	0 – 180, 1.0	–
Integr. param. A, B, EMS	13.0; 3.0; 0.012	–
F(000), e	712	724
Crystal size, μm^3	20 × 20 × 60	20 × 20 × 60
Transm. ratio (max/min)	3.15	1.86
θ range, deg	4 – 32	4 – 30
Range in *hkl*	±10, ±6, ±11	±9, 0 – 6, ±10
Total no. reflections	2523	1331
Independent reflections / $R_{\rm int}$	435 / 0.1337	358 / 0.0779
Reflections with $I \geq 2\sigma(I)/R_\sigma$	372 / 0.0705	279 / 0.0499
Data / parameters	435 / 20	358 / 20
Goodness-of-fit on F^2	0.935	1.105
$R1/wR2$ for $I \geq 2\sigma(I)$	0.0302 / 0.0501	0.0324 / 0.0634
$R1/wR2$ for all data	0.0396 / 0.0523	0.0500 / 0.0696
Extinction coefficient	0.0031(2)	0.0062(4)
Largest diff. peak / hole, e Å^{-3}	2.52 / −4.12	2.79 / −3.98

The scans were taken in the $\omega/2\theta$ mode, and an empirical absorption correction was applied on the basis of ψ-scan data, accompanied by a spherical absorption correction. The ErPtGe crystal was measured at r. t. by use of a Stoe IPDS-II imaging plate diffractometer in oscillation mode (graphite-monochromatized MoK_α radiation). A numerical absorption correction was applied to the data set. All relevant details concerning the data collections and evaluations are listed in Table 2.

Structure refinements

Although isotypy of ErPtGe and LuPtGe with the TiNiSi type [29], space group *Pnma*, could already be assumed from

Atom	x	z	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
ErPtGe							
Er	0.00231(8)	0.70421(8)	83(2)	91(3)	92(3)	5(2)	89(2)
Pt	0.29561(6)	0.41643(7)	96(2)	81(2)	86(2)	0(2)	88(2)
Ge	0.1914(2)	0.0894(2)	111(5)	66(6)	92(7)	−2(5)	90(3)
LuPtGe							
Lu	0.00203(15)	0.70404(12)	55(4)	93(4)	79(4)	−2(3)	76(3)
Pt	0.29512(14)	0.41631(12)	71(4)	83(4)	67(4)	5(4)	74(3)
Ge	0.1928(4)	0.0899(3)	101(12)	63(9)	57(10)	−7(11)	74(5)

Table 3. Atomic coordinates and anisotropic displacement parameters (pm^2) of ErPtGe and LuPtGe. All atoms lie on Wyckoff positions 4*c* (x, 1/4, z). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{12} = U_{23} = 0$.

Table 4. Interatomic distances (pm), calculated with the powder lattice parameters of ErPtGe and LuPtGe. Standard deviations are all equal or smaller than 0.3 pm. All distances within the first coordination spheres are listed.

		ErPtGe	**LuPtGe**
RE: 1	Pt	297.0	294.4
2	Ge	298.0	296.1
2	Pt	302.9	301.0
1	Ge	308.5	305.4
2	Pt	312.1	308.9
2	Ge	314.8	311.2
1	Ge	318.3	317.5
1	Pt	319.5	318.0
2	*RE*	352.8	348.5
2	*RE*	375.9	373.9
Pt: 2	Ge	252.4	251.2
1	Ge	256.7	254.7
1	Ge	273.9	271.7
1	*RE*	297.0	294.4
2	*RE*	302.9	301.0
2	*RE*	312.1	308.9
1	*RE*	319.5	318.0
Ge: 2	Pt	252.4	251.2
1	Pt	256.7	254.7
1	Pt	273.9	271.7
2	*RE*	298.0	296.1
1	*RE*	308.5	305.4
2	*RE*	314.8	311.2
1	*RE*	318.3	317.5

the Guinier patterns, the data sets were carefully evaluated. Indeed both crystals showed primitive orthorhombic lattices, and the systematic extinctions were compatible with space group *Pnma*. The atomic parameters of isotypic YbPtGe [25] were taken as starting values, and the two structures were refined using SHELXL-97 [30] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. As a check for Pt/Ge mixed sites, the occupancy parameters were refined in separate series of least-squares cycles. Since all sites were fully occupied within two standard deviations, in the final cycles the ideal occupancy parameters were assumed again. The final difference Fourier syntheses were flat (Table 2). The positional parameters and interatomic distances are listed in Tables 3 and 4. Further details on the structure refinements are available.

Further details of the crystal structure investigations 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 numbers CSD-420231 (ErPtGe) and CSD-420232 (LuPtGe).

type \ *RE*	Sc	Y	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
LaPtSi			×														
LaIrSi									×								
TiNiSi	×	×						HT		×	×	×	×	×	×	×	×
YPdSi				×	×	×		LT									

Fig. 1. Structure types for the *RE*PtGe germanides. The low- and high-temperature modifications of SmPtGe are indicated.

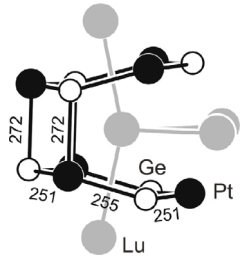

Fig. 2. Coordination of the lutetium atoms in the germanide LuPtGe. Relevant interatomic distances are given (pm). For details see text.

Discussion

By the synthesis and structure determination of the new germanide LuPtGe the series of *RE*PtGe germanides has been completed. Exemplarily, the single crystal data of ErPtGe and LuPtGe and those recently reported for YbPtGe [25] clearly manifest the TiNiSi-type structure for the *RE*PtGe germanides with the smaller rare earth elements, in full agreement with the X-ray powder data originally reported by Hovestreydt *et al.* [1]. The structure predictions [4] for YbPtGe and LuPtGe have also been confirmed. Powder neutron diffraction data had been reported for TbPtGe, DyPtGe [20, 21], and ErPtGe [17], however, the refinements yielded poor resolution for the positional parameters.

So far seven ordered orthorhombic superstructure variants of the KHg_2 type are known, *i. e.* the structure types TiNiSi [29], CaCuGe [31, 32], CaAuSn [32], YPdSi [33], EuAuGe [34], EuAuSn [35], and YbAuSn [36]. Except LaPtGe and EuPtGe, all other *RE*PtGe germanides crystallize with one of these superstructures. The diagram given in Fig. 1 shows the structure types as a function of the rare earth element.

Finally, as an example, we briefly discuss the crystal chemistry of the new germanide LuPtGe. The near-neighbor coordination of the lutetium atoms in LuPtGe is presented in Fig. 2. This Figure shows the close structural relationship with the AlB_2 type. The platinum and germanium atoms build up strongly puckered Pt_3Ge_3 hexagons, two of which coordinate a lutetium atom. The Pt–Ge distances of 251 and 255 pm within the hexagons are close to the sum of the covalent radii of 251 pm [37], indicating strong covalent Pt–Ge bonding. The interlayer Pt–Ge distances of 272 pm are slightly larger. The bonding of the lutetium atoms to the three-dimensional [PtGe] network proceeds *via* one shorter Lu–Pt distance of 294 pm, only slightly longer than the sum of the covalent radii of 285 pm [37]. Each lutetium atom has four nearest lutetium neighbors at 349 and 374 pm. The shorter distances compare well with the average Lu–Lu distance of 347 pm in *hcp* lutetium [38]. For further details on chemical bonding in TiNiSi-type intermetallics we refer to [39, 40].

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