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Structure Refinement of CePtSi and Hydrogenation Behavior of CePdGe, CePtSi and CePtGe

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The intermetallic cerium compounds CePdGe, CePtSi, and CePtGe were synthesized from the elements by arc-melting and subsequent annealing. The structure of CePtSi was refined from single crystal X-ray diffraction data: LaPtSi-type (ordered α -ThSi₂ version), $I4_1md$, $a = 419.6(1)$ and $c = 1450.0(5)$ pm, $wR2 = 0.0490$, 362 F^2 values and 16 variables. The Pt–Si distances within the three-dimensional [PtSi] network are 242 pm, indicating strong Pt–Si interactions. Hydrogenation of the three compounds at 623 K and 4 MPa H₂ gave no indication for hydride formation.

Key words: Cerium Intermetallics, Hydrogenation

Introduction

The equiatomic cerium based intermetallics CeTX ($T =$ late transition metal, $X =$ element of the 3rd, 4th, or 5th main group) display highly interesting magnetic and electrical properties like intermediate valence characteristics, antiferromagnetism, ferromagnetism, Kondo- or heavy fermion-type behavior. The magnetic behavior is mainly determined by the hybridization strength J_{cf} between the cerium $4f$ and the conduction electrons. Thus, the nature of the transition metal T and the X component and the Ce- T / Ce- X coordination considerably influence the J_{cf} exchange parameter. Literature overviews are given in [1–3, and refs. therein].

The magnetic ground state of these CeTX intermetallics can be influenced by (i) application of high temperature and high pressure (HP), leading to new

HP-phases (recent examples are HP-CePdSn [4], HP-CePtSn [5], or HP-CeAuGe [6]), or (ii) hydrogenation [7–11, and refs. therein]. In the family of CeTX silicides and CeTGe germanides the quaternary hydrides CeMnSiH_{1.0}, CeMnGeH_{1.1}, CeNiSiH_{0.8}, CeNiGeH_{1.6}, CeCuSiH_{1.35}, and CeCuGeH_{1.0} have been reported [10, 11]. The unit cell volume changes $\Delta V/V$ upon hydrogenation range from 0.1 % for CeNiSiH_{0.8} to 11.6 % for CeNiGeH_{1.6}. The most interesting hydride in this family is CeNiSiH_{0.8} [8], where an increase of the cerium valence is observed upon hydrogenation, suggesting a higher Kondo effect in CeNiSiH_{0.8} as compared to CeNiSi.

We have now extended our investigations to include the $4d$ and $5d$ transition metals. Herein we report on the hydrogenation behavior of CePdGe [12], CePtSi [13], and CePtGe [14]. The two ternary germanides adopt complicated orthorhombic superstructures of the KHg₂-type [15] with different ordering patterns of the transition metal and germanium atoms. The heavy-fermion compound CePtSi [16] had only been characterized on the basis of X-ray powder data [13, 17]. A single crystal structure refinement is presented in the present work.

Experimental Section

Synthesis

Starting materials for the synthesis of CePdGe, CePtSi, and CePtGe were cerium ingots (Chempur or Johnson Matthey), palladium and platinum powder (Degussa-Hüls, 200 mesh), and silicon and germanium lumps (Wacker), all with stated purities better than 99.9 %. The larger cerium ingots were mechanically cut into smaller pieces under paraffin oil and cleaned with n -hexane. Both the paraffin oil and n -hexane were dried over sodium wire. The small cerium pieces were subsequently arc-melted under an atmosphere of *ca.* 600 mbar argon [18]. The argon was purified before over molecular sieves, silica gel, and titanium sponge (900 K). The pre-melting procedure for the cerium pieces strongly reduces a shattering during the exothermic reaction with palladium or platinum and silicon or germanium. The cerium buttons, cold-pressed pellets of palladium (platinum) (\varnothing 6 mm) and pieces of silicon (germanium) were then mixed in the ideal 1 : 1 : 1 atomic ratio and the samples were synthesized by arc-melting of the mixtures. The samples were then flipped over and remelted up to three times in order to achieve homogeneity. After the arc-melting the samples were sealed in evacuated silica ampoules and inductively

Table 1. Crystal data and structure refinement for CePtSi.

Empirical formula	CePtSi
Molar mass [g mol ⁻¹]	358.29
Unit cell dimensions [pm]	$a = 419.6(1)$
(Guinier data) [pm]	$c = 1450.0(5)$
[nm ³]	$V = 0.2553$
Space group	$I4_1md$
Pearson symbol, Z	tI12, 4
Calculated density [g cm ⁻³]	9.32
Crystal size [μm^3]	$15 \times 20 \times 40$
Transmission ratio (max/min)	1.72
Radiation	AgK α ($\lambda = 0.56086$ pm)
Absorption coefficient	38.2 mm^{-1}
$F(000)$	592
θ range [°]	3 to 28
Range in hkl	$\pm 6, \pm 6, \pm 23$
Total no. reflections	2206
Independent reflections	362 ($R_{\text{int}} = 0.1448$)
Reflections with $I \geq 2\sigma(I)$	259 ($R_{\text{sigma}} = 0.0730$)
Data/parameters	362 / 16
Goodness-of-fit on F^2	0.968
Final R indices [$I \geq 2\sigma(I)$]	$R1 = 0.0353$; $wR2 = 0.0446$
R indices (all data)	$R1 = 0.0678$; $wR2 = 0.0490$
Extinction coefficient	0.0020(3)
BASF	0.13(3)
Largest diff. peak / hole [e \AA^{-3}]	2.38 / -3.03

annealed for 5 h slightly below the melting points in a special water-cooled sample chamber [12]. The light grey polycrystalline, moisture-stable samples were obtained in amounts of 1 g. Single crystals have metallic luster while ground powders are dark grey.

X-Ray diffraction

The samples were studied through Guinier powder patterns (imaging plate technique, Fujifilm BAS-1800) using CuK α_1 radiation and α -quartz ($a = 491.30$ and $c = 540.46$ pm) as an internal standard. The lattice parameters ($a = 2191.4(5)$, $b = 449.2(1)$ and $c = 768.0(2)$ pm for CePdGe, $a = 419.6(1)$ and $c = 1450.0(5)$ pm for CePtSi, and $a = 445.2(1)$, $b = 1467.4(4)$ and $c = 762.5(2)$ pm for CePtGe) were obtained from least-squares fits of the powder data. The correct indexing of the patterns was ensured through intensity calculations [19] taking the atomic positions from the structure refinements. The powder lattice parameters compared well with the previous literature data [12–14]. For CePtSi the powder and the single crystal data ($a = 419.15(7)$ and $c = 1449.8(1)$ pm) agreed well.

Single crystal intensity data were collected at r.t. by use of a four-circle diffractometer (CAD4) with graphite-monochromatized AgK α (56.086 pm) radiation and a scintillation counter with pulse height discrimination. The scans were taken in the $\omega/2\theta$ mode and an empirical absorption correction was applied on the basis of ψ scan data, followed by a spherical absorption correction. All relevant details concerning the data collection are listed in Table 1.

Table 2. Atomic coordinates and isotropic displacement parameters (pm^2) for CePtSi. All atoms lie on Wyckoff sites $4a$. U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
Ce	0	0	0*	75(6)
0.939(15) Pt + 0.061(15) Si	0	0	0.4139(1)	79(4)
0.970(6) Si + 0.030(6) Pt	0	0	0.5807(5)	123(19)

* arbitrarily fixed.

Table 3. Interatomic distances (pm) in CePtSi calculated with the powder lattice parameters. Standard deviations are given in parentheses.

Ce:	2	Pt	317.1(1)	Pt:	2	Si	241.9(6)
	4	Si	319.0(3)		1	Si	242.0(3)
	4	Pt	321.9(1)		2	Ce	317.1(1)
	2	Si	322.9(5)		4	Ce	321.9(1)
	4	Ce	418.8(1)	Si:	2	Pt	241.9(6)
	4	Ce	419.6(1)		1	Pt	242.0(3)
					4	Ce	319.0(3)
					2	Ce	322.9(5)

Structure refinement of CePtSi

Small, irregularly shaped single crystals of CePtSi were isolated from the annealed sample by mechanical fragmentation and examined by use of a Buerger camera equipped with an image plate system (Fujifilm BAS-1800) in order to establish suitability for intensity data collection. The isotopy with the tetragonal LaPtSi-type [13], space group $I4_1md$, was already evident from the powder pattern.

The atomic parameters of LaPtSi [13] were taken as starting values and the structure was refined using SHELXL-97 [20] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all atoms. Refinement of the Flack parameter [21, 22] indicated twinning by inversion (due to the *translationsgleiche* symmetry reduction, see Discussion). In the final cycles the structure was then refined as an inversion twin. The displacement parameters indicated a small mixed Pt/Si occupancy on both the platinum and the silicon site. Both sites were subsequently refined with Pt/Si mixing, resulting in the composition CePt_{0.97(1)}Si_{1.03(1)} for the investigated crystal. A similar effect was also observed for the crystal of the prototype LaPtSi [13]. The final difference Fourier synthesis was flat (Table 1). The positional parameters and interatomic distances of the refinement are listed in Tables 2 and 3. Further details on the structure refinement are available.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (e-mail: crys data@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-417451.

Scanning electron microscopy

The bulk sample of CePtSi and the single crystal investigated on the four-circle diffractometer were analyzed in a LEICA 420 I scanning electron microscope equipped with an OXFORD EDX analyzer. Since the crystal was mounted by beeswax on a glass fibre, it was first coated with a carbon film. CeO₂, Pt, and SiO₂ were used as standards for the semi-quantitative EDX measurements. The analyses were in good agreement with the equiatomic composition and no impurity elements were observed.

Hydrogenation experiments

Hydrogen absorption experiments were performed using the apparatus described previously [23]. In different runs, annealed ingots and powders of CePdGe, CePtSi, and CePtGe were heated under vacuum at 623 K for 12 h and then exposed to 4 MPa of hydrogen gas at the same temperature for two days. The amount of hydrogen absorbed could be determined volumetrically by monitoring pressure changes in a calibrated volume.

Results and Discussion

Crystal chemistry

CePtSi crystallizes with the tetragonal LaPtSi-type structure [13], a ternary ordered version of the α -ThSi₂-type [24]. Due to the ordering of the platinum and silicon atoms, the space group symmetry is reduced from $I4_1/amd$ via a *translationsgleiche* transition to the non-centrosymmetric space group $I4_1md$. Each platinum (silicon) atom has three silicon (platinum) neighbours in slightly distorted trigonal planar coordination with Si–Pt–Si angles differing slightly from 120° and Pt–Si distances of 242 pm, slightly smaller than the sum of the covalent radii (246 pm) [25], indicating strong Pt–Si interactions. Together, the platinum and silicon atoms build up a three-dimensional [PtSi] network (Fig. 1) in which the cerium atoms fill prismatic voids. For further crystal chemical details we refer to the original work on LaPtSi [13].

Hydrogenation behavior

In contrast to CeNiSi which absorbs hydrogen already at 2 MPa and 393 K [8], no reaction was evident

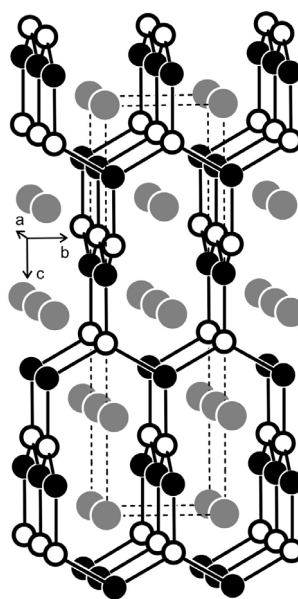


Fig. 1. The crystal structure of CePtSi. The cerium, platinum, silicon atoms are drawn as medium grey, black, open circles, respectively. The three-dimensional [PtSi] network is emphasized.

for CePtSi under similar conditions, even not at 4 MPa and 623 K. Similar behavior was observed for CePdGe and CePtGe. The hydrogenation did not induce a decrepitation of the starting ingots and no volume change of the initial hydrogen content was observed. The lattice parameters determined for the hydrogenated samples ($a = 2193(1)$, $b = 449.0(4)$ and $c = 765.6(4)$ pm for CePdGe, $a = 419.92(9)$ and $c = 1449.0(4)$ pm for CePtSi, and $a = 444.7(1)$, $b = 1467.6(4)$ and $c = 761.1(2)$ pm for CePtGe) were very close to the values of the initial products. So far we can give no structural reason for the strongly differing hydrogenation behavior. Probably, for the platinum metal containing compounds much higher temperature and hydrogen pressure are required for hydrogenation to occur, similar to the observations for many alkali metal-platinum metal-hydrides [26, 27].

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