Crystal Structure of Eu_2PdSi_3

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Single crystals of Eu_2PdSi_3 were obtained from an arc-melted sample that was further annealed at 1020 K for seven days in a silica tube. The structure of Eu_2PdSi_3 was refined from single crystal X-ray diffractometer data: $P6/mmm$, a = 831.88(12), c = 435.88(9) pm, $wR2$ = 0.1175, 265 F^2 values, and 13 variable parameters. It crystallizes with the U_2RuSi_3 structure, a superstructure of the AlB_2 type. The palladium and silicon atoms form a planar two-dimensional [$PdSi_3$] network. The two crystallographically different europium atoms have hexagonal prismatic coordinations $Eu1Si_{12}$ and $Eu2Pd_4Si_8$. The Pd–Si and Si–Si distances within the [$PdSi_3$] network are 244 and 236 pm, respectively.

Key words: Silicide, Crystal Structure, Solid State Synthesis

Introduction

The AlB_2 structure type allows a variety of different colorings on the boron network. Assuming a given REX_2 (RE = rare earth element; X = element of the 3rd, 4th or 5th main group) compound, it is sometimes possible to substitute some of the X atoms by a T atom (T = transition metal) resulting in ternary intermetallic $RETX$ or RE_2TX_3 compounds. The structures of these compounds are ordered substitution variants of the aristotype AlB_2 and their space groups derive from $P6/mmm$ by symmetry reduction. In a recent review article [1] we discussed 46 structure types which belong to this family of compounds. The space group relations have been discussed according to the Bärnighausen formalism [2, 3].

In many cases, the symmetry reduction leads to two or more crystallographically independent rare earth sites, leading to interesting magnetic properties. This is also the case for the structure types U_2RuSi_3 and Ce_2CoSi_3 ($P6/mmm$) [4 – 6], Er_2RhSi_3 ($P6_3/mmc$) [7, 8], $Ba_4Li_2Si_6$ ($Fddd$) [9], and $Ca_4Ag_2Si_6$ ($Fmmm$) [10] which all have two uranium (Er, Ba, Ca) sites. Although the four structures have the same composition, they exhibit a different puckering and packing of the [TX_3] networks. So far it is not possible to predict which of the four structure types a given RE_2TX_3 compound adopts. The superstructure reflections resulting from the *klassengleiche* symmetry reductions are all very weak and can easily be overlooked in an X-ray powder pattern. Only precise single crystal X-ray data can help to unambiguously determine the correct superstructure.

Also the silicide Eu_2PdSi_3 [11 – 13] belongs to this family of AlB_2 superstructures. So far Eu_2PdSi_3 has only been characterized on the basis of X-ray powder data. Herein we report on the structure refinement based on single crystal diffractometer data.

Experimental Section

Synthesis

Starting materials for the preparation of Eu_2PdSi_3 were europium ingots, palladium powder, and silicon pieces. A polycrystalline Eu_2PdSi_3 sample was obtained by arc-melting of the elements under purified argon as described previously [14]. An excess of 5% europium was used to compensate the loss during the arc-melting process. The arc-molten button was subsequently sealed in an evacuated silica ampoule and annealed at 1020 K for 7 d. Compact pieces of Eu_2PdSi_3 are light gray with metallic luster. The sample is stable in moist air. No decomposition was observed after several months.

X-ray film data and structure refinement

Irregularly shaped single crystals were isolated from the annealed sample by mechanical fragmentation. They were

Table 1. Crystal data and structure refinement for Eu_2PdSi_3.

Empirical formula	Eu_2PdSi_3
Molar mass	494.59 g/mol
Unit cell dimensions	a = 831.88(12) pm
(IPDS data)	c = 435.88(9) pm
	V = 0.2612 nm^3
Space group	$P6/mmm$ (No. 191)
Calculated density	6.29 g/cm^3
Crystal size	$30 \times 40 \times 45\ \mu$m^3
Transm. ratio (max/min)	1.27
Absorption coefficient	27.6 mm^{-1}
θ Range	4° to 35°
Range in hkl	$-11 \le h \le 13$,
	$-13 \le k \le 12$, $-6 \le l \le 7$
Total no. reflections	3834
Independent reflections	265 (R_{int} = 0.0895)
Reflections with $I > 2\sigma(I)$	246 (R_{sigma} = 0.0389)
Data/parameters	265 / 13
Goodness-of-fit on F^2	0.882
Final R indices $[I > 2\sigma(I)]$	$R1$ = 0.0316
	$wR2$ = 0.1127
R Indices (all data)	$R1$ = 0.0354
	$wR2$ = 0.1175
Extinction coefficient	0.0004(11)
Largest diff. peak and hole	2.29 and -1.93 e/Å^3

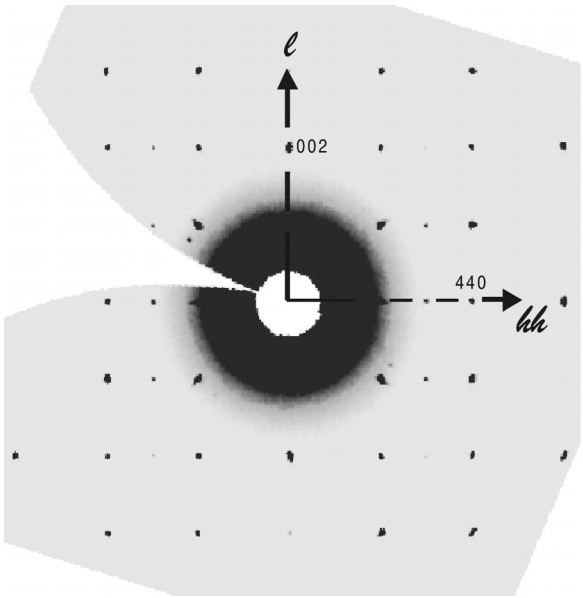

Fig. 1. Reconstructed reciprocal hhl layer of Eu_2PdSi_3. Superstructure reflections are those with h = 2n + 1.

first examined on a Buerger precession camera in order to establish both symmetry and suitability for intensity data collection. Single crystal intensity data were collected at room temperature by use of a Stoe IPDS–II diffractometer with graphite monochromatized Mo-K_α radiation (71.073 pm) at a detector distance of 60 mm, an exposure time of 30 min, and an omega range from 0 to 180° ($\Delta\omega$ = 1°). The integration parameters were A = 14.5, B = 5.0, and EMS = 0.02. A numerical absorption correction was applied to the data. All relevant details concerning the data collection are listed in Table 1.

Careful analyses of the data set showed a pronounced AlB_2 type subcell and weak reflections doubling the a and b axes. The reciprocal layers $hk0$ and $hk1$ showed high Laue

Table 2. Atomic coordinates and anisotropic displacement parameters (pm^2) for Eu_2PdSi_3. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. $U_{13} = U_{23} = 0$.

Atom	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{eq}
Eu1	1a	0	0	0	80(4)	U_{11}	92(5)	40(2)	84(3)
Eu2	3f	1/2	0	0	89(4)	106(4)	109(5)	53(2)	100(3)
Pd	2d	1/3	2/3	1/2	68(4)	U_{11}	120(5)	34(2)	85(3)
Si	6m	0.1638(2)	2x	1/2	86(11)	73(12)	183(18)	37(6)	116(7)

Table 3. Interatomic distances (pm), calculated with the single crystal lattice parameters of Eu_2PdSi_3. All distances within the first coordination sphere are listed (standard deviations in parentheses).

Eu1:	12	Si	321.2(2)	Pd:	3	Si	244.3(3)
	6	Eu2	415.94(6)		6	Eu2	324.30(4)
	2	Eu1	435.88(9)	Si:	2	Si	236.0(3)
Eu2:	4	Pd	324.30(4)		1	Pd	244.3(3)
	8	Si	325.9(1)		2	Eu1	321.2(2)
	4	Eu2	415.94(6)		4	Eu2	325.9(1)
	2	Eu1	415.94(6)				
	2	Eu2	435.88(9)				

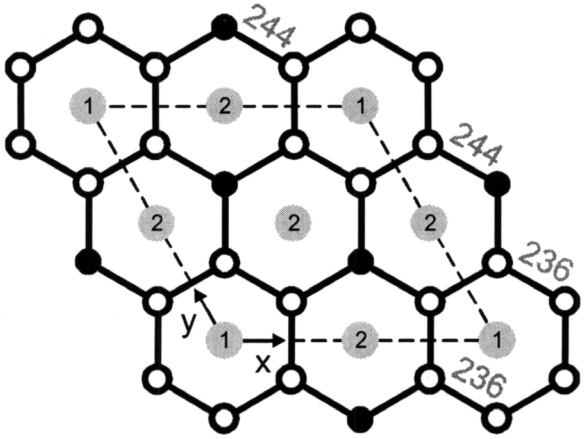

Fig. 2. Projection of the Eu_2PdSi_3 structure onto the ab plane. Large gray, black filled, and medium open circles represent europium, palladium, and silicon, respectively. The two-dimensional $[PdSi_3]$ network at z = 1/2 is emphasized. Some relevant interatomic distances are indicated in units of pm.

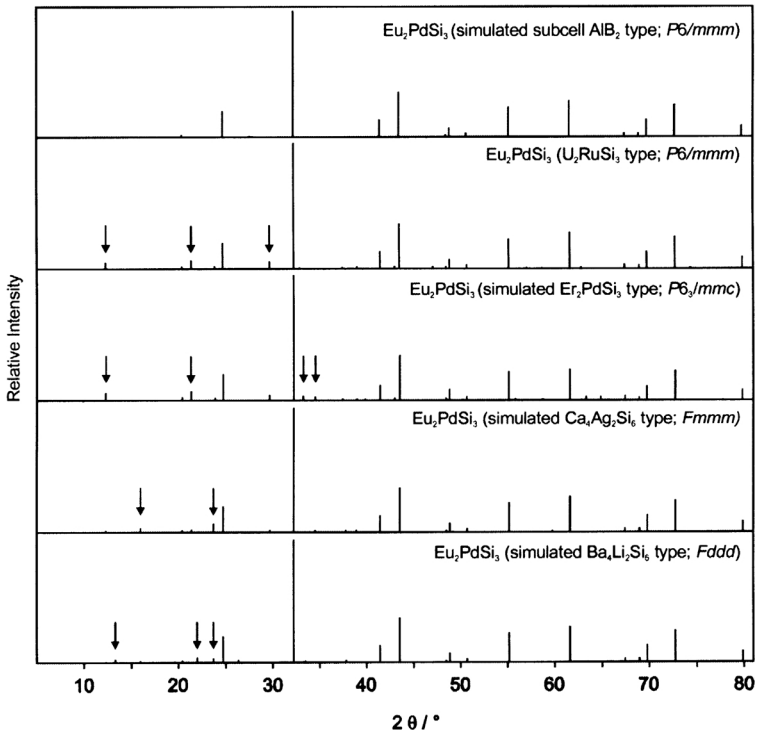

Fig. 3. Calculated powder patterns (Cu-$K_{\alpha 1}$ radiation) for the AlB_2 type subcell and the U_2RuSi_3 type superstructure of Eu_2PdSi_3. The other three diagrams are simulations for a possible Er_2RhSi_3, $Ba_4Li_2Si_6$, or $Ca_4Ag_2Si_6$ type superstructure for Eu_2PdSi_3. The unequivocal superstructure reflections for each superstructure model are marked by arrows. The observed powder pattern of ref. [11] is best matched by the calculation with the U_2RuSi_3 type.

symmetry and no systematic extinctions, compatible with space groups $P6/mmm$, $P6mm$, $P\bar{6}2m$, and $P\bar{6}m2$. The space group with the highest symmetry, $P6/mmm$ was found to be correct during the structure refinements. As mentioned in the introduction, four different structure types are known for the composition RE_2TX_3. We have therefore carefully analysed the reciprocal space. As is evident from the reconstructed *hhl* layer in Fig. 1, no doubling is observed for the *c* lattice parameter. Also no diffuse scattering is observed in this direction as well as in other directions, which would be relevant to a doubling of the *c* axis.

The atomic positions of Ce_2CoSi_3 [6] were taken as starting values and the structure was successfully refined using SHELXL-97 (full-matrix least-squares on F_o^2) [15] with anisotropic atomic displacement parameters for all sites. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. All sites were fully occupied within two standard deviations. A final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The positional parameters and interatomic distances are listed in Tables 2 and 3. Listings of the observed and calculated structure factors are available.*

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), E-mail: crysdata@fiz-karlsruhe.de by quoting the Registry No. CSD-391246.

Although the refinement converged to quite low residuals for all reflections, we prefer to calculate separate residuals for the superstructure reflections [16], since the overall residual is strongly affected by the dominating subcell reflections. For a 1σ cutoff we got a residual of 0.0742 for 182 superstructure reflections accounting for 27% of the total scattered intensity. The 83 subcell reflections yield a *R*1 of 0.0174.

Discussion

A projection of the Eu_2PdSi_3 structure is shown in Fig. 2. The palladium and silicon atoms build a two-dimensional $[PdSi_3]$ network. Within these networks the silicon atoms build discrete Si_6 rings and the palladium atoms have a trigonal-planar silicon coordination at Pd–Si distances of 244 pm, close to the sum of the covalent radii of 246 pm [17]. The structure contains two crystallographically independent europium sites which both have a hexagonal prismatic coordination, Eu1 by 12 silicon atoms and Eu2 by four palladium and eight silicon atoms.

Such a two-dimensional network also occurs in $Ca_4Ag_2Si_6$ [10]. Electron counting in the calcium compound may be written as $(4Ca^{2+})^{8+}(2Ag^{+})^{2+}[Si_6]^{10-}$. According to magnetic suscepti-

bility measurements [11], the europium atoms in Eu_2PdSi_3 are divalent, leading to a formulation $(4Eu^{2+})^{8+}(2Pd^{+})^{2+}[Si_6]^{10-}$ with a formal charge of +1 per palladium atom. The Si–Si distance within the 10π-electron Hückel arenes $[Si_6]^{10-}$ is 236 pm, similar to those in $Ba_4Li_2Si_6$ [9] and $Ca_4Ag_2Si_6$ [10], and elemental silicon [18]. The ionic formula splitting is certainly only a first rough approximation. Besides the strong Si–Si bonding we have to consider also the strong covalent Pd–Si bonds within the network.

The U_{33} displacement parameters of the palladium and silicon atoms are about two times larger than the U_{11} values. This might indicate a tendency for puckering of the $[PdSi_3]$ network as it is realized in the Er_2RhSi_3 structure [7, 8]. The X-ray powder (see below) and single crystal data, however, give no indication for an enlargement of the unit cell along the *c* direction. A similar behavior was recently observed for the $[CoSi_3]$ network in Ce_2CoSi_3 [6]. The displacements of the silicon atoms are much more pronounced in U_2RuSi_3 [4]. Here, the structure was even refined with a split position *x* 2*x z* instead of *x* 2*x* 1/2. However, the X-ray powder and single crystal data and electron diffraction patterns gave also no hint for a unit cell enlargement.

Finally we present calculated X-ray powder patterns (Cu-$K_{\alpha 1}$ radiation) [19] for the AlB_2 type subcell and the U_2RuSi_3 type superstructure of Eu_2PdSi_3 in Fig. 3. The other three diagrams in that Figure are simulations for a possible Er_2RhSi_3, $Ba_4Li_2Si_6$, or $Ca_4Ag_2Si_6$ type superstructure for Eu_2PdSi_3. From the calculated patterns it can be seen that the different superstructures can clearly be distinguished from high quality X-ray powder data. The superstructure model derived here from the single crystal data is in excellent agreement with the powder pattern reported in ref. [11].

Acknowledgements

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