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Crystal structure of Dy_2PdGe_6

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ABSTRACT

The crystal structure of Dy_2PdGe_6 was studied by X-ray diffraction on single crystal. Space group *Cmca* (No. 64), $a = 8.1337(16)$, $b = 8.0208(16)$, $c = 21.441(4)$ Å, $V = 1398.8$ Å^3, $Z = 8$, 1259 unique reflections with $I > 2\sigma(I_0)$ in refinement ($2\Theta_{max} = 75.81°$), down to $R1 = 0.029$, $wR2 = 0.071$. The title compound represents an ordered derivative from the Ce_2GaGe_6-type. The crystal structure can be presented as a sequence of the AlB_2-type slabs, quadrangular antiprisms slabs, and distorted αPo-type slabs along the *c* direction. The atomic order in Dy_2PdGe_6 derived from the single crystal data was confirmed by X-ray powder diffraction with cell parameters $a = 8.1348(6)$, $b = 8.0145(5)$, $c = 21.4396(14)$ Å.

1. Introduction

The ternary intermetallic compounds with R_2TGe_6 formulas (R = Y, La-Sm, Gd-Yb; T = Pd, Pt) were known to crystallize in the crystal structures of Ce_2CuGe_6-type (*Amm*2 symmetry) [1]. This knowledge was based on the powder diffraction data. Later for Yb_2PdGe_6 compound two polymorphic modifications were studied by single crystal X-ray diffraction technique. Each modification differed from Ce_2CuGe_6-model of atomic order: Ce_2GaGe_6-type (*Cmca* symmetry) [2] and $SmNiGe_3$-type (*Cmmm* symmetry) [3] of structure were announced. In our work four alloys of the stoichiometry composition 2:1:6, namely $La_{22.2}Pd_{11.1}Ge_{66.7}$, $La_{22.2}Pt_{11.1}Ge_{66.7}$, $Dy_{22.2}Pd_{11.1}Ge_{66.7}$, and $Dy_{22.2}Pt_{11.1}Ge_{66.7}$ (at.%) were prepared in order to check their crystal structures and physical properties. Two of them ($Dy_{22.2}Pd_{11.1}Ge_{66.7}$ and $La_{22.2}Pd_{11.1}Ge_{66.7}$) were quite suitable for the physical measurements after annealing at 700 °C during 15 days, so their physical properties were recently studied and published in [4], where Cmca space group and lattice parameters were reported based on the X-ray powder diffraction test. Simultaneously with the physical measurements we had attempted to get the suitable single crystal for precise structure determination, that is why two samples, $Dy_{22.2}Pd_{11.1}Ge_{66.7}$ and $Dy_{22.2}Pt_{11.1}Ge_{66.7}$ were synthesized again and annealed at higher temperature, 950 °C, during longer time – 30 days. A good single crystal was found and investigated for $Dy_{22.2}Pd_{11.1}Ge_{66.7}$ alloy. The atomic order for the corresponding compound Dy_2PdGe_6 was studied by both X-ray single crystal and X-ray powder diffraction techniques, and data obtained are reporting in the present paper. As a result, for Dy_2PdGe_6 compound Ce_2GaGe_6-type of crystal structure is established.

2. Experimental details

Four alloys of the stoichiometry composition 2:1:6, namely $La_{22.2}Pd_{11.1}Ge_{66.7}$, $La_{22.2}Pt_{11.1}Ge_{66.7}$, $Dy_{22.2}Pd_{11.1}Ge_{66.7}$, and $Dy_{22.2}Pt_{11.1}Ge_{66.7}$ (at.%) with a weight of 1 g each were synthesized from pure elements (La and Dy 99.8, Pd, Pt and Ge more than 99.9 mass%) by arc melting under argon atmosphere on a water-cooled copper hearth. To ensure homogenization, the alloys were re-melted three times. All prepared samples were annealed at 700 °C in evacuated quartz tube (15 days). Two Dy-containing samples were also annealed at 950 °C (30 days). After annealing all samples were quenched in cold water.

Single crystal for structural studies was isolated from the surface of the alloy $Dy_{22.2}Pd_{11.1}Ge_{66.7}$ (at.%) after long term annealing at 950 °C. X-ray intensity data collection was performed at 25 °C using a Bruker APEX-II diffractometer equipped with a CCD area detector and employing graphite monochromated MoK radiation ($\lambda = 0.71073$ Å). Unit cell parameters were derived using program Bruker SAINT [5]. Absorption correction was performed with SADABS program [6]. The structure was solved by direct methods [7] and refined with the SHELXL-97 program [8].

X-ray powder diffraction (XPD) data were collected at 22 °C with a STOE STADI P transmission diffractometer, equipped with a linear PSD, (monochromated CuK_1-radiation; $7° < 2\theta < 100°$). Lattice parameters were calculated using program STOE-WinXpow [9]. Quantitative Rietveld refinement of the powder X-ray pattern was performed with the FULLPROF program [10,11], employing internal tables for X-ray atomic form factors. Atomic parameters were standardized with the aid of program STRUCTURE TIDY [12]. Structure and polyhedra were visualized using program DIAMOND [13].

The sample $Dy_{22.2}Pd_{11.1}Ge_{66.7}$ (at.%) was cut, grinded and polished via standard procedures and has been examined by scanning electron microscopy (SEM). Phase compositions were determined via Electron Probe Microanalyses (EPMA) on a Carl Zeiss LEO EVO 50XVP instrument with a Link EDX INCA Energy 450 system (Q-BSD detector).

3. Results and discussion

Previously the crystal structure of Dy_2PdGe_6 was determined by powder diffraction as isotypic with Ce_2CuGe_6 [1]. In the present investigation the crystal structure of Dy_2PdGe_6 was solved from the single crystal X-ray diffraction experiment by direct methods and found to be the ordered version of the Ce_2GaGe_6-type:

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Table 1
X-ray crystallographic data and structure refinement parameters for Dy_2PdGe_6 (single crystal X-ray diffraction experiment).

Alloy composition [at.%]	$Dy_{22.2}Pd_{11.1}Ge_{66.7}$
Crystal size [μm]	50 × 30 × 20
Space group	*Cmca*, Origin at centre (2/m)
Prototype	Ce_2GaGe_6
Pearson symbol	*oC*72
Lattice parameters [Å]	
a	8.1337(16)
b	8.0208(16)
c	21.441(4)
Cell volume [Å^3]	1398.8 (5)
Chemical formula	Dy_2PdGe_6
Formula weight, *M*	6935.52
Number of formula units in unit cell, *Z*	8
Calculated density [g/cm^3]	8.233
Absorption coefficient, μ_{abs} [mm^{-1}]	48.87
2θ Range up to [°]	75.81
Reflections in refinement	1259 $\geqslant$ 2 (I_0) of 1980
Index range	$-13 \leqslant h \leqslant 14$ $-13 \leqslant k \leqslant 13$ $-36 \leqslant l \leqslant 36$
Number of variables	50
$R1 = \|\|F_0\| - \|F_c\|\|/\|F_0\|$	0.029
R_{int}	0.050
w*R*2	0.071
Goodness of fit, $S = \{[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$	0.974
Extinction (Zachariasen)	0.00028(2)
Residual density; *e*/Å^3 max; min	3.34; −2.83

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for Dy_2PdGe_6.

Atom	Wyckoff position	*x*/*a*	*y*/*b*	*z*/*c*	Occ.	U_{eq} (Å^2)
Dy	16*g*	0.25101(2)	0.37552(6)	0.08119(1)	1.0(−)	0.00367(6)
Pd	8*f*	0	0.12695(8)	0.14228(2)	1.0(−)	0.00415(9)
Ge1	16*g*	0.27704(6)	0.1264(1)	0.19286(2)	1.0(−)	0.0045(1)
Ge2	8*f*	0	0.1191(2)	0.45757(4)	1.0(−)	0.0052(1)
Ge3	8*f*	0	0.1317(2)	0.02864(3)	1.0(−)	0.0048(1)
Ge4	8*f*	0	0.3474(1)	0.30763(4)	1.0(−)	0.0045(2)
Ge5	8*f*	0	0.4049(1)	0.19317(4)	1.0(−)	0.0048(2)

orthorhombic *Cmca* space group (No. 64), *Z* = 8. Parameters for single crystal X-ray data collection, structure refinement and obtained crystallographic data for Dy_2PdGe_6 are presented in Tables 1–3. The structure results (symmetry, cell dimensions and the atomic order) afterwards were confirmed by X-ray powder diffraction experiment with cell parameters *a* = 8.1348(6), *b* = 8.0145(5), *c* = 21.4396(14) Å. The interatomic distances and coordination numbers of atoms for the Dy_2PdGe_6 are collected in the Table 4 (in these calculations cell parameters values from XPD experiment were used). Observed interatomic distances are typical for intermetallic compounds existing in the R-T-Ge ternary systems (T-transition metal). The unit cell and coordination polyhedra of Dy_2PdGe_6 are presented on Fig. 1. Dy atoms are surrounded by 2 Pd atoms and 10 Ge atoms, coordination number CN = 12 (Fig. 1a). Pd atoms are located inside the quadrangular antiprisms with one additional Ge atom – $Pd[Dy_4Ge_5]$ (CN = 9) (Fig. 1b), whereas all Ge atoms are situated inside the triangular prisms:

Table 4
Selected interatomic distances and coordination numbers of atoms for the Dy_2PdGe_6 compound (Δ < 0.002 Å).

Couple of atoms	*d* (Å)	CN	Couple of atoms	*d* (Å)	CN
Dy–Ge2	2.945				
–Ge2	3.003		Ge2–Ge3	2.512	
–Ge3	3.043		–Ge2	2.637	
–Ge3	3.096		–2 Dy	2.945	8
–Ge3	3.107		–2 Dy	3.003	
–Ge1	3.125	12	–2 Dy	3.346	
–Ge1	3.135		Ge3–Pd	2.437	
–Ge4	3.136		–Ge3	2.442	
–Pd	3.139		–Ge2	2.512	9
–Pd	3.143		–2 Dy	3.043	
–Ge5	3.161		–2 Dy	3.096	
–Ge2	3.346		–2 Dy	3.107	
Pd–Ge3	2.437				
–Ge5	2.480		Ge4–Pd	2.485	
–Ge4	2.485	9	–Ge5	2.497	8
–2 Ge1	2.501		–2 Ge1	2.535	
–2 Dy	3.139		–2 Dy	3.136	
–2 Dy	3.143		–2 Ge1	3.175	
Ge1–Ge1	2.489				
–Pd	2.501		Ge5–Pd	2.480	
–Ge4	2.535		–Ge4	2.497	
–Ge5	2.538	8	–2 Ge1	2.538	8
–Dy	3.125		–2 Dy	3.161	
–Dy	3.135		–2 Ge1	3.172	
–Ge5	3.172				
–Ge4	3.175				

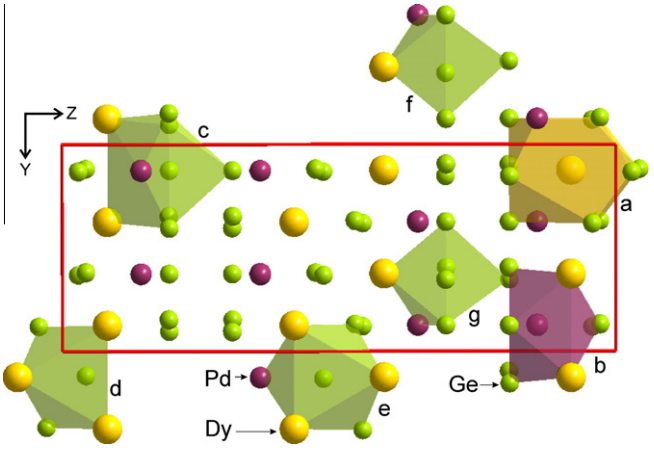

Fig. 1. The projection of the unit cell on YZ-plane and coordination polyhedral for the Dy_2PdGe_6 crystal structure: (a) – coordination polyhedron for Dy atoms, (b) – coordination polyhedron for Pd atoms, (c–g) – coordination polyhedra for Ge1, Ge2, Ge3, Ge4 and Ge5, respectively.

Table 3
The anisotropic displacement parameters for Dy_2PdGe_6.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Dy	0.0034(1)	0.00345(9)	0.00413(9)	−0.0001(2)	−0.00009(6)	−0.00027(6)
Pd	0.0041(2)	0.0043(2)	0.0040(2)	0.0001(2)	0	0
Ge1	0.0043(2)	0.0044(2)	0.0049(2)	−0.0000(2)	−0.0005(2)	0.0003(3)
Ge2	0.0045(3)	0.0039(3)	0.0070(3)	−0.0008(3)	0	0
Ge3	0.0059(3)	0.0041(3)	0.0045(3)	0.0004(3)	0	0
Ge4	0.0045(3)	0.0039(4)	0.0053(3)	0.0000(3)	0	0
Ge5	0.0043(3)	0.0047(4)	0.0053(3)	−0.0007(3)	0	0

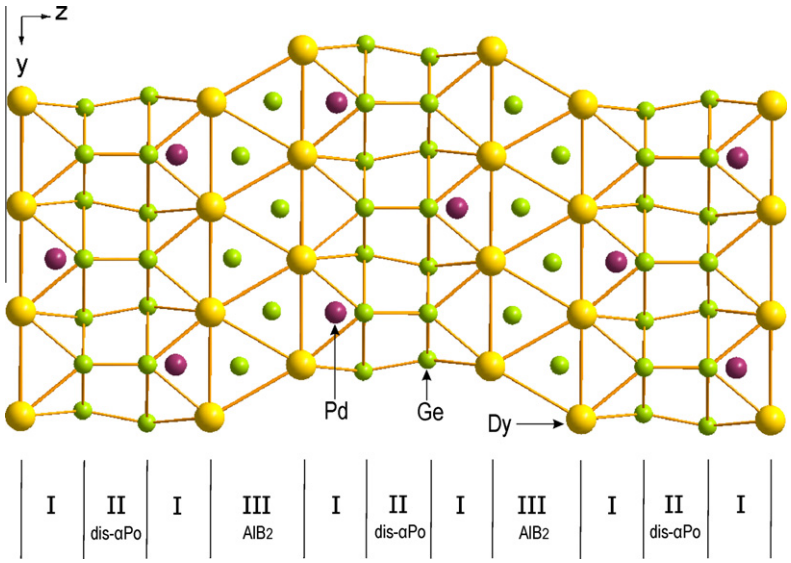

Fig. 2. Packing of layers in the Dy_2PdGe_6 crystal structure (for comments see text).

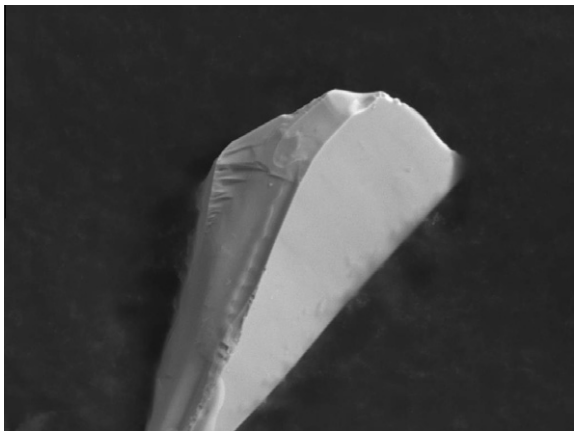

Fig. 3. Investigated single crystal of Dy_2PdGe_6 (SEM-image).

Ge1, Ge4 and Ge5 – inside distorted triangular prisms with two additional atoms Ge1[$Dy_2Pd_1Ge_5$], Ge4[$Dy_2Pd_1Ge_5$], Ge5[$Dy_2Pd_1Ge_5$] (CN = 8) (Fig. 1c,f,g); Ge2 and Ge3 – inside trigonal prisms with two additional atoms Ge2[Dy_6Ge_2] (CN = 8) (Fig. 1d) and three additional atoms Ge3[Dy_6PdGe_2] (CN = 9) (Fig. 1e).

Earlier Ce_2GaGe_6-type was described [2,14] as alternating layers of AlB_2-type, slabs of quadrangular antiprisms (both filled and empty), and the layers of distorted αPo-type (Fig. 2): the slab (I) consists of alternating filled and empty quadrangular antiprisms, the slab (II) can be considered as distorted αPo-type of structure (labeled as "dis-αPo"), the slab (III) represents AlB_2-type. The distortion of the αPo-blocks has been induced due to absence of the atom inside the each second quadrangular antiprism in the neighboring slab.

After completing the X-ray single crystal experiment the same single crystal was unglued from the holder and studied in scanning electron microscope (Fig. 3). Its chemical composition was mea-

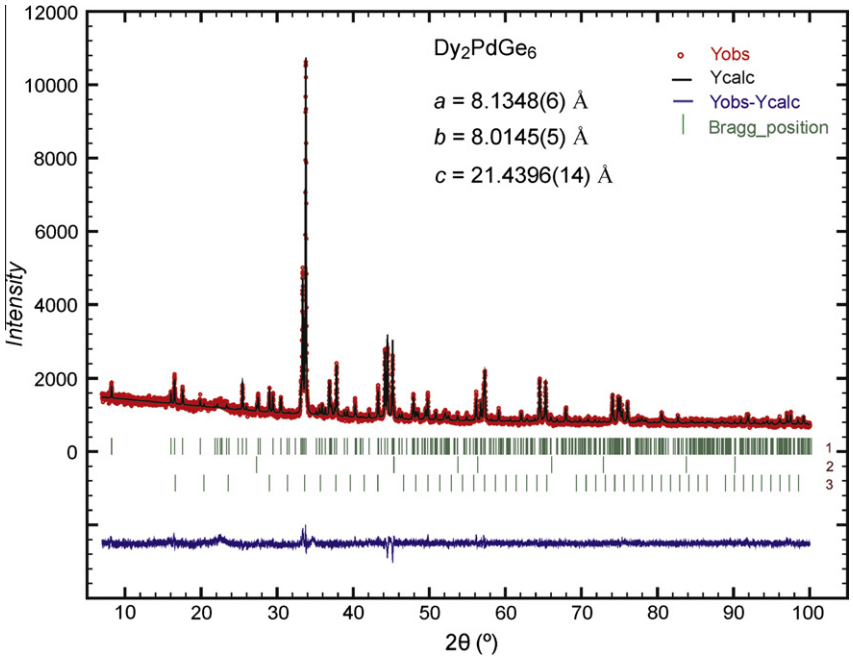

Fig. 4. Experimental powder diffraction pattern (red), calculated diffraction pattern (black), difference curve (blue) for $Dy_{22.2}Pd_{11.1}Ge_{66.7}$ alloy in Rietveld refinement (1 – Dy_2PdGe_6, 2 – Ge, 3 – Dy_2O_3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

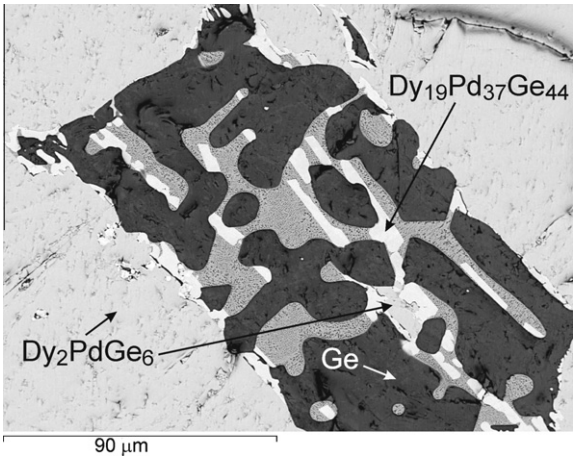

Fig. 5. Microstructure of $Dy_{22.2}Pd_{11.1}Ge_{66.7}$ alloy (SEM-image and EPMA data).

sured with the EPMA equipment. The obtained chemical composition Dy:Pd:Ge ratios in both X-ray structural (2:1:6) and EPMA quantitative (Dy – 23(1), Pd – 12(1), Ge – 65(1) at.%) studies coincide well.

From the literature it is known, that in the case of related Yb-containing germanide,Yb_2PdGe_6, two polymorphic modifications were detected by single crystal X-ray diffraction technique: (1) with the same type of the crystal structure – Ce_2GaGe_6 [2], and (2) with $SmNiGe_3$-type (*Cmmm* symmetry, Yb in Sm (4*j*) site, Pd with one-half occupation factor in Ni (4*i*) site and Ge in one 4(*j*) and two 4(*i*) Ge sites: $Yb_4Pd_2Ge_{12} = Yb_2PdGe_6$) [3]. In the present investigation, the X-ray powder diffraction test revealed the single case of atomic order corresponding to Ce_2GaGe_6-type. Except the main phase Dy_2PdGe_6 (96.3%) two impurity phases – Ge (0.4%) and Dy_2O_3 (3.3%) were detected using Rietveld refinement method. Fig. 4 illustrates the Dy_2PdGe_6 powder diffraction pattern and Rietveld refinement result for the Ce_2GaGe_6-type model with specified amount of Ge and Dy_2O_3. The appearance of small quantities of dysprosium oxide in the sample may be due to partial oxidation of the powder at its preparation in air. However, SEM/EPMA-examination of the bulk specimen except of main matrix Dy_2PdGe_6 and Ge particles revealed presence of trace amount of unknown phase of $Dy_{19}Pd_{37}Ge_{44}$ composition (at.%, Fig. 5) which can probably be $DyPd_2Ge_2$. X-ray diffraction peaks for that phase were not detected in XPD experiment due to its very low content in the bulk specimen.

Powder diffraction data for two another 2-1-6 compounds, namely La_2PdGe_6 and Dy_2PtGe_6, suggest structure also isotopic with Ce_2GaGe_6 (*Cmca* symmetry), while La_2PtGe_6 was not detected either in the as-cast, nor in the annealed specimen. Cell dimension parameters for observed isotypic compounds are presented in Table 5.

Table 5
Cell dimension parameters for observed compounds with Ce_2GaGe_6-type of structure (XPD data).

Compound	Annealing temperature (°C)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)
La_2PdGe_6	700	8.4301(11)	8.2180(7)	22.192(3)	1537.4(4)
La_2PtGe_6	700	*Was not detected*			
Dy_2PdGe_6	950	8.1348(6)	8.0145(5)	21.4396(14)	1397.8(1)
Dy_2PtGe_6	950	8.0896(5)	8.0098(5)	21.6074(15)	1400.1(1)

4. Conclusion

The crystal structure of the Dy_2PdGe_6 compound was determined from both X-ray single crystal and X-ray powder diffraction experiments. It represents an ordered derivative from the Ce_2GaGe_6-type.

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