

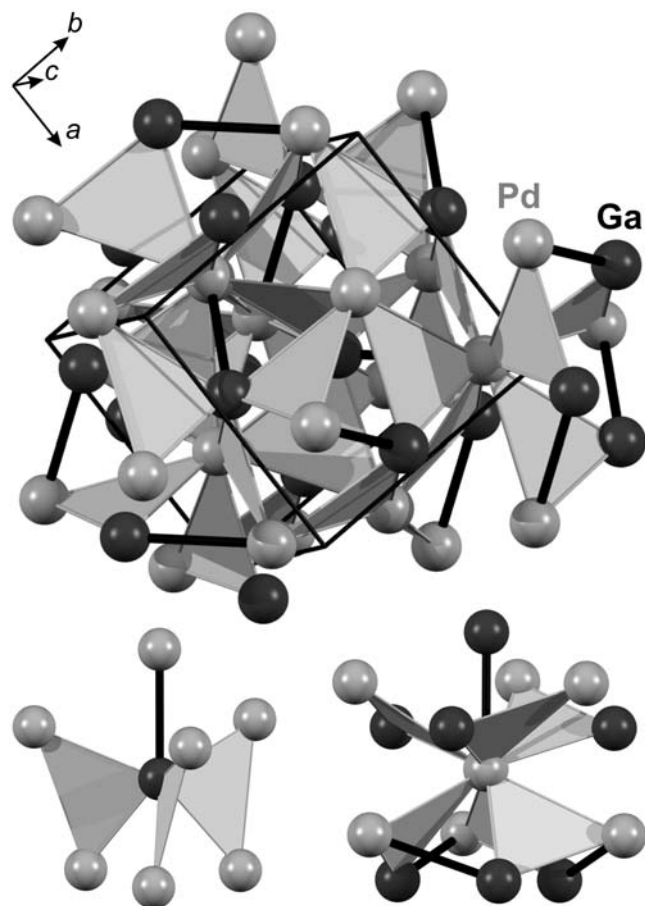
# Refinement of the crystal structure of palladium gallium (1:1), PdGa

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## Abstract

PdGa, cubic,  $P2_13$  (no. 198),  $a = 4.89695(6)$  Å,  $V = 117.4$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{gt}(F) = 0.024$ ,  $wR_{ref}(F^2) = 0.035$ ,  $T = 295$  K.

## Source of material

Large single crystals of PdGa were obtained by Czochralski growth from the melt as described in [1]. The melt consisted of Pd (99.9 %, ChemPur) and Ga (99.99 %, ChemPur) in an atomic ratio of 45:55. The metals were pre-reacted in glassy carbon crucibles under inert argon atmosphere in a high-frequency induction furnace. Single crystals used in this study were obtained from the bottom of the as grown Czochralski crystal and were annealed at 800 °C for 24 h in dynamic vacuum at  $10^{-6}$  mbar prior to the X-ray diffraction experiments. For the lattice parameter determination a small part of the bottom of the large crystal was crushed and an-

nealed as described above. WDXS measurements were performed on a CAMECA SX100 (W filament, 25 kV) with Pd50Ga50 (by chemical analysis via ICP-OES) as standard.

## Experimental details

Single crystal data were collected using a Rigaku R-axis SPIDER diffractometer with monochromated Ag  $K\alpha$  radiation. Determination and refinement of the crystal structure were performed with the *SHELX-97* software [2]. Spence [3] defined the two absolute structures of the FeSi type as form A (Fe in  $4a$  with  $x = 0.1358$ , Si in  $4a$  with  $x = 0.844$ ) and form B (Fe in  $4a$  with  $x = 0.8642$ , Si in  $4a$  with  $x = 0.156$ ). Models of both absolute structures were refined for PdGa without twin model and resulted in considerable differences in  $R_{gt,A} = 0.028$  and  $R_{gt,B} = 0.040$ , respectively. Further refinement of form A as inversion twin resulted in a Flack parameter of 0.05(1), confirming the proper parameter set. Refining site occupancy for both atoms resulted in fully occupied sites within one e.s.d. This excludes mutual site occupation in the crystal as is expected due to the covalent interactions in the compound [4].

To verify the absolute structure refinement, the mean-square Friedel intensity difference was determined according to Flack and Shmueli [5]. The resulting value of  $10^4 \chi = 261$  is sufficiently high to confirm the selected set of parameters and setting of the crystal structure.

The lattice parameters were determined by least-squares refinement of 18 reflections from powder X-ray diffraction data obtained from the annealed PdGa sample (Huber Image Plate Guinier camera G670, Cu  $K\alpha_1$  radiation,  $\lambda = 1.540562$  Å, LaB<sub>6</sub> as internal standard,  $a = 4.15692$  Å, WinCSD [6]). WDXS measurements resulted in a composition of Pd<sub>51.3(4)</sub>Ga<sub>48.7(4)</sub>.

## Discussion

To understand the excellent heterogeneous catalytic properties of the intermetallic compound PdGa [6–8] in detail, large single crystals are necessary to conduct surface investigations. According to references [9] and [10], PdGa crystallizes in the FeSi type of structure [11,12]. The absence of an inversion centre implicates two possible absolute structures, each with a characteristic but inverse stacking sequence of Pd and Ga atoms along the polar [111] direction. An unambiguous determination of the absolute structure is necessary prior to the surface investigations, since the knowledge of the sequence forms the basis for interpretation of the results. The FeSi type of structure may be considered as strongly distorted NaCl type with associated increase in coordination number from 6 to 7 for both atom sites [13]. The coordination shell of Pd or Ga, respectively, consists exclusively of atoms of the other kind and may be described as distorted monocapped trigonal prism. The capping atom represents the shortest contact between Pd and Ga at 2.5399(2) Å (black bonds in the figure) and is located on the threefold axis. The prism is completed by three

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slightly longer contacts of 2.5726(2) Å and three significantly longer contacts at 2.7058(1) Å. The rather unbalanced coordination of the atoms is a result of two-center Pd–Ga and three-center Pd–Ga–Pd covalent interactions [6]. The larger distance among Pd atoms (3.0084(1) Å) in comparison to elemental palladium along with the high stability [7] make PdGa a highly selective and stable hydrogenation catalyst [8].

**Table 1.** Data collection and handling.

Crystal:	metallic gray prism, size 0.028 × 0.028 × 0.030 mm
Wavelength:	Ag $K_{\alpha}$ radiation (0.56087 Å)
$\mu$ :	196.20 cm <sup>-1</sup>
Diffractometer, scan mode:	Rigaku R-axis SPIDER, $\omega$
$2\theta_{\max}$ :	99.64°
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ :	2834, 765
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 714
$N(\text{param})_{\text{refined}}$ :	9
Programs:	SHELXL-97 [2], WinCSD [5]

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Pd(1)	4a	0.39240(2)	<i>x</i>	<i>x</i>	0.00651(3)	<i>U</i> <sub>11</sub>	<i>U</i> <sub>11</sub>	0.00003(2)	<i>U</i> <sub>12</sub>	<i>U</i> <sub>12</sub>
Ga(1)	4a	0.09295(2)	<i>x</i>	<i>x</i>	0.00753(3)	<i>U</i> <sub>11</sub>	<i>U</i> <sub>11</sub>	-0.00099(3)	<i>U</i> <sub>12</sub>	<i>U</i> <sub>12</sub>

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