Redetermination of the crystal structure of RhPb$_2$ from single-crystal X-ray diffraction data, revealing a rhodium deficiency

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RhPb$_2$ (rhodium dilead) is a superconductor crystallizing in the CuAl$_2$ structure type (space group $I4/mcm$). The Rh and Pb atoms are located at the 4$a$ (site symmetry 422) and 8$h$ ($m.2m$) sites, respectively. The crystal structure is composed of [RhPb$_8$] antiprisms, which share their square faces along the $c$ axis and the edges in the direction perpendicular to the $c$ axis. We have succeeded in growing single crystals of RhPb$_2$ and have re-determined the crystal structure on basis of single-crystal X-ray diffraction data. In comparison with the previous structure studies using powder X-ray diffraction data [Wallbaum (1943). Z. Metallkd. 35, 218–221; Havinga et al. (1972). J. Less-Common Met. 27, 169–186], the current structure analysis of RhPb$_2$ leads to more precise unit-cell parameters and fractional coordinates, together with anisotropic displacement parameters for the two atoms. In addition and likewise different from the previous studies, we have found a slight deficiency of Rh in RhPb$_2$, leading to a refined formula of Rh$_{0.950(9)}$Pb$_2$.

1. Chemical context
A large number of binary intermetallic compounds with the CuAl$_2$ structure type have been reported (Wallbaum, 1943; Havinga et al., 1972; Havinga, 1972), and several of them exhibit superconductivity (Gendron & Jones, 1962). RhPb$_2$ is one of them, with a superconducting transition temperature ($T_c$) of 2.66 K (Gendron & Jones, 1962). $\beta$-RhPb$_2$ adopting the $\beta$-PdBi$_2$ structure type (space group $I4/mmm$) has been reported as a candidate material for topological superconductors (Zhang et al., 2019), and RhPb$_2$ crystallizing in the CuAl$_2$ structure type has also attracted much attention. While the previous powder X-ray studies of RhPb$_2$ (Wallbaum, 1943; Havinga et al., 1972) used polycrystalline material prepared by a melting method, we have grown RhPb$_2$ single crystals by application of a vertical pulling mechanism using an infrared mirror furnace. Here we report on the redetermined crystal structure of RhPb$_2$ based on single-crystal X-ray data.

2. Structural commentary
The crystal structure of RhPb$_2$, refined from single-crystal data is essentially the same as determined previously (Wallbaum, 1943; Havinga et al., 1972). RhPb$_2$ is composed of [RhPb$_8$] antiprisms, which share the square faces along the $c$ axis and the edges in the direction perpendicular to the $c$ axis (Fig. 1).
The Rh atom (site symmetry 422) is surrounded by eight Pb atoms occupying the edges of the \([\text{RhPb}_8]\) antiprism, and two Rh atoms are spaced along the \(c\) axis at a distance of half of the unit-cell parameter \(c\). The Pb—Pb distance in the adjacent \([\text{RhPb}_8]\) antiprism is the shortest among the Pb—Pb distances (Table 1; Fig. 1b, Pb—Pb\text{ix}); all Pb—Pb distances belonging to the shared square faces of the \([\text{RhPb}_8]\) antiprism are equal (Fig. 1b, Pb—Pb\text{x}), while the Pb—Pb distances belonging to the sides of the triangle of the \([\text{RhPb}_8]\) antiprism are all different (Fig. 1c, Pb—Pb\text{ix}, Pb—Pb\text{xi} and Pb\text{x}—Pb\text{xi}).

While RhPb\(_2\) has been reported to be single phase only in a Pb-deficient sample (Havinga et al., 1972), we have found a deficiency of Rh rather than a deficiency of Pb in the grown single crystals. The chemical composition obtained from the analysis of the occupancy of Rh is Rh\(_{0.950 (9)}\)Pb\(_2\). Hamilton’s \(R\) factor ratio test (Hamilton, 1965) was used to compare the \(R\) factors for the models with and without a deficiency of Rh. The result rejected the model without deficiency of Rh at a significance level of less than 0.005.

Table 1 shows the unit-cell parameters and interatomic distances (Å) at room temperature in RhPb\(_2\) determined in previous and the present studies.

|                  | Wallbaum (1943) | Havinga et al. (1972) | This work          |
|------------------|-----------------|-----------------------|--------------------|
| \(a\)            | 6.651 (3)       | 6.674 (3)             | 6.7068 (4)         |
| \(c\)            | 5.853 (3)       | 5.831 (3)             | 5.8623 (6)         |
| Pb—Pb            | 2.902           | 2.885 (6)             | 2.9016 (2)         |
| Pb—Pb\text{ix}  | 2.972           | 3.134 (14)            | 3.1313 (13)        |
| Pb—Pb\text{x}   | 3.544           | 3.520 (10)            | 3.5416 (4)         |
| Pb—Pb\text{xi}  | 3.603           | 3.662 (9)             | 3.6734 (6)         |
| Pb\text{x}—Pb\text{xi} | 3.400       | 3.319 (7)             | 3.3448 (7)         |

Symmetry codes: (ix) \(-x + 1, -y, -z + 1\); (x) \(-x + 1, -z + \frac{1}{2}\); (xi) \(y + \frac{1}{2}, -x + \frac{1}{2}, -z + \frac{1}{2}\).

3. Synthesis and crystallization

Single crystals of RhPb\(_2\) were grown from the Pb-rich melt (molar ratio Rh:Pb = 1:8) by a slow cooling process in a steep temperature gradient infrared furnace according to the Pb–Rh binary phase diagram (El-Boragy et al., 1992), where RhPb\(_2\) is shown to grow through the peritectic reaction incongruently melting between 593 and 913 K. The raw materials of Rh and Pb were of 99.9% purity in powder form (300 mesh) and 99.99% in shots, respectively, purchased from Furuiuchi Chemical Co. Prior to crystal growth, Rh and Pb were melted together in an evacuated silica tube by heating with a flame torch. The obtained ingot was then put into a new silica tube and was vacuum sealed. The silica tube was hung in an infrared mirror furnace, which generally has a strong temperature gradient around the focal point. The sample silica tube was heated above 913 K, where the sample became completely liquid. Then, the silica tube was placed at the

![Figure 1](image_url)
position where the temperature gradient is the highest. The silica tube was rotated slowly (~10 r.p.m.) to promote single crystals to grow in a uniform temperature horizontally with a steep temperature gradient vertically. A silica tube with a cone-shaped bottom was used. The furnace temperature was slowly decreased with a constant rate of 0.5 K h⁻¹ until it reached the temperature well below 593 K, then it was lowered to room temperature.

After removing the silica tube carefully, the grown boule showed clearly the liquid–solid phase boundary as a horizontal line in the upper part of the boule, indicating that the single-crystal growth had progressed as planned according to the phase diagram (El-Boragy et al., 1992). More than half of the grown boule from the bottom appeared to have turned into a single crystal of RhPb₂. The latter cleaves easily, showing shiny reflection with a silvery luster from the cleaved surface. The single crystal was rather soft and could easily be scratched by tweezers. The product seems to be stable in air because the color of the cleaved surface did not change over time. In Fig. 2 photographs of the grown single crystals of RhPb₂ are shown.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The equivalent isotropic atomic displacement parameter \( U_{eq} \) of the Rh sites for the model without deficiency of Rh was 0.0131 (5) Å², which was larger than that of Pb (0.0107 (3) Å²). We refined the occupancies of Rh and Pb. While the refined occupancy of Pb was very close to full occupation, the refined occupancy of Rh indicated a significant deficiency of this site. The final \( wR(F^2) \) value for the model without deficiency of Rh was 0.047, and that for the model with deficiency of Rh was 0.042. In the final model [occupancy of Rh = 0.950 (9); full occupancy of Pb] the atomic displacement parameter \( U_{eq} \) of the Rh site is the same as that of the Pb site.

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Table 2

| Crystal data | Rh₀.₉₅Pb₂ |
|--------------|-----------|
| Chemical formula | Rh₀.₉₅Pb₂ |
| \( M \) | 512.14 |
| Crystal system, space group | Tetragonal, \( I\bar{4}mcm \) |
| Temperature (K) | 295 |
| \( a \), \( c \) (Å) | 6.7068 (4), 5.8623 (6) |
| \( V \) (Å³) | 263.69 (4) |
| \( Z \) | 4 |
| Radiation type | Mo Kα |
| \( \mu \) (mm⁻¹) | 132.87 |
| Crystal size (mm) | 0.11 x 0.05 x 0.03 |

Data collection

Diffractometer | XtaLAB Mini II
Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2019)
\( T_{\text{min}}, T_{\text{max}} \) | 0.123, 1.000 |
No. of measured, independent and observed \([I > 2\sigma(I)]\) reflections | 461, 117, 88 |
\( R_{\text{int}} \) | 0.033 |
\( \langle \sin \theta / \lambda \rangle_{\text{max}} \) (Å⁻¹) | 0.708 |

Refinement

\( wR(F^2) \), \( S \) | 0.021, 0.042, 1.01 |
No. of reflections | 117 |
No. of parameters | 9 |
\( \Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} \) (e Å⁻³) | 1.96, −1.56 |

Computer programs: CrysAlis PRO (Rigaku OD, 2019), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b) and OLEX2 (Dolomanov et al., 2009).
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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2019); cell refinement: CrysAlis PRO (Rigaku OD, 2019); data reduction: CrysAlis PRO (Rigaku OD, 2019); program(s) used to solve structure: ShelXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Rhodium dilead

Crystal data

Rh₉₅Pb₂  
$M_r = 512.14$  
Tetragonal, I₄/mcm  
a = 6.7068 (4) Å  
c = 5.8623 (6) Å  
$V = 263.69$ (4) Å³  
Z = 4  
$F(000) = 827$

Data collection

XtaLAB Mini II diffractometer  
Detector resolution: 10.0000 pixels mm⁻¹  
$\omega$ scans  
Absorption correction: multi-scan  
(CrysAlisPro; Rigaku OD, 2019)  
$T_{\text{min}} = 0.123$, $T_{\text{max}} = 1.000$  
461 measured reflections

Refinement

Refinement on $F^2$  
Least-squares matrix: full  
$R[F^2 > 2\sigma(F^2)] = 0.021$  
wR($F^2$) = 0.042  
$S = 1.01$  
117 reflections  
9 parameters  
0 restraints  
Primary atom site location: iterative  

$D_a = 12.900$ Mg m⁻³  
Mo Ka radiation, $\lambda = 0.71073$ Å  
Cell parameters from 295 reflections  
$\theta = 6.1–30.2^\circ$  
$\mu = 132.87$ mm⁻¹  
$T = 295$ K  
Irregular, metallic dark grey  
$0.11 \times 0.05 \times 0.03$ mm

$R_{\text{int}} = 0.033$  
$\theta_{\text{max}} = 30.2^\circ$, $\theta_{\text{min}} = 4.3^\circ$  
h = −9→8  
k = −7→9  
l = −8→7

$w = 1/[\sigma^2(F_o^2) + (0.013P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta \sigma)_{\text{max}} < 0.001$

$\Delta \rho_{\text{max}} = 1.96$ e Å⁻³

$\Delta \rho_{\text{min}} = -1.56$ e Å⁻³

Extinction correction: SHELXL2018/3 (Sheldrick 2015b),  
$Fc^* = kFc[1+0.001xFc^2/sin(2\theta)]^{1/4}$

Extinction coefficient: 0.0030 (3)
Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x    | y    | z    | U(eq)/Ueq | Occ. (<1) |
|---|------|------|------|------------|-----------|
|Rh| 0.500000 | 0.500000 | 0.750000 | 0.0103 (7) | 0.950 (9) |
|Pb| 0.66507 (7) | 0.16507 (7) | 0.500000 | 0.0103 (3) |           |

Atomic displacement parameters (Å²)

|   | U¹¹ | U¹² | U¹³ | U¹² | U¹³ | U¹³ |
|---|-----|-----|-----|-----|-----|-----|
|Rh| 0.0111 (8) | 0.0111 (8) | 0.0088 (11) | 0.000 | 0.000 | 0.000 |
|Pb| 0.0091 (3) | 0.0091 (3) | 0.0128 (4) | 0.0013 (3) | 0.000 | 0.000 |

Geometric parameters (Å, °)

|   | Rh—Rh' | Rh—Pbvi | Rh—Pb |   |
|---|--------|---------|--------|---|
|Rh—Rhii | 2.9312 (3) | 2.9016 (2) | 2.9016 (2) | 2.9016 (2) |
|Pb—Rh | 59.663 (4) | 59.663 (4) | 59.663 (4) | 59.663 (4) |
|Pb—Rh | 120.337 (4) | 120.337 (4) | 120.337 (4) | 120.337 (4) |
|Pb—Rh | 99.966 (13) | 96.44 (2) | 96.44 (2) | 96.44 (2) |
|Pb—Pb | 107.993 (18) | 106.118 (12) | 106.118 (12) | 106.118 (12) |

*Acta Cryst.* (2021). E77, 1327-1329
| Bond                  | Distance (Å) | Standard Deviation (Å) |
|-----------------------|--------------|------------------------|
| Pb—Rh—Pb^vii         | 119.326 (8)  |                        |
| Pb—Rh—Pb^viii        | 70.390 (11)  |                        |
| Pb—Rh—Pb^vii         | 70.390 (11)  |                        |
| Pb^v—Rh—Pb^i         | 75.220 (4)   |                        |
| Pb^iv—Rh—Pb^v        | 135.14 (2)   |                        |
| Pb—Rh—Pb^vi          | 78.54 (2)    |                        |
| Pb^iv—Rh—Pb^ii       | 75.220 (4)   |                        |
| Pb^iv—Rh—Pb^v        | 135.14 (2)   |                        |
| Pb^iv—Rh—Pb^vii      | 78.54 (2)    |                        |
| Pb^iv—Rh—Pb^vii      | 75.220 (4)   |                        |
| Pb^iv—Rh—Pb^vi       | 78.54 (2)    |                        |
| Pb^iv—Rh—Pb^v        | 147.76 (2)   |                        |
| Pb^iv—Rh—Pb^viii     | 119.326 (8)  |                        |
| Pb^viii—Rh—Pb^vi     | 75.220 (3)   |                        |
| Pb^v—Rh—Pb^iv        | 75.220 (3)   |                        |
| Pb^v—Rh—Pb^iv        | 147.76 (2)   |                        |
| Pb—Rh—Pb^iii         | 75.220 (3)   |                        |
| Pb^v—Rh—Pb^vii       | 119.326 (8)  |                        |
| Pb^viii—Rh—Pb^v      | 147.76 (2)   |                        |
| Pb^v—Rh—Pb^v         | 75.220 (4)   |                        |
| Pb^iv—Rh—Pb^vi       | 78.54 (2)    |                        |
| Pb—Rh—Pb^i           | 70.390 (12)  |                        |
| Pb^v—Rh—Pb^vii       | 70.390 (11)  |                        |
| Pb—Rh—Pb^iv          | 147.76 (2)   |                        |
| Pb^v—Rh—Pb^vi        | 119.326 (8)  |                        |
| Pb^v—Rh—Pb^v         | 78.54 (2)    |                        |
| Pb—Rh—Pb^v           | 147.76 (2)   |                        |
| Pb—Rh—Pb^v           | 75.220 (3)   |                        |
| Rh—Pb—Rh^i           | 109.610 (11) |                        |
| Rh—Pb—Rh^iv          | 109.610 (12) |                        |
| Rh—Pb—Rh^iv          | 147.76 (2)   |                        |
| Rh^vi—Pb—Rh^iv       | 147.76 (2)   |                        |
| Rh^v—Pb—Rh^iv        | 60.674 (8)   |                        |
| Rh^v—Pb—Rh^iv        | 109.610 (12) |                        |
| Rh^vi—Pb—Rh^iv       | 147.76 (2)   |                        |
| Rh^v—Pb—Rh^iv        | 60.674 (8)   |                        |
| Rh^v—Pb—Pb^v         | 52.390 (2)   |                        |
| Rh^vi—Pb—Pb^v        | 54.805 (6)   |                        |
| Rh^vi—Pb—Pb^v        | 148.841 (9)  |                        |

Symmetry codes: (i) −x+1, −y+1, −z+2; (ii) −x+1, −y+1, −z+1; (iii) x−1/2, y+1/2, z+1/2; (iv) y, −x+1, −z+1; (v) −x+3/2, −y+1/2, −z+3/2; (vi) y+1/2, −x+3/2, −z+3/2; (vii) −y+1, x, z; (viii) −y+1/2, x−1/2, z+1/2; (ix) −x+1, −y, −z+1; (x) −y+1, x−1, z; (xi) y+1/2, −x+1/2, −z+1/2; (xii) y+1, −x+1, −z+1; (xiii) −x+3/2, −y+1/2, −z+1/2; (xiv) x+1/2, y−1/2, z−1/2.