

Structures of Superconducting Palladium Selenides, Pd<sub>7</sub>Se<sub>2</sub> and Pd<sub>34</sub>Se<sub>11</sub>

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(Received 26 May 1988; accepted 2 August 1988)

**Abstract.** (I) Pd<sub>7</sub>Se<sub>2</sub>,  $M_r = 902.72$ , monoclinic,  $P2_1/a$ ,  $a = 9.441$  (7),  $b = 5.370$  (5),  $c = 5.495$  (4) Å,  $\beta = 93.61$  (7)°,  $V = 278.0$  (4) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 10.78$  Mg m<sup>-3</sup>,  $\lambda(\text{Ag } K\alpha) = 0.5608$  Å,  $\mu(\text{Ag } K\alpha) = 17.5$  mm<sup>-1</sup>,  $F(000) = 780$ , 298 K,  $R = 0.042$  for 863 unique reflections. (II) Pd<sub>34</sub>Se<sub>11</sub>,  $M_r = 4486.16$ , monoclinic,  $P2_1/n$ ,  $a = 21.413$  (5),  $b = 5.504$  (1),  $c = 12.030$  (2) Å,  $\beta = 99.44$  (2)°,  $V = 1398.6$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 10.65$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu(\text{Mo } K\alpha) = 35.2$  mm<sup>-1</sup>,  $F(000) = 3876$ , 298 K,  $R = 0.032$  for 2591 reflections. In Pd<sub>7</sub>Se<sub>2</sub>, the Se atom is surrounded by seven Pd atoms, and the Pd atom has eight or nine Pd neighbors. In Pd<sub>34</sub>Se<sub>11</sub>, the Se atom is surrounded by five to seven Pd atoms, and the Pd atom has five to ten Pd neighbors. In both crystals, each Pd atom is coordinated by two Se atoms with a few exceptions in Pd<sub>34</sub>Se<sub>11</sub>. The Pd-Se bonds are essentially covalent with the bond lengths ranging from 2.4 to 2.6 Å; the Pd-Pd bonds with interatomic distances 2.7-3.2 Å are considered to be metallic. Irregular three-dimensional networks of Pd-Se chains are formed.

**Introduction.** In the phase diagram of the Pd-Se system (Olsen, Røst & Grønvold, 1979), there exist four compounds in the narrow range of Se concentration from 18 to 25 at.%, Pd<sub>9</sub>Se<sub>2</sub>, Pd<sub>4</sub>Se, Pd<sub>7</sub>Se<sub>2</sub> and Pd<sub>3</sub>Se. Among these compounds, Pd<sub>4</sub>Se is the only one for which a detailed crystal structure has so far been reported (Grønvold & Røst, 1962). Recently, Takabatake, Ishikawa & Jorda (1987) confirmed the phase diagram and revealed that the Pd<sub>9</sub>Se<sub>2</sub> phase is stabilized only by forming a lamellar structure with the neighboring phase of Pd<sub>4</sub>Se. They found the symmetry of Pd<sub>9</sub>Se<sub>2</sub> to be trigonal but could not determine the crystal structure owing to the presence of microtwins. Olsen *et al.* (1979) reported that Pd<sub>7</sub>Se<sub>2</sub> was monoclinic with lattice parameters  $a = 9.462$ ,  $b = 5.354$ ,  $c = 5.501$  Å and  $\beta = 86.50$ °. They also presented X-ray powder diffraction data of Pd<sub>3</sub>Se, which could not be indexed. We will show in this paper that the compound described as Pd<sub>3</sub>Se has a stoichiometry

slightly shifted to palladium-rich composition, Pd<sub>34</sub>Se<sub>11</sub>.

Superconductivity in the Pd-Se system was investigated by Takabatake *et al.* (1987). The compounds Pd<sub>9</sub>Se<sub>2</sub>, Pd<sub>7</sub>Se<sub>2</sub> and Pd<sub>34</sub>Se<sub>11</sub> were found to exhibit superconductivity below 0.64, 0.53 and 2.66 K, respectively. Superconducting, magnetic and transport properties of these compounds have been further studied by Takabatake, Ishikawa & Junod (1988). In order to understand the marked difference in the physical properties such as  $T_c$  values, it is important to know their structural details. We report here the crystal structures of Pd<sub>7</sub>Se<sub>2</sub> and Pd<sub>34</sub>Se<sub>11</sub> determined by four-circle X-ray diffraction with single crystals.

**Experimental.** According to the phase diagram established by Takabatake *et al.* (1987), Pd<sub>7</sub>Se<sub>2</sub> and Pd<sub>34</sub>Se<sub>11</sub> are formed by peritectic reaction at 803 and 698 K, respectively. The compounds were prepared by a direct reaction of the constituents in silica-glass tubes at 1423 K, followed by quenching. Nearly stoichiometric compositions with slightly excess contents of selenium were used. The crystals for this X-ray study were then grown by annealing the samples at temperatures several tens of degrees lower than the peritectic temperatures: Pd<sub>7</sub>Se<sub>2</sub> at 773 K for 6 d and Pd<sub>34</sub>Se<sub>11</sub> at 673 K for 18 d.

Crystals shaped in a spherical form, then chemically etched. Rigaku AFC-3 diffractometer, graphite monochromated, scan speed 2° min<sup>-1</sup> in  $\omega$ . The space groups and preliminary lattice constants determined by oscillation and Weissenberg photographs, the lattice constants finally determined by least-squares calculations on the basis of  $\theta$  values of some reflections measured on the diffractometer. Four standard reflections monitored every 50 reflections: no significant intensity fluctuations. Reflections with  $|F_o| \geq 3\sigma(|F_o|)$  regarded as observed, Lp and absorption corrections. The structures solved by the direct method (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least squares with anisotropic thermal parameters. Function minimized  $\sum w(|F_o| - |F_c|)^2$ ,  $w = [\sigma^2(|F_o|) + 0.04|F_o|^2]^{-1}$ .

(I) Pd<sub>7</sub>Se<sub>2</sub>: diameter 0.32 mm, Ag  $K\alpha$  radiation,  $\omega$ -2 $\theta$  scan,  $\Delta\omega = (1.6 + 1.6 \tan\theta)^\circ$ ,  $2\theta_{\max} = 50^\circ$ , 863 unique reflections ( $h - 14 \rightarrow 14$ ,  $k 0 \rightarrow 8$ ,  $l 0 \rightarrow 8$ ; possible

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1004), transmission factor 0.031–0.049; 35 reflections to determine the cell dimensions ( $19.6 < \theta < 22.0^\circ$ );  $R = 0.042$ ,  $wR = 0.087$ ,  $S = 1.6$ , secondary-extinction parameter  $g = 0.16 \times 10^{-4}$ ,  $(\Delta/\sigma)_{\max} = 0.07$ ,  $\Delta\rho_{\max} = 4.2$ ,  $\Delta\rho_{\min} = -3.1 \text{ e } \text{Å}^{-3}$  (large residual densities are observed near the Pd atoms).

(II) Pd<sub>34</sub>Se<sub>11</sub>: diameter 0.29 mm, Mo *K* $\alpha$  radiation,  $\omega$  scan,  $\Delta\omega = 2.5^\circ$ ,  $2\theta_{\max} = 70^\circ$ , 2591 unique reflections ( $h 0 \rightarrow 34$ ,  $k -8 \rightarrow 0$ ,  $l -19 \rightarrow 19$ ; possible 6153); transmission factor 0.007–0.027; 35 reflections to determine the cell parameters ( $20.0 < \theta < 23.0^\circ$ );  $R = 0.032$ ,  $wR = 0.055$ ,  $S = 1.0$ ,  $g = 0.07 \times 10^{-4}$ ,  $(\Delta/\sigma)_{\max} = 0.04$ ,  $\Delta\rho_{\max} = 2.8$ ,  $\Delta\rho_{\min} = -3.0 \text{ e } \text{Å}^{-3}$ .

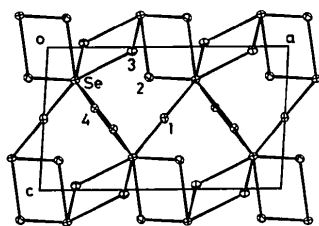
The atomic scattering factors and  $f'$ ,  $f''$  values taken from *International Tables for X-ray Crystallography* (1974). The calculations performed on FACOM M-360 and M-380R computers at this Institute; programs used were UNICSII (Sakurai, 1967), RADIEL (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) and local programs prepared at ISSP.\*

\* Lists of structure factors, anisotropic thermal parameters and Se–Pd–Se bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51309 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

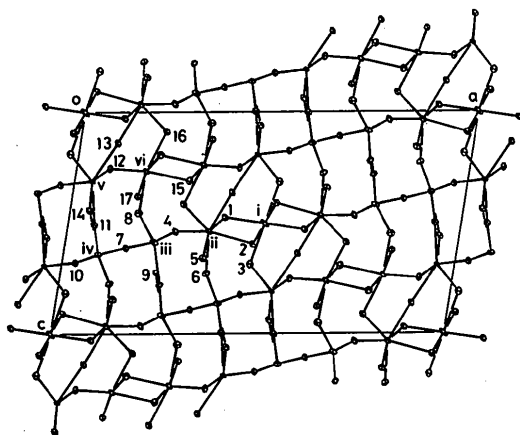
Table 1. Atomic parameters ( $\times 10^5$  for Pd<sub>7</sub>Se<sub>2</sub>,  $\times 10^4$  for Pd<sub>34</sub>Se<sub>11</sub>,  $\times 10^4$  for  $U_{eq}$ ) with their *e.s.d.*'s in parentheses

$$U_{eq} = (\sum \sum U_i a_i^* a_j^* a_i \cdot a_j) / 3.$$

|                                       | x         | y          | z          | $U_{eq}(\text{Å}^2)$ |
|---------------------------------------|-----------|------------|------------|----------------------|
| <b>Pd<sub>7</sub>Se<sub>2</sub></b>   |           |            |            |                      |
| Pd(1)                                 | 50000     | 50000      | 50000      | 104 (4)              |
| Pd(2)                                 | 42738 (7) | 92084 (13) | 20758 (13) | 115 (4)              |
| Pd(3)                                 | 35143 (7) | 40151 (13) | 3078 (14)  | 123 (4)              |
| Pd(4)                                 | 20870 (6) | 65724 (13) | 42762 (12) | 98 (4)               |
| Se                                    | 12188 (9) | 27175 (16) | 22675 (15) | 97 (4)               |
| <b>Pd<sub>34</sub>Se<sub>11</sub></b> |           |            |            |                      |
| Pd(1)                                 | 3962 (1)  | 6808 (5)   | 4718 (2)   | 143 (7)              |
| Pd(2)                                 | 4789 (1)  | 1125 (5)   | 5927 (2)   | 150 (7)              |
| Pd(3)                                 | 4789 (1)  | 6244 (4)   | 6856 (2)   | 145 (6)              |
| Pd(4)                                 | 2755 (1)  | 7945 (4)   | 5360 (2)   | 139 (7)              |
| Pd(5)                                 | 3566 (2)  | 4194 (5)   | 6575 (3)   | 131 (8)              |
| Pd(6)                                 | 3707 (1)  | 9091 (4)   | 7269 (2)   | 128 (7)              |
| Pd(7)                                 | 1561 (2)  | 7466 (6)   | 6094 (3)   | 109 (3)              |
| Pd(8)                                 | 1747 (1)  | 1097 (4)   | 4521 (2)   | 143 (6)              |
| Pd(9)                                 | 2431 (2)  | 856 (4)    | 7193 (3)   | 110 (8)              |
| Pd(10)                                | 338 (1)   | 7228 (4)   | 6751 (3)   | 120 (6)              |
| Pd(11)                                | 664 (2)   | 4158 (4)   | 5028 (3)   | 113 (8)              |
| Pd(12)                                | 856 (1)   | 2028 (4)   | 2514 (2)   | 125 (7)              |
| Pd(13)                                | 952 (2)   | 6835 (2)   | 1375 (4)   | 147 (4)              |
| Pd(14)                                | 493 (2)   | 9217 (4)   | 4397 (3)   | 116 (8)              |
| Pd(15)                                | 2915 (1)  | 8556 (5)   | 3083 (2)   | 165 (7)              |
| Pd(16)                                | 2142 (2)  | 8489 (3)   | 863 (3)    | 151 (6)              |
| Pd(17)                                | 1655 (1)  | 5942 (5)   | 3772 (2)   | 117 (7)              |
| Se(1)                                 | 5000      | 5000       | 5000       | 244 (15)             |
| Se(2)                                 | 3614 (1)  | 763 (5)    | 5355 (2)   | 116 (8)              |
| Se(3)                                 | 2259 (1)  | 4149 (4)   | 5839 (3)   | 125 (9)              |
| Se(4)                                 | 887 (1)   | 881 (3)    | 6386 (3)   | 100 (6)              |
| Se(5)                                 | 440 (1)   | 5844 (5)   | 3098 (2)   | 73 (7)               |
| Se(6)                                 | 1782 (1)  | 9503 (5)   | 2635 (2)   | 118 (7)              |



(a)



(b)

Fig. 1. Crystal structures viewed down the *b* axis: (a) Pd<sub>7</sub>Se<sub>2</sub> and (b) Pd<sub>34</sub>Se<sub>11</sub>. Bonds are limited to those shorter than 2.58 Å. The numbering scheme of the Pd atoms is indicated by arabic figures, the Se atoms in (b) by roman numerals.

**Discussion.** Fig. 1 shows projections of the structures of Pd<sub>7</sub>Se<sub>2</sub> and Pd<sub>34</sub>Se<sub>11</sub>. The final atomic parameters are listed in Table 1; selected Pd–Se bond lengths are given in Table 2. In both crystals, most of the Pd atoms are coordinated by two Se atoms as in Pd<sub>4</sub>Se (Grønvold & Røst, 1962) and Pd<sub>7</sub>Se<sub>4</sub> (Matković & Schubert, 1978), and have several Pd neighbors. The Se atoms are surrounded polyhedrally by some Pd atoms; the polyhedra formed by the Pd environments are much distorted; neighboring polyhedra are linked by corner-sharing with each other. The Pd–Se bonds are essentially covalent, because their bond lengths are nearly equal to 2.45 Å, the sum of the covalent radii of both atoms. The Pd–Pd distances are close to or slightly longer than 2.74 Å which is twice the metallic radius of Pd. The metallic character of the Pd–Se systems is presumably due to these metallic contacts. Various interatomic distances are observed, probably being affected by the local packing geometries. There are three-dimensional networks of zigzag chains in which the Pd and Se atoms are alternately bonded.

(I) Pd<sub>7</sub>Se<sub>2</sub>. The cell dimensions agree well with those reported by Olsen *et al.* (1979) (the obtuse angle of  $\beta$  was adopted in the present work). The Se atom is surrounded by seven Pd atoms and linked to adjacent Se atoms through these Pd atoms. The Pd–Se bonds have a mean value of 2.488 (2) Å; the Se–Pd–Se

Table 2. *The Pd–Se bonds (Å) within 2.58 Å*

|                                 |           |                         |           |
|---------------------------------|-----------|-------------------------|-----------|
| Pd <sub>7</sub> Se <sub>2</sub> |           |                         |           |
| Pd(1)–Se                        | 2.434 (2) | Pd(2 <sup>II</sup> )–Se | 2.532 (2) |
| Pd(2 <sup>III</sup> )–Se        | 2.467 (2) | Pd(3)–Se                | 2.576 (2) |
| Pd(3 <sup>II</sup> )–Se         | 2.462 (2) | Pd(4)–Se                | 2.462 (2) |
| Pd(4)–Se                        | 2.482 (2) |                         |           |

Symmetry operations: (i)  $\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$ ; (ii)  $\frac{1}{2}-x, -\frac{1}{2}+y, -z$ ; (iii)  $-\frac{1}{2}+x, \frac{3}{2}-y, z$ .

|                                   |           |                              |           |
|-----------------------------------|-----------|------------------------------|-----------|
| Pd <sub>34</sub> Se <sub>11</sub> |           |                              |           |
| Pd(1)–Se(1)                       | 2.408 (2) | Pd(2)–Se(1)                  | 2.482 (3) |
| Pd(3)–Se(1)                       | 2.447 (2) | Pd(1 <sup>I</sup> )–Se(2)    | 2.463 (4) |
| Pd(2)–Se(2)                       | 2.505 (3) | Pd(4)–Se(2)                  | 2.407 (3) |
| Pd(5)–Se(2)                       | 2.404 (4) | Pd(6 <sup>I</sup> )–Se(2)    | 2.457 (3) |
| Pd(13 <sup>II</sup> )–Se(2)       | 2.485 (5) | Pd(16 <sup>II</sup> )–Se(2)  | 2.498 (4) |
| Pd(4)–Se(3)                       | 2.455 (3) | Pd(7)–Se(3)                  | 2.411 (4) |
| Pd(8)–Se(3)                       | 2.443 (3) | Pd(9)–Se(3)                  | 2.424 (4) |
| Pd(9 <sup>III</sup> )–Se(3)       | 2.532 (5) | Pd(6 <sup>IV</sup> )–Se(4)   | 2.456 (3) |
| Pd(7)–Se(4)                       | 2.430 (4) | Pd(10 <sup>I</sup> )–Se(4)   | 2.406 (3) |
| Pd(11)–Se(4)                      | 2.428 (4) | Pd(14 <sup>I</sup> )–Se(4)   | 2.572 (5) |
| Pd(3 <sup>V</sup> )–Se(5)         | 2.462 (3) | Pd(10 <sup>II</sup> )–Se(5)  | 2.401 (3) |
| Pd(11)–Se(5)                      | 2.473 (4) | Pd(12)–Se(5)                 | 2.430 (4) |
| Pd(13)–Se(5)                      | 2.557 (6) | Pd(14)–Se(5)                 | 2.417 (4) |
| Pd(8 <sup>III</sup> )–Se(6)       | 2.445 (3) | Pd(12 <sup>III</sup> )–Se(6) | 2.406 (3) |
| Pd(15)–Se(6)                      | 2.453 (3) | Pd(15 <sup>III</sup> )–Se(6) | 2.515 (4) |
| Pd(16)–Se(6)                      | 2.447 (5) | Pd(17)–Se(6)                 | 2.431 (4) |

Symmetry operations: (i)  $x, -1+y, z$ ; (ii)  $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$ ; (iii)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$ ; (iv)  $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z$ ; (v)  $-\frac{1}{2}+x, \frac{3}{2}-y, -\frac{1}{2}+z$ ; (vi)  $-x, 1-y, 1-z$ ; (vii)  $x, 1+y, z$ ; (viii)  $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ .

angles of non-linear bonds are between 110.12 (4) and 137.02 (4)°. The numbers of neighboring Pd atoms within 3.2 Å around the individual Pd atoms are: Pd(1) 8, Pd(2) 9, Pd(3) 8 and Pd(4) 9. The Pd–Pd distances range from 2.743 (2) to 3.069 (2) Å.

(II) Pd<sub>34</sub>Se<sub>11</sub>. We found that the compound formerly characterized as Pd<sub>3</sub>Se by Olsen *et al.* (1979) has a

composition slightly shifted towards the palladium-rich region as Pd<sub>34</sub>Se<sub>11</sub>: the powder pattern listed in their report can be interpreted well by our structural data for Pd<sub>34</sub>Se<sub>11</sub>. The Pd(5) and Pd(17) atoms are bonded to a single Se atom; the rest of the Pd atoms are coordinated by two Se atoms as mentioned above. The number of Pd neighbors is five to seven around the Se atom, and between five and ten within 3.2 Å around Pd. The values of Pd–Se and Pd–Pd bonds are widely distributed in contrast to those of Pd<sub>7</sub>Se<sub>2</sub>. The average Pd–Se bond length is 2.455 (4) Å. The Pd–Pd distances range between 2.778 (4) and 3.191 (3) Å.

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*Acta Cryst.* (1989). **C45**, 3–7

## Oxygen Vacancy Ordering in the Defect Pyrochlore Pb<sub>2</sub>[TiSb]O<sub>6.5</sub>: A Rietveld Refinement of Neutron Powder Diffraction Data

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(Received 5 May 1988; accepted 9 August 1988)

**Abstract.**  $M_r = 688.13$ , cubic,  $F\bar{4}3m$ ,  $a = 8.10$  Mg m<sup>-3</sup>, neutron powder diffraction (Rietveld method),  $\lambda = 1.9109$  Å,  $T = 295$  K,  $R_p = 5.40$ ,  $R_{wp} = 7.14$ ,  $R_e = 5.48$ ,  $R_f = 1.69\%$  for 52 integrated Bragg intensities, goodness of fit  $R_g = 1.70$ . Oxygen coordination polyhedra for Ti, Sb are nearly regular octahedra, whereas that for Pb is a scalenohedron with the

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