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The Crystal Structure of $PdSe_2$ and PdS_2

BY FREDRIK GRØNVOLD AND ERLING RØST*

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Norway

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The compounds $PdSe_2$ and PdS_2 have orthorhombic structures with the following cell dimensions:

$PdSe_2$: $a = 5{\cdot}741$, $b = 5{\cdot}866$, $c = 7{\cdot}691$ Å;
PdS_2: $a = 5{\cdot}460$, $b = 5{\cdot}541$, $c = 7{\cdot}531$ Å.

The probable space group is $Pbca$–D_{2h}^{15} with 4 Pd in special positions (*a*) and 8 Se(S) in general positions (*c*) with the following parameters:

$PdSe_2$: $x = 0{\cdot}112$, $y = 0{\cdot}117$, $z = 0{\cdot}407$;
PdS_2: $x = 0{\cdot}107$, $y = 0{\cdot}112$, $z = 0{\cdot}425$.

Each Pd atom is surrrounded by four Se(S) atoms at the corners of a square. The metalloid atoms are bonded into pairs. The shortest interatomic distances are

Pd–4Se = 2·44, Se–Se = 2·36, Pd–4S = 2·30 Å; S–S = 2·13 Å.

Introduction

In a recent study of the palladium chalcogenides (Grønvold & Røst, 1956) the phases $PdSe_2$ and PdS_2 were identified by means of X-rays. The structures are orthorhombic with the following cell dimensions:

	a (Å)	*b* (Å)	*c* (Å)
$PdSe_2$	5·741	5·866	7·691
PdS_2	5·460	5·541	7·531

Considerable interest is connected with the atomic arrangement in these structures, especially if it might bear some resemblance to that of RhS_2 (Thomassen, 1929) and $RhSe_2$ (Geller & Cetlin, 1955) with the pyrite-type structure.

The present investigation shows that this is the case to some extent, but that the nearly regular octahedral arrangement around the metal atom, characteristic of the pyrite-type structure, is transformed into a square arrangement as two of the six metalloid atoms have moved away. At the same time, the configuration around the metalloid atom has lost its regular tetrahedral character.

Determination of the structure

Powder photographs of $PdSe_2$ and PdS_2 were taken with filtered iron radiation in cameras of 11·48 cm. diameter. The relative intensities of the reflexions were determined from photometer recording of the films. In the case of $PdSe_2$ a small crystal flake was investigated on the Weissenberg goniometer with copper radiation. Even though not a single crystal, it was of some help in the structure determination.

Missing reflexions on the photographs were $0kl$ when $k = 2n+1$, $h0l$ when $l = 2n+1$ and $hk0$ when $h = 2n+1$. The characteristic space group is thus $Pbca$–D_{2h}^{15}. On the basis of the observed densities, 6·77 g.cm.$^{-3}$ for $PdSe_2$ (Grønvold & Røst, 1956) and 4·833 g.cm.$^{-3}$ for PdS_2 (Biltz & Laar, 1936), the unit cell contains four palladium atoms and eight selenium (sulphur) atoms.

In the space group *Pbca* the palladium atoms are supposedly located in fourfold, special positions and the metalloid atoms in eightfold general positions as follows:

4 Pd in (*a*): $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$.
8 Se(S) in (*c*): $\pm(x, y, z$; $\frac{1}{2}+x, \frac{1}{2}-y, -z$; $-x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}-x, -y, \frac{1}{2}+z)$.

The parameters of the metalloid atoms were determined by trial and error, and the best agreement between observed and calculated intensities was obtained with the following parameters:

	x	*y*	*z*
$PdSe_2$	0·112	0·117	0·407
PdS_2	0·107	0·112	0·425

Tables 1 and 2 show the comparison between the intensities, which gives good support to the correctness of the assumed structure. The intensities of the strongest low-angle reflexions (002 for $PdSe_2$, 002 and 111 for PdS_2) are considerably lower than calculated, probably because of lack of proportionality between density and intensity of the lines, and because of extinction. In addition, the observed intensities are slightly reduced at low angles by absorption.

* Present address: Haldor Topsøe, Raadgivende Ingeniører, Hellerup, Danmark.

Table 1. *Observed and calculated intensities for* $PdSe_2$

hkl	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c
002	54	100	124	—	0·1	143	—	0·0	512 } 244 }	15	6·6, 11
111	11	13	214	5·5	4·3	234 } 242 }	12	4·0, 5·5	251	—	3·1
102	29	32	133	11	8·0	324	—	0·0	424	13	10
020	22	25	232	—	1·8	225	—	0·0	306	—	0·7
200	25	29	313	9·0	7·7	413	—	0·7	045 } 117 }	18	0·0, 16
112	26	31	322	—	0·1	116 } 422 }	11	0·4, 5·9	343	—	0·0
021	17	20	040	—	0·3	333	10	7·4	521	—	1·7
210	21	25	115 } 041 }	31	27, 0·1	135	—	1·0	433	—	0·6
121	23	27	400	—	0·2	026 } 315 }	3·8	2·5, 1·6	136	—	0·8
211	14	15	224	8·2	7·7	206	—	2·0	153	8·8	6·5
022	19	21	141	—	0·2	044	13	13	316	—	0·3
202	20	23	410	—	0·4	243	—	0·0	252	—	0·7
113	37	42	411	—	0·3	430	—	0·4	145	—	0·3
122	—	0·0	042 } 233 }	6·6	0·8, 5·0	423	—	0·0	415	—	0·0
212	3·3	4·0	025	—	0·4	341		0·3	513	8·8	7·2
220	11	14	323 } 304 }	4·4	0·4, 2·8	126 } 404 }	22	0·0, 12	522	—	0·1
221	—	4·1	331	4·4	3·0	216 }		5·0	027	9·3	6·6
023	23	21	402	—	0·8	431	—	0·1	440	26	28
004	—	0·0	134 } 142 }	8·2	1·0, 5·2	144	—	0·2	335	21	22
123	—	0·5	125	8·2	5·5	151	22	22	441	—	0·2
104 } 213 }	21	3·8, 19	314	—	0·9	414	—	0·3	127	—	0·3
222	21	17	215	—	0·4	511 } 334 } 235 } 342 }	33	24, 1·2, 0·2, 8·4	217	9·3	8·2
131	37	40	412	—	0·1				236	9·3	14
311	33	35	240	—	2·0				326	—	0·0
114	7·4	4·1	420 } 332 } 241 }	5·5	2·6, 1·9, 0·0				253	14	19
302	11	8·9							344 } 245 }	8·2	10, 0·0
132	9·3	8·4				325	13	9·7	351	—	4·1
312	4·4	2·6				432	—	0·1	434 } 442 }	24	1·0, 37
230	7·7	7·2				152	—	0·3	425	—	1·4
024	5·5	4·8				502	—	0·8	154	—	2·7
223	—	0·6	006	—	0·2	226	8·2	7·4			
204	4·9	4·2	043 } 421 }	3	0·3, 3·6	250	—	2·2			
231	—	2·2									
321	12	11	106	—	0·4						

Discussion of the structure

A projection of the structure of $PdSe_2$ is shown in Fig. 1. Each palladium atom is surrounded by four selenium atoms in a planar, nearly square configuration. The distances Pd–4Se are 2·44 Å. Two more selenium atoms are found on an axis through the palladium atom and almost normal to the plane through the other four selenium atoms, at the distance 3·25 Å from the palladium atom.

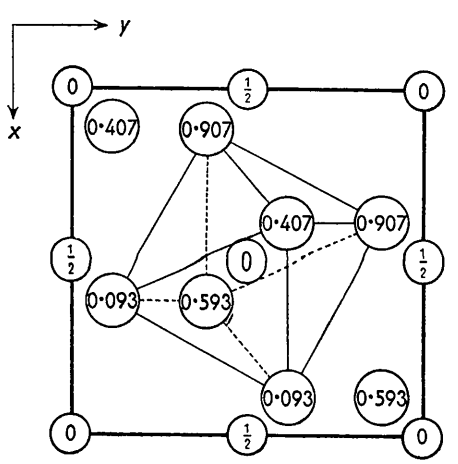

Fig. 1. Projection of the $PdSe_2$ structure on (001). The large circles indicate the selenium atoms and the small circles the palladium atoms. Figures in the circles give the z parameters of the atoms.

Each selenium atom has another selenium atom as nearest neighbour at the distance 2·36 Å, two palladium atoms at 2·44 Å and one at 3·25 Å at the corners of a tetrahedron. The Se–Se distance is slightly longer than the tetrahedral covalent distance 2·28 Å (Pauling & Huggins, 1934).

The structure might be looked at as a deformed pyrite-type structure, with such weak bonds between atoms in the c direction that a layer lattice is formed. This explains the flaky appearance of some of the $PdSe_2$ preparations.

In applying the valence bond description (Pauling, 1945) the palladium atom probably can be said to form dsp^2 bonds and the selenium atom to form sp^2 bonds, or sp^3 bonds with an inert electron pair. None of the atomic electrons of palladium needs to be excited to outer orbitals and the radius of square Pd(II) is expected to be the same as that of octahedral Pd(IV) with a radius of 1·31 Å. This gives a Pd–Se distance of 1·31+1·14 = 2·45 Å, in essentially exact agreement with the observed values. The same agreement is obtained with the use of the metallic radii of the elements (Pauling, 1947), giving a radius sum Pd+Se of 1·23+1·22 = 2·45 Å. The observed Se–Se distance

Table 2. *Observed and calculated intensities for* PdS_2

hkl	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c	*hkl*	I_o	I_c
002	52	100	230	3	1·7	332	—	0·2	325	—	1·6
111	44	77	231	—	0·2	420 }	6·5	{ 3·9	334	—	0·5
102	5	5·8	124	—	0·0	106 }		{ 0·1	511	27	24
020	25	28	214 }	5	{ 0·1	214	—	0·0	342	—	2·0
200	26	28	321 }		{ 2·9	043	—	0·1	226 }	9	{ 12
112	6·5	5·2	133	11	13	421	—	0·5	432 }		{ 0·2
021	3·5	2·8	313	11	13	116	—	0·1	502	—	0·1
210	4·5	4·5	232	—	1·2	225	—	0·1	152	—	0·2
121	5·5	4·6	322	—	0·0	234	—	0·2	117	16	25
211	3·5	2·2	115	14	17	143	—	0·0	306 }	16	{ 0·1
022	20	27	040	—	0·5	324	—	0·1	244 }		{ 17
202	20	27	400	—	0·6	242	9	7·9	512	—	1·3
113	27	35	041	—	0·0	413	—	0·3	250 }	11	{ 2·1
122	—	0·1	224	8·5	10	422	9·5	8·5	424 }		{ 16
212	—	0·1	410	—	0·1	333	9	9·0	136	—	0·2
220	17	16	025	—	0·9	026	6·5	4·0	045	—	0·3
221	—	0·1	141	—	0·0	135 }	9	{ 6·6	251	—	0·9
004	5·5	4·5	304	—	1·3	206 }		{ 3·7	316	—	0·1
023	5	4·2	233	—	0·9	315	6·5	7·3	343	—	0·0
104	—	1·3	411	—	0·1	126	—	0·0	521	—	0·2
123	—	0·1	323 }	3	{ 0·1	216	—	1·4	433	—	0·3
213	4	4·0	042 }		{ 2·1	044	8	6·9	027	—	0·0
222	19	21	125 }		{ 0·7	243	—	0·0	145	—	0·6
131	29	29	402 }	5	{ 2·3	404	7·5	7·3	153	12	24
114	—	1·5	215 }		{ 0·9	423	—	2·8	415	—	0·4
311	26	26	134	—	1·4	430	—	0·3	252	—	0·4
302	3	1·5	331	10	7·7	144	—	1·2	127	—	3·3
132	3	1·6	314	—	0·6	341	—	0·3	513	15	31
312	—	0·3	142	—	0·8	431	—	0·0	217	—	0·1
024	7	6·9	006	—	1·6	414	—	0·0	335	16	36
204	7	6·9	412	—	0·1	151	25	22	522	—	0·0
223	—	0·2	240	5·5	3·6	235	—	0·5	440	29	58

is, however, somewhat smaller than 2·44 Å, but slight errors in the parameter values have a marked influence on that distance.

In the structure of PdS_2 the interatomic distances are correspondingly shorter. Here palladium is surrounded by four sulphur atoms at the distance 2·30 Å and two more sulphur atoms at the distance 3·28 Å. The expected covalent radius sum Pd+S is 1·31+1·04 = 2·35 Å, which is slightly larger than observed. The observed S–S distance is 2·13 Å, or slightly larger than the tetrahedral covalent distance 2·08 Å, in analogy with what was found for $PdSe_2$. By using the metallic radii (Pauling, 1947) the Pd–S distances are expected to be 1·23+1·09 = 2·32 Å, in very good agreement with those observed. The S–S distance, 2·18 Å, is slightly larger than the observed value.

Palladium diselenide and disulphide have structures which resemble that of palladium monosulphide as far as the palladium coordination is concerned. In PdS the sulphur atoms are arranged in deformed squares around the palladium atoms (Gaskell, 1937). Furthermore, the sulphur atoms are surrounded by palladium atoms at the corners of deformed tetrahedra. The four different Pd–S distances are 2·26, 2·29, 2·34 and 2·43 Å. The average of the three first is equal to the distances 2·30 Å found for PdS_2.

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