ACTA CHEMICA SCANDINAVICA 10 (1956) 1620—1634

On the Sulfides, Selenides and Tellurides of Palladium

FREDRIK GRØNVOLD and ERLING RØST

Kjemisk Institutt A, Universitetet i Oslo, Blindern, Norway

The phase relationships in the systems palladium sulfur, palladium selenium and palladium tellurium have been studied by means of X-rays. Density determinations and magnetic susceptibility measurements have also been carried out.

In the Pd-S system five intermediate phases were identified:

1. Pd_4S, with tetragonal structure, $a = 5.1147$ Å, $c = 5.5903$ Å. The observed density is 10.27 g cm^{-3}.
2. $Pd_{2.8}S$, which is only present in quenched preparations. Its structure is unknown.
3. $Pd_{2.2}S$, with cubic structure, $a = 8.9300$ Å and a density of 8.67 g cm^{-3}.
4. PdS, with tetragonal structure. The redetermined lattice constants are $a = 6.4287$ Å, $c = 6.6082$ Å.
5. PdS_2, with orthorhombic structure and unit cell dimensions $a = 5.460$ Å, $b = 5.541$ Å, $c = 7.531$ Å.

In the Pd-Se system four intermediate phases were identified:

1. Pd_4Se, isomorphous with Pd_4S, $a = 5.2324$ Å, $c = 5.6470$ Å. The observed density is 10.74 g cm^{-3}.
2. $Pd_{2.8}Se$, with unknown structure.
3. $Pd_{1.1}Se$, with cubic structure and lattice constant $a = 10.604$ Å. It has a density of 8.30 g cm^{-3}.
4. $PdSe_2$, isomorphous with PdS_2 and with lattice constants $a = 5.741$ Å, $b = 5.866$ Å, $c = 7.691$ Å. The observed density is 6.77 g cm^{-3}.

In the Pd-Te system six intermediate phases were identified:

1. Pd_4Te, with cubic structure, $a = 12.674$ Å. The observed density is 11.40 g cm^{-3}. The structure might be looked at as an approximately body-centered arrangement of palladium atoms of which one fifth has been substituted by tellurium atoms.
2, 3 and 4. Three phases have been identified in the range between Pd_4Te and PdTe. Their approximate compositions are Pd_3Te, $Pd_{2.5}Te$ and Pd_2Te.
5. PdTe, with structure of the NiAs-type. The redetermined lattice constants are $a = 4.1521$ Å, $c = 5.6719$ Å.
6. $PdTe_2$, with structure of the $Cd(OH)_2$-type. The redetermined lattice constants are $a = 4.0365$ Å, $c = 5.1262$ Å. No extended mutual solubility of PdTe and $PdTe_2$ was observed.

The magnetic susceptibility of Pd_4S,$Pd_{2.2}S$,Pd_4Se, $Pd_{1.1}Se$, $PdSe_2$ and Pd_4Te has been measured between −183° and 450°C. The compounds Pd_4S, Pd_4Se and Pd_4Te are weakly ferromagnetic with Curie temperatures in the range 20° to 300°C. Above this temperature they have almost zero magnetic susceptibility like the compounds $Pd_{2.2}S$, $Pd_{1.1}Se$ and $PdSe_2$.

Palladium monosulfide was prepared by direct combination of the elements by Berzelius [1] in 1813. It has been studied by many investigators since that time, and the results have been reviewed by Gmelin [2]. Three other palladium sulfides, Pd_2S, Pd_3S_4 and PdS_2, were obtained by Schneider [3]. The existence of the compound Pd_2S has later been confirmed by Petrenko-Kritschenko [4] and Roessler [5]. Furthermore, the compound Pd_4S exists according to Maxted [6], and the compound Pd_3S according to Iwanoff [7].

The region Pd to PdS of the palladium sulfur system was studied by Weibke and Laar [8] by means of thermal, metallographic and X-ray methods. The compounds Pd_4S and PdS were found in slowly cooled samples, and in addition, a phase with composition around 73.5 atomic per cent palladium ($Pd_{2.8}S$) which disproportionated into Pd_4S and PdS at temperatures below 554°C.

A tensimetric analysis of the sulfur-rich part of the system was carried out by Biltz and Laar [9]. No intermediate compounds between PdS and PdS_2 were found.

The crystal structure of PdS was determined by Gaskell [10] by means of single crystals. The structure of the other palladium sulphides are unknown.

Palladium monoselenide was obtained by Rössler [11] as an insoluble product after heating some precipitates containing palladium and selenium and treating them with nitric acid. The existence of PdSe has later been confirmed by Roessler [5] and by Moser and Atynski [12]. Roessler [5] also found a phase with composition Pd_4Se by heating dichlorodiammine palladium with selenium.

Thomassen [13] did not succeed in preparing stoichiometric palladium diselenide from the elements. Laue photographs taken of the crystals showed only twofold symmetry. $PdSe_2$ was later prepared by Wöhler, Ewald and Krall [14] by heating palladium dichloride with excess selenium. As a result of microscopic examination they concluded that the crystals were hexagonal and of the $Cd(OH)_2$-(*C*6)-type.

Palladium monotelluride was prepared by Tibbals, Jr.[15] by precipitation, and later by Thomassen [13] by heating a mixture of the elements. In the same way Thomassen prepared palladium ditelluride. By means of X-ray powder photographs he found that PdTe had a hexagonal structure of the NiAs-(*B*8-) type, and that $PdTe_2$ had a structure of the $Cd(OH)_2$-(*C*6-) type.

EXPERIMENTAL

The *palladium* metal used in this study was kindly placed at our disposal by Falconbridge Nikkelverk A/S, Kristiansand S. To remove adsorbed hydrogen, the metal was heated at 900°C at a pressure of the order 10^{-6} cm Hg. A spectrographic analysis showed that Ag was present in the order of 0.01 % and Cu, Mg, Fe, Si and Na in less than 0.01 % each.

Sulfur from Schering-Kahlbaum A.G. (Sulfur cryst. puriss.) was purified by double distillation in a silica apparatus. Only the middle fractions were used. The highly purified *selenium* was a gift from Bolidens Gruvaktiebolag, Sweden. It carried the analysis: 0.0002 % Cu, 0.0007 % Fe, 0.003 % Te, 0.01 % S and 0.003 % non volatile matter. *Tellurium* from The British Drug Houses Ltd. was subjected to vacuum distillation in silica vessels. According to the spectrographic analysis it contained less than 0.01 % Fe and only traces of Al, Mg and Pb. This analysis and the palladium analysis were kindly carried out by siv.ing. S. Rutlin, Sentralinstitutt for Industriell Forskning, Blindern.

Alloys were prepared by heating mixtures of palladium and sulfur, selenium or tellurium, respectively, in the stoichiometric ratio 1:1 in evacuated and sealed silica tubes.

After being heated for a few days at temperatures ranging between 500° and 800°C the samples were cooled and finely ground. Alloys with other desired compositions were obtained by adding Pd, S, Se or Te in the right proportions to the mono compounds and heating the samples for some days at 600°C. Most of the samples were afterwards annealed at temperatures ranging between 250° and 650°C and cooled slowly to room temperature. In some cases the samples were quenched in ice water. During some of the heat treatments single crystals were formed.

X-Ray single crystal photographs were taken in an oscillation camera with 6.0 cm diameter and a Weissenberg camera with 5.73 cm diameter. The powdered samples were investigated by X-rays in cameras with 11.46 cm effective diameter and asymmetric film mounting. Lattice constants are expressed in Ångström units on basis of the wave lengths $\lambda \mathrm{Cu}K\alpha_1 = 1.54051$ Å, $\lambda \mathrm{Fe}K\alpha_1 = 1.93597$ Å and $\lambda \mathrm{Cr}K\alpha_1 = 2.28962$ Å. Results from earlier investigations, expressed in kX, have been transformed to Å by multiplication by the factor 1.00202.

Lattice constants of the cubic phases were found by extrapolation according to the method given by Nelson and Riley [16]. In this way the lattice constant of palladium was determined as $a = 3.8902$ Å, in perfect agreement with the high precision value $a = 3.89022$ Å given by Owen and Yates [17] for spectrographically pure palladium at 18°C.

The density of the samples was determined by the pycnometric method at 25°C with kerosene as displacement liquid. To remove gases adsorbed by the sample, the pycnometer was filled under vacuum with kerosene. Each sample weighed around 1.5 g.

The magnetic susceptibility of the samples was measured by the Gouy method at three different maximum field strengths at −183°, −78°, 20°, 150°, 300° and 450°C. The samples were filled in thin walled silica tubes of about 0.10 cm internal diameter and to a height of about 8.5 cm.

X-RAY RESULTS

A. Palladium sulfides

In the system palladium sulfur five intermediate phases were identified by means of X-rays: Pd_4S, $Pd_{2.2}S$, PdS, PdS_2 and a high temperature phase with composition around $Pd_{2.8}S$. PdS and samples richer in palladium were brittle and of gray, metallic color. The existence of a compound Pd_3S_4, claimed by Schneider [3], was not confirmed, while all the other palladium sulfides described earlier exist if one associates the compound Pd_3S by Iwanoff [7] with $Pd_{2.8}S$, and Pd_2S by Schneider[3], Petrenko-Kritschenko [4] and Roessler [5] with $Pd_{2.2}S$.

The lattice constant found for palladium in equilibrium with Pd_4S was equal to that of pure palladium within the limits of experimental error. This confirms the observations by Jedele [18] and Weibke and Laar [8] that sulfur is practically insoluble in solid palladium.

The Pd_4S phase. The Pd_4S phase could be indexed on basis of a tetragonal unit cell with dimensions:

$$a = 5.1147 \text{ Å}, \qquad c = 5.5903 \text{ Å}, \qquad c/a = 1.0930.$$

Results of the measurements are listed in Table 1. The systematic missing reflections are of the type $h\,h\,l$ with $l = 2n+1$ and $h\,0\,0$ with $h = 2n+1$. They characterize the space group $P\,\bar{4}\,2_1c$ (D_{2d}^4). The Pd_4S phase is isomorphous with the Pd_4Se phase.

The density of Pd_4S was determined to be 10.27 g cm^{-3} at 25°C, which gives a unit cell content of eight (7.90) palladium and two (1.97) sulfur atoms.

Table 1. Powder photograph data of Pd_4S annealed at 450°C, CuKa radiation. The a_2 reflections have been omitted.

I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*
vw	421	101	m	4175	214	vw	7575	424
w	763	002	vw	4541	420	st	7610	513
st	913	200	vw	4622	412	w	7699	325
st	992	102	m	4663	323	w	7743	206
m	1101	201	m	4732	421	w	7903	531
vst	1139	210	w	4847	332	m	7969	216
vst	1219	112	w	5084	304	m	8014	442
st	1330	211	vw	5306	422	vw	8285	523
m	1672	202	w	5571	413	w	8357	601
w	1818	220	vw	5658	205	st	8376	405
st	1899	212	st	5862	501 413	m	8472	532
w	1940	103				m	8580	611
vw	2240	301	m	5890	215 501	vw	8649	226
vw	2277	310				w	8708	504 434
m	2468	311	m	5994	324			
vw	2579	222	m	6093	511	vw	8876	306
m	2808	302	vw	6248	423	w	8933	514
vw	2847	213	w	6443	502 432	w	9102	316
w	2953	320				w	9152	612
w	3035	312	vw	6580	520	m	9260	621
m	3143	321	vw	6658	512	st	9281	425
vw	3269	104	m	6773	521	w	9421	533
m	3500	114	w	6841	006	m	9487	541
m	3718	322	w	6902	412	w	9612	520
m	3824	401	vw	7127	334	m	9782	326
w	3866	410	vw	7268	440	m	9830	622
w	3951	204	w	7385	503 430			
m	3982	313						

The $Pd_{2.8}S$ phase. When samples with composition Pd_3S were quenched from 580° and 600°C their X-ray photographs showed the presence of a phase which was not found in the furnace cooled samples. Weak reflections from the Pd_4S phase were found in the quenched Pd_3S sample, while rather strong reflections from the $Pd_{2.2}S$ phase were found in the quenched $Pd_{2.5}S$ sample. The high temperature phase thus seems to have a composition in the vicinity of $Pd_{2.8}S$. This agrees well with the results of Weibke and Laar [8]. We have not yet been able to determine the structure of this phase and only its characteristic reflections are listed in Table 2.

The $Pd_{2.2}S$ phase. In contrast to the results by Weibke and Laar, another intermediate phase between Pd_4S and PdS was found both in slowly cooled samples and in samples quenched from 600°C. The composition of the phase is probably close to $Pd_{2.20}S$ as the powder photograph of this sample contains no lines from other phases, while that of $Pd_{2.25}S$ shows some weak Pd_4S lines and that of Pd_2S shows many lines from the PdS phase.

The powder photograph of $Pd_{2.20}S$ could be indexed as cubic with lattice constant $a = 8.9300$ Å. No significant variation in lattice constant with composition was observed, and in Table 3 is given the indexing for the $Pd_{2.25}S$ sample.

Table 2. Characteristic low angle reflections and interplanar spacings of the $Pd_{2.8}S$ phase as found from a powder photograph of Pd_3S quenched from 600°C, CuKα radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	d in Å	I_{obs}	$\sin^2\Theta \cdot 10^4$	d in Å	I_{obs}	$\sin^2\Theta \cdot 10^4$	d in Å
m	314	4.341	vw*	1216	2.209	vw*	2464	1.552
w	474	3.539	m	1250	2.178	w	2617	1.506
m	643	3.037	vst	1332	2.110	w	2687	1.486
vw	764	2.788	st	1413	2.049	vw*	2808	1.454
w*	908	2.556	w	1472	2.008	vw	3041	1.397
st	954	2.494	vw	1724	1.855	vw	3171	1.368
st	985	2.452	vw	1817	1.807	m	3450	1.311
st	1072	2.353	vw*	1898	1.768	w	3529	1.296
w*	1134	2.287	m	1965	1.738	w	3726	1.262
m	1173	2.249	vw	2279	1.614	w	4351	1.168

* Reflections probably from the Pd_4S phase.

Reflections $h\,k\,l$ of the type $h+k+l = 2n+1$ are missing, which is characteristic of a body centered unit cell. The experimentally found density of $Pd_{2.20}S$ is 8.67 g cm^{-3} and the unit cell accordingly contains 30.7 palladium and 13.9 sulfur atoms.

The PdS phase. A redetermination of the lattice constant of the tetragonal PdS phase gave the values:

$$a = 6.4287 \text{ Å}, \qquad c = 6.6082 \text{ Å}, \qquad c/a = 1.0279.$$

Table 3. Powder photograph data of $Pd_{2.25}S$ annealed at 300°C, CuKα radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$	I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$	I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$
w	300	4	st	2835	38	m	6409	86
st	449	6	vw	2982	40	vw	6707	90
w	748	10	vw	3135	42	w	7002	94
m	898	12	w	3277	44	w	7152	96
vst	1045	14	m	3430	46	m	7301	98
vw*	1137		w	3580	48	vw	7596	102
m	1193	16	m	3726	50	m	7747	104
vw*	1216		st	4023	54	st	8042	108
st	1347	18	m	4321	58	w	8190	110
w	1493	20	vw	4618	62	w	8489	114
w	1643	22	m	4915	66	vw	8635	116
m	1790	24	vw	5072	68	w	8784	118
vw*	1898		vw	5220	70	vw	8931	120
m	1944	26	w	5368	72	st	9082	122
w	2237	30	m	5514	74	st	9376	126
m	2390	32	m	5667	76	m	9525	128
m	2533	34	st	5817	78	w	9673	130
w	2687	36	vw	6107	82	w	9821	132

* Reflections from the Pd_4S phase.

The determination by Bannister[19] gave $a = 6.44$ Å, $c = 6.60$ Å and the values reported by Gaskell[10], who determined the atomic arrangement in PdS, were $a = 6.44$ Å, $c = 6.64$ Å.

The complete indexing of a powder photograph of PdS taken with chromium radiation is given in Table 4.

*Table 4. Powder photograph data of PdS annealed at 300°C, Cr*K*a radiation.*

I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*
vw	936	111	w	4432	321	vw	8552	511
vw	1273	200	w	4815	004	w	8778	205
st	1521	102	m	5085	400	st	8929	324
st	1573	201	vw	5399	410	m	9050	423
st	1592	210	vw	6297	402	m	9093	215
m	1840	112	vw	6361	420	st	9132	502 432
vst	1893	211	w	6407	214			
w	2794	212	w	6611	412	vw	9200	520
m	3745	222	vw	6661	421	m	9449	512
w	3975	203	w	6844	323	m	9497	521
w	4061	302	vw	6921	332	vst	9875	404
w	4130	320	vw	8238	501 431			
st	4294	213						
st	4376	312	vw	8417	333			

The PdS_2 phase. Experiments to get the PdS_2 phase by heating the components were not entirely successful. Even after treating PdS with excess of sulfur for six months at various temperatures between 300° and 500°C, reflections from unreacted PdS could still be seen on the X-ray photographs together with those from another phase, probably PdS_2.

It was then tried to prepare PdS_2 by the method of Wöhler, Ewald and Krall[14] by heating palladium dichloride with excess of sulfur for four days at 450°C in an evacuated silica tube. The product was obtained in form of a black, crystalline powder after washing with carbon disulfide. The X-ray photographs resembled the earlier ones, but all the reflections from PdS had disappeared, and the sample was supposedly pure PdS_2.

The powder photograph could be indexed as orthorhombic with unit cell dimensions:

$$a = 5.460 \text{ Å}, \qquad b = 5.541 \text{ Å}, \qquad c = 7.531 \text{ Å},$$

$$a{:}b{:}c = 0.9854{:}1{:}1.3591.$$

In Table 5 are found the results of film measurements and indexing.

According to Biltz and Laar[9] the density of PdS_2, synthesized from $PdCl_2$ and sulfur, is 4.833 g cm^{-3}. The unit cell should then contain four (3.883) formula units of PdS_2.

The systematic missing reflections on the powder photograph seem to be the same as those for the $PdSe_2$ phase. Since the number of atoms in the unit cell and the axial ratios are about the same as found for $PdSe_2$, these phases are probably isomorphous.

Table 5. Powder photograph data of PdS_2 annealed at 450°, FeKa radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*
vst	674	002
vst	798	111
vw	987	102
st	1238	020
st	1273	200
vw	1403	021
w	1577	210
w	1720	121
vw	1746	211
st	1899	022
st	1941	202
vst	2128	113
st	2502	220
w	2665	004
w	2732	023
vw	3073	213
st	3159	222
vst	3244	131
st	3317	311
vw	3505	302
vw	3740	132
w	3885	024
w	3919	204
vw	4014	130
w	4228	214 321
m	4566	133
m	4646	313
st	4778	115
m	5145	224
vw	5560	323 042
vw	5699	125 402 215
m	5751	331
w	6169	240
w	6282	420 106
m	6824	242
m	6936	422
m	7087	333
vw	7203	026
w	7214	135 206
vw	7288	315
w	7543	044
w	7684	404
vst	8210	151
vst	8340	511
m	8437	226 432
st	8723	117
m	8791	306 244
m	8898	250 424
m	9435	153
st	9653	513
st	9706	335
vst	9912	440

B. Palladium selenides

Four intermediate phases were identified in the palladium selenium system: Pd_4Se, $Pd_{2.8}Se$, $Pd_{1.1}Se$ and $PdSe_2$. The phases were all obtained both in quenched and slowly cooled preparations. They were of gray, metallic color and also brittle, except $PdSe_2$ which formed soft, platelike crystals.

The $Pd_{2.8}Se$ phase was not found by earlier investigators and the $Pd_{1.1}Se$ phase was given the composition PdSe by Roessler [5], Rössler [11] and Moser and Atynski [12].

The Pd_4Se phase. Powder photographs of Pd_4Se showed great similarities with those of Pd_4S and could be indexed as tetragonal. The unit cell dimensions were found to be:

$$a = 5.2324 \text{ Å}, \qquad c = 5.6470 \text{ Å}, \qquad c/a = 1.0792.$$

A record of the interferences which occur on a powder photograph of Pd_4Se taken with copper radiation is found in Table 6.

After annealing a Pd_4Se sample at 450°C for forty-five days some small crystals had been formed. Weissenberg photographs with the b-axis as rotation axis confirmed that the systematic missing reflections were of the type $h\,h\,l$ absent when $l = 2n+1$ and $h\ 0\ 0$ absent when $h = 2n+1$. The characteristic space group is thus $P\,\bar{4}\,2_1c$ (D_{2d}^4) as found for Pd_4S.

The pycnometric density of Pd_4Se is 10.74 g cm^{-3} which means that eight (7.95) palladium and two (1.99) selenium atoms are present in the unit cell. A discussion of the atomic arrangement in the two isomorphous phases Pd_4S and Pd_4Se will be given in a later paper.

Table 6. Powder photograph data of Pd$_4$Se annealed at 300°C, CuKa radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*
vw	437	110	w	3569	322	m	7473	325
vw	746	002	m	3661	401	vw	7563	531
m	872	200	st	3850	313	w	7685	442
st	965	102			204	m	7785	216
st	1056	201	w	4066	214	m	7965	523
vst	1092	210	w	4336	420	vst	8121	532
vst	1183	112	m	4498	323			405
vst	1275	211	m	4523	421	st	8208	611
m	1618	202	w	4651	332	w	8614	443
vw	1746	220	vw	4933	304			514
st	1830	212	m	5363	413	vw	8766	612
m	1896	103	vw	5525	205	w	8867	316
w	2148	301	m	5611	431	m	8988	425
w	2177	310	w	5741	215	w	9075	541
m	2362	311	w	5830	511	w	9265	524
vw	2482	222	w	6482	521	w	9414	622
m	2704	302	w	6702	006	m	9516	326
vw	2766	213	w	6876	334	m	9632	542
w	2821	320	vw	7037	522	m	9754	630
m	3011	321	w	7100	503	st	9914	444
vw	3200	104			433			
m	3419	114	st	7314	513			

The Pd$_{2.8}$Se phase. Powder photographs of samples in the composition range between Pd$_4$Se and Pd$_{1.1}$Se contain reflections from a phase with composition around Pd$_{2.8}$Se. The photographs of Pd$_3$Se show some additional very weak reflections that are probably from the Pd$_4$Se phase, and the photograph of Pd$_{2.5}$Se shows rather strong reflections from a phase richer in selenium.

In Table 7 are listed the lines found in the low angle region on a powder photograph of the Pd$_{2.5}$Se sample. The structure of this phase is unknown. On some photographs a few additional reflections were found that are possibly due to an unidentified phase, perhaps only stable at higher temperatures.

Table 7. Low angle reflections on a powder photograph of Pd$_{2.5}$Se annealed at 450°C, CuKa radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	*d* in Å	I_{obs}	$\sin^2\Theta \cdot 10^4$	*d* in Å	I_{obs}	$\sin^2\Theta \cdot 10^4$	*d* in Å
vw	478	3.523	st*	902	2.564	st	1226	2.199
w*	531	3.341	st	989	2.449	vw	1294	2.142
m*	585	3.184	m	1007	2.428	st	1361	2.088
vw	635	3.056	m	1044	2.384	m*	1426	2.040
vw*	690	2.932	st	1069	2.356			
w*	745	2.820	vst	1190	2.233			

* Reflections probably from the Pd$_{1.1}$Se phase.

The $Pd_{1.1}Se$ phase (Pd_9Se_8?). Powder photographs of PdSe samples contain some of the strongest reflections from the $PdSe_2$ phase in addition to the characteristic pattern of a cubic phase. These additional reflections are absent on photographs of $Pd_{1.1}Se$ and the cubic phase is therefore assumed to have a composition close to Pd_9Se_8.

A record of the reflections observed for $Pd_{1.1}Se$ is found in Table 8. The unit cell is primitive with lattice constant a = 10.604 Å.

A density determination on $Pd_{1.1}Se$ gave 8.30 g cm^{-3} and thus a cell content of 33.7 palladium atoms and 30.0 selenium atoms.

It is interesting to note that Juza, Hülsmann, Meisel and Biltz [20] found a phase at the composition Rh_9S_8 by tensimetric analysis of the rhodium sulfur system. According to X-ray studies by Mr. Ø. Steen in this institute the structure of Rh_9S_8 is also cubic and probably closely related to that of Pd_9Se_8.

Table 8. Powder photograph data of $Pd_{1.1}Se$ annealed at 450°C, CuKa radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$	I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$	I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$
vw	215	4	w	2753	52	vw	6764	128
vw	426	8	vw	3009	57	w	6918	131
vw	478	9	vw	3065	58	w	7078	134
st	532	10	st	3122	59	w	7181	136
vst	586	11	vw	3224	61	w	7344	139
vw	632	12	vw	3277	62	w	7602	144
vw	660	?	w	3384	64	vw	7706	146
m	690	13	vw	3433	65	vw	7764	147
st	742	14	w	3488	66	w	8027	152
vw	787	?	w	3538	67	vw	8182	155
vst	903	17	w	3597	68	m	8344	158
m	956	18	vw	3647	69	vw	8446	160
m	1008	19	w	3810	72	w	8497	161
m	1061	20	w	3909	74	w	8553	162
m	1114	21	vw	3962	75	vw	8656	164
vw	1161	22	vw	4226	80	w	8709	165
w	1324	25	vw	4278	81	vw	8925	169
w	1379	26	vw	4330	82	w	8973	170
vst	1430	27	vw	4434	84	st	9025	171
vw	1550	?	w	4541	86	m	9075	$\alpha_2$171
vst	1695	32	vw	4645	88			172
vw	1748	33	vw	4706	89	w	9290	176
w	1801	34	vw	4759	90	m	9395	178
m	1906	36	m	5073	96	vst	9446	179
vw	1962	37	m	5232	99	vst	9497	$\alpha_2$179
m	2017	38	vw	5606	106			180
w	2115	40	w	5658	107	w	9605	182
m	2170	41	vw	5814	110	m	9762	185
m	2222	42	vw	5968	113	st	9815	$\alpha_2$185
vw	2277	43	m	6130	116			186
w	2383	45	vw	6450	122	m	9866	187
vw	2540	48	w	6495	123	w	9916	$\alpha_2$187
w	2648	50	vw	6608	125			

The $PdSe_2$ phase. After annealing $PdSe_2$ for fifty days at 650°C some small, badly developed crystals were obtained. Weissenberg photographs showed that the crystals were orthorhombic and gave the approximate cell dimensions. The powder photograph of $PdSe_2$ could then be indexed as shown in Table 9 and these lattice constants were arrived at:

$$a = 5.741\ \text{Å}, \qquad b = 5.866\ \text{Å}, \qquad c = 7.691\ \text{Å},$$

$$a{:}b{:}c = 0.9787{:}1{:}1.3111.$$

Missing reflections are of the type $0\,k\,l$ absent when $k = 2n+1$, $h\,0\,l$ absent when $l = 2n+1$ and $h\,k\,0$ absent when $h = 2n+1$. The characteristic space group is thus $P\ b\ c\ a$ (D_{2h}^{15}) and on basis of the observed density 6.77 g cm^{-3} the unit cell contains four (4.00) palladium and eight (8.00) selenium atoms.

Table 9. Powder photograph data of $PdSe_2$ annealed at 450°C, FeKα radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*	I_{obs}	$\sin^2\Theta \cdot 10^4$	*hkl*
vst	638	002	w	3815	321	w	7076	341
w	718	111	w	3952	214			126
st	922	102	w	4170	133			404
m	1092	020	w	4267	313	w	7113	216
m	1136	200	st	4526	115	m	7254	151
m	1196	112			041	st	7545	511
m	1253	021	w	4765	224			334
m	1415	210	vw	5005	042			235
m	1537	121			233			342
w	1571	211	vw	5087	323	w	7615	325
m	1730	022			304	vw	7935	226
m	1777	202	vw	5174	331	w	8030	512
st	1988	113	w	5279	134			244
vw	2047	212			142	w	8176	424
m	2233	220	w	5340	125	m	8320	045
m	2522	023	vw	5654	332			117
w	2837	104			241	vw	8808	513
		213	vw	5799	043	vw	8853	027
vw	2868	222			421	m	8908	440
st	2903	131	w	6137	234	vw	8974	335
st	2998	311			242	w	9174	217
vw	3100	114	w	6269	116	w	9295	236
w	3200	302			422	w	9375	253
w	3377	132	w	6445	333	w	9453	344
vw	3469	312	vw	6792	026			245
vw	3597	230			315	m	9540	434
vw	3630	024	w	6897	044			442
vw	3677	204						

C. Palladium tellurides

In the palladium tellurium system the following intermediate phases were found: Pd_4Te, Pd_3Te, Pd_2Te, PdTe and $PdTe_2$. In addition, a sixth phase probably exists in the range between Pd_3Te and Pd_2Te. The exact composition limits of the phases have not been determined, and the formulae only indicate the approximate composition of the phases. All phases have been found both in quenched and in slowly cooled preparations. The samples are gray in color and apart from $PdTe_2$ they are brittle.

The only palladium tellurides described earlier are the monotelluride by Tibbals, Jr.[15] and Thomassen [13] and the ditelluride by Thomassen [13].

The Pd_4Te phase. Single crystals of the Pd_4Te phase were obtained in a sample with gross composition Pd_6Te that had been heated at 550°C for fifty days. Weissenberg photographs showed primitive cubic symmetry, and by means of powder photographs the lattice constant of Pd_4Te was found to be $a = 12.674$ Å.

The single crystal photographs show strong reflections only in the equatorial and fourth layer line while those in the first, second, third, fifth and sixth layer line are weak. This suggests that the true unit cell is a superstructure cell, and as apparent from Table 10 the strong reflections are multiples of $h^2+k^2+l^2 = 32$, indicating that the "subcell" with $a' = 3.168$ Å is approximately body centered.

Table 10. Powder photograph data of Pd_4Te annealed with excess Pd at 500°C, CuKa radiation.

I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$	I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$	I_{obs}	$\sin^2\Theta \cdot 10^4$	$h^2+k^2+l^2$
vw	1002	27	vw	4504	122	w	8092	219
vw	1150	?	m	4730	128	vst	8274	224
vst	1193	32	vw	5149	139	w	8681	235
vw	1529	41	m	5922	160	w	8721	236
w	2193	59	w	6330	171	w	9130	?
m	2376	64	vw	6915	187	st	9270	251
vw	3064	83	w	7092	192	vw	9381	254
vw	3141	85	vw	7239	196	m	9453	256
st	3557	96	vw	7460	202	vw	9751	264
w	3962	107	vw	7505	203	w	9861	267
vw	4190	113	vw	7613	206			
vw	4319	117	vw	7831	212			

In agreement with this, the observed density 11.40 g cm^{-3} of Pd_4Te confirms that the number of atoms in the subcell is close to two (1.575 Pd atoms and 0.394 Te atoms). The structure can probably be looked at as a body centered arrangement of palladium atoms of which one fifth has been substituted by tellurium atoms in an ordered way. However, the atoms are slightly displaced from the ideal positions as evidenced especially by the strong $h^2+k^2+l^2 = 251$ reflection.

The phases between Pd_4Te and $PdTe$. Samples in this range give very complicated powder photographs and the phases are not easily identified. The Pd_4Te reflections are found in $Pd_{3.5}Te$ but are absent in Pd_3Te. No lines from a tellurium richer phase are presumably present in Pd_3Te since the powder photographs of Pd_3Te and $Pd_{2.75}Te$ are alike. The low angle reflections found on a powder photograph of Pd_3Te are collected in Table 11.

There also exists a phase with composition around Pd_2Te. Its characteristic low angle reflections are listed in Table 11 too. A sample with composition $Pd_{1.5}Te$ was found to contain both the Pd_2Te and the PdTe phase.

The powder photograph of $Pd_{2.5}Te$ is markedly different from that of Pd_2Te and does not resemble that of $Pd_{2.75}Te$ either, see Table 11. Probably therefore a third phase exists in this range.

Table 11. Characteristic low angle reflections on powder photographs of Pd_3Te, $Pd_{2.5}Te$ and Pd_2Te.

Pd_3Te			$Pd_{2.5}Te$			Pd_2Te		
I_{obs}	$\sin^2\Theta \cdot 10^4$	d in Å	I_{obs}	$\sin^2\Theta \cdot 10^4$	d in Å	I_{obs}	$\sin^2\Theta \cdot 10^4$	d in Å
vw	446	3.65	vw	460	3.59	vw	308	4.39
vw	588	3.18	vw	602	3.14	vw	354	4.09
w	683	2.95	vw	703	2.90	w	525	3.36
w	929	2.53	vw	917	2.54	w	553	3.28
w	958	2.49	w	953	2.50	vw	627	3.08
m	991	2.45	w	986	2.45	vw	732	2.85
w	1101	2.32	vw	1128	2.29	vw	765	2.79
w	1128	2.29	vst	1165	2.26	w	800	2.72
vst	1162	2.26	vw	1192	2.23	m	919	2.54
st	1192	2.23	w	1215	2.21	w	960	2.49
w	1271	2.16	m	1232	2.19	w	1007	2.43
w	1426	2.04	w	1306	2.13	vw	1074	2.35
m	1502	1.99	vw	1343	2.10	m	1117	2.30
vw	1531	1.97	m	1512	1.98	w	1147	2.27
w	1594	1.93	vw	1587	1.93	m	1173	2.25
m	1628	1.91	vw	1654	1.89	st	1198	2.23
vw	1667	1.89	vw	1690	1.87	w	1226	2.20
						vw	1247	2.18
						m	1306	2.13
						w	1349	2.10
						w	1428	2.04
						w	1508	1.98
						m	1539	1.96

The PdTe and $PdTe_2$ phase. A redetermination of the lattice constants of hexagonal PdTe with structure of the NiAs-($B8$-)type gave the result:

$$a = 4.1521 \text{ Å}, \qquad c = 5.6719 \text{ Å}, \qquad c/a = 1.3660.$$

These values are in good agreement with those determined by Thomassen[13] ($a = 4.135 \pm 0.004$ Å, $c = 5.674 \pm 0.005$ Å).

The homogeneity range of the PdTe phase is apparently rather narrow since the lattice constants of the PdTe phase are equal within the limits of experimental error both in $Pd_{1.5}Te$, PdTe and $PdTe_{1.5}$.

The structure of $PdTe_2$ is also hexagonal and for a sample that had been heated with excess tellurium at 300°C for 30 days the following lattice constants were computed:

$$a = 4.0365 \text{ Å}, \qquad c = 5.1262 \text{ Å}, \qquad c/a = 1.2700.$$

According to Thomassen [13] the structure is of the $Cd(OH)_2$-($C6$-) type and the lattice constants given by him ($a = 4.036 \pm 0.003$ Å, $c = 5.128 \pm 0.004$ Å) are in excellent agreement with ours.

A continuous solid solution between PdTe and $PdTe_2$ is not found, and in general it seems like none of the palladium chalcogenides have extended ranges of homogeneity. Among the chalcogenides of the 3d transition elements solid solutions involving a continuous transition from the $B8$ to $C6$ structure type are quite common. As examples might be mentioned the CoTe - $CoTe_2$ and NiTe - $NiTe_2$ transitions found by Tengnér [21] and the TiTe - $TiTe_2$ transition studied by Ehrlich [22]. Recently, the phases RhTe and $RhTe_2$ have been identified by Geller [23]. RhTe was found to have a structure of the $B8$ type and the high temperature form of $RhTe_2$ a structure of the $C6$ type. No samples with intermediate compositions were studied so it is not known to what extent these phases show mutual solubility.

MAGNETIC PROPERTIES OF THE PALLADIUM CHALCOGENIDES

The magnetic susceptibility of Pd_4S, $Pd_{2.2}S$, Pd_4Se, $Pd_{1.1}Se$, $PdSe_2$ and Pd_4Te was measured at six different temperatures from —183° to 450°C and the results are listed in Tables 12 and 13.

Table 12. Magnetic susceptibility of the palladium chalcogenides, $\chi_g \times 10^6$.

Compound	Temperature °C					
	−183	−78	20	150	300	450
Pd_4S	*	*	*	0.20	0.01	0.06
$Pd_{2.2}S$	0.27	0.25	0.17	0.17	0.14	0.12
Pd_4Se	*	*	*	0.18	0.04	0.00
$Pd_{1.1}Se$	0.07	0.05	0.02	0.00	−0.01	−0.01
$PdSe_2$	−0.26	−0.26	−0.26	−0.26	−0.26	−0.27
Pd_4Te	*	*	*	*	0.51	0.14

* The field strength dependent susceptibilities are listed in Table 13.

Table 13. The field strength dependent susceptibility of the Pd_4X compounds, $\chi_g \times 10^6$.

Compound	T°C	H_{max}		
		4 015 Ø	4 700 Ø	5 110 Ø
Pd_4S	−183	19.9	17.5	16.4
	− 78	16.7	14.6	13.5
	20	7.0	6.0	5.4
Pd_4Se	−183	26.2	22.8	21.2
	− 78	11.0	9.5	8.5
	20	1.9	1.7	1.6
Pd_4Te	−183	5.1	4.5	4.3
	− 78	4.7	4.2	3.6
	20	4.3	3.8	3.6
	150	3.6	3.2	3.1

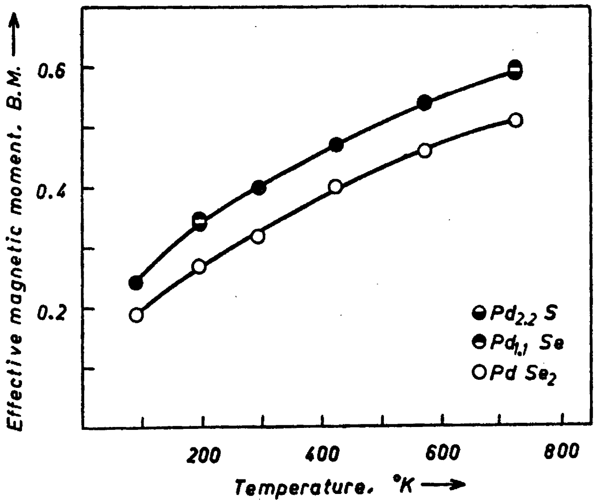

Fig. 1. Effective magnetic moments of the compounds $Pd_{2.2}S$, $Pd_{1.1}Se$ and $PdSe_2$ as functions of temperature.

Disregarding the peculiar behavior of the Pd_4X compounds at low temperatures, the magnetic susceptibilities are exceedingly low. If one subtracts the induced diamagnetism in the palladium (—21.3 × 10^{-6} per mole Pd^0 according to Hoare and Matthews [24]) and in the chalcogen (—32.6 × 10^{-6} per mole S^{-2}, —47.6 × 10^{-6} per mole Se^{-2} and —70.6 × 10^{-6} per mole Te^{-2} according to Angus [25]) one finds effective magnetic moments in the range 0.19 to 0.60 Bohr magnetons for the compounds $Pd_{2.2}S$, $Pd_{1.1}Se$ and $PdSe_2$, see Fig. 1. Considerable uncertainty is connected with the diamagnetic corrections. They are most probably too high since they refer to completed electron shells, thus resulting in too high effective magnetic moments.

Even so, the magnetic moments are rather small and show that the compounds are of an essentially metallic or covalent type. In case the bonds had been of the ionic type, a magnetic moment of 2.83 B.M. was expected for the Pd^{+2} ion and 4.90 B.M. for the Pd^{+4} ion according to the "spin only" theory. The tendency, present among the nickel chalcogenides, for the magnetism to be weaker than expected, is even more pronounced among the palladium chalcogenides. One possible explanation for this behavior is that interaction between the atoms changes the coupling of the 4d electrons of palladium so that the stable configuration does not have the maximum multiplicity required by the Hund rule.

Below certain temperatures, the magnetic susceptibilities of Pd_4S, Pd_4Se and Pd_4Te are field strength dependent and increase with decreasing temperature. The field strength dependence is observed at room temperature for Pd_4S and Pd_4Se and also at 150°C for Pd_4Te.

The authors should like to express their appreciation to professor Haakon Haraldsen for his interest in this study. They wish to thank Falconbridge Nikkelverk A/S for generously supplying palladium metal and to thank Bolidens Gruvaktiebolag for the selenium. They also wish to thank siv.ing. Sigurd Rutlin, Sentralinstitutt for Industriell Forskning, for carrying out the spectrographic analysis.

REFERENCES

1. Berzelius, J. *Kgl. Svenska Vetenskapsakad. Handl.* **1813** 204.
2. Gmelins *Handbuch der anorganischen Chemie*, System-Nummer 65: Palladium, Berlin 1942.
3. Schneider, R. *Ann. Physik.* **141** (1870) 519; **148** (1873) 625.
4. Petrenko-Kritschenko, P. *Z. anorg. Chem.* **4** (1893) 247.
5. Roessler, F. *Z. anorg. Chem.* **9** (1895) 31.
6. Maxted, E. B. *J. Chem. Soc.* **1919** 1050.
7. Iwanoff, W. N. *Chem.-Ztg*, **47** (1923) 209.
8. Weibke, F. and Laar, J. *Z. anorg. u. allgem. Chem.* **224** (1935) 49.
9. Biltz, W. and Laar, J. *Z. anorg. u. allgem. Chem.* **228** (1936) 257.
10. Gaskell, T. F. *Z. Krist.* **96** (1937) 203.
11. Rössler, H. *Ann.* **180** (1876) 240.
12. Moser, C. and Atynski, K. *Monatsh.* **45** (1924) 235.
13. Thomassen, L. *Z. physik. Chem.* **B2** (1929) 349.
14. Wöhler, L., Ewald, K. and Krall, H. G. *Ber.* **66B** (1933) 1638.
15. Tibbals, C. A. Jr. *J. Am. Chem. Soc.* **31** (1909) 902.
16. Nelson, J. B. and Riley, D. P. *Proc. Phys. Soc. London* **57** (1945) 160.
17. Owen, E. A. and Yates, E. L. *Phil. Mag.* [7] **16** (1933) 606.
18. Jedele, A. *Z. Metallkunde* **27** (1935) 271.
19. Bannister, F. A. *Z. Krist.* **96** (1937) 201.
20. Juza, R., Hülsmann, O., Meisel, K. and Biltz, W. *Z. anorg. u. allgem. Chem.* **225** (1935) 369.
21. Tengnér, S. *Z. anorg. u. allgem. Chem.* **239** (1938) 126.
22. Ehrlich, P. *Z. anorg. Chem.* **260** (1949) 1.
23. Geller, S. *J. Am. Chem. Soc.* **77** (1955) 2641.
24. Hoare, F. E. and Matthews, J. C. *Proc. Roy. Soc. London* **A212** (1952) 137.
25. Angus, W. R. *Proc. Roy. Soc. London* **A136** (1932) 573.

Received July 3, 1956.