ACTA CHEMICA SCANDINAVICA 14 (1960) 1879–1893

On the Sulfides, Selenides and Tellurides of Platinum

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The phase relationships in the systems platinum sulfur, platinum selenium and platinum tellurium have been studied by means of X-rays. Density determinations and magnetic susceptibility measurements have been carried out. Two new, intermediate phases were identified:

1. $PtSe_{0.80}$, with monoclinic structure, $a = 6.5806$ Å, $b = 4.6248$ Å, $c = 11.145$ Å, $\beta = 78.40°$. The pycnometric density is 12.79 g cm^{-3} at 25°C. The unit cell contains ten formula units and the probable space group is Pc or $P2/c$.
2. PtTe, with orthorhombic structure, $a = 6.6144$ Å, $b = 5.6360$ Å, $c = 11.865$ Å. The observed density is 12.01 g cm^{-3}. The unit cell contains ten formula units.

The earlier known phases PtS, PtS_2, $PtSe_2$ and $PtTe_2$ have been reinvestigated. The lattice constants and the observed densities are:

PtS, $a = 3.4700$ Å, $c = 6.1096$ Å
PtS_2, $a = 3.5432$ Å, $c = 5.0388$ Å, density: 7.83 g cm^{-3}
$PtSe_2$, $a = 3.7278$ Å, $c = 5.0813$ Å, density: 9.53 g cm^{-3}
$PtTe_2$, $a = 4.0259$ Å, $c = 5.2209$ Å, density: 10.16 g cm^{-3}

The correctness of the earlier assumed, tetragonal structure of PtS has been confirmed as result of intensity measurements and calculations.

The value $z = 0.250$ of the parameter in the $Cd(OH)_2$-type structures of PtS_2, $PtSe_2$ and $PtTe_2$ gives the best agreement between observed and calculated X-ray intensities.

The magnetic susceptibilities of the different phases have been measured between −183 and 450°C. The compounds show almost zero magnetic susceptibility.

EARLIER RESULTS

Platinum monosulfide was first prepared by Davey [1] by heating platinum sponge and sulfur in a closed tube. Vauquelin [2] prepared it by heating ammonium hexachloroplatinate(IV) with sulfur and sodium carbonate. According to Schneider [3] such products contain more sulfur than corresponding to the formula PtS, and are better described by the formula $4PtS \cdot PtS_2$, *i.e.* Pt_5S_6. At red heat the reported compound looses one sixth of its sulfur and

PtS is formed. Platinum monosulfide occurs in nature as cooperite and its crystal structure was determined by Bannister and Hey[4].

Platinum disulfide was prepared by Davey[1] by heating ammonium hexachloroplatinate(IV) with sulfur at red heat in the absence of air. Berzelius[5] prepared it by treating a solution of hexachloroplatinum(IV) acid with hydrogen disulfide or alkali metal sulfides. Thomassen[6] tried to make PtS_2 by heating stoichiometric amounts of the elements in an evacuated and sealed quartz tube. He obtained a product with composition $PtS_{1.94}$ and found from X-ray powder photographs that it had a hexagonal structure of the $Cd(OH)_2$-type.

In addition to postulating the existence of Pt_5S_6, Schneider[3] also reported a platinum sulfide with composition Pt_2S_3. Neither of these compounds were found by Wöhler, Ewald and Krall[7], who studied the platinum sulfur system by preparative-analytic methods, or by Biltz and Juza[8], who studied the system by tensimetric analysis. The latter authors found no indications of other compounds than PtS and PtS_2. For further references to earlier studies of the platinum-sulfur system, see Gmelin[9].

The reaction between platinum and selenium was observed by Berzelius[10]. The first analyzed compound in this system was platinum monoselenide, prepared from the elements by Roessler[11]. Its existence has not been confirmed by other investigators.

Platinum diselenide has, however, been described by several investigators. Minozzi[12] synthesized $PtSe_2$ from the elements, while Moser and Atynski[13] prepared the compound by precipitation with hydrogen selenide in aqueous solution. Wöhler *et al.*[7] obtained $PtSe_2$ by heating platinum tetrachloride with a large amount of selenium. Thomassen[6] studied $PtSe_2$ by means of X-rays and found that it had a structure of the $Cd(OH)_2$-type.

Minozzi[12] reports also the existence of $PtSe_3$. This compound was prepared by reacting pctassium hexachloroplatinate(IV) with selenium dioxide in an alkaline formaldehyde solution.

Platinum ditelluride was prepared by Roessler[14] by heating platinum and tellurium. Wöhler *et al.*[7] synthesized $PtTe_2$ from platinum tetrachloride and tellurium. In contrast to Tibbals, Jr.[15], who reported that sodium telluride reduced platinum tetrachloride solutions to elemental platinum, Brukl[16] claimed that $PtTe_2$ could be precipitated from aqueous solutions by means of hydrogen telluride. Thomassen[6] determined the crystal structure of $PtTe_2$ and found that it was of the same type as PtS_2 and $PtSe_2$. The lattice constants of $PtTe_2$ were redetermined by Groeneveld Meijer[17].

Experiments to obtain other platinum tellurides have been less successful. Roessler[14] claims that the compounds PtTe and Pt_2Te are formed by decomposing platinum tellurides richer in tellurium. Attempts by Thomassen[6] to make PtTe resulted in heterogeneous products with $PtTe_2$ as the main constituent.

The existence of a platinum telluride mineral with composition $PtTe_3$ was claimed by Scholtz[18]. The reported X-ray data for the mineral, named niggliite, were interpreted by Groeneveld Meijer[19] as mainly caused by a hexagonal NiAs-like structure. On this basis Groeneveld Meijer assigned the composition PtTe to the mineral.

EXPERIMENTAL

Most of the platinum metal used in this study was kindly placed at our disposal by Falconbridge Nikkelverk A/S, Norway. A spectrographic analysis showed presence of the following impurities: about 0.07 % Au, 0.02 % Ir, 0.01 % Pd, 0.01 % Rh, 0.001 % Cu and less than 0.001 % Ag. Some platinum thermocouple wire was also used. A spectrographic analysis of this platinum showed about 0.05 % Au, 0.05 % Cu, 0.02 % Ir, 0.01 % Pd and 0.01 % Rh.

An X-ray powder photograph of the Falconbridge platinum taken at 19 ± 2°C gave a lattice constant of 3.9232 Å, in close agreement with the value 3.9231 Å by Swanson and Tatge [20].

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 purified by vacuum distillation in a silica apparatus. According to the spectrographic analysis the distilled product contained less than 0.01 % Fe and only traces of Al, Mg and Pb.

The alloys were prepared by heating accurately weighed quantities of platinum and sulfur, selenium or tellurium, respectively, in evacuated and sealed silica tubes.

In the platinum-sulfur system alloys with 25.00, 33.33, 40.00, 47.37, 48.72, 50.00, 51.22, 52.38, 54.55, 60.00, 66.10, 66.67 and 75.00 atomic % sulfur were made. All samples except those with 25.00, 40.00 and 54.55 atomic % S were heated at 825°C for 30 days and cooled slowly to room temperature over a period of another 30 days. The samples with 66.67 and 75.00 atomic % S were afterwards annealed for 50 days at a temperature of 650°C. The samples with 25.00, 40.00 and 54.55 atomic % S were quenched in ice water from 1 150, 825 and 650°C, respectively.

In the platinum-selenium system alloys with 25.00, 33.33, 37.11, 38.65, 40.00, 41.18, 42.86, 43.50, 44.44, 45.95, 47.61, 50.00, 60.00, 66.67, 75.00 atomic % selenium were made. All samples except those with 25.00, 40.00 and 50.00 atomic % Se were heated at 825°C for 30 days and cooled slowly to room temperature over a period of another 30 days. The samples with 44.44, 50.00, 66.67 and 75.00 atomic % Se were also heated at 1 000 and 600°C for 20 to 30 days. The alloy with 44.44 atomic % Se was furthermore heated at 400°C for 60 days. The samples with 25.00, 40.00, 44.44 and 50.00 atomic % Se were quenched in ice water from 1 200, 825, 1 155 and 825°C, respectively. For density measurements samples with 41.18, 42.28, 44.44 and 45.95 atomic % Se were heated at 1 150°C for 2 days. The melted alloys were afterwards crushed and annealed at 850°C for 10 days and slowly cooled to room temperature over a period of 14 days.

In the platinum-tellurium system alloys with 33.33, 40.00, 47.37, 50.00, 52.24, 60.00, 66.67, 67.74 and 75.00 atomic % tellurium were synthesized. The alloys were heated for 30 days at 825°C and cooled slowly to room temperature over a period of another 30 days. The samples with 40.00 and 50.00 atomic % Te were afterwards annealed at 750°C for 20 and 30 days, respectively. The alloy with 50.00 atomic % Te was also heated at 400°C for 40 days. The samples with 33.33, 50.00 and 60.00 atomic % Te were quenched in ice water from 750, 925 and 825°C, respectively.

During the heat treatments some of the samples were subject to sintering or melting. The alloys with 33.33 atomic % selenium or tellurium had melted at 825 and 750°C, respectively. In both samples a lump of elemental platinum was present, indicating that during cooling platinum was primarily deposited from the melt. The melting point of the alloys with 44.44 atomic % Se and 50.00 atomic % Te was determined to be 1 055 ± 15 and 925 ± 15°C, respectively. Thus, the composition of the eutectic alloy lies between 33.33 and 44.44 atomic % Se in the platinum-selenium system and between 33.33 and 50.00 atomic % Te in the platinum-tellurium system. The alloys were black or grey in colour. When heated to 825°C and above the platinum tellurium alloys showed metallic lustre.

All samples were crushed and X-ray photographs taken in cameras with 114.6 mm effective diameter and asymmetric film mounting. X-Ray photographs were also taken in a Weissenberg camera with 57.3 mm diameter. X-Ray powder data on PtTe were obtained with a Guinier focusing camera of 80 mm diameter and strictly monochromatized Cu$K\alpha_1$ radiation. Guinier photographs of the $PtSe_{0.80}$-phase were taken in a Nonius camera of 114.6 mm diameter. Spectrometer diagrams were taken in a Philips Geiger spectrometer. For the calculation of lattice constants by the Guinier method, potassium chloride (Analar, The British Drug Houses Ltd. a = 6.2919 Å[21]) was added to the specimen as an internal standard. The lattice constant of the different samples of platinum was found by extrapolation according to the method of Nelson and Riley[22].

Lattice constants are expressed in Ångström units on the basis of $\lambda_{CuK\alpha_1} = 1.54050$ Å. Results from earlier investigations expressed in kX-units have been transformed to Å by multiplication by the factor 1.00202.

The density of the phases 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 from 2 to 3 g. The magnetic susceptibilities of the phases were 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 2 mm internal diameter and to a height of about 85 mm.

X-RAY RESULTS

A. Platinum sulfides

In agreement with the results by Biltz and Juza[8] only the PtS-phase and PtS_2-phase were found in the platinum sulfur system. The existence of the compounds Pt_2S_3 and Pt_5S_6, claimed by Schneider[3], was thus not confirmed.

The lattice constant of platinum was found to be 3.9234 Å in an alloy with 33.33 atomic % S, containing Pt and PtS in equilibrium. Within the limits of experimental error this value is equal to that of pure platinum, and indicates that sulfur is practically insoluble in solid platinum.

The PtS-phase. Powder photographs of the PtS-phase were indexed on the basis of a tetragonal unit cell, *cf.* Table 1. The lattice constants of the sample with composition $PtS_{1.00}$ are found in Table 2 together with the lattice constants of the PtS-phase in the samples $PtS_{0.90}$ and $PtS_{1.10}$, in which PtS is in equilibrium with Pt and PtS_2, respectively. As the lattice constants do not vary with composition, the homogeneity range of the PtS-phase is not noticeable. The only previous determinations, due to Bannister and Hey[4], are also given in Table 2. The accordance is very satisfactory.

The systematic missing reflections were of the type (hkl) absent when $l = 2n + 1$. The highest symmetric space group is thus $P4_2/mmc$ (D_{4h}^9).

Bannister and Hey[4] described the structure of PtS by means of a C-centered unit cell to bring out the relationships with the face-centered unit cell of platinum. In Table 1 the C-centered indices (HKL) are also listed. The corresponding extinctions are of the type (HKL) absent when $H + K = 2n + 1$ and $(H0L)$ absent when $H = 2n + 1$ and $L = 2n + 1$. The corresponding space group orientation is $C4/mcm$. By the transformation to the C-centered unit cell only the a-axis is changed, and

$$A = a\sqrt{2} \quad , \quad C = c$$

with numerical values

$$A = 4.9073 \text{ Å} \quad , \quad C = 6.1096 \text{ Å}$$

for $PtS_{1.00}$.

Table 1. Powder photograph data of PtS taken with Cu*K*-radiation, α_2 and β lines omitted.

$\sin^2\Theta \times 10^4$	*HKL*	*hkl*	I_{obs}	I_{calc}
493	110	100	1	0.9
—	002	002	37	1.1
651	111	101		40.2
987	200	110	5	7.9
1131	112	102	1	0.5
1627	202	112	13.5	14.6
1929	113	103	7.5	8.2
1976	220	200	5	5.3
—	221	201	0	0.00
—	310	210	0	0.1
2550	004	004	2	1.8
2612	222	202	13.5	3.5
2627	311	211		9.9
—	114	104	0	0.1
—	312	212	0	0.2
—	223	203	0	0.00
3533	204	114	2.5	2.1
3901	313	213	6	5.2
3947	400	220	2	1.7
—	330	300	0	0.03
4472	115	105	3	2.1
4521	224	204	3.5	2.8
4585	402	222	4	1.5
4599	331	301		2.1
—	420	310	0	0.05
—	314	214	0	0.1
—	332	302	0	0.05
—	421	311	0	0.00
5575	422	312	6	4.6
5727	006	006	0.1	0.3
5873	333	303	2	1.6
—	225	205	0	0.00
—	116	106	0	0.04
—	423	313	0	0.00
—	510	320	0	0.04
6442	315	215	4.5	3.2
6486	404	224	3.5	2.1
6573	511	321	4	3.2
6713	206	116	3.5	2.2
—	334	304	0	0.04
—	512	322	0	0.08
7473	424	314	3.5	2.5
7697	226	206	1.5	1.3
7840	513	323	4.5	3.7
7883	440	400	1.5	1.3
—	441	401	0	0.00
—	316	216	0	0.1
8284	117	107	3	2.1
—	530	410	0	0.05
8414	335	305	3	2.2
8524	442	402	6	1.6
8540	531	411		4.5
—	514	324	0	0.1
—	425	315	0	0.00
8875	600	330	1	0.9
—	532	412	0	0.1
—	443	403	0	0.00
9505.4	602	332	5	5.2
9664.8	406	226	3.5	3.4
—	227	207	0	0.00
9806.3	533	413	9	12.5
9854.1	620	420	9	11.0

Bannister and Hey based their structure determination on the intensities of a few reflections only. For this reason a new comparison of observed and calculated intensities of the reflections was carried out. In terms of the space group $P4_2/mmc$ (D_{4h}^9) the atomic arrangement in PtS is as follows:

2 Pt in (*c*) $0,\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$, and 2 S in (*e*) $0,0,\frac{1}{4}$; $0,0,\frac{3}{4}$.

The intensities of the reflections were calculated using the formula

$$I_{calc} = 10^{-5} \times |F|^2 \times Lp \times \nu$$

No corrections for absorption and temperature factors were thus applied. The observed intensities were obtained from photometer recordings and referred to a relative, absolute scale by making the sums of I_{obs} and I_{calc} equal. As can be seen from Table 1 the agreement between the two sets of values is very good, and leaves no doubt about the correctness of the proposed structure.

Table 2. Lattice constants of the PtS-phase.

Sample	a(Å)	c(Å)	Reference
$PtS_{0.90}$	3.4695	6.1087	Present
$PtS_{1.00}$	3.4700	6.1096	Present
$PtS_{1.10}$	3.4701	6.1089	Present
$PtS_{1.02}$ (Cooperite)	3.48	6.11	Bannister and Hey [4]
$PtS_{1.29}$ (Cooperite)	3.48	6.11	Bannister and Hey [4]
$PtS_{1.10}$ (Synthetic)	3.49	6.13	Bannister and Hey [4]
$PtS_{1.27}$ (Synthetic)	3.49	6.13	Bannister and Hey [4]

Table 3. Powder photograph data of PtS_2 taken with CuK-radiation, α_2 and β lines omitted.

$\sin^2 \Theta \times 10^4$	hkl	I_{obs}	I_{calc}
234	001	7	8.7
632	100	5.5	5.4
865	101	10.5	11.2
934	002	6.5	6.9
1565	102	5.5	5.8
1891	110	4.5	5.6
2124	003	3	0.4
	111		2.7
2525	200	1	0.7
2733	103	4	1.9
2759	201		1.9
2827	112	1	0.8
3463	202	1.5	1.6
3742	004	0.3	0.3
3997	113	1	1.3
4373	104	0.5	0.6
4418	210	0.5	0.6
4636	203	2.5	0.8
4654	211		1.7
5356	212	2	1.8
5630	114	1	1.1
5682	300	0.5	0.6
—	005	0	0.1
5915	301	1	0.6
6263	204	0.4	0.4
6476	105	0.5	0.7
6517	213	1.5	1.3
6608	302	0.3	0.3
7569	220	0.5	0.6
7732	115	0.5	0.7
7781	303	1	0.7
7802	221	1	0.7
8150	214	1	1.1
8194	310	0.5	0.5
8364	205	0.5	0.8
—	006	0	0.1
8431	311	2	1.8
8501	222	0.5	0.4
9042.1	106	1.5	1.4
9127.1	312	2.5	2.9
9410.0	304	2	2.3
9664.9	223	1.5	1.8

Table 4. Lattice constants of the PtS_2-phase.

Sample	a(Å)	c(Å)	Reference
$PtS_{1.50}$	3.543	5.040	Present
$PtS_{1.94}$	3.5431	5.0389	Present
$PtS_{2.00}$	3.5432	5.0388	Present
$PtS_{3.00}$	3.5428	5.0415	Present
$PtS_{1.94}$	3.544 ± 0.004	5.029 ± 0.005	Thomassen [6]
$PtS_{2.00}$	3.55	5.03	Bannister and Hey [4]

The interatomic distances are only slightly altered by the new data. Four sulfur atoms are arranged around each platinum atom at the corners of a rectangle (3.040 × 3.470 Å^2). The shortest interatomic distances are: platinum-sulfur 2.312 Å, sulfur-sulfur 3.040 and 3.470 Å, and platinum-platinum 3.470 and 3.907 Å.

The PtS_2-phase. Powder photographs of the PtS_2-phase were indexed as hexagonal, *cf.* Table 3. The lattice constants of $PtS_{2.00}$ are listed in Table 4 together with the lattice constants of the PtS_2-phase for the samples $PtS_{1.50}$ and $PtS_{3.00}$ in which PtS_2 is in equilibrium with PtS and S, respectively. In addition, a sample with 24.2 weight % sulfur, corresponding to the non-stoichiometric composition $PtS_{1.94}$, found for the PtS_2-phase by Thomassen [6] was prepared and examined. The lattice constants of this sample are listed in Table 4 together with previous lattice constant values by Thomassen [6] and Bannister and Hey [4]. The difference between the values for the *c*-axis in the samples $PtS_{2.00}$ and $PtS_{3.00}$ might indicate a narrow range of homogeneity for the PtS_2-phase.

The pycnometric densities of $PtS_{1.94}$ and $PtS_{2.00}$ at 25°C were found to be 7.80 and 7.83 g cm^{-3}, respectively, in close agreement with the density 7.86 g cm^{-3} calculated for $PtS_{2.00}$ from the X-ray data. Earlier values by Biltz and Juza [8] for samples with composition $PtS_{2.00}$ are about 2 % lower.

According to Thomassen the structure of PtS_2 is of the $Cd(OH)_2$-type. The space group is $P\bar{3}m1$ (D_{3d}^3) with

1 Pt in *(a)* 0,0,0 and 2 S in *(d)* $2/3,1/3,z;1/3,2/3,\bar{z}$.

Thomassen obtained good agreement between I_{obs} and I_{calc} using the parameter value $z = 1/4$. In order to check the parameter value intensities were calculated for $z = 0.240$, 0.245, 0.250, 0.255 and 0.260. The value $z = 0.250$ gives indeed the best agreement between I_{obs} and I_{calc}. The corresponding calculated intensities are listed in Table 3 together with the observed ones.

The interatomic distances are only slightly altered by the new lattice constant values. Each platinum atom is surrounded octahedrally by six sulfur atoms at the distance 2.402 Å. The twelve shortest sulfur-sulfur distances are 3.245 Å and the six shortest platinum-platinum distances are 3.543 Å.

B. Platinum selenides

In the platinum-selenium system two intermediate phases, the $PtSe_{0.80}$-phase and the $PtSe_2$-phase, were identified. This is in accordance with earlier results if the $PtSe_{0.80}$-phase is identified with the monoselenide described by Roessler [11]. The existence of $PtSe_3$, claimed by Minozzi [12], could not be confirmed.

The lattice constant of platinum was found to be 3.9233 Å in an alloy with 33.33 atomic % Se, in which Pt is in equilibrium with $PtSe_{0.80}$. This indicates that selenium is practically insoluble in solid platinum.

The $PtSe_{0.80}$-phase. Powder photographs of different samples of PtSe and $PtSe_{0.909}$ contain some of the strongest reflections from the $PtSe_2$-phase, while powder photographs of $PtS_{0.50}$, $PtSe_{0.667}$ and $PtSe_{0.70}$ contain reflections from pure platinum. The additional reflections are very weak on photographs of samples with composition $PtSe_{0.75}$ and $PtSe_{0.85}$ and are absent on photographs of samples with composition $PtSe_{0.80}$. Thus the composition of the phase is provisionally designated $PtSe_{0.80}$. As the specific volume turned out to be an approximately linear function of atomic % Se in the whole concentration range from 0 to 66.67 atomic % Se, density determinations alone could not be used for an accurate determination of the composition of the phase.

Since no unit cell fitting all lines on the complex powder photographs could be found, it was tried to isolate crystallites large enough for single crystal work. After several unsuccessful attempts, a fairly useful fragment of a crystal was obtained. Oscillation photographs contained reflections from several crystals and traces of powder lines. By means of Weissenberg photographs the crystal was found to exhibit monoclinic symmetry and these photographs also gave the approximate cell dimensions. The Guinier photographs could then be indexed as shown in Table 5.

The lattice constants of the $PtSe_{0.80}$-phase in the samples $PtSe_{0.70}$, $PtSe_{0.75}$, $PtSe_{0.80}$ and $PtSe_{0.85}$, annealed at 850°C, are listed in Table 6. The slight

Table 5. Guinier powder photograph data of $PtSe_{0.80}$ taken with Cu*K*α-radiation.

I_{obs}	$\sin^2 \Theta \times 10^4$		*hkl*
	obs	calc	
vw	143.2	143.0	100
m	199.1	199.4	002
w	273.9	274.6	$10\bar{2}$
vw	327.3	327.8	011
w	409.5	410.2	102
w	420.7	420.9	110
w	477.2	476.8	012
m	505.1	504.7	111
st	552.5	552.5	$11\bar{2}$
vw	571.1	572.0	200
vw	636.2	635.8	$20\bar{2}$
st	688.1	688.1	112
vw	726.9	726.6	013
st	767.9	767.9	$11\bar{3}$
vw	798.4	797.8	004
vw	806.0	805.2	$10\bar{4}$
st	831.7	832.0	$21\bar{1}$
st	849.4	849.9	210
m	913.2	913.7	$21\bar{2}$
m	968.1	967.6	211
m	972.2	971.3	113
w	1075.9	1075.7	014
		1076.4	104
w	1082.9	1083.1	$11\bar{4}$
vw	1097.1	1095.3	$21\bar{3}$
		1098.7	$20\bar{4}$
vw	1255.2	1254.6	120
w	1283.6	1283.1	$30\bar{2}$
		1287.0	300
w	1355.1	1354.3	114
vw	1377.4	1376.6	$21\bar{4}$
vw	1387.5	1386.2	$12\bar{2}$
vw	1497.5	1498.2	$11\bar{5}$
w	1525.6	1524.4	015
w	1562.0	1561.0	$31\bar{2}$
		1564.9	310
w	1602.3	1601.6	$12\bar{3}$
vw	1663.4	1665.7	$22\bar{1}$
st	1679.2	1678.1	$30\bar{4}$
st	1688.5	1683.6	220
		1689.7	302
vw	1714.4	1716.5	311
vw	1755.9	1757.5	$21\bar{5}$
m	1796.1	1795.0	006
m	1803.1	1801.3	221
		1805.0	123
m	1917.1	1916.8	$12\bar{4}$
		1918.8	214
vw	2186.1	2188.0	124
w	2212.3	2210.3	$22\bar{4}$
		2216.3	$40\bar{2}$
w	2236.4	2238.2	$21\bar{6}$
vw	2289.3	2288.0	400
vw	2437.8	2435.3	215
m	2475.5	2472.0	$30\bar{6}$
m	2492.4	2491.5	304
m	2552.2	2550.2	321

Table 6. Lattice constants of the $PtSe_{0.80}$-phase.

Sample	a(Å)	b(Å)	c(Å)	β (°)
$PtSe_{0.70}$	6.5812	4.6255	11.147	78.39
$PtSe_{0.75}$	6.5812	4.6252	11.148	78.39
$PtSe_{0.80}$	6.5806	4.6248	11.145	78.40
$PtSe_{0.85}$	6.5805	4.6244	11.144	78.41

variations in unit cell dimensions indicate that the homogeneity range of the phase is rather narrow.

The $h0l$ reflections are absent when $l = 2n + 1$. The probable space group is thus Pc (C_s^2) or $P2/c$ (C_{2h}^4).

The density of $PtSe_{0.80}$ was determined to be 12.79 g cm^{-3}. This corresponds to 9.91 Pt and 7.93 Se atoms in the unit cell. If the composition of the phase was assumed to be $PtSe_{0.75}$, the observed density 12.92 g cm^{-3} would give a cell content of 10.18 Pt and 7.64 Se atoms, and for $PtSe_{0.85}$ with observed density of 12.41 g cm^{-3}, 9.47 Pt and 8.05 Se atoms. As the probable space groups Pc and $P2/c$ only have four-fold and two-fold point symmetry, a composition $Pt_{10}Se_8$ seems most reasonable. The calculated density for $Pt_{10}Se_8$ from the X-ray measurements is 12.90 g cm^{-3}.

Samples with composition $PtSe_{0.80}$, heated at 400°C for two months, gave diffuse X-ray photographs indicating some sort of disorder in the structure. The annealing time was probably not sufficiently long to establish equilibrium at that temperature.

Heat treatment at 1 050 and 1 150°C of the samples $PtSe_{0.667}$, $PtSe_{0.70}$, $PtSe_{0.75}$, $PtSe_{0.80}$, $PtSe_{0.85}$ and $PtSe_{0.909}$ indicates that the $PtSe_{0.80}$-phase is formed peritectically, as the X-ray photographs show presence of considerable amounts of Pt and $PtSe_2$.

The $PtSe_2$-phase. Powder photographs of $PtSe_2$ were indexed as hexagonal, *cf.* Table 7. The lattice constants of $PtSe_{2.00}$ are listed in Table 8 together with the lattice constants of $PtSe_{1.50}$ and $PtSe_{3.00}$. From these values the homogeneity range of the $PtSe_2$-phase is not noticeable. In the quenched $PtSe_{1.00}$-sample, however, the c-axis of the $PtSe_2$-phase has a smaller value, indicating a slight change in composition of the $PtSe_2$-phase with temperature. The only previous lattice constant determination of $PtSe_2$, due to Thomassen [6] is also listed in Table 8. The values agree best with those for the quenched sample.

The pycnometric density of $PtSe_2$, 9.53 g cm^{-3}, is in close agreement with the density 9.59 g cm^{-3} calculated on the basis of the X-ray data.

Thomassen found that $PtSe_2$ was isostructural with PtS_2. In order to verify the parameter value, intensities were calculated in the same way as for PtS_2. Also here the parameter value $z = 0.250$ gives the best agreement, I_{obs} and I_{calc}, *cf.* Table 7.

The corresponding interatomic distances are: platinum-selenium 2.499 Å, selenium-selenium 3.330 Å and platinum-platinum 3.728 Å.

Table 7. Powder photograph data of PtSe$_2$ taken with Cu*K*-radiation, α_2 and β lines omitted.

$\sin^2 \Theta \times 10^4$	*hkl*	I_{obs}	I_{calc}
230	001	7	9.0
570	100	3	3.1
800	101	17	17.0
—	002	0	0.1
1492	102	8.5	8.9
1710	110	6	6.1
1941	111	3.5	3.0
2074	003	0.5	0.5
2283	200	0.5	0.4
2510	201	3	2.9
—	112	0	0.1
2643	103	3	2.6
3200	202	3	2.5
3682	004	0.5	0.6
3780	113	1.5	1.0
3988	210	0.5	0.4
4220	211	2.5	2.4
4240	104	0.5	0.3
4353	203	1.5	1.2
4904	212	3	2.7
5122	300	1	1.0
5363	301	1	0.7
5389	114	2.5	2.0
—	005	0	0.1
5961	204	0.2	0.2
6060	213	2	1.7
	302		0.03
6318	105	1	0.8
6836	220	1	0.9
7064	221	0.5	0.6
7195	303	1	0.6
7406	310	0.3	0.3
7456	115	0.5	0.7
7630	311	2	1.9
7666	214	0.3	0.5
—	222	0	0.1
8024	205	1	1.0
—	006	0	0.01
8323	312	3	3.0
8800	304	2.5	2.9
8842	106	1.5	1.8
8899	223	1.5	1.0
9108	400	0.2	0.2
9337.8	401	1.5	1.8
9468.3	313	3	3.9
9729.2	215	3.5	5.5

Table 8. Lattice constants of the PtSe$_2$-phase.

Sample	*a*(Å)	*c*(Å)	Reference
PtSe$_{1.50}$	3.7279	5.0808	Present
PtSe$_{2.00}$	3.7278	5.0813	Present
PtSe$_{3.00}$	3.7283	5.0812	Present
PtSe$_{1.00}$ (quenched)	3.7279	5.0722	Present
PtSe$_{2.00}$	3.732 ± 0.004	5.072 ± 0.004	Thomassen [6]

C. Platinum tellurides

In the system platinum-tellurium the existence of two of the earlier reported intermediate phases, *i.e.*, the PtTe-phase and the PtTe$_2$-phase, was confirmed. A phase with composition Pt$_2$Te, described by Roessler [14], was not found.

The lattice constant of platinum was found to be 3.9234 Å in an alloy with 33.33 atomic% Te, in which Pt exists in equilibrium with PtTe. Evidently, platinum does not dissolve any appreciable amounts of tellurium.

The PtTe-phase. Samples with the composition PtTe, heated at 825°C for 30 days, give powder photographs containing very few lines. In order

Table 9. Guinier powder photograph data of PtTe taken with strictly monochromatized Cu$K\alpha_1$-radiation.

I_{obs}	$\sin^2 \Theta \times 10^4$		hkl
	obs	calc	
st	135.5	135.6	100
vw	168.2	168.5	002
vw	187.1	186.7	010
vw	305.2	304.0	102
vw	378.0	379.2	003
w	517.9	514.7	103
w	541.8	542.4	200
w	563.2	565.9	013
w	727.8	729.1	210
st	747.1	747.1	020
m	1243.7	1240.7	015
vw	1295.4	1289.5	220
vw	1425.8	1421.4	024
m	1459.8	1458.0	222
vst	1517.2	1517.2	006
m	1649.6	1652.7	106
vw	2010.8	2009.7	321
w	2055.3	2055.0 2059.6 2060.2	007 206 033
vw	2080.5	2081.5	314
vw	2169.7	2169.7	400
m	2261.1	2264.3	026
m	2339.0	2338.3	402
st	2986.6	2988.4	040
w	3392.1	3390.2	500
m	3577.7	3575.7	334
vw	3686.4	3686.9	406
st	3773.8	3769.5	503
w	3848.2	3850.6	430
m	4253.5	4251.2	514
m	4507.9	4505.6	046
m	4538.5	4536.8	1,1,10
vw	4672.8	4669.4	050

to grow single crystals, the samples were heated to a temperature just below the melting point, 925 ± 15°C. After many trials some crystals with platy, hexagonal habit were obtained. When slowly cooled to room temperature these crystals disintegrated to a powder after some time. In quenched samples the crystals retained their habit at room temperature. Oscillation photographs of the crystals gave only powder lines, some times with preferred orientation. A possible explanation of these phenomena might be sought in a phase transition.

In order to determine the unit cell dimensions of the unknown structure powder photographs were taken in a Guinier focusing camera of high resolution. Using the Lipson [23] method the unit cell of PtTe could be indexed as orthorhombic, *cf.* Table 9. The lattice constants of PtTe and of the PtTe-phase in the samples $\text{PtTe}_{0.90}$ and $\text{PtTe}_{1.10}$, in which it exists in equilibrium with Pt or PtTe_2, respectively, are listed in Table 10. The slight variations in unit cell dimensions between the three samples indicate that the homogeneity range of the PtTe-phase is rather narrow. The reflections observed in the powder photographs show that the unit cell is primitive.

Table 10. Lattice constants of the PtTe-phase.

Sample	a(Å)	b(Å)	c(Å)
$\text{PtTe}_{0.90}$	6.6132	5.6351	11.858
$\text{PtTe}_{1.00}$	6.6144	5.6360	11.865
$\text{PtTe}_{1.10}$	6.6157	5.6369	11.869

On the basis of the observed density, 12.01 g cm^{-3}, the unit cell contains ten platinum and ten tellurium atoms. The calculated density for $Pt_{10}Te_{10}$ from the X-ray measurements is 12.11 g cm^{-3}.

The pronounced orientation effects observed for the PtTe-phase in form of variable intensities for some of the reflections indicate that it must have a typical layer structure. Thus, the same powder sample as was used for the Guinier photographs gave pronounced enforcements of the ($h00$) reflections ($h = 1, 2, 4$ and 5) when using a Geiger spectrometer. In contrast to this, a sample of PtTe that had been melted, formed mica-like flakes, which mounted on a glass plate gave a Geiger-spectrogram with ($00l$) reflections only ($l = 1, 2, 3, 4, 6, 7$, and 9). The direction of cleavage therefore seems to change as result of melting.

These preliminary results about the structure of PtTe are not consistent with earlier statements. Both Hume-Rothery [24] and Zhdanov and Gladoleva [25], list PtTe among substances having NiAs-type structure. Apparently, no structure determination of PtTe has been made before 1955 when Groeneveld Meijer [19] interpreted the X-ray photograph of niggliite as due to a phase with NiAs-like structure and composition PtTe. It should, however be remarked, that neither Thomassen [6] nor Groeneveld Meijer [17,19] succeeded in

Table 11. Powder photograph data of $PtTe_2$ taken with CuK-radiation, α_2 and β lines omitted.

$\sin^2 \Theta \times 10^4$	hkl	I_{obs}	I_{calc}	$\sin^2 \Theta \times 10^4$	hkl	I_{obs}	I_{calc}
218	001	6	9.5	5935	105	2	1.3
488	100	1	1.5	6079	221	1	0.6
708	101	19.5	30.2	—	310	0	0.1
—	002	0	0.1	6356	303	1	0.6
872	200	1	0.7	6567	311	3	2.6
1366	102	13.5	14.2	—	222	0	0.04
1466	110	10	12.3	—	214	0	0.2
1688	111	3.5	3.8	6908	115	1	0.6
1966	003	0.5	0.5	7221	312	4	3.3
2175	201	5.5	5.6	7398	205	2.5	1.4
—	112	0	0.1	—	400	0	0.1
2453	103	5	4.6	7822	223	1	0.7
2829	202	3.5	4.3	—	006	0	0.01
—	210	0	0.2	7879	304	5.5	3.5
3429	113	1.5	1.2	8030	401	2	1.6
3486	004	1.5	1.0	8306	313	6	3.4
3641	211	4.5	4.7	8329	106		2.1
3914	203	3.5	4.2	8684	402	3	2.3
—	104	0	0.1	8862	215	5.5	4.1
4292	212	4	4.4	—	320	0	0.2
4400	300	1.5	2.1	—	116	0	0.1
4620	301	1	0.8	9340.7	224	8	6.2
4956	114	4.5	3.6	9492.8	321	6.5	6.1
—	302	0	0.04	9766.5	403	5	4.4
5382	213	3	2.8	9787.9	206	6.5	5.7
—	204	0	0.1	9834.7	314	3.5	0.8
—	005	0	0.1		305		2.5
5865	220	1.5	1.6				

Table 12. Lattice constants of the $PtTe_2$-phase.

Sample	a(Å)	c(Å)	Reference
$PtTe_{1.50}$	4.0261	5.2212	Present
$PtTe_{2.00}$	4.0259	5.2209	Present
$PtTe_{2.10}$	4.0267	5.2221	Present
$PtTe_{3.00}$	4.0269	5.2224	Present
$PtTe_{2.00}$	4.018 ± 0.004	5.212 ± 0.005	Thomassen[6]
$PtTe_{2.00}$	4.010	5.201	Groeneveld Meijer[17]

synthesizing any other platinum telluride phases than the ditelluride, and that the monotelluride reported here gives a completely different X-ray picture from that of niggliite. Nevertheless, a PtTe-phase with NiAs-like structure might possibly exist at higher temperatures, and thus explain the observed hexagonal habit of the crystals.

The $PtTe_2$-phase. The lattice constants of the hexagonal $PtTe_2$-phase were redetermined. The results of the X-ray measurements are given in Table 11 and the lattice constant values are listed in Table 12 for samples of various compositions. The homogeneity range of the phase is apparently narrow, and slightly on the tellurium-rich side of the composition $PtTe_2$. The previous determinations by Thomassen[6] and Groeneveld Meijer[17], also given in Table 12, differ to some extent from the values found here for the $PtTe_2$-phase.

The observed density, 10.16 g cm^{-3}, is in close agreement with the density 10.20 g cm^{-3} calculated assuming one platinum and two tellurium atoms in the unit cell.

According to Thomassen, $PtTe_2$ is isostructural with PtS_2 and $PtSe_2$. In order to verify the parameter value, intensities were calculated in the same way as for PtS_2 and $PtSe_2$. Here too, the parameter value $z = 0.250$ gives the best agreement between I_{obs} and I_{calc}, *cf.* Table 11.

The shortest interatomic distances are: platinum-tellurium 2.666 Å, tellurium-tellurium 3.495 Å and platinum-platinum 4.026 Å.

Table 13. Magnetic susceptibilities of the platinum chalcogenides, $\chi_g \times 10^6$.

Compound	Temperature °C						Induced diamagnetism
	−183	−78	20	150	300	450	
PtS		−0.14	−0.14	−0.13	−0.14	−0.14	−0.26
PtS_2	−0.28	−0.28	−0.28	−0.28	−0.28	−0.28	−0.36
$PtSe_{0.80}$		−0.12	−0.12	−0.11	−0.11	−0.10	−0.25
$PtSe_2$	−0.12	−0.12	−0.13	−0.13	−0.13	−0.13	−0.35
PtTe		−0.13	−0.13	−0.12	−0.12	−0.12	−0.30
$PtTe_2$	−0.05	−0.05	−0.05	−0.05	−0.05	−0.05	−0.37

Table 14. The field strength dependent susceptibilities of PtS, $PtSe_{0.80}$ and PtTe, $\chi_g \times 10^6$, at liquid air temperature.

H_{max} (Ø)	PtS	$PtSe_{0.80}$	PtTe
4 015	0.20	0.10	0.02
4 700	0.16	0.08	0.01
5 110	0.14	0.06	0.01

MAGNETIC PROPERTIES OF THE PLATINUM CHALCOGENIDES

The magnetic susceptibilities of PtS, PtS_2, $PtSe_{0.80}$, PtTe and $PtTe_2$ were measured at six different temperatures between — 183 and 450°C. The results are listed in Table 13. With three exceptions they are mean values of the susceptibilities at three different field strengths (H_{max} = 4 015, 4 700 and 5 110 Ø, respectively).

The measured susceptibilities are all exceedingly low and almost balanced by the diamagnetism induced in the compounds. The diamagnetic corrections are -27.3×10^{-6} per mole Pt° according to Hoare and Matthews[26], -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[27]. The corrections are listed for one gram of the compounds in the far right column of Table 13. By subtracting these values from the measured susceptibilities, the susceptibilities of the paramagnetic ions are obtained. These corrected susceptibilities increase from sulfide *via* selenide to telluride both for the di- and »mono»-compounds in accordance with the more metallic behavior of the tellurides.

The effective magnetic moments, ranging from 0.11 to 0.91 Bohr magnetons, show that the compounds are of an essentially metallic or covalent type. In case the bonds had been of ionic type, the »spin only» theory demands a magnetic moment of 2.83 μB for compounds containing the Pt^{2+}-ion and 4.90 μB for compounds containing the Pt^{4+}-ion.

The only irregularities observed are that the susceptibilities of all three »mono»-compounds are slightly field strength dependent at liquid air temperature, *cf.* Table 14. Similar effects, but of a much larger magnitude, have earlier been observed for the palladium chalcogenides Pd_4S, Pd_4Se and Pd_4Te[28].

Acknowledgements. The authors wish to thank Falconbridge Nikkelverk A/S for placing platinum metal at their disposal and to thank Bolidens Gruvaktiebolag for the selenium. They also wish to express their thanks to Dr. Arne Magnéli, Stockholms Høgskola, Sweden, for taking Guinier photographs of PtTe, to Siv.ing. Sigurd Rutlin, Sentralinstitutt for Industriell Forskning, for carrying out the spectrographic analysis and to Mr. Håkon Mohn for carrying out some of the magnetic measurements.

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Received April 9, 1960.