Palladium and Platinum Phosphochalcogenides—Synthesis and Properties*

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Three new PdP_yS_{2-y} $(0 < y \leqslant 1)$ compounds have been prepared between the known end members, PdP_2 and PdS_2, as well as certain selenide isotypes. The semiconductors, PdPS (orthorhombic, $P2_1ca$ or $Pmca$) and PdPSe, were obtained from the elements by reaction at autogenous pressure. The metallic, pyrite-type compounds $PdP_{0.67}S_{1.33}$ and $PdP_{0.59}Se_{1.41}$, as well as a second metallic type phase of approximate composition $PdP_{0.33}S_{1.67}$, were prepared under high pressure in a tetrahedral anvil device. The unrelated thiophosphate $Pd_3(PS_4)_2$ (trigonal, $P\bar{3}m1$) was also obtained at autogenous pressure. The crystal structure of this semiconductor was solved by refinement of X-ray powder intensity data using trial and error methods. Reactivity was much lower in the related Pt systems and only substitution of small amounts of S for P in pyrite-type PtP_2 was observed.

Introduction

Ternary pnictide chalcogenides MZX of the d^{6-8} transition metals have been studied by Hulliger (1-3), Hahn and Klingen (4), and Banus and Lavine (5). Essentially the complete series of phosphosulfides and selenides for the d^6 iron group, i.e., the semiconducting arsenopyrite-type compounds FePX, RuPX, and OsPX (X = S, Se), and for the d^7 cobalt group, i.e., the semiconducting pyrite-type compounds CoPS, RhPS, and IrPS as well as the pyrite-related ullmannite-type compounds RhPSe and IrPSe, are reported. Of the possible d^8-nickel group phosphosulfides and selenides, however, only the metallic pyrite-type compound NiPS is described. In contrast, pyrite- or ullmannite-type arsenic, antimony, and bismuth sulfides and selenides of both palladium and platinum form readily (1), i.e., PdAsS, PdAsSe, PdSbS, PdSbSe, PdBiSe, PtAsS, PtSbS, PtSbSe, etc. In view of this discrepancy, it was of interest to investigate the reactivity of Pd and Pt with P plus S or Se under a wide range of reaction temperatures and pressures in an effort to obtain further information on this series of compounds.

Experimental Section

Preparation of Compounds

Reactions were carried out at autogenous to 3 kbar pressure in sealed and evacuated silica tubes,

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or at pressures of 20–65 kbar in a tetrahedral anvil device of National Bureau of Standards design (6). Sealed-tube reactions at autogenous pressure were run in a unit capable of being heated to 1100°C and pressured to 200 atm with argon to act as a back-up to prevent rupture of the silica tubes from internally developed pressure. At 3 kbar pressure, reactions were also run in sealed, evacuated silica tubes in a bomb pressured with argon and capable of being internally heated by a platinum resistance furnace to a temperature of about 1400°C. The silica flowed around the sample, thus allowing transmittal of this higher pressure. The high-pressure runs were made in boron nitride crucibles. The operating procedures and calibration points for the tetrahedral anvil have been described previously (7).

Reactants (>99.99% pure) in elemental form were ground together and pelleted prior to reaction. Depending upon reactant densities, pellets charged in anvil reactions weighed about 0.5–1 g. and those in sealed-tube reactions about 0.5–2 g. Heating cycles were as follows: (1) 20–65 kbar pressure/heat 2 hr at 1000–1200°C/cool 4 hr to 400°C/quench; (2) 3 kbar pressure/heat 2 hr at 1200°C/cool 4 hr to 400°C/heat off; and (3) autogenous pressure/heat 2 hr at 900°C/cool 3 hr to 600°C/heat off. Impurities in the reaction products such as sulfur and unstable phosphorus sulfides and selenides were removed by an initial extraction with CS_2 followed by treatment with warm water or water–acetone mixtures. An

ultrasonic bath was used to aid in dispersing the impurities for subsequent decantation. Products were then air dried following a final acetone treatment.

Analytical

Following digestion of the phosphochalcogenides with an oxidizing acid, palladium was determined by the standard dimethylglyoxime precipitation technique. A sodium peroxide-Parr bomb fusion was used to convert S and P in these materials to sulfate and phosphate. Palladium was removed from the acidified oxidation products with an ion-exchange resin. Sulfur was then determined as $BaSO_4$ and phosphorus by the ammonium phosphomolybdate procedure.

Density measurements were made on 10–100 mg of solid sample pieces by a liquid displacement technique using bromoform.

X-Ray Data

Single-crystal data were obtained from precession photographs. X-Ray powder diffraction patterns were taken at 25°C with a Debye–Scherrer camera or a Hagg–Guinier camera which used monochromatic CuK_{α_1} radiation and a KCl internal standard ($a = 6.2931$ Å). Films were read on a David Mann film reader, model No. 1222. Cell dimensions were refined by a least-squares method and showed a standard deviation of ±0.001 Å or less.

Electrical and Optical Measurements

Electrical resistivity was measured on single crystals using a four-probe technique. Activation energy of resistivity, E_a, is defined by the relation $\rho = \rho_0 e^{E_a/kT}$.

The optical band gap of some of the phosphosulfides was determined from absorbance measurements made on thin (25–35 μ) single-crystal platelets with a Cary 14 Spectrophotometer over the wavelength range 0.2–2 μ. The index of refraction of PdPS could be adventitiously derived from one such measurement in which a periodic variation of transmission with wavelength occurred because of interference between directly transmitted light and that internally reflected from the fairly smooth, plane-parallel crystal platelet faces.

Results

PdPS

With an atom ratio of reactants of Pd:P:S = 1:1:1, the compound PdPS was obtained essentially as single-phase material at reaction pressures ranging from autogenous to 65 kbar. Crystals were usually in the form of silvery, laminar platelets, but small parallelepipeds were also isolated from some runs at autogenous pressure. The compound PdPS mixed with other Pd phosphosulfides was also obtained from reaction charges of Pd:P:S = 1:1:>2 that were heated at pressures below 40 kbar. It was not observed to form when these same reaction charges rich in sulphur were heated at 600–1200°C and a pressure of 65 kbar.

Elemental analyses were made on crystals prepared at 65 kbar/1200°C. Analyses calculated for PdPS: Pd, 62.80; P, 18.28; S, 18.92. Found: Pd, 60.92; P, 17.80; S, 20.31. This compound was stable to about 800°C when heated in an argon atmosphere.

Single crystal X-ray data indicated PdPS to have orthorhombic symmetry in space group $P2_1ca$ or $Pmca$. Cell dimensions $a = 5.693$, $b = 13.305$, and $c = 5.678$ Å were obtained by refinement of Guinier X-ray powder data (Table I). A unique composition is indicated by the fact that these same cell dimensions were obtained on products prepared throughout the pressure range autogenous to 65 kbar. In addition, variations in the ratio of starting materials, which still gave this orthorhombic phase as one of the reaction products, led to no variation in these cell dimensions. Crystals had a measured density of 5.13 g/cm^3; the calculated density for eight formula weights of PdPS per unit cell is 5.22 g/cm^3.

Four-probe resistivity measurements on single-crystal PdPS showed it to be a semiconductor with resistivities $\rho_{298°K}$ 9 × 10^7 and $\rho_{425°K}$ 3 × 10^4 ohm-cm, and an activation energy of resistivity, E_a, of 0.7 eV. From optical transmission measurements on a crystal platelet, a band edge near 0.9μ was observed, indicating an optical band gap, ΔE, of about 1.38 eV. The geometry of the crystal used in this optical measurement was such that the refractive index, n, of PdPS could be determined from the same data. A value of n between 3.1 and 3.6 was calculated. Magnetic susceptibility measurements showed PdPS to be diamagnetic.

PdPSe

With an atom ratio of reactants of Pd:P:Se = 1:1:1, the compound PdPSe was isolated at reaction pressures ranging from autogenous to 20 kbar. Silvery, blade-like crystals were obtained. Traces of PdPSe were also observed in products prepared at 45 kbar pressure, but not in those heated at 1000–1200°C and 65 kbar pressure. Analyses calculated for PdPSe: Pd, 49.18; P, 14.32. Found: Pd, 49.94, 49.96; P, 15.11, 15.18.

TABLE I
X-Ray Diffraction Powder Patterns of PdPX

h k l	PdPS d_{obs}	I/I_0	PdPSe d_{obs}	I/I_0	$PdPS_{0.67}Se_{0.33}$ d_{obs}	I/I_0
0 2 0	6.6500	5	--	--	6.7350	15
0 1 1	5.2171	15	--	--	5.2507	5
1 2 0	--	--	--	--	4.4208	5
1 1 1	3.8465	100	3.9515	55	3.8858	75
---	--	--	--	--	3.7416	5
0 3 1	--	--	3.5680	20	--	--
1 2 1	3.4413	20	--	--	3.4689	30
0 4 0	3.3250	15	3.3980	100	3.3684	100
1 3 1	2.9773	5	3.0475	10	3.0010	25
2 0 0	2.8443	5	--	--	--	--
0 0 2	2.8380	50	2.9131	55	2.8528	80
2 1 0	2.7826	75	2.8621	60	2.8014	50
0 5 0	--	--	2.7127	30	2.7000	40
2 2 0	2.6167	5	2.6932	20	--	--
1 4 1	--	--	2.6199	35	2.5949	10
2 1 1	2.4981	50	--	--	2.5252	25
1 1 2	2.4948	50	2.5633	65	--	--
2 3 0	2.3975	10	2.4571	25	2.4156	25
1 2 2	2.3739	5	--	--	--	--
2 3 1	--	--	2.2653	35	--	--
1 5 1	--	--	--	--	2.2389	35
0 4 2	2.1591	10	2.2103	25	2.1764	35
2 4 1	--	--	2.0697	2	--	--
2 0 2	2.0099	10	--	--	2.0191	20
2 1 2	1.9873	75	2.0407	30	1.9999	25
2 5 0	--	--	1.9895	10	--	--
0 5 2	--	--	--	--	1.9529	15
3 0 0	--	--	1.9497	5	--	--
3 1 0	--	--	--	--	1.8912	10
1 5 2	--	--	1.8795	50	--	--
2 5 1	--	--	--	--	1.8616	20
2 3 2	1.8310	5	--	--	1.8434	25
1 1 3	1.7798	75	1.8263	40	1.7892	40
2 6 0	--	--	--	--	1.7715	60
0 3 3	--	--	1.7843	85	1.7487	70
3 2 1	1.7376	50	--	--	--	--
1 2 3	1.7341	20	--	--	--	--
1 6 2	--	--	1.7089	15	--	--
3 3 1	--	--	--	--	1.6784	5
1 3 3	1.6648	2	--	--	--	--
2 5 2	--	--	1.6427	5	--	--
3 0 2	1.5777	15	1.6218	15	--	--
3 1 2	--	--	1.6098	15	--	--
2 1 3	1.5648	2	--	--	--	--
1 8 1	--	--	1.5693	15	--	--
2 6 2	1.4895	2	1.5249	20	--	--
---	--	--	--	--	1.5126	5
2 3 3	--	--	--	--	1.4951	5
4 0 0	1.4235	2	1.4643	5	--	--
0 0 4	1.4194	5	--	--	--	--
4 2 0	--	--	1.4311	20	1.4036	15
1 9 1	--	--	1.4155	15	--	--
3 5 2	--	--	1.3914	5	--	--
0 7 3	--	--	1.3731	5	--	--
0 3 4	--	--	--	--	1.3582	2
1 3 4	--	--	1.3475	5	--	--
3 2 3	1.3138	20	--	--	1.3215	5
2 0 4	--	--	1.3041	5	1.2761	5
1 4 4	1.2725	5	--	--	--	--
4 1 2	1.2665	10	--	--	--	--
2 1 4	1.2646	15	--	--	--	--
1 5 4	--	--	1.2541	5	--	--

The Debye–Scherrer X-ray diffraction powder pattern of PdPSe (Table I) could be indexed on the basis of an orthorhombic unit cell with $a = 5.856$,

$b = 13.569$, and $c = 5.824$ Å. As with PdPS, variations in both reaction pressures and the ratio of starting materials, which still gave this phase as one of the reaction products, led to no variation in equivalent d values in the X-ray diffraction patterns. The similarity in the powder patterns of PdPS and PdPSe suggests that these two compounds are isotypic. A structure determination will be done on PdPSe.

Four-probe resistivity measurements on single-crystal PdPSe showed it also to be a semiconductor with resistivities $\rho_{60°K}$ 4×10^3, $\rho_{300°K}$ 30, and $\rho_{400°K}$ 1 ohm-cm, and an activation energy of resistivity, E_a, of 0.15 eV over the temperature range 300–400°K.

$PdPS_xSe_{1-x}$

Reactions of Pd:P:S:Se in 1:1:0.75:0.25; 1:1:0.5:0.5, and 1:1:0.25:0.75 atom ratios at 20 kbar/1000°C gave similar products comprising silvery, blade-like crystals. Like PdPSe, these quaternaries also had X-ray diffraction powder patterns that appeared to be isotypic with that of PdPS and the majority of their reflections could be indexed on the basis of orthorhombic unit cells similar to those of PdPS and PdPSe, i.e., $a = 5.738$–5.788, $b = 13.499$–13.544, and $c = 5.698$–5.770 Å. The diffraction pattern for a phase of approximate composition $PdPS_{0.67}Se_{0.33}$ is listed (Table I).

$PdP_{0.67}S_{1.33}$

In contrast to the formation of PdPS at 1000–1200°C/65 kbar from an atom ratio of Pd:P:S = 1:1:1, a change in reactants so that the ratio of S:P is greater than unity gives, under the same high-pressure conditions, several new phases including silvery crystals of a pyrite-type compound $PdP_{0.67}S_{1.33}$. An essentially unique composition for this latter product is suggested by the fact that the same cell dimension, $a = 5.844$ Å (Table II), was obtained on products prepared from a range of starting materials in which the charge ratio of S:P varied from 1.5:1 to 3:1 and the charge ratio of Pd:P varied from 1.5:1 to 1:1. Analytical and density data confirmed the approximate nonstoichiometric composition $PdP_{0.67}S_{1.33}$, in contrast to the stoichiometric pyrite-type phase PdPS hypothesized in the literature (I). Analyses were obtained upon small lots of crystals isolated from runs prepared from the following atom ratios of the elements: Pd:P:S = (a) and (b) 1:1:2, (c) 1:1:1.5, (d) 1:0.67:1.33. The data indicate a S:P ratio of 2:1 in the pyrite phase. Analyses calculated for pyrite-type $PdP_{0.67}S_{1.33}$ with $a = 5.844$ Å; P, 12.17; S,

TABLE II

X-Ray Diffraction Powder Patterns of PdP_yX_{2-y} Pyrite-Type Phases

h k l	$PdP_{0.67}S_{1.33}$		$PdP_{0.59}Se_{1.41}$	
	d_{obsd}	I/I_0	d_{obsd}	I/I_0
1 1 1	3.3870	85	3.4938	35
2 0 0	2.9315	90	3.0269	100
2 1 0	2.6204	45	2.7071	70
2 1 1	2.3913	45	2.4711	70
2 2 0	2.0702	90	2.1395	60
2 2 1	1.9535	10	2.0202	5
3 1 1	1.7644	100	1.8252	100
2 2 2	1.6889	60	1.7471	25
3 2 0	1.6224	25	1.6789	40
3 2 1	1.5632	30	1.6183	50
4 0 0	1.4622	10	—	—
4 1 0	1.4180	5	1.4676	2
3 3 1	1.3419	60	1.3887	20
4 2 0	1.3077	50	1.3539	25
4 2 1	1.2767	5	1.3208	15
3 3 2	1.2464	5	1.2902	10
4 2 2	1.1937	70	1.2358	15
5 1 1	1.1251	60	1.1648	50
5 2 0	1.0859	10	1.1237	15
5 2 1	1.0679	10	1.1057	10
4 4 0	1.0332	25	1.0700	30
5 3 1	.9878	30	1.0230	10
6 0 0	.9742	25	1.0094	20
6 1 0	—	—	.9959	5
6 1 1	.9485	5	.9819	15
6 2 0	.9242	10	.9578	10
6 2 1	.9125	2	.9463	5
5 3 3	.8913	20	.9240	15
6 2 2	.8812	15	—	—
4 4 4	.8434	5	—	—
6 3 2	.8352	5	—	—
7 1 1	.8184	70	.8477	5
6 4 0	.8104	70	.8397	20
7 2 0	.8027	10	.8319	10
7 2 1	.7953	5	.8241	10
6 4 2	.7810	50	.8091	15
7 3 1	—	—	.7885	25

25.17; density, 5.65 g/cm³. Found: (a) P, 12.4; (b) P, 13.03; S, 26.36; S:P = 1.95:1 atom ratio; (c) P, 12.47; S, 27.57; S:P = 2.14:1 atom ratio; (d) density, 5.66 g/cm³.

High pressure is necessary and the ratio of starting materials is critical in the preparation of $PdP_{0.67}S_{1.33}$. Thus, this phase was obtained at 65 kbar but not at 40 kbar from the atom-charge ratios Pd:P:S = 1:1:1.5–3.0 and 1:0.67:1.33. Under the same reaction conditions and at atom-charge ratios of

Pd:P:S = 1:1:1 or 1:2:1, the compounds PdPS (orthorhombic) or PdPS plus PdP_2 (monoclinic) were obtained instead.

Four-probe resistivity measurements on a single crystal of this pyrite-type phase showed it to be metallic with an essentially invariant resistivity, $\rho_{4.2°K}$ 1.7 × 10⁻⁴, $\rho_{298°K}$ 2 × 10⁻⁴ ohm-cm. Magnetic susceptibility measurements indicated Pauli paramagnetism with a temperature-independent value of χ_g 0.20 × 10⁻⁶ emu/g over the measured range 77–300°K.

PdP_ySe_{2-y} (0 < y < 1)

Selenide-containing, pyrite-type phases PdP_ySe_{2-y} were also obtained at high pressure. In contrast to $PdP_{0.67}S_{1.33}$, a variable ratio of Se:P is indicated since unit cell dimensions over the range $a = 6.05$–6.13 Å were observed in products prepared from different ratios of starting materials and at different temperatures and pressures. Thus, pyrite-type PdP_ySe_{2-y} was obtained from such atom-charge ratios as Pd:P:Se = 1:1:1, 1:0.5:1.5, and 1:0.67:1.33–2.67 and at pressures of 40–65 kbar. Traces of this phase were also detected in runs made at 25 kbar but not at 20 kbar pressure.

Reaction of Pd:P:Se = 1:1:1 at 1000°C/65 kbar gave silvery, crystalline material as one phase. Debye–Scherrer X-ray diffraction powder data indicated these silvery crystals to have a pyrite-type structure of cell dimension $a = 6.056$ Å (Table II). Their measured density was 7.06 g/cm³, indicating an approximate composition $PdP_{0.59}Se_{1.41}$. Golden crystals also present were identified as monoclinic PdP_2. The presence of PdP_2 along with the pyrite phase confirms the fact that the stoichiometry of the latter has a ratio of Se to P greater than unity. This phase also showed metallic conductivity.

$PdP_{\sim0.33}S_{\sim1.67}$

In addition to the pyrite-type compound $PdP_{0.67}S_{1.33}$ obtained at 65 kbar pressure, reaction of an atomic ratio of Pd:P:S = 1:1:3 at 1200–1000°C/65 kbar gave a second silvery, crystalline phase. X-Ray patterns of these materials could be indexed for the most part on the basis of tetragonal cells whose dimensions ($a \sim 5.63$–5.67, $c \sim 6.48$–6.43 Å) related to those of orthorhombic PdPS. Variations observed in the X-ray patterns of these "tetragonal" materials as obtained from different syntheses suggested changes in composition and probable crystal symmetry as well. Analyses on one product made at 1000°C/65 kbar indicated a higher sulfur content than in the pyrite phase $PdP_{0.67}S_{1.33}$ but with the essential 2:1 ratio of anions to cation

$h\,k\,l$	d_{obsd}	I/I_0
1 1 1	3.395	100
0 0 2	3.245	60
2 0 0	2.817	85
– – –	2.712	2
2 0 1	2.591	5
1 1 2	2.511	10
2 1 1	2.351	10
2 0 2	2.126	70
2 2 0	1.992	40
2 2 1	1.901	35
3 1 1	1.718	80
2 2 2	1.698	40
– – –	1.567	15
3 2 1	1.518	10
4 0 0	1.408	10
3 1 3	1.374	20
3 3 1	1.300	10
4 2 0	1.259	10
3 3 2	1.230	5
4 2 2	1.173	20
3 3 3	1.131	10
– – –	1.093	15
2 2 5	1.086	15
4 0 4	1.062	5
4 2 4	.9949	10
– – –	.9531	10

[a] Tetragonal cell dimensions:
$a = 5.63$Å and $c = 6.48$Å.

still pertaining. Analyses calculated for PdP$_{0.33}$S$_{1.67}$: P, 6.06; S, 31.41. Found: P, 6.41; S, 31.81. The Debye–Scherrer X-ray powder pattern of this composition is given in Table III. Like the pyrite phase, an essentially invariant resistivity was observed on this material, $\rho_{4.2°K}$ 9.3 × 10^{-4}, $\rho_{298°K}$ 8.5 × 10^{-4} ohm-cm.

High pressure (above 40 kbar) was found to be necessary for the synthesis of this phase rich in sulfur and high temperature also favored its formation. Thus at 65 kbar pressure, runs at 1000, 800, and 600°C gave decreasing yields with PdS being the main product formed at 600°C.

Pd$_3$(PS$_4$)$_2$

Reaction of an atom ratio of Pd:P:S = 1:1:2.5–3.5 in sealed silica tubes at 900°C/autogenous pressure or 1200°C/3 kbar pressure gave the compound Pd$_3$(PS$_4$)$_2$ in the form of red–purple crystals, with

many as hexagonal platelets. Small amounts of silvery PdPS plus yellow–orange phosphorus sulfides formed at the same time. This latter impurity was removed by hot water treatment as described in the Experimental Section. Reaction pressures up to 25 kbar have given products containing Pd$_3$(PS$_4$)$_2$ as one of the phases but at 45 kbar or higher formation of this composition was not observed. Reactant ratios of S:P greater than unity are also a requisite to obtain this phase.

Elemental analyses were made on several batches of crystals prepared at autogenous pressure. Analyses calculated for Pd$_3$(PS$_4$)$_2$: Pd 50.06; P, 9.72; S, 40.23. Found: Pd, 49.43, 51.10, 51.89; P, 9.05, 9.38, 9.67, 9.69, 9.90, 9.91; S, 41.51, 41.53. This compound was stable to about 730°C when heated in an argon atmosphere. In oxygen, oxidation commenced around 450°C.

Single-crystal X-ray data indicated Pd$_3$(PS$_4$)$_2$ to have trigonal symmetry in space group $P321$, $P3m1$, or $P\bar{3}m1$. Hexagonal cell dimensions $a = 6.836$ and $c = 7.239$ Å were obtained by refinement of Debye–Scherrer X-ray powder data. A unique composition is indicated by the fact that the same cell dimensions were obtained from products prepared over the pressure range autogenous to 25 kbar as well as from a variety of reactant ratios. These included Pd:P:S = 1:1:1.5–3.5, 1:0.5–0.67:1.5–1.33, and 1:0.67:3. Other phases including PdPS and PdS formed in variable amounts at the same time. Crystals had a measured density of 3.57 g/cm^3; the calculated density for one formula weight of Pd$_3$(PS$_4$)$_2$ per unit cell is 3.61 g/cm^3.

The crystal structure was solved by refinement of X-ray powder intensity data (Table IV) using trial and error methods. Relative intensities were collected from a diffractometer tracing by obtaining relative weights of the peaks. The sample was prepared by grinding, passing through a 325-mesh screen, and sprinkling on a glass slide coated with vaseline. A Norelco diffractometer was used at a scanning rate of $\frac{1}{4}$ deg/min with the chart scaled to 1 in./deg. Twenty-one pieces of data were collected. Least-squares refinements were done using a program written by Dr. C. T. Prewitt which handles the sums of nonequivalent overlapping reflections. Atomic scattering factors were obtained from "International Tables for X-Ray Crystallography," Volume III, Tables 3.3.1 and 3.3.1B. The real and imaginary parts of the anomalous dispersion correction and Lorentz and polarization factors were applied during the refinements.

Atomic positions were chosen on the assumption that the structure was related to the CdI$_2$-type since

TABLE IV

X-RAY DIFFRACTION POWDER PATTERN AND OBSERVED
AND CALCULATED INTENSITIES OF $Pd_3(PS_4)_2$

h	k	l	$d_{obs.}$	$d_{calc.}$	$I_{obs.}$	$I_{calc.}$
0	0	1	7.2313	7.2390	100.0	99.5
1	0	0	5.9272	5.9285	39.0	40.3
1	0	1	4.5911	4.5866	21.0	18.3
1	0	1̄				1.0
0	0	2	3.6172	3.6195	6.0	5.5
1	1	0	3.4387	3.4228	.7	.75
1	1	1		3.0943		32.7
1	0	2	3.0926	3.0894	44.0	11.2
1	0	2̄				.7
2	0	0	2.9623	2.9642	6.0	7.4
2	0	1	2.7416	2.7432	58.0	8.5
2	0	1̄				49.4
1	1	2	2.4902	2.4869	1.2	2.7
0	0	3	2.4078	2.4130	3.4	2.0
2	0	2	2.2944	2.2933	49.0	10.4
2	0	2̄				36.4
1	0	3	2.2352	2.2349	13.0	.5
1	0	3̄		2.2420		8.4
2	1	0				3.8
3	0	0	1.9830	1.9762	< .5	--
2	1	2	1.9051	1.9051	12.0	4.5
2	1	2̄				1.0
3	0	1		1.9072		2.5
3	0	1̄				4.4
2	0	3	1.8714	1.8714	21.0	7.7
2	0	3̄				13.2
0	0	4	1.8076	1.8097	2.2	1.3
3	0	2	1.7343	1.7345	< .5	--
2	2	0	1.7105	1.7114	13.0	20.0
2	2	1	1.6624	1.6655	7.0	9.6
3	1	0	1.6439	1.6442	9.0	2.0
2	1	3		1.6425		.8
2	1	3̄				6.5
1	1	4	1.5994	1.5999	3.5	1.0
3	1	1		1.6042		.0
3	1	1̄				1.6
2	0	4	1.5452	1.5446	19.0	12.5
2	0	4̄		1.5465		.3
2	2	2				2.4
0	0	5	1.4487	1.4478	8.0	1.7
4	0	1		1.4527		4.8
4	0	1̄				1.1
2	1	4	1.4096	1.4079	--	--
2	2	3	1.3945	1.3960	--	--
4	0	2	1.3722	1.3716	--	--
3	0	4	1.3346	1.3346	--	--
2	0	5	1.2993	1.3009	--	--
3	2	2	1.2731	1.2732	--	--
2	2	5	1.1054	1.1053	--	--

it is layer-like and has the same space group ($P\bar{3}m1$). In comparison to the CdI_2-type, the a axis is doubled and the compound is cation deficient. In CdI_2, there is one formula per unit cell, and the cations are placed at 0, 0, 0 and the anions at $\frac{1}{3}, \frac{2}{3}, z$; $\frac{2}{3}, \frac{1}{3}, \bar{z}$ with $z = \frac{1}{4}$. In $Pd_3P_2S_8$, the three Pd atoms were placed in the special positions $3e$; $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; and $\frac{1}{2}, \frac{1}{2}, 0$. Six S atoms were placed in positions $6i$; $x, \bar{x}, z$ with $x = \frac{1}{6}$ and $z = \frac{1}{6}$. The remaining two S atoms were placed in positions $2d$; $\frac{1}{3}, \frac{2}{3}, z$ where

$z = \frac{5}{8}$. This assignment results in a square-planar arrangement of the sixfold group of S atoms about the Pd atoms; the remaining two S atoms are at an angle of 102° from the plane and bonded at a much longer distance from the Pd. The coordination of each Pd may be considered a very distorted, elongated octahedron. The two P atoms were placed at positions $2d$; $\frac{1}{3}, \frac{2}{3}, z$ with $z = 0.3$. This places the P atoms in sites surrounded tetrahedrally by four S atoms.

Refinements of these positions and isotropic temperature factors were carried out, and an R factor of 0.07 was obtained based on intensities. The temperature factors, however, behaved badly and rose to 6 and 7 for the S atoms and became negative (−0.65) for the P atoms. This behavior of the temperature factors could be caused by insufficient data or by disorder in the structure due to stacking faults. The structure, however, appears to be essentially correct. Another refinement was done in which the temperature factors of the S atoms were held at 2.5 and those of the P atoms at 1.0. The positional parameters and isotropic temperature factors of Pd were refined, and an R factor of 0.065 was obtained. These parameters were used for calculation of bond distances and angles.

The intensity data are shown in Table IV. Refined parameters and bond distances and angles are shown in Table V. The numbers of the atoms correspond to the numbers of the atoms on the structure (Fig. 1). The errors in bond angles and distances are quite

TABLE V

REFINED PARAMETERS AND BOND DISTANCES AND ANGLES
FOR $Pd_3(PS_4)_2$

Atom	Wyckoff notation	(Space group $P\bar{3}m1$)			Temperature factor
		x	y	z	
Pd	$3e$	1/2	0	0	2.1(6)
S	$6i$	0.174(2)	$\bar{x}$	0.177(5)	2.5
S	$2d$	1/3	2/3	0.58(1)	2.5
P	$2d$	1/3	2/3	0.30(1)	1.0

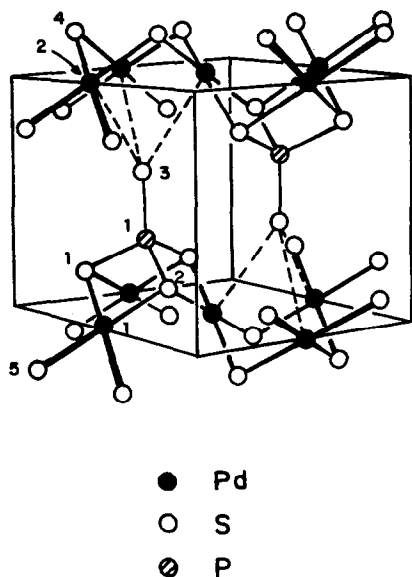| Atoms[a]	Distance in Å	Angle in degrees
S(1)–Pd(1)–S(2)	2.32(3) 2.32(3)	90(1)
S(1)–Pd(1)–S(5)	2.32(3) 2.32(3)	90(1)
S(1)–P(1)–S(2)	2.10(5) 2.10(5)	102(3)
S(1)–P(1)–S(3)	2.10(5) 2.00(10)	116(3)
S(4)–Pd(2)–S(3)	2.32(3) 3.59(8)	102(1)

[a] Atom numbers correspond to numbers in Fig. 1.

● Pd

○ S

⊘ P

Fig. 1. Crystal structure of $Pd_3(PS_4)_2$.

large, and refinement from single-crystal data is indicated.

Four-probe resistivity measurements on single-crystal $Pd_3(PS_4)_2$ showed it to be a semiconductor with resistivities $\rho_{279°K}$ 7×10^7, $\rho_{300°K}$ 4×10^6, $\rho_{345°K}$ 3×10^4 ohm-cm and activation energy of resistivity, E_a, of 1 eV. Optical transmission was measured on a flat platelet some 25 μ thick and a band edge of 0.55 μ was observed, indicating an optical band gap, ΔE, of about 2.2 eV. Magnetic susceptibility measurements showed $Pd_3(PS_4)_2$ to be diamagnetic.

PdP_2S_7

In addition to the silvery, crystalline $PdP_{0.67}S_{1.33}$ and $PdP_{\sim0.33}S_{\sim1.67}$ phases obtained at 65 kbar pressure, reaction at 1200°C/65 kbar of an atom ratio of Pd:P:S = 1:1:3 also gave a glassy-appearing, blue–black product in the form of irregularly shaped and conchoidally fractured chunks. This material was amorphous to X-rays. Analyses approximated the polyanion composition PdP_2S_7. Calculated: Pd, 27.09; P, 15.77; S, 57.14. Found $Pd_{max} \sim 25$ by emission spectroscopy; P, 16.59; S, 55.60; density, 2.90 g/cm³. Slow hydrolytic decomposition of this material was observed.

PtP_yS_{2-y}

Analogous reactions to those forming new Pd phosphosulfides were also carried out between Pt, P, and S. Thus such atomic ratios of Pt:P:S as 2:1:3, 1:0.67:1.33, 1:1:1, and 1:1:3 were heated

at 1000°C/65 kbar and 900–1000°C/200 atm backup pressure in sealed silica tubes. At autogenous pressures, the known CdI_2-type PtS_2 and pyrite-type PtP_2 ($a = 5.696$ Å) phases were obtained with PtS also being identified at times. At 65 kbar pressure, a small amount of S was forced into the PtP_2 pyrite-type lattice since the unit cell size increased to 5.729 Å. None of the other intermediate phosphosulfides obtained in the Pd system was observed to form with Pt.

Discussion

PdP_yS_{2-y} Compounds ($0 \leqslant y \leqslant 2$)

The three compounds PdPS, $PdP_{0.67}S_{1.33}$, and $PdP_{\sim0.33}S_{\sim1.67}$ having essentially a 2:1 ratio of anions to cation have now been found to exist between the known end members, PdP_2 and PdS_2. Certain selenide isotypes have also been obtained. Both stoichiometry of reactants and reaction pressure are critical to the preparation of each of these compounds with the reaction pressure being varied from autogenous to 65 kbar. Reactivity is much lower in the related Pt system and only substitution of small amounts of S for P in pyrite-type PtP_2 was observed.

In monoclinic PdP_2 (8), the P atoms form continuous zig-zag chains along the a axis leading to a polyanion structure in which each P may be considered to have a formal valence of -1. The coordination of Pd^{+2} is square-planar with each metal atom being bonded to four P atoms, each from a separate chain. This PdP_2 compound is a diamagnetic semiconductor (9) in accord with the electronic structure of this type of d^8 configuration. The NiP_2 isotype of PdP_2 converts to the pyrite-type structure at pressures above 15 kbar (10), but the inherent stability of Pd in a square-planar arrangement seems to preclude a similar transition in PdP_2, at least to pressures near 65 kbar (10).

The other end member of this series, orthorhombic PdS_2 (11), may be considered to have a distorted pyrite-type structure. Each Pd atom is surrounded by four S atoms, again in an essentially square-planar configuration. Two additional S atoms lie at a greater distance from the Pd on an axis approximately perpendicular to the plane of the other four S atoms. In this c direction, weak bonding between atoms leads to a layer-type material. This compound also shows the expected properties of a diamagnetic semiconductor (12). In contrast to PdP_2, the application of 65 kbar pressure to PdS_2 has been observed in this laboratory and elsewhere (13) to lead to an appreciable shortening of the

Pd–S distances in the c direction. This reduction in distortion of the anion octahedron about Pd leads to metallic rather than semiconducting behavior in this high-pressure form of PdS_2.

Although structural studies will be necessary for positive confirmation, the following hypothesis is proposed to account for the properties of the three PdP_yS_{2-y} phases obtained in this work as intermediates between PdP_2 and PdS_2. The apparent absence of any phases between PdP_2 and PdPS suggests that the anions in these two compounds occupy distinct positions such that neither compound allows any range of substitution. The semiconductivity and lamellar crystalline habit of the orthorhombic PdPS phase are indicative of the presence of square-planar Pd^{+2} and the existence of polyanions. The most probable anion configuration is a combination of $[P^{-1}]_n$ chains as in PdP_2 and $[S–S]^{-2}$ pairs as in PdS_2. Thus formal valencies in PdPS would be Pd^{+2}, P^{-1}, and S^{-1}.

The effect of increasing the S content is to form at high pressure a pyrite-type phase of composition $PdP_{0.67}S_{1.33}$. Since no solid solutions of S in PdPS and no intermediate compositions are found, it seems that a specific excess of S is necessary to disrupt the $[P^{-1}]_n$ chains in PdPS to form this new compound. In pyrite-type $PdP_{0.67}S_{1.33}$, the anions are all paired; consequently, the *formal* valence of Pd is $+2\frac{2}{3}$ with each atom having an average of $7\frac{1}{3}d$ electrons. According to the molecular orbital diagram for pyrite-type compounds *(14)*, six electrons occupy the t_{2_g} levels leaving $1\frac{1}{3}$ electrons in the e_g conduction band. Thus the material exhibits metallic conductivity.

The composition $PdP_{0.33}S_{1.67}$ may have an intermediate structure between the pyrite type and that of PdS_2 in which the *formal* valence of Pd is $+2\frac{1}{3}$. The coordination of Pd may also be intermediate between octahedral and square-planar as in the high-pressure forms of PdS_2. In any case, metallic conductivity would be expected because of the odd valence. Reasons for these compositions occurring at stoichiometries that leave Pd with valencies at approximate increments of thirds are beyond consideration here.

In PdPSe, as in PdPS, no substitution of P by Se seems to be allowed. However, in the pyrite-type composition PdP_ySe_{2-y} $(0 < y < 1)$, the presence of the more polarizable selenide ion does lead to a modest range in stoichiometry.

Thiophosphates

In addition to the unusual PdP_yX_{2-y} series of phases, the unrelated compounds $Pd_3(PS_4)_2$ and PdP_2S_7 have also been prepared. Although errors in the bond angles and distances of $Pd_3(PS_4)_2$ as derived from the present structure determination are relatively large, the structure obtained readily explains the semiconducting and diamagnetic properties of this compound. The data show $Pd_3(PS_4)_2$ to be a thiophosphate and thus the valences $2\cdot(PS_4)^{-3}$ and $3\cdot Pd^{+2}$ may be assigned. Data on structure and properties of other thiophosphates including Cu_3PS_4 *(15, 16)*, BPS_4 *(17)*, $AlPS_4$ *(18)*, $GaPS_4$ *(16)*, $InPS_4$ *(16)*, and $BiPS_4$ *(16, 19)*, are reported throughout the literature. Pyrothiophosphates $M_2P_2S_7$ of Fe, Ni, Zn, Cd, and Pb are also indicated *(20)*.

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