

The Structure of PdPS and the Crystal Chemistry of Late Transition-Metal Dipnictides and Dichalcogenides

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PdPS crystallizes with orthorhombic symmetry, space group $Pbcn$ (D_{2h}^{14}) and lattice constants $a=13.3045$ (37), $b=5.6777$ (5), $c=5.6932$ (5) Å, $Z=8$. The structure was determined from single-crystal counter data by Patterson and Fourier methods. Full-matrix least-squares refinements with ellipsoidal thermal parameters resulted in a conventional R value of 0.040 for 1194 structure amplitudes greater than three standard deviations. The distinction between the P and S atoms was made by analogy with isostructural PdPSe for which the ordering of the P and Se atoms was determined from powder patterns. Palladium is in square-planar coordination of two P and two S atoms. The P and S atoms may be considered as forming $[S-P-P-S]^{4-}$ polyanions. Phosphorus is tetrahedrally coordinated to one P, one S, and two Pd atoms. The S atom can be described as being tetrahedrally coordinated by two Pd atoms, one P atom, and a lone electron pair as fourth ligand. A puckered net of pentagons forms the basic building element of the structures of most late transition-metal dipnictides and dichalcogenides. These structures can be characterized by the relative orientation of the nets and by the kind of bonds formed between them. Strong two-electron bonds connect the nets in the pyrite, marcasite, arsenopyrite, parammelsbergite and PdP₂ type structures. In PdS₂ the nets are held together mainly by the interaction of the lone pair of S of one layer with the Pd atom of another layer. PdPS forms double nets, thus combining the bonding characteristics of PdP₂ and PdS₂.

Introduction

Bither, Donohue & Young (1971) studied the pseudo-binary sections of PdP₂ with PdS₂ and PdSe₂ at various temperatures and pressures and described the preparation and properties of PdPS and PdPSe. Both compounds can be prepared at normal pressure; they have graphite-like habit. PdPS is a diamagnetic semiconductor, and isostructural PdPSe was also found to be semiconducting. Results indicating solid solutions between the two compounds were reported.

Experimental

Well crystallized samples of PdPS and PdPSe, prepared from the elements in sealed silica tubes, were kindly provided by T. A. Bither of this laboratory. The flake-like crystals are easily deformed and after mounting on glass fibers, examination with X-rays usually showed angular spreads of up to 20°. After many attempts a relatively thick crystal of PdPS was found to be undeformed after mounting. It had the form of a prismatic plate with a height of 0.06 mm and an irregular pentagonal cross section with overall dimensions 0.13 by 0.13 mm. The crystal was examined with a Buerger precession camera and Mo $K\alpha$ radiation. Intensity data were measured on an automated four-circle diffractometer with Zr-filtered Mo radiation. Scans were along 2θ with a scan angle of 1.0° and a scan speed of 0.3° min⁻¹. Background was counted

for 30 s at beginning and end of each scan. An absorption correction was made using a program by Prewitt (1967) based on a procedure described by Wuensch & Prewitt (1965). Transmission values were found to vary between 34 and 54%.

Structure determination

Single crystals of PdPS and PdPSe have orthorhombic diffraction symmetry. Systematic absences ($hk0$ observed only with $h+k=2n$, $h0l$ only with $l=2n$, and $0kl$ only with $k=2n$) are characteristic of space group $Pbcn$ (D_{2h}^{14}). Cell dimensions, refined from Hagg-Guinier powder data with KCl ($a=6.2931$ Å) as standard, are listed in Table 1, which also lists the values for PdPSe obtained by Bither *et al.* (1971). The calculated density of 5.23 g cm⁻³ for eight formula units PdPS compares well with the measured density of 5.13 g cm⁻³.

Table 1. Lattice constants of PdPS and PdPSe

	PdPS	PdPSe
a	13.3045 (37) Å	13.569 (4) Å
b	5.6777 (5)	5.824 (1)
c	5.6932 (5)	5.856 (1)
V	430.06 (11) Å ³	462.8 (2) Å ³

The position of the Pd atom was deduced from the three-dimensional Patterson function and the light atoms were located on a difference-Fourier synthesis computed with a program written by Fritchie &

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Guggenberger (1967). The structure was refined with a full-matrix least-squares program by Finger (1969). Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968), corrected for anomalous dispersion (Cromer & Liberman, 1970). The function minimized was sum(w(KF_o - |F_c|)^2) where w is the weight based on counting statistics and K is a scale factor. An extinction correction in the form of I_cor = I_uncor / (1 - cI_uncor) was used (Zachariasen, 1963a). Reflections where this correction was greater than 20% and reflections where F_o was less than three standard

deviations (in F) were given zero weight and are marked with an asterisk in Table 2.

In order to distinguish the P and S atoms, the structure was also refined with the scattering curves of P and S interchanged. Conventional R values for the 1194 structure factors included in the refinement, are 0.0397 for the model finally judged to be correct* and 0.0403 for the model with interchanged occupancies.

* The R value for all 1779 reflections listed in Table 2 is 0.070.

Table 2. Observed and calculated structure factors of PdPS

The columns contain the values h, k, F_o and F_c.

Table with columns for h, k, F_o, and F_c. The table contains a large number of rows of numerical data representing structure factors for various h and k values.

An unambiguous decision about the position of the anions was made by an intensity calculation for the powder pattern of PdPSe (Table 3) with positional parameters as obtained for PdPS (Table 4). It can be assumed that the position of the S atom in PdPS will correspond to the position of Se in PdPSe. It should also be mentioned that anisotropic thermal parameters obtained in the refinements of PdPS are more meaningful for the correct model. The R value for 165 low-angle reflections is 0.060 for the correct model and 0.065 for the other model. The correct model also puts

Table 3. *Calculated and observed powder patterns of PdPS and PdPSe*

The observed values are taken from Bither, Donohue & Young (1971). In the Hagg-Guinier pattern of PdPS observed intensities are strongly affected by preferred orientation of the flake-like crystals. For the Debye-Scherrer pattern of PdPSe intensities were calculated (Yvon, Jeitschko & Parthé, 1969) for two models which differ in the positions of the P and Se atoms. It can be seen that one model can definitely be ruled out.

PdPS				PdPSe						
hkl	d_c	d_o	I_c	hkl	d_c	d_o	I_c^*	I_o	I_c^{**}	
200	6.6525	6.6500	10	5	200	6.7845	-	<1	-	38
110	5.2223	5.2171	2	15	110	5.3519	-	1	-	30
111	3.8484	3.8465	54	100	111	3.9506	3.9515	28	55	5
310	3.4952	-	5	-	310	3.5723	3.5680	18	20	4
211	3.4408	3.4413	30	20	211	3.5274	-	1	-	34
400	3.3262	3.3250	100	15	400	3.3923	3.3980	100	100	100
311	2.9786	2.9773	26	5	311	3.0496	3.0475	11	10	22
002	2.8465	2.8443	6	5	002	2.9280	-	<1	-	21
020	2.8390	2.8380	41	50	020	2.9120	2.9131	31	55	34
102	2.7835	2.7826	32	75	102	2.8621	2.8621	35	60	19
202	2.6170	2.6167	5	5	202	2.6883	2.6932	6	20	11
220	2.6112	-	1	-	220	2.6759	-	<1	-	1
411	2.5628	-	12	-	411	2.6212	2.6199	20	35	12
021	2.5406	-	1	-	021	2.6074	-	<1	-	15
112	2.4993	2.4981	7	50	112	2.5687	2.5633	10	65	20
121	2.4955	2.4948	8	50	121	2.5606	-	25	-	-
510	2.4095	-	2	-	510	2.4599	-	2	-	7
302	2.3955	2.3975	22	10	302	2.4579	2.4571	17	25	10
212	2.3767	-	2	-	212	2.4408	-	5	-	4
221	2.3734	2.3739	2	5	221	2.4339	-	3	-	11
511	2.2190	-	27	-	511	2.2679	2.2653	18	35	6
600	2.2175	-	3	-	312	2.2645	-	7	-	1
312	2.2071	-	2	-	600	2.2615	-	<1	-	11
321	2.2045	-	1	-	321	2.2589	-	3	-	3
402	2.1627	-	4	-	402	2.2165	-	<1	-	8
420	2.1594	2.1591	34	10	420	2.2096	2.2103	24	25	26
412	2.0211	-	<1	-	412	2.0716	-	<1	-	<1
421	2.0190	-	<1	-	421	2.0673	2.0697	<1	2	3
022	2.0101	2.0099	4	10	022	2.0647	-	2	-	4
122	1.9876	1.9873	20	75	122	2.0412	2.0407	14	30	15
502	1.9439	-	9	-	502	1.9904	-	11	-	9
611	1.9417	-	8	-	611	1.9835	1.9895	2	10	6
222	1.9242	-	<1	-	222	1.9753	-	<1	-	<1
130	1.8738	-	<1	-	130	1.9218	-	<1	-	3
512	1.8391	-	1	-	512	1.8834	-	<1	-	5
521	1.8376	-	3	-	521	1.8802	1.8795	12	50	1
322	1.8308	1.8310	25	5	322	1.8783	-	16	-	18
710	1.8024	-	2	-	710	1.8392	-	4	-	5
113	1.7836	-	1	-	113	1.8338	-	<1	-	5
131	1.7799	1.7798	26	75	131	1.8260	1.8263	17	40	32
602	1.7493	-	8	-	602	1.7898	-	10	-	15
620	1.7476	-	3	-	620	1.7861	-	1	-	2
330	1.7408	-	1	-	213	1.7856	1.7843	45	85	49
213	1.7373	1.7376	54	50	330	1.7840	-	4	-	1
231	1.7339	1.7341	15	20	231	1.7783	-	16	-	9
422	1.7204	-	5	-	422	1.7637	-	2	-	4
711	1.7183	-	5	-	711	1.7547	-	2	-	11
612	1.6718	-	<1	-	313	1.7129	-	2	-	<1
621	1.6706	-	3	-	612	1.7108	-	<1	-	<1
313	1.6677	-	<1	-	-	-	-	-	-	-
331	1.6647	1.6648	8	2	-	-	-	-	-	-
800	1.6631	-	4	-	-	-	-	-	-	-

* correct model

** model with interchanged occupancies of P and Se

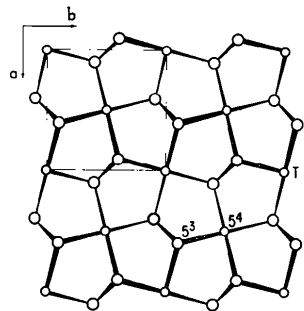


Fig. 1. Projection of the (3+4)-connected pentagonal net which occurs as a building element of most late transition-metal dipnictides and dichalcogenides (TX_2). This net can be described with the Schläfli symbol $5^4 + 5^3$ (2:3). Wells (1965) has shown that this symbol also applies for another (3+4)-connected pentagonal net. This, however, does not occur for transition-metal dimetalloids.

the lone pair on the anion with the higher electronegativity. A decision on the ordering of the anions by comparing interatomic distances, however, would not have been conclusive, as will be discussed below.

Table 4. *Positional and thermal parameters of PdPS*

Numbers in parentheses are e.s.d.'s in the least significant digits. Vibrational parameters ($\times 10^6$) are defined through $T = \exp(-h_i h_j \beta_{ij})$. Equivalent isotropic thermal parameters $B(\text{\AA}^2)$ are also listed.

$Pbcn (D_{2h}^{14})$	Pd	P	S
	8(d)	8(d)	8(d)
x	0.11372 (2)	0.41818 (9)	0.34694 (8)
y	0.25292 (5)	0.12974 (20)	0.36324 (18)
z	0.15907 (5)	0.28111 (19)	0.04553 (17)
β_{11}	122 (2)	101 (4)	125 (4)
β_{22}	256 (7)	291 (20)	318 (19)
β_{33}	261 (7)	266 (20)	298 (19)
β_{12}	23 (3)	-4 (9)	4 (8)
β_{13}	-6 (2)	-7 (8)	-14 (8)
β_{23}	-1 (5)	-19 (19)	-33 (18)
B	0.51	0.48	0.56

Discussion of the PdPS structure

Palladium is in square-planar coordination of two S and two P atoms. Phosphorus is tetrahedrally coordinated to one S, one P, and two Pd atoms. Sulfur may also be described as tetrahedral with one P, two Pd, and a lone pair of electrons as fourth ligand.

As could be expected from the graphite-like habit and deformability, PdPS has a layer structure. The layers consist of pentagons which are joined to form puckered two-dimensionally infinite nets as shown in Fig. 1. Each pentagon consists of two Pd atoms and either one P and two S, or one S and two P atoms. Ideal bonding angles are 90° at the two Pd corners and 109.5° at the three metalloloid corners. The sum of these angles is 508° which is somewhat smaller than the angle sum of 540° for a two-dimensional pentagon. Therefore, the nets are puckered. Each two nets are connected *via* P-P bonds, thus forming double layers as shown in Figs. 2 and 3. No strong bonds exist between neighboring double layers.

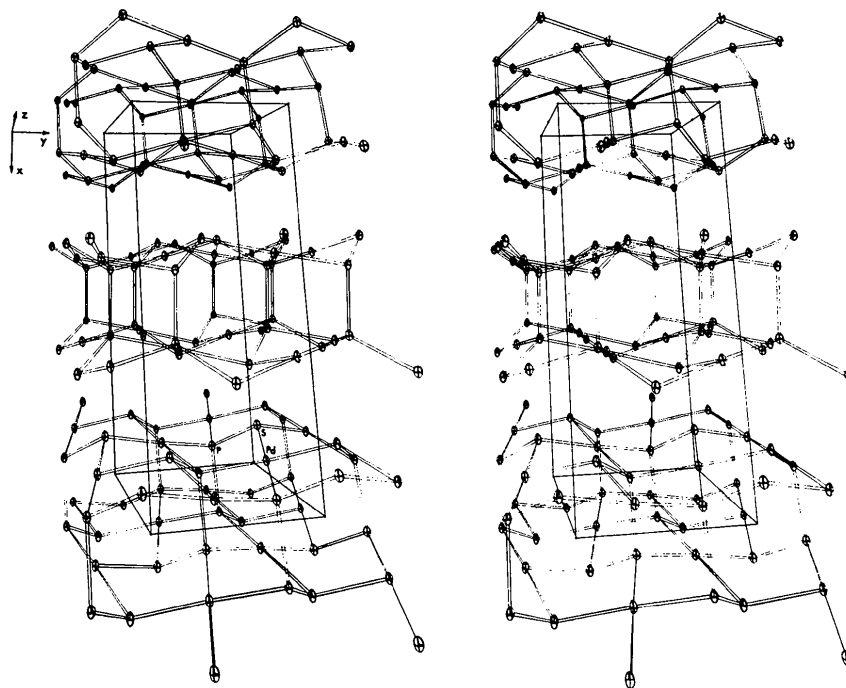


Fig. 2. Stereodrawing of the PdPS structure prepared with Johnson's (1965) program. Thermal ellipsoids are drawn at the 50% probability limit. Only two-electron bonds are drawn to emphasize the layers.

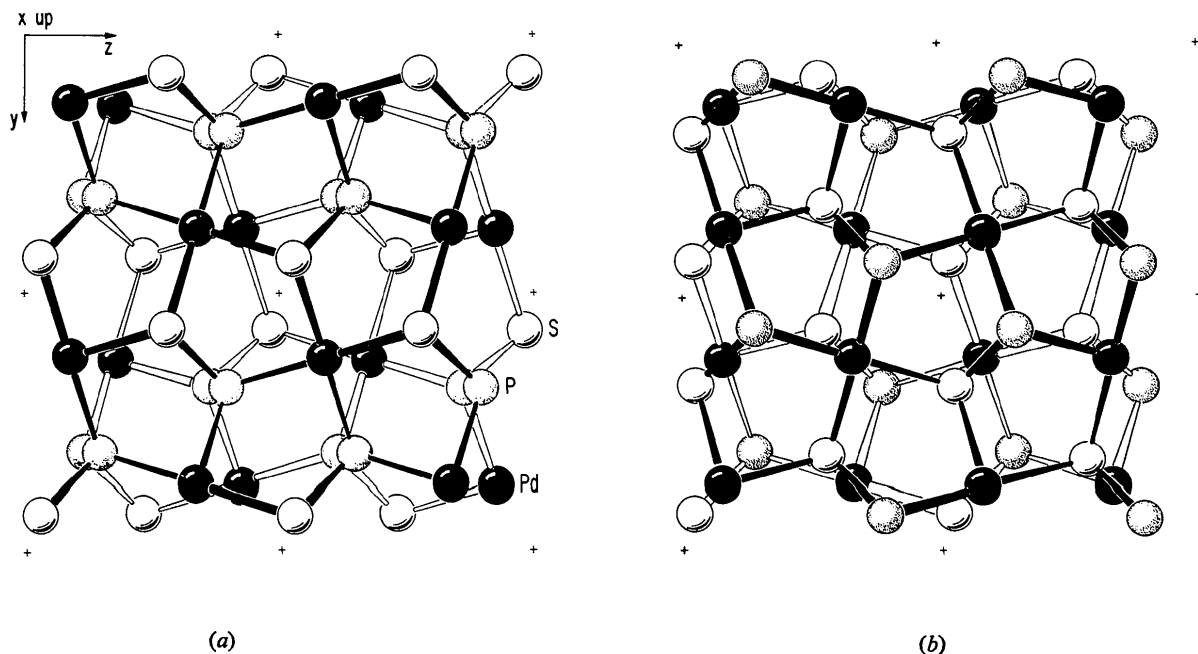


Fig. 3. Relative positions of atomic layers in the PdPS structure. Atoms in the upper layers are connected by solid lines and in the lower layers by double lines. Two layers (at $x \sim 0.9$ and $x \sim 0.1$) held together by bonds between the nearly superimposed P atoms are shown in (a). Additional weak bonding between these layers occurs *via* Pd-Pd interactions. (b) illustrates the relative positions of two layers (at $x \sim 0.1$ and $x \sim 0.4$) which are held together mainly by weak interactions of the lone pair of S of one layer with the Pd atom of the other layer. The relative positions of the layers as shown in (a) and (b) correspond to the interactions between layers in the PdP₂ and PdS₂ structures respectively. The stacking in the pyrite structure is the same as in PdS₂ (b) except that the spacings between the nets are short in pyrite, due to strong metal-metalloid bonds.

Interatomic distances

During recent years the crystal structures of more than 20 molecular inorganic complexes with Pd in an approximately square-planar configuration and P and/or S atoms as ligands have been determined (Kennard & Watson, 1971; Kennard, Watson & Town, 1973). In these complexes the Pd–P distances vary from 2.23 to 2.29 Å and Pd–S distances vary from 2.30 to 2.47 Å. The greater length of Pd–S bonds as compared with Pd–P bonds in molecular (relatively unstrained) structures is therefore well documented. These distances also compare well with the corresponding distances in PdPS (Table 5). As will be discussed later, the PdPS structure is closely related to the structures of PdP₂ (Zachariassen, 1963*b*) and PdS₂ (Grønvold & Røst, 1957). It is remarkable that both the Pd–P distance of 2.34 Å in PdP₂ and the Pd–S distance of 2.30 Å in PdS₂ fall outside the ranges found in molecular Pd compounds and differ by about 0.05 Å each from the corresponding distance in PdPS. There is no reason to question seriously the Pd–P and Pd–S distances in PdP₂ and PdS₂, although the accuracy of the structure determination of PdS₂ was possibly not very high by modern standards. In molecular structures few restraints are operating and interatomic distances will be close to the optimal bonding distances. This is not necessarily true for a solid-state compound where the rigidity of the structure may prevent optimization of bonding distances. The fact that the free energy of PdPS is lower (as proven by its formation) than the free energy of a mixture of PdP₂ and PdS₂ is an indication that interatomic distances in the ternary compound are closer to the ideal bonding distances than the distances in PdP₂ or PdS₂.^{*} Thus it would be more surprising if the Pd–P and Pd–S distances in the binary compounds were close to the ideal bonding distances and those in PdPS were not. Distance least-squares (DLS) refinements (Shoemaker & Shoemaker, 1967; Meier & Villinger, 1969; Baur, 1971) of the PdP₂ and PdS₂ structures should be of interest.

The P–P distance of 2.21 Å in PdPS compares well with the P–P distances of 2.21 ± 0.02 Å in elementary modifications of phosphorus as well as in many phosphorus-rich compounds (Dahl, 1969; Jeitschko & Donohue, 1972). The P–S distance of 2.11 Å is close to the sum of the covalent radii of P (1.10 Å) and S (1.03 Å) as found in the various modifications of phosphorus and sulfur (Schmidt, 1973).

Thermal vibrations

In general, amplitudes of thermal motion are larger in directions perpendicular to strong bonds than in the bonding direction. Since the PdPS structure has strong bonds only within the double layers, thermal motion is larger in the direction perpendicular to the layers.

^{*} In addition, the ternary compound is of course also stabilized by P–S interactions which take the place of P–P and S–S interactions of the binary compounds.

Table 5. *Interatomic distances and angles in PdPS*

Standard deviations, computed from e.s.d.'s of positional parameters and lattice constants, are all less than 0.002 Å and 0.2°, respectively. All distances less than 3.4 Å are given. Interatomic angles are listed only to the four nearest neighbors of each central atom.

Pd–Pd	3.198 Å	P–Pd–P'	88.8°
P	2.289	P–Pd–S	91.1
P'	2.292	P–Pd–S'	177.3
P''	3.386	P'–Pd–S	177.8
S	2.356	P'–Pd–S'	93.2
S'	2.364	S–Pd–S'	86.8
S''	3.231		
P–Pd	2.289	Pd–P–Pd'	121.5
Pd'	2.292	Pd–P–P	97.7
Pd''	3.386	Pd'–P–P	109.5
P	2.206	Pd–P–S	108.1
P'	3.205	Pd'–P–S	109.3
P''	3.205	P–P–S	110.0
S	2.111		
S'	3.317		
S''	3.384		
S–Pd	2.356	Pd–S–Pd'	117.9
Pd'	2.364	Pd–S–Pd''	110.2
Pd''	3.231	Pd'–S–Pd''	109.8
P	2.111	Pd–S–P	108.5
P'	3.317	Pd'–S–P	108.3
P''	3.384	Pd''–S–P	100.5
S	3.243 (2 ×)		

Calculation of the root-mean-square amplitudes of the thermal ellipsoids showed that the ratio of the long to the average of the short axes is 1.63 ± 0.02 , 1.41 ± 0.04 , and 1.50 ± 0.04 for Pd, P, and S respectively, with the direction of the long axes being in all cases less than 8° off the *a* axis.

Bonding description

In stressing ionicity, PdPS may be formulated as Pd₂²⁺[S–P–P–S]⁴⁻, thus emphasizing the polyanion. The structure can also be described by a covalent model where two-electron bonds account for all short interactions. Of the total of 21 valence electrons (Pd: 10, P: 5, S: 6) 11 electrons are needed to form two-electron bonds for the 5½ short bonding interactions per formula unit (the P–P bond of the polyanion belongs to 2 formula units); two electrons form a lone pair on S. The remaining 8 electrons occupy non-bonding *d* orbitals of Pd. In accordance with the geometry of the structure, *dsp*² hybridization can be deduced for Pd and *sp*³ mixing for P and S. This crude description is also in agreement with the diamagnetic behavior of the compound.

Parthé (1973) used the then unknown structure of PdPS to demonstrate the usefulness of simple algebraic formulas for predicting near-neighbor environments. Assuming square-planar coordination for Pd, tetrahedral coordination for P and S, and knowing that PdPS is semiconducting, he correctly deduced the presence of one lone pair on one of the anions, and the number of cation–anion bonds (4) and anion–anion bonds (1½) per formula unit. He also suggested the correct crystal-chemical formula Pd^[4]Pt^[2+2]S^[2+1] as

the most likely realization for the deduced bonding scheme.

In addition to the two-electron bonds, weak bonding also occurs between the Pd atom of one layer and the Pd and S atoms of the adjacent layers, as indicated by broken lines in Fig. 4. Although the distances of 3.2 Å are rather large, the bonding character of these interactions must be concluded from the large number of solid-state compounds where Ni^{2+} , Pd^{2+} , or Pt^{2+} with square-planar nearest-neighbor coordination is always packed in such a way as to allow interactions between the metal atoms. With these two additional near neighbors, the coordination of the metal atoms is better described by an octahedron stretched along one four-fold axis. Since the $4d_{z^2}$ orbital (which is directed towards the additional two neighbors) is filled in the simple two-electron bonding description given above, bonding most likely involves the $5p_z$ orbitals of Pd.

Similar interactions occur between the metal atoms in many square-planar molecular complexes (Rundle, 1957; Miller, 1962; Krogmann, 1969) as for instance in nickel dimethylglyoxime and Magnus's green salt $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, where optical spectra (Ohashi, Hanazaki & Nagakura, 1970; Miller, 1965) and semiconducting properties (Gomm, Thomas & Underhill, 1971) were extensively studied. In a simple molecular-orbital description, the interaction between the nd_{z^2} and $(n+1)p_z$ orbitals of the neighboring metal atoms results in a filled dp band with primarily d_{z^2} character and an unfilled dp^* band which has predominantly p_z character. The band gap as determined by optical transitions or by the temperature dependence of semiconductivity along the metal-metal chains is determined by the metal-metal distances. Pressure decreases the distances and the band gap (Zahner & Drickamer, 1960; Interrante & Bundy, 1971). The conductivity is very anisotropic and highest along the metal-metal chains.

In PdPS the situation is somewhat different since the d_{z^2} and p_z orbitals of Pd interact only on one side with the corresponding orbitals of another Pd atom; on the other side the interaction occurs with the lone pair of the S atom. Thus no continuous Pd-Pd chains exist and the electrical conductivity is probably less anisotropic than in some of the complex salts where the conductivity along the metal-metal chains is about two to three orders of magnitude greater than in directions perpendicular to the metal chains (Monteith, Ballard, Pitt, Klein, Slifkin & Collman, 1968). In PdP_2 the metal chains are infinite, but the compound is still semiconducting (Hulliger, 1963).

Crystal chemistry of late transition-metal dipnictides and dichalcogenides

Coordination and conductivity

For transition-metal dimetalloids there is a systematic change from high to low coordination for both the metal and the metalloid components. The disili-

cides, digermanides, distannides, and diplumbides are all high coordinated compounds with coordination numbers (CN) greater than six, as is typical of intermetallic phases. In transition-metal diphosphides, diarsenides, and diantimonides, high coordination occurs for the early (Groups IV to VI), low-coordination for the late (Group VIII) transition metals (Jeitschko & Donohue, 1973). The transition-metal dichalcogenides are all low-coordinated. In these compounds 'low coordination' means octahedral or trigonal prismatic metalloid environment for the metal atoms (with the exception of Ni and Pd which frequently have square-planar coordinations) and tetrahedral coordination for the metalloid atoms (counting lone pairs as neighbors; Andersson & Åström, 1972).

Although the transition-metal dimetalloids with high CN's are usually metallic conductors, a few exceptions are known where band saturation occurs also in high-coordinated compounds, as is the case for semiconducting CrSi_2 and $\beta\text{-FeSi}_2$. Thus for high-coordinated compounds, electrical properties cannot be predicted by simple rules (high coordination occurs for metallic and ionic bonding). Low coordination allows rationalization of bonding in terms of covalent models; the compounds may of course still exhibit metallic conductivity due to a zero band gap (semimetal) or to a partially filled valence or conduction band. The general $(8-N)$ rule for predicting semiconducting or metallic behavior (Mooser & Pearson, 1960; Hulliger, 1968) can be used reliably only for low-coordinated compounds with nonzero band gap. Since the crude bonding model given above for PdPS accommodates all valence electrons in two-electron bonds and lone

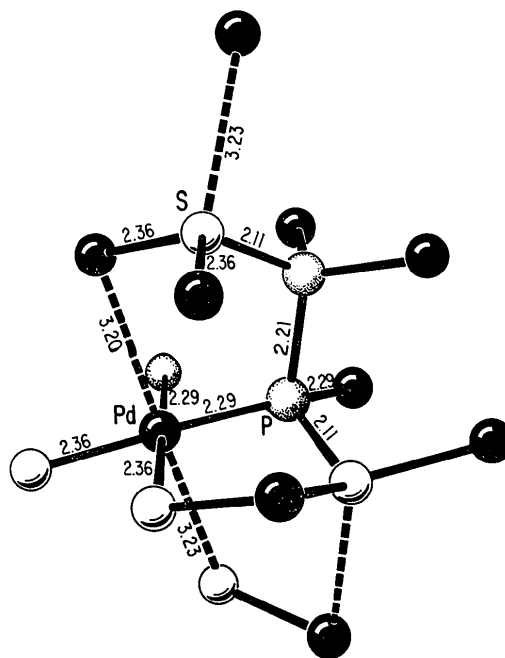


Fig. 4. Near-neighbor environments in PdPS.

pairs, the conduction band is empty. The band gap reported by Bither *et al.* (1971) decreases from PdPS ($E_g=0.7$ eV) to PdPSe ($E_g=0.15$ eV). For a hypothetical isostructural PdAsSe or PdPTe, a zero band gap could be extrapolated. Indiscriminate use of the (8-N) rule of course would wrongly predict semiconductivity also for PdAsSe or PdPTe.

Structural relationships

Of the 135 possible compositions TX_2 , TX_2Y , and TY_2 (where T=Group VIII transition metal, X=P,

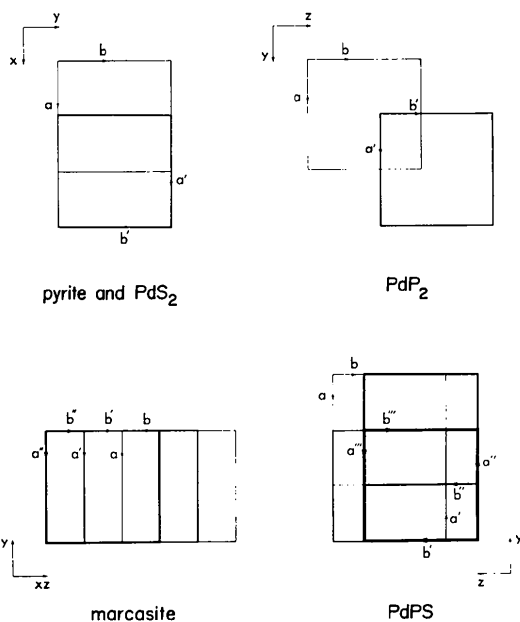


Fig. 5. Stacking of the unit mesh of Fig. 1 in some TX_2 structures.

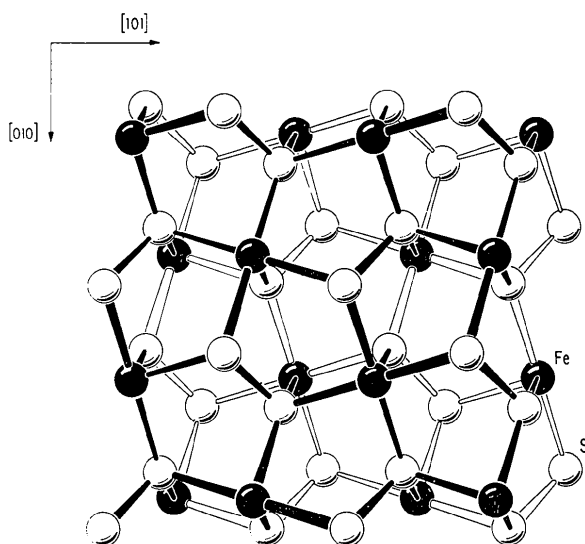


Fig. 6. Relative positions of atomic layers in the marcasite structure.

As, Sb, and Y=S, Se, Te) about 110 have been prepared and their structures were determined.* Most crystallize with the pyrite structure and its ternary ordered and/or distorted versions (cobaltite, ullmannite) or with the marcasite and distorted marcasite (arsenopyrite) structure. Since for the purpose of the following discussion ordering of the metalloid atoms and lattice distortions are not important these structures will be referred to briefly as pyrite and marcasite type structures. Only a few representatives each are found for the parammelsbergite (α -NiAs₂), PdP₂, PdS₂, PdPS, IrSe₂, and CdI₂ type structures which are the only other structural types reported for these compositions.

The puckered net shown in Fig. 1 may be regarded as the basic building element of the pyrite, marcasite, parammelsbergite, PdP₂, PdS₂, and PdPS type structures.† The differences between these structures arise from the various ways these nets can be stacked on top of each other and the kind of bonds formed between them.

In PdP₂ the nets are parallel and shifted by $\frac{1}{2}$ and about $\frac{2}{3}$ translation periods in the *a* and *b* directions, respectively, of the basic unit mesh (Fig. 5). This type of stacking puts the metal atoms approximately on top of each other, allowing weak metal-metal interactions as discussed above. The metalloid atoms of each layer alternately form strong bonds with the metalloid atoms of the layers above and below. This type of stacking occurs also in PdPS [Fig. 3(a)].

In the pyrite and PdS₂ type structures, adjacent nets are antiparallel oriented and shifted by $a/2$ relative to each other. This results in metal-metalloid interactions between neighboring layers. In the pyrite structure these interactions correspond to two-electron bonds; in PdS₂ these interactions are weak, as discussed above for PdPS [Fig. 3(b)].

The marcasite structure represents the third type of stacking (Fig. 6), where adjacent layers are parallel and shifted by about $b/3$ relative to each other.‡ This type of stacking permits metal-metal interactions between the edge-sharing TX₆ octahedra, in contrast to the pyrite structure where the octahedra share only corners.

The PdPS and parammelsbergite structures have mixed stacking sequences. In PdPS the stacking alternates between the PdP₂ and the PdS₂ type, while marcasite and pyrite type stacking alternates in the parammelsbergite structure. In both structures four layers are needed to complete one unit cell. More complicated stacking sequences can be envisioned for

* References may be found in Pearson's (1967) handbook and in the reviews by Hulliger (1968), Jelinek (1972), Ward (1972), and Jeitschko (1974).

† The IrSe₂ and CdI₂ type structures are not built up of such nets and will not be discussed further.

‡ The symbol *b* designates the axis of the unit mesh which corresponds to the [101] direction of the usual *Pnmm* setting of marcasite. For the axial ratio $a/c=1/2$ of marcasite the layers are shifted by exactly $b/3$ relative to each other.

compounds with more than one kind of transition metal and/or different pnictogen/chalcogen ratios.

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References

- ANDERSSON, S. & ÅSTRÖM, A. (1972). *Proc. 5th Mater. Res. Symp.* 1971. *Natl. Bur. Stand. Spec. Publ.* **364**, pp. 3–14.
- BAUR, W. H. (1971). *Nature Phys. Sci.* **233**, 135–137.
- BITHER, T. A., DONOHUE, P. C. & YOUNG, H. S. (1971). *J. Solid State Chem.* **3**, 300–307.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DAHL, E. (1969). *Acta Chem. Scand.* **23**, 2677–2684.
- FINGER, L. W. (1969). Unpublished computer program for the least-squares refinement of crystal structures.
- FRITCHIE, C. J. & GUGGENBERGER, L. J. (1967). Unpublished electron summation program.
- GOMM, P. S., THOMAS, T. W. & UNDERHILL, A. E. (1971). *J. Chem. Soc. (A)*, pp. 2154–2157.
- GRØNVOLD, F. & RØST, E. (1957). *Acta Cryst.* **10**, 329–331.
- HULLIGER, F. (1963). *Nature, Lond.* **200**, 1064–1065.
- HULLIGER, F. (1968). In *Structure and Bonding*, Vol. 4, pp. 83–229. New York: Springer.
- INTERRANTE, L. V. & BUNDY, F. P. (1971). *Inorg. Chem.* **10**, 1169–1174.
- JEITSCHKO, W. (1974). In *Med. Tech. Publ. Co. International Review of Science: Inorg. Chem.*, Series 2, Vol. 5, pp. 219–281. London: Butterworths.
- JEITSCHKO, W. & DONOHUE, P. C. (1972). *Acta Cryst.* **B28**, 1893–1898.
- JEITSCHKO, W. & DONOHUE, P. C. (1973). *Acta Cryst.* **B29**, 783–789.
- JELLINEK, F. (1972). In *Med. Tech. Publ. Co. International Review of Science: Inorg. Chem.*, Series 1, Vol. 5, pp. 339–396. London: Butterworths.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- KENNARD, O. & WATSON, D. G. (1971). *Molecular Structures and Dimensions*, Vol. 3. Utrecht: Oosthoek.
- KENNARD, O., WATSON, D. G. & TOWN, W. G. (1973). *Molecular Structures and Dimensions*, Vol. 4. Utrecht: Oosthoek.
- KROGMANN, K. (1969). *Angew. Chem. Int. Ed.* **8**, 35–42.
- MEIER, W. M. & VILLIGER, H. (1969). *Z. Kristallogr.* **129**, 411–423.
- MILLER, J. R. (1962). *Advanc. Inorg. Radiochem.* **4**, 133–195.
- MILLER, J. R. (1965). *J. Chem. Soc.* pp. 713–720.
- MONTEITH, L. K., BALLARD, L. F., PITT, C. G., KLEIN, B. K. SLIFKIN, L. M. & COLLMAN, J. P. (1968). *Solid State Commun.* **6**, 301–304.
- MOOSER, E. & PEARSON, W. B. (1960). *Prog. Semicond.* **5**, 103–139.
- OHASHI, Y., HANAZAKI, I. & NAGAKURA, S. (1970). *Inorg. Chem.* **9**, 2551–2556.
- PARTHÉ, E. (1973). *Acta Cryst.* **B29**, 2808–2815.
- PEARSON, W. B. (1967). *Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2. New York: Pergamon Press.
- PREWITT, C. T. (1967). Unpublished computer program.
- RUNDLE, R. E. (1957). *J. Phys. Chem.* **61**, 45–50.
- SCHMIDT, M. (1973). *Angew. Chem. Int. Ed.* **12**, 445–455.
- SHOEMAKER, C. B. & SHOEMAKER, D. P. (1967). *Acta Cryst.* **23**, 231–238.
- WARD, R. (1972). In *Med. Tech. Publ. Co. International Review of Science: Inorg. Chem.*, Series 1, Vol. 5, pp. 93–174. London: Butterworths.
- WELLS, A. F. (1965). *Acta Cryst.* **18**, 894–900.
- WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.
- YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1969). *A Fortran IV Program for the Intensity Calculation of Powder Patterns*. Report of the Laboratory for Research on the Structure of Matter, Univ. of Pennsylvania, Philadelphia, Pa.
- ZACHARIASEN, W. H. (1963a). *Acta Cryst.* **16**, 1139–1144.
- ZACHARIASEN, W. H. (1963b). *Acta Cryst.* **16**, 1253–1255.
- ZAHNER, J. C. & DRICKAMER, H. G. (1960). *J. Chem. Phys.* **33**, 1625–1628.