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Preparation, Crystal Structure, and Properties of $HgSnP_{14}$ and Other Polyphosphides with $HgPbP_{14}$-Type Structure

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The new compound $HgSnP_{14}$ and the known isotypic polyphosphides $HgPbP_{14}$ and $MM'P_{14}$ (M = Zn, Cd; M' = Sn, Pb) were prepared by reaction of the elemental components in evacuated silica tubes. They are diamagnetic semiconductors with bandgaps ranging from 0.4 ± 0.2 eV for $HgPbP_{14}$ to 1.6 ± 0.1 eV for $ZnSnP_{14}$. The crystal structure of $CdSnP_{14}$ was refined from single-crystal X-ray counter data to a residual of $R = 0.040$ for 83 variable parameters and 1182 structure factors. The crystal structure and physical properties of these polyphosphides are briefly discussed.

Introduction

The compounds $MPbP_{14}$ (M = Zn, Cd, Hg) were first prepared by Krebs, Pakulla, and Zürn (*1*). Their crystal structure was determined from single-crystal data of $HgPbP_{14}$ in 1958 (*2*). Much later the isotypic compounds $ZnSnP_{14}$ and $CdSnP_{14}$ were briefly described in conference abstracts (*3*). We have prepared $CdSnP_{14}$ accidentally in well crystallized form during our search for ternary polyphosphides like $MoFe_2P_{12}$ (*4*), $TiMn_2P_{12}$ (*5*), or $NbMn_2P_{12}$ (*6*) with Cd as a metal component using tin as a reaction medium. Since the structure of $HgPbP_{14}$ was determined only from film data with rather high residuals varying between $R = 0.14$ and $R = 0.26$ for various fractions of the data set (*2*), we decided to refine the structure for $CdSnP_{14}$ using modern counter and computing techniques. We also determined the electrical conductivity and magnetic properties for the whole isotypic series, including the new compound $HgSnP_{14}$.

Sample Preparation

Starting materials were powders of zinc and cadmium (up to 0.07 mm, 99.999%), tin 99.9%), lead (99.999%), mercury ("zur Polarographie," Merck), and red phosphorus ("ultrapure," Hoechst). The components were mixed and annealed in evacuated, closed silica tubes. The reaction times were in all cases two weeks followed by slow cooling (10°/hr) to room temperature.

The starting compositions for the preparation of $ZnSnP_{14}$ and $CdSnP_{14}$ were in the atomic ratios Zn(Cd) : Sn : P = 1 : 20 : 30. Annealing at 700°C yielded larger crystals than annealing at 500°C. $HgSnP_{14}$ was obtained only with small yields. The starting ratio was Hg : Sn : P = 10 : 1 : 30. For 0.3 g P the reaction volume was 3 cm^3.

The preparation of the ternary lead com-

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pounds was essentially as previously reported (*1*). The starting compositions for $ZnPbP_{14}$ varied between Zn : Pb : P = 1 : 97 : 50 and 3 : 97 : 100 with annealing at 630°C. For $CdPbP_{14}$ starting ratios of Cd : Pb : P = 1 : 99 : 50 and 1 : 99 : 100 were used; annealing at 600°C. Well developed crystals of $HgPbP_{14}$ were obtained from samples with Hg : Pb : P = 3 : 97 : 50 and 3 : 97 : 100, annealed at 630°C.

The matrix of the tin containing samples was dissolved in slightly diluted (1 : 1) hydrochloric acid. The samples containing lead were treated with a mixture (1 : 1) of aqueous solutions of acetic acid (25%) and hydrogen peroxide (15%).

Properties

The ternary compounds crystallize in the form of black needles which easily disintegrate into very thin fibers. They withstand diluted acids (HCl, H_2SO_4) and bases and dissolve slowly in cold concentrated nitric acid, aqua regia, and hydrogen peroxide (30%). They are indefinitely stable in dry air, but are slightly attacked in moist air, probably through the formation of phosphoric acid (*1*). However, even after a year only the surface of the crystals was corroded.

Lattice constants were determined from Guinier powder patterns with use of α-quartz (a = 0.49130 nm, c = 0.54046 nm) as a standard (Table I). To assure proper indexing intensities were calculated (*7*) using the positional parameters as obtained in the structure refinement of $CdSnP_{14}$. As an example the evaluation of the diagram of $HgSnP_{14}$ is shown in Table II.

Magnetic susceptibility measurements were carried out at room temperature with a Faraday balance. The sample weights were about 30 to 40 mg with the exception of the zinc containing samples which were smaller. This resulted in larger error limits. All compounds are diamagnetic. The results are as follows (all values $\times 10^{-6}$ in cm^3/mole): $ZnSnP_{14}$: −490 ± 100; Cd SnP_{14}: −380 ± 20; $HgSnP_{14}$: −330 ± 30; $ZnPbP_{14}$: −210 ± 100; $CdPbP_{14}$: −390 ± 20; $HgPbP_{14}$: −450 ± 20. Using the increments ($\chi \times 10^{-6}$ cm^3/mole) of the metal ions for Zn^{2+} (−10), Cd^{2+} (−22), Hg^{2+} (−37),

TABLE I

LATTICE CONSTANTS OF COMPOUNDS WITH $HgPbP_{14}$-TYPE STRUCTURE[a]

Compound	a (nm)	b (nm)	c (nm)	V (nm^3)	Reference
$ZnSnP_{14}$	1.2619(3)	0.9794(2)	1.0496(2)	1.297(1)	[b]
$ZnSnP_{14}$	1.25954(5)	0.98264(7)	1.05192(9)	1.302	(*3*)
$CdSnP_{14}$	1.2817(3)	0.9826(2)	1.0775(2)	1.357(1)	[b]
$CdSnP_{14}$	1.272	0.989	1.056	1.328	(*3*)
$CdSnP_{14}$	1.2820(1)	0.9831(6)	1.0789(4)	1.360	(*26*)
$HgSnP_{14}$	1.2775(2)	0.9834(1)	1.0717(2)	1.346(1)	[b]
$ZnPbP_{14}$	1.2621(2)	0.9811(1)	1.0548(2)	1.306(1)	[b]
$ZnPbP_{14}$	1.272(2)	0.987(2)	1.057(2)	1.327	(*1, 2*)
$CdPbP_{14}$	1.2865(2)	0.9850(1)	1.0815(2)	1.371(1)	[b]
$CdPbP_{14}$	1.283(2)	0.993(2)	1.073(2)	1.367	(*1, 2*)
$HgPbP_{14}$	1.2816(4)	0.9852(2)	1.0745(3)	1.357(1)	[b]
$HgPbP_{14}$	1.280(2)	0.993(2)	1.071(2)	1.361	(*1, 2*)

[a] Setting *Pnma*; standard deviations in the least significant digits are listed in parentheses.

[b] This work.

TABLE II

EVALUATION OF A POWDER PATTERN OF $HgSnP_{14}$ WITH $HgPbP_{14}$-TYPE STRUCTURE[a]

hkl	Q_c	Q_o	I_c	I_o	*hkl*	Q_c	Q_o	I_c	I_o
101	148	149	57	s	214	1742	1743	35	m
011	191	191	17	w	323	1749	1745	26	w
111	252	252	81	vs	141	1803	1805	15	vw
201	332	332	57	s	502	1880	1878	13	vw
020	414	413	73	vs	240	1900	1900	13	vw
121	562	562	36	m	042	2003	2001	15	vw
202	593	594	62	s	521	2033	2033	38	m
301	639	639	83	vs	142	2064	2064	9	vw
220	659	658	49	s	423	2178	2176	9	vw
212	697	697	25	w	600	2206	2207	12	vw
022	762	762	69	s	242	2248	2250	16	vw
122	823	823	10	vw	601	2293	2291	45	s
113	948	948	74	vs	115	2341	2343	40	m
312	1003	1007	13	s	414	2477	2479	43	m
222	1007		49		234	2569	2573	20	w
031	1018	1019	12	vw	620	2620	2621	16	vw
203	1029	1030	66	s	243	2683	2681	9	vw
321	1052	1052	100	vs	334	2875	2877	13	vw
401	1068	1067	60	s	622	2968	2966	16	w
123	1259	1261	13	vw	035	3107	3101	18	w
231	1263	—	15	—	135	3169	3166	57	s
303	1335	1335	38	m	631	3224	3224	32	m
132	1340	1341	71	vs	533	3246	3248	17	w
412	1432	1432	27	w	541	3273	3273	18	w
232	1524	1522	55	s	434	3303	3304	84	vs
331	1569	1570	11	vw	153	3430	3427	12	vw
501	1619	1619	36	m	216	3483	3486	19	w
040	1654	1658	31	m	060	3722	3725	34	m

[a] The pattern was recorded in a Guinier camera with Cu$K\alpha_1$ radiation. All observed reflections and all reflections with calculated intensities $I_c > 12$ are listed. The Q values are defined by $Q = 100/d^2$ (nm^{-2}). Observed intensities: vw, very weak; w, weak; m, medium; s, strong; vs, very strong.

Sn^{2+} (−20), Pb^{2+} (−28), and (for simplicity) the Pascal increment of −26 for P^0 (*8, 9*), one obtains calculated values of between −394 and −429 in good agreement with the observed values, considering the relatively large error limits of our measurements.

Electrical conductivities were determined for polycrystalline pellets. The determination for single crystals was not possible because of the tendency for fibrous cleavage of the crystals. The samples were ground up with a small amount of paraffin oil, which was washed away by repeated treatment with petrol ether. The cold pressed pellets were squeezed between flat tungsten electrodes. Independent current and voltage probes were used and the potential differences were determined with a compensator. Because of the uncertainty of the contacting areas and the porosities of the pellets the absolute resistivity values are estimated to be correct only within a factor of three. The specific resistivities at room temperature thus calculated varied between 6 × 10^4 Ω cm for $HgPbP_{14}$ and 3 × 10^5 Ω cm for $ZnSnP_{14}$.

Relative values for one sample at different temperatures were judged to be much more reliable. All samples were measured between liquid nitrogen temperature and 600 K. Only slight increases of the conductivities were observed for the six compounds between 77 K and room temperature. The onsets of the intrinsic conductivities occurred for the zinc compounds at about 370 K, for the cadmium compounds at about 400 K, and for the mercury compounds at about 480 K. Activation energies E_a with estimated error limits (Table III) were calculated from the straight slopes of the ln ρ vs $1/T$ plots at higher temperatures according to $\rho = \rho_0 \exp E_a/2kT$.

Structure Refinement of $CdSnP_{14}$

The single crystal of $CdSnP_{14}$ used for the structure refinement was isolated from a sample which had been annealed at 500°C. Precession diagrams confirmed the orthorhombic symmetry, and the space group extinctions were compatible with space group *Pnma*-D_{2h}^{16}. We have used this setting throughout rather than the nonstandard setting *Pbnm* adopted previously (*1–3*).

The crystal (dimensions 0.02 × 0.04 ×

TABLE III

ACTIVATION ENERGIES E_a (eV) FOR SEMICONDUCTORS WITH $HgPbP_{14}$-TYPE STRUCTURE

M =	Zn	Cd	Hg
$MSnP_{14}$	1.6 ± 0.1	1.0 ± 0.1	0.4 ± 0.2
$MPbP_{14}$	0.8 ± 0.1	0.7 ± 0.1	0.4 ± 0.2

0.11 mm^3) was mounted with the needle axis parallel to the phi axis of an automated four-circle diffractometer. All reflections within one-half of the reciprocal space were measured up to $2\theta = 90°$ with $\theta/2\theta$-scans, Mo$K\alpha$ radiation, a graphite monochromator, a scintillation counter, and a pulse height discriminator. Background counts were taken at both ends of each scan. An empirical absorption correction was applied from psi scan data. Of the total of 23,233 reflections 1182 independent structure factors remained after averaging of equivalent reflections and omitting those with intensities smaller than three standard deviations.

After transforming the atomic positions as given by Krebs and Ludwig (*2*) to the standard description of space group *Pnma*, the structure was refined by a full-matrix least-squares program supplied by the Enraf-Nonius Company. Atomic scattering factors (*10*), corrected for anomalous dispersion (*11*) were used. Weights were assigned according to counting statistics. A parameter for an isotropic secondary extinction correction was also refined. The residual for a refinement with isotropic thermal parameters was $R = 0.053$ (40 variables); it was lowered to $R = 0.040$ by allowing for ellipsoidal thermal parameters (83 variables, 1182 structure factors). A refinement of occupancy parameters for all positions did not result in any significant deviations from full occupancy: the occupancy parameters (with standard deviations) varied between 97.8 (1.2)% for P(3) and 102.2 (1.2)% for P(4). A final difference Fourier analysis showed the small value of 1.6×10^3 e/nm^3 as highest peak. The atomic parameters are listed in Table IV, interatomic distances and angles in Table V. A listing of observed and calculated structure factors can be obtained from the authors (*12*).

Discussion

The HgPbP$_{14}$-type structure consists of tubes of condensed five- and six-membered rings of strongly bonded atoms (Fig. 1). The tubes have pentagonal cross section; they extend parallel to the *y* direction and are linked to each other via Hg(Zn, Cd)–P bonds (Fig. 2). Similar tubes with pentagonal cross section occur in the Hittorf modifi-

TABLE IV

POSITIONAL AND THERMAL PARAMETERS OF CdSnP$_{14}$[a]

Atom	*Pnma*	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	*B*
Cd	4*c*	0.1832(1)	$\frac{1}{4}$	0.0048(1)	14.5(4)	12.8(4)	13.0(4)	0	5.0(5)	0	1.06(1)
Sn	4*c*	0.3294(1)	$\frac{1}{4}$	0.5989(1)	16.0(4)	24.4(5)	13.8(4)	0	−4.1(5)	0	1.42(2)
P(1)	4*c*	0.0305(3)	$\frac{1}{4}$	0.8372(4)	14(2)	8(1)	10(1)	0	0(1)	0	0.82(6)
P(2)	4*c*	0.4442(3)	$\frac{1}{4}$	0.2206(4)	14(2)	10(2)	15(2)	0	−1(2)	0	1.01(6)
P(3)	4*c*	0.0857(3)	$\frac{1}{4}$	0.4007(4)	15(2)	8(1)	11(1)	0	−2(2)	0	0.90(6)
P(4)	4*c*	0.3314(3)	$\frac{1}{4}$	0.8477(4)	11(1)	7(1)	12(1)	0	2(2)	0	0.79(5)
P(5)	8*d*	0.4700(2)	0.0752(3)	0.3479(3)	15(1)	8(1)	13(1)	−1(1)	2(1)	−2(1)	0.94(4)
P(6)	8*d*	0.0685(2)	0.0824(3)	0.7099(3)	10(1)	7(1)	14(1)	−1(1)	1(1)	−1(1)	0.82(4)
P(7)	8*d*	0.4256(2)	0.0804(3)	0.9176(2)	15(1)	8(1)	9(1)	0(1)	0(1)	0(1)	0.84(4)
P(8)	8*d*	0.1789(2)	0.0756(3)	0.3341(3)	11(1)	7(1)	17(1)	−1(1)	−3(1)	0(1)	0.93(4)
P(9)	8*d*	0.1395(2)	0.0433(3)	0.1393(3)	17(1)	8(1)	13(1)	0(1)	4(1)	2(1)	0.99(4)

[a] The standard deviations in the positions of the least-significant digits are given in parentheses. Ellipsoidal thermal parameters ($\times 10^3$) are defined by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)]$. The last column contains the equivalent isotropic thermal parameter $B(\times 100$, nm$^2)$.

TABLE V

INTERATOMIC DISTANCES (pm) AND ANGLES (°) IN $CdSnP_{14}$[a]

Cd:	1P(4)	254.5	P(4)–Cd –P(9)	122.7	(2*x*)
	2P(9)	255.8	P(4)–Cd –P(1)	95.6	
	1P(1)	266.3	P(9)–Cd –P(9)	105.2	
			P(9)–Cd –P(1)	102.9	(2*x*)
Sn:	1P(1)	266.7	P(1)–Sn –P(4)	74.5	
	1P(4)	268.1	P(1)–Sn –P(9)	80.3	(2*x*)
	2P(9)	294.1	P(4)–Sn –P(9)	81.4	(2*x*)
			P(9)–Sn –P(9)	156.8	
P(1):	2P(6)	219.8	P(6)–P(1)–P(6)	97.0	
	1Cd	266.3	P(6)–P(1)–Cd	105.1	(2*x*)
	1Sn	266.7	P(6)–P(1)–Sn	112.0	(2*x*)
			Cd– P(1)–Sn	122.3	
P(2):	2P(5)	222.3	P(5)–P(2)–P(5)	101.2	
	1P(3)	223.6	P(5)–P(2)–P(3)	103.8	(2*x*)
P(3):	2P(8)	220.9	P(8)–P(3)–P(8)	101.7	
	1P(2)	223.6	P(8)–P(3)–P(2)	104.4	(2*x*)
P(4):	2P(7)	219.2	P(7)–P(4)–P(7)	99.0	
	1Cd	254.5	P(7)–P(4)–Cd	100.5	(2*x*)
	1Sn	268.1	P(7)–P(4)–Sn	110.4	(2*x*)
			Cd– P(4)–Sn	131.2	
P(5):	1P(9)	219.8	P(9)–P(5)–P(6)	99.4	
	1P(6)	220.3	P(9)–P(5)–P(2)	107.3	
	1P(2)	222.3	P(6)–P(5)–P(2)	95.3	
P(6):	1P(1)	219.8	P(1)–P(6)–P(5)	93.2	
	1P(5)	220.3	P(1)–P(6)–P(7)	101.8	
	1P(7)	228.9	P(5)–P(6)–P(7)	102.7	
P(7):	1P(4)	219.2	P(4)–P(7)–P(8)	93.0	
	1P(8)	222.6	P(4)–P(7)–P(6)	103.1	
	1P(6)	228.9	P(8)–P(7)–P(6)	104.2	
P(8):	1P(9)	218.2	P(9)–P(8)–P(3)	107.5	
	1P(3)	220.9	P(9)–P(8)–P(7)	98.6	
	1P(7)	222.6	P(3)–P(8)–P(7)	94.4	
P(9):	1P(8)	218.2	P(8)–P(9)–P(5)	98.5	
	1P(5)	219.8	P(8)–P(9)–Cd	112.3	
	1Cd	255.8	P(8)–P(9)–Sn	104.7	
	1Sn	294.1	P(5)–P(9)–Cd	98.0	
			P(5)–P(9)–Sn	106.4	
			Cd– P(9)–Sn	131.6	

[a] All distances shorter than 300 pm are listed. Standard deviations computed from those of the lattice and the positional parameters are all equal or less than 0.6 pm and 0.2°, respectively. The distances of the Sn atoms to P atoms in neighboring tubes are 367.5 pm (2*x*) to P(5), 378.1 pm (1*x*) to P(3), and 384.5 pm (2*x*) to P(8).

cation of phosphorus (*13*), in KP_{15} (*14*), CsP_{11} (*15*), BaP_{10} (*16*), TlP_5 (*17*), and $Cu_2P_3I_2$ (*18*). In the $HgPbP_{14}$-type compounds the metal atoms participate in the formation of the tubes.

The P–P bonds in $CdSnP_{14}$ cover the range from 218.2 to 228.9 pm. The average bond length of 221.4 pm corresponds to the usual average bond lengths of 222 ± 2 pm for P–P bonds in elementary phosphorus modifications (*13, 19*) and other polyphosphides, e.g., $TiMn_2P_{12}$: 222.9 pm (*5*), $Cu_2P_3I_2$: 222.8 pm (*18*), VP_4: 222.0 pm (*20*), $MoFe_2P_{12}$: 224.8 pm (*4*), TcP_3: 220.6 pm (*21*), Cu_2P_7: 220.1 pm (*22*). The P–P–P bond angles extend from 93.2 to 107.5° with an average of 100.7°. They are thus all smaller than the ideal tetrahedral angle of 109.5°.

In assigning oxidation number zero to each phosphorus atom with three P neighbors and oxidation number −1 to each phosphorus atom with two P and two metal neighbors, both cadmium and tin obtain oxidation number +2.

The tin atoms have a typical coordination for Sn^{2+} with a stereoactive lone pair. The cadmium atoms have four close P neighbors which belong to three tubes and which form a distorted tetrahedron. The tetrahedral coordination of the cadmium atoms is remarkable, since in CdP_4 (*23*), the coordination of the Cd atoms (also with oxidation number +2) is octahedral. The average Cd–P bond lengths of 258.1 pm in $CdSnP_{14}$ and 277.9 pm in CdP_4, however, reflect the differing coordination numbers. In $CdGeP_2$ (*24*) the Cd atoms are also tetrahedrally coordinated by P atoms. The slightly shorter (unique) Cd–P distance of 255.4 pm in that compound compares favorably with the average Cd–P distance of 258.1 pm in $CdSnP_{14}$ considering the spread (*25*) of these distances in $CdSnP_{14}$.

It is interesting to compare the cell volumes of the six $HgPbP_{14}$ type compounds (Fig. 3). Although the atomic and ionic radii of Zn, Cd, and Hg increase in that order, the cell volumes of the mercury compounds are smaller than those of the cadmium com-

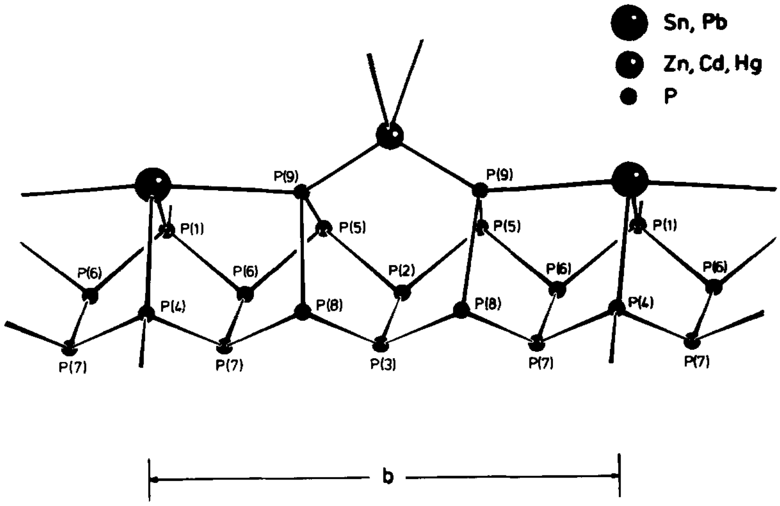

FIG. 1. A cut-out of the tube-like chains with pentagonal cross section of the $HgPbP_{14}$-type structure. The length of one translation period consisting of one formula unit is indicated.

pounds. In comparing our lattice constants—which we hold more reliable, since they were all determined the same way and thus subject to the same systematic errors (if any)—it can be seen (Table I) that, in going from the Cd to the Hg compound, the *a* and *c* lattice constants decrease, while *b* increases. This is probably caused by the tendency of Hg^{2+} for coordination number two with linear coordination. If the P(9)–Hg(Cd)–P(9) angle increases from 105.2° in the Cd compound to a value closer to 180° in the Hg compound (Fig. 1), the tubes and thus the *b* axis expands, while the packing of the tubes becomes denser, which results in a decrease of the *a* and *c* axes.

In agreement with the rationalization of chemical bonding all $HgPbP_{14}$-type compounds are diamagnetic semiconductors. The bandgaps decrease in going from the cadmium to the mercury and from the tin to the lead compounds. This is in accord with the general observation of a diminishing band gap for the heavier elements within

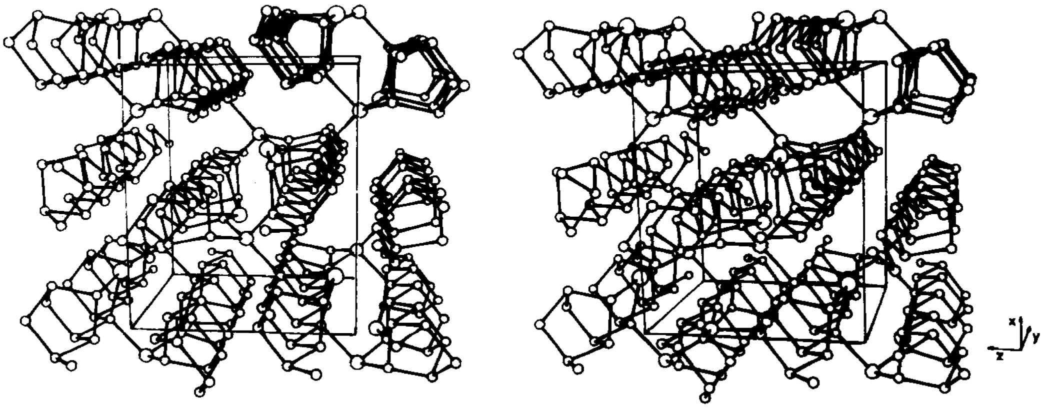

FIG. 2. Stereoplot of the structure of $CdSnP_{14}$. Large, medium, and small spheres correspond to the Sn, Cd, and P atoms, respectively.

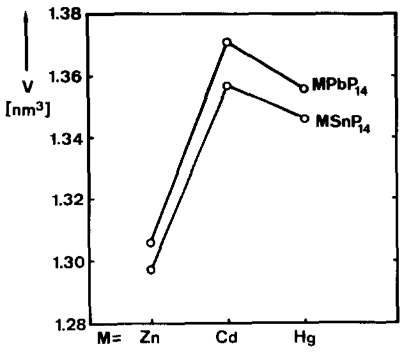

FIG. 3. Cell volumes of HgPbP$_{14}$-type compounds.

one main group of the periodic system, as it is best known for the diamond modification of carbon, silicon, and germanium.

Note added after completion of the manuscript. Some excerpts of a doctoral thesis by Ott (*26*) were made available to us by a reviewer. Ott had refined the crystal structures of ZnSnP$_{14}$ and CdSnP$_{14}$ from single-crystal counter data. The accuracy of these refinements is difficult to assess since no standard deviations of the positional parameters, interatomic distances, and interatomic angles were reported. However, judging from the only slightly higher residuals of 0.041 and 0.042 for the Zn and Cd compound, respectively, the accuracy is comparable, albeit probably somewhat lower, to that obtained by us for CdSnP$_{14}$. Interatomic distances and angles of the two refinements of CdSnP$_{14}$ agree all within 0.6 pm and 0.4°. The differences in interatomic angles for the corresponding metal atoms in ZnSnP$_{14}$ and CdSnP$_{14}$ are all less than 3.8°. Ott (*26*) has pointed out, that the thermal parameters of the Sn atoms (with the designation of our present setting) U_{22} are unusually large: 0.0304 for the Zn compound and 0.0227 for the Cd compound. This is also the case for the corresponding value of $U_{22} = 0.0244$ for our refinement of CdSnP$_{14}$. These large thermal amplitudes of the Sn atoms along the *b* axis are most likely due to the weak bonds of the Sn atoms to the P(9) atoms. This distance is 294.1 pm in CdSnP$_{14}$ and even greater (299.8 pm) in ZnSnP$_{14}$.

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