

# The Crystal Structure of the Tetragonal Modification of $\text{ZnP}_2$

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The crystal structure of the tetragonal modification of  $\text{ZnP}_2$  has been determined from three-dimensional single-crystal X-ray data. All the atoms are tetrahedrally coordinated. Each zinc atom is bonded to four phosphorus atoms while each phosphorus atom is bonded to two zinc and two phosphorus atoms. The structure has no pronounced anisotropic features. One physical difference between the tetragonal  $z$  direction and the  $x$  and  $y$  directions is that continuous chains of phosphorus atoms run through the crystal parallel to  $a$  and  $b$ , but all chains parallel to  $c$  are interrupted by zinc atoms. The bond distances are in good agreement with those calculated from covalent radii but the bond angles show rather wide variations.

## Introduction

In a recent investigation of the physical properties of the zinc phosphides it became necessary to determine the crystal structures of both the red tetragonal modification and a new black monoclinic modification of  $\text{ZnP}_2$ . A preliminary account of these structures has been given together with the preparation of the crystals and their optoelectronic properties (Hegyi, Loebner, Poor & White, 1963). In the present paper the detailed crystal structure of the tetragonal modification, after further refinement, is described.

The unit-cell dimensions and space group of tetragonal  $\text{ZnP}_2$  were first determined by Stackelburg & Paulus (1935) and the corresponding data given below are almost identical with those published by these authors.

## Experimental measurements

### Crystal data

$\text{ZnP}_2$ , M.W. 127.33.

Orthorhombic,

$a = 5.08 \pm 0.01$ ,  $c = 18.59 \pm 0.05$  Å,  $V = 479.8$  Å<sup>3</sup>.

Absent spectra:  $00l$  with  $l \neq 4n$ ,  $h00$  with  $h$  odd.

Space group  $P4_12_12$  (or  $P4_32_12$ ).

8 formula units per unit cell.

$d_c = 3.536$  g.cm<sup>-3</sup>.

$\mu$  (Cu  $K\alpha$ ) = 233 cm<sup>-1</sup>.

The crystals were in the form of thick orange-red plates with the large face (001). They cleaved easily on both (100) and (110) to give suitable specimens for X-ray examination. Most of the crystals had growth ridges or striations in the [001] and [110] directions.

All the X-ray measurements were made with Ni filtered Cu  $K\alpha$  radiation. Three-dimensional intensity data were collected on six sets of equi-inclination Weissenberg photographs from two crystals. The crystal used for the  $0kl$ ,  $1kl$  and  $2kl$  reflections measured  $0.03 \times 0.05$  mm in cross section and that for the

$hhl$ ,  $h, h \pm 1, l$  and  $h, h \pm 2, l$  reflections had a square cross section of edge 0.04 mm. Both crystals were about 0.2 mm in length. The intensities were estimated visually by comparison with a standard intensity scale prepared by recording a single reflection for varying times and the strongest and weakest intensities were correlated by the use of a multiple film technique. Of the 313 observed reflections 68 were

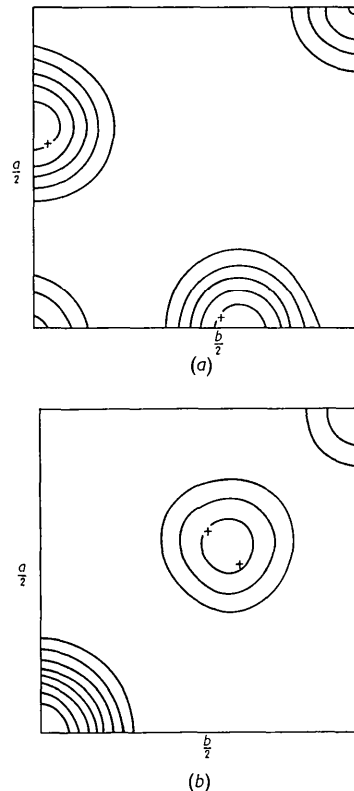


Fig. 1. Sections of the three-dimensional Patterson map, (a) at  $z = \frac{1}{4}$ , (b) at  $z = \frac{1}{2}$ . The crosses mark Zn-Zn vectors, other peaks being due to superposed Zn-P and P-P vectors.

estimated on three different photographs, 82 on two and 163 only once. For the crystal used in the  $a$  axis settings absorption corrections were made from the measured shape of the crystal (Evans, 1952) while for the other a cylindrical approximation was made.

### Structure determination and refinement

A Patterson projection of the  $0kl$  zone was first prepared. For such a simple structure, involving only three crystallographically independent atoms (although with nine free parameters in this projection), the vector map proved surprisingly difficult to interpret. In fact the Zn-Zn projection vectors could not be unambiguously assigned. This difficulty was due actually to the fact that many parameters are close to rational fractions of the cell edges and many coincidences occurred in projection among vectors involving phosphorus atoms.

Accordingly sections of the three-dimensional Patterson function, with the  $F^2$  data sharpened to

Table 1. *Coordinates of the atoms and standard deviations*

Atom	$x$	$y$	$z$	$\sigma$
Zn	0.154	-0.366	0.0503	0.005 Å
P(1)	-0.185	0.298	0.0597	0.009
P(2)	-0.010	-0.020	0.1261	0.009

correspond to atoms at rest, were prepared at  $z = \frac{1}{4}$ ,  $z = \frac{1}{2}$  and  $x = \frac{1}{2}$  and the structure was very easily solved. Two of these Harker sections are shown in Fig. 1.

All the atoms were found to be in the eightfold ( $b$ ) positions with coordinates close to those of Table 1. The structure was refined first by means of the centrosymmetric  $0kl$  projection through four cycles of  $\rho_o$  and  $\rho_o - \rho_c$  series. Then when no further atomic movements occurred two cycles of three-dimensional refinement were carried out again by difference Fourier methods, by computing sections through the center of each atom perpendicular to both  $b$  and  $c$ . Between the two- and three-dimensional refinements the atom Zn and P(2) moved less than 0.01 Å but the atom P(1) moved about 0.04 Å. For this atom a third three-dimensional refinement was carried out but further change was negligible. Initially a single temperature factor was used for all atoms but in the later stages an attempt was made to refine the temperature factors separately for each atom (Hamilton, 1955). The individual differences were obviously small and in the finally adopted values of  $B$ , 0.60 Å<sup>-2</sup> for Zn and 0.75 Å<sup>-2</sup> for P(1) and P(2), they cannot be considered outside experimental error. The difference electron density maps suggested no clear anisotropy of thermal vibrations between directions parallel and perpendicular to the  $c$  axis and it appears that the structure can be described to a fair approximation

Table 2. *Calculated and observed values of the structure factors*

$hkl$	$ E_c $	$E_o$	$hkl$	$ E_c $	$E_o$	$hkl$	$ E_c $	$E_o$	$hkl$	$ E_c $	$E_o$	$hkl$	$ E_c $	$E_o$	$hkl$	$ E_c $	$E_o$	$hkl$	$ E_c $	$E_o$
004	33	36	02,13	46	49	04,10	8	119	119	44	41	133	29	31	154	38	45	22,21	14	16
008	139	125	02,14	8	<12	04,11	24	18	11,10	133	128	134	36	39	155	23	21	230	9	7
00,12	175	170	02,15	19	19	04,12	16	<17	11,11	62	66	135	11	12	156	28	26	231	4	7
00,16	137	130	02,16	4	<12	04,13	20	19	11,12	19	21	136	10	10	157	35	35	232	17	16
00,20	51	52	02,17	11	<13	04,14	2	<15	11,13	33	36	137	19	18	158	44	46	233	53	52
011	16	16	02,18	7	<14	04,15	21	20	11,14	6	<13	138	19	20	159	56	54	234	64	60
012	5	5	02,19	42	42	04,16	20	22	11,15	15	19	139	29	28	15,10	58	60	235	59	56
013	24	27	02,20	65	67	05,18	27	11,16	30	36	13,10	16	17	15,11	28	26	236	29	28	
014	146	130	02,21	50	54	05,19	26	11,17	22	19	13,11	40	41	15,12	37	41	237	43	42	
015	50	53	02,22	2	<10	05,20	50	56	11,18	79	88	13,12	97	91	15,13	13	<10	238	20	19
016	2	<8	031	7	<14	054	29	31	11,19	24	26	13,13	36	37	15,14	11	<9	239	31	30
017	57	60	032	14	15	055	47	42	11,20	70	73	13,14	21	20	160	7	<9	23,10	8	10
018	61	61	033	57	63	056	5	<17	11,21	26	29	13,15	30	31	161	5	<10	23,11	20	17
019	30	33	034	174	152	057	29	26	11,22	20	20	13,16	69	72	162	14	<11	23,12	43	40
01,10	1	<11	035	66	70	058	2	<16	11,23	32	35	13,17	17	18	163	21	20	23,13	27	24
01,11	11	15	036	8	<16	059	26	25	120	3	<6	164	31	36	23,14	22	18	262	19	21
01,12	70	72	037	33	37	05,10	23	20	121	30	30	13,19	22	25	165	34	35	23,15	37	37
01,13	19	19	038	69	71	05,11	6	<13	122	107	114	13,20	7	<9	166	15	12	23,16	22	20
01,14	9	<13	039	19	24	05,12	28	32	123	49	51	140	21	19	167	24	25	23,17	42	42
01,15	39	39	03,10	8	<18	05,13	38	36	124	43	51	141	38	37	168	17	16	23,18	21	24
01,16	65	65	03,11	44	47	05,14	3	<9	125	53	59	142	57	55	220	110	106	23,19	23	25
01,17	44	48	03,12	98	93	05,15	39	32	126	143	134	143	41	42	221	20	21	240	64	66
01,18	6	<13	03,13	30	27	060	93	103	127	43	43	144	51	51	222	133	133	241	69	67
01,19	39	41	03,14	4	<19	061	71	81	128	15	17	145	53	52	223	27	28	242	60	58
01,20	15	17	03,15	26	24	062	21	19	129	30	30	146	71	68	224	59	65	243	41	40
01,21	10	11	03,16	80	77	063	4	<15	12,10	26	29	147	57	55	225	21	24	244	42	44
01,22	2	<7	03,17	28	27	064	17	22	12,11	14	14	148	32	31	226	59	64	245	29	29
01,23	13	10	03,18	12	<15	065	4	<12	12,12	26	28	149	8	<17	277	4	<12	246	34	36
020	22	25	03,19	9	<12	066	21	20	12,13	38	36	14,10	25	26	228	20	26	247	24	24
021	71	75	03,20	31	31	067	36	34	12,14	102	94	14,11	8	<14	229	14	15	248	32	33
022	7	7	03,21	14	10	068	20	21	12,15	39	39	14,12	26	21	22,10	129	113	249	49	44
023	57	56	040	40	39	069	35	32	12,16	17	17	14,13	38	37	22,11	9	13	24,10	60	53
024	93	98	041	6	<14	110	10	11	12,17	29	31	14,14	57	63	22,12	61	56	24,11	61	52
025	24	28	042	2	<16	111	64	64	12,18	23	21	14,15	42	41	22,13	41	41	24,12	51	50
026	14	14	043	4	<17	112	153	130	12,19	16	19	14,16	34	36	22,14	15	15	24,13	21	19
027	47	51	044	80	85	113	47	53	12,20	10	12	14,17	18	19	22,15	5	<14	24,14	4	<12
028	142	133	045	17	20	114	109	109	12,21	20	20	14,18	3	<9	22,16	68	69	24,15	23	25
029	70	71	046	0	<18	115	17	15	12,22	49	47	150	33	42	22,17	11	15	24,16	36	40
02,10	2	<12	047	37	38	116	78	83	130	160	143	151	34	39	22,18	72	77	24,17	38	38
02,11	56	54	048	111	103	117	9	9	131	52	61	152	57	62	22,19	5	<8	341	14	12
02,12	24	28	049	10	<18	118	129	124	132	18	19	153	48	55	22,20	25	29	251	30	32

by a single isotropic temperature factor. Accurate counter measurements would probably be required to define precisely the fine differences which undoubtedly exist.

The refined coordinates of the atoms are given in Table 1 with their corresponding standard deviations (Cruickshank, 1949) and the final observed and calculated structure factors are listed in Table 2. The scattering factors used are those given in *International Tables for X-ray Crystallography* (1962) and anomalous dispersion corrections were applied (Dauben & Templeton, 1955). For all the observed data  $R$  is 0.077 and a plot of  $R$  as a function of  $\sin \theta$  is shown in Fig. 2 (Luzzati, 1952).

The final electron density map is shown in Fig. 3. This is a composite map of different sections perpendicular to the  $c$  axis and includes a zinc-centered and a phosphorus-centered tetrahedron.

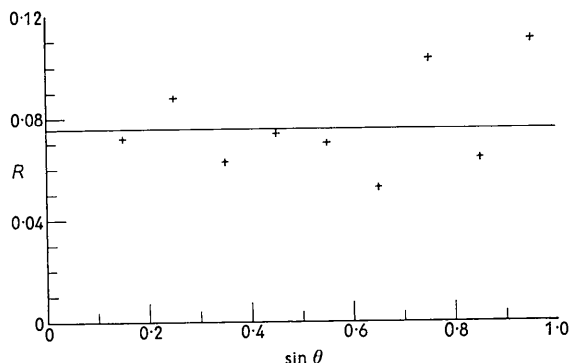


Fig. 2. The discrepancy index  $R$  plotted as a function of  $\sin \theta$ .

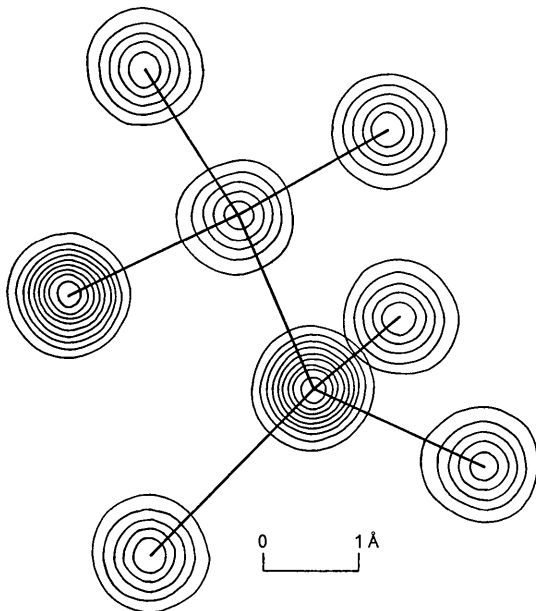


Fig. 3. The electron density over a Zn-centered and a P-centered tetrahedron viewed in the direction of the crystal  $c$  axis. Contours are drawn at intervals of  $10 \text{ e. \AA}^{-3}$  starting at the 2-electron contour.

## Description of the structure

A view of the atomic arrangement within one unit cell of  $\text{ZnP}_2$  is shown in Fig. 4. All atoms are tetrahedrally

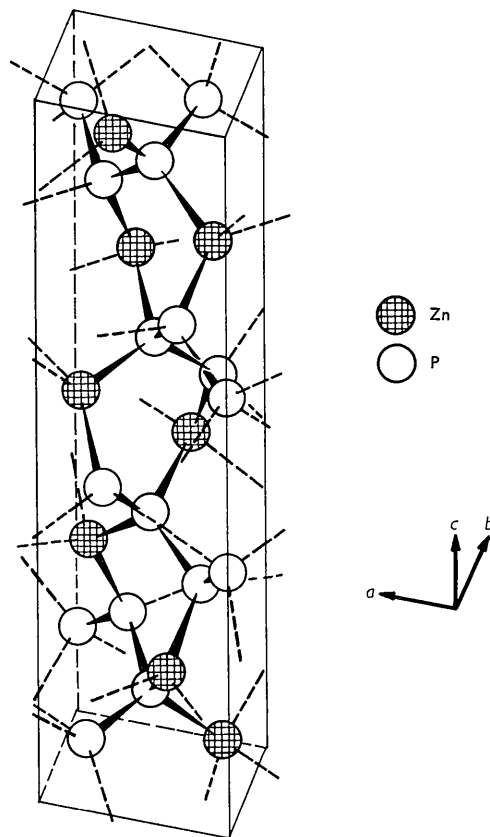


Fig. 4. View of the atomic arrangement in one unit cell of  $\text{ZnP}_2$ . Dotted lines complete the tetrahedral bonding to atoms outside the cell.

bonded. Each zinc atom is bonded to four phosphorus atoms, while each phosphorus atom is bonded to two zinc atoms and two phosphorus atoms. A pseudo halving of the  $c$  axis occurs because for each atom at  $x, y, z$  there is an atom close to  $x, y, \frac{1}{2} + z$  but in some cases it is a zinc and a phosphorus atom rather than two identical atoms which are related in this way. The dimensions of the different tetrahedra are listed in Table 3.

A physical distinction between the  $z$  direction and the  $x$  and  $y$  directions arises from the arrangement of the different tetrahedra. Continuous bonded chains of phosphorus atoms run through the crystal in the  $x$  and  $y$  directions only, while in the  $z$  direction all such chains are interrupted by zinc atoms. There are four phosphorus chains per unit cell running alternately parallel to  $a$  and  $b$ .

## Discussion

Since the Zn-P and P-P bond distances differ on average by about 10% the tetrahedra must necessarily

Table 3. *Bond distances and bond angles*

Tetrahedron surrounding Zn		
Atoms	Distance	$\sigma$
Zn-P(1)	2.36 Å	} 0.010 Å
Zn-P(1')	2.43	
Zn-P(2)	2.40	
Zn-P(2')	2.40	
Atoms	Angle	$\sigma$
P(1)-Zn-P(1')	123.8°	} 0.4°
P(1)-Zn-P(2)	109.3	
P(1')-Zn-P(2)	103.1	
P(1')-Zn-P(2')	105.3	
P(1)-Zn-P(2')	112.7	
P(2)-Zn-P(2')	99.5	
Tetrahedron surrounding P(1)		
Atoms	Distance	$\sigma$
P(1)-Zn	2.36 Å	} 0.010 Å
P(1)-Zn'	2.43	
P(1)-P(2)	2.17	} 0.013
P(1)-P(2')	2.22	
Atoms	Angle	$\sigma$
P(2)-P(1)-P(2')	107.0°	} 0.6°
P(2)-P(1)-Zn	109.5	
P(2)-P(1)-Zn'	104.1	
Zn-P(1)-Zn'	115.5	
Zn-P(1)-P(2')	114.4	
Zn'-P(1)-P(2')	105.6	
Tetrahedron surrounding P(2)		
Atoms	Distance	$\sigma$
P(2)-Zn	2.40 Å	} 0.010 Å
P(2)-Zn'	2.40	
P(2)-P(1)	2.17	} 0.013
P(2)-P(1')	2.22	
Atoms	Angle	$\sigma$
P(1)-P(2)-Zn	111.4°	} 0.6°
P(1)-P(2)-Zn'	104.9	
P(1)-P(2)-P(1')	109.4	
P(1')-P(2)-Zn'	110.2	
Zn-P(2)-Zn'	108.2	
P(1')-P(2)-Zn	112.6	

be somewhat distorted in forming a continuous network. The measured distortions are, in fact, very large particularly for some of the P-Zn-P bond angles. The distortions from the tetrahedral angles, however, are of about the same magnitude as those found

for the high pressure form of germanium (Bundy & Kasper, 1963) where only one type of atom is present.

The average Zn-P distance is 2.40 Å while the average P-P distance is 2.19 Å. These values are in excellent agreement with the distances 2.41 Å and 2.20 Å respectively calculated from Pauling's (1960) tetrahedral radii for wurtzite and zinc blende type structures, although the Zn-P bonds must, of course, have some fraction of ionic type bond character. The extreme variations in bond length, having a maximum difference of seven times the standard deviations, are probably real. The wide variations in the bond angles must give rise to different bond strengths.

The space group has not been determined on an absolute basis, and the atomic coordinates given above refer to an arbitrarily chosen enantiomorph. For Cu  $K\alpha$  radiation used in the experimental work the imaginary component of the anomalous dispersion is zero for the Zn  $K$  shell though there is a small  $L$ -shell contribution. The use of the  $WL$  series would distinguish the enantiomorph existing for a given crystal. However, this does not seem to be of any fundamental importance, for growth of both enantiomorphs probably takes place in the same preparation owing to random nucleation.

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