

Refined Crystal Structures of  $\text{PtP}_2$  and  $\text{FeP}_2$ 

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The crystal structures of  $\text{PtP}_2$  (C2 pyrite type) and  $\text{FeP}_2$  (C18 marcasite type) have been refined by least-squares methods from single-crystal X-ray diffraction data. The P—P bond distances in the two compounds are briefly discussed.

The pyrite type crystal structure of  $\text{PtP}_2$  was originally determined by Thomassen<sup>1</sup> and later confirmed by Biltz *et al.*<sup>2</sup> In this structure (space group:  $Pa\bar{3}$ ) the platinum atoms are in fixed positions, while the phosphorus atoms have one positional parameter ( $x$ ). The platinum atoms are surrounded by six phosphorus neighbours situated at the corners of a slightly distorted octahedron. The pyrite structure might be described as being built up of such octahedra sharing corners. The phosphorus atoms are surrounded by one phosphorus and three platinum neighbours situated at the corners of a distorted tetrahedron. Thus P—P bonds appear in the structure, forming  $\text{P}_2$  pairs. Approximate values for the  $x$  parameter have been given by Rundqvist<sup>3</sup> and by Kjekshus *et al.*<sup>4</sup> These investigations were carried out using estimated intensities of reflexions from X-ray powder diffraction films. The results are listed in Table 1. Kjekshus compared his P—P distance with

Table 1. The  $x$  parameter and P—P distance obtained in former investigations of  $\text{PtP}_2$ .

	$x$	$d_{\text{P-P}}$
Rundqvist	$0.390 \pm 0.005$	$2.17 \pm 0.10$
Kjekshus <i>et al.</i>	$0.394 \pm 0.004$	$2.09 \pm 0.08$

other P—P bond distances found in the literature. This comparison showed that the value for  $\text{PtP}_2$  seems to be significantly shorter than all P—P distances previously reported. However, as he also points out,  $\text{PtP}_2$  is rather unfavourable for an accurate determination of the P—P distance, due to the large difference in the scattering factors for platinum and phosphorus.

In the course of recent studies of platinum phosphides (Dahl<sup>5</sup>), single-crystals of  $\text{PtP}_2$  were obtained. In connection with Kjekshus' discussion it

seemed to be of interest to improve the determination of the bond distance in the  $P_2$  pairs. This bond distance depends on the unit cell parameter  $a$  ( $5.6955 \pm 0.0005$  Å according to Kjekshus *et al.*<sup>4</sup> and the atomic parameter  $x$ . The accuracy with which  $a$  is known is so great that the accuracy of the P—P distance is almost exclusively dependent on the accuracy of the determination of the  $x$  parameter. In order to get a more accurate value of this parameter, a refinement of the  $PtP_2$  crystal structure was undertaken using single-crystal methods.

In connection with work on chemical transport reactions at this Institute (M. Richardson and S. Rundqvist) single-crystals of  $FeP_2$  have been prepared.  $FeP_2$  crystallizes with the marcasite (C 18) structure (Meisel<sup>6</sup>) but accurate structure data are lacking. (The lattice constants have been redetermined by Rundqvist<sup>7</sup>). The marcasite structure (space group:  $Pn\bar{m}$ ) is closely related to the pyrite structure. The iron atoms have six phosphorus neighbours arranged at the corners of a distorted octahedron and the phosphorus atoms have one phosphorus and three iron neighbours situated at the corners of a deformed tetrahedron. In contrast to the pyrite structure, the  $FeP_6$  octahedra share edges so that chains of octahedra run parallel to the shortest unit cell axis. However, both structure types exhibit  $P_2$  pairs and it seemed interesting to make a closer structural comparison. Therefore a single-crystal refinement was made for  $FeP_2$  and the result is reported together with the result of the refinement of  $PtP_2$ .

#### EXPERIMENTAL

The  $PtP_2$  crystal was obtained from an alloy prepared by mixing 70 at. % platinum metal powder (Johnson, Matthey & Co. Ltd, spectroscopic pure) and 30 at. % red phosphorus (better than 99 %) and heating for three weeks in an evacuated and sealed silica tube at about 570°C. The crystal had the dimensions 0.11 mm  $\times$  0.09 mm  $\times$  0.07 mm. Multiple-film Weissenberg photographs were recorded about the  $a$  axis (corresponding to the 0.09 mm edge of the crystal) using Zr-filtered MoK radiation. Thin iron foils were interleaved with the films. The relative intensities of 48 independent  $hk0$  reflexions were estimated visually using an intensity scale obtained by exposing one of the reflexions during measured time intervals. The estimations were carried out over a 180° interval and mean values were then calculated to obtain independent reflexions only.

The  $FeP_2$  single-crystals were prepared by a halogen transport reaction using an experimental arrangement similar to the one described in Ref. 8. The crystal selected had the dimensions 0.4  $\times$  0.07  $\times$  0.07 mm. Multiple-film Weissenberg photographs were recorded about the  $c$  axis (corresponding to the 0.04 mm crystal edge) in the same manner as described for  $PtP_2$ . The relative intensities of  $hk0$  and  $hkl$  reflexions were measured visually and mean values were calculated. 246 independent intensities were obtained.

The intensity data for  $PtP_2$  and  $FeP_2$  were corrected for Lorentz and polarization effects and the  $|F|$ -values were used as input in least-squares refinements. For information regarding the programs and computer used, see Table 2. In the least-squares refinements, weights for the reflexions were assigned according to the formula  $w = 1/(a + |F_o| + c \cdot |F_o|^2)$  following a suggestion by Cruickshank.<sup>9</sup> Final values assigned for the constants were for  $PtP_2$   $a = 19.7$  and  $c = 0.04$  and for  $FeP_2$   $a = 20$  and  $c = 0.5$ . In the structure factor calculations, values for the atomic scattering factors as given in Intern. Tables<sup>10</sup> were used. The value used for the  $PtP_2$  cell parameter was obtained from Ref. 4. The cell parameters for  $FeP_2$  were refined using a powder pattern recorded in a Guinier-Hägg type focussing camera with  $CuK\alpha_1$  radiation ( $\lambda = 1.54051$  Å). Silicon was used as an internal calibration standard ( $a = 5.43054$  Å). The following values were obtained:  $a = 4.9729$  Å  $\pm$  0.0007 Å;  $b = 5.6568$  Å  $\pm$  0.0008 Å;  $c = 2.7230$  Å  $\pm$  0.0004 Å.

Table 2. All the calculations have been carried out on a CDC 3600 electronic computer using the following programs (all programs are written in Fortran IV).

<i>Program</i>	<i>Authors</i>
Lorentz-polarization corrections	A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Absorption correction	P. Coppens, L. Leiserowitz and D. Rabinovich, Rehovoth, Israel; modified by O. Olofsson Uppsala, Sweden.
Least squares refinements of positional parameters and temperatur factors	P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden.
Interatomic distances	A. Zalkin, Berkeley, U.S.A.
Least squares refinement of unit-cell dimensions	J. Tegenfeldt, Uppsala, Sweden.

#### REFINEMENTS OF THE CRYSTAL STRUCTURES

*The PtP<sub>2</sub>-structure.* The intensity material obtained could be divided into two groups, one group with rather strong reflexions and one group with weak reflexions. In the case of the first group, which consists of  $hk0$  having  $k=2n$ , both platinum and phosphorus atoms contribute to the intensity, while the second group of reflexions, consisting of  $hk0$  having  $k=2n+1$ , have intensities depending on the phosphorus atoms only.

A preliminary refinement of the positional parameter for the phosphorus atom, the temperature factors and the scale factor, was made using all reflexions. The  $R$  value ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) obtained was 0.153. The reason for this rather high figure is probably the strong extinction and absorption in the crystal. (The linear absorption coefficient  $\mu=810$ ). A smaller crystal would of course diminish the absorption error but it would also decrease the number of measurable reflexions, especially reducing the number of very useful weak reflexions, which would hardly be visible. In fact a trial with a rather small crystal has been made at this Institute.<sup>11</sup> This trial gave a rather poor result and an  $R$  value of about 0.20.

An attempt was made to improve the intensity material by introducing an absorption correction. As the crystal has rather irregular faces this correction was not very accurate. The  $R$  value for the subsequent refinement did not decrease, but rather increased to 0.157. The temperature factors were, however, less negative than before correction.

It was then decided to make a refinement using only  $hk0$  reflexions with  $k=2n+1$ . As mentioned above, the intensities of these reflexions (18 were obtained) are not dependent on any contribution from the platinum atoms. These intensities should therefore be most sensitive to small changes in the  $x$  parameter for the phosphorus atoms. In addition the low intensities of all these reflexions lead to a smaller extinction error. Refinements using the reduced material were made both excluding and including the absorption correction. The  $R$  values obtained were 0.118 and 0.153, respectively.

Table 3. Result of the refinements of PtP<sub>2</sub>.

Reflexions used	Abs. corr.	$x_P$	$\sigma(x_P)$	$B_{Pt}$	$\sigma(B_{Pt})$	$B_P$	$\sigma(B_P)$	R
All reflexions	No	0.3900	0.0017	-0.34	0.05	-0.65	0.09	0.153
All reflexions	Yes	0.3909	0.0019	0.12	0.06	-0.26	0.11	0.157
Odd reflexions	No	0.3899	0.0007	—	—	-0.35	0.06	0.118
Odd reflexions	Yes	0.3906	0.0011	—	—	0.06	0.10	0.153

Table 4. Structural data for PtP<sub>2</sub>. Space group *Pa*3;  $Z=4$ ;  $a=5.6956$  Å;  $\sigma(a)=0.0005$  Å.

Atom	Position	$x$	$\sigma(x)$	$B$ Å <sup>2</sup>	$\sigma(B)$
Pt	4(a)	—	—	—	—
P	8(c)	0.3899	0.0007	-0.347	0.063

Table 5. Interatomic distances and standard deviations (Å units) in PtP<sub>2</sub>. Distances less than 4 Å listed.

		Dist.	St.dev.
Pt	- 6 P	2.391	0.002
	- 6 P	3.586	0.006
	- 2 P	3.846	0.007
P	- P	2.172	0.015
	- 3 Pt	2.391	0.002
	- 6 P	3.263	0.004
	- 6 P	3.496	0.001
	- 3 Pt	3.586	0.006
	- Pt	3.846	0.007

Table 6. Observed and calculated structure factors for PtP<sub>2</sub>.

Original material														
h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $
2	0	0	197.24	287.17	4	2	0	175.68	203.32	1	4	0	32.20	16.15
4	0	0	163.51	159.25	5	2	0	32.93	19.38	3	4	0	37.53	21.02
6	0	0	176.86	159.05	6	2	0	176.25	182.00	4	4	0	207.48	251.07
8	0	0	213.38	211.97	7	2	0	86.36	55.93	6	4	0	184.01	207.27
10	0	0	200.40	199.97	8	2	0	189.53	177.24	7	4	0	39.20	20.99
12	0	0	161.93	133.58	10	2	0	186.50	166.26	8	4	0	166.09	129.53
14	0	0	133.87	106.08	11	2	0	67.63	45.73	10	4	0	166.37	120.15
1	2	0	72.86	53.58	12	2	0	168.59	149.82	12	4	0	174.09	171.99
2	2	0	191.30	252.05	14	2	0	140.91	144.65	14	4	0	157.52	199.31
3	2	0	60.99	61.72	15	2	0	35.91	41.10	1	6	0	54.91	33.03

  

Reduced material														
h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $
1	2	0	14.89	52.99	11	2	0	41.65	34.08	7	4	0	18.60	17.13
3	2	0	49.85	59.82	15	2	0	22.12	24.05	1	6	0	33.82	30.34
5	2	0	20.28	16.24	1	4	0	19.83	15.45	3	6	0	36.84	39.54
7	2	0	53.19	49.32	3	4	0	23.11	19.69	7	6	0	35.89	35.50

The results of the refinements made are listed in Table 3. The temperature factors obtained have hardly any physical significance. There is good agreement between the different  $x$  parameters obtained, and it seems reasonable to adopt a final value of  $x_p = 0.390 \pm 0.001$ . Interatomic distances based on this value are listed in Table 5. A summary of structure data for PtP<sub>2</sub> is given in Table 4. In Table 6 observed and calculated structure factors are listed for the original and reduced material obtained in the refinements using the uncorrected intensity material.

*The FeP<sub>2</sub>-structure.* The parameters refined consist of two scale factors, isotropic temperature factors for the platinum and phosphorus atoms, and the  $x$  and  $y$  parameters for the phosphorus atoms. The  $R$  value obtained was 0.058. As neither the linear absorption coefficient ( $\mu = 114$ ), nor the crystal size is very large, no absorption correction seemed necessary. It seems likely that the extinction error is small as well and no correction for extinction was made. (The very strong 101 reflexion was too strong to be accurately estimated and is therefore not included). Positional parameters and temperature factors are listed in Table 7. Interatomic distances are given in Table 8. Table 9 contains a list of observed and calculated structure factors for FeP<sub>2</sub>.

Table 7. Structural data for FeP<sub>2</sub>. Space group  $Pn\bar{m}$ ;  $Z=2$ .

		$a = 4.9729 \text{ \AA}$		$\sigma(a) = 0.0007 \text{ \AA}$			
		$b = 5.6568 \text{ \AA}$		$\sigma(b) = 0.0008 \text{ \AA}$			
		$c = 2.7230 \text{ \AA}$		$\sigma(c) = 0.0004 \text{ \AA}$			
Atom	Position	$x$	$\sigma(x)$	$y$	$\sigma(y)$	$B \text{ \AA}^2$	$\sigma(B)$
Fe	2(a)	—	—	—	—	0.172	0.008
P	4(g)	0.1683	0.0002	0.3689	0.0002	0.244	0.011

Table 8. Interatomic distances and standard deviations ( $\text{\AA}$  units) in FeP<sub>2</sub>. Distances less than 4  $\text{\AA}$  listed.

		Dist.	St.dev.
Fe	— 2 P	2.248	0.001
	— 4 P	2.264	0.001
	— 2 Fe	2.723	0.0004
	— 4 P	3.351	0.001
	— 6 P	3.667	0.001
P	— P	2.237	0.002
	— Fe	2.248	0.001
	— 2 Fe	2.264	0.001
	— 2 P	2.723	0.0004
	— 4 P	3.138	0.001
	— 4 P	3.242	0.001
	— 2 P	3.524	0.001
	— 2 Fe	3.531	0.001
	— P	3.617	0.002
	— 3 Fe	3.667	0.001

Table 9. Observed and calculated structure factors for FeP<sub>2</sub>.

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	
0	2	0	31.07	30.21	4	10	0	14.09	13.09	10	2	0	11.18	11.03	2	9	1	15.44	15.87	7	3	1	9.15	8.61	
0	6	0	29.28	26.20	4	12	0	12.99	12.70	10	2	0	5.22	5.11	2	10	1	9.16	9.00	7	4	1	8.09	7.30	
0	10	0	30.08	32.16	4	14	0	5.60	5.76	10	4	0	14.09	13.71	2	11	1	6.27	6.23	7	5	1	10.65	9.84	
0	14	0	7.62	7.76	4	13	0	6.65	6.73	10	4	0	6.40	6.09	2	12	1	3.70	3.08	7	5	1	23.44	13.24	
0	18	0	11.80	11.78	5	1	0	13.64	12.40	10	6	0	15.26	8.88	2	13	1	8.85	8.14	7	7	1	4.89	4.75	
0	1	1	26.10	28.60	5	2	0	20.21	19.89	10	8	0	5.97	6.25	2	14	1	4.36	4.32	7	8	1	14.07	14.73	
0	1	2	32.88	35.31	5	3	0	31.50	28.93	10	9	0	4.83	4.74	2	15	1	9.63	10.15	7	9	1	6.70	6.81	
0	1	3	40.86	47.39	5	5	0	22.36	23.07	10	10	0	7.99	8.50	3	2	1	33.18	29.44	7	10	1	8.51	8.29	
0	1	4	3.92	4.05	5	6	0	13.66	13.68	11	1	0	6.65	6.65	3	4	1	43.85	46.79	7	12	1	5.47	5.96	
0	1	5	35.67	31.49	5	7	0	6.61	6.69	11	2	0	6.16	6.17	3	6	1	12.48	12.64	7	13	1	4.11	4.34	
0	1	6	40.65	19.95	5	9	0	9.48	9.11	11	3	0	13.35	13.05	3	10	1	15.89	15.55	8	1	1	18.75	19.51	
0	1	7	8.40	8.80	5	10	0	5.50	7.33	11	5	0	11.33	11.29	3	12	1	17.58	16.68	8	2	1	11.63	10.95	
0	1	8	4.55	4.56	5	11	0	14.69	14.11	11	6	0	4.98	4.93	3	14	1	5.26	5.26	8	3	1	7.53	6.91	
0	1	9	10.18	10.54	5	13	0	9.21	9.39	11	7	0	5.16	5.29	4	1	1	34.73	32.71	8	5	1	8.93	8.17	
0	1	10	10.17	9.85	5	14	0	3.50	3.77	11	9	0	5.98	6.23	4	2	1	25.21	22.95	8	6	1	8.89	8.10	
0	1	11	15.98	15.90	6	0	0	37.97	39.34	12	0	0	15.35	15.39	4	3	1	13.02	12.45	8	7	1	15.29	15.18	
0	1	12	10.21	10.40	6	2	0	16.41	15.88	12	2	0	8.11	8.39	4	4	1	3.37	3.06	8	9	1	11.50	11.26	
0	1	14	0	4.59	4.60	6	6	0	17.18	16.88	12	6	0	8.82	9.12	4	5	1	11.53	12.25	8	10	1	5.14	4.96
0	1	15	0	4.75	5.25	6	8	0	22.16	22.49	13	1	0	6.04	6.57	4	6	1	14.70	15.64	8	11	1	5.18	5.17
0	1	16	0	23.61	18.65	6	10	0	7.10	7.06	13	3	0	5.22	4.97	4	7	1	19.39	20.7	9	2	1	13.41	13.51
0	2	1	23.18	24.62	6	14	0	8.28	9.87	13	3	0	8.40	9.30	4	8	1	3.91	3.66	9	4	1	21.02	20.90	
0	2	2	35.64	36.57	7	1	0	10.91	10.21	13	5	0	7.07	8.37	4	9	1	14.84	14.34	9	6	1	8.95	8.34	
0	2	3	17.36	16.98	7	3	0	15.20	15.20	0	3	1	12.00	12.03	4	10	1	18.50	18.20	9	10	1	10.38	10.40	
0	2	4	43.30	41.25	7	3	0	20.36	19.99	0	5	1	44.92	56.94	4	11	1	7.30	6.87	10	1	1	44.25	13.24	
0	2	5	17.75	18.17	7	5	0	17.34	16.48	0	5	1	36.50	37.39	4	13	1	8.09	7.55	10	2	1	9.30	8.25	
0	2	6	16.88	16.88	7	7	0	11.07	10.88	0	9	1	9.34	9.34	4	14	1	4.01	3.5	10	3	1	10.0	10.0	
0	2	7	0	8.19	8.22	7	7	0	8.35	8.72	0	11	1	20.61	20.38	5	0	1	35.79	33.47	10	5	1	8.34	8.03
0	2	8	0	6.92	6.64	7	9	0	8.35	8.72	0	13	1	12.02	11.30	5	1	1	14.00	14.41	10	6	1	7.23	6.45
0	2	9	0	17.36	16.98	7	10	0	6.17	6.31	0	15	1	18.67	2.61	5	2	1	18.50	18.50	10	7	1	11.57	11.37
0	2	10	0	14.61	14.37	7	10	0	11.71	11.64	1	1	1	26.08	26.67	5	3	1	11.27	11.17	10	9	1	9.30	9.07
0	2	12	0	14.55	14.01	7	13	0	7.87	8.26	1	2	1	28.53	33.40	5	4	1	7.06	6.41	10	10	1	4.12	4.32
0	2	13	0	5.66	5.79	8	0	0	8.18	8.26	1	4	1	15.80	17.16	5	5	1	12.10	12.10	11	0	1	14.01	14.1
0	2	14	0	5.41	5.41	8	1	0	6.76	6.78	1	4	1	12.86	12.87	5	6	1	16.30	16.48	11	1	1	5.11	4.50
0	3	1	48.97	54.37	8	2	0	14.88	13.87	1	5	1	16.70	18.42	5	7	1	9.05	8.84	11	2	1	9.48	9.24	
0	3	2	4.37	4.17	8	2	0	6.76	6.78	1	6	1	19.14	21.78	5	8	1	18.75	18.13	11	3	1	3.79	2.61	
0	3	3	7.03	7.03	8	3	0	20.69	19.50	1	7	1	6.01	6.34	5	9	1	8.15	8.03	11	4	1	4.90	2.10	
0	3	5	31.07	31.66	8	5	0	7.86	7.84	1	8	1	20.45	22.54	5	10	1	10.75	10.75	11	5	1	4.67	4.16	
0	3	7	17.82	18.44	8	6	0	10.22	10.02	1	9	1	10.81	11.02	5	12	1	5.92	5.77	11	8	1	4.82	4.45	
0	3	13	0	6.56	6.56	8	8	0	11.08	11.08	1	10	1	10.15	9.89	5	13	1	27.10	26.73	11	9	1	10.33	10.85
0	3	15	0	12.02	12.43	8	8	0	6.09	5.61	1	12	1	6.74	6.47	5	14	1	8.84	8.05	11	9	1	3.41	3.55
0	4	0	14.81	13.41	8	9	0	5.69	5.60	1	13	1	6.24	5.87	6	1	1	4.89	4.66	12	1	1	4.01	3.88	
0	4	1	20.44	18.78	8	10	0	11.08	10.43	1	14	1	10.06	9.96	6	2	1	16.03	16.02	13	0	1	13.05	13.22	
0	4	2	28.55	25.79	8	12	0	9.89	10.47	2	1	1	50.17	46.03	6	5	1	21.83	22.83	12	5	1	10.84	11.17	
0	4	3	15.86	14.19	9	1	0	21.04	19.97	2	2	1	27.87	27.60	6	9	1	6.84	6.78	12	7	1	3.20	3.18	
0	4	4	37.83	31.59	9	5	0	6.38	5.54	2	4	1	15.07	15.90	6	11	1	16.03	16.02	13	1	1	15.50	9.90	
0	4	5	16.29	15.76	9	7	0	16.84	16.96	2	4	1	3.53	3.55	6	13	1	9.55	9.50	13	1	1	4.01	3.83	
0	4	6	14.82	14.43	9	9	0	11.86	11.69	2	5	1	13.25	14.14	6	7	0	21.57	22.34	13	2	1	7.57	7.62	
0	4	7	7.15	7.23	10	1	0	7.53	6.99	2	6	1	16.22	17.89	7	1	1	11.23	11.03	13	3	1	11.04	8.96	
0	4	9	9.87	9.75	10	1	0	6.47	6.42	2	7	1	22.39	24.54	7	2	1	14.66	14.04	13	4	1	4.97	5.61	

## DISCUSSION

The P—P distance in PtP<sub>2</sub> obtained in this investigation ( $2.165 \pm 0.017 \text{ \AA}$ ) is normal for P—P bonds in the transition metal phosphides. The value found for the  $x$  parameter is also in agreement with a study made by Kjekshus *et al.*<sup>12</sup> regarding several solid-solid solubility equilibria, including the solid solubility of arsenic in PtP<sub>2</sub>. A function giving the relation between the  $x$  parameter in phases with the pyrite-type crystal-structure and the lattice constant was derived. The experimental and calculated lattice constants for various compositions were then shown to obey Vegard's law. The results for PtP<sub>2- $v$</sub> As <sub>$v$</sub>  showed discrepancies, however, when the  $x_p$  value of 0.394 was used. As Kjekshus *et al.* pointed out, the discrepancies are very much reduced if the  $x_p$  value is changed to 0.390.

The P—P distance in FeP<sub>2</sub> (obtained value  $2.237 \pm 0.002 \text{ \AA}$ ) seems to be significantly larger than the corresponding distance in PtP<sub>2</sub>. However, both these P—P distances seem to be normal as compared with other transition metal phosphides. As little is at present known regarding the influence of the structural environment on the length of the P—P bond it would be of great interest to compare such distances in a larger number of chemical compounds. Kjekshus *et al.*<sup>4</sup> made an attempt to summarize available data in the literature by calculating mean values for different classes of compounds. They found no significant differences between transition metal phosphides and non-transition metal phosphides. However, since most determinations reported have rather low accuracy, such mean values probably have a limited significance. Table 10 is an attempt to summarize some of the more accurate results

Table 10. P—P distances in some crystalline phases obtained with rather high accuracy (single-crystals used in most cases).

Compound	P—P distance and standard deviation (Å units)	Reference
Hittorf's phosphorus	2.219 ± 0.003 <sup>a</sup>	30
Black phosphorus	2.244 ± 0.002	13
	2.224 ± 0.002	
FeP <sub>2</sub>	2.237 ± 0.002	
PtP <sub>2</sub>	2.172 ± 0.015	
Cub. NiP <sub>2</sub>	2.12 ± 0.03	14
SiP <sub>2</sub>	2.13 ± 0.03	15
NiP	2.430 ± 0.008	16
monocl. NiP <sub>2</sub>	2.220 ± 0.004	16
Ni <sub>5</sub> P <sub>4</sub>	2.189 ± 0.011	17
CuP <sub>2</sub>	2.193 ± 0.008	18
	2.205 ± 0.008	
	2.207 ± 0.008	
PdP <sub>2</sub>	2.201 ± 0.010	19
	2.224 ± 0.010	
TiP <sub>2</sub>	2.257 ± 0.022	20
ZrP <sub>2</sub>	2.410 ± 0.024	20
CdP <sub>4</sub>	2.18 ± 0.02	21
	2.21 ± 0.02	
	2.24 ± 0.02	
tetr. ZnP <sub>2</sub>	2.17 ± 0.013	22
	2.22 ± 0.013	
MoP <sub>2</sub>	2.17	23
CoP <sub>3</sub>	2.24 <sub>0</sub>	24
	2.34 <sub>0</sub>	
NiP <sub>3</sub>	2.21 <sub>6</sub>	24
	2.28 <sub>3</sub>	
RhP <sub>3</sub>	2.22 <sub>7</sub>	24
	2.32 <sub>3</sub>	
IrP <sub>3</sub>	2.23 <sub>3</sub>	24
	2.34 <sub>0</sub>	
P <sub>4</sub> S <sub>3</sub>	2.235 ± 0.005	25
P <sub>4</sub> S <sub>5</sub>	2.205 ± 0.025	26
P <sub>4</sub> S <sub>7</sub>	2.35 ± 0.01	27
P <sub>4</sub> Se <sub>3</sub>	2.25 ± 0.03	28
P <sub>4</sub> S <sub>3</sub> I <sub>2</sub>	2.20 ± 0.04	29

<sup>a</sup> Mean value of 32 independent distances.

obtained to date regarding P—P bond distances in crystalline phases. This table shows that significant deviations in the length of the P—P bond do appear for some compounds, but for most compounds the differences fall within the calculated experimental errors. Some deviations (as for example the large value for ZrP<sub>2</sub>) can possibly be accounted for by simple geometrical considerations while in other cases (as for example the small values for PtP<sub>2</sub>, cub. NiP<sub>2</sub>, and SiP<sub>2</sub>, all exhibiting the pyrite structure) the cause of the deviations is still not clear.

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