

The Crystal Structure of a New MnP₄ Modification Determined by Direct Methods Applied to Powder Data

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In the phosphorus-rich part of the Mn-P system the occurrence of the phases MnP₃ and MnP₄ has been reported.^{1,2} The structure of MnP₃ is not known. In attempts to grow crystals of this compound, a new triclinic modification of MnP₄ was obtained. The present paper reports the determination of the crystal structure of this phase using direct methods applied to X-ray powder diffraction data. A complete single-crystal structure refinement based on X-ray diffractometer intensity data is in progress and a more detailed discussion of the triclinic MnP₄ structure is deferred to a forthcoming paper.

Experimental. The MnP₄ sample was prepared from red phosphorus (Koch-Light, claimed purity 99.999%) and electrolytic manganese (99.9% further purified by a sublimation process) by heating the powdered elements (molar ratio 1:4) in an evacuated and sealed silica tube at 730 °C for 320 h. The powder was then used as feedstock in chemical vapour transport experiments. Silica tubes with a length of 13 cm and an internal diameter of 6 mm were used. The transporting component used was iodine with a filling concentration of 3.9 mol m⁻³ (I₂). The source temperature was 735 °C and crystals of MnP₄ were formed in the coldest part of the tube at temperatures of 620–585 °C. The crystals were in the shape of long thin plates and were heavily twinned. No traces of the monoclinic form² were found. The powder pattern was indexed from preliminary single-crystal parameters. Refined lattice parameters were determined from a least-squares refinement of *Q*-values (=1/*d*²) obtained from a Guinier-Hägg powder film. The exposure was performed at 25 °C using monochromatized CrKα₁ radiation (λ=2.289753 Å) and with silicon (a=5.431065 Å) as the internal calibration standard. The cell dimensions are: a=5.8622(3) Å, b=5.1059(3) Å, c=5.8360(4) Å, α=93.803(4)°, β=107.338(4)°, γ=115.830(5)°.

Because of the similarity between this new triclinic modification of MnP₄ and the monoclinic form,² the cell was chosen such that the triclinic *ab* plane corresponds to the *ab* plane in the monoclinic MnP₄, where a(monocl.) ≈ 2a(tricl.)+b(tricl.) and b(monocl.) ≈ b(tricl.). The numbers of formula

units in the monoclinic and the triclinic cell are 16 and 2, respectively. The corresponding cell volumes are 1163.8(1) Å³ and 146.08(2) Å³.

The intensity profile was measured on a SAAB Mk II Model 2 automatic film scanner³ coupled on-line to an IBM 1800 computer. In all 70 reflections with sin θ/λ < 0.306 were covered by the profile.

Structure determination and refinement. The integrated intensities for the 35 strongest reflections were evaluated using the computer program LINNE.⁴ For a few overlapping reflections the intensities were attributed to the appropriate reflections according to intensity ratios estimated from Weissenberg photographs. The structure was (provisionally)

Table 1. Evaluation of a Guinier-Hägg powder pattern of MnP₄ (triclinic). The *Q*-values have been multiplied by 10⁶.

H	K	L	D(OBS)	Q(OBS)	Q(CALC)	I(OBS)	I(CALC)
0	0	0	5.4265	33960	33994	4	3
0	0	1	4.5225	41334	41378	37	30.1
0	0	2	4.5726	47827	47859	37	33
0	0	3	—	—	48086	3	1
0	0	4	—	—	49950	4	1
0	0	5	3.9189	65114	65128	43	41
0	0	6	—	—	73571	0.0	0.6
0	0	7	—	—	80357	0.0	0.0
0	0	8	—	—	102709	0.0	0.1
0	0	9	—	—	102760	0.0	0.3
0	0	10	2.8545	122723	122715	20	2
0	0	11	—	—	122756	0.0	0.3
0	0	12	2.8087	126761	126773	66	64
0	0	13	2.7893	128529	128572	64	64
0	0	14	2.7238	134790	134850	87	84
0	0	15	2.7124	135928	135976	100	100
0	0	16	—	—	144986	0.1	0.2
0	0	17	—	—	152125	0.0	0.3
0	0	18	—	—	152125	0.1	0.3
0	0	19	2.4573	165602	165616	5	4
0	0	20	2.4480	166863	166845	5	3
0	0	21	2.3708	177910	177888	29	24
0	0	22	2.3667	178526	178526	29	24
0	0	23	2.2853	191480	191436	48	40
0	0	24	2.2796	192441	192345	48	40
0	0	25	—	—	192937	0.5	0.0
0	0	26	2.2570	196300	196163	44	3
0	0	27	—	—	198330	0.3	0.1
0	0	28	—	—	198330	0.0	0.6
0	0	29	2.2373	199781	199802	22	18
0	0	30	2.2313	200856	200825	24	21
0	0	31	—	—	208440	0.1	0.3
0	0	32	2.1570	214925	214972	11	9
0	0	33	2.1155	223457	223360	3	2
0	0	34	2.0765	231909	232003	3	2
0	0	35	—	—	242420	0.1	0.0
0	0	36	1.9833	254235	254233	0.1	0.0
0	0	37	1.9594	260477	260511	11	10
0	0	38	—	—	262975	0.5	0.5
0	0	39	1.9498	263049	263111	5	5
0	0	40	1.9409	265445	265415	5	5
0	0	41	1.9259	269596	269548	2	0.9
0	0	42	—	—	271428	8	8
0	0	43	—	—	291653	6	3
0	0	44	1.8507	291962	292100	9	8
0	0	45	1.8461	293409	293432	9	8
0	0	46	1.8341	297273	297246	37	36
0	0	47	1.8275	299432	299446	40	38
0	0	48	1.8223	301146	301158	40	39
0	0	49	—	—	302210	3	0.9
0	0	50	—	—	302210	4	3
0	0	51	1.8074	306111	305946	0.1	0.0
0	0	52	1.8026	307757	307694	0.0	0.0
0	0	53	—	—	311465	0.1	0.9
0	0	54	1.7549	324697	324694	52	55
0	0	55	1.7483	327149	327101	56	60
0	0	56	—	—	328196	2	1
0	0	57	—	—	328319	2	1
0	0	58	1.7294	334364	334283	8	8
0	0	59	1.7249	336104	336165	2	2
0	0	60	1.7031	344743	344741	0.1	0.6
0	0	61	1.6804	354158	354198	0.1	0.2
0	0	62	—	—	358377	3	2
0	0	63	1.6656	360469	360333	34	37
0	0	64	—	—	361392	42	51
0	0	65	1.6595	363131	363082	71	61
0	0	66	1.6541	365490	365328	5	5
0	0	67	—	—	372634	11	11

Table 2. Atomic parameters of MnP_4 ($\text{P}\bar{1}$). All atoms are on position 2(i). The fractional coordinates are multiplied by 10^3 . The standard deviations are 2 units for all the positional parameters.

Atom	x	y	z	B (\AA^2)
Mn	228	224	756	3.0(2)
P(1)	485	922	306	2.7(3)
P(2)	132	257	359	0.5(3)
P(3)	433	324	191	2.0(4)
P(4)	45	592	201	2.3(3)

assumed to be centrosymmetric and reflections with normalized structure factors greater than 0.9 (25 refl.) were included in the sign determination using the program MULTAN 71.⁵ Of the four solutions obtained, the one with the highest absolute figure of merit (1.46) was used in Fourier calculations, from which approximate coordinates for all atoms were obtained. It was later found that only two of the 25 signs were incorrectly determined. This is, to our knowledge, the first time that X-ray powder data have been used for a structure determination by means of direct methods.

For the final refinement the complete intensity profile was used (including the standard substance silicon) in a full profile refinement program.⁶ The function minimized is

$$\sum_i w_i [y_i(\text{obs}) - K^{-1}y_i(\text{calc})]^2$$

where w_i is the weight assigned to an individual observed net intensity $y_i(\text{obs})$, $y_i(\text{calc})$ the calculated intensity and K is a scale factor. Scattering factors, corrected for anomalous dispersion, were taken from the *International Tables*.⁷ A total of 37 parameters for the two phases were refined. These were: profile parameters: halfwidth (3+3), asymmetry (1+1), structure parameters: overall scale factor (1), lattice parameters (6+0), positional parameters (15+0), temperature factors (5+1), and "occupancy factor" for Si (1). The final agreement factors obtained (for definitions see Ref. 6) were: $R(I)=0.090$, $R(F)=0.097$, $R(P)=0.137$, and $R(WP)=0.185$. The largest deviation from zero in a final difference Fourier synthesis was equivalent to 5% of a phosphorus peak in the $F(\text{obs})$ Fourier maps. A list of observed and calculated structure factors can be obtained on request from the authors.

The structure shows great similarities with the monoclinic MnP_4 , which can be described as a stacking of eight MnP_4 layers parallel to the ab plane. The stacking sequence consists of four layers of almost the same kind followed by the same four layers rotated 180° . In the triclinic MnP_4 there are

only two layers, both of them of the same type. Two-layer structures are also found in CrP_4 and MoP_4 ,⁸ but in these compounds there are only two phosphorus sites in special positions. In the triclinic MnP_4 all four phosphorus atoms are in general positions. The manganese atoms are surrounded by six phosphorus atoms at distances ranging from 2.22 \AA to 2.37 \AA at the corners of a slightly distorted octahedron. Two of the phosphorus atoms are surrounded by two manganese atoms and two phosphorus atoms, while the other two phosphorus atoms are surrounded by one manganese and three phosphorus atoms in a distorted tetrahedral arrangement. The average P–P distance is 2.25 \AA . The monoclinic form contains manganese pairs with an Mn–Mn distance of 2.94 \AA .² Due to small differences between the layers in the two forms and the different stacking, the shortest Mn–Mn distance in the triclinic form is 3.21 \AA .

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1. Biltz, W., Wiechmann, F. and Meisel, K. *Z. Anorg. Allg. Chem.* 234 (1937) 117.
2. Jeitschko, W. and Donohue, P. C. *Acta Crystallogr. B* 31 (1975) 574.
3. Abrahamsson, S. *J. Sci. Instrum.* 43 (1966) 931.
4. Ersson, N.-O. Inst. of Chemistry, Univ. of Uppsala, Sweden. *Personal communication*.
5. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
6. Malmros, G. and Thomas, J. O. *J. Appl. Crystallogr.* 10 (1977) 7.
7. Ibers, J. A. and Hamilton, W. C. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV.
8. Jeitschko, W. and Donohue, P. C. *Acta Crystallogr. B* 28 (1972) 1893.

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