The Missing Stacking Variant 4-MnP$_4$, Realized for the Solid Solution Cr$_{1-x}$Mn$_x$P$_4$ (*x* = 0.3–0.7)

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The polyphosphides of the solid solution series Cr$_{1-x}$Mn$_x$P$_4$ were prepared by reaction of chromium–manganese alloys with phosphorus in a tin flux. The crystal structures of three members of this series with the compositions Cr$_{0.41}$Mn$_{0.59}$P$_4$, Cr$_{0.66}$Mn$_{0.34}$P$_4$, and Cr$_{0.68}$Mn$_{0.32}$P$_4$ were refined from single-crystal X-ray data to residuals of $R = 0.024$ (2129 structure factors), $R = 0.033$ (1158), and $R = 0.039$ (2052), respectively, for 94 variable parameters each. The lattice constants of the triclinic structure (space group $P\bar{1}$, $Z = 4$) vary as follows: $a = 512.7(1)$–$514.5(3)$ pm, $b = 588.3(1)$–$591.3(2)$ pm, $c = 1125.0(2)$–$1129.5(6)$ pm, $\alpha = 101.12(3)$–$101.59(3)°$, $\beta = 94.01(3)$–$94.21(4)°$, $\gamma = 115.57(3)$–$115.62(3)°$; and $V = 0.2958$–0.2985 nm^3 for the compositions Cr/Mn from 0.41/0.59 to 0.68/0.32. The structure has the same near-neighbor coordinations as were previously found for the three modifications of the manganese polyphosphides 2-MnP$_4$, 6-MnP$_4$, and 8-MnP$_4$, and it corresponds to that of the missing modification 4-MnP$_4$. Again the transition metal atoms (*T*) form pairs with *T*–*T* distances varying between 293.9 and 298.1 pm. The new chromium-containing modification is a semiconductor like 2-, 6-, and 8-MnP$_4$. While the binary modifications of MnP$_4$ are diamagnetic, the new chromium-containing phase is paramagnetic, in agreement with a simple bonding model for these compounds, where two electrons are counted for each short *T*–*T*, *T*–*P*, and *P*–*P* interaction. © 1996 Academic Press, Inc.

INTRODUCTION

The previously reported modifications of the manganese polyphosphide MnP$_4$ can be described as stacking variants of a two-dimensionally infinite puckered net of pentagons and hexagons formed by manganese and phosphorus atoms. In the three modifications 2-MnP$_4$(1), 6-MnP$_4$(2), and 8-MnP$_4$(3), two, six, and eight such nets are stacked on top of each other to complete one translation period. We have now prepared a solid solution series of ternary chromium manganese polyphosphides Cr$_{1-x}$Mn$_x$P$_4$, which crystallize with a structure corresponding to that of the missing modification 4-MnP$_4$.

SAMPLE PREPARATION

Various compositions of the solid solution series Cr$_{1-x}$Mn$_x$P$_4$ were obtained in well-crystallized form by reacting chromium–manganese alloys with red phosphorus in a tin flux. Starting materials were powders of manganese (99.95%), chromium (99.9%), red phosphorus ("ultrapure," Hoechst), and tin (99.9%). At first chromium–manganese alloys were prepared by arc-melting cold-pressed pellets with atomic ratios Cr/Mn varying between 2/8 and 8/2. The products were ground to fine powders and reacted with red phosphorus and tin in the ratio (Cr/Mn)/P/Sn = 1/20/25 in evacuated, sealed silica tubes (tube volume 5 cm^3, phosphorus content 0.3 g). The samples were annealed for 24 hr at 450°C followed by 2 weeks at 675°C, and cooled to room temperature in 3 hr. The tin matrix was dissolved in slightly diluted (1/1) hydrochloric acid.

The limits of the solid solution series Cr$_{1-x}$Mn$_x$P$_4$ could not be well established from the X-ray powder data, due to the small differences of the lattice constants. Samples with *x* smaller than 0.25 and higher than 0.75 showed the diffraction patterns of CrP$_4$(4) and 6-MnP$_4$(2). This suggests that the solid solution extends approximately between the limits *x* = 0.3 and *x* = 0.7, which are expected to depend on the annealing temperature. Unfortunately single crystals for a structure refinement could not be obtained from samples with high manganese content.

The crystals of the phosphides Cr$_{1-x}$Mn$_x$P$_4$ are black with metallic luster and they have no preferred growth directions. They are stable in air for long periods of time and they are not attacked by nonoxidizing acids. To facilitate the identification of these phosphides the evaluation of a Guinier powder pattern of Cr$_{0.41}$Mn$_{0.59}$P$_4$ is given in Table 1.

MAGNETIC PROPERTIES

The magnetic susceptibilities of several polycrystalline samples of the solid solution series were determined by a
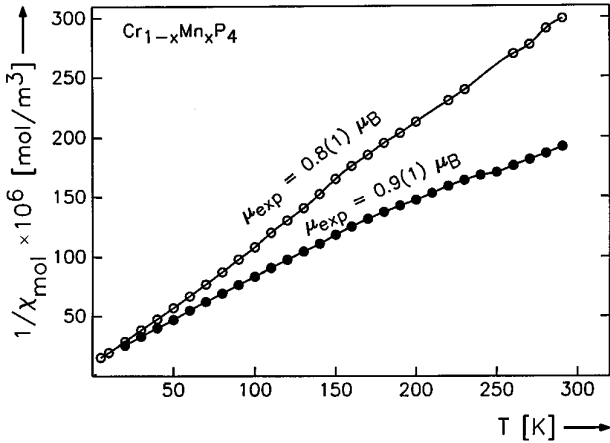
FIG. 1. Inverse magnetic susceptibilities of two samples of the solid solution series Cr$_{1-x}$Mn$_x$P$_4$ with the nominal composition Cr$_{0.5}$Mn$_{0.5}$P$_4$ as a function of the temperature measured with a magnetic flux density of 5 T.

FIG. 2. Cell volumes per formula unit in the pseudobinary system CrP$_4$–MnP$_4$. The volumes of 2-MnP$_4$, 6-MnP$_4$, and 8-MnP$_4$ are practically the same. The volumes of the three crystals I, II, and III of the solid solution series Cr$_{1-x}$Mn$_x$P$_4$ are shown as horizontal lines and their interceptions with the line connecting the volumes of CrP$_4$ and MnP$_4$ were used to obtain what are believed to be the most reliable compositions of the crystals. The results for the compositions as obtained from the structure refinements (open circles) and from EDAX analyses (heavy horizontal bars) are also indicated.

SQUID magnetometer in the temperature range between 2 and 300 K with magnetic flux densities of 1 to 5 T. All samples contained small amounts of ferromagnetic impurities, as revealed by the field dependence of the magnetic susceptibilities. These impurities—possibly MnP(5)—were not visible on the Guinier films. For two different samples, both with the overall Cr/Mn ratio of 0.5/0.5, the amounts of these impurities were so small that the magnetic susceptibilities measured in magnetic fields of 3 and 5 T were already indistinguishable. The reciprocal susceptibilities of these samples did not entirely follow the Curie–Weiss law (Fig. 1) and for that reason we evaluated these data by assuming a temperature-independent contribution
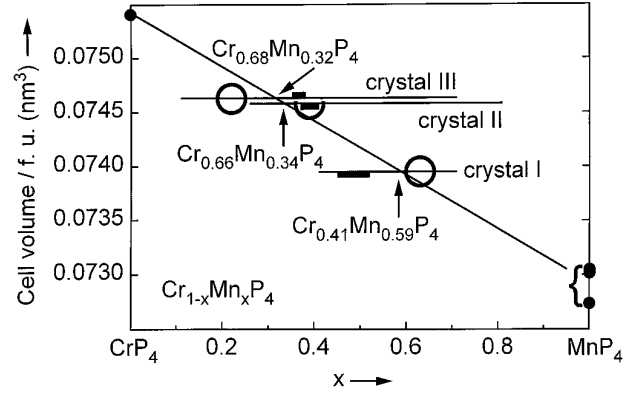
χ_0 to the susceptibilities. The fit of the data to the corresponding equation $\chi = \chi_0 + C/(T - \Theta)$ resulted in magnetic moments of $\mu_B = (8C)^{1/2} = 0.8(1)$ and $0.9(1)$ μ_B with χ_0 values of $0.2(1) \times 10^{-9}$ and $1.5(5) \times 10^{-9}$ m^3/formula unit and a Weiss constant of $\Theta = -6(2)$ K for both samples.

CHEMICAL COMPOSITIONS

The three crystals used for the structure determination and the refinements were subsequently analyzed in a scanning electron microscope. The energy dispersive analyses

TABLE 1
Powder Pattern of Cr$_{0.41}$Mn$_{0.59}$P$_4$[a]

h	k	l	$2\theta_0$	Q_c	Q_o	I_c	I_o	h	k	l	$2\theta_0$	Q_c	Q_o	I_c	I_o
1	0	−1	19.78	496	497	29	m	2	−2	−3	—	2756	—	8	—
1	−1	−1	21.27	574	574	34	s	2	1	−1	49.38	2938	2941	22	s
1	1	−2	25.87	846	844	7	vw	2	−3	1	49.58	2960	2963	22	s
1	1	0	31.59	1249	1249	83	vs	0	3	−2	51.74	3210	3209	38	s
1	−2	2	32.78	1342	1342	87	vs	1	1	4	52.00	3237	3239	44	s
0	0	4	32.89	1353	1351	100	vs	2	0	−5	52.84	3338	3337	11	vw
2	−1	−2	37.75	1763	1764	17	m	0	3	0	53.38	3403	3400	5	vw
2	0	−1	38.90	1872	1869	24	s	1	−2	6	55.24	3621	3622	35	s
2	−2	1	39.58	1935	1937	12	m	3	−2	1	55.39	3639	3640	15	m
2	0	−2	40.15	1985	1985	8	vw	0	3	−4	—	3693	—	6	—
2	−2	−1	—	2007	—	7	—	3	−1	1	56.33	3758	3756	12	w
1	−2	4	40.78	2144	2143	8	vw	2	1	−5	58.72	4050	4052	15	w
1	0	−5	42.77	2243	2241	17	m	2	−3	−3	59.38	4135	4135	18	m
1	−1	−5	46.96	2676	2676	19	m								

[a] The Q values are defined by $Q = 100/d^2$ (nm^{-2}).

FIG. 3. Near-neighbor environments of the transition metal atoms in $Cr_{0.41}Mn_{0.59}P_4$. The bonding and antibonding metal–metal distances (pm) as well as the corresponding bond angles (°) are indicated.

obtained from the structure refinements are the least reliable ones. For simplicity and also to avoid confusion we therefore designate the three crystals with the compositions as obtained from the volume plot for most purposes.

STRUCTURE DETERMINATION AND REFINEMENTS

Two single crystals (crystals I and II) were isolated from a sample with the initial Cr/Mn ratio of 0.5/0.5. Apparently this sample was not in equilibrium, since both structure refinements and the EDAX (energy dispersive analysis of the X-ray fluorescence) results showed them to have different compositions. A third single crystal (III) was picked from a sample with the overall Cr/Mn ratio 0.7/0.3.

These single crystals were investigated with a precession camera to establish their symmetry and suitability for the intensity data collections. The cell dimensions (Table 2) were obtained from least-squares fits of 25 well-centered reflections for each crystal. Intensity data were collected on an automated four-circle diffractometer with graphite-monochromated $MoK\alpha$ radiation and a scintillation counter with pulse-height discrimination. Background counts were recorded at both ends of each $\theta/2\theta$ scan. Empirical absorption corrections were carried out using psi scan data. Further details of the data collections of the three crystals are summarized in Table 2.

The structure was solved by Patterson and difference Fourier syntheses. Full-matrix least-squares refinements were carried out with atomic scattering factors (6), corrected for anomalous dispersion (7). The weighting scheme was based on the counting statistics and a parameter correcting for isotropic secondary extinction was optimized. The metal positions were refined with mixed Cr/Mn occupancy together with anisotropic displacement parameters. Because of the similar scattering power of chromium and manganese the standard deviations for the Cr/Mn ratios are rather high. Nevertheless, meaningful results were obtained, which are consistent with the differences of the lattice constants of the three crystals. The occupancy parameters of the phosphorus positions were also allowed to vary together with the ellipsoidal thermal parameters in one series of least-squares cycles. They varied between the values of 99.5(2) and 100.6(2)% for crystal I, between 98.9(5) and 100.9(5)% for crystal II, and between 99.2(4) and 101.3(4)% for crystal III. Because these deviations were considered insignificant, the ideal occupancies were resumed for the phosphorus positions in the final least-squares cycles. The highest residual electron densities amounted to 0.60, 0.87, and 2.04 e/Å^3 for the three crystals. These peaks were too small and too close to the occupied atomic positions to be suitable for additional atomic sites. The final conventional residuals $R = \Sigma(\|F_o\| - |F_c\|)/\Sigma|F_o|$ are listed in Table 2; the atomic parameters and interatomic distances are listed in Tables 3 and 4. The near-neighbor

of the X-ray fluorescence (EDAX) showed no impurity elements with atomic numbers greater than 11 (Na). The Cr/Mn ratios were determined five times for each of the three crystals. These ratios varied between the values 48/52 and 55/45 for crystal I, later designated with the formula $Cr_{0.41}Mn_{0.59}P_4$, between 59/41 and 63/37 for crystal II ($Cr_{0.66}Mn_{0.34}P_4$), and between 62/38 and 64/36 for crystal III ($Cr_{0.68}Mn_{0.32}P_4$).

The most reliable results for the compositions of the three crystals were obtained from the interpolation of the cell volumes. The structures of CrP_4, 2-MnP_4, 6-MnP_4, and 8-MnP_4 may be regarded as stacking variants of each other (2), and it can be assumed that the cell volumes per formula unit directly correspond to the Cr/Mn ratios, especially since the three known modifications of MnP_4 have practically the same cell volumes per formula unit. Figure 2 shows the results of this interpolation together with the results of the EDAX analyses and of the structure refinements. Since the scattering powers of chromium and manganese differ by only one electron, the Cr/Mn ratios
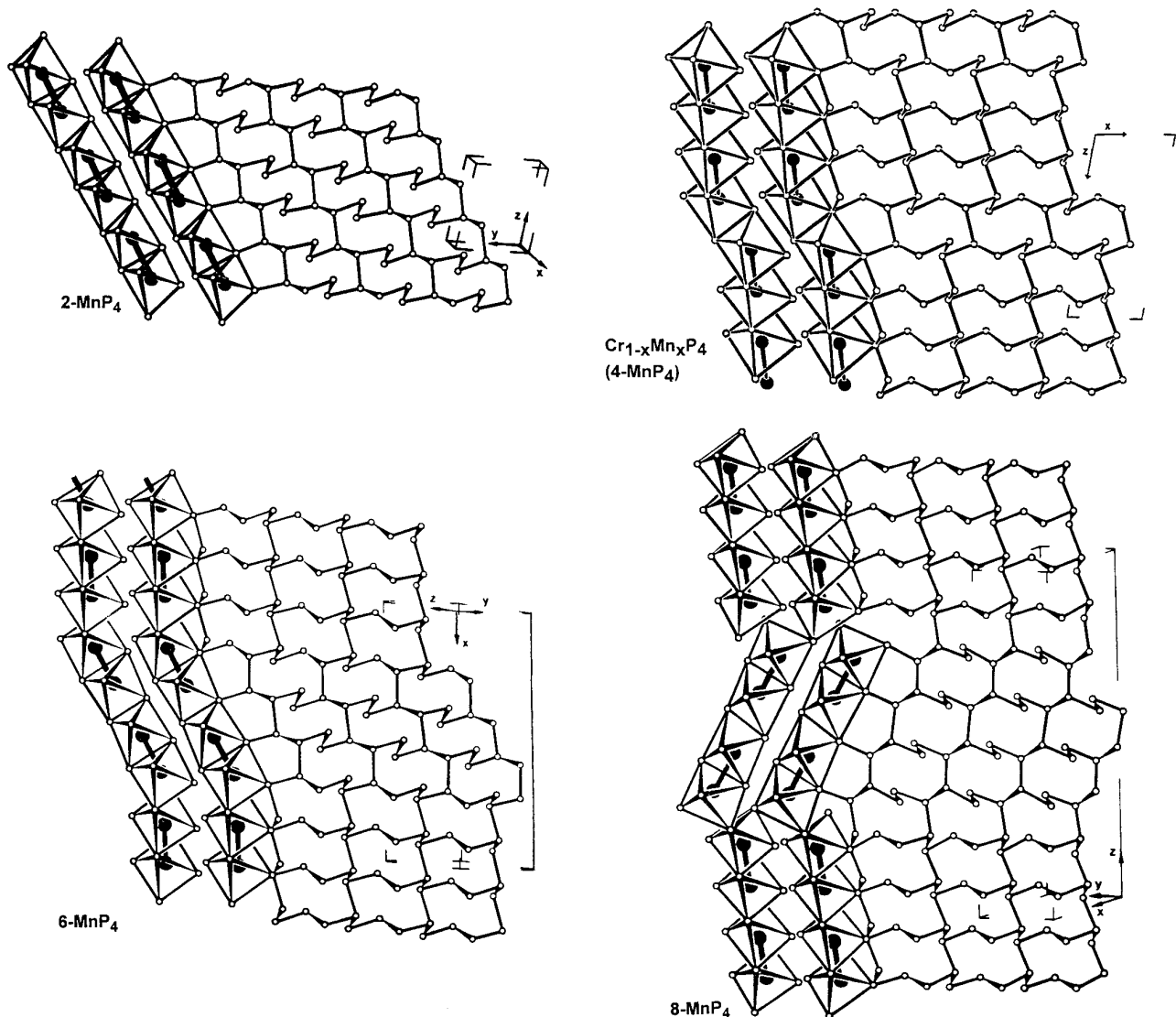
FIG. 4. Comparisons of the crystal structures of the three modifications of MnP$_4$ and the new stacking variant realized for Cr$_{1-x}$Mn$_x$P$_4$. On the left-hand sides of each drawing the arrangements of the TP$_6$ octahedra are shown. The right-hand sides show the condensed P$_{10}$ rings. The projection directions are chosen such that the phosphorus atoms of the puckered rings do not overlap.

environments of the new structure type "4-MnP$_4$" are shown in Fig. 3, and a comparison of that structure with the structures of 2-, 6-, and 8-MnP$_4$ is made in Fig. 4. The structure factor tables and anisotropic displacement parameters are available from the authors upon request.

DISCUSSION

We will first briefly compare the results of the three structure refinements of the new structure, which are quite consistent. In all three refinements the $T1$ (= Cr1/Mn1) site has a higher chromium content than the $T2$ site. The $T1$ site also always has the higher equivalent thermal pa-

rameter B_{eq}. Among the phosphorus atoms the P4 atom always has the greatest thermal parameter and the thermal parameters of the P1, P3, P6, and P8 atoms are always smaller than those of the other phosphorus atoms. The average bonding P–P distances are practically the same with 222.3, 222.4, and 222.1 pm for crystals I, II, and III, respectively, while the average T–P distances increase from 229.7 pm for crystal I, to 230.5 pm for crystal II, to 230.9 pm for crystal III, which has the highest chromium content. This is consistent with the higher average Cr–P distance of 233.6 pm in CrP$_4$(4) as compared to the average Mn–P distances of 227.3 pm in 2-MnP$_4$(1), 227.5 pm in 6-MnP$_4$(2), and 228.2 pm in 8-MnP$_4$(3). Similarly, the short T–T dis-
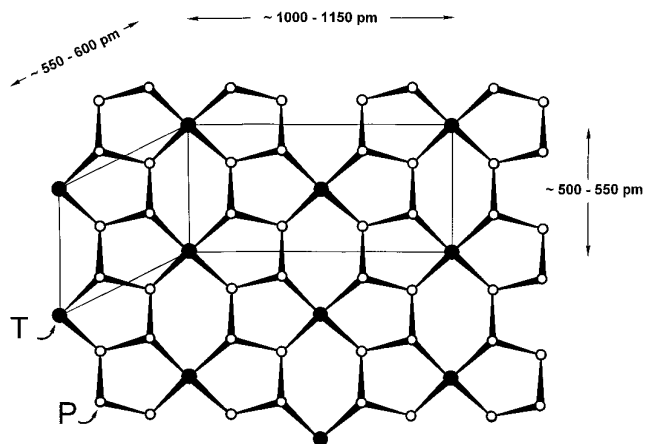
FIG. 5. The puckered net of pentagons and hexagons, which can be considered the basic building element of several TP_4 compounds. The cell dimensions a and b of CrP_4, 8-MnP_4, β-FeP_4, and γ-FeP_4 correspond to the centered rectangular mesh. The cell dimensions a and b of 2-MnP_4, $Cr_{1-x}Mn_xP_4$, and 6-MnP_4 correspond to the primitive mesh outlined in the left-hand side of the figure.

tances increase from 293.9 to 296.2 to 298.1 pm with increasing chromium content of the three crystals.

Three modifications of MnP_4, i.e., 2-MnP_4(1), 6-MnP_4(2), and 8-MnP_4(3) have been described previously. The presently determined structure of the solid solution series $Cr_{1-x}Mn_xP_4$ represents the missing stacking variant 4-MnP_4. Unfortunately, we have not been successful in preparing a sample with this structure without chromium. The four different structures of n-MnP_4 ($n = 2, 4, 6, 8$) have

similar powder patterns. The greatest differences between these patterns occur for the weak lines in the front reflection regions. The three strongest lines are always at the d values around 277 pm (Table 5). The strongest reflection always has an index which corresponds to the number of atomic layers of the respective stacking variant.

In the structures of the transition metal polyphosphides each near neighbor T–T, T–P, and P–P interaction can be rationalized by classical two-electron bonds, as was discussed previously for numerous examples (Refs. 1–4, 8–14, and references cited therein). Nevertheless, we will briefly show how this result is arrived at in the case of the three binary modifications 2-MnP_4, 6-MnP_4, and 8-MnP_4 as well as in the case of CrP_4. In all of these compounds the phosphorus atoms have four neighbors, and in assuming the octet rule to be valid, one counts two valence electrons for each of these four interactions. There are two kinds of phosphorus atoms in each of these TP_4 compounds in equal amounts: one with $1T$ and $3P$ neighbors, and one with $2T$ and $2P$ neighbors. In ascribing oxidation numbers (formal charges) one counts the electrons of the T–P bonds at the phosphorus atoms, while the P–P bonds are split homolytically. In this way the phosphorus atoms with one T neighbor obtain the oxidation number zero, while those with two T neighbors obtain the oxidation number -1. The formulas can therefore be written as $T^{+2}P^0P^0P^{-1}P^{-1}$. The important result of this simple rationalization is that the transition metal atoms have the oxidation number $+2$, i.e., the chromium atoms obtain a (so called) d^4 system, while the manganese atoms have a d^5 system. This means

TABLE 2
Crystallographic Data for $Cr_{0.41}Mn_{0.59}P_4$, $Cr_{0.66}Mn_{0.34}P_4$, and $Cr_{0.68}Mn_{0.32}P_4$

Cr/Mn	41/59	66/34	68/32
a (pm)	512.7(1)	514.44(6)	514.5(3)
b (pm)	588.3(1)	590.48(9)	591.3(2)
c (pm)	1125.0(2)	1128.9(3)	1129.5(6)
α (°)	101.12(3)	101.37(2)	101.59(3)
β (°)	94.01(3)	94.07(1)	94.21(4)
γ (°)	115.57(3)	115.64(1)	115.62(3)
V (nm^3)	0.2958	0.2983	0.2985
Formula units/cell	$Z = 4$	$Z = 4$	$Z = 4$
Calculated density (g/cm^3)	3.99	3.94	3.93
Crystal dimensions (μm^3)	$80 \times 130 \times 40$	$20 \times 40 \times 40$	$40 \times 40 \times 20$
$\theta/2\theta$ scans up to	$2\theta = 75°$	$2\theta = 73°$	$2\theta = 90°$
Range in h, k, l	$\pm 8, \pm 10, \pm 19$	$\pm 8, \pm 9, \pm 18$	$+10 - 6, \pm 11, \pm 22$
Total no. of reflections	6202	5945	9016
Transm. coeff. (highest/lowest)	1.15	1.19	1.10
Unique reflections	3079	2523	4917
Inner residual	0.023	0.036	0.033
Reflections with $I > 3\sigma(I)$	2129	1158	2052
No. of variables	94	94	94
Conventional residual	$R = 0.024$	$R = 0.033$	$R = 0.039$
Weighted residual	$R_w = 0.026$	$R_w = 0.033$	$R_w = 0.039$

TABLE 3
Atomic Parameters of Three Crystals of the Solid Solution Series Cr$_{1-x}$Mn$_x$P$_4$[a]

Atom	Occup. (%)	x	y	z	B_{eq}
Cr$_{0.37(3)}$Mn$_{0.63(3)}$P$_4$ (crystal I, "Cr$_{0.41}$Mn$_{0.59}$P$_4$")
Cr1/Mn1	46(3)/54(3)	0.25765(6)	0.23373(5)	0.63575(3)	0.308(5)
Cr2/Mn2	29(3)/71(3)	0.41075(6)	0.09906(5)	0.86002(3)	0.248(5)
P1	100	0.0509(1)	0.21273(9)	0.14920(5)	0.332(8)
P2	100	0.0888(1)	0.51797(9)	0.59637(5)	0.353(8)
P3	100	0.1173(1)	0.58504(9)	0.09802(5)	0.347(8)
P4	100	0.2191(1)	0.10187(9)	0.41850(5)	0.439(8)
P5	100	0.2852(1)	0.43820(9)	0.33956(5)	0.367(8)
P6	100	0.4292(1)	0.18190(9)	0.07489(5)	0.355(8)
P7	100	0.5849(1)	0.06212(9)	0.34185(5)	0.373(8)
P8	100	0.7339(1)	0.59983(9)	0.16361(5)	0.346(8)
Cr$_{0.61(6)}$Mn$_{0.39(6)}$P$_4$ (crystal II, "Cr$_{0.66}$Mn$_{0.34}$P$_4$")
Cr1/Mn1	80(6)/20(6)	0.2503(2)	0.2274(2)	0.63383(8)	0.38(1)
Cr2/Mn2	43(6)/57(6)	0.4082(2)	0.0981(2)	0.86003(8)	0.29(1)
P1	100	0.0534(3)	0.2152(3)	0.1492(1)	0.40(2)
P2	100	0.0844(3)	0.5145(3)	0.5962(1)	0.43(2)
P3	100	0.1184(3)	0.5860(3)	0.0985(1)	0.38(2)
P4	100	0.2261(3)	0.1068(3)	0.4174(1)	0.52(2)
P5	100	0.2893(3)	0.4422(3)	0.3396(1)	0.45(2)
P6	100	0.4307(3)	0.1831(3)	0.0756(1)	0.37(2)
P7	100	0.5903(3)	0.0671(3)	0.3418(1)	0.44(2)
P8	100	0.7357(3)	0.6017(3)	0.1637(1)	0.38(2)
Cr$_{0.78(4)}$Mn$_{0.22(4)}$P$_4$ (crystal III, "Cr$_{0.68}$Mn$_{0.32}$P$_4$")
Cr1/Mn1	84(4)/16(4)	0.2428(1)	0.2210(1)	0.63174(6)	0.398(9)
Cr2/Mn2	71(4)/29(4)	0.4066(1)	0.0968(1)	0.86023(5)	0.227(8)
P1	100	0.0561(2)	0.2173(2)	0.1492(1)	0.36(2)
P2	100	0.0798(2)	0.5113(2)	0.5958(1)	0.39(2)
P3	100	0.1201(2)	0.5866(2)	0.0980(1)	0.36(2)
P4	100	0.2334(2)	0.1116(2)	0.4158(1)	0.51(2)
P5	100	0.2933(2)	0.4459(2)	0.3399(1)	0.39(2)
P6	100	0.4326(2)	0.1848(2)	0.0760(1)	0.37(2)
P7	100	0.5972(2)	0.0711(2)	0.3416(1)	0.40(2)
P8	100	0.7396(2)	0.6039(2)	0.1642(1)	0.37(2)

[a] Standard deviations in the place values of the last listed positions are listed in parentheses throughout the paper. The last column lists the equivalent isotropic displacement parameters ($\times 10^4$, pm^2).

that four of the valence electrons of the chromium atoms and five of the valence electrons of the manganese atoms do not participate in the bonding to the phosphorus atoms. These electrons have to be accommodated in either nonbonding orbitals or in T–T bonding orbitals. In all of these polyphosphides the transition metal atoms make full use of their 3d, 4s, and 4p orbitals, i.e., they obey the 18-electron rule: Twelve electrons are accommodated in the six bonds from the transition metal atoms to the octahedrally coordinating phosphorus atoms. In CrP$_4$ each chromium atom forms two Cr–Cr bonds; for these we have to count four electrons. Two more electrons are nonbonding (12 + 4 + 2 = 18). In the three binary modifications of MnP$_4$ each manganese atom forms one Mn–Mn bond, which accounts for two electrons, and in addition each

manganese atom has four electrons in nonbonding orbitals (12 + 2 + 4 = 18). As a consequence, in none of the binary compounds TP$_4$ do the transition metal atoms carry magnetic moments.

Obviously this beautiful systematics is not applicable for the solid solution Cr$_{1-x}$Mn$_x$P$_4$ of the present paper. The crystal structure of these compositions corresponds to those of the binary modifications of MnP$_4$, i.e., every transition metal forms one T–T bond. Therefore the compounds could be expected to be diamagnetic or Pauli paramagnetic, if the transition metal sites were occupied only by manganese atoms. The presence of chromium atoms means that not all transition metal atoms reach the 18-electron count, and this cannot be compensated for by additional T–T bonding as is the case in CrP$_4$. Therefore the composi-

TABLE 4
Interatomic Distances in $Cr_{0.41}Mn_{0.59}P_4$, $Cr_{0.66}Mn_{0.34}P_4$, and $Cr_{0.68}Mn_{0.32}P_4$[a]

Cr1/Mn1:	P5	225.7/227.5/229.0	Cr2/Mn2:	P8	224.7/224.9/225.7
	P7	225.8/227.3/227.1		P1	226.3/227.1/227.8
	P8	227.2/229.2/230.7		P3	227.0/227.9/227.8
	P2	228.6/229.5/230.0		P7	229.4/229.6/229.1
	P4	232.5/232.3/231.9		P6	234.4/235.7/235.8
	P4	238.5/238.4/238.6		P6	236.0/236.9/236.8
	Cr2/Mn2	293.9/296.2/298.1		Cr1/Mn1	293.9/296.2/298.1
P1:	P5	222.7/223.1/223.0	P2:	P5	219.5/220.0/219.7
	P6	223.0/223.2/222.9		P2	222.6/222.6/221.5
	P3	226.2/226.3/226.3		P7	223.5/222.9/222.2
	Cr2/Mn2	226.3/227.1/227.8		Cr1/Mn1	228.6/229.5/230.0
P3:	P8	217.9/218.2/218.2	P4:	P7	220.2/219.7/219.1
	P3	224.7/226.1/225.1		P5	222.7/222.9/222.1
	P1	226.2/226.3/226.3		Cr1/Mn1	232.5/232.3/231.9
	Cr2/Mn2	227.0/227.9/227.8		Cr1/Mn1	238.5/238.4/238.6
P5:	P2	219.5/220.0/219.7	P6:	P1	223.0/223.2/222.9
	P1	222.7/223.1/223.0		P8	223.7/223.9/224.0
	P4	222.7/222.9/222.1		Cr2/Mn2	234.4/235.7/235.8
	Cr1/Mn1	225.7/227.5/229.0		Cr2/Mn2	236.0/236.9/236.8
P7:	P4	220.2/219.7/219.1	P8:	P3	217.9/218.2/218.2
	P2	223.5/222.9/222.2		P6	223.7/223.9/224.0
	Cr1/Mn1	225.8/227.3/227.1		Cr2/Mn2	224.7/224.9/225.7
	Cr2/Mn2	229.4/229.6/229.1		Cr1/Mn1	227.2/229.2/230.7

[a] The shortest nonbonding distances in the three refinements are $T–T$: 363.9/356.1/347.4, $T–P$: 370.7/371.6/371.6, and P–P: 283.9/307.9/309.7. Standard deviations are all equal to 0.2 pm or less.

TABLE 5
The Three Strongest Reflections of 2-MnP_4, 6-MnP_4, and 8-MnP_4 as Well as Those of Three Chromium-Containing Samples with "4-MnP_4"-Type Structure

Compound	h	k	l	2θ (Cu$K\alpha_1$)	d (pm)	I_c
2-MnP_4	2	$\bar{1}$	$\bar{1}$	31.85	280.8	78
	1	1	1	32.86	272.3	95
	0	0	2	33.00	271.2	100
$Cr_{0.41},Mn_{0.59}P_4$	1	1	0	31.59	283.0	83
	1	$\bar{2}$	2	32.78	273.0	87
	0	0	4	32.93	271.8	100
$Cr_{0.66}Mn_{0.34}P_4$	1	1	0	31.55	283.3	82
	1	$\bar{2}$	2	32.62	274.3	86
	0	0	4	32.86	272.3	100
$Cr_{0.68}Mn_{0.32}P_4$	1	1	0	31.57	283.2	81
	1	$\bar{2}$	2	32.56	274.8	85
	0	0	4	32.90	272.0	100
6-MnP_4	2	$\bar{1}$	$\bar{1}$	32.04	279.2	79
	2	2	$\bar{1}$	32.58	274.6	75
	6	0	0	33.00	271.2	100
8-MnP_4	3	1	$\bar{2}$	31.57	283.1	20
	3	1	1			54
	3	1	$\bar{3}$	32.65	274.0	44
	3	1	2			18
	0	0	8	32.95	271.6	100

tions of the solid solution series $Cr_{1-x}Mn_xP_4$ have uncompensated spins, in agreement with the paramagnetism found experimentally.

The crystal structures of 2-, 6-, and 8-MnP_4 as well as those of CrP_4 and the β- and γ-modifications of FeP_4 (15, 16) may be considered as stacking variants of a two-dimensionally infinite, puckered net of pentagons and hexagons of transition metal and phosphorus atoms (Fig. 5), although the chemical bonding is of equal strength within and between the nets. A nomenclature distinguishing the various ways these nets can be stacked on top of each other has been developed (2). Using this nomenclature the "4-MnP_4-type" structure reported here for the three structure refinements of the solid solution series $Cr_{1-x}Mn_xP_4$ can be represented by the stacking sequence ppo'o, ppo'o.

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