Phosphides of the *B*31 (MnP) Structure Type

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The mono-phosphides of Cr, Mn, Fe, Co, W, and Ru crystallize in the *B*31 (MnP) structure type. The unit cell dimensions of these phosphides have been measured, and the structures of MnP, FeP and CoP have been determined accurately by single-crystal methods. Some data for unit cell variations accompanying isomorphous substitution are presented and discussed.

The first X-ray investigation of a phase crystallizing in the *B*31 structure type was made by Hägg [1], who proposed a tentative structure for FeAs. Later, Fylking [2] investigated several arsenides and phosphides isomorphous with FeAs, in particular MnP, and the approximate structure of this phase was determined by single-crystal and powder methods.

Among the phases with the *B*31 structure (a list is given in Ref.[3]) there are six phosphides, *viz.* CrP, MnP, FeP, CoP, WP and RuP. MnP, FeP and CoP were investigated by Fylking [2], CrP by Nowotny and Henglein [4] and by Schönberg [5], WP by Schönberg [5] and RuP by the present author [6].

The present investigation was undertaken in order to provide data for crystal-chemical comparisons in the series of isomorphous *B*31 phosphides.

EXPERIMENTAL

Preparation. The starting materials for the preparation of MnP, FeP and CoP were electrolytic manganese (AB Ferrolegeringar, Stockholm, claimed purity higher than 99.9 %), spectrographically standardized iron and cobalt rods (Johnson, Matthey & Co. Ltd., London) and red phosphorus (purity higher than 99 %). The phosphides were prepared by dropping pellets of red phosphorus into melts of the appropriate metals, contained in crucibles of pure alumina (Degussit Al 23 from Degussa, Frankfurt, Germany). The metals were melted by induction heating in a closed chamber filled with purified argon. No chemical analyses were made. Earlier preparations [7-9] using the technique described above have yielded products with purities higher than 99.5 %.

On account of the high phosphorus pressures over the molten mono-phosphides it was not possible to prepare single-phase MeP alloys [1,10]. The alloys, from which the single-crystals were selected, contained primary MeP crystals embedded in a Me$_2$P + MeP eutectic. Alloys with higher phosphorus contents were prepared by heating the crushed master alloys and red phosphorus in evacuated and sealed silica tubes at temperatures between 900°C and 1 150°. The phosphides of chromium, tungsten and ruthenium were

prepared by heating metal powder (electrolytic chromium from Gesellschaft für Elektro-metallurgie m.b.H., Werk Nürnberg, Germany; tungsten powder, claimed purity 99.9 %, from Söderfors Bruk, Sweden; ruthenium sponge, claimed purity 99.8 %, from Heraeus, Hanau, Germany) and red phosphorus in silica tubes at 1 000°C.

X-Ray work. X-Ray powder photographs were taken with Guinier-type focussing came-ras using $CrK\alpha_1$ radiation, and with silicon ($a = 5.4305$ Å) as the internal calibration standard. The accuracy of the lattice parameter determinations is estimated to be 0.04 %. For the single-crystal work, needle-shaped crystals of MnP, FeP and CoP(maximum thickness not exceeding 0.05 mm) were used, in which the needle axis corresponded to the b axis of the crystal. Weissenberg photographs were taken about the b axis using zirconium-filtered MoK radiation, and the multiple-film technique with thin iron foils between successive films. The intensities were estimated by visual comparison with cali-brated spots. Corrections for Lorentz and polarisation factors, Fourier series summations, structure factor calculations and calculations of interatomic distances were made by the electronic digital computer BESK using programmes available at BESK. Atomic scatter-ing factors were taken from tables given by Watson and Freeman [11] for manganese, Tho-mas and Umeda [12] for iron and cobalt and Tomiie and Stam [13] for phosphorus. The real part of the dispersion correction, calculated by Dauben and Templeton [14] for each of the metals, was included in the structure factor calculations. Standard deviations of he atomic parameters were estimated by Cruickshank's [15] equation. (Lists of observed and calculated structure factors can be obtained from this Institute on request).

STRUCTURE DETERMINATIONS

According to Hägg [1] and Fylking [2], the $B31$ (MnP) structure, which has the symmetry *Pnma*, can be regarded as an orthorhombic distortion of the hexagonal $B8$ (NiAs) structure. The $B8$ structure (unit cell dimensions a_{B8} and c_{B8}) can also be described by the space group *Pnma* (unit cell dimensions $a = c_{B8}$, $b = a_{B8}$, $c = a_{B8} \times \sqrt{3}$), and the relation between the atomic posi-tions in the NiAs and MnP structures is as follows.

NiAs	x	z	MnP	x	z
4 Ni in 4 *(c)*	0	1/4	4 Mn in 4 *(c)*	0.005	0.20
4 As in 4 *(c)*	1/4	7/12	4 P in 4 *(c)*	0.19	0.57

Starting with the approximate atomic parameters quoted above, the struc-tures of MnP, FeP and CoP were refined by successive electron density pro-jections and difference syntheses on the ac-plane, until no appreciable shifts in the atomic positions were indicated in the difference maps. An isotropic temperature factor for each crystal was applied in the structure factor cal-culations.

Table 1. Atomic positions and standard deviations in MnP, FeP and CoP.

Phos-phide	Parameters for the metal atoms				Parameters for the phosphorus atoms			
	x	$\sigma(x)$	z	$\sigma(z)$	x	$\sigma(x)$	z	$\sigma(z)$
MnP	0.0049	0.0002	0.1965	0.0002	0.1878	0.0005	0.5686	0.0005
FeP	0.0016	0.0002	0.2006	0.0002	0.1913	0.0005	0.5684	0.0004
CoP	0.0007	0.0002	0.1984	0.0002	0.1917	0.0006	0.5814	0.0006

Table 2. Number of observed $(h0l)$ reflexions, reliability index, and temperature factor for MnP, FeP and CoP.

Phos-phide	Number of observed $(h0l)$ reflexions	Reliability index $\Sigma|F_o - F_c|/\Sigma|F_o|$	Temperature factor B (Å^2)
MnP	119	0.075	0.29_0
FeP	106	0.054	0.25_7
CoP	101	0.072	0.29_6

Table 3. Unit cell dimensions for $B31$ type phosphides (Å units. Estimated accuracy 0.04 %).

Phosphide	Unit cell dimensions			Volume U	$c/(b \times \sqrt{3})$
	a	b	c		
CrP	5.362	3.113	6.018	100.5	1.116
MnP	5.258	3.172	5.918	98.7	1.077
FeP	5.191	3.099	5.792	93.2	1.079
CoP	5.077	3.281	5.587	93.1	0.983
WP	5.734	3.249	6.222	115.9	1.106
RuP	5.520	3.168	6.120	107.0	1.115

Table 4. Interatomic distances in MnP, FeP and CoP (Å) (Distances shorter than 3.5 Å listed).

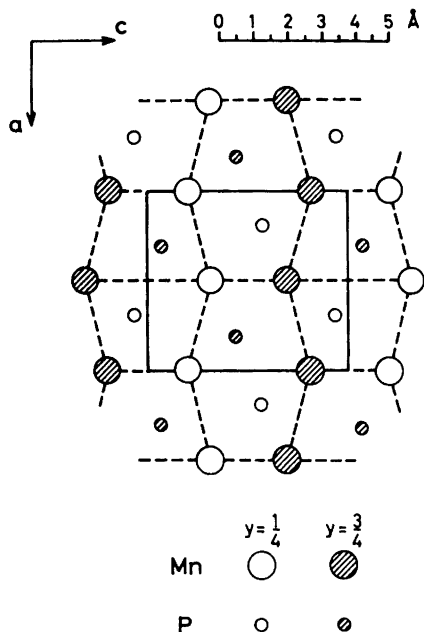| Type of distance	Number of equivalent distances	MnP	FeP	CoP
Me-Me	2	2.70_4	2.65_8	2.60_3
	2	2.81_6	2.79_3	2.75_8
	2	3.17_2	3.09_9	3.28_1
Me-P	1	2.28_9	2.24_1	2.21_5
	2	2.34_0	2.27_9	2.27_1
	1	2.40_3	2.34_7	2.34_9
	2	2.38_7	2.35_1	2.35_7
P-P	2	2.66_0	2.64_1	2.70_3
	2	3.17_2	3.09_9	3.28_1
	2	3.39_4	3.34_1	3.16_1
	4	3.42_0	3.34_1	3.29_3

Fig. 1. The structure of MnP projected on (010).

The final atomic parameters are given in Table 1. The number of recorded $F(h0l)$-values, the temperature factor and the reliability index for each crystal are given in Table 2. Unit cell dimensions are listed in Table 3 and interatomic distances in Table 4.

DESCRIPTION OF THE STRUCTURES

A projection of the MnP structure on the ac-plane is shown in Fig. 1. The metal atoms have four near metal neighbours, while another two metal neighbours (in the b direction) are more distant. Each metal atom has six near phosphorus neighbours situated in a distorted octahedral configuration. The phosphorus atoms are surrounded by six metal atoms at the corners of a highly distorted triangular prism. The triangular prismatic metal coordination about the phosphorus atoms has been found in several phosphides, *e.g.* in Fe₂P ($C22$ type)[16], Co₂P ($C23$ type)[7], Pd₃P (DO_{11} type)[17] and in Rh₄P₃[8]. In the last-mentioned phosphides, the phosphorus atoms have no phosphorus neighbours closer than 3.0 Å. In the $B31$ type phosphides, however, there are zig-zag chains of phosphorus atoms extending in the b direction with the P-P distance 2.66 Å in MnP, 2.64 Å in FeP and 2.70 Å in CoP. This may indicate a tendency to P-P bond formation in these phases. ,

ISOMORPHOUS SUBSTITUTION IN *B*31 STRUCTURES

Unit cell dimensions (as determined in the present investigation) for the six phosphides crystallizing in the *B*31 structure are given in Table 3. The values for MnP, FeP and CoP are in good agreement with those obtained by Fylking[2], whereas the values for CrP and WP are somewhat different from those quoted by Nowotny and Henglein[4] and by Schönberg[5]. Lattice parameter variations indicating extended homogeneity ranges were not observed for any of these phases. As seen from Table 3, the unit cell volumes follow the same sequence as the radii of the metal constituents, but the values for the *b* axis display irregularities. For instance, the largest *b* axis is found for CoP, which has the smallest unit cell volume.

The structural properties of the *B*31 phases have been given particular consideration by Schubert *et al.*[18-21] Schubert divides the *B*31 phases into two classes. In one class, denoted *B*31 *(l)*, the ratio *c/b* is larger than $\sqrt{3}$ (the value for the ideal *B*8 structure), in the other, denoted *B*31 *(k)* the radio is smaller than $\sqrt{3}$. Schubert points out that *B*31 *(l)* seems to be stable at lower, and *B*31 *(k)* at higher electron concentrations.

Among the phosphides, CoP is the only *B*31 *(k)* phase (see Table 3). The present author has found complete solid solubility of FeP, MnP and CrP in CoP. It is therefore possible to study the "transition" from the *B*31 *(k)* to the *B*31 *(l)* class by the substitution of iron, manganese or chromium for cobalt. Lattice parameter measurements on (Co,Me)P alloys (Me = Fe, Mn, Cr) indicate deviations from Vegard's law. It is interesting to note that the compositions for the alloys with $c/b = \sqrt{3}$ were found to be approximately $Co_{0.6}Fe_{0.4}P$, $Co_{0.8}Mn_{0.2}P$ and $Co_{0.87}Cr_{0.13}P$, which implies that the number of electrons is roughly constant at this *c/b* ratio.

It is also possible to study the effect of isomorphous substitution for phosphorus by other non-metals in the *B*31 type phosphides. There is, for instance, a considerable solubility of silicon in FeP and CoP, and boron dissolves to some extent in CoP[9]. (There are, however, no indications of any appreciable solubility of sulphur in FeP or CoP). Since the atomic radius of silicon is larger,

Table 5. Unit cell dimensions for ternary *B*31 type phases. (Å units. Estimated accuracy 0.04 %).

Composition	Unit cell dimensions			Volume	$c/(b \times \sqrt{3})$
	a	b	c	U	
CoP	5.077	3.281	5.587	93.0_7	0.983
$CoP_{0.6}Si_{0.4}$	5.060	5.264	5.653	93.4	1.000
$CoP_{0.9}B_{0.1}$	5.050	3.277	5.623	93.0_5	0.991
FeP	5.191	3.099	5.792	93.2	1.079
$FeP_{0.5}Si_{0.5}$	5.242	3.059	5.853	93.9	1.105

and the boron radius is smaller than that of phosphorus, the volume of the CoP unit cell should increase on P/Si substitution and decrease on P/B substitution. If Schubert's hypothesis is correct, the c/b ratio should increase in both cases. The values given in Table 5 show that this is in fact the case. (The compositions given in the table are only approximate).

From the above-mentioned observations it is clear that the unit cell dimensions for $B31$ phases are dependent on "electronic factors" as stressed by Schubert.

The data from the structure determinations do not indicate any marked structural difference between $B31$ *(l)* and $B31$ *(k)* phases.

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