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Preparation and Properties of a New Iron Phosphide FeP_4

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The new iron phosphide with the highest phosphorus content of known ion phosphides, FeP_4, was synthesized by the reaction of elemental components at 60 kbar in a cubic anvil device. Its space group was found to be C_{222_1}, with four formula units in the unit cell ($a = 0.5005(1)$, $b = 1.0213(3)$, $c = 0.530(1)$ nm). The structure of FeP_4 was analysed by standard Patterson and Fourier techniques and refined by a block-diagonal least-squares method to a final conventional R value of 0.067 for 546 reflections. The coordination around Fe and P in FeP_4 is very similar to that of Cr, Mn, and P in CrP_4 and MnP_4. The difference in structure between these compounds is discussed and correlated to the electronic configuration.

Introduction

Studies on the synthesis of transition metal phosphides under atmospheric conditions have been reviewed by Rundqvist (*1*) and Lundström (*2*). The metal : phosphorus ratios of the compounds described in these papers are ≤1 : 2. In recent years the phosphides with higher proportions of phosphorus content such as CrP_4 or MnP_4 have been introduced by Jeitschko and Donohue (*3*, *4*), but the synthesis of FeP_4 has not been reported to date. This paper reports on the high-pressure synthesis of FeP_4 and its crystal structure.

Sample Preparation and Experimental

Starting material was prepared by mixing Fe and red P powders in the ratio varying between 1 : 3 and 1 : 8. The starting material was charged into a cylindrical BN tube, 3 mm long and 2.8 mm in diameter and inserted into a carbon tube for heating. This assemblage was placed in a hole drilled in the center of a pyrophyllite cube 12.5 mm on an edge. Using a cubic anvil device, the cube was subjected to high temperature and pressure (1100°C and 60 kbar). The temperature of the sample was evaluated from the electric current through the carbon heater and calibrated by inserting a Pt–Pt–13% Rh thermocouple in the assemblage. The emf was not corrected for pressure effect. After 30 min under these conditions the temperature and pressure were lowered and the sample was taken out of the cell.

A more detailed description of the experimental technique for such high-pressure synthesis is given by Yanagisawa and Kume (*5*).

The product was a mixture of black crystals with irregular shape and metallic luster and black phosphorus which was dissolved from

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the product by HNO_3 solution. This purified sample was calcined with $NaHSO_4$ in an Al_2O_3 crucible, dissolved in water, and analyzed by the permanganate method for iron. The iron content in this compound was found to be 31.7 wt% as compared with the calculated value of 31.1 wt%, which showed this new compound had a composition of FeP_4.

Characterization

Electrical resistivity measurements were carried out on a sintered specimen with a four-probe technique from 77°K to room temperature. The specimen was prepared at 1100°C and 60 kbar from purified FeP_4 powder, and its dimension and density were 4*mm*ø × 3*mmh* and 4.2 g/cm^3, respectively. From Fig. 1, it is seen that FeP_4 is a semiconductor with a room-temperature resistivity of 3×10^4 Ω-cm and an activation energy (from $\rho = \rho_0 \exp E_a/kT$) of 0.052 eV.

The magnetization of FeP_4 from 77°K to room temperature is weak.

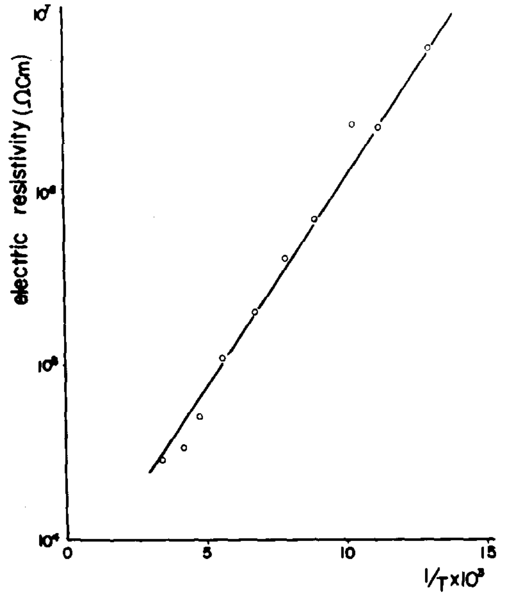

FIG. 1. Variation of the logarithm of resistivity vs the reciprocal absolute temperature for FeP_4.

The Mössbauer effect was examined at room temperature for the material under investigation, and the velocity was calibrated with stainless steel. An isomer shift and a quadrupole splitting were found to be 0.09 and 0.64 mm/sec, respectively.

Structure Determination

The X-ray powder pattern of FeP_4 was indexed as the orthorhombic cell. The lattice constants were refined by a least-squares procedure, using Fe-filtered Co*Kα* radiation and silicon as a standard. Lattice constants and the powder pattern are shown in Table I. With four formula units in the unit cell assumed, the density was calculated to be 4.22 g/cm^3, in good agreement with the observed density of 4.2 g/cm^3.

As shown in Table II, the similarity of lattice constants between the three transition

TABLE I

X-RAY POWDER PATTERN AND LATTICE CONSTANTS OF FeP_4[a]

h k l	I_{obs}	d_{obs}	d_{calc}
0 2 0	vw	0.512	0.511
1 1 0	m	0.450	0.449
0 2 1	vw	0.376	0.375
1 1 1	m	0.349	0.349
1 3 0	vs	0.2817	0.2816
0 0 2	s	0.2765	0.2765
1 3 1	m	0.2506	0.2510
2 0 0			0.2503
1 1 2	m	0.2356	0.2355
2 0 1	vw	0.2279	0.2280
2 2 0	vw	0.2248	0.2247
2 2 1	vw	0.2083	0.2082
1 3 2	w	0.1973	0.1973
1 5 1	w	0.1789	0.1789
2 2 2	w	0.1744	0.1744
1 1 3	s	0.1702	0.1705
0 6 0			0.1703
2 4 1			0.1701
3 1 1	vw	0.1578	0.1578
1 3 3	w	0.1542	0.1542

[a] $a = 0.5005(1)$ nm, $b = 1.0212(3)$ nm, and $c = 0.5530(1)$ nm.

TABLE II

LATTICE PARAMETERS AND DENSITIES OF MP_4 (M: Cr, Mn, Fe)

						d (g/cm^3)	
	a (nm)	b (nm)	c (nm)	β (°)	V (nm^3)	Obs	Calc
CrP_4[a]	0.5191	1.0760	0.5771	110.65	0.3017	3.88	3.87
MnP_4[b]	0.5094	1.0513	2.1804	$\alpha = 94.71$	1.1638	4.05	4.08
FeP_4[c]	0.5005	1.0212	0.5530		0.2826	4.2	4.22

[a] Reference (*3*).

[b] Reference (*4*). A modified unit cell is chosen here in order to make comparison with other compounds.

[c] This work.

metal polyphosphides (CrP_4, MnP_4, and FeP_4), implies that the structure of FeP_4 should be closely related to that of other transition metal polyphosphides.

The systematic lack of reflections observed by Weissenberg and Buerger precession techniques were hkl with $h + k \neq 2n$ and $00l$ with $l \neq 2n$. Space group C_{222_1} is indicated by those diffraction extinctions.

The three-dimensional intensity data for the analysis of the crystal structure were collected using a 20 × 30 × 50-μm single crystal. Zr-filtered Mo$K\alpha$ radiation was used with a four-circle automated diffractometer. The scan speed was 2° (2θ) min^{-1}, and the background was counted for 20 sec at both ends of each scan.

All reflections within the hemisphere $2\theta < 110°$ were collected. The Lorentz-polarization correction was made. The absorption correction was not applied because of the small size of the crystal.

After the interpretation of a three-dimensional Patterson function computed with a program given by Sakurai (*6*), the structure was refined using Ashida's block-diagonal least-squares program (*7*). Atomic scattering factors for neutral atoms and dispersion correction were taken from the "International Tables for X-Ray Crystallography" (*8*, *9*).

The sum $\Sigma w(|F_0| - k|F_c|)$ where w is the weight based on counting statistics and k is the scale factor, was minimized. Observed structure factors which were smaller than twice the standard deviation were excluded from the calculation.

The refinement with anisotropic temperature factors resulted in a final R value of 0.067 for 546 reflections and an Rw of 0.087 (Table III).

The atomic parameters and anisotropic temperature factors are listed in Table IV. Since space group C_{222_1} is noncentrosymmetric, the refinement for another configuration was carried out. Final R value was calculated to be 0.084 and Rw, 0.111.

Discussion

As shown in Fig. 2, the density value of FeP_4 lies on the smooth curve obtained from the relation between densities and atomic contents for iron phosphides which were prepared previously. Similar phenomena were found in the Cr–P and Mo–P systems (*3*).

The structure of FeP_4 is shown in Figs. 3 and 4. Each Fe atom is surrounded octahedrally by six P atoms. These octahedra share corners with each other, forming a plane parallel to (010). P atoms are located at the center of two types of tetrahedron. One tetrahedron has two P atoms and two Fe atoms at its apices, and the other is composed of three P atoms and one Fe atom located at its vertices.

Table III. Observed and calculated structure factors of FeP_4

H	FO	FC
K,L=	0	0
2	467	501
4	780	773
6	689	728
8	124	137
K,L=	1	0
1	384	353
3	501	498
5	84	119
7	510	507
9	175	157
K,L=	2	0
0	250	209
2	760	797
6	494	501
K,L=	3	0
1	1145	1394
3	393	428
5	1124	1278
7	127	79
9	298	271
K,L=	4	0
0	394	394
2	723	742
4	106	126
6	202	197
8	150	168
K,L=	5	0
1	612	602
3	265	237
5	193	227
7	491	481
9	180	132
K,L=	6	0
0	1449	1773
2	217	213
4	578	585
6	538	584
K,L=	7	0
1	80	39
3	465	448
5	290	275
7	265	282
K,L=	8	0
0	643	642
2	384	356
6	534	564
K,L=	9	0
1	675	669
5	675	706
7	115	106
K,L=	10	0
0	410	420
2	328	344
6	108	90
8	163	128
K,L=	11	0
1	531	518
3	115	51
5	436	439
7	256	292
K,L=	12	0
0	586	580
2	160	143
4	320	296
6	295	316
K,L=	13	0
1	150	150
3	235	226
5	235	205
K,L=	14	0
0	638	650
2	108	100
4	195	226
6	409	412
K,L=	15	0
1	263	240
3	219	229
5	204	193
K,L=	16	0
0	230	242
K,L=	17	0
1	368	380
K,L=	18	0
0	102	46
2	308	291
K,L=	19	0
1	190	125
K,L=	0	1
2	572	544
4	579	553
6	286	288
K,L=	1	1
1	538	489
3	1050	1070
5	164	196
7	336	345
9	317	325
K,L=	2	1
0	417	388
2	768	767
4	579	596
6	98	84
8	387	403
K,L=	3	1
1	738	737
3	276	274
5	180	188
7	239	244
9	201	203
K,L=	4	1
0	187	225
2	1115	1230
4	430	412
6	141	180
8	479	512
K,L=	5	1
1	527	529
3	454	423
5	402	401
7	226	224
9	347	295
K,L=	6	1
0	302	304
2	352	321
4	524	522
6	194	199
8	131	114
K,L=	7	1
1	369	381
3	1039	1109
5	147	182
7	497	527
K,L=	8	1
0	653	673
2	234	261
4	498	485
6	117	145
8	198	190
K,L=	9	1
1	352	319
3	198	220
5	265	273
7	158	144
K,L=	10	1
0	328	333
2	952	1008
4	238	235
8	423	398
K,L=	11	1
1	391	412
5	454	465
7	156	211
K,L=	12	1
0	291	307
4	386	410
K,L=	13	1
1	241	286
3	691	721
5	135	98
7	452	402
K,L=	14	1
0	547	555
2	271	283
4	302	292
K,L=	15	1
1	161	174
3	182	205
5	245	246
K,L=	16	1
0	120	107
2	578	589
4	206	158
K,L=	17	1
1	273	242
3	184	178
K,L=	18	1
0	227	231
2	126	145
K,L=	19	1
1	208	194
K,L=	0	2
0	1343	1635
2	190	154
4	764	748
6	390	381
8	153	169
K,L=	1	2
1	749	734
3	654	631
5	317	320
7	502	519
9	153	188
K,L=	2	2
0	117	137
2	913	942
4	350	311
6	289	295
8	241	277
K,L=	3	2
1	897	892
3	220	185
5	790	810
9	371	341
K,L=	4	2
0	286	287
2	813	837
4	620	664
6	339	319
8	201	170
K,L=	5	2
1	401	388
3	583	574
5	175	139
7	442	468
K,L=	6	2
0	1001	1046
2	234	183
4	572	596
6	321	340
8	234	191
K,L=	7	2
1	773	765
3	399	431
5	232	246
7	364	379
K,L=	8	2
0	209	191
2	550	562
4	190	205
6	299	299
K,L=	9	2
1	499	489
3	198	212
5	517	542
7	223	184
K,L=	10	2
0	163	165
2	458	467
4	520	531
6	301	295
K,L=	11	2
1	394	393
3	384	397
5	220	211
7	279	284
K,L=	12	2
0	428	396
2	256	259
4	334	345
6	217	249
K,L=	13	2
1	457	472
3	205	208
5	98	79
K,L=	14	2
0	319	339
2	293	288
4	368	387
6	301	245
K,L=	15	2
1	205	225
3	265	239
5	317	276
K,L=	16	2
2	171	209
4	257	216
K,L=	17	2
1	387	356
3	228	264
K,L=	18	2
2	246	230
K,L=	0	3
2	684	680
4	782	807
6	499	499
K,L=	1	3
1	846	856
3	378	321
5	584	593
7	320	276
9	149	97
K,L=	2	3
0	941	961
2	289	249
4	394	395
6	456	459
8	302	329
K,L=	3	3
1	980	992
3	493	465
5	204	220
7	301	291
K,L=	4	3
0	819	810
2	502	492
4	384	359
6	590	604
8	256	193
K,L=	5	3
1	565	542
3	204	244
5	534	549
7	197	244
K,L=	6	3
0	558	554
2	472	470
4	579	606
6	395	373
K,L=	7	3
1	706	726
3	356	326
5	360	385
7	397	397
K,L=	8	3
0	628	614
2	209	221
4	350	339
6	228	217
8	224	211
K,L=	9	3
1	526	519
3	268	282
5	413	423
K,L=	10	3
0	417	415
2	464	500
4	286	267
6	438	473
K,L=	11	3
1	332	333
5	306	333
7	183	196
K,L=	13	3
1	415	432
3	294	292
5	206	224
K,L=	14	3
0	230	246
2	209	207
4	293	268
6	110	100
K,L=	15	3
1	301	300
5	372	347
K,L=	16	3
0	194	213
2	346	381
4	190	158
K,L=	17	3
1	221	231
3	132	77
K,L=	18	3
0	408	389
K,L=	0	4
0	186	151
2	784	772
4	595	585
6	99	60
8	465	487
K,L=	1	4
1	236	188
3	558	534
5	135	103
7	272	231
K,L=	2	4
0	236	235
2	687	679
4	227	228
6	102	20
8	347	349
K,L=	3	4
1	413	401
3	823	847
5	104	179
7	242	240
K,L=	4	4
2	379	374
4	290	295
6	235	181
8	149	167
K,L=	5	4
1	250	216
3	756	795
5	99	124
7	272	281
K,L=	6	4
0	154	145
2	619	624
4	493	480
6	219	248
8	424	375
K,L=	7	4
1	445	438
3	276	269
7	123	128
K,L=	8	4
0	163	210
2	656	663
4	365	409
6	158	177
K,L=	9	4
1	406	429
3	560	558
5	205	234
7	231	223
K,L=	10	4
0	138	161
2	219	233
4	331	322
6	272	283
K,L=	11	4
1	338	333
3	654	683
K,L=	12	4
0	198	171
2	356	370
4	299	299
6	271	282
K,L=	13	4
1	380	362
3	306	301
5	113	122
K,L=	14	4
0	135	56
2	443	442
4	378	406
K,L=	15	4
1	256	321
3	294	261
K,L=	16	4
0	171	170
2	205	244
K,L=	17	4
1	283	231
K,L=	0	5
2	108	55
4	135	159
6	257	255
8	257	249
K,L=	1	5
1	894	929
3	361	330
5	543	573
7	246	283
K,L=	2	5
0	753	757
2	391	352
4	569	602
6	569	552
8	194	240
K,L=	3	5
1	263	278
3	272	282
5	213	238
7	116	101
K,L=	4	5
0	869	907
2	297	321
4	447	401
6	595	638
8	127	115
K,L=	5	5
1	682	687
3	352	384
5	362	355
7	194	219
K,L=	6	5
0	326	340
2	72	23
4	87	125
6	247	256
K,L=	7	5
1	635	658
3	183	147
5	542	564
7	350	244
K,L=	8	5
0	334	314
2	316	297
4	405	424
6	305	296
K,L=	9	5
1	273	266
3	183	162
5	276	276
7	160	109
K,L=	10	5
0	661	666
4	250	259
6	432	454
K,L=	11	5
1	278	278
3	212	236
5	123	136
K,L=	12	5
0	393	413
4	97	103
K,L=	13	5
1	368	376
5	387	358
K,L=	14	5
2	204	182
4	131	159
K,L=	15	5
1	269	274
K,L=	16	5
0	380	362
2	216	156
K,L=	0	6
2	646	647
4	321	300
6	212	212
K,L=	1	6
1	402	415
5	305	282
7	234	248
K,L=	2	6
0	315	316
2	327	296
4	450	474
6	202	170
K,L=	3	6
1	424	433
3	599	594
5	138	114
7	361	380
K,L=	4	6
0	243	275
2	219	250
4	299	263
6	134	90
K,L=	5	6
1	472	445
3	334	351
5	221	248
7	193	126
K,L=	6	6
0	82	130
2	605	616
4	413	396
6	326	355
K,L=	7	6
1	134	145
3	105	105
5	242	257
7	153	170
K,L=	9	6
1	591	623
3	447	432
5	169	158
K,L=	8	6
0	249	242
2	310	294
4	405	434
6	243	211
K,L=	10	6
0	134	132
K,L=	11	6
1	336	306
3	386	390
5	180	181
K,L=	12	6
0	164	198
2	436	457
4	405	404
K,L=	13	6
1	150	79
3	135	147
K,L=	14	6
0	183	185
2	272	285
K,L=	15	6
1	426	462
K,L=	0	7
2	167	144
4	98	95
K,L=	1	7
1	523	569
3	460	443
5	195	199
7	246	233
K,L=	2	7
0	119	119
2	508	494
4	494	519
6	276	271
K,L=	3	7
3	184	182
5	191	222
K,L=	4	7
0	304	294
2	360	381
4	398	385
6	271	300
K,L=	5	7
1	509	498
3	461	472
K,L=	6	7
0	142	139
2	272	291
4	145	66
6	142	44
K,L=	7	7
1	350	352
3	339	313
5	293	327
K,L=	8	7
2	453	438
4	356	403
K,L=	9	7
3	306	312
5	138	113
K,L=	10	7
0	372	366
2	190	204
4	352	369
K,L=	11	7
1	319	278
3	261	283
K,L=	12	7
0	156	119
2	342	348
K,L=	13	7
1	283	274
3	216	186
K,L=	0	8
0	362	346
2	368	375
4	108	122
6	454	389
K,L=	1	8
1	305	309
3	173	167
5	404	426
K,L=	2	8
0	665	697
2	216	210
4	304	308
6	263	212
K,L=	3	8
1	390	402
3	167	205
5	236	255
K,L=	4	8
0	393	410
2	165	173
4	239	209
K,L=	5	8
1	389	389
3	215	207
5	497	488
K,L=	6	8
0	324	322
2	360	353
4	171	151
K,L=	7	8
1	115	86
5	165	150
K,L=	8	8
0	610	636
2	124	71
4	249	268
K,L=	9	8
1	328	389
3	182	186
K,L=	11	8
1	341	328
K,L=	12	8
0	243	228
K,L=	0	9
2	119	86
K,L=	1	9
1	164	174
3	449	457
K,L=	2	9
2	412	423
4	235	212
K,L=	3	9
3	184	185
K,L=	4	9
0	126	131
2	313	335
4	362	308
K,L=	5	9
1	110	125
3	395	411
K,L=	6	9
0	198	238
2	287	307
K,L=	7	9
1	176	230
3	317	312
K,L=	8	9
0	113	93
2	364	336
K,L=	10	9
0	268	213
K,L=	0	10
2	330	359
K,L=	1	10
1	236	241
K,L=	2	10
0	476	470
2	198	181
K,L=	3	10
1	252	233
K,L=	4	10
0	326	290
2	187	142
K,L=	5	10
1	283	266
K,L=	12	3
0	597	614
2	179	154
4	278	285
6	265	244

TABLE IV

FINAL POSITIONAL AND THERMAL PARAMETERS OF THE FeP_4 STRUCTURE[a, b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	0.0	0.1741(1)	0.25	5(3)	4(4)	1(3)	0	0(1)	0
P_1	0.1804(4)	0.1824(2)	0.6338(3)	38(5)	54(4)	32(4)	−1(4)	−3(4)	3(4)
P_2	0.2104(4)	0.5180(2)	0.3020(3)	32(4)	46(4)	34(4)	−2(4)	−4(4)	2(3)

[a] Errors in the last place are given in parentheses.

[b] The thermal parameters are defined through $T = \exp 10^{-4} \times \frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)$.

P atoms are bound to each other by covalent bonds with an average bond distance of 0.2234 nm and construct the three-dimensional network. Interatomic distances are given in Table V. The P_1–P_2 distance of 0.2315 nm is a little longer than the P–P distances observed in elemental phosphorus (0.223 nm for black phosphorus and 0.222 for Hittsorfs phosphorus) (*10*, *11*) and phosphides with a P—P bond such as FeP_2 (0.2237 nm) (*12*). However, the P_1—P_2 bond may still be considered as weakly covalent. The bond angles around the P atoms vary from 87.68 to 127.45°, which is within the allowable range for sp^3 hybridized bond angles consistent with a covalent character. The Fe–P distances range from 0.2308 to 0.2175 nm with an average distance of 0.2249 nm. This value is smaller than the sum of Pauling's covalent radii and the mean Fe–P bond distance observed for FeP_2.

The structure of FeP_4 is delineated as a layered structure like the descriptions for the crystal structures of CrP_4 and MnP_4 (*3*, *4*). These three structures are composed of almost the same layer, with the composition of M_2P_8 (M = Mn, Cr, and Fe). The stacking of this layer is a little different in each compound.

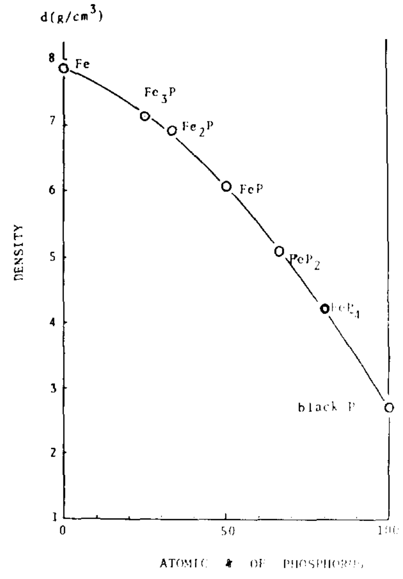

FIG. 2. Relation between density and atomic percentage of phosphorus in various kinds of iron phosphides.

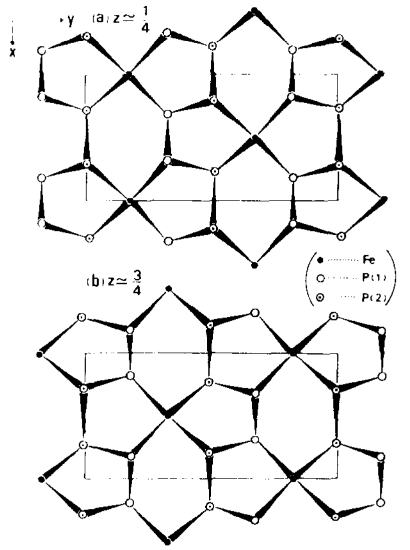

FIG. 3. Structure of FeP_4. The structure is formed by the stacking of two layers at $Z\frac{1}{4}$ and $Z\frac{3}{4}$. They are correlated by rotation of 180°.

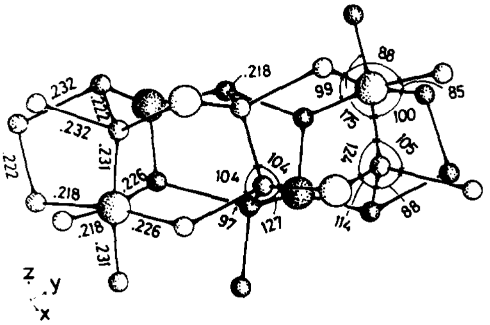

FIG. 4. A perspective view of the linkage between Fe and P atoms and between P atoms. Large spheres indicate Fe atoms, and small spheres indicate P atoms. P_1 is surrounded by two Fe and two P atoms. P_2 is surrounded by one Fe atom and three P atoms. A decimal fraction means the bond distance in nanometers, and an integer means the bond angle in degrees.

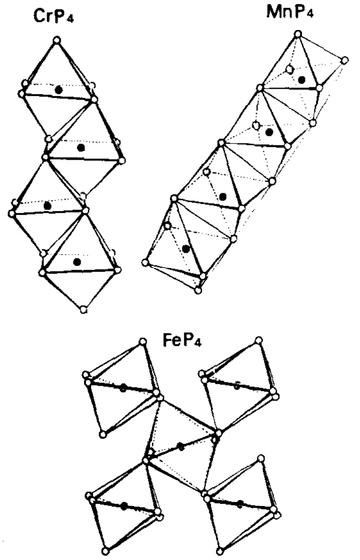

FIG. 5. Crystal structures of FeP_4, CrP_4, and MnP_4.

The crystal structure of CrP_4 is formed by a parallel stacking of layers which are slightly shifted relative to adjacent layers. The octahedra are connected only by edge sharing and form zigzag chains along the *z* axis in CrP_4.

In addition to parallel transfer, rotational operation around an axis perpendicular to the layer is needed to compose the structure of MnP_4. As a result of the rotation, octahedra share edges and corners in MnP_4.

In the case of FeP_4, each layer is rotated by 180° relative to the adjacent layers above and below around an axis whose position differs from that of MnP_4. So, the octahedra share

TABLE V

INTERATOMIC DISTANCES (nm) AND ANGLES (°) IN THE FeP_4 STRUCTURE[a]

Fe:4Fe 0.4039(2)	P_1: Fe 0.2308(2)	P_2: Fe 0.2175(2)
$2P_1$ 0.2308(2)	Fe 0.2263(2)	P_1 0.2305(2)
$2P_1$ 0.2263(2)	P_1 0.2216(3)	P_2 0.2221(2)
$2P_2$ 0.2175(2)	P_2 0.2315(2)	P_2 0.2183(2)

P_1–Fe–P_1	89.52(8) (2×)	Fe–P_1–Fe	124.15(9)
P_1–Fe–P_1	175.79 (9)	Fe–P_1–P_1	114.28(10)
P_1–Fe–P_1	87.76(8) (2×)	Fe–P_1–P_2	107.00(9)
P_1–Fe–P_2	83.56(8) (2×)	Fe–P_1–P_1	102.38(9)
P_1–Fe–P_2	88.10(8) (2×)	Fe–P_1–P_2	105.42(9)
P_1–Fe–P_1	99.22(8)	P_1–P_1–P_2	87.68(9)
P_1–Fe–P_2	169.74(9) (2×)		
P_1–Fe–P_2	99.56(8) (2×)	Fe–P_2–P_1	116.01(9)
P_2–Fe–P_2	85.62(8)	Fe–P_2–P_2	104.59(9)
		Fe–P_2–P_2	127.45(10)
		P_1–P_2–P_2	104.45(9)
		P_1–P_2–P_2	97.00(9)
		P_2–P_2–P_2	101.06(8)

[a] Standard deviations in the last place are given in parentheses.

only corners in FeP_4 and form the corrugated plane parallel to (010) (Fig. 5).

The stacking sequence in these three compounds is as follows, $AA'AA' \cdots$ for CrP_4, $AA'A''A'''BB'B''B''' \cdots$ for MnP_4, and $ABAB \cdots$ for FeP_4. From the viewpoint of the connection of octahedra, FeP_4 seems to be a companion of CdP_4 (*13*). But, the linkage of P in FeP_4 has very little resemblance to that in CdP_4. FeP_4 should be considered to be a companion of CrP_4 and MnP_4. Jeitschko and Donohue (*3*) gave a formal valence of zero to the P atoms surrounded by three P atoms and one Cr atom, and a formal valence of -1 to the P atoms bonded to two P and two Cr atoms. From this consideration, the formal valence of Fe is deduced to be $+2$ in FeP_4 as well as Cr in CrP_4 and Mn in MnP_4.

A d^6 configuration of Fe with a low spin state fits well to the very weak magnetization observed for FeP_4. The isomer shift of FeP_4 fell into the range of isomer shifts reported for the compounds with low-spin-state Fe^{2+}.

Here, we can see a clear example of the effect of the electronic configuration on the crystal structure. In a series of MP_4 compounds, Cr, Mn, and Fe have d^4, d^5, and d^6 configurations, respectively. The d^4 configuration makes it possible to form two metal–metal bondings through shared edges as seen in the CrP_4 with zigzag chains. In the case of the d^5 configuration, only one metal–metal bonding is acceptable. MnP_4 has the alternate metal–metal bonding in the straight link of four edge-shared MnP_6 octahedra. In FeP_4, no half-filled orbital which is available for metal–metal bonding is conceivable because of a d^6 configuration with a low spin state. Then, the FeP_6 octahedra share only corners, as seen in CdP_4 with a d_{10} configuration.

This fact is comparable to the structural change of MX_2 (M: Fe, Co, and Ni; X: P, As, and Sb) due to an electronic configuration as reported by Hulliger and Mooser (*14*).

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