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The Crystal Structure of Manganese Fluorophosphate, $Mn_2(PO_4)F$

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Manganese fluorophosphate, $Mn_2(PO_4)F$, crystallizes in the space group $C2/c$, with cell dimensions $a=13{\cdot}410$ (4), $b=6{\cdot}5096$ (5), $c=10{\cdot}094$ (2) Å, and $\beta=119{\cdot}99$ (1)° ($Z=8$). A three-dimensional structural analysis using automatic diffractometer data has been completed and refined by full-matrix least-squares procedures to a residual $R=0{\cdot}023$ ($R_w=0{\cdot}046$). $Mn_2(PO_4)F$ is found to be isostructural with the mineral triplite, except that there is no disorder in the fluorine position. A possible explanation for the disorder in triplite is given, and the relationships between the structures of $Mn_2(PO_4)F$, triplite, triploidite, and wagnerite are discussed.

Introduction

As part of a continuing study of the crystal chemistry of halophosphates with the composition $M_2(PO_4)X$, where M is a divalent metal or metals and X is a halogen (Rea & Kostiner, 1972, and references therein), we have grown single crystals of manganese fluorophosphate $Mn_2(PO_4)F$; this paper describes its crystal structure.

Manganese fluorophosphate represents a pure end member of the phosphate mineral triplite, $(Mn,Fe)_2(PO_4)F$, whose structure was recently determined by Waldrop (1969). The materials are isotypic with an interesting difference reflected in the position of the fluorine atoms. The possible cause of this difference is discussed in detail.

Experimental

Preparation and crystal growth

Single crystals of manganese fluorophosphate were grown by standard flux melt techniques using excess manganese fluoride as the flux. Manganese(II) phosphate trihydrate was prepared in aqueous solution at 100°C by reaction of manganese(II) sulfate monohydrate and disodium hydrogen phosphate (starting materials were Analytical Reagent Grade, Mallinckrodt Chemical Works) and was then dehydrated at 750°C. Anhydrous manganese(II) fluoride (Ozark-Mahoning Co.) was used as received.

A mixture of 20 mole.% $Mn_3(PO_4)_2$–80 mole.% MnF_2 was placed in a tightly covered 25 cm^3 platinum crucible and inserted into a silicon carbide resistance-heated furnace which was brought to a temperature of 1150°C under a flowing dry nitrogen atmosphere. After soaking at this temperature for four hours, the furnace was cooled at a rate of 8°C per hour to 650°C and then shut off. The irregularly shaped crystals, up to 1 mm thick, were separated from the melt by repeated washing with hot distilled water; no attempt was made to maximize crystal size.

X-ray diffraction data

A crystal was ground to a sphere of 0·013 (2) cm; Weissenberg and precession photographs revealed monoclinic symmetry with systematic absences corresponding to the space groups $C2/c$ or Cc. No measurable piezoelectric effect could be detected using a sensitive Giebe–Scheibe detector designed by H. Diamant.

The lattice parameters were determined in a *PICK* II least-squares refinement program, using 48 reflections within the angular range $35° < 2\theta < 54°$; the reflections were automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation. At 22°C the lattice parameters are $a=13{\cdot}410$ (4), $b=6{\cdot}5096$ (5), $c=10{\cdot}094$ (2) Å, and $\beta=119{\cdot}99$ (1)°, where the figures in parentheses represent the standard deviations in the last reported figure. The calculated density, with $Z=8$, is 3·896 g.cm^{-3} and the measured density (buoyant force) is 3·88 (1) g.cm^{-3}.

Diffraction intensities were measured using Zr filtered Mo $K\alpha$ radiation at a take-off angle of 2·5° with the diffractometer operating in the θ–2θ scan mode. Scans were made at 1° per min over 1·5° with allowance for dispersion, and with 40-sec background counts taken at both ends of the scan. Of the 1614 independent data investigated in the angular range $2\theta < 71°$, 1588 were considered observable according to the criterion $|F_o| > 0{\cdot}675\sigma_F$, where σ_F is defined as $0{\cdot}02|F_o| + [C + k^2B]^{1/2}/2|F_o|\text{Lp}$; the total scan count is C, k is the ratio of scanning time to the total background time, and B is the total background count. Three reflections were systematically monitored and no random variations in intensity greater than 3·5% were observed over the entire data collection period; the mean variation was very much smaller.

The intensity data were corrected for Lorentz and polarization effects, and absorption corrections (*Inter-*

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Table 1. *Observed and calculated structure factor*

H	K	L	FOBS	FCAL
0	0	2	234	244
0	0	4	980	952
0	0	6	2291	2333
0	0	8	688	707
0	0	10	398	405
0	0	12	454	465
0	0	14	777	782
0	2	0	505	503
0	2	2	1577	1585
0	2	3	70	43
0	2	4	1687	1685
0	2	5	1902	1916
0	2	6	882	897
0	2	7	673	679
0	2	8	805	817
0	2	9	160	179
0	2	10	553	552
0	2	11	84	69
0	2	12	449	454
0	2	13	190	190
0	2	14	265	254
0	4	0	736	733
0	4	1	1148	1143
0	4	2	1654	1641
0	4	3	87	100
0	4	4	1513	1533
0	4	5	948	963
0	4	6	186	178
0	4	7	222	227
0	4	8	841	841
0	4	9	246	243
0	4	10	415	425
0	4	11	63	50
0	4	12	355	361
0	4	13	252	259
0	6	0	2036	2010
0	6	1	848	861
0	6	2	285	282
0	6	3	111	97
0	6	4	48	30
0	6	5	643	644
0	6	6	802	816
0	6	7	228	228
0	6	8	289	290
0	6	9	58	57
0	6	10	333	330
0	6	11	167	173
0	8	0	655	660
0	8	1	563	574
0	8	2	198	186
0	8	3	98	68
0	8	4	143	127
0	8	5	328	336
0	8	6	592	589
0	8	7	312	315
0	8	8	328	335
0	8	9	61	58
0	10	0	560	581
0	10	1	44	47
0	10	2	446	460
0	10	3	166	170
0	10	4	546	563
1	1	-11	806	802
1	1	-10	698	689
1	1	-9	400	403
1	1	-8	591	605
1	1	-7	193	177
1	1	-6	1118	1153
1	1	-5	1521	1523
1	1	-4	582	621
1	1	-3	58	51
1	1	-2	456	462
1	1	0	88	280
1	1	1	550	560
1	1	2	309	313
1	1	3	591	619
1	1	4	738	761
1	1	5	703	707
1	1	6	1006	1038
1	1	7	491	495
1	1	8	992	1012
1	1	9	288	300
1	1	10	42	26
1	1	11	175	168
1	1	12	596	590
1	1	13	385	384
1	3	-10	519	511
1	3	-9	523	517
1	3	-8	272	258
1	3	-7	1154	1165
1	3	-6	448	444
1	3	-5	978	977
1	3	-4	1083	1070
1	3	-3	753	746
1	3	-2	687	686
1	3	-1	2169	2071
1	3	0	478	454
1	3	1	696	669
1	3	2	412	393
1	3	3	1004	984
1	3	4	705	717
1	3	5	198	199
1	3	6	387	383
1	3	7	1205	1227
1	3	8	235	221
1	3	9	568	579
1	3	10	309	312
1	3	11	225	213
1	3	12	405	401
1	3	13	640	636
1	5	-9	451	458
1	5	-8	52	58
1	5	-7	545	551
1	5	-6	1181	1178
1	5	-5	64	49
1	5	-4	228	233
1	5	-3	357	356
1	5	-2	367	377
1	5	-1	549	545
1	5	0	900	895
1	5	1	161	158
1	5	2	621	605
1	5	3	161	154
1	5	4	115	105
1	5	5	418	433
1	5	6	184	180
1	5	7	106	100
1	5	8	1193	1207
1	5	9	123	124
1	5	10	94	97
1	5	11	104	72
1	5	12	219	222
1	7	-7	185	172
1	7	-6	80	92
1	7	-5	1005	1016
1	7	-4	424	422
1	7	-3	48	44
1	7	-2	350	356
1	7	-1	399	400
1	7	0	386	391
1	7	1	233	232
1	7	2	312	314
1	7	3	642	656
1	7	4	606	602
1	7	6	508	513
1	7	7	568	580
1	7	8	116	93
1	7	9	536	551
1	7	10	308	304
1	9	-7	143	123
1	9	-6	274	280
1	9	-5	219	217
1	9	-4	577	602
1	9	-3	384	380
1	9	-2	707	720
1	9	-1	244	239
1	9	0	49	24
1	9	1	118	121
1	9	2	24	7
1	9	3	125	118
1	9	4	773	787
1	9	5	107	97
1	9	6	469	479
1	9	7	232	239
2	0	-12	478	474
2	0	-10	442	445
2	0	-8	603	638
2	0	-6	495	512
2	0	-4	1881	1948
2	0	-2	223	242
2	0	4	198	182
2	0	6	174	88
2	0	8	1610	1603
2	0	10	345	347
2	0	12	187	189
2	2	-11	83	75
2	2	-10	233	227
2	2	-9	110	94
2	2	-8	209	169
2	2	-7	93	98
2	2	-6	1015	1031
2	2	-5	1199	1193
2	2	-4	1016	1000
2	2	-3	164	221
2	2	-2	1031	1035
2	2	-1	98	97
2	2	0	1204	1181
2	2	1	1452	1468
2	2	2	1114	1083
2	2	3	1753	1751
2	2	4	1100	1124
2	2	5	116	79
2	2	6	518	514
2	2	7	1158	1164
2	2	8	601	614
2	2	9	238	236
2	2	10	702	714
2	2	11	89	69
2	2	12	318	319
2	2	13	29	28
2	4	-10	223	213
2	4	-9	428	428
2	4	-8	513	471
2	4	-7	294	305
2	4	-6	746	730
2	4	-5	348	351
2	4	-4	138	133
2	4	-3	779	780
2	4	-2	1408	1395
2	4	-1	30	18
2	4	0	1631	1600
2	4	1	117	106
2	4	2	725	731
2	4	3	1407	1411
2	4	4	1127	1132
2	4	5	57	37
2	4	6	1207	1219
2	4	7	314	316
2	4	8	87	61
2	4	9	230	236
2	4	10	426	424
2	4	11	108	93
2	4	12	574	576
2	6	-8	193	193
2	6	-7	60	54
2	6	-6	151	151
2	6	-5	47	8
2	6	-4	1106	1109
2	6	-3	1138	1146
2	6	-2	368	370
2	6	-1	135	139
2	6	0	98	74
2	6	1	686	609
2	6	2	1664	1645
2	6	3	1108	1111
2	6	4	69	44
2	6	5	457	462
2	6	6	208	214
2	6	7	525	542
2	6	8	725	726
2	6	9	302	307
2	6	10	253	243
2	6	11	451	450
2	8	-8	116	100
2	8	-7	243	246
2	8	-6	234	236
2	8	-5	856	862
2	8	-4	464	469
2	8	-3	308	305
2	8	-2	126	111
2	8	-1	376	380
2	8	0	148	145
2	8	1	860	860
2	8	2	614	621
2	8	3	633	640
2	8	4	180	175
2	8	5	266	271
2	8	6	77	65
2	8	7	604	611
2	8	8	447	457
2	10	-5	63	80
2	10	-4	467	472
2	10	-3	221	232
2	10	-2	687	692
2	10	-1	222	214
2	10	0	438	433
2	10	1	211	206
2	10	2	644	658
2	10	3	378	384
2	10	4	507	518
3	1	-12	91	81
3	1	-11	118	125
3	1	-10	1028	1032
3	1	-9	1248	1250
3	1	-8	795	807
3	1	-7	1078	1094
3	1	-6	731	733
3	1	-5	579	594
3	1	-4	949	963
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3	1	0	80	61
3	1	1	1054	1053
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3	1	3	1130	1133
3	1	4	133	143
3	1	5	896	928
3	1	6	838	858
3	1	7	560	556
3	1	8	413	413
3	1	9	119	113
3	1	10	734	731
3	1	11	651	649
3	1	12	255	245
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3	3	-10	374	371
3	3	-9	387	381
3	3	-8	185	181
3	3	-7	1232	1247
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3	3	-2	104	102
3	3	-1	1029	1025
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3	3	1	1899	1867
3	3	2	159	150
3	3	3	835	832
3	3	5	74	58
3	3	6	331	338
3	3	7	698	710
3	3	8	229	224
3	3	9	1054	1056
3	3	10	104	101
3	3	11	498	494
3	3	12	93	76
3	5	-10	1082	1083
3	5	-9	442	443
3	5	-8	389	380
3	5	-7	269	271
3	5	-6	443	434
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3	5	-4	672	655
3	5	-3	776	768
3	5	-2	73	57
3	5	-1	391	383
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3	5	2	379	359
3	5	3	450	448
3	5	4	578	563
3	5	5	304	303
3	5	6	169	165
3	5	7	409	408
3	5	8	369	367
3	5	9	254	266
3	5	10	796	807
3	5	11	345	350
3	7	-8	455	452
3	7	-7	328	336
3	7	-6	160	142
3	7	-5	227	176
3	7	-4	111	108
3	7	-3	858	851
3	7	-2	430	428
3	7	-1	570	547
3	7	0	102	97
3	7	1	238	242
3	7	2	187	186
3	7	3	70	65
3	7	4	59	48
3	7	5	658	654
3	7	6	353	354
3	7	7	302	306
3	7	8	471	461
3	7	9	337	340
3	9	-8	488	480
3	9	-7	374	368
3	9	-6	351	353
3	9	-5	337	324
3	9	-4	398	398
3	9	-3	93	50
3	9	-2	308	289
3	9	-1	303	310
3	9	0	497	490
3	9	1	51	38
3	9	2	61	43
3	9	3	484	482
3	9	4	169	155
3	9	5	160	153
3	9	6	496	503
4	0	-12	455	448
4	0	-10	573	569
4	0	-8	168	161
4	0	-6	1543	1552
4	0	-4	194	157
4	0	0	1002	994
4	0	2	833	833
4	0	4	1735	1729
4	0	6	377	357
4	0	8	218	212
4	0	10	849	846
4	0	12	436	426
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4	2	-11	747	747
4	2	-10	83	60
4	2	-9	78	74
4	2	-8	259	261
4	2	-7	813	823
4	2	-6	191	190
4	2	-5	297	304
4	2	-4	559	551
4	2	-3	1566	1552
4	2	-2	916	895
4	2	-1	534	571
4	2	0	275	279
4	2	1	436	426
4	2	2	830	821
4	2	3	1260	1270
4	2	4	42	23
4	2	5	822	841
4	2	6	446	453
4	2	7	36	13
4	2	8	275	279
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4	2	10	127	126
4	2	11	58	42
4	2	12	169	154
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4	4	-10	278	277
4	4	-9	328	326
4	4	-8	272	277
4	4	-7	955	961
4	4	-6	371	381
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4	4	-4	378	376
4	4	-3	528	518
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4	4	1	141	91
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4	4	7	253	247
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4	4	10	108	93
4	4	11	224	208
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4	6	-8	105	87
4	6	-7	637	649
4	6	-6	280	284
4	6	-5	133	119
4	6	-4	357	362
4	6	-3	221	186
4	6	-2	1226	1203
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4	6	0	366	361
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4	6	2	309	304
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4	6	4	857	864
4	6	5	765	770
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4	6	7	271	266
4	6	8	148	160
4	6	9	137	72
4	6	10	511	513
4	8	-9	471	480
4	8	-8	101	97
4	8	-6	236	246
4	8	-5	71	68
4	8	-4	62	37
4	8	-3	1086	1088
4	8	-2	197	165
4	8	-1	69	67
4	8	0	87	86
4	8	1	434	437
4	8	2	25	49
4	8	3	823	822
4	8	4	342	347
4	8	5	310	315
4	8	6	150	131
4	8	7	427	437
4	10	-5	519	524
4	10	-4	241	252
4	10	-3	284	288
4	10	-2	645	657
4	10	-1	219	225
4	10	0	425	430
4	10	1	198	199
4	10	2	331	337
5	1	-12	619	620
5	1	-11	493	498
5	1	-10	228	232
5	1	-9	304	301
5	1	-8	1433	1451
5	1	-7	1643	1661
5	1	-6	366	386
5	1	-5	1538	1526
5	1	-4	971	958
5	1	-3	517	524
5	1	-2	506	513
5	1	-1	946	976
5	1	0	356	327
5	1	1	1956	1980
5	1	2	403	398
5	1	3	1284	1313
5	1	4	193	212
5	1	5	531	529
5	1	6	632	656
5	1	7	889	903
5	1	8	136	139
5	1	9	519	529
5	1	10	348	360
5	1	11	165	154
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5	3	-10	246	251
5	3	-9	1330	1338
5	3	-8	423	424
5	3	-7	785	789
5	3	-6	307	307
5	3	-5	1234	1234
5	3	-4	172	151
5	3	-3	2818	2694
5	3	-2	741	730
5	3	-1	812	794
5	3	0	125	120
5	3	1	454	406
5	3	2	504	510
5	3	3	801	787
5	3	4	339	339
5	3	5	1087	1114
5	3	6	288	270
5	3	7	184	196
5	3	8	353	350
5	3	9	567	568
5	3	10	59	37
5	3	11	955	953
5	5	-10	327	329
5	5	-9	345	356
5	5	-8	1066	1064
5	5	-7	612	608
5	5	-6	780	781
5	5	-5	616	612
5	5	-4	595	589
5	5	-3	799	791
5	5	-2	478	461
5	5	-1	543	542
5	5	0	249	239
5	5	1	482	492
5	5	2	259	257
5	5	3	1183	1194
5	5	4	193	193
5	5	5	442	441
5	5	6	483	485
5	5	7	166	175
5	5	8	209	207
5	5	9	574	569
5	5	10	354	346
5	7	-9	149	155
5	7	-8	618	624
5	7	-7	1352	1351
5	7	-6	253	243
5	7	-5	153	149
5	7	-4	196	200
5	7	-3	273	259
5	7	-2	300	305
5	7	-1	897	893
5	7	0	304	295
5	7	1	598	587
5	7	2	228	223
5	7	3	284	278
5	7	5	173	164
5	7	6	158	163
5	7	7	678	681
5	7	8	76	92
5	9	-8	733	743
5	9	-7	332	336
5	9	-6	425	426
5	9	-5	557	552
5	9	-4	118	123
5	9	-3	516	504
5	9	-2	667	676
5	9	-1	41	26
5	9	0	69	39
5	9	1	367	381
5	9	2	238	236
5	9	3	32	34
5	9	4	137	149
5	9	5	283	284
6	0	-12	868	864
6	0	-8	46	47
6	0	-6	406	416
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14	2	-11	570	572
14	2	-10	513	517
14	2	-9	130	126
14	2	-8	221	214
14	2	-7	103	101
14	2	-6	218	211
14	2	-5	467	470
14	2	-4	118	118
14	2	-3	569	563
14	2	-2	180	190
14	2	-1	400	400
14	2	0	254	246
14	2	1	371	379
14	2	2	145	141
14	2	3	816	823
14	2	4	179	185
14	4	-14	232	222
14	4	-13	218	220
14	4	-12	234	236
14	4	-11	80	91
14	4	-10	633	633
14	4	-9	583	591
14	4	-8	475	482
14	4	-7	85	74
14	4	-6	255	241
14	4	-5	27	16
14	4	-4	110	98
14	4	-3	292	300
14	4	-2	689	685
14	4	-1	296	310
14	4	0	115	103
14	4	1	479	478
14	4	2	560	564
14	4	3	178	173
14	4	4	441	433
14	6	-12	447	449
14	6	-11	113	122
14	6	-10	352	351
14	6	-9	344	349
14	6	-8	296	292
14	6	-7	535	553
14	6	-6	258	258
14	6	-5	76	49
14	6	-4	195	198
14	6	-3	33	22
14	6	-2	59	40
14	6	-1	555	564
14	6	0	177	160
14	6	1	363	376
14	6	2	453	459
14	[illegible]	[illegible]	[illegible]	[illegible]
15	1	-6	270	271
15	1	-5	816	817
15	1	-4	579	573
15	1	-3	93	95
15	1	-2	1001	1000
15	1	-1	734	744
15	1	0	39	35
15	1	1	673	684
15	1	2	442	436
15	1	3	196	193
15	1	4	160	136
15	3	-15	239	239
15	3	-14	255	247
15	3	-13	155	141
15	3	-12	72	58
15	3	-11	206	207
15	3	-10	48	52
15	3	-9	974	993
15	3	-8	360	351
15	3	-7	126	82
15	3	-6	64	9
15	3	-5	155	133
15	3	-4	66	58
15	3	-3	1298	1288
15	3	-2	276	286
15	3	-1	146	140
15	3	0	61	47
15	3	1	218	216
15	3	2	84	69
15	[illegible]	[illegible]	[illegible]	[illegible]
15	5	-1	388	393
15	5	1	378	374
15	5	2	549	561
15	7	-10	98	89
15	7	-9	295	305
15	7	-8	111	109
15	7	-7	479	478
15	7	-6	206	212
15	7	-5	616	620
15	7	-4	74	68
15	7	-3	341	344
15	7	-2	461	474
16	0	-14	254	258
16	0	-12	676	704
16	0	-10	1007	1003
16	0	-8	246	248
16	0	-6	541	539
16	0	-4	397	401
16	0	-2	730	740
16	0	0	202	81
16	0	2	341	337
16	2	-15	788	785
16	2	-14	729	718
16	2	-13	358	360
16	2	-12	534	529
16	2	-11	263	245
16	2	-10	134	137
16	2	-9	399	396
16	2	-8	613	614
16	2	-7	128	126
16	4	-11	242	233
16	4	-10	68	47
16	4	-9	158	156
16	4	-8	669	664
16	4	-7	306	299
16	4	-6	479	486
16	4	-5	71	49
16	4	-4	362	359
16	4	-3	35	26
16	4	-2	175	172
16	4	-1	82	73
16	4	0	635	641
16	4	1	134	126
16	4	2	233	233
16	6	-11	58	39
16	6	-10	686	687
16	6	-9	108	95
16	6	-8	70	30
16	6	-7	263	255
16	6	-6	361	348
16	6	-5	117	112
16	6	-4	247	240
16	6	-3	76	38
16	6	-2	270	272
17	1	-15	147	138
17	1	-14	148	147
17	1	-13	313	308
17	1	-12	372	367
17	1	-11	307	306
17	1	-10	251	252
17	3	-13	166	161
17	3	-12	275	281
17	3	-11	252	251
17	3	-10	90	85
17	3	-9	436	434
17	3	-8	66	45
17	3	-7	808	827
17	3	-6	497	499
17	3	-5	116	70
17	3	-4	66	49
17	3	-3	163	163
17	3	-2	102	64
17	3	-1	619	617
17	3	0	428	436
17	3	1	285	290
17	5	-12	236	223
17	5	-10	219	220
17	5	-9	139	116
17	5	-8	852	853
17	5	-7	92	80
17	5	-6	442	451
17	5	-5	126	129
17	5	-4	200	204
17	5	-3	164	151
17	5	-2	899	909
17	5	-1	294	268
18	0	-14	786	786
18	0	-12	432	436
18	0	-11	47	0
18	0	-10	727	740
14	8	-6	289	299
14	8	-5	353	359
14	8	-4	86	57
14	8	-3	553	565
15	1	-15	78	94
15	1	-14	326	323
15	1	-13	552	558
15	1	-12	34	41
15	1	-11	469	473
15	1	-10	348	351
15	1	-9	183	177
15	1	-8	595	598
15	1	-7	891	883
18	2	-6	550	548
18	2	-5	176	179
18	2	-4	513	514
18	2	-3	167	129
18	2	-2	463	473
18	2	-1	237	242
18	2	0	398	394
18	4	-12	1079	1084
18	4	-11	131	127
18	4	-10	369	371
18	4	-9	118	109
18	4	-8	122	98
18	4	-7	238	251
18	4	-6	593	592
18	4	-5	96	71
18	4	-4	549	546
18	4	-3	56	54
15	3	4	97	74
15	5	-13	98	89
15	5	-12	106	99
15	5	-11	302	311
15	5	-10	742	751
15	5	-9	248	244
15	5	-8	326	325
15	5	-7	277	266
15	5	-6	254	221
15	5	-5	540	528
15	5	-4	932	928
15	5	-3	258	255
15	5	-2	580	593
18	4	-2	412	412
18	4	-1	69	40
18	6	-8	639	635
18	6	-7	322	331
18	6	-6	286	285
19	1	-14	78	68
19	1	-13	483	470
19	1	-12	25	19
19	1	-11	503	510
19	1	-10	286	284
19	1	-8	82	75
19	1	-7	95	37
19	1	-6	537	531
19	1	-5	847	855
19	1	-4	729	736
19	1	-3	58	12
19	1	-2	132	129
16	2	-6	700	[illegible]
16	2	-5	54	65
16	2	-4	485	492
16	2	-3	54	20
16	2	-2	266	255
16	2	-1	575	579
16	2	0	510	510
16	2	1	205	200
16	2	2	413	416
16	2	3	429	440
16	4	-14	889	888
16	4	-13	201	203
16	4	-12	289	291
19	1	[illegible]	145	148
19	3	-13	142	111
19	3	-12	78	72
19	3	-11	52	62
19	3	-10	130	126
19	3	-9	562	575
19	3	-8	202	197
19	3	-7	622	609
19	3	-6	110	101
19	3	-5	471	475
19	3	-4	209	214
19	3	-3	444	456
19	3	-2	176	186
19	5	-9	89	79
19	5	-8	252	265
19	5	-7	213	212
19	5	-6	757	704
17	[illegible]	[illegible]	[illegible]	[illegible]
17	1	-8	565	557
17	1	-7	668	667
17	1	-6	585	588
17	1	-5	314	319
17	1	-4	72	74
17	1	-3	437	439
17	1	-2	466	468
17	1	-1	308	320
17	1	0	483	484
17	1	1	405	406
17	1	2	46	54
17	3	-14	115	112
19	5	-5	203	204
20	0	-12	739	748
20	0	-10	481	478
20	0	-8	902	904
20	0	-6	682	689
20	0	-4	86	94
20	0	-2	210	216
20	2	-11	589	593
20	2	-10	492	502
20	2	-9	614	608
20	2	-8	283	289
20	2	-7	378	379
20	2	-6	103	113
20	2	-5	469	468
20	2	-4	258	263
20	2	-3	34	10
20	4	-10	783	795
18	0	-8	908	925
18	0	-6	262	258
18	0	-4	701	713
18	0	-2	283	289
18	0	0	543	541
18	2	-14	243	248
18	2	-13	742	743
18	2	-12	714	707
18	2	-11	583	588
18	2	-10	426	430
18	2	-9	232	229
18	2	-8	287	279
18	2	-7	468	468
20	4	-9	173	123
20	4	-8	160	166
20	4	-7	155	155
20	4	-6	179	183
21	1	-11	536	536
21	1	-10	80	57
21	1	-9	580	588
21	1	-8	188	180
21	1	-7	215	214
21	1	-6	58	69
21	1	-5	292	288
21	1	-4	388	391
21	3	-9	126	124
21	3	-8	72	78
21	3	-7	[illegible]	49

Table 2. *Fractional atomic coordinates and anisotropic thermal parameters*

Numbers in parentheses are estimated standard deviations in the last significant figure.

	$10^4 x$	$10^4 y$	$10^4 z$	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn(1)	558·2 (2)	2666·0 (5)	9951·5 (4)	0·57 (1)	0·85 (1)	0·60 (1)	0·20 (1)	0·29 (1)	0·13 (1)
Mn(2)	3442·1 (3)	3957·0 (5)	6486·0 (4)	0·67 (1)	0·45 (1)	0·68 (1)	−0·05 (1)	0·37 (1)	0·02 (1)
P	1757·1 (4)	4058·2 (8)	8060·1 (6)	0·34 (2)	0·34 (2)	0·40 (2)	−0·03 (1)	0·14 (1)	−0·01 (1)
O(1)	3069 (1)	816 (2)	5828 (2)	0·86 (5)	0·56 (4)	0·59 (5)	−0·07 (4)	0·23 (4)	0·19 (4)
O(2)	2101 (1)	1441 (3)	1880 (2)	0·55 (5)	1·04 (5)	0·93 (6)	0·15 (4)	0·51 (4)	0·12 (4)
O(3)	4157 (1)	367 (2)	3582 (2)	0·67 (5)	0·72 (5)	0·46 (5)	−0·14 (4)	0·01 (4)	0·11 (4)
O(4)	3677 (1)	2825 (2)	1451 (2)	0·81 (5)	0·41 (4)	0·94 (6)	−0·09 (4)	0·55 (4)	0·01 (4)
F	140 (1)	970 (2)	3918 (2)	0·91 (5)	1·34 (5)	1·64 (6)	−0·03 (4)	0·79 (4)	−0·52 (4)

national Tables for X-ray Crystallography, 1968) were applied for a spherical crystal with $\mu R = 0·94$; the maximum absorption correction applied was 5·0% of $|F_o|$.

Determination and refinement of the structure

A straightforward analysis of the Patterson map revealed the positions of the three heavy atoms in the asymmetric unit. A least-squares refinement in the centric space group $C2/c$ and a difference Fourier synthesis were then calculated, using manganese atoms in the two positions which contributed most strongly to the Patterson map and a phosphorus atom in the other position. Of the five most intense image peaks in the difference Fourier map, four were within 1·6 Å of the phosphorus and were assigned to oxygen atoms. The fifth was assigned to a fluorine atom.

Three cycles of least-squares refinement (Busing, Martin & Levy, 1962*a*) of these positions, using a $1/\sigma^2$ weighting scheme, zerovalent scattering factors for Mn, P, F and O (Cromer & Mann, 1968), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0·044$ and a weighted residual $R_w = 0·072$. The anisotropic refinement, based on a data to parameter ratio of 21 to 1 with 74 independently varied parameters, yielded a final $R = 0·023$ and $R_w = 0·046$ for the observed data. Calculated and observed structure factors are listed in Table 1. In the final refinement, the maximum extinction correction (Zachariasen, 1968) was 42% of $|F_c|$ for the $60\bar{4}$ reflection.

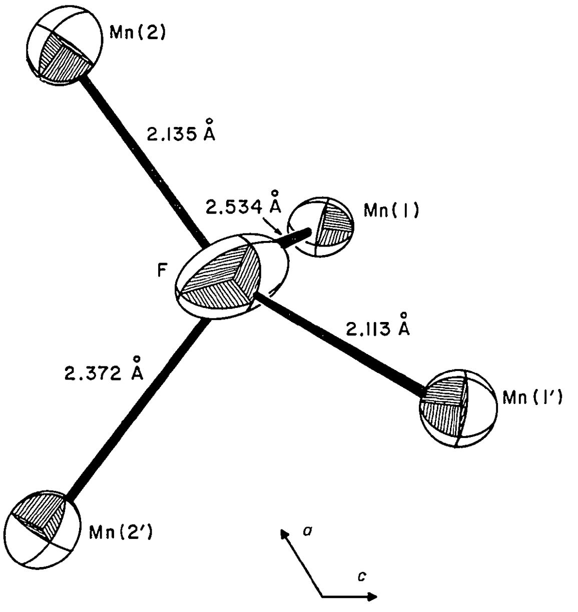

Fig. 1. The fluorine environment in $Mn_2(PO_4)F$ viewed down the *b* axis. 98% probability ellipsoids are shown.

Table 2 presents the final atomic coordinates and anisotropic thermal parameters.

Discussion

The manganese atoms lie at the centers of highly distorted octahedra. Mn(1) is coordinated by four oxygen atoms at an average distance of 2·158 Å and two fluorine atoms at 2·113 and 2·534 Å. Mn(2) is coordinated by four oxygen atoms at an average distance of 2·145 Å and two fluorine atoms at 2·135 and 2·372 Å. The fluorine atoms are *cis* in both cases. Table 3 lists angles and distances for the manganese polyhedra.

Table 3. *Bond distances, polyhedral edge lengths, and bond angles for manganese polyhedra*

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Interatomic distances

Mn(1)–O(2)	2·163 (2) Å	Mn(2)–O(1)	2·131 (2) Å
Mn(1)–O(3)	2·205 (2)	Mn(2)–O(1′)	2·202 (2)
Mn(1)–O(3′)	2·117 (2)	Mn(2)–O(2)	2·126 (2)
Mn(1)–O(4)	2·147 (2)	Mn(2)–O(4)	2·121 (2)
Mn(1)–F	2·113 (2)	Mn(2)–F	2·135 (2)
Mn(1)–F′	2·534 (2)	Mn(2)–F′	2·372 (2)

Mn(1) octahedron		Mn(2) octahedron	
O(2)–O(3)	2·968 (2) Å	O(1)–O(1′)	2·716 (3) Å
O(2)–O(4)	3·019 (3)	O(1)–O(2)	3·020 (3)
O(2)–F	2·713 (3)	O(1)–F	3·097 (2)
O(2)–F′	3·234 (3)	O(1)–F′	3·628 (3)
O(3)–O(3′)	2·657 (3)	O(1′)–O(2)	3·544 (3)
O(3)–O(4)	3·870 (3)	O(1′)–O(4)	3·030 (3)
O(3)–F	3·098 (2)	O(1′)–F	3·402 (3)
O(3′)–O(4)	3·331 (2)	O(2)–O(4)	3·351 (2)
O(3′)–F	3·250 (2)	O(2)–F′	2·713 (3)
O(3′)–F′	3·836 (2)	O(4)–F	2·727 (2)
O(4)–F′	2·727 (2)	O(4)–F′	3·059 (2)
F——F′	2·707 (4)	F——F′	2·695 (4)

Table 3 (*cont.*)

(ii) Angles

Mn(1) octahedron		Mn(2) octahedron	
O(2)–Mn(1)–O(3)	85·59 (6)°	O(1)–Mn(2)–O(1′)	77·60 (7)°
O(2)–Mn(1)–O(4)	88·93 (6)	O(1)–Mn(2)–O(2)	90·38 (7)
O(2)–Mn(1)–F	78·72 (7)	O(1)–Mn(2)–F	93·13 (6)
O(2)–Mn(1)–F′	86·64 (6)	O(1)–Mn(2)–F′	107·24 (6)
O(3)–Mn(1)–O(3′)	75·84 (7)	O(1′)–Mn(2)–O(2)	109·91 (7)
O(3)–Mn(1)–O(4)	125·57 (6)	O(1′)–Mn(2)–O(4)	88·95 (6)
O(3)–Mn(1)–F	91·66 (7)	O(1′)–Mn(2)–F	103·34 (7)
O(3′)–Mn(1)–O(4)	102·72 (7)	O(2)–Mn(2)–O(4)	104·17 (7)
O(3′)–Mn(1)–F	100·36 (7)	O(2)–Mn(2)–F′	73·95 (7)
O(3′)–Mn(1)–F′	110·77 (6)	O(4)–Mn(2)–F	79·69 (6)
O(4)–Mn(1)–F′	70·72 (5)	O(4)–Mn(2)–F′	88·62 (6)
F——Mn(1)–F′	70·60 (7)	F——Mn(2)–F′	73·23 (8)
O(2)–Mn(1)–O(3′)	161·39 (9)	O(1)–Mn(2)–O(4)	162·96 (7)
O(3)–Mn(1)–F′	161·73 (7)	O(1′)–Mn(2)–F′	174·03 (9)
O(4)–Mn(1)–F	139·91 (7)	O(2)–Mn(2)–F	146·53 (6)

The phosphate tetrahedra are very regular with an average bond length of 1·537 Å (+0·003, −0·001 Å) and an average angle of 109·5° (+1·3, −1·9°). Table 4 lists the tetrahedral bond angles and distances. The standard deviations for all bond lengths and angles were computed by the function and error program (*ORFFE*) of Busing, Martin & Levy (1962*b*).

Table 4. *Bond distances, polyhedral edge lengths, and bond angles for the phosphate tetrahedron*

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Interatomic distances

P–O(1)	1·537 (2) Å	O(1)–O(2)	2·520 (3) Å
P–O(2)	1·536 (2)	O(1)–O(3)	2·529 (2)
P–O(3)	1·536 (2)	O(1)–O(4)	2·483 (3)
P–O(4)	1·540 (2)	O(2)–O(3)	2·511 (2)
		O(2)–O(4)	2·526 (2)
		O(3)–O(4)	2·494 (2)

(ii) Angles

O(1)–P–O(2)	110·1 (1)°
O(1)–P–O(3)	110·8 (1)
O(1)–P–O(4)	107·6 (1)
O(2)–P–O(3)	109·6 (1)
O(2)–P–O(4)	110·4 (1)
O(3)–P–O(4)	108·3 (1)

Mn$_2$(PO$_4$)F is isostructural with the mineral triplite, (Mn, Fe)$_2$(PO$_4$)F (Waldrop, 1969), except that there is no disorder in the fluorine site as in triplite (*vide infra*). The Mn(2) octahedra are linked by edge sharing to form zigzag chains which run perpendicular to the *b* axis; the Mn(1) octahedra are linked by edge sharing to form chains which run parallel to the *b* axis; the Mn(1) and Mn(2) chains are connected by edge sharing (see Waldrop, 1969). The phosphate tetrahedra share only corners with other polyhedra.

It is possible to transform the atomic coordinates reported for triplite to coordinates referred to the conventional *C*-centered cell by using the following equations:

$$x_C = x_I - 0{\cdot}25$$
$$y_C = y_I + 0{\cdot}25$$
$$z_C = x_I - z_I - 0{\cdot}50$$

The subscripts *C* and *I* refer to the *C*-centered and *I*-centered unit cells of the equivalent space groups *C*2/*c* and *I*2/*a* respectively.

A comparison of atomic coordinates for triplite and Mn$_2$(PO$_4$)F show the atomic positions to be virtually identical except in the case of fluorine. The fluorine in Mn$_2$(PO$_4$)F occupies a position between the half-occupied fluorine sites in triplite; this position is designated by Waldrop as F(av). Although the fluorine in Mn$_2$(PO$_4$)F is anisotropic in the direction of the splitting in triplite (the root-mean-square displacement in this direction is approximately twice that of the shortest direction), the corresponding isotropic thermal parameter ($B = 1{\cdot}07$ Å^2) is far less than the isotropic thermal parameter for a fluorine at the F(av) site in triplite (4·2 Å^2). This fact and the very low *R* for the Mn$_2$(PO$_4$)F structure as described indicate that there is only one fluorine position present in this structure. The fluorine environment is shown in Fig. 1, which is a view of the thermal ellipsoids (98 %) down the *b* axis. The pertinent angles and distances are given in Table 5.

Table 5. *Bond distances and angles for the fluorine environment*

Numbers in parentheses are estimated standard deviations in the last significant figure.

(i) Interatomic distances

F–Mn(1)	2·534 (2) Å
F–Mn(1′)	2·113 (2)
F–Mn(2)	2·135 (2)
F–Mn(2′)	2·372 (2)

(ii) Angles

Mn(1)–F–Mn(1′)	109·40 (7)°
Mn(1)–F–Mn(2)	93·70 (6)
Mn(1)–F–Mn(2′)	110·18 (6)
Mn(1′)–F–Mn(2)	140·26 (7)
Mn(1′)–F–Mn(2′)	95·34 (6)
Mn(2)–F–Mn(2′)	106·72 (8)

The relationship among the structures of Mn$_2$(PO$_4$)F triplite, triploidite, and wagnerite (Coda, Giuseppetti & Tadini, 1967) is interesting. The space groups and compositions of these materials are given in Table 6. As pointed out by Waldrop (1970) and Engel (1970), the structures in the two space groups differ only in the positions of the fluorine (or hydroxyl group). For triploidite and wagnerite the fluorine position of triplite has completely split so that F (or OH) occupies one site in the lower part of the doubled cell and the other site in the upper part, giving rise to five- and six-coordinated metals and lower symmetry.

Table 6. *Space groups and compositions of the related structures*

	Composition		Space group
	Cations	Anion	
$Mn_2(PO_4)F$	Mn_2	F	$C2/c$
Triplite	$Mn_{.95}Fe_{.25}Mg_{.7}Ca_{.1}$	F	$C2/c$
Triploidite	$Mn_{1.5}Fe_{.5}$	OH	$P2_1/c$
Wagnerite	Mg_2	F	$P2_1/c$

The driving force for this situation in wagnerite is probably the smaller size of the Mg^{2+} cation relative to Mn^{2+} in the $Mn_2(PO_4)F$. In triploidite a contribution to the effect by the large amount of Fe^{2+} present (slightly smaller in ionic radius than Mn^{2+}) must be ruled out, since the iron-rich triplite, zwieselite, $(Fe,Mn)_2PO_4F$ falls into the space group $C2/c$ and seems to be isotypic with triplite. Therefore the effect must be due to the dipolar anion OH^-. Waldrop (1970) postulates that the hydroxyl group moves into the nearest face of the distorted tetrahedron, reducing the repulsion between the hydrogen, which is probably out of the plane, and the far manganese.

It is possible that the site splitting in triplite is caused by the presence of different sizes of metal cations. It seems that the predominant metals manganese and iron cause the basic structure to be the same as the end-member $Mn_2(PO_4)F$, but there are large amounts of the smaller Mg^{2+} and a significant amount of the larger Ca^{2+} (see Table 5). Different arrangements of the different sized metal cations about the fluorine site may lead the fluorine to prefer slightly different positions. Mössbauer effect measurements on triplite (Kostiner, 1972) indicate a high degree of disorder about the metal sites.

Engel (1970) has reported that $Cd_2(PO_4)F$ has cell constants similar to $Mn_2(PO_4)F$ and crystallizes in the space group $C2/c$. They are most probably isotypic, but some minor differences might be expected, since Cd^{2+} is larger than Mn^{2+}. It would be very interesting to see if the fluorine position in this compound is single (as expected) and, further, if the unusually long metal–fluorine distances for one of the two fluorines in each of the octahedra are shortened.

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