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Refinement of the Structure of $LiMnPO_4$

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The least-squares technique applied to three-dimensional X-ray diffraction data has been used to refine the structure of $LiMnPO_4$. The crystal belongs to space group D_{2h}^{16}–*Pmnb*; the unit cell with

$$a = 6\cdot10 \pm 0\cdot02,\ b = 10\cdot46 \pm 0\cdot03,\ c = 4\cdot744 \pm 0\cdot010\ \text{Å}$$

contains four formula units. The structure is closely related to that of olivine (Mg_2SiO_4). It consists of discrete PO_4 tetrahedral complexes and highly distorted oxygen octahedra about the Li^+ and Mn^{2+} ions. The average P–O distance is 1·54 Å with no significant differences among the three non-equivalent P–O distances. The PO_4 tetrahedron is not regular, however, there being two significantly different sets of O–O distances or O–P–O angles.

For this structure, neglect of off-diagonal terms of the normal equations matrix of the least-squares calculation does not significantly affect the results. Furthermore the least-squares calculation with use of only the [001], [010], and [100] zonal data and neglect of the off-diagonal terms of the normal equations matrix gives results differing in only a minor way from those obtained by use of three-dimensional data and inclusion of the off-diagonal terms of the normal equations matrix.

Introduction

The observations of second-nearest-neighbor nuclear magnetic resonance shifts in iron group phosphates have recently been reported by Mays (1957). Crystals of $LiMnPO_4$ become antiferromagnetic at 34·8 °K. (Mays, 1959). A mineral specimen had a somewhat higher Néel temperature: approximately 42 °K. (Bozorth & Kramer, 1959). In the antiferromagnetic state the size of the P^{31} shift indicates that the magnetization of the Mn^{2+} is being felt by the P atom which is a second-nearest-neighbor (Mays, 1957).

Mays made his original measurements on mineral specimens of lithiophilite, which always, apparently, contain some Fe^{2+} ion. Nielsen synthesized some pure $LiMnPO_4$ crystals by the method of Zambonini & Malossi (1931). These crystals are isostructural with the mineral. Mays' subsequent measurements and those described in this paper were made on specimens of the synthetic $LiMnPO_4$.

Certain of the nuclear magnetic resonance observations are very sensitive to atomic positions. Thus the atomic parameters of heterosite, $(Mn_x^{3+}Fe_{1-x}^{3+})PO_4$ (Björling & Westgren (1938)) as suggested by Byström (1943) for lithiophilite were not of adequate accuracy. The refinement of the $LiMnPO_4$ structure was undertaken mainly for the purpose of aiding in an ultimate understanding of the magnetic interactions in this crystal.

The mineral triphylite, which is $LiFePO_4$ containing varying amounts of Mn^{2+} ion, is also isostructural with $LiMnPO_4$. An X-ray structural investigation was made on a triphylite specimen by Destenay (1950). Some of the distances found by Destenay in triphylite are not in accord with analogous distances found in the present study.

Experimental

Powder photographs of samples from the specimens synthesized by Nielsen indicated that the $LiMnPO_4$ was isostructural with the lithiophilite mineral. Using the lithiophilite cell dimensions (Gossner & Strunz, 1932),* crystals were aligned by means of a single crystal spectrometer and (100) and (001) plates were cut. These were polished to thicknesses of 0·10 and 0·12 mm. respectively. The plates were very nearly square of about 2 mm. on the side.

The Buerger precession camera was used to obtain the intensity data. With Mo $K\alpha$ radiation the 0th, 1st and 2nd layers about [100] and 0th and 1st layers about [001] were accessible. The largest values observed for h, k, l were 8, 14, 6 respectively. The total number of independent observable reflections is 329. Of these 61 were too weak to be observed.

The symmetry of the X-ray diffraction effects is D_{2h}–*mmm*. Reflections $hk0$ are present only for k even, and $h0l$ only for $h+l$ even. Thus the probable space groups are D_{2h}^{16}–*Pmnb* or C_{2v}^{9}–$P2_1nb$. It will be shown subsequently that the data are compatible with *Pmnb*, which may therefore be taken as the most probable space group. From the Buerger precession camera photographs, the cell dimensions of the synthetic $LiMnPO_4$ are

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* These are $a = 6\cdot05$, $b = 10\cdot37$, $c = 4\cdot72$ Å. The a and c dimensions were close enough to those of the synthetic so that no ambiguity occurred. Adjustments to the correct angles were, of course, necessary.

$a = 6·10 \pm 0·02,\quad b = 10·46 \pm 0·03,\quad c = 4·744 \pm 0·010$ Å .

With four formula units per cell, the X-ray density is 3·44 g.cm.$^{-3}$*

The photographed plate specimens were both considerably larger than the impinging X-ray beam, thus yielding data which were quite uniform in intensity (Donnay & Donnay, 1954). This was not quite the case for the very weak intensities.

Intensities were measured with a Leeds–Northrup photodensitometer. A simple modification was made, however, which permitted efficient measurement of even the weakest intensities. When the long thin slit is used as a viewing aperture, a very noisy background is obtained. This occurs because the grain size of the X-ray film (Eastman Kodak old Type *K* and new No Screen) emulsion is large: because the small slit sees only a small number of grains at any instant, it necessarily sees a nonrandom distribution which results in noise.

This noise is greatly reduced by substituting for the slit a circular hole of diameter smaller than the length of the originally used slit. The original light source is a sharply focused image of a single straight wire filament. In order to illuminate the entire area of the hole, the diameter of which is about one hundred times the thickness of the focused filament image, the filament is simply moved back to cause the blurred filament image to be wider than the diameter of the hole. In this way an area at least ten times larger than the former slit area is used, with proportionally less variation of density due to the larger number of grains under observation. Experiments show that the two methods give closely the same results, but that the new method makes determination of the background much easier and cuts in half the time needed to measure a film. Previously each spot was scanned, and a visually integrated peak height was used as the density of the spot. Now, with the absence of noise, the viewing hole can be moved into the center of the spot, and the peak density read at once. Scanning is needed only for the background, where, even though much reduced, there is still some residual noise.

Usually exposures of the layers were taken as follows: 8, 4, 2, 1, ½ hours. In a few cases, X-ray tube current and both voltage and current were decreased in order to obtain measures of the strongest intensities.

After obtaining the intensities, the relative $|F_{hkl}|^2$ were obtained by applying the Lorentz-polarization corrections as obtained from Waser (1951, 1952) and Grenville-Wells & Abrahams (1952) charts.† Because, with the above described method of photography the absorption correction is constant for each layer (Donnay & Donnay, 1954), no absorption correction was needed and the $|F^2_{hkl}|$ were put on the same scale by the method of cross-comparison of values common to more than one layer.

Refinement of the structure

The parameters given by Björling & Westgren (1938) for heterosite and by Destenay for triphylite are listed in Table 1. Some re-estimates were made (Table 1) and *hk*0 and 0*kl* structure amplitudes calculated.* The comparison with observed structure amplitudes indicated the correctness of the structure. Signs were applied to the observed amplitudes, and the (100) and (001) projections of relative electron density were calculated.† These gave convincing evidence that the general features of the structure were correct but also that some significant changes in oxygen parameters were indicated. Also because of overlap, the parameters of the oxygens in the 4*c* positions could not be accurately determined.

Table 1. *Initial atomic parameters of* $LiMnPO_4$ *compared with those of Björling & Westgren for heterosite and of Destenay for triphylite*

		Parameters				
Atom	Position	*x*	*y*	*z*	*B* (Å^2)	Reference
Li	4*a*	0	0	0		B&W
		0	0	0		D
		0	0	0	1·5	Initial
Mn	4*c*	0·250	0·278	−0·028		B&W
Fe		0·250	0·282	−0·023		D
Mn		0·250	0·278	−0·028	0·5	Initial
P	4*c*	0·250	0·097	0·417		B&W
		0·250	0·095	0·418		D
		0·250	0·097	0·417	0·8	Initial
O	4*c*	0·250	0·056	−0·250		B&W
		0·250	0·107	−0·268		D
		0·250	0·056	−0·268	1·2	Initial
O	4*c*	0·250	0·444	0·250		B&W
		0·250	0·460	0·208		D
		0·250	0·444	0·232	1·2	Initial
O	8*d*	0·028	0·167	0·194		B&W
		0·043	0·165	0·288		D
		0·046	0·167	0·268	1·2	Initial

Initially an IBM 704 least-squares program devised by Busing & Levy (1959) was used. The weighting used was simply in accord with the multiplicity except for those amplitudes of reflections too weak to be observed. These were put into the calculation as half the threshold value and given extremely low weights. As indicated (Table 1), isotropic temperature factors were used, and in the initial calculation these were held constant. These calculations also permitted us to make extinction corrections as described elsewhere (Geller & Booth, 1959). The reflections for which these corrections were made and the values before and after correction are listed in Table 2. Including these cor-

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* The range of densities for triphylites measured by Destenay (1950) is 3·42–3·56 g.cm.$^{-3}$.

† These charts are supplied by Nies.

* The IBM 704 programs used in these calculations were devised by Dr R. G. Treuting.

† The atomic scattering factors used were as follows: Li^+, James & Brindley, 1931; Mn^{2+}, Thomas & Umeda, 1957; P, Viervoll & Øgrim, 1949; and O, Berghuis *et al.*, 1955.

rections, the R value was 12% for the 329 amplitudes included in the calculation and multiplicity ignored (that is, each amplitude is counted exactly once). The parameters obtained in this calculation are listed in Table 3, 1. It should be mentioned that when this calculation was stopped, some significant changes had still taken place in oxygen coordinates, e.g., $-0{\cdot}005$ in z_{O_1}, but it appeared sensible at this point to allow the temperature factors of all but the Li^+ atoms to vary. After one cycle the temperature factor of the P became negative and the calculation stopped.* For interest these parameters are also listed in Table 3, 2. This time the largest change was again that of the z_{O_1} which was $+0{\cdot}006$.

Table 2. *Extinction corrected amplitudes (after first refinements)*

hkl	$\|F_o\|$	$\|F'_o\|$	*w*	*hkl*	$\|F_o\|$	$\|F'_o\|$	*w*
020	42·7	47·5	0·20	071	62·7	68·8	0·50
120	37·5	40·2	0·50	131	76·3	90·0	0·80
140	59·5	66·1	0·45	151	33·2	35·8	1·00
160	81·8	95·0	0·40	271	56·3	64·7	0·80
200	86·2	136·0	0·10	331	55·4	71·2	0·70
260	77·0	86·8	0·45	012	49·1	53·0	0·50
340	69·8	77·0	0·50	022	53·6	58·8	0·50
360	65·6	75·4	0·40	042	61·2	68·1	0·45
400	95·0	118·6	0·15	142	59·6	65·4	1·00
011	48·2	56·4	0·40	202	35·2	49·7	0·10
031	55·4	64·4	0·40	212	22·2	23·3	1·00
041	50·6	55·9	0·50	222	68·0	95·7	0·20
051	23·4	24·0	0·50				

$|F'_o|$ = corrected $|F_o|$. w = weight in L.S. calculation.

We then decided to use Sayre's NYXR2 least-squares refinement program on the data. Except for the amplitudes corrected for extinction (Table 2) the weighting scheme was the same. For the extinction corrected amplitudes, the weighting was taken in accord with the percentage correction (Table 2) and superposed on the multiplicity weight.†

In the first calculation with Sayre's program, the starting parameters were those in Table 3, 1, and only 100, 010, and 001 pinacoidal data were used. After five iterations, the R value decreased to 9% for these data. Again this R value includes all unobserved data and ignores multiplicity. The resulting parameters are listed in Table 3, 3.

The next calculation was made with Sayre's program including all the data. The temperature factor for Li^+ was held constant at 1·0 Å². The results of this calculation are listed in Table 3, 4. The R value calculated as before is 9%.

The final calculation was made with the Busing–Levy program with a modification introduced by us. This is already part of the Sayre program and is concerned with the temperature factor refinement. The

Table 3. *Parameters obtained from the various least-squares calculations*

Atom	Parameters	1	2	3	4	5	$\|\Delta\|$ 4 & 5	Largest $\|\Delta\| \times 10^4$*	σ_4	σ_5	Last recorded applied changes 4	Last recorded applied changes 5
Li	*B*	1·5	1·5	1·0	1·0	1·0						
Mn	*y*	0·2818	0·2817	0·2817	0·2817	0·2817	0·0000	1	0·0002	0·0001	0·00001	0·00000
	z	−0·0285	−0·0283	−0·0282	−0·0282	−0·0281	0·0001	4	0·0004	0·0004	0·00002	0·00000
	B	0·5	0·17	0·31	0·32	0·22	0·10		0·02	0·04	0·01	−0·01
P	*y*	0·0921	0·0924	0·0921	0·0924	0·0923	0·0001	3	0·0003	0·0003	0·00000	0·00000
	z	0·4090	0·4082	0·4056	0·4081	0·4081	0·0000	34	0·0007	0·0007	0·00001	0·00000
	B	0·8	−0·02	0·17	0·17	0·04	0·13		0·04	0·05	−0·02	−0·02
O_1	*y*	0·0986	0·0966	0·0972	0·0964	0·0968	0·0004	28	0·0009	0·0009	0·00004	0·00000
	z	−0·2703	−0·2658	−0·2629	−0·2658	−0·2664	0·0006	74	0·0022	0·0021	0·00016	0·00000
	B	1·2	0·59	0·47	0·70	0·51	0·19		0·14	0·14	0·00	−0·03
O_2	*y*	0·4571	0·4558	0·4562	0·4563	0·4561	0·0002	13	0·0008	0·0008	−0·00002	0·00000
	z	0·2078	0·2069	0·2083	0·2072	0·2073	0·0001	14	0·0021	0·0020	0·00005	0·00000
	B	1·2	0·48	0·28	0·63	0·50	0·13		0·14	0·14	−0·02	−0·04
O_3	*x*	0·0493	0·0510	0·0497	0·0493	0·0492	0·0001	18	0·0012	0·0012	0·00006	0·00001
	y	0·1610	0·1610	0·1602	0·1609	0·1609	0·0000	7	0·0006	0·0006	0·00001	0·00001
	z	0·2778	0·2795	0·2788	0·2778	0·2781	0·0003	17	0·0014	0·0014	0·00008	0·00001
	B	1·2	0·51	0·56	0·60	0·47	0·13		0·10	0·10	−0·02	−0·02

1 B&L program, *B*'s held constant.
2 B&L program, only B_{Li} held constant.
3 S program, only 0*kl*, *h*0*l*, and *hk*0 data.
4 S program, all data.
5 B&L program, modified.
* Coordinates only.

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* This stop is built into the Busing & Levy program we used.

† When the correction was greater than 10%, $w = \frac{1}{2}p(2|F_o| - |F'_o|)/|F_o|$ to the nearest 0·05, where p is the multiplicity.

Table 4. *Calculated and observed amplitudes*

$\ell=0$

h	k	Fo	Fc
0	2	48.8	-44.4
0	4	5.5	- .2
0	6	39.0	-36.4
0	8	10.0	-12.0
0	10	33.2	29.5
0	12	<10.9	1.2
0	14	18.5	17.1
1	2	41.3	-36.0
1	4	68.0	-69.4
1	6	97.7	95.9
1	8	7.9	- 9.0
1	10	61.3	60.1
1	12	47.9	-44.4
1	14	22.5	-19.7
2	0	140.	-128
2	2	17.8	20.6
2	4	33.6	-33.3
2	6	89.2	91.3
2	8	11.7	5.9
2	10	46.4	-49.4
2	12	24.6	21.8
2	14	16.3	-16.3
3	2	14.9	-12.4
3	4	79.2	84.1
3	6	77.5	-73.9
3	8	15.2	-13.6
3	10	45.9	-44.0
3	12	50.7	46.9
4	0	122.	133
4	2	25.1	-26.0
4	4	13.5	10.7
4	6	45.3	-45.5
4	8	< 9.0	- 6.7
4	10	36.6	32.7
4	12	6.6	- 6.7
5	2	32.0	-30.5
5	4	41.7	-35.6
5	6	61.5	63.6
5	8	13.8	-15.3
5	10	54.2	51.9
5	12	29.1	-33.0
6	0	78.7	-89.5
6	2	26.4	21.7
6	4	7.9	- 5.2
6	6	42.9	39.2
6	8	8.8	6.5
6	10	30.1	-27.2
7	2	< 9.0	0.5
7	4	50.0	48.0
7	6	44.9	-44.4
7	8	12.6	- 6.9
8	0	58.1	55.5
8	2	9.3	-10.3
8	4	15.4	12.6

$\ell=1$

h	k	Fo	Fc
0	1	58.0	-58.4
0	2	40.7	-36.9
0	3	66.2	61.4
0	4	57.5	58.0
0	5	24.7	-25.1
0	6	12.5	9.6
0	7	70.7	72.6
0	8	< 9.0	1.4
0	9	46.7	-50.0
0	10	12.0	11.9
0	11	15.8	12.9
0	12	<10.9	6.8
0	13	22.9	-22.7
0	14	24.8	-22.5
1	3	92.5	96.5
1	4	6.3	6.7
1	5	36.8	-34.9
1	6	10.7	- 7.2
1	7	16.2	-14.4
1	8	13.7	10.4
1	9	14.8	-12.2
1	10	12.4	10.0
1	11	21.6	-21.2
1	12	10.1	- 8.1
1	13	46.3	46.3
1	14	15.2	8.6
2	2	34.9	-35.9
2	3	28.9	-32.3
2	4	< 3.9	1.4
2	5	25.9	25.5
2	6	< 6.6	1.9
2	7	66.5	-68.5
2	8	36.8	-38.0
2	9	53.3	56.0
2	10	< 8.6	7.0
2	11	9.7	-11.3
2	12	<10.1	3.3
2	13	21.6	19.7
2	14	<10.9	2.3
3	0	23.1	-20.9
3	1	50.0	53.3
3	2	35.9	37.5
3	3	73.2	-77.2
3	4	13.3	11.2
3	5	24.3	23.6
3	6	21.3	-20.8
3	7	17.3	16.2
3	8	< 9.7	- 4.2
3	9	14.9	12.4
3	10	<10.5	4.1
3	11	15.4	16.8
3	12	<11.5	- 4.5
3	13	41.4	-42.2
3	14	<11.1	- 7.9

$\ell=1$

h	k	Fo	Fc
4	1	33.4	-36.2
4	2	10.1	- 8.6
4	3	37.3	36.4
4	4	17.9	17.4
4	5	14.8	-15.4
4	6	< 8.8	3.4
4	7	52.3	57.7
4	8	8.9	14.3
4	9	40.3	-44.1
4	10	<10.9	3.8
4	11	12.6	10.7
4	12	<11.1	2.4
4	13	13.5	-19.1
5	0	27.2	-27.4
5	1	30.9	-30.9
5	2	11.6	-10.0
5	3	54.8	60.2
5	4	16.3	15.9
5	5	22.7	-22.8
5	6	12.6	-11.4
5	7	8.2	-10.2
5	8	8.5	9.1
5	9	8.9	- 9.4
5	10	8.9	12.8
5	11	19.7	-18.4
5	12	13.1	-13.4
6	1	31.7	30.4
6	2	7.6	8.0
6	3	23.1	-24.6
6	4	9.8	- 9.9
6	5	14.7	12.6
6	6	<10.5	- 2.3
6	7	42.2	-45.0
6	8	13.5	-12.9
6	9	38.9	38.0
6	10	<11.1	- 2.7
6	11	8.9	- 8.8
7	0	<10.5	- 5.2
7	1	26.1	26.2
7	2	19.0	18.6
7	3	44.7	-46.1
7	4	<10.5	1.6
7	5	14.2	13.6
7	6	16.3	-13.3
7	7	12.6	10.8
7	8	<11.1	- 2.5
7	9	9.4	8.6
8	1	20.2	-20.9
8	2	<11.1	4.0
8	3	19.3	18.0
8	4	<11.1	- 2.3
8	5	<11.1	- 8.6
8	6	<11.1	- 0.8

$\ell=2$

h	k	Fo	Fc
0	0	11.1	14.9
0	1	54.5	52.3
0	2	60.5	-58.5
0	3	< 8.4	3.4
0	4	70.0	62.3
0	5	< 8.6	1.5
0	6	39.9	-40.7
0	7	24.3	-22.5
0	8	12.1	7.8
0	9	24.7	-24.2
0	10	39.5	35.7
0	11	<10.9	3.7
0	12	24.1	-25.1
0	13	12.1	10.4
0	14	35.3	31.7
1	1	34.4	32.1
1	2	34.2	31.0
1	3	13.4	11.1
1	4	67.2	-62.3
1	5	42.4	-41.0
1	6	37.2	34.5
1	7	< 8.2	1.6
1	8	44.2	-43.4
1	9	9.5	- 9.4
1	10	34.1	32.1
1	11	29.1	26.9
1	12	23.0	-22.8
1	13	<10.5	- 1.7
1	14	10.7	12.5
2	0	51.1	-68.9
2	1	24.0	-27.8
2	2	98.4	83.8
2	3	< 5.6	- 2.4
2	4	15.7	-19.0
2	5	18.5	-17.6
2	6	8.2	3.9
2	7	31.0	30.8
2	8	< 9.4	3.2
2	9	24.8	26.5
2	10	14.2	-12.8
2	11	11.8	-12.0
2	12	9.7	6.3
2	13	<10.9	- 6.1
2	14	27.6	-29.9

$\ell=3$

0	1	24.3	18.7
0	2	37.7	-36.8
0	3	25.7	21.8
0	4	36.1	-34.4
0	5	38.4	-38.2
0	6	22.4	-19.7
0	7	43.7	40.3
0	8	57.5	64.3
0	9	39.4	-40.7
0	10	15.0	-14.4
0	11	29.5	26.2
0	12	10.7	- 9.6
0	13	10.3	-11.5
1	0	< 7.8	2.1
1	1	56.7	-56.8
1	2	41.8	-39.5
1	3	39.4	37.9
1	4	50.2	47.9
1	5	17.6	-14.5
1	6	33.4	30.5
1	7	19.5	16.9
1	8	< 9.4	- 4.2
1	9	15.6	15.2
1	10	29.2	-26.1
1	11	19.0	-15.9
1	12	28.4	-31.5
1	13	15.7	15.2
2	1	< 7.8	1.5
2	2	61.6	69.8
2	3	34.2	-37.4
2	4	< 7.8	4.2
2	5	44.9	45.8
2	6	12.5	11.8
2	7	22.4	-24.5
2	8	36.2	-37.3
2	9	28.7	27.7
2	10	<10.1	0.6
2	11	22.0	-23.0
2	12	<10.9	1.8
2	13	22.0	19.8

$\ell=4$

0	0	54.6	50.3
0	1	39.5	36.1
0	2	36.9	-39.0
0	3	<10.9	4.0
0	4	28.8	24.7
0	5	38.6	38.5
0	9	20.3	-20.4
0	10	< 9.7	- 6.0
0	11	22.3	22.0
1	1	< 9.2	4.0
1	2	24.8	21.1
1	3	14.0	10.5
1	4	< 9.5	- 9.1
1	5	52.3	-48.0
1	6	34.1	31.5
1	7	14.3	12.9
1	8	38.5	-37.8
1	9	<10.3	- 5.5
1	10	23.2	20.3
1	11	41.4	37.5
1	12	11.7	-11.0
2	0	13.8	-16.2
2	1	52.7	-53.2
2	2	31.0	28.6
2	3	< 9.9	- 6.2
2	4	35.0	-36.0
2	5	18.9	-18.3
2	6	14.2	11.9
2	7	12.2	9.4
2	8	<10.1	- 0.9
2	9	17.7	15.0
2	10	<10.9	- 5.8
2	11	<10.9	- 8.5
2	12	32.7	31.5

$\ell=5$

0	1	<10.9	- 0.9
0	2	19.4	-19.1
0	3	20.8	18.1
0	4	30.5	29.2
0	5	39.8	-42.0
0	6	22.7	-22.9
0	7	8.9	5.9
0	8	21.3	19.0
0	9	< 7.6	0.8
1	0	30.2	26.4
1	1	35.2	-34.5
1	2	30.3	-28.2
1	3	<10.3	- 4.2
1	4	22.8	20.5
1	5	29.6	-26.9
1	6	13.8	-11.8
1	7	17.3	13.7
1	8	<10.5	1.9
1	9	18.3	16.3
1	10	15.3	12.3
2	1	<10.9	- 8.9
2	2	<10.9	3.4
2	3	< 9.7	3.7
2	4	16.1	-15.5
2	5	34.7	35.4
2	6	25.5	25.3
2	7	15.7	-16.6
2	8	31.1	-31.3
2	9	16.1	14.3
2	10	21.6	22.1

$\ell=6$

0	0	17.2	-13.8
0	1	29.6	30.3
0	2	21.0	-21.3
0	3	37.8	-36.6
0	4	33.1	31.5
0	5	< 7.6	- 1.7
0	6	14.2	10.4
1	1	<10.7	- 6.6
1	2	33.8	30.4
1	3	19.4	18.7
1	4	<10.5	4.6
1	5	14.4	-11.6
1	6	<10.5	5.7
2	0	<11.7	3.6
2	1	14.5	-13.6
2	2	26.4	26.0
2	3	36.9	37.3
2	4	20.5	-23.6
2	5	14.9	-14.7
2	6	20.0	-18.6

Table 5. *Interatomic distances and standard deviations*

	Atom pair (no.)	Distance	σ		Atom pair (no.)	Distance	σ
PO_4 tetrahedron	P–O$_1$	1·545 Å	0·010 Å	MnO_6 octahedron	Mn–O$_1$	2·240 Å	0·010 Å
	P–O$_2$	1·526	0·010		Mn–O$_2$	2·139	0·010
	P–O$_3$ (2)	1·547	0·007		Mn–O$_3$ (2)	2·283	0·007
	O$_1$–O$_2$	2·558	0·014		Mn–O$_3$ (2)	2·130	0·007
	O$_1$–O$_3$ (2)	2·573	0·011		O$_1$–O$_3$ (2)	2·936	0·011
	O$_2$–O$_3$ (2)	2·469	0·012		O$_1$–O$_3$ (2)	3·135	0·011
	O$_3$–O$_3$	2·450	0·018		O$_2$–O$_3$ (2)	2·996	0·012
					O$_2$–O$_3$ (2)	3·339	0·012
					O$_3$–O$_3$ (2)	3·076	0·018
					O$_3$–O$_3$	3·650	0·018
					O$_3$–O$_3$	2·450	0·018
				Averages			
LiO_6 octahedron	Li–O$_1$ (2)	2·224 Å	0·010 Å	PO_4 tetrahedron	P–O	1·54 Å	
	Li–O$_2$ (2)	2·113	0·009		O–O	2·52	
	Li–O$_3$ (2)	2·160	0·007	MnO_6 octahedron	Mn–O	2·20	
	O$_1$–O$_2$ (2)	3·034	0·014		O–O	3·09	
	O$_1$–O$_2$ (2)	3·102	0·014	LiO_6 octahedron	Li–O	2·17	
	O$_1$–O$_3$ (2)	2·936	0·011		O–O	2·99	
	O$_1$–O$_3$ (2)	3·244	0·011				
	O$_2$–O$_3$ (2)	2·469	0·012				
	O$_2$–O$_3$ (2)	3·133	0·012				

computed least-squares correction on the temperature factor is recorded but only half of it is applied to the old value. However, no correction is ever allowed to be greater than 0·5 in absolute value. Furthermore (and this is not in Sayre's program), the temperature factor is never permitted to go negative. If the correction indicates that it should, it is automatically set equal to +0·01. This calculation also gave an R value of 9% calculated as before. The parameters are listed in Table 3, 5. The differences in geometric coordinates (Table 3) obtained by the last two calculations are not significant as can be seen from the listed (Table 3) standard deviations. The largest difference is equivalent to 0·004 Å in y_{O_1}. Thus the off-diagonal terms (used in the Busing–Levy but not in the Sayre program) in the least-squares matrix are not important in the adjustment of atomic coordinates for this structure.

As to the temperature factors, even though the crystals are hard, these appear to be low. For the oxygens, the differences obtained are within one standard deviation of each other, for Mn^{2+} and P, two standard deviations. It is noteworthy that the B's for the three nonequivalent oxygens as calculated by either of the last two methods are not significantly different. In both methods all the changes in parameters in the final iteration were very much less than a standard deviation (Table 3).

Actually, it is clear that convergence was simple for this structure and the data obtained. The largest difference for *all five* calculations is equivalent to only 0·035 Å in z_{O_1}, and we know that the first three were only approximate. Especially noteworthy is the fact that the $0kl$, $hk0$, and $h0l$ data alone gave results differing almost insignificantly from those obtained with the three-dimensional data. The largest difference in atomic coordinate between the results of this calculation and the final one is equivalent to 0·014 Å in z_{O_1}.

The calculated and observed amplitudes obtained from the Busing–Levy program are given in Table 4. (These are on an absolute scale.) The discrepancy factor calculated with the inclusion of the multiplicity but excluding amplitudes for reflections to weak to be observed is 7·6%. Although all calculated amplitudes for the unobserved reflections are less than the threshold values, if these are compared with half the threshold values and included, the discrepancy factor then is 9·0%. The higher value results in this case from the situation that the calculated values of amplitudes corresponding to the weak reflections are almost all very low.

Interatomic distances

The estimated standard deviations of the positions of the atoms are (from the Busing–Levy program calculation): 0·001, 0·003, 0·010, 0·009 and 0·007 Å for Mn^{2+}, P, O_1, O_2 and O_3 respectively. The standard deviations for Li^+–O distances will be those of the oxygen atoms. For Mn^{2+}–O, P–O and O–O distances within a given mirror plane $\sigma(d_{12}) = [\sigma^2(x_1) + \sigma^2(x_2)]^{\frac{1}{2}}$. For equivalent oxygen atoms $\sigma(d_{11'}) = 2\sigma(x_1)$. This result is obtained by considering that the variance of two dependent variables is given by:

$$\sigma^2(X+Y) = \sigma^2(X) + \sigma^2(Y) + 2\varrho\sigma(X)\sigma(Y)\ ,$$

where ϱ is the correlation coefficient, which apparently in this case is +1. For a distance between an atom constrained to lie in the mirror plane and an oxygen in $8d$; the variance is less than the sum of the estimated variances of position. The contribution from the atom lying in the plane will be a component properly depending on the angle the distance makes with the plane. However, because calculations of such angles are tedious (especially as compared with what is to be gained from them) we shall take the conservative estimate that $\sigma^2(d_{12}) = \sigma^2(x_1) + \sigma^2(x_2)$. The interatomic distances and standard deviations are given in Table 5.

To facilitate later discussion the O–P–O angles in the PO_4 tetrahedron are given in Table 6.

Table 6. O–P–O *angles in* PO_4 *tetrahedron*

Atoms involved	Angle	σ (′)
O_1–P–O_2	112° 48′	40
O_1–P–O_3	112° 37′	32
O_2–P–O_3	106° 53′	34
O_3–P–O_3	104° 44′	41

Discussion

As is now known (e.g., see Byström, 1943) the structure of $LiMnPO_4$ (Fig. 1) is closely related to that of olivine, essentially Mg_2SiO_4 (Bragg & Brown, 1926; Belov *et al.*, 1951). There are apparently independent tetrahedral $(PO_4)^{3+}$ complexes in the structure. The Li^+ and Mn^{2+} ions are ordered and each is surrounded by a highly distorted octahedron of oxygens. Two of the twelve edges of an octahedron about a Li^+ ion are shared with two different PO_4 tetrahedra. The octahedron of oxygens about an Mn^{2+} ion shares only one edge of a PO_4 tetrahedron.

The PO_4 tetrahedron is a tightly bonded complex and there is indication that the P–O bonds are largely covalent.* The differences in P–O distances are not significant (Cruickshank, 1949), the average being 1·54 Å. There are two groups of O–O distances (Table 5) in the PO_4 tetrahedron which are reliably different. This is also true, of course, of the O–P–O angles. The two average O–O distances in the tetrahedron are 2·46 and 2·57 Å and the overall average O–O distance in the tetrahedron is 2·52 Å. The two average O–P–O angles are 112·7 and 105·8°. These dimensions are in striking agreement with those (Table 7) obtained in several recently determined structures containing discrete phosphate tetrahedra.

The mineral triphylite, $Li(Fe_xMn_{1-x})PO_4$, in which the Fe^{2+} ion content predominates, is also isostructural with $LiMnPO_4$. An X-ray structural investigation was made on a triphylite specimen by Destenay (1950). It has turned out that the parameters reported for triphylite are much closer to those of $LiMnPO_4$ reported

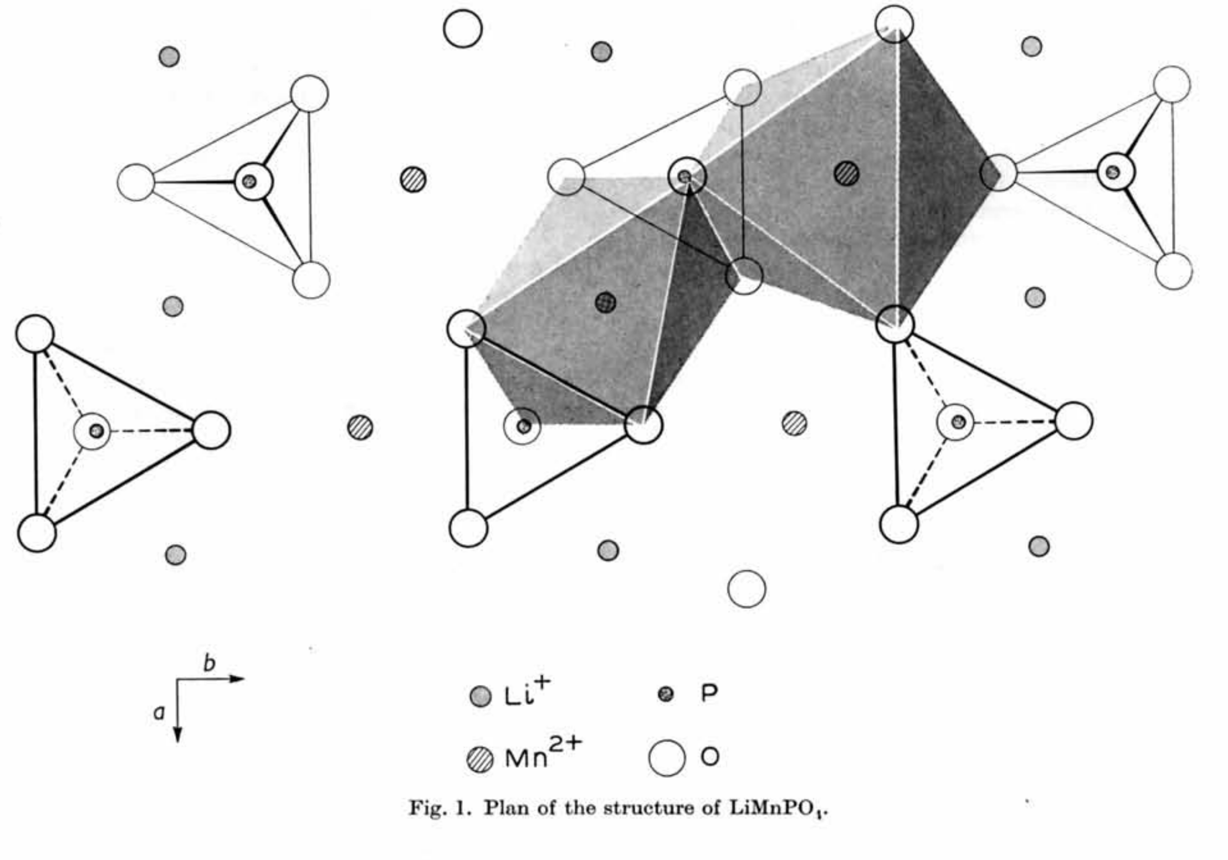

Fig. 1. Plan of the structure of $LiMnPO_4$.

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* With regard to obtaining some idea about the bond type from Fourier synthesis, it appears that this would not prove too fruitful. The differences between the scattering factors for P^{5+} and P^0 occur only for $\sin \theta/\lambda \leq 0{\cdot}2$. Several of the intensities in this region are apt to be off because of extinction effects and because of the error in the estimate of the Lorentz-polarization factors. Furthermore, the P atom which is so tightly bonded to four oxygens may have a scattering factor which differs substantially from those calculated for either P^{5+} or P^0. Thus a difference synthesis may be misleading.

Table 7. *Average* PO_4 *tetrahedron dimensions in various recently determined structures*

Crystal	*d*(P–O)	*d*(O–O)	O–P–O*	O–P–O†	Ref.
$LiMnPO_4$	1·54 Å	2·52 Å	106°	113°	
$NH_4H_2PO_4$	1·54	2·52	109	111	1
KH_2PO_4	1·54	2·52	109	111	2
$CaHPO_4.2\,H_2O$	1·53	2·51	110		3
$CaHPO_4$	1·54	2·51	106 105	115 111	4

1. Tenzer, Frazer & Pepinsky (1958).
2. Bacon & Pease (1955).
3. Beevers (1958).
4. MacLennan & Beevers (1955).

* Average of three smaller angles.

† Average of three larger angles.

herein than those reported by Björling & Westgren for heterosite. However, the Li^+–O and PO_4 group interatomic distances found in triphylite by Destenay are not in accord with those found in $LiMnPO_4$, unless it is assumed that Destenay's limits of error are wide enough to allow overlapping with those of the present determination. In any case, the purpose for the refinement of the $LiMnPO_4$ structure appears to be adequately served. Highly accurate positions of the atoms must be known for calculations of internal magnetic field to be compared with those observed by nuclear magnetic resonance measurements.*

Note added in proof—In the writing of this paper we inadvertently omitted mentioning that we had applied the correction for dispersion (Dauben and Templeton (1955)) to the atomic scattering factors of the Mn^{2+} ion.

It will be noticed (Table 3) that the temperature factors obtained by means of Sayre's program are uniformly lower than those obtained by the Busing-Levy program. In a private communication to us from Dr Busing, he surmised correctly that the Sayre program refined a scale factor applied directly to the F_o; the Busing-Levy program does the inverse. This was independently discovered by Dr Sayre who mentioned this during the discussion following the oral presentation of this paper at the Washington Meeting of the American Crystallographic Association (January 24-27, 1960). All agree with Dr Busing that the scale factor should be applied to the F_c.

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* To be discussed in a paper on this work by J. M. Mays.