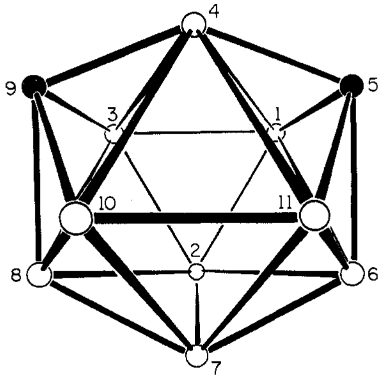

Figure 3.—Molecular structure of $B_9C_2H_{11}$. The hydrogen atoms have been omitted.

C atoms at positions 5 and 9 (Figure 3). However, the chemical and nuclear magnetic resonance evidence did not rule out the possibility[18] that the C atoms of $B_9C_2H_{11}$ are at positions 6 and 8. If the removal of B atoms from $B_9C_2H_{11}$ occurs without rearrangement of the boron framework, then the structure found here for $B_7C_2H_{11}(CH_3)_2$ and hence inferred for $B_7C_2H_{13}$ supports positions 5 and 9 for C atoms in $B_9C_2H_{11}$ (Figure 3). After completion of this study, we have received results of an X-ray diffraction study of $B_9C_2H_{11}$ itself by Tsai and Streib,[19] who have proved that the structure shown in Figure 3 for $B_9C_2H_{11}$ is correct.

Acknowledgment.—We wish to thank the Office of Naval Research, the National Institutes of Health, and the Advanced Research Projects Agency for support of this study.

[18] Refer to footnote 3 of ref 12.

[19] C-c. Tsai and W. E. Streib, private communication, Aug 1966; see also *J. Am. Chem. Soc.*, **88**, 4513 (1966).

CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C.

The Crystal Structure of Twinned Low-Temperature Lithium Phosphate

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It is shown that lithium phosphate (Li_3PO_4) prepared by precipitation from an aqueous solution differs from the form that has been described in the literature. When heated it transforms irreversibly at 502 ± 5° to the familiar form. The low-temperature form crystallizes in space group $Pmn2_1$ with $a_0 = 6.1150 \pm 0.0010$ A, $b_0 = 5.2394 \pm 0.0011$ A, and $c_0 = 4.8554 \pm 0.0010$ A; $Z = 2$. It exhibits merohedral twinning with the twin plane normal to the z axis. The multiplicity of the predominant image is 0.75. All atoms are tetrahedrally coordinated. The final reliability index is 0.054.

Introduction

The assumption of Zambonini and Laves[2] that lithium phosphate (Li_3PO_4) crystallizes with a structure similar to that of olivine (Mg_2SiO_4) was generally accepted prior to 1960. In that year, Zemann[3] determined the structure for a single crystal obtained by recrystallization of a precipitate of lithium phosphate from molten lithium chloride. He showed conclusively that the lithium atoms are in tetrahedral coordination, thus ruling out the olivine-type structure.

In 1963 Swanson, *et al.*,[4,5] reported the existence of a second form of lithium phosphate prepared by precipitation from an aqueous solution. From the powder diffraction data it appeared to have the same space group and nearly the same lattice parameters as the phase described by Zemann. Speculation arose as to the relationship of the two forms and an investigation of the crystal structure was undertaken.

Experimental Section

Sample Preparation.—Samples of low-temperature lithium phosphate (Li_3PO_4) were prepared by neutralizing a slurry of lithium carbonate by slowly adding phosphoric acid. The mixture was boiled for a few minutes and the precipitate was washed with water and centrifuged. Spectrographic analysis indicated no impurities greater than 0.01%. A few crystals, large enough for X-ray studies, were grown by slow evaporation over a period of 2 months from a 1-l. water solution of the very slightly soluble lithium phosphate. The one selected for intensity measurements was tabular with nicely formed prism faces, probably {110}. The over-all dimensions were 0.07, 0.16, and 0.05 mm in the *a*, *b*, and *c* directions, respectively.

A study by the differential thermal analysis technique using 12°/min and 1°/min heating rates showed that the new form of lithium phosphate transforms at 502 ± 5° to the form described by Zemann (see Figure 1). The transformation does not appear to be reversible. There is no weight change associated with it, so both phases are assumed to have the same composition. A second transition was observed at 1183 ± 5° by differential thermal anaysis and confirmed by high-temperature powder diffraction. It has not been shown that the phase that occurs above 1183° has the Li_3PO_4 composition, and it will not be considered here. The discussion will be limited to the low-temperature form as prepared by Swanson, *et al.*, by precipita-

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[1] National Research Council–National Bureau of Standards Postdoctoral Research Associate, 1964–1966.

[2] F. Zambonini and F. Laves, *Z. Krist.*, **83**, 26 (1932).

[3] J. Zemann, *Acta Cryst.*, **13**, 863 (1960).

[4] H. E. Swanson, M. C. Morris, E. H. Evans, and L. Ulmer, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards Monograph 25, Section 3, U. S. Government Printing Office, Washington, D. C., 1964, p 38.

[5] H. E. Swanson, M. C. Morris, and E. H. Evans, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards, Monograph 25, Section 4, U. S. Government Printing Office, Washington, D. C., 1966, p 21.

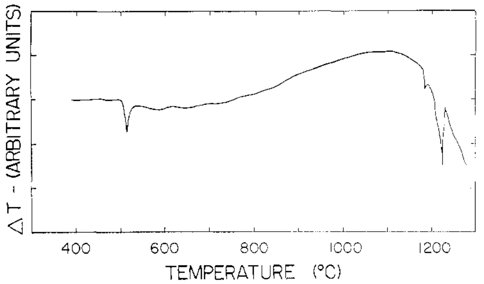

Figure 1.—Differential thermal analysis curve for lithium phosphate prepared by precipitation from aqueous solution. The three endothermic heat effects shown are: the transition at 502° from the low-temperature form described here to the form described by Zemann, the transition at 1183° to a crystalline form that has not yet been studied, and melting at 1215°. The samples were heated at 12°/min in air.

tion from aqueous solution, and its relation to the high-temperature form described by Zemann.

Space Group and Unit-Cell Dimensions.—Precession films indicate that there are two formula units per cell and that the space group for low-temperature lithium phosphate ($h0l$ absent for $h + l$ odd) is either the acentric space group Pmn2$_1$ (P2$_1$nm) or the centric space group Pmnm.

Analysis of the three-dimensional Patterson map clearly defined the approximate positions and orientation of the two PO_4^{3-} tetrahedra in the unit cell. These positions are consistent only with the acentric space group. Further, the space group was determined to be Pmn2$_1$ rather than the alternative setting P2$_1$nm as the positioning of the phosphate tetrahedra required the space group mirror to be normal to the a axis.

The cell parameters were determined with a single crystal diffractometer using copper radiation, (λ_{α_1} 1.54051 A, λ_{α_2} 1.54178 A). Twelve reflections having 2θ angles greater than 140° and peak intensities of 200 counts/sec or greater were measured. The peak width at half-height was unusually large (approximately 0.8° in 2θ) and the α_1,α_2 doublet could not be resolved at angles below about 150° in 2θ. The mosaic spread, determined by scanning reflections such as the 200, 020, and 002 in the low 2θ region, was no greater than 0.2–0.3°, so the poor resolution in the high 2θ region is believed to be associated with lattice strain which results in a variation in the interplanar spacing of a given set of planes from point to point throughout the crystal. A variation of 0.1% in d could prevent resolution of α_1 and α_2 at 150° in 2θ, but would increase the width of a peak at 35° in 2θ by only about 0.05°.

Because of the limitation on resolution imposed by lattice strain the use of a 1° take-off angle was not justified, and measurements were made at a take-off angle of 4° (which corresponds to a beam divergence of 0.4°) in order to take advantage of the increase in intensity. In each case, the 2θ angle was measured after centering the reflection in the counter window. Whenever the α_1,α_2 doublet could not be resolved the Bragg angle was corrected by subtracting one-third of the α_1,α_2 separation. The largest correction was 0.3° in 2θ. An alignment check was made immediately after these measurements and a correction of 0.06° was added to compensate for a zero shift on the 2θ scale. Finally, the lattice constants were calculated using a least-squares refinement program incorporated in the X-ray 63 system.[6] The cell parameters reported by Swanson, *et al.*,[5] were taken as the initial values. The best fit was obtained by assuming that α_1 and α_2 are resolved for lines above 152° in 2θ and are not resolved for those below 145° (no lines in the range 145–152° were used). In all, five cases were calculated in order to treat two doubtful reflections as both α_1 (resolved) and α_1,α_2 (unresolved) and to fit the remaining reflections without these two. The cell parameters were quite similar in all cases and showed significant differences from those reported by Swanson, *et al.*,[5] for the low-temperature form. They are, however, distinctly different from the cell parameters of the high-temperature form (Table I). The differences are believed to result from the small particle size of the powder diffraction sample, which limits the accumulation of strain and the consequent variation in interplanar spacings. Consistent with this interpretation is the observation that Swanson, *et al.*,[5] did not encounter the loss of resolution at high 2θ angles that characterized the single crystal work.

Table I

Cell Dimensions for High- and Low-Temperature Lithium Phosphate

High	Low	
Swanson, *et al.*[a] (powder)	Swanson, *et al.*[b] (power)	This work (single crystal)
6.1147 ± 0.0005	6.1155 ± 0.0004	6.1150 ± 0.0010
10.475 ± 0.001	5.2340 ± 0.0005	5.2394 ± 0.0011
4.9228 ± 0.0005	4.8452 ± 0.0005	4.8554 ± 0.0010

[a] H. E. Swanson, M. C. Morris, E. H. Evans, and L. Ulmer, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards Monograph 25, Section 3, U. S. Government Printing Office, Washington, D. C., 1964. [b] H. E. Swanson, M. C. Morris, and E. H. Evans, "Standard X-ray Diffraction Powder Patterns," National Bureau of Standards Monograph 25, Section 4, U. S. Government Printing Office, Washington, D. C., 1966.

Intensity Measurements.—A semiautomatic diffractometer was used in measuring the diffraction data for low-temperature lithium phosphate. The χ, ϕ, and 2θ angles, the Miller indices, and the scalar readings were automatically recorded on punched paper tape. Measurements were made with unfiltered radiation from a molybdenum tube operating at 45 kv, 22 ma, with full wave rectification. The detector was a scintillation counter used in conjunction with a pulse height analyzer set at $E = 2.80$ v and at $\Delta E = 1.40$ v. No attenuation filters were used. The maximum counting rate was 5640 counts/sec on the 002 reflection and counting losses did not exceed 1%. The crystal was mounted with the b^* axis along the ϕ axis of the diffractometer.

The stationary-crystal, stationary-counter method was used in measuring intensities. The number of counts obtained by this method was converted to the number that would have been obtained by scanning through the reflection to obtain the integrated intensity. The correction factors were determined empirically for this crystal.[7] A 4° take-off angle was used so that the angle subtended by the source was approximately 0.4°. The weighted average of the α_1–α_2 doublet was used as the wavelength (λ 0.710688 A) in calculating the settings for measuring the peak intensity. Measurements were restricted to the range below $2\theta = 60°$ so that separation of the α_1,α_2 doublet did not become a problem. Background measurements were made at $2\theta - (\Delta 2\theta/2)$ and at $2\theta + (\Delta 2\theta/2)$ where $\Delta 2\theta = 1.80° + 1.00° \times \tan\theta$ is the scan range recommended by Alexander and Smith.[8] The counting time was 10 sec for each peak and each background. The intensities were corrected for Lorentz and polarization factors. Since the μR based on the longest dimension was less than 0.1, no absorption correction was applied to the observed data.

Solution of the Crystal Structure

Analysis of the Patterson map and the $hk0$ projection electron density map, supplemented by knowledge of the structure of the high-temperature form of lithium phosphate,[3] led rapidly to a trial model for the low-temperature form. However, efforts to refine the trial model failed. A more detailed analysis of the Pat-

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(6) "Technical Report TR-64-6," University of Maryland Computer Science Center (1964).

(7) L. E. Alexander and G. S. Smith, *Acta Cryst.*, **15**, 983 (1962).

(8) L. E. Alexander and G. S. Smith, *ibid.*, **17**, 1195 (1964).

terson map indicated that certain vectors parallel to the w axis were inconsistent with the trial model. Analysis of a $(F_o - F_c)$ difference map revealed a few large peaks that suggested disorder. Several types of disordered models were next refined by the full-matrix least-squares technique. Each model was rejected, however, because the phosphate tetrahedra became seriously distorted.

Twinning was next suspected as the low-temperature form of lithium phosphate is a derivative structure.[9] Moreover, it is possible to have twinning by merohedry because the point group is 2/m 2/m 2/m for the high-temperature form and mm2 for the low-temperature form. This would require the twin plane to be normal to the c axis. Placing the twin mirror normal to the z axis accounts for the additional vectors parallel to the w direction of the Patterson map. Furthermore, the reciprocal lattice from the main image and the one from the mirror image superimpose and produce diffraction with no streaking.

Assuming that the structure is twinned and that the twin mirror is normal to the z axis, the x,y projection coordinates should be unaffected by the twinning. For this reason, a two-dimensional $hk0$ Patterson projection using $53|F|^2$ was calculated. The model obtained from this Patterson projection was refined by full-matrix least-squares to $R = 3.5\%$. The x,y coordinates of the atoms in the asymmetric unit were, within experimental error, the same as those proposed by Zemann for the high-temperature form. The electron density projection showed no evidence of anything unusual about the structure and was consistent with placing the twin plane normal to the z axis.

From the electron-density projection, it was evident that the apex of the phosphate tetrahedron points in a direction parallel to the z axis. Using reasonable bond angles and distances, it was possible to estimate the z parameter for each atom. Since the positioning of the initial z coordinate is arbitrary in the space group $Pmn2_1$, the z parameter for the phosphorus atom in the tetrahedron was assigned the value of zero. The z parameters for the oxygen atoms in the tetrahedron were calculated assuming that tetrahedral angles and distances were ideal and that the apical P–O bond was parallel to the z axis. The z parameters for each of the crystallographically independent lithium atoms were determined by adjusting z to give the most reasonable set of tetrahedral Li–O bond distances. The reliability index calculated on the basis of these atomic coordinates was 25%.

The calculation of electron-density and difference electron-density maps clearly indicated the complete mirror image of the structure in the three-dimensional model. The mirror was normal to the z axis and located at $z \cong 0.94$. The electron densities for atoms in the mirror image came to the appropriate relative heights. Structure factor calculations using both images of the structure gave $R = 8\%$. A series of electron-density and difference maps was calculated to adjust further the multiplicities of the two images. The values settled to approximately $^3/_4$ and $^1/_4$. At this point all the atoms in the unit cell were located, and isotropic full-matrix least-squares refinement could be used.

Least-Squares Refinement

The full-matrix least-squares program[6] was used to refine positional parameters, individual isotropic temperature factors for the predominant image, the z parameter for the mirror normal to the z axis, the multiplicity factor, and the over-all scale factor. The program minimizes the quantity $R' = \Sigma w(F_o - F_c)^2$. Unit weights were used. The scattering factors were those listed in the International Tables for X-ray Crystallography[10a] for oxygen (O^-), neutral phosphorus, and lithium (Li^+).

TABLE II

FINAL ATOMIC PARAMETERS FOR TWINNED LOW-TEMPERATURE LITHIUM PHOSPHATE[a]

	x/a	y/b	z/c	B
2 P	0	0.82430 (42)	0	0.034 (32)
4 O(1)	0.20777 (78)	0.68676 (84)	0.8961 (12)	0.556 (75)
2 O(2)	0	0.1052 (12)	0.9004 (18)	0.273 (97)
2 O(3)	$^1/_2$	0.1814 (15)	0.8172 (16)	0.47 (12)
4 Li(1)	0.2481 (20)	0.3277 (21)	0.9860 (41)	0.98 (18)
2 Li(2)	$^1/_2$	0.8428 (32)	0.9893 (56)	0.86 (24)
Twin mirror[b] (normal to z axis)			0.9370 (30)	

Multiplicity predominant image = 0.755 (16)

Scale on F_o = 0.4051 (58)

[a] The errors derived from full-matrix least-squares refinement are given in parentheses and refer to the last significant figures quoted. [b] Since the mirror is normal to the z axis, the x,y parameters for the atoms in the mirror image are the same as for the predominant image. The z parameters may be calculated from the position of the mirror given in this table.

TABLE III

FINAL STRUCTURE FACTORS FOR TWINNED LOW-TEMPERATURE LITHIUM PHOSPHATE[a]

0,0,L		
2	502	524
4	67	63
6	106	92
1,0,L		
1	279	305
3	189	188
5	18	13
2,0,L		
0	227	226
2	74	64
4	98	103
6	94	97
3,0,L		
1	68	77
3	110	115
5	52	48
4,0,L		
0	461	455
2	259	268
4	50	55
6	92	84
5,0,L		
1	231	228
3	146	156
5	18*	12
6,0,L		
0	220	206
2	116	118
4	37	38
7,0,L		
1	57	58
3	70	77
8,0,L		
0	176	167
2	97	101
0,1,L		
0	168	174
1	212	242
2	66	59
3	154	151
4	32	35
5	17	17
6	46	40
1,1,L		
0	290	301
1	109	113
2	92	93
3	77	76
4	78	81
5	15*	7
6	85	89
2,1,L		
0	376	367
1	114	124
2	203	202
3	136	165
4	28	32
5	98	108
6	40	38
3,1,L		
0	47	48
1	151	143
2	55	54
3	90	89
4	118	123
5	25	9
6	95	101
4,1,L		
0	131	121
1	93	93
2	66	65
3	87	94
4	16*	20
5	26	35
5,1,L		
0	222	217
1	44	41
2	116	119
3	47	43
4	36	34
5	9*	15
6,1,L		
0	134	134
1	105	106
2	86	86
3	100	102
4	29	22
7,1,L		
0	44	47
1	89	84
2	38	38
3	56	58
8,1,L		
0	99	93
1	30	35
2	63	61
0,2,L		
0	396	387
1	123	130
2	211	196
3	130	156
4	22	31
5	101	109
6	64	59
1,2,L		
0	63	68
1	74	72
2	40	40
3	75	79
4	101	105
5	12*	25
6	87	90
2,2,L		
0	7*	13
1	95	95
2	54	47
3	87	92
4	88	90
5	30	36
6	69	69
3,2,L		
0	179	167
1	63	59
2	74	72
3	64	71
4	58	58
5	44	48
6	69	73
4,2,L		
0	208	190
1	70	74
2	105	106
3	100	111
4	44	40
5	68	80
5,2,L		
0	29	22
1	103	98
2	50	47
3	73	74
4	100	100
5	16*	7
6,2,L		
0	84	82
1	43	41
2	32	40
3	53	64
4	46	40
7,2,L		
0	116	114
1	34	27
2	65	62
3	51	50
8,2,L		
0	68	65
1	80	76
0,3,L		
0	119	105
1	137	125
2	44	45
3	92	80
4	110	111
5	28	30
6	95	99
1,3,L		
0	157	144
1	80	88
2	93	87
3	99	108
4	16	18
5	49	43
6	20	11
2,3,L		
0	448	446
1	37	34
2	257	263
3	38	34
4	44	53
5	15*	7
6	89	86
3,3,L		
0	83	72
1	181	176
2	44	41
3	123	129
4	15*	6
5	19	12
4,3,L		
0	144	146
1	70	66
2	68	71
3	53	49
4	70	72
5	22	20
5,3,L		
0	106	105
1	45	48
2	75	74
3	80	82
4	18	24
6,3,L		
0	208	205
1	47	45
2	119	125
3	37	36
7,3,L		
0	39	38
1	129	132
2	23	23
0,4,L		
0	161	142
1	94	95
2	100	96
3	124	131
4	21*	24
5	79	79
1,4,L		
0	189	184
1	69	69
2	95	90
3	49	42
4	70	64
5	17*	5
2,4,L		
0	103	96
1	184	180
2	69	64
3	129	129
4	21*	13
5	20*	3
3,4,L		
0	257	255
1	58	59
2	152	150
3	38	37
4	30	23
5	16*	4
4,4,L		
0	110	106
1	119	117
2	80	74
3	105	111
4	17*	20
5,4,L		
0	84	94
1	62	54
2	48	48
3	28	34
4	79	76
6,4,L		
0	74	67
1	81	83
2	47	47
3	79	75
7,4,L		
0	176	182
1	42	43
0,5,L		
0	18	7
1	94	88
2	70	58
3	65	66
4	109	105
1,5,L		
0	111	102
1	38	38
2	57	55
3	71	69
4	34	38
2,5,L		
0	179	174
1	86	80
2	100	99
3	76	78
4	43	42
3,5,L		
0	69	67
1	72	71
2	36	36
3	64	66
4	54	50
4,5,L		
0	41	36
1	72	66
2	30	28
3	53	54
5,5,L		
0	102	100
1	54	46
2	65	59
3	70	70
6,5,L		
0	82	78
1	85	72
0,6,L		
0	214	203
1	20	18
2	131	125
3	29	33
1,6,L		
0	83	77
1	73	66
2	51	44
3	73	69
2,6,L		
0	59	62
1	82	75
2	46	38
3	64	59
3,6,L		
0	111	112
1	38	37
2	78	74
3	64	67
4,6,L		
0	158	150
1	32	29
2	94	91
0,7,L		
0	19*	39
1	140	143
2	23	24
1,7,L		
0	164	169
1	15*	10
2,7,L		
0	11	2
1	88	86

[a] The three columns are L, F_o, and F_c, respectively. $F(000) = 1120$. Reflections marked with an asterisk were unobservable and received no weight in the least-squares refinement.

Because of a high correlation between parameters, the structure was refined in three steps: first, the posi-

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(9) M. J. Buerger, "Crystal-Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, p 55.

(10) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962: (a) p 202; (b) p 271.

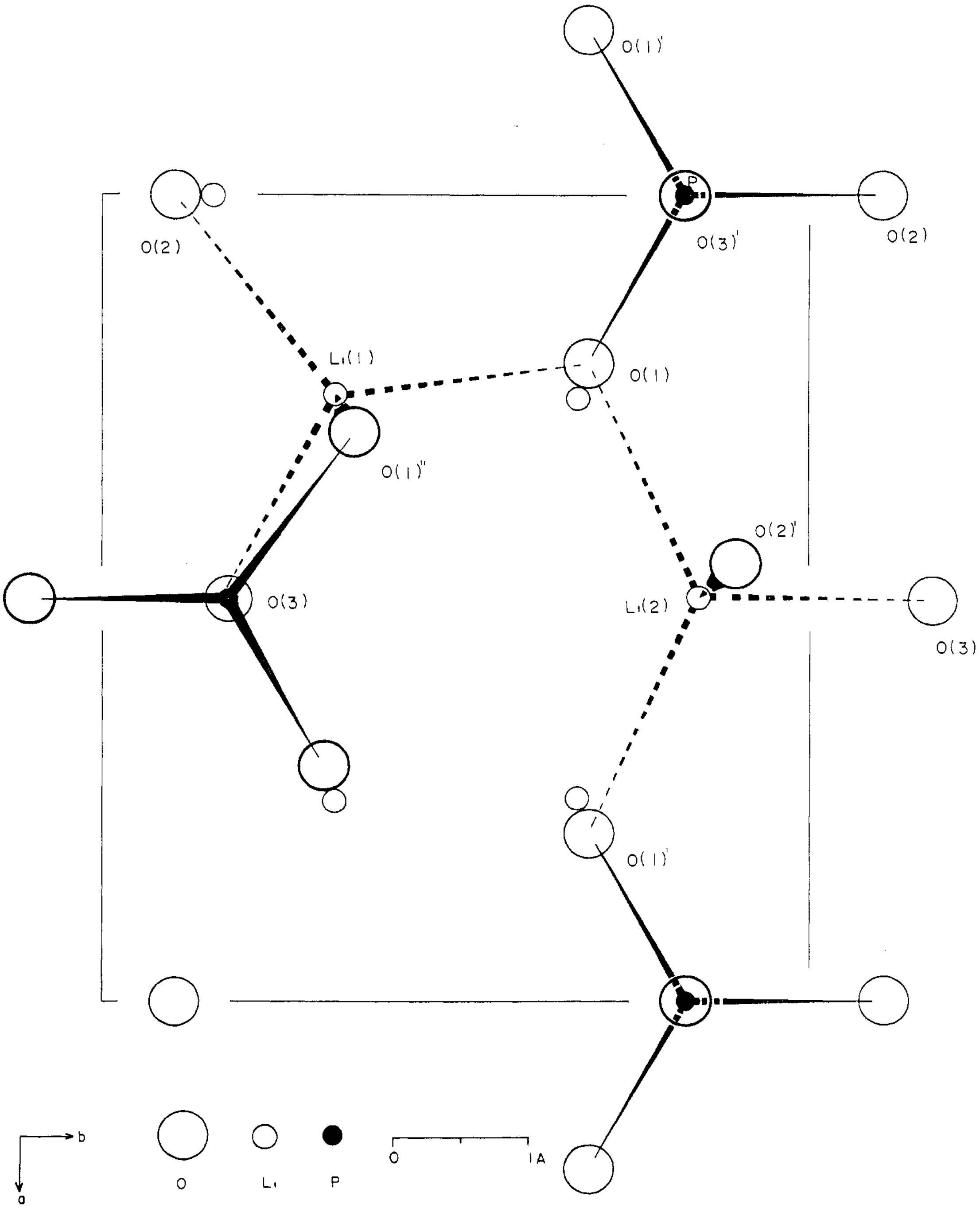

Figure 2.—*hk*0 projection of the final structure for twinned low-temperature lithium phosphate. Both images coincide in this projection

tional parameters and the isotropic temperature factors for the predominant image, second the multiplicity factor, and third the position of the mirror. This series of steps was repeated until no further significant parameter shifts occurred. Each final shift was less than 0.025 of this standard deviation.

The final reliability index, $R = \Sigma|\Delta F|/\Sigma|F_o|$, for 273 observed reflections is 5.4%. The final least-squares results are given in Table II for the atomic parameters of the six atoms in the asymmetric unit, for the position of the mirror, and for the multiplicities. The final observed and calculated structure factors are listed in Table III. A three-dimensional difference map based on the parameters reported in Table II showed no significant maxima or minima.

Discussion and Conclusion

If the high- and low-temperature forms of a crystal are related by a disordering transformation, invariably there is a basic structure for the high-temperature form and a derivative structure for the low-temperature form.[9] Low-temperature lithium phosphate is a derivative structure and represents an example of twinning by merohedry. The crystal used in this study is probably a twinned intergrowth on a submicroscopic scale. Thus the twinning would occur at the unit cell level

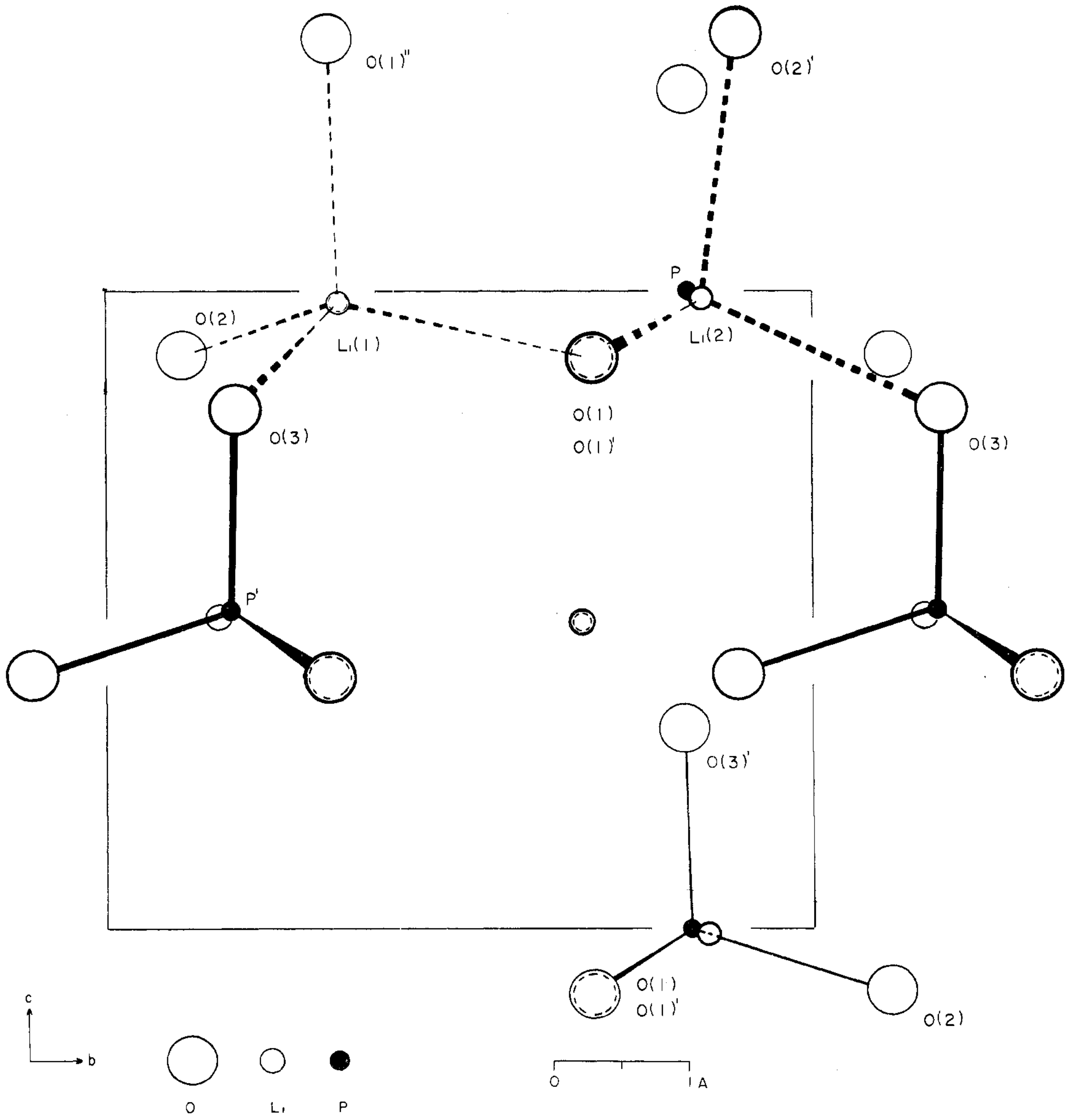

Figure 3.—0*kl* projection of the final structure for twinned low-temperature lithium phosphate. This shows one image only. The twin mirror is normal to the *c* axis at $z = 0.94$. The mirror image is left out for clarity.

and not between a large number of unit cells. In this case it is permissible to use coherent phase relations between the diffracted spectra of both twins just as is done in the case of a disordered structure.

In this type of twinning one would ordinarily expect a multiplicity ratio of 50:50 for the two images. The fact that the ratio refined by least squares to 75:25 in this instance should not be disturbing, however, because we are dealing with a disordered structure in which a general lack of uniqueness is common. The multiplicity ratio of 75:25 could be accounted for by assuming a model for low-temperature Li_3PO_4 in which part of the coherent domains are untwinned and part are 50:50 twinned. In addition a small amount of incoherent twinning may be present which would cause the multiplicity ratio to differ from 50:50. If a second sample of low-temperature Li_3PO_4 were prepared it would undoubtedly be twinned but with a still different multiplicity ratio.

The twin mirror as determined by least-squares refinement is normal to the z axis at $z = 0.937$. (In this space group ($Pmn2_1$), it is the relative set of z parameters that one determines. For this reason one could equally well assign the twin mirror a $z = 0$ and then add $(1.000 - 0.937)$ to the z parameter of each atom in the main image.) Figure 2 shows the projection down the c axis in which both images exactly coincide (the same projection for the high-temperature form is identical). Figure 3 shows the projection down the a axis for one image of the twin. Figure 4 compares the low-temperature form of lithium phosphate with the high-temperature form described by Zemann.[3] Table IV compares the final atomic coordinates of the two forms. Table V shows the final bond angles and distances, and their estimated standard deviations, for the low-temperature form of lithium phosphate.

In these structures the lithium atoms are in tetrahedral coordination. Both structures are tightly held together by corner sharing of the lithium and phosphate tetrahedra (see Figure 3). Also, the oxygen

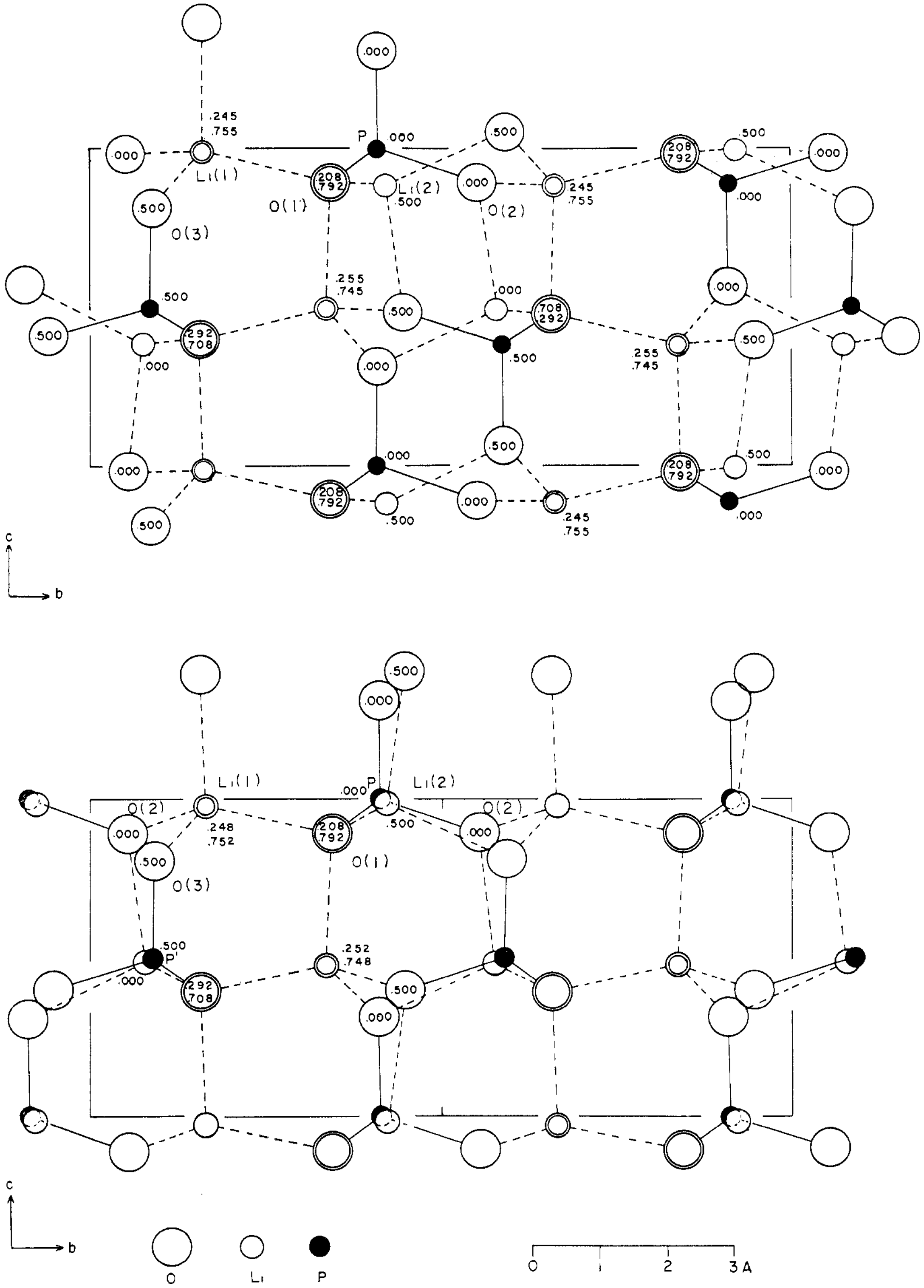

Figure 4.—Comparison of the 0*kl* projections for the high- and low-temperature forms of lithium phosphate. The 0*kl* projection for the high-temperature form of lithium phosphate is shown in the upper diagram. The coordinates indicated are derived from those reported by Zemann[3] by shifting the origin in the *ac* plane so that his atomic parameters can be compared with those of the low-temperature form of lithium phosphate. The 0*kl* projection for the low-temperature form of lithium phosphate is shown in the lower diagram. Two unit cells along *b* are shown. The twin mirror is normal to the *c* axis at $z = 0.94$. The twin mirror and the twin image are left out for clarity.

atoms are tetrahedrally coordinated by three lithium atoms and one phosphorus atom. This is consistent with the low values of the isotropic temperature parameters.

The average P–O bond distances in the orthophosphate group for the low-temperature and high-temperature forms of lithium phosphate are 1.546 ± 0.007 A and 1.555 ± 0.020 A, respectively. Thus, the average P–O bond distance in both forms of lithium phosphate is somewhat greater than the average orthophosphate

TABLE IV

COMPARISON OF THE FINAL ATOMIC PARAMETERS FOR THE HIGH- AND LOW-TEMPERATURE FORMS OF LITHIUM PHOSPHATE. THE VALUES FOR THE HIGH FORM ARE GIVEN IN PARENTHESES

Atom	x/a	y/b	z/c	B
P	0 (0)[a]	0.824 (0.822)	0 (O)	0.03 (0.5)
O(1)	0.792 (0.792)	0.687 (0.684)	0.896 (0.897)	0.55 (0.9)
O(2)	0 (0)	0.105 (0.104)	0.900 (0.987)	0.27 (0.9)
O(3)	$^1/_2$ ($^1/_2$)	0.181 (0.180)	0.817 (0.817)	0.47 (0.9)
Li(1)	0.248 (0.245)	0.328 (0.324)	0.986 (0.996)	0.98 (1.1)
Li(2)	$^1/_2$ ($^1/_2$)	0.843 (0.844)	0.989 (0.888)	0.86 (1.1)

[a] The parameters for the high form are derived from those reported by Zemann[3] by a translation of the origin. Only half the parameters can be compared because the cell is halved in the low-temperature form.

TABLE V

FINAL BOND DISTANCES AND BOND ANGLES FOR ONE IMAGE OF TWINNED LOW-TEMPERATURE LITHIUM PHOSPHATE[a]

Distances, A			Angles, deg	
Phosphate Tetrahedron				
P–O(1)	1.546 (5)	(2×)		
P–O(2)	1.550 (7)	(1×)		
P–O(3)′	1.542 (8)	(1×)		
O(1)–O(1)′	2.542 (7)	(1×)	O(1)–P–O(1)′ =	110.59 (28)
O(1)–O(2)	2.535 (7)	(2×)	O(1)–P–O(2) =	109.92 (24)
O(1)–O(3)′	2.507 (9)	(2×)	O(1)–P–O(3)′ =	108.52 (27)
O(2)–O(3)′	2.522 (11)	(1×)	O(2)–P–O(3)′ =	109.32 (44)
Coordination Polyhedra about Li(1)				
Li(1)–O(1)″	2.014 (21)			
Li(1)–O(1)	1.948 (13)			
Li(1)–O(2)	1.959 (13)			
Li(1)–O(3)	1.907 (15)			
O(1)–O(1)″	3.164 (8)		O(1)–Li(1)–O(1)″ =	105.99 (75)
O(1)–O(2)	3.303 (7)		O(1)–Li(1)–O(2) =	115.43 (72)
O(1)–O(3)	3.219 (8)		O(1)–Li(1)–O(3) =	113.22 (81)
O(1)″–O(2)	3.193 (9)		O(1)″–Li–O(2) =	106.97 (79)
O(1)″–O(3)	3.165 (9)		O(1)″–Li(1)–O(3) =	107.62 (73)
O(2)–O(3)	3.111 (2)		O(2)–Li(1)–O(3) =	107.18 (73)
Coordination Polyhedra about Li(2)				
Li(2)–O(1)	2.018 (10)	(2×)		
Li(2)–O(2)′	2.017 (28)	(1×)		
Li(2)–O(3)	1.962 (21)	(1×)		
O(1)–O(1)′	3.576 (7)	(1×)	O(1)–Li(2)–O(1)′ =	124.77 (102)
O(1)–O(2)′	3.225 (9)	(2×)	O(1)–Li(2)–O(2)′ =	106.11 (82)
O(1)–O(3)	3.172 (8)	(2×)	O(1)–Li(2)–O(3) =	105.71 (76)
O(2)′–O(3)	3.209 (12)	(1×)	O(2)′–Li(2)–O(3) =	107.49 (97)

[a] Standard deviation for each value is given in parentheses and refers to the last significant figures quoted. Primes refer to atoms related by symmetry to those given in Table II.

P–O distance of 1.534 A listed in the International Tables of X-ray Crystallography.[10b]

Now that it has been established that lithium phosphate can exist in two forms additional insight can be gained by reviewing earlier work and attempting to determine, from the method of preparation and from the X-ray patterns, which phase was studied in each case. Solid-state reactions or crystallization from the melt at temperatures above the transition temperature are known to produce the high-temperature form, while precipitation from an aqueous solution at or near room temperature results in the low-temperature form.

Thus, Zambonini and Laves,[2] who prepared their sample by a solid-state reaction in an electric furnace (probably at a temperature near 850°), must have obtained the high-temperature form, although the indications from lattice constant data are ambiguous. Matias and Bondareva[11] described a new mineral, lithophosphate, and presented the X-ray powder diffraction data of Denisov, which generally seems to agree with that of the low-temperature form, although the intensity data are not entirely consistent with either. Fisher[12] published a powder pattern of synthetic lithium phosphate (the preparation is not described) that agrees well with that of the low-temperature form. Tien and Hummel[13] prepared samples both by solid-state reaction at 800° and by crystallization from the melt. Excluding diffraction peaks that indicate the presence of lithium pyrophosphate ($Li_4P_2O_7$), their pattern agrees well with that of the high-temperature polymorph of lithium phosphate. Because the samples were prepared above the transition temperature, their differential thermal analysis studies did not show the phase transition at 502°.

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