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Structure of α-LiZnPO$_4$

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Abstract. α-LiZnPO$_4$, M_r = 167·280, monoclinic, Cc, a = 17·250 (6), b = 9·767 (3), c = 17·106 (6) Å, β = 110·9 (3)°, V = 2691·8 (1) Å^3, Z = 32, D_x = 3·30 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 77·9 cm^{-1}, F(000) = 2560, T = 298 K, R = 0·0289 for 4739 independent reflections with $I > 3\sigma(I)$. The structure consists of discrete PO$_4$ tetrahedra linked by ZnO$_4$ and LiO$_4$ distorted tetrahedra such that three tetrahedra, one of each kind, share one corner. Although layers of tetrahedra parallel to (001) can be recognized in the structure, the PO$_4$ tetrahedra form a slightly distorted cubic closest packing, with Zn and Li occupying all of its tetrahedral voids.

Introduction. The present work on the systems $A^{\rm I}B^{\rm II}$PO$_4$ ($A^{\rm I}$ = monovalent cation, $B^{\rm II}$ = divalent cation) is part of our broad programme of crystallographic investigations, carried out in order to establish the structural relations within this phosphate family especially with respect to the origin of their phase transitions and ferroic properties (Elammari, 1983; Elammari, Durand, Cot & Elouadi, 1987; Elouadi, Elammari & Ravez, 1984; Elammari & Elouadi, 1987). During the study of the phase diagram in the system Li$_3$PO$_4$–Zn$_3$(PO$_4$)$_2$, Torres-Trevinos & West (1986) have determined the transition temperatures of (α, β, γ)-LiZnPO$_4$ and the unit-cell parameters of α-LiZnPO$_4$. The transition temperatures and the melting point in their and our work are identical as are the unit-cell parameters. We report here the crystal structure of α-LiZnPO$_4$; the structures of the β and γ modifications are under investigation.

Experimental. The LiZnPO$_4$ powder used for crystal growth has been synthesized according to the following chemical reaction:

$$\mathrm{Li_2CO_3 + 2ZnO + 2(NH_4)_2HPO_4 \rightarrow 2LiZnPO_4 + 4NH_3 + 3H_2O + CO_2}.$$

Stoichiometric mixtures were submitted to various heat treatments at temperatures ranging from 623 to 1123 K. The powder sample was melted and heated to 1510 K (m.p. 1458 K) and then slowly (6 K h^{-1}) cooled to 770 K, then rapidly to room temperature. A suitable single crystal was selected and ground to a sphere of approximate radius 0·205 mm. Precession and Weissenberg photographs revealed monoclinic Laue symmetry and showed the reflection conditions hkl: $h + k = 2n$ with $h + k = 4n$ reflections very intense; $h0l$: $l = 2n$, ($h = 2n$); $0k0$: ($k = 2n$), consistent with space groups Cc and $C2/c$. Unit-cell parameters were obtained by least-squares refinement of the accurately determined angles of 25 independent reflections ($9 \leq 2\theta \leq 26°$). The values agree with those determined from a previous Guinier powder photograph at room temperature. Data collection: 8413 reflections ($4·5 \leq 2\theta \leq 60°$; $-25 \leq h \leq 25$, $0 \leq k \leq 14$, $-25 \leq l \leq 25$) collected, ω scans, scan width 0·9°, variable scan speed 4–15° min^{-1}, background measured on both sides of the reflection, total background time = 0·5 times the time used for the peaks; automated Syntex R3 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Three standard reflections (400, 040, 008) measured periodically after every 200 reflections, no significant change. Data corrected for Lorentz and polarization effects; spherical absorption correction, μR = 1·60; maximum, minimum transmission 0·263, 0·204; $R_{\rm int}$ =

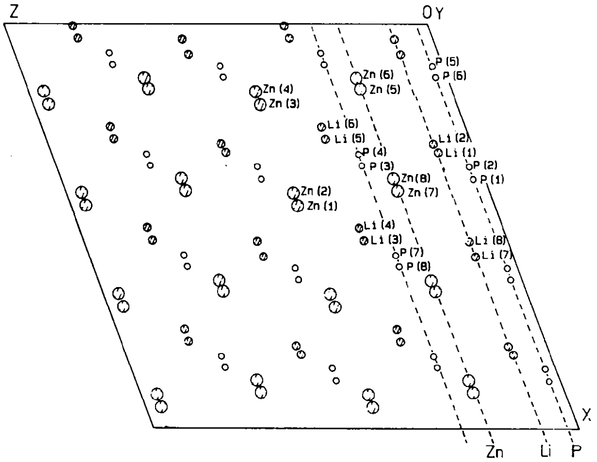

Fig. 1. Projection of the α-LiZnPO$_4$ structure without O atoms onto (010) showing the cationic order.

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0·0475, 6975 independent reflections of which 4739 with $I > 3\sigma(I)$ were used for the refinement. A positive second-harmonic-generation (SHG) test performed on powder samples indicated the absence of a centre of symmetry, thus *Cc* was used in the subsequent analysis. The Zn atoms were found by direct methods, several cycles of refinement followed by difference Fourier maps located the P, O and Li atoms; the $x = 0{\cdot}9490$ and $z = 0{\cdot}4639$ coordinates of Zn(1) have been fixed to determine the origin of the space group. Scattering factors for neutral atoms including f' and f'' terms for anomalous dispersion from *International Tables for X-ray Crystallography* (1974); cascade least squares (*R* isotropic = 0·066); $\sum w(|F_o| - |F_c|)^2$ minimized; weighting scheme $w = [\sigma^2(F_o) + 0{\cdot}00055(F_o)^2]^{-1}$; empirical isotropic extinction correction; anisotropic displacement parameters for all atoms; 504 least-squares parameters; $R = 0{\cdot}0289$, $wR = 0{\cdot}0334$.* Maximum shift/e.s.d. = 0·053 after the final cycle; maximum residual electron density 1·38 e Å^{-3}, 0·78 Å from Zn(1). The program system *SHELXTL* (Sheldrick, 1983) was used for all calculations on a Data General Nova 3 computer.

Discussion. The Weissenberg photographs showed very intense reflections *hkl* with $h + k = 4n$; this suggests a pseudo periodicity of the cation arrangement with half the unit cell. Fig. 1 shows the succession of the lines with P,Li,Zn,P,... running parallel to **a**. Final atomic coordinates are listed in Table 1. Interatomic distances and angles are given in Table 2. The α-LiZnPO$_4$ structure consists of relatively regular discrete PO$_4$ tetrahedra linked by distorted ZnO$_4$ and LiO$_4$ tetrahedra. The Zn—O and Li—O bond lengths range from 1·920 to 1·992 (5) Å and from 1·889 to 2·024 (14) Å, respectively. The P—O bond lengths vary in the range 1·517–1·569 (5) Å. Three tetrahedra, one of each kind, share one corner; they are arranged in interconnected layers parallel to (001). The layers limit small channels of which the diameter is equal to the edge of a PO$_4$ tetrahedron. Fig. 2 shows a stereoplot of the α-LiZnPO$_4$ structure viewed along [010].

According to Durif (1961) and Blasse (1963), LiZn*X*O$_4$ compounds (*X* = V, As, P) have a phenacite structure (Be$_2$SiO$_4$). The lithium monophosphate type (Li$_3$PO$_4$) is found in γ_{II}-Li$_2$ZnSiO$_4$, β_{II}-Li$_2$CoSiO$_4$ (Yamaguchi, Akatsuka & Setoguchi, 1979*a*,*b*) and a complex Zn Li silicate (Yu, Smith & Austerman, 1978). In all these structures, each cation has tetrahedral coordination, but the O atom is

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

	x	*y*	*z*	*U**
Zn(1)	9490	−2863 (1)	4639	14 (1)
Zn(2)	1987 (1)	−361 (1)	4645 (1)	14 (1)
Zn(3)	−833 (1)	−1828 (1)	−364 (1)	15 (1)
Zn(4)	1620 (1)	−6894 (1)	2146 (1)	14 (1)
Zn(5)	−902 (1)	624 (1)	2148 (1)	14 (1)
Zn(6)	−3692 (1)	−7141 (1)	2140 (1)	15 (1)
Zn(7)	1674 (1)	−5703 (1)	4633 (1)	15 (1)
Zn(8)	−1160 (1)	−4659 (1)	2151 (1)	14 (1)
P(1)	−1467 (1)	630 (2)	252 (1)	13 (1)
P(2)	−1189 (1)	−4686 (2)	268 (1)	13 (1)
P(3)	−1493 (1)	−1881 (2)	2775 (1)	12 (1)
P(4)	−1797 (1)	−7159 (2)	2756 (1)	13 (1)
P(5)	1332 (1)	−2826 (2)	5269 (1)	12 (1)
P(6)	−3982 (1)	−6886 (1)	247 (1)	12 (1)
P(7)	723 (1)	−4680 (2)	2759 (1)	12 (1)
P(8)	990 (1)	612 (2)	2777 (1)	12 (1)
O(11)	−1644 (3)	−353 (4)	−495 (3)	16 (1)
O(12)	−2227 (2)	1544 (4)	94 (3)	15 (1)
O(13)	−1301 (3)	−290 (4)	1048 (3)	19 (1)
O(14)	−689 (2)	1502 (4)	384 (3)	16 (1)
O(21)	−426 (2)	−5325 (4)	156 (3)	18 (1)
O(22)	−1964 (2)	−4987 (5)	−518 (3)	16 (1)
O(23)	−1046 (3)	−3134 (4)	404 (3)	17 (1)
O(24)	−1366 (3)	−5342 (5)	1010 (3)	20 (1)
O(31)	−1577 (3)	−2792 (4)	2010 (3)	17 (1)
O(32)	−1326 (2)	−2848 (4)	3522 (3)	16 (1)
O(33)	−2285 (3)	−1035 (4)	2610 (3)	16 (1)
O(34)	−748 (2)	−904 (4)	2945 (3)	16 (1)
O(41)	−1024 (2)	−7516 (4)	3524 (3)	17 (1)
O(42)	−1654 (3)	−7812 (5)	1993 (3)	18 (1)
O(43)	−2570 (3)	−7747 (4)	2875 (3)	17 (1)
O(44)	−1903 (2)	−5611 (4)	2628 (3)	16 (1)
O(51)	1190 (3)	−2273 (4)	6036 (3)	13 (1)
O(52)	2094 (3)	−2193 (4)	5154 (3)	18 (1)
O(53)	1461 (3)	−4377 (4)	5396 (3)	17 (1)
O(54)	548 (3)	−2503 (5)	4504 (3)	18 (1)
O(61)	−3839 (3)	−7771 (4)	1014 (3)	14 (1)
O(62)	−3213 (3)	−6008 (4)	390 (3)	17 (1)
O(63)	−4131 (3)	−7835 (4)	−510 (3)	16 (1)
O(64)	−4745 (2)	−5953 (4)	95 (3)	16 (1)
O(71)	597 (2)	−3121 (4)	2627 (3)	17 (1)
O(72)	1503 (2)	−4987 (5)	3533 (3)	19 (1)
O(73)	−51 (2)	−5289 (4)	2868 (3)	17 (1)
O(74)	871 (3)	−5285 (5)	2000 (3)	18 (1)
O(81)	198 (2)	1471 (4)	2613 (3)	18 (1)
O(82)	854 (3)	−269 (5)	1999 (3)	16 (1)
O(83)	1732 (2)	1591 (4)	2935 (3)	16 (1)
O(84)	1151 (3)	−366 (4)	3526 (3)	19 (1)
Li(1)	−2127 (8)	−6937 (10)	903 (9)	23 (1)
Li(2)	−1766 (6)	−2188 (9)	880 (6)	17 (1)
Li(3)	346 (5)	−1781 (10)	3393 (6)	18 (1)
Li(4)	30 (7)	−7098 (12)	3380 (7)	31 (1)
Li(5)	−2152 (6)	−4332 (11)	3395 (7)	22 (1)
Li(6)	−2441 (5)	392 (9)	3399 (7)	16 (1)
Li(7)	447 (6)	636 (10)	890 (6)	21 (1)
Li(8)	694 (6)	−4640 (10)	862 (7)	18 (1)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

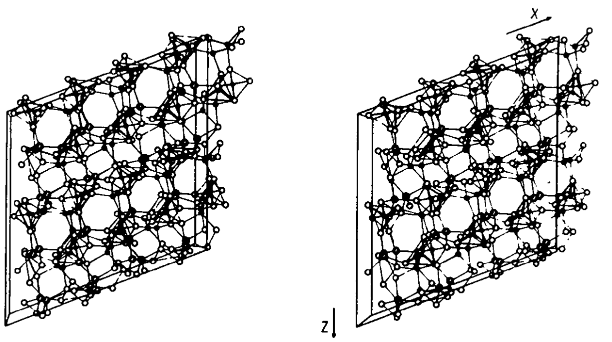

Fig. 2. A stereoplot of the α-LiZnPO$_4$ structure viewed along [010]. Empty circles represent O, hatched circles (small) Li and (large) Zn atoms, respectively. The black knots represent P atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52013 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the* α-LiZnPO$_4$ *structure*

P—O distances

P(1)—O(11)	1·540 (5)	P(5)—O(51)	1·517 (5)
P(1)—O(12)	1·527 (4)	P(5)—O(52)	1·528 (5)
P(1)—O(13)	1·569 (5)	P(5)—O(53)	1·535 (4)
P(1)—O(14)	1·537 (4)	P(5)—O(54)	1·541 (4)
P(2)—O(21)	1·530 (5)	P(6)—O(61)	1·517 (5)
P(2)—O(22)	1·548 (4)	P(6)—O(62)	1·524 (5)
P(2)—O(23)	1·539 (4)	P(6)—O(63)	1·537 (4)
P(2)—O(24)	1·548 (5)	P(6)—O(64)	1·546 (4)
P(3)—O(31)	1·547 (5)	P(7)—O(71)	1·544 (4)
P(3)—O(32)	1·531 (4)	P(7)—O(72)	1·542 (4)
P(3)—O(33)	1·535 (4)	P(7)—O(73)	1·531 (5)
P(3)—O(34)	1·543 (4)	P(7)—O(74)	1·530 (6)
P(4)—O(41)	1·541 (4)	P(8)—O(81)	1·540 (4)
P(4)—O(42)	1·550 (6)	P(8)—O(82)	1·531 (5)
P(4)—O(43)	1·531 (5)	P(8)—O(83)	1·542 (4)
P(4)—O(44)	1·529 (4)	P(8)—O(84)	1·541 (5)

O—P—O angles

O(11)—P(1)—O(12)	108·4 (2)	O(51)—P(5)—O(52)	112·3 (2)
O(11)—P(1)—O(13)	106·4 (2)	O(51)—P(5)—O(53)	106·8 (3)
O(11)—P(1)—O(14)	111·7 (3)	O(51)—P(5)—O(54)	107·3 (3)
O(12)—P(1)—O(13)	116·6 (3)	O(52)—P(5)—O(53)	109·2 (3)
O(12)—P(1)—O(14)	110·6 (2)	O(52)—P(5)—O(54)	110·0 (3)
O(13)—P(1)—O(14)	108·1 (2)	O(53)—P(5)—O(54)	111·2 (2)
O(21)—P(2)—O(22)	109·2 (3)	O(61)—P(6)—O(62)	108·6 (2)
O(21)—P(2)—O(23)	108·8 (3)	O(61)—P(6)—O(63)	108·2 (2)
O(21)—P(2)—O(24)	111·4 (3)	O(61)—P(6)—O(64)	110·2 (3)
O(22)—P(2)—O(23)	111·1 (3)	O(62)—P(6)—O(63)	110·4 (3)
O(22)—P(2)—O(24)	105·8 (2)	O(62)—P(6)—O(64)	109·6 (2)
O(23)—P(2)—O(24)	110·6 (3)	O(63)—P(6)—O(64)	109·8 (2)
O(31)—P(3)—O(32)	106·5 (2)	O(71)—P(7)—O(72)	110·5 (2)
O(31)—P(3)—O(33)	110·2 (2)	O(71)—P(7)—O(73)	108·5 (2)
O(31)—P(3)—O(34)	109·5 (3)	O(71)—P(7)—O(74)	108·3 (3)
O(32)—P(3)—O(33)	112·1 (3)	O(72)—P(7)—O(73)	110·6 (3)
O(32)—P(3)—O(34)	109·2 (2)	O(72)—P(7)—O(74)	107·1 (3)
O(33)—P(3)—O(34)	109·2 (2)	O(73)—P(7)—O(74)	111·8 (3)
O(41)—P(4)—O(42)	106·0 (3)	O(81)—P(8)—O(82)	107·3 (2)
O(41)—P(4)—O(43)	109·3 (3)	O(81)—P(8)—O(83)	108·7 (2)
O(41)—P(4)—O(44)	111·7 (2)	O(81)—P(8)—O(84)	111.9 (3)
O(42)—P(4)—O(43)	111·4 (3)	O(82)—P(8)—O(83)	111·1 (3)
O(42)—P(4)—O(44)	109·5 (3)	O(82)—P(8)—O(84)	107·4 (3)
O(43)—P(4)—O(44)	108·9 (3)	O(83)—P(8)—O(84)	110·4 (2)

Zn—O distances

Zn(1)—O(14^{vii})	1·940 (4)	Zn(5)—O(13)	1·971 (4)
Zn(1)—O(21^{viii})	1·961 (4)	Zn(5)—O(34)	1·974 (4)
Zn(1)—O(32^{iv})	1·926 (4)	Zn(5)—O(81)	1·960 (4)
Zn(1)—O(54^{iv})	1·952 (5)	Zn(5)—O(42^{iii})	1·959 (5)
Zn(2)—O(52)	1·969 (4)	Zn(6)—O(43)	1·984 (4)
Zn(2)—O(84)	1·942 (4)	Zn(6)—O(61)	1·950 (5)
Zn(2)—O(22^{i})	1·958 (5)	Zn(6)—O(71^{ii})	1·962 (5)
Zn(2)—O(62^{i})	1·961 (5)	Zn(6)—O(82^{ii})	1·969 (5)
Zn(3)—O(11)	1·964 (4)	Zn(7)—O(53)	1·965 (5)
Zn(3)—O(23)	1·958 (5)	Zn(7)—O(72)	1·929 (5)
Zn(3)—O(41^{v})	1·920 (4)	Zn(7)—O(12^{i})	1·956 (4)
Zn(3)—O(64^{ii})	1·954 (4)	Zn(7)—O(63^{ix})	1·945 (4)
Zn(4)—O(74)	1·992 (5)	Zn(8)—O(24)	1·971 (5)
Zn(4)—O(33^{ii})	1·957 (4)	Zn(8)—O(31)	1·944 (4)
Zn(4)—O(51^{v})	1·953 (4)	Zn(8)—O(44)	1·981 (5)
Zn(4)—O(83^{iii})	1·964 (4)	Zn(8)—O(73)	1·966 (4)

O—Zn—O angles

O(14^{vii})—Zn(1)—O(21^{viii})	109·0 (2)	O(13)—Zn(5)—O(34)	103·4 (2)
O(14^{vii})—Zn(1)—O(32^{iv})	114·5 (2)	O(13)—Zn(5)—O(81)	122·4 (2)
O(14^{vii})—Zn(1)—O(54^{iv})	109·2 (2)	O(13)—Zn(5)—O(42^{iii})	103·6 (2)
O(21^{viii})—Zn(1)—O(32^{iv})	111·4 (2)	O(34)—Zn(5)—O(81)	99·6 (2)
O(21^{viii})—Zn(1)—O(54^{iv})	107·1 (2)	O(34)—Zn(5)—O(42^{iii})	127·0 (2)
O(32^{iv})—Zn(1)—O(54^{iv})	105·3 (2)	O(81)—Zn(5)—O(42^{iii})	102·9 (2)
O(52)—Zn(2)—O(84)	110·7 (2)	O(43)—Zn(6)—O(61)	106·5 (2)
O(52)—Zn(2)—O(22^{i})	106·0 (2)	O(43)—Zn(6)—O(71^{ii})	101·6 (2)
O(52)—Zn(2)—O(62^{i})	110·0 (2)	O(43)—Zn(6)—O(82^{ii})	127·6 (2)
O(84)—Zn(2)—O(21^{i})	105·0 (2)	O(61)—Zn(6)—O(71^{ii})	112·6 (2)
O(84)—Zn(2)—O(62^{i})	113·7 (2)	O(61)—Zn(6)—O(82^{ii})	105·5 (2)
O(22^{i})—Zn(2)—O(62^{i})	111·2 (2)	O(71^{ii})—Zn(6)—O(82^{ii})	102·9 (2)
O(11)—Zn(3)—O(23)	104·9 (2)	O(53)—Zn(7)—O(72)	114·2 (2)
O(11)—Zn(3)—O(41^{v})	105·6 (2)	O(53)—Zn(7)—O(12^{i})	113·2 (2)
O(11)—Zn(3)—O(64^{ii})	105·5 (2)	O(53)—Zn(7)—O(63^{ix})	105·9 (2)
O(23)—Zn(3)—O(41^{v})	116·1 (2)	O(72)—Zn(7)—O(12^{i})	109·5 (2)
O(23)—Zn(3)—O(64^{ii})	113·5 (2)	O(72)—Zn(7)—O(63^{ix})	106·8 (2)
O(41^{v})—Zn(3)—O(64^{ii})	110·2 (2)	O(12^{i})—Zn(7)—O(63^{ix})	106·7 (2)
O(74)—Zn(4)—O(33^{ii})	101·6 (2)	O(24)—Zn(8)—O(31)	105·4 (2)
O(74)—Zn(4)—O(51^{v})	101·7 (2)	O(24)—Zn(8)—O(44)	109·6 (2)
O(74)—Zn(4)—O(83^{iii})	125·5 (2)	O(24)—Zn(8)—O(73)	107·6 (2)
O(33)—Zn(4)—O(51^{v})	123·3 (2)	O(31)—Zn(8)—O(44)	103·1 (2)

Table 2 (*cont.*)

O(33)—Zn(4)—O(83^{iii})	101·6 (2)	O(31)—Zn(8)—O(73)	127·3 (2)
O(51)—Zn(4)—O(83^{iii})	105·3 (2)	O(44)—Zn(8)—O(73)	103·0 (2)

Li—O distances

Li(1)—O(24)	2·003 (12)	Li(5)—O(32)	1·989 (11)
Li(1)—O(42)	1·042 (14)	Li(5)—O(44)	1·967 (13)
Li(1)—O(62)	1·983 (12)	Li(5)—O(22^{v})	1·889 (12)
Li(1)—O(12^{iii})	1·992 (13)	Li(5)—O(83^{ii})	2·015 (10)
Li(2)—O(13)	2·000 (10)	Li(6)—O(33)	2·024 (11)
Li(2)—O(23)	1·944 (12)	Li(6)—O(11^{vi})	1·902 (10)
Li(2)—O(31)	1·933 (11)	Li(6)—O(43^{iii})	2·003 (10)
Li(2)—O(52^{i})	2·008 (9)	Li(6)—O(72^{ii})	1·951 (11)
Li(3)—O(34)	1·961 (10)	Li(7)—O(14)	2·022 (10)
Li(3)—O(54)	1·938 (12)	Li(7)—O(82)	1·980 (11)
Li(3)—O(71)	2·005 (12)	Li(7)—O(51^{vi})	2·008 (11)
Li(3)—O(84)	1·914 (11)	Li(7)—O(64^{ii})	2·011 (11)
Li(4)—O(41)	1·964 (15)	Li(8)—O(21)	1·992 (9)
Li(4)—O(73)	1·955 (13)	Li(8)—O(74)	1·963 (12)
Li(4)—O(63^{ix})	1·934 (11)	Li(8)—O(53^{v})	2·016 (12)
Li(4)—O(81^{iii})	2·007 (14)	Li(8)—O(61^{ii})	1·974 (11)

O—Li—O angles

O(24)—Li(1)—O(42)	102·5 (5)	O(32)—Li(5)—O(44)	102·6 (6)
O(24)—Li(1)—O(62)	99·7 (5)	O(32)—Li(5)—O(22^{v})	106·6 (5)
O(24)—Li(1)—O(12^{iii})	122·3 (9)	O(32)—Li(5)—O(83^{ii})	105·3 (5)
O(42)—Li(1)—O(62)	129·1 (9)	O(44)—Li(5)—O(22^{v})	115·5 (5)
O(42)—Li(1)—O(12^{iii})	104·0 (5)	O(44)—Li(5)—O(83^{ii})	115·4 (5)
O(62)—Li(1)—O(12^{iii})	101·6 (5)	O(22^{v})—Li(5)—O(83^{ii})	110·3 (6)
O(13)—Li(2)—O(23)	102·6 (5)	O(33)—Li(6)—O(11^{vi})	115·4 (5)
O(13)—Li(2)—O(31)	102·9 (4)	O(33)—Li(6)—O(43^{iii})	110·2 (6)
O(13)—Li(2)—O(52^{i})	128·5 (5)	O(33)—Li(6)—O(72^{ii})	107·5 (4)
O(23)—Li(2)—O(31)	103·2 (5)	O(11^{vi})—Li(6)—O(43^{iii})	112·9 (4)
O(23)—Li(2)—O(52^{i})	103·2 (5)	O(11^{vi})—Li(6)—O(72^{ii})	104·6 (6)
O(31)—Li(2)—O(52^{i})	107·7 (6)	O(43^{iii})—Li(6)—O(72^{ii})	105·4 (4)
O(34)—Li(3)—O(54)	110·7 (6)	O(14)—Li(7)—O(82)	123·7 (7)
O(34)—Li(3)—O(71)	115·5 (5)	O(14)—Li(7)—O(51^{vi})	101·4 (5)
O(34)—Li(3)—O(84)	106·6 (5)	O(14)—Li(7)—O(64^{ii})	97·6 (4)
O(54)—Li(3)—O(71)	113·4 (5)	O(82)—Li(7)—O(51^{vi})	104·2 (4)
O(54)—Li(3)—O(84)	106·1 (4)	O(82)—Li(7)—O(64^{ii})	102·7 (5)
O(71)—Li(3)—O(84)	103·4 (6)	O(51^{vi})—Li(7)—O(64^{ii})	129·9 (7)
O(41)—Li(4)—O(73)	108·9 (6)	O(21)—Li(8)—O(74)	105·5 (6)
O(41)—Li(4)—O(63^{ix})	105·7 (7)	O(21)—Li(8)—O(53^{v})	103·4 (5)
O(41)—Li(4)—O(81^{iii})	107·1 (6)	O(21)—Li(8)—O(61^{ii})	130·7 (5)
O(73)—Li(4)—O(63^{ix})	112·3 (6)	O(74)—Li(8)—O(53^{v})	110·3 (5)
O(73)—Li(4)—O(81^{iii})	109·9 (7)	O(74)—Li(8)—O(61^{ii})	104·7 (5)
O(63^{ix})—Li(4)—O(81^{iii})	112·7 (6)	O(53)—Li(8)—O(61^{ii})	101·4 (5)

Symmetry code: (i) $x \pm 0{\cdot}5$, $-(y + 0{\cdot}5)$, $z \pm 0{\cdot}5$; (ii) $x \pm 0{\cdot}5$, $y \pm 0{\cdot}5$, z; (iii) x, $y \pm 1$, z; (iv) $x + 1$, y, z; (v) x, $-(y + 1)$, $z \pm 0{\cdot}5$; (vi) x, $-y$, $z + 0{\cdot}5$; (vii) $x + 1$, $-y$, $z + 0{\cdot}5$; (viii) $x + 1$, $-(y + 1)$, $z + 0{\cdot}5$; (ix) $x + 0{\cdot}5$, $-(y + 0{\cdot}5) - 1$, $z + 0{\cdot}5$.

shared by three tetrahedra in the phenacite and α-LiZnPO$_4$ structures and four tetrahedra in the Li$_3$PO$_4$ structure type. The structure of the title compound belongs to the family of so-called tetrahedral structures (Parthé, 1964). Evidently the size of a PO$_4$ tetrahedron is smaller than that of SiO$_4$, VO$_4$ and AsO$_4$. All these compounds are built up of LiO$_4$, MO$_4$ (M = Be, Co, Zn) and XO$_4$ (X = P, Si, V, As) tetrahedra with different arrangements. This arrangement depends on the temperature and on the proportion and the size of the tetrahedra. Thus in phenacite and Li$_3$PO$_4$ structures all the tetrahedra are oriented with one vertex in the **c** direction whereas in the α-LiZnPO$_4$ structure only one of two tetrahedra is oriented in this way.

The structure of α-LiZnPO$_4$ can be described as a cubic closest packing of the PO$_4$ tetrahedra with complete occupation of its tetrahedral voids by the Li and Zn atoms (see Fig. 3*b*). As an example, Fig. 3(*a*) shows the 12 neighbouring P atoms of a P(3) atom arranged as a cuboctahedron.

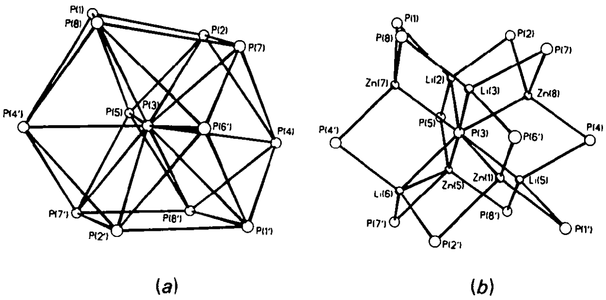

Fig. 3. (*a*) Cuboctahedral surroundings of the P(3) atom in the cubic closest packing of PO_4 tetrahedra. (*b*) Occupation of the tetrahedral voids of the PO_4 packing by Li and Zn.

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u Parameters for the Wurtzite Structure of ZnS and ZnO using Powder Neutron Diffraction

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Abstract. The crystal structures of hexagonal ZnS [$M_r = 97{\cdot}44$, $P6_3mc$, $a = 3{\cdot}8227$ (1). $c = 6{\cdot}2607$ (1) Å, $V = 79{\cdot}23$ Å^3, $Z = 2$, $D_x = 4{\cdot}08$ Mg m^{-3}, $R_{wp} = 0{\cdot}058$, $R_B = 0{\cdot}017$] and ZnO [$M_r = 81{\cdot}38$, $P6_3mc$, $a = 3{\cdot}2501$ (1), $c = 5{\cdot}2071$ (1) Å, $V = 47{\cdot}63$ Å^3, $Z = 2$, $D_x = 5{\cdot}67$ Mg m^{-3}, $R_{wp} = 0{\cdot}078$, $R_B = 0{\cdot}012$] at 295 K have been refined by Rietveld analysis of 1·500 (1) Å neutron powder diffraction data containing 50 and 33 independent reflections respectively. Zinc atoms occupy the special position 2(*b*) with coordinates $\frac{1}{3}, \frac{2}{3}, 0$. Oxygen and sulfur also occupy special position 2(*b*) with coordinates $\frac{1}{3}, \frac{2}{3}, u$. For ZnS, $u = 0{\cdot}3748$ (2) and for ZnO $u = 0{\cdot}3817$ (3). Both compounds have u and $\frac{c}{a}$ which conform to the known correlation between these parameters. It is shown that this correlation is equivalent to $\frac{uc}{a}$ remaining constant at or near its ideal value $(\frac{3}{8})^{1/2}$. The JCPDS file No. for ZnS is 10-434 and for ZnO is 21-1486.

Introduction. Hexagonal ZnS is the prototype for the wurtzite structure ($P6_3mc$, Zn at $\frac{1}{3}, \frac{2}{3}, 0$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$, and S at $\frac{1}{3}, \frac{2}{3}, u$ and $\frac{2}{3}, \frac{1}{3}, u + \frac{1}{2}$), the high-temperature polymorphic modification of zincblende. Surprisingly, a thorough literature search has failed to reveal a precisely determined value for u which is often taken to have the ideal value $\frac{3}{8}$. A recent NMR study (Bastow & Stuart, 1988) proposed a value of 0·373 for ZnS. In materials with the wurtzite structure, there is an approximately linear relationship between the value of u and the $\frac{c}{a}$ ratio as shown in Fig. 1. This figure has been used to estimate u for ZnS from published $\frac{c}{a}$ ratios. $\frac{c}{a} = 1{\cdot}6407$ (*Handbook of Physics*

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