present, but arranged in different ways. Isolated pairs of tetrahedra joined by a face are found in Ba_3Al_5 and in Ba_4Al_5 (Fornasini, 1975), while $BaAl_2$, formed only in high-pressure conditions (Cordier, Czech & Schäfer, 1984), shows the infinite framework of tetrahedra joined by vertices typical of the cubic Laves phase $MgCu_2$. The Ba_7Al_{13} structure (Fornasini & Bruzzone, 1975) contains some face-sharing tetrahedra and some of the $MgCu_2$ framework, and can be built up by intergrowth of segments of the Ba_3Al_5 and $MgCu_2$ structures, as outlined in the figure. Alternatively, it can be described as formed by cells of Ba_3Al_5 separated one from the other by insertion of an aluminium Kagomé net. Recognizable segments of the Ba_3Al_5 structure are also found in Ba_4Al_5, but in the boundary region between two segments of Ba_3Al_5 two Ba layers are inserted instead of one.

Very recently the structure of the rhombohedral Sr_5Al_9 phase has been published (Manyako, Zarechnyuk & Yanson, 1987), described by the authors as an intergrowth of segments of $MgZn_2$ and a hypothetical R_3X_5 structure, while the structure of Ba_7Al_{13} is shown as an intergrowth of the $MgCu_2$ and the same hypothetical R_3X_5 structure. Interestingly, this hypothetical structure corresponds to that of the Ba_3Al_5 phase. So here again is an event common in crystal structure determination: the more complex examples of a structural family are found before the discovery of the simplest parent member!

The coordination polyhedra in Ba_3Al_5 are very similar to those of the related Ba–Al structures. Ba1 is coordinated with 10 Al + 4 Ba in the same manner as Ba2 in Ba_4Al_5 with a further Al atom; the Ba2 polyhedron, formed by 12 Al + 6 Ba is identical to that of Ba1 in Ba_7Al_{13}. The Al1 atoms forming Kagomé nets are icosahedrally surrounded by 6 Al + 6 Ba. The same coordination is found also around Al in h.p. $BaAl_2$, Al2 in Ba_4Al_5 and Al2, Al3, Al4 in Ba_7Al_{13}. Finally, the environment of Al2, coordinated with 3 Al + 7 Ba, is identical to those of Al1 in Ba_4Al_5 and Al1 in Ba_7Al_{13}. Neither Ba_3Al_5 nor Ba_4Al_5 show Friauf polyhedra around the large atoms, a characteristic feature of the Laves phases; they are present, though, in Ba_7Al_{13} and Sr_5Al_9 structures.

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Structure of $LiCdPO_4$

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Abstract. $M_r = 214{\cdot}31$, orthorhombic, space group $Pna2_1$, $a = 10{\cdot}713$ (4), $b = 4{\cdot}801$ (1), $c = 6{\cdot}284$ (3) Å, $V = 323{\cdot}2$ (1) Å^3, $Z = 4$, $D_x = 4{\cdot}40$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}7107$ Å, $\mu = 70{\cdot}59$ cm^{-1}, $F(000) = 392$, $T = 298$ K, $R = 0{\cdot}0206$ for 1079 independent reflections with $I > 1{\cdot}5\sigma(I)$. The structure consists of discrete PO_4 tetrahedra linked by CdO_6 octahedra and distorted LiO_6 octahedra. The Cd—O and Li—O bond lengths

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range from 2·178 to 2·390 Å and from 2·082 to 2·388 Å, respectively. The P—O bond lengths are in the range 1·518–1·567 Å. The structure of $LiCdPO_4$ can be regarded as a heavily distorted olivine structure.

Introduction. In previous studies we investigated the crystal structures and phase transitions of some members of the mixed phosphate family with the formula: $A^{I}B^{II}PO_4$ (A = Li, Na, K, Rb, Cs; B = Mg, Ca, Sr, Ba, Zn, Cd, Pb) (Elammari, 1983; Elammari, Durand, Cot & Elouadi, 1987; Elouadi, Elammari & Ravez, 1984; Elammari & Elouadi, 1987). Furthermore, Blum, Peuzin & Henry (1984) and Blum, Durif & Averbuch-Pouchot (1986) have recently confirmed the ferroic properties of $CsCoPO_4$ and $CsZnPO_4$. The determination of the crystal structure of $LiCdPO_4$ has been carried out in order to enhance our understanding of the crystal chemistry and of the origin of the ferroelectric properties found in this phosphate family.

Experimental. The $LiCdPO_4$ powder used for crystal growth has been synthesized according to the following chemical reaction:

$$Li_2CO_3 + 2CdCO_3 + 2(NH_4)_2HPO_4 \rightarrow 2LiCdPO_4 + 4NH_3 + 3H_2O + 3CO_2.$$

Stoichiometric mixtures were submitted to various heat treatments at temperatures ranging from 473 to 1123 K. The powder sample was melted at 1273 K and then slowly ($6 K h^{-1}$) cooled to room temperature. A suitable single crystal was selected and ground to an ellipsoid of approximate mean radius 0·125 mm.

Precession photographs revealed orthorhombic Laue symmetry and showed the reflection conditions $0kl$: $k+l = 2n$, $h0l$: $h = 2n$ ($h00$: $h = 2n$, $0k0$: $k = 2n$), consistent with space groups $Pna2_1$ and $Pnam$. Cell parameters were obtained by least-squares refinement of the accurately determined angles of 22 independent reflections ($7 \leq 2\theta \leq 40°$). The values agree with those determined from a previous Guinier powder photograph with silicon (a_{Si} = 5·430 Å) as internal standard: a = 10·713 (4), b = 4·801 (1) and c = 6·284 (3) Å at room temperature.

2049 reflections ($5 \leq 2\theta \leq 70°$, $-18 \leq h \leq 18$, $0 \leq k \leq 8$, $0 \leq l \leq 11$) collected, ω scans, automated Syntex $R3$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Three standard reflections (006, 020, 400) measured periodically after every 200 reflections, no significant change. Eleven forbidden but observed reflections (001, 029, 009, 047, 070, 17,0,0, 17,0,0, 15,0,0, 15,0,0, 102 and 102) have been shown (ψ scan) to be caused by the Renninger effect. Data corrected for Lorentz and polarization effects; empirical absorption correction (ψ scan), μR = 0·882; max., min. transmission 0·141, 0·084; R_{int} = 0·0187, 1079 unique reflections with $I > 1·5\sigma(I)$ were obtained (28 unobserved reflections). Statistical tests indicated the absence of a centre of symmetry in accordance with a positive second-harmonic-generation test achieved on powder samples, thus $Pna2_1$ was used. Patterson method, several cycles of refinement with isotropic displacement parameters located the O and Li atoms (R isotropic = 0·04). The z (0·25) coordinate of Cd has been fixed to determine the origin of the space group. Refinement on F_o to R = 0·0206 and wR = 0·0212* has been obtained with anisotropic displacement parameters for all atoms. Weighting scheme $w = [\sigma^2(F_o) + 0·0002(F_o)^2]^{-1}$. Extinction was corrected by an empirical parameter according to Sheldrick (1983). Table 1 lists the refined fractional coordinates and equivalent displacement parameters, Table 2 lists bond lengths and angles. Scattering factors for neutral atoms including f' and f'' terms for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). After the final cycle max. shift/e.s.d. = 0·042, max. and min. residual electron density 1·99 e Å^{-3} 0·51 Å from Cd and −0·75 e Å^{-3}, respectively. The program system *SHELXTL* (Sheldrick, 1983) was used for all calculations.

Discussion. The $LiCdPO_4$ structure consists of discrete PO_4 tetrahedra linked by CdO_6 octahedra and distorted LiO_6 octahedra. The Cd—O and Li—O bond lengths range from 2·178 to 2·390 Å and from 2·082 to 2·388 Å, respectively. The P—O bond lengths vary in the range 1·518–1·567 Å. The projection of the structure onto (010) is shown in Fig. 1. The structure of $LiCdPO_4$ can be regarded as a heavily distorted olivine structure. It is interesting to compare the title compound with Mg_2SiO_4 and the lithiophilite $LiMnPO_4$ (Wenk & Raymond, 1973; Geller & Durand, 1960). The latter compound is only slightly distorted with respect to Mg_2SiO_4, because the difference between the ionic radii of the cation occupying the octahedral sites (r_{Li} = 0·74, r_{Mn} = 0·67 Å; Shannon & Prewitt, 1969) is small compared with that of Li and Cd (r_{Cd} = 0·95 Å) in $LiCdPO_4$. Therefore the strong distortion of $LiCdPO_4$ is not surprising.

Griffen & Ribbe (1979) have introduced parameters for describing the deformation of the bond length (BLDP) and of the edge length (ELDP) of various tetrahedral oxyanions and have, in particular, given grand mean values for the PO_4 tetrahedron (<BLDP> = 0·0168, <ELDP> = 0·0150). The values calculated for the PO_4 tetrahedron in $LiCdPO_4$ demonstrate that the angular distortion (ELDP = 0·0246) is more pronounced than the bond-length distortion (BLDP = 0·0133). It is clear from Table 2 that the CdO_6

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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 44651 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

E.s.d.'s are in parentheses and refer to the final digits quoted.

	x	y	z	U_{eq}*
Cd	2156 (1)	450 (1)	2500	12 (1)
P	9107 (1)	−1046 (1)	2475 (4)	10 (1)
O(1)	9067 (2)	2114 (4)	2509 (10)	16 (1)
O(2)	10440 (2)	−2253 (4)	2482 (12)	15 (1)
O(3)	8475 (4)	−2464 (10)	556 (8)	14 (1)
O(4)	8414 (4)	−2249 (10)	4471 (7)	13 (1)
Li	9976 (30)	−5137 (48)	48 (52)	30 (2)

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

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

PO$_4$ tetrahedra			
P–O(1)	1·518 (2)	P–O(3)	1·542 (5)
P–O(2)	1·541 (2)	P–O(4)	1·567 (5)
O(1)–P–O(3)	116·1 (3)	O(2)–P–O(3)	104·1 (3)
O(1)–P–O(2)	113·7 (1)	O(3)–P–O(4)	104·8 (2)
O(1)–P–O(4)	110·1 (3)	O(2)–P–O(4)	107·3 (3)
CdO$_6$ octahedra			
Cd–O(1^{ii})	2·358 (2)	Cd–O(3^{iii})	2·254 (5)
Cd–O(2^{iv})	2·251 (2)	Cd–O(4^{ii})	2·390 (5)
Cd–O(3^{ii})	2·354 (5)	Cd–O(4^{iii})	2·178 (5)
O(1^{ii})–Cd–O(2^{iv})	274·5 (1)	O(2^{iv})–Cd–O(4^{iii})	89·7 (2)
O(1^{ii})–Cd–O(3^{ii})	77·4 (1)	O(3^{ii})–Cd–O(3^{iii})	152·1 (2)
O(1^{ii})–Cd–O(3^{iii})	92·6 (2)	O(3^{ii})–Cd–O(4^{ii})	62·6 (2)
O(1^{ii})–Cd–O(4^{ii})	80·1 (1)	O(3^{ii})–Cd–O(4^{iii})	87·5 (2)
O(1^{ii})–Cd–O(4^{iii})	92·8 (2)	O(3^{iii})–Cd–O(4^{ii})	90·2 (2)
O(2^{iv})–Cd–O(3^{ii})	97·8 (2)	O(3^{iii})–Cd–O(4^{iii})	119·4 (2)
O(2^{iv})–Cd–O(3^{iii})	90·4 (2)	O(4^{ii})–Cd–O(4^{iii})	150·0 (2)
O(2^{iv})–Cd–O(4^{ii})	95·3 (2)		
LiO$_6$ octahedra			
Li–O(2)	2·122 (30)	Li–O(1^{iii})	2·388 (30)
Li–O(3)	2·082 (29)	Li–O(2^{v})	2·090 (30)
Li–O(1^{i})	2·254 (30)	Li–O(4^{v})	2·163 (30)
O(2)–Li–O(3)	70·6 (9)	O(3)–Li–O(4^{v})	177·4 (14)
O(2)–Li–O(1^{i})	89·3 (12)	O(1^{i})–Li–O(1^{iii})	178·4 (15)
O(2)–Li–O(1^{iii})	89·1 (9)	O(1^{i})–Li–O(2^{v})	94·9 (10)
O(2)–Li–O(2^{v})	175·6 (17)	O(1^{i})–Li–O(4^{v})	96·9 (10)
O(2)–Li–O(4^{v})	108·2 (14)	O(1^{iii})–Li–O(2^{v})	86·6 (12)
O(3)–Li–O(1^{i})	85·5 (12)	O(1^{iii})–Li–O(4^{v})	84·2 (11)
O(3)–Li–O(1^{iii})	93·4 (10)	O(2^{v})–Li–O(4^{v})	72·1 (9)
O(3)–Li–O(2^{v})	108·8 (15)		

Symmetry code: (i) $x, y-1, z$; (ii) $x-0{\cdot}5, -y\pm0{\cdot}5, z$; (iii) $1-x, -y, z\pm0{\cdot}5$; (iv) $x-1, y, z$; (v) $1-x, -1-y, z-0{\cdot}5$.

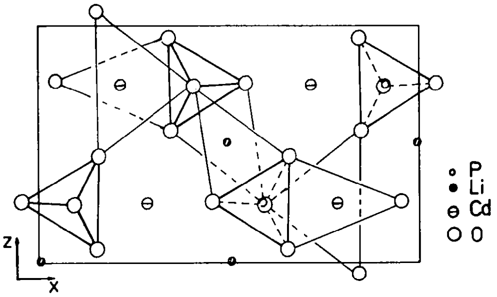

Fig. 1. Projection of the LiCdPO$_4$ structure onto (010) showing the discrete PO$_4$ tetrahedra (thick solid lines) and distorted LiO$_6$ and CdO$_6$ octahedra (at the centre and on the upper left- and the lower right-hand side, respectively).

octahedron is more regular than the LiO$_6$ octahedron. The deformation of the latter results from two relatively long bonds and two O—Li—O angles with values close to that of a regular tetrahedron. One might argue, therefore, that the coordination of Li in LiCdPO$_4$ is somewhat in between octahedral and tetrahedral.

The space group of LiCdPO$_4$, $Pna2_1$, allows the occurrence of ferroelectricity. Tentatively, we have calculated the spontaneous polarization using a formula and the corresponding approximations proposed by Jeitschko (1972). The value found for LiCdPO$_4$ ($P_m = 1{\cdot}93\ \mu\mathrm{C\,cm^{-2}}$) compares well with values for well known improper ferroelectrics, *e.g.* $Cu_3B_7O_{13}Cl$ ($P_m = 1{\cdot}85\ \mu\mathrm{C\,cm^{-2}}$; Schmid & Tippmann, 1978) and $Gd_2(MoO)_4$ ($P_m = 1{\cdot}6\ \mu\mathrm{C\,cm^{-2}}$; Jeitschko, 1972). Up to now we have not been able to grow crystals suitable for an experimental verification of the above value, but further growth experiments are to be performed.

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