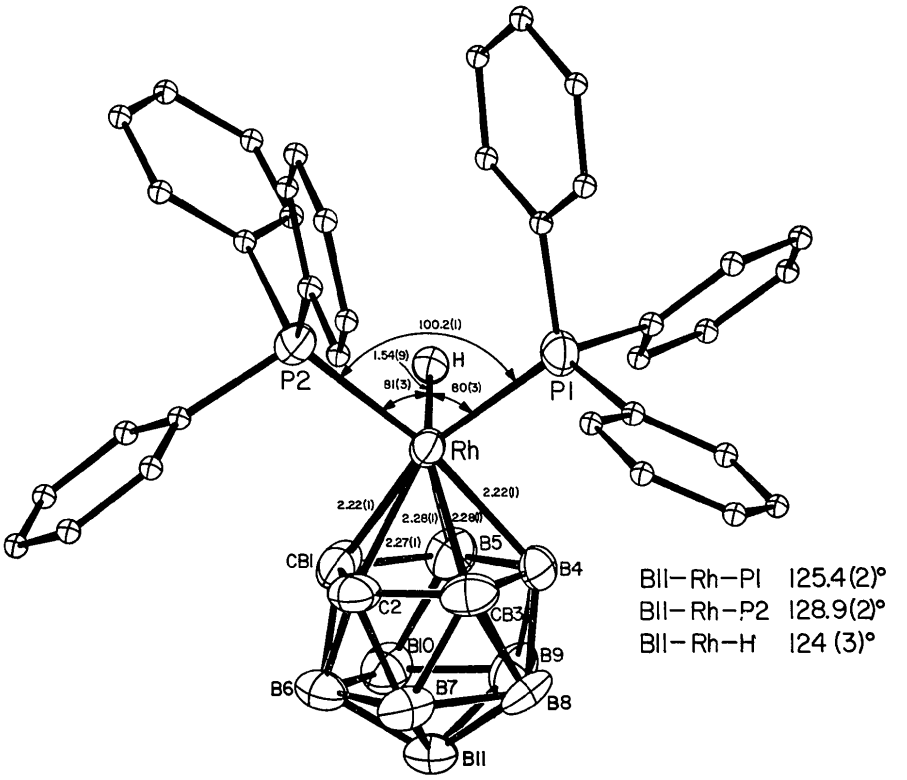


Fig. 1. The molecular structure of $RhH(PPh_3)_2(C_2B_9H_{11})$. All hydrogen atoms except the hydride are omitted for clarity. A atoms except the phenyl carbon atoms are depicted as 50% probability ellipsoids.

Dr Timm Paxson for supplying the crystals used in this investigation.

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# An Efficient Laser Material, Lithium Neodymium Phosphate $LiNdP_4O_{12}$

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**Abstract.** Monoclinic, $I2/c$ ($C_{2h}^6$), $a=9{\cdot}844$ (2), $b=7{\cdot}008$ (3), $c=13{\cdot}25$ (2) Å, $\beta=90{\cdot}1$ (2)°, $Z=4$, $D_c=3{\cdot}39$, $D_o=3{\cdot}38$ g cm$^{-3}$, $\mu$(Mo $K\alpha$)$=62{\cdot}0$ cm$^{-1}$. Structural framework is helical chains of $(PO_3)_\infty$ along the $b$ axis. Both $Nd^{3+}$ and $Li^+$ ions alternate on twofold axes in the middle of four such chains. $NdO_8$ dodecahedra and considerably distorted $LiO_4$ tetrahedra form linear chains sharing their edges. The refinement converged to $R=0{\cdot}035$ for 1095 independent observed reflexions.

**Introduction.** Recently a phosphate laser material with high Nd concentration, $LiNdP_4O_{12}$, was produced in our laboratory and is reported to have a high laser performance (Yamada, Otsuka & Nakano, 1974), comparable to or better than that of $NdP_5O_{14}$.

Specimens were selected from the crystals grown from the melt of $Li_2O$–$Nd_2O_3$–$P_2O_5$ by the Kyropolous technique (Yamada *et al.*, 1974). Precession and Weissenberg photographs exhibited $2/m$ Laue symme-

try with the following systematic absences: $hkl$ when $h+k+l=2n+1$, $0kl$ when $k+l=2n+1$, $h0l$ when $h=2n+1$, $l=2n+1$, $hk0$ when $h+k=2n+1$.*

A prismatic crystal of dimensions $0{\cdot}23\times0{\cdot}35\times0{\cdot}63$ mm was mounted so that its $b$ axis was along the $\varphi$ axis of the Rigaku Denki automatic four-circle X-ray diffractometer. Reflexions within $(\sin\theta/\lambda)=0{\cdot}60$ Å$^{-1}$ were measured using $\omega$–$2\theta$ scan technique with a Ge monochromator. The intensities were corrected for Lorentz–polarization, absorption and extinction effects.

The locations of the heavier atoms, $Nd^{3+}$ and P, were determined by the three-dimensional Patterson method. Structure factors based on the Patterson coordinates gave the conventional $R$ value of 0·231. Successive Fourier synthesis clearly revealed the O atoms' positions indicating tetrahedral coordination around each P atom. Then atomic positional and thermal parameters were refined by a full-matrix least-squares method (Busing, Martin & Levy, 1962) to give $R=0{\cdot}067$. The location of the $Li^+$ ion was selected from among several possible sites on the basis of symmetry and bonding considerations. All parameters including those for the $Li^+$ ion were refined by two further cycles of least-squares methods and a final $R$ value of 0·035 was obtained.

The final atomic positional and thermal parameters are listed in Table 1.*

**Discussion.** Bond distances and angles calculated from the final parameters are given in Table 2. Views of the structure projected along each axis are shown in Figs. 1, 2 and 3.

* The symmetry of the crystal was erroneously reported as orthorhombic (Yamada *et al.*, 1974). The relations between pseudo-orthorhombic axes and monoclinic axes are as follows. $a_{\text{pseudo orth.}} \parallel [100]_{\text{monocl.}}$; $b_{\text{pseudo orth.}} \parallel c_{\text{monocl.}}$; $c_{\text{pseudo orth.}} \parallel b_{\text{monocl.}}$.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31343 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters obtained in the final least-squares refinement*

Estimated standard deviations are given in parentheses. Anisotropic thermal factors ($\times10^5$) are given by the expression:
$T=\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2kl\beta_{23}+2hl\beta_{13})]$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ or $B$(Å$^2$) | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Nd | ½ | 0·5501 (1) | ¼ | 231 (6) | 471 (12) | 86 (3) | 0 | 8 (3) | 0 |
| P(1) | 0·2247 (2) | 0·3070 (2) | 0·3889 (1) | 261 (14) | 614 (30) | 91 (8) | 8 (15) | 20 (8) | 15 (11) |
| P(2) | 0·3021 (2) | 0·9081 (3) | 0·3990 (1) | 287 (15) | 594 (28) | 91 (8) | −6 (16) | 7 (8) | 3 (12) |
| O(1) | 0·1193 (5) | 0·2551 (6) | 0·3153 (3) | 328 (39) | 630 (79) | 105 (20) | 121 (41) | 31 (22) | 26 (33) |
| O(2) | 0·3155 (5) | 0·4689 (6) | 0·3651 (4) | 448 (50) | 548 (92) | 188 (27) | −172 (46) | 49 (30) | 42 (34) |
| O(3) | 0·1554 (4) | 0·8642 (6) | 0·3806 (3) | 334 (41) | 627 (86) | 171 (23) | 26 (47) | −91 (25) | 20 (35) |
| O(4) | 0·4072 (4) | 0·8490 (6) | 0·3238 (3) | 370 (42) | 634 (84) | 176 (23) | 17 (44) | 104 (25) | 15 (36) |
| O(5) | 0·1488 (4) | 0·3364 (7) | 0·4937 (3) | 333 (40) | 985 (90) | 64 (20) | 23 (48) | −15 (23) | −36 (35) |
| O(6) | 0·3231 (4) | 0·1321 (6) | 0·4095 (3) | 329 (4) | 163 (5) | 208 (3) | 85 (41) | 1 (80) | −3 (23) |
| Li | ½ | 0·0536 (18) | ¼ | [0·98 (9)] | | | | | |

Table 2. *Bond distances and angles in* $LiNdP_4O_{12}$ *with standard deviations in parentheses*

Dodecahedron around Nd

| | | | |
|---|---|---|---|
| Nd–O(1) | 2×2·571 (4) Å | O(1)–O(1)′ | 2·854 (7) Å |
| Nd–O(2) | 2×2·421 (5) | O(1)–O(2) | 2·934 (6) |
| Nd–O(3) | 2×2·404 (4) | O(1)–O(3) | 2·904 (6) |
| Nd–O(4) | 2×2·480 (4) | O(2)–O(4) | 2·863 (6) |
| Nd–Nd | 6·474 (1) | O(3)–O(4) | 2·971 (6) |
| | 5·644 (1) | O(3)–O(4) | 3·162 (6) |
| | 6·662 (1) | O(4)–O(4)′ | 2·655 (6) |

Tetrahedron around P(1)

| | | | | | |
|---|---|---|---|---|---|
| P(1)–O(1) | 1·519 (5) Å | O(1)–O(2) | 2·581 (7) Å | O(1)–P(1)–O(2) | 119·1 (3)° |
| P(1)–O(2) | 1·475 (5) | O(1)–O(5) | 2·461 (6) | O(1)–P(1)–O(5) | 105·1 (3) |
| P(1)–O(5) | 1·580 (4) | O(1)–O(6) | 2·574 (6) | O(1)–P(1)–O(6) | 111·8 (2) |
| P(1)–O(6) | 1·589 (4) | O(2)–O(5) | 2·574 (6) | O(2)–P(1)–O(5) | 111·3 (3) |
| | | O(2)–O(6) | 2·434 (6) | O(2)–P(1)–O(6) | 105·1 (3) |
| | | O(5)–O(6) | 2·485 (6) | O(5)–P(1)–O(6) | 103·3 (2) |

Tetrahedron around P(2)

| | | | | | |
|---|---|---|---|---|---|
| P(2)–O(3) | 1·500 (4) Å | O(3)–O(4) | 2·581 (6) Å | O(3)–P(2)–O(4) | 119·6 (2)° |
| P(2)–O(4) | 1·484 (4) | O(3)–O(5) | 2·575 (6) | O(3)–P(2)–O(5) | 112·6 (2) |
| P(2)–O(5) | 1·590 (4) | O(3)–O(6) | 2·533 (6) | O(3)–P(2)–O(6) | 110·1 (3) |
| P(2)–O(6) | 1·590 (5) | O(4)–O(5) | 2·473 (6) | O(4)–P(2)–O(5) | 107·2 (3) |
| | | O(4)–O(6) | 2·425 (6) | O(4)–P(2)–O(6) | 104·1 (3) |
| | | O(5)–O(6) | 2·455 (6) | O(5)–P(2)–O(6) | 101·1 (2) |

Tetrahedron around Li

| | | | | | |
|---|---|---|---|---|---|
| Li—O(1) | 2×1·958 (12) Å | O(1)–O(4) | 2×3·441 (6) Å | O(1)–Li—O(4) | 2×123·2 (2)° |
| Li—O(4) | 2×1·954 (9) | O(1)–O(4)′ | 2×3·339 (6) | O(1)–Li—O(4)′ | 2× 93·6 (6) |
| | | O(1)–O(1)′ | 2·854 (6) | O(1)–Li—O(1)′ | 117·2 (2) |
| | | O(4)–O(4)′ | 2·655 (6) | O(4)–Li—O(4)′ | 85·6 (5) |

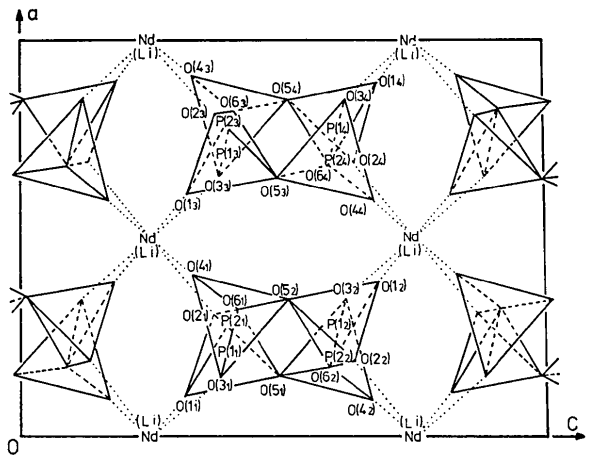


Fig. 1. [010] projection of the $LiNdP_4O_{12}$ structure.

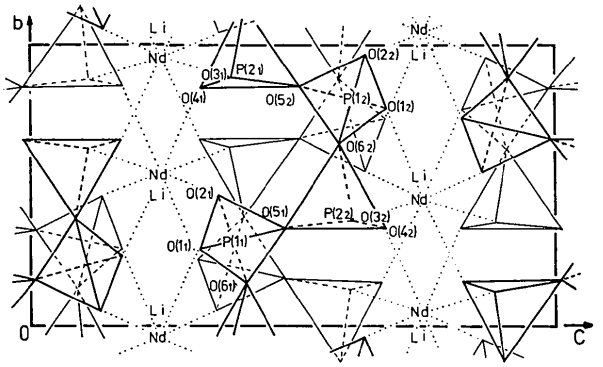


Fig. 2. [100] projection of the $LiNdP_4O_{12}$ structure.

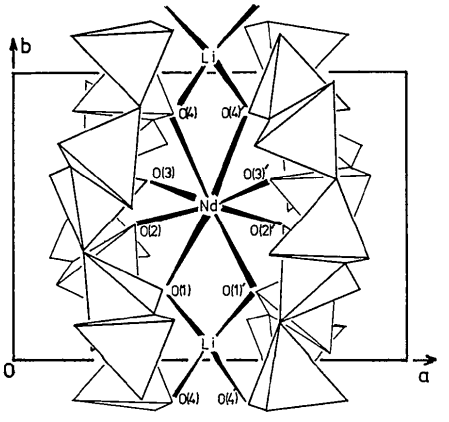


Fig. 3. Schematic view of the $-NdO_8-LiO_4-$ chain in the [001] direction.

Each $NdO_8$ dodecahedron on the twofold axes also has an approximate $\bar{4}$ symmetry along the *b* axis. Such a configuration can be seen also in the crystal structure of $NdNa_5(WO_4)_4$ (Hong & Dwight, 1974). The polyhedra share all their oxygen atoms with the corners and edges of neighbouring $PO_4$ and $LiO_4$ tetrahedra respectively. It is to be noted that the adjacent $NdO_8$ polyhedra do not share any oxygen atoms among them. The shortest Nd–Nd distance 5·644 Å is an intermediate value of those in $NdNa_5(WO_4)_4$ (6·450 Å) and $NdP_5O_{14}$ (5·194 Å) (Albrand, Attig, Fenner, Jeser & Mootz, 1974).

$LiO_4$ tetrahedra have a considerably distorted shape with a somewhat shorter average Li–O distance (1·956 Å) than that quoted in the literature (1·98 Å), *International Tables for X-ray Crystallography* (1962).

The helical arrangement of the corner-shared $PO_4$ tetrahedra chains can be clearly shown on [100] and [001] projection (Figs. 2 and 3). In comparison, helical chains in the $NdP_3O_9$ structure involve two more $PO_4$ groups in each chain unit and in the structure of $NdP_5O_{14}$ there is cross-linking of $(PO_3)_\infty$ ribbons (Hong, 1974).

The helical $(PO_3)_\infty$ chains in the structure and significant difference in Nd–Nd separation along each axis (5·644, 7·008, 6·621 Å) may be closely related to the observed strong anisotropy in laser characteristics (Otsuka, Yamada, Saruwatari & Kimura, 1975).

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