The Na position is of interest in such a tunnel structure. It is probable that the Na ion is, as seen in the sodium titanium bronze Na_xTiO_2 (Andersson & Wadsley, 1962*b*), located at the 'cubic position': the center of the oxygen pseudo-cube. (The Na occupancy, then, may be reduced to one half in order to relieve electrostatic repulsion between Na ions at the neighboring cubic positions at the same level of *y*.) In practice, however, Na is at the 2(*a*) site which is the center of a pseudo-square consisting of four O(2) atoms. One of the reasons why Na is actually found at the 2(*a*) site only may be that the 2(*a*) site is preferable to the 'cubic position' for Na to be accommodated in view of the electrostatic stability. If Na is located at the 'cubic position', Na again forms a square-planar coordination with two O(2) and two O(6) atoms at a distance of 2.540 (1) Å due to the striking distortion of the cube. Although the value of 2.540 Å would also be probable for the distance between Na and O atoms, Na is more stabilized at the 2(*a*) site, surrounded by four O(2) atoms, at a distance of 2.429 (1) Å.

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Structure of Lithium Niobium Nitride

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Abstract. Lithium niobium(V) nitride, Li_7NbN_4, $M_r = 197.49$, cubic, $Pa3$, $a = 9.829\ (1)$ Å, $V = 949.6\ (4)$ Å^3, $Z = 8$, $D_x = 2.77$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 22.8$ cm^{-1}, $F(000) = 720$, $T = 298$ K, final $R = 0.031$ for 369 unique reflections. Li_7NbN_4 crystallizes as a superstructure of the *anti*-fluorite structure. Each octant of the cubic structure contains a distorted Li_7Nb cube, which is oriented so that the eight Nb atoms in the unit cell occupy successively each of the distorted cube vertices. The Li_7Nb cube is further surrounded by a larger cube with N atoms at the vertices and face center positions. The Nb ordering produces rows along [100] containing three Li atoms and one Nb atom per unit cell, and an equal number of rows containing only Li atoms. The structure obtained differs from those previously proposed for cubic Li_7VN_4 and for distorted Li_7NbN_4 and Li_7TaN_4 [Juza, Giernn & Haug (1959). *Z. Anorg. Allg. Chem.* **300**, 61–71].

Introduction. Recently we have reported structures and properties of ternary transition-metal nitrides containing electropositive metals. These compounds are relatively simple to prepare as polycrystalline powders; however, in only a few instances have we been able to prepare single crystals (Vennos, Badding & DiSalvo, 1990). In an attempt to grow crystals of Ca_2ZnN_2 (Chern & DiSalvo, 1990) in an Nb tube using Li_3N as a flux, Ca was excluded and crystals of Li_7NbN_4 grew. Many of the known Li–transition-metal nitrides adopt superstructures of the *anti*-fluorite type; these include Li_3FeN_2 (Gudat, Kneip, Rabenau, Bronger & Ruschewitz, 1990), Li_6MoN_4 and $Li_{15}Cr_2N_9$ (Gudat, Haag, Kneip & Rabenau,

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Table 1. *Final atomic positions and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
Nb(1)	0.3722 (1)	0.3722	0.3722	0.0030 (1)
N(1)	0.2561 (4)	0.0143 (5)	−0.0117 (4)	0.0078 (11)
N(2)	0.2589 (4)	0.2589	0.2589	0.0046 (8)
Li(1)	0.6320 (10)	0.1397 (10)	0.1151 (10)	0.0175 (26)
Li(2)	0.1190 (11)	−0.0988 (10)	−0.1348 (11)	0.0171 (26)
Li(3)	0.1321 (9)	0.1321	0.1321	0.0125 (17)

* Equivalent isotropic U defined as $\frac{1}{3}$ of the trace of the orthogonalized U_{ij} tensor.

1990), and Li_5TiN_3 (Juza, Weber & Meyer-Simon, 1953). The structure of Li_7VN_4 has been reported, as determined by powder diffraction, to be the cubic *anti*-fluorite type, and the Li_7NbN_4 and Li_7TaN_4 phases were proposed to be rhombohedrally or tetragonally distorted superstructures of the fluorite lattice (Juza, Giernn & Haug, 1959). Here, we report the single-crystal structure of Li_7NbN_4 as a cubic superstructure of the fluorite lattice.

Experimental. All manipulations were carried out in an Ar-filled glove box due to the air sensitivity of reactants and product. Single crystals of Li_7NbN_4 were grown by heating Li_3N in an Nb container, using Zn_3N_2 and Ca_3N_2 as sources of nitrogen. An intimate mixture of the binary nitrides was sealed under argon in an Nb tube, which in turn was sealed in an evacuated quartz tube. The reaction mixture was heated from room temperature to 1273 K in 10 h, soaked at 1273 K for 30 h, cooled to 773 K in 15 h, and finally cooled to room temperature in 5 h. Microprobe analysis showed the crystals contained no Ca or Zn.

An irregularly shaped (approximately 0.19 × 0.16 × 0.27 mm), clear, colorless crystal was sealed in a 0.3 mm glass capillary; four-circle Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation, graphite monochromator; 24 independent reflections in 2θ range 15–25° used for refinement of cell dimensions, θ–2θ scan mode; scan speed variable from 1.5–29.30° min^{-1}, $3 \leq 2\theta \leq 55°$; $0 \leq h \leq 12$, $0 \leq k \leq 12$, $-12 \leq l \leq 12$; three standard reflections measured every 50 reflections; average standard reflection intensities varied ±2%; 2436 reflections collected. Empirical absorption correction applied to isotropically refined data; min. and max. correction factors were 0.830 and 0.892. After averaging symmetry-related reflections ($R_{\text{int}} = 0.028$) 369 unique reflections, of which 336 had $F_o > 3\sigma(F_o)$, were used to solve the structure.

Structure solved by direct methods using Nicolet *SHELXTL-Plus* software on a MicroVAX computer. Function minimized in least-squares refinement $\sum w(|F_o| - |F_c|)^2$, with $w = \sigma^{-2}$. Anisotropic refinement of all atoms, 37 parameters, converged to $R = 0.031$, $wR = 0.036$ and $S = 2.52$. Largest shift/e.s.d. = 0.009, max. and min. electron density in final difference Fourier map was 0.63 and -1.37 e Å^{-3} respectively. Scattering factors and f' and f'' values were taken from *International Tables for X-ray Crystallography* (1962, Vol. III). Final atomic positions are listed in Table 1.*

Discussion. The structure of the title compound can be described as a cubic superstructure of the *anti*-CaF_2 type. The superstructure doubles the basic *anti*-CaF_2 axes. In each octant of the superstructure, four nitrogen atoms occupy Ca sites of a CaF_2 cell, and the seven Li and one Nb atoms occupy F sites. The N atoms are slightly displaced from their ideal sites of a face-centered cubic cell, repeating at $a/2$. Note that in Table 1 and Fig. 1 the usual origin for the *anti*-CaF_2 lattice (anion at 0,0,0) has been shifted to ($\frac{1}{4}$,0,0) and that N(1) is slightly displaced from this position. The Nb and Li atoms are tetrahedrally coordinated by N. Fig. 1 shows how eight Li_7Nb distorted cubes are stacked in the unit cell. N atoms are omitted for clarity. The eight Nb atoms are distributed on each possible corner position of the smaller cubes. The Li_7Nb units are distorted due to the positive charge repulsion and the size difference of Li^+ and Nb^{5+} (smallest Li—Li distance 2.24, Li—Nb distance 2.69 Å); however, each Li_7Nb

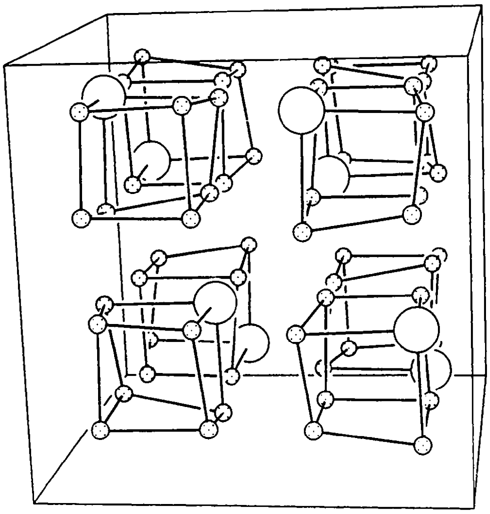

Fig. 1. Projection of the structure along [100]. N atoms are omitted for clarity; Nb atoms and Li atoms are represented by large open circles and small dotted circles, respectively.

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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 54713 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0379]

cube retains threefold symmetry with Nb and Li(3) lying on the threefold axis. Along [100], alternating zigzag chains of all Li atoms and chains containing one Nb atom per unit cell are apparent. Half the chains contain Li atoms exclusively; the other half contain one Nb atom and three Li atoms per unit cell. Each Nb atom is coordinated tetrahedrally by nitrogen at an average distance of 1.95 Å. This distance is much smaller than that found in the sixfold coordinate Nb in NbN (2.35 Å) (Christensen, 1977), but as expected for a lower coordination number, the Nb—N bond length is comparable to the W—N bond length (1.86 Å) in the $[WN_4]^{6-}$ tetrahedra found in Ba_3WN_4 (Gudat, Hohn, Kneip, Rabenau, 1991).

It is interesting to note that Li_7VN_4 (space group $P43n$, $a = 9.60$ Å) is not reportedly isostructural with the title phase (Juza, Giernn & Haug, 1959). Along [100] in the Nb phase, the closest Nb—Nb distance is 5.50 Å. In the vanadium phase, there is an irregular distribution of V atoms with the closest V—V distance (4.80 Å) equal to half the lattice constant. We find it questionable that the V atoms are so close, and because the structure of the vanadium phase was determined by powder methods in which Laue symmetries *m*3*m* and *m*3 are not easily distinguished, we suggest that the reported positions may be incorrect and should be redetermined by a single-crystal structural analysis. Juza *et al.* (1959) also report that Li_7NbN_4 and Li_7TaN_4 are isostructural and are rhombohedrally or tetragonally distorted structures based on Li_7VN_4. Because we have determined that Li_7NbN_4 is cubic, we also suggest that the structure of the Li_7TaN_4 phase should be determined by single-crystal studies.

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Structure of the Sodium Salt of *m*-Xylenesulfonate Monohydrate

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Abstract. Sodium 4-*m*-xylenesulfonate monohydrate, $Na^+.C_8H_9SO_3^-.H_2O$, $M_r = 226.2$, monoclinic, $P2_1/c$, $a = 15.750$ (5), $b = 8.783$ (2), $c = 7.625$ (2) Å, $\beta = 99.82$ (3)°, $V = 1039$ (1) Å^3, $Z = 4$, $D_x = 1.45$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 3.23$ cm^{-1}, $F(000) = 472$, $T = 294$ K, $R = 0.036$, $wR = 0.036$ for 2434 observations. The structure is formed by alternative stacks of *m*-xylenesulfonate and water molecules along the *c* axis, with O—H···O hydrogen bonds. The Na ions are situated at the centres of octahedra formed with O atoms of the SO_3 group and water molecule.

Introduction. It has already been established (Marder, Perry & Schaefer, 1989) that noncentrosymmetric organic salts can be used in optical information processing owing to their second-order nonlinear optical properties (NLO) (Chemla & Zyss,

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