JOURNAL OF SOLID STATE CHEMISTRY **65**, 63–71 (1986)

The Structure of the Lithium-Inserted Metal Oxide δLiV_2O_5

R. J. CAVA,* A. SANTORO,† D. W. MURPHY,* S. M. ZAHURAK,*
R. M. FLEMING,* P. MARSH,* AND R. S. ROTH†

**AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974, and †U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. 20234*

Received November 25, 1985; in revised form March 3, 1986

Employing neutron and X-ray powder diffraction analysis we have found that the compound at composition LiV_2O_5 formed at ambient temperature on insertion of Li into V_2O_5 has a structure which has been significantly altered from that of the original V_2O_5. The V_2O_5 host acts as a layered compound at high lithium contents: weak V–O bonds are broken and neighboring layers both shift and buckle to accommodate the inserted lithium ions. The inserted Li ions are in tetrahedral coordination with oxygen. © 1986 Academic Press, Inc.

Introduction

The insertion of lithium into the channels and cavities of transition-metal compounds at ambient temperature forms the basis for the potential use of these compounds as the active cathode materials in rechargeable electrochemical cells. The chemical, electrochemical, structural, and transport properties of these compounds have been studied extensively in recent years. We have been particularly interested in the crystal structures of lithium-inserted metal oxides in order to better understand the microscopic features of the insertion process through the characterization of the lithium–oxygen coordination polyhedra and changes in the geometry of the host structure of the accommodation of additional ions. In general, the materials are available only in polycrystalline powder (and not single-crystal) form due to volume changes which break up crystals during insertion. Thus we have employed neutron diffraction powder profile analysis to determine the structures of various compounds. The same technique, combined with X-ray diffraction, was employed to study LiV_2O_5.

The case of lithium insertion into V_2O_5 is of interest from both the electrochemical and the structural points of view. The reaction is important as it forms the basis for part of the discharge of Li/V_2O_5 primary cells (*1*) which are of significant commercial importance. Structurally, the V_2O_5 host is unusual as it falls in a category somewhere between a layered compound and a crystallographic shear (*CS*) structure. The ideal basic structure is that of a *CS* based on ReO_3: VO_6 "octahedra" form corner-shared blocks two octahedra wide and infinite in the two remaining directions. The blocks share edges with each other, resulting in planes of edge sharing octahedra running perpendicular to the short block dimension. In real V_2O_5, however, the VO_6

0022-4596/86 $3.00
Copyright © 1986 by Academic Press, Inc.
All rights of reproduction in any form reserved.

"octahedra" all have one long V–O bond as the V^{5+} ion is displaced toward one apex of the oxygen octahedron, making the coordination pyramidal. The result is that there are layers in the structure which are bound together only by the weak V–O bonds (*2*, *3*). Earlier studies have shown that transition metal oxide hosts with two intersecting sets of shear planes are generally structurally stable on insertion of lithium, basically only changing size on Li accommodation (*4*, *5*). Structures which are exclusively corner shared, such as ReO_3, can twist about shared corners to distort significantly on insertion of Li (*6–8*). Thus one might expect some distortion of the V_2O_5 host on insertion of Li if the V_2O_5 acts as a crystallographic shear structure, but considerably more distortion if it acts as a layer structure.

There have been several studies of the phases formed on ambient temperature insertion of Li into V_2O_5 (*9–11*), employing electrochemical and chemical synthesis, and powder X-ray diffraction for phase characterization. They have found the existence of three phases at ambient temperature, of approximate stoichiometries $Li_xV_2O_5$: $0.0 \leq x \leq 0.1$ (α), $0.35 \leq x \leq 0.70$ (ε), and $0.9 \leq x \leq 1.0$ (δ). The X-ray diffraction characterization found the α phase to show little change in lattice parameter from the pure V_2O_5 host. In the ε phase, the powder pattern remains similar to that of pure V_2O_5, indicating negligible structural distortion of the host. There is a significant increase in the lattice parameter parallel to the long V–O bond, indicating a weakening of the interlayer coupling. For the δ phase, however, a significant change in the X-ray powder diffraction pattern was reported. Although the pattern could be accounted for by a unit cell similar to those of α and ε $Li_xV_2O_5$, there were extra reflections present suggesting the possibility of significant structural distortion. Our earliest attempts to determine the structure of δLiV_2O_5 were frustrated by the similarities of the X-ray patterns of the ε and δ phases which suggest the two compounds to be more similar in structure than they actually are. The process of structure solution for δLiV_2O_5 involved several steps. These included determination of the true unit cell from the powder diffraction data, determination of a structural model by use of Patterson synthesis and least-squares structure refinement based solely on unambiguous structure factors, and finally Rietveld powder profile analysis.

Experimental

To synthesize LiV_2O_5, an excess of LiI in acetonitrile solution was added to powdered V_2O_5, and the resulting mixture was stirred for 24 hr at room temperature. The V_2O_5 used was prepared from reagent grade (Alfa) NH_4VO_3; reagent grade acetonitrile was distilled from P_2O_5 under Ar; and anhydrous LiI was dried at 150°C *in vacuo*. The product of the reaction was isolated by filtration and washed in acetonitrile. The filtrate and washings were combined, and the quantity of I_2 released during the reaction was determined by titration with a standardized aqueous $Na_2S_2O_3$ solution. The indicated stoichiometry was $Li_{1.0}V_2O_5$.

Neutron diffraction measurements were performed on the high resolution five counter powder diffractometer at the NBS Reactor, with neutrons of wavelength 1.5416(3) Å. The experimental conditions used to collect the data are presented in Table I. The powder profile refinement was performed using the Rietveld program (*12*) adapted to the 5 detector diffractometer design and modified to allow the refinement of background intensity (*13*). The high-resolution diffractometer when used with the experimental conditions described in Table I, gives Gaussian instrumental profiles over the entire 2θ angular range within a very good approximation. The peak profiles

TABLE I

EXPERIMENTAL CONDITIONS USED TO COLLECT THE NEUTRON POWDER INTENSITY DATA FOR LiV$_2$O$_5$

	Monochromatic beam:	
Wavelength	1.5416(3) Å	
Horizontal divergences	(a) In-pile collimator:	10′ arc;
	(b) Monochromatic beam collimator:	20′ arc
	(c) Diffracted beam collimator:	10′ arc
Monochromator mosaic spread	~15′ arc	
Sample container	Vanadium can ~10 mm in diameter	
Angular ranges scanned by each detector	10–40, 30–60, 50–80, 70–100, 90–120	
Angular step	0.05°	

from LiV$_2$O$_5$ were not described well by the standard Gaussian function. We therefore employed for the refinement of the neutron diffraction data the modification of the Rietveld program describing non-Gaussian profiles with the Pearson type VII distribution, which allows the lineshape to be varied continuously from Gaussian to Lorentzian by changing one additional profile parameter (*14*).

The neutron scattering amplitudes employed were $b(\mathrm{Li}) = -0.214$, $b(\mathrm{V}) = -0.038$, and $b(\mathrm{O}) = 0.58$ ($\times 10^{-12}$ cm) (*15*). Initial lattice parameters were obtained from the least-squares fit to the positions of the uniquely indexed lines. Approximate values of the background parameters were obtained at positions in the patterns free from diffraction effects. The background was assumed to be a straight line with finite slope and was refined separately for each counter. This description is quite adequate for the compounds studied and for the small angular interval scanned by each counter. In the refinement of the structural models, all structural, lattice, and profile parameters were refined simultaneously. Refinements were terminated when in two successive cycles the factor R_w (see Table III) varied by less than one part in a thousand.

X-ray diffraction measurements were performed by illumination of a sample of LiV$_2$O$_5$ powder enclosed in a 0.5-mm quartz capillary with the Cu$K\alpha$ radiation from a 15-kW X-ray source. Incident radiation was monochromated by (002) reflection from a focusing graphite crystal. The diffraction pattern was recorded in 0.05° increments in the range of 2θ between 10 and 90°. Twenty-six X-ray structure factors were obtained by fitting peaks of unambiguously indexed diffraction lines to Gaussian functions. The structure factors were corrected for Lorentzian and polarization effects and for absorption, and were then employed in a standard crystallographic refinement program to determine the vanadium positions.

Procedure and Results

Initial attempts to refine the structure from the neutron diffraction data and published unit cell parameters proved unsuccessful even when various monoclinic distortions were considered. The correct unit cell was finally found by using the indexing program of Visser (*16*) with 18 low-angle diffraction lines (<54° 2θ) whose positions had been precisely determined (±0.02° 2θ) from a fit of single neutron powder diffraction lines to Gaussian functions. The unit cell determined by that program was then employed in a second refinement which included a set of line positions up to 2θ of 90°. The positions and intensities of these peaks were determined by fitting the neutron data with the Pearson type VII function. The cell thus obtained allowed the unambiguous indexing and intensity measurement of 34 reflections to $2\theta = 90°$.

After correction for angular and multiplicity factors, a set of sharpened structure factors was obtained for use in a Patterson synthesis (*17*) by assuming the scattering to be dominated by oxygen and factoring out the effects of an approximate isotropic thermal parameter. The major features of the Patterson synthesis could all be attributed to the fact that the line of VO_5 edge-shared pyramids in V_2O_5 was retained in δLiV_2O_5 except that (a) the layers in V_2O_5 had become separated, and (b) there was buckling in the line of pyramids where they shared only corners. Employing that information, and the unit cell dimensions and centering, an initial model for the V_2O_5 host structure was devised. A probable position for Li, of tetrahedral coordination, was easily found in the interstices of the new V_2O_5 host array. A more accurate set of starting positional parameters for the Rietveld refinement were obtained by employing the same data in a standard structure refinement. Only three orthorhombic space groups were consistent with the observed reflections and the symmetry of the structural model: *Cmcm* (63), *Cmc*2_1 (36), and *Ama*2 (40). We chose the centrosymmetric space group *Cmcm* and refined the structural model to an acceptable starting point, $R(F) = 13\%$, for input to the Rietveld program, leaving the noncentrosymmetric space groups for later tests with the complete data set.

To maintain the relationship with the labeling adopted for the V_2O_5 unit cell axes ($a_0 = 11.510$, $b_0 = 4.369$, $c_0 = 3.563$) (2), we have assigned the unit cell of δLiV_2O_5 as $a_0 = 11.2423(8)$, $b_0 = 9.9054(9)$, and $c_0 = 3.6018(3)$ with 4 formula units per cell. This requires refinement and reporting of the structure in a nonstandard setting of the space groups listed above. The centrosymmetric space group is *Amam*: the general position (xyz) is repeated to $(x + \frac{1}{2}, \bar{y}, \bar{z})$, $(\bar{x} + \frac{1}{2}, y, \bar{z})$, $(\overline{xy}\ z)$ plus cell centering $(0\ \frac{1}{2}\ \frac{1}{2})$ and inversion. The Li atom and the oxygen atom O(3) are in positions 4*c* $(\frac{1}{4}, y, 0)$, and the two oxygen atoms (O1, O2) and the vanadium atom are in positions 8*f* $(x, y, 0)$. The total profile refinement (isotropic) in the centrosymmetric space group with vanadium omitted led to a structural model with final parameters very similar to those initially estimated. Difference Fourier synthesis for the structure showed a large anomaly at the vanadium site. Agreement indexes with vanadium included at the site determined from the difference map, but its position not refined, indicated the structure to be well determined ($\chi = 1.99$) but suggested further refinement might be possible. The difference Fourier synthesis revealed that the anomalies were associated with the oxygen atom positions. Refinements in the two noncentered space groups *A*2_1*am* and *Ama*2 did not shift the atoms from their *Amam* positions. For the final structural model, the oxygen atoms were described by anisotropic thermal parameters in the centrosymmetric space group *Amam*, with final agreement indexes of $R_N = 6.70\%$, $R_p = 5.96\%$, $R_w = 7.69\%$, $R_E = 4.37\%$, $\chi = 1.76$). The atom positions were within two standard deviations of those of the isotropic model except for the *y* parameter of O3, which shifted six standard deviations. Final structural and thermal parameters for δLiV_2O_5 are presented in Table II. We have not generally found anisotropic thermal parameters to be significant in previous structural refinements of lithium inserted metal oxides from neutron powder diffraction data. For δLiV_2O_5, however, where there can be bending of the V–O–V bond between corner-shared pyramids within the host layers, we are not surprised to find evidence for either the thermal or the positional disorder implied in the observation of significant anisotropy in the oxygen thermal parameters. Figure 1 presents the observed and calculated neutron diffraction profile for δLiV_2O_5 for the final structural model presented in Table II.

The neutron diffraction data indicated that the position of the vanadium atom was very close to (0.4, 0.2, 0) in positions 8*f*. To refine the position of the vanadium atom further, the structure factors from the X-ray powder diffraction pattern were employed in a conventional structure refinement program. Initial positional parameters

TABLE II

FINAL STRUCTURAL MODEL FOR δLiV_2O_5 IN SPACE GROUP *Amam*

$a = 11.2423(8)$			$b = 9.9054(9)$			$c = 3.6018(3)$		
Atom	Position	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}
Li	4*c*	0.75	0.109(2)	0	4.0(3)	—	—	—
O1	8*f*	0.1269(3)	0.0464(4)	0	1.2(1)	2.4(2)	4.3(2)	0.1(2)
O2	8*f*	0.0729(3)	0.2626(5)	0.5	0.5(1)	4.4(2)	0.5(1)	0.7(2)
O3	4*c*	0.25	0.2855(5)	0	0.1(2)	1.9(3)	1.6(3)	—
V[a]	8*f*	0.401(3)	0.206(3)	0	—			

[a] From X-ray diffraction data, thermal parameter not refined.

Pearson type VII lineshape: $2M = 3$

$R_N = 6.70\%$; $R_p = 5.96\%$; $R_w = 7.69\%$; $R_E = 4.37\%$.

$$R_N = \frac{\Sigma|I(\text{obs}) - I(\text{calc})|}{\Sigma I(\text{obs})}$$

$$R_p = \frac{\Sigma|y(\text{obs}) - y(\text{calc})|}{\Sigma y(\text{obs})}$$

$$R_w = \left\{\frac{\Sigma w[y(\text{obs}) - y(\text{calc})]^2}{\Sigma w[y(\text{obs})]^2}\right\}^{1/2}$$

$$R_e = \left\{\frac{N - P + C}{\Sigma w[y(\text{obs})]^2}\right\}^{1/2}$$

where N = number of independent observations, P = number of parameters, C = number of constraints, y = counts at angle 2θ, I = integrated Bragg intensities, and w = weights.

for all atoms were those of the neutron refinement. The thermal parameters for all atoms which were not varied in the X-ray refinement, were set at their (isotropic) neutron diffraction values, with that of Vanadium set to 0.5. Refinement of the positions of all atoms (excluding Li) led to an agreement between observed and calculated structure factors of 10.5% (R_F) and left all atoms, including vanadium, within two standard deviations of the positions determined by the neutron diffraction study. The position for the vanadium atom reported in Table II, and its standard deviation, are from the X-ray structure refinement. A representation of the structure projected down the c axis is presented in Fig. 2, and characteristics of the metal–oxygen coordination polyhedra are presented in Table III and Figs. 3 and 4.

Discussion

The insertion of Li into V_2O_5 at ambient temperature results in a separation, shifting, (by $\frac{1}{2}c$ for alternate layers) and puckering of the VO_5 layers to accommodate Li in a favorable coordination geometry with oxygen. If the insertion reaction giving $Li_xV_2O_5$ goes no further than $x = 1$, the reaction can be reversed with the V_2O_5 host returning to its original configuration. During this process, one long (2.79 Å (2)) V–O bond is broken; the bond is then reformed, with the shift of the layers back to their original positions, as the lithium is removed. The shift of the layers at ambient temperature occurs for Li content on the order of $x \sim 0.9$ in $Li_xV_2O_5$, the phase boundary between the ε and δ phases. At temperatures only slightly higher than ambient (*10*), 1Li/formula unit is accommodated by the V_2O_5 host without separation and slip of the layers; the ε phase is maintained. Although the characteristics of δLiV_2O_5 indicate a layer like nature for insertion into V_2O_5, the V_2O_5 host cannot be considered as layered in the sense that the transition metal dicalchogenides can be. Larger cations than Li cannot be inserted into V_2O_5 at ambient temperature, nor can organic molecules (*10*). The layer-like nature is also not displayed in the early stages of insertion of Li into V_2O_5. It is only at Li contents near 0.5/V, and then only at lower temperatures, that this happens.

TABLE III

METAL–OXYGEN COORDINATION POLYHEDRA GEOMETRY IN δLiV_2O_5

Li–O1	2 × 2.04(3) Å	V–O1	1.62(2) Å
Li–O2	2 × 2.38(3) Å	V–O2	2 × 1.91(2) Å
Li–O3	2 × 2.10(3) Å	V–O2	1.96(2) Å
O1–Li–O1	85.4(5)°	V–O3	1.87(2) Å
O3–Li–O3	118.6(7)°	O1–V–O2	69.6(4)°
O1–Li–O3	67.9(4)°	O1–V–O2	2 × 71.6(4)°
		O1–V–O4	76.1(5)°
		O2–V–O2	2 × 78.5(5)°
		O2–V–O3	2 × 89.0(5)°

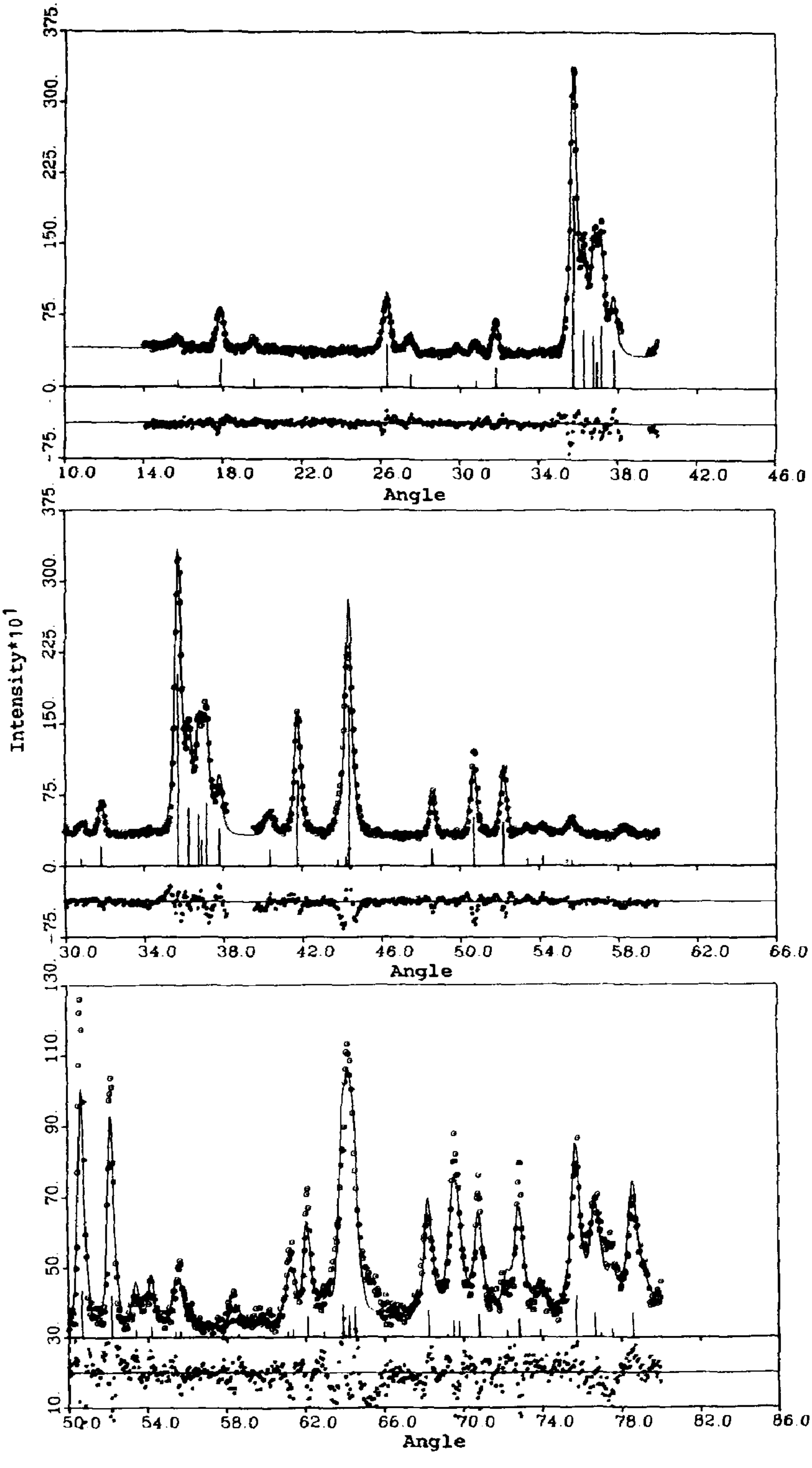

FIG. 1. Observed and calculated powder neutron diffraction profile intensities for δLiV_2O_5. Under the profile for each of the five detectors, plotted on the same scale, are the differences between the observed and calculated profiles.

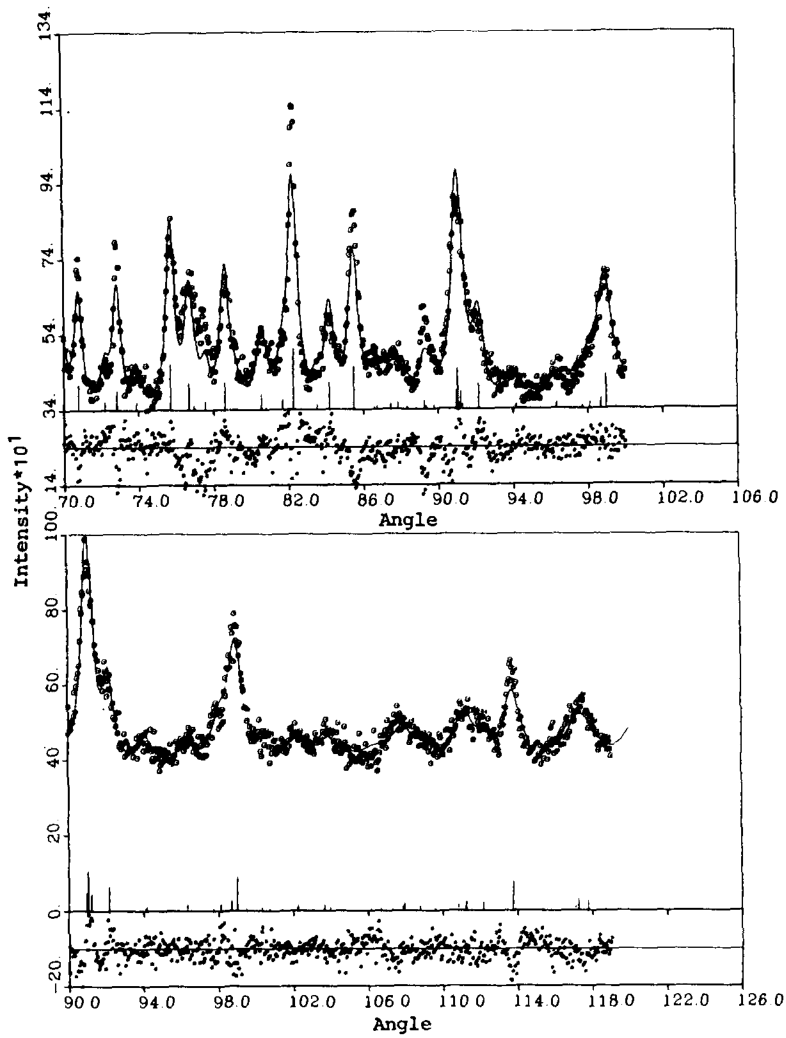

FIG. 1.—*Continued.*

The vanadium–oxygen coordination polyhedron in δLiV_2O_5 is presented in Fig. 3. The average V–O bond length to the oxygens in the base of the pyramid in δLiV_2O_5, 1.91 Å, is essentially unchanged from the 1.89 Å average found for V_2O_5 (*2*). In addition the short vanadyl V=O bond in δLiV_2O_5, at 1.62 Å, is not much different from that reported (*2*) for V_2O_5, 1.59 Å. This is in good agreement with the infrared V=O bond stretch near 1015 cm^{-1} which has been reported to be unchanged on insertion of V_2O_5 to δLiV_2O_5 (*10*). There is no oxygen at the apex opposite the short vanadyl bond, due to the shifting of the layers, and the coordination is pyramidal.

The lithium coordination polyhedron in δLiV_2O_5 is presented in Fig. 4. The coordination is tetrahedral, with bond distances between 2.04 and 2.10 Å to the nearest oxy-

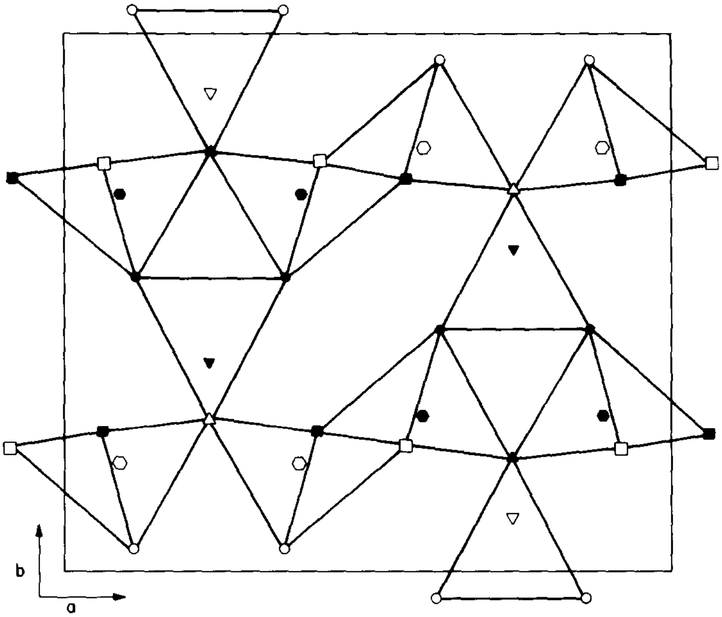

FIG. 2. The crystal structure of δLiV_2O_5 viewed down the c (3.6 Å) axis. Vanadium atoms are hexagons; lithium are triangles down; O1, O2, and O3 are circles, squares, and triangles up, respectively. Open symbols indicate $z = 0$ and closed symbols indicate $z = 0.5$. The vanadium–oxygen and lithium–oxygen coordination polyhedra are emphasized by solid lines.

gen atoms. Two second nearest oxygen atoms are at 2.38 Å but we do not consider this to be a bonding distance due to the four closer oxygens and include them with dotted lines in Fig. 4. Although the Li–O distances in the tetrahedron are quite regular, the bond angles are distorted from the ideal 109° (Table III). The lithium coordination polyhedron is comparable in size and geometry to coordination polyhedra commonly

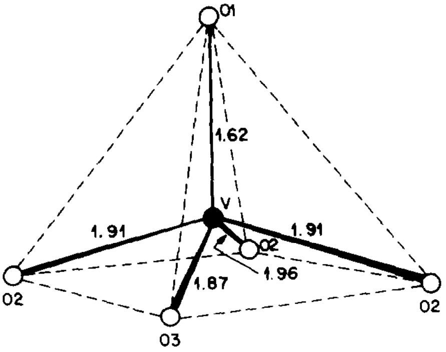

FIG. 3. Vanadium–oxygen coordination polyhedron in δLiV_2O_5. The closed circle indicates vanadium; the open circles, oxygen.

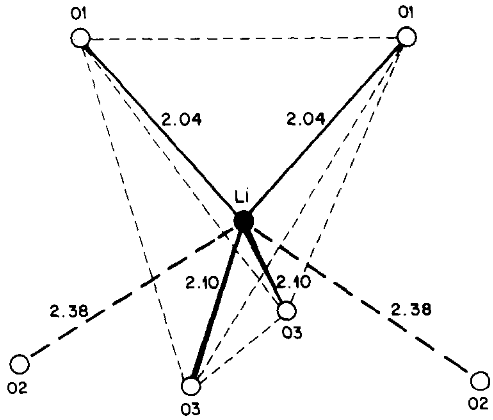

FIG. 4. Lithium–oxygen coordination polyhedron in δLiV_2O_5. The closed circle indicates lithium; the open circles, oxygen.

found in equilibrium lithium ternary metal oxides (*18*). We have now found Li to occupy four-, five-, and six-coordinate polyhedra with oxygen of various geometries in the lithium inserted metal oxides. The geometrical requirement for lithium accommodation appears only to be the existance of a coordination polyhedron with four to six near oxygen neighbors at distances of approximately 2 Å, a common occurrence in transition metal oxides. This ability of Li to have equilibrium coordination polyhedra of different geometry is probably one key factor in its accommodation into a wide variety of insertion hosts. The case of lithium insertion into V_2O_5 seems especially remarkable because of the large distortion of the host induced by the inserted Li ions to create interstitial positions of a favorable coordination geometry.

References

1. C. R. Walk and J. S. Gore, Electrochemical Society Extended Abstracts, Electrochemical Society Meeting, Toronto, Canada, May 11–16, 1975, paper No. 27.

2. H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Kristallogr.* **115,** 110 (1961).

3. A. Bystrom, K-A. Wilhelmi, and O. Brtozen, *Acta. Chem. Scand.* **4,** 1119 (1950).

4. R. J. Cava, A. Santoro, D. W. Murphy, S. Zahurak, and R. S. Roth, *J. Solid State Chem.* **48,** 309 (1983).

5. R. J. Cava, D. W. Murphy, and S. M. Zahurak, *J. Electrochem. Soc.* **130,** 2345 (1983).

6. P. J. Wiseman and P. G. Dickens, *J. Solid State Chem.* **17,** 91 (1976).

7. R. J. Cava, A. Santoro, D. W. Murphy, S. M. Zahurak, and R. S. Roth, *J. Solid State Chem.* **50,** 121 (1983).

8. R. J. Cava, A. Santoro, D. W. Murphy, S. M. Zahurak, and R. S. Roth, *J. Solid State Chem.* **42,** 251 (1982).

9. P. G. Dickens, S. J. French, A. T. Hight, and M. F. Pye, *Mat. Res. Bull.* **14,** 1295 (1979).

10. D. W. Murphy, P. A. Christian, F. J. DiSalvo and J. V. Waszczak, *Inorg. Chem.* **18,** 2800 (1979).

11. M. S. Whittingham, *J. Electrochem. Soc.* **123,** 316 (1976).

12. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).

13. E. Prince, "U. D. Tech. Note 1117" (F. J. Shorten, Ed.), pp. 8–9, National Bureau of Standards, Washington, D.C., 1980.

14. A. Santoro, R. J. Cava, D. W. Murphy, and R. S. Roth, "Neutron Scattering" (J. Faber, Ed.), p. 162, American Institute of Physics, Conf. Proc. No. 89, 1982.

15. G. E. Bacon, *Acta Crystallogr. Sect. A* **28,** 357 (1972).

16. J. W. Visser, *J. Appl. Crystallogr.* **2,** 89 (1969).

17. See, for instance, G. H. Stout and L. H. Jensen, "X-ray Structure Determination," pp. 270–288, Macmillan, New York, 1968.

18. See, for instance, D. Tranqui, R. D. Shannon, H. Y. Chen, S. Iijima, and W. H. Baur, *Acta Crystallogr. Sect. B* **35,** 2479 (1979).