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Superlattice formation in the lithiated vanadium oxide phases $Li_{0.67}V_6O_{13}$ and LiV_6O_{13}

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Two new lithiated phases of V_6O_{13} were formed by carefully tuning the temperature of electrochemical lithiation in a 'coffee-bag' type Li-ion battery at 2.78 V *versus* Li/Li^+. These were studied by single-crystal X-ray diffraction. A phase with the composition $Li_{2/3}V_6O_{13}$ was obtained at 308 K with a unit cell three times the volume of the original V_6O_{13} cell. A single crystal discharged at ambient temperature was shown to be LiV_6O_{13} and twice the unit-cell volume of the original V_6O_{13} cell. On lithiation, the structures retain their basic V_6O_{13} structure of alternating single and double layers of VO_6 octahedra. The lithium ions occupy chemically equivalent sites, where they coordinate fivefold to O atoms, and associate with the single layers of VO_6 octahedra. The insertion of lithium causes a significant elongation of one of the V—O bonds in each structure, which expands from 1.65 to 1.89 Å; this is due to the charge reduction of a specific V atom.

1. Introduction

There are several different vanadium oxides, all of which have long been investigated as potential cathode materials in Li-polymer batteries; a recent review of V—O structures, including vanadium with oxidation state greater than 3+, has been made by Zavalij & Whittingham (1999), where the V—O frameworks are divided into five classes by type of coordination polyhedra. In a battery context, V_6O_{13} has one of the highest theoretical capacities, 860 Wh kg^{-1}, of the vanadium oxides. The electrochemical properties of V_6O_{13} were first investigated by Murphy *et al.* (1979). The structure was refined by Wilhelmi *et al.* (1971) and can be described as consisting of alternating single and double layers of VO_6 octahedra parallel to (001). The octahedra are edge-sharing within the layers and corner-sharing between the layers (Fig. 1). The single layer (at $z = 0$) contains the V1 atom (suggested by an earlier electron density study by Bergström *et al.*, 1998*b*, to have oxidation state 4+) and the double layer at $z = 0.5$ includes the V2 (5+) and V3 (4+) atoms; the space group is $C2/m$ with the unit-cell dimensions $a = 11.922$ (2), $b = 3.680$ (1), $c = 10.138$ (2) Å and $\beta = 100.88$ (1)°. The discharge curve for a V_6O_{13} Li-ion battery (Fig. 2) shows that several different $Li_xV_6O_{13}$ phases occur as lithium is inserted, *e.g.* $x = 1, 2, 3$. The *quasi*-vertical sections of the discharge curves correspond to single-phase regions and the plateaus to two-phase regions. The phase transformations are closely reversible, which is an important requirement of an electrode material in a Li-ion battery. Clearly, a more detailed understanding of insertion/extraction mechanisms is important to understand the electrochemical cycling behaviour of

Li-ion batteries. Several researchers have examined these phases by different techniques: cyclic voltammetry and impedance spectroscopy (West *et al.*, 1985), X-ray powder diffraction (Gustafsson *et al.*, 1992), magnetic measurements, X-ray absorption and magnetic spectroscopic studies (Stallworth *et al.*, 1998). The precise structures of the phases formed in the low lithium-content region are still not determined, however. Single-crystal X-ray diffraction (XRD) provides a superior tool for this purpose. Previous single-crystal studies have been performed for the lithium-rich phases $Li_2V_6O_{13}$ (Bergström *et al.*, 1997) and $Li_3V_6O_{13}$ (Bergström *et al.*, 1998*a*). The basic structural framework of V—O octahedra in $Li_2V_6O_{13}$ is, in principle, the same as for V_6O_{13}; the lithium ions in $Li_2V_6O_{13}$ associate with the single layer. The insertion of lithium between the layers causes a *c*-axis expansion from $c = 10.140$ (1) Å in pure V_6O_{13} to $c = 10.892$ (3) Å in $Li_2V_6O_{13}$. An electron-density study of the $Li_2V_6O_{13}$ structure shows that as lithium ions are inserted in the material, the V2 atom would appear to be reduced from 5+ to 4+ (Bergström *et al.*, 1999). In the $Li_3V_6O_{13}$ structure, the lithium ions move into the single layers and the *c* axis contracts. This paper describes detailed studies of the two low lithium phases $Li_{2/3}V_6O_{13}$ and LiV_6O_{13}.

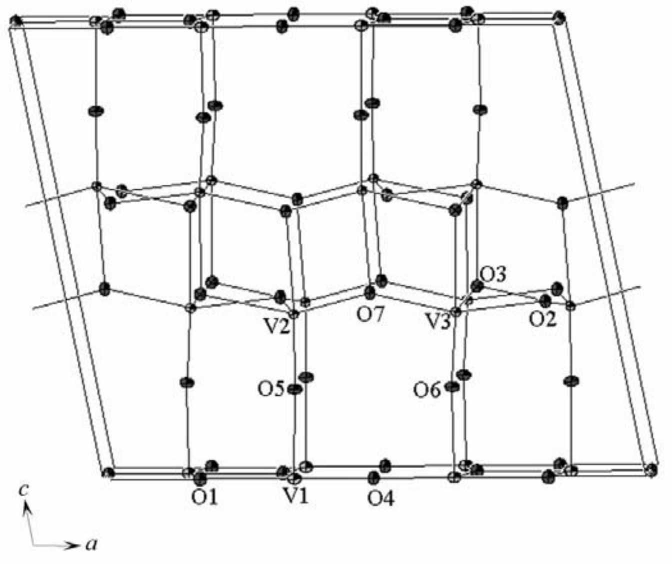

Figure 1
The crystal structure of V_6O_{13} viewed along the *b* axis. Displacement ellipsoids are drawn at 90% probability.

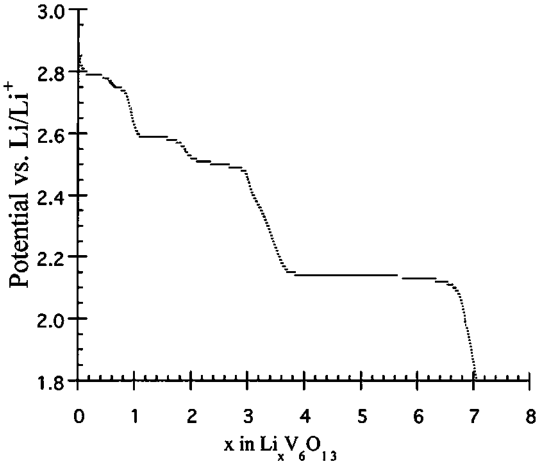

Figure 2
Discharge curve of a ⟨Li | liquid electrolyte | V_6O_{13}⟩ ‘coffee-bag’ type cell.

2. Experimental

2.1. Growth of V_6O_{13} single crystals

V_6O_{13} powder was prepared by controlled thermal decomposition of ammonium vanadate, NH_4VO_3 (Lampe-Önnerud & Thomas, 1995). The powder was used together with a $TeCl_4$ transport agent (Merck, as received) as the starting materials for growth of V_6O_{13} single crystals by chemical vapour transport (CVT). The starting materials were mixed in a 20:1 mass ratio and placed at one end of a sealed silica tube, which was subjected to a temperature gradient of 943–923 K along the furnace axis (Saeki *et al.*, 1973). The crystals thus obtained were of approximate size 0.1 × 0.1 × 0.2 mm.

2.2. Lithiation of V_6O_{13} single crystals

Electrochemical lithiation of V_6O_{13} single crystals was performed by incorporating single crystals into the composite cathode of ⟨Li | liquid electrolyte | V_6O_{13}⟩ ‘coffee-bag’ type electrochemical cells. The electrochemically active material in the cathode consisted of the phase-pure V_6O_{13} powder referred to above. One of the cells was placed in a furnace at slightly elevated temperature (308 K) to enhance the lithium diffusion in the single crystals and the reaction kinetics of the cell. The other cell was held at room temperature. The cells were then discharged slowly to the selected voltage of 2.78 V, starting at 3.0 V *versus* Li/Li$^+$. The discharge was controlled by a Mac Pile II® potentiostat, where the potential was changed in steps of −10 mV when the current density had fallen to 2 μA cm^{-2}. The cell was thus kept close to electrochemical equilibrium during the entire discharge. The lithiated single crystals were then recovered from the cathode under a microscope and mounted on an X-ray goniometer.

2.3. Single-crystal X-ray diffraction of $Li_{2/3}V_6O_{13}$

The single crystal discharged at 308 K was mounted on a Stoe image-plate detector system (IPDS) diffractometer with graphite-monochromated Mo $K\bar{\alpha}$ radiation. The crystal was twinned and had several overlapping reflections. All overlapping reflections were excluded from the data; this explains the small number of integrated reflections. A list of experimental and refinement details is presented in Table 1. Intensities were corrected for Lorentz, polarization and absorption factors using the Stoe programs *X-red* and *X-prep* (Stoe & Cie, 1998).

Table 1
Experimental details.

	$Li_{0.67}V_6O_{13}$	LiV_6O_{13}
Crystal data		
Chemical formula	$Li_{0.67}V_6O_{13}$	LiV_6O_{13}
Chemical formula weight	518.30	520.57
Cell setting, space group	Monoclinic, $C2/m$	Monoclinic, $C2/m$
a, b, c (Å)	21.848 (2), 3.6904 (3), 17.245 (2)	21.955 (10), 3.686 (2), 11.850 (6)
β (°)	105.01 (1)	110.656 (10)
V (Å^3)	1343.0 (2)	897.3 (8)
Z	6	4
D_x (Mg m^{-3})	3.861	3.852
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	3403	50
θ range (°)	2.45–28	17.50–39.0
μ (mm^{-1})	6.09	6.07
Temperature (K)	293	293
Crystal form, colour	Needle, black	Needle, black
Crystal size (mm)	0.2 × 0.1 × 0.1	0.28 × 0.11 × 0.11
Data collection		
Diffractometer	Stoe IPDS	Stoe four-circle
Data collection method	Omega scan	$\theta/2\theta$ scan
Absorption correction	Numerical	Integration
T_{min}	0.2695	0.3780
T_{max}	0.4440	0.5855
No. of measured, independent and observed parameters	3403, 1197, 1150	10 855, 5464, 10 855
Criterion for observed reflections	$I_{net} > -15.0\sigma(I_{net})$	$I_{net} > -15.0\sigma(I_{net})$
R_{int}	0.0563	0.0328
θ_{max} (°)	28	52.00
Range of h, k, l	$-28 \rightarrow h \rightarrow 28$	$-24 \rightarrow h \rightarrow 48$
	$-4 \rightarrow k \rightarrow 4$	$0 \rightarrow k \rightarrow 8$
	$-21 \rightarrow l \rightarrow 22$	$-25 \rightarrow l \rightarrow 26$
No. and frequency of standard reflections	–	5 every 180 min
Intensity decay (%)	–	11.3
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0356, 0.0838, 3.78	0.0269, 0.0573, 2.34
No. of reflections and parameters used in refinement	1197, 179	5464, 122
Weighting scheme	$w = 1/[\sigma^2(I) + (0.01I)^2]$	$w = 1/[\sigma^2(F) + 0.0150F^2]$
$(\Delta/\sigma)_{max}$	0.0008	0.0021
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.78, −0.98	1.504, −1.675
Extinction method	None	Becker & Coppens (1974), anisotropic type II
Extinction coefficient	–	0.7502E-07; 0.6778E-07 0.1111E-07; 0.6345E-07 −0.2642E-07; −0.2650E-07

Computer programs used: *STOEDATR*, *MULTAN*80, *DUPALS*, *DISTAN* (Lundgren, 1983).

2.4. Single-crystal X-ray diffraction of LiV_6O_{13}

The single crystal which was lithiated at room temperature had the composition LiV_6O_{13}. It was mounted on a Stoe & Cie four-circle diffractometer. The cell parameters were refined by a least-squares method using data from 50 reflections in the range $17 < \theta < 39°$. Standard reflections were measured every 180 min during the data collection; these showed only minor variations (< 2%) during the first part of the data collection. After *ca* 4600 reflections (~42% of the total data set) larger variations indicated the onset of crystal decomposition. This part of the intensity data was appropriately corrected. Data reduction was carried out using the *STOEDATRED*, *LSQLIN* and *ABSSTOE* programs (Lundgren, 1983). Experimental and refinement details are summarized in Table 1.

3. Symmetry and refinements

One can reasonably assume that on insertion or extraction of lithium, the basic V_6O_{13} structural host remains virtually intact with its alternating single and double layers of VO_6 octahedra. However, it is equally reasonable that the most appropriate choice of unit-cell axes will change for $Li_{2/3}V_6O_{13}$ and LiV_6O_{13} as new symmetries are created on the successive introduction of lithium.

3.1. The $Li_{2/3}V_6O_{13}$ structure

From the symmetry and systematic extinctions in the diffraction pattern, a monoclinic unit cell was chosen with the space group $C2/m$. This new cell has a volume three times that of the original V_6O_{13} unit cell and is related to it as given below.

$$\begin{pmatrix} \mathbf{a}_{new} \\ \mathbf{b}_{new} \\ \mathbf{c}_{new} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 2 \\ 0 & 1 & 0 \\ 1 & 0 & -1 \end{pmatrix} \times \begin{pmatrix} \mathbf{a}_{orig} \\ \mathbf{b}_{orig} \\ \mathbf{c}_{orig} \end{pmatrix} \tag{1}$$

The atomic coordinates of V_6O_{13} (Wilhelmi *et al.*, 1971) were thus transformed and the number of atoms in the new cell tripled to fill it with the basic V_6O_{13} structure. The labelling of the new atoms is such that V1 of V_6O_{13} becomes V11, V12 and V13 in $Li_{2/3}V_6O_{13}$ *etc*. The structure is shown in Fig. 3. The $Li_{2/3}V_6O_{13}$ structure was solved using difference Fourier syntheses using the *JANA*98 refinement program (Petriçek & Dušek, 1997). The refinements, using 1197 reflections and 180 independent parameters, led to $R(F) = 0.035$ and $wR(F^2) = 0.090$. The final refined fractional coordinates are given in Table 2; selected geometrical parameters are given in Table 3.[1]

3.2. The LiV_6O_{13} structure

The space group $C2/m$ was chosen on the basis of the symmetry and systematic extinctions in the diffraction data.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS0075). Services for accessing these data are described at the back of the journal.

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the $Li_{2/3}V_6O_{13}$ structure.

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
V11	0.12135 (3)	0	0.23855 (4)	0.0063 (2)
V12	0.44842 (3)	0	−0.09924 (4)	0.0084 (2)
V13	0.79923 (3)	0	0.54822 (3)	0.0061 (2)
V21	0.25918 (3)	0	0.15174 (4)	0.0050 (2)
V22	0.58889 (3)	0	−0.17546 (4)	0.0049 (2)
V23	0.94004 (3)	0	0.47324 (4)	0.0108 (2)
V31	0.36205 (3)	0	0.34553 (4)	0.0065 (2)
V32	0.69178 (3)	0	0.02124 (4)	0.0053 (2)
V33	0.02271 (3)	0	0.69348 (4)	0.0051 (2)
O11	0.38940 (14)	0	−0.2145 (2)	0.0072 (16)
O12	0.0625 (2)	0	0.1202 (3)	0.0121 (15)
O13	0.7298 (2)	0	0.4499 (2)	0.0069 (13)
O21	0.4251 (2)	0	0.4574 (3)	0.0051 (13)
O22	1.0865 (2)	0	0.7966 (2)	0.0051 (11)
O23	0.7577 (2)	0	0.1254 (2)	0.0054 (12)
O31	0.5485 (2)	0	−0.2998 (2)	0.0059 (12)
O32	0.2182 (2)	0	0.0309 (3)	0.0063 (14)
O33	0.8861 (2)	0	0.3553 (3)	0.0071 (12)
O41	1/2	0	0	0.015 (2)
O42	0.82961 (19)	0	0.6653 (2)	0.0081 (16)
O51	0.52580 (15)	0	−0.13944 (18)	0.0103 (10)
O52	0.20042 (15)	0	0.19700 (18)	0.0109 (10)
O53	0.86374 (16)	0	0.5180 (2)	0.0140 (11)
O61	0.62703 (16)	0	0.05310 (18)	0.0106 (10)
O62	0.29444 (16)	0	0.3696 (2)	0.0132 (10)
O63	0.95526 (15)	0	0.71941 (18)	0.0111 (10)
O71	0.6539 (2)	0	−0.0908 (3)	0.0065 (13)
O72	0.3280 (2)	0	0.2331 (2)	0.0080 (12)
O73	1.0085 (2)	0	0.4234 (3)	0.0065 (12)
Li1	0.7379 (6)	0	0.3396 (6)	0.036 (4)

The unit cell has twice the volume of the original V_6O_{13} cell and is related to it by the equation

$$\begin{pmatrix} \mathbf{a}_{\rm new} \\ \mathbf{b}_{\rm new} \\ \mathbf{c}_{\rm new} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 2 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \times \begin{pmatrix} \mathbf{a}_{\rm orig} \\ \mathbf{b}_{\rm orig} \\ \mathbf{c}_{\rm orig} \end{pmatrix}. \qquad (2)$$

The atomic coordinates of V_6O_{13} (Wilhelmi *et al.*, 1971) were transformed correspondingly and the number of atoms required to fill the LiV_6O_{13} unit cell was thus doubled (Fig. 4). The labelling of the atoms was performed in the same way as mentioned above. Anisotropic extinction correction was used since there were large intensity deviations in certain groups of reflections. The refined extinction coefficients differ from each other and show that the extinction is different in different directions. By using the anisotropic extinction correction the R value decreased significantly. The structure was again solved using difference Fourier syntheses using the *DUPALS* program package (Lundgren, 1983). The refinements led to $R(F) = 0.027$ and $wR(F^2) = 0.057$, using 5464 reflections and refining 122 independent parameters. The final refined fractional coordinates are given in Table 4; Table 5 gives selected geometrical parameters.

Table 3
Selected geometric parameters (Å) for the $Li_{2/3}V_6O_{13}$ structure.

V11—O11$^{\rm i}$	1.8923 (8)	V21—O32	2.044 (4)
V11—O11$^{\rm ii}$	1.8923 (8)	V21—O52	1.666 (3)
V11—O12	2.112 (4)	V21—O71$^{\rm iv}$	2.396 (6)
V11—O42$^{\rm iii}$	1.726 (3)	V21—O72	1.770 (4)
V11—O52	2.034 (3)	V22—O22$^{\rm ix}$	1.9044 (11)
V11—O63$^{\rm iii}$	1.989 (3)	V22—O22$^{\rm x}$	1.9044 (11)
V12—O11	2.071 (3)	V22—O31	2.096 (4)
V12—O12$^{\rm i}$	1.8835 (10)	V22—O51	1.652 (3)
V12—O12$^{\rm ii}$	1.8835 (10)	V22—O71	1.754 (5)
V12—O41	1.7888 (6)	V22—O72$^{\rm iv}$	2.284 (5)
V12—O51	1.986 (3)	V23—O21$^{\rm xi}$	1.8815 (9)
V12—O61$^{\rm iv}$	2.008 (3)	V23—O21$^{\rm xii}$	1.8815 (9)
V13—O13	1.960 (4)	V23—O33	2.069 (4)
V13—O13$^{\rm v}$	1.9540 (18)	V23—O53	2.011 (4)
V13—O13$^{\rm vi}$	1.9540 (18)	V23—O73	1.909 (6)
V13—O42	1.955 (3)	V23—O73$^{\rm xiii}$	1.845 (5)
V13—O53	1.624 (4)	O13—Li1	1.956 (12)
V13—O62$^{\rm iii}$	2.775 (4)	O42—Li1$^{\rm v}$	2.350 (9)
V21—O23$^{\rm vii}$	1.8985 (12)	O42—Li1$^{\rm vi}$	2.350 (9)
V21—O23$^{\rm viii}$	1.8985 (12)	O62—Li1$^{\rm vii}$	2.206 (7)
		O62—Li1$^{\rm viii}$	2.206 (7)

Symmetry codes: (i) $\frac{1}{2}-x, -\frac{1}{2}-y, -z$; (ii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iii) $1-x, -y, 1-z$; (iv) $1-x, -y, -z$; (v) $\frac{3}{2}-x, -\frac{1}{2}-y, 1-z$; (vi) $\frac{3}{2}-x, \frac{1}{2}-y, 1-z$; (vii) $x-\frac{1}{2}, y-\frac{1}{2}, z$; (viii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (ix) $x-\frac{1}{2}, y-\frac{1}{2}, z-1$; (x) $x-\frac{1}{2}, \frac{1}{2}+y, z-1$; (xi) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (xii) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (xiii) $2-x, -y, 1-z$.

Full occupation of lithium ions was confirmed by refining the occupancy factors for both structures. The maximum deviation of the occupancy factors was 0.5% for the $Li_{2/3}V_6O_{13}$ structure. In both structures the anisotropic displacement parameters for the lithium ions are somewhat elongated towards neighbouring O atoms in the *a*-axis direction; this behaviour has previously been observed in other lithiated V_6O_{13} compounds (Bergström *et al.*, 1997).

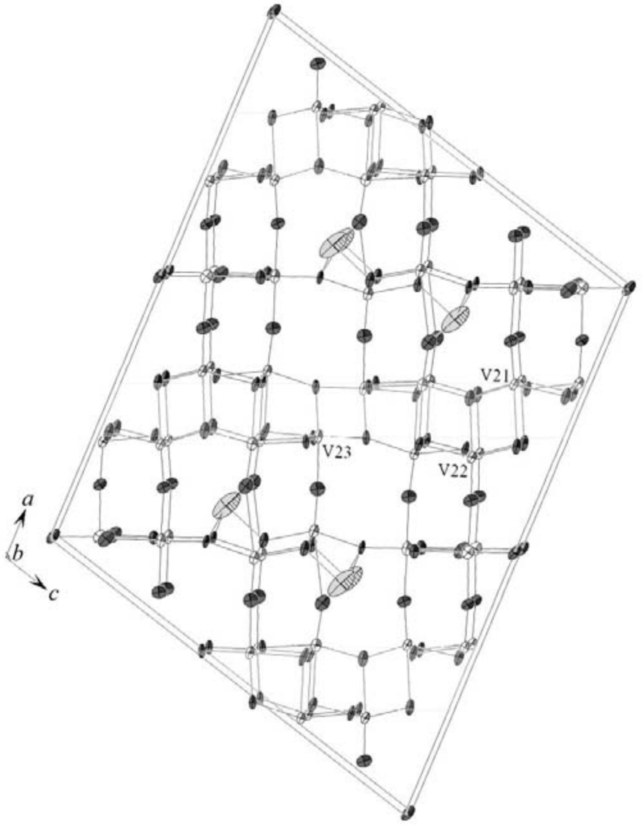

Figure 3
The crystal structure of $Li_{2/3}V_6O_{13}$ viewed along the *b* axis. The double layers are shaded and displacement ellipsoids are drawn at 90% probability.

4. Discussion

The structures of $Li_xV_6O_{13}$ for x = 0, 2/3 and 1 are closely similar in terms of V—O coordination. They can all be described in terms of alternating single and double layers of edge-sharing VO_6 octahedra; the layers are connected *via* corner-sharing octahedra. In both lithiated phases the lithium ions insert between the single and double layers and coordinate to the O atoms in the single layer and to the O atoms between the layers. The lithium ions distribute regularly through the structure in fully occupied, chemically equivalent sites with fivefold oxygen coordination in tetragonal pyramids; Li—O distances are in the range 1.966 (1)–2.345 (1) Å for x = 1, and 1.95 (1)–2.353 (8) Å for x = 2/3.

Commonly in a V^{5+} coordination polyhedra a vanadyl group (V═O) is present, whose bond length (1.55–1.75 Å) is short compared with other bonds in the polyhedra (1.9–2.0 Å; Zavalij & Whittingham, 1999). This bond is very often termed a double bond (Shriver *et al.*, 1994). From earlier electron density studies of $Li_2V_6O_{13}$ (Bergström *et al.*, 1998*b*), it was concluded that insertion of lithium caused a formal reduction of the V2 atom from +5 to +4. This reduction was also expressed in the V2—O5 bond length, which was significantly elongated. Only one of the chemically equivalent but crystallographically independent V atoms in each of the two new structures presented here, related to V2 in the original V_6O_{13} structure, exhibits this same increase in V—O bond length. The elongation seems to relieve some distortion in the octahedra and allows the angles to come closer to 90°. The coordination octahedron for V2 in V_6O_{13} is shown in Fig. 5. The corresponding octahedra for V21 and V22 in $Li_{2/3}V_6O_{13}$ are very similar (Figs. 6*a* and *c*, respectively), while the elongation of the V23—O53 bond due to the reduction of the V atom is shown in Fig. 6(*b*). In the LiV_6O_{13} structure there are two independent V atoms for which the V21 shows the same elongation as mentioned above. In both structures the reduced

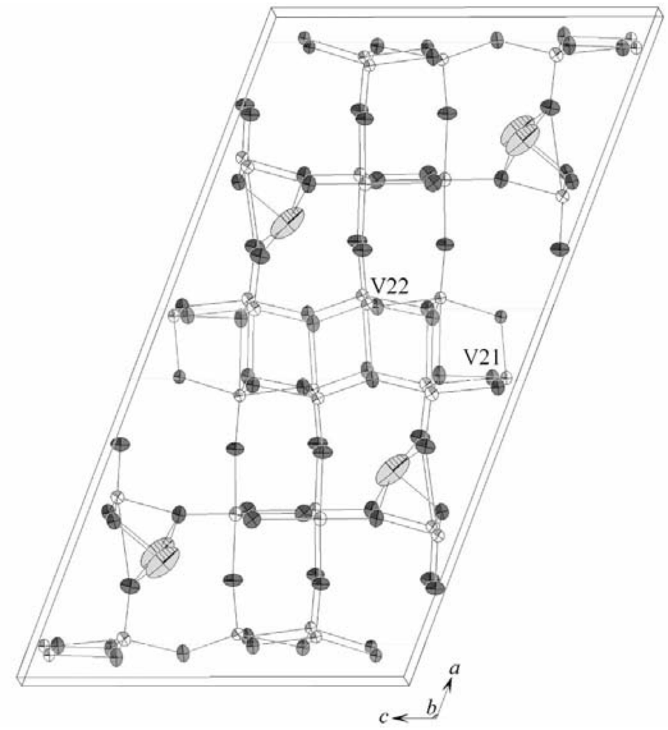

Figure 4
The crystal structure of LiV_6O_{13} viewed along the *b* axis. The double layers are shaded and displacement ellipsoids are drawn at 90% probability.

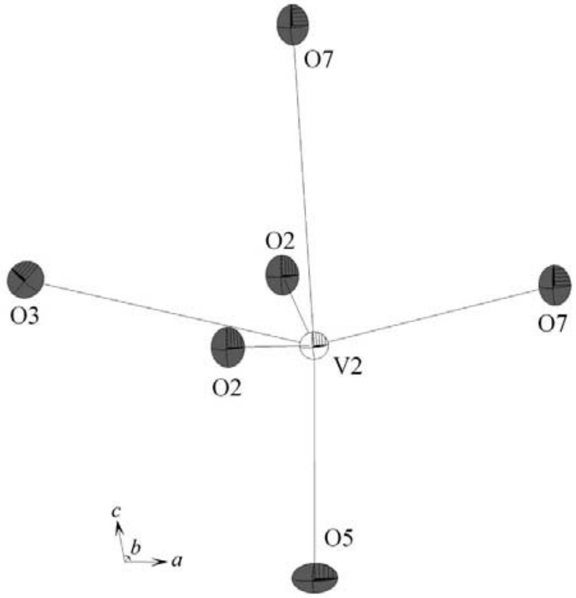

Figure 5
VO_6 octahedra for the V2 atom in V_6O_{13}.

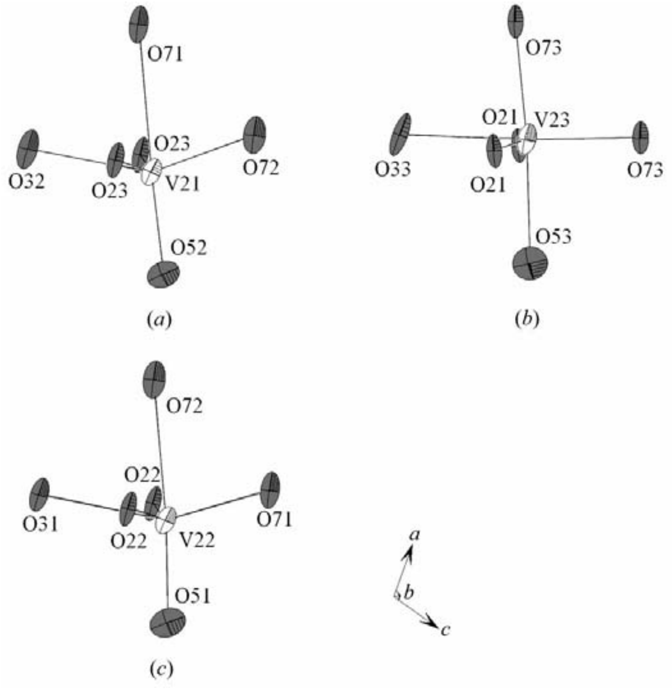

Figure 6
VO_6 octahedra in the $Li_{2/3}V_6O_{13}$ structure for (*a*) the V21 atom, (*b*) the reduced V23 atom and (*c*) the V22 atom.

Table 4
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the LiV_6O_{13} structure.

$U_{eq} = (1/3)\Sigma_i\Sigma_jU^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
V11	−0.22440 (1)	0	−0.0728	0.0057
V12	0.24978 (1)	0	0.39391 (1)	0.00609 (5)
V21	−0.04686 (1)	0	0.03972 (1)	0.00820 (5)
V22	0.42919 (1)	0	0.51767 (1)	0.00497 (4)
V31	−0.07310 (1)	0	−0.28880 (1)	0.00478 (4)
V32	0.43618 (1)	0	0.22826 (1)	0.00613 (5)
O11	0.75350 (4)	0	1.07500 (6)	0.0072 (2)
O12	0.24874 (4)	0	0.56894 (7)	0.0095 (3)
O21	−0.06013 (4)	0	−0.44368 (6)	0.0071 (2)
O22	0.44623 (4)	0	0.06385 (6)	0.0073 (2)
O31	−0.04309 (4)	0	0.21544 (6)	0.0080 (2)
O32	0.44950 (4)	0	0.69911 (6)	0.0068 (2)
O41	0.74967 (4)	0	0.75183 (6)	0.0109 (3)
O51	−0.14567 (4)	0	−0.02786 (7)	0.0111 (3)
O52	0.34862 (4)	0	0.45210 (7)	0.0103 (3)
O61	−0.15270 (4)	0	−0.32901 (7)	0.0098 (3)
O62	0.35732 (4)	0	0.19222 (8)	0.0132 (3)
O71	−0.04508 (4)	0	−0.11457 (6)	0.0071 (2)
O72	0.45801 (4)	0	0.39539 (6)	0.0085 (2)
Li1	−0.1849 (2)	0	0.2422 (3)	0.041 (2)

V atoms move very close to each other and form what can be considered a metal–metal bond with bond distances 2.543 (1) Å for the V23—V23 bond in the $Li_{2/3}V_6O_{13}$ structure and 2.547 (1) Å for V21—V21 in the LiV_6O_{13} structure. The coordination polyhedron for the V1 atom in the V_6O_{13} structure is a slightly distorted octahedron with bond distances in the range 1.766 (1)–2.064 (4) Å (Wilhelmi *et al.*, 1971; Fig. 7*a*). As lithium ions are inserted and the V2—O5 bond is elongated, the V1—O5 bond is shortened from 1.9722 (5) to 1.639 (1) Å (Bergström *et al.*, 1998*b*), which means that the V1—O5 bond is a double bond rather than a V2—O5 bond. There is also an increase in the V1—O4 bond from 1.7639 (2) to 1.887 (1) Å. The coordination for the V1 atom hereby changes and forms a square pyramid. This occurs for the V13 atom in the $Li_{2/3}V_6O_{13}$ structure (Fig. 7*b*) and for the V11 in the LiV_6O_{13} structure. The coordination change for the V1 atom is a consequence of the reduction of the V2 atom and its adherent coordination changes.

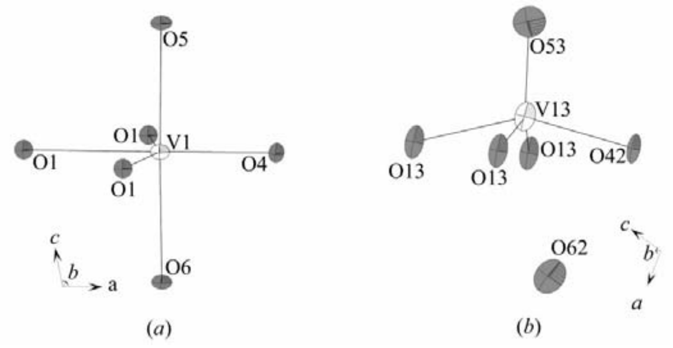

Figure 7
Coordination polyhedra for (*a*) V1 in V_6O_{13} and (*b*) V13 in $Li_{2/3}V_6O_{13}$.

Table 5
Selected geometric parameters (Å) for the LiV_6O_{13} structure.

V11—O11^{i}	1.9758 (12)	V21—O31	2.0546 (13)
V11—O11^{ii}	1.9478 (10)	V21—O51	2.0303 (12)
V11—O11^{iii}	1.9478 (10)	V21—O71	1.8424 (12)
V11—O41^{i}	1.9510 (13)	V21—O71^{iv}	1.8968 (12)
V11—O51	1.6193 (11)	V22—O21^{viii}	1.8936 (10)
V11—O62^{iv}	2.7576 (14)	V22—O21^{ix}	1.8936 (10)
V12—O12	2.0823 (13)	V22—O32	2.0360 (13)
V12—O12^{ii}	1.8925 (10)	V22—O52	1.6622 (11)
V12—O12^{iii}	1.8925 (10)	V22—O72	1.774 (4)
V12—O41^{v}	1.7313 (12)	V22—O72^{v}	2.323 (4)
V12—O52	2.0320 (12)	Li1—O11^{x}	1.9658 (11)
V12—O61^{iv}	1.9946 (13)	Li1—O41^{ii}	2.3447 (10)
V21—O22^{vi}	1.8794 (10)	Li1—O41^{iii}	2.3447 (10)
V21—O22^{vii}	1.8794 (10)	Li1—O62^{xi}	2.2341 (9)
		Li1—O62^{xii}	2.2341 (9)

Symmetry codes: (i) $x-1, y, z-1$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, 1-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (v) $\frac{3}{2}+x, \frac{1}{2}+y, 1+z$; (vi) $-1-x, y-1, -z$; (vii) $-1-x, y, -z$; (viii) $-x, y-1, 1-z$; (ix) $-x, y, 1-z$; (x) $1+x, y, 1+z$; (xi) $-x, y-1, -z$; (xii) $-x, y, -z$.

4.1. Phase transformation between $Li_{2/3}V_6O_{13}$ and LiV_6O_{13}

The phase transformation from $Li_{2/3}V_6O_{13}$ to LiV_6O_{13} requires the intercalation of one more lithium ion for every 18 V atoms. This new lithium ion coordinates to the single layer of VO_6 octahedra, in the same way as the existing lithiums. A careful study of the structures in Fig. 3 and 4 shows that a rearrangement of the lithiums already present in the structure is necessary to form the new phase. This rearrangement occurs within the single layer of VO_6 octahedra. We can also note that the reduced V atoms always occur in the double layer between pairs of Li^+ ions occurring in different layers. It can thus be concluded that the rearrangement of the Li^+ ions is coupled to an electron redistribution within the double layer of VO_6 octahedra.

In conclusion, two new lithiated phases of V_6O_{13} have been identified by single-crystal XRD. The lithium ions coordinate to O atoms in the single layer and to the O atoms lying between the layers. The insertion of lithium into the structures causes a significant elongation of one of the V2—O distances, implying the reduction of this vanadium, as indeed suggested by earlier electron density studies. The phase transformation from $Li_{2/3}V_6O_{13}$ to LiV_6O_{13} has been shown to be accompanied by a rearrangement of the lithium ions already present and by a redistribution of electrons associated with the reduction of specific V atoms in the structure.

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