

Lithium divanadate spinel,  $\text{LiV}_2\text{O}_4$ Yoshitaka Matsushita,\* Jun-Ichi  
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## Key indicators

Single-crystal X-ray study  
 $T = 295 \text{ K}$   
Mean  $\sigma(\text{V}-\text{O}) = 0.0007 \text{ \AA}$   
 $R$  factor = 0.026  
 $wR$  factor = 0.076  
Data-to-parameter ratio = 24.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

For the first time, large single crystals of lithium divanadate spinel,  $\text{LiV}_2\text{O}_4$ , showing heavy-fermion behavior down to 20 K, have been grown by a flux method using an effective  $\text{LiCl-Li}_2\text{MoO}_4\text{-LiBO}_2$  solvent system.  $\text{LiV}_2\text{O}_4$  belongs to the normal spinel structure type. The V atoms ( $16d$ ) have octahedral coordination [ $\text{V}-\text{O} = 1.9709(7) \text{ \AA}$ ] and are arranged in a pyrochlore-type sublattice [ $\text{V}\cdots\text{V} = 2.9147(4) \text{ \AA}$ ]. The Li atoms ( $8a$ ) have tetrahedral coordination [ $\text{Li}-\text{O} = 1.9487(5) \text{ \AA}$ ] and are located in channels running parallel to  $[110]$ .

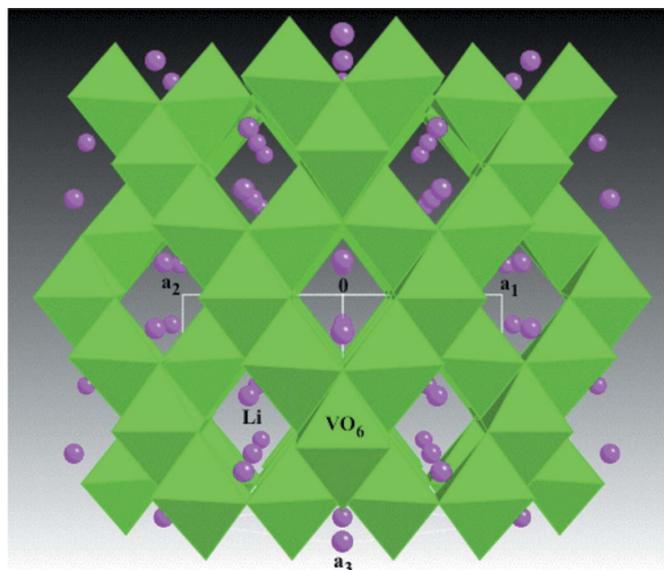
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## Comment

Lithium spinel oxides,  $\text{LiM}_2\text{O}_4$  ( $M =$  transition metal), show a variety of interesting physical and chemical properties. For example,  $\text{LiTi}_2\text{O}_4$  shows BCS-type superconductivity at  $T_c = 13.7 \text{ K}$ , the highest in oxides before the discovery of high- $T_c$  cuprates (Moshopoulou, 1999).  $\text{LiMn}_2\text{O}_4$  is a strong candidate for solid-state electrolytes in lithium secondary batteries (Kumagai & Komaba, 2002, and references therein). In the  $\text{LiM}_2\text{O}_4$  normal spinel structure, the Li ions have tetrahedral coordination. When there are excess Li ions, they are disordered within the  $16c$  sites. The  $M$  ions are octahedrally coordinated by O atoms. If only nearest neighbor  $M\cdots M$  distances are considered, they form a pyrochlore-type sublattice with corner-sharing  $M_4$  tetrahedra. This sublattice is important for physical properties, because it shows a high degree of frustration that is three-dimensional, combined with anti-



**Figure 1**  
Perspective view of  $\text{LiV}_2\text{O}_4$  crystal structure. View direction is parallel to  $[110]$ . Purple circle: Li; green polyhedron:  $\text{VO}_6$ .

ferromagnetic interactions and/or valence ordering. One of the characteristic features of this geometrical frustration is the absence of long-range magnetic order (implying no Néel temperature) (Johnston, 1976).

The title compound,  $\text{LiV}_2\text{O}_4$ , also belongs to the normal spinel structure. The V formal oxidation state of +3.5 (corresponding to 1.5*d* electrons per V) implies a mixed valence of  $\text{V}^{3+}$  and  $\text{V}^{4+}$ . This compound is a second example in spinel oxides that shows metallic conduction down to 300 mK. However, no structural transition is observed even at low temperatures, down to 4 K, by powder neutron diffraction (Chmaissem *et al.*, 1997). The most interesting physical property is heavy-fermion behavior below  $\sim 25$  K with an extremely large quasiparticle specific heat coefficient  $\gamma$ ,  $\sim 420 \text{ mJ mol}^{-1} \text{ K}^2$  (Kondo *et al.*, 1997, 1999; Johnston *et al.*, 1999; Takagi *et al.*, 1999; Urano *et al.*, 2000; Matsushita *et al.*, 2005). This large value is close to those of typical heavy-fermion compounds containing Ce, Yb and U, which have two types of electrons (localized *f* electrons and conduction *s/p* electrons) near the Fermi level. Anomalous physical properties such as this heavy-fermion behavior at low temperature arise from the competition between the Kondo screening effect of the localized electrons by the conduction electrons and the RKKY (Ruderman–Kittel–Kasuya–Yosida) interactions among neighbor localized spins (Grewe & Steglich, 1991). On the other hand,  $\text{LiV}_2\text{O}_4$  has only *d* electrons near the Fermi level, so the observation of heavy-fermion behavior is surprising. To understand the origin of these physical properties, experiments using single crystals are required. Accurate crystallographic details are also necessary to carry out theoretical band-structure calculations.

Unfortunately, reports on the crystal growth of  $\text{LiV}_2\text{O}_4$  are limited. Difficulties in crystal growth arise from high volatility at high temperatures, high reactivity with air, moisture or vessels, and mixed valency of V ions. Thus, all previous structural studies on  $\text{LiV}_2\text{O}_4$  have been on polycrystalline samples (Chmaissem *et al.*, 1997). There has been only one report of the crystal growth of  $\text{LiV}_2\text{O}_4$ , performed under hydrothermal conditions (Rogers *et al.*, 1967). However, with this method, it is difficult to optimize growth conditions and there is a greater possibility for the crystals to be deficient in Li. Recently, we have succeeded in developing a reproducible crystal growth technique with the use of a flux in the multi-compositional solvent system  $\text{LiCl-Li}_2\text{MoO}_4\text{-LiBO}_2$ , giving high yield and relatively large single crystals of  $\text{LiV}_2\text{O}_4$  (Matsushita *et al.*, 2005).

In our structural study, no Li-deficient or excess sites were observed. The V atoms have octahedral coordination [ $\text{V-O} = 1.9709$  (7) Å] and the octahedra link to form a three-dimensional framework. If nearest neighbor  $\text{V}\cdots\text{V}$  contacts are considered [2.9147 (4) Å],  $\text{V}_4$  tetrahedra are formed, having a coordination volume of  $2.918 \text{ \AA}^3$  without any atom at the centroid position ( $\frac{3}{8}, \frac{3}{8}, \frac{3}{8}$ ), and these tetrahedra are arranged in a three-dimensional pyrochlore-type sublattice. The Li atoms are coordinated tetrahedrally [ $\text{Li-O} = 1.9487$  (5) Å] with a coordination volume of  $3.797 \text{ \AA}^3$ . The Li atoms occupy one-dimensional channels running parallel to [110], having a cross-

sectional area of  $4.319 \times 3.182 \text{ \AA}^2$ , consistent with the observation of Li ion conductivity (Pistoia *et al.*, 1991; Li *et al.*, 1996). This area is smaller than that of other lithium oxide normal spinels [ $4.429 \times 3.277 \text{ \AA}^2$  in  $\text{LiTi}_2\text{O}_4$  (Takahashi *et al.*, 2002) and  $4.353 \times 3.224 \text{ \AA}^2$  in  $\text{LiMn}_2\text{O}_4$  (Akimoto *et al.*, 2001)].

## Experimental

Single crystals of  $\text{LiV}_2\text{O}_4$  were grown by a flux method with the eutectic solvent in  $\text{LiCl-Li}_2\text{MoO}_4\text{-LiBO}_2$ . The shiny black octahedral crystals have well developed {111} faces and sizes of up to 1.0 mm across corners. Chemical analysis using ICP revealed stoichiometric compositions. The crystals showed metallic conductivity and heavy-fermion behavior with an extremely large specific heat coefficient,  $\gamma$ , reaching up to  $\sim 460 \text{ mJ mol}^{-1} \text{ K}^2$  at 2 K. Details of the crystal growth and chemical and physical properties have been reported by Matsushita *et al.* (2005).

### Crystal data

$\text{LiV}_2\text{O}_4$	Cell parameters from 2848 reflections
$M_r = 172.82$	$\theta = 9.3\text{--}53.2^\circ$
Cubic, $Fd\bar{3}m$	$\mu = 6.47 \text{ mm}^{-1}$
$a = 8.2437$ (2) Å	$T = 295 \text{ K}$
$V = 560.23$ (2) Å <sup>3</sup>	Octahedron, black
$Z = 8$	$0.01 \times 0.01 \times 0.01 \text{ mm}$
$D_x = 4.098 \text{ Mg m}^{-3}$	
Mo $K\alpha$ radiation	

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	194 independent reflections
$\varphi$ and $\omega$ scans	183 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Shelldrick, 1996)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.878$ , $T_{\text{max}} = 0.937$	$\theta_{\text{max}} = 53.2^\circ$
2848 measured reflections	$h = -17 \rightarrow 18$
	$k = -17 \rightarrow 18$
	$l = -18 \rightarrow 13$

### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{\text{max}} = 0.94 \text{ e \AA}^{-3}$
$wR(F^2) = 0.076$	$\Delta\rho_{\text{min}} = -1.11 \text{ e \AA}^{-3}$
$S = 0.85$	Extinction correction: Zachariasen (1968) type 2 Gaussian isotropic
194 reflections	Extinction coefficient: 0.009 (1)
8 parameters	
$w = 1/(\sigma^2(F_o^2) + \{0.07[\text{Max}(F_o^2, 0) + 2F_c^2]/3\})$	

**Table 1**

Selected interatomic distances (Å).

$\text{V-V}^i$	2.9147 (4)	$\text{Li-O}^{\text{ii}}$	1.9487 (5)
$\text{V-O}$	1.9709 (7)		

Symmetry codes: (i)  $x, -y + \frac{5}{8}, -z + \frac{5}{8}$ ; (ii)  $x, -y + \frac{1}{8}, -z + \frac{1}{8}$ .

The deepest hole is located 0.78 Å from atom V.

Data collection: SMART (Bruker, 1997); cell refinement: S<sub>A</sub>I<sub>N</sub>T (Bruker, 1997); data reduction: S<sub>A</sub>I<sub>N</sub>T and T<sub>E</sub>X<sub>S</sub>A<sub>N</sub> (Molecular Structure Corporation, 2001); program(s) used to solve structure: S<sub>I</sub>R<sub>9</sub>7 (Altomare *et al.*, 1999); program(s) used to refine structure: T<sub>E</sub>X<sub>S</sub>A<sub>N</sub>; molecular graphics: C<sub>r</sub>ystalM<sub>a</sub>ker (Palmer, 2005); software used to prepare material for publication: T<sub>E</sub>X<sub>S</sub>A<sub>N</sub>.

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