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New Refinement of the Room-Temperature Structure of LiCuVO$_4$

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Abstract. Lithium copper(II) vanadate, $M_r = 207.43$, orthorhombic, *Imma*, $a = 5.662$ (1), $b = 5.809$ (1), $c = 8.758$ (2) Å, $V = 288.0$ (2) Å^3, $Z = 4$, $D_x = 4.78$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 10.4$ mm^{-1}, $F(000) = 348$, $R = 0.040$ for 461 unique reflections. The sample was prepared by hydrothermal growth ($T = 919$ K, $P = 190$ MPa, 48 h) of 1.5 g of a powder of LiCuVO$_4$ in 1.65 cm^3 of 0.1 M NaF aqueous solution. LiCuVO$_4$ is an orthorhombic distortion of the cubic spinel structure, with V^{5+} on tetrahedral sites and Li$^+$ and Cu^{2+} distributed in an ordered way on the octahedral sites. This leads to edge-sharing chains of Li$^+$ and Cu^{2+} octahedra running along [100] and [010], respectively.

Experimental. Powder sample prepared as previously described (Joubert, Grenier & Durif, 1965). Hydrothermal growth (919 K, 190 MPa, 48 h) performed in a platinum tube (1.5 g LiCuVO$_4$ powder, 1.65 cm^3 of 0.1 M NaF aqueous solution). Dark-brown platelet (0.14 × 0.08 × 0.03 mm). Data collected on a Siemens AED-2 four-circle diffractometer. ω–2θ step-scan mode in N steps of $\Delta\omega^\circ$, $38 \le N \le 47$, $0.023 \le \Delta\omega \le 0.045^\circ$; time per step 2 s. Profile-fitting data analysis (Clegg, 1981); isotropic linewidth $\Gamma = (1.15 + 0.32\tan\theta)^\circ$. Aperture $D = 4.5$ mm.

Lattice constants based on 28 reflections measured in double step-scan mode at $\pm(2\theta \simeq 30^\circ)$; absorption correction by the Gaussian method, $A_{max} = 0.70$, $A_{min} = 0.40$. Intensity measurement to $2\theta \le 90^\circ$ of five independent sets of reflections within range $|h| \le 11$, $|k| \le 11$, $|l| \le 16$. Standard reflections ($\bar{2}20$, 220, 004), intensity variation 1.0%; 3458 reflections measured, 461 independent reflections used for refinements [$|F| > 6\sigma(|F|)$], $R_{int} = 0.050$.

Structure solved by direct methods with *TANG* option of *SHELX76* (Sheldrick, 1976). F magnitudes used in least-squares refinements, 23 parameters refined; max. $|\Delta/\sigma| = 0.001$; secondary-extinction factor $x = 2.1 \times 10^{-7}$; atomic scattering factors for Li, Cu, V and O from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX76* program (Sheldrick, 1976); all atoms, except Li, refined anisotropically [$R = 0.040$, $wR = 0.035$, $w = 1/\sigma^2(F)$].

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* ($\mathring{A}^2$) *for* LiCuVO$_4$ (*e.s.d.'s in parentheses*)

$$B_{eq} = \tfrac{4}{3}\Sigma_{ij}\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j) \text{ (Hamilton, 1959)}.$$

		x	y	z	B_{eq}
Li$^+$	4(d)	$\tfrac{1}{4}$	$\tfrac{1}{4}$	$\tfrac{3}{4}$	1·0 (2)
Cu^{2+}	4(a)	0	0	0	0·50 (2)
V^{5+}	4(e)	0	$\tfrac{1}{4}$	0·3860 (1)	0·41 (3)
O(1)	8(h)	0	0·0164 (5)	0·2748 (4)	0·73 (8)
O(2)	8(i)	0·2352 (4)	$\tfrac{1}{4}$	−0·0007 (3)	0·59 (7)

Table 2. *Selected bond lengths* ($\mathring{A}$) *and angles* (°) *in* LiCuVO$_4$ (*e.s.d.'s in parentheses*)

Ionic radii are from Shannon (1976).

V^{5+} tetrahedron

2 × V—O(1)	1·670 (3)	O(1)—O(1)	2·714 (4)	O(1)—V—O(1)	108·8 (2)
2 × V—O(2)	1·804 (2)	O(2)—O(2)	2·999 (3)	O(2)—V—O(2)	112·3 (2)
		O(1)—O(2)	2·829 (2)	O(1)—V—O(2)	108·9 (2)

$<d_{V-O}> = 1\cdot737$
$d_{Shannon} = 1\cdot735$

Li$^+$ octahedron

4 × Li—O(1)	2·108 (2)	O(1)—O(1)	2·864 (0)	O(1)—Li—O(1)	85·6 (1)
2 × Li—O(2)	2·185 (2)	O(1)—O(2)	2·917 (3)	O(1)—Li—O(2)	85·6 (2)

$<d_{Li-O}> = 2\cdot134$
$d_{Shannon} = 2\cdot140$

Cu^{2+} octahedron

4 × Cu—O(1)	2·409 (3)	O(2)—O(2)	2·663 (3)	O(2)—Cu—O(2)	85·0 (2)
2 × Cu—O(2)	1·970 (1)	O(1)—O(2)	3·072 (3)	O(1)—Cu—O(2)	88·5 (2)

$<d_{Cu-O}> = 2\cdot116$
$d_{Shannon} = 2\cdot110$

Attempts to take into account some degree of disorder between the Li and Cu sites led to increased R values. Max. and min. heights in final difference map 2·49 and −1·85 e $\mathring{A}^{-3}$ in the vicinity of V and Cu atoms. The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, and some characteristic distances and angles are listed in Table 2.*

The elongation of copper octahedra along **c** is related to the Jahn–Teller effect, and induces an axial [001] distortion of Li$^+$ octahedra and V^{5+} tetrahedra.

The structure (Fig. 1) is an orthorhombic distortion of the cubic spinel structure (*Fd*3*m*). The distortion results from the strict cationic ordering between Li$^+$ and Cu^{2+} which leads to a lowering of symmetry and a group–subgroup relation *Fd*3*m*→*Imma*. Each octahedral subnetwork can therefore be described as independent chains of edge-sharing octahedra running along [100] and [010] for Li$^+$ and Cu^{2+}, respectively, the two subnetworks being edge-shared.

Related literature. Until now, very few compounds with the general formula LiM^{II}VO$_4$ have been reported;

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51756 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
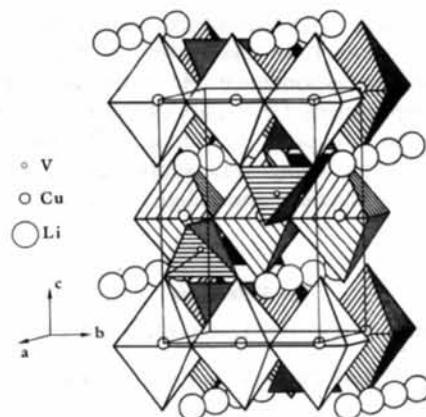

Fig. 1. Perspective view of LiCuVO$_4$ with Cu octahedra and V tetrahedra; Li ions are represented as open circles. Light-, medium- and dark-hatched Cu and V polyhedra lie at $x = 1, 0\cdot5$ and 0, respectively.
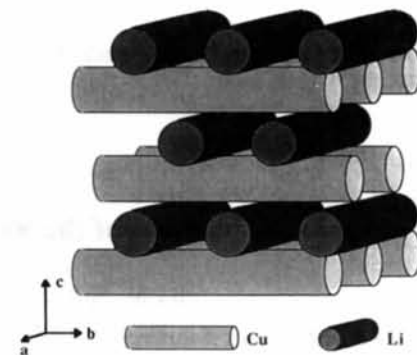

Fig. 2. Diagram showing LiCuVO$_4$ in terms of ordered rod packing (O'Keeffe & Andersson, 1977).

these include M^{II} = Co, Ni (Bernier, Poix & Michel, 1961) and Cu (Joubert, Grenier & Durif, 1965; Durif, Grenier, Joubert & Tran-Qui, 1966). The structure described here (Fig. 2), illustrates the concept of rod packing (O'Keeffe & Andersson, 1977) and exhibits one-dimensional magnetic behaviour whose study is currently in progress.

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