

# Structure and magnetic properties of $\text{LiMVO}_4$ ( $M = \text{Co}, \text{Ni}, \text{Cu}$ ) spinels

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The two-dimensional antiferromagnetic correlations found for  $\text{LiCuVO}_4$  below 30 K have been explained by considering the ordered distribution of lithium and copper in the octahedral sites.

## 1. Introduction

In the ideal cubic  $\text{AB}_2\text{X}_4$  spinel structure (space group  $Fd\bar{3}m$ ) the oxygen ions form a cubic close-packed sublattice with the A and B cations occupying, respectively, one-eighth of the tetrahedrally and one-half of the octahedrally coordinated interstices. Jahn–Teller distortions in the spinel structure have been widely studied from the viewpoint of the arrangement in a lattice of the orbital directions of certain anisotropic ions, such as  $d^4$ ,  $d^9$  in a high spin state [1, 2].

The crystal structure of orthorhombic spinel  $\text{LiCuVO}_4$  (space group  $Imma$ ) has been previously reported [3, 4] showing that lithium and copper ions are located in an ordered way on the octahedral sites, whereas vanadium ions occupy the tetrahedral ones. The orthorhombic distortion is attributed to the Jahn–Teller effect of  $\text{Cu}^{2+}$  cations and to the one-dimensional ordering for both octahedral cations. This order leads to edge-sharing chains of lithium octahedra running along  $[100]$  and copper octahedra along  $[010]$ . This structure suggests a one-dimensional magnetic behaviour.

This paper describes the synthesis, crystal structure and magnetic properties of  $\text{LiMVO}_4$  ( $M = \text{Co}, \text{Ni}$ ) and the magnetic properties of  $\text{LiCuVO}_4$ .

## 2. Experimental procedure

The  $\text{LiMVO}_4$  ( $M = \text{Co}, \text{Ni}, \text{Cu}$ ) system has been obtained from mixtures, in appropriate stoichiometric ratio, of  $\text{Li}_2\text{CO}_3$  (Merck, 99%),  $\text{CoCO}_3$  (Probus, 99%),  $\text{NiCO}_3$  (Riser, 99%),  $\text{CuO}$  (Merck, 99%) and  $\text{V}_2\text{O}_5$  (Riedel de Haën AG, 99%). These mixtures were heated at 803 K for several days. X-ray powder diffraction (XRD) data showed that the products were single phase.

Powder XRD patterns were obtained at room temperature at a rate of  $0.1^\circ (2\theta) \text{ min}^{-1}$  by means of a Siemens Kristalloflex diffractometer powered by a D500 generator using nickel-filtered  $\text{CuK}_\alpha$  radiation

(tungsten was employed as a standard for calibration). A  $2\theta$ -step size of  $0.04^\circ$  was used. The Rietveld's profile analysis method [5] was employed for refinement of the XRD results.

The magnetic susceptibility measurements were made in the temperature range 4.2–300 K, using a DSM-8 pendule magnetometer. The maximum magnetic field was 14 kG with  $H(dH/dz) = 29 \text{ kG}^2 \text{ cm}^{-1}$ . The unit was calibrated with  $\text{Hg}[\text{Co}(\text{SCN})_4]$  and  $\text{Gd}_2(\text{SO}_4) \cdot 8\text{H}_2\text{O}$  and the susceptibility was independent of the magnetic field in the temperature range used in these experiments [6].

## 3. Results

The unit cell parameters of  $\text{LiMVO}_4$  ( $M = \text{Co}, \text{Ni}$ ) were refined to the values 0.827 9(1) and 0.821 6(1) nm, respectively. All the atoms in the spinel unit cell occupy special positions in the space group  $Fd\bar{3}m$  (no. 227, origin at 16c). For the oxide  $\text{LiCoVO}_4$ , these positions are: lithium and cobalt ( $16d$ ,  $1/2$ ,  $1/2$ ,  $1/2$ ), vanadium ( $8a$ ,  $1/4$ ,  $1/4$ ,  $1/4$ ) and oxygen ( $32e$ ,  $x$ ,  $x$ ,  $x$ ). The Rietveld analysis confirms this hypothesis. Table I shows the final parameters, the reliability factors, the atomic positions for oxygen atoms and bond distances. A structural model for these materials is given in Fig. 1, in which white octahedra represent the coordination polyhedra of Li/Co or Li/Ni atoms, randomly distributed. The differences between this structure and that previously described for  $\text{LiCuVO}_4$ , in which copper and lithium octahedra are ordered, can be seen in Fig. 2.

The temperature dependence of the reciprocal molar susceptibility of  $\text{LiNiVO}_4$ ,  $\text{LiCoVO}_4$  and  $\text{LiCuVO}_4$  is shown in Fig. 3. In the case of  $\text{LiCuVO}_4$  the susceptibility obeys a Curie–Weiss behaviour, between 300 and 40 K, and the calculated magnetic moment ( $2.14 \mu_B$ ) agrees approximately with that expected for the  $^2E$  term, which is the ground crystal field state of  $\text{Cu}^{2+}$ . The minimum observed around 30 K agrees with the magnetic susceptibility data,

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reported earlier for these compounds [7]. However, the broadening feature of this minimum, which is characteristic of the so-called low-dimensional antiferromagnetic ordering, is rather surprising, taking into ac-

count the three-dimensional network of the spinel structure-type. The different superexchange pathways which are present in this complex structure-type are discussed below.

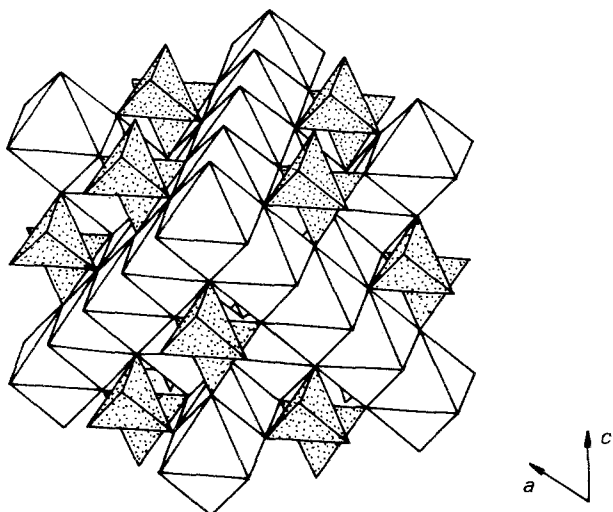


Figure 1 Structural model for  $\text{LiMVO}_4$  ( $M = \text{Co, Ni}$ ). V, Shadow tetrahedra; Li/Co, octahedra.

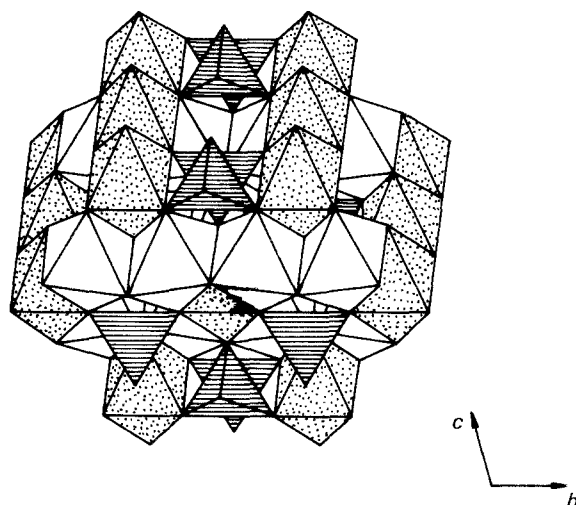


Figure 2 Structural model for  $\text{LiCuVO}_4$ . V, Shadow tetrahedra; Li, white octahedra; Cu, shadow octahedra.

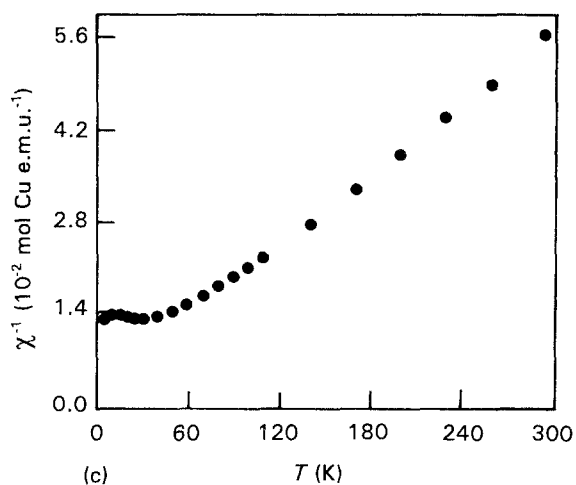
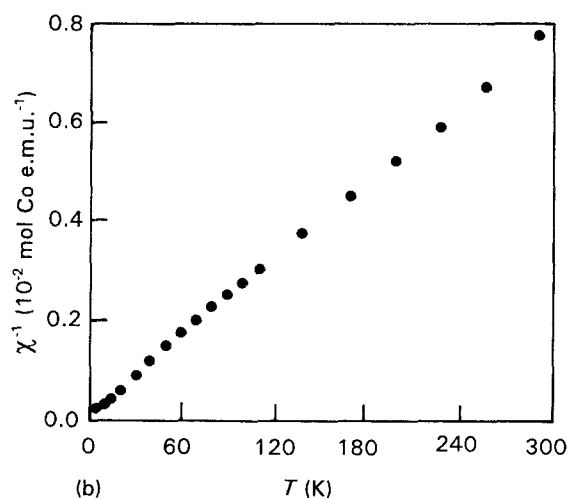
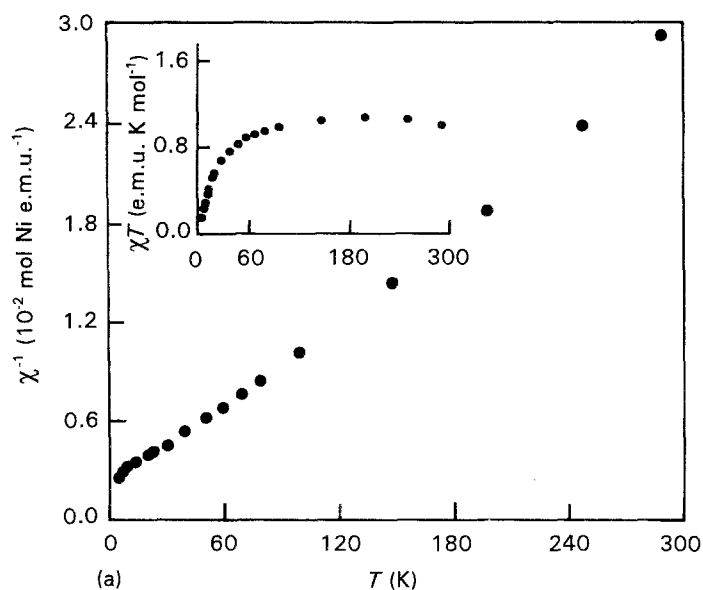


Figure 3 Temperature dependence of the reciprocal molar susceptibility for (a)  $\text{LiNiVO}_4$  (b)  $\text{LiCoVO}_4$  and (c)  $\text{LiCuVO}_4$ .

TABLE I Crystallographic data for LiCoVO<sub>4</sub> from Rietveld refinement

Space group	$Fd\bar{3}m$	$R_p$	8.19
Z	8	$R_{wp}$	10.9
a (nm)	0.831 5(1)	$R_B$	3.52
V (nm <sup>3</sup> )	0.575	$R_c$	5.62
Number of steps	2727	Limits of 2 $\theta$	10°–119°
Number of variables	16	Oxygen position	0.245(1)
Mean distances		Weiss constant	– 6.07 K
(Li/Co–O)	2.109(× 6)	Distances(V–O)	1.725(× 4)

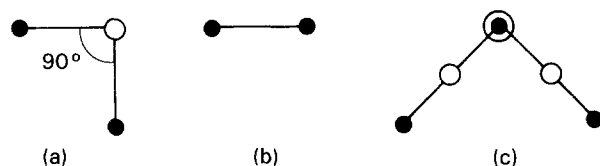


Figure 4 Possible operative magnetic interactions in the spinel structure: (a) Ferromagnetic interaction; (b) direct antiferromagnetic interaction; (c) long-range superexchange through V<sup>5+</sup> ion.

In this sense, it is well known that, in the case of spinels A<sub>2</sub>BX<sub>4</sub>, the interaction between the A and B sublattices is stronger than those within the sublattices; furthermore, the interactions between ions in A sites are the weakest of all. Because, in our case, A (V<sup>5+</sup>) cation is diamagnetic and the B sites are occupied by Li<sup>+</sup> and paramagnetic Cu<sup>2+</sup> ions in an ordered fashion, the only possible operative magnetic pathways for this oxide are sketched in Fig. 4. All these interactions are in the *ab* plane and for this reason this spinel, LiCuVO<sub>4</sub>, has been considered earlier as a two-dimensional antiferromagnet [8], related to the classical K<sub>2</sub>NiF<sub>4</sub> structure-type. However, this comparison is too strong because, for the two-dimensional K<sub>2</sub>NiF<sub>4</sub>, there is only one possible pathway for the superexchange process. Moreover, this pathway is of the type Ni–F–Ni and the angle is 180°, giving rise to very strong interactions. For example, in the case of the isostructural Ln<sub>2</sub>NiO<sub>4</sub> [9] and Ln<sub>2</sub>CuO<sub>4</sub> [10], the reported Néel temperatures were 325 and 320 K, respectively.

In the present case, because the Cu–Cu distance is quite large, about 0.215 nm, the A and B interactions (Fig. 4) will be very weak and can be neglected. Then it appears that the main interaction should be the long-range superexchange between two copper atoms of different rows of octahedra in the *ab* plane (Fig. 2), giving rise to a two-dimensional antiferromagnetic correlation below 30 K.

The magnetic susceptibility for both LiCoVO<sub>4</sub> and LiNiVO<sub>4</sub> follows a Curie–Weiss behaviour in a very wide temperature range. The obtained magnetic moments agree fully with those expected for the octahedral field term <sup>4</sup>T<sub>1</sub> (for Co<sup>2+</sup>) or <sup>3</sup>A<sub>2</sub> (for Ni<sup>2+</sup>).

On the other hand, the very different magnetic behaviour found at low temperatures for these LiMVO<sub>4</sub> (M = Co, Ni) oxides, compared with that of LiCuVO<sub>4</sub>, as discussed earlier, can be explained by considering the disordered distribution of lithium and Ni/Co in the B sites. Because of this random distribution, all the possible pathways for the magnetic interactions [11] will be operative, although the presence of lithium will diminish greatly the strength of these interactions. In this sense, no minima are found in the susceptibility for both cobalt and nickel spinels down to 3.6 K. However, these antiferromagnetic interactions appear to be operative, as can be deduced from the upward deviations found in the reciprocal susceptibility graphs for the cobalt (at 14 K) and nickel (at 4.4 K) spinels.

This assumption even agrees with the negative values of the Weiss constant for both spinels (Table I) and with the very low values at lower temperatures, as is shown in Fig. 3a, inset.

Neutron diffraction studies are in progress in order to determine the magnetic structure and the Néel temperatures of these compounds.

## References

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Received 6 May  
and accepted 29 October 1993