Incommensurate antiferromagnetic order in the $S = \frac{1}{2}$ quantum chain compound LiCuVO$_4$

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Stimulated by the vivid search for a theoretical understanding of high-T_c superconductivity, the magnetic properties of low-dimensional quantum antiferromagnetic (afm) systems that contain $S = \frac{1}{2}$ moments on Cu^{2+}, V^{4+}, or Ti^{3+} ions have attracted particular attention. Unusual ground-state properties have been seen to evolve due to the proximity of such systems to quantum criticality via mainly a considerable sensitivity to higher-order effects in the exchange coupling but also to coupling to lattice or charge degrees of freedom. For example, the spin-Peierls transition observed in the inorganic one-dimensional Heisenberg antiferromagnet CuGeO$_3$ leaves a nonmagnetic singlet ground state below ≈ 14 K, which was suggested to arise from the interplay of the nearest neighbor (NN) and the next-nearest neighbor (NNN) Cu–Cu superexchange and magnetoelastic coupling.
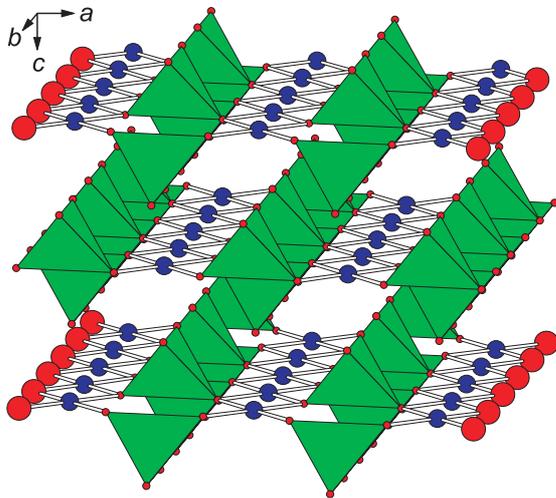

Figure 1: Crystal structure of LiCuVO$_4$. VO$_4$ tetrahedra (green), Cu atoms (blue), O atoms (red). Li atoms not shown.

LiCuVO$_4$ (V[LiCu]O$_4$ in the standard spinel notation) crystallizes in an orthorhombically distorted inverse spinel structure (Fig. 1) [1]. The nonmagnetic V^{5+} ions occupy tetrahedrally coordinated sites. Li$^+$ and Cu^{2+} ($3d^9$ configuration, $S = \frac{1}{2}$) occupy in an ordered way

sites which are octahedrally coordinated by O atoms. The Jahn-Teller elongated CuO$_6$ octahedra connect via trans-edges to form infinite Cu^{2+} chains along the b-axis leaving two nearly rectangular ($\approx 95°$) Cu-O-Cu super-exchange paths between NN Cu ions. The resulting CuO$_2$ ribbons are connected by VO$_4$ tetrahedra which alternate up and down along the chain direction. The topology of the CuO$_2$ ribbons is identical to that found in CuGeO$_3$, however somewhat different bonding distances and angles are observed. It has been suggested that LiCuVO$_4$ behaves as a quasi one-dimensional $S = \frac{1}{2}$ Heisenberg afm with uniform NN coupling [2] although details of NNN, anisotropic and antisymmetry exchange components remained to be clarified. In contrast to CuGeO$_3$, LiCuVO$_4$ shows no evidence of a diamagnetic ground state but rather anomalies in the heat capacity and the susceptibility which indicate the onset of long-range afm ordering below ≈ 2.5 K.
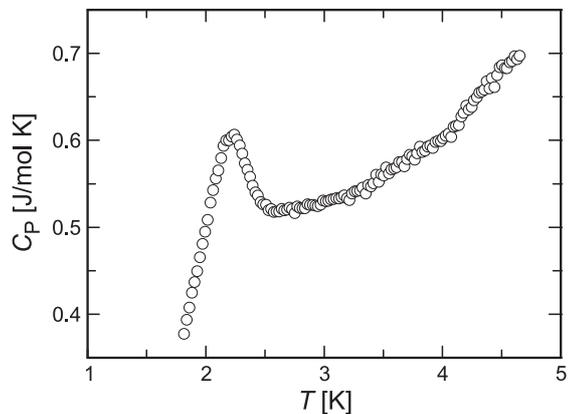

Figure 2: Heat capacity of an end-piece cut from the crystal of LiCuVO$_4$ used for the neutron diffraction study.

We have performed an investigation of the ordered magnetic structure by means of elastic neutron diffraction on single crystals. For the neutron diffraction experiment, a large single crystal of LiCuVO$_4$ was grown by a flux method. The magnetic susceptibility of our

single crystals shows a broad maximum centered around 27 K due to afm short-range ordering. Kinks in the susceptibility at ≈ 2.2 K along all crystal axes indicate long-range afm ordering. Heat capacity measurements on a small piece cut from this crystal show an anomaly at ≈ 2.2 K (Fig. 2) consistent with findings on powder samples.

In the neutron diffraction experiment carried out on ILL's D10 four-circle diffractometer about 200 independent nuclear reflections were collected at 1.6 K. A full refinement of the nuclear structure was carried out in the distorted orthorhombic spinel structure and the results were in very good agreement with previous X-ray structure determinations with a slight temperature-induced lattice contraction. Scans through reciprocal space were performed at 1.6 K to search for additional reflections arising from the Cu^{2+} moment ordering. We initially found a weak peak at the approximate position, $(1, \approx\frac{1}{2}, 0)$ which disappeared upon heating to 2.5 K. We then checked for further peaks at $(h, \approx\frac{1}{2}, l)$ positions and observed a family of magnetic reflections which satisfied the general condition, $h + l = 2n + 1$.
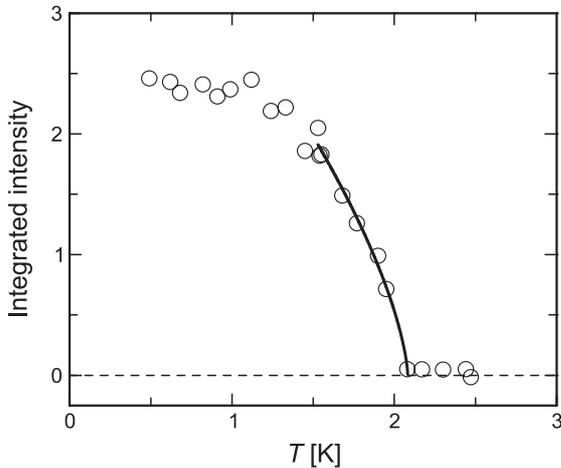

Figure 3: Integrated intensity of the magnetic reflection '$(1, \frac{1}{2}, 0)$'. The full line represents a fit to a power law with critical exponent $\beta \approx 0.3$.

Closer inspection of the magnetic reflections revealed an incommensurate magnetic structure that can be described by the propagation vector $k = (0, 0.532, 0)$ about the fundamental body-centered nuclear reflections. Subsequently, the temperature dependence of the intensity of the reflection '$(1, \frac{1}{2}, 0)$' was measured

from which we determined the Néel temperature to be $T_N = 2.1(1)$ K. Detailed scans of various allowed magnetic reflections at 0.2 K and 1.2 K were made (the ordering is nearly complete at 1.2 K – see Fig. 3) and the profile was fitted to a Gaussian.

A magnetic structure of $LiCuVO_4$ compatible with the underlying crystal symmetry (i.e. that satisfies $h + l = 2n$) can be generated by symmetry operations based on space group *Imma*, with the centering removed. Using this magnetic symmetry the refinement based on 14 unique allowed magnetic reflections at 0.2 and 1.2 K with two free variables converged to a magnetic structure with the spins in the *ab*-plane enclosing a polar angle of $\Phi = 44(5)°$ with the *a*-axis. The average Cu^{2+} magnetic moment is $0.31(1)\mu_B$. Neighboring moments along the chains along *b* enclose an angle of $\approx 90°$ (Fig. 4).
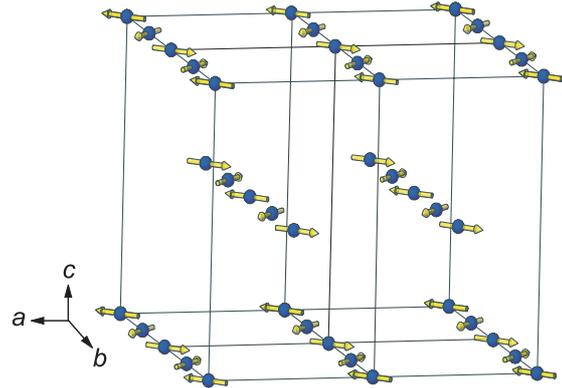

Figure 4: Magnetic structure of $LiCuVO_4$, only Cu atoms are shown. The moments are confined to the *ab*-plane: NN moments enclose an angle of $\approx 90°$.

As indicated by the characteristic maximum in the susceptibility and the broad Schottky-like anomaly in the magnetic part of the heat capacity, $LiCuVO_4$ shows features typical of a one-dimensional afm system with predominant exchange coupling along the Cu chains. Assuming a Heisenberg $S = \frac{1}{2}$ chain behavior with uniform NN coupling, the temperature of the maximum in the magnetic susceptibility T_{max} implies an intrachain exchange constant J_{intra} of ≈ 42 K. Long-range afm ordering of the short-range correlated chains had been concluded from the magnetic susceptibility and the anomaly in the heat capacity is now

conclusively confirmed by our neutron diffraction study. Long-range correlation between the chains is due to weaker interchain coupling. J_{inter} can be estimated from T_N and the intrachain coupling to be $\lesssim 1\,K$.

The surprising result of the present investigation is the unusual ordering scheme of the Cu spins along b. This arrangement can be interpreted as resulting from a stacking of two individual chains each consisting of NNN Cu atoms of the original chain. Such 'sub-chains' show a collinear antiparallel arrangement of neighboring moments. When the two chains stack, NN spins enclose an angle of $\approx 90°$ to minimize the exchange energy between the NN moments. This finding suggests that NNN exchange coupling via a Cu–O–O–Cu path is afm and dominates the NN coupling. Irrespective of the sign of the NN exchange the latter is frustrated and, in order to minimize the exchange energy, the moments assume a noncollinear arrangement. NNN coupling arises from hybridization of NN O $2p_x$-orbitals resulting in a sizable $p_x - p_x$ hopping parameter between O

atoms along the chain. For a certain parameter range of the NN and NNN exchange constants, $J_{NNN}\,J_{NN}$, the Hamiltonian

$$H = \sum_1 J_{NN}\,S_i \cdot S_{i+1} + J_{NNN}\,S_i \cdot S_{i+2} \qquad (1)$$

has been found to describe magnetic phases with incommensurate spiral spin correlations along the chain [3]. Magnetic frustration in an afm chain due to NNN coupling therefore is suggested to be the origin for the experimentally observed incommensurability of the moment order along the Cu chains. This assumption meanwhile was confirmed by an inelastic neutron scattering investigation indicating a ratio $J_{NN}/J_{NNN} \approx -0.3$.

[1] *Durif, A., J.C. Grenier, J.C. Joubert and T.Q. Duc.* Bulletin de la Societe Francaise de Mineralogie et de Cristallographie **89**, 407–409 (1966).

[2] *Vasil'ev, A.N., L.A. Ponomarenko, H. Manaka, I. Yamada, M. Isobe and Y. Ueda.* Physical Review B **64**, 024419 (2001).

[3] *White, S.R. and I. Affleck.* Physical Review **54**, 9862–9869 (1996).