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# High field magnetization of the frustrated one-dimensional quantum antiferromagnet $\text{LiCuVO}_4$

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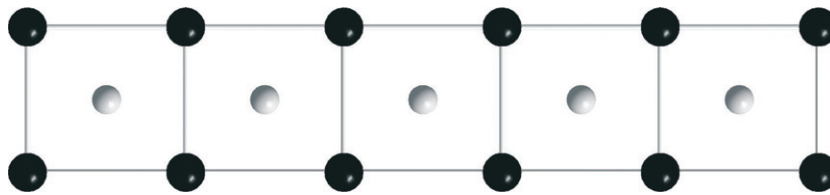
## Abstract

We have investigated the high field magnetization of the frustrated one-dimensional compound  $\text{LiCuVO}_4$ . In zero field,  $\text{LiCuVO}_4$  undergoes long range antiferromagnetic order at  $T_N \approx 2.5$  K with a broad short range Schottky type anomaly due to one-dimensional correlations in the specific heat at 32 K. Application of a magnetic field induces a rich phase diagram. An anomaly in the derivative of the magnetization with respect to the applied magnetic field is seen at  $\sim 7.5$  T with  $H \parallel c$  in the long range order phase. We investigated this in terms of a first experimental evidence of a middle field cusp singularity (MFCS). Our numerical density matrix renormalization group results show that in the parameter range of  $\text{LiCuVO}_4$  as deduced by inelastic neutron scattering (INS), there exists no MFCS. The anomaly in the derivative of the magnetization at  $\sim 7.5$  T is therefore assigned to a change in the spin structure from the  $ab$  plane helix seen in zero field neutron diffraction.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

In the course of the vivid search for a theoretical understanding of high- $T_c$  oxocuprate superconductors, the magnetic properties of low-dimensional quantum  $S = \frac{1}{2}$  antiferromagnetic (afm) systems play a prominent role. Attention has been focused on theoretical and experimental investigations especially of quasi-one-dimensional afm systems since it became clear that electronic phase separation creating for example doping induced ‘stripe-like’ aggregates may be essential in the formation of the superconducting phase [16, 17, 29, 36]. A larger number of new quasi-one-dimensional copper oxides



**Figure 1.** Schematic view of a  $\text{CuO}_2$  ribbon chain made up of edge-sharing  $\text{CuO}_4$  squares. The grey spheres represent the  $\text{Cu}^{2+}$  ions, the black spheres the  $\text{O}^{2-}$  ions.

structurally closely related to high- $T_c$  oxocuprates have since been prepared and their magnetic properties were investigated in detail [14]. Unusual ground-state properties have been seen to evolve due to the proximity of such systems to quantum criticality via for example a considerable sensitivity to higher-order effects in the exchange coupling but also to coupling to lattice or charge degrees of freedom.

Most of the quasi-one-dimensional copper oxide systems investigated so far contain more or less *stretched* Cu–O–Cu bonds with bonding angles close to  $\sim 180^\circ$ , which leads to super-exchange with exchange constants of the order of 100 meV [13], very similar to that found in the undoped parent compounds of the high- $T_c$  oxocuprate superconductors [6].

Less broadly investigated are quasi-one-dimensional systems which contain isolated  $\text{CuO}_2$  ribbon chains made up of edge-sharing (slightly stretched or deformed)  $\text{CuO}_4$  squares (see figure 1). For an isolated  $\text{CuO}_2$  ribbon chain, the spin exchange interactions of interest are the nearest-neighbour (NN) interaction  $J_1$ , which takes place through the two Cu–O–Cu super-exchange paths, and the next-nearest-neighbour (NNN) interaction  $J_2$ , which takes place through the two Cu–O  $\cdots$  O–Cu super-super-exchange (SSE) paths [22, 7].

A broadly investigated system which contains such  $\text{CuO}_2$  ribbon chains which are connected via  $\text{GeO}_4$  tetrahedra is for example the inorganic spin Peierls compound  $\text{CuGeO}_3$  ( $T_{\text{SP}} \approx 14$  K) [31, 11]. The importance of the NNN interaction in  $\text{CuGeO}_3$  has first been discussed by Castilla *et al* [5].

Quasi-one-dimensional systems containing isolated  $\text{CuO}_2$  ribbon chains offer the possibility to study one-dimensional compounds with frustrated magnetism. Magnetic frustration is brought about by the competition of the NN and NNN interactions. If  $J_1$  and  $J_2$  are both afm, frustration primarily does not emerge from the geometry of the lattice as for example is realized with the triangular or the Kagomé lattices in two dimensions, or with a pyrochlore lattice in three dimensions, but rather from the topology of the Hamiltonian which can be mapped to that of a zigzag chain with NN interactions only.

It can easily be shown that one-dimensional classical magnets with competing interactions may result in a helicoidal ground state. In the quantum case with  $S = \frac{1}{2}$ , strong frustration can not only lead to a helicoidal ground state but also to gapped spin liquid phases or states with local spin correlations, depending on the frustration ratio  $\alpha (= J_2/J_1)$  [34, 3].

Theoretically, much work has been carried out on a  $J_1$ – $J_2$  model for a one-dimensional Heisenberg  $S = \frac{1}{2}$  antiferromagnet ever since the discovery of non-classical ground states [3, 21]. Calculation of the thermodynamic properties resulted in possible novel excitations of a domain wall type [27]. More recently, much work has been carried out employing density-matrix renormalization group (DMRG) [33, 20] which does not suffer from the sign problem as in the case of Monte Carlo (MC) simulations, and also gives results on substantially larger system sizes than those accessible with full diagonalization techniques.

Special attention has been paid to the magnetization process of a one-dimensional chain with both afm ( $J_1, J_2 > 0$ ) competing NN and NNN exchange interactions. For special

values of  $\alpha$ , so-called additional ‘middle-field cusp singularities’ (MFCS) at magnetic fields significantly below the saturation field can appear in the magnetization ( $M$ – $H$  curve). The origin of the MFCS is a double-minimum shape of the energy dispersion of the low-lying excitations.

The  $M$ – $H$  curve of an afm zigzag chain at zero and finite temperatures was calculated using DMRG in the thermodynamic limit for various values of  $\alpha$  by Okunishi and collaborators [23, 24, 19, 25]. At zero temperature an MFCS was seen in the  $M$ – $H$  curve for  $\alpha > 0.25$ . For  $\alpha \leq 0.25$ , the dispersion of a ‘one down spin’ has one minimum. For  $\alpha > 0.25$ , we have at  $k = \pi$  a local maximum and two minima that appear at either side of the maximum.

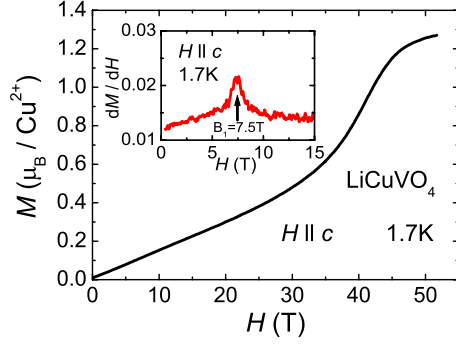
Recently, it was shown that the compound  $\text{LiCuVO}_4$  represents an example of a quasi-one-dimensional Heisenberg  $S = \frac{1}{2}$  antiferromagnet in which such a frustrated situation is realized.  $\text{LiCuVO}_4$  ( $\equiv \text{V}[\text{LiCuO}_4]$  in the standard spinel notation) crystallizes in an orthorhombically distorted inverse spinel structure, with the non-magnetic  $\text{V}^{5+}$  ions at the tetrahedrally coordinated sites and  $\text{Li}^+$  and  $\text{Cu}^{2+}$  ( $3d^9$  configuration) occupying in an ordered way the octahedrally coordinated sites [8, 18]. The Jahn–Teller distorted  $\text{CuO}_6$  octahedra connect via *trans* edges to form infinite  $\text{Cu}^{2+}$  chains along the crystallographic  $b$  direction, leaving two nearly rectangular ( $\sim 95^\circ$ ) Cu–O–Cu super-exchange paths between NN Cu ions. The resulting  $\text{CuO}_2$  ribbons are connected by  $\text{VO}_4$  tetrahedra that alternate up and down along the chain direction.  $\text{LiCuVO}_4$  exhibits the typical features of a quasi-one-dimensional Heisenberg  $S = \frac{1}{2}$  antiferromagnet, e.g. a broad short range Schottky type anomaly in the specific heat at 32 K [1] and a broad short range ordering maximum in the magnetic susceptibility. In fact, initially  $\text{LiCuVO}_4$  was described as a quasi-one-dimensional Heisenberg  $S = \frac{1}{2}$  afm with NN interactions only [2, 35, 30, 15, 28, 32].

$\text{LiCuVO}_4$  undergoes long range afm order at  $\sim 2.5$  K due to interchain interactions. The magnetic structure of  $\text{LiCuVO}_4$  was first determined by single crystal neutron diffraction and found to realize an incommensurate helix polarized along the chain direction [10]. The incommensurability was proposed to be caused by a scenario of frustration involving an NN and NNN interaction along the chain. Subsequent inelastic neutron scattering determined the NN exchange to be ferromagnetic ( $J_1 \approx -12$  K), rather than the expected afm interaction, and the NNN exchange to be substantially larger and afm ( $J_2 \approx 41$  K), thus confirming unquestionably this scenario of magnetic frustration along the chain [9].

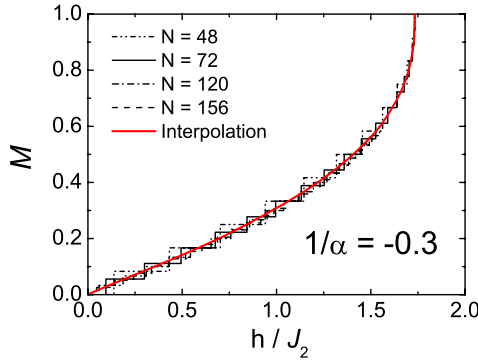
Here we report high field magnetization measurements on single crystals of  $\text{LiCuVO}_4$  in the magnetically ordered phase. We found an anomaly in the derivative of the magnetization at  $\sim 7.5$  T with  $H \parallel c$ . Using the exchange integrals from INS experiments we have calculated the magnetization process for several system sizes by means of DMRG calculations. Our results suggest that the anomaly seen at 7.5 T in the derivative of the magnetization is most likely *not* due to an MFCS but rather originates from a change of the magnetic structure. The true nature of the phase transition and the magnetic structure in this high field phase is unclear at present.

## 2. Experimental details

Single crystals of  $\text{LiCuVO}_4$  (space group *Imma*) were grown from solutions of  $\text{LiCuVO}_4$  in a  $\text{LiVO}_3$  melt according to the procedures described elsewhere [26]. Magnetization was measured down to 1.8 K in a magnetic field up to 7 T. Heat capacity and susceptibility measurements both revealed a transition at 2.5 K due to afm long range order. High field magnetization was carried out up to a maximum field of 55 T, at the Laboratoire National des Champs Magnétiques Pulsés Toulouse, France.



**Figure 2.** High field magnetization of LiCuVO<sub>4</sub> with  $H \parallel c$  at 1.7 K. Inset: derivative of the magnetization with respect to the applied field for  $H \parallel c$  showing a clear anomaly at  $\sim 7.5$  T.



**Figure 3.** DMRG calculations of the magnetization of a one-dimensional  $S = \frac{1}{2}$  Heisenberg chain using  $1/\alpha = -0.3$  for  $N = 48, 72, 120$  and  $156$  sites. The solid (red) line is an interpolation taking the midpoint of each plateau in the magnetization for  $N = 72$  sites.

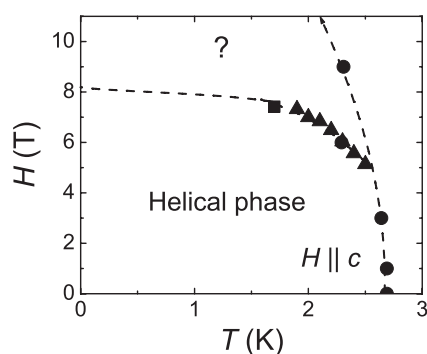
### 3. Results and discussion

Figure 2 shows the magnetization as a function of applied magnetic field up to 55 T for  $H \parallel c$  at 1.7 K. Differentiating the magnetization with respect to the field shows a saturation of the magnetization at 40.7 T [9]. Using the results of the DMRG calculations,  $H_{\text{sat}} = 1.73 J_2$ , and the dominant exchange integral,  $J_2 \approx 41$  K with a  $g$ -factor of  $g_c = 2.313$  [32], we arrive at a saturation field of  $H_{\text{sat}}^c = 46.2$  T. This gives a  $\sim 4$  T discrepancy in the saturation field between theory and experiment. The insert of figure 2 shows a clear anomaly in the derivative of the magnetization at  $\sim 7.5$  T. To investigate whether this corresponds to an MFCS we have carried out DMRG calculations in the parameter regime ( $1/\alpha = J_1/J_2 = -0.3$ ) relevant for LiCuVO<sub>4</sub> as deduced by INS experiments, based on the following one-dimensional Hamiltonian.

$$H = \sum_i (J_1 \vec{S}_i \cdot \vec{S}_{i+1} + J_2 \vec{S}_i \cdot \vec{S}_{i+2}) - h \sum_i S_i^z \quad (1)$$

where  $\vec{S}_i$  are spin 1/2 operators,  $J_i$ ,  $i = 1, 2$ , are the exchange integrals and  $h$  is the magnetic field.

The results of our calculations for four different system sizes,  $N = 48, 72, 120$  and  $156$ , are shown in figure 3. In all cases we see no change of the magnetization by a jump or singularity in the middle field region. An interpolation of the magnetization for  $N = 72$  using the midpoint



**Figure 4.** Phase diagram of LiCuVO<sub>4</sub> with  $H \parallel c$ . Closed circles: specific heat measurements. Closed triangles: magnetic susceptibility measurements. Closed squares: pulsed high field measurements. Dashed lines are tentative phase boundaries.

of every plateau [4] results in a smooth curve. Differentiating this curve with respect to the field ( $dM/dh$ ) does not indicate any singularities or jumps. Any experimental uncertainty in the values of  $J_1$  and  $J_2$  does not affect this result, because the frustrated ferromagnetic  $J_1$ - $J_2$  chain for  $0 > J_1/J_2 \gtrsim -1$  exhibits only one phase in a finite magnetic field until saturation is reached [12]. Therefore, we conclude in the parameter range of LiCuVO<sub>4</sub> we have no occurrence of a middle field cusp singularity within the  $J_1$ - $J_2$  model.

Failing the observation of an MFCS in the DMRG calculations, we suggest the anomaly most likely represents a reorientation of the magnetic structure. To gain more insight into this we have constructed the low temperature phase diagram of LiCuVO<sub>4</sub> for  $H \parallel c$  as deduced by three different experimental techniques: specific heat, high field magnetization and magnetic susceptibility. The data points from the specific heat, as shown in figure 4, were taken from the maximum in  $C_p$  when passing through the sharp transition temperature at a constant magnetic field. The data points for the susceptibility were taken from  $M$ - $H$  scans at constant temperature. The differential  $dM/dH$  was calculated numerically and the maximum of the peak was taken as the magnetic field of the transition. The data points for the high field magnetization were taken in a similar way to the magnetic susceptibility. Two distinct phases are shown in figure 4; the first is the helical long range order phase as solved by neutron diffraction. The second phase, observed for  $H \geq 7.5$  T, increases in field with decreasing temperature and then saturates to reach, at  $T = 0$ , approximately 8 T, as shown in figure 4. To deduce the nature of this phase from the magnetic structure, a field of  $H > 7.5$  T would be quite large to represent a spin flop phase resulting from local anisotropies; therefore the change in the magnetization in this phase most likely represents an essential reorientation of the magnetic structure from the  $ab$  plane helix or alternatively a spin liquid state. Further neutron scattering experiments are needed in order to investigate the interesting phase diagram of LiCuVO<sub>4</sub> in terms of its magnetic structure in applied fields.

#### 4. Summary

We have shown that the frustrated one-dimensional quantum antiferromagnet LiCuVO<sub>4</sub> has a complex ( $H$ - $T$ ) phase diagram. The application of a magnetic field larger than  $\sim 7.5$  T at 1.7 K, with  $H \parallel c$ , induces an anomaly in the derivative of the magnetization. Our DMRG calculations, by using a frustration parameter of  $1/\alpha = -0.3$  as derived from inelastic neutron scattering, showed no evidence of a middle field cusp singularity. The anomaly seen in the

derivative of the magnetization at  $\sim 7.5$  T could indicate a significant change of the magnetic structure from the *ab* plane incommensurate magnetic helix seen in zero field. Further neutron investigations are planned in order to elucidate the magnetic structure of this unknown high field phase.

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