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High field magnetisation of the frustrated one dimensional quantum antiferromagnet $LiCuVO_4$

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Abstract. We have investigated the high field magnetisation of the frustrated one dimensional compound $LiCuVO_4$. In zero field, $LiCuVO_4$ 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 magnetisation with respect to the applied magnetic field is seen at ~ 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 DMRG results show that in the parameter range of $LiCuVO_4$ as deduced by inelastic neutron scattering (INS), there exists no MFCS. The anomaly in the derivative of the magnetisation at ~ 7.5 T is therfore assigned to a change in the spin structure from the *ab* plane helix seen in zero field neutron diffraction.

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 focussed on theoretical and experimental investigations especially of quasi one-dimensional afm systems since it became clear that electronic phase separation creating e.g. doping induced 'stripe-like' aggregates may be essential in the formation of the superconducting phase [1, 2, 3, 4]. A larger number of new quasi one-dimensional copper oxides structurally closely related to high-T_c oxocuprates have since been prepared and their magnetic properties were investigated in detail [5]. Unusual ground-state properties have been seen to evolve due to the proximity of such systems to quantum criticality via e.g. 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° which leads to superexchange with exchange constants of the order of 100 meV [6], very

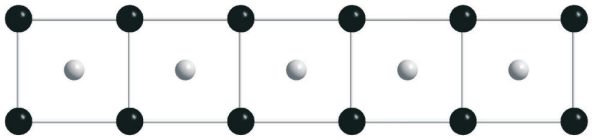

Figure 1. Schematic view of a CuO_2 ribbon chain made up of edgesharing CuO_4 squares. The grey spheres represent the Cu^{2+} ions, the black spheres the O^{2-} ions.

similar to that found in the undoped parent compounds of the high-T_c oxocuprate superconductors [7].

Less broadly investigated are quasi one-dimensional systems which contain isolated CuO_2 ribbon chains made up of edge-sharing (slightly stretched or deformed) CuO_4 squares (see Fig. 1). For an isolated CuO_2 ribbon chain, the spin exchange interactions of interest are the nearest-neighbor (NN) interaction J_1, which takes place through the two Cu-O-Cu superexchange paths, and the next-nearest neighbor (NNN) interaction J_2, which takes place through the two Cu-O $\cdots$ O-Cu super-superexchange (SSE) paths [8, 9].

A broadly investigated system which contains such CuO_2 ribbon chains which are connected via GeO_4 tetrahedra is e. g. the inorganic spin Peierls compound $CuGeO_3$ ($T_{SP} \approx 14$ K) [10, 11]. The importance of the NNN interaction in $CuGeO_3$ has first been discussed by Castilla *et al.* [12].

Quasi one-dimensional systems containing isolated 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 interaction. 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 in 2D, or with a pyrochlore lattice in 3D, 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 α ($= J_2/J_1$) [13, 14].

Theoretically, much work has been carried out on a J_1-J_2 model for a one-dimensional Heisenberg $S = \frac{1}{2}$ afm ever since the discovery of non-classical ground states [14, 15]. Calculation of the thermodynamic properties resulted in possible novel excitations of a domain wall type [16]. More recently, much work has been carried out employing the density-matrix renormalization group (DMRG) [17, 18] 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 accessible with full diagonalization techniques.

Special attention has been paid to the magnetisation process of a one-dimensional chain with both afm (J_1, $J_2 > 0$) competing NN and NNN exchange interactions. For special values of α, so-called additional 'middle-field cusp singularities' (MFCS) at magnetic fields significantly below the saturation field can appear in the magnetisation ($M - H$ 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 antiferromagnetic zigzag chain at zero and finite temperatures was calculated using DMRG in the thermodynamic limit for various values of α by Okunishi and collaborators [19, 20, 21, 22]. At zero temperature a 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 $LiCuVO_4$ represents an example of a quasi one-dimensional Heisenberg $S = \frac{1}{2}$ afm in which such a frustrated situation is realized. $LiCuVO_4$ (≡V[LiCu]O4) in the standard spinel notation) crystallizes in an orthorhombically distorted inverse spinel structure, with the non-magnetic V^{5+} ions at the tetrahedrally coordinated sites and Li^+ and Cu^{2+} ($3d^9$ configuration) occupying in an ordered way the octahedrally coordinated sites [23, 24]. The Jahn-Teller distorted CuO_6 octahedra connect via trans edges to form infinite Cu^{2+} chains along the crystallographic b direction leaving two nearly rectangular (∼95°) Cu-O-Cu super-exchange paths between NN Cu ions. The resulting CuO_2 ribbons are connected by VO_4 tetrahedra that alternate up and down along the chain direction. $LiCuVO_4$ exhibits the typical features of a quasi one-dimensional Heisenberg $S = \frac{1}{2}$ afm, e. g. a broad short range Schottky type anomaly in the specific heat at 32 K [25] and a broad short range ordering maximum in the magnetic susceptibility. In fact, initially $LiCuVO_4$ was described as a quasi one-dimensional Heisenberg $S = \frac{1}{2}$ afm with NN neighbor interactions only [26, 27, 28, 29, 30, 31].

$LiCuVO_4$ undergoes long range afm order at ∼2.5 K due to interchain interactions. The magnetic structure of $LiCuVO_4$ was first determined by single crystal neutron diffraction and found to realize an incommensurate helix polarized along the chain direction [32]. The incommensurability was proposed to be caused by a scenario of frustration involving a 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 being substantially larger and antiferromagnetic ($J_2 \approx 41$ K), thus confirming unquestionably this scenario of magnetic frustration along the chain [33].

Here we report high field magnetisation measurements on single crystals of $LiCuVO_4$ in the magnetically ordered phase. We found an anomaly in the derivative of the magnetisation at $\sim$ 7.5 T with $H \parallel c$. Using the exchange integrals from INS experiments we have calculated the magnetisation 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 magnetisation is most likely *not* due to a 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

Single crystals of $LiCuVO_4$ (space group Imma) were grown from solutions of $LiCuVO_4$ in a $LiVO_3$ according to the procedures described elsewhere [34]. Magnetisation 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 antiferromagnetic long range order. High field magnetisation was carried out until a maximum field of 55 T, at the Laboratoire National des Champs Magnétiques Pulsés Toulouse, France.

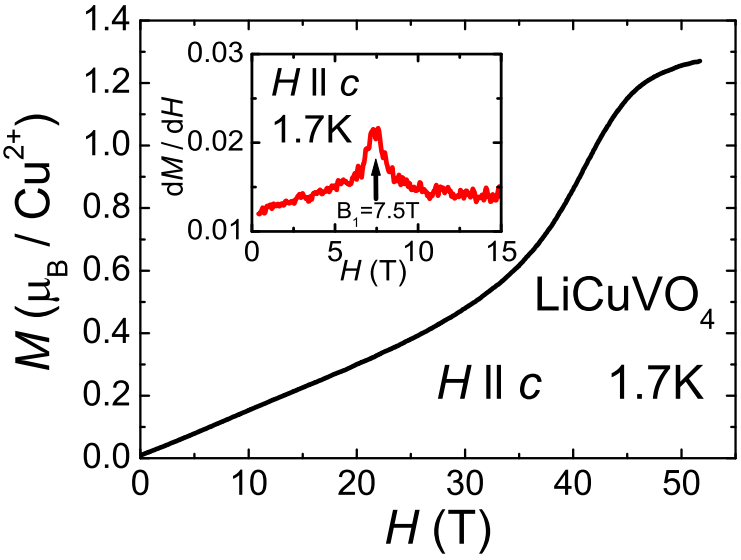

Figure 2. High field magnetisation of $LiCuVO_4$ with $H \parallel c$ at 1.7 K. Insert: derivative of the magnetisation with respect to the applied field for $H \parallel c$ showing a clear anomaly at $\sim$ 7.5 T.

3. Results and discussion

Fig 2 shows the magnetisation as a function of applied magnetic field up to 55 T for $H \parallel c$ at 1.7K. Differentiating the magnetisation with respect to the field shows a saturation of the magnetisation at 40.7 T [33]. Using the results of the DMRG calculations, $H_{sat} = 1.73\ J_2$, and the dominant exchange integral, $J_2 \approx 41$ K with a g-factor of $g_c = 2.313$ [31] we arrive at a saturation field of $H^c_{sat} = 46.2$ T. This gives a ~ 4 T discrepancy in the saturation field between theory and experiment. The insert of Fig 2 shows a clear anomaly in the derivative of the magnetisation at ~ 7.5 T. To investigate whether this corresponds to a MFCS we have carried out DMRG calculations in the parameter regime ($1/\alpha = J_1/J_2 =$ -0.3) relevant for $LiCuVO_4$ as deduced by INS experiments, based on the following one dimensional hamiltonian.

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

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 4 different system sizes, $N = 48$, 72, 120 and 156 are shown in Fig 3. In all cases we see no change of the magnetisation by a jump or singularity in the middle field region. An interpolation of the magnetisation for $N = 72$ using the midpoint of every plateau [35] results in a smooth curve. Differentiating this curve with respect to the field ($\mathrm{d}M/\mathrm{d}h$) does not indicate any singularities or jumps. Any experimental uncertainty in the values of J_1 and J_2 does not affect this result as for $0 > J_1/J_2 \gtrsim$ -1, the frustrated ferromagnetic J_1-J_2 chain exhibits only one phase in a finite magnetic field until saturation is reached [36]. Therefore, we

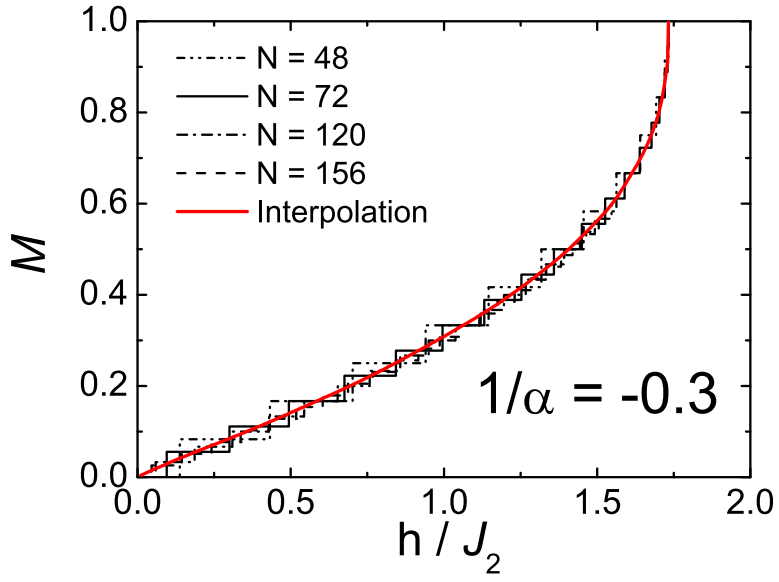

Figure 3. DMRG calculations of the magnetisation of a one- dimensional $S=\frac{1}{2}$ Heisenberg chain using $1/\alpha$ = -0.3 for N = 48, 72, 120 and 156 sites. Solid red line is an interpolation taking the midpoint of each plateau in the magnetisation for $N = 72$ sites.

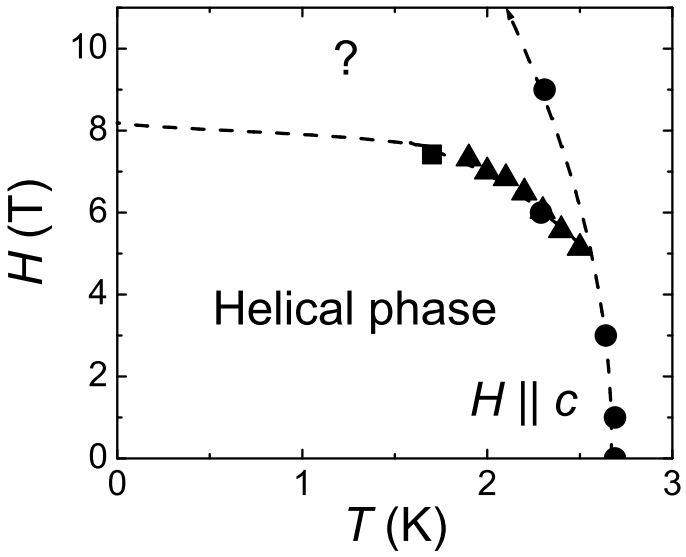

Figure 4. Phase diagram of $LiCuVO_4$ with $H \parallel c$. Closed circles: specific heat measurements. Closed triangles: magnetic susceptibility measurements. Closed squares: pulsed high field measurements. Dashed lines are tentative phase boundaries.

conclude in the parameter range of $LiCuVO_4$ we have no occurrence of a middle field cusp singularity within the J_1-J_2 model.

Failing the observation of a 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 $LiCuVO_4$ for $H \parallel c$ as deduced by three different experimental techniques, specific heat, high field magnetisation and magnetic susceptibility. The data points from the specific heat, as shown in Fig 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 magnetisation was taken in a similar way to the magnetic susceptibility. Two distinct phases are shown in Fig 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 Fig 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 magnetisation 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 $LiCuVO_4$ in terms of its magnetic structure in applied fields.

4. Summary

We have shown that the frustrated one dimensional quantum antiferromagnet $LiCuVO_4$ has a complex $(H - T)$ phase diagram. With the application of a magnetic field larger than ~ 7.5 T at 1.7 K with $H \parallel c$, induces an anomaly in the derivative of the magnetisation. 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 magnetisation 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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References

[1] Kremer R K, Sigmund E, Hizhnyakov V, Hentsch F, Simon A, Müller K A and Mehring M 1992 *Z. Phys. B - Cond. Mat.* **86** 319
[2] Kremer R K, Simon A, Hizhnyakov V, Sigmund E and Müller K A 1993 *Z. Phys. B - Cond. Mat.* **91** 169
[3] Tranquada J M, Sternlieb B J, Axe J D, Nakamura Y and Uchida S 1995 *Nature* **375** 561
[4] Zaanen J and Gunnarsson O 1989 *Phys. Rev. B* **40** 7391
[5] Johnston D C 1997 *Handbook of Magnetic Materials* vol 10 (Elsevier, Amsterdam)

[6] Johnston D C 1996 *Phys. Rev. B* **54** 13009
[7] Coldea R, Hayden S M, Aeppli G, Perring T G, Frost C D, Mason T E, Cheong S W and Fisk Z 2001 *Phys. Rev. Lett.* **86** 5377
[8] Mizuno Y, Tohyama T, Maekawa S, Osafune T, Motoyama N, Eisaki H and Uchida S 1998 *Phys. Rev. B* **57** 5326
[9] Dai D, Koo H J and Whangbo M H 2004 *Inorg. Chem.* **43** 4026
[10] Völlenkle H, Wittmann A and Nowottny H 1967 *Monatsh. Chem.* **89** 1352
[11] Hase M, Terasaki I and Uchinokura K 1993 *Phys. Rev. Lett.* **70** 3651
[12] Castilla G, Chakravarty S and Emery V J 1995 *Phys. Rev. Lett.* **75** 1823
[13] White S R and Affleck I 1996 *Phys. Rev. B* **54** 9862
[14] Bursill R, Gehring G A, Farnell D J J, Parkinson J B, Xiang T and Zeng C 1995 *J. Phys. Cond. Mat.* **7** 8605
[15] Majumdar C K and Ghosh D K 1969 *J. Math. Phys.* **10** 1388
[16] Shastry B S and Sutherland B 1981 *Phys. Rev. Lett.* **47** 964
[17] White S 1992 *Phys. Rev. Lett.* **69** 2863
[18] Maisinger K and Schollwöck U 1998 *Phys. Rev. Lett.* **81** 445
[19] Okunishi K, Hieida Y and Akutsu Y 1999 *Phys. Rev. B* **60** R6953
[20] Okunishi K and Tonegawa T 2003 *Phys. Rev. B* **68** 224422
[21] Maeshima N and Okunishi K 2000 *Phys. Rev. B* **62** 934
[22] Okunishi K and Tonegawa T 2003 *J. Phys. Soc. Jpn.* **72** 479
[23] Durif A, Grenier J C, Joubert J C and Duc T Q 1966 *Bull. Soc. Fr. Mineral. Crystallogr.* **89** 407
[24] Lafontaine M, Leblanc A and Ferey G 1989 *Acta Crystallogr. C* **45** 1205
[25] Banks M G, Honecker A, Heidrich-Meisner F and Kremer R K to be published
[26] Blasse G 1965 *J. Phys. Chem. Solids* **27** 612
[27] Yamaguchi M, Furuta T and Ishikawa M 1996 *J. Phys. Soc. Jpn.* **65** 2998
[28] Vasilev A N, Ponomarenko A L, Manaka H, Yamada I, Isobe M and Ueda Y 2001 *Phys. Rev. B* **64** 024419
[29] Kegler C, Büttgen N, von Nidda H A K, Krimmel A, Svistov L, Kochelaev B I, Loidl A, Prokofiev A and Assmus W 2001 *Eur. Phys. J. B* **22** 321
[30] Tanaka T, Ispida H, Matsumoto M and Wada S 2002 *J. Phys. Soc. Jpn.* **71** 308
[31] von Nidda H A K, Svistov L E, Eremin M V, Eremina R M, Loidl A, Kataev V, Validov A, Prokofiev A and Assmus W 2002 *Phys. Rev. B* **65** 134445
[32] Gibson B J, Kremer R K, Prokofiev A V, Assmus W and McIntyre G J 2004 *Physica B* **350** e253
[33] Enderle M, Mukherjee C, Fåk B, Kremer R K, Broto J M, Rosner H, Drechsler S L, Richter J, Malek J, Prokofiev A, Assmus W, Pujol S, Raggazzoni J L, Rakoto H, Rheinstädter M and Rønnow H M 2005 *Europhys. Lett.* **70** 237
[34] Prokofiev A V, Wichert D and Assmus W 2000 *J. Cryst. Growth* **220** 345
[35] Cabra D C, Honecker A and Pujol P 2000 *Eur. Phys. J. B* **13** 55
[36] Heidrich-Meisner F, Honecker A and Vekua T 2006 *Phys. Rev. B* **74** 020403