Magnetic ordering in the frustrated Heisenberg chain system cupric chloride, $CuCl_2$

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The interplay of magnetic and ferroelectric ordering in so-called multiferroic compounds as basis of possible data storage devices has recently attracted particular attention. The majority of the multiferroic systems identified so far are transition or mixed rare earth transition metal oxides. In an ongoing effort to identify unconventional magnetic low-dimensional systems with competing interactions and helicoidal incommensurate antiferromagnetic (AFM) ordering as possible candidates for multiferroic behavior we recently focussed our attention on the binary Cu halides, $CuCl_2$ and $CuBr_2$ [1]. Here, we report on a detailed investigation of the magnetic properties of cupric chloride $CuCl_2$ which has a crystal structure (Fig. 1) in which layers of composition $CuCl_2$ stack along the *c*-direction with van-der-Waals interactions between them [2].

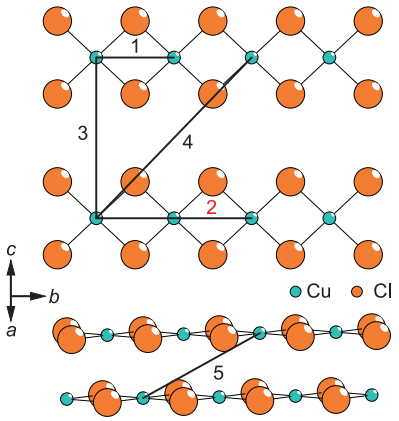

Figure 1: Crystal structure of $CuCl_2$ [2]. The Cu atoms are represented by small (blue), and the Cl atoms by large (orange) circles. The lower part of the figure highlights a $CuCl_2$ ribbons with the *b*-axis along the ribbons. The planes of the ribbons are parallel to the *bc*-plane. the definition of the five exchange paths $J_1 - J_5$ of $CuCl_2$, where the numbers $1 \ldots 5$ represent $J_1 \ldots J_5$, respectively as used for the DFT calculations (see below) are indicated.

Each $CuCl_2$ layer consists of $CuCl_2$ ribbons made up of edge-sharing $CuCl_4$ square planes such that the axial positions of each $CuCl_4$ square are capped by the Cl atoms of its adjacent ribbons with long Cu…Cl distances. Thus, each Cu^{2+} (d^9, $S = 1/2$) ion is contained in an axially elongated $CuCl_6$ octahedron, as expected for a Jahn-Teller active Cu^{2+} ion.

In view of its crystal structure, the early magnetic susceptibility and heat capacity measurements, $CuCl_2$ was historically one of the first systems which has been discussed in terms of a one-dimensional AFM with uniform nearest neighbor (NN) Heisenberg exchange [3].

On the other hand, by analogy to the CuO_2 ribbon chains found in other magnetic oxocuprates such as $LiCuVO_4$ or $NaCu_2O_2$ [4], the next-nearest neighbor (NNN) spin exchange coupling along the chain may be essential in addition to the nearest neighbor (NN) spin exchange in understanding the magnetic properties of $CuCl_2$. For such CuO_2 chains, made up of edge-sharing CuO_4 square planes, the NN spin exchange has been found to be ferromagnetic (FM), while the NNN spin exchange has been observed to be AFM and even stronger than NN superexchange. The resulting geometric spin frustration may give rise to an incommensurate spiral spin ordering and multiferroic behavior.

Our own magnetic susceptibility data measured on melt-grown single crystals of $CuCl_2$ reveal short-range antiferromagnetic ordering features in the magnetic susceptibility i.e., a typical broad maximum at ≈ 70 K (Fig. 2). A careful comparison of our data with recent exact diagonalization results obtained by Heidrich *et al.* [5] suggest a description within terms of a $S = 1/2$ Heisenberg chain with NN and NNN spin exchange interaction equivalent to a frustrated zig-zag chain arrangement. Additional, interchain superexchange interactions which lead to AFM long-range ordering has been taken care of by applying a mean-field correction for the magnetic susceptibility according to Eq. (1):

$$\chi^{\rm cor}_{\rm spin}(T) = \frac{\chi_{\rm spin}(T)}{1-(zJ/N_{\rm A}g^2_{\perp}\mu^2_{\rm B})\chi_{\rm spin}(T)} \qquad (1)$$

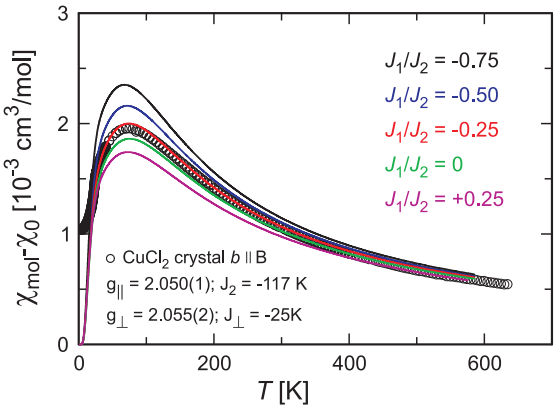

Figure 2: Temperature dependence of the magnetic susceptibility of a crystal of $CuCl_2$ measured with magnetic field aligned along the crystal b-axis corrected for the sum of diamagnetic and Van Vleck contributions ($\chi_0 \approx -18(1)\cdot10^{-6}$ cm^3/mole) (○) compared with the results of exact diagonalization calculations of $S = 1/2$ Heisenberg chains with NN and NNN exchange J_1 and J_2, respectively, defining the ratio $\alpha = J_1/J_2$. The (colored) solid lines were calculated according to Eq. (1) with $\chi_{\rm spin}(T)$ taken from [5] for $J_2 = -117$ K and $\alpha = J_2/J_1$ as given in the inset. From top to bottom α amounts to –0.75 . . . +0.25, respectively.

Long-range AFM ordering below a Néel temperature of ≈ 24 K has previously been observed in heat capacity measurements on powder samples [3,6]. Figure 3 displays our data measured on a single crystal of $CuCl_2$. Entropy considerations indicate substantial AFM short-range ordering to occur above the Néel temperature. Short-range ordering removes about 90% of the spin-entropy (Fig. 3).

In order to establish the magnetic structure we have performed neutron diffraction experiments on single crystals and powder samples of $CuCl_2$ and found an incommensurate AFM long-range ordering with a helicoidal spin structure below $T_{\rm N} = 24.7(0.1)$ K, in good agreement with the heat capacity and susceptibility measurements [7]. All magnetic Bragg reflections can be indexed with a magnetic propagation vector (1,0.225,0.5) indicating a doubling of the magnetic cell along the c-axis and an incommensurate AFM ordering along b.

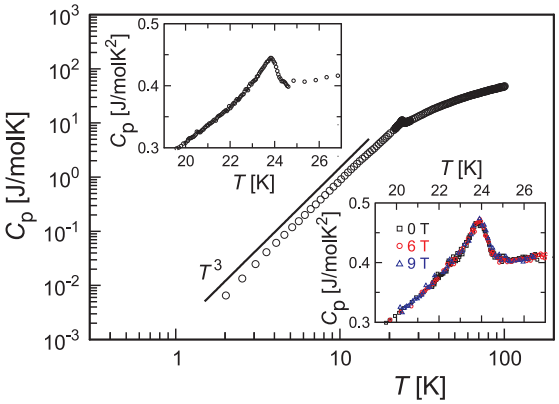

Figure 3: Temperature dependence of the specific heat of $CuCl_2$. The main frame shows the heat capacity of a crystal, the lower inset gives the magnetic field dependence of the anomaly at the Néel temperature $T_{\rm N} = 23.85(3)$ K. The magnetic field was directed perpendicular to the b-axis. The upper inset displays the heat capacity near $T_{\rm N}$ of a polycrystalline sample.

Figure 4 depicts the magnetic structure of $CuCl_2$ and the temperature dependence of the order parameter. The magnetic moments ($\approx 0.50(1)\mu_{\rm B}$) are confined to the $CuCl_2$ ribbon-planes and arrange with an incommensurate helix along b. Neighboring moments enclose a pitch of $\approx 81°$, thus reducing NN spin exchange energy.

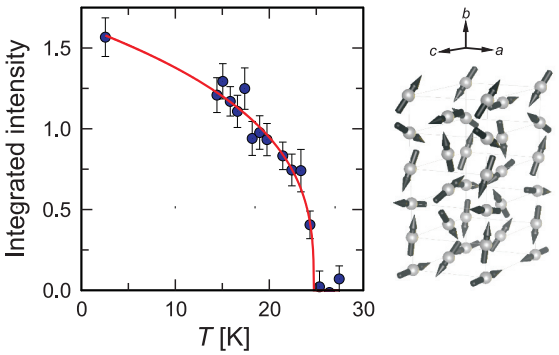

Figure 4: (l.h.s.) Temperature dependence of the integrated intensity of the (–1,0.225,0.5) magnetic reflection. The solid line is a fit to a critical power law with $T_{\rm N} = 24.7(1)$ K. (r.h.s.) Magnetic structure of $CuCl_2$ at 2 K. A helix propagating along b is observed with the moments confined to the bc-plane. Neighboring moments along b enclose an angle of $\approx 81°$.

To understand the magnetic arrangement in $CuCl_2$ we performed first principles DFT electronic structure calculations using the Vienna *ab initio* simulation package with the pro-

jected augmented-wave method and the generalized gradient approximation (GGA) for the exchange and correlation functionals.

The strong electron correlation associated with the Cu 3*d* state was taken into consideration by performing GGA plus on-site repulsion (GGA + U) calculations with $U = 3$, 5, and 7 eV on Cu. We investigated the relative energies of six ordered spin configurations and obtained from our GGA+U calculations relative energies which written in terms of a Heisenberg exchange Hamiltonian give exchange constants (for definition cf. Fig. 1) summarized in Tab. 1. For all values of U employed, the two strongest spin exchange interactions are the intrachain interactions J_1 (FM) and J_2 (AFM), with J_2 being larger in magnitude than J_1 in agreement with our experimental findings.

Table 1: Values of the spin exchange parameters J_1–J_5 (in meV) in $CuCl_2$ obtained from the GGA + U calculations

state	$U = 3$ eV	$U = 5$ eV	$U = 7$ eV
J_1	23.3	21.4	18.4
J_2	–41.4	–31.9	–24.5
J_3	–9.1	–7.0	–5.3
J_4	–0.2	–0.1	–0.1
J_5	–0.8	–0.7	–0.5

All helicoidal systems investigated so far contain oxygen anions to provide superexchange between the Cu^{2+} moments. Clear proof of the helicoidal ground state by magnetic neutron scattering is available only for a few of them. Evidence for systems containing anions other than O^{2-} has not been reported yet. Our electronic structure calculations for $CuCl_2$ give clear theoretical evidence for a scenario of competing FM NN and AFM NNN exchange interactions. Our experimental results for the bulk magnetic properties and the comparison with their predictions for a $S = 1/2$ AFM Heisenberg chain with competing FM NN and AFM NNN exchange interactions support the theoretical predictions. Clear proof for the helicoidal AFM ground state comes from the neutron diffraction work on powder and single crystals. We find a magnetic structure indicating a $S = 1/2$ helix in the $CuCl_2$ ribbon chains. With respect to the helix this scenario is analogous to that in $LiCuV_4$ (propagation vector (0 0.468 0)) and $NaCu_2O_2$ (propagation vector (0.5,0.227,0) [4]. Anhydrous $CuCl_2$ appears to be the first halide quantum system containing Cu-ribbon chains for which a helicoidal magnetic ground state is realized and may be expected to be ferroelectric below 23.9 K. Investigations of the low-temperature dielectric properties of $CuCl_2$ are currently underway.

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[1] *Banks, M.G.,* Ph.D. Thesis, Loughborough University, Loughborough, U.K. (2007).

[2] *Wells, A.F.* Journal of the Chemical Society **1947**, 1670–1674 (1947).

[3] *Stout, J.W. and R.C. Chisholm.* The Journal of Chemical Physics **36**, 979–991 (1962).

[4] *Gibson, B.J., R.K. Kremer, A.V. Prokofiev, W. Assmus and G.J. McIntyre.* Physica B **350**, e253–e256 (2004); *Enderle, M., C. Mukherjee, B. Fåk, R.K. Kremer, J.-M. Broto, H. Rosner, S.-L. Drechsler, J. Richter, J. Malek, A. Prokofiev, W. Assmus, S. Pujol, J.-L. Raggazzoni, H. Rakoto, M. Rheinstädter and H.M. Rønnow.* Europhysics Letters **70**, 237–243 (2005); *Capogna, L.,M. Mayr, P. Horsch, M. Raichle, R.K. Kremer, M. Sofin, A. Maljuk, M. Jansen and B. Keimer.* Physical Review B **71**, 140402(R) (2005).

[5] *Heidrich-Meisner, F., A. Honecker and T. Vekua.* Physical Review B **74** 020403(R) (2006).

[6] *Billerey, D., C. Terrier, R. Mainard and N. Criet.* Journal of Magnetism and Magnetic Materials **30**, 55–57 (1982).

[7] *Banks, M.G., R.K. Kremer, C. Hoch, A. Simon, B. Ouladdiaf, J.-M. Broto, H. Rakoto, C. Lee and M.-H. Whangbo.* Physical Review B **80**, 024404 (2009).