Crystal water induced switching of magnetically active orbitals in CuCl₂

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The dehydration of CuCl₂·2H₂O to CuCl₂ leads to a dramatic change in magnetic behavior and ground state. Combining density functional electronic structure and model calculations with thermodynamical measurements we reveal the microscopic origin of this unexpected incident – a crystal water driven switching of the magnetically active orbitals. This switching results in a fundamental change of the coupling regime from a three-dimensional antiferromagnet to a quasi one-dimensional behavior. CuCl₂ can be well described as a frustrated J₁–J₂ Heisenberg chain with ferromagnetic exchange J₁ and J₂/J₁ ~ −1.5 for which a helical ground state is predicted.

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I. INTRODUCTION

Low-dimensional spin 1/2 magnets are of wide interest in solid state physics since they are ideal objects to study the interplay of dimensionality, magnetic frustration and strong quantum fluctuations. These compounds can be described often very successfully based on their magnetically active structural building blocks and their linking. Typical examples for such building blocks are Ti(III)O₅ octahedra, V(IV)O₅ square pyramids or Cu(II)O₄ plaquettes that form various spin 1/2 networks like quasi one-dimensional (1D) chains or ladders. Nevertheless, for a reliable and accurate description of such networks, precise model parameters are a precondition, especially in the vicinity of quantum critical points. However, since for new compounds these parameters are unknown, it is common to transfer the known parameters from related, similar systems in a slightly renormalized form according to changed distances and/or bond angles.

A typical example for the application of this strategy are compounds that contain crystal water in different amounts. Although in some cases the topology of the magnetic network and the related magnetic properties totally change upon dehydration like in the case of CuSiO₂·H₂O and CuSiO₂·2H₂O, for most compounds only moderate structural changes with respect to the magnetic network are observed. It is generally assumed that in this case crystal water leads mainly to a modest change of the crystal field for the magnetic ion. In turn, small changes in the crystal field only, would directly suggest a description within the same model with slightly revised parameters. This leads to the common belief that crystal water plays only a minor role regarding the magnetic properties for compounds where crystal structure is basically preserved upon water intercalation.

Here, in contrast, we show that the hydration of CuCl₂ to CuCl₂·2H₂O fundamentally changes the magnetic properties, although the topology of the covalent Cu-Cl network is seemingly unchanged. Whereas CuCl₂·2H₂O is a classical three-dimensional (3D) anti-ferromagnet (AFM) with a Neél temperature of 4.3 K, we establish the dehydrated species as an example for a quasi 1D chain compound. The results of susceptibility measurements, density functional and model calculations can be consistently understood from a reorientation of the magnetically active Cu orbital driven by the hydration. Regarding the well known 3D magnetic nature of CuCl₂·2H₂O we predict a helical magnetic order below the observed transition at 24 K. Earlier studies that tried to model CuCl₂ as a spin 1/2 chain found considerable deviations from a 1D behavior since in these investigations only NN AFM coupling was considered. Alternatively a 1D model with AFM NN and NNN exchanges was suggested, but this model yields far too large couplings.

II. CRYSTAL STRUCTURE

The crystal structure of CuCl₂ is presented in Fig. 1. Cu and Cl form a covalent network of edge shared CuCl₄ plaquettes running along b direction. Such fourfold planar Cu²⁺ coordination suggests a strong analogy to the undoped cuprates. The Cu-Cl-Cu bond angle is 93.6° and thus very similar to that in the CuO₂ chain cuprate family, where bond angles close to 90° result in FM NN exchange like in Li₂CuO₂, LiCu₂O₄, and Li₂ZrCuO₄. As in the latter two compounds, these chains are arranged in layers (Fig. 1 top), suggesting a rather weak exchange between the layers. Since even the arrangement of the chains within the layers is very similar, a quasi 1D behavior might be expected from a mere comparison with these cuprate crystal structures.

When CuCl₂ is exposed to moisture, H₂O enters the space between the chain layers, finally forming the fully hydrated CuCl₂·2H₂O (Fig. 1 bottom). Although the crystal structure seems very similar at a first glance, the crystal water induces several changes: (i) The inter-layer distance increases, (ii) the CuCl₂ chains shift with respect to each other and, (iii) the Cu-Cl distances within
the chains are modified. Whereas the structural changes can be easily understood by packing and electrostatics (negatively polarized $O^{2-}$ is situated close to the $Cu^{2+}$ ions, $H^+$ is attracted by $Cl^-$), the origin of the drastic change of magnetic properties – 1D versus 3D – is far from obvious. Unraveling the underlying microscopic physics is the aim of our joint theoretical and experimental study.

III. METHODS

Polycrystalline CuCl$_2$ was prepared by dehydration of CuCl$_2$·2H$_2$O (Alfa Aesar 99.999%) under vacuum at 390 K. Single crystals were grown by chemical transport in a temperature gradient from 650 K to 575 K with AlCl$_3$ (Alfa Aesar 99.999%, ultra dry) as transport agent. The chemical characterization of CuCl$_2$·2H$_2$O and of the CuCl$_2$ crystals was carried out by X-ray powder diffraction, DSC/TG-methods and chemical analysis. The heat of dehydration was determined by DSC. Based on five independent measurements, the heat of dehydration is $\Delta H^{\text{dehyd.}} = (117 \pm 2)$ kJ/mol at 400 K.

Magnetization was measured in a SQUID magnetometer (1.8 – 300 K) in magnetic fields up to 7 T. Heat capacity was determined by a relaxation method in the same temperature range up to $\mu_0 H = 9$ T.

Exact diagonalization (ED) of the $J_1$–$J_2$ Heisenberg Hamiltonian has been performed on $N = 16$ sites clusters using the ALPS code. The low-temperature behavior of the magnetic susceptibility has been simulated using the transfer-matrix density-matrix renormalization-group (TMRG) method.

For the electronic structure calculations the full-potential local-orbital scheme FPLO (version: fplo7.00-28) within the local (spin) density approximation (L(S)DA) was used. In the scalar relativistic calculations the exchange and correlation potential of Perdew and Wang was chosen. To consider the strong electron correlations for the Cu 3$d^9$ configuration, we use the LSDA+$U$ approximation varying $U_d$ in the physically relevant range from 6 – 8.5 eV. The LDA results were mapped onto an effective tight-binding model (TB) and subsequently to a Hubbard and a Heisenberg model.
IV. RESULTS AND DISCUSSION

A. Thermodynamic measurements

The susceptibility data for both compounds are shown in Fig. 2. CuCl₂ exhibits a broad maximum at $T_{\text{max}} \approx 75\, \text{K}$ as a fingerprint of quasi 1D behavior. An AFM Curie-Weiss temperature $\Theta_{\text{CW}} = +107\, \text{K}$ has been extracted from the high temperature region. A sharp kink at $T_N = 24\, \text{K}$ (see Fig. 2 and inset $d\chi/dT$) followed by a rapid drop of $\chi$ indicates a magnetic phase transition as earlier suggested.

The measured zero-field specific heat as a function of temperature for CuCl₂ is shown in Fig. 3. Our data agree well with earlier studies. The specific heat curve shows a pronounced lambda shape anomaly at $T_N = 24\, \text{K}$ due to the onset of long range AFM ordering. The ordering temperature from $C_p$ is in perfect agreement with $T_N$ evaluated from susceptibility. Well below $T_N$ the total specific heat is described by $C_p = \beta T^3$ with $\beta = 0.8514(3)\, \text{mJ mol}^{-1} \, \text{K}^{-1}$ (fit for $T < 10\, \text{K}$), indicating that both phononic and magnetic contributions to $C_p(T)$ are $\propto T^3$. The data in a field $\mu_0 H = 9\, \text{T}$ show no visible differences to the zero-field data.

In contrast to the quasi 1D susceptibility of CuCl₂, the hydrated system shows an increasing $\chi$ down to low temperatures right above the AFM phase transition at $4.3\, \text{K}$ (see Fig. 2 and inset $d\chi/dT$) in perfect agreement with earlier measurements. A Curie-Weiss temperature $\Theta_{\text{CW}} = +5.3\, \text{K}$ indicating weak AFM interactions has been evaluated.

B. Band structure calculations

The essentially different character of the susceptibility of both compounds points to a changed coupling regime rather than to a mere re-scaling according to the modified atomic distances. To construct an appropriate microscopic model based on the relevant interactions we perform $ab$-initio electronic structure calculations, as successfully demonstrated earlier for the closely related CuO₂ chain compound family.

Total and partial densities of states (DOS) for both compounds are pictured in Fig. 4. On a coarse energy scale both systems are similar, the contribution of the additional H states to the valence region is negligible. Both compounds show half-filled, well separated anti-bonding bands at the Fermi level. This metallic behavior is in contrast to the experiment and is a well known shortcoming of the LDA due to the underestimation of the strong Coulomb repulsion for the Cu²⁺ 3d⁹ configuration. The observed insulating ground state is obtained (i) within the LDA+U approximation or (ii) by a model approach mapping the relevant low lying LDA states onto an effective TB model, and, including the correlations, subsequently onto a Hubbard and a Heisenberg model.

A closer inspection of the DOS and the related band structure reveals two important differences: (i) Whereas the width of the anti-bonding band in CuCl₂ is 0.8 eV – rather typical for 1D edge-shared CuO₂ chains – the bandwidth in CuCl₂·2H₂O is reduced by more than a factor of three to about 0.25 eV (Fig. 4). (ii) The magnetically active anti-bonding band in CuCl₂ is formed exclusively by Cu-Cl d$p\sigma$ states (inset Fig. 4a) corresponding to the bonds pictured in Fig. 1. In contrast, for CuCl₂·2H₂O the O 2p orbitals that are directed towards the Cu contribute significantly to this band (inset.
The leading transfer integrals and fitted it to the relevant LDA bands (Fig. 4e,f). Constructed a TB model (Fig. 4c) for both compounds, the plaquettes in CuCl$_2$·H$_2$O are isolated resulting in weak, but 3D interactions. For an independent evaluation of the leading exchange interactions confirm the intuitive picture of a quasi 1D chain model compound with small inter-chain coupling, very similar to LiCu$_2$O$_2$·H$_2$O. Therefore, the magnetic ground state is mainly determined by the ratio $\alpha = J_2/J_1$ of the frustrating main interactions along the chains. For CuCl$_2$, we find $\alpha = -(1.0 \pm 0.1)$ and predict a ground state well in the helical ordered region of the $J_1$–$J_2$-phase diagram.

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The calculated leading hopping integrals $t_i$ for the effective TB model shown in Fig. 4c.

| $t_i$/meV | $t_1$ | $t_2$ | $t_1^c$ | $t_2^c$ | $t_1^d$ |
|---|---|---|---|---|---|
| CuCl$_2$ | 34 | 117 | 61 | -19 | 8 |
| CuCl$_2$·2H$_2$O | 17 | 6 | 4 | 16 | 20 |

These $J$’s are perfectly in line with the experimentally observed $T_N = 4.3$ K as could be expected for an almost isotropic 3D coupling. For CuCl$_2$, the leading NNN $t_2$ results in $J_2 = 160 - 180$ K. Although of the correct order of magnitude compared to $T_{\text{max}}$ and $\Theta_{\text{CW}}$, this would clearly exceed the “overall AFM coupling” in the compound without additional FM interactions. Sizable FM interactions are typical for close to 90° bond angles according to the Goodenough-Kanamori-Anderson rules and therefore expected for the NN $J_1$ in CuCl$_2$. For a quantitative estimate of the FM contributions to the leading $J$’s we apply LSDA+$U$ calculations for different spin arrangements in magnetic super cells.

Mapping the resulting total energy differences to the Heisenberg model, we obtain the following total exchange integrals ($U_{\text{ic}} = 7 \pm 0.5$ eV$^{23}$, $J_1 = -(150 \pm 10)$ K, $J_2 = 155 \pm 25$ K and $J_1^c = 35 \pm 5$ K. Within the error bars, the latter two agree very well with the $J$ values calculated from the corresponding $t$’s of the TB approach indicating that FM contributions beyond NN are rather small. In contrast, we find a large FM contribution of about 175 K to $J_1$ as expected from the Cu-Cl-Cu bond angle of 93.6°. The size of the FM contribution to $J_1$ fits well to related edge-shared CuO$_2$ chain compounds.

The strongly correlated limit ($U_{\text{eff}} \gg t_i$) at half filling, the TB model can be mapped via a Hubbard model to a Heisenberg model with resulting AFM exchange couplings $J_i = 4t_i^2/U_{\text{eff}}$ where $U_{\text{eff}}$ is the correlation in the effective one-band description. Depending on the choice of $U_{\text{eff}}$ within a reasonable range ($U_{\text{eff}} = 3.5 - 4$ eV) this leads to exchange constants $J_i = 3 - 5$ K for the three leading couplings in CuCl$_2$·2H$_2$O (Table 1).

C. Model analysis of magnetic susceptibility

For an independent evaluation of the leading exchange interactions in CuCl$_2$ we simulated $\chi(T)$ within a spin-1/2 $J_1$–$J_2$ Heisenberg model for various $J_2/J_1$ ratios using the TMRG technique and fitted the resulting $\chi^\prime(T)/J$ curves to the measured $\chi(T)$. Rather typical for the $J_1$–$J_2$ Heisenberg model we find two possible solutions for the fit: (i) $\alpha = +3.0$ with $J_1 = 120$ K and $J_2 = 40$ K (AFM solution) and (ii) $\alpha = -1.5$ with...
$J_1 = -90$ K and $J_2 = 135$ K (FM solution). The FM solution (ii) is in rather good agreement with the estimates from our \textit{ab-initio} calculations. The corresponding fits are shown in Fig. 2. The AFM solution (i) can be discarded regarding our calculational results and the close to $90^\circ$ Cu-O-Cu bond angle.

In a naive approach, using the relation $\Theta_{\text{CW}} \approx 1/2(J_1 + J_2 + J_{ic})$, the theoretically estimated $\Theta_{\text{CW}}^{\text{exp}} \approx +30 \pm 10$ K seems to be inconsistent with the experimental $\Theta_{\text{CW}} \approx +100$ K. Thus, we choose a more sophisticated procedure performing ED studies for the FM solution, which yield the expected $\Theta_{\text{CW}} \approx 1/2(J_1 + J_2)$, but only at high temperatures $T > 10 J_2$. Since this high temperature region is inaccessible to experiments, we choose a temperature window of the Curie-Weiss fit in order to obtain $\Theta_{\text{CW}}$ for the highest temperatures measured ($225$ K < $T$ < $300$ K corresponding to $1.7 J_2 < T < 2.2 J_2$). Using $J_1$ and $J_2$ from the TMRG, we obtain $\Theta_{\text{CW}}^{\text{tho}} = +72$ K. The remaining difference between $\Theta_{\text{CW}}^{\text{tho}}$ and $\Theta_{\text{CW}}^{\text{exp}}$ of about $30$ K corresponds in very good agreement to the inter-chain coupling $J_{ic}$ of about $35$ K neglected in the ED simulations.

D. Thermochemical properties

The dramatic effect of the dehydration of CuCl$_2$·2H$_2$O certainly raises the question whether this is really a typical dehydration process or if the involvement of the crystal water related oxygen in the magnetic exchange via covalent Cu-O bonds is an indication for a chemical reaction on a different energy scale. The dehydration enthalpy $\Delta H_{\text{dehyd}}^{\text{tho}} = 117$ kJ/mol of CuCl$_2$·2H$_2$O is a typical (small) value for this class of materials. Our \textit{ab-initio} estimate for the dehydration enthalpy yields $\Delta H_{\text{dehyd}}^{\text{tho}} = 95$ kJ/mol which is in quite good agreement with the measured value, providing additional confidence to the reliability of the calculational procedure.

V. SUMMARY

In summary, our joint theoretical and experimental study provides a consistent explanation for the fundamentally different magnetic properties of CuCl$_2$·2H$_2$O and CuCl$_2$. Whereas CuCl$_2$·2H$_2$O is a quite isotropic 3D AFM with small exchange couplings due to the orientation of neighboring isolated CuCl$_2$O$_2$ plaquettes, CuCl$_2$ can be well understood in terms of a 1D FM-AFM $J_1$–$J_2$ chain model. This extension of the originally, critically discussed 1D AFM-NN only model re-establishes the pronounced 1D nature of the magnetism in CuCl$_2$. The dramatic change of magnetic properties between both compounds can be traced back to a switch of the magnetically active orbital induced by crystal water. From our \textit{ab-initio} calculations and model studies of the measured susceptibility using the transfer-matrix density-matrix renormalization-group and exact diagonalization techniques we predict a helical ground state and likely related multiferroic behavior for CuCl$_2$ driven by strong in-chain frustration originating from FM nearest neighbor and AFM next-nearest neighbor exchange interactions. Our study reveals that crystal water can have crucial influence on the electronic and magnetic properties of low dimensional magnets. More general, our work emphasizes that a transfer of model parameters from seemingly closely related systems is rather dangerous. The unaware neglect of this fact will lead to an at best inaccurate description of the physical properties in many cases.

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\textit{Note added in revision: While revising our manuscript, we learned that our magnetic model and predicted ground state was confirmed by an independent study.}\(^{27}\)}

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28 These compounds are known as $J_1$–$J_2$ chain models with FM NN and AFM NNN exchange, where the different $J_2/J_1$ ratios lead to different ground states.
29 Netzsch DSC 204 thermocouple, platinum crucible, heating rate 10 K/min, dry argon atmosphere, 10 mg sample.
30 The absence of an impurity related Curie tail at low temperatures indicates the high quality of the sample.
31 For comparison, CuGeO₃ shows a bandwidth of 0.95 eV for the anti-bonding band, CuSiO₃ about 0.65 eV and LiCuVO₄ about 0.7 eV.
32 The chosen region for $U_d$ covers the experimental NN exchange $J_1$ in La$_2$CuO$_4$.
33 This good agreement justifies a posteriori the transfer of the $U_{\text{eff}}$ and $U_d$ values from the CuO$_2$ chain compounds.
34 Even for medium size clusters ($N = 16$), ED perfectly describes the high-temperature region of $\chi(T)$ which obeys a Curie-Weiss law.