

Crystal water induced alteration of magnetic exchange interactions

Miriam Schmitt^a, Marcus Schmidt^a,
Walter Schnelle^a, Stefan-Ludwig Drechsler^b and
Helge Rosner^{a,*}

^a MPI-CPFS Dresden, Nöthnitzer Straße 40, 01187 Dresden

^b IFW Dresden, Helmholtzstraße 20, 01069 Dresden

E-mail: rosner@cpfs.mpg.de

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Cuprates show an intimate interplay between the crystal structure and their magnetism, particularly with respect to frustration and dimensionality. On the other hand, it is a widespread belief that crystal water has just a moderate and quantitative influence to the magnetic properties of these compounds caused by the modification of interatomic distances. In contrast, the hydration of CuCl_2 leads to a dramatic change in magnetic behaviour and ground state. While $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is a classic example for a three-dimensional antiferromagnet ($T_N = 4.3$ K) [1] with small exchange couplings, CuCl_2 is a quasi-one dimensional chain compound that exhibits long-range order at $T \approx 24$ K [2].

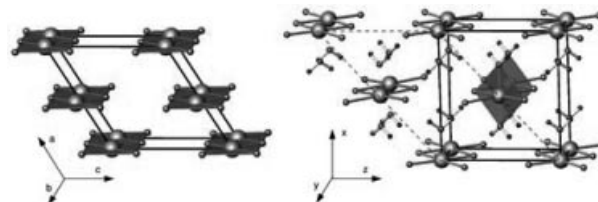


Figure 1 Left: CuCl_2 : The ligand field of Cl atoms forms an octahedral surrounding with four short (and two long) bonds leading to planar CuCl_4 subunits (orange) forming chains along b direction. Right: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: The crystal water changes the planar CuCl_4 coordination. The new planar $\text{Cu-Cl}_2\text{O}_2$ subunits are perpendicular to the former CuCl_4 blocks due to a strong increase (shown in blue) of two of the original Cu-Cl bond length. (Cu orange, Cl green, O red, H blue spheres)

Combining electronic structure calculation based on DFT, model calculation and thermodynamic measurements we investigate the microscopic origin of this surprising alteration of the magnetic interactions induced by the crystal water. Based on our calculations, the magnetically active orbital in CuCl_2 is formed by the Cu $3d$ and Cl $3p$ σ bonds in the bc plane (Fig. 1 left). For the resulting picture of magnetic chains with ferromagnetic nearest neighbour and antiferromagnetic next-nearest neighbour exchange we predict a helical ground state. Unexpectedly, the hydration of CuCl_2 modifies the coordination of the Cu^{2+} drastically, leading to a flip of the magnetically active orbital (Fig. 1 right). In turn, this causes a fundamental change in the coupling regime by strong reduction of the former in-chain interactions, yielding an almost isotropic three-dimensional coupling in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, consistent with the thermodynamic data and the antiferromagnetic ground state.

[1] W. Marshall, *J. Phys. Chem. Solids* **1958**, 7, 159.

[2] J. W. Stout et al., *J. Chem. Phys.* **1962**, 36, 979.