Quantum magnetism in spin ½ Cu-minerals and related compounds – a playground for the study of exotic ground states

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The study of low-dimensional spin-1/2 magnets has developed into a field of its own because these materials provide a unique possibility to study ground and excited states of a large variety of quantum models with very high accuracy [1, 2]. Despite their conceptual simplicity, these models provide rich magnetic phase diagrams [3, 4] arising from a complex interplay of quantum fluctuations and exchange interactions, which often result in magnetic frustration. In particular, dimensionality and lattice topology are decisive for the observed plethora of quantum phenomena like the spin-Peierls transition in $CuGeO_3$ [5], the possible quantum spin liquid state in the Cu-minerals Herbertsmithite [6] and Barlowite [7] or the formation of skyrmions in Cu_2SeO_3 [8-10].

Due to the rigid nature of chemical bonds for given valences of 3*d* transition metal compounds, in many cases the concept of rigid structural building blocks, connected in a large variety of different patterns, can be successfully applied for an analysis of the resulting exchange interaction, determining the magnetic lattice topology and the respective ground state. Spin ½ compounds are of particular interest for the study of quantum ground states because of the intrinsic strong quantum fluctuations due to the small local magnetic moment. Depending on dimensionality, lattice symmetry and structural peculiarities, magnetic frustration can strongly enhance the quantum fluctuations, finally resulting in exotic ground states. Here, we present a joined theoretical and experimental approach to study microscopically the ingredients and origins of unusual quantum phenomena.

One way to encounter new exotic ground states is the synthesis of new compounds. Alternatively, nature has done this demanding job for us in hundreds of millions of years by mere chance. Even restricting our search to Cu^{2+} spin ½ compounds, more than 900 Cu-minerals are known, and many of them are still completely unexplored. Since their essential building block, a Cu^{2+} $3d^9$ ion, fourfold coordinated by O-ligands, can be linked in a huge number of different ways, these minerals are a real treasure trove for the emergence of new magnetic model compounds.

The natural growth of minerals provides in many cases large and on the first glance perfect single crystals (see Fig. 1). However, substitutional disorder or an undefined water content of the samples can be an issue. Therefore, a detailed characterization of the investigated samples by X-ray diffraction, chemical analysis and EDX is essential. In addition, the size of the impurity contribution in the low temperature magnetic susceptibility is a very good fingerprint for the sample quality. Measurements of the thermodynamic properties, like magnetic susceptibility, specific heat or field dependent magnetization often yield ambiguous data for the interpretation of the underlying magnetic model. Therefore, we have chosen a combined theoretical and experimental approach to establish a microscopically justified magnetic model for the compounds under investigation.

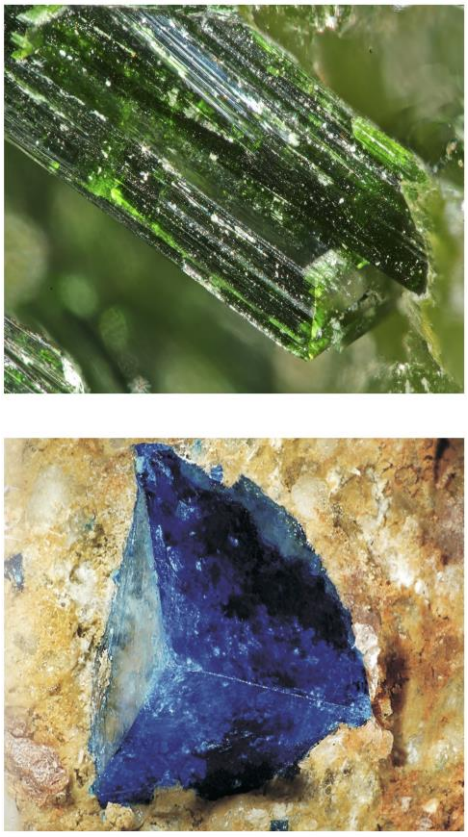

Fig.-1: Examples of the investigated mineral samples: the triple chain system Szenicsite $Cu_3(MoO_4)(OH)_4$ (upper panel) and the cuboctahedral molecular magnet Boleite $KPb_{26}Cu_{24}Ag_9(OH)_{48}Cl_{62}$ in a matrix (lower panel).

Applying state of the art density functional electronic structure calculations, we obtain a semi-quantitative regime of exchange interactions for a given crystal lattice. The mayor challenges here are the strong electronic correlations, intrinsically present in these compounds, which can be only taken into account rather approximately in a mean field way in the self- consistent calculations. Although the calculations yield for most geometries a rather good estimate of magnetic exchange couplings, a refinement of the models to fit the thermodynamic data is crucial. To relate the theoretically estimated exchange constants and the experimental observations, we apply numerical simulations like high-temperature series expansion (HTSE), exact diagonalization (ED) or density matrix renormalization group (DMRG) approaches. In the following, we want to illustrate our procedure by a few examples.

Boleite - a frustrated molecular Archimedean nano magnet

Molecular spin ½ quantum magnets with the structure of Archimedean solids are not only esthetically pleasing, but due to distinct frustration effects also magnetically very attractive. Synthetical efforts in the lab yielded only two such compounds so far: an icosidodecahedron of vanadium 4+ as well as a cuboctahedron of copper 2+ ions. However, mother nature - using her own recipes - created a third model compound, a truncated cube, which is at the heart of the mineral Boleite ($KPb_{26}Cu_{24}Ag_9(OH)_{48}Cl_{62}$). The perfect bright blue crystalline cubes (see Fig. 1) receive their magnetic properties from a spin lattice of truncated cubes that embody 24 copper spin ½ ions, thereby forming molecule-like units in the three-dimensional solid structure (see Fig. 2).

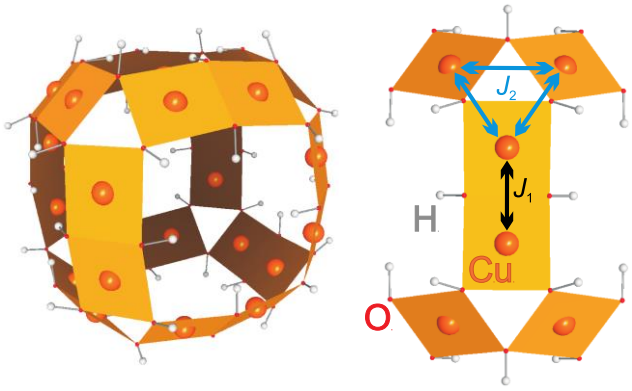

Fig.-2: Left panel: Geometric structure of the isolated Cu_{24}-cuboctahedron built from 24 CuO_4-plaquette building blocks (filled orange rectangles). Grey spheres represent the adjacent H-atoms which have a strong influence on the leading exchanges. Right panel: Leading exchange terms; ferromagnetic J_1 on the structural Cu_2O_6-dimer forming the edge of the cubeoctahedron and antiferromagnetic J_2 connecting the dimers by frustrated triangles at the edges of the cubeoctahedron.

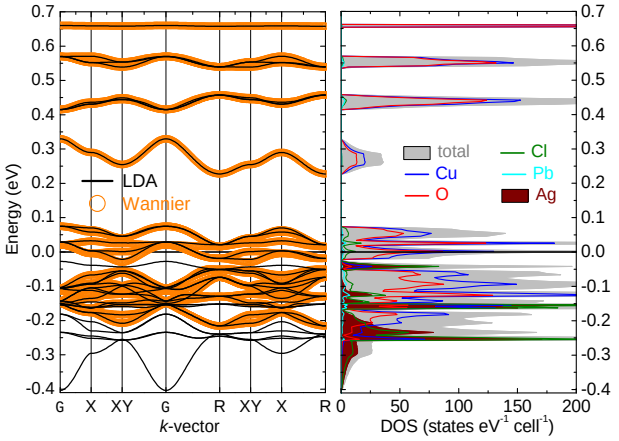

Fig.-3: Electronic structure of the antibonding states of boleite responsible for the magnetic properties. Left panel: LDA band structure (full black lines) and bands derived from the 24 Cu centered Wannier functions of the local CuO_4 plaquette orbitals (orange circles). Right panel: Total and partial DOS of the antibonding band complex, showing a weak mixing, only, between the Cu-O derived bands and the Ag-Cl bands.

To estimate the relevant magnetic exchange couplings, we start with a density functional electronic structure calculation. We use the experimental crystal structure, but optimize the hydrogen positions with respect to the total energy, since in the available experimental data the H positions are often ill defined or even unknown. For the calculation of the exchange couplings, however, accurate H positions are crucial.

Fig. 3 shows the calculated band structure and the bands derived from the 24 Cu centered Wannier functions of the local CuO_4 plaquette orbitals. The Wannier-derived bands are basically identical with the LDA bands of the respective CuO_4 plaquete states, demonstrating the suitability of an effective single band model. The dispersion of the individual bands is very small, reminescent to localized molecular states, thus showing the tiny interaction between the Cu_{24} cuboctahedra. Although forming a three-dimensional crystal lattice, the system can be considered as molecular magnet in very good approximation. A closer inspection of the related tight-binding model (calculated from the Wannier functions) yields two leading coupling parameters (see Fig. 3): t_2=177 meV between two adjacent dimers and t_1=115 meV within

the dimers. For these leading couplings, LDA+*U* total energy calculations for different spin configurations yield a ferromagnetic J_1~75+-5 K and an antiferromagnetic J_2 ~ 240+-30 K. In conclusion, the magnetic model for the cuboctahedron can be well described in terms of 8 strongly frustrated, antiferromagnetically coupled triangles at the corners of the cuboctahedron that are ferromagnetically coupled via the edges. For the estimated exchange parameters, exact diagonalization studies estimate a magnetization plateau at ⅓ of the total saturation magnetization in moderate magnetic fields. Applying pulsed high-field measurements up to 60 T in the Dresden High-field-Lab, an extended plateau was experimentally observed above 35 T, verifying the peculiar molecular magnetic state of this system.

Frustrated spin chain physics near the Majumdar-Ghosh point in szenicsite $Cu_3(MoO_4)(OH)$

Taking a similar combined theoretical and experimental approach we investigated the magnetic behavior and microscopic magnetic model of the rare Cu^{2+} mineral szenicsite (see Fig. 1), whose crystal structure features isolated triple chains. These chains consist of a central chain formed by edge-sharing CuO_4 plaquettes and two side chains built of corner-sharing plaquettes with MoO_4 groups attached (see Fig. 4). A consistent magnetic model could be derived on the basis of LDA and LSDA+U calculations of exchange coupling constants, fits of susceptibility data, and model analysis of the magnetization and heat capacity [11].

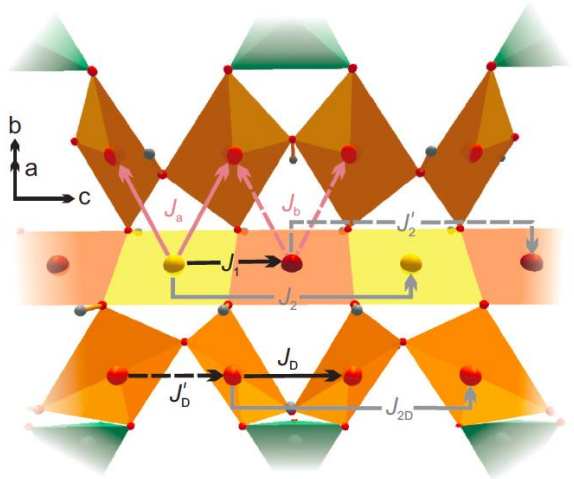

Fig.-4: Crystal structure and exchange pathways within the structural triple chain of szenicsite. The crystallographically different CuO_4 plaquettes, resulting in an alternating next-nearest neighbor exchange J_2, are shown in different colors. The MoO_4 side groups are shown in green.

Even though the crystal structure suggests a three-leg ladder magnetic model, it turns out that the side chains can be reduced to AFM dimers with a coupling strength of about 200 K, where the central chain features an AFM next neighbor coupling of about 68 K and alternating next-nearest neighbor couplings. The couplings between the chains are quite small, below 30 K, and of minor importance for the magnetic model because of the frustration and different energy scales in the side chains versus the central chain. Accordingly, the low-temperature physics of szenicsite is well described by an original version of the AFM J_1-J_2 model with alternating J_2 -J_2 couplings. According to the J_2/J_1 ratio of about 0.45, the system is in close vicinity to the Majumdar-Ghosh point of 0.5. A small spin gap should be present in szenicsite. Its upper limit of about 4 K is consistent with our magnetization measurements. A similar mechanism of gap opening is likely responsible for the formation of idle spins in the closely related mineral antlerite.

However, the physics of side chains is largely different in the two minerals. We ascribed these differences to the effects of side groups and hydrogen positions that play a crucial role for magnetic interactions in cupric minerals.

External Cooperation Partners

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