# Electronic structure and magnetic properties of melanothallite ($Cu_2OCl_2$), a gateway to understanding copper oxychlorides

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Transition-metal-based minerals show a variety of crystal structures and offer unique possibilities for the investigation of interesting physical phenomena caused by strong electronic correlations. The Cu-containing compounds are especially interesting with respect to their low-temperature magnetic properties that are essentially governed by quantum effects. In this contribution, we present a combined experimental and computational study of melanothallite and apply the gained insight to other copper oxychlorides with exotic low-temperature properties.

Melanothallite is a simple copper oxychloride $Cu_2OCl_2$. Copper atoms have planar coordination with two O and two Cl atoms surrounding each Cu. The resulting $CuO_2Cl_2$ plaquettes share edges and form crossing chains. Our x-ray and neutron diffraction experiments evidence a non-trivial evolution of the crystal structure below room temperature and show the formation of an incommensurate magnetic structure below $T_N$ = 70 K. To explore the magnetic ground state, we calculated the band structure of $Cu_2OCl_2$ within the framework of density functional theory (DFT) and evaluated the electronic state of Cu along with the leading magnetic exchange couplings. The oxidation state of Cu is +2 (electronic configuration $3d^9$, spin-1/2). The half-filled $d$ orbital has the $x^2–y^2$ symmetry and lies in the $CuO_2Cl_2$ plane. The magnetic interactions are highly non-trivial. Each chain of edge-sharing plaquettes is a frustrated spin chain with competing ferromagnetic nearest-neighbor ($J_1 \sim -$ 180 K) and next-nearest-neighbor ($J_2 \sim$ 100 K) interactions. Moreover, sizable interchain interactions ($J_i \sim$ 220 K) are found. The resulting spin lattice features an unusual quantum spin model. The magnetic frustration readily leads to the incommensurate magnetic structure that can cause strong magnetoelectric coupling.

The crystal structure of melanothallite is a key to understanding synthetic copper oxychlorides. For example, the crystal structure of a quantum magnet $(CuCl)LaNb_2O_7$ remains controversial due to the uncertainty in the Cl position. Since the $CuO_2Cl_2$ plaquette is the preferential copper coordination in melanothallite, a similar local environment can be proposed for the $(CuCl)LaNb_2O_7$ structure. We confirmed this conjecture using DFT structure relaxation and synchrotron x-ray diffraction at different temperatures. The resulting structural model is in agreement with the available data from nuclear magnetic resonance and Raman spectroscopy. The proposed crystal structure leads to non-trivial magnetic superexchange couplings that explain the puzzling results of magnetization and inelastic neutron scattering measurements. We show that the precise crystal structure solution along with the quantitative information on the band structure are essential for understanding the physical properties of Cu-based compounds.