Magnetically-Driven Phase Transitions in Cu Halides and the Role of Spin-Lattice Coupling

Musfeldt, J.L., Hughey, K.D., Harms, N.C., O'Neal, K.R., Clune, A.J., Blockman, A., Monroe, J.C., Liu, Z. (Univ. of Tennessee); Ozerov, M., (NHMFL); Landee, C. (Clark Univ.)

Introduction

Molecule-based materials offer exciting opportunities to explore the interplay between structure and magnetism. Soft ligands, which link the metal centers, introduce characteristically low energy scales, flexible architectures and externally-tunable properties, all of which are crucial to driving into new states of mater and revealing exotic properties. Complex copper halides have attracted attention due to their inherently quantum (S=1/2) nature and low-dimensional magnetic character.[1] By modifying stoichiometry and chemical composition, both hydrogen-bonding interactions and spin exchange pathways can be altered. This provides an effective platform for the control of structural and magnetic dimensionality. The role of external stimuli is especially important in the investigation of quantum phase transitions. Copper halide complexes manifest in multiple dimensions, ranging from zero-dimensional systems to square lattices. Although the spin behavior of 1D and 2D systems have been extensively explored, less is known about how the spin-lattice interactions that develop across the quantum phase transitions vary as a function of dimensionality. At the same time, the lack of a systematic series of magneto-infrared measurements on a full set of chemically-similar materials has been a significant impediment to the development of structure-property relationships. The recent development of a Cu halide spin ladder provides an intermediate dimensionality system with which we can explore these entanglements.

Results and Discussion

We combined magneto-infrared spectroscopy and high field magnetization to explore spin-lattice coupling in a series of copper halide complexes including the two-leg ladder system $[Cu(pyz)_{1.5}(4\text{-}OHpy)_2](ClO_4)$. Analysis of the out-of-plane pyrazine bending modes reveal that local lattice distortions are an integral part of the magnetically-driven transitions to the fully saturated state [Fig. 1(a, b, c)]. Using the field-induced frequency shifts, we extract spin-phonon coupling constants for this and several other copper halides of varying dimensionality. Figure 1(d) summarizes the results. $[Cu(pyz)_{1.5}(4\text{-}OHpy)_2](ClO_4)$ sports the largest effects, with the important distortions occurring within the rails and runs of individual ladders. That a single vibrational mode is sensitive to field suggests that the ladder tends toward Cu dimer formation – which have only one important super-exchange interaction along the rungs and thus require simpler distortions to achieve magnetic saturation.

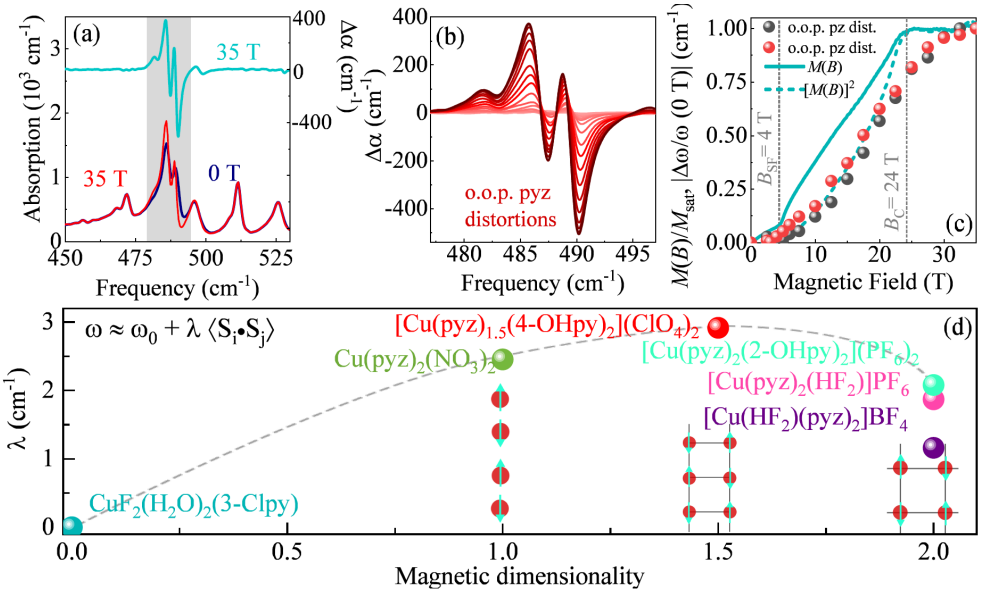

Figure 1: (a) Absorption of $[Cu(pyz)_{1.5}(4\text{-}OHpy_2](ClO_4)_2$ at 0 and 35 T along with the 35 T absorption difference spectra. A vertical gray band highlights the field-induced changes. (b) Absorption difference of the magneto-active modes with increasing field. (c) Overlay of magnetic field-induced frequency shifts of the out-of-plane pyrazine distortions plotted with magnetization and the square of magnetization at 1.5 K. (d) Comparison of spin-phonon coupling constants of the out-of-plane pyrazine distortion between several known Cu halides as a function of magnetic dimensionality.

Acknowledgements

This research is supported by DMR-1707846 from the National Science Foundation and the Materials Research Fund at the University of Tennessee. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida.

References

[1] Landee, C. P. and Turnbull, M. A., J. Coord. Chem. **67**, 375 (2014).