Magnetization Study of $Ni(HF_2)_2(H_2O)(3\text{-fluoropyridine})_3$ Single Crystals

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Introduction

$[Ni(HF_2)(pyz)_2]SbF_6$ (pyz = pyrazine = $N_2C_4H_4$) was recently synthesized and its crystal structure determined to consist of a tetragonal MOF-like 3D network. This network can be deconvoluted into linear Ni-FHF-Ni chains along the *c*-axis that are cross-linked by pyz ligands to form 2D square lattice propagating in the *ab*-plane [1]. Evidence provided by various magnetic property measurements establish quasi-1D magnetic exchange along the Ni-FHF-Ni chains (J_{1D}) with a much weaker coupling along Ni-pyz-Ni (J_{pyz}). Despite this, a relatively high T_N of 12.2 K was found which is the highest such temperature observed in materials of this type. We have also found that this and other related systems possess sizeable zero-field splitting (ZFS) of up to 11 K. Substitution of the pyz ligands for 3-fluoropyridine (3-Fpy) leads to the coordination complex $Ni(HF_2)_2(H_2O)(3\text{-Fpy})_3$ [2]. Although the crystal structure contains the desired F···H···F^- ligands, they are non-bridging. However, the coordinated H_2O ligand forms bifurcated hydrogen bonds with fluorides coordinating adjacent NiN_4F_2 octahedra to form zig-zag chains with the closest Ni···Ni intrachain distance being 5.35 Å. As an initial means to try to determine the relative magnitude of the ZFS, we used pulsed magnetic fields to characterize the magnetization of $Ni(HF_2)_2(H_2O)(3\text{-Fpy})_3$.

Experimental

Magnetization studies were provided by a 60 T short-pulse magnet located at the Pulsed Field Facility, National High Magnetic Field Laboratory, Los Alamos, NM. The susceptometer was placed within a ^{3}He cryostat providing temperatures down to as low as 0.5 K. The field *B* was measured by integrating the voltage induced in a ten-turn coil calibrated by observing the de Haas–van Alphen oscillations of the belly orbits of the copper coils of the susceptometer.

Results and Discussion

Magnetization (*M*) measurements (**Figure 1**) performed on oriented single crystals of $Ni(HF_2)_2(H_2O)(3\text{-Fpy})_3$ reveals some slight differences in behavior. With the field applied is along the chain-axis, the magnetization exhibits a pronounced concavity with saturation (B_c) occurring at 10 T. For a crystal aligned perpendicular to the chains, *M* displays a more subtle concavity and then broadens as saturation is reached at 10.2 T. From these data there is no evidence for a spin-gap which precludes the existence of the Haldane phase whereas the similar B_c's for the two unique axes suggests very little *g*-factor anisotropy of the Ni(II) ion as expected.

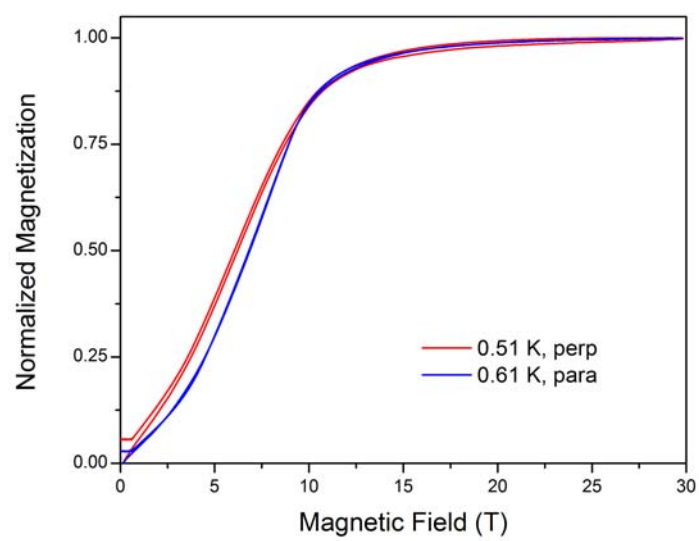

Figure 1. Magnetization data for $Ni(HF_2)_2(H_2O)(3\text{-Fpy})_3$ measured parallel and perpendicular to the Ni-F···H-O-Ni chains.

Conclusions

We find evidence for gapless magnetic behavior in $Ni(HF_2)_2(H_2O)(3\text{-Fpy})_3$. Future experiments aimed at better understanding the ZFS, including high-field/frequency electron-spin resonance, are being pursued.

Acknowledgements

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References

[1] J.L. Manson, *et al.*, *Inorg. Chem.* **2011**, *50*, 5990.
[2] J.L. Manson, *et al.*, unpublished results.