Magnetization Study of $[Ni(HF_2)(3\text{-chloropyridine})_4]BF_4$ 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. Substitution of the pyz ligands for 3-chloropyridine (3-Clpy) leads to the quasi-1D chain compound $[Ni(HF_2)(3\text{-Clpy})_4]BF_4$ which retains the same NiF_2N_4 coordination environment but only the Ni-FHF-Ni bridges [2]. The chemical tunability of this system allows us to directly examine the Ni-FHF-Ni magnetic interaction in order to assess the exchange efficiency of these strong hydrogen bonds.

Experimental

Magnetization studies were provided by a 65 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**) conducted on oriented single crystals of $[Ni(HF_2)(3\text{-Clpy})_4]BF_4$ reveals stark differences in behavior. With the field applied along the chain-axis, a nearly linear rise in *M* suggests the presence of low-dimensional spin correlations with saturation (B_c) occurring at ~18 T. For a crystal oriented perpendicular to the chains, *M* exhibits a slight concavity and then broadens as saturation is reached near 11 T. From the data in hand there is no evidence for a spin-gap precluding the existence of the Haldane phase whereas the large variation in B_c for the two axes exceeds expectation for g-factor anisotropy of the Ni(II) ion. With an estimated crystal field splitting (*D*) of ~4.3 K and J_{1D} ~4.9 K, we arrive at a *D*/*J* ratio close to unity which is unique among Ni(II)-chain materials [2].

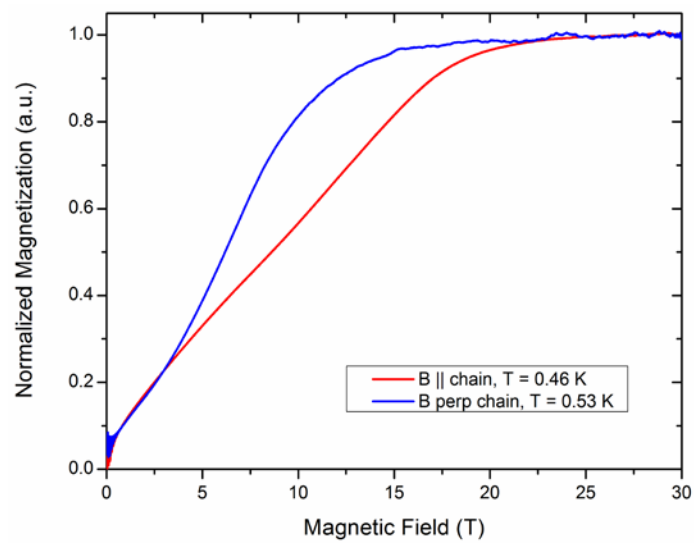

Figure 1. Raw magnetization data for $[Ni(HF_2)(3\text{-Clpy})_4]BF_4$ measured parallel and perpendicular to the Ni-FHF-Ni chains.

Conclusions

We find evidence for gapless magnetic behavior and moderate intrachain coupling in $[Ni(HF_2)(3\text{-Clpy})_4]BF_4$. Future experiments aimed at better understanding these data, including high-field/frequency electron-spin resonance, will be pursued.

Acknowledgements

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References

[1] J.L. Manson, *et al.*, *Inorg. Chem.* **2011**, *50*, 5990.
[2] J.L. Manson, *et al.*, *Inorg. Chem.* **2012**, *51*, 7520 and unpublished results.