A disordered polymorph of $[Ni(HF_2)(pyz)_2]PF_6$ (pyz = pyrazine)

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Introduction

Under ambient conditions, $[Ni(HF_2)(pyz)_2]PF_6$ exists as two polymorphs, monoclinic and tetragonal, and both have been structurally and magnetically characterized [1, 2]. We have recently discovered a second monoclinic phase (Fig. 1) of this material which possesses a disordered structure [3]. The pyrazine ligands exist in two possible orientations and the PF_6^- anion exhibits four-fold positional disorder; shaded atoms in Fig. 1. As compared to the originally reported monoclinic phase (T_N = 6.2 K), the new polymorph has a slightly lower T_N of 5.1 K [3], likely attributed to disordered superexchange pathways. Herein, we employ high-field magnetization to complement its temperature-dependent magnetic properties.

Experimental

Pulsed-field magnetization measurements of powdered **1** and **2** were performed using a short-pulse 65 T magnet at NHMFL Los Alamos. The samples were cooled and measurements made at a variety of temperatures in the range 0.6 < T < 15 K using a ^{3}He cryostat. SQUID data obtained at 1.8 K were used to calibrate the pulsed-field $M(H)$ data in order to quantify the saturated moment.

Results and Discussion

Fig. 2 shows the T < 2 K pulsed-field magnetization for $[Ni(HF_2)(pyz)_2]PF_6$ [3]. As the field increases, M increases slowly until ~2.6 T wherein the magnetization rises more abruptly. This kink near 2.6 T is likely due to a spin-flop transition, $\mu_0 H_{c1}$. Beyond this point, M rises nearly linearly and broadens as the saturation field, $\mu_0 H_{c2}$, is reached at ~15 T. The saturated moment is ~ 2.2 μ_B as expected for a Ni(II) ion in a near-octahedral crystal field with g ~ 2.2. The transition fields, $\mu_0 H_{c1}$ and $\mu_0 H_{c2}$, occur at reduced values relative to the original monoclinic phase [1].

Conclusions

A third polymorph of $[Ni(HF_2)(pyz)_2]PF_6$ has been synthesized and characterized by pulsed-field magnetization. We observe a field-induced phase transition near 2.6 T owing to a probably spin-flop phase. Magnetic saturation occurs near 15 T. Heat capacity measurements are planned in the near future to further characterize the magnetic ground-state of this material.

Acknowledgments

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References

[1] Manson, J.L., *et al*., *Inorg. Chem*. **50**, 5990 (2011).
[2] Manson, J.L., *et al*. *Dalton Trans*. **41**, 7235 (2012).
[3] Manson, J.L., *et al*. manuscript in preparation (2018).

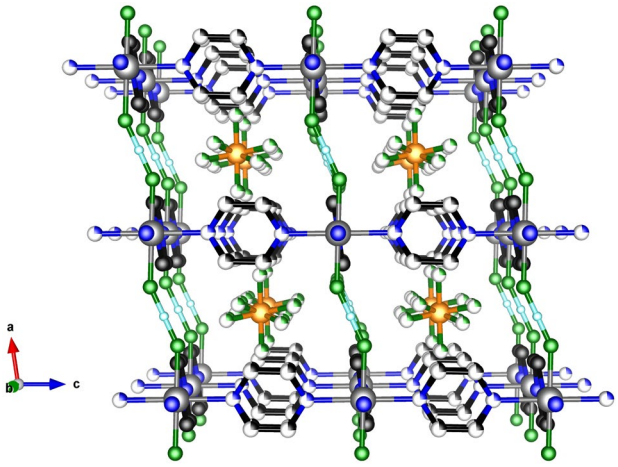

Fig. 1 Crystal structure of $[Ni(HF_2)(pyz)_2]PF_6$. Positionally disordered atoms are octant shaded. Ni, C, N, F, H and P atoms are delineated as gray, black, blue, green, cyan and orange spheres, respectively.

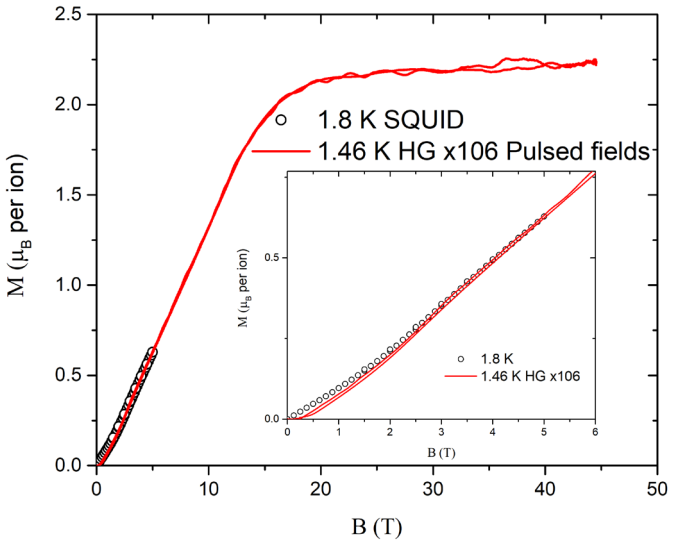

Fig. 2 Pulsed-field $M(H)$ data for $[Ni(HF_2)(pyz)_2]PF_6$.