Pulsed-field Magnetization of the S = 1 Square Lattices $NiX_2(pyrazine)_2$ (X = Cl^-, Br^-)

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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]. The SbF_6^- anions are non-coordinating and occupy interpore sites. 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. Complications in data analyses stemming from the lack of single crystals, as well as crystal field splitting (D) of the octahedral Ni(II) ion, necessitated studies of model compounds. In this case, we desired to better understand the Ni-pyz-Ni functionality of $[Ni(HF_2)(pyz)_2]SbF_6$ while retaining a similar tetragonal NiX_2N_4 crystal field. Thus, $NiX_2(pyz)_2$ square lattices were synthesized so as to reduce the strong spin correlations exemplified by the HF_2-containing polymer.

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 measurements (**Figure 1**) conducted on powder samples of the isomorphous title complexes revealed B_c's of ~6.8 and 6.3 T for $NiCl_2(pyz)_2$ and $NiBr_2(pyz)_2$, respectively. These data, combined with preliminary theoretical analyses of magnetic susceptibility and heat capacity data, suggest J_{pyz} ~1 K. The sharper critical field observed in the Br-material implies more 3D-like magnetic behavior relative to the Cl-analog which exhibits a much broader saturation. Moreover, $NiCl_2(pyz)_2$ may exhibit a larger D relative to Br which may further contribute to the more rounded magnetization behavior.

Conclusions

Not surprisingly, the magnetic susceptibility data for the $NiX_2(pyz)_2$ polymers reveal similar characteristics. However, clear differences in the low temperature magnetization for $NiCl_2(pyz)_2$ and $NiBr_2(pyz)_2$ suggest that D_{Cl} may be significantly larger than D_{Br} such that the latter exhibits 3D long-range magnetic order while the Cl-system may not.

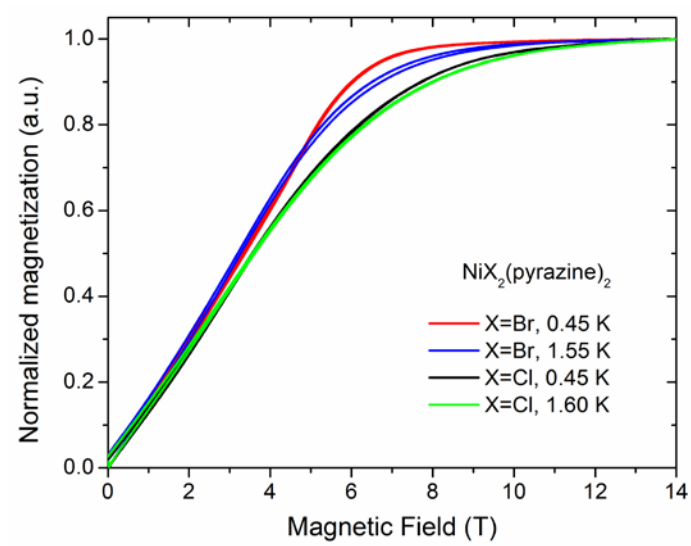

Figure 1. Pulsed-field magnetization data for the S = 1 square lattice antiferromagnets $NiX_2(pyz)_2$.

Acknowledgements

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References

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[2] P. Goddard, *et al.*, manuscript in preparation.