**Anomalous Behavior of Spin Dynamics in the Metal-Organic Framework (MOF)
Dimethylammonium Manganese Formate (DMMnF) from 1H and 55Mn NMR**

Reyes, R.R.(NYU/NHMFL); Ramakrishna, S.K.(FSU/NHMFL); Haddock, J.(FSU); Reyes, A.P. (NHMFL) and Dalal, N. (FSU/NHMFL)

**Introduction**

 Multiferroics have been of great recent interest for their unique simultaneous demonstration of both electric and magnetic properties which has potential technological applications. Recently, multiferroic behavior has been observed in Metal Organic Framework (MOF) compound Dimethylammonium Manganese Formate (DMMnF). [1] This system exhibits a dielectric transition around 184K and a weak canted antiferromagnetic (AF) behavior at *T*C = 8.4K. The microscopic details of these phase transitions are studied using 1H and 55Mn NMR technique.

**Experimental**

 Crystals were synthesized via hydrothermal process. [1] The NMR spectra and relaxation time T1 were taken in a 12T superconducting magnet by sweeping the frequency from 30-116 MHz over different set fields.

**Results and Discussion**



**Fig. 1** 1H NMR spectra at 1.2T as a function of temperature.



**Fig. 2** Temperature dependence of the outermost 1H peak position.



**Fig. 3** Plot of both long and short T1 for the central peak (**o ~ 51.45 MHz).

**Fig. 1** shows the temperature dependence of the 1H spectra as the system crosses the magnetic ordering temperature. Above *T*C, the spectra simplify to a three-peak signal: (Left) amine H, (Central) methyl, (Right) formate. Below *T*C, the position of the outermost peak fits with a critical scaling with exponent ** ~ ¼, compared with the Mean Field (MF) model (**= ½) (**Fig. 2**). Spectra for 55Mn (not shown) were obtained at zero-field and was interpreted to originate from AF ordered Mn moments producing 8T hyperfine field. This signal is suppressed above 0.3T, consistent with the spin-flop transition. [2] The proton relaxation of the methyl line exhibits double exponential behavior. **Fig. 3** shows the short component (red) is weakly temperature dependent at high temperatures but undergoes critical fluctuations as the system crosses the magnetic boundary (*T*C = 8.32K), consistent with a spin gap model. The long T1 component (blue) on the other hand shows a dip below 150K near the FE transition and is not sensitive to the magnetic order. This difference is not yet clearly understood.

**Conclusions**

 The 55Mn and 1H NMR provided microscopic details on the AF phase transitions of DMMnF. Strong hyperfine fields from local Mn moments are observed whose fluctuations are faster than MF prediction. The fast relaxation data suggest a spin gap in the density of states while the long component probably samples a different part of the spin fluctuation spectrum.

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**References**

[1] P. Jain *et al*., J. Am. Chem. Soc. **131**, 13625 (2009).

[2] Clune *et al*., Physical Review B*,***96,** 104424, (2017).