Glassy Behavior in the Metal Organic Framework [(CH$_3$)$_2$NH$_2$]Zn(HCOO)$_3$

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**Introduction**

We report on a glassy behavior in a metal organic framework (MOF) with a perovskite architecture (Fig. 1), [(CH$_3$)$_2$NH$_2$]Zn(HCOO)$_3$ (DMAZF) [1]. MOFs are extended organic-inorganic crystalline solids with strong bonding providing robustness and a geometrically well defined structure. Glassy behavior related to orientational ordering is observed in many polymeric systems and plastic crystals. A knowledge of the orientational ordering is important because it influences the properties and phase diagrams of such systems. DMAZF undergoes an order-disorder phase transition at 156 K, and we report here on solid state proton NMR spin-lattice relaxation time measurements of this transition and other ordering processes observed [2].

**Experimental**

The sample consisted of 20-30 sub-mm sized single crystals. The spin-lattice relaxation time ($T_1$) of DMAZF was measured over a wide temperature range (4-250 K), using a spectrometer available at the NHMFL. Measurements were taken at $H=6.267$ T (266.8 MHz for protons). The standard $\pi/2-\tau-\pi/2$ saturation recovery procedure was used.

**Results, Discussion and Conclusions**

The $T_1$ of the CH$_3$ protons was used as a probe of the local order and molecular dynamics of the (CH$_3$)$_2$NH$_2^+$ (DMA) unit. Fig. 2 shows the $T$ dependence of the spin-lattice relaxation rate ($T_1^{-1}$). The main graph has been divided into three regions guided by natural breaks in the slope. In region C, DMAZF is in the paraelectric phase. On lowering $T$, $T_1^{-1}$ increases to a maximum around $T_c$ and thereafter decreases as DMAZF enters the antiferroelectric regions (A and B). In the range $T=65$-250 K, $T_1^{-1}$ is completely reversible along the main path. This reversibility holds as long as the sample is not cooled below 40 K. The $T$ dependence of $T_1$ for the PE phase and for the main path in region B was analyzed using the BPP formalism [3], in which the relaxation rate is related to the correlation time $\tau_c$:

$$\frac{1}{T_1} = \frac{9}{20} \left( \frac{\mu_0^2 \gamma^2 h}{4 \pi^3} \right)^2 \left( \frac{T_c}{1 + \omega^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega^2 \tau_c^2} \right).$$  \[1\]

The $T$ dependence of $\tau_c$ follows an Arrhenius-like behavior with $\tau_c = \tau_o \exp(E_a/RT)$, where $E_a$ is the activation energy. $\tau_c$ experiences an anomalous increase across $T_c$, implying that the AFE transition results from a freezing of the DMA hopping motion between its three sites. In region B, $T_1$ becomes multivalued over the range 65 K - $T_c$, depending on cooling history. Two such paths are shown in the inset to Fig. 2, obtained while raising $T$, after the sample was cooled to ~4 K. $T_1$ shows sudden jumps from the metastable paths to the main path at unpredictable temperatures, implying that the structures attained are very close in energy. This existence of several different local structures is consistent with glassy behavior. A new relaxation pathway begins to operate in region A, with a maximum at ~40 K. This is analogous to relaxation processes found in many methyl-containing solids [4].

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**References**