

Spin dynamics in the molecule-based ferromagnet decamethylferrocenium tetracyanoethanide $[\text{FeCp}_2^*][\text{TCNE}]$, as probed by ^1H NMR relaxation

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This contribution is dedicated to Dr. Aris Terzis for the occasion of his retirement.

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ABSTRACT

A ^1H Nuclear Magnetic Resonance study of the molecule-based ferromagnet decamethylferrocenium tetracyanoethanide, $[\text{FeCp}_2^*][\text{TCNE}]$, is reported. The dynamics of the electronic spin system is investigated by performing T_1 and T_2 relaxation time measurements. A strong peak in the temperature dependence of the ^1H T_1^{-1} spin–lattice relaxation rate is observed at a temperature above the zero-field critical transition temperature T_c . The T_2^{-1} spin–spin relaxation rate also exhibits a weaker peak at the same temperature. It is proposed that the relaxation rate maxima are associated with the temperature dependence of the static uniform susceptibility of a ferromagnetic Ising linear chain and also to the development of short range order at temperatures above T_c for this low-dimensional Ising-like compound.

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1. Introduction

Magnetism in molecule-based materials has been a challenging field for both theorists and experimentalists since the realization of molecule-based ferromagnets exhibiting a spontaneous magnetization below a critical temperature T_c [1,2]. The mixed-stack electron transfer salt decamethylferrocenium tetracyanoethanide, $[\text{FeCp}_2^*][\text{TCNE}]$, was the first reported molecule-based ferromagnet undergoing a phase transition to a ferromagnetically ordered state at $T_c = 4.8$ K [3,4]. This system forms a one-dimensional structure with stacks of alternating $[\text{FeCp}_2^*]^+$ (containing Fe^{3+} in a low spin $S = 1/2$ state) and $[\text{TCNE}]^{*-}$ (with $S = 1/2$) ions. The intrachain $\text{Fe} \cdots \text{Fe}$ distance is 10.45 Å at 12 K [5]. The chains pack in a pseudo-triangular lattice (Fig. 6 in Ref. [5]) with a shortest $\text{Fe} \cdots \text{Fe}$ inter-chain distance of 8.205 Å. The compound has been extensively studied using magnetization [3,4,6], specific heat [7], neutron diffraction [8] and muon-spin-relaxation (μSR) [9] measurements. These studies have shown that the magnetic properties of $[\text{FeCp}_2^*][\text{TCNE}]$ can be explained by using a spin-1/2 Heisenberg ferromagnetic chain model including a substantial uniaxial anisotropy with exchange interactions, $J_{\parallel} = 27.4$ K and $J_{\perp} = 8.1$ K. Nonetheless, while the static magnetic properties are well described, the spin dynamics of the system is not. Only μSR investigations [9] revealed the presence of thermally activated slow spin fluctua-

tions at temperatures above the transition temperature. In this work we report ^1H Nuclear Magnetic Resonance (NMR) experiments on $[\text{FeCp}_2^*][\text{TCNE}]$. The NMR technique, like μSR , probes the low-frequency spin dynamics in magnetically ordered and paramagnetic materials.

2. Experimental

The synthesis and crystal structure of $[\text{FeCp}_2^*][\text{TCNE}]$ is described elsewhere [3,5]. ^1H NMR experiments were performed at magnetic fields $H_0 = 2.35$ and 4.7 T using a coherent pulsed NMR spectrometer, at Larmor resonance frequencies $\omega_L/2\pi = 100.17$ and 200.17 MHz, respectively. An Oxford 1200CF continuous flow cryostat was employed for measurements from 3 to 300 K. At high temperatures, the NMR spectra were obtained by the Fourier transform of the nuclear free induction decay at the Larmor frequency, since a single pulse of around 1 μs was sufficient to irradiate the whole NMR line. At low temperatures, the spectra were obtained by the spin-echo point to point method while varying the frequency across the inhomogeneously broadened line. T_1 spin–lattice and T_2 spin–spin relaxation times were measured using standard spin-echo pulse sequences.

3. Results and discussion

^1H NMR spectra of $[\text{FeCp}_2^*][\text{TCNE}]$ in a powder sample were acquired between room and liquid helium temperatures at applied

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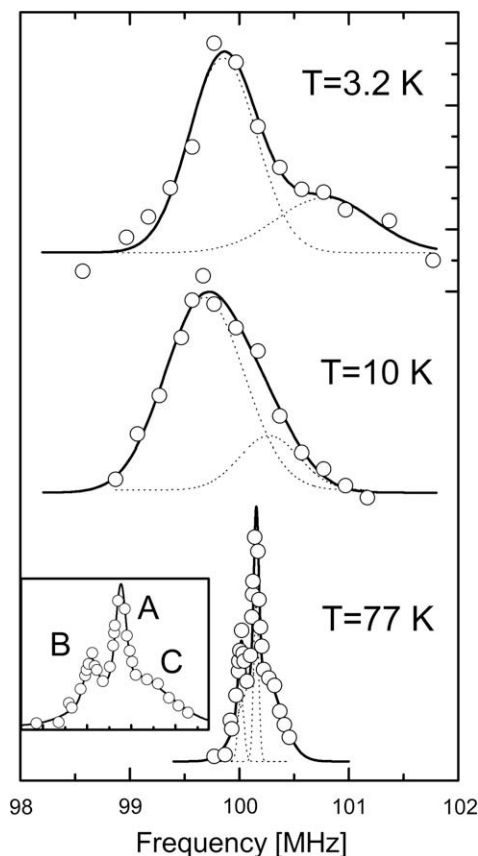


Fig. 1. ^1H NMR spectra at $H_0 = 2.35$ T for selected temperatures for $[\text{FeCp}_2][\text{TCNE}]$. The open circles are the experimental data acquired by the point-by-point spin-echo method. The solid lines are fits to the spectra using Gaussian functions. The inset shows the expanded NMR lineshape at 77 K, where three peaks A, B, and C are clearly identified.

magnetic field $H_0 = 2.35$ T. Fig. 1 shows typical ^1H NMR spectra for selected low temperatures. Similar results were obtained at $H_0 = 4.7$ T applied magnetic field. The high temperature spectra (not shown) are narrow with a width in the kilohertz range, whereas the low temperature spectra are broadened with a width in the megahertz range.

Fig. 1 clearly shows that the NMR resonance lines exhibit a structure at low temperatures, due to the large number of protons in the system situated at magnetically inequivalent crystallographic sites. At 77 K three peaks (A, B, and C) could be resolved whereas at liquid helium temperatures the line is further broadened and shifted to lower frequencies and could be decomposed into two Gaussian line profiles. The protons are coupled to the electronic spin system through the hyperfine electron–nucleus dipolar interaction. The different hyperfine couplings lead to a distribution of paramagnetic shifts and result in an inhomogeneous broadening of the NMR line. It is also evident from Fig. 1 that the linewidth of the spectra increases substantially below liquid nitrogen temperatures signifying the onset of strong magnetic interactions in the low temperature regime, since the overall width of the inhomogeneous broadened NMR line is proportional to the magnitude of the local magnetic moment.

In order to study the low-energy spin dynamics of $[\text{FeCp}_2][\text{TCNE}]$ we performed ^1H T_1 spin–lattice and T_2 spin–spin relaxation time measurements, shown in Fig. 2 as a function of temperature at $H_0 = 2.35$ and 4.7 T.

Both T_1 and T_2 relaxation times at the two applied fields decrease on cooling and exhibit minima at around 15–20 K. Before analyzing the temperature dependence of the relaxation times,

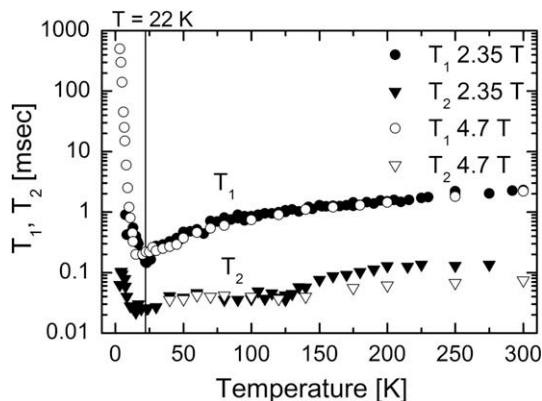


Fig. 2. Temperature dependence of ^1H NMR T_1 and T_2 relaxation times for $[\text{FeCp}_2][\text{TCNE}]$ at two applied magnetic fields $H_0 = 2.35$ and 4.7 T.

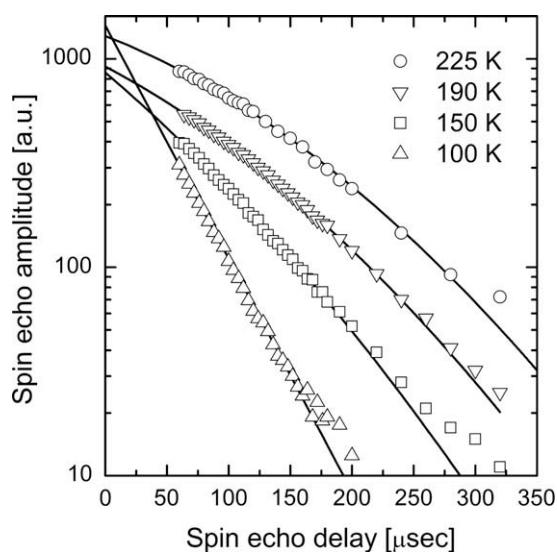


Fig. 3. Spin–echo decays of $[\text{FeCp}_2][\text{TCNE}]$ at $H_0 = 2.35$ T for selected temperatures. The data have been shifted for clarity. The solid lines are fits using a product of a Gaussian and an exponential function (see text). For temperatures between 50 and 100 K, the decays are double exponentials. For the decay at 100 K, only the fast component of the double exponential relaxation (solid line) is shown.

we first consider the analysis of the relaxation decays which determine the values of T_1 and T_2 . The longitudinal relaxation decays were single exponentials thus providing a unique value of T_1 , whereas the transverse relaxation decays were in general non-exponential functions. The T_2 spin–echo decays for selected temperatures in the high temperature regime at $H_0 = 2.35$ T are shown in Fig. 3.

The spin–echo decays between 100 and 300 K could be analyzed using a function that is a product of a Gaussian and an exponential function shown as solid lines in Fig. 3. Below 100 K we observe a distinct crossover from the Gaussian–exponential to double exponential decay. The Gaussian–exponential function has been frequently encountered in the NMR literature (e.g. high temperature cuprate superconductors), and in general signifies the coupling of the nuclei through the electron spins (Gaussian contribution, T_{2G}) weighted by the T_1 relaxation (Redfield contribution, T_{2R}) [10,11]. The temperature behavior of echo decay can be understood if the measured ^1H nuclei are coupled to neighboring spins that experience a fast relaxation time. For very long T_1 the echo decay is Gaussian. As T_1 decreases, the echo decay becomes exponential. However, in our present system, although T_1 decreases

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