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Spin dynamics in mesoscopic size magnetic systems: A ^{1}H NMR study in rings of iron (III) ions

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Two magnetic molecular clusters containing almost coplanar rings of iron (III) ions with spin $S=5/2$ have been investigated by ^{1}H NMR and relaxation measurements. The first system, which will be referred to as Fe6, is a molecule of general formula $[\mathrm{NaFe_6(OCH_3)_{12}(C_{17}O_4H_{15})_6}]^+\mathrm{ClO_4}^-$ *or* $[\mathrm{NaFe_6(OCH_3)_{12}(C_{15}H_{11}O_2)_6}]^+\mathrm{ClO_4}^-$ *or* $[\mathrm{LiFe_6(OCH_3)_{12}(C_{15}H_{11}O_2)_6}]^+\mathrm{ClO_4}^-$ while the second type of ring, denoted Fe10, corresponds to the molecule $[\mathrm{Fe_{10}(OCH_3)_{20}(C_2H_2O_2Cl)_{10}}]$. The ^{1}H NMR linewidth is broadened by the nuclear dipolar interaction and by the dipolar coupling of the protons with the iron (III) paramagnetic moment. It is found that the nuclear spin-lattice relaxation rate, $T_1{}^{-1}$, of the proton is a sensitive probe of the Fe spin dynamics. In both clusters, $T_1{}^{-1}$ decreases with decreasing temperatures from room temperature, goes through a peak just below about 30 K in Fe6 and 10 K in Fe10, and it drops exponentially to very small values at helium temperature. The temperature dependence of the relaxation rate is discussed in terms of the fluctuations of the local spins within the allowed total spin configurations in the framework of the weak collision theory to describe the nuclear relaxation. We use the calculated energy levels for the Fe6 ring based on a Heisenberg Hamiltonian and the value of J obtained from the fit of the magnetic susceptibility to describe semiquantitatively the behavior of $T_1{}^{-1}$ vs T. The exponential drop of $T_1{}^{-1}$ at low temperature is consistent with a nonmagnetic singlet ground state separated by an energy gap from the first excited triplet state. The values obtained for the gap energies are $E_T/k=12$ K for Fe10 and $E_T/k=38$ K for Fe6 which are almost twice as big as the values deduced from susceptibility measurements. At all temperatures the relaxation rate decreases with increasing magnetic field, i.e., NMR resonance frequency. This effect could be related to the long time persistence of the spin correlation functions typical of diffusive modes in low dimensional magnetic systems. It is argued that the data presented are a direct experimental study of spin dynamics in mesoscopic spin rings and should afford a test for exact analytical and/or numerical solutions. [S0163-1829(97)08621-9]

I. INTRODUCTION

The magnetic properties of metal ion clusters are largely studied for their implications in fundamental physics and magnetochemistry.[1–6] These systems provide mesoscopic size magnetic particles which have been recently recognized as very interesting systems both for the study of fundamental magnetism and for possible applications. The attention has been focused mainly on the very low temperature region where clusters of high-spin ground state and Ising-type anisotropy (examples are Fe8 and Mn12 clusters) can display superparamagneticlike behavior[7,8] with phenomena like bistability and macroscopic quantum tunneling.[9–11]

The investigation of the spin dynamics over the whole temperature range should also be of great interest. In fact one can follow the evolution from the high temperature behavior of uncorrelated spins to the low temperature collective behavior. The condensation of the magnetic cluster into its ground state configuration could be viewed as the equivalent of the magnetic phase transition into a short range or long range ordered state and the study of these finite systems can provide a guide for the extrapolation of exact results on a limited number of spins to the thermodynamic limit.

Measurements of nuclear spin-lattice relaxation rate, $T_1{}^{-1}$, afford a powerful tool to investigate the spin dynamics since the nuclei probe the fluctuation spectrum of the local field induced at the nuclear site by the hyperfine interaction with the localized magnetic moments. Since the relaxation rate, $T_1{}^{-1}$, is determined by the low frequency part of the fluctuation spectrum one can probe the long time behavior of the local auto and pair correlation functions of the magnetic moments which is not easily accessible with other techniques. For example in one-dimensional (1D) magnetic chains, $T_1{}^{-1}$ measurements have proved the long time diffusive behavior of the two spin correlation function at high temperature.[12] Furthermore, in two-dimensional (2D) and three-dimensional (3D) magnetic systems, the slowing down of the spin fluctuations on approaching from the high temperature side the phase transition to long range order is manifested by a divergence of $T_1{}^{-1}$ (Ref. 13).

Crystals formed of large magnetic molecules containing anywhere from 6 to 20 magnetic ions in simple geometric arrangements are very attractive for NMR studies. In fact, since generally the magnetic properties do not depend on intermolecular interactions one has access to the intrinsic magnetic behavior of each individual cluster although the NMR parameters are averages over all the nuclei in the crystal. Ring shaped clusters appear to be particularly attractive. In fact they have been long used to extrapolate the thermodynamic properties of one-dimensional magnets.[14,15] Now the developments in synthetic chemistry provide real objects on which experiments can be performed to measure the transition from isolated spins to collective behavior. In the present paper we report the results of an NMR investigation of the spin dynamics in iron (III) clusters in which the paramagnetic ions form rings lying in a single plane.[16–18] We have concentrated our attention on four different samples which we label here and in the following with the letters A to D and whose general formula is

(A) $[NaFe_6(OCH_3)_{12}(C_{17}O_4H_{15})_6]^+ClO_4^-$,

(B) $[NaFe_6(OCH_3)_{12}(C_{15}H_{11}O_2)_6]^+ClO_4^-$,

(C) $[LiFe_6(OCH_3)_{12}(C_{15}H_{11}O_2)_6]^+ClO_4^-$,

(D) $[Fe_{10}(OCH_3)_{20}(C_2H_2O_2Cl)_{10}]$.

The structural and magnetic properties of these systems have been already investigated.[16–18] Here we summarize the features which are most relevant for our spin dynamical investigation. Samples A,[18(a)] B,[17] and C [Ref. 18(b)] consist of rings of six iron (III) ions arranged at the vertices of an almost regular hexagon with a small deviation from coplanarity (less than 0.1 Å) and with the alkali ion at the center. The clusters have either crystallographically imposed (sample A) or approximate (samples B,C) S_6 point-group symmetry and show very similar magnetic behaviors. The Fe ions have spin $S=5/2$ and are coupled by nearest neighbor antiferromagnetic exchange interaction estimated at $J=28.6$ K for sample A, $J=28.8$ K for sample B, and $J=20.6$ K for sample C (the spin Hamiltonian being in the form $H=\Sigma_{ij}J\mathbf{S}_i\cdot\mathbf{S}_j$). The ground state is a nonmagnetic singlet state with total $S=0$ and the energies of the lowest-lying exchange multiplets obey a Lande's interval rule. In order to fit the susceptibility data it was necessary to introduce a small anisotropy of the order of 1% of the exchange interaction due to single ion plus dipolar anisotropic terms.[18(a)]

The sample D contains molecules in which 10 Fe ions form an almost coplanar ring (deviation 0.009 Å, referred to in the literature as the ''molecular ferric wheel'') [Ref. 16(a)] with approximate D_{5d} symmetry.[16] Each ion carries a spin $S=5/2$ and the moments are coupled by antiferromagnetic exchange interaction estimated to be $J=13.8$ K. The ground state is a nonmagnetic singlet state of total spin $S=0$.[16(b)]

The measurements of proton spin-lattice relaxation rate, T_1^{-1}, are used here to investigate the spin dynamics of the rings of six and ten magnetic moments, respectively. Although there are many nonequivalent protons in the molecule we will argue that the parameters measured are averages which are uniquely related to the spin fluctuation spectrum of the iron rings. In Sec. II we discuss the experimental details while in Sec. III we present the experimental results for T_1^{-1} as a function of temperature and external magnetic field. No theory of nuclear relaxation in mesoscopic magnetic clusters is currently available. Thus in Sec. IV we discuss the results qualitatively pointing out similarities and differences with the results in infinite linear chains for which theories do exist.

II. EXPERIMENTAL DETAILS

For the methods of synthesis, for the solid state structure and for the magnetic properties of the compounds investigated we refer to the other publications.[16–18]

^1H pulsed NMR experiments were performed on powdered samples by using a Stelar Spinmaster/BHH broadband pulse Fourier transform (FT) spectrometer in conjunction with a variable field electromagnet which allowed to vary the ^1H NMR frequency in the range 7–60 MHz. The temperature was varied in the range 4–298 K with an Oxford Instruments CF1200S cryostat using helium gas as heat exchanger and the temperature was controlled and measured by means of two thermocouples.

The $\pi/2$ pulse length was between 2 and 6 μs depending on the operating frequency of the spectrometer. In all cases the intensity of the radiofrequency field, H_1, is sufficiently strong to irradiate the whole NMR line. Thus the spectrum was obtained directly from the FT of the free precession decay (FID). The spin-lattice relaxation rate was obtained from the recovery of the nuclear magnetization following a short sequence of saturating radio frequency pulses.

III. PROTON NMR RESULTS

A. Line shapes and linewidth

The ^1H NMR spectrum in all the samples investigated has a width which changes from a minimum of about 20 kHz at room temperature and low applied magnetic field up to a maximum of about 100 kHz at low temperature and at the higher fields. Thus in all cases the full spectrum could be reproduced by Fourier transformation of the free precession decay or of half of the echo signal. The shape of the signal also depends somewhat on temperature and applied field. In most cases the signal is slightly asymmetric with two or three unresolved components. Due to the large number of protons present in the molecule, the shape of the spectrum results from an average of the shapes typical of CH_3, CH_2, CH groups with the further broadening due to the dipolar interaction among protons of different groups and of the protons with the Fe magnetic moments.[19]

In Fig. 1 and in Fig. 2 we plot the full width at half maximum (FWHM) for the A (Fig. 1) and for the D (Fig. 2) samples as a function of temperature for the lowest and for the highest frequency investigated. Data taken at intermediate frequencies fall in between and are not shown for sake of clarity. The uncertainty in the experimental values is due to the difficulty in defining a linewidth for shapes which are not symmetric and contain some unresolved structure. However, the general trend appears to be well defined. At low magnetic field (i.e., low resonance frequency: 7 MHz) the width is about 45 kHz which is the order of magnitude of the rigid lattice nuclear dipolar broadening of CH_3 and CH_2 groups in

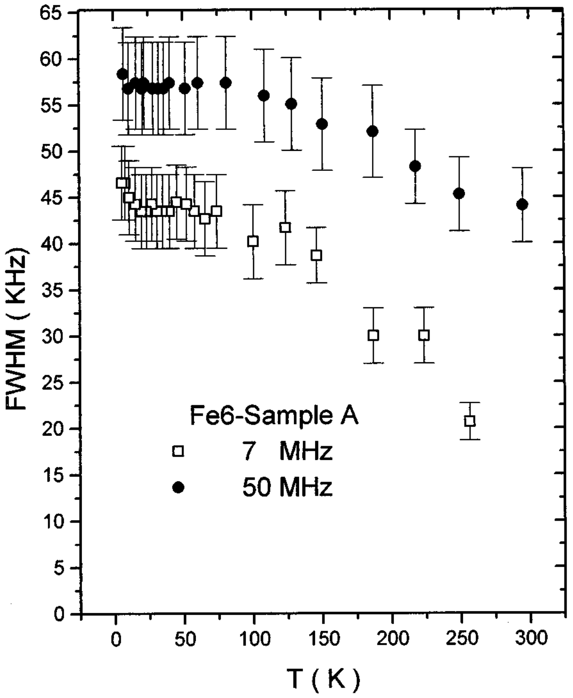

FIG. 1. Full width at half maximum of the ^{1}H NMR line in Fe6 cluster (sample A) plotted as a function of temperature for two different values of the applied magnetic field.

organic molecules.[19] At temperatures above 150 K the line narrows because of the onset of hindered rotations in the CH_3 and CH_2 groups (see Figs. 1 and 2). This again is consistent with what is generally observed in organic compounds containing similar proton arrangements.[19] At low fields only a dipolar solid echo is present while at high fields one can observe a Hahn echo[19] due to magnetic inhomogeneous broadening. We conclude that at high magnetic field the spectrum is broadened inhomogeneously by the dipolar interaction of the ^{1}H with the Fe moments which produce a distribution of local fields at the proton sites.

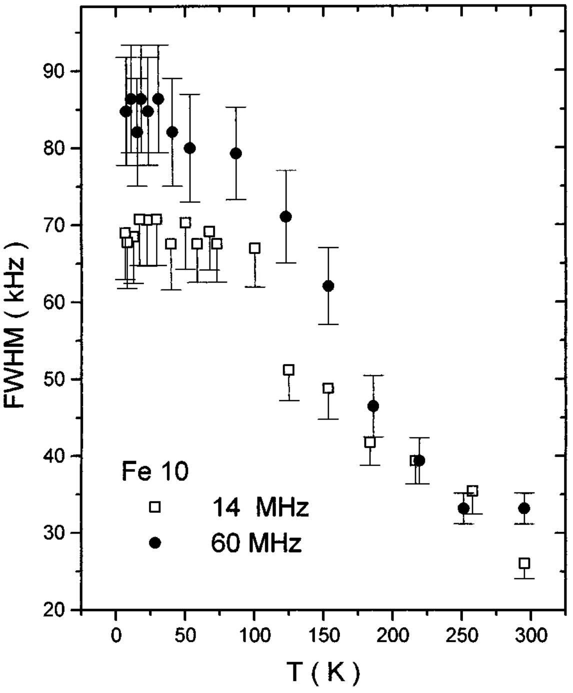

FIG. 2. Full width at half maximum of the ^{1}H NMR line for the cluster Fe10 (sample D) plotted as a function of temperature for two different values of the applied magnetic field.

B. Nuclear spin-lattice relaxation rates

The recovery of the nuclear magnetization was almost exponential for the measurements at low magnetic field and at higher temperature but a departure from exponentiality was observed in the measurements at low temperature and/or high magnetic field. There are two sources for nonexponential recovery. The first is due to incomplete saturation of the broad NMR spectrum which leads to an initial fast recovery of the nuclear magnetization due to spectral diffusion. The effect of spectral diffusion was minimized in most cases by using a saturation sequence of short radio frequency pulses. Whenever a residual effect due to spectral diffusion was present we disregarded the initial fast recovery of the magnetization which accounted for 20% of the total nuclear magnetization in the most unfavorable case. The second source of nonexponential recovery is due to the presence in the molecule of nonequivalent protons, i.e., protons having a different environment of magnetic Fe ions and thus having a different relaxation rate. At high temperature and/or low magnetic field the spin diffusion process characterized by T_2 is fast compared to T_1 and all ^{1}H nuclei relax back to equilibrium with a common spin temperature. In this case the recovery is exponential and the relaxation rate measured, $T_1{}^{-1}$, is a weighted average of the rates of the inequivalent protons in the molecule.[19] At low temperature and/or at high magnetic field the width of the spectrum increases as discussed in the previous paragraph and, as a consequence, energy conserving spin flip-flop processes are no longer allowed and the spin diffusion becomes less effective. Furthermore in some cases T_1 becomes very short. Both circumstances prevent the inequivalent nuclei from reaching a common spin temperature and the recovery of the nuclear magnetization results in the sum of more than one exponential. Whenever the recovery was nonexponential we derived the T_1 parameter from the recovery of the nuclear magnetization at short times. In fact for a nonexponential recovery described by a weighted sum of exponentials:

$$n(t)=[M(\infty)-M(t)]/M(\infty)=\Sigma_i p_i \exp(-t/T_{1i}). \quad (1)$$

The slope at $t \rightarrow 0$ of the semilog plot of $n(t)$ vs t yields an average relaxation rate $T_1{}^{-1}=\Sigma_i p_i T_{1i}{}^{-1}$. Thus the relaxation rate results shown in what follows are the average relaxation rates for the different nonequivalent ^{1}H nuclei in the molecule in all cases.

The temperature dependence of the nuclear spin-lattice relaxation rate, $T_1{}^{-1}$, is shown in Figs. 3–6 for the different iron clusters. Figure 3 shows the results in the Fe6 ring (sample A) for different values of the applied magnetic field. The amplitude of the peak at low temperature, although not its position, is affected by the external magnetic field. Figures 4 and 5 show the results in the Fe6 rings (samples B and C, respectively). We replot in the same figure also the results for sample A obtained at the same external magnetic field in order to compare sample A with samples B and C, respec-

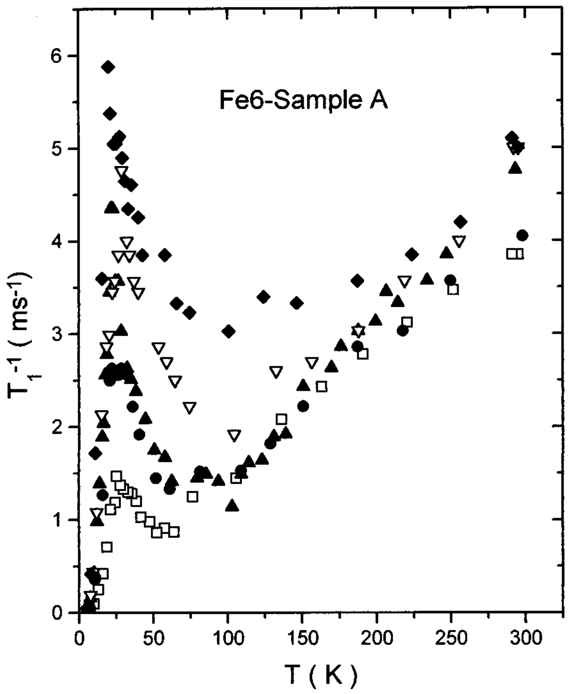

FIG. 3. ^{1}H nuclear spin-lattice relaxation rate, $T_1{}^{-1,}$ plotted as a function of temperature for the Fe6 ring (sample A) for different resonance frequencies: (◆) 7 MHz, (▽) 14 MHz, (▲) 31 MHz, (●) 50 MHz, and (□) 60 MHz.

tively. The magnetic properties of the three types of Fe6 rings are very similar to each other while the structure and thus the number and the location of the protons are slightly different in the three samples. The fact that the temperature behavior of $T_1{}^{-1}$ and its value is comparable in all cases supports our assumption that the proton average relaxation rate probes the spin dynamics independently of the exact location of the protons with respect to the Fe(III) ions. There are other features which are worth pointing out and that are discussed in the following section. First the relaxation rate drops rapidly to a very low value below 20–30 K in all samples. This is consistent with the notion that the ground state is a nonmagnetic singlet state $(S=0)$. A similar exponential decrease of the relaxation rate at low temperature is observed in linear antiferromagnetic chains with a spin gap such as the one found in spin-1 systems[20] and in spin-1/2 coupled chains.[21,22] However, contrary to the linear chain case, we observe a strong enhancement of $T_1{}^{-1}$ which precedes the low temperature drop. We argue in the following section that the enhancement is a typical feature of the spin dynamics of a finite size magnetic cluster and is related to the discreteness of the energy levels. A strong field dependence is observed in all cases whereby the intensity of the peak at low temperature is suppressed at high fields. Experimental features quite similar to those of Fe6 rings, were observed in the $T_1{}^{-1}$ relaxation rate of Fe10 ring (Fig. 6). Because of this fact, the physical principles leading to $T_1{}^{-1}$ behavior will be assumed to be the same as for Fe6 (see next section).

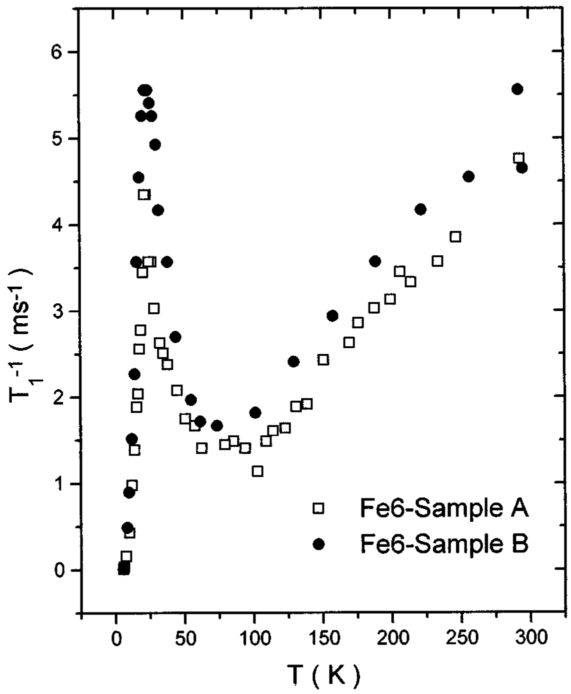

FIG. 4. ^{1}H nuclear spin-lattice relaxation rate, $T_1{}^{-1,}$ plotted as a function of temperature for two different Fe6 rings. The measuring resonance frequency is 31 MHz in both cases.

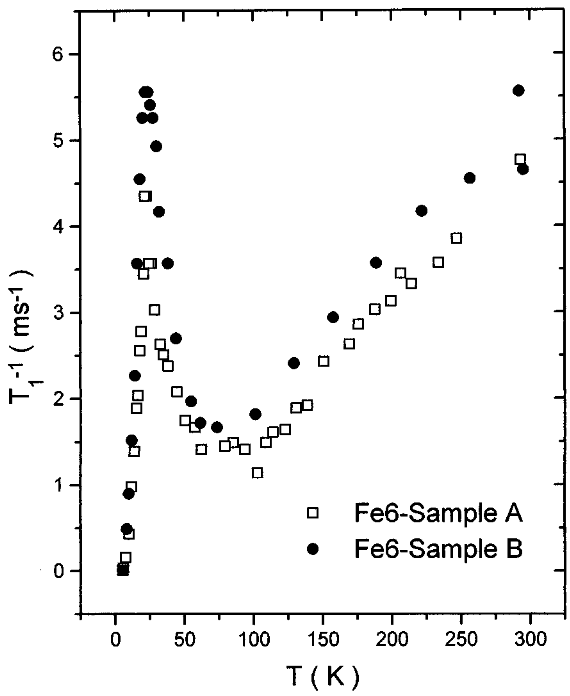

FIG. 5. ^{1}H nuclear spin-lattice relaxation rate, $T_1{}^{-1,}$ plotted as a function of temperature for two different Fe6 rings. The measuring resonance frequency is 14 MHz in both cases.

IV. DISCUSSION

The data for the linewidth presented in Sec. III A show that the ^{1}H nuclei are coupled to the Fe(III) magnetic moments and can thus provide information about the spin dynamics through the nuclear relaxation $T_1{}^{-1}$ measurements. No specific theory has been yet developed to describe the nuclear-spin lattice relaxation in mesoscopic magnetic systems. We will use as a guideline the expressions for $T_1{}^{-1}$

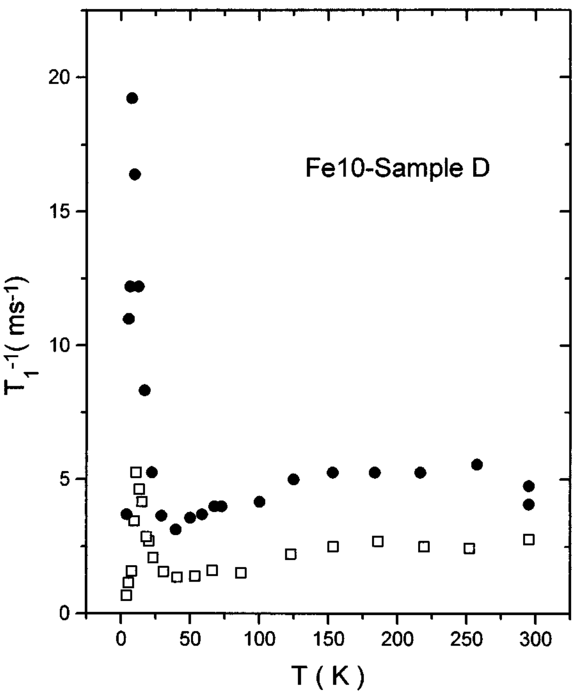

FIG. 6. ^{1}H nuclear spin-lattice relaxation rate, $T_1{}^{-1}$, plotted as a function of temperature for the Fe10 cluster at two different resonance frequencies: (●) 14 MHz and (□) 60 MHz.

which are used to interpret the data in dense paramagnetic systems, with particular reference to 1D magnetic chains without long range order.[13]

In the weak collision approximation we can write[23]

$$T_1{}^{-1}=\frac{\gamma_N}{4}\int_{-\infty}^{+\infty}\langle h_+(t)h_-(0)\rangle\exp(i\omega_L t)dt, \qquad (2)$$

where $\omega_L=\gamma_N\ H$ is the nuclear Larmor frequency and $h_\pm(t)$ is the component, perpendicular to the external magnetic field H, of the hyperfine interaction between the nucleus and the Fe(III) magnetic moment. Since the protons do not bond directly to the Fe(III) ions in neither Fe6 nor Fe10 clusters we assume that the contact hyperfine interaction is negligible with respect to the dipolar interaction. This is confirmed by the observation that the ^{1}H NMR line is broadened but not shifted by the magnetic interaction with the Fe(III) moment (see Sec. III A). By expressing the local dipolar field in Eq. (2) in terms of the components S_α^j of the local electronic spins at site j we can write

$$\begin{aligned}T_1{}^{-1}=2\gamma_N^2\gamma_S^2\hbar^2 S(S+1)\Bigg\{&\Sigma_{j,j'}\alpha_{jj'}\int_{-\infty}^{+\infty}\langle S_+^j(t)S_-^{j'}(0)\rangle\\ &\times\exp[i(\omega_S\pm\omega_L)t]dt+\Sigma_{j,j'}\beta_{j,j'}\\ &\times\int_{-\infty}^{+\infty}\langle S_z^j(t)S_z^{j'}(0)\rangle\exp(-i\omega_L)t\ dt\Bigg\},\end{aligned} \qquad (3)$$

where $\omega_S=\gamma_S\ H$ is the electronic Larmor frequency and the coefficients $\alpha_{j,j'}$ and $\beta_{j,j'}$ are the geometrical coefficients of the dipolar interaction.[19,13]

Equation (3) is the starting point to calculate the relaxation rate in dense paramagnets. For example, in the linear antiferromagnetic chain tetramethel ammonium chloride (TMMC), a detailed calculation based on collective variables and the use of the random phase approximation to evaluate the correlation function gave good agreement with the experimental data.[24]

The coupling coefficients are different for inequivalent protons in the molecule and this is the reason why we observe nonexponential recovery of the nuclear magnetization under certain conditions, whereby we always measure an average relaxation rate (see Sec. III B). If the pair correlation terms, $j\neq j'$, in Eq. (3) vanish as expected at high temperature, then the geometrical coefficients can be factored out and calculated independently of the spin dynamics. However, when correlation effects become important at low temperature the geometrical coefficient become weighting factors in the summation over the pair correlation functions. Since there is a very large number of protons in the molecule and we measure an average relaxation rate it should be a reasonable approximation to factor out the geometrical coefficients for all temperatures and introduce a single constant representing an average over all protons and all pair correlations. Thus we rewrite Eq. (3) as

$$\begin{aligned}T_1{}^{-1}=\Sigma_{j,j'}[AJ_\pm^{j,j'}(\omega_L\pm\omega_S)+BJ_z^{j,j'}(\omega_L)]=\Sigma_{j,j'}\Sigma_{n,m}\ &\exp(-\beta E_n)[A\langle n|S_\pm^j|m\rangle\langle m|S_\pm^{j'}|n\rangle\delta(E_n-E_m-(\omega_L\pm\omega_S))\\ &+B\langle n|S_z^j|m\rangle\langle m|S_z^{j'}|n\rangle\delta(E_n-E_m-\omega_L)]/\Sigma_n\ \exp(-\beta E_n).\end{aligned} \qquad (4)$$

The first term in Eq. (4) expresses the relaxation rate in terms of the spectral density $J(\omega)$ of the electronic spin fluctuations. The second term in Eq. (4) is obtained by expressing the correlation function in Eq. (3) as

$$\begin{aligned}\langle S_j^\alpha(t)S_{j'}^\alpha\rangle=\mathrm{Tr}\{&\exp(-\beta H)\exp(iHt/\hbar)S_j^\alpha\\ &\times\exp(-iHt/\hbar)S_{j'}^\alpha\}/\mathrm{Tr}\ \exp(-\beta H)\end{aligned} \qquad (5)$$

and can thus be written in terms of the matrix elements of the local spin components between eigenstates of the total cluster spin system $\langle n|,\langle m|$.

In the case of the Fe6 cluster and possibly for the Fe10 cluster, one should be able to calculate the correlation functions exactly from the calculated energy levels (see below) and compare with the $T_1{}^{-1}$ data by using Eq. (4) although in practice this could be a formidable task. Another theoretical approach would be to expand the local spin variables in terms of collective q-dependent variables and make assumptions about the spectrum of the collective excitations.[23,24] However, this collective approach should be explored first theoretically in view of the objection that a small number of coupled spins may not sustain collective excitations at all. In view of the complexity of the theory we limit ourselves here to a semiquantitative analysis of the problem based on some simplifying assumptions and on the comparison with results obtained in 1D magnetic chains.

Let us first consider the room temperature results for ${T_1}^{-1}$ shown in Figs. 3–6. Since $J/k \ll 300$ K the Fe spins are uncorrelated in this high temperature limit. From the expansion of the correlation function in Eq. (5) for short times Moriya[23] obtained the expression valid for dense 3D paramagnets:

$$ {T_1}^{-1} = \frac{\gamma^2}{4} A^2 \frac{\sqrt{2\pi}}{\omega_{\text{ex}}}, \tag{6} $$

where γ is the nuclear gyromagnetic ratio, A is the local field at the nuclear site, and the exchange frequency is given by $\omega_{\text{ex}}^2 = 2zJ^2k^2S(S+1)/3\hbar^2$ with z the number of nearest neighbors of a given Fe spin. For $z=2$, $S=5/2$, and $J=30$ K one has $\omega_{\text{ex}} = 1.3 \times 10^{13}$ Hz. Assuming $A=350$ G, which is the dipolar field created by one Bohr magneton at a distance of 3 Å, one has from Eq. (6) ${T_1}^{-1} = 4\ \text{sec}^{-1}$, which is three orders of magnitude smaller than the room temperature measured ${T_1}^{-1}$ (see Figs. 3–6). This order of magnitude estimate indicates that the correlation function for a ring must decay much more slowly than the Gaussian decay obtained from the short time expansion of Eq. (5). A slow decay in time of the correlation function corresponds to an enhancement of the spectral density at low frequency and thus to an enhancement and a frequency dependence of the relaxation rate. This is confirmed by the magnetic field dependence of ${T_1}^{-1}$ which is also observed in infinite chains.[12,13,20,24] A systematic study of the high temperature spin dynamics in the Mn molecular cluster, Mn12, as well as in Fe6 and Fe10 will be presented in a separate publication.

Regarding the temperature dependence, let us first recall the phenomenology observed in the temperature dependence of ${T_1}^{-1}$ in infinite antiferromagnetic chains. For quantum spin-1/2 chains, ${T_1}^{-1}$ is practically temperature independent from $T \cong J/k$ down to a few degrees from the 3D ordering temperature which is related to the coupling between chains.[25,26] For classical spin-5/2 chains, ${T_1}^{-1}$ shows a strong enhancement on lowering the temperature below $T=J/k$ which can be interpreted in terms of slowing down of the antiferromagnetic collective fluctuations at wave vector q at border zone.[24] In spin-1 chains with Haldane gap[20] and for coupled spin-1/2 chains (two-leg ladders)[21] with a nonmagnetic ground state, ${T_1}^{-1}$ is weakly temperature dependent down to a temperature of order of the energy gap and then it decreases exponentially. The temperature and magnetic field dependence of ${T_1}^{-1}$ observed here in magnetic rings (Figs. 3–6) have features which are similar to the ones observed in infinite spin chains with some important differences. We argue that the differences stem mainly from the discreteness of the low lying magnetic states in finite rings to be contrasted with the quasicontinuum of states with or without gap to the ground state present in infinite chains.

For a ring of N spins with $S_i = 5/2$ the total number of states is 6^N. The energy levels for rings of spins coupled by nearest neighbor exchange coupling constant J were calculated for $N=6$(Ref. 18) and extrapolated to the $N=10$ ring.[16(b)] For a cluster of six $S=5/2$ spins the energy levels are calculated using the Heisenberg Hamiltonian $\mathcal{H} = J\Sigma_{j=1}^{5} \mathbf{S}_j \cdot \mathbf{S}_{j+1} + J\mathbf{S}_6 \cdot \mathbf{S}_1$ which describes nearest-neighbor interactions and assumes sixfold symmetry. The size of the matrices can be reduced using the symmetry properties of the total spin operator $\mathbf{S} = \Sigma_j \mathbf{S}_j$. In this way sixteen matrices, with size ranging from 1×1 to 609×609 and S values ranging from 15 to 0 must be calculated and diagonalized. This can be done very effectively using irreducible tensor operator techniques.[27] The calculated levels were used to express the magnetic susceptibility χ of the clusters. A best fit to the temperature dependence of χ yielded the value of the coupling constant J. The energies of the first excited levels were checked also through magnetization measurements at 1.5 and 0.6 K for sample B [Ref. 18(a)] and for sample D [Ref. 16(b)], respectively, which showed steps attributed to the crossover from the S to the $S+1$ energy levels in presence of the applied magnetic field. The energy levels of the lowest lying $S=1,2,3$ for sample B [Ref. 18(a)] and $S=1,2,3,\ldots,9$ for sample D [Ref. 16(b)] were observed. A scheme of the low lying energy levels for Fe6 is shown in Fig. 7(a). In Fig. 7(b) we show the distribution of energy levels as a function of energy in the form of an histogram. By dividing the number of states on the y axis by the size of the interval of the histogram, $\Delta E/k = 19$ K, one obtains the density of states which can be fitted well with a Gaussian function centered at $E/k = 1270$ K and with standard deviation $\sigma = 370$ K as shown in Fig. 7(b). It is apparent that the low lying levels are well separated in energy from the strongly overlapping higher energy states.

If one takes the energy of the $S=0$ ground state as zero then the first $S \neq 0$ excited states are given by Lande's rule:

$$ E(S) = \frac{P}{2} S(S+1), \tag{7} $$

where S is the total spin value and the parameter P is $=4J/N$. For $N=6$ and $S \leqslant 4$ the energy levels given by Eq. (7) are lying lowest in energy, well separated from other excited states and have only the magnetic degeneracy $2S+1$. For higher values of S, Eq. (7) gives energies which overlap with other excited states as shown in Fig. 7(a). From fits of the magnetic susceptibility a value of the parameter was derived: $P=5.5$ K (corresponding to $J=13.8$ K) for the Fe10 ring (sample D), $P=19.1$ K (corresponding to $J=28.6$ K) for the Fe6 ring (sample A), $P=19.2$ K (corresponding to $J=28.8$ K) for Fe6 (sample B), and $P=13.7$ K (corresponding to $J=20.6$ K) for Fe6 (sample C).

The nuclear relaxation process can be viewed as the result of scattering between the nuclear spin and the local electronic spin S_j. As a result of the energy conservation requirement in Eq. (4) one can infer that at high temperature most of the states in the quasicontinuum will contribute while at lower temperatures only fluctuations of the local spin within the same low lying energy level would contribute. We assume that ${T_1}^{-1}$ has contributions proportional to the probability of occupation of the different energy levels with different strength for the first excited triplet state (total

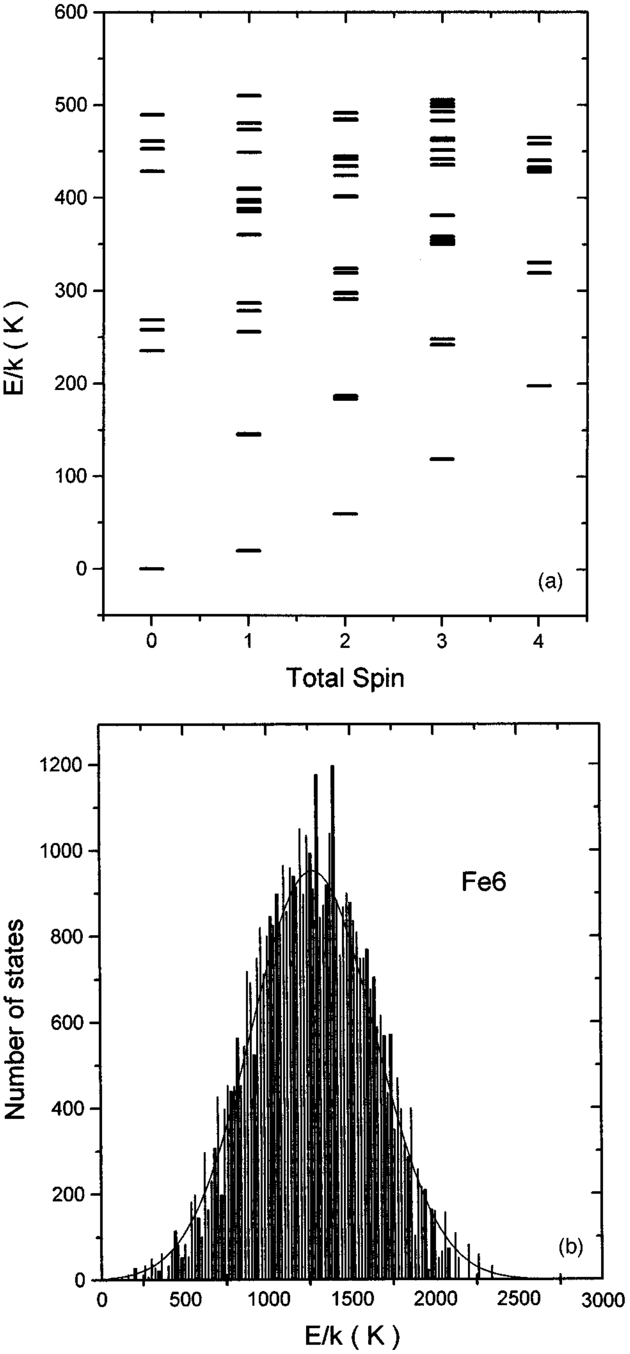

FIG. 7. Calculated magnetic energy levels for the Fe6 ring. (a) Diagram of the low lying levels as a function of the total spin value of the ring. (b) Histogram of the distribution of energy levels as a function of energy. The amplitude of the interval in the histogram is $\Delta E/k = 19$ K. The curve represents a Gaussian function which best fits the histogram corresponding to a normalized density of states given by

$$D\left(\frac{E}{k}\right)=\frac{6^6}{\sqrt{2\pi}}\,\frac{1}{370(K)}\,\exp-\frac{[1270(K)-E/k]^2}{2.370^2(K^2)}.$$

spin $S=1$) than for the remaining distribution of levels which is approximated by a continuum. For the energy of the excited triplet state we assume from Eq. (7) $E_T/k=19.1$ K for Fe6 (sample A). For the remaining states we use the continuous distribution $D(E)$ expressed by the normalized Gaussian function given in the caption of Fig. 7(b). Thus we write

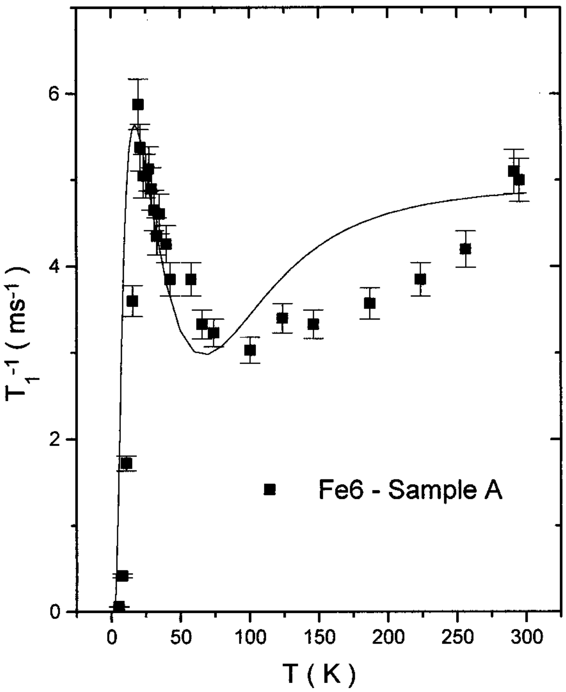

FIG. 8. The experimental data for the ^{1}H nuclear spin-lattice relaxation rate, T_1^{-1}, in Fe6–sample A are compared with the curve obtained from Eq. (8) with parameters $d=200$ K, $A=7.3$ msec^{-1}, and $B=5$ msec^{-1}. The data shown in this figure are the same as the ones shown in Fig. 3 for the resonance frequency 7 MHz.

$$T_1^{-1}=\left\{A\ \exp(-\beta E_T)+B\int_d^{\infty}D(E)\exp(-\beta E)dE\right\}Z^{-1}, \tag{8}$$

where $Z=\int_0^{\infty}D(E)\exp(-\beta E)dE$ is the partition function and A,B are adjustable parameters which give the relative contribution to nuclear relaxation from the triplet state and from all other states respectively. It is noted that the lower limit, d, of the integral in Eq. (8) is also treated as an adjustable parameter since it represents the minimum energy above which the distribution of energy levels can be approximated by the continuous function $D(E)$. The curve calculated from Eq. (8) is compared to the experimental data, for the lowest external magnetic field, for Fe6 (sample A) in Fig. 8. This purely phenomenological approach appears to reproduce the general trend of the experimental data particularly regarding the peak in T_1^{-1} and point out the role of the lowest lying excited states in the spin dynamics of the spin ring. An analogous comparison for the Fe10 ring is not possible since the distribution of energy levels, $D(E)$, cannot be calculated.

From the exponential drop of T_1^{-1} at low temperature one can estimate the size of the energy gap from the nonmagnetic ground state to the first excited state. From the semilog plot of T_1^{-1} vs $1000/T$ in Fig. 9 we estimate a gap E_T/k of 12 K for Fe10 and 38 K for Fe6 which are considerably higher than the values 5.5 K (sample D) and 19.1 K (sample A), 19.2 K (sample B), 13.8 K (sample C), respec-

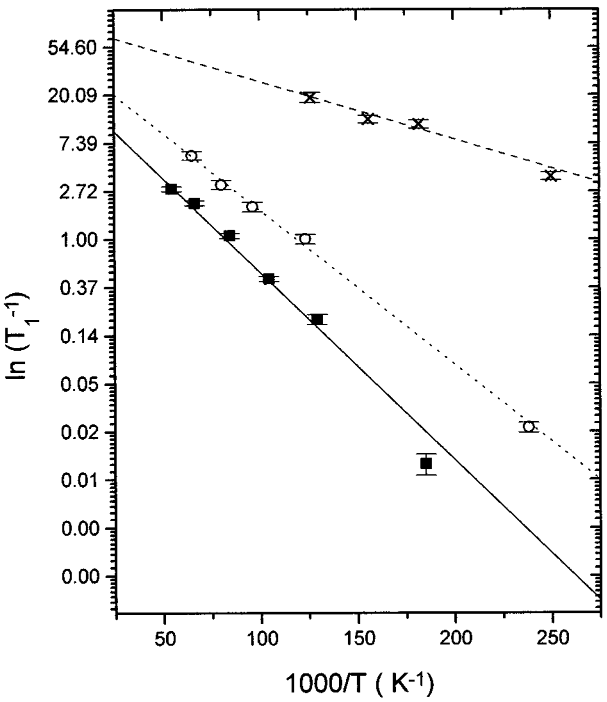

FIG. 9. Semilog plot of ^{1}H nuclear spin lattice relaxation rate, T_1^{-1}, vs 1000/T: (■) Fe6–sample A; (○) Fe6–sample C; (×) Fe10–sample D. The data shown in this figure are the lowest temperature data also shown in Figs. 3 and 6, respectively, at 14 MHz. The straight lines in the semilog plot are exponential fits $T_1^{-1} \propto \exp(-E_T/kT)$ yielding gap parameters: (—) $E_T/k = 39$ K (sample A); (···) $E_T/k = 32$ K (sample C); (----) $E_T/k = 12$ K (sample D) with estimated error of ±2 K in all cases.

tively, obtained from the fit of the susceptibility and used in the calculation of the theoretical curves in Fig. 8. The reason for this discrepancy cannot be understood in absence of a more detailed theory for the spin dynamics in the ring which should include also the effect of the external magnetic field.

V. SUMMARY AND CONCLUSIONS

We have presented the proton ^{1}H NMR linewidth and relaxation results vs temperature and external magnetic field in two types of molecular clusters containing almost coplanar rings of six and ten magnetic spin-5/2 iron (III) ions, respectively. We have shown that the T_1^{-1} results allow to probe the spin dynamics in these finite size rings. The salient features of our results are (i) a strong dependence of the relaxation rate on the applied magnetic field, (ii) an exponential drop of T_1^{-1} at the lowest temperatures, (iii) a peak in the relaxation rate just preceding the exponential drop, and (iv) the partial quenching of the peak in the relaxation rate when the external magnetic field is increased.

We have discussed the way to solve exactly the spin dynamical problem and efforts in that direction are underway. A preliminary qualitative discussion of the data leads to the following conclusions. The field dependence of T_1^{-1} at room temperature is similar to what is observed in infinite spin chains and should arise from the long time persistence of the correlation function due to $q=0$ diffusive modes. The exponential drop of T_1^{-1} at low temperature is consistent with the presence of a nonmagnetic total spin $S=0$ ground state as already deduced from susceptibility measurements. However, the value of the energy gap to the first triplet excited state derived from T_1^{-1} measurements is almost twice as big as the value derived from susceptibility measurements. The peak in T_1^{-1} appears to be due to an enhancement of the nuclear relaxation at the temperature corresponding to the maximum fractional occupation of the triplet state. The quenching of the peak when the magnetic field is increased could be due to the magnetic splitting of the triplet state which reduces the possibility of energy conserving scattering processes between the ^{1}H nuclear spin and the local iron (III) electronic spin.

The studies presented here of the spin dynamics in a well defined cluster of few localized magnetic moments should provide an ideal test for exact analytical and/or numerical solutions on a finite spin system.

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