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Ground-state magnetization of the molecular cluster $Mn_{12}O_{12}$-acetate as seen by proton NMR

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^{1}H nuclear magnetic resonance (NMR) measurements have been carried out in $Mn_{12}O_{12}$-acetate clusters at low temperature in order to investigate microscopically the static and dynamic magnetic properties of the molecule in its high-spin $S=10$ ground state. Below liquid helium temperature it is found that the local hyperfine fields at the proton sites are static as expected for the very slow superparamagnetic relaxation of $Mn_{12}O_{12}$ at low temperature. The magnitude and distribution of the hyperfine fields can be reproduced to a good approximation by considering only the dipolar interaction of protons with the local Mn magnetic moments and by assigning the magnitude and orientation of the local moments of the different Mn^{3+} and Mn^{4+} ions according to an accepted coupling scheme for the total $S=10$ ground state. The relaxation time of the macroscopic magnetization of the cluster was measured by monitoring the change of the intensity of the ^{1}H-NMR shifted lines following inversion of the applied magnetic field. This is possible because the sudden change of the field orientation changes the sign of the shift of the NMR lines in the proton spectrum. Although important differences are noticed, the relaxation time of the magnetization as measured indirectly by the ^{1}H-NMR method is comparable to the one obtained directly with a superconducting quantum interference device magnetometer. In particular we could reproduce the minima in the relaxation time as a function of magnetic field at the fields for level crossing, minima which are considered to be a signature of the quantum tunneling of the magnetization.

I. INTRODUCTION

Quantum tunneling of the magnetization (QTM) in mesoscopic molecular magnets has recently attracted much interest since several experiments have indicated evidence of QTM in some magnetic cluster.[1] Among the magnetic clusters, $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$ (henceforth abbreviated as $Mn_{12}O_{12}$) is one of the most investigated molecular magnets and the first where quantum tunneling phenomena have been reported.[2,3] The magnetic core of the cluster is made up of a tetrahedron of Mn^{4+} ($S=3/2$) at the center and eight Mn^{3+} ($S=2$) on the outside.[4,5] The ground state is determined by the relative strength of at least four antiferromagnetic intramolecular superexchange interactions of the order of hundreds kelvin. A simple coupling scheme which explains successfully the magnetic properties[5] describes the cluster as four dimers Mn^{3+}-Mn^{4+} with spin $s=1/2$ (resulting from a very strong antiferromagnetic intradimer exchange interaction J) and four Mn^{3+} ions, coupled together by an effective ferromagnetic isotropic exchange interaction. This is equivalent to considering the four inner Mn^{4+} moments ferromagnetically aligned and the eight outer Mn^{3+} also ferromagnetically aligned with the two subsystems antiferromagnetically aligned. The result of this coupling scheme is a high total spin ground state, i.e., $S=10$. The $S=10$ ground state is split into 11 sublevels by a strong easy-axis anisotropy.[5] The remaining Kramers degeneracy is removed by an external magnetic field yielding energy levels for the 21 magnetic sublevels m expressed as $E_m=-Dm^2-Bm^4+hm\cos\theta$. The most recent determination of the parameters obtained from neutron scattering[6,7] yielded $D=0.55$ K, $B=1.2\times10^{-3}$ K. We will neglect here the very small nondiagonal transverse term detected in a recent experiment.[7] Assuming a gyromagnetic ratio $g=2$ one has $h=g\mu_B H/k_B=1.33H$ (K) for H in tesla and θ is the angle between the easy axis (c axis) of the cluster and the external magnetic field. Below liquid helium temperature the clusters occupy mostly the $m=\pm10$ states and the reorientation of the magnetization between these two states becomes extremely long—about 1 day at 2.4 K—due to the anisotropy barrier giving rise to a pronounced superparamagnetic behavior.[8] When the relaxation rate of the magnetization is measured in response to a varying magnetic field H_z along the easy axis peaks are observed which have been interpreted as a manifestation of resonant tunneling of the magnetization.[1,9] The qualitative explanation is that the relaxation rate of the magnetization increases at field values where the spin states become pairwise degenerate. It is this degeneracy which increases the tunneling probability and thus shortens the relaxation time. The size of the effect is reduced by the smearing out of the energy levels of the spin states due to spin-phonon coupling, intermolecular interactions, and/or hyperfine interactions with the nuclei.[10]

Nuclear magnetic resonance (NMR) is a suitable microscopic probe to investigate the electronic states of the cluster from the microscopic point of view. For example, from an investigation of the temperature dependence in the range 2–30 K of the nuclear spin-lattice relaxation rate it was possible to determine the lifetime broadening of the molecular spin states due to spin-phonon interactions.[11] The results turned out to be in good agreement with recent theoretical calculations.[10] More recently we have reported a time dependence of the NMR proton spin-echo signal measured at the center of the spectrum when the measurements are done in off-equilibrium conditions.[12] It was shown that the exponential fit of the time dependence of the echo intensity yields the relaxation rate of the magnetization of the molecule. In the present paper we report a systematic study of the low-temperature proton NMR spectrum both in equilibrium conditions and during the thermal equilibration of the magnetization of the molecules. From the equilibrium spectrum we obtain the hyperfine field at the proton sites in the superparamagnetic frozen state of the $Mn_{12}O_{12}$ cluster due to the local magnetic moment on the different Mn^{3+-4+} ions. Furthermore, from the evolution in time of the intensity of the proton NMR shifted lines we can determine the relaxation time of magnetization of the $Mn_{12}O_{12}$ cluster in the temperature and magnetic field range where quantum tunneling is important, thus leading to a microscopic determination of the QTM phenomenon.

II. EXPERIMENT

Polycrystalline samples of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\ 2CH_3COOH\cdot 4H_2O$ were prepared as described in Ref. 5. A part of the powdered material was mixed with Stycast 1266 and allowed to set in a magnetic field of 9 T at 300 K for several hours in order to obtain a sample with rigid orientation of the crystallites with their easy axis (*c* axis) along the field direction. This sample was used in experiments where a sudden rotation of the sample by 180° with respect to the applied field is necessary to bring the system off equilibrium. The obvious disadvantage of using a sample embedded in Stycast is the presence of a huge proton NMR signal from the glue. Therefore whenever possible we used a loosely packed powder sample where the crystallites are oriented only for the time during which the sample sits in the applied magnetic field. In both cases the NMR spectrum in equilibrium conditions is the same. The ^{1}H-NMR measurements were carried out utilizing a phase-coherent spin-echo pulse spectrometer. The spectra were obtained by sweeping in steps the external magnetic field at constant frequency. The intensity of the NMR spin-echo signal at each field step was collected and averaged using a boxcar integrator. The resulting average speed for the field sweep was 15 G/sec. The echo was obtained with two pulses $\pi/2$, π in phase (Hahn echo) with a typical pulse length for the $\pi/2$ pulse of $\sim 2\ \mu$sec. The range of temperature explored is 1.4–4.2K and the external magnetic field was varied up to 5 T. The dc magnetization measurements were performed in the sample oriented in Stycast by means of a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS).

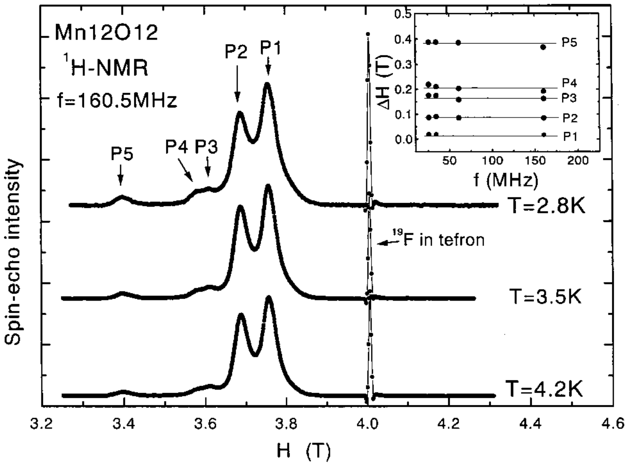

FIG. 1. ^{1}H-NMR spectra in $Mn_{12}O_{12}$ measured at 160.5 MHz for three different temperatures. The inset shows the shift of the resonance field as a function of resonance frequency, $\Delta H = H_0 - H_i$, at about 2.4 K. The average rate of sweep of the field is 15 Oe/sec.

III. RESULTS AND DISCUSSIONS

A. ^{1}H-NMR spectra in the thermal equilibrium state

Figure 1 shows several ^{1}H-NMR spectra at different temperatures measured at 160.5 MHz for a loosely packed powder sample. In this case, most of small particles are aligned with the *c* axis along the magnetic field because of the strong magnetic field. As can be seen in the figure two strong peaks and three weak peaks are observed at low temperature. The two main peaks denoted P1, close to the Larmor frequency, and P2 with positive shift agree with the spectrum previously reported.[11] The shift for peak P2 increases with decreasing *T* and it levels off to a value of about 0.07 T, which becomes temperature and field independent below about 5 K in agreement with a previous report.[11] The peaks P3, P4, and P5 in Fig. 1 also reach a constant shift with decreasing *T* below 4.2 K as can be seen in Fig. 1.

The inset in Fig. 1 shows the resonance frequency dependence at 2.4 K of $\Delta H = H_0 - H_i$ where H_i is the magnetic field at the each peak (P_i) and H_0 is the Larmor field. The fact that the absolute shift for each peak is the same for any value of the applied magnetic field indicates clearly that the shift arises from a spontaneous hyperfine field at the proton sites due to the frozen orientation of the magnetization of the $Mn_{12}O_{12}$ molecules. This is expected since, in agreement with the superparamagnetic behavior of the magnetization for $Mn_{12}O_{12}$ clusters,[8] the frequency of the reorientation of the magnetic moment of the total $S = 10$ spin at low tempera-

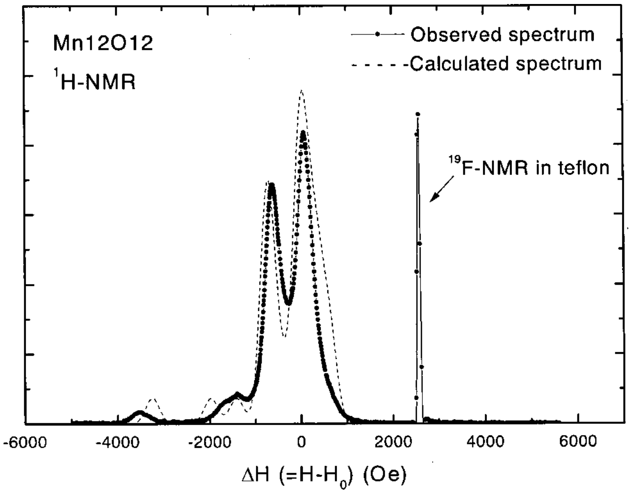

FIG. 2. Comparison of the experimental ^{1}H-NMR spectrum measured at 160.5 MHz and $T=4.2$ K with the spectrum calculated on the basis of a dipolar hyperfine field at the proton sites (see text) in $Mn_{12}O_{12}$. The calculated spectrum was obtained by weighting the peaks by the relative abundance of the different proton sites, indicating that the agreement is satisfactory both regarding the peak positions and their relative intensity.

ture is much smaller than the NMR frequency (of the order of 10^6 Hz). This is also a direct confirmation that the local orientation of the Mn moments, which is responsible for the hyperfine field at the proton site, follows the orientation of the total $S=10$ spin quantum state. The hyperfine field at each proton site can be estimated to be 0.7, 1.7, 1.9, and 3.7 kOe for the P2, P3, P4, and P5 peaks, respectively. In general, there are two possibilities for the origin of hyperfine field at proton sites, that is, dipole fields and contact hyperfine fields from the Mn^{3+}-Mn^{4+} magnetic ions. The dipolar field at the proton site can be calculated by summing up the contributions at each proton site from the different Mn ions. We used the crystal coordinates reported by Lis.[4] The only adjustable parameters are thus the values assigned to the local magnetic moments of the Mn ions. Following the proposed coupling scheme[5] we assigned four Bohr magnetons to the eight Mn^{3+} $(S=2)$ outer ions and three Bohr magnetons to the four inner Mn^{4+} ions. We further assumed in the calculation that the magnetic moment on Mn^{3+} ions is along the magnetic field while that on Mn^{4+} is antiparallel to H. The intermolecular dipole field is neglected and the dipole field at proton sites of solvent molecules located between the clusters is assumed to be zero for simplicity. The calculated spectrum using the above assignments is shown in Fig. 2. In simulating the NMR spectrum we have introduced a broadening of each component described by a Gaussian having full width at half maximum (FWHM) of ~300 Oe. This broadening includes both nuclear dipole-dipole interactions and the effect of misalignment of the particles in the powder sample. The relatively good agreement between the observed and calculated spectra suggests that the main part of the hyperfine field at the proton site is due to the dipole field from the spin moments on local Mn ions. The most shifted peak P5 is attributed to one of the protons of the water molecules directly bonded to a manganese ion (H2 in the original labeling by Lis[4]). The other water proton H1 corresponds to P4, while P3 is attributed to the H4 proton of the solvation water molecule. The other proton H3 of the solvation water is expected to be less shifted and to merge in the P2 peak, together with the signals originating from the protons of the eight acetate groups, whose CO_2 plane is essentially parallel to the tetragonal axis. Finally the almost unshifted P1 peak should include the protons of the eight acetate groups, whose CO_2 plane is almost perpendicular to the tetragonal axis, and those of the solvation acetic acid molecules. It is noted that the present analysis is based on room-temperature x-ray crystal data[4] and thus small differences can be expected at 2.4 K due to thermal expansion. The remaining discrepancy between the dipolar calculated spectrum and the experimental one can be ascribed to a small contribution from the transferred hyperfine field due to a small overlap of the wave function of the Mn ion at the proton site. We have checked the sensitivity of the dipole field distribution to the assignment of the local magnetization to the Mn ions. If one assigns one Bohr magneton shared between the two Mn^{3+}-Mn^{4+} ions of each of the four dimers and four Bohr magnetons to the remaining four Mn^{4+} ions, the result is still in reasonable agreement with the experimental spectrum. On the other hand, if one assigns a uniform average moment of 20/12 Bohr magnetons to the 12 Mn ions, the shifted lines P5, P4, and P3 cannot be reproduced at all. Thus one may conclude that the NMR proton spectrum is a confirmation of the coupling scheme previously suggested[5] and mentioned in the Introduction.

It should be noted that the spectra reported here might not correspond exactly to a thermal equilibrium state because they are obtained by sweeping the magnetic field at a rate (15 Oe/sec) which, at such low temperature, could be faster than the equilibration time of the magnetization. However, at a field of about 4 T for which the spectra in Fig. 1 and Fig. 2 were taken, the ground state is $m=-10$ separated from the first excited state $m=-9$ by ~20 K, a value much larger than the temperature of the measurement. Therefore, for our experimental condition, most of the clusters are in the $m=-10$ sublevel, and the changes of the thermal population of the excited states when the magnetic field is swept is negligible.

B. ^{1}H-NMR spectra in off-equilibrium condition and relaxation of the magnetization

The magnetization of the clusters is initially prepared in equilibrium conditions with the magnetic field along the easy c crystal axis. By inverting the magnetic field one creates off-equilibrium conditions whereby the magnetization of each molecule wants to realign along the external field ($m=-10$ to $m=+10$ transition). At low temperature and in magnetic fields less than 1 T this process is prevented by the crystal field anisotropy and proceeds very slowly via spin tunneling and phonon-assisted relaxation.[10] Since the direction of the local hyperfine field at the proton sites with respect to the external field depends upon the relative orientation of the magnetization of the molecule with respect to the external field, one can study the microscopic relaxation of the cluster magnetization by looking at the proton NMR spectrum. In order to detect this effect, we measured the ^{1}H-NMR spectrum using the oriented sample in Stycast to avoid reorientation of the particles due to the magnetic field

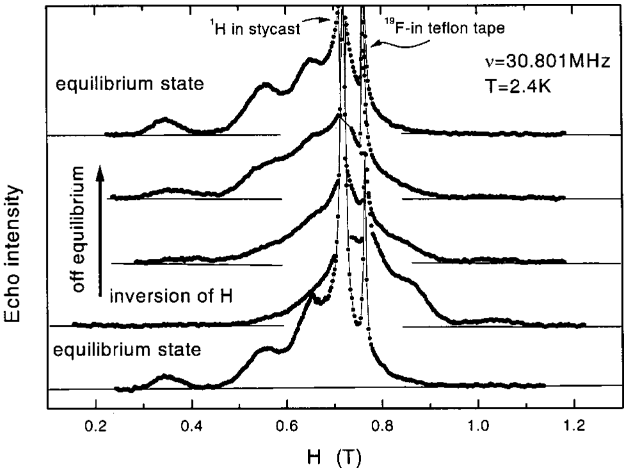

FIG. 3. Time evolution of ^{1}H-NMR spectrum measured at 30.801 MHz and $T=2.4$ K. The spectrum at the bottom corresponds to the thermal equilibrium state. The second lowest spectrum corresponds to the off-equilibrium situation following the field inversion. The remaining spectra from bottom up are taken at different times after the field inversion.

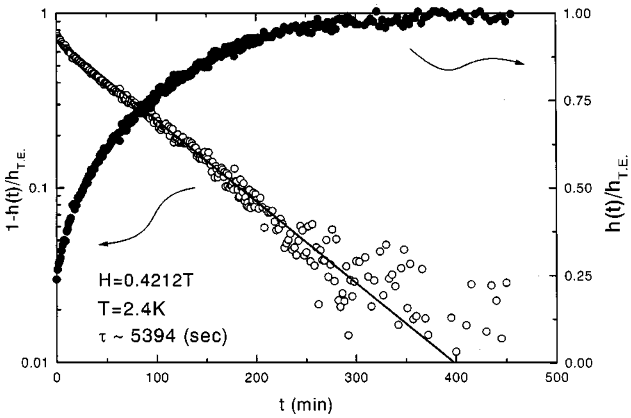

FIG. 4. Time dependence of the echo intensity taken at $H=0.4212$ T (21.85 MHz) and $T=2.4$ K following the sudden inversion of the orientation of the z axis of the sample with respect to the applied magnetic field: (●) $h(t)/h_{\mathrm{T.E.}}$, (○) $1-h(t)/h_{\mathrm{T.E.}}$.

after field inversion. Instead of inverting H, we quickly invert the direction of the oriented sample. Figure 3 shows the experimental results. The spectrum at the bottom of Fig. 3 corresponds to the thermal equilibrium state before inversion, where the easy axis of the clusters is along the magnetic field. The observed spectrum is the same as the one observed in loosely packed powder (Fig. 1) except that now we have a very strong ^{1}H-NMR signal from the Stycast centered at the Larmor field. This ^{1}H signal as well as the ^{19}F signal coming from the Teflon tape should be disregarded in the discussion, which follows.

Just after inversion of the direction of the sample, the observed spectrum changes drastically as shown in the second spectrum from the bottom of Fig. 3. In the figure, the time evolution is from the bottom up. Since the spectra were obtained by sweeping the magnetic field, a process, which takes about 30 min for each spectrum, does not correspond to a precise off-equilibrium state. However, since the overall process of relaxation of the magnetization at this temperature takes 200–300 min, the different spectra give a qualitative idea of the evolution of the NMR spectrum in time. The signals of the shifted peaks with positive hyperfine fields disappear, while new signals can be observed at magnetic fields higher than the Lamor field H_0, where no signal could be detected before the inversion. After a long time (for example, 400 min for this case), the spectrum becomes independent of time and it recovers the initial shape before the field inversion. The drastic change of the spectrum after the inversion can be explained simply as the inversion of the orientation of the hyperfine fields at each proton sites in $\mathrm{Mn}_{12}\mathrm{O}_{12}$ clusters i.e., from $H_{\mathrm{local}}=H_{\mathrm{hf}}+H_0$ to $H_{\mathrm{local}}=-H_{\mathrm{hf}}+H_0$, giving rise to a spectrum inverted with respect to the Lamor field (H_0). It should be noted that the proton spin-lattice relaxation time in the equilibrium state is shorter by about six orders of magnitude[11] than the time scale for the changes in the spectrum and thus plays no role here.

In order to investigate the effect quantitatively one can sit at a fixed field on one of the shifted lines (see Fig. 1) and follow its amplitude as a function of time without the need for recording the full spectrum. The signal intensity for each shifted peak, P2–P5, in the spectrum at thermal equilibrium corresponds to the total number of clusters occupying the magnetic $m=-10$ ground state. Immediately after the 180° rotation of the sample the state $m=-10$ becomes $m=+10$. Then the growth of the signal intensity for each peak after the inversion is proportional to the increase of the number of clusters which return to the $m=-10$ new ground state. Therefore, we can measure the relaxation time of the magnetization by monitoring the echo intensity as a function of time. We find that the results are independent, within our experimental uncertainty, of the radio frequency pulse width used to generate the echo signal. Figure 4 shows a typical time dependence of the echo intensity $h(t)$ measured at 0.4212 T (at the position of the P2 peak) and at $T=2.4$ K. The experimental results can be fitted tentatively by the expression

$$h(t)=a\{1-\exp[-t/\tau(H)]\}+b, \tag{1}$$

where $\tau(H)$ is a relaxation time and $a+b$ is the echo intensity for the thermal equilibrium state, $h_{\mathrm{T.E.}}$. As can be seen in Fig. 4, the growth of the signal intensity is well fitted by a single exponential function [Eq. (1)] except for an initial fast growth, which accounts for about 30% of the signal. From the slope of the $1-h(t)/h_{\mathrm{T.E.}}$ on a semilogarithmic plot, we can estimate $\tau(H)$. The time dependence of the echo intensity at a field corresponding to the position of the peak P5 (see Fig. 1) was also measured, yielding similar results. However, for this peak it is found that there is a slight but measurable shift as a function of time. The shift could be due to the effect of the relaxation of neighboring clusters and thus of interest by itself. A combined study of the intensity and of the shift is currently underway.

In order to verify if $\tau(H)$ corresponds to the relaxation time of the macroscopic magnetization, as one would expect, we measured τ directly using the SQUID magnetometer. The time dependence of the magnetization, $M(t)$, is shown in Fig. 5. The $M(t)$ increases up to the thermal equilibrium value $M_{\mathrm{T.E.}}$. For this measurement the sample oriented in Stycast was cooled down to 2.4 K under zero magnetic field

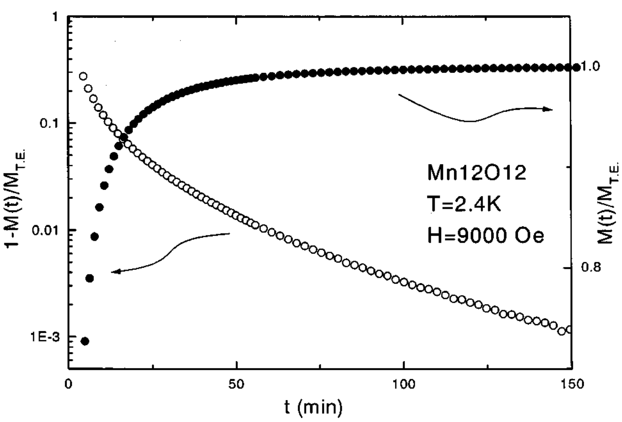

FIG. 5. Time dependence of the magnetization, $M(t)$, measured by SQUID at $T=2.4$ K and $H=9000$ Oe. (●) $M(t)/M_{\mathrm{T.E.}}$, (○) $1-M(t)/M_{\mathrm{T.E.}}$.

(zero magnetization) and was kept for several hours at this temperature, and then $M(t)$ was monitored after the magnetic field was raised up to the desired value. Contrary to the case of the NMR signal intensity, the relaxation behavior of the magnetization, $[1-M(t)/M_{\mathrm{T.E.}}]$ in Fig. 5, is described better by a stretched exponential. A similar behavior was reported by Friedman *et al.*[2] A stretched exponential relaxation of the magnetization was previously observed in the Fe8 molecular cluster in the low-temperature quantum tunneling regime.[13] The result was explained[13] in terms of a redistribution of the local fields during the relaxation process which affects locally the tunneling rate and thus makes the relaxation transition probability time dependent.[14] The average relaxation time $\tau(H)$ from SQUID measurements was estimated from a fit of the recovery curves (see Fig. 5) to a stretched exponential $\exp\{-[t/\tau(H)]^{\beta}\}$ and the results are shown in Fig. 6. In the same figure is shown a comparison of the field dependence of the relaxation time measured with both methods, NMR and SQUID. Although the two sets of data refer to two different ways of extracting the relaxation time from the recovery curves, one can conclude that the results from both methods are in good agreement. In particular, in both cases one sees minima of $\tau(H)$ at the level crossing fields, i.e., $H=0$ (only for the magnetization), $H=0.45$ T, and $H=0.9$ T. Except for the minima, indicated by the arrows in Fig. 6, the H dependence of $\tau(H)$ follows a thermal activated law $\tau(H)=\tau_0\exp[(67-13.3H)/k_{\mathrm{B}}T]$ with $\tau_0\sim 10^{-6}$ (sec) which is consistent with background thermal excitations over the barrier due to the anisotropy as modified by the applied magnetic field. The field values corresponding to the minima in the relaxation time agree with critical fields where the magnetic level crossing occurs.[3] It is noteworthy that the β exponent is also field dependent with minima at the level crossing fields. Since the minima observed in the H dependence of both $\tau(H)$ and β are indicative of quantum tunneling effects, there is the interesting possibility of investigating the relaxation of the magnetization of the cluster from the microscopic point of view with the NMR method. It is pointed out that the difference in the shape of the recovery curves obtained from the NMR signal intensity (Fig. 4) and the one from the magnetization (Fig. 5) is significant. The recovery of the NMR signal intensity in Fig. 4 is exponential if one excludes the first 30% of the recovery which could simply be due to the presence in the sample of fast relaxing species of Mn_{12}.[15] On the other hand, the recovery of the magnetization in Fig. 5 is stretched exponentially over the whole time interval. One simple explanation could be found in the slight misalignment of the oriented powder sample. Since the relaxation time of the magnetization is expected to be a sensitive function of the orientation of the magnetic field with respect to the anisotropy axis, a distribution of relaxation times would result in a stretched exponential recovery curve. In the NMR case the distribution of relaxation times would be less severe since the NMR echo signal at a given resonance frequency selects already only the crystallites properly oriented. More experiments are underway to clarify this point.

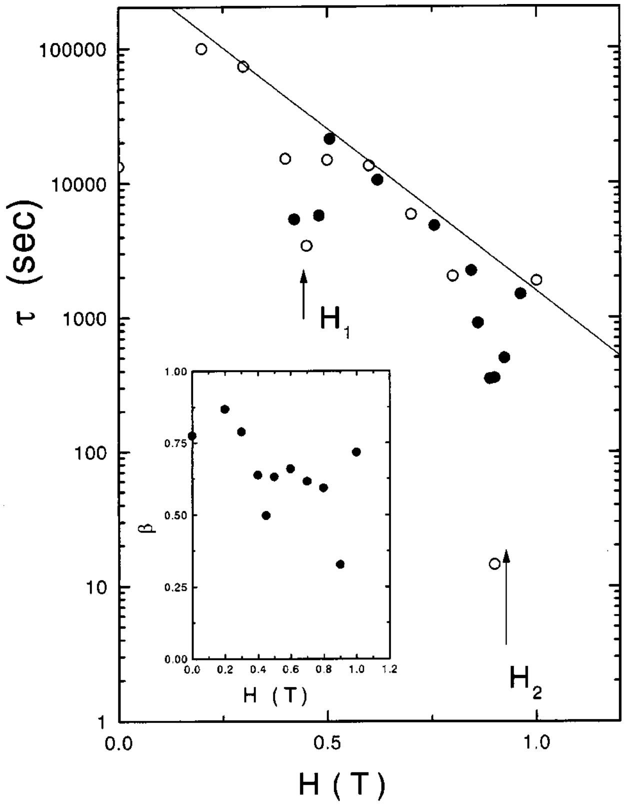

FIG. 6. Field dependence of the relaxation time for magnetization measured at $T=2.4$ K by (●) ^{1}H-NMR, (○) SQUID. The solid line corresponds to the equation $\tau(H)=4\times 10^{5}\exp[(-13.3H)/2.4]$ (sec) with H in tesla. The inset shows the stretched exponent β used to fit the SQUID recovery curves for the different fields.

IV. SUMMARY AND CONCLUSIONS

We have carried out ^{1}H-NMR at low temperature in order to investigate the magnetic state of $\mathrm{Mn}_{12}\mathrm{O}_{12}$ clusters in its ground state. The equilibrium proton NMR spectrum displays several shifted lines besides the weakly shifted main resonance line. The spectrum could be explained almost entirely by considering the dipolar local fields created at the proton sites by Mn magnetic ions in the frozen superparamagnetic state. It was shown that the shifted proton lines reverse sign of the shift when the easy c axis of the sample is rotated by 180° with respect to the external magnetic field.

By monitoring the subsequent growth of the shifted lines (or decrease of the mirror image ones with respect to the Larmor field) one can follow the relaxation of the magnetization of the molecules from a microscopic point of view. The relaxation time measured by monitoring the time evolution of the echo intensity as a function of magnetic field shows the expected minima at the critical magnetic fields for level crossings which originate from quantum tunneling of the magnetization. It is noted that a similar NMR method to study the relaxation of the $Mn_{12}O_{12}$ magnetization was recently reported.[12] However, in Ref. 12 the echo intensity was measured at the weakly shifted main proton line (see P1 in Fig. 1) whose position is not significantly affected by the sudden change of orientation or intensity of the magnetic field, thus requiring a more elaborate explanation of the experimental observations. With the present paper a complete experimental characterization of the time dependence of the NMR parameters in off-equilibrium conditions is made available. We have observed significant differences in the shape of the recovery of the magnetization monitored by NMR and SQUID which requires more measurements and a detailed theoretical analysis to be elucidated. These circumstance, together with the possibility of following separately different parts of the NMR spectrum during the recovery, may open up the possibility of studying the evolution in time for each magnetic sublevel.

ACKNOWLEDGMENTS

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