Nuclear Spin-Lattice Relaxation by Solitons in the Antiferromagnetic Chains $(CH_3)_4NMnCl_3$

J. P. Boucher

Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, F-38041 Grenoble, France

and

J. P. Renard

Institut d'Electronique Fondamentale, Université Paris XI, F-91405 Orsay, France

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The first evidence of nuclear spin-lattice relaxation (NSLR) by magnetic soliton fluctuations is presented. The NSLR rate T_1^{-1} of ^{15}N in an enriched crystal of $(CH_3)_4NMnCl_3$ is measured versus field ($20 \lesssim H \lesssim 80$ kOe) and temperature ($2 \lesssim T \lesssim 4.2$ K). At a given temperature an exponential divergence of T_1^{-1} is observed as a function of H. This drastic behavior is in complete agreement with the soliton model for planar antiferromagnetic chains.

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Nuclear spin-lattice relaxation (NSLR) time (T_1) measurements give a way to probe the very low-frequency fluctuations undergone by the nuclei in a sample. In ordered ferromagnets and antiferromagnets, information is thus obtained on the direct or induced multimagnon processes.[1] In paramagnets the low-frequency fluctuations are essentially given by the hydrodynamic modes while near a transition the critical fluctuations become dominant.[2] This technique has been shown to be a powerful tool in one-dimensional (1D) systems where in the high-temperature limit the spin diffusion leads to a drastic divergence of the local fluctuations as the frequency $\omega \to 0$.[3] At lower temperature when substantial 1D short-range order is present in the chains the main contribution to the relaxation rate T_1^{-1} is given by "diffuse" modes peaked at $\omega = 0$. Quasimagnons contribute also to the dynamics in magnetic chains and multimagnon processes can explain the drastic decrease of T_1^{-1} observed as a function of the field, at a given temperature, on some 1D ferro- and antiferromagnetic compounds.[4] In all cases the theoretical description of these low-frequency contributions can be given by use of linear-mode approximations. Recently a new class of excitations has been shown to take place in 1D planar magnetic chains.[5] In presence of magnetic field H, nonlinear modes occur which can be described in terms of magnetic solitons. Their contribution to the NSLR as a direct process has been already considered in the case of ferromagnetic chains[6]: T_1^{-1} is predicted to be proportional to the soliton density and therefore to *decrease* exponentially as a function of $H^{1/2}$ at a given temperature T. In this Letter we consider the case of antiferromagnetic (AF) chains where the situation is completely different. It will be shown that magnetic solitons in antiferromagnetic chains give rise to a rather unusual behavior: T_1^{-1} *increases* exponentially as a function of H/T. In practice this allows us to follow the soliton regime on a large scale of the soliton density.

NSLR measurements have already been performed on different nuclei (^1H; ^2D; ^{14}N) of $(CH_3)_4NMnCl_3$ (TMMC) showing a drastic behavior of T_1^{-1} versus field and temperature.[7] In order to get very accurate information on the spin dynamics we have measured the NSLR rate T_1^{-1} of ^{15}N-nuclear spins in an enriched single crystal of TMMC. Its chemical purity was appreciated by measuring the 3D ordering temperature T_N in low field: $T_N \simeq 0.83$ K. This value is lower than the value for pure TMMC ($0.84 \lesssim T_N \lesssim 0.85$).[8] The small difference can be attributed to a very low concentration of impurities ($x \simeq 10^{-4}$) due probably to residual diamagnetic Hg^{++} ions.

During the measurements, the magnetic field $\vec{H}$ was applied perpendicular to the chain axis ($\vec{H} \perp \vec{c}$). Since the ^{15}N spin value is $I = \frac{1}{2}$, there is no quadrupolar interaction and the nuclear resonance is made of a single line. The time T_1 was measured as a function of the field ($20 \lesssim H \lesssim 80$ kOe) and the temperature T ($2 \lesssim T \lesssim 4.2$ K). The recovery of the nuclear magnetization following a π-$\frac{1}{2}\pi$ pulse sequence was found to be exponential. The data are shown in Fig. 1. At a given temperature a drastic increase of T_1^{-1} is observed with increasing H. The divergence is limited only by the 3D magnetic ordering which

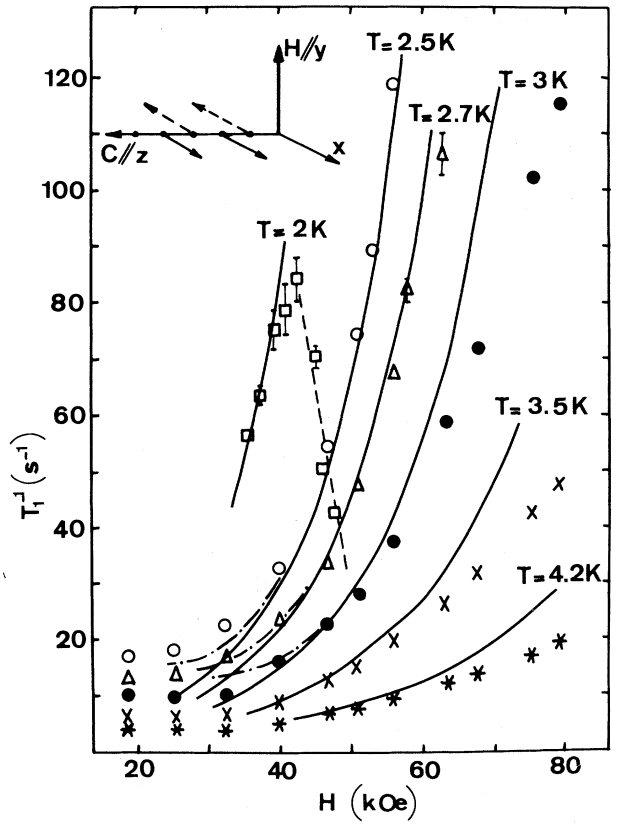

FIG. 1. NSLR rate T_1^{-1} of ^{15}N in TMMC vs magnetic field H at different temperatures. The full lines represent the contribution of the spin fluctuations perpendicular to $\vec{H}$ predicted by the soliton model for planar antiferromagnetic chains. The dot-dashed lines include the fluctuations parallel to $\vec{H}$. The dashed line is an aid to the eye which displays the T_1^{-1} behavior at the 3D magnetic ordering.

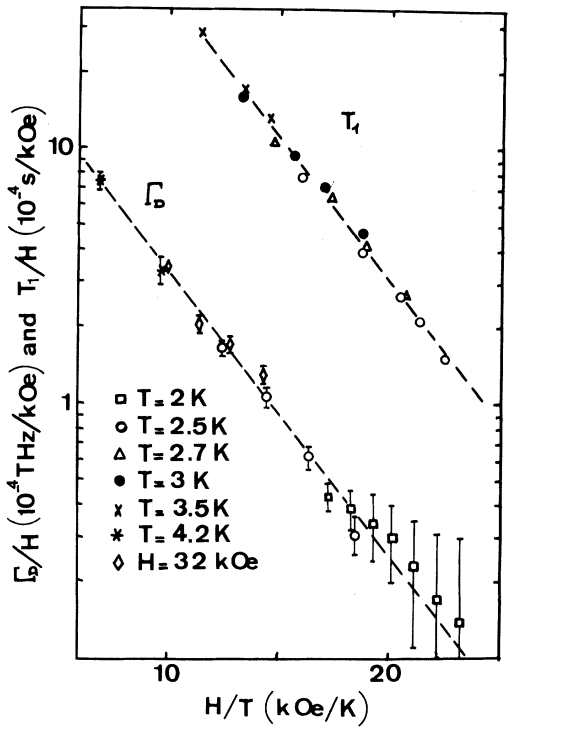

FIG. 2. Experimental values of T_1/H and Γ_D/H as a function of H/T, where Γ_D represents the width of the central peak observed by neutron measurements (Ref. 9) in the same conditions. The slopes of the two dashed lines are the same: $\alpha \simeq 0.26$ K/kOe.

is associated with a rapid drop of T_1^{-1} (cf. data for $T = 2$ K). In Fig. 2, the quantity T_1/H is plotted as a function of H/T in such a way as to establish its exponential behavior. In the same figure, recent neutron results[9] are also reported: Γ_D represents the width of the central peak which has been shown to account for the π flipping of the AF sublattices each time a soliton has passed along the chains. The two quantities T_1/H and H/Γ display clearly the same behavior.

For magnetic solids the NSLR rate can be written as

$$T_1^{-1} = 2\pi N^{-1} \sum_q A_q S_{\parallel}(\vec{q}, \omega_N) + B_q S_{\perp}(\vec{q}, \omega_N), \quad (1)$$

where the coefficients A_q and B_q are related to the hyperfine coupling between ^{15}N nuclear and electron spins. The functions $S_{\parallel,\perp}(q, \omega)$ are the dynamic structure factors associated with the fluctuations parallel and perpendicular to $\vec{H}$. The wave vector $\vec{q}$ refers to the chain axis and ω_N is the nuclear Larmor frequency. Below $T \lesssim 5$ K, TMMC can be considered as a planar system with the spins lying in the XY plane perpendicular to the chain axis ($\hat{c} \equiv \hat{z}$).[10] As a consequence the low-frequency fluctuations associated with the residual S^z components are completely negligible.[11] In Eq. (1), $S_{\perp}(q, \omega)$ represents the fluctuations of the spin components along x if the field is applied in the y direction (cf. Fig. 1).

In a crystal of TMMC the location of the nitrogen atoms is well defined. They are surrounded by three equivalent magnetic chains at a distance $l = 5.269$ Å.[12] If we assume that the hyperfine coupling is of dipolar origin, the terms A_q and B_q in Eq. (1) can be evaluated easily. Two remarks are in order: (i) For $\vec{H} \parallel \vec{c}$, the coefficients A_q and B_q are q independent around $q = \pi$.[13] Since one expects the low-temperature fluctuations to be dominated by the AF modes ($q \simeq \pi$), one can replace A_q and B_q by A_π and B_π in Eq. (1). (ii) For one chain the coefficients A_π and B_π depend on the angle between $\vec{H}$ and the vector joining the ni-

trogen atom to the chain. However, when the three nearest chains are considered together, these coefficients become angular independent: A_π and B_π are fully isotropic in the XY plane. Finally, one has $B_\pi = A_\pi$ and

$$B_\pi = 27\pi/2(\hbar\gamma_e\gamma_N/l^3)^2 \times\sum_n(-1)^n \sin\theta_n\cos\theta_n/|\vec{r}_n|^3,$$

where γ_e and γ_N are the gyromagnetic ratios of the electron and nuclear spins, respectively. In the sum, n labels the electron spins of one chain which interacts with a ^{15}N spin whose position is determined by the vector $\vec{r}_n$ making the angle θ_n with the chain axis. For an infinite chain the coefficients A_π and B_π depend only but rather sensitively on l and $c = 3.213$ Å[12] the distance between two neighboring spins in a chain. We obtained $B_\pi = 2.0\times10^{11}$ (rad/sec)^2.

At low temperature the spins in an AF chain tend to lie perpendicular to the applied field $\vec{H}$. Magnetic solitons are nonlinear excitations which correspond to a π-rad turn of the spins. Moving Bloch walls are thus created between two antiphased ordered domains. The creation of solitons results from a thermally activated process with an energy proportional to H: $E_s = \alpha H$.[9] In the classical spin model, the soliton density n_s is given by

$$2n_s/\kappa(XY) = a(\alpha H/T)^{3/2}\exp(-\alpha H/T), \quad (2)$$

with $\kappa(XY) = T/4JS^2$, where J is the exchange coupling and S the spin value ($J\simeq6.8$ K and $S=\frac{5}{2}$ for TMMC). Unlike the ferromagnetic case, the soliton fluctuations give rise to different expressions for $S_\parallel(q,\omega)$ and $S_\perp(q,\omega)$. One can write[14,15]

$$2\pi N^{-1}\sum_q S_\parallel(q,\omega_N) = (\hbar/k)S^2(\pi/32)^{1/2}(aS/T)\exp(-\alpha H/T)I(\Delta), \quad (3)$$

with

$$I(\Delta) = \int_{-\infty}^{+\infty} dx|x|^{-1}\operatorname{sech}^2 x\exp[-(\Delta/x)^2]$$

and $\Delta = \pi/\sqrt{8}(\gamma_N/\gamma_e)(\alpha H/T)^{1/2}$. For $S_\perp(q,\omega)$ slightly different descriptions have been given by Mikeska[14] and Maki.[15] However, after integration over q, one obtains the same result:

$$2\pi N^{-1}\sum_q S_\perp(q,\omega_N) = S^2\pi^{-1}\Gamma_D/[\Gamma_D{}^2+\omega_N{}^2], \quad (4)$$

with $\hbar\Gamma_D/k = 2n_s v$ where $v = (2/\pi)^{1/2}4JS/(\alpha H/T)^{1/2}$ is the soliton velocity. The fluctuation mode $S_\perp(q,\omega)$ which results from the π flipping of the two sublattices defines unambiguously the soliton regime. Such a contribution does not exist in ferromagnetic chains where the solitons are defined by a 2π-rad turn of the spins. In this case no change can be seen on the spin correlation after a soliton has passed since the spins are found in the same position. In Eq. (4) ω_N which represents the ^{15}N Larmor frequency (6–35 MHz) is much smaller than Γ_D(0.3–20 GHz) and can be neglected. Finally the contribution of the fluctuations perpendicular to $\vec{H}$, $(T_1^{-1})_\perp = B_\pi S^2/\pi\Gamma_D$, can be expressed as

$$(T_1^{-1})_\perp = (\hbar/k)B_\pi S^3/[a(2\pi)^{1/2}\alpha H] \times\exp(+\alpha H/T). \quad (5)$$

It increases exponentially with H/T while $(T_1^{-1})_\parallel = A_\pi 2\pi N^{-1}\sum_q S_\parallel(q,\omega_N)$ can be seen from Eq. (3) to be exponentially decreasing. For large values of H/T one expects therefore $T_1^{-1}\simeq(T_1^{-1})_\perp$ and the quantity $\ln(H/T_1)$ to behave linearly. This result is established in Fig. 2 from which an experimental value for α is obtained: $\alpha_{\text{expt}} = 0.26\pm0.01$ K/kOe. This value compares perfectly well with the neutron data which give the same value but with less accuracy.[9] From Eq. (4) the theory predicts $\Gamma_D/T_1 = B_\pi S^2/\pi = 2.5\times10^{-12}$ (rad/sec)^2 while experimentally we obtain $\Gamma_D/T_1 = (2.0\pm0.3)\times10^{-12}$ (rad/sec)^2. The agreement is still quite good.

The excellent agreement between neutron and NSLR data justifies our description of T_1 in terms of solitons. However, numerical discrepancies occur in the value of the coefficients α and a. Theoretically they are predicted to be: $\alpha_{\text{th}} = g\mu_B S/k \simeq 0.336$ K/kOe and $a_{\text{th}} = 8/(2\pi)^{1/2}\simeq3.19$. Recently, Maki has shown that the expression of the soliton density given by Eq. (2), with the theoretical values for α and a, is numerically correct only for $H/T \gtrsim 30$ kOe/K[14] which is beyond our experimental conditions. For smaller values of H/T, we have suggested in Ref. 9 that Eq. (2) is a good approximation if adequate values are used for α and a. For $10\lesssim H/T\lesssim20$ kOe/K a fit can actually be obtained with a numerical calculation performed by Loveluck[16] for $\alpha\simeq0.32$ K/kOe and $a\simeq2.15$. This value of α is closer but still larger than our experimental evaluation. In order to get a quantitative description for T_1^{-1} we use for α the experimental value $\alpha_{\text{expt}} = 0.26$ K/kOe. The coefficient a is determined by fitting the expression for $(T_1^{-1})_\perp$ to one experimental point. We choose the value for $H\simeq54$ kOe and $T = 2.5$ K, where we expect $(T_1^{-1})_\parallel$ to be negligible: $a_{\text{expt}} \simeq 2.0$. All the curves on Fig. 1 are deduced from this one-point fitting. The full lines correspond to $(T_1^{-1})_\perp$ while the dot-dashed lines are the sum

of the two contributions $(T_1^{-1})_{\parallel}$ and $(T_1^{-1})_{\perp}$. At low temperature, a very good agreement is obtained with the experiments. The NSLR rate is essentially dominated by the soliton fluctuations perpendicular to $\vec{H}$. The deviation which occurs for the highest values of H could be attributed to a small amount of defects in the chains.[17] Before ending the discussion we have to mention that an uncertainty might exist on the value of the effective field undergone by the electron spins. Below 120 K, three crystallographic domains co-exist in a single crystal of TMMC and in each domain a small magnetic anisotropy d is present in the XY plane.[18] As shown in Ref. 17, the effect of d can be described in terms of an internal field $|\vec{H}_d| \simeq 11$ kOe and one can define an effective field by $H_{\text{eff}} = (|H^2 \pm H_d^2|)^{1/2}$ (the sign + or − depends on whether $\vec{H}$ is $\parallel$ or $\perp$ to $\vec{H}_d$, respectively). The T_1 data reported on Fig. 2 corresponds to $H \gtrsim 40$ kOe: the maximum uncertainty on H resulting from H_d is definitely less than 3% on each point and does not affect the final accuracy on α: $\alpha_{\text{expt}} = 0.26 \pm 0.01$ K/kOe.

For the conclusion we point out that the present experimental study gives the first evidence of NSLR induced by the fluctuations of magnetic solitons as a direct process. It is shown that in AF chains the soliton fluctuations lead to an exponential divergence of T_1^{-1} as a function of H/T. As a consequence T_1 measurements allow us to define the soliton regime with great accuracy. For the range of H/T explored in this work, the soliton density has been changed by more than a factor of 20. The experimental value obtained for the soliton energy ($E_s = \alpha H$) is definitely smaller than the theoretical predictions for the classical spin model. In real systems such as TMMC we may have to account for possible quantum effects which can actually reduce the soliton energy and possibly explain our results.

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