Diffusion of Solitons in the Antiferromagnetic Chains of $(CD_3)_4NMnCl_3$: A Study by Neutron Spin Echo

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Quasi one-dimensional magnetic compounds have given good examples of soliton excitations. We present new results on soliton dynamics obtained by the neutron-spin-echo method. This technique allowed a unique accurate line-shape analysis of the antiferromagnetic mode (centered at $q=\pi/a$ in reciprocal space) in the time domain 0.02–1.7 nsec. Thus we could directly probe the antiferromagnetic short-range order in the chains. The analysis of the relaxation line shape of this order in $(Cd_3)_4NMnCl_3$ doped with copper reveals an exp $(-\sqrt{t})$ time decay—a signature of diffusive soliton dynamics—and does not show the conventional exp$(-t)$ decay expected for ballistic solitons.

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In the past few years, a great deal of effort in condensed matter has been devoted to the study of the "soliton" phenomenon.[1] In the case of one-dimensional (1D) magnetic compounds, "topological" solitons can be viewed as domain walls moving almost freely along chains having substantial internal magnetic order. The dynamics of solitons, especially in real systems, remains one of the most interesting problems to be studied.[2] Essentially, two models can be considered: the "coherent" and "incoherent" models.[3] In the coherent model, the solitons are assumed to follow a ballistic behavior, while in the incoherent or diffusive model the solitons are expected to move randomly along the chains. For a study of the soliton dynamics antiferromagnetic (AF) compounds deserve special attention since they offer a definite experimental advantage. In AF chains, a soliton corresponds to a π rotation of the spins. Therefore, as the solitons travel along the chains they induce rapid spin flips which finally reverse the spin direction in the magnetic sublattices. This flipping process limits in time the AF short-range order yielding a frequency (energy) broadening of the "staggered"—or "AF"—mode occurring in reciprocal space at the wave vector $q=\pi/a$ (a is the distance between two neighboring spins). In particular, the frequency width of the AF mode gives a direct evaluation of the flipping rate. However, it is only the frequency (time) line shape that distinguishes the two kinds of soliton behavior: ballistic or diffusive. The purpose of this work was to perform such a line-shape analysis making use of the unique capabilities of the neutron-spin-echo (NSE)[4] method. This technique allows a combination of the exploration of the reciprocal wave-vector space with a real-time analysis in a very low frequency range [90 MHz–8 GHz]. The first point is definitely needed in order to observe the AF mode at $q=\pi/a$ and the second one will be shown to offer the best approach to the line-shape problem.

It is generally accepted that in the AF compound $(CD_3)_4NMnCl_3$ (TMMC) the low-frequency spin dynamics is governed by thermally excited solitons in a well-known temperature-applied field domain.[5] Furthermore, it has been concluded from indirect evidence[3] that a small amount of impurities turns the soliton motion from ballistic into diffusive. Until now, however, no frequency analysis of the AF mode has been possible. This mode becomes actually too narrow to be probed by conventional neutron diffraction measurements, even under high resolution conditions.[6] The data reported in the present Letter provide the first direct observation of the predicted exp$(-\sqrt{t})$-type relaxation of the AF mode, an unambiguous signature of diffusive dynamics.[2] In particular, it will be shown that by use of an appropriate scaling, the line-shape analysis can be extended over more than four orders of magnitude in time.

The experiment has been performed on the IN 11 NSE spectrometer at the Institut Laue Langevin in Grenoble. It was used in a triple-axis-type configuration (Fig. 1) with a 0.4°-mosaic graphite analyzer crystal. The sample

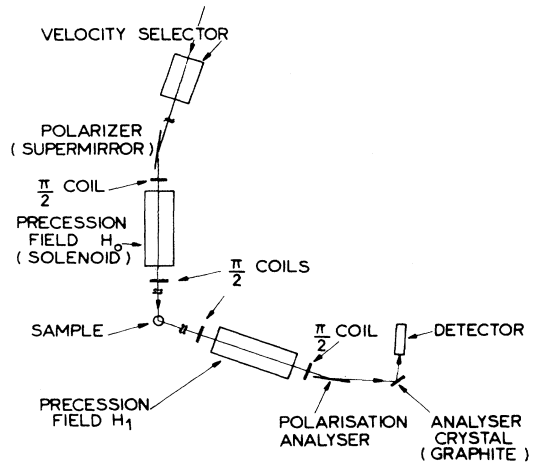

FIG. 1. Triple-axis-type configuration of the spectrometer used in this ferromagnetic NSE experiment.

was a ^{37}Cl-enriched single crystal of TMMC (about 0.5 cm^3) containing a small concentration ($c \simeq 0.5\%$) of magnetic impurities (Cu) on Mn sites. The crystal was oriented with the chain axis in the horizontal plane and the scattering vector **Q** was fixed at the position $\mathbf{Q}_0 = [0.15, 0, 1]$ in reciprocal lattice units (rlu). Thus, we observed the magnetic fluctuations $S_\perp$ practically perpendicular to the chain direction [0,0,1]. In order to reach the desired soliton regime, a vertical field $H = 38$ kOe was applied to the sample.[5] With a temperature-independent background of 6 counts/min (room background plus elastic nuclear scattering) we found a strongly temperature-dependent spin-flip scattering contribution of maximum 18-counts/min intensity at 1.3 K. This corresponds to the AF mode with spins ordering in the direction perpendicular to both the chain and the magnetic field, as expected. A contribution from direct scattering on the solitons was negligible.[5]

Because of the applied field, ferromagnetic neutron spin echo[4] had to be used in order to avoid the dephasing of Larmor precessions in the strong inhomogeneities of the sample field. As a result of the very strong stray fields of the asymmetric split-coil cryomagnet the available time range was limited to between 0.02 nsec (equivalent to 8 GHz) and 1.7 nsec (90 MHz).[7] Nevertheless, at least two of the three key parameters, i.e., energy resolution (90 MHz), dynamic range ($\sim$1:100), and counting rate, were much superior to those obtainable with any of the other neutron scattering techniques, at comparable q resolution.

In this experiment, we made use of the capability of neutron scattering to explore a feature with a well-defined wave number: i.e., the $q = \pi/a$ AF mode. However for the incident wavelength used, $\lambda = 6.04$ Å, the instrumental wave-vector resolution in the chain direction was $\delta q \simeq 0.041/a$ (0.013 rlu) (HWHM). This value must be compared to the physical q width of the AF mode. In the soliton regime and in the presence of impurities, it is given approximately by[8] $\Delta q \simeq (c + 2n_s)/a$ where c is the impurity and n_s the soliton concentration. Within our experimental conditions, the instrumental resolution δq was always worse than Δq ($\Delta q \lesssim 0.008/a$). This means that what we really observed was the AF *local order,* local in the sense that it was defined over a range of about $1/\delta q \sim 25$ lattice spacings, i.e., small compared with the expected range of ordered chain sections ($\gtrsim 120$ lattice spacings).[9] In other words, the observed quantity corresponded to the intensity "integrated" in q (but around $q = \pi/a$). On the other hand, our spectrometer configuration allowed collection of neutrons within an energy window $\Delta\omega \simeq 24$ GHz HWHM at a given q. We have observed a small decrease of the AF scattering intensity with increasing temperature, which therefore indicates inelastic scattering outside our window. For relaxation-type processes this decrease is an approximate measure of the time decay of the local AF order $S_\perp(t)$, at a time t close to $\hbar/\Delta\omega$. The points around $t = 0.0035$ nsec in Fig. 2 represent this decrease of the measured scattering intensity relative to that at $T = 1.3$ K, and the large error bars in the time variable (based on numerical estimates) take into account the approximate character of this information. All other points in Fig. 2 represent $S_\perp(t)$ as directly measured by NSE.

In the soliton regime, the local AF order decays in time as a result of the flipping process described above. One expects that the corresponding correlation function $S_\perp(t)$ relaxes exponentially as a function of the average number of spin flips $N(t)$ occurring at *a given point in space* during the time t. Indeed, it can be shown that

$$S_\perp(t) \simeq \exp[-2N(t)]$$

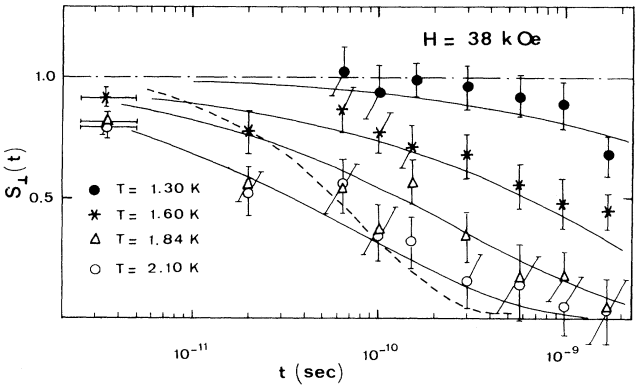

FIG. 2. Time decay of the local antiferromagnetic order at different temperatures, as directly measured by NSE (except for the points at $t \sim 0.0035$ nsec, as explained in the text). The solid curves correspond to the diffusive soliton model and the dashed curve to the conventional exponential relaxation predicted for the ballistic soliton model.

(the factor 2 in the exponent is related to the fact that the flip process is an exact spin reversal). $N(t)$ depends on the soliton dynamics. In the coherent model, the solitons after they have been created are assumed to retain their initial velocity both in amplitude and in direction. With n_s being the soliton density, the number of flips is simply given by $N(t)=n_s V_0 t$, where V_0 represents the average velocity in a soliton gas. One is led to

$$S_\perp(t)\simeq\exp(-At)\ , \tag{1}$$

with $A=2n_s V_0$. In contrast, for a diffusive behavior (incoherent model), within a period t a soliton covers an average distance of $(\langle r^2\rangle)^{1/2}=(Dt)^{1/2}$ where D is the diffusion coefficient. One gets

$$S_\perp(t)\simeq\exp[-(Bt)^{1/2}]\ , \tag{2}$$

with $B=4n_s^2 D$. Note that $N(t)$ counts only the number of "uncorrelated" flippings (see Ref. 2).

The two expressions (1) and (2) differ appreciably by their time dependence. In Fig. 2 the dashed line gives the shape of the curve corresponding to Eq. (1), and its steep slope is clearly inconsistent with the experimental results. On the other hand, the shape of the full lines which are obtained from Eq. (2) reproduces well the observed time dependence at all temperatures. It is worth noting that in NSE the data reduction does not involve deconvolution[4] and, therefore, it can be performed point by point without fitting to a model.

Quantitative analysis reinforces this conclusion. Referring to the sine-Gordon description for the soliton gas,[10] one can write

$$n_s=(8/\pi)^{1/2}m(E_s/T)^{1/2}\exp(-E_s/T)\ ,$$

$$V_0\simeq(2/\pi)^{1/2}4JS(E_s/T)^{-1/2}\ ,$$

where E_s is the soliton energy, m is the soliton mass ($m=E_s/4JS^2$), J is the exchange coupling, and $S=\frac{5}{2}$ is the spin value (for TMMC $JS^2\simeq 42.5$ K). In AF chains, E_s is proportional to H: $E_s=\alpha H$ (for TMMC, we have obtained experimentally[10] $\alpha=0.26\pm0.02$ K/kOe). The coefficient A in Eq. (1) is therefore given by

$$A=(8/\pi S)\alpha H\exp(-\alpha H/T)\ . \tag{3}$$

The dashed curve in Fig. 2 was calculated for $T=2.10$ K. Definitely, the coherent model cannot explain our results, neither qualitatively nor quantitatively.

For completing the description of the diffusive model, we make explicit the coefficient D as $D=V_0^2\zeta_D$ where ζ_D^{-1} characterizes the damping rate associated with the diffusion. The coefficient B in Eq. (2) becomes

$$B=4n_s^2V_0^2\zeta_D=(8/\pi S)^2(\alpha H)^2\zeta_D\exp(-2\alpha H/T)\ . \tag{4}$$

It is remarkable that the different full curves in Fig. 2 were obtained by use of Eq. (4) with the *same* value of the only free parameter $\zeta_D^{-1}=10^{10}$ rad/sec. A more striking representation of this point is shown in Fig. 3 where the same data are plotted as a function of the "extended time" scale $x=[\exp(-2\alpha H/T)]t$. With this scaling, specific to the diffusive model, the line-shape analysis covers more than four orders of magnitude: The theoretical diffusive prediction (full curve) is in very good agreement with the data. Thus our results provide direct, unambiguous evidence that in our doped TMMC sample, the spin-flip relaxation of the AF short-range order is induced by diffusive particles. This result is fully consistent with the soliton picture and corroborates previous conclusions obtained rather indirectly from nuclear magnetic resonance measurements.[3]

It remains to elucidate by a systematic study on various magnetic chain systems, what is the heretofore unknown origin of the diffusion. The variation with impurity concentration is certainly essential. In particular, one should

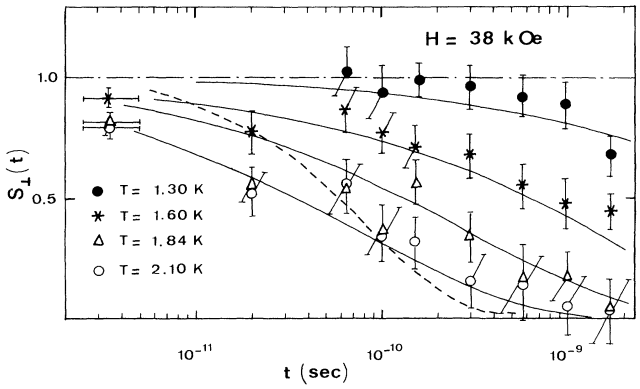

FIG. 3. Same data as in Fig. 2 plotted as a function of the "extended" time scale x specific to the diffusive model. The solid curve is obtained for the value $\zeta_D^{-1}=10^{10}$ rad/sec. The dashed curves with $\zeta_D^{-1}=1.8\times10^{10}$ and 6.2×10^{10} rad/sec, respectively, illustrate the accuracy of the determination of ζ_D^{-1}.

be able to observe directly the crossover between the coherent $\exp(-t)$ and incoherent $\exp(-\sqrt{t})$ behaviors, expected to occur in compounds with lower impurity concentrations. The present results also show that the NSE method is a well-adapted, powerful tool for this kind of research.

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[6]For instance, for the triple-axis spectrometer IN 12 at the Institut Laue-Langevin, the best instrumental energy resolution is about $\delta\omega \simeq 2.5$ GHz (HWHM).

[7]This value is three times less than usual on IN 11 at the used wavelength.

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[9]In contrast, in NMR work, such as Ref. 3, no selection can be made in the q space, i.e., fluctuations local on the scale of atomic distances are observed.

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