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Direct-Process NMR Relaxation by Spin Waves in a One-Dimensional Antiferromagnet*

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Measurements of the proton relaxation time T_1 in $(CH_3)_4NMnCl_3$ are reported as a function of temperature between 4.0 and 1.2 K. Results are interpreted in terms of a direct relaxation process with spin waves in a one-dimensional antiferromagnet. They represent the first observation of direct-process NMR relaxation by magnons in any system and show that any gap in the spectrum at $q=\pi/a$ has to be less than 0.07 meV.

We report low-temperature NMR measurements of the proton longitudinal relaxation time T_1 in the one-dimensional antiferromagnet $(CH_3)_4NMnCl_3$ (TMMC). These are consistent with a direct-process coupling of the nuclear spin system to antiferromagnetic magnons. As such, they represent the first known observation of this kind of relaxation in a magnetic substance and verify the existence of a gapless spin-wave mode at the antiferromagnetic wave vector $q=\pi/a$ (a is the lattice spacing so that $q=2\pi/2a$ is the reciprocal-lattice vector for the magnetic unit cell of an antiferromagnet). The latter verification is in accord with simple spin-wave theory and contrary to a recently proposed temperature-dependent gap by the author.[1] It also agrees with the theory of Lovesey and Meserve.[2]

Lively interest has centered around the existence[3] of spin waves in a one-dimensional antiferromagnet. The standard antiferromagnetic spin-wave spectrum for an ordered system,[4]

$$\hbar\omega_q = 4JS|\sin qa|\,, \tag{1}$$

predicts a zero-frequency mode at $q=\pi/a$, and whether this is appropriate for TMMC at finite temperature has been of particular concern. In Ref. 1 we noted that a second-order Green-function theory predicts a gap at $q=\pi/a\equiv q_0$ and that $\omega_{q_0}\propto T$, where T is the absolute temperature. This leads to a natural interpretation of static correlations[5,6] at low temperature in terms of noninteracting spin waves. Parameters of the theory included nearest- and next-nearest-neighbor static correlation functions, which were obtained from the classical theory.[6] Scales and Gersch[7] have since shown that a self-consistent solution for quantum spins produces a gap at q_0 even for $T=0$. Lovesey and Meserve,[2] on the other hand, have used a continued fraction expansion which allows for damping—something absent in the treatments of Refs. 1 and 7. They find the $q=\pi/a$ mode to be strongly peaked at $\omega=0$ for temperatures below about 20 K in TMMC.

Inelastic neutron scattering data[3] exist for $q^*a \geq 0.05\pi$, where $q^*=\pi/a-q$, at temperatures down to 1.9 K. At $q^*a=0.05\pi$ the observed magnon energy is 1 meV. Since the predicted gap energy of Ref. 1 is 0.1 meV at 1.9 K, and that of Ref. 7 is

0.3 meV at $T=0$, the gap would probably have been undetected by the neutron scattering at the lowest temperatures, especially since the energy varies as $(\omega_{q_0}^2+D^2q^{*2})^{1/2}$ near $q^*=0$, where D is an appropriate constant; so even a gap as large as that found by Scales and Gersch would produce only a 5% effect. Data of Hutchings *et al.*[3] at 20 K definitely rule out a gap of 1 meV, as results from the theory of Ref. 1; but it is at the lowest temperatures, where damping is least likely to be important, where the simple Green-function theories are most likely to be valid, and thus where crucial experiments need be performed.

NMR provides a powerful tool for probing very low-energy parts of the spectrum and thus can be utilized to resolve the question of a gap at $q_0=\pi/a$. The relaxation time T_1 may be expressed in the general form[8]

$$1/T_1=\sum_j[A_jf_j(0)+B_jf_j(\omega_0)] \tag{2}$$

for an electronic system described by an isotropic Heisenberg exchange Hamiltonian $\mathcal{H}_{ex}$ plus Zeeman interaction with an applied field H in the z direction. In the above,

$$f_j(\omega)=\int_{-\infty}^{\infty}dt\,\langle S_i^z(t)S_{i+j}^z(0)\rangle e^{-i\omega t} \tag{3}$$

is the spectral density at frequency ω of the pair correlation between the electronic spin operator S_i^z at site i and the one j sites removed, and where $\omega_0=\gamma_eH$ is the *electron* spin resonance frequency in the applied field (γ_e is the electronic gyromagnetic ratio). The NMR frequency has been taken as negligibly small. Time dependence shown in Eq. (3) is governed solely by $\mathcal{H}_{ex}$, the Zeeman term having been explicitly accounted for by the spectral component at ω_0. For an isotropic hyperfine interaction, $A_j=0$; but this is not the case for dipolar coupling of protons to Mn electron spins in TMMC. Isotropy [$\langle S_i^\alpha(t)S_{i+j}^\alpha(0)\rangle$ independent of $\alpha=x$, y, or z] has been assumed, as is correct for the one-dimensional Heisenberg antiferromagnet with no long-range order.

A direct-process contribution to T_1 requires there to be an elementary excitation of $\mathcal{H}_{ex}$ with energy 0 or $\hbar\omega_0$. The typical antiferromagnet usually has an anistropy gap larger than $\hbar\omega_0$, and even if—as in a ferromagnet—energy conservation is allowed, it generally occurs for wave vectors $q\approx 0$ so that the three-dimensional density of states is too small for the process to be effective. Thus NMR relaxation in ordered magnetic systems has been analyzed in terms of Raman and other multimagnon processes[9] with the direct interaction rightly ignored.

But the situation is different in a one-dimensional antiferromagnet because there is no anisotropy gap[10] at $q=0$ and because the one-dimensional density of states does not discriminate against $q=0$ or π/a.

Temperature dependence of T_1 is readily established for a noninteracting spin-wave spectrum

$$\langle S_q^z(t)S_{-q}^z(0)\rangle=\langle S_q^zS_{-q}^z\rangle\exp(i\omega_qt), \tag{4}$$

where $\langle S_q^zS_{-q}^z\rangle$ is the static correlation function at wave vector q. Since

$$\langle S_i^z(t)S_{i+j}^z(0)\rangle$$

$$=(a/\pi)\int_0^{\pi/a}dq\,\langle S_q^z(t)S_{-q}^z(0)\rangle\cos qaj, \tag{5}$$

and in our experiments $\hbar\omega_0=0.07$ meV $\ll 4JS$, use of Eqs. (1), (4), and (5) in Eq. (2) yields the approximate relation

$$1/T_1=C(\langle S_0^zS_0^z\rangle+\epsilon\langle S_{q_0}^zS_{-q_0}^z\rangle), \tag{6}$$

where $q_0=\pi/a$, C is an appropriate constant, and where $\epsilon=0$ if $\omega_0<\omega_{q_0}$, so that no direct process is possible for q_0 magnons, and $\epsilon=1$ if $\omega_{q_0}=0$, a gapless spectrum. At low temperature exact results for classical spins[5] show $\langle S_0^zS_0^z\rangle\propto T$ and $\langle S_{q_0}^zS_{-q_0}^z\rangle\propto 1/T$, so the conditions $\omega_0<\omega_{q_0}$ and $\omega_0>\omega_{q_0}$ produce completely different temperature dependences for T_1. That the low-temperature direct process at $q=0$ is much weaker than at q_0 is a consequence of the uniform ($q=0$) susceptibility being much less then the staggered ($q=q_0$) susceptibility for an antiferromagnet.

Measurements of the proton T_1 were performed on a polycrystalline sample of TMMC between 4.0 and 1.19 K at a frequency of 25 MHz. Recovery of a two-pulse echo was observed following saturation by a prepulse. The resulting T_1 from the exponential (over at least one decade) recovery is shown in Fig. 1. An approximately linear relation $T_1\propto T$ is seen, so we conclude that a direct process is occurring at q_0.

Our experiments show that the q_0 mode has appreciable spectral density near $\omega=0$. They do not necessarily imply an infinite-lifetime mode as suggested by Eq. (4). To investigate this point we have also considered the spectrum

$$\langle S_q^z(t)S_{-q}^z(0)\rangle=\frac{\langle S_{q_0}^zS_{-q_0}^z\rangle\kappa^2}{q^{*2}+\kappa^2}\times\exp(i\omega_qt)\exp(-\Gamma t) \tag{7}$$

near $q^*=0=q_0-q$, which includes a finite inverse correlation length κ and damping constant Γ. Analysis shows that the linear temperature de-

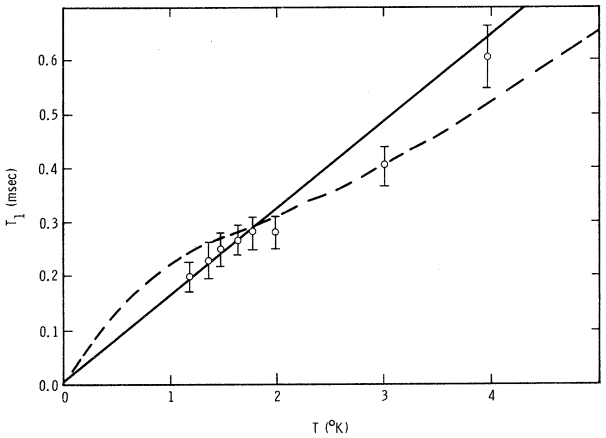

FIG. 1. Relaxation time T_1 (in milliseconds) versus temperature T. Solid line, simple linear relation. Dashed curve includes corrections for nonzero ω_0 as explained in text. Each curve is multiplied by a *different* constant to obtain a best fit.

pendence of T_1 is valid provided $\hbar\Gamma/\kappa aJ$ is either constant or approaches zero as $T \to 0$. Physically this means that the correlation length must not become large compared to the spin-wave mean free path as $T \to 0$. The theory of Lovesey and Meserve may be shown to give $\hbar\Gamma/\kappa aJ \propto T^{1/2}$ and thus is consistent with our results. Given that $\hbar\Gamma/\kappa aJ \ll 1$, a further condition for validity of Eq. (6) is that $(\hbar\omega_0)^2 \ll (4JS\kappa a)^2$. Since the two quantities are about equal at 1.2 K, this is a non-negligible effect. The dashed curve of Fig. 1 includes this correction and is obtained by noting that the term $f_j(\omega_0)$ samples a q_1^* such that $\omega_{q_1^*} = Dq_1^* = \omega_0$ and, thus, the appropriate amplitude is $\langle S_{q_0} S_{-q_0} \rangle (1 + q_1^{*2}/\kappa^2)^{-1}$. We also used $B_j = \frac{7}{3} A_j$ in Eq. (2), the result for a powder average and dipolar coupling. Data are not sufficiently accurate and do not exyend to low enough temperatures to choose between the finite-ω_0 dashed curve and the simple linear dependence.

Calculation of the numerical value for T_1 is complicated by inequivalent and unknown sites for the methyl protons at low temperatures. Recent work of Mangum and Utton[11] does show that the protons are stationary at these temperatures. Also, both the magnitude and temperature dependence of T_1 are such that the only plausible source of relaxation is coupling of the protons to electron spins on the Mn^{++} ions. This is further strengthened by the fact that room-temperature measurements of the proton T_1 in the diamagnetic isomorphous compound TMCC show it to be orders of magnitude longer than for TMMC. For a rough estimate we take the average position of the protons to be at the carbon sites[12]—as is the case at high temperature—and consider classical dipolar coupling of a proton spin to electron spins of the neighboring manganous ions. The polycrystalline average then gives $T_1 = 0.9$ msec at $T = 4.0$ K upon using Fisher's classical value for $\langle S_{q_0}^z S_{-q_0}^z \rangle$. This is in reasonable accord with the measured number 0.6 msec.

In conclusion, we have established that any gap at $q_0 = \pi/a$ in the antiferromagnetic spin-wave spectrum of TMMC must have an energy less than 0.07 meV, at temperatures between 4.0 and 1.19 K. On the other hand, the theory of Ref. 1 predicted a gap of 0.2 meV at 4.0 K. Furthermore, the q_0 spin-wave mode appears to be well defined in the sense that its mean free path is of the same order as or larger than the correlation length. These results are consistent with the spectral density recently proposed by Lovesey and Meserve. Finally, we stress that the temperature dependence $T_1 \propto T$ rules out Raman-like processes in which a nuclear spin flip is induced by an incident magnon since such interactions must give $T_1 \to \infty$ as $T \to 0$ and the density of excitations approaches zero. NMR relaxation via direct process with magnons has been observed, and this is possible only because of the unique characteristics of a one-dimensional system.

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Antiferromagnetic-Resonance Linewidths in MnF_2 †

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The fundamental relaxation mechanisms by which the uniform and magnetostatic modes decay in an antiferromagnet are identified by antiferromagnetic-resonance linewidth observations in MnF_2 at 4.2°K in fields of 85 kOe. The dependence of the linewidth—0.2 Oe in the narrowest instance—on sample geometry, surface preparation, and impurity concentrations makes quantitative comparison with the Loudon-Pincus theory possible. The predominant relaxation process is surface pit scattering into the degenerate spin-wave manifold in all but the most impure crystals.

While the linewidth and relaxation of magnetic resonance modes in ferromagnetic and ferrimagnetic insulators have been both well studied and explained,[1] little attention has been given to the problem of antiferromagnetic-resonance (AFMR) linewidth, despite the existence of a quantitative theory[2] for the nonthermal relaxation processes. Here we report the results of an extensive study of the AFMR linewidths of the uniform and magnetostatic modes in pure and impurity-doped MnF_2 at 4.2°K.[3] The various mechanisms (e.g., pit scattering and spatial variations in the local field) that contribute to the linewidths have been isolated and identified.

The AFMR frequencies in an easy axis, uniaxial antiferromagnet (AFM) with the external field H_0 applied collinear with the spin moments are, at 0°K,[4]

$$\omega/\gamma = (H_C^2 + 2H_A N_\perp M_S)^{1/2} \pm H_0, \qquad H_0 < H_C = (H_A^2 + 2H_A H_E)^{1/2}; \tag{1}$$

here H_A and H_E are the anisotropy and exchange fields, respectively, M_S the sublattice magnetization, and $N_\perp$ the perpendicular demagnetizing factor. In MnF_2 $H_E \simeq 515$ kOe, $H_A \simeq 8.4$ kOe, $H_C \simeq 93$ kOe, and $M_S \simeq 600$ Oe. To minimize the effects of rf field variations across the sample, the downgoing AFMR branch was studied at high fields ($H_0 \sim 85$ kOe) and relatively low frequencies (~23 GHz). The samples were cut cylindrically symmetric with respect to the c axis, highly polished, and strain-free mounted. Because of the strong angular dependence of the AFMR at high fields[5] the c axis was made collinear with the field to better than 0.1° by tilting the sample, *in situ*, while observing the resonance.

The following qualitative features associated with the uniform mode were noted immediately. Resonance half-widths ΔH are smallest in flat disks ($c \perp$ plane)—$\Delta H \simeq 5.0$ Oe—and the line profiles are Lorentzian as expected for relaxation broadening. These widths are nearly two orders of magnitude smaller than were previously found in AFMR studies of MnF_2.[6,7] Small misalignment in the field causes severe broadening and, with increasing misalignment, the uniform mode splits up into many distinct modes. The linewidth is temperature independent below 8°K. It can be increased by an order of magnitude by roughening the surface of the samples. The substitution for Mn of 1% Fe, Zn, or Ni impurities causes negligible linewidth changes despite resonance-field shifts of as much as 7 kOe. Only in samples with Co impurities (~1%) does the linewidth increase fourfold.

The experimental results strongly indicate that the relaxation of the AFMR is dominated by its decay into the degenerate manifold of $k \neq 0$ magnons via surface pit scattering. This mechanism has been found to be an important source of linewidth in ferromagnets[1] and has been theoretically explored for the AFMR by Loudon and Pincus (LP).[2] LP showed that in a finite sample volume dipolar fields cause the AFM spin-wave spectrum to become anisotropic. The dispersion relation for long-wavelength magnons $[r_0^{-1} \ll k \ll (H_A/2H_E b^2)^{1/2}]$ is, assuming $2\pi M_S \ll H_E$ and