# Electron-spin-lattice relaxation in a one-dimensional system

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We have measured by the modulation technique at the $X$ band the spin-lattice relaxation rate
in the one-dimensional $(CH_3)_4NMnCl_3$, in the temperature range 20–300 K. The experimental
data are well described by the Bloembergen and Wang model. Below 45 K, an exchange-lattice
relaxation process has been evidenced.

The spin dynamics in one-dimensional (1D) materials has been extensively studied by magnetic resonance[1,2] and neutron diffusion techniques.[3] In these materials, the exchange-narrowed electron-spin resonance shows marked properties; they concern the angular and frequency dependences of the linewidth, the line shape, and other effects such as line shifts and half-field transitions. They are consequences of the long-time diffusive decay of spin correlations in Heisenberg 1D systems.[1]

In this paper, we present the first study of the electron-spin-lattice relaxation time $T_1$ in a quasiperfect 1D system. We have measured $T_1$ at $X$ band as a function of crystal orientation and temperature (Figs. 1 and 2) in tetramethylammonium trichloromanganate $(CH_3)_4NMnCl_3$ (TMMC). This compound consists of $MnCl_3$ chains well separated from each other. The Heisenberg exchange coupling is very strong within the chains ($J = -6.7$ K) but about $10^4$ smaller between the chains.[4] We took great care to operate on perfect crystals to avoid the presence of a 3D species which was described in another publication.[5]

In concentrated magnetic materials, the relaxation time $T_1$ is usually very short. Its measurement by conventional techniques is rather difficult and very few experimental data are available. However, precise measurements can be obtained by the "modulation method" which was originally devised by Hervé and Pescia.[6] In a "modulation spectrometer," the amplitude of the microwave field is modulated at a frequency $\Omega$. A coil placed in the cavity, around the sample and coaxial to the magnetic field, picks up a signal $S$ proportional to the time derivative of the longitudinal magnetization $dM_z/dt$. For $\Omega T_1 \ll 1$, the magnetization follows the modulation and $S \propto \Omega$;

on the other hand, for $\Omega T_1 \gg 1$, the relaxation is effective and $S$ tends towards a value $S_0$. In the general case, two data, the low-$\Omega$ slope and the asymptotic value $S_0$ are sufficient to the determination of $T_1$. The upper values of $\Omega$ are limited by technical difficulties and $S_0$ cannot be obtained directly in samples where $T_1 < 10^{-8}$ s. Meanwhile, it can be shown[7] that there is a constant ratio between $S_0$ and the ESR signal delivered by the apparatus used just like a con-
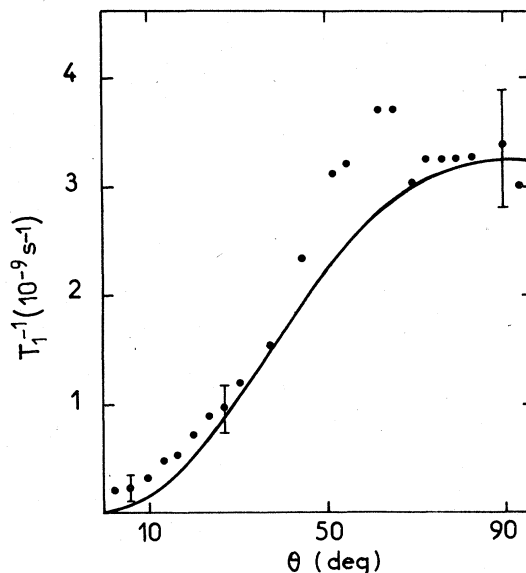


FIG. 1. Angular variation of the spin-lattice relaxation rate in TMMC at 300 K and 9 GHz. The solid curve is obtained from Eq. (3) without adjustable parameters. $\theta$ is the angle between the Zeeman field and the chain axis.
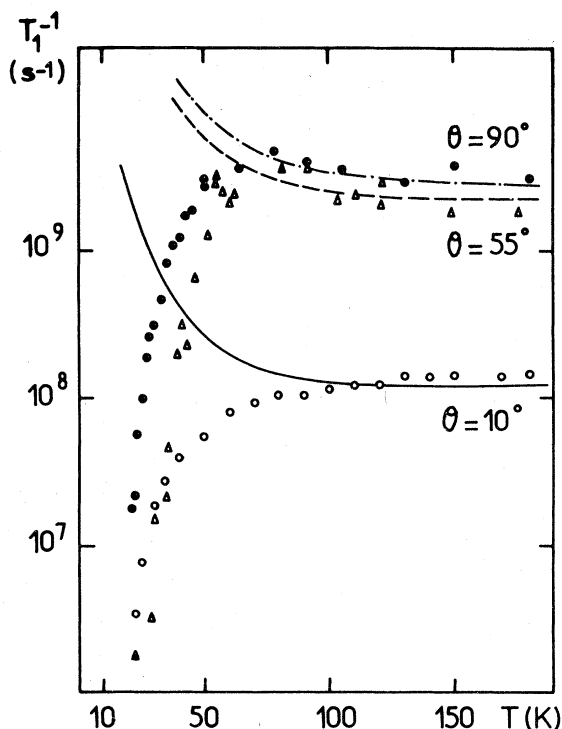
FIG. 2. Temperature dependence of the spin-lattice relaxation rate in TMMC for the orientations $\theta = 10°$ (open circles), $55°$ (triangles), and $90°$ (black circles). The corresponding theoretical curves, obtained from Eq. (3), are, respectively, solid, dashed, and dot-dashed. Above 100 K, the agreement between theory and experiment is good. Below 70 K, the observed $T^7$ dependence is well explained assuming an exchange-lattice relaxation.

ventional spectrometer. This ratio is measured using a test sample (with a long $T_1$) and $S_0$ can be determined indirectly for the sample of interest. This improvement of the method allows the measurement of $T_1$ as short as $10^{-10}$ s, such as those encountered in TMMC, with an error which does not exceed 20%.

When a strong exchange is present, spin-lattice relaxation is usually depicted by the three-reservoir model of Bloembergen and Wang.[8] The effective $T_1$ is[9]

$$T_1 = T_{ZE} + \left[\frac{\omega_z}{\omega_{ex}}\right]^2 T_{EL} \ , \qquad (1)$$

$\omega_z$ and $\omega_{ex}$ being the Larmor and exchange frequencies, respectively; in TMMC, their ratio is about $10^{-2}$ at $X$ band. The exchange-lattice relaxation time $T_{EL}$ is due to the modulation of exchange by the lattice vibrations. At high temperatures, the exchange reservoir is strongly coupled to the lattice and $T_1$ is equal to the Zeeman-exchange relaxation time $T_{ZE}$.

The energy transfer between the Zeeman and the exchange systems takes place because the exchange interaction randomly modulates the dipolar interaction; the relaxation is adequately described by the Kubo-Tomita approach[10]

$$T_1^{-1} = \int_0^\infty \psi(\tau)\,d\tau \ ,$$

$$\psi(\tau) = \langle [S^Z, H_D(\tau)][H_D, S^Z]\rangle / \langle S^Z S^Z \rangle \ , \qquad (2)$$

where $S^Z$ is the total spin component, along the applied field. The time evolution of the dipolar term $H_D(\tau)$ is governed by the unperturbed Hamiltonian (Zeeman plus exchange). For the study of the temperature dependence it is convenient to separate $\psi(\tau)$ into a Gaussian short-time part and a diffusive long-time part.[11] We have then

$$T_1^{-1}(T) = T_{1S}^{-1}G_S(T) + T_{1D}^{-1}G_D(T) \ , \qquad (3)$$

$G_S$ and $G_D$ are temperature-dependent functions, which are unity in the infinite temperature limit.[12]

$$T_{1S}^{-1} = 6S(S+1)\omega_D^2\zeta(6)(\tfrac{1}{2}\pi)^{1/2}\omega_{ex}^{-1}\sin^2\theta \ ,$$

$$T_{1D}^{-1} = 3S(S+1)\omega_D^2\zeta^2(3)$$

$$\times [\sin^2\theta\cos^2\theta\phi(\omega_z) + \sin^4\theta\phi(2\omega_z)] \ ,$$

with

$$\phi(\omega_z) = (D\omega_z)^{-1/2}[1 - 4(\omega_z/\pi\omega_{ex})^{1/2}] \ ,$$

$\omega_D = \hbar\gamma^2/c^3$, $\gamma$ is the gyromagnetic ratio, and $c$ is the distance between neighboring ions along a chain. $\zeta(x) = \sum_n n^{-x}$. $\theta$ is the angle between the magnetic field and the chain axis. $D$ is the spin-diffusion coefficient.[13]

The curve in Fig. 1 is calculated from Eq. (3) with $T = 300$ K. The agreement between theory and experiment for both the magnitude and the angular variation of $T_1^{-1}$ is quite satisfactory. Furthermore, no parameter has been adjusted in this comparison. In the calculation we have considered only intrachain relaxation, so the theoretical value vanishes for $\theta = 0°$. The small nonzero experimental value obtained for this orientation is due to interchain relaxation. $T_1$ does not vary significantly between 300 and 100 K in agreement with the theory, but below 70 K a strong disagreement occurs (Fig. 2). The sudden increase of the relaxation time is certainly related to the preponderance of the exchange-lattice relaxation [Eq. (1)]. An "exchange-bottleneck" effect[9] results from it. The corresponding value of $T_{EL}$ is comparable to the relaxation times encountered in ionic crystals. We find $T_1^{-1} \propto T^{7\pm0.5}$ for all the orientations and at temperatures as high as 45 K. This law is consistent with a two-phonon relaxation process.[14] The original theory of exchange-lattice relaxation is due to Griffiths.[14] This theory neglects the correlations

between different pairs of spins and, in the case of a two-phonon relaxation process, gives a $T^7$ law in agreement with our experimental result. Richards[15] has extended the work of Griffiths by including the correlations. He has shown that, in the case of linear chains with interactions restricted to nearest neighbors, the $T^7$ term vanishes and the relaxation rate is proportional to $T^9$. The $T^7$ law is recovered if one takes into account next-neighbor interactions. However, in the calculation, it is assumed that the four-spin correlation function $\langle \vec{S}_i(t) \cdot \vec{S}_j(t) \vec{S}_k \cdot \vec{S}_l \rangle$ be-

comes negligible in a time of the order of $1/J$. This assumption is certainly inexact here, since it is known that the 1D correlation functions follow at long times an unidimensional diffusion law. A remarkable feature is the high temperature for which the two-phonon process sets in. To our knowledge, it is the first direct observation of an exchange-bottlenecked electron-spin-lattice relaxation occurring in this temperature range.[16] This implies the existence of high-energy phonons. Such an effect may be related to the dimensionality of the system.[17]

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