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Observation of solitons in the $S = \frac{1}{2}$ antiferromagnetic chain $[CuPM(NO_3)_2(H_2O)_2]_n$ by ^{13}C-NMR

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Abstract

We present ^{13}C-NMR investigations of the $S = \frac{1}{2}$ antiferromagnetically coupled Heisenberg chain system $[CuPM(NO_3)_2(H_2O)_2]_n$, ($PM = C_4N_2H_4$ = pyrimidine). For this material, as result of the Dzyaloshinskii–Moriya interaction and an alternating g-tensor, the ground state is characterized by a giant static spin canting and an anisotropic magnetic field-induced spin excitation gap. We measured the spin–lattice relaxation rate $1/T_1$ at three inequivalent carbon sites in the pyrimidine molecule as function of temperature. From these studies we deduce the magnetic excitation spectrum of copper pyrimidine dinitrate at a constant applied magnetic field of 9.3 T. The experimental data are discussed in context with recent ESR investigations, which have been interpreted in terms of breather, soliton and multi-particle excitations based on the quantum sine-Gordon field theory.

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Quantum fluctuations, which are significantly enhanced in systems with reduced dimensionality, give rise to a variety of strongly correlated states and make low-dimensional magnets an ideal ground for testing various theoretical concepts [1,2]. A well-known example is the uniform $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain with a gapless continuum of spin excitations, since it is exactly solvable using the so-called Bethe ansatz equations [3,4].

For $S = \frac{1}{2}$ antiferromagnetic Heisenberg chains on low symmetry crystallographic lattices, such as copper pyrimidine dinitrate, $[CuPM(NO_3)_2{\cdot}(H_2O)_2]_n$ (CuPM), it has been demonstrated that the residual spin–orbit coupling fundamentally changes the magnetic properties. As a consequence, the Dzyaloshinskii–Moriya interaction D and an anisotropy of the g-tensor have to be taken into account [5,6]. These contributions lead to an effective staggered field h perpendicular to the external field H, with $h = \text{const}{\cdot}H$ resulting in an additional contribution to the susceptibility $\propto 1/T$, a giant spin canting, and an anisotropic magnetic field-induced spin gap $\Delta \propto H^{2/3}$ [6]. The gapped phase can be effectively described by the quantum sine-Gordon field theory and the excitation spectrum is represented by

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solitons, antisolitons and their bound states called breathers [5,7]. In fact, recent ESR investigations on CuPM identified signatures of three breather branches and a soliton, as well as several multi-particle excitation modes [8].

In this paper, we present the spin–lattice relaxation rate $1/T_1$ as a function of temperature on $[CuPM(NO_3)_2{\cdot}(H_2O)_2]_n$ at a constant external magnetic field of 9.3 T at three inequivalent carbon sites in the pyrimidine molecule. Four distinct spin excitation modes are extracted from a fit of the data using a superposition of various activation laws. Our results are discussed in context with recent ESR data from Ref. [8]. Concerning the four modes resolved in NMR we find very good agreement between the two experimental techniques.

Single crystals of $[CuPM(NO_3)_2{\cdot}(H_2O)_2]_n$ have been grown as described previously [6]. The Cu ions form uniformly spaced chains running parallel to the short *ac*-diagonal of the monoclinic crystal structure. The intrachain magnetic pathway is provided by the pyrimidine ring $C_4N_2H_4$, which connects two neighboring Cu ions as shown in Fig. 1. From a single crystal magnetization study a magnetic exchange parameter $J/k_B = 36.3(5)$ K along the chain is derived [6,9].

As is evident from the structure plot of PM, for a given field in the plane perpendicular to the molecule, i.e. in the *ac*-plane, the carbon sites C1, C2 and C3 are inequivalent, with additional hyperfine coupling to the nearest proton ($I = \frac{1}{2}$). In consequence, in a NMR study, we expect to observe three sets of double pairs of lines from the three inequivalent sites and the line splitting due to the hydrogen spin direction [10].

The NMR measurements were carried out using a home-built spectrometer in quadrature detection and a superconducting magnet operating at a constant field of 9.3 T. For the experiments the sample was oriented along the Cu chain direction and placed inside a teflon tube. Nuclear spin–lattice relaxation rates were measured by a progressive saturation method and an echo subsequence at the end using phase cycling to cancel parasitic ^{13}C signal from the teflon tube around the sample.

The spin–lattice relaxation rate $1/T_1$ as function of temperature is shown in Figs. 1 and 2. Here, each set of hyperfine doublets is represented by its averaged value for $1/T_1$. The spin–lattice relaxation rate can be expressed in terms of the imaginary part of the dynamical susceptibility as [11]

$$\frac{1}{T_1} = \frac{\gamma_n^2 k_B T}{2\mu_B^2} \sum_q A(q)^2 \frac{\chi''(q,\omega)}{\omega_n}, \tag{1}$$

where γ_n is the nuclear gyromagnetic ratio of ^{13}C and $A(q)$ is the q-dependent form factor. ω_n is the nuclear Larmor frequency. Direct spin excitation processes involving excitations from the ground state to the soliton and breather branches do not contribute to $1/T_1$ since the frequencies of such processes are much larger than the nuclear Larmor frequency ω_n. The only relevant relaxation channels in 1D spin-chain systems with a spin gap are those which are quasielastic and involve a scattering between two excited states. Taking into account only these processes [12] and following the quantum sine-Gordon model which predicts multiple spin excitation modes, the scattering process leads to a

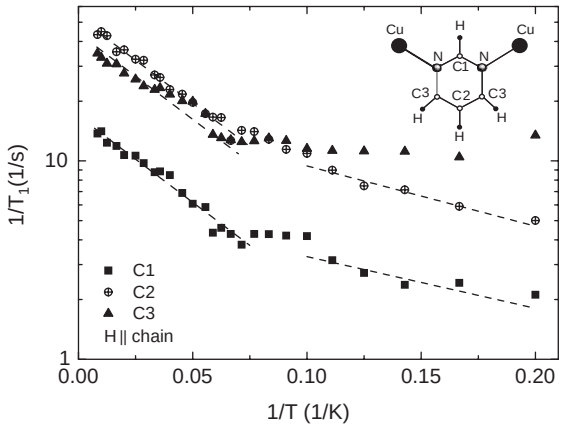

Fig. 1. Logarithmic plot of the spin–lattice relaxation rate $1/T_1$ against $1/T$ at the three inequivalent ^{13}C sites in CuPM with the external field $H \parallel$ to the Cu chains. Here, each dashed line indicates a single activated behavior. In the inset a schematic picture of the different carbon sites C1, C2 and C3 in the pyrimidine molecule is displayed.

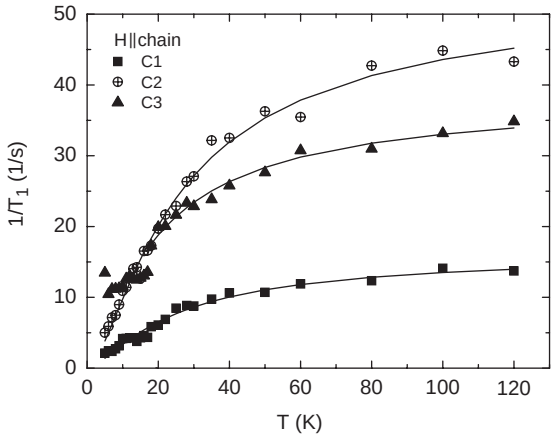

Fig. 2. The temperature dependent spin–lattice relaxation rate $1/T_1$ in $[CuPM(NO_3)_2(H_2O)_2]_n$ with the external field $H \parallel$ to the Cu chains. The solid lines are fits to Eq. (2) in (i) the whole temperature range $5\,K \leqslant T \leqslant 120\,K$ for C1 and C2 and (ii) $18\,K \leqslant T \leqslant 120\,K$ for site C3, respectively.