Magnetic behavior of a two-leg organic spin-ladder compound

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Zero-field and longitudinal field μ^+SR measurements as a function of temperature on $[(DT\text{-}TTF)_2][Au(mnt)_2]$ have confirmed that this compound is a molecular material with a two-leg spin-ladder configuration. The results corroborate the theoretical expectations for the absence of magnetic order in even-leg spin ladders with the quantum spin-liquid state realized, despite the somewhat strong ladder-ladder interactions present. Slowly fluctuating local fields are evident below 20 K and could originate from chain breaks. [S0163-1829(99)13729-9]

The magnetic properties of low dimensional [one- and two-dimensional (1D) and (2D)] quantum antiferromagnets have attracted a lot of interest both from the theoretical and the experimental point of view. The behavior of 1D strongly correlated systems and spin chains is by now relatively well understood.[1] This is not the case for 2D strongly correlated systems, in which many questions still remain. In view of this, spin-ladder systems, which consist of a finite number of strongly coupled chains are intermediate between 1D and 2D systems and their magnetic properties are of particular interest. Theoretical calculations[2–9] have predicted that spin ladders with an even number of legs have a ground state of correlated spin singlet pairs. The first excited state is separated from the singlet ground state by a spin gap energy of $\approx 0.5J$, where J is the intraladder antiferromagnetic coupling constant.[2,4,9] It has been also predicted that light hole doping of two-leg ladders can even lead to superconductivity due to the remaining spin gap. On the other hand, spin-ladder compounds with odd number of legs are in a magnetically ordered state because singlet pair formation on their rungs is not possible.[4]

Examples of families of compounds, which possess spin-ladder structures have been extremely rare. The first experimentally realized series of even- and odd-leg ladder structures was provided by the cuprates $Sr_{n-1}Cu_{n+1}O_{2n}$ ($n=3,5,...$).[10] μSR experiments revealed both the occurrence of static magnetic order below 52 K in $Sr_4Cu_6O_{10}$ (the three-leg ladder) and the absence of any magnetic order down to 25 mK in $Sr_2Cu_4O_6$ (the two-leg ladder),[11] in excellent agreement with the theoretical predictions. Another cuprate system, $LaCuO_{2.5}$ (Ref. 12) was also originally described in the literature as a two-leg spin ladder on the basis of the observed temperature dependence of the magnetic susceptibility. However, both μSR (Ref. 13) and NMR (Ref. 14) experiments later revealed the presence of static magnetic order below 125 K, despite the absence of an anomaly in the measured susceptibility at this temperature. This behavior was rationalized by Troyer *et al.*[15] who proposed a nearly critical ground state for $LaCuO_{2.5}$, as a result of the ladder-ladder interaction, J' being larger than the critical value, $J'_c \approx 0.11J$. In such a case, a quantum phase transition between the spin liquid and a magnetically ordered state occurs.

The family of potential spin-ladder compounds was recently enriched with the synthesis of the organic charge-transfer salt, $[(DT\text{-}TTF)_2][Au(mnt)_2]$ (DT-TTF =dithiophenetetrathiafulvalene, mnt=maleonitrile dithiolate).[16] At room temperature, the DT-TTF and $Au(mnt)_2$ molecules form regular stacks of donor DT-TTF and acceptor $Au(mnt)_2$ units along the monoclinic crystallographic b axis. The DT-TTF stacks are arranged in pairs related by a twofold screw axis and are isolated from each other by the $Au(mnt)_2$ stacks. Pairs of organic donor molecules are strongly linked by three interstack $S\ldots S$ close contacts, resulting in a structural two-leg ladder. Below 220 K, the DT-TTF stacks are dimerized giving rise to the two-leg spin ladder in which the $[(DT\text{-}TTF)_2^{+\cdot}]$ dimers are the spin carrying units. Magnetic measurements[16] revealed that the electronic static susceptibility shows a Curie-Weiss behavior at high temperatures and a thermally activated temperature dependence below 70 K. The susceptibility data were successfully fitted with the Troyer expression[7] for a two-leg spin ladder system with the energy gap, Δ in the spin-excitation spectrum found to be equal to 78 K.[16] The exchange interactions along the leg, $J_\parallel$ and along the rung, $J_\perp$ (Fig. 1) of the ladder were also extracted for this system, as -83 and -142 K, respectively. These values are qualitatively in agreement with the calculated transfer integrals, $t_\parallel = 36$ meV and $t_\perp = 21$ meV, once the dimeric nature of the spin carrier units of the spin ladder is taken into account.[16] The temperature dependence of the susceptibility was thus interpreted as providing clear evidence that $[(DT\text{-}TTF)_2][Au(mnt)_2]$ is the first purely organic system with a two-leg spin-ladder configuration. However, the calculated interladder transfer integral, $t' = 6$ meV (Ref. 16) implies that the ladder-ladder interactions, J' (Fig. 1) are quite

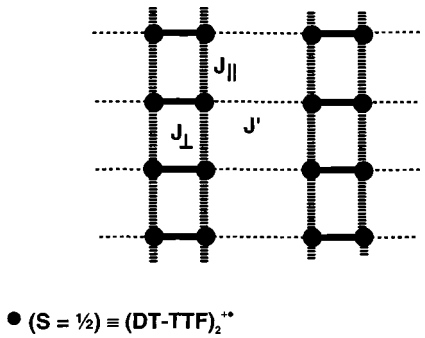

FIG. 1. Schematic representation of the spin-ladder structure in $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$, showing the intraladder couplings, $J_{\parallel}$ and $J_{\perp}$ together with the ladder-ladder interactions, J'.

sizeable and their effect on the nature of the low-temperature magnetic state of this compound needs to be explored.

In this paper, we employ the positive muon spin relaxation (μ^+SR) technique in its zero field (ZF) and longitudinal field (LF) variants in an attempt to authenticate the true magnetic ground state of $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$. The μ^+SR technique in its various forms has proven extremely powerful in the field of small-moment magnetism and, in all cases, when magnetic order is of random, very short range, spatially inhomogeneous or incommensurate nature.[17] It is also valuable for studying local-field fluctuations with a characteristic time window between 10^{-6} to 10^{-9} s, where other experimental techniques may be insensitive. In $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$, the μ^+SR results suggest that the electronic local fields remain dynamic on the μSR time scale down to 85 mK, in agreement with the proposed quantum spin-liquid state.

The $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$ sample used in the present work was synthesized by electrocrystallization from a CH_2Cl_2 solution containing the DT-TTF donor and the tetrabutylammonium salt of $[\text{Au(mnt)}_2]^-$ using H-shaped cells and Pt-wire electrodes. The crystalline material obtained from different batches was characterized by infrared, near-infrared, and electron-spin resonance spectroscopy and showed the same behavior, as reported before.[16] Powder x-ray-diffraction profiles of the whole sample (mass $=118$ mg) were in excellent agreement with that simulated from the single-crystal x-ray-diffraction data, confirming its high-quality single phase nature. Static magnetic susceptibility of the sample follows the same magnetic behavior previously reported.[16] Analysis of the susceptibility data in the temperature range 2–50 K shows the presence of ~2% of paramagnetic defects, resulting from crystalline defects and chain breaks that disrupt the ladder. We collected ZF and LF (10 to 1000 G) μ^+SR data on $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$ at the Paul Scherrer Institute (PSI), Villigen, Switzerland with the GPS (2–100 K) and the LTF (0.085–0.8 K) spectrometers using low-energy (surface) muons on the μ^+SR-dedicated $\pi M3$ beamline on the PSI 600 MeV proton accelerator. 100% spin-polarized positive muons (μ^+) are implanted into the solid sample and, after they come to rest at an interstitial site, they can act as highly sensitive microscopic local probes. In the presence of local magnetic fields, $\langle B_\mu \rangle$, they will precess with a frequency given by $\nu_\mu = (\gamma_\mu/2\pi)\langle B_\mu \rangle$, where $(\gamma_\mu/2\pi) = 13.55$ kHz G^{-1}. In the absence of an applied external field, the appearance of a precession signals the onset of an ordering transition. Moreover, application of a magnetic-field parallel to the initial μ^+ spin polarization (LF) allows the decoupling of the μ^+ spin from the static internal fields.

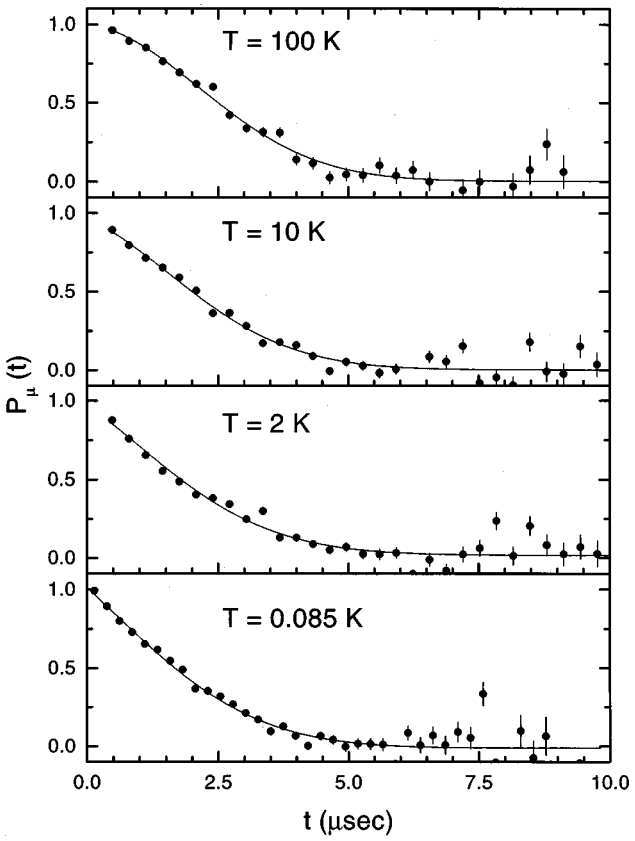

FIG. 2. The time evolution of the zero-field μ^+ spin polarization in $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$ at selected temperatures.

In Fig. 2, we show representative ZF time-dependent μ^+SR spectra of $[(\text{DT-TTF})_2][\text{Au(mnt)}_2]$ at various temperatures between 0.085 and 100 K. No oscillating signal is seen at any temperature. The μ^+SR spectra at 100 K were best fitted by the double-relaxation function:[18]

$$P_\mu(t) = A\exp(-\lambda t)\exp\left(-\frac{1}{2}\sigma^2 t^2\right), \tag{1}$$

where A is the magnitude of the asymmetry, and λ and σ are Lorentzian and Gaussian relaxation rates, respectively. The second Gaussian term with a relaxation rate, $\sigma = 0.44(1)\ \mu\text{s}^{-1}$ is characteristic of the presence of weak static nuclear dipole moments. This muon relaxation arises principally from the hydrogen nuclear moments, which appear frozen into a disordered spin configuration, producing an essentially temperature-independent distribution of local fields with a width, $\langle \Delta B^2 \rangle^{1/2} \approx 15$ G. In addition, the μ^+ spin is also relaxed by the rapidly fluctuating electron spins, which give rise to the $\exp(-\lambda t)$ component in Eq. (1) with $\lambda = 0.04(2)\ \mu\text{s}^{-1}$. Above 20 K, λ is temperature independent. This suggests that the relaxation at high temperatures is probably due to the exchange fluctuations of the ladder spins.

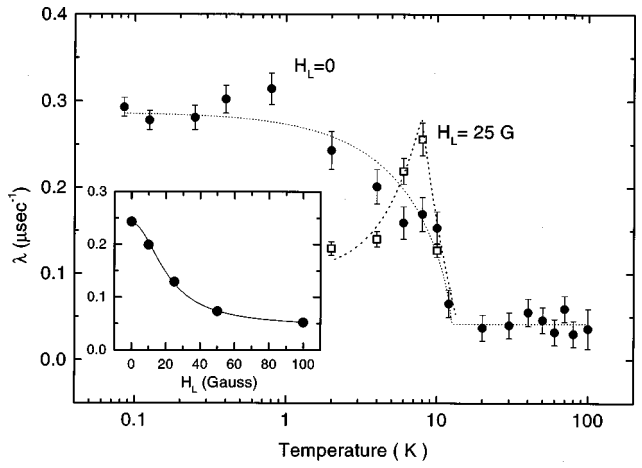

FIG. 3. Temperature dependence of the μ^+ spin depolarization rate, λ in zero-field ($H_L=0$ G, solid circles) and in a longitudinal field ($H_L=25$ G, open squares). The dotted lines are guides to the eye. The inset shows the field dependence of λ at 2 K. The solid line is a fit to Eq. (2).

We can estimate[19] the exchange fluctuation rate, $\nu=\sqrt{Z}k_BJ_{i,j}S/\hbar\approx10^{13}\,\mathrm{s}^{-1}$ with $Z=3$, $J_{i,j}=100$ K and $S=1/2$. This enables us to calculate the width of the random-field distribution in the narrowing limit with the expression, $\lambda=2\Delta^2/\nu$, to be $\Delta/\gamma_\mu\approx5$ kG.

The time-dependent μ^+SR spectra remained essentially unchanged down to 20 K. Below this temperature, their shape begins to change considerably (Fig. 2). We find that the double-relaxation function of Eq. (1) still describes the data well. However, while the Gaussian relaxation rate σ remains temperature independent, the $\exp(-\lambda t)$ part damps faster with decreasing temperature. The relaxation rate λ increases continuously below 20 K as T decreases, finally approaching a value of 0.29(1) μs^{-1} below 1 K (Fig. 3). The source of the observed relaxation can be either fluctuating and/or static internal fields. If the local fields would be static the value of the relaxation rate λ implies a distribution of local fields with a width, $\langle\Delta B^2\rangle^{1/2}\approx6.8(2)$ G at the muon site. On the other hand, if the local fields were still fluctuating, the observed increase in λ would signify a slowing down of the local-field fluctuations, as they now fall inside the μ^+SR time window.

In order to distinguish between the static and dynamic nature of the internal fields, we performed complementary longitudinal field (LF) μ^+SR experiments between 10 and 1000 G at a temperature of 2 K. These experiments allow the depolarization due to dynamic or fluctuating moments to be decoupled from that due to static components. In the case of static order, the effect of applied LF is to lead to a recovery of the asymmetry at long times. The typical longitudinal field which decouples the μ^+ spin relaxation in the static case is in the order of the field distribution width, Δ(~10 G) estimated from the ZF experiments above. On the other hand, if the μ^+ spin relaxation is of dynamic origin, the relaxation persists to longitudinal fields much larger than those suggested by the ZF relaxation rate. Fits of the μ^+SR spectra obtained with applied longitudinal fields, $H_L>50$ G, with the Kubo-Toyabe relaxation function appropriate for the static local field case, failed to describe the μ^+ spin polarization at

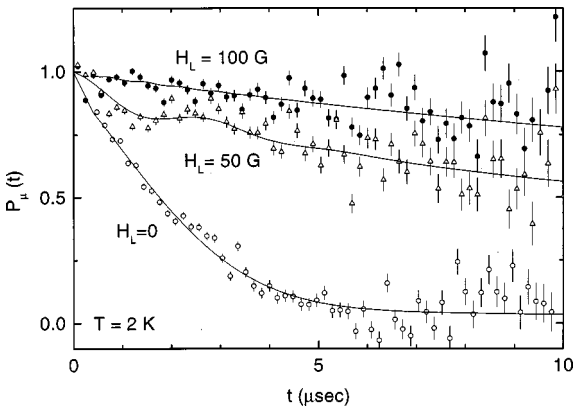

FIG. 4. The time evolution of the longitudinal field μ^+ spin polarization in $[(DT\text{-}TTF)_2][Au(mnt)_2]$ at 2 K and applied fields, $H_L=0$, 50, and 100 G.

longer times. Instead it was found that the electronic contribution still causes some slow relaxation, up to a longitudinal field of 100 G, as shown in Fig. 4. This observation suggests that the source of the observed relaxation is dynamic.

Further support for the fluctuating nature of the local fields experienced by the muons below 20 K in $[(DT\text{-}TTF)_2][Au(mnt)_2]$, comes from the field dependence of λ at $T=2$ K (Fig. 3 inset). When the μ^+ spin is exposed to randomly fluctuating local magnetic fields, the field dependence of the relaxation rate, $1/T_1$ is given by

$$\lambda=\frac{1}{T_1}=\gamma_\mu^2(\langle B_x^2\rangle+\langle B_y^2\rangle)\,\frac{\tau_c}{1+(\omega_L\tau_c)^2}. \qquad (2)$$

Here B_x and B_y are the fluctuating transverse field components, τ_c is the correlation time, and $\omega_L=\gamma_\mu H_L$ is the muon Larmor frequency. From the fit of the experimental data (Fig. 3 inset), we estimate the correlation time at 2 K to be $\tau_c=6(1)\times10^{-7}$ s. Equation (2) also predicts a maximum in λ when $\omega_L\tau_c=1$. The temperature dependence of λ in a longitudinal field, $H_L=25$ G indeed shows a maximum at $T=8$ K (Fig. 3). The correlation time at this temperature is $\tau_c=1/\omega_L=5\times10^{-7}$ s.

The indicated dynamic nature of the electronic local fields at the muon site has important consequences for the understanding of the low-temperature magnetic properties of $[(DT\text{-}TTF)_2][Au(mnt)_2]$. It confirms the spin-liquid nature of the magnetic ground state. Unlike $LaCuO_{2.5}$,[12–15,20] which becomes antiferromagnetic at low temperatures, the ladder-ladder interactions in the present sample, while sizeable, are not strong enough to destroy the spin-liquid ground state at low temperatures. The overall temperature and longitudinal field dependence of the relaxation rate, λ resembles those measured in other spin-liquid systems.[13,21] In these systems, the increase of λ at low temperatures was ascribed to unpaired spins, which originate from chain breaks. The presence of chain breaks in $[(DT\text{-}TTF)_2][Au(mnt)_2]$ is indeed quite pronounced, as evidenced by diffuse x-ray-scattering experiments, and limits the effective length of the ladders to about 40 rungs on average (~150 Å).[16] The presence of chain breaks is also evident in the susceptibility measurements, in which a Curie tail appears below 14 K. The ex-

tracted magnitude of the correlation time, τ_c also favors the defect origin of the local-field fluctuations, as it is much too long to be associated with the fluctuation rate of the triplet excitations. On the other hand, it is comparable with the fluctuation rate found in the Haldane system, $(Y_{2-x}Ca_x)Ba(Ni_{1-y}Mg_y)O_5$.[21]

In conclusion, the present ZF and LF μ^+SR measurements on the $[(DT\text{-}TTF)_2][Au(mnt)_2]$ microcrystalline sample identify it as the first two-leg organic spin-ladder compound. No static magnetic order appears down to the lowest temperature of the present experiment (85 mK) with the slow relaxation observed below 20 K in the ZF experiments being principally of dynamic nature and most likely associated with chain breaks, present in the ladders of the investigated sample.

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