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Low-Temperature Spin Diffusion in a Highly Ideal $S = \frac{1}{2}$ Heisenberg Antiferromagnetic Chain Studied by Muon Spin Relaxation

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The organic radical-ion salt DEOCC-$TCNQF_4$ contains linear chains of stacked molecules with significant Heisenberg antiferromagnet interactions along the chain and extremely weak interactions between the chains. Zero-field μSR has confirmed the absence of long-range magnetic order down to 20 mK and field-dependent μSR is found to be consistent with diffusive motion of the spin excitations. The anisotropic spin dynamics and the upper boundary for magnetic ordering temperature both indicate interchain magnetic coupling $|J'| < 7$ mK. As the intrachain coupling J is 110 K, $|J'/J|$ is significantly less than 10^{-4}. This system therefore provides one of the most ideal examples of the one-dimensional $S = 1/2$ Heisenberg antiferromagnet yet discovered.

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One-dimensional $S = 1/2$ Heisenberg antiferromagnets (1DHAF) described by the Hamiltonian

$$H = J\sum_i \mathbf{S}_i \cdot \mathbf{S}_{i+1} \tag{1}$$

have attracted much interest, both theoretically and experimentally, as examples of a simple but nontrivial class of model magnetic system in which fluctuations associated with quantum criticality provide the dominant feature [1,2]. Usually real systems only follow ideal 1DHAF behavior down to some minimum temperature, below which additional weak interactions produce a new ground state, e.g., finite interchain coupling leading to long-range magnetic order (LRMO) [3,4].

One way to minimize interchain couplings and suppress LRMO is to arrange to have bulky spacers between the magnetic chains. Following this approach a molecular ion-radical salt was prepared in which the large donor diethyloxacarbocyanine (DEOCC) and the acceptor tetrafluorotetracyanoquinodimethane ($TCNQF_4$) were combined to give DEOCC-$TCNQF_4$ [5]. In this salt the planar molecules are stacked separately along the a axis forming segregated columns and it was found to behave as an $S = 1/2$ 1DHAF with $J/2 = 55$ K [5]. No LRMO was found down to 1.1 K and logarithmic behavior of the low-temperature susceptibility was observed [5], following predictions for the $S = 1/2$ 1DHAF [6]. Here we describe muon studies that demonstrate the absence of static LRMO down to $T = 20$ mK, thus extending the T range over which theoretical predictions for the 1DHAF system may be tested down to $0.0002J$. From probing the spin dynamics at low T we find that diffusive spin transport is dominant at T down to at least $0.004J$, with no significant ballistic contribution.

Muon-spin relaxation (μSR) measurements [7] were carried out using the LTF instrument at the SμS, Paul Scherrer Institute, Switzerland and using the EMU and ARGUS instruments at the ISIS Facility, Rutherford Appleton Laboratory, UK. In these experiments a spin polarized muon beam was implanted into the polycrystalline sample, cooled by one of several cryostats: a 20 mK dilution refrigerator (LTF), a 300 mK ^{3}He cryostat (EMU), and a helium flow cryostat (ARGUS).

For quantitative analysis of the muon data it is important to have an idea of the nature and location of the muon probe states. When a muon first thermalizes in a sample it either remains as a free μ^+ or else captures an electron to form muonium (Mu). In the case of DEOCC-$TCNQF_4$ a μ^+ will be attracted to the $TCNQF_4{}^-$, forming a muoniated molecular radical state. The resulting reaction is equivalent to the addition of muonium to a neutral $TCNQF_4$ and the associated scalar and dipolar hyperfine parameters A and D can be measured using muon level-crossing-resonance spectroscopy on the muoniated radical formed in the neutral molecule. The values $A = 60$ MHz and $D = 9$ MHz were obtained in this way for $TCNQF_4$ in the region below 8 K [8]. These values are slightly smaller than those of TCNQ ($A = 82$ MHz, $D = 10$ MHz [9]). In the case of muonium addition to $TCNQF_4{}^-$, a local spin singlet is expected. This will weaken the exchange coupling along the chain at this point and also weaken the coupling of the muon to 1DHAF spins, as there is now only weak dipolar coupling to the next neighbor spins. Some muonium addition to the $DEOCC^+$ molecule may also occur, but these states would only couple very weakly to the 1DHAF spins. Hence we expect that the relaxation contribution from the molecular $\mu^+TCNQF_4{}^-$ state will be the most sensitive probe of the 1DHAF spin dynamics.

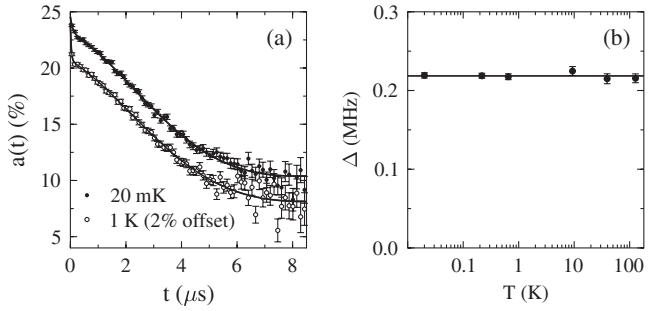

FIG. 1. (a) Zero-field muon-spin relaxation for DEOCC-$TCNQF_4$ at 20 mK and 1 K. (b) The T dependence of Δ.

In order to check for the possibility of a transition to LRMO at low T, a zero-field study was carried out using the LTF dilution refrigerator. The μSR relaxation measured in this way for DEOCC-$TCNQF_4$ at the 20 mK base temperature and at 1 K are shown in Fig. 1(a). The data are almost identical between 20 mK and 1.0 K. Since no precession signal or drop of asymmetry appears at low T, it is concluded that there is no LRMO down to 20 mK in this salt.

The main relaxation signal from the sample was fitted to the function:

$$a(t) = a_0 G_z^{\mathrm{KT}}(\Delta, B) e^{-\lambda t}, \tag{2}$$

where $G_z^{\mathrm{KT}}(\Delta, B)$ is the Kubo-Toyabe relaxation function [10]. The fitted value $\Delta = 0.22$ MHz is consistent with relaxation in the local field distribution from nuclei surrounding the muon site. Figure 1(b) shows the T dependence of Δ, showing little variation from 20 mK to above 100 K. The predominant Kubo-Toyabe relaxation is evidence of an environment that is effectively diamagnetic for the majority of the muons stopping in the sample and is a signature that there is no static magnetic order in the sample, even down to 20 mK. The contribution from the electronic moments on the $TCNQF_4$ is reflected in λ and is small compared to the nuclear moments because the electronic moments are rapidly fluctuating at all T, leading to a motionally narrowed contribution to the muon-spin relaxation.

The nuclear dipole fields at the muon site are $\sim$1 mT, whereas the electronic fields will be orders of magnitude larger. By applying longitudinal fields $B > 1$ mT it is possible to quench the nuclear contribution to the relaxation and thus focus on the residual electronic contribution. The T dependence of λ has been measured at $B = 3$ mT and low T data are shown in Fig. 2(a). As a local probe, the muon is not selective for the wave vector q of the spin excitations and can respond to the full spectrum [Fig. 2(b)]. Excitations close to $q = 0$ produce a contribution to λ with first linear [11,12] and then quadratic [12] T behavior. Excitations close to $q = \pi/a$ produce essentially T-independent λ, but low T corrections to the theory of spin correlations for the $S = 1/2$ 1DHAF lead to a rise in λ

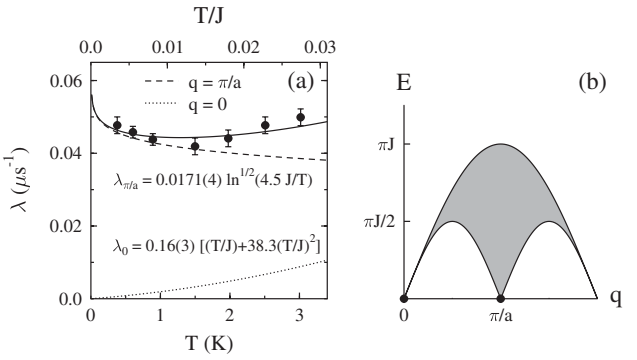

FIG. 2. (a) T dependence of λ at 3 mT with contributions from $q = \pi/a$ [13] and $q = 0$ [12]. (b) The spin excitation spectrum contributing to λ [11,26].

at small T/J, following $\ln^{1/2}(\Lambda/T)$, where $\Lambda \sim 4.5J$ [11,13]. This effect was previously observed experimentally in NMR studies of Sr_2CuO_3 [14]. Figure 2(a) shows that the μSR data can be represented by a sum of $q = 0$ and $q = \pi/a$ terms, with the relaxation in this T range being dominated by the $q = \pi/a$ contribution.

One key question about the spin excitations in the ideal $S = 1/2$ 1DHAF is whether they propagate diffusively or ballistically. Fluctuations at $q = 0$ are expected to be diffusive at higher temperatures and ballistic in the low T limit, whereas fluctuations at $q = \pi/a$ are diffusive, but ballistic as q moves away from this point [11]. Previous ^{63}Cu NMR studies on the 1DHAF system Sr_2CuO_3, however, suggested that the behavior of the $q = \pi/a$ mode is ballistic [14]. Field-dependent studies can be used to distinguish between these types of spin transport, since their spin autocorrelation functions have different associated spectral densities $f(\omega)$: $f(\omega) \sim \omega^{-1/2}$ for 1D diffusion and $f(\omega) \sim \ln(J/\omega)$ for ballistic motion.

To gain more information about the spin dynamics we studied the B dependence of λ. Figure 3 shows data at 1 K. The B dependence for ballistic transport (Fig. 3, dotted

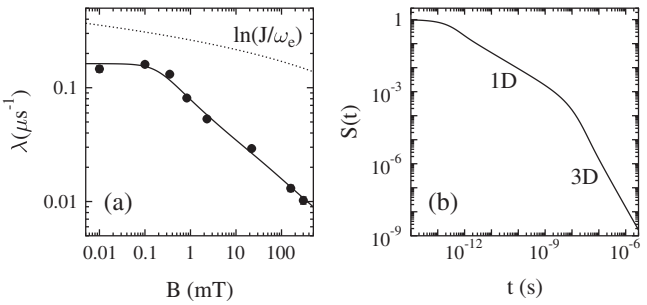

FIG. 3. (a) B dependence of λ at 1 K. The dotted line illustrates the behavior expected for ballistic spin transport. The solid line is a fit to the anisotropic spin diffusion model (4). (b) The form of the spin correlation function $S(t)$ that is consistent with the data. Crossover between 1D and 3D diffusion takes place for time scales longer than $\sim$10 ns.

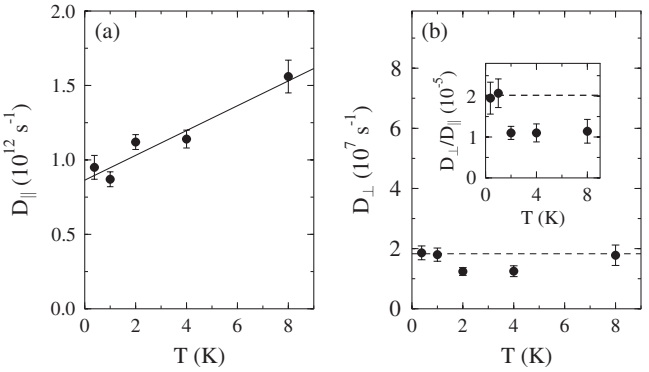

FIG. 4. Anisotropic spin diffusion parameters derived from the B dependence of λ. (a) The on-chain spin diffusion rate with linear fit and (b) the interchain diffusion rate. The inset shows the diffusion rate anisotropy. Dashed lines indicate average parameter values measured for the region below 2 K.

line) is clearly a poor description of the data. The data above ~0.2 mT are fitted well by the power law $\lambda \propto B^{-n}$ with $n = 0.350(7)$. Although n is a little lower than the ideal value 0.5, it is still broadly consistent with a 1D diffusive picture of the spin fluctuations. A frequency domain power law ω^{-n} corresponds to a power law t^{-m} for the spin autocorrelation function, where $m = 1 - n$. Thus our data gives $m = 0.650(7)$, which is comparable with values obtained from exact diagonalization of finite quantum chains ($m = 0.705$ [15]) and from classical simulation of large chains [$m = 0.609(5)$ [16]].

The presence of a low B cutoff to the power law dependence of λ allows an estimate of the anisotropy of the spin diffusion to be made [17]. For a static hyperfine-coupled spin 1/2 probe such as a muon in the presence of anisotropic electronic spin diffusion, λ follows [18]

$$\lambda(B) = 1/20[3D^2 f(\omega_\mu) + (5A^2 + 7D^2) f(\omega_e)], \quad (3)$$

where $\omega_\mu = \gamma_\mu B$ and $\omega_e = \gamma_e B$; A and D are the scalar and dipolar hyperfine coupling parameters; and $f(\omega)$ is the spectral density. In our case $A^2 \gg D^2$ and the term $(A^2/4) f(\omega_e)$ in (3) dominates $\lambda(B)$. For anisotropic spin diffusion, $f(\omega)$ can be expressed in terms of fast on-chain and slow interchain diffusion rates $D_\parallel$ and $D_\perp$ as

$$f(\omega) = \frac{1}{\sqrt{2D_\parallel D_\perp}} \left(\frac{1 + \sqrt{1 + (\omega/2D_\perp)^2}}{2[1 + (\omega/2D_\perp)^2]} \right)^n. \quad (4)$$

This shows a transition from a constant low frequency value $(2D_\parallel D_\perp)^{-1/2}$ to a power law behavior above a crossover frequency proportional to $D_\perp$ [19,20]. When $n = 0.5$ the ideal 1D power law $(2D_\parallel \omega)^{-1/2}$ is obtained. Using the reduced value $n = 0.349$ ensures that the high B behavior of (4) matches that determined experimentally. The corresponding spin correlation function $S(t)$ is illustrated in Fig. 3(b), showing the crossover from 1D to 3D diffusion at longer times.

Spin diffusion rates obtained in this way for several temperatures between 0.38 and 8 K are plotted in Fig. 4. It is found that $D_\parallel$ shows a linear increase with T [Fig. 4(a)]. At low T the intrachain intersite diffusion time $D_\parallel^{-1} \sim 1$ ps, which can be compared with the classical spin diffusion time $(2/\pi)^{1/2}/J$ or the spinon intersite transit time $(2/\pi)/J$, which are both around 0.3 ps. The interchain rate $D_\perp$ shows little T dependence and is smaller than $D_\parallel$ by a factor of 5×10^4 at 1 K and below. The anisotropy ratio $D_\perp/D_\parallel$ is shown in the inset to Fig. 4(b).

Since diffusion rates and exchange couplings are directly proportional, the diffusion rate anisotropy $D_\perp/D_\parallel$ gives a direct measure of the magnetic coupling anisotropy $|J'/J|$. At low T we obtain $|J'/J| = 2.0(3) \times 10^{-5}$ and $|J'| = 2.2(3)$ mK. An alternative estimate of $|J'/J|$ can be provided by the observation that no LRMO appears above 20 mK. In recent Monte Carlo studies of the relation between T_N and $|J'|$, Yasuda *et al.* [21] found an empirical relation between these parameters. This can be used to estimate an upper limit for $|J'|$ from our experimental upper limit for T_N. From this we obtain $|J'| < 7$ mK and hence $|J'/J| < 6 \times 10^{-5}$, which is also consistent with our estimate from the spin diffusion.

As the expected size of any ordered moment is $1.017|J'/J|^{1/2}$ [22], a reduced moment of 10^{-2} would result if there was a transition to LRMO in the 20 mK region. When scaled by A, this translates into a muon precession frequency of 0.6 MHz, which would have

TABLE I. Experimental magnetic parameters for DEOCC-TCNQF$_4$ compared with theoretical estimates. The T_N estimate is obtained from the experimental $|J'/J|$ estimate. The upper limit estimate for $|J'|$ is obtained from the experimental upper limit for T_N. For comparison, parameters are also shown for the 1DHAF Cu chain systems Sr_2CuO_3 [23,24], copper pyrazine dinitrate (CuPzN) [3] and $KCuF_3$ [25].

	T_N (mK)	$\|J'\|$ (mK)	J (K)	T_N/J (10^{-2})	$\|J'/J\|$ (10^{-3})
Experiment	<20	2.2	110	<0.018	0.020
Estimate	7	<7		0.006	<0.06
Sr_2CuO_3	5.4 K	2 K	2200	0.25	0.93
CuPzN	107	46	10.3	1.0	4.4
$KCuF_3$	39 K	21 K	406	9.6	52

been easily observable if such a transition were present in our experimental T range. Taking the $|J/J'|$ estimate from the spin diffusion and using the Yasuda relation for T_N/J' [21] gives an estimate of 7 mK for T_N, which is below the region accessible at current μSR facilities.

The low value $|J'| = 2.2$ mK obtained from the spin dynamics is suggestive of dipolar coupling and calculation of the interchain dipolar coupling energy from the crystal structure gives a ferromagnetic coupling of 2.0 mK, in excellent agreement with $|J'|$ obtained from the spin dynamics. The measured and estimated parameters for DEOCC-TCNQF$_4$ are summarized in Table I, along with those of some other benchmark 1DHAF systems.

In conclusion, the molecular ion-radical salt DEOCC-TCNQF$_4$ has been demonstrated to be an almost perfect example of an $S = 1/2$ 1DHAF. As the anisotropy ratio $|J'/J|$ in this material is below 10^{-4} and approaching 10^{-5}, it is significantly closer to the ideal case than the ratios of other well-studied 1DHAF systems such as $KCuF_3$ and Sr_2CuO_3. This system should therefore prove valuable for further testing of 1DHAF theory.

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