Spin dynamics in the organic spin - Peierls system $MEM(TCNQ)_2$ studied using muon-spin relaxation

1997 J. Phys.: Condens. Matter 9 L119

(http://iopscience.iop.org/0953-8984/9/9/002)

J. Phys.: Condens. Matter **9** (1997) L119–L124. Printed in the UK PII: S0953-8984(97)80800-4

LETTER TO THE EDITOR

Spin dynamics in the organic spin–Peierls system $MEM(TCNQ)_2$ studied using muon-spin relaxation

S J Blundell†, F L Pratt†, P A Pattenden†, M Kurmoo‡, K H Chow†, S Takagi§, Th Jestädt† and W Hayes†

† University of Oxford, Department of Physics, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK

‡ IPCMS, 23, rue du Loess, BP 20/CR, 67037 Strasbourg, France

§ Department of Physics, Kyushu Institute of Technology, Tobata, Kitakyushu 804, Japan

Received 9 January 1997

Abstract. We report the first muon-spin relaxation study of an organic spin–Peierls system, the linear-chain compound $MEM(TCNQ)_2$. Our results show a crossover from a Gaussian relaxation to an exponential relaxation as the temperature is lowered below the spin–Peierls transition. We associate this behaviour with the slowing down of the electronic fluctuations resulting from the opening of a gap in the magnetic excitation spectrum.

The spin–Peierls transition is an intrinsic lattice instability in spin-$\frac{1}{2}$ antiferromagnetic Heisenberg chains; the driving force is the magnetoelastic coupling between the one-dimensional electronic structure and the three-dimensional lattice vibrations [1]. Above the transition temperature T_{SP}, there is a uniform antiferromagnetic next-neighbour exchange in each chain; below T_{SP} there is an elastic distortion resulting in dimerization, and hence two, unequal alternating exchange constants. The dimerization increases progressively as the temperature is lowered and reaches a maximum at zero temperature. The alternating chain possesses an energy gap between the singlet ground state and the lowest lying band of triplet excited states. The magnitude of the gap is related to the degree of dimerization and hence to the degree of lattice distortion, becoming zero for the uniform chain (zero dimerization). Thus the magnetic susceptibility $\chi(T)$ shows a knee at T_{SP}, with a rather abrupt fall of χ below T_{SP}, corresponding to the opening of the gap. Whereas the normal Peierls distortion (the electronic analogue of the spin–Peierls transition) occurs at a temperature T_P of the order of $k_B T_P \sim E_F \exp(-1/\lambda)$, where λ is the electron–phonon coupling constant, the spin–Peierls transition will occur at $k_B T_{SP} \sim |J| \exp(-1/\lambda)$, where J is the exchange interaction between adjacent spins; since $J \ll E_F$ (e.g. J is typically 50 K, E_F is typically 500–5000 K), T_{SP} is always small in comparison with T_P.

There are only very few materials which show a spin–Peierls transition. This is because antiferromagnetic chains usually form three-dimensional order at low temperature due to interchain coupling. Only in very few materials is the spin–phonon coupling able to dominate the interchain spin–spin coupling and allow the formation of a spin–Peierls ground state. Examples of such materials are mainly organic systems, e.g. $MEM(TCNQ)_2$ (T_{SP} = 18 K) [2], TTF-$CuS_4C_4(CF_3)_4$ (T_{SP} = 12 K) [3], TTF-$AuS_4C_4(CF_3)_4$ (T_{SP} = 2 K) [3, 4], α'-$(ET)_2Ag(CN)_2$ (T_{SP} = 7 K) [5, 6, 7], $(BCPTTF)_2X$ with X = PF_6,AsF_6 (T_{SP} =36 K, 32.5 K) [8, 9]. This is because such materials contain flat organic molecules in columnar stacks. The large interchain separation and weak van der Waals intermolecular interactions

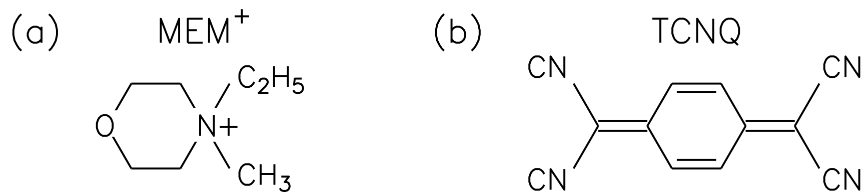

Figure 1. Molecular structure of (a) MEM^+ and (b) TCNQ.

favour the dominance of magnetoelastic effects over interchain ordering. In contrast the chains in corresponding inorganic materials, such as copper chain compounds, are quite rigid due to the ionic bonding and only a single example of an inorganic spin–Peierls material is known ($CuGeO_3$, with $T_{SP} = 14$ K [10]).

In this letter we report the results of the first muon-spin relaxation (μSR) study of an *organic* spin–Peierls system, the linear chain compound methyl-ethyl-morpholinium-(tetracyanoquinodimethanide)$_2$ (MEM(TCNQ)$_2$). The molecular structures of the molecules MEM and TCNQ are shown in figure 1. The planar TCNQ molecules stack face-to-face to form one-dimensional chains. These chains are uniform above 335 K and the material is metallic, but a dimerization of the chains occurs at this temperature below which the conductivity decreases by a factor of $\sim 10^4$ [2] (this transition is a conventional electronic Peierls transition). A further distortion occurs at 18 K [11], leading to a tetramerized structure (representing a further dimerization of the dimer units, see figure 1 of [11]), which is accompanied by a drop in χ, the electron spin susceptibility, and also the Knight shift, together with an anomaly in the specific heat; all of these agree well with expected behaviour for a spin–Peierls system [2].

In figure 2(a) we show the measured magnetic susceptibility of our sample of MEM(TCNQ)$_2$ which clearly shows the spin–Peierls transition at $\sim$18 K. The high-temperature ($T > T_{SP}$) behaviour closely follows a Bonner–Fisher expression (with the fitted $J/k_B = 46$ K), as expected for a uniform antiferromagnetic chain [12]. χ drops suddenly below T_{SP}, consistent with the opening of a singlet–triplet gap. The result is in agreement with previous measurements [2].

Zero- and longitudinal-field μSR measurements were carried out at ISIS (Rutherford Appleton Laboratory, UK) and also at PSI (Switzerland). Spin-polarized positive muons were implanted in the sample of MEM(TCNQ)$_2$ (mounted on a silver backing plate and cooled in a He^4 cryostat) and the depolarization of the muon spin was measured by monitoring the time-dependence of the angle-dependent decay positron emission (this occurs predominantly along the instantaneous direction of the muon spin). For the zero-field measurements the earth's magnetic field was compensated to less than 10 μT. The data are conventionally presented by comparing the positron counts in the forward and backward detectors and forming an asymmetry function $G_z(t)$, a quantity which is then proportional to the time-evolution of the muon-spin polarization [13]. We note that μSR has been used extensively to study subtle magnetic properties in a wide range of materials [14]. The main results of our μSR study are shown in figure 2(b)–(d) which illustrate the temperature dependence of parameters extracted from fitting the μSR data. These will be discussed in detail below.

In figure 3 we show zero-field μSR data for two temperatures, one well below and the other well above T_{SP}. Below the transition the relaxation of the muon depolarization is well fitted by an exponential, while above the transition the relaxation is Gaussian. We can

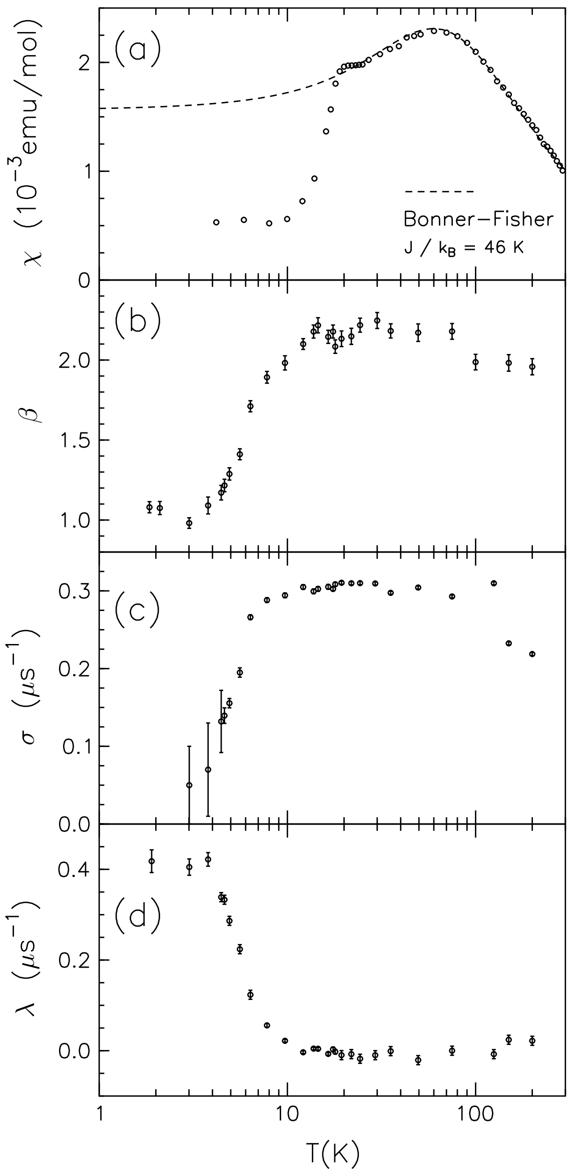

Figure 2. (a) Magnetic susceptibility of MEM-(TCNQ)$_2$. The dashed line at high temperatures is a fit of the data above 20 K to the Bonner–Fisher expression assuming $J/k_B = 46$ K. (b) The temperature dependence of the parameter β which is extracted from fitting the μSR data using equation (1). $\beta = 2$ corresponds to a Gaussian relaxation, $\beta = 1$ to an exponential relaxation. Using an alternative fitting form (equation (2)) yields the temperature dependence of (c) the Gaussian relaxation rate and (d) the exponential relaxation rate.

follow this crossover in relaxation form by fitting our data over the complete temperature range using a variable lineshape

$$G_z(t) = A_S e^{-(\alpha t)^\beta} + A_{Ag} \quad (1)$$

where α is a temperature-dependent relaxation rate (not shown) and A_S and A_{Ag} are

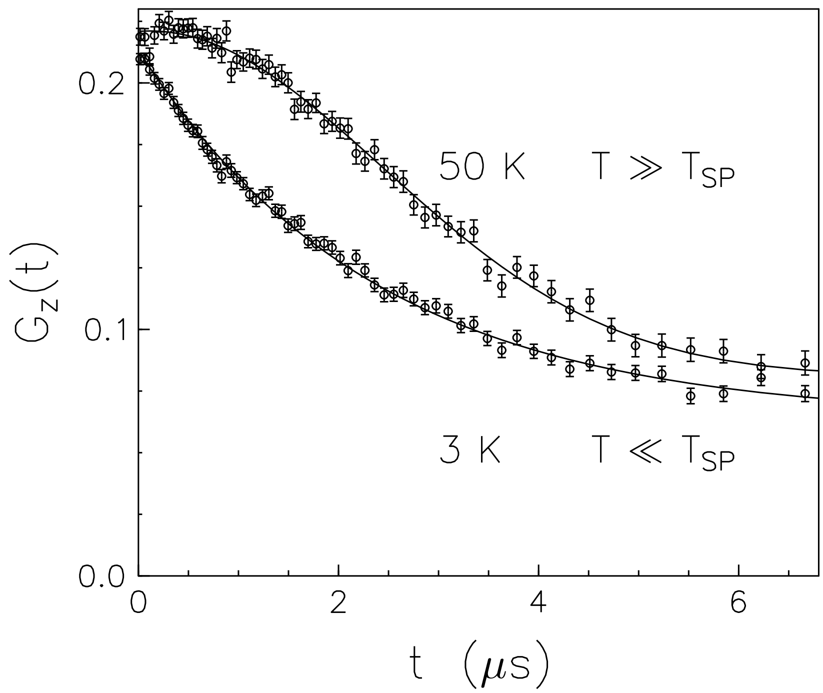

Figure 3. The decay positron asymmetry $G_z(t)$ as a function of time for MEM-(TCNQ)$_2$ at 50 K (a temperature well above T_{SP}) and 3 K (a temperature well below T_{SP}). The data are well fitted by Gaussian and exponential forms respectively.

temperature-independent amplitudes reflecting the relative fraction of muons stopping in the sample (A_S) and in the silver backing plate (A_{Ag}). Hence $\beta \sim 2$ corresponds to a Gaussian relaxation, $\beta \sim 1$ corresponds to an exponential relaxation. The temperature dependence of our fitted values of β is shown in figure 2(b) and indicates that the crossover happens between 4 and 15 K, which is somewhat below T_{SP}.

There are two mechanisms which contribute to the muon relaxation in our sample, corresponding to the effect of (1) the neighbouring nuclear spins and (2) the fluctuating electronic spins. We can model this by fitting the muon data by using the functional form

$$G_z(t) = A_S e^{-\lambda t} e^{-(\sigma t)^2} + A_{Ag} \qquad (2)$$

where the Gaussian relaxation arises from the random fields from surrounding nuclear dipoles (static over the muon lifetime) and the exponential relaxation is ascribed to the effect of the fluctuating electronic moments. This expression assumes that the nuclear and electronic sources of relaxation are uncorrelated. Equation (2) fits the data well over the entire temperature range studied (A_S and A_{Ag} are kept fixed) so that σ and λ are the only two adjustable parameters. Their temperature dependences are shown in figure 2(c) and 2(d).

Above the spin–Peierls transition we find $\lambda \sim 0$ and $\sigma \sim 0.3\ \mu s^{-1}$. The functional form of the relaxation and the observation that it is quenched in a longitudinal field of a few tens of Gauss suggest that the relaxation is due to randomly oriented quasistatic nuclear spins. The result $\lambda \sim 0$ in this temperature range indicates that the electronic spins are likely to be fluctuating extremely rapidly (motional narrowing limit).

Below the spin–Peierls transition dimerization occurs and the electronic spins begin to freeze out into spin–singlet pairs. We find in this case that the relaxation is predominantly exponential and our fitted value of σ decreases sharply (though at the lowest temperatures it is difficult to determine reliably) while λ increases up to $\sim$0.4 μs^{-1}. The relaxation can be decoupled in a field of 50–100 G. The opening up of the gap in the magnetic excitation spectrum at T_{SP} is expected to have a dramatic effect on the spin dynamics. In NMR experiments on spin–Peierls systems a sharp decrease in T_1^{-1} is found just below T_{SP} since the main relaxation mechanism of the nuclear spin is being destroyed [15, 16]. In contrast, we find an *increasing* relaxation rate below T_{SP}. This difference may reflect the differing time windows of the two probes. For the muon case we observe a crossover from a regime in which the fluctuations are so fast that the relaxation is very weak (motionally narrowed limit) to a regime in which the correlation time of the electronic fluctuations is slow enough that it falls into the μSR time window; thus the relaxation rate increases as the electronic fluctuation rate decreases, but the crossover to exponential relaxation only happens when the fluctuation rate is slow enough; hence the crossover is observed at a temperature somewhat lower than T_{SP}.

In general we expect that thermally activated excitations across the magnetic gap are responsible for the relaxation [15, 17]. We associate the slowing down of the electronic spin-fluctuations with the opening of the gap in the magnetic excitation spectrum. As the temperature decreases, and the gap widens, the fluctuations are progressively suppressed. Thus in contrast with NMR experiments which usually focus on the very fast fluctuations for $T > T_{SP}$, we have observed the slower fluctuations which occur in the spin–Peierls state. An interesting feature of the data is the apparent saturation in the relaxation rate λ at the lowest temperatures measured (see figure 2(d)). If the gap in this region were fully open one would expect λ to begin to fall with decreasing temperature, but this is not observed. This saturation effect is not understood at present; it may be that the muon spin itself may perturb its local environment so as to break up and interact with nearby singlet pairs, causing some residual relaxation.

Although this is the first μSR study of an organic spin–Peierls, system there have been several investigations concerning the inorganic spin–Peierls material $CuGeO_3$ [18, 19, 20]. A similar crossover from Gaussian to exponential relaxation was observed in zero-field [19, 20] and transverse-field [18] experiments where a similar slowing-down of fluctuations was assumed. Our work shows that this effect in the muon-spin relaxation may not therefore be peculiar to $CuGeO_3$ but could be a general characteristic of spin–Peierls systems.

We are grateful to P J C King (ISIS), U Zimmermann (PSI) and R Poinsot (IPCMS) for technical assistance. We would like to thank Merton College (SJB), NSERC Canada (KHC) and EPSRC for support.

References

[1] Bray J W, Interrante L V, Jacobs I S and Bonner J C 1983 *Extended Linear Chain Compounds* vol 3 (New York: Plenum) p 353
[2] Huizinga S, Kommandeur J, Sawatzky G A, Thole B T, Kopinga K, de Jonge W J M and Roos J 1979 *Phys. Rev.* B **19** 4723
[3] Bray J W, Hart H R, Interrante L V, Jacobs I S, Kasper J S, Watkins G D, Wee S H and Bonner J C 1975 *Phys. Rev. Lett.* **35** 744
[4] Jacobs I S, Bray J W, Hart H R, Interrante L V, Kasper J S, Watkins G D, Prober D E and Bonner J C 1976 *Phys. Rev.* B **14** 3036
[5] Obertelli S D, Friend R H, Talham D R, Kurmoo M and Day P 1989 *J. Phys.: Condens. Matter* **1** 5671
[6] Parker I D, Friend R H, Kurmoo M and Day P 1989 *J. Phys.: Condens. Matter* **1** 5681

[7] Kurmoo M, Green M A, Day P, Bellitto C, Staulo G, Pratt F L and Hayes W 1993 *Synth. Met.* **55–57** 2380
[8] Ducasse L, Coulon C, Chasseau D, Yagbasan R, Fabre J M and Gouasmia A K 1988 *Synth. Met.* **27** B543
[9] Liu Q, Ravy S, Pouget J P, Coulon C and Bourbonnais C 1993 *Synth. Met.* **55–57** 1840
[10] Hase M, Terasaki I and Uchinokura K 1993 *Phys. Rev. Lett.* **70** 3651
[11] van Bodegom B, Larson B C and Mook H A 1981 *Phys. Rev.* B **24** 1520
[12] Bonner J C and Fisher M E 1964 *Phys. Rev.* **135** A640
[13] Cox S F J 1987 *J. Phys. C: Solid State Phys.* **20** 3187
[14] Schenck A and Gygax F N 1995 *Handbook of Magnetic Materials* vol 9 ed K H J Buschow (Oxford: Elsevier)
[15] Smith L S, Ehrenfreund E, Heeger A J, Interrante L V, Bray J W, Hart H R and Jacobs I S 1976 *Solid State Commun.* **19** 377
[16] Itoh M, Hirashima S and Motoya K 1995 *Phys. Rev.* B **52** 3410
[17] Ehrenfreund E and Smith L S 1977 *Phys. Rev.* B **16** 1870
[18] Lappas A, Prassides K, Amato A, Feyerherm R, Gygax F N and Schenck A 1994 *Z. Phys. B* **96** 223
[19] García-Muñoz J L, Suaadi M and Martínez B 1995 *Phys. Rev.* B **52** 4288
[20] Tchernyshyov O, Blaer A S, Keren A, Kojima K, Luke G M, Wu W D, Uemura Y J, Hase M, Uchinokura K, Ajiro Y, Asano T and Mekata M 1995 *J. Magn. Magn. Mater.* **140–144** 1687