ELSEVIER

Synthetic Metals 135–136 (2003) 649–650

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Evidence for spin solitons in spin-Peierls system $(DMe\text{-}DCNQI)_2Li$

M. Hiraoka [a*], H. Sakamoto [a], K. Mizoguchi [a], R. Kato [b]

[a] *Dept. of Phys., Tokyo Metropolitan Univ., Hachioji, Tokyo, 192-0397, Japan*
[b] *RIKEN, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan*

Abstract

$(DMe\text{-}DCNQI)_2Li$ has a 1/4-filled π electron system and a spin-Peierls ground state. At low temperatures below 30K, the quasi-one dimensional spin diffusive motion of Curie electron spins are observed with variable frequency ESR measurement. It is a strong evidence for a presence of the spin solitons in a spin gap state of the tetramerized DCNQI chains. The intrachain diffusion rate obeys $\sim T^2$ below 30 K. The interchain hopping would be originated by the exchange interaction. Under pressure up to 1.5GPa, $(DMe\text{-}DCNQI)_2Li$ maintains highly one dimensional, and the spin soliton diffusion is affected only a little by the pressures.

Keywords: Electron spin resonance, Magnetic phase transitions, Organic conductors based on radical cation and/or anion salts

1. Introduction

$(DMe\text{-}DCNQI)_2Li$ is a 1/4-filled one-dimensional π electron system. At ambient pressure, a spin-Peierls (SP) transition takes place at 65 K. This material has no d electrons. NMR Knight shift suggested that the only π electron spins are responsible for almost all the magnetic properties in this material [1]. The characteristic properties are understood by strong Coulomb correlation and highly one dimensionality. In this report, we assign the spin diffusive motion below the SP transition temperature T_{sp} to be spin solitons. Validity of this assignment is owing to the quite simple magnetic structure which come from only π electron spins of this material.

2. Experimental

The electron spin susceptibility was measured by ESR at 50 MHz. The ESR intensity was calibrated with the intensity of ^{19}F-NMR in a sample tube for the magnetic susceptibility measurements. The frequency dependence of the ESR linewidth was measured between 10 MHz and 2 GHz. ESR at higher frequency ranges was also studied. Pressure is applied with Cu-Be cell up to 1.5 GPa. The spectra taken at various frequencies provide useful information about spin dynamics.

2. Results and Discussion

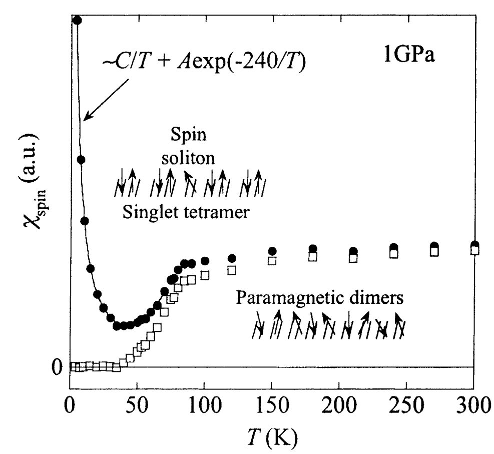

Fig. 1 The temperature dependence of the electron spin susceptibility obtained by ESR at 50 MHz under 1GPa. Closed circles show the raw data. SP transition occurs at T_{sp} = 80 K. Open squares show those obtained by subtracting Curie contributions from the raw data. They disappear exponentially below T_{sp} and 1/2 spin solitons remain.

Figure. 1 shows the spin susceptibility at 1 GPa in $(DMe\text{-}DCNQI)_2Li$. Measurements are also done at ambient pressure and 1.5 GPa. Figure. 2 shows frequency dependence of ESR linewidth between 14 MHz and 2 GHz. Above $\sim$400 MHz (0.5 $1/\sqrt{MHz}$), a contribution from g-valueanisotropy dominates the linewidth, where the contribution from Q1D diffusion is smeared out by this brodening and cannot be obserbed. The ESR linewidth

* e-mail: m-hira@comp.metro-u.ac.jp

doi:10.1016/S0379-6779(02)00761-0

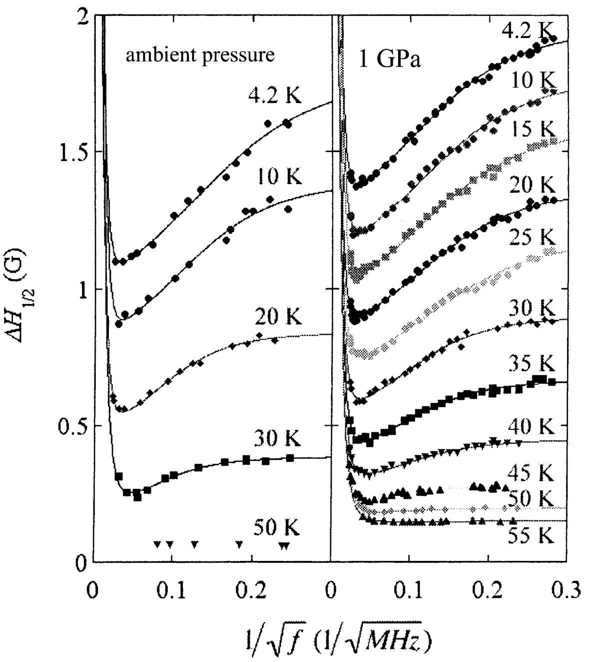

Fig. 2. The frequency dependence (14 MHz∼2 GHz) of ESR linewidth under ambient pressure and 1 GPa. The slope between about $1/\sqrt{f}$ ∼ 0.05 and ∼0.2 ($1/\sqrt{MHz}$) is proportional to $1/\sqrt{D_{//}}$ in Eq. (1). The upturn at higher frequencies above $1/\sqrt{f}$ ∼0.05 (400 MHz) arises from the g-shift anisotropy broadening in the powder sample. The linewidth increases with decreasing temperatures because of motional broadening of the trapped spins [3].

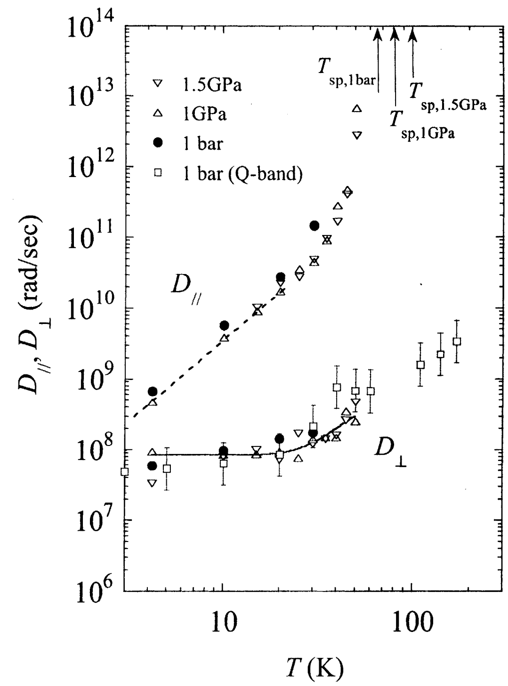

Fig. 3. The temperature dependence of $D_{//}$ and $D_{\perp}$. Open down triangles, open up triangles and closed circles were obtained from Fig. 2. Open squares show the results from motional broadening at Q-band (35 GHz) ESR. The details will be published in anyhere.

can be understood with the diffuse-trap model for the quasi-one dimensional (Q1D) diffusion of the electron spins [2]. The diffuse-trap model was adopted to the neutral solitons in t-$(CH)_x$ [3]. The ESR linewidth in the diffuse trap model is dominated by two different broadening mechanisms. One is a trapped spin broadening ΔH_{trap} which is independent of frequency. We assume an electron spin dipolar broadening for a main contribution of ΔH_{trap}. Another is the relaxation by the Q1D diffusive motion,

$$\Delta H_{Q1D}(\omega) \propto c\left[0.3\phi(0) + 0.5\phi(\omega) + 0.2\phi(2\omega)\right], \quad (1a)$$

$$\phi(\omega) = \sqrt{\frac{1}{4D_{//}D_{\perp}}}\sqrt{\frac{1+\sqrt{1+(\omega/2D_{\perp})^2}}{1+(\omega/2D_{\perp})^2}}, \quad (1b)$$

where c is the concentration of $S = 1/2$ spins, $\omega = 2\pi f$, and $D_{//}$ and $D_{\perp}$ the diffusion rates along and across the 1D chain(s), respectively. The spectral density $\phi(\omega)$ corresponds to the Fourier spectrum of the fluctuating dipolar field produced by the Q1D spin motion.

Since the trapped spins increase with decreasing temperatures, the diffusing spins decrease with decreasing temperatures. Therefore we have to correct this effect on the concentration c for the diffusing spins in Eq. (1), to obtain $D_{//}$ from Fig. 2. Figure. 3 shows the temperature dependence of $D_{//}$ and $D_{\perp}$. $D_{//}$ is obtained from the corrected concentration c. The temperature dependence of $D_{//}$ below 30 K, where the spin solitons are dominant, is similar to the neutral solitons in t-$(CH)_x$, which follows to $\sim T^2$.

The temperature dependence of $D_{\perp}$ below 40 K under 1 GPa can be reproduced with an empirical formula of $9\times 10^7 + A\exp(-150/T)$ as shown by the solid line in Fig. 3. If $D_{\perp}$ is dominated with the inter-chain exchange interaction, the activattion type behavior suggests a thermal creation of the spin solitons which enhaces the exchange coupling. The constant $9\times 10^7/\hbar \sim 0.5$ meV is consistent with the reported Curie-Weiss temperature Θ at 1 % impurity concentration of less than 1 K [4]. The activation energy 150 K is consistent with the spin gap of ∼240 K in Fig. 1. Above T_{sp}, another mechanism will dominate the spin diffusion. This is now under study.

References

[1] K. Miyagawa, A. Kawamoto, K. Kanoda, Phys. Rev. **B60**, (1999) 14847(5).
[2] M. Hiraoka, H. Sakamoto, K. Mizoguchi, R. Kato, Phys. Rev. **B65** (2002) 174413(4).
[3] K. Mizoguchi, S. Masubuchi, K. Kume, Phys. Rev. **B51**, (1995) 8864.
[4] T. Yamamoto, H. Tajima, J. Yamaura, S. Aonuma, R. Kato, JPSJ, **68**, (1999) 1384-1391.