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Spin soliton dynamics and magnetic susceptibility of $(DMe\text{-}DCNQI)_2Li$ by ESR under pressure☆

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Abstract

At ambient pressure, a 1/4 filled spin-Peierls system $(DMe\text{-}DCNQI)_2Li$ shows spin-Peierls transition at $T_{sp} \sim 65$ K, which increases by about 15 K at 10 kbar. Below T_{sp}, Curie susceptibility emerges. We measured a frequency dependence of ESR line width of Curie spins, and found a quasi-one-dimensional (Q1D) diffusive motion. We propose that the Curie spins are spin solitons as a domain wall spread over several units. The chains with $4N + n$ units, where $N =$ integer, $n = 1$, 2, or 3, caused by possible structural defects could provide the spin solitons. The average domain size is ~100 DCNQI molecules deduced from the Curie constant and the extension of domain wall is found to be several units from the frequency dependence of ESR line width at 4.2 K. The diffusion rate of the spin solitons increases with temperature, suggesting a motion of the spin soliton dominated by phonons, which is similar to the neutral solitons in polyacetylene. It was also found that the pressure tends to suppress the spin soliton motion.

Keywords: Spin soliton; ESR; Spin-Peierls; Pressure; Antiferromagnetic order

1. Introduction

We have studied the electronic states of one-dimensional (1D) system of $(DMe\text{-}DCNQI)_2Li$ in powder form with ESR under atmospheric pressure and 10 kbar using a Be–Cu clamp-type pressure cell with Daphne 7373 oil. Relative spin susceptibility was obtained by ESR and NMR (^{19}F in a sample tube) integrated intensity. Spin dynamics of spin solitons were investigated with a frequency dependence of ESR line width $\Delta H_{1/2}$. In case of quasi-one-dimensional (Q1D) spin diffusion, $\Delta H_{1/2}$ behaves as follows, where ω is the frequency, and $D_\perp$ and $D_{//}$ the diffusion rates of inter- and intrachain [1]:

$$\Delta H_{1/2}(\omega_0) \propto [0.3\phi(0) + 0.5\phi(\omega_0) + 0.2\phi(2\omega_0)],$$

$$\phi(\omega) = \frac{1}{\sqrt{4D_\perp D_{//}}}\sqrt{\frac{1+\sqrt{1+(\omega/2D_\perp)^2}}{1+(\omega/2D_\perp)^2}}. \qquad (1)$$

2. Results and discussion

The spin susceptibility is shown in Fig. 1. The spin-Peierls transition temperature, T_{sp} increases from 65 K at ambient pressure to 80 K at 10 kbar. Below T_{sp}, about 1 Curie spin per 100 dimers are observed. A mechanism of pressure dependence in T_{sp} is not quite simple. For example, T_{sp} decreases by 10% at 6 kbar in (TTF)(CuBDT) [2]. A

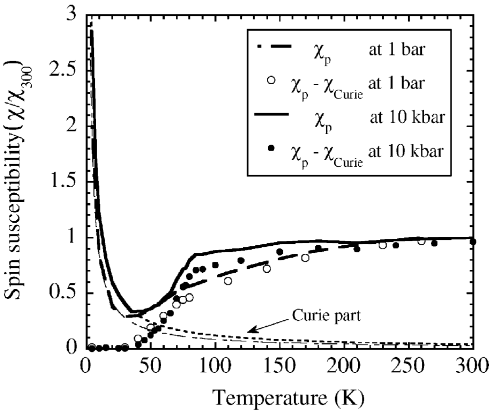

Fig. 1. Spin susceptibility of $(DMe\text{-}DCNQI)_2Li$ normalized at 300 K obtained from ESR.

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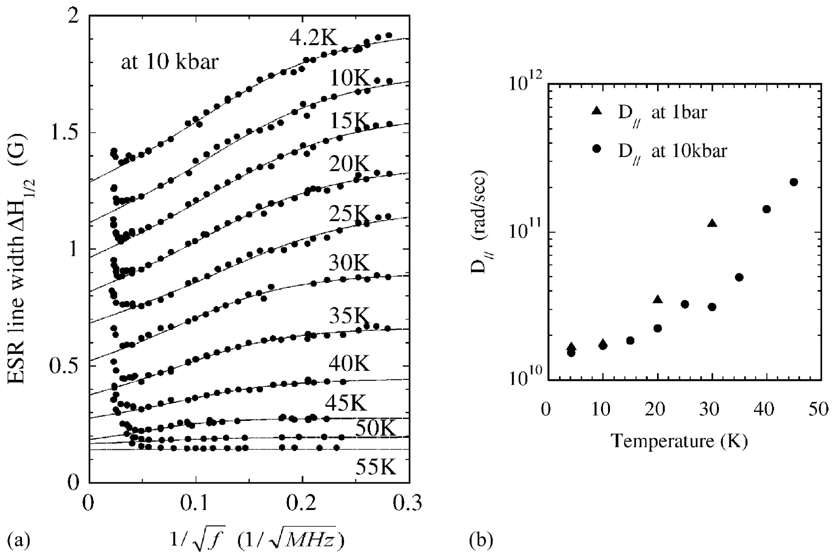

Fig. 2. (a) Frequency dependence of $\Delta H_{1/2}$. The solid curves indicate Q1D parts. Deviations at high frequencies are caused by anisotropy of g shift. (b) $D_{//}$ derived from the solid curves in (a) is plotted vs. T.

possible factor on this difference is a higher one-dimensionality in $(\text{DMe-DCNQI})_2\text{Li}$ than in (TTF)(CuBDT). Pressure induces mainly intrachain interactions in $(\text{DMe-DCNQI})_2\text{Li}$, which can enhance Peierls gap [3], but 3D couplings in (TTF)(CuBDT), as expected from their structures.

The frequency dependence of $\Delta H_{1/2}$ below T_{sp} is shown in Fig. 2(a). The observed line shape is Lorentzian under all the conditions studied. The solid curves demonstrate the Q1D prediction of Eq. (1), which reproduces $\Delta H_{1/2}$ below 500 MHz and 45 K. Fig. 2(b) shows the temperature dependence of $D_{//}$ deduced from the fitting parameters. A monotonous increase of $D_{//}$ suggests phonon-assisted diffusion mechanism, similar to the neutral soliton in *trans*-polyacetylene. Above T_{sp} in $(\text{DMe-DCNQI})_2\text{Li}$, the electronic states with large Coulomb repulsion U is an insulating dimer phase with $4k_{\text{F}}$ gap. Each dimer, carrying one spin, turns into singlet tetramers below T_{sp}. The rapid $D_{//}$ suggests an origin of the Curie spins to be movable domain walls arising from defect-origin finite size domains, roughly 100 molecules, that could contain odd number of dimers. In addition to such spin solitons, spin-soliton pairs can also be excited thermally near T_{sp}. The prediction of Eq. (1) is only valid if the spin soliton is localized on a single site. If it delocalized over W dimers, ESR broadening due to Q1D mechanism goes out at higher frequencies than $2D_{//}/\pi W^2 = 10^{10}/50\pi = 60$ MHz [1], with $D_{//} = 10^{10}$ rad/s at 4.2 K and $W = 10$ dimers. This suggests W to be less than 3 dimers. Such a narrow extent is consistent if a relatively large exchange interaction is assumed between the next-nearest neighboring dimers, which can enhance T_{sp} [3]. The smallness of W could be the reason why antiferromagnetic (AF) ordering below T_{sp} was not observed in $(\text{DMe-DCNQI})_2\text{Li}$, even with 1% of the spin solitons (impurities). In the case of CuGeO_3 [4], 1% of impurity is an enough high concentration to observe AF ordering below T_{sp} with W of more than 10.

3. Conclusion

1. The spin-Peierls gap is enhanced by 15 K, with the hydrostatic pressure. This concerns with an enhancement of the intrachain interaction, between not only nearest neighbors but also next-nearest neighbors, by pressure.
2. Translational dynamics of the spin soliton in the spin-Peierls state was observed.
3. The spin soliton motion is derived by phonon scattering, as in the case of neutral solitons in *trans*-polyacetylene [1], and suppressed by pressure [5].
4. The extension of spin soliton is narrower than 3 units. This is a key parameter to realize AF ordering by impurities introduced to the spin-Peierls systems and can account for the difference between the present and CuGeO_3 systems [4].

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