

Charge Transport in the Insulating State of (DMe-DCNQI)₂Li above T_{SP} : A Possible Fractional Charge Soliton Conduction with $\pm\frac{1}{2}e$

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A spin-Peierls system (DMe-DCNQI)₂Li is studied with *W*-band electron paramagnetic resonance (EPR) (≈ 94 GHz) to unveil a charge transport mechanism in the insulating $4k_F$ charge density wave state above T_{SP} . The electron hopping between the neighbor DCNQI columns provides an additional broadening of the EPR linewidth, since the neighbor columns are generally nonequivalent to each other with respect to *g* shift. The obtained intercolumn hopping rates lead us to the conclusion that the electron hopping to a hole soliton carrying a fractional charge of $\frac{e}{2}$ in the neighbor column dominates the intercolumn charge transport.

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It is known that a quasi-one-dimensional (*Q1D*) π -electronic system, lithium salt with dimethyl-dicyanoquinone-diimine (DMe-DCNQI)₂Li, shows relatively high electrical conductivity from 10 to 150 S/cm with a weak temperature dependence above the paramagnetic to nonmagnetic transition temperature $T_{MN} \approx 65$ K [1], which led us in the early stages to the conclusion that this system was *metallic* above T_{MN} . Recently, however, from the semiconducting temperature dependence in the electrical resistivity of higher purity materials, it is unveiled that the system is *insulating* in the sense that the charge gap of ≈ 270 K is open even above T_{MN} [2]. It is also reported that the $2k_F$ Peierls gap with tetramerization opens at $T_{MN} \approx 65$ K in the $\frac{1}{4}$ -filled π band [2]. These facts suggest that T_{MN} corresponds to a spin-Peierls (SP) transition to the spin gap ground state from the insulating dimerized $4k_F$ charge density wave (CDW) states in the lower Hubbard band where the spin degree of freedom is preserved, as sketched roughly in Fig. 1, typical for the strongly correlated *Q1D* electronic systems. The observation of the $4k_F$ superstructure has been suggested in Li salt [3], and has been reported at room temperature in Ag salt [4], which is isoelectronic with Li salt.

Then, the question is what kind of charge carriers could play a role in such 1D Mott-insulating $4k_F$ CDW states above T_{SP} . The DCNQI dimer possesses one electron and $S = \frac{1}{2}$. The hopping of these electrons to the neighbor DCNQI dimers is substantially forbidden by the large on-site Coulomb repulsion energy U , as in the usual Mott-Hubbard insulators. Therefore, the possible charge transport mechanism is a sliding motion of the charged solitons with the Goldstone mode. Thermal dissociation of a dimer to a couple of DCNQI monomers could provide a fractionally charged soliton pair of the midgap states in the $4k_F$ CDW gap, as shown in Fig. 2; a spin soliton with $S = \frac{1}{2}$ and excess fractional charge of $-\frac{1}{2}e$, and a hole soliton with $S = 0$ and $\frac{1}{2}e$, since the average charge in a DCNQI molecule is $-\frac{1}{2}e$. Although the charge transport

carried by the fractional charges has been proposed theoretically [5,6], it is generally difficult to observe directly the charge of the domain wall soliton. We have succeeded to give one experimental evidence for this issue, though it is indirect. Here, we propose the fractional charged soliton conduction could be a common mechanism in the strongly correlated $1/4$ -filled systems.

In this Letter, we demonstrate the evidence for the transport carried by the fractionally charged solitons, that is, the spin and hole solitons in the insulating state of (DMe-DCNQI)₂Li with the $4k_F$ CDW gap. The temperature dependence of the total intercolumn hopping rate $2D_{\perp}$ is determined by analyzing the frequency dependent anisotropy of electron paramagnetic resonance (EPR) linewidth at *Q* and *W* bands. The obtained D_{\perp} above T_{SP} can be reproduced by the activation-type expression with $T_{\perp} \approx 242 \pm 40$ K which agrees well with 270 K for the dc conductivity above T_{SP} [2]. A collective motion of CDW [2] is not the case, but the presence of the

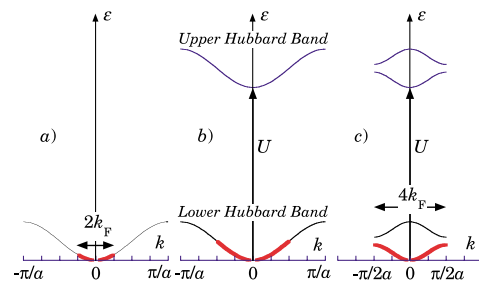


FIG. 1 (color online). (a) A 1D $1/4$ -filled band where each state can be occupied doubly with up and down spins. (b) Hubbard band where on-site Coulomb U limits not only occupancy to single electron with up or down spin but also charge transport. (c) Dimerized $4k_F$ CDW states where the spin degree of freedom is preserved. The spin and hole solitons are excited as midgap states. Note that these pictures have only a meaning of intuitive help for understanding of the $4k_F$ CDW, because the electron correlation is not taken into account correctly.

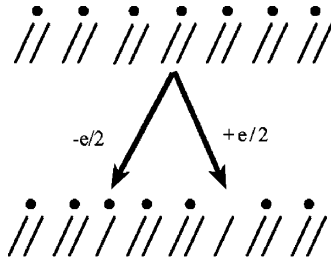


FIG. 2. A conceptual picture for the spin soliton and hole soliton pair creation. A dimer with one $S = \frac{1}{2}$ spin dissociates to a pair of the spin soliton and the hole soliton, with the excess charge of $-\frac{1}{2}e$ and $\frac{1}{2}e$, respectively. Note that this process does not change the total number of spins, that is, the spin susceptibility in the system.

holes is essential for the intercolumn hopping of charges to avoid the cost of U . Then, the activation-type D_{\perp} could be a strong evidence for the fractionally charged soliton transport, because creation mechanisms of the solitons are mainly the thermal dissociation of DCNQI dimers. The observed activation energy of $T_{\perp} \approx 242$ K corresponds to the creation energy of the soliton pair, relating to the $4k_F$ CDW gap.

Small needlelike single crystals prepared with a reported technique [7] were used for the EPR study with Q - and W -band spectrometers operated around 35 and 94 GHz, respectively, made by Bruker Instruments installed at Institute for Molecular Science (IMS). The single crystal less than 1 mm long can be rotated in a transverse magnetic field of 1.2 T for the Q band and 3.4 T for the W band. The temperature was changed from 300 K down to 10 K. Inhomogeneity of the magnetic field over the crystal is found to be of the order of 0.1–0.2 G in the W band, but negligibly small in the Q band.

Figure 3 shows a schematic structure of $(\text{DMe-DCNQI})_2\text{Li}$ demonstrating the presence of non-equivalent DCNQI columns with respect to the angle α between the π -orbital axis and the external magnetic field H . Experimental data will be shown as a function of the angle θ between the 1D DCNQI stacking c axis and H . The angular dependence of the g factor,

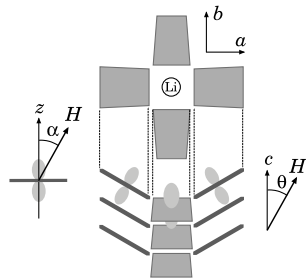


FIG. 3. A schematic structure of $(\text{DMe-DCNQI})_2\text{Li}$. The square plates represent the DCNQI molecules that tilt alternately by $\pm 33^\circ$ out of the plane normal to the one-dimensional stacking c axis. π -orbital direction is also shown schematically.

$2.00340 - 0.00070 \cos 2\theta$ is consistent with the reported data [8].

The angular dependence of the EPR half width at half maximum obtained at Q and W bands are shown in Fig. 4. A characteristic feature from Q to W band is a strong dependence on θ and frequency f ; at $\theta = 0^\circ$, a weak increase caused by inhomogeneity of H , but a strong enhancement at $\theta = 45^\circ$. The origin of this anomaly can be accounted for with the electron hopping between the neighbor columns with different g values because of alternating tilt of the DCNQI molecular plane by 33° [9,10], as shown in Fig. 3.

If the spins localize in each column, the EPR spectrum should have some structure corresponding to the different resonance fields of the four nonequivalent columns, arising from the anisotropic g shifts. Since single Lorentzian is observed in this study, the spins do not localize, but hop to the neighbor columns faster than the frequency corresponding to the difference of their resonance fields. Such a motional narrowing was first discussed by Anderson and Weiss [11], and the resultant spectrum has a Lorentzian line shape with the width expressed by the relation [12]

$$\Delta H_{\text{IC}} = \frac{\gamma \delta^2}{2(2D_{\perp})}, \quad (1)$$

where γ is the electron gyromagnetic ratio, D_{\perp} the intercolumn hopping rate for one direction, and 2δ the difference of the resonance fields proportional to the frequency f . Then, the ΔH_{IC} depends on f^2 , which actually holds in the present case; $\Delta H_{\text{IC,W}}/\Delta H_{\text{IC,Q}} \sim (f_W/f_Q)^2 \sim (94 \text{ GHz}/35 \text{ GHz})^2 = 7.4$, consistent with the amplitude of the solid curves in Fig. 4. It is also consistent with Eq. (1) that the enhancement is substantially absent at $\theta = 0^\circ$, where all the columns are equivalent, namely $\delta = 0$. Then, it is concluded that Eq. (1) is the mechanism

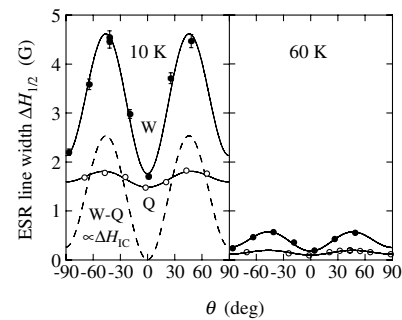


FIG. 4. The angular dependences of the EPR linewidth at Q (open circles) and W (closed circles) bands are shown for two typical temperatures. The data can be reproduced well by the solid curves representing $\Delta H_W = 3.28 - 0.185 \cos 2\theta - 1.33 \cos 4\theta$ and $\Delta H_Q = 1.67 - 0.0551 \cos 2\theta - 0.134 \cos 4\theta$ at 10 K. The dashed curve at 10 K shows the remainder of them, which equals $0.86 \Delta H_{\text{IC}}$ at W band, where $0.86 = (f_W^2 - f_Q^2)/f_W^2$. The magnetic field inhomogeneity has been corrected.

for the anomalous line broadening depending on the angle and the frequency. From the comparison between the angular dependence of the linewidth and a prediction of Eq. (1), the hopping mode can be discussed. If the spins hop to the second nearest neighbor (snn) columns over the Li ion, the observed ΔH_{IC} in Fig. 4 goes to zero at $\theta = \pi/2$, where the snn columns are equivalent to each other. It is, however, finite for the hopping to the nearest neighbor (nn) columns which are nonequivalent to each other. Figure 4 is consistent with the equal probability to hop to each neighbor column of the Li ion; in total, twice hopping probability to nn than to snn.

The temperature dependence of ΔH_{IC} is shown in Fig. 5 together with the hopping rate D_{\perp} deduced from ΔH_{IC} and Eq. (1). Note a curious feature around 40 K. D_{\perp} steeply increases with T approaching 40 K, but above 40 K, suddenly slows down the rate to no less than $1/50$ of that below 40 K. This acute change suggests the presence of some transition around it. Although the spin-Peierls transition takes place at 65 K, there is a clear discrepancy in temperature between them by more than 20 K. Then, the anomaly would be a crossover between two different hopping mechanisms. The possible mechanisms are the exchange interaction and the actual hopping of the electron or hole between the neighbor columns.

At the lowest temperatures, the hopping rate approaches the constant value of $D_{\perp} \approx 1.3 \times 10^8$ rad/s that is consistent with the previously reported value $\approx 1.0 \times 10^8$ rad/s derived from the cutoff frequency of the spectral density for the $Q1D$ diffusive motion of the dimer spin solitons in the tetramerized spin-Peierls state below $T_{SP} \approx 65$ K [13]. Since, in this case, hole solitons could not be created even by the dissociation of the tetramer, the mechanism of the D_{\perp} below T_{SP} should be dominated by the exchange interaction. In contrast, at

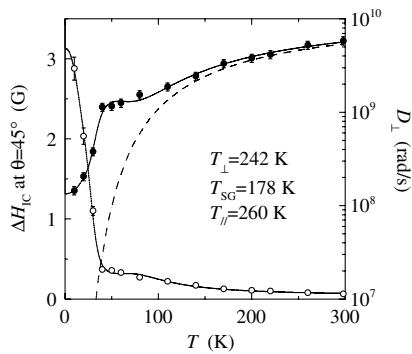


FIG. 5. The temperature dependence of ΔH_{IC} at W band (open circles) and the intercolumn hopping rate D_{\perp} (closed circles) deduced from ΔH_{IC} . The solid curves represent the prediction of Eq. (4) along with Eq. (1) and the parameters determined experimentally in Ref. [13]. The dashed curve represents the activated behavior corresponding to thermal creation of the spin- and hole-soliton pair carrying the fractional charges, $\pm \frac{1}{2}e$.

$T \gg T_{SP}$, the real particle hopping should be a leading mechanism, because the observed rates could not be accounted for by the exchange interaction between the moving spin carriers, which is limited by several factors, such as (i) the largest exchange frequency ω_J at the nearest distance, (ii) the number of spins c , (iii) the diffusion rate D_{\parallel} along the column, and (iv) the stay period $\tau_c = 1/D_{\parallel}$ to interact with another spin. Therefore, D_{\perp} caused by the effective exchange interaction is expressed by [14]

$$D_{\perp,ex} \propto \frac{\frac{9}{4} \omega_J^2 / D_{\parallel}}{1 + \frac{9}{4} \omega_J^2 / D_{\parallel}^2} c. \quad (2)$$

This formula shows a peak around $D_{\parallel} \approx \omega_J$, where the spin exchange with the spins in the neighbor columns occurs most effectively because of the optimum diffusion rate in the column, that is, the fastest diffusion rate D_{\parallel} ensuring the minimum stay time τ_c required to exchange the spins. This peak could correspond to the hump of D_{\perp} around 40 K in Fig. 5.

Above T_{SP} , the observed D_{\perp} shows a monotonic increase which tends to an activation-type formula:

$$D_{\perp,IC}(T) = D_{\perp,IC}(\infty) e^{-T_{\perp}/T}, \quad (3)$$

where T_{\perp} is the activation temperature in the temperature range above T_{SP} . This feature requires a new mechanism for the intercolumn hopping. The most probable scenario is an intercolumn spin transport in terms of the fractionally charged spin and hole solitons produced by thermal dissociation of the dimers in the $4k_F$ CDW states. In this case, T_{\perp} relates to the pair creation energy of these solitons, which might be the order of the $4k_F$ CDW gap. This scenario has the advantage of no cost of U for the electrons to hop to the neighbor columns by virtue of the hole solitons. Here, note that this electron hopping corresponds to the exchange of the spin soliton ($S = \frac{1}{2}$ and $-\frac{1}{2}e$) in one column for the hole soliton ($S = 0$ and $\frac{1}{2}e$) in the neighbor column. This also corresponds to a transfer of the electron with both the spin $\frac{1}{2}$ and the charge $-e$. Then, this hopping mechanism could provide a 3D charge transport combined with the sliding transport of these solitons within the column. Consequently, the temperature dependence of D_{\perp} would relate to that of the dc conductivity [2] as discussed later.

With these hopping mechanisms, we tried to reproduce the experimental data in Fig. 5 and to estimate several parameters. The solid curves represent

$$D_{\perp}(T) = D_{\perp,ex0} + D_{\perp,ex}(T) + D_{\perp,IC}(T), \quad (4)$$

and Eq. (1), where $D_{\perp,ex0}$ is the temperature independent static term corresponding to the exchange interaction between the trapped solitons enough below T_{SP} [13], and the second and the third terms represent Eqs. (2) and (3), respectively. The reported empirical formula for the on-chain diffusion rate D_{\parallel} composed of a power

law and an exponential term is utilized in the second term; $D_{\parallel} = 1.8 \times 10^7 T^{2.4} + 7.7 \times 10^{13} e^{-T_{\parallel}/T}$ (rad/s), derived from the ambient pressure data below T_{SP} [13]. On the spin concentration $c(T)$, a spin-gap behavior below T_{SP} and leveling off above T_{SP} in the spin susceptibility are taken into account [15]. Thus, three characteristic energy parameters were determined as follows: (i) the thermal activation with $T_{\parallel} = 260 \pm 60$ K in the on-chain diffusion rate near T_{SP} , (ii) the spin-gap temperature $T_{SG} = 178 \pm 40$ K below T_{SP} , and (iii) the thermal activation with $T_{\perp} = 242 \pm 40$ K in the intercolumn hopping rate. The agreement between the prediction of Eq. (4) and the data in Fig. 5 is satisfactory, but accuracies of the obtained values are not high because of the fitting with as many as eight parameters correlating with each other. $T_{SG} = 178 \pm 40$ K, which causes the spin-Peierls transition at 65 K, is well consistent with 150 ± 25 K derived from the susceptibility below T_{SP} . The activation temperature $T_{\parallel} = 260 \pm 60$ K for D_{\parallel} is also consistent with 190 ± 100 K deduced from the temperature dependence of D_{\parallel} [13].

The most interesting parameter is the activation temperature $T_{\perp} = 242 \pm 40$ K for the intercolumn hopping rate, since it would be concerned with the charge transport in the Mott-Peierls insulating state carried by the fractionally charged solitons; spin and hole solitons. The thermal activation of D_{\perp} in the $4k_F$ CDW, Mott-like insulator can be reasonably understood by the presence of the hole soliton to avoid the cost of U . The soliton pairs created by thermal dissociation of the dimers substantially contribute to the soliton charge transport not only along the column, but also across the columns. Such a conclusion is additionally supported by the coincidence of the obtained activation energy for D_{\perp} , 242 ± 40 K with 270 K for the electrical conductivity σ [2]. This activation energy would correspond to the creation energy of the spin and hole soliton pair, because both σ and D_{\perp} have to be proportional to the number of hole solitons as the charge carriers without the cost of U . These kink solitons travel within a column with Goldstone sliding motion, conveying the charges $\pm \frac{1}{2}e$. Here, note that a single electron transfers from the spin soliton to the electrode or the hole soliton in the neighbor column, leaving another hole soliton and vice versa. For the realistic charge transport through a macroscopic sample, the intercolumn hopping D_{\perp} should play a critical role. At the moment, however, it is not self-evident if σ is limited by D_{\perp} or simply by the number of the fractionally charged solitons. It is, however, shown that even in the D_{\perp} -limited case the conductivity of the order of 100 S/cm can be easily accounted for with appropriate parameters given in Ref. [13]. The final answer to this issue will be provided by a future study on the temperature dependence of D_{\parallel} . Finally, from the simulation of Eq. (4), the *maximum*

exchange temperature $\hbar\omega_J/k_B$ appeared in Eq. (2) is estimated to be 2 K which should be concerned with the antiferromagnetic ordering under the spin-Peierls state as an upper limit.

In conclusion, it was demonstrated that the charge transport in the insulating state of 1/4-filled (DMe-DCNQI)₂Li is dominated by the fractionally charged hole solitons to make the charge movable without the cost of U . With additional suppliers for the hole solitons such as impurities, the reported weakly metallic temperature dependence of the conductivity [1] might also be accounted for with phonon scattering of the solitons. This type of fractional charged soliton conduction could be a common mechanism in the 1/4-filled systems with strong correlations.

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 - [15] An experimental formula for c in Eq. (2) is converted from the spin susceptibility χ . $e^{-T_{SG}/T} / \exp(-T_{SG}/\{T/[1 + (1.1T_{SP}/T)^m] + 1.08T_{SP}/[1 + (T/1.2T_{SP})^n]\})$ is used for χ with spin-Peierls transition. With increasing power m ($= 4$) and n ($= 3$), the transition from the exponential to the constant becomes sharp.