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

Maki Hiraoka,[1] Hirokazu Sakamoto,[1] Kenji Mizoguchi,[1] and Reizo Kato[2]
[1]*Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan*
[2]*RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama, 351-0198, Japan*
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A spin-Peierls system $(DMe\text{-}DCNQI)_2Li$ has been studied with electron paramagnetic resonance (EPR) under hydrostatic pressure. A definite frequency dependence of the EPR linewidth is observed for the Curie spins that appear below T_{SP}, demonstrating a clear one-dimensional diffusive character similar to $t\text{-}(CH)_x$. This is strong evidence for Curie spins to arise from spin solitons as domain walls caused by structural defects. The estimated extent of the spin soliton is less than several molecular units. A relation with the antiferromagnetic ordering provoked by impurities as found in $CuGeO_3$ is discussed.

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Lithium salt of dimethyl-dicyanoquinone-diimine $[(DMe\text{-}DCNQI)_2Li]$ is a one-dimensional (1D) π-band system composed of 1D stacks of DMe-DCNQI molecules, where one electron transferred from each Li counter ion to each couple of DMe-DCNQI molecules. At room temperature this system is an insulator[1] with a probable $4k_F$ dimerization gap at the Fermi energy, suggested from quite similar physical properties to $(DMe\text{-}DCNQI)_2Ag$.[2] A relatively higher electrical conductivity is believed to arise from a collective mode of domain walls excited thermally.[1] In an iodized system $(DI\text{-}DCNQI)_2Ag$ with a narrower bandwidth, the Wigner crystallization of electrons occurs below 220 K, demonstrating the crucial role of the long-range Coulomb interaction between DCNQI molecules in these systems.[3] Magnetic properties suggest $(DMe\text{-}DCNQI)_2Li$ has a nonmagnetic ground state below 60 K accompanied by a $2k_F$ superstructure, corresponding to tetramerization of DCNQI molecules,[4] ascribable to a spin-Peierls transition like the Ag-salt.[5] If the number of DCNQI molecules in a chain is $4N+n$, where N is an integer and n is 1, 2, or 3, the spin soliton could be present in the spin-Peierls state. Such a spin soliton might be mobile with the Goldstone mode of kink solitons, as actually observed in *trans*-polyacetylene $[t\text{-}(CH)_x]$.[6,7] The spin solitons induced by impurity doping would be concerned with the appearance of a long-range antiferromagnetic (AF) ordering below T_{SP}, as in the inorganic spin-Peierls system $CuGeO_3$ doped with impurities such as Zn or Si.[8–11] To induce AF long-range ordering in the spin-Peierls state, the spatial extent of the spin solitons becomes crucial. In this meaning, it is interesting to investigate the nature of spin solitons in spin-Peierls systems. Since the magnitude of the Curie tail in $(DMe\text{-}DCNQI)_2Li$ depends on sample quality, the Curie tail has been assigned to localized impurity spins. From such a reason, the dynamics of the Curie spins, that is, the spin solitons, has remained unclear.[12]

In this report, we demonstrate evidence for spin solitons and their dynamics in the spin-Peierls system $(DMe\text{-}DCNQI)_2Li$ with electron paramagnetic resonance (EPR) in a wide frequency range from 10 to 20 000 MHz. Strong evidence for the presence of spin solitons is obtained from a definite quasi-one-dimensional diffusive motion of the Curie spins coming out below T_{SP}, which is deduced from the frequency dependence of the EPR linewidth.[7] The observed behavior of the diffusion rate similar to $t\text{-}(CH)_x$ reminds us that the present system has the same degeneracy in the ground-state energy as $t\text{-}(CH)_x$. In addition, the frequency spectrum at the lowest temperature 4.2 K tells us that the spin soliton extent should be less than several molecular units. A weak intra- and interchain interaction between the solitons arising from such a small extent elucidates why AF long-range ordering was not observed in $(DMe\text{-}DCNQI)_2Li$, although it takes place in $CuGeO_3$ systems doped with impurity concentrations less than 1 at. % which is comparable to that for the present spin solitons. The small extent of the spin soliton would be consistent with the crucial role of the long-range Coulomb interaction in systems such as the Li and Ag salts of DCNQI.[4,13]

A powder sample of small crystallites prepared with a reported technique[14] was used for the present EPR study. The EPR intensity proportional to the spin susceptibility was calibrated relative to the NMR intensity of the known number of ^{19}F in a Teflon sample tube at 40–50 MHz. The frequency was varied from 10 MHz to 8 GHz with a coil and trimmer capacitors or stub tuners. EPR spectra were analyzed with a least-squares fit to Lorentzian functions. For pressure experiments, a clamp-type cell made of CuBe alloy is used with Daphne 7373 oil as a pressurizing medium. Figures for the pressure shown in this work are nominal values clamped at room temperature. Pressure loss caused by thermal contraction is estimated with the values reported by Murata *et al.*[15]

Figure 1 shows the temperature dependence of the spin susceptibility in $(DMe\text{-}DCNQI)_2Li$ measured at 1 GPa. Except for the Curie tail below 50 K, the paramagnetic susceptibility disappears exponentially below 80 K at 1 GPa as represented by the open circles, which might be ascribed to the spin-Peierls transition, on the basis of a semiconducting behavior of the electrical conductivity.[1] The transition temperature increases from 65 K at ambient pressure to 80 K at 1 GPa. Schematic features are also shown in Fig. 1: the spins on dimers are strongly coupled antiferromagnetically to each other in the paramagnetic region, and the Curie spins are conveyed by the spin solitons caused, for instance, by a dimer in a chain with a length of $4N+2$. To investigate the spin soliton dynamics, the frequency dependence of the EPR linewidth is examined below 50 K.

Figure 2 shows the EPR linewidth taken at 1 GPa as a

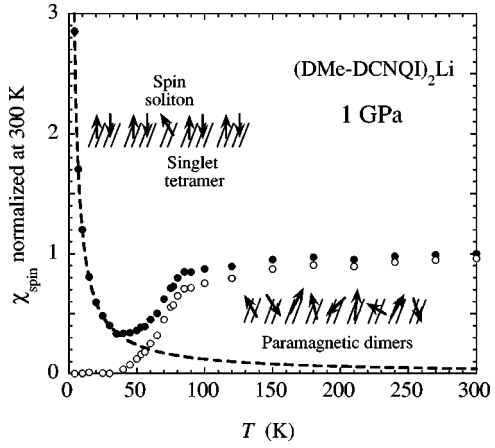

FIG. 1. The temperature dependence of $\chi_{\rm spin}$ in $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ measured around 50 MHz and at 1 GPa. The exponential decay below 80 K is superimposed by a Curie tail shown by the dashed line. The open circles show $\chi_{\rm spin}$-$\chi_{\rm Curie}$. In the paramagnetic state above 80 K, each DCNQI dimer has one paramagnetic spin. Below 80 K, the singlet tetramers of DCNQI molecules develop. A deficient unit with fewer than four DCNQI molecules, for example, an isolated dimer in the 1D chain, behaves as a kink soliton with spin $\frac{1}{2}$.

function of $1/\sqrt{f}$, where f is the EPR frequency. A typical frequency-dependent width $\Delta H_{\rm Q1D}$, caused by the electronic dipolar interaction modulated with the quasi-one-dimensional (Q1D) diffusive motion of the spin soliton, is expressed as[6,16,17]

$$\Delta H_{\rm Q1D}(\omega) \propto c_{//} c \Sigma_l [0.3\phi(0) + 0.5\phi(\omega) + 0.2\phi(2\omega)], \tag{1a}$$

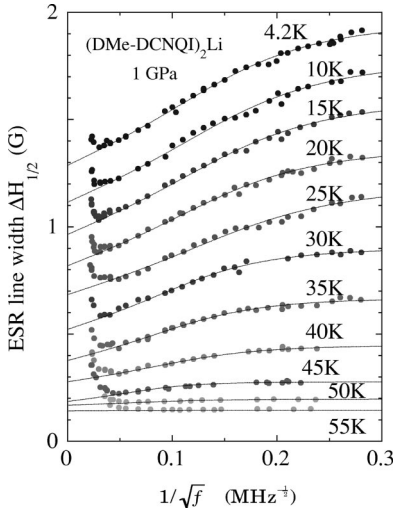

FIG. 2. The EPR linewidth in $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ as a function of $1/\sqrt{f}$, where f is the EPR frequency, measured at 1 GPa, and several temperatures below 55 K. The dotted curves represent the Q1D behavior expected from Eq. (1). The upturn at higher frequencies than 1 GHz arises from the g-shift anisotropy distribution in the powder sample.

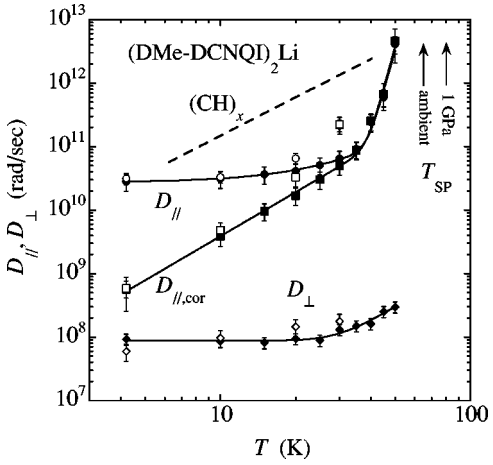

FIG. 3. The temperature dependence of the diffusion rates at ambient pressure (open symbols) and 1 GPa (solid ones) deduced from the ESR linewidth with Eq. (1), together with $D_{//,\rm cor}$ corrected on the trapping effect. The solid curves represent the experimental formulas, Eq. (2) for $D_{//,\rm cor}$ (squares) and Eq. (3) for $D_\perp$ (diamonds). The dashed line represents $D_{//}$ for t-$(\mathrm{CD})_x$ (Refs. 6 and 7). The line for $D_{//}$ (circles) is a guide for the eyes.

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

where $c_{//} = 4 \times 3.788$ Å is the unit hopping length, c the concentration of $S=\frac{1}{2}$ spins, Σ_l the lattice sum, $\omega = 2\pi f$, 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. $\phi(\omega)$ is frequency dependent, $1/\sqrt{2D_{//}\omega}$ at $\omega \gg D_\perp$ (1D regime), and approaches a constant value independent of ω, $1/\sqrt{2D_{//}D_\perp}$ at $\omega \ll D_\perp$ (3D regime). The curves in Fig. 2 definitely demonstrate such a feature, representing a Q1D diffusive motion of the Curie spins as clear evidence for the spin soliton. $D_\perp$ could also be characterized as the ''escape time'' from the 1D motion in a chain to the 3D motion between chains. Then, $D_\perp$ corresponds to the crossover frequency between the 1D and 3D regimes and $D_{//}$ is proportional to the inverse of the slopes at $\omega \gg D_\perp$. With using $c = 0.9\%$ deduced from $\chi_{\rm Curie} = 7.7 \times 10^{-4}$ emu/mol at 4.2 K and $\Sigma_l = 2.00 \times 10^{43}$ cm^{-6} calculated for the structure of $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$,[18] the diffusion rates $D_{//}$ and $D_\perp$ are successfully derived at ambient pressure and 1 GPa with a weak pressure dependence from the parameters obtained by the least-squares fitting to Eq. (1), as shown in Fig. 3.

A characteristic feature in the temperature dependence of $D_{//}$ is as follows: $D_{//}$ is almost temperature independent up to 30 K and increases steeply above 25 K at ambient pressure and 35 K at 1 GPa by nearly two orders of magnitudes. A similar behavior to the former has been reported on the dynamics of neutral solitons in t-$(\mathrm{CH})_x$ below 100 K, which is a domain-wall soliton of bond alternation with $S=\frac{1}{2}$.[6] The diffusion rate $D_{//}$ along the chain was concluded to be proportional to T^2 with a diffuse-trap model that takes into account an effect of the trapped solitons. The diffuse-trap

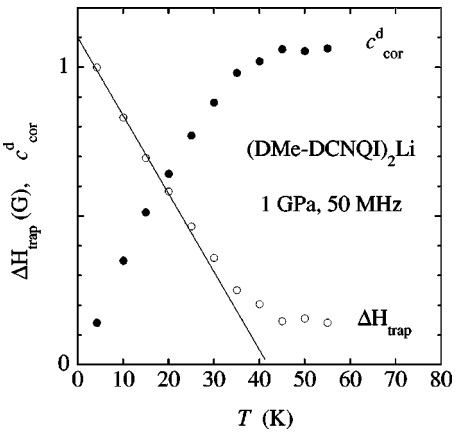

FIG. 4. The temperature dependence of $\Delta H_{\rm trap}$ caused by the static broadening when the spin soliton is trapped. The correction factor $c^{\rm d}_{\rm cor}$ to multiply to Eq. (1) is also shown by the solid circles.

model assumes that the neutral soliton stays for long duration in the trapping sites compared with when diffusing, resulting in static broadening when trapped, instead of the Q1D relaxation broadening when diffusing.[6,7,19] Then, the linewidth is a sum of the broadenings with the two different mechanisms. With decreasing temperature, the period spent at the trapping sites increases at the cost of decreasing Q1D broadening. A similar interpretation can be applied to $D_{//}$ in the present system. Figure 4 shows the temperature dependence of $\Delta H_{\rm trap}$ at 1 GPa, obtained by subtraction of $\Delta H_{\rm Q1D}$ from the observed. A correction factor $c^{\rm d}_{\rm cor}$ to give an effective concentration of the diffusing spins $c_{\rm dif}=cc^{\rm d}_{\rm cor}$ can be deduced from $\Delta H_{\rm trap}$ in the same way as that reported,[6] as shown in Fig. 4. Then, the corrected diffusion rate $D_{//,\rm cor}$ in Fig. 3 is given by $(c^{\rm d}_{\rm cor})^2 D_{//}$.

The solid curve successfully reproduces $D_{//,\rm cor}$ at 1 GPa with the two terms

$$D_{//,\rm cor}=A_{//}T^{p}+B_{//}e^{-T_{//}/T}, \tag{2}$$

where $A_{//}=2\times10^{7}$ rad/s, $p=2.3\pm0.3$, $B_{//}=7\times10^{18}$ rad/s, and $T_{//}=(7\pm1.5)\times10^{2}$ K. The first term $T^{2.3}$ of Eq. (2) is a similar dependence to T^2 for the neutral soliton in t-$(\rm CH)_x$ and actually T^2 can reproduce the data within uncertainty. The second one is simply assumed to reproduce the steep increase above 35 K at 1 GPa and, similarly, above 20 K at ambient pressure. From the first term, it is concluded that the dynamics of the spin solitons is the same as the neutral soliton in the temperature dependence, but is slower by two orders of magnitude than that at least below 20–30 K where the spin solitons are sufficiently isolated from each other. This suggests that the spin solitons are driven by the phonons similarly as the neutral soliton in t-$(\rm CH)_x$.[20,21] This is consistent with the fact that the CH unit has a markedly lighter mass than two (DMe-DCNQI) molecules, since the soliton diffusion rate is proportional to $1/m^2$, where m is the ionic mass. The steep increase of $D_{//}$ above 20 K (35 K at 1 GPa) would suggest some change of the electronic states, probably concerned with the spin-Peierls transition. With approaching $T_{\rm SP}$, soliton (dimer) pair formation takes place exponentially and almost all the tetramers dissociate into dimers at $T_{\rm SP}$ with AF correlation between the dimers that strongly suppresses the spin susceptibility. Then, 10%–20% of the dimers could be excited around 35 K (50 K at 1 GPa), which makes the 1D chain a mixture of tetramers and dimers, such as the liquid state, giving rise to the possiblity of enhanced diffusion rates for the spin solitons. Here, there is an interesting coincidence in the activation energy around 50 K: 700 ± 150 K for $D_{//}$ and 630 ± 50 K for the electrical conductivity at ambient pressure,[1] which suggests some connection of the spin soliton diffusion to the electrical conductivity.

The solid curve for $D_{\perp}$ at 1 GPa in Fig. 3 represents the relation

$$D_{\perp}=A_{\perp}+B_{\perp}e^{-T_{\perp}/T}, \tag{3}$$

where $A_{\perp}=9\times10^{7}$ rad/s, $B_{\perp}=4\times10^{9}$ rad/s, and $T_{\perp}=150$ $(+100,-50)$ K. The maximum of $\approx4\times10^{9}$ rad/s for $D_{\perp}$ with $T_{\perp}=200$ K is consistent with the NMR T_1^{-1} result to be less than 5×10^{10} rad/s.[22] The constant term can be assigned to the cutoff frequency caused by interchain interactions, such as the dipolar interaction between the spin solitons, etc.[23] The second term represents the thermal activation with $T_{\perp}=E_{\perp}/k_{\rm B}=150$ K, which is a similar magnitude to the spin excitation gap $E_{\rm SP}/k_{\rm B}=230\pm30$ K below $T_{\rm SP}$ (Fig. 1). This interesting coincidence suggests for the cutoff mechanism to be the exchange interaction between the spin soliton and the thermally excited dimer soliton, but not actual hopping. The interchain exchange interaction would be proportional to the number of excited spin solitons, as represented by the second term in Eq. (3), since the number of excited solitons governs the frequency to meet each other. Besides, π-electron-vacant, spinless solitons on the neighbor chains are inevitable for the interchain hopping of spin solitons to avoid the expense of the Coulomb repulsion energy U. They, however, could not be created by the thermal dissociation of the tetramers nearby $T_{\rm SP}$. Meanwhile, $A_{\perp}/\hbar\approx0.5$ meV below 30 K provides us only the upper bound for the exchange interaction which is consistent with the reported Curie-Weiss temperature Θ of less than 1 K.[4] This figure is naturally ascribed to the interchain exchange interaction between the spin solitons whose concentration is 0.9%.

Finally, we discuss an effect of delocalization of the spin soliton. It is known that the frequency spectrum of Q1D motion for the solitons with finite extent is modified to an approximate expression[7,19,23] $\phi(\omega)=1/\sqrt{2D_{//}\omega}-0.33L_{\rm eff}/D_{//}$ valid at $\omega_0>\omega>D_{\perp}$, where $L_{\rm eff}$ is the effective soliton extent measured by the number of tetramers, which approximately equals the actual extent L for $L\geqslant5$ and $\omega_0=5D_{//}/L^2_{\rm eff}$. To be exact, $\phi(\omega)$ gradually loses its frequency dependence above ω_0, where the displacement for the Larmor period is too small compared with the soliton extent to produce a sizable variation of the local field. This effect becomes pronounced at the lowest temperature, where $D_{//}$ becomes smallest, as demonstrated in t-$(\rm CH)_x$.[19] With $D_{//}\approx6\times10^{8}$ rad/s at 4.2 K, $f_0=\omega_0/2\pi\approx4.5\times10^{8}/L^2_{\rm eff}$ MHz is obtained, which corresponds to $1/\sqrt{f_0}\approx0.046$ $\rm MHz^{-1/2}$ for $L_{\rm eff}=1$ or $L\approx1.6$. Compared with Fig.

2, this value seems to be acceptable as a maximum, but not for $L_{\mathrm{eff}}=2$ or $1/\sqrt{f_0}\approx 0.09$ $\mathrm{MHz}^{-1/2}$. Therefore, it is concluded that the spin soliton in $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ is localized in a tetramer.

A coexistence of the spin-Peierls distortion and the AF long-range ordering has been found in the inorganic spin-Peierls system $CuGeO_3$ with impurities such as Si or Zn,[8–11] where the required impurity concentration is around 1% for several K of T_{SP}. Although it is a similar concentration to that for the present spin solitons, no AF long-range ordering, but $\Theta<1$ K, was found so far. According to the model where a 3D ordering of alternating magnetization of the spin soliton is the origin of the observed AF ordering in $CuGeO_3$, the well-localized spin soliton in $(\mathrm{DMe\text{-}DCNQI})_2\mathrm{Li}$ should play a key role in the missing AF long-range ordering, along with the weak interchain exchange interaction less than 0.5 meV at 4.2 K. It is suggested theoretically that the exchange interaction between the second-neighbor spins in a chain would cause a small extent for the spin soliton and could enhance T_{SP},[13] which provides a consistent picture with the present experimental data, in comparison with the case of $CuGeO_3$.

In conclusion, we demonstrated that the Curie susceptibility observed below T_{SP} is of the spin solitons arising from the effective finite chain lengths. The diffusion mechanism below 30 K was concluded to be the same as that in $t\text{-}(\mathrm{CH})_x$, but a strong enhancement was observed above it. The cutoff frequency is dominated by the exchange interaction between the spin solitons. The extent of the spin soliton was estimated to be less than several molecules.

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[1] T. Yamamoto, H. Tajima, J. Yamaura, S. Aonuma, and R. Kato, J. Phys. Soc. Jpn. **68**, 1384 (1999).
[2] R. Moret, P. Erk, S. Hunig, and J. U. von Schutz, J. Phys. A **49**, 1925 (1988).
[3] K. Hiraki and K. Kanoda, Phys. Rev. Lett. **80**, 4737 (1998).
[4] T. Yamamoto, H. Tajima, and R. Kato, Solid State Commun. **114**, 281 (2000).
[5] R. T. Henriques, S. Tomic, W. Kang, D. Jerome, F. Brisset, P. Batail, P. Erk, S. Hunig, and J. U. von Schutz, Synth. Met. **27**, B333 (1988).
[6] K. Mizoguchi, S. Masubuchi, K. Kume, K. Akagi, and H. Shirakawa, Phys. Rev. B **51**, 8864 (1995). Supply a missing coefficient $c_{//}$ in Eqs. (3), (4), (10), and (11) in this reference, as appeared in Eq. (1).
[7] K. Mizoguchi and S. Kuroda, in *Conductive Polymers: Spectroscopy and Physical Properties*, edited by H. S. Nalwa (Wiley, Sussex, 1997), Vol. 3, p. 251.
[8] L. P. Regnault, M. Ain, B. Hennion, G. Dhalenne, and A. Revcolevschi, Phys. Rev. B **53**, 5579 (1996).
[9] Y. Sasago, N. Koide, K. Uchinokura, M. C. Martin, M. Hase, K. Hirota, and G. Shirane, Phys. Rev. B **54**, R6835 (1996).
[10] M. Weiden, R. Hauptmann, W. Richter, C. Geibel, P. Hellmann, M. Koppen, F. Steglich, M. Fischer, P. Lemmens, G. Guntherodt, A. Krimmel, and G. Nieva, Phys. Rev. B **55**, 15 067 (1997).
[11] A. K. Hassan, L. A. Pardi, G. B. Martins, G. Cao, and L.-C. Brunel, Phys. Rev. Lett. **80**, 1984 (1998).
[12] W. Bietsch, J. U. von Schutz, and H. C. Wolf, Appl. Magn. Reson. **7**, 271 (1994).
[13] M. Ohira, Master thesis, Osaka City University, 2001.
[14] R. Kato, H. Kobayashi, A. Kobayashi, T. Mori, and H. Inokuchi, Chem. Lett. **1987**, 1579 (1987).
[15] K. Murata, H. Yoshino, H. O. Yadav, Y. Honda, and N. Shirakawa, Rev. Sci. Instrum. **68**, 2490 (1997).
[16] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, 1961).
[17] C. A. Sholl, J. Phys. C **14**, 447 (1981).
[18] R. Kato, H. Kobayashi, A. Kobayashi, T. Mori, and H. Inokuchi, Synth. Met. **27**, B263 (1988).
[19] M. Nechtschein, F. Devreux, F. Genoud, M. Guglielmi, and K. Holczer, Phys. Rev. B **27**, 61 (1983).
[20] Y. Wada, Prog. Theor. Phys. Suppl. **113**, 1 (1993).
[21] S. Jeyadev and E. M. Conwell, Phys. Rev. B **36**, 3284 (1987).
[22] M. Bair, J. U. von Schutz, H. C. Wolf, P. Erk, H. Meixner, and S. Hunig, Synth. Met. **41-43**, 1801 (1991).
[23] F. Devreux, Phys. Rev. B **25**, 6609 (1982).