

Spin density distribution and electronic states in $(\text{DMe-DCNQi})_2M$ ($M=\text{Li, Ag, Cu}$) from high-resolution solid-state NMR

Yukie Shinohara and Shigeo Kazama

Department of Physics, Chuo University, Bunkyo-ku, Tokyo 112-8557, Japan

Kenji Mizoguchi,* Maki Hiraoka,† and Hirokazu Sakamoto

Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

Shin-ichi Masubuchi

Department of Physics, Tokyo Medical University, Shinjuku-ku, Tokyo 160-8402, Japan

Reizo Kato

RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan

Koichi Hiraki and Toshihiro Takahashi

Department of Physics, Gakushuin University, Toshima-ku, Tokyo 171-8588, Japan

(Received 2 May 2006; revised manuscript received 30 March 2007; published 31 July 2007)

We experimentally determined the spin density distribution to investigate the electronic states of the $(\text{DMe-DCNQi})_2M$ systems, where M is Li, Ag, and Cu. The Knight shift is measured with solid-state high-resolution NMR of ^1H and ^{13}C and is analyzed together with the reported ^{15}N data. The Knight shift data at each atom of the DMe-DCNQi molecule give the π -electron spin distribution of the Li salt, which might correspond to the charge distribution in the insulating and localized spin system of the Li salt. The average fraction of the spin susceptibility $\chi_{\text{DCNQi}}/\chi_0$ in the DMe-DCNQi molecule of the Ag and Cu salts relative to that of the Li salt is obtained to be 0.82 and 0.71, respectively. Thus, if the valence of the Ag ion is unity, the DMe-DCNQi molecule of the Ag salt has the missing spin fraction by 0.18. One possible origin of this missing spin is a modification of the lowest unoccupied molecular orbital of the DMe-DCNQi molecule due to the π - d hybridization with the Ag d_{xy} orbitals, which could be one of the origins for the difference of the physical properties from the Li salt, as in the enhancement of the charge hopping rate between the neighboring DMe-DCNQi columns in the Ag salt. In the Cu salt case, the missing spin fraction of 0.29 would correspond to the d -spin hole number of 0.28 of the Cu d_{xy} orbital. Finally, it is stressed that all the present results are consistent with both the first-principles calculation and the X-ray photoelectron spectroscopy study.

DOI: [10.1103/PhysRevB.76.035128](https://doi.org/10.1103/PhysRevB.76.035128)

PACS number(s): 71.45.Lr, 72.80.Le, 73.90.+f, 76.60.Cq

I. INTRODUCTION

The charge transfer salts $(2,5-R_1, R_2\text{-DCNQi})_2M$, where R_1 and R_2 is methyl group or halogen, and M is metal ion such as Li, Ag, or Cu, have attracted much interest in their peculiar physical properties based on the strong electron-electron correlation effects between the molecules. Here, DCNQi is dicyanoquinonediimine. Hereafter, these salts will be abbreviated as $R_1, R_2\text{-}M$ in general or M salt in the DMe- M , for example, DMe-Li or Li salt. Metal ions in the DMe-Li and the DMe-Ag have been known to be monocations providing one electron for two DCNQi molecules, which results in a quarter-filled one-dimensional (1D) π -electron band. Thus, these two salts have been understood as a dimer-type Mott insulator with a phase transition from $4k_F$ charge density wave (CDW) state to a spin-Peierls ground state at about 60 K for the DMe-Li and 80 K for the DMe-Ag.^{1,2} In contrast to these, the DMe-Cu with an average Cu valence of $\approx +4/3$ (Refs. 3 and 4) has a three-dimensional metallic band structure in addition to a 1D band because of a strong π - d hybridization effect. This salt shows a remarkably sharp metal-insulator reentrant transition under the tiny physical pressure much less than 1 kbar or the

chemical pressure caused by partial deuteration of hydrogens in DMe-DCNQi molecule.⁵ In the opposite limit, the Ag salt of diiodo-DCNQi (DI-Ag) has a narrower band width along the DCNQi stacking axis because of a larger ionic radius of iodine anion than that of methyl group, giving rise to an enhanced electronic correlation not only within the molecule but also between the molecules. The Wigner-lattice-type charge disproportionation dominated by the intermolecular Coulomb repulsion has been found in this system by Hiraki and Kanoda with ^{13}C NMR.⁶

There had been a remaining open question in the simple systems, the DMe-Li and the DMe-Ag of the dimer Mott insulators. These salts have insulating electronic states apparently with a small $4k_F$ -CDW gap. However, the charges excited over the gap would still be immobile because of the intradimer repulsive Coulomb interaction of the order of $t + V$, corresponding to the on-site Coulomb interaction U in the half-filled Mott insulators, where t is the transfer integral and V is the intermolecular repulsive Coulomb interaction, within the dimer. Thus, the question is the relatively high dc conductivity of the order of 1–100 S/cm in these *insulating* systems.^{1,7} Recent development in the spin dynamics study with the EPR linewidth depending on the observed fre-

quency between Q (34 GHz) and W (94 GHz) bands revealed that, irrespective of the Coulomb correlation, the charges can move by virtue of the hole solitons created thermally in the $4k_F$ -CDW gap as a pair of a hole soliton and a charged soliton with possible fractional charges of $e/2$ and $-e/2$, respectively.^{8–10}

In the case of the DMe-Li, a situation seems to be the simplest among the DCNQI systems, since the Li monocation has only a closed $1s$ shell, making bondings purely ionic. However, the DMe-Ag has $4d$ electrons which form directional bondings with the nitrogens of DCNQI molecules. Physical properties of the two salts are apparently similar to each other, especially, spin susceptibility, dc conductivity, and structure with the $4k_F$ superlattice scatterings.^{1,2,11–14} In more detail, the DMe-Ag differs from the DMe-Li in several points, such as metallic temperature dependence of the resistivity only in the DMe-Ag around RT, the higher T_{SP} for the DMe-Ag in spite of the longer 1D lattice constant than that of the DMe-Li, and the two peaks of specific heat in the DMe-Ag, in contrast to the single peak in the DMe-Li.¹⁵ One of the possible origins of the differences between the DMe-Li and the DMe-Ag might be the difference of the electronic structures caused by the presence of $4d$ orbitals in the DMe-Ag. For example, on T_{SP} , a d -orbital bonding between Ag ions could enhance the spin-lattice coupling, because the reduced separation of the Ag ions caused by dimerization increases the transfer integral between Ag ions preferable to dimerization, in contrast to the DMe-Li case where the Coulomb repulsion between the neighboring two Li monocations destabilizes dimerization. Furthermore, Miyazaki and co-workers have pointed out the presence of a sizable contribution of $4d$ band at the Fermi energy in the DMe-Ag with first-principles theoretical studies.^{16,17} However, none of the experimental study on this issue has been reported yet.

In this paper, we demonstrate the spin density distribution of the DCNQI molecule in the DMe-Li, and the fraction of the spin susceptibility of the DMe-DCNQI molecule χ_{DCNQI}/χ_0 for the DMe-Ag, and Cu, relative to that of the DMe-Li, using the Knight shifts of ^1H , ^{13}C (the present work), and ^{15}N (from Ref. 18) induced by the spin densities. The obtained spin distribution of the DMe-Li is consistent with that of the charge density estimated by the first-principles studies.^{16,17} The most remarkable point found in this paper is the missing fraction $(\chi_0 - \chi_{DCNQI})/\chi_0 = 0.18$, in the spin susceptibility of the DMe-Ag, relative to that of the DMe-Li case. This observation suggests that the d band should be taken into account to understand the nature of the DMe-Ag correctly.

II. EXPERIMENT

A bundle of small needlelike crystals was used for solid-state high-resolution NMR, and low frequency EPR to estimate the spin susceptibility. The crystals were prepared with the reported techniques.^{5,11} To achieve a definite site assignment for the observed NMR peaks, two deuterated Li salts were prepared; d2-Li and d6-Li, as shown in Fig. 1. The spin susceptibility was measured with a homebuilt EPR-NMR

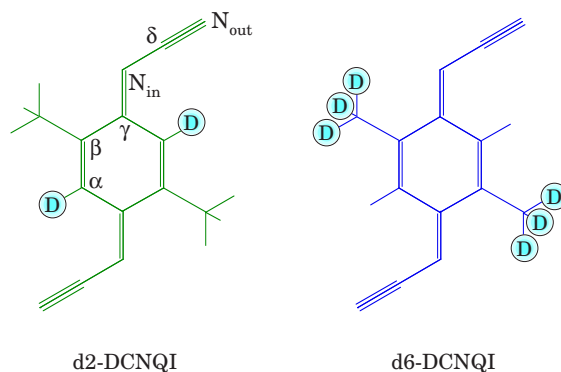


FIG. 1. (Color online) Chemical structures for the partially deuterated DCNQIs; d2-DCNQI and d6-DCNQI. A label is shown to specify each carbon or nitrogen site.

spectrometer at low frequency, typically at 50 MHz. The high-resolution ^1H magic angle spinning (MAS) and ^{13}C cross polarization (CP)/MAS NMR were carried out with Bruker DSX 300 spectrometer at 7 T, corresponding to 300 MHz for ^1H and 75 MHz for ^{13}C . Resonance shift is measured from tetramethylsilane (TMS) standard. Rotor speed was changed from 9 to 11 kHz to discriminate spinning sidebands (SSBs) from NMR signals. For the Ag and Cu salts, the small crystals were mixed into alumina powder to avoid radio frequency sample heating. Actually, without alumina powder crystals of the Ag salt melted after a CP/MAS experiment, resulting in a black melted solid without original electrical conductivity and spin susceptibility. In this paper, we use the terminology of Knight shift as the resonance shift caused by the electron spins.

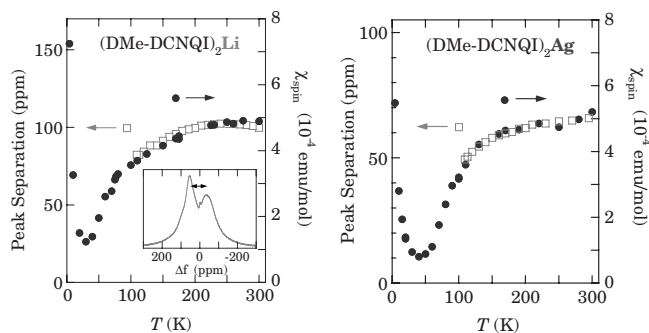


FIG. 2. The peak separation (square) of ^1H NMR doublet, corresponding to the powder patterns of anisotropic Knight shift (Ref. 19) as defined in the inset, along with the spin susceptibility (circle) measured with ESR-NMR technique is plotted as a function of temperature both for the DMe-Li (left) and the DMe-Ag (right). The ESR-NMR technique provides purely the spin susceptibility, independent of diamagnetic contribution (Ref. 20). Note a good coincidence of those, suggesting that the peak separation is dominated by the spin susceptibility. The temperature dependence of the spin susceptibility is dominated by the antiferromagnetic spin-spin correlation between the neighbor molecular dimers in the one-dimensional dimer Mott insulator. The isotropic Knight shifts will be obtained from Figs. 3 and 4 taken with the magic angle spinning (MAS) technique and will be discussed later quantitatively.

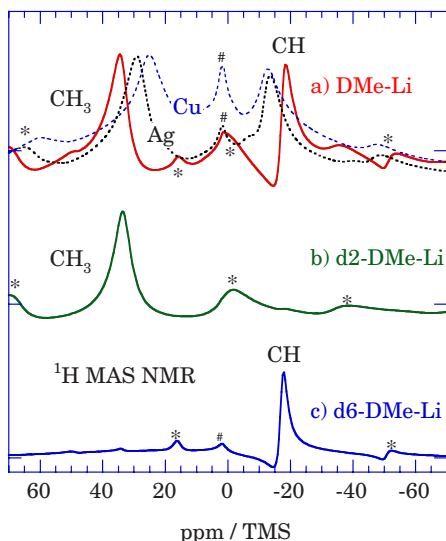


FIG. 3. (Color online) ^1H MAS NMR spectra for the three Li salts with partially deuterated groups, along with the Ag and the Cu salts. The chemical shifts of the neutral DMe-DCNQI molecule are 2 ppm for CH_3 and 7 ppm for CH, as shown in Fig. 4. The observed shifts which are the sum of the chemical shift and the Knight shift are much larger than the chemical shifts of the neutral molecule. Signs of the shifts in the CH_3 and CH peaks are opposite to each other because of the opposite sign of the coupling constants, see the text for details. Note that the negative shift (right hand side) corresponds to the high magnetic field. The marks * and # represent spinning sidebands (SSBs) and impurity signals, respectively.

III. RESULTS AND DISCUSSION

A. ^1H NMR (Reference 21)

All the observed proton NMR spectra in the M (M is Li, Ag, or Cu) salt consist of two peaks with the negative (high field) and the positive (low field) shifts. Figure 2 demonstrates that the temperature dependence of the peak separation is proportional to the spin susceptibility. These peaks originated from the powder patterns of the anisotropic Knight shift for the protons of CH and CH_3 , which is a sum of the isotropic and the anisotropic shifts, along with the chemical shift in Fig. 4. Thus, these separations are approximately proportional to the local spin susceptibility of the π -electron density at the corresponding carbon site but are not suitable for a quantitative analysis. The good coincidence above 100 K in Fig. 2 suggests that the spin density distribution is approximately independent of the temperature in this range. This observation is accountable from the consideration that the wave function, that is, the probability density distribution of the π -electron molecular orbital, is determined by the intramolecular Coulomb interaction energy between the π electron and the ion charges of the molecule which is much larger than $k_B T$. Surely, the wave function might be modified in part by the intermolecular Coulomb interaction which depends on the crystal structure. Assignment of each peak is carried out by comparison with the MAS spectra of the deuterated samples, d2- and d6-Li in Fig. 3; the peak with the negative shift corresponds to the α proton in the C-H bond and the positively shifted peak is as-

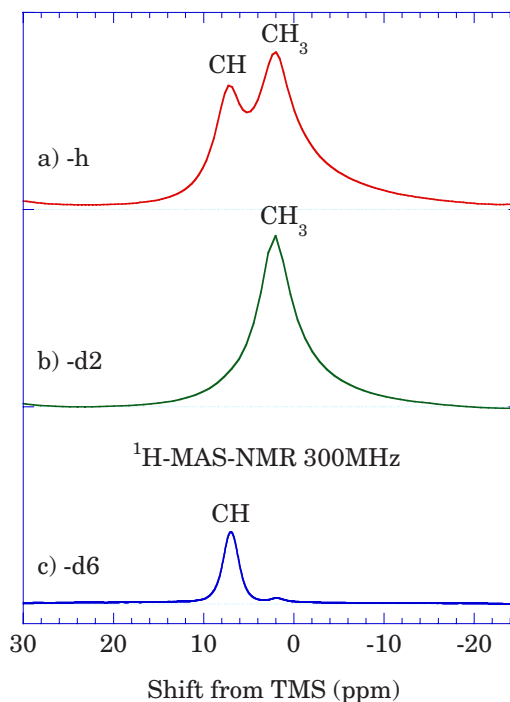


FIG. 4. (Color online) ^1H MAS NMR spectra for the neutral DMe-DCNQI molecules with two deuterated moieties, d2- and d6-DCNQI's.

signed to the β methyl protons. The ^1H NMR Knight shift is measured from the chemical shifts of the neutral molecules; 7 ppm for the α proton and 2 ppm for the β proton, as shown in Fig. 4. There are some advantageous points in evaluation of the spin densities with ^1H NMR; (1) The π -electron densities at the proton and the methyl-carbon sites are negligibly small, (2) the chemical shift of proton is very small, and (3) then, the ^1H NMR shift usually reflects mainly the π -electron spin density, i.e., Knight shift at the aromatic carbon atom. A MAS NMR spectrum reflects only the isotropic Knight shift, since the anisotropic part is averaged by the magic angle spinning.²² It is known that the isotropic part of the hyperfine coupling constant $2A_{hf}^{iso}/2\pi\hbar = -69.8$ and 71.0 MHz for the α proton in C-H bond and the β proton in methyl group, respectively, deduced from the EPR splittings caused by the coupled proton nuclear spins.²³ Here, note the opposite signs for these coupling constants caused by the different magnetization transfer mechanism,²³ and the prefactor of 2, corresponding to the EPR splitting, that is, the difference between the local fields by the nuclei with spin up and down. With the interaction energy $\mathcal{H} = A_i \mathbf{S} \cdot \mathbf{I}_i$, where A_i is the hyperfine coupling energy, \mathbf{S} the electron spin, and \mathbf{I}_i the i nuclear spin, the Knight shift K_i of the i nucleus is obtained as

$$K_i = \frac{\Delta H}{H_0} = \frac{A_i \langle S_z \rangle_i}{\gamma_i \hbar H_0} = \frac{A_i}{\gamma_i \gamma_e \hbar^2} \frac{\chi_i}{2N_A}, \quad (1)$$

where $\chi_i = 2N_A \gamma_e \hbar \langle S_z \rangle_i / H_0$ is the local spin susceptibility of the i nucleus, ΔH the resonance field shift from H_0 with no π -electron spin, γ_i the gyromagnetic ratio for the i nucleus,

TABLE I. The total spin susceptibilities of one mole of (DMe-DCNQI)₂M at RT for the three salts. Note that the same values are used for the analysis of the charge transfer, see the text for details.

	Li	Ag	Cu ^a
χ_{spin} (emu/mol)	4.90×10^{-4}	5.0×10^{-4}	5.1×10^{-4}

^aReference 18.

γ_e for the electron, $\langle S_z \rangle_i$ the expectation value of the electron spin at the i nucleus, and \hbar the Planck constant. Here, note that χ is measured per one (DMe-DCNQI)₂M unit. In this paper, the fraction of the π -electron spin susceptibility $n_\pi(i)$ is defined by the ratio χ_i/χ_0 , where χ_0 is the total spin susceptibility. Then, the observed Knight shift is written by the fraction of the π -electron spin susceptibility $n_\pi(i)$ as

$$K_i = \frac{A_i}{\gamma_i \gamma_e \hbar^2} \frac{\chi_0}{2N_A} n_\pi(i). \quad (2)$$

Thus, we can deduce the fraction of the π -spin susceptibility at the i site of the DMe-DCNQI molecule with Eq. (2) and $\chi_0 = 4.90 \times 10^{-4}$ emu/mol (Fig. 2) at RT for the Li salt, provided that the Li ion is fully ionized. The total spin susceptibility is shown in Fig. 2 and in Table I for the other salts. The small scattering is found between the salts. Possible sources of the scattering are (1) the difference in the charge transfer from the metal ion to the DMe-DCNQI molecules, combined with (2) the difference in the magnetic interaction within the DCNQI column or the metal ion column, and (3) systematic errors of the measurements. Actually, it is known that the d -spin susceptibility of the metal ion column strongly depends on the temperature, but the π -spin susceptibility is almost independent of the temperature, as demonstrated by the independent estimation of the d -spin susceptibility in the Cu salt.¹⁸

The obtained Knight shifts are summarized in Table II. It is interesting to note that the Knight shift of ¹H NMR shows a definite tendency to decrease from the Li to the Cu salt. This tendency is also valid in the other data sets of ¹³C and ¹⁵N NMR.¹⁸

B. ¹³C NMR

The ¹H NMR analysis of the π -electron fraction has some advantage over the ¹³C NMR case, as mentioned in the previous section. The best point in ¹H case is simplicity, but a number of available ¹H sites are limited by the molecular structure. This means that, ¹³C NMR in the organic substances could be advantageous (surely, this could be disadvantage, too; requires complex site assignment) if the Knight shift were enough larger than the chemical shift which is usually ten times larger than that of ¹H NMR. Thus, it is important to subtract the chemical shift from the observed shift to extract the Knight shift by using the shift of neutral molecules where there exist no π -electron spins which produce the Knight shift. In some cases, however, it should be considered how the charge transfer affects the chemical shift.

TABLE II. The Knight shift of each nucleus of the DCNQI molecule in the Li, Ag, or Cu salt, relative to the chemical shift of the neutral DMe-DCNQI molecule. The ratio of the Knight shifts for the Ag and Cu salts against that of the Li salt is shown in the parentheses. Note that the π -charge density at the carbon site with asterisk mainly dominates the observed Knight shift. The second row for the ¹H nucleus represents the Knight shifts corrected for the induced chemical shift, -3 ppm. See Sec. III D for details.

Nucleus	Nuclear site	Knight shift (ppm)		
		Li salt	Ag salt	Cu salt
¹ H	C*-H(α)	-25	-20.5 (0.82)	-19.5 (0.78)
	C*-H (corr)	-22	-17.5 (0.80)	-16.5 (0.75)
	C*-CH ₃	32	27 (0.84)	23 (0.72)
¹³ C	C-H(α)	-48.4	-42.4 (0.88)	-29.4 (0.61)
	C=N(δ)	-454	-342 (0.75)	-289 (0.64)
	C*- ¹³ CH ₃	-64.1	-52.9 (0.83)	-45.4 (0.71)
¹⁵ N ^a	N ^{out} _{aniso}	500		370 (0.74)
	N ⁱⁿ _{aniso}	780		580 (0.74)
Ratio		1.00	0.82	0.71

^aThe figures for ¹⁵N are anisotropic Knight shift reported by Miyagawa *et al.* (Ref. 18).

1. Neutral DCNQI

Figure 5 shows the ¹³C CP/MAS NMR spectra for the three DMe-DCNQI molecules. Five peaks are found corresponding to the five chemically different carbon sites of the neutral DMe-DCNQI molecule, as labeled in Fig. 1. The labels represent the assignment of peaks on the basis of the observed modification by CP, deuteration, and so on. The expected effects of the deuteration are (1) a loss of intensity enhancement due to the CP from ¹H nuclear magnetization to ¹³C and (2) a loss of some line broadening caused by proton nuclear dipole moments. Here, note that the peaks without the CP effects by the deuteration, the “CD₃” in the d6 spectrum, and the “ α ” in the d2 spectrum in Fig. 5 have the weaker integrated intensity and the narrower linewidth than the other two spectra with the CP effect. The peak assigned to “CN” shows asymmetric line shape which is typical of a ¹⁴N cyanocarbon with $S=1$. Thus, the two leftmost peaks should correspond to the β and γ sites. These carbons have no nearby protons and could not be assigned by these effects. Thus, we tried to assign them on the basis of a database with a pretty good dependence of the ¹³C chemical shifts on the variety of chemical bondings.²⁴ The present assignment of the ¹³C chemical shifts for the neutral DMe-DCNQI molecule agrees with that reported by Köngeter *et al.*²⁵ The assigned chemical shifts of the neutral DMe-DCNQI are summarized in Table III.

2. (DMe-DCNQI)₂Li

Figure 6 shows the spectra for the three Li salts. The same policy as the neutral molecules is applied to the site assign-

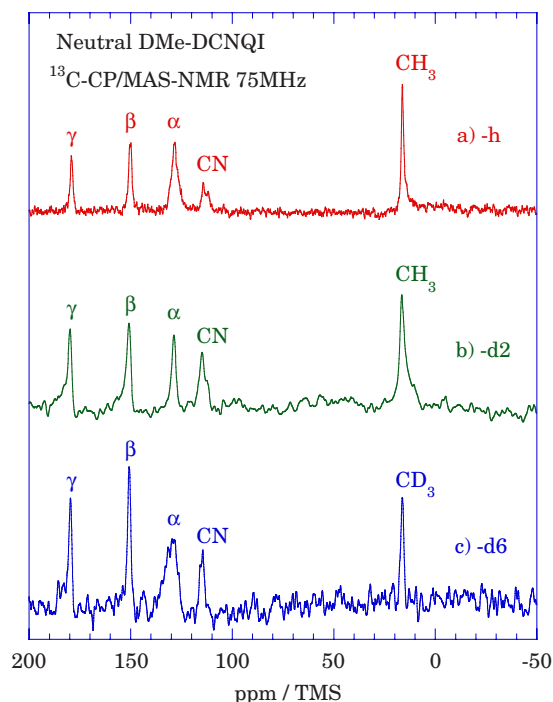


FIG. 5. (Color online) ^{13}C CP/MAS NMR spectra in the neutral DMe-DCNQI, DMe-DCNQI(d2), and DMe(d6)-DCNQI molecules, which helps us to assign each peak to a corresponding carbon site. See the text for details.

ment for these spectra. The rightmost asymmetric peak is assigned to the cyanocarbon. The deuteration helps us assign the methyl carbon to the second rightmost peak, the smallest in the d6 spectrum, and the α carbon should correspond to the third leftmost peak which is extremely narrow in the d2 spectrum. The present assignment is consistent with the reported result by Helmle *et al.*²⁶ Unfortunately, the two leftmost peaks cannot be assigned by the present policy. Then, hereafter, we do not try to analyze these two peaks because of this ambiguity and relatively small possible Knight shifts. Unlike the simplicity of the ^1H NMR analysis, the hyperfine field felt by the carbon nucleus is quite complicated.²³ The reason is the multiple interaction paths with the π electrons on the carbon itself and the neighboring carbons and/or nitrogens. The π -electron spin polarizes $1s$ and $2s$ electron cores with two interaction paths through the exchange interaction. One is the direct path from π orbital to $1s$ or $2s$ orbital, $A_{\text{dir}}^{\text{C}} = S^{\text{C}} \rho_{\pi}^{\text{C}}$, and the other is the indirect one from π to three σ orbitals and then to s cores, $A_{\text{indir}}^{\text{C}} = Q_{\text{CX}}^{\text{C}} \rho_{\pi}^{\text{C}}$, where the C represents carbon atom and the X the bonding atom, car-

TABLE III. The chemical shift for the neutral DMe-DCNQI molecule in Fig. 5.

Chemical shift (ppm)				
α	β	γ	$\delta(\text{CN})$	CH_3
128.4	150.2	179.3	114.0	16.4

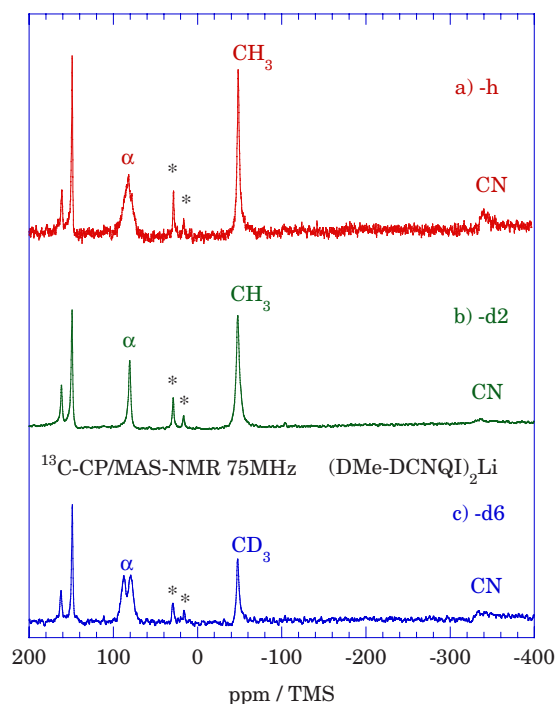


FIG. 6. (Color online) ^{13}C CP/MAS NMR spectra in $(\text{DMe-DCNQI})_2\text{Li}$. The partially deuterated spectra make it possible to assign CH_3 and α proton sites from the signal intensity and linewidth. The asterisk marks represent the spinning sidebands (SSBs). See the text for details.

bon, nitrogen, etc. The third path is the π orbitals of the neighboring atoms which polarize the σ orbital and then the s cores, $A_{\text{indirX}}^{\text{C}} = Q_{\text{XC}}^{\text{C}} \rho_{\pi}^{\text{X}}$. The signs of these couplings are estimated to be negative for S^{C} and positive for Q 's with comparable magnitudes to each other.²³

Thus, it is almost impossible to estimate the π -electron spin densities accurately with the analysis of the ^{13}C Knight shifts, since the delicate balance of these couplings controls the total coupling constant, even in its sign, positive or negative. Therefore, we treat only the ratio of the Knight shift between the Li salt and the other salts, provided that the distribution function of π electron on the DMe-DCNQI molecule is independent of a species of the metal ions. To this purpose, the averages of the ratios listed in Table II will be utilized to discuss the missing local spin susceptibility of the DCNQI molecule in these salts.

A characteristic point of Fig. 6 or Table II is that the largest negative (high field) deviation is found in the CN peak. The tricky reason of this large shift is the absence of the hyperfine field cancellation through the multiple coupling paths. The local field at the $\text{N}-\text{C}\equiv\text{N}$ carbon site is additively produced by the π -electron spins on both the neighboring nitrogen atoms because of the small π -electron density on the CN carbon atom itself.¹⁷

3. Ag and Cu salts

Figure 7 shows the CP/MAS spectra for the Li, Ag, and Cu salts, together with the chemical shifts of the neutral DMe-DCNQI molecule for comparison. Note that the same

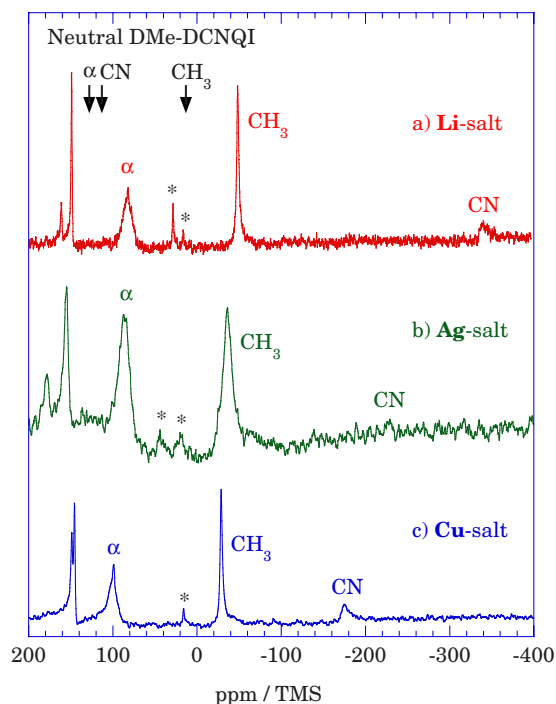


FIG. 7. (Color online) ^{13}C CP/MAS NMR spectra for $(\text{DMe-DCNQI})_2M$. Here, M is Li, Ag, and Cu. The shifts for the neutral DMe-DCNQI molecule are indicated by the arrows.

tendency as in the ^1H NMR case of Fig. 3 is found; the largest Knight shift in the Li salts and the smallest in the Cu salts, typically in the CN peaks. Since these salts carry the spin susceptibility of the same orders of magnitude as listed in Table I, it is suggested that the number of spins on the DMe-DCNQI molecule is smaller in the Ag salt than in the Li salt and the smallest in the Cu salt. Generally, it should be considered that the chemical shift could be affected by the π -electron charge transfer to the DMe-DCNQI molecule. Fortunately, it is expected that the CN spectra contain the smallest effect caused by the charge transfer, since the CN-carbon site has small π -electron density suitable for the origin of the chemical shift. Actually, the estimated Knight shift of 454 ppm (Table II) at RT relative to that of the neutral DMe-DCNQI molecule agrees well with 465 ± 10 ppm determined relative to the zero Knight shift in the spin-Peierls state below 50 K.¹⁸ This means that the Knight shift at the “ CH_3 ” site with low π charge density¹⁷ could also provide good ratios for the π -electron spin fraction at the aromatic carbon, “ $\text{C}-\text{CH}_3$ ” site. In contrast, that of α site (“ CH ”) could be affected with the chemical shift change due to the π -charge transfer from the metal ions.

Contrary to these three sites, CN, CH_3 , and CH, no such systematic tendency is found in the rest of the sites, “ β ” and “ γ .” This might result from a metal ion dependence of the charge distribution which causes the change of the hyperfine field standing on a delicate balance of the multiple path interactions, as discussed in Sec. III B 2.

C. ^{15}N NMR (Reference 18)

Estimation of the π -electron spin fraction at the nitrogen sites is important to determine the distribution of the local

π -spin susceptibility of the $(\text{DMe-DCNQI})_2M$ systems. To this purpose, we analyzed the reported data of ^{15}N NMR by Miyagawa *et al.*¹⁸ The isotropic hyperfine interaction of the ^{15}N is greatly complicated than that of the carbons and is difficult to give a systematic interpretation because of the unshared electron pair in the valence shell of the nitrogen. It is known that the extent of the s - σ hybridization strongly depends on the molecular systems.²³ On the other hand, fortunately, the anisotropic hyperfine coupling of the dipolar field produced by the π orbital can be utilized as a reliable analysis of the spin density instead of the isotropic one.

Miyagawa *et al.* reported the ^{15}N NMR spectrum broadened more than 1000 ppm at 80 K and the temperature dependences of the isotropic and anisotropic Knight shifts in the systematic study of the ^{15}N enriched $(\text{DMe-DCNQI})_2M$ ($M=\text{Li}$ and Cu) systems.¹⁸ In Table II, the anisotropic Knight shifts are listed for both the nitrogen sites of the Li and Cu salts. Thus, we can estimate the π -electron fraction at both the nitrogen sites with the anisotropic hyperfine coupling constant of the ^{15}N known to be $B_{hf}^{aniso}/2\pi\hbar=67$ MHz.²³

D. π -electron spin distribution

We can estimate the π -electron spin fraction at the α - and β -carbon sites and the two “in-nitrogen” and “out-nitrogen” sites with the isotropic Knight shifts of the ^1H NMR and the anisotropic one of the ^{15}N NMR, respectively, and Eq. (2). The Knight shifts of the ^{13}C NMR will not be discussed here but are utilized as the ratio only for comparison of the local spin susceptibility of the DMe-DCNQI molecule between the salts. The estimated fraction of the π -electron spin is listed in Table IV. To estimate the $n_\pi(i)$ for the γ and the “ δ ” sites which are not available in Table IV, we assumed that the valence of the Li ion is +1, that is, the whole spin susceptibility χ_0 resides on the DMe-DCNQI molecule. Thus, $n_\pi(\gamma + \delta) = (1 - 2n_\pi[\alpha + \beta + N_{in} + N_{out} + (\text{H} + \text{CH}_3)]) / 2 = 0.15$ does hold. Since the $n_\pi[\delta + (\text{H} + \text{CH}_3)]$ is reported to be small,¹⁷ we assumed $n_\pi(\gamma) = 0.15$ and zero for the rest in the Li salt. Figure 8 represents the obtained π -electron spin distribution $n_\pi(i)$ which is proportional to the area of the circles. It is interesting to note that the result is quite similar to the distribution of the π -electron density obtained by the first-principles calculation,¹⁷ except for the smaller fraction of the spin susceptibility $n_\pi(N_{out})$. The other characteristic point is that almost 50% of the π -electron spin locates in the $\text{C}=\text{N}_{in}$ double bonds. These features are similar to that of the DBr-DCNQI molecule calculated on the HF/STO-3G level.²⁷ To our knowledge, there is no systematic experimental determination of the π -electron spin distribution in this system to compare with the present result.

Finally, we discuss the possible contribution of the induced chemical shift caused by the π -charge injection to DMe-DCNQI molecule. This issue is always present in the quantitative estimation of the Knight shift. In the ^1H NMR case, the chemical shift is less than 10 ppm in almost cases, except for the $\text{C}-\text{OH}$ bonds which might give less than 20 ppm. The order of -6 ppm/electron of the induced chemical shift is suggested from our study on the ^1H NMR of the $\text{C}-\text{H}$ group in the K-TCNQ system where one electron

TABLE IV. The estimated π -electron spin fraction $n_{\pi}(i)$ at the i -carbon site in $(\text{DMe-DCNQI})_2\text{Li}$, derived from the Knight shift K_i , the isotropic A_{hf} and anisotropic B_{hf} hyperfine coupling constants, and the spin susceptibility χ_0 in Table I with Eq. (2). The column “corrected” represents the induced chemical shift correction. See Sec. III D for details.

	Isotropic ^1H		Anisotropic ^{15}N	
	$\alpha(\text{C}^*\text{H})$	$\beta(\text{C}^*-\text{CH}_3)$	N_{in}	N_{out}
K_i (ppm)	-25	32	500 ^a	780 ^a
Corrected	-22			
$A_{hf}^i/2\pi\hbar$ (MHz) ^b	-69.8	71.0		
$B_{hf}^i/2\pi\hbar$ (MHz) ^b			67	
$n_{\pi}(i)$	0.072	0.088	0.114	0.074
Corrected	0.064			

^aReference 18.

^bReference 23.

transfers from the K to the TCNQ molecule. If this is the case in the present study with 0.5 electrons in DMe-DCNQI molecule, the order of -3 ppm of the induced chemical shift might be subtracted from the Knight shift for $\text{C}-^1\text{H}$ site of the three salts in Table II. This would correspond to around -10% of the deviation in the α carbon of the $\text{C}-\text{H}$ group as shown in Table IV, which suppresses the $n_{\pi}(\alpha)$ and enhances the $n_{\pi}(\gamma)$. The anisotropic Knight shift of ^{15}N NMR is not affected by the chemical shift, since it originates from the electron dipolar field. Thus, in total, the induced chemical shift might cause the order of $+5\%$ error in the $n_{\pi}(\gamma)$.

E. Missing π -spin susceptibility of DMe-DCNQI molecules

In this section, we focus on the missing fraction $(\chi_0 - \chi_{\text{DCNQI}})/\chi_0$ of the spin susceptibility in the Ag and Cu salts, using the average ratios of the Knight shifts relative to that of the Li salt in Table II. In this paper, we assume the charge

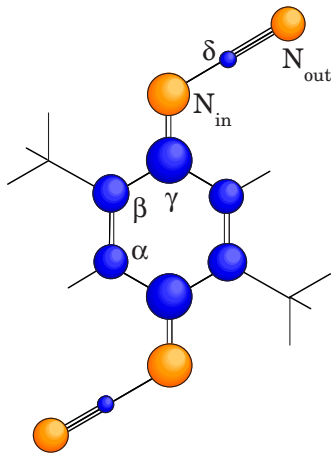


FIG. 8. (Color online) The π -electron spin distribution of $(\text{DMe-DCNQI})_2\text{Li}$ molecule, determined with the observed Knight shifts. Area of circles represents the π -electron spin fraction at a carbon (blue) or a nitrogen (ocher) site.

transfer of one electron from the Li to the two DCNQI molecules in the Li salt.

The average Knight shift ratio of 0.71 relative to that of the Li salt is obtained for the Cu salt, as shown in Table II. Taking account of the total spin susceptibility nearly independent of the salts with Li, Ag, and Cu as shown in Table I, this fraction of 0.71 less than unity means the presence of the missing fraction $(\chi_0 - \chi_{\text{DCNQI}})/\chi_0 = 0.29$ for the spin susceptibility of the DMe-DCNQI molecule in the Cu salt. This figure can be compared with the 0.28 holes in the Cu d orbital derived from the x-ray photoelectron spectroscopy (XPS) study,^{4,5} which has been understood in relation to the CDW state of $\text{Cu}^+-\text{Cu}^+-\text{Cu}^{2+}$ periodic sequence.⁵ It has been pointed out that the deviation of the observed number of 1.28 from $4/3 \approx 1.33$ expected for the CDW state stabilizes the metallic states down to low temperatures. Thus, we conclude that the missing fraction of 0.29 from the DMe-DCNQI molecule in the spin susceptibility is ascribable to the spin susceptibility of the 0.28 hole in the Cu d orbital, as reported with the NMR analysis.¹⁸

In the Ag salt, the ratio of 0.82 is obtained. This figure is significantly smaller than the unity for the Li salt, which is expected for the spin-Peierls ground state along the c axis below ≈ 80 K.^{8,9} However, the first-principles calculation by Miyazaki and co-workers reported the charge state of Ag to be 1.19 because of the weak π - d hybridization, while its formal value is unity.^{16,17} Thus, it is interesting to compare the missing fraction from the DCNQI molecule $(\chi_0 - \chi_{\text{DCNQI}})/\chi_0 = 0.18$ with the difference from the formal charge state. This observation suggests that the missing spin susceptibility is caused by the modification of the π -electron wave function of the molecular orbital due to the weak but finite π - d hybridization effect in the $(\text{DMe-DCNQI})_2\text{Ag}$. One possible interpretation of the missing susceptibility is that the largest change induced by the π - d hybridization locates in between the outer nitrogen and the Ag ion. As a result, both of the π electron on the DMe-DCNQI molecule and the d_{xy} electron reduce their amplitude by 0.18–0.19. This scenario is consistent with the fourfold periodicity of the nesting vector in the π band by the first-principles calculation.^{16,17}

The other possible interpretation is the actual charge transfer by 0.18–0.19 electrons from the Ag d_{xy} orbital to the π band of the DMe-DCNQI molecule, which provides the net number of 0.82 spins on the DMe-DCNQI molecule, consistent with the present experimental observation. However, in this case, the $2k_F$ nesting condition required for the established spin-Peierls ground state below 80 K is not fulfilled. One possibility is a temperature dependence of the charge transfer from the Ag ion; the charge transfer of 0.18 at 300 K changes to 0.0 around 100 K where the $4k_F$ diffuse scattering changes into the satellite reflections.² In contrast, however, the recent study on the electronic states of the Li and Ag salts deduced from the frequency dependence of EPR linewidth is consistent with the presence of the $4k_F$ Peierls gap resulting in the dimer Mott insulating state of this salt even above 80 K.^{9,10} In this context, the $4k_F$ satellite reflections fade into the diffuse scattering because of the thermal excitation of the spin and hole soliton pairs from the DCNQI dimers.^{9,10} The hole solitons provide the hole sites essential for the intercolumn charge transport in the strongly correlated dimer Mott systems which carry a relatively high electrical conductivity from 1 to 100 S/cm.¹ Thus, the band near the Fermi energy should be filled up to a quarter, whereas the DCNQI molecule has apparently 0.82 π electrons, as fulfilled in the first possible scenario.

Thus, it is suggested that the π - d hybridization effect should be taken into account for the physical properties of this system, as observed in the strongly enhanced charge hopping rate between the neighboring DMe-DCNQI columns via the Ag ion in the Ag salt more than that via the Li ion in the Li salt.^{9,10}

IV. CONCLUSION

The π -electron spin distribution of the DCNQI molecule in the Li salts is determined experimentally. The result is

consistent with the charge density distribution predicted by the first-principles calculation reported by Miyazaki and co-workers.^{16,17} The fraction of the spin susceptibility at the several carbon and nitrogen sites of the Li salt is compared with that in the Ag and Cu salts. The definite differences from the Li salt are found in the average fraction of the local spin susceptibility, which are consistent with the reports on the XPS study^{4,5} and the calculation.^{16,17} This good consistency with the two experimental studies and the theoretical prediction strongly supports the finite hybridization between the DCNQI π band and the Ag d band, which is not recognized well because of really similar physical properties of the Li and the Ag salts, in strong contrast to the Cu salt case. The apparent metallic temperature dependence of the conductivity in the Ag salt can be well accounted for with the present conclusion of the finite d - π hybridization. That is, the recent spin dynamics study with the frequency dependent EPR linewidth proportional to the number of thermally activated hole solitons successfully and systematically reproduces the observed temperature dependence of the conductivity for both the salts.^{9,10,28} The Knight shift of ¹⁰⁹Ag NMR and the x-ray analysis of the charge distribution help to confirm the proposed scenario, which is planned in the near future.

ACKNOWLEDGMENTS

One of the authors (K.M.) would like to thank Hidetoshi Fukuyama, Hiroshi Sawa, Toshio Naito, and Hiroshi M. Yamamoto for valuable discussions on the Ag salts and Atsushi Kawamoto for useful comments on the induced chemical shift. This work was supported by MEXT KAKENHI on Priority Areas (17067015) and (16038220), and by JSPS KAKENHI (C) (17540334) and (17540332).

*mizoguchi@phys.metro-u.ac.jp; URL: <http://spinman.phys.metro-u.ac.jp>

†maki-hiraoka@aist.go.jp

¹T. Yamamoto, H. Tajima, J. Yamaura, S. Aonuma, and R. Kato, *J. Phys. Soc. Jpn.* **68**, 1384 (1999).

²R. Moret, P. Erk, S. Hunig, and J. U. von Schutz, *J. Phys. (Paris)* **49**, 1925 (1988).

³I. H. Inoue, A. Kakizaki, H. Namatame, A. Fujimori, A. Kobayashi, R. Kato, and H. Kobayashi, *Phys. Rev. B* **45**, 5828 (1992).

⁴A. Tanaka, A. Chainani, T. Yokoya, T. Takahashi, T. Miyazaki, S. Hasegawa, and T. Mori, *Phys. Rev. B* **52**, 7951 (1995).

⁵R. Kato, *Bull. Chem. Soc. Jpn.* **73**, 515 (2000).

⁶K. Hiraki and K. Kanoda, *Phys. Rev. Lett.* **80**, 4737 (1998).

⁷S. Hnig *et al.*, *Synth. Met.* **27**, B181 (1988).

⁸M. Hiraoka, H. Sakamoto, K. Mizoguchi, and R. Kato, *Phys. Rev. B* **65**, 174413 (2002).

⁹M. Hiraoka, H. Sakamoto, K. Mizoguchi, T. Kato, and R. Kato, *Phys. Rev. Lett.* **91**, 056604 (2003).

¹⁰M. Hiraoka, H. Sakamoto, K. Mizoguchi, T. Kato, K. Furukawa, R. Kato, K. Hiraki, and T. Takahashi, *J. Magn. Magn. Mater.*

272, 1077 (2004).

¹¹R. Kato, H. Kobayashi, A. Kobayashi, T. Mori, and H. Inokuchi, *Chem. Lett.* **16**, 1579 (1987).

¹²H.-P. Werner, J. U. von Schütz, H. C. Wolf, R. Kremer, M. Gehrke, A. Aumüller, P. Erk, and S. Hünig, *Solid State Commun.* **65**, 809 (1988).

¹³W. Bietsch, J. U. von Schütz, and H. C. Wolf, *Appl. Magn. Reson.* **7**, 271 (1994).

¹⁴S. Tomic, N. Biskup, M. Pinteri, J. U. v. Schütz, H. Schmitt, and R. Moret, *Europhys. Lett.* **38**, 219 (1997).

¹⁵Y. Nakazawa, A. Sato, M. Seki, K. Saito, K.-I. Hiraki, T. Takahashi, K. Kanoda, and M. Sorai, *Phys. Rev. B* **68**, 085112 (2003).

¹⁶T. Miyazaki, K. Terakura, Y. Morikawa, and T. Yamasaki, *Phys. Rev. Lett.* **74**, 5104 (1995).

¹⁷T. Miyazaki and K. Terakura, *Phys. Rev. B* **54**, 10452 (1996).

¹⁸K. Miyagawa, A. Kawamoto, and K. Kanoda, *Phys. Rev. B* **60**, 14847 (1999).

¹⁹M. Mehring, *Principles of High Resolution NMR in Solids* (Springer, Berlin, 1983).

²⁰R. T. Schumacher and C. P. Slichter, *Phys. Rev.* **101**, 58 (1956).

- ²¹A part of the present work has appeared in K. Mizoguchi, Y. Shinohara, S. Kazama, M. Hiraoka, H. Sakamoto, R. Kato, K. Hiraki, and T. Takahashi, *J. Low Temp. Phys.* **142**, 625 (2006).
- ²²C. P. Slichter, *Principles of Magnetic Resonance* (Springer, Berlin, 1989).
- ²³W. Gordy, *Theory and Application of Electron Spin Resonance* (Wiley, New York, 1980).
- ²⁴SDBS Web: <http://www.aist.go.jp/RIODB/SDBS/> (National Institute of Advanced Industrial Science and Technology).
- ²⁵D. Köngeter, F. Hentsch, H. Seidel, M. Mehring, P. Erk, and S. Hünig, *Solid State Commun.* **65**, 453 (1988).
- ²⁶M. Helmle, J. Reiner, H. Seidel, M. Mehring, P. Erk, and S. Hünig, *Synth. Met.* **41**, 1763 (1991).
- ²⁷Y. Yamakita, Y. Furukawa, A. Kobayashi, M. Tasumi, R. Kato, and H. Kobayashi, *J. Chem. Phys.* **100**, 2449 (1994).
- ²⁸M. Hiraoka *et al.*, *J. Low Temp. Phys.* **142**, 617 (2006).