Wigner Crystal Type of Charge Ordering in an Organic Conductor with a Quarter-Filled Band: $(\mathrm{DI\text{-}DCNQI})_2\mathrm{Ag}$

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^{13}C-NMR measurements have been performed to investigate the nature of the insulating state of a quasi-one-dimensional conductor, (DI-DCNQI)$_2$Ag, with a quarter-filled band. The $4k_F$ charge-density wave has been evidenced below about 220 K by the line separation of the ^{13}C-NMR spectra, which shows a clear charge disproportionation instead of the lattice dimerization encountered in most cases. The present case demonstrates the Wigner crystallization of electrons in the charge-transfer salt and a crucial role of the long-range Coulomb interaction. [S0031-9007(98)06168-7]

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R^1,R^2-DCNQI (2,5-R^1,R^2-dicyanoquinonediimine) with $R^1/R^2 = \mathrm{CH_3}$ (methyl group), I (iodine), etc., is an organic π acceptor molecule, which affords organic charge transfer salts with metallic countercations, M = Ag and Cu. The M complexes of R^1,R^2-DCNQI, (R^1,R^2-DCNQI)$_2M$, have the same crystal symmetry with the space group $I4_1/a$, irrespective of the kind of M or the substitution group R^1/R^2 [1]. In the crystal, planar DCNQI molecules are uniformly stacked along the crystallographical c axis and form one-dimensional (1D) columns [2]. In (R^1,R^2-DCNQI)$_2$Ag, the monovalent Ag does not contribute to the conduction band, which is constructed by the π electrons in DCNQI columns with a quarter filling [3]. The (R^1,R^2-DCNQI)$_2$Ag systems are advantageous to investigate the properties of the quasi-1D electronic system with respect to the controllability of the intracolumn bandwidth and the dimensionality of the electronic systems, namely, the ratio of the transfer integrals $t_\perp/t_\parallel$, by changing the substitution group R^1/R^2 [4,5]. Such systems show a variety of electronic phases in the presence of the electron correlation. The concern of the present paper is the origin of the insulating state in (R^1,R^2-DCNQI)$_2$Ag. It is noted that these uniformly stacking systems have a different nature from the well-known quasi-one-dimensional quarter-filled TMTTF/TMTSF systems with dimerization and inherent $4k_F$ anion potential, which are discussed to be crucial to the appearance of the insulating ground state. (The TMTTF/TMTSF stands for tetramethyltetrathiafulvalene/tetramethyltetrasalenafulvalene.) In fact, the charge ordering is uncovered in this Letter.

(DMe-DCNQI)$_2$Ag ($R^1/R^2 = \mathrm{CH_3}$) behaves metallic at higher temperatures while it becomes insulating at lower temperatures [6]. The ground state is the nonmagnetic Peierls (or spin-Peierls) state with a $2k_F$ lattice distortion, which follows a $4k_F$ lattice distortion [7]. The size of the iodine is much larger than that of the methyl group as the substitution group R^1/R^2. Consequently, the intrachain overlap integral $t_\parallel$ is expected to be smaller in (DI-DCNQI)$_2$Ag (R^1/R^2 = iodine) than in (DMe-DCNQI)$_2$Ag. Indeed, the bandwidth is predicted to be narrower in the DI-DCNQI system than in the DMe-DCNQI by the first principles band calculation [5].

The behaviors of resistivity, magnetic susceptibility, and ^{1}H-NMR of (DI-DCNQI)$_2$Ag were revealed in our previous work [8]. The resistivity is insulating at least below room temperature. The susceptibility shows no spin gap and an antiferromagnetic ordering at 5.5 K is evidenced by ^{1}H-NMR measurements. These form a striking contrast to the properties of (DMe-DCNQI)$_2$Ag. (DI-DCNQI)$_2$Ag is the first case of the π electron antiferromagnet among the DCNQI-metal complex family. All of the results indicate that the electron correlation is crucial in the (DI-DCNQI)$_2$Ag. The enhanced correlation effect in this salt is reasonably related to the narrow band as evaluated in the band calculation. If the molecular stacking and charge density are uniform, the filling of the 1D π electronic band in (DI-DCNQI)$_2$Ag is a quarter, which would give a metallic state. Considering the insulating state without spin gap unlike (DMe-DCNQI)$_2$Ag, one expects occurrence of the $4k_F$ charge density wave (CDW), which leads to electron localization with the spin degree of freedom remained. Unfortunately, the hyperfine coupling between ^{1}H nuclei and lowest unoccupied molecular orbital (LUMO) electrons is too small to characterize the detailed electronic state by the ^{1}H-NMR technique.

To examine the electronic structure and clarify the origin of the insulating state of the compound, ^{13}C-NMR measurements have been performed at the cyano site in the DI-DCNQI molecule, which has large hyperfine coupling with electrons. We have succeeded in observing the $4k_F$ charge ordering which is qualitatively different from the frequently encountered molecular dimerization. In this Letter, we report the first NMR observation of the Wigner crystal type of charge ordering in the charge transfer organic salt. The present observation is an evidence for the decisive role of the long-range nature of the electron correlation in this salt.

The carbon site in the cyano group in the DI-DCNQI molecule was enriched by a ^{13}C isotope with the synthetic route given in Ref. [9]. The ^{13}C-NMR measurements were made for a powdered sample weighing $\sim$20 mg in a temperature range between 1.7 and 280 K under an external field of 8.2 T, which corresponds to an NMR frequency of 87.6 MHz. The NMR spectra were obtained by the fast Fourier transformation of the spin echo signal following the $\pi/2$-π pulse sequence in a higher temperature region, where the present $\pi/2$ pulse width of 4 μs corresponding to the spectral width of $\sim$120 kHz can cover the whole spectra. At lower temperatures, where the spectra become split and broader, the spectra were constructed by scanning the echo intensity as a function of frequency at the fixed field. The time interval τ between $\pi/2$ and π pulses in our experiments is 50 μs. We confirmed that τ is much smaller than T_2 of the spectra in the whole temperature range so that the spectra can be regarded as those in the limit of $\tau \to 0$; e.g., 980 and 570 μs for two split lines (see below) at 67 K.

^{13}C-NMR spectra are shown in Fig. 1, where the shift is from the center of the gravity of the spectra of the nonmagnetic neutral DI-DCNQI powder. According to the first principles calculation [5], the cyano carbon site is a node of the LUMO profile. Therefore, the hyperfine field at the ^{13}C nuclear site is mainly due to the through-bond core polarization and the dipole field from the spin on the neighboring nitrogen atom, which give an isotropic field and an anisotropic field, respectively. As seen in the room temperature spectrum in Fig. 1, the isotropic shift (-830 ppm) is several times larger than the width coming from the anisotropic shift. This situation is similar to the DMe-DCNQI molecule [10]. At higher temperatures above 220 K, ^{13}C-NMR spectra are single lines, which is consistent with the fact that all of the ^{13}C sites are crystallographically equivalent. Below 220 K, however, the spectra get split into two lines with different shift K. The narrower line with a smaller shift and the broader one with a larger shift are called the inner line and the outer one hereafter. Although the outer line is much broader than the inner line, the intensities of the two lines are comparable. Therefore, the line splitting indicates separation of the carbon sites into two different electronic circumstances with equal populations. As shown in Fig. 1, the outer line becomes remarkably broadened with the width nearly proportional to the central shift down to 45 K and finally spreads out beyond the proportionality below 30 K, and the inner line also shows appreciable broadening well below 20 K although remaining observable down to the lowest temperature available. As suggested by the susceptibility and evidenced by the ^{1}H-NMR [8], the ground state is an antiferromagnetically ordered state. In this context, the low-temperature line broadening, which is not scaled to the central shift, is attributed to the $2k_F$ antiferromagnetic fluctuations and ordering. The existence of the fluctuations well above the ordering temperature 5.5 K reflects the low dimensionality of the electronic system. On the other hand, the NMR line splitting is a manifestation of the $4k_F$ CDW, which had been expected as an origin of the insulator with no spin gap. A $4k_F$ x-ray scattering is observed by Nogami *et al.* [11].

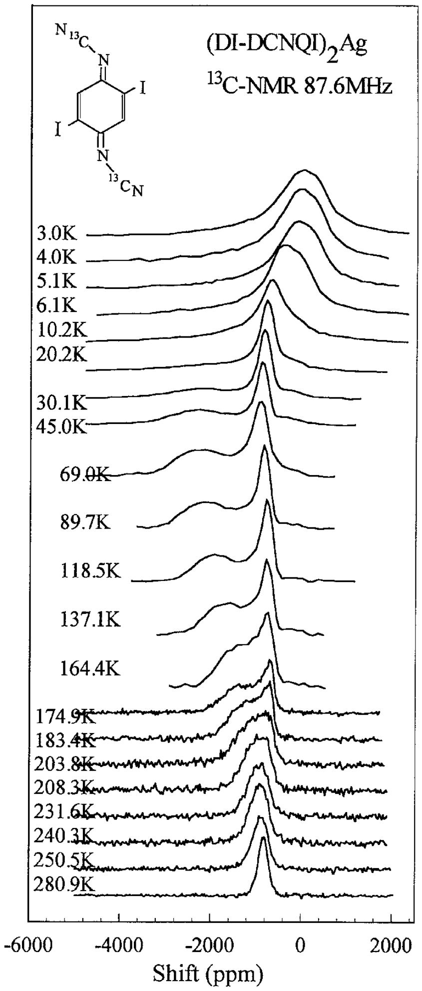

FIG. 1. ^{13}C-NMR spectra of the cyano carbon in the DI-DCNQI molecule of (DI-DCNQI)$_2$Ag at various temperatures. The origin of the horizontal axis is taken to the first moment of the powder pattern of the chemical shift, which was measured for neutral DI-DCNQI molecules.

There are two types of $4k_F$ CDW as depicted in Fig. 2(a), which shows the molecular dimerization, and Fig. 2(b), which shows the spontaneous charge modulation. The separation of the NMR spectra itself can occur in both types of CDW through the following mechanisms. As seen in Fig. 2, the DCNQI molecules containing two ^{13}C sites stack with the molecular faces inclined with respect to the stacking axis. In this situation, even if the dimerization pairing of molecules occurs as shown in Fig. 2(a), the DCNQI molecule essentially stays equivalent. However, the two ^{13}C sites denoted by $C(A)$ and $C(B)$ within a molecule become nonequivalent and can give splitting of the spectra. In the charge-modulation type [Fig. 2(b)], where the ^{13}C sites within a molecule

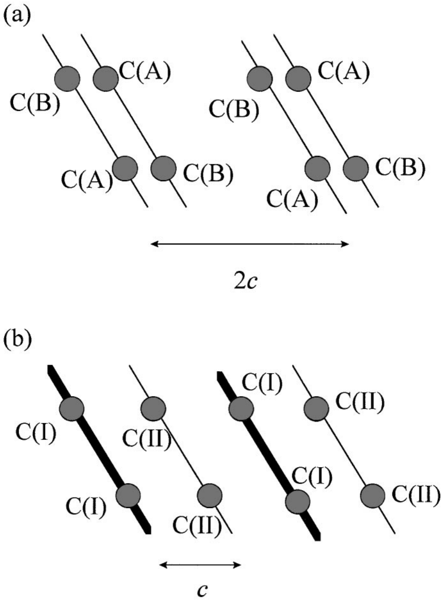

FIG. 2. Schematics of two representatives of $4k_F$ CDW; (a) molecular-dimerization type, and (b) charge-modulation type. The solid lines and shaded circles represent the DI-DCNQI molecules and ^{13}C atoms, respectively, in side view. The bold and thin lines in (b) correspond to the "rich electron" and "poor electron" sites, respectively.

are equivalent, the molecule becomes separated into two kinds with rich and poor electron densities, giving splitting of spectra.

However, if the difference between the low-temperature linewidth profiles of the two lines is taken into consideration, the former case is ruled out in the present system. As mentioned above, the excess broadening starts at 30 K for the broad line, while there is no excess broadening down to 20 K for the inner line. The different behaviors at further lower temperatures are obvious. In the case of the dimer type of CDW, the two lines originating from the same molecule probe the electron spin on the identical LUMO and therefore would have the same profile of low-temperature line broadening. The observation cannot be reconciled by the dimer type of CDW. In the context of the charge-modulation type of CDW, the "rich electron" site experiences serious fluctuations of local field, which makes the broadening prominent, while, at the "poor electron" site situated in between the rich electron site, the local hyperfine field due to the antiferromagnetic short-range order should be canceled out because the form factor of the $2k_F$ spin fluctuations vanishes at the site in question. This explains why the inner line alone is free from spreading out at low temperatures. The dipole field from the neighboring spin-rich molecules is negligible in the paramagnetic state. With the magnetic ordering approached, however, the staggered moment gives an appreciable anisotropic local field, which is not canceled away because the $C(II)$ site is off-center of the DCNQI molecule, as seen in Fig. 2(b). The line broadening below 10 K is attributable to this contribution. Thus, it is concluded that the $4k_F$ charge ordering is realized in (DI-DCNQI)$_2$Ag.

The NMR shifts of the inner and outer lines defined by the peak positions K_i and K_o are plotted as a function of temperature in Fig. 3(a). The averaged shift $(K_i + K_o)/2$ is well scaled to the spin susceptibility shown in the inset in the whole temperature range. The hyperfine field at the ^{13}C nucleus is $-1.0\ \mathrm{T}/\mu_{\mathrm{B-DI\text{-}DCNQI}}$. The $K_i/(K_i + K_o)$ and $K_o/(K_i + K_o)$, which measures relative populations of electron in the respective molecules, are shown in Fig. 3(b). The charge disproportionation starting around 220 K saturates to ~3:1 below 140 K. The electrons are localized at the rich site with extension to the neighboring poor sites. This charge ordering with a $4k_F$ modulation is concluded to be responsible for the nonmetallic state of the material. This is a kind of Wigner crystallization [12] of electrons in nature and the first NMR evidence among the organic charge transfer salts to the

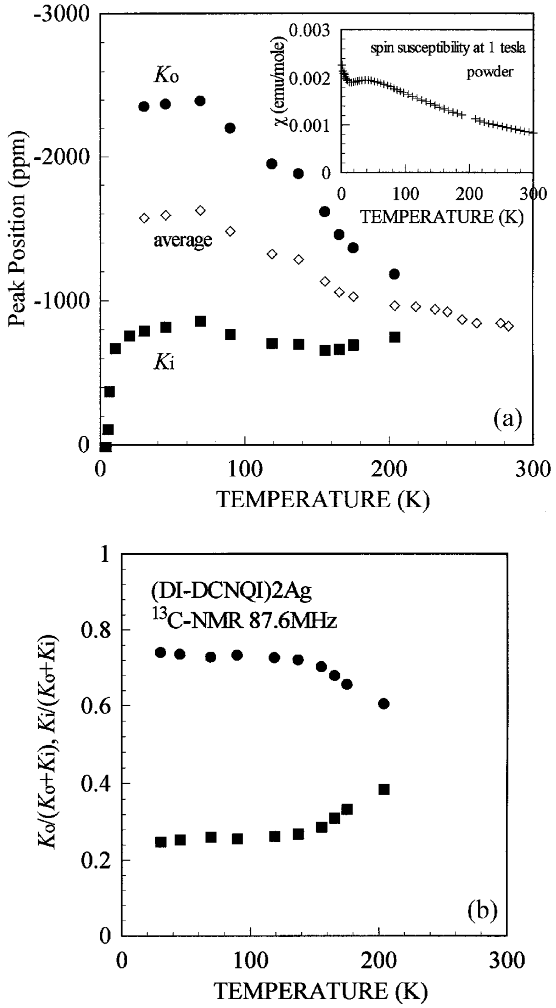

FIG. 3. (a) Temperature dependence of the peak positions of the inner and outer lines, K_i and K_o, and the averaged one, $(K_i + K_o)/2$. The susceptibility χ with correction of core diamagnetism is shown in the inset. (b) Temperature dependence of $K_i/(K_i + K_o)$ and $K_o/(K_i + K_o)$, which measure the relative populations of electron in the respective molecular species.

author's knowledge, while the lattice modulation type of $4k_F$ CDW is widely observed in many organic systems with a quarter-filled band. Seo and Fukuyama theoretically showed a manner in which the intersite Coulomb interaction V leads to the charge disproportionation in quarter-filled one-dimensional systems [13]. The present result is viewed as an experimental demonstration of this prediction.

It is mentioned that the presence of lattice deformation is not ruled out because the present NMR technique does not probe the molecular displacement. However, it is emphasized that the observed large charge disproportionation ($\sim$3:1) is not explained by lowering of the crystal symmetry caused by a molecular displacement. The hyperfine field at the ^{13}C site in question is made mainly by the spin on neighboring nitrogen sites via the through-bond core polarization. It is not acceptable that a minor molecular displacement such as the $4k_F$ superlattice leads to such modification of LUMO that the local electron population on the nitrogen site becomes different by as much as 3 times. Moreover, the nonequivalence in the hyperfine coupling cannot give such qualitatively different behaviors of the two lines as observed at low temperatures.

The Wigner crystallization of electrons shows the crucial role of the long-range Coulomb interaction between electrons in the present system. In $(\text{DMe-DCNQI})_2$Ag, the dimer type of $4k_F$ CDW was suggested to occur at 100 K, which is higher by 20 K than the paramagnetic-to-nonmagnetic transition at 80 K [7]. Thus, the correlation effect manifests itself in a different manner, depending on the bandwidth.

Next, our attention is directed to the spin-ordered state at low temperatures. As discussed above, the spectra observed at low temperatures are for the sites in between the Wigner lattice of electrons, which eventually undergoes the long-range antiferromagnetic order. In the paramagnetic state at higher temperatures, the shift of the intermediate site K_i is proportional to the charge density there. As seen in Figs. 1 and 3, however, it turns toward zero with gradual broadening below 10 K. Curious is the vanishing of the central shift in the spin-ordered state. As seen in the spectra of the powdered sample in the paramagnetic state, the isotropic term is dominant in the hyperfine field. This means that the central shift should be scaled to the spin susceptibility given in the inset of Fig. 3(a) even in the ordered state, since the field-parallel component of the antiferromagnetic moment is responsible for the central shift; the perpendicular component gives only the width of the spectra through the off-diagonal hyperfine tensor. Therefore, the present observation is not trivial but means that the spin at the intermediate site with a finite charge density, which gives paramagnetic susceptibility at higher temperatures, behaves as if it were in a local singlet in the ordered state. According to the theoretical investigation on the spin structure in the V-driven charge ordered state by Seo and Fukuyama [13], a spin configuration like ($\uparrow 0 \downarrow 0$) is realized in the nondimeric chains. Our observation may be understood along this line.

In conclusion, ^{13}C-NMR experiments on $(\text{DI-DCNQI})_2$Ag have demonstrated a $4k_F$ charge ordering below 220 K with a charge disproportionation ratio of 3:1. This Wigner crystallization evidences the decisive role of the long-range Coulomb interaction of electrons in the present system with a narrow band. The local spin susceptibility at the intermediate site in between the Wigner lattice is found to vanish in the spin-ordered state as if a local singlet is formed there. The present observation of the Wigner crystallization in a molecular conductor possibly opens a way to a systematic investigation of the role of the long-range nature of the Coulomb interaction in the electronic phase, which was missing in experiments until now, by controlling the bandwidth or dimensionality in the $(\text{DCNQI})_2$Ag family. The present finding may have some connection with the recent observation of the charge-density modulation in the $2k_F$ spin-density wave (SDW) state of $(\text{TMTSF})_2\text{PF}_6$ although it occurs simultaneously with the SDW transition in the latter case [14].

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