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Band-Selective NMR of a π - d Hybridized Electronic System

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A π - d hybrid electronic system, (DMe-DCNQI)₂Cu, where the π orbital of the organic molecule, DMe-DCNQI, is strongly hybridized with the d_{xy} orbital of Cu, has been studied by ¹⁵N and ¹³C NMR at three sites. The analysis of Knight shift, K , local spin susceptibilities in the π and d orbitals were determined separately. The π and d spin susceptibilities were found to be quite different in magnitude and temperature dependence. Moreover, the Knight shift was separated into those of two constituent bands; a one-dimensional π band and a three-dimensional π - d band. The relative weight of the band susceptibilities is strongly temperature-dependent.

Keywords: DCNQI; d - π Interaction; antiferromagnetic and ferromagnetic fluctuations; ¹³C and ¹⁵N-NMR

INTRODUCTION

The metallic properties of (DMe-DCNQI)₂Cu is very attractive in point of view of the d - π interacting system^[1]. Indeed, applying physical/chemical pressure, this system showed the curious metal-insulator or metal-insulator-metal re-entrant transition^[2,3]. From

the ^{13}C -NMR study on the partially deuteration $\text{DMe-DCNQI}_2\text{Cu}$, we suggested that the combination of the lattice instability and the on-site Coulomb repulsion on Cu ion plays the important role in these transitions^[4].

Many theoretical studies clarified that the electronic structure of $(\text{DMe-DCNQI})_2\text{Cu}$ consist of the two kinds of electronic band^[5]. One has one-dimensional nature of π -orbital in DMe-DCNQI's stacking structure and another has three-dimensional nature of the mixing between π -orbital in DMe-DCNQI molecules and d -orbital in Cu ions. Even in metallic state, the electronic properties showed the complicated behaviors. It is an important for the study of the d - π electron system to extract the static and dynamic properties of these electronic bands separately.

Unfortunately, not only macroscopic measurements, (*ex.* magnetic susceptibility), but also the site selective NMR, which is a powerful approach to study the electronic structure using microscopic probe can detect the sum of the contributions from all bands. In order to separate the contributions of these electronic bands, as described in this article, the multi-site NMR and its quantitative interpretation is necessary.

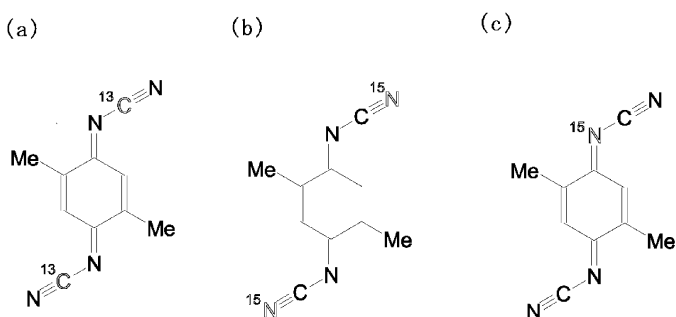


FIGURE 1 Isotope substituted DMeDCNQI molecules

EXPERIMENT

In this purpose, as shown in Figure 1, we synthesized two type of ^{15}N labeled DMe-DCNQI molecules and ^{13}C enriched DMe-DCNQI molecule and performed ^{13}C and ^{15}N -NMR at selective nuclear sites using FFT method. According to Aumuller procedure from *p*-phenylenediamine^[1]. The molecule (a) and (b) was prepared using K^{13}CN and KC^{15}N , respectively. The molecule (c) was prepared using H^{15}NO_3 . $(\text{DMe-DCNQI})_2\text{Cu}$ salts were prepared with chemical oxidation method.

RESULTS AND DISCUSSION

Due to the small spin-orbital contribution, the quantitative interpretations of NMR results in organic π conductors are relatively easy than that in the inorganic systems. For quantitative interpretation of NMR results, it is necessary to determine all hyperfine-coupling constants. We already estimated hyperfine-coupling constants in our previous work^[4,6]. Here we summarized the results briefly. There are two types of hyperfine coupling constants in this system. One is the coupling between the nuclear spin and electrons on π -orbital of DMeDCNQI molecule, which are defined in this article, as $^i a$ and $^i B$. Another is the coupling between the nuclear and electrons on d -orbital on Cu ions through CN --- Cu covalent bond, which were defined here as $^i a_d$ and $^i B_d$.

The nuclear spin-lattice relaxation rates at each site are expressed as,

$$\left[\frac{1}{T_1(\theta)T} \right] \left(\frac{\gamma_e^2}{\gamma_i^2} \right) = \frac{2k_B}{\hbar^2} \left\{ ^i a^2 - \frac{2 ^i a ^i B (1 + 3 \cos 2\theta) + (3 \cos 2\theta - 7) ^i B^2}{4} \right\} \sum_{\mathbf{q}} \frac{\chi''_{1D}(\mathbf{q}, \omega_I)}{\omega_I} \\ + \frac{2k_B}{\hbar^2} \left\{ ^i a_{3D}^2 - \frac{2 ^i a_{3D} ^i B_{3D} (1 + 3 \cos 2\theta) + (3 \cos 2\theta - 7) ^i B_{3D}^2}{4} \right\} \sum_{\mathbf{q}} \frac{\chi''_{3D}(\mathbf{q}, \omega_I)}{\omega_I}, \\ ^i a_{3D} = ^i a(1-c) + ^i a_d c, \\ ^i B_{3D} = ^i B(1-c),$$

here, c is the fraction of electron on Cu atom in the hybridized band, ω_l is a Lamohr frequency. and $\chi''_{1D}(\mathbf{q}, \omega_l)$ and $\chi''_{3D}(\mathbf{q}, \omega_l)$ are imaginary parts of dynamic susceptibility with \mathbf{q} vector on one dimensional and the hybridized band, respectively.

The Knight shifts on $(\text{DMe-DCNQI})_2\text{Cu}$ are also written using the mixing ratio c and the static susceptibility on one dimensional (χ_{1D}) and hybridized band (χ_{3D}) as follow,

$$^iK(\theta) = \left(^i a + \frac{^i B(1 + 3 \cos 2\theta)}{2} \right) \chi_{1D} + \left\{ ^i a(1 - c) + ^i a_d c \right\} \chi_{3D}$$

As χ_d is defined as the susceptibility on Cu ion, χ_d is relates to χ_{3D} by the equation, $c\chi_{3D} = \chi_d$. Solving simultaneous equations for for $i = *N\text{-CN}$, $N\text{-}^*CN$ or $N\text{-C}^*N$, we can extract the c , the temperature dependence of the dynamic susceptibility $\Sigma \chi''_{1D}(\mathbf{q}, \omega_l)/\omega_l$ and $\Sigma \chi''_{3D}(\mathbf{q}, \omega_l)/\omega_l$ and the band selective susceptibility χ_{1D} and χ_{3D} , as shown in Figure 2.

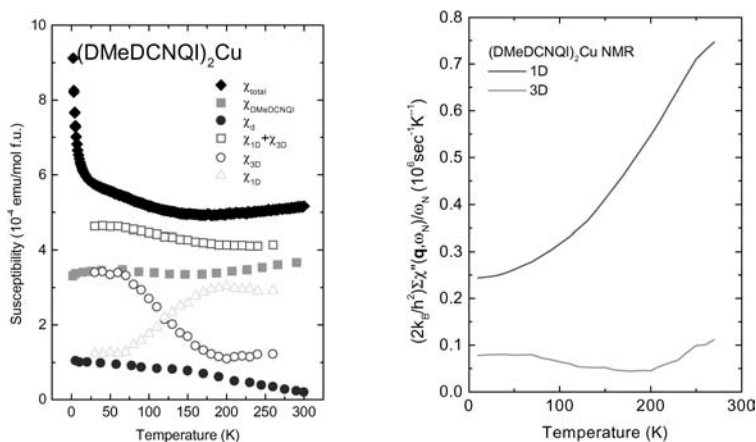


FIGURE 2 The temperature dependence of the susceptibility (left panel) and the dynamic susceptibility (right panel)

The difference of the total susceptibility χ_{total} and $\chi_{1D} + \chi_{3D}$ is considered to be the contribution of the almost temperature

independence orbital part on Cu ions.

The almost temperature independent static susceptibility was interpreted as the normal Pauli-like behavior. However the Knight shift in ^{63}Cu -NMR and ^{13}C -NMR showed the different temperature behavior. We solved this mystery experimentally in term of that the compensation of the susceptibilities between one-dimensional band and the hybridized band. Here we separate experimentally the contributions from two types of band using NMR results only and made it possible to discuss the electric properties of each band. The one dimensional band of $(\text{DMe-DCNQI})_2\text{Cu}$, which consist of DMe-DCNQI's orbital, showed the typical characters of the one dimensional electron system.

The most important thing in $(\text{DMe-DCNQI})_2\text{Cu}$ or these π - d electron systems, is the electronic properties of this mixing band. The susceptibility on the mixing band decreases with increasing temperature. The electronic properties on one-dimensional band show the typical one-dimensional nature, these on the mixing band shows the abnormal behavior described in the term of anti-ferromagnetic fluctuation. Compared with the dynamic susceptibility of one-dimensional band, that on the hybridized band is relatively small. The Korriga Factor, K_α^{-1} , for mixing 3D continues to increase up to 2.5 across the unity at low temperature. This result suggested the existence of the ferromagnetic fluctuation on 3D band. Thus, the ground state of this material is a curious hybrid-band state with contrasting spin-fluctuations

Theoretically, the strange and interesting phenomenon on $(\text{DMe-DCNQI})_2\text{Cu}$ was explained by the mixing of d - π orbital and the one-site Coulomb repulsion on Cu ions which is relatively larger than that on DMe-DCNQI's π -electron system. Experimentally, the evidence of this hybridized band suggested by SdH oscillation measurement, however, owing to the mask by the contribution from one-dimensional band, there are no more information about the character of this band. This is the first experimental results of the magnetic properties and it's

dynamics the d - π hybridized band. The site selective NMR is a powerful tool of studying the magnetic structure and dynamics. For the study of multi-band electronic system, it is not sufficient to measure at only selective single site, which give local spatial information. The systematic measurement on multi sites and the quantitative analysis are necessary.

CONCLUSION

From the site selective NMR and the quantitative analysis of the Knight shift and the spin lattice relaxation rate, we extract the contribution of one-dimensional band and the d - π hybridized band, separately. The static susceptibilities on one-dimensional and the d - π hybridized band are compensated and result in almost temperature independence susceptibility. The electronic properties on one-dimensional band show the typical behavior of one-dimensional electronic system. Our band selective NMR was demonstrated for an organic π -inorganic d electron hybrid, (DMe-DCNQI)₂Cu, where the exotic coexistence of the ferromagnetic and antiferromagnetic fluctuations in separate bands is uncovered. Finally, we also demonstrated that the site selective NMR is not only the spatial local probe for the static and dynamic susceptibility, but also the powerful method for studying the multi-band electronic system.

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