

Ferromagnetic and Antiferromagnetic Fluctuations of π - d Itinerant Electrons Disclosed by Band-Selective NMR

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We present a band-selective NMR method to probe the constituent electronic bands separately in the condensed molecular matter. This method is applied to an organic-inorganic π - d hybrid metal, and its utility to give the static and dynamic spin susceptibilities for the constituent bands is demonstrated. The analysis of the results uncovers an exotic feature; the antiferromagnetic and ferromagnetic correlations are enhanced in separate bands in a single material. This finding provides a novel scope connecting the metal-insulator transitions in this system and the manganese oxides.

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The research on the condensed molecular matters affords a variety of synthetic metals with interesting properties and functionalities. Some of them have several electronic bands with different characters. For attribution of the properties to the constituent bands, the experimental probe of the electronic state with the band selectivity is required. The nuclear magnetic resonance (NMR) probes the electronic state of the material at the nuclear sites. The nucleus feels hyperfine fields made by the electrons on different orbitals through the orbital-dependent hyperfine coupling constants, which are defined by the ratio of the hyperfine field at the nuclear site to the electron spin moment on each orbital. This electron moment-hyperfine field correspondence gives the NMR utility of the orbital attribution of the magnetism, as was recently utilized for the organics [1] and the oxides [2] to yield the orbital-dependent magnetism. In the present Letter, we show that NMR can acquire the higher level of utility that is probing the constituent electronic bands separately. The point of the method is to take advantage of a distinctive feature of the molecular matters; the molecular orbital as a minimum electronic entity extends over the molecule, which can have several NMR-active nuclei to see the identical molecular orbital by the isotope-label technique. In this Letter, we demonstrate that application of this method to an organic-inorganic hybrid metal affords a new phase of information for the condensed molecular matters.

The material studied here is an organic π electron-inorganic d electron hybrid system, $(\text{DMe-DCNQI})_2\text{Cu}$, where DMe-DCNQI is 2,5-dimethyl- N,N' -dicyanoquinonediimine [3]. The organic π acceptor molecule, DMe-DCNQI, is uniformly stacked along the crystallographic c axis with the inclined face-to-face stacking, and the Cu ion located in between the adjacent DMe-DCNQI columns is coordinated by the N atom of CN in the DMe-DCNQI molecules [3,4], as shown in Fig. 1(a). The band structure profile along the stacking c axis is simplified in Fig. 1(b) [4–6]. The π orbital of DMe-DCNQI forms a one-dimensional band along the stacking c axis.

The d_{xy} orbital level, which is the highest among the d levels of Cu in this crystal field, is situated just below the π bands [4,5]. According to the 2:1 stoichiometry of DMe-DCNQI and Cu, the π band is doubly degenerate while the d_{xy} band is nondegenerate. In this situation, one of the degenerate π bands is hybridized to the d_{xy} band and is energetically lifted around the bottom [6]. This π - d band is three-dimensional (3D), as was evidenced by the dH-vA oscillation [7]. The other π band keeps unchanged because of the nonbonding nature and holds

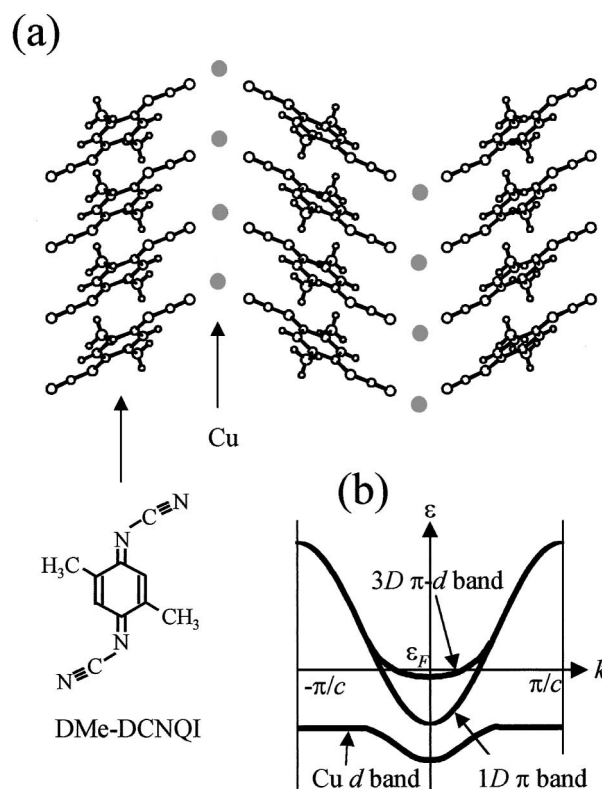


FIG. 1. (a) Crystal structure of $(\text{DMe-DCNQI})_2\text{Cu}$. (b) Schematic of the electronic band structure along the stacking c axis of $(\text{DMe-DCNQI})_2\text{Cu}$ [3,5,6].

one-dimensionality (1D). Thus, the 3D π - d band and the 1D π band crossing the Fermi level are responsible for the conductive and magnetic properties. At ambient pressure, the conductivity increases monotonously with temperature and the magnetic susceptibility is temperature insensitive [4]. They look like nothing curious. However, application of the following NMR method to probe the respective bands discloses that the seemingly conventional metal is really an anomalous metal having two contrasting electronic bands with ferromagnetic and antiferromagnetic fluctuations.

The first step to the “band-selective NMR” is isotope enrichment of the three atomic sites of $=N-C\equiv N$ in DMe-DCNQI by ^{15}N and ^{13}C , as shown in Fig. 2(a). The π spin extending over the molecule makes a local field on each site, i , of $=N-C\equiv N$ with site-dependent hyperfine coupling constants, which are denoted by $^i a_\pi$ and $^i B_\pi$ for the isotropic and anisotropic parts. The Cu d spin, although it is outside the molecule, also makes a local field on each site of $=N-C\equiv N$ via the through-bond core polarization. In this case, the hyperfine coupling constant has only an isotropic term, $^i a_d$, for every site of i . The values of $^i a_\pi$, $^i B_\pi$, and $^i a_d$ were obtained in our previous work [1,8]. Because the π and d orbitals are hybridized to form the two different bands, the local field at site i is made by the 1D π band spin and the 3D π - d band spin. Since the 1D band is made only from the π orbital [4–6], the hyperfine coupling constants of the 1D band spin are given by $^i a_{1D} = ^i a_\pi/2$ and $^i B_{1D} = ^i B_\pi/2$ [9]. The 3D band is made of the π and d orbitals [4–7]. Supposing that the spin fraction on the π and d sites in the 3D band is $1 - c : c$, the 3D band hyperfine coupling constant on site i is expressed by $^i a_{3D} = (1 - c)^i a_\pi/2 + c^i a_d$ and $^i B_{3D} = (1 - c)^i B_\pi/2$ [9]. Then, the nuclear spin-lattice

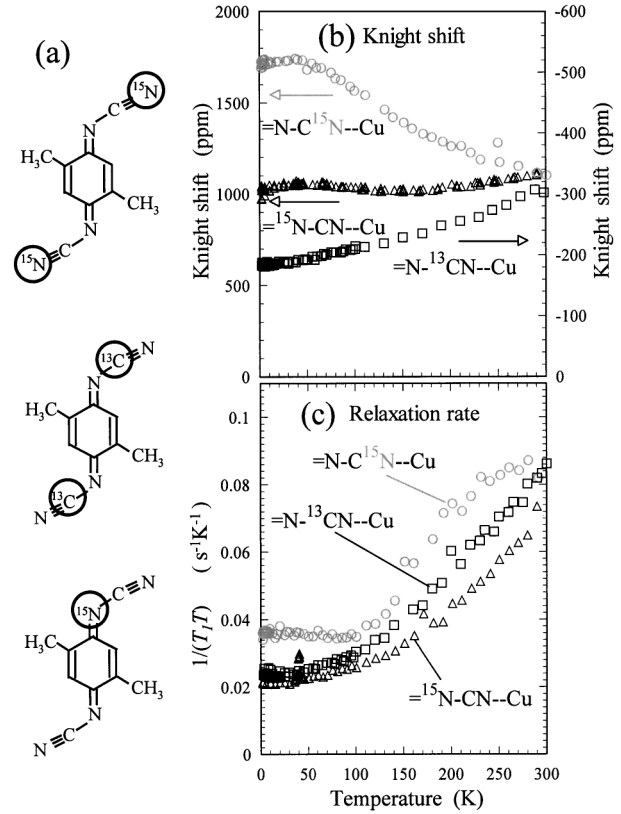


FIG. 2. (a) DMe-DCNQI molecules prepared for NMR at the three selective sites. (b) Knight shift at each site of $=N-CN$. The origin of the Knight shift is determined by the NMR line position of a nonmagnetic $(DMe-DCNQI)_2Li$. (c) Nuclear spin-lattice relaxation rate divided by temperature at each site of $=N-CN$.

relaxation time on site i , $^i T_1(\theta)$, is expressed as a summation of the 1D and 3D band contributions in terms of the imaginary parts of the dynamic susceptibilities, $\chi''_{1D}(\mathbf{q}, \omega_1)$ and $\chi''_{3D}(\mathbf{q}, \omega_1)$ [10]:

$$\left[\frac{1}{^i T_1(\theta) T} \right] \left(\frac{\gamma_e^2}{\gamma_I^2} \right) = \frac{2k_B}{\hbar^2} \left[^i a_{1D}^2 - \frac{2^i a_{1D} ^i B_{1D} (1 + 3 \cos 2\theta) + (3 \cos 2\theta - 7)^i B_{1D}^2}{4} \right] \sum_{\mathbf{q}} \frac{\chi''_{1D}(\mathbf{q}, \omega_1)}{\omega_1} + \frac{2k_B}{\hbar^2} \left[^i a_{3D}^2 - \frac{2^i a_{3D} ^i B_{3D} (1 + 3 \cos 2\theta) + (3 \cos 2\theta - 7)^i B_{3D}^2}{4} \right] \sum_{\mathbf{q}} \frac{\chi''_{3D}(\mathbf{q}, \omega_1)}{\omega_1}. \quad (1)$$

The Knight shift, $^i K(\theta)$, is expressed in terms of the static susceptibilities of the 1D and 3D bands, χ_{1D} and χ_{3D} :

$$^i K(\theta) = \frac{1}{\mu_B} \left[^i a_{1D} + \frac{^i B_{1D} (1 + 3 \cos 2\theta)}{2} \right] \chi_{1D} + \frac{1}{\mu_B} \left[^i a_{3D} + \frac{^i B_{3D} (1 + 3 \cos 2\theta)}{2} \right] \chi_{3D}. \quad (2)$$

Here, θ is the angle between the applied magnetic field and the uniaxial symmetry axis of the hyperfine coupling tensor, T is temperature, and ω_1 is NMR frequency. The γ_e and γ_I are the gyromagnetic ratios for the electron and nuclear spins. The static and dynamic susceptibilities, χ and χ'' , are defined for the formula unit of the compound.

When T and θ are experimentally set and $^i T_1(\theta)$ is measured, parameters remaining unknown in Eq. (1) are $\sum \chi''_{1D}(\mathbf{q}, \omega_1)/\omega_1$, $\sum \chi''_{3D}(\mathbf{q}, \omega_1)/\omega_1$, and c . They are obtained by solving the three equations for the three sites at each temperature. With the knowledge of the c value, χ_{1D} and χ_{3D} are deduced through Eq. (2) in a similar manner [11]. Following the above procedure at each temperature measured, one obtains the mixing parameter, c , the band-dependent static susceptibilities, χ_{1D} and χ_{3D} , and the dynamic susceptibilities, $\sum \chi''_{1D}(\mathbf{q}, \omega_1)/\omega_1$ and $\sum \chi''_{3D}(\mathbf{q}, \omega_1)/\omega_1$, as a function of temperature. It is emphasized that the negligible orbital magnetism in the molecule enables one to construct the above formulations only with the spin contribution.

The measurements of ^{13}C and ^{15}N NMR Knight shift, K , and relaxation time, T_1 , were performed for powders at an external magnetic field of 8 T, where the powdered grains were aligned with the c axis parallel to the magnetic field due to the anisotropic susceptibility. Because the symmetry axis of the hyperfine field is that of the p_z orbital on the carbon and nitrogen, θ for the present case is estimated at 35° from the crystallographic data. The measured K and $1/(T_1T)$ are shown in Figs. 2(b) and 2(c). After smoothing the data with polynomials, we followed the above procedures to obtain the five quantities at each temperature. Figure 3(a) shows the resultant static band susceptibilities, $\chi_{1\text{D}}$ and $\chi_{3\text{D}}$, along with the total susceptibility measured with a SQUID magnetometer. The strongly temperature-dependent interplay between $\chi_{1\text{D}}$ and $\chi_{3\text{D}}$ hidden inside the temperature-independent total susceptibility is uncovered. The $\chi_{1\text{D}}$ is 2–3 times greater than $\chi_{3\text{D}}$ above 200 K while the relation becomes the contrary below 100 K. As for the dynamic band susceptibilities, $\sum \chi''_{1\text{D}}(\mathbf{q}, \omega_1)/\omega_1$ and $\sum \chi''_{3\text{D}}(\mathbf{q}, \omega_1)/\omega_1$, different interplay is evident [Fig. 3(b)]; the former exceeds the latter in the whole temperature range and they have distinct temperature dependence. To see the validity of

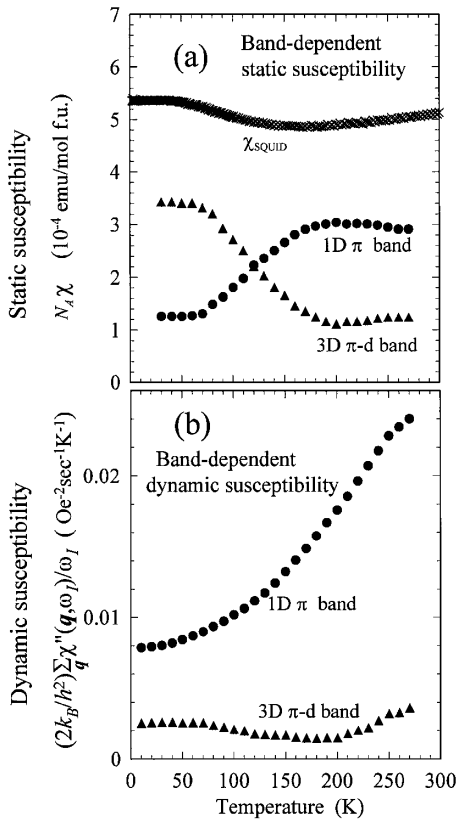


FIG. 3. Band-selective NMR results. (a) Band-dependent (molar) static spin susceptibility deduced from the site-selective Knight shift data. N_A is Avogadro's number. The total susceptibility (with the core contribution corrected) measured independently with the SQUID magnetometer is also shown. (b) Band-dependent dynamic spin susceptibility deduced from the site-selective nuclear relaxation data.

the present analysis, we calculated the Cu-site $1/(T_1T)$, which is evaluated by $c^2 \sum \chi''_{3\text{D}}(\mathbf{q}, \omega_1)/\omega_1$, since the Cu d orbital solely contributes to the 3D band with fraction c . The resultant values of $c^2 \sum \chi''_{3\text{D}}(\mathbf{q}, \omega_1)/\omega_1$ reproduced the profile of the experimental Cu $1/(T_1T)$, which does not vary up to 100 K and then increases [12], supporting the validity of the present method.

From the above results, one can draw an important consequence on the spin correlations of this material. The ratio of the squared static susceptibility to the dynamic susceptibility defined by $K_\alpha^{-1} = (h/\mu_B^2) \chi^2 / [\sum \chi''(\mathbf{q}, \omega_1)/\omega_1]$ reflects the \mathbf{q} profile of the spin fluctuations. If $K_\alpha^{-1} > 1$, it tells that the spin fluctuations are enhanced at $\mathbf{q} = 0$ relative to other wave vectors, while the contrary relation, $K_\alpha^{-1} < 1$, tells enhancement of the fluctuations at finite \mathbf{q} vectors. The former is ferromagnetic while the latter is antiferromagnetic. Figure 4(a) shows K_α^{-1} for each band. With temperature decreased, they both increase gradually down to 200 K with the magnitude much less than unity, indicative of the antiferromagnetic nature. Below 200 K, however, they are branched off; the 3D-band K_α^{-1}

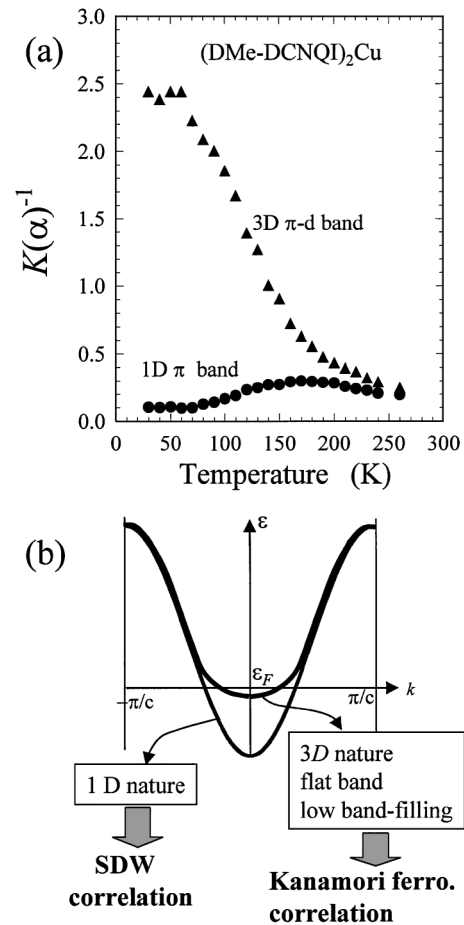


FIG. 4. Band-dependent spin fluctuation profile. (a) Band-dependent K_α^{-1} defined by $(h/\mu_B^2) \chi^2 / [\sum \chi''(\mathbf{q}, \omega_1)/\omega_1]$, which measures the \mathbf{q} vector profile of the spin fluctuations. (b) Correspondence between the band-structure characteristics and the spin correlation profiles.

continues to increase up to 2.5 across unity while the 1D-band K_{α}^{-1} keeps well below unity and decreases down to 0.1 at low temperatures. Thus, at low temperatures the antiferromagnetic fluctuations are enhanced in the 1D band while the ferromagnetic fluctuations are enhanced in the 3D band. The behavior of the 1D band is understood in terms of spin density wave (SDW) fluctuations due to the nesting instability of the 1D Fermi surface. As for the 3D band, this is the first evidence of the enhanced ferromagnetic correlations among the metallic organics to the authors' knowledge. The three dimensionality and the incommensurate low filling of this band, which are unusual for molecular conductors, make this system against the nesting or Mott instability with the antiferromagnetic spin correlations. Then the electron correlation should lead to the so-called Stoner enhancement of the uniform susceptibility. Considering that the Fermi level is near the flat bottom of the 3D band [see Fig. 1(b)], the enhanced ferromagnetic fluctuations of the 3D band can be viewed as a trend toward the so-called Kanamori ferromagnetism [13]. Thus, the electron correlation gives the contrasting effects to the two bands in a single material, antiferromagnetic or ferromagnetic depending on the band structure [see Fig. 4(b)].

The present finding widens the scope to view the metal-to-insulator (M-I) transition appearing under pressure [14–16] or with deuteration of the molecule [4]. This M-I transition is beyond the conventional framework of the organics such as charge density wave, SDW, or Mott transitions because of the unconventional features of the insulating state [4,16]; (i) threefold charge ordering, $\text{Cu}^+\text{Cu}^+\text{Cu}^{2+}$, occurs along the c axis, (ii) the spins on the Cu^{2+} sites form an antiferromagnetic lattice, and (iii) the DMe-DCNQI sites become nonmagnetic. It is obvious that the charge and spin states of the metallic phase revealed here have no continuation to those of the insulating phase; the π electron, which is partially ferromagnetic and partially antiferromagnetic in the metallic phase, becomes nonmagnetic and the d electron, which contributes to the ferromagnetic fluctuations in the metallic phase, becomes antiferromagnetic in the insulating phase. This feature is compared with the case of the colossal-magnetoresistive manganese oxides, where the ferromagnetic metal undergoes a transition to the antiferromagnetic insulator with charge ordering, orbital ordering, and the (cooperative Jahn-Teller-like) lattice distortion [17]. The underlying physics is considered to be shared by the two systems as follows. In the insulating phase of $(\text{DMe-DCNQI})_2\text{Cu}$, the tetrahedral coordination angle of CN to Cu is modulated with threefold periodicity along the c axis [16]. This results in the Peierls instability for the nearly $1/3$ -filled 1D π band and makes the filling of the 3D π - d band a half, which enhances the electron correlation effect [6]. At the same time, the modulation of the coordination angle around Cu makes the partially occupied d_{xy} energy level split with threefold periodicity

(a kind of cooperative Jahn-Teller effect), which aids charge ordering on the Cu site. Namely, this M-I transition is attributable to the cooperative instabilities in the lattice, charge, and 1D Fermi surface in presence of the Coulomb repulsion. Supposing that the orbital instability in the manganites is replaced by the 1D Fermi surface instability in $(\text{DMe-DCNQI})_2\text{Cu}$, one acquires a new scope that the M-I transitions of the present transition-metal organics and the extensively studied transition-metal oxides belong to the same class of cooperative instability.

In conclusion, we presented a method by which the conventional site-selective NMR gets the band selectivity for molecular materials. The method allows one to pick up the characteristics of the constituent bands in the multiband system separately. Its utility was demonstrated for an organic π -inorganic d electron hybrid, $(\text{DMe-DCNQI})_2\text{Cu}$, by the finding of exotic coexistence of the ferromagnetic and antiferromagnetic fluctuations in separate bands. This method is widely applicable to other molecular systems.

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