Extremely Slow Charge Fluctuations in the Metallic State of the Two-Dimensional Molecular Conductor θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$

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Large charge disproportionation has been confirmed in the metallic state of a 1/4-filled organic conductor θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ by means of ^{13}C-NMR analysis on a selectively ^{13}C-enriched single crystal sample. By comparing the homogeneous and inhomogeneous linewidths, the temperature dependence of the extremely slow dynamics of charge fluctuations has been determined first. The exotic nature of the metallic state of this salt is discussed.

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Charge ordering has become one of the important keywords in understanding the low temperature properties of organic conductors. It is a novel manifestation of Coulomb correlation in low-dimensional electronic systems. The first observation of charge ordering of the Wigner crystal type was reported for a quasi-one-dimensional (Q1D) conductor (DI-DCNQI)$_2$Ag, where the ^{13}C-NMR spectrum from selectively ^{13}C-enriched cyano groups was split into two peaks corresponding to charge-rich and charge-poor sites below 220 K [1]. Similar charge ordering was suggested to explain the magnetic structure in the commensurate spin-density wave (SDW) state of (TMTTF)$_2$Br [2]. Later, charge ordered states in (TMTTF)$_2X$ [$X = \mathrm{PF}_6, \mathrm{AF}_6$] were observed by ^{13}C-NMR [3,4] and confirmed by dielectric measurements [5,6]. These phenomena in Q1D systems were theoretically discussed on the basis of the 1D scattering approach [7], the Mott-Hubbard model [8], and the mean-field theory [9].

In two-dimensional (2D) systems, a charge ordered state was theoretically predicted by Kino and Fukuyama [10] as a ground state of the α-type BEDT-TTF salt, by taking account of on-site Coulomb interaction and asymmetric intermolecular transfers within a framework of Hartree-Fock approximation. This prediction was actually confirmed in α-(BEDT-TTF)$_2$I$_3$ [11]; the metal-insulator (MI) transition at 135 K in this salt was identified by ^{13}C-NMR measurements as a charge ordering transition. Similar charge ordering was also confirmed in θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ below 190 K by ^{13}C-NMR [12,13].

The mechanism of the MI transition in the α- and the θ-phase salts had been unclear for a long time. In the case of κ- and β-type BEDT-TTF salts with strong dimerization, insulating states are considered as the Mott-Hubbard insulator, since the electronic systems become effectively half-filled. In contrast, the α- and the θ-phase salts have no appreciable dimerization and thus have a quarter-filled band. Now, the charge ordered state is the most possible candidate of insulating states in nondimerized quarter-filled systems.

The ^{13}C-NMR measurements for θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ mentioned above [12,13] had also found an anomalous broadening of the ^{13}C-NMR spectrum above the transition. This phenomenon was explained as a precursor of the charge ordering below the transition. However, such a large broadening is quite unusual since the system is believed to be metallic above the transition temperature. The purpose of this work is to clarify the origin of this anomalous broadening above the transition from precise analysis of the angular dependence of the linewidth, and to determine the dynamics

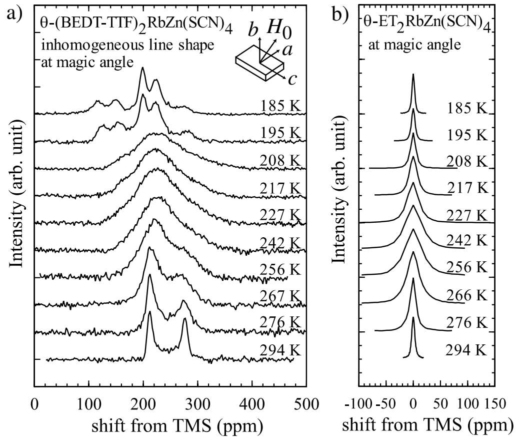

FIG. 1. Temperature dependence of (a) inhomogeneous and (b) homogeneous line shapes of ^{13}C-NMR. The external field was precisely tuned in the *ab* plane to give a magic angle for nuclear dipolar coupling between ^{13}C nuclei.

of charge fluctuations through the measurements of transverse relaxation rate, T_2^{-1}, defined as a decay rate of the spin-echo signal.

Single crystals of θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ were prepared with the use of a BEDT-TTF molecule in which the central double-bonded carbon sites were selectively replaced with a ^{13}C isotope ($I = 1/2$). ^{13}C-NMR measurements were performed on single crystal samples of a few milligrams in weight. Resonance frequency was 88 MHz, which corresponds to a resonance field of 8.2 T. The absorption spectrum was obtained by fast Fourier transformation (FFT) of the spin-echo signal following a $\pi/2$-π pulse sequence. A single crystal sample could be rotated in the external field with respect to a certain axis (c axis, mainly in this work).

Figure 1(a) shows the temperature dependence of the ^{13}C-NMR spectrum obtained by FFT of the spin-echo signal. Here, the external field was oriented to give a magic angle for nuclear dipolar coupling between the central carbon pairs on a BEDT-TTF molecule. At room temperature, the spectrum consists of two sharp peaks, which correspond to two ^{13}C sites on a BEDT-TTF molecule, which are crystallographically not equivalent with each other. (For a general field direction, the spectrum becomes a quartet, characteristic of dipolar-coupled ^{13}C nuclei.) As the temperature decreases, the spectrum is gradually broadened, as already reported [12,13]. At the MI transition temperature, the spectrum exhibits a drastic change; the observed sharp and broad components have been assigned to the signals from charge-poor and charge-rich sites, respectively. This was considered as a direct indication of the charge ordering in the insulating state [12,13].

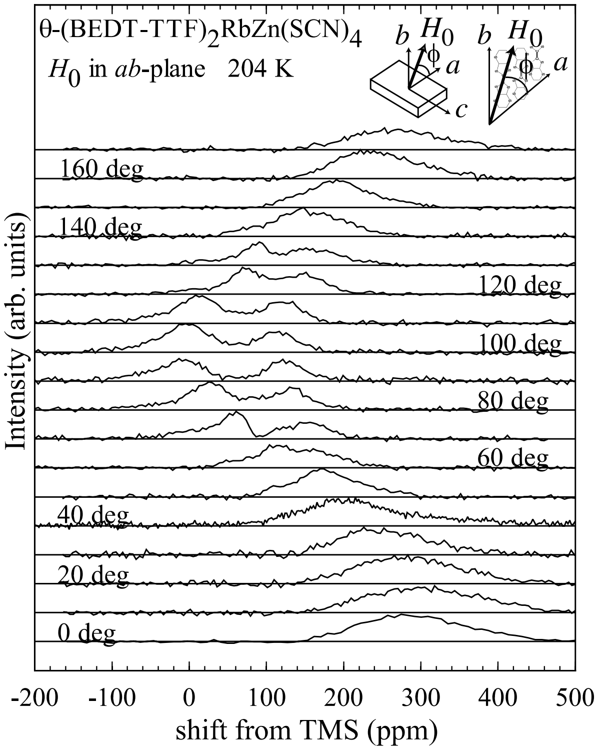

FIG. 2. Angular dependence of the NMR line shape at 204 K in the ab plane.

To find the mechanism of the line broadening above the MI transition, we measured the angular dependence of the ^{13}C spectrum when the external field was rotated in the ab plane at 204 K. The results are shown in Fig. 2.

It is clearly seen that the line shape, the linewidth, and the center of mass of the spectrum are remarkably angular dependent. The shift of the center of mass is consistent with the anisotropic Knight shift expected for ^{13}C nuclei on the BEDT-TTF molecule [14]. The line splitting observed around $H_0 \parallel b$ ($\phi \sim 90°$) is due to nuclear dipolar coupling. We found that excess broadening is also angular dependent. In order to analyze it quantitatively, we calculated the second moment of the observed spectrum. The total second moment contains a trivial contribution of nuclear dipolar structure, $\langle \Delta f^2 \rangle_{\text{dip}}$, which can be calculated as $\langle \Delta f^2 \rangle_{\text{dip}} = (1/4)(\Delta f_{\text{dip}})^2$, where Δf_{dip} is the separation of the Pake doublet observed at room temperature. Figure 3 shows the angular dependence of the excess broadening, $\langle \Delta f^2 \rangle_{\text{excess}} = \langle \Delta f^2 \rangle_{\text{obs}} - \langle \Delta f^2 \rangle_{\text{dip}}$. $\langle \Delta f^2 \rangle_{\text{excess}}$ shows clear minimums around 60° and 130°. Since the chemical shift in these directions is constant at $\sim$135 ppm, as found in the analysis of room temperature data [13], one can see that the minimums of $\langle \Delta f^2 \rangle_{\text{excess}}$ appear at angles where the Knight shift vanishes ($K = 0$). We have plotted the square of the Knight shift to compare with the behavior of the excess second moment in Fig. 3; these quantities scale well to each other. An offset of the second moment of $\sim$10 kHz^2 is observed at the minimum positions. We consider that this is caused by the difference of the central shift, ΔK, for the coupled ^{13}C nuclei. Since $\Delta K \sim 6.2$ kHz at angles for $K = 0$, the contribution of the second moment is estimated as $\sim(1/4)(6.2\ \text{kHz})^2 \sim 9.6$ kHz^2, which agrees with the observed offset of the second moment. These results clearly indicate that the excess line broadening is caused by the inhomogeneous change in the Knight shift, that is, the inhomogeneity of local susceptibility. This fact strongly suggests that

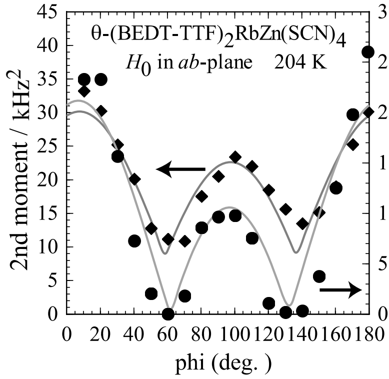

FIG. 3. Diamonds indicate the second moment of the spectrum and closed circles the square of the Knight shift.

charge disproportionation with large fluctuations in space already appears above the MI transition. From the observed excess second moment, the effective charge per molecules should be distributed in a range of $+0.3$–$+0.7$. It should be noted that the fluctuations of charge disproportionation in time should be extremely slow with a correlation frequency, τ_c^{-1}, much less than the observed width ~6 kHz; otherwise, the inhomogeneous width should have been narrowed by the motion, at least, at temperatures just above the MI transition. This picture strongly contradicts the expectation that this system should be metallic above the MI transition.

However, the excess broadening is reduced as temperature increases. The spectrum at room temperature is very compatible with a model of equally charged molecules. The charge disproportionation should fluctuate rapidly in time as the temperature increases. It is quite important to determine the dynamics of these charge disproportionation.

In order to address this issue, we have measured the transverse relaxation rate, T_2^{-1}, which contains only a homogeneous contribution to the linewidth. In order to eliminate the nuclear dipolar contribution to the echo decay, the external field was precisely oriented in the *ab* plane to give a magic angle for dipolar coupling between ^{13}C pairs on a BEDT-TTF molecule. A pulse sequence, $\pi/2$-τ'-π, was used to create spin echo at $2\tau'$, where τ' is a time interval between the $\pi/2$ and π pulses.

We measured the integrated intensity of the echo spectrum as a function of $2\tau'$. At all measured temperatures, echo decay was single exponential, which means that homogeneous line shape was pure Lorentzian within experimental accuracy. By Fourier transforming echo decay curves, we obtained homogeneous spectra, which are shown in Fig. 1(b) in comparison to inhomogeneous ones shown in 1(a). The scales of the horizontal axes of 1(a) and 1(b) have been chosen to be the same.

At low temperatures, the homogeneous spectrum is much narrower than the inhomogeneous one. As the temperature increases, the homogeneous width increases rapidly, making a peak around 250 K, and then decreases again. At room temperature, the homogeneous width explains well the observed width of each peak of the inhomogeneous spectrum. The temperature dependence of the homogeneous width, T_2^{-1}, is shown in Fig. 4.

The peak behavior of T_2^{-1} can be explained as follows. T_2^{-1} corresponds to the inverse of the lifetime of Zeeman levels according to the uncertainty principle. It is usually determined by nuclear dipolar coupling and is called the spin-spin relaxation rate. However, when inhomogeneous fields start to fluctuate in time, the characteristic frequency of the fluctuations, τ_c^{-1}, should contribute to reduce the lifetime of Zeeman levels. As inhomogeneous fields fluctuate more rapidly with increasing temperature, T_2^{-1} also increases. A peak should appear at a temperature where the characteristic frequency becomes comparable to the inhomogeneous width itself (in a frequency scale), since at higher temperatures the inhomogeneous field should be averaged in time by a well-known motional narrowing process.

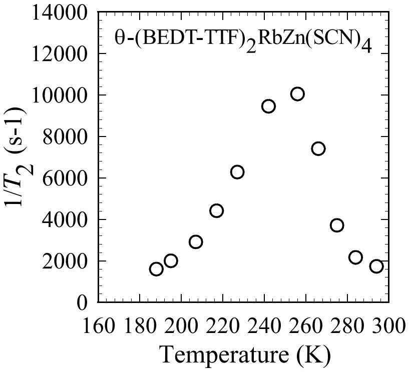

FIG. 4. Temperature dependence of the homogeneous width, T_2^{-1}.

The model proposed above to explain the peak behavior of T_2^{-1} leads to a well-known Bloembergen-Purcell-Pound (BPP)-type behavior assuming an activation-type temperature dependence of $\tau_c = \tau_\infty \exp(\Delta/k_B T)$ [15]. We plotted the results of T_2^{-1} in a semilogarithmic scale against the inverse of the temperature in Fig. 5. Here, we have subtracted the contribution of the intrinsic homogeneous width, which was estimated as 1×10^3 s^{-1}. It can be seen that the curve is asymmetric and different from a well-known BPP-type behavior.

We have found that the asymmetric behavior can be explained with the use of the so-called expanded exponential correlation function [16]. In this model, the correlation function of fluctuating local fields is assumed to be

$$\Phi(t) = \gamma_n^2 \langle H_{\mathrm{loc}}(t) H_{\mathrm{loc}}(0) \rangle = \langle \Delta\omega^2 \rangle \exp(-(|t|/\tau_c)^\beta). \quad (1)$$

Here, $\langle \Delta\omega^2 \rangle$ is the second moment for the inhomogeneous width. The homogeneous relaxation rate is obtained by Fourier transformation of this correlation function as

$$\frac{1}{T_2} = \int_{-\infty}^{\infty} \Phi(t) \cos(\sqrt{\langle \Delta\omega^2 \rangle} t) dt,$$

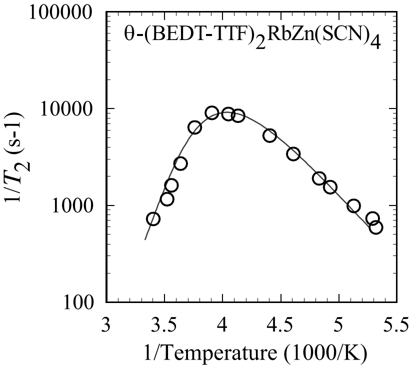

FIG. 5. T_2^{-1} in semilogarithmic scale against the inverse of the temperature.

which can be calculated numerically. Asymptotic behaviors are given as

$$\frac{1}{T_2} = 2\Gamma(\beta + 1)\sin\left(\frac{\beta\pi}{2}\right)\langle\Delta\omega^2\rangle^{(1-\beta)/2}\tau_c^{-\beta}, \qquad (\tau_c \to \infty),$$
$$= 2\Gamma\left(\frac{1}{\beta} + 1\right)\langle\Delta\omega^2\rangle\tau_c, \qquad (\tau_c \to 0). \qquad (2)$$

The asymmetry in Fig. 5 is determined by the parameter, β; we obtain a BPP-type behavior for $\beta = 1$. The solid curve in Fig. 5 is obtained by taking parameters $\Delta/k_B = 7600$ K, $\beta = 0.4$, and $\sqrt{\langle\Delta\omega^2\rangle}/2\pi = 3.3$ kHz. Agreement with the observed data is satisfactory.

The physical meaning of the expanded exponential correlation is not clear, but this behavior has been observed almost universally in various types of dynamics in various random systems. In ionic conductors, for example, diffusion properties of mobile ions were found to follow this type of correlation [17]. It is believed that strong correlations in ionic motions are responsible for this correlation. It is also known that similar correlation is obtained in the dielectric response of complex systems with a large distribution of the dielectric relaxation rate, $1/\tau_c$ [18,19]. This system has close similarity to ionic conducting systems and dielectric systems since large charge disproportionations are fluctuating in time. We believe that short-range charge orderings have developed well at high temperatures. The transition at 190 K may be the formation of three-dimensional long-range ordering assisted by lattice dimerization along the c axis. Fluctuations of charge ordering should cost a large amount of Coulomb energy, which seems consistent with the rather large amount of activation energy, $\Delta \sim 7600\ \text{K} \sim 0.65$ eV. The observed charge fluctuation should not be considered as the usual precursor effect of the transition at 190 K, which is believed to be of first order [20].

It should be noted that these charge fluctuations do not contribute to the spin-lattice relaxation rate, T_1^{-1}: From the BPP relation and the parameters obtained above, the maximum of T_1^{-1} will be $\langle\Delta\omega^2\rangle\tau_c/2 \sim 0.4\ \text{s}^{-1}$ when $\omega_N\tau_c \sim 1$ is satisfied around 364 K, where ω_N is the Larmor frequency. The observed T_1^{-1} is $\sim 100\ \text{s}^{-1}$ and almost temperature independent above 230 K [21].

This observation is quite consistent with the recent dielectric measurements which have revealed an unusually large dielectric constant with Debye-type relaxation even above T_{MI} [22]. The authors suggested that insulating and metallic phases coexist in the "metallic" state. We claim that the transport properties in this region should be seriously reconsidered.

In conclusion, we have confirmed that large charge disproportionations, which are very probably short-range charge orderings, are developed far above the transition temperature. We have determined the dynamical properties of the charge disproportionation, by comparing the temperature dependence of homogeneous and inhomogeneous line widths precisely. We have found that the charge dynamics is well explained by an expanded exponential correlation model, which is generally applied in strongly correlated systems such as ionic conductors. This work is the first microscopic determination of the dynamics of short-range charge orderings in the metallic state and the first direct evidence of the existence of a novel type of conducting state in organic molecular conductors.

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[1] K. Hiraki and K. Kanoda, Phys. Rev. Lett. **80**, 4737 (1998).
[2] T. Nakamura, T. Nobutoki, Y. Kobayashi, T. Takahashi, and G. Saito, Synth. Met. **70**, 1293 (1995).
[3] D.S. Chow, F. Zamborszky, B. Alavi, D.J. Tantillo, A. Baur, C.A. Merlic, and S.E. Brown, Phys. Rev. Lett. **85**, 1698 (2000).
[4] F. Zamborszky, W. Yu, W. Raas, S.E. Brown, B. Alavi, C.A. Merlic, and A. Baur, Phys. Rev. B **66**, 081103 (2002).
[5] F. Nad, P. Monceau, C. Carcel, and J.M. Fabre, Phys. Rev. B **62**, 1753 (2000).
[6] P. Monceau, F.Y. Nad, and S. Brazovskii, Phys. Rev. Lett. **86**, 4080 (2001).
[7] H.J. Schulz, Int. J. Mod. Phys. B **5**, 57 (1991).
[8] R.T. Clay, A.W. Sandvik, and D.K. Campbell, Phys. Rev. B **59**, 4665 (1999).
[9] H. Seo and H. Fukuyama, J. Phys. Soc. Jpn. **66**, 1249 (1997).
[10] H. Kino and H. Fukuyama, J. Phys. Soc. Jpn. **65**, 2158 (1996).
[11] T. Takano, K. Hiraki, H. Yamamoto, T. Nakamura, and T. Takahashi, J. Phys. Chem. Solids **62**, 389 (2001).
[12] K. Miyagawa, A. Kawamoto, and K. Kanoda, Phys. Rev. B **62**, R7679 (2000).
[13] R. Chiba, H. Yamamoto, K. Hiraki, T. Takahashi, and T. Nakamura, J. Phys. Chem. Solids **62**, 393 (2001).
[14] A. Kawamoto, K. Miyagawa, Y. Nakazawa, and K. Kanoda, Phys. Rev. B **52**, 15 522 (1995).
[15] N. Bloembergen, E.M. Purcell, and R.V. Pound, Phys. Rev. **73**, 679 (1948).
[16] G. Williams and D.C. Watts, Trans. Faraday Soc. **66**, 80 (1970).
[17] C. León, M.L. Lucia, J. Santamaría, M.A. París, J. Sanz, and A. Várez, Phys. Rev. B **54**, 184 (1996).
[18] K.S. Cole and R.H. Cole, J. Chem. Phys. **9**, 341 (1941).
[19] S. Havriliak and S. Negami, J. Polym. Sci., Part C: Polym. Symp. **14**, 99 (1966).
[20] H. Mori, S. Tanaka, and T. Mori, Phys. Rev. B **57**, 12 023 (1998).
[21] K. Miyagawa (private communication).
[22] K. Inagaki, I. Terasaki, and H. Mori, Physica (Amsterdam) **329-333B**, 1162 (2002).