Role of hydrogen bonding in charge-ordered organic conductor $\alpha$-(BEDT-TTF)$_2$I$_3$ probed by $^{127}$I nuclear quadrupole resonance

T. Kobayashi,1,2,3,* Y. Kato,1 H. Taniguchi,1 T. Tsumuraya,4 K. Hiraki,5 and S. Fujiyama3

1Graduate School of Science and Engineering, Saitama University, Saitama, 338-8570, Japan
2Research and Development Bureau, Saitama University, Saitama 338-8570, Japan
3Meson Science Laboratory, RIKEN, Saitama 351-0198, Japan
4Magnesium Research Center, Kumamoto University, 860-8555, Japan
5Center for Integrated Science and Humanities, Fukushima Medical University, Fukushima, 960-1295, Japan
(Dated: August 31, 2023)

We present $^{127}$I nuclear quadrupole resonance spectra and nuclear relaxation of $\alpha$-(BEDT-TTF)$_2$I$_3$ that undergoes a charge-ordering transition. Only one of the two I$_3$ anion sites shows a significant differentiation in the electric field gradients across the first-order transition. The charge modulation only in the BEDT-TTF layers can not reproduce; instead, an anion-donor interaction accompanied by hydrogen bonding is necessary. The dominating source for the nuclear relaxation is the local libration of the I$_3$ anions, but an anomalous peak is detected just below the transition, as observed by $^{13}$C NMR.

I. INTRODUCTION

Electronic correlation in a quasi-two-dimensional organic conductor (BEDT-TTF)$_2$X stabilizes various ground states, including quantum spin liquids or Dirac electron systems. Molecular arrangements of the BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene, hereafter abbreviated as ET] in the alternating conducting planes specify the electronic correlation leading to various physical properties [1, 2]. Of these, $\alpha$, $\beta''$, or $\theta$ type molecular arrangements establish two-dimensional 3/4-filled (1/4-filled hole) electronic bands. Long-range Coulomb interactions cause ground states such as charge ordering (CO), ferroelectricity [3, 4], charge glass [5], and superconductivity [6–9].

A quasi-two-dimensional organic conductor $\alpha$-ET$_2$I$_3$, shown in Fig. 1(a), is one of the most studied organic conductors [10]. This material has a quarter-filled electronic band, showing a Mott-insulating instability. One prominent property of $\alpha$-ET$_2$I$_3$ is the realization of a Dirac electron system under applied pressure [11–15]. At ambient pressure, the system shows a metal-insulator transition at $T_{CO} \approx 135$ K associated with the CO transition [3, 4, 16]. It is widely accepted that the modulation pattern of the CO is not checkerboardlike but zigzag-chain-like with charge-rich sites A and B, and charge-poor sites A’ and C [Fig. 1(b)], as revealed by x-ray structural analysis [17], infrared and Raman spectroscopies [18–20], and $^{13}$C-NMR spectroscopy [21–24].

Despite the consensus on the modulation pattern, issues remain regarding the mechanism of the CO transition. Many theoretical studies have been conducted and a variety of proposals have been made. Coulomb repulsion in the quarter-filled band of the ET layers has been proposed [1, 26–29], followed by a claim that the electron-phonon interaction plays a crucial role to reproduce the CO pattern [30–33]. While these theories consider only interactions within the intra-ET layers, some approaches actively incorporate the role of the anion layer through hydrogen bonding. Reference [34] pointed out the significant role of the H-I$^{-1/2}$ $\sigma$ bond between the anion and edge protons in the ET molecule. Since the energy difference between the $\sigma$ bond and $\pi$ electrons of donor molecules are far apart, the $\sigma$ hybridization is expected to conserve the total charge density in the ET layers. However, the $\sigma$ bond can constrain atomic positions across the structural phase transition, and also the problem regarding the stability of the Mottness of the quarter-filled band perturbed by the hydrogen bond attracts much attention.

In this paper, we propose $^{127}$I-nuclear quadrupole resonance (NQR) as a microscopic tool to examine the specific H-I$^{-1/2}$ bonds. The NQR spectra of $\alpha$-ET$_2$I$_3$...
are qualitatively reproduced using first-principles calculations, which enables us to claim the microscopic interactions that occur during the CO transition. Utilizing another merit of NQR, unlike with $^{13}$C NMR, we can directly observe static and dynamic charge properties via an electric field gradient (EFG), and we found the zigzaglike charge modulation in the CO state across a first-order transition. Only one of two I-spectral lines shows significant splitting at $T_{\text{CO}}$, which cannot be reproduced by an electrostatic interaction only from the ET layers, and an interaction between the ET and $I_3$ layers through such a hydrogen bonding is necessary. The nuclear spin-lattice relaxation rate ($1/T_1$) is dominated by local fluctuation of the $I_3$ anions, of which the energy is five times smaller than the Debye frequency. We also found enhancements of $1/T_1$ just below $T_{\text{CO}}$.

II. EXPERIMENTS

Single crystals of $\alpha$-ET$_2$I$_3$ were grown by the standard electrochemical reaction [16]. The $^{127}$I-NQR experiment was performed on a polycrystalline sample of 14.2 mg under zero magnetic fields. The NQR spectrum was obtained by fast Fourier transformation of the spin-echo signal with a $\pi/2$ pulse sequence, where the typical $\pi/2$ pulse length was 2.5 $\mu$s. The $1/T_1$ times were measured using the inversion and saturation recovery methods and were obtained by fitting the magnetization curves using

$$1 - \frac{M(t)}{M(\infty)} = \frac{3}{28} \exp \left( -\frac{3t}{T_1} \right) + \frac{25}{28} \exp \left( -\frac{10t}{T_1} \right)$$

(see the Supplemental Material [35] and also Refs. [36, 37] therein). Here, $t$ is the interval between inversion (saturation) and the first $\pi/2$ pulses, and $M(t)$ is the magnetization at time $t$. We confirmed that the same $T_1$ values were obtained by both methods in the appropriate temperature range. EFGs at the iodine sites of $\alpha$-ET$_2$I$_3$ were calculated using the first-principles calculations based on the full-potential linearized augmented plane-wave (FLAPW) method [38, 39]. The calculations are based on density-functional theory (DFT), and the exchange and correlation potential is represented by a generalized gradient approximation in the Perdew-Burke-Ernzerhof formula [35, 40].

III. RESULTS AND DISCUSSION

A. NQR spectra

We found two $^{127}$I-NQR spectral lines at 172.2 and 173.1 MHz at 150 K, as shown in Fig. 2(a), while sweeping in the range of 170–176 MHz. Reported $^{127}$I-NQR studies of $I_3$ anions in quaternary ammonium salts indicated that the observed resonances are ascribed to $\pm 1/2 \leftrightarrow \pm 3/2$ transitions of the terminal iodines [41, 42]. At a terminal iodine, the EFG tensor is nearly axially symmetric [12] [i.e., $\eta = (V_{xx} - V_{yy})/V_{zz} \approx 0$, where $V_{\alpha i}$ ($i = x, y, z$) are the diagonal components of the EFG tensor]. The NQR frequency, $\nu_Q$, is expressed as $\nu_Q = \frac{eQV}{2\hbar}$, where $e$, $Q$, and $\hbar$ are the elementary charge, the nuclear quadrupole moment of the $^{127}$I nucleus $\left[ -680(10) \text{ mb} \right]$, and Planck’s constant, respectively.

In $\alpha$-ET$_2$I$_3$, two crystallographically independent $I_3$ anions, D and E, exist [Fig. 1(c)]. Since the central iodine of each anion is located at the inversion center (1c and 1d sites in Wyckoff positions), the terminal iodines of each anion group are equivalent and occupied at 2i sites above $T_{\text{CO}}$. As a result, two independent terminal iodines exist, holding relations $I_1 = I_3$ and $I_2 = I_4$ (”$=$” denotes the site equivalency), which agrees with the two distinct lines observed in our NQR spectra. As discussed below, the signals at the high and low frequencies can be assigned to the D and E sites, respectively, from the calculation of the EFG using first-principles method.

At 139 K, five distinct lines are observed, as shown in Fig. 2(a), and the three lines remain at the lowest temperature. The temperature of 139 K corresponds to $T_{\text{CO}}$, and the coexistence of high-temperature and low-temperature peaks in the spectrum indicates that the phase transition is a first-order transition. Below $T_{\text{CO}}$, four lines are expected according to the loss of the inversion center by the CO transition [17]. Although the number of observed lines below $T_{\text{CO}}$ is three, the intensities are approximately 1:2:1 from the low-frequency side, suggesting that the NQR spectra consist of four lines. The central peak below $T_{\text{CO}}$ splits slightly, as shown in the inset of Fig. 2(a). We considered that two lines nearly overlap at $\nu_Q \approx 173$ MHz because they exhibit nearly the same magnitude of EFG at the terminal iodine sites.

All the $\nu_Q$’s increase upon cooling as a result of lattice contraction, as shown in Fig. 2(b). The slope of $\nu_Q$ at the
D site is larger than that at the E site above $T_{\text{CO}}$, and below $T_{\text{CO}}$, the slopes of $\nu_Q$ at the high- and low-frequency signals are larger than that at the central frequency. An empirical formula for temperature-dependent $\nu_Q(T)$ considering thermal expansion of the unit cell \[ rarr \]

\[ \nu_Q(T) = \nu_0(1 - \alpha T^{3/2}) \] \( \text{(2)} \)

fits the experiments well [solid lines in Fig. 2(b)], and we summarize the fitted parameters in Table I. Comparing $\alpha$ values, $\alpha$ at the D site is 1.5 times larger than at the E site above $T_{\text{CO}}$, and $\alpha$ at the two outer lines is also 1.5 times larger than at the central line below $T_{\text{CO}}$. The $\alpha$ value that is dependent on the iodine site can be attributed to the distinct principal axes of the EFG at D and E, relative to that of the thermal expansion. We concluded that the two outer lines originate from the D anion (hereafter, we refer to them as $D_H$ and $D_L$), and the overlapped central line originates from the E anion ($E_H$ and $E_L$). These results show that $\nu_Q$ of the D site changes significantly because of the CO transition, whereas the change in $\nu_Q$ of the E site is negligible.

We calculated the EFG at each iodine position using the FLAPW method to clarify the relationship between the measured NQR signals and the actual iodine positions \[ rarr \]. Since the EFG is usually very sensitive to internal atomic coordinates \[ rarr \] and hydrogen atom positions determined from x-ray diffraction were not so accurate \[ rarr \], we performed structural optimization for iodine and hydrogen atom positions. The relaxed structures with the Crystallographic Information File format and detailed calculation method are included in the Supplemental Material \[ rarr \]. The calculated NQR frequencies $\nu_Q$’s are summarized in Table II along with the experimental values. At 150 K, the calculations show that $\nu_Q = 174.0 \text{ MHz}$ at the D site, which is 0.4% larger than $\nu_Q = 173.3 \text{ MHz}$ at the E site. Experimentally, the difference in frequency between the two NQR lines is approximately 0.5%, which is in good quantitative agreement. Hence, the high- and low-frequency lines are interpreted as signals originating from D and E anions.

At 30 K, the calculated $\nu_Q$ at the D site splits significantly into two lines with higher and lower frequencies, while the change at the E site is small. To discuss the amount of change in the D and E sites during the CO transition, we define

\[ \left( \frac{\Delta \nu}{\nu} \right)_{Q,k} = \frac{(\nu_{Q,k,D} - \nu_{Q,k,E})_{30 \text{K}}}{(\nu_{Q,k,E})_{150 \text{K}}} \] \( \text{(3)} \)

where $k = D, E$ sites, resulting in experimental values: $(\Delta \nu/\nu)_{Q,D} = 1.75\%$ and $(\Delta \nu/\nu)_{Q,E} = 0.02\%$; calculated values: $(\Delta \nu/\nu)_{Q,D} = 0.74\%$ and $(\Delta \nu/\nu)_{Q,E} = 0.19\%$. The first-principles DFT calculations show that $(\Delta \nu/\nu)_{Q,D}$ is larger than $(\Delta \nu/\nu)_{Q,E}$, which qualitatively explain the experimental results, although $\nu_Q$ at the E site still split in the calculations.

In order to explore the cause behind the different conduct of the D and E sites, we performed calculations on the EFG that governs $\nu_Q$, as a function of the charge-disproportionation ratio in the ET layer, by utilizing the point charge model (see the Supplemental Material \[ rarr \]) \[ rarr \]. Figures 3(a) and (b) show $\nu_{Q,p}$ ($p = I_1–I_4$) only from the ET layers at 150 K [Fig. 3(a)] and 30 K [Fig. 3(b)] as a function of $\Delta \rho$ with $\rho = 0.5 \pm \Delta \rho$ $(0 < \Delta \rho < 0.5)$. Here, the positive sign represents rich charge densities $\rho$ for molecules A and B, while the negative sign corresponds to $\rho$ for molecules A’ and C in the CO state. $\Delta \rho = 0$ is at a high-temperature electronic state, and $\Delta \rho = 0.2–0.3$ is reported in the CO state. At 150 K, because of $\Delta \rho = 0$ and the existence of the inversion symmetry, $\nu_{Q,11}$ and $\nu_{Q,13}$ ($\nu_{Q,12}$ and $\nu_{Q,14}$) must agree. The agreement of them at $\Delta \rho = 0$, indicated by the arrow [Fig. 3(a)], shows the validity of the calculation. There is no clear difference when we compare the $\nu_Q$ at 150 and 30 K. Moreover, as $\Delta \rho$ increases, the difference within each anion, i.e., $\nu_{Q,11} - \nu_{Q,13}, \nu_{Q,12} - \nu_{Q,14}$, increases [two-headed arrows in Fig. 3(b)].

---

**TABLE I.** Fitted parameters obtained by fitting $\nu_Q(T)$ at each site with Eq. (2).

|       | $\nu_0$ (MHz) | $\alpha$ (K$^{-3/2}$) |
|-------|---------------|-----------------------|
| D     | $T > T_{\text{CO}}$ | 173.94(1)             |
|       | $T < T_{\text{CO}}$ | 172.493(6)            |
| E     | $T > T_{\text{CO}}$ | 172.72(1)             |
|       | $T < T_{\text{CO}}$ | 173.081(7)            |

---

**FIG. 3.** (a)–(c) $\nu_{Q,p}$ calculated by the point charge model as a function of $\Delta \rho$ with $\rho = 0.5 \pm \Delta \rho$ $(0 < \Delta \rho < 0.5)$. (a) and (b) show the calculation results based on the 150 and 30 K structures, respectively, taking into account only the charge of the ET layers. (c) shows the results for 150 and 30 K calculated by incorporating the charge of the I3 layers in addition to the ET layers.
consistent with the experimental results, in which the E line hardly changes in the temperature-dependent spectra and the D line changes significantly.

Next, we computed the EFG incorporating the EFG from the negative charges of the I\(_3\) layers and show \(\nu_{Q,p}\) in Fig. 3(c). The magnitudes of the change in \(\nu_{Q,12}\) and \(\nu_{Q,14}\) across the CO transition differ significantly: \(\nu_{Q,12} - \nu_{Q,14} = 0\) at \(\Delta \rho = 0\) for 150 K, and that at \(\Delta \rho = 0.4\) for 30 K. On the other hand, \(\nu_{Q,11} - \nu_{Q,13}\) is minimized at \(\Delta \rho = 0\) both for 150 and 30 K, and \(\nu_{Q,11} - \nu_{Q,13}\) at all \(\Delta \rho\) for 30 K is greater than zero. The less pronounced differentiation in \(\nu_Q\) at the E site compared to the D site in the CO state is replicated, indicating the substantial role of the interaction between the anion and cation in reproducing the microscopic spectroscopy.

As the origin of this anion–cation interaction, Alemen et al. [34] pointed out that the hydrogen bonding is important and that the E anion is more strongly bound to hydrogen atoms than the D anion. The presence of hydrogen bonding would enhance the anion-cation interaction. The observed larger change in \(\nu_Q\) at the E site is consistent with this argument. Hydrogen bonding has been discussed experimentally from a structural analysis [34] and also by transport measurements [49]. In this study, we were able to explore the hydrogen bonding from a microscopic point of view.

### B. Relaxation rate

In Fig. 4, we show the temperature-dependent nuclear spin-lattice relaxation rate \(1/T_1\) for each spectral line. No significant variation in \(1/T_1\) for the distinct lines is observed. The \(1/T_1\) nearly follows power relations in regards to temperature, \(1/T_1 \propto T^\beta\), which differs from \(^{13}\text{C}\) NMR [24]. The \(\beta\) changes from high temperature, \(\beta = 2\), to low temperature, \(\beta \approx 7\), suggesting that the relaxation mechanism is quadrupolar relaxation of nuclei by two-phonon Raman processes [50, 51]. The \(1/T_1\) originating from this process is expressed as [52]

\[
\left( \frac{1}{T_1} \right)_Q \approx \frac{81 \pi}{2} \left( \frac{F_2 h}{m v^2} \right)^2 \int_0^\Omega \frac{e^{\omega/k_B T}}{(e^{\omega/k_B T} + 1)^2} \frac{\omega}{\Omega} d\omega,
\]

where \(k_B, m, \Omega\) are the Boltzmann constant, the mass of the \(^{127}\text{I}\) nucleus, and a cutoff frequency, respectively. \(v\) is the sound velocity in the crystal, which is an order of \(10^3\) m/s in organic conductors [53]. \(\Omega\) is represented by the temperature \(\Theta = (\hbar/k_B)\Omega\) and can be estimated as the Debye temperature, \(\Theta = \Theta_D = 200\) K, which is obtained by heat capacity measurements of ET organic conductors. \(F_2\) characterizes the phonon modulation of the EFG and is difficult to determine precisely; however, the simplest estimate, \(F_2 = 2\pi \nu Q\), works well [51, 54].

The calculated \((1/T_1)_Q\) is plotted as the blue dashed line in Fig. 4 using \(\nu_Q = 173\) MHz and \(\Theta = 200\) K, which is significantly smaller than the experimental \(1/T_1\). Instead, the calculated \((1/T_1)_Q\) using \(\Theta = 45\) K (green dashed line) reproduces the experiments well. This discrepancy suggests that the local \(\Theta\) at iodine sites in Eq. (4) can be smaller than the global Debye temperature \(\Theta_D\) estimated from macroscopic measurements. We can cite several related experiments. The \(^{129}\text{I-}\)Mössbauer results of \(\beta\text{-ET}_{2}\text{I}_3\) have been explained using the local Debye temperature of \(\sim 100\) K [55], which is smaller than \(\Theta_D \sim 200\) K estimated from the heat capacity measurement [56]. Raman spectra also showed a low-lying molecular vibration mode with 27 cm\(^{-1}\) (= 38 K) assigned to the libration of \(\text{I}_3\) anions, a reciprocating motion with a fixed position in the middle of the \(\text{I}_3\) “stick” (i.e., the central iodine). These arguments are consistent with our observations.

Around the \(T_{CO}\), we found small peaks for \(1/T_1\) of the charge-sensitive \(\text{D}_H\) and \(\text{D}_L\) lines, as shown in the inset of Fig. 4. Notably, that the peak temperature is located just below \(T_{CO}\), by which we consider the source for the additional relaxation is not a critical slowing down for the CO. A similar peak for \(1/T_1\) just below the \(T_{CO}\) was observed by \(^{13}\text{C}\)-NMR for the charge-rich site [24]. Reference [24] argues that an emergent antiferromagnetic zigzag chain \((S = 1/2)\) for \(T < T_{CO}\) undergoes a singlet state with a sizable gap of \(\Delta = 40\) meV [29]. We plot \(1/T_1 = (1/T_1)_Q + \text{const.} \times \exp(-\Delta/k_B T)\) as the solid lines in the inset of Fig. 4 and find good agreements with the experimental \(1/T_1\) for the \(\text{D}_H\) and \(\text{D}_L\) sites. However, we cannot conclude that magnetic fluctuation from charge-ordered ET layers is the source for the peaks of \(1/T_1\) because \(1/T_1\) for \(\text{D}_Q\) and \(\text{D}_L\) sites that are close to charge-rich and charge-poor ET molecules show comparable enhancements.

When we consider the difference in the relaxation mechanisms of \(^{13}\text{C}\) and \(^{127}\text{I}\) (i.e., magnetic fluctuation of the local spin density for the former and EFG fluctuation for the latter), we can point out another possibility.

### TABLE II. NQR frequencies of experiments \((\nu_Q^{exp})\) and calculation \((\nu_Q^{cal})\) for terminal iodines of \(\text{I}_3\) anions.

|       | D \(\nu_Q^{exp}\) (MHz) | D \(\nu_Q^{cal}\) (MHz) | E site | E \(\nu_Q^{exp}\) (MHz) | E \(\nu_Q^{cal}\) (MHz) | site |
|-------|--------------------------|--------------------------|--------|--------------------------|--------------------------|------|
| 150 K \((T > T_{CO})\) | 173.10 | 174.0 | I1(=13) | 172.17 | 173.3 | I2(=14) |
| 30 K \((T < T_{CO})\) | 175.40 | 175.2 | I1 | 173.04 | 172.9 | I2 |
|       | 172.38 | 173.8 | I3 | 173.00 | 172.6 | I4 |
between the energy gaps in the CDW and spin-singlet Mott systems. The first-principles calculations also show a similar singularity for the gap opening due to Coulomb repulsion \cite{60, 61}. Detailed theoretical analyses considering the gap structures and the relationships between the magnitudes of the gap and leading electronic/magnetic interactions are necessary to determine the origins of the gap.

In summary, we obtained $^{127}$I-NQR spectra and $1/T_1$ for $\alpha$-ET$_2$I$_3$ that undergoes a CO transition at ambient pressure. The first-principles calculations accurately reproduced the NQR frequency of each spectral line, which enabled us to examine the microscopic interactions. The spectral line at the D site splits significantly, while that at the E site is negligibly small. These results are qualitatively reproduced by EFG calculations based on a point-charge model that incorporates contributions from both ET and I$_3$ layers, suggesting the importance of the anion-cation interaction. Furthermore, $1/T_1$ is predominantly determined by a two-phonon process characterized by the local vibration of I$_3$ anions. The charge order phase transition is first-order, without a critical slowing down of the electronic charges. Just below the $T_{CO}$, $1/T_1$ shows an additional relaxation similar to the reported $^{13}$C NMR.

ACKNOWLEDGMENTS

We are grateful to H. Sawa and H. Seo for their helpful discussions. The computations in this study were mainly conducted using the computer facilities of MASAMUNE at IMR, Tohoku University, Japan. This work was partially supported by the Japan Society for the Promotion of Science KAKENHI Grants No. 20K14401, No. 21K03438, No. 20K03870, No. 21K03426, and No. 19K21860.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure.png}
\caption{Temperature dependence of $1/T_1$. The dashed lines are calculated $(1/T_1)_Q$ with $\Theta = 45$ K and 200 K. The inset shows the temperature dependence of $1/T_1$ in the vicinity of $T_{CO}$. For clarity, the $D_H$ and $D_L$ data are multiplied and divided by 1.5, respectively. The solid curves are $1/T_1 = (1/T_1)_Q + \text{const.} \times \exp(-\Delta/k_BT)$.}
\end{figure}

\begin{itemize}
\item [1] H. Seo, Charge ordering in organic ET compounds, Journal of the Physical Society of Japan 69, 805 (2000).
\item [2] K. Miyagawa, A. Kawamoto, and K. Kanoda, Charge ordering in a quasi-two-dimensional organic conductor, Physical Review B 62, R7679 (2000).
\item [3] K. Yamamoto, S. Iwai, S. Boyko, A. Kashiwazaki, F. Hirramatsu, C. Okabe, N. Nishi, and K. Yakushi, Strong optical nonlinearity and its ultrafast response associated with electron ferroelectricity in an organic conductor, Journal of the Physical Society of Japan 77, 074709 (2008).
\item [4] S. Tomić and M. Dressel, Ferroelectricity in molecular solids: a review of electrodynamic properties, Reports on Progress in Physics 78, 096501 (2015).
\item [5] F. Kagawa, T. Sato, K. Miyagawa, K. Kanoda, Y. Tokura, K. Kobayashi, R. Kumai, and Y. Murakami, Charge-cluster glass in an organic conductor, Nature Physics 9, 419 (2013).
\item [6] H. Mori, S. Tanaka, and T. Mori, Systematic study of the electronic state in $\theta$-type BEDT-TTF organic conductors by changing the electronic correlation, Physical Review B 57, 12023 (1998).
\item [7] J. Merino and R. H. McKenzie, Superconductivity mediated by charge fluctuations in layered molecular crystals, Physical Review Letters 87, 237002 (2001).
\item [8] A. F. Bangura, A. I. Coldea, J. Singleton, A. Ardashan, A. Akutsu-Sato, H. Akutsu, S. S. Turner, P. Day, T. Yamamoto, and K. Yakushi, Robust superconducting state in the low-quasiparticle-density organic metals $\beta''$-(BEDT-TTF)$_4$[(H$_2$O)$_3$M(C$_2$O$_4$)$_3$]Y: Superconductivity due to proximity to a charge-ordered state, Physical Review B 72, 014543 (2005).
\item [9] A. Pustogow, K. Treptow, A. Rohwer, Y. Saito, M. Sanz Alonso, A. Löhle, J. A. Schmeler, and M. Dressel, Charge order in $\beta''$-phase BEDT-TTF salts, Physical Review B 99, 155144 (2019).
\item [10] M. Dressel and S. Tomić, Molecular quantum materials: electronic phases and charge dynamics in two-dimensional organic solids, Advances in Physics 69, 1 (2020).
\item [11] N. Tajima, M. Tamura, Y. Nishio, K. Kajita, and Y. Iye, Transport property of an organic conductor $\alpha$-(BEDT-TTF)$_2$I$_3$ under high pressure -Discovery of a novel type of conductor-, Journal of the Physical Society of Japan 86, 014544 (2001).
\end{itemize}
[12] S. Katayama, A. Kobayashi, and Y. Suzumura, Pressure-induced zero-gap semiconducting state in organic conductor \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) salt, Journal of the Physical Society of Japan 75, 054705 (2006).

[13] K. Kajita, Y. Nishiho, N. Tajima, Y. Suzumura, and A. Kobayashi, Molecular Dirac fermion systems - Theoretical and experimental approaches-, Journal of the Physical Society of Japan 83, 072004 (2012).

[14] M. Hirata, K. Ishikawa, G. Matsuno, A. Kobayashi, K. Miyagawa, M. Tamura, C. Berthier, and K. Kanoda, Anomalous spin correlations and excitonic instability of interacting 2D Weyl fermions, Science 358, 1403 (2017).

[15] S. Fujiyama, H. Maebashi, N. Tajima, T. Tsumuraya, H.-B. Cui, M. Ogata, and R. Kato, Large diamagnetism and electromagnetic duality in two-dimensional dirac electron system, Phys. Rev. Lett. 128, 027201 (2022).

[16] K. Bender, I. Hennig, D. Schweitzer, K. Dietz, H. Endres, and H. J. Keller, Synthesis, structure and physical properties of a two-dimensional organic metal, \(\text{dil}[\text{bis(ethylenedithio)tetraethylvalene}](\text{triiodide})\), (BEDT-TTF)\(_2\)I\(_3\), Molecular Crystals and Liquid Crystals 108, 359 (1984).

[17] T. Kakiuchi, Y. Wakabayashi, H. Sawa, T. Takahashi, and T. Nakamura, Charge ordering in \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) by synchrotron x-ray diffraction, Journal of the Physical Society of Japan 76, 113702 (2007).

[18] R. Wojciechowski, K. Yamamoto, K. Yakushi, M. Inokuchi, and A. Kawamoto, High-pressure Raman study of the charge ordering in \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\), Physical Review B 67, 224105 (2003).

[19] T. Ivec, B. Korin-Hamzić, O. Milat, S. Tomic, C. Clauss, N. Drichko, D. Schweitzer, and M. Dressel, Electrodynamic response of the charge ordering phase: Dielectric and optical studies of \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\), Physical Review B 83, 165128 (2011).

[20] K. Yakushi, Infrared and Raman studies of charge ordering in organic conductors, BEDT-TTF salts with quarter-filled bands, Crystals 2, 1291 (2012).

[21] Y. Takano, K. Hiroki, H. M. Yamamoto, T. Nakamura, and T. Takahashi, Charge disproportionation in the organic conductor, \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\), Journal of Physics and Chemistry of Solids 62, 393 (2001).

[22] S. Hirose and A. Kawamoto, Local spin susceptibility in the zero-gap-semiconductor state of \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) probed by \(^{13}\)C NMR under pressure, Physical Review B 82, 115114 (2010).

[23] M. Hirata, K. Ishikawa, K. Miyagawa, K. Kanoda, and M. Tamura, \(^{13}\)C NMR study on the charge-disproportionated conducting state in the quasi-two-dimensional organic conductor \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\), Physical Review B 84, 125133 (2011).

[24] K. Ishikawa, M. Hirata, D. Liu, K. Miyagawa, M. Tamura, and K. Kanoda, Spin excitations in the quasi-two-dimensional charge-ordered insulator \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\) probed via \(^{13}\)C NMR, Physical Review B 94, 085154 (2016).

[25] S. Kitou, T. Tsumuraya, H. Sawahata, F. Ishii, K.-i. Hiraki, T. Nakamura, N. Katayama, and H. Sawa, Ambient-pressure Dirac electron system in the quasi-two-dimensional molecular conductor \(\alpha\)-(BETS)\(_2\)I\(_3\), Physical Review B 103, 035135 (2021).

[26] H. Kino and H. Fukuyama, On the phase transition of \(\alpha\)-(ET)\(_2\)I\(_3\), Journal of the Physical Society of Japan 64, 1877 (1995).

[27] H. Kino and H. Fukuyama, Phase diagram of two-dimensional Organic Conductors: (BEDT-TTF)\(_2\)X, Journal of the Physical Society of Japan 65, 2158 (1996).

[28] H. Seo and H. Fukuyama, Antiferromagnetic phases of one-dimensional quarter-filled organic conductors, Journal of the Physical Society of Japan 66, 1240 (1997).

[29] Y. Tanaka and M. Ogata, Correlation Effects on Charge Order and Zero-Gap State in the Organic Conductor \(\alpha\)-(BEDT-TTF)\(_2\)X, Journal of the Physical Society of Japan 85, 104706 (2016).

[30] R. Torsten Clay, S. Mazumdar, and D. K. Campbell, Charge Ordering in \(\theta\)-(BEDT-TTF)\(_2\)X Materials, Journal of the Physical Society of Japan 71, 1816 (2002).

[31] Y. Tanaka and K. Yonemitsu, Charge order with structural distortion in organic conductors: Comparison between \(\theta\)-(ET)\(_2\)RbZn(SCN)\(_4\) and \(\alpha\)-(ET)\(_2\)I\(_3\), Journal of the Physical Society of Japan 77, 034708 (2008).

[32] S. Miyashita, Y. Tanaka, S. Iwai, and K. Yonemitsu, Charge, lattice, and spin dynamics in photoinduced phase transitions from charge-ordered insulator to metal in quasi-two-dimensional organic conductors, Journal of the Physical Society of Japan 79, 034708 (2010).

[33] M. Udagawa and Y. Motome, Charge ordering and coexistence of charge fluctuations in quasi-two-dimensional organic conductors \(\theta\)-(BEDT-TTF)\(_2\)X, Phys. Rev. Lett. 98, 206405 (2007).

[34] P. Alemany, J.-P. Pouget, and E. Canadell, Essential role of anions in the charge ordering transition of \(\alpha\)-(BEDT-TTF)\(_2\)I\(_3\), Physical Review B 85, 195118 (2012).

[35] See the Supplemental Material for detailed calculation of EFG and relaxation curves.

[36] D. E. MacLaughlin, J. D. Williamson, and J. Butterworth, Nuclear spin-lattice relaxation in pure and impure indium. I. Normal state, Physical Review B 4, 60 (1971).

[37] A. C. Daniel and W. G. Moulton, Temperature dependence of pure nuclear quadrupole spin—lattice relaxation in SnI\(_4\), The Journal of Chemical Physics 41, 1833 (1964).

[38] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Full-potential self-consistent linearized-augmented-plane-wave method for calculating the electronic structure of molecules and surfaces: \(\text{O}_2\) molecule, Physical Review B 24, 864 (1981).

[39] J. Yu, A. J. Freeman, R. Podloucky, P. Herzig, and P. Weinberger, Origin of electric-field gradients in high-temperature superconductors: \(\text{YBa}_2\text{Cu}_3\text{O}_7\), Physical Review B 43, 532 (1991).

[40] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Physical Review Letters 77, 3865 (1996).

[41] Y. Yoshioka, N. Nakamura, and H. Chihara, On the correlation between NQR frequency and bond length in \(\text{I}_3\), Journal of Molecular Structure 111, 151 (1983).

[42] G. A. Bowmaker and S. Hacobian, Nuclear quadrupole resonance of charge transfer complexes. I. The trihalide ions, Australian Journal of Chemistry 21, 551 (1968).

[43] H. Yakobi, E. Eliav, L. Visscher, and U. Kaldor, High-accuracy calculation of nuclear quadrupole moments of atomic halogens, The Journal of Chemical Physics 126, 054301 (2007).

[44] J. Christiansen, P. Heubes, R. Keitel, W. Klinger, W. Loeffler, W. Sandner, and W. Wittthuhn, Temperature dependence of the electric field gradient in noncubic met-
[45] P. Blaha, D. J. Singh, P. I. Sorantin, and K. Schwarz, Electric-field-gradient calculations for systems with large extended-core-state contributions, Phys. Rev. B 46, 1321 (1992).

[46] P. T. Edwards, L. K. Saunders, D. C. Grinter, P. Ferrer, G. Held, E. J. Shotton, and S. L. M. Schroeder, Determination of H-atom positions in organic crystal structures by nexas combined with density functional theory: a study of two-component systems containing isonicotinamide, The Journal of Physical Chemistry A 126, 2889 (2022), pMID: 35537046.

[47] W. Gabes and M. A. M. Nijman-Meester, Semiempirical molecular orbital calculation of symmetrical trihalide ions, Inorganic Chemistry 12, 589 (1973).

[48] T. Mori, A. Kobayashi, Y. Sasaki, H. Kobayashi, G. Saito, and H. Inokuchi, The intermolecular interaction of tetrathiafulvalene and bis(ethylenedithio)tetrathiafulvalene in organic metals. Calculation of orbital overlaps and models of energy-band structures, Bulletin of the Chemical Society of Japan 57, 627 (1984).

[49] T. Ivek, M. Čulo, M. Kuveždić, E. Tutiš, M. Basletić, B. Mihaljević, E. Tafra, S. Tomić, A. Löhle, M. Dressel, D. Schweitzer, and B. Korin-Hamzić, Semimetallic and charge-ordered α-(BEDT-TTF)2I3: On the role of disorder in dc transport and dielectric properties, Physical Review B 96, 075141 (2017).

[50] F. Iwase, K. Miyagawa, S. Fujiyama, K. Kanoda, S. Hiroiuchi, and Y. Tokura, Neutral-ionic phase transition in DMTTF-QCl4 investigated by 35Cl NQR, Journal of the Physical Society of Japan 76, 073701 (2007).

[51] T. Kobayashi, Q.-P. Ding, H. Taniguchi, K. Satoh, A. Kawamoto, and Y. Furukawa, Charge disproportionation in the spin-liquid candidate κ-(ET)2Cu2(CN)3 at 6 K revealed by 63Cu NQR measurements, Physical Review Research 2, 042023(R) (2020).

[52] A. A. Abragam, The Principles of Nuclear Magnetism (Oxford University Press, Oxford, U.K., 1961).

[53] S. Imajo, private communication.

[54] M. Klanjšek, A. Zorko, R. Žitko, J. Mravlje, Z. Jagličič, P. K. Biswas, P. Prelovšek, D. Mihailović, and D. Arčon, A high-temperature quantum spin liquid with polaron spins, Nature Physics 13, 1130 (2017).

[55] G. Wortmann, E. Bychkov, and Y. S. Grushko, 129I-Mössbauer study of molecular dynamics in the organic superconductor β-(BEDT-TTF)2I3, Hyperfine Interactions 70, 1179 (1992).

[56] G. Gruner, The dynamics of charge-density waves, Reviews of modern physics 60, 1129 (1988).

[57] P. Matus, P. Bánki, and G. Kriza, 87Rb NMR spin-lattice relaxation in the charge-density wave phase of Rb0.3MoO3, Le Journal de Physique IV 09, Pr10 (1999).

[58] T. Maniv, Effect of a spin density wave instability on the nuclear spin-lattice relaxation in quasi 1-d conductors, Solid State Communications 43, 47 (1982).

[59] T. Tsumuraya, H. Seo, and T. Miyazaki, First-principles study of the charge ordered phase in κ-D3(Cat-EDT-TTF/ST)2: Stability of π-electron deuterium coupled ordering in hydrogen-bonded molecular conductors, Physical Review B 101, 045114 (2020).

[60] T. Tsumuraya, H. Seo, and T. Miyazaki, First-principles study on the stability and electronic structure of the charge-ordered phase in α-(BEDT-TTF)2I3, Crystals 11, 1109 (2021).
