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Charge disproportionation in the spin-liquid candidate κ – (ET)2Cu2(CN)3 at 6 K revealed by 63Cu NQR measurements

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Abstract
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Rapid Communications

Charge disproportionation in the spin-liquid candidate κ-(ET)$_2$Cu$_2$(CN)$_3$ at 6 K revealed by ^{63}Cu NQR measurements

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The spin-liquid candidate κ-(ET)$_2$Cu$_2$(CN)$_3$ [ET: bis(ethylenedithio)tetrathiafulvalene] does not exhibit magnetic ordering down to a very low temperature, but shows a mysterious anomaly at 6 K. The origin of the so-called 6-K anomaly is still under debate. We carried out nuclear quadrupole resonance (NQR) measurements on the copper sites of the insulating layers, which are sensitive to the charge dynamics unlike conventional spin-1/2 nuclear magnetic resonance (NMR). The main finding of this Rapid Communication is that the observation of a sharp peak behavior in the nuclear spin-lattice relaxation rate T_1^{-1} of ^{63}Cu NQR at 6 K while T_1^{-1} of both ^{13}C and ^{1}H NMR show no clear anomaly. This behavior can be understood as a second-order phase transition related to charge disproportionation in the ET layers.

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Quasi-two-dimensional organic charge transfer salts κ-(ET)$_2X$ [ET and X denote bis(ethylenedithio) tetrathiafulvalene and monovalent anion, respectively] possess half-filled bands owing to the strong dimeric structures of the donor molecules. In a typical phase diagram, antiferromagnetic and superconducting phases are adjacent to each other, and the phase transition between them has been discussed in terms of the bandwidth and on-site Coulomb repulsion [1], where the magnetic properties mainly originate from an antiferromagnetic interaction between (ET)$_2^+$ dimers with $S = 1/2$. The role of the charge degree of freedom has also been pointed out to explore the recent observations of dielectric anomaly with antiferromagnetic ordering [2], charge order [3,4], and quantum dipole liquid [5].

Such complex physical properties related to spin and charge degrees of freedom have also been discussed in a representative spin-liquid candidate κ-(ET)$_2$Cu$_2$(CN)$_3$. This material does not show long-range magnetic ordering down to $T = 32$ mK despite a large antiferromagnetic exchange interaction of ~250 K [6], and therefore it has attracted much attention as a quantum spin liquid. κ-(ET)$_2$Cu$_2$(CN)$_3$ showed a relaxorlike dielectric response below 60 K, and intradimer charge disproportionation (CD) was proposed [7] although the mechanism is under debate [8–10]. It is also pointed out that the mysterious anomaly at 6 K could be related to charge properties. This anomaly was initially detected by the hump structure in the T dependence of specific heat whereby a crossover from a thermal disordered to a quantum spin-liquid state was suggested [11]. On the other hand, the thermal expansion measurements indicate a phase transition, and the importance of charge degrees of freedom was suggested [12]. Whereas many experimental and theoretical efforts have been devoted to elucidating the origin of the so-called "6-K anomaly" [13–24], it is not even clear whether it is a phase transition or a crossover phenomenon.

Nuclear magnetic resonance (NMR) is an effective technique for providing microscopic evidence of charge and/or spin anomalies. Up to now, there have been several NMR reports using ^{13}C and ^{1}H nuclei with nuclear spin $I = 1/2$. However, such NMR measurements cannot probe the charge directly because of no direct interaction between the $I = 1/2$ nucleus and charge, whereas one can obtain information of the charge distributions through the change in the hyperfine coupling constants [25]. Therefore NMR measurements using nuclei with $I = 1/2$ are less sensitive to a charge anomaly. In fact, no clear anomaly at 6 K has been observed in ^{1}H- and ^{13}C-NMR measurements, especially in nuclear spin-lattice relaxation measurements [6,26–28]. Here, we focus on the nuclear quadrupole resonance (NQR) technique, which is a charge-sensitive probe offering a different perspective. This is because the NQR technique directly detects the electric field gradient (EFG) through the nuclear quadrupole moment Q ($\neq 0$ when $I > 1/2$). Until now, the NQR method has attracted less attention in the field of organic conductors since there is no NQR-active nuclei in the ET molecule. In this Rapid Communication, we report a NQR experiment in the ET-based charge transfer salts using copper nuclei located at the insulating layer in κ-(ET)$_2$Cu$_2$(CN)$_3$. Our NQR results elucidate that the 6-K anomaly can be understood as a phase transition related to the charge degree of freedom in the molecular layers.

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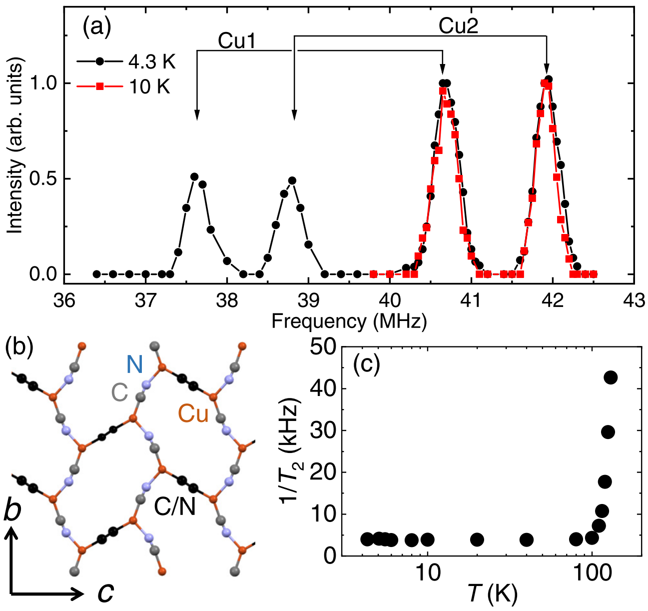

FIG. 1. (a) ZF NQR spectra at 4.3 K (black circles) and 10 K (red squares). (b) Structure of the $Cu_2(CN)_3$ insulating layer. (c) T dependence of T_2^{-1} measured at the peak around 40.7 MHz.

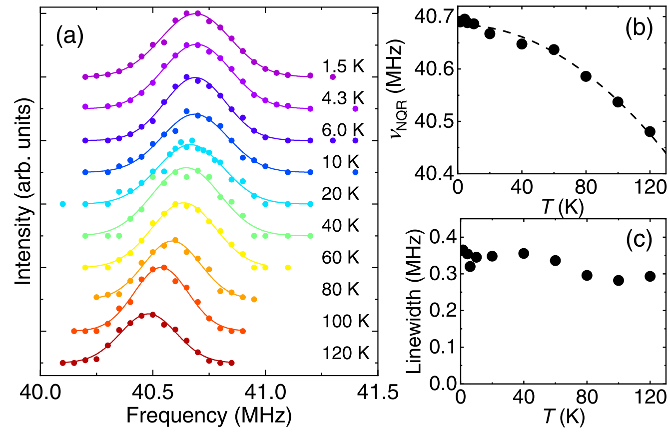

FIG. 2. (a) T evolution of NQR spectra. Solid lines are the fitting curves using the Gaussian function. (b) T dependence of ν_{NQR}. The dashed curve is the calculated result with the empirical formula $\nu_{NQR} = \nu_0 \exp(-\alpha T^2)$ (see text). (c) T dependence of the linewidth.

Polycrystalline samples were prepared by the standard electrochemical reaction [29]. Zero-magnetic-field (ZF) NQR experiments of ^{63}Cu ($I = 3/2$, $Q = -0.21$ barns) and ^{65}Cu ($I = 3/2$, $Q = -0.195$ barns) were performed by using a home-made phase-coherent spin-echo pulse spectrometer. ^{63,65}Cu-NQR spectra were obtained in steps of frequency by measuring the intensity of the Hahn spin echo. The nuclear spin-lattice relaxation rate of ^{63}Cu, ${}^{63}T_1^{-1}$, was measured with a saturation recovery method and determined by fitting $M(t)$ using the stretched exponential function $1 - M(t)/M(\infty) = \exp[-(3t/T_1)^\beta]$, where $M(t)$ and $M(\infty)$ are the nuclear magnetization at time t after the saturation and the equilibrium nuclear magnetization at $t \to \infty$, and β is the stretched exponent, respectively. The nuclear spin-echo decay rate T_2^{-1} was determined by the spin-echo signal $M(2\tau)$ as a function of time 2τ, where τ is the interval between the first exciting and refocusing pulses.

Figure 1(a) shows the NQR spectra at 4.3 K where four lines are observed in the frequency range of 36–43 MHz. In the case of $I = 3/2$, one expects a single NQR line at a resonance frequency of $\nu_{NQR} = \nu_Q\sqrt{1 + \eta^2/3}$, where ν_Q is the nuclear quadrupole frequency defined by $\nu_Q = eQV_{ZZ}/2h$. Here, e, V_{ZZ}, h, and η are the elementary charge, the principal value of the EFG tensor, Planck's constant, and asymmetry parameter of EFG, respectively. Since there are two isotopes ^{63}Cu and ^{65}Cu, the NQR spectrum must be a pair of lines with different intensities where the ^{63}Cu-NQR intensity is about double that of the ^{65}Cu-NQR one due to the natural abundances of the two nuclei (viz., ^{63}Cu: 69%; ^{65}Cu: 31%). Therefore, the observation of four lines clearly indicates the existence of two Cu sites with slightly different environments. By taking the difference in Q between ^{63}Cu and ^{65}Cu into consideration, we can assign the two pairs (defined by Cu1 and Cu2 sites) as shown in Fig. 1(a).

In κ-$(ET)_2Cu_2(CN)_3$, as shown in Fig. 1(b), there are three cyano groups around a Cu nucleus, and one of them is considered to be positionally disordered with a 50% carbon and 50% nitrogen distribution (depicted by black symbols) due to an inversion point at the center of the cyano groups [30,31]. Consequently, Cu^+ ions are expected to be trigonally coordinated with two carbons and one nitrogen, or with one carbon and two nitrogens, making two copper sites with slightly different environments (i.e., slightly different EFG) with equal probability. This is consistent with the observed NQR spectrum including the intensity ratio of 1:1 for Cu1 and Cu2. Although we do not know which one is which, our observation directly evidences the disorder of carbon and nitrogen ions due to the inversion symmetry in κ-$(ET)_2Cu_2(CN)_3$.

It is noted that one cannot determine the values of ν_Q and η for the Cu ions separately from only the NQR spectrum. A finite value of η, the lack of axial symmetry of EFG, is expected from the local symmetry at the Cu sites. With the help of the NMR spectrum measurements described below, η is estimated to be $\sim$0.5, and thus the values of ν_Q are estimated to be 36.2 (37.3) MHz and 39.1 (40.3) MHz for ^{65}Cu and ^{63}Cu, respectively, for the Cu1 (Cu2) sites. The direction of V_{ZZ} is considered to be parallel to the a^* axis, perpendicular to the insulating layers.

As shown in Fig. 1(a), there is no significant difference in the spectra between 4.3 and 10 K for the two Cu sites, and hereafter, we show the T dependence of spectra and ${}^{63}T_1^{-1}$ measured at the peak at around 40.7 MHz (^{63}Cu ions at the Cu1 site). NQR experiments were able to be conducted between 1.5 and 120 K. Above 100 K, T_2^{-1} suddenly increases as shown in Fig. 1(c), and eventually the NQR signals disappeared above 130 K owing to the shortening of T_2. This is probably due to the vibrational motion of the ethylene end groups of the ET molecule at high T [32].

Figure 2(a) shows the T evolution of ^{63}Cu-NQR spectra for the Cu1 site. There is no drastic change in the NQR spectra, suggesting no structural phase transition in the T range. The peak position is slightly shifted to a lower frequency with

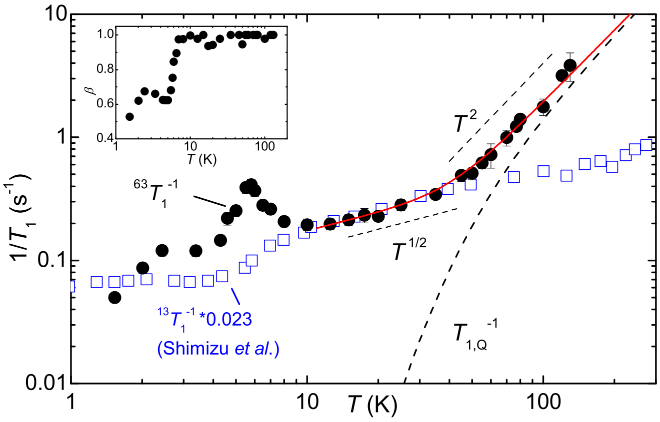

FIG. 3. T dependencies of $^{63}T_1^{-1}$ (black circles) and $^{13}T_1^{-1}$ (open blue squares) from Ref. [27]. The values of $^{13}T_1^{-1}$ are reduced by a factor of 0.023. Dashed black and solid red curves represent $T_{1,Q}^{-1}$ due to the thermal lattice vibration, and $T_{1,Q}^{-1} + 0.055T^{1/2}$, respectively. The inset shows the T dependence of β.

increasing T, corresponding to the decrease in $\nu_{\rm NQR}$ as shown in Fig. 2(b). The T dependence of $\nu_{\rm NQR}$ is considered to be originated from the thermal lattice expansion and can be described by the empirical formula [33,34] $\nu_{\rm NQR} = \nu_0 \exp(-\alpha T^2)$. As shown by the curve in Fig. 2(b), the T dependence of $\nu_{\rm NQR}$ is well reproduced with the formula with $\nu_0 = 40.68$ MHz and $\alpha = 3.58 \times 10^{-7}$ K^{-2}. Figure 2(c) shows the T dependence of the linewidth [full width at half maximum (FWHM)] determined by the fitting of the spectra with a Gaussian function. With decreasing T, the linewidth increases from 0.3 MHz at 120 K to 0.36 MHz at around 60 K, and is nearly independent of T below 60 K.

Figure 3 shows the T dependence of ZF $^{63}T_1^{-1}$. For comparison, the T dependence of T_1^{-1} of ^{13}C, $^{13}T_1^{-1}$, is also plotted [27]. Note that the values of $^{13}T_1^{-1}$ are reduced by a factor of 0.023. The T dependences are quite different from each other. $^{63}T_1^{-1}$ shows a T^2 dependence above 60 K, below which it is proportional to $T^{1/2}$ coinciding with that of $^{13}T_1^{-1}$. With further decreasing T below 10 K, $^{63}T_1^{-1}$ starts to increase and then shows a pronounced peak at 6 K, whereas $^{13}T_1^{-1}$ decreases monotonically. The exponent β deviates from unity below 6 K as shown in the inset of Fig. 3, indicating a development of inhomogeneity in $^{63}T_1$. A similar inhomogeneity below ∼6 K was also observed in the ^{13}C- and ^{1}H-NMR measurements [6,27].

The $T^{\sim 2}$ dependence of $^{63}T_1^{-1}$ observed above 60 K can be explained by the thermal vibrations of the three nearest-neighbor CN$^-$ ions with respect to the Cu ion. A similar T dependence has been reported in other kinds of diamagnetic insulators [34–36], whose T dependence was explained by the quadrupolar relaxation due to the two-phonon Raman process [37]. In this case, the quadruple relaxation ($T_{1,\rm Q}^{-1}$) is described as $T_{1,\rm Q}^{-1} = \frac{81\pi}{2}\left(\frac{F_2\hbar}{mv^2}\right)^2 \int_0^{\Omega} e^{\hbar\omega/k_BT}(e^{\hbar\omega/k_BT} - 1)^{-2}(\omega/\Omega)^6 d\omega$. Here, m, v, and Ω are the atomic mass of ^{63}Cu, sound velocity in the crystal, and cutoff frequency related to the Debye temperature (Θ), respectively. F_2 is a parameter which can be approximated by $2\pi\nu_{\rm Q}$ [37,38]. Assuming $v = 10^3$ m/s [39], and a typical value $\Theta = \hbar\Omega/k_B = 200$ K for κ-(ET)$_2X$ [40,41], we have calculated the T dependence of $T_{1,\rm Q}^{-1}$. The dashed black curve is the calculated result without a free parameter, which reproduces the experimental data very well by adding another contribution as described below.

From the calculated result of $T_{1,\rm Q}^{-1}$, $^{63}T_1^{-1}$ is expected to decrease drastically at low T due to the suppression of thermal vibrations. However, $^{63}T_1^{-1}$ gradually deviates from $T_{1,\rm Q}^{-1}$ below ∼60 K and shows a $T^{1/2}$ dependence between 10 and 40 K, which is the same as that of $^{13}T_1^{-1}$ [27]. Since $^{13}T_1^{-1}$ originates from the magnetic fluctuations from the π electrons of the ET layers [27,42], the similar T dependence of $^{63}T_1^{-1}$ indicates that the magnetic fluctuations become dominant at the Cu site. In fact, this interpretation can be confirmed by looking at the ratio of $^{63}T_1^{-1}/^{13}T_1^{-1}$. Since T_1^{-1} is proportional to the square of the gyromagnetic ratio γ and hyperfine coupling constant A, the ratio of $(^{63}\gamma^{2\ 63}T_1)^{-1}/(^{13}\gamma^{2\ 13}T_1)^{-1} \sim 0.02$ should be proportional to $|^{63}A/^{13}A|^2$. To estimate the ^{63}A, we performed ^{63}Cu-NQR measurements on the antiferromagnet κ-(ET)$_2$Cu[N(CN)$_2$]Cl (Néel temperature ∼22 K [43,44]) whose interlayer distance is close to the case of κ-(ET)$_2$Cu$_2$(CN)$_3$ [45]. We found the internal field at the ^{63}Cu site to be $^{63}H_{\rm int} \sim 70$ G [46]. According to the ^{13}C-NMR measurement by Smith *et al.*, the mean internal field at the ^{13}C site is estimated to be $^{13}H_{\rm int} \sim 750$ G [47]. Since the ratio of the internal magnetic field ($|^{63}H_{\rm int}/^{13}H_{\rm int}| \sim 0.1$) is considered to be proportional to the hyperfine coupling constant ratio, $|^{63}A/^{13}A|^2$ is evaluated to be 0.01, which is in good agreement with $(^{63}\gamma^{2\ 63}T_1)^{-1}/(^{13}\gamma^{2\ 13}T_1)^{-1} \sim 0.02$. Therefore, the observed $^{63}T_1^{-1}$ between 10 and 40 K can be interpreted as the magnetic fluctuations originating from the π electrons on the ET layers. The red solid curve shown in Fig. 3 is the sum of the two contributions of the magnetic relaxation ($^{63}T_1^{-1} \propto T^{1/2}$) and the quadruple relaxation $T_{1,\rm Q}^{-1}$: $T_1^{-1} = aT^{1/2} + T_{1,\rm Q}^{-1}$ (with $a = 0.055$), which reproduces the experimental data quite well.

The most striking feature in the T dependence of $^{63}T_1^{-1}$ is the observation of a sharp peak around 6 K, indicating a second-order phase transition. We exclude the possibility of a crossover phenomenon for the anomaly by measuring the resonance frequency dependence of $^{63}T_1^{-1}$. In the case of crossover, we expect a Bloembergen-Purcell-Pound-like behavior where a frequency-dependent T_1^{-1} is expected [48]. Since one cannot change the resonance frequency in the NQR experiment, we have carried out NMR measurements. Figure 4(a) shows the field-swept ^{63,65}Cu-NMR spectrum measured at a fixed frequency 75 MHz at 1.7 K where a broad and complicated spectrum is observed. This is due to large $\nu_{\rm NQR}$ and a finite value of η as well as the superposition of four NMR lines (^{63,65}Cu ions for the two Cu sites). The red curve is the sum of the four calculated powder-pattern spectra [49]. As observed in the figure, the calculated spectrum well reproduces the characteristic shape of the observed spectrum. $^{63}T_1$ was measured at the relatively sharp peak appearing at the lower magnetic field side of the main broad peak [around 6 T for 75 MHz in Fig. 4(a)] while changing the frequency [50].

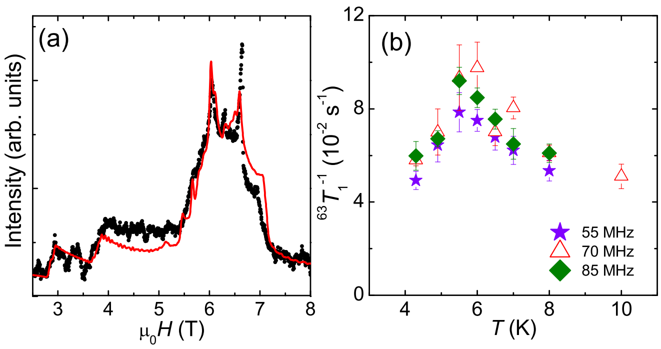

FIG. 4. (a) Field-swept ^{63,65}Cu-NMR spectra at 75 MHz and 1.7 K (black symbols) and the simulation result of four observed NQR frequencies and $\eta = 0.5$ (red line). (b) T dependence of $^{63}T_1^{-1}$ in the magnetic fields.

As shown in Fig. 4(b), no obvious frequency dependence in $^{63}T_1$ was observed within our experimental uncertainty, evidencing again that the anomaly at 6 K is not due to a crossover but to a phase transition with a critical slowing down.

What then is the origin of the phase transition? $^{13}T_1^{-1}$ measurements could not clearly detect the anomaly at 6 K [6,27], suggesting that the 6-K anomaly is not due to the magnetic fluctuation of the ET layers. Furthermore, magnetic fluctuations originating from the anion insulating layers are also unlikely because Cu^+ ion is nonmagnetic, and also $^{1}T_1^{-1}$ performed on the ethylene end groups of the ET molecules near the anion layer showed no clear anomaly [6]. Therefore, it is concluded that the peak in the T dependence of $^{63}T_1^{-1}$ originates from the EFG fluctuation. There are three possible scenarios: The first one is the charge fluctuations due to the disorder of C and N ions in the anion layers, the second one is a structural phase transition, and the last one is due to CD in the ET layers.

Regarding the first one, since two Cu sites, Cu1 and Cu2, caused by the disorder of C and N ions in the anion layers were observed below and above 6 K, no change in the disorder is expected at 6 K. In addition, no change in $\nu_{\rm NQR}$ and linewidth at 6 K also will exclude the possibility of a structural phase transition at 6 K.

Hence, the most probable explanation is the CD in the ET layers. To check whether or not a CD on the conduction layers actually affects the EFG value at the Cu site, we have calculated the EFG while assuming a CD of $\pm 0.1e$ on the ET molecules. From our simple point charge calculation, we found that the EFG at the Cu sites is modulated by 0.5×10^{18} V/m^2. The value is comparable to that from the thermal displacement of CN^- ions which modulates the EFG by 2.2×10^{18} V/m^2 at the Cu site [51]. Since we actually observed the $T^{\sim 2}$ dependence of $^{63}T_1^{-1}$ due to the thermal vibration of CN^- ions at high T, we conclude that the critical slowing down of the CD on the ET molecules should be detected by ^{63}Cu NQR at low T when the lattice vibration is suppressed.

According to previous ^{13}C-NMR studies, the ^{13}C-NMR linewidth discontinuously increases below 6 K [26,27]. Since the linewidth relates to the distribution of charge density through the hyperfine couplings [26,27], the value of the discontinuous jump of the linewidth divided by the Knight shift (corresponding to the mean value of the charge density) will give an estimate of the degree of charge distribution. Using the data from Ref. [26], we estimate the charge distribution from the average valence of the ET molecules to be $(0.5 \pm 0.13)e$ [52]. The decrease in β both in ^{13}C NMR and ^{63}Cu NQR can also be understood by the CD due to the phase transition at 6 K. Therefore, it is quite reasonable that the charge degree of freedom in the ET layer is responsible for the observed phase transition. CD within dimers has been proposed experimentally [7,15] and theoretically [53–57], and a recent structural analysis also pointed out the possibility of CD between dimers [31]. On the other hand, a powder transmission measurement detected no CD [8]. Further studies are required to clarify what kind of CD occurs.

Finally, we comment on the small humps around 3 K observed in $^{63}T_1^{-1}$ and β. The anomaly at the same temperature was also observed in measurements such as thermal expansion, dielectric function, and muon spin relaxation measurements, indicating it is intrinsic [12,14,58]. At present, we cannot conclude the origin of the hump behavior in $^{63}T_1^{-1}$ from our NQR experiments. Detailed low-T Cu-NQR measurements down to temperatures such as 0.1 K are interesting to shed light on the physical properties of the compound at low T. This is a future work.

In conclusion, we performed a ^{63}Cu-NQR measurement on the quantum spin-liquid candidate κ-$(ET)_2Cu_2(CN)_3$ to investigate the charge dynamics. Two different Cu sites are observed in the ^{63,65}Cu NQR spectrum, which is direct evidence for the disorder of C and N atoms in the cyanide groups. $^{63}T_1^{-1}$ shows a T^2 dependence, indicating the EFG fluctuation due to the lattice vibration above 60 K, below which $^{63}T_1^{-1}$ changes from T^2 to $T^{1/2}$ dependence with the suppression of lattice vibration. The $T^{1/2}$ dependence of $^{63}T_1^{-1}$ observed in $T = 10$–40 K was ascribed to the magnetic fluctuation of π electrons of the ET layers. Below 10 K, $^{63}T_1^{-1}$ increases and divergent behavior was observed at 6 K, evidencing a phase transition with a critical slowing down derived from the EFG fluctuation. Based on our NQR data, we attributed the 6-K anomaly to the phase transition of CD originating from the π electrons in the ET layers. Our results require one to reconsider the current interpretation of the low-T electronic state of κ-$(ET)_2Cu_2(CN)_3$, which was thought to exhibit a paramagnetic spin state without the phase transition down to a very low T due to the spin frustration.

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[1] K. Kanoda, Recent progress in NMR studies on organic conductors, Hyperfine Interact. **104**, 235 (1997).
[2] P. Lunkenheimer, J. Müller, S. Krohns, F. Schrettle, A. Loidl, B. Hartmann, R. Rommel, M. de Souza, C. Hotta, J. A. Schlueter, and M. Lang, Multiferroicity in an organic charge-transfer salt that is suggestive of electric-dipole-driven magnetism, Nat. Mater. **11**, 755 (2012).
[3] N. Drichko, R. Beyer, E. Rose, M. Dressel, J. A. Schlueter, S. A. Turunova, E. I. Zhilyaeva, and R. N. Lyubovskaya, Metallic state and charge-order metal-insulator transition in the quasi-two-dimensional conductor κ-(BEDT-TTF)$_2$Hg(SCN)$_2$Cl, Phys. Rev. B **89**, 075133 (2014).
[4] E. Gati, J. K. H. Fischer, P. Lunkenheimer, D. Zielke, S. Köhler, F. Kolb, H. A. K. von Nidda, S. M. Winter, H. Schubert, J. A. Schlueter, H. O. Jeschke, R. Valentí, and M. Lang, Evidence for Electronically Driven Ferroelectricity in a Strongly Correlated Dimerized BEDT-TTF Molecular Conductor, Phys. Rev. Lett. **120**, 247601 (2018).
[5] N. Hassan, S. Cunningham, M. Mourigal, E. I. Zhilyaeva, S. A. Torunova, R. N. Lyubovskaya, J. A. Schlueter, and N. Drichko, Evidence for a quantum dipole liquid state in an organic quasi-two-dimensional material, Science **360**, 1101 (2018).
[6] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Spin Liquid State in an Organic Mott Insulator with a Triangular Lattice, Phys. Rev. Lett. **91**, 107001 (2003).
[7] M. Abdel-Jawad, I. Terasaki, T. Sasaki, N. Yoneyama, N. Kobayashi, Y. Uesu, and C. Hotta, Anomalous dielectric response in the dimer Mott insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **82**, 125119 (2010).
[8] K. Sedlmeier, S. Elsässer, D. Neubauer, R. Beyer, D. Wu, T. Ivek, S. Tomić, J. A. Schlueter, and M. Dressel, Absence of charge order in the dimerized κ-phase BEDT-TTF salts, Phys. Rev. B **86**, 245103 (2012).
[9] M. Pinterić, T. Ivek, M. Čulo, O. Milat, M. Basletić, B. Korin-Hamzić, E. Tafra, A. Hamzić, M. Dressel, and S. Tomić, What is the origin of anomalous dielectric response in 2D organic dimer Mott insulators κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl and κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. B: Condens. Matter **460**, 202 (2015).
[10] M. Dressel, P. Lazić, A. Pustogow, E. Zhukova, B. Gorshunov, J. A. Schlueter, O. Milat, B. Gumhalter, and S. Tomić, Lattice vibrations of the charge-transfer salt κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: Comprehensive explanation of the electrodynamic response in a spin-liquid compound, Phys. Rev. B **93**, 081201(R) (2016).
[11] S. Yamashita, Y. Nakazawa, M. Oguni, Y. Oshima, H. Nojiri, Y. Shimizu, K. Miyagawa, and K. Kanoda, Thermodynamic properties of a spin-1/2 spin-liquid state in a κ-type organic salt, Nat. Phys. **4**, 459 (2008).
[12] R. S. Manna, M. de Souza, A. Brühl, J. A. Schlueter, and M. Lang, Lattice Effects and Entropy Release at the Low-Temperature Phase Transition in the Spin-Liquid Candidate κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. Lett. **104**, 016403 (2010).
[13] F. L. Pratt, P. J. Baker, S. J. Blundell, T. Lancaster, S. Ohira-Kawamura, C. Baines, Y. Shimizu, K. Kanoda, I. Watanabe, and G. Saito, Magnetic and non-magnetic phases of a quantum spin liquid, Nature (London) **471**, 612 (2011).
[14] M. Poirier, S. Parent, A. Côté, K. Miyagawa, K. Kanoda, and Y. Shimizu, Magnetodielectric effects and spin-charge coupling in the spin-liquid candidate κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **85**, 134444 (2012).
[15] K. Itoh, H. Itoh, M. Naka, S. Saito, I. Hosako, N. Yoneyama, S. Ishihara, T. Sasaki, and S. Iwai, Collective Excitation of an Electric Dipole on a Molecular Dimer in an Organic Dimer-Mott Insulator, Phys. Rev. Lett. **110**, 106401 (2013).
[16] M. Poirier, M. de Lafontaine, K. Miyagawa, K. Kanoda, and Y. Shimizu, Ultrasonic investigation of the transition at 6 K in the spin-liquid candidate κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **89**, 045138 (2014).
[17] T. Isono, T. Terashima, K. Miyagawa, K. Kanoda, and S. Uji, Quantum criticality in an organic spin-liquid insulator κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Nat. Commun. **7**, 13494 (2016).
[18] T. Furukawa, K. Kobashi, Y. Kurosaki, K. Miyagawa, and K. Kanoda, Quasi-continuous transition from a Fermi liquid to a spin liquid in κ-(ET)$_2$Cu$_2$(CN)$_3$, Nat. Commun. **9**, 307 (2018).
[19] H. Kawamura and S. Miyashita, Phase transition of the two-dimensional Heisenberg antiferromagnet on the triangular lattice, J. Phys. Soc. Jpn. **53**, 4138 (1984).
[20] G. Baskaran, Novel Local Symmetries and Chiral-Symmetry-Broken Phases in $S = 1/2$ Triangular-Lattice Heisenberg Model, Phys. Rev. Lett. **63**, 2524 (1989).
[21] S.-S. Lee, P. A. Lee, and T. Senthil, Amperean Pairing Instability in the U(1) Spin Liquid State with Fermi Surface and Application to κ(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. Lett. **98**, 067006 (2007).
[22] Y. Qi and S. Sachdev, Insulator-metal transition on the triangular lattice, Phys. Rev. B **77**, 165112 (2008).
[23] T. Grover, N. Trivedi, T. Senthil, and P. A. Lee, Weak Mott insulators on the triangular lattice: Possibility of a gapless nematic quantum spin liquid, Phys. Rev. B **81**, 245121 (2010).
[24] K. Riedl, R. Valentí, and S. M. Winter, Critical spin liquid versus valence-bond glass in a triangular-lattice organic antiferromagnet, Nat. Commun. **10**, 2561 (2019).
[25] K. Miyagawa, A. Kawamoto, and K. Kanoda, Charge ordering in a quasi-two-dimensional organic conductor, Phys. Rev. B **62**, R7679 (2000).
[26] A. Kawamoto, Y. Honma, and K.-I. Kumagai, Electron localization in the strongly correlated organic system κ-(BEDT-TTF)$_2X$ probed with nuclear magnetic resonance ^{13}C-NMR, Phys. Rev. B **70**, 060510(R) (2004).
[27] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, Emergence of inhomogeneous moments from spin liquid in the triangular-lattice Mott insulator κ-(ET)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **73**, 140407(R) (2006).
[28] Y. Saito, T. Minamidate, A. Kawamoto, N. Matsunaga, and K. Nomura, Site-specific ^{13}C NMR study on the locally distorted triangular lattice of the organic conductor κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **98**, 205141 (2018).
[29] U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, H. A. Charlier, J. E. Heindl, G. A. Yaconi, B. J. Love, M. W. Lathrop, J. E. Schirber, D. L. Overmyer, J. Ren, and M. H. Whangbo, Superconductivity at 2.8 K and 1.5 kbar in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: The first organic superconductor containing a polymeric copper cyanide anion, Inorg. Chem. **30**, 2586 (1991).
[30] H. O. Jeschke, M. de Souza, R. Valentí, R. S. Manna, M. Lang, and J. A. Schlueter, Temperature dependence of structural and electronic properties of the spin-liquid candidate κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, Phys. Rev. B **85**, 035125 (2012).

[31] P. Foury-Leylekian, V. Ilakovac, V. Balédent, P. Fertey, A. Arakcheeva, O. Milat, D. Petermann, G. Guillier, K. Miyagawa, K. Kanoda, P. Alemany, E. Canadell, S. Tomic, J.-P. Pouget, P. Foury-Leylekian, V. Ilakovac, V. Balédent, P. Fertey, A. Arakcheeva, O. Milat *et al.*, $(BEDT\text{-}TTF)_2Cu_2(CN)_3$ spin liquid: Beyond the average structure, Crystals **8**, 158 (2018).

[32] Y. Kurosaki, Y. Shimizu, K. Miyagawa, K. Kanoda, and G. Saito, Mott Transition from a Spin Liquid to a Fermi Liquid in the Spin-Frustrated Organic Conductor κ-$(ET)_2Cu_2(CN)_3$, Phys. Rev. Lett. **95**, 177001 (2005).

[33] A. A. Koukoulas and M. Whitehead, Observations in nuclear quadrupole resonance frequency temperature dependence, Chem. Phys. Lett. **167**, 379 (1990).

[34] F. Iwase, K. Miyagawa, S. Fujiyama, K. Kanoda, S. Horiuchi, and Y. Tokura, Neutral-ionic phase transition in DMTTF-QCl_4 investigated by ^{35}Cl NQR, J. Phys. Soc. Jpn. **76**, 073701 (2007).

[35] H. Nakayama, N. Nakamura, and H. Chihara, Coordination bonds in $KCu(CN)_2$ as studied by ^{14}N and ^{63}Cu NQR, J. Mol. Struct. **83**, 281 (1982).

[36] F. Iwase, K. Miyagawa, K. Kanoda, S. Horiuchi, and Y. Tokura, Charge-lattice-coupled quantum fluctuations in DMTTF-2,6-QBr_2Cl_2, J. Phys. Soc. Jpn. **79**, 043709 (2010).

[37] A. A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, Oxford, UK, 1961).

[38] M. Klanjšek, A. Zorko, R. Žitko, J. Mravlje, Z. Jagličić, P. K. Biswas, P. Prelovšek, D. Mihailovic, and D. Arčon, A high-temperature quantum spin liquid with polaron spins, Nat. Phys. **13**, 1130 (2017).

[39] S. Imajo (private communication).

[40] Y. Nakazawa and K. Kanoda, Low-temperature specific heat of κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ in the superconducting state, Phys. Rev. B **55**, R8670 (1997).

[41] B. Andraka, J. S. Kim, G. R. Stewart, K. D. Carlson, H. H. Wang, and J. M. Williams, Specific heat in high magnetic field of κ-di[bis(ethylenedithio)tetrathiafulvalene]-di(thiocyano)cuprate [κ-$(ET)_2Cu(NCS)_2$]: Evidence for strong-coupling superconductivity, Phys. Rev. B **40**, 11345 (1989).

[42] A. Kawamoto, Y. Honma, K. I. Kumagai, N. Matsunaga, and K. Nomura, Suppression of inhomogeneous electron localization in κ-$(BEDT\text{-}TF)_2Cu_2(CN)_3$ under pressure, Phys. Rev. B **74**, 212508 (2006).

[43] F. Kagawa, Y. Kurosaki, K. Miyagawa, and K. Kanoda, Field-induced staggered magnetic moment in the quasi-two-dimensional organic Mott insulator κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$, Phys. Rev. B **78**, 184402 (2008).

[44] M. Ito, T. Uehara, H. Taniguchi, K. Satoh, Y. Ishii, and I. Watanabe, Zero-field magnetism of a two-dimensional antiferromagnet, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$, determined by muon spin rotation and magnetization measurements, J. Phys. Soc. Jpn. **84**, 053703 (2015).

[45] In κ-$(ET)_2Cu[N(CN)_2]Cl$, the two nearest-neighbor magnetic moments for the Cu site are ferromagnetically ordered in the antiferromagnetic state [R. Ishikawa, H. Tsunakawa, K. Oinuma, S. Michimura, H. Taniguchi, K. Satoh, Y. Ishii, and H. Okamoto, Zero-field spin structure and spin reorientations in layered organic antiferromagnet, κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$, with Dzyaloshinskii-Moriya interaction, J. Phys. Soc. Jpn. **87**, 064701 (2018)]. Thus, there is no cancellation of the internal field at the Cu sites. No cancellation of the internal field at the C sites on the ET molecules is also expected. Therefore, the ratio of the internal field at the Cu and C sites ($|^{63}H_{\rm int}/^{13}H_{\rm int}|$) in κ-$(ET)_2Cu[N(CN)_2]Cl$ is considered to be scaled to the ratio of the hyperfine coupling constants $|^{63}A/^{13}A|$.

[46] We have observed a clear splitting of the ^{63}Cu NQR spectrum due to the internal field in the antiferromagnetic state in κ-$(ET)_2Cu[N(CN)_2]Cl$ [T. Kobayashi *et al.* (unpublished)]. From the magnitude of the splitting, we estimate an internal field of $\sim$70 G.

[47] D. F. Smith, S. M. De Soto, C. P. Slichter, J. A. Schlueter, A. M. Kini, and R. G. Daugherty, Dzialoshinskii-Moriya interaction in the organic superconductor κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Cl$, Phys. Rev. B **68**, 024512 (2003).

[48] N. Bloembergen, E. M. Purcell, and R. V. Pound, Relaxation effects in nuclear magnetic resonance absorption, Phys. Rev. **73**, 679 (1948).

[49] The NMR spectrum was calculated with a nuclear spin Hamiltonian including Zeeman and quadrupolar interactions without perturbation. In the calculation, we used the four values of ν_Q determined by the NQR measurements and also $\eta = 0.5$ for each.

[50] T_1 was estimated from the fitting with $1 - M(t)/M(\infty) = 0.1\exp[-(t/T_1)^{\beta}] + 0.9\exp[-(6t/T_1)^{\beta}]$, where the β values change from 0.7 to 1.0 depending on temperature and also resonance frequency.

[51] We assumed an amplitude of 5 pm, which is estimated from $\sqrt{k_B T/k}$, where k is the force constant. k of the cyano group can be estimated from the vibrational mode of Cu-CN-Cu motion $\sim$500 cm^{-1} [10].

[52] From Figs. 3 and 4 in Ref. [26], the Knight shift and linewidth jump at 6 K are 270 ppm and 7 kHz (corresponding to 70 ppm), respectively, which give a fractional charge ratio of $\sim$0.26.

[53] M. Naka and S. Ishihara, Electronic ferroelectricity in a dimer Mott insulator, J. Phys. Soc. Jpn. **79**, 063707 (2010).

[54] C. Hotta, Quantum electric dipoles in spin-liquid dimer Mott insulator κ-$ET_2Cu_2(CN)_3$, Phys. Rev. B **82**, 241104(R) (2010).

[55] S. Dayal, R. T. Clay, H. Li, and S. Mazumdar, Paired electron crystal: Order from frustration in the quarter-filled band, Phys. Rev. B **83**, 245106 (2011).

[56] H. Gomi, M. Ikenaga, Y. Hiragi, D. Segawa, A. Takahashi, T. J. Inagaki, and M. Aihara, Ferroelectric states induced by dimer lattice disorder in dimer Mott insulators, Phys. Rev. B **87**, 195126 (2013).

[57] H. Gomi, T. J. Inagaki, and A. Takahashi, Ferroelectric charge order enhanced by magnetic frustration in dimer Mott insulators, Phys. Rev. B **93**, 035105 (2016).

[58] S. Nakajima, T. Suzuki, Y. Ishii, K. Ohishi, I. Watanabe, T. Goto, A. Oosawa, N. Yoneyama, N. Kobayashi, F. L. Pratt, and T. Sasaki, Microscopic phase separation in triangular-lattice quantum spin magnet κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ probed by muon spin relaxation, J. Phys. Soc. Jpn. **81**, 063706 (2012).