Charge disproportionation in the spin-liquid candidate $\kappa-(ET)2Cu2(CN)3$ at 6 K revealed by $^{63}$Cu NQR measurements

Takeshi Kobayashi  
*Ames Laboratory and Saitama University, takeshi@ameslab.gov*

Qing-Ping Ding  
*Iowa State University and Ames Laboratory, qpding@ameslab.gov*

H. Taniguchi  
*Saitama University*

K. Satoh  
*Saitama University*

A. Kawamoto  
*Hokkaido University*

See next page for additional authors

Follow this and additional works at: [https://lib.dr.iastate.edu/ameslab_manuscripts](https://lib.dr.iastate.edu/ameslab_manuscripts)

Part of the Condensed Matter Physics Commons

**Recommended Citation**

Kobayashi, Takeshi; Ding, Qing-Ping; Taniguchi, H.; Satoh, K.; Kawamoto, A.; and Furukawa, Yuji, "Charge disproportionation in the spin-liquid candidate $\kappa-(ET)2Cu2(CN)3$ at 6 K revealed by $^{63}$Cu NQR measurements" (2020). Ames Laboratory Accepted Manuscripts. 750.  
[https://lib.dr.iastate.edu/ameslab_manuscripts/750](https://lib.dr.iastate.edu/ameslab_manuscripts/750)

This Article is brought to you for free and open access by the Ames Laboratory at Iowa State University Digital Repository. It has been accepted for inclusion in Ames Laboratory Accepted Manuscripts by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Charge disproportionation in the spin-liquid candidate $\kappa - (ET)2Cu2(CN)3$ at 6 K revealed by $^{63}$Cu NQR measurements

Abstract

The spin-liquid candidate $\kappa - (ET)2Cu2(CN)3$ [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 $T^{-1}$ of $^{63}$Cu NQR at 6 K while $T^{-1}$ 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.

Disciplines

Condensed Matter Physics

Authors

Takeshi Kobayashi, Qing-Ping Ding, H. Taniguchi, K. Satoh, A. Kawamoto, and Yuji Furukawa
Charge disproportionation in the spin-liquid candidate $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ at 6 K revealed by $^{63}$Cu NQR measurements

T. Kobayashi $^{1,2,*}$, Q.-P. Ding $^2$, H. Taniguchi $^{1,*}$, K. Satoh $^{1,*}$, A. Kawamoto $^3$, and Y. Furukawa $^2$

$^1$Graduate School of Science and Engineering, Saitama University, Saitama 338-8570, Japan
$^2$Ames Laboratory, U.S. DOE, and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA
$^3$Department of Condensed Matter Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

(Rceived 30 March 2020; revised 26 September 2020; accepted 14 October 2020; published 30 October 2020)

The spin-liquid candidate $\kappa$-(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.

DOI: 10.1103/PhysRevResearch.2.042023

Quasi-two-dimensional organic charge transfer salts $\kappa$-(ET)$_2$X [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 metallic 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 $\kappa$-(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 $\sim 250$ K [6], and therefore it has attracted much attention as a quantum spin liquid. $\kappa$-(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 $\kappa$-(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.

*tkobayashi@phy.saitama-u.ac.jp

Published by the American Physical Society under the terms of the Creative Commons Attribution 4.0 International license. Further distribution of this work must maintain attribution to the author(s) and the published article’s title, journal citation, and DOI.
dependence of (red squares). (b) Structure of the Cu$_2$(CN)$_3$ insulating layer. (c) $T$ dependence of $T_1^{-1}$ measured at the peak around 40.7 MHz.

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 quadrupole frequency is

$$\nu = \frac{eQV_{ZZ}}{2h}$$

where $e$, $Q$, $V_{ZZ}$, $h$, and $\eta$ 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 $\kappa$-(ET)$_2$Cu$_2$(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 $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$.

It is noted that one cannot determine the values of $\nu_Q$ and $\eta$ for the Cu ions separately from only the NQR spectrum. A finite value of $\eta$, 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, $\eta$ is estimated to be $\sim 0.5$, and thus the values of $\nu_Q$ 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 $\nu_Q$. The dashed curve is the calculated result with the empirical formula

$$\nu_Q = \nu_0 \exp(-\alpha T^2)$$

where $\alpha$ is an adjustable parameter of EFG, respectively. Since there are two isotopes $^{63}$Cu and $^{65}$Cu, respectively, for the Cu ions separately from only the NQR spectrum. 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).

![Figure 1](image1.png)

**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 $T_1^{-1}$ measured at the peak around 40.7 MHz.

![Figure 2](image2.png)

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

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 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, $^{63}T_1^{-1}$ 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...
The inset shows the blue squares from Ref. [27]. The values of \( \nu_{13T_1^{-1}} \) to the thermal lattice vibration, and \( \nu_{13T_1^{-1}} + 0.055T^{1/2} \), respectively. The inset shows the \( T \) dependence of \( \beta \).

Increasing \( T \), corresponding to the decrease in \( v_{\text{NQR}} \) as shown in Fig. 2(b). The \( T \) dependence of \( v_{\text{NQR}} \) is considered to be originated from the thermal lattice expansion and can be described by the empirical formula \([33,34] v_{\text{NQR}} = \nu_0 \exp(-\alpha T^2) \). As shown by the curve in Fig. 2(b), the \( T \) dependence of \( v_{\text{NQR}} \) is well reproduced with the formula with \( \nu_0 = 40.68 \text{MHz} \) and \( \alpha = 3.58 \times 10^{-7} \text{ K}^{-2} \). 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 \( Z \) \( 63T_1^{-1} \). For comparison, the \( T \) dependence of \( T_1^{-1} \) of \( ^{13}C \), \( 13T_1^{-1} \), is also plotted [27]. Note that the values of \( 13T_1^{-1} \) are reduced by a factor of 0.023. The \( T \) dependences are quite different from each other. \( 63T_1^{-1} \) shows a \( T^2 \) dependence above 60 K, below which it is proportional to \( T^{1/2} \) coinciding with that of \( 13T_1^{-1} \). With further decreasing \( T \) below 10 K, \( 63T_1^{-1} \) starts to increase and then shows a pronounced peak at 6 K, whereas \( 13T_1^{-1} \) decreases monotonically. The exponent \( \beta \) deviates from unity below 6 K as shown in the inset of Fig. 3, indicating a development of inhomogeneity in \( 63T_1 \). A similar inhomogeneity below \( \sim 6 \text{ K} \) was also observed in the \(^{13}\text{C}\)- and \(^{3}\text{H}\)-NMR measurements [6,27].

The \( T^{-2} \) dependence of \( 63T_1^{-1} \) observed above 60 K can be explained by the thermal vibrations of the three nearest-neighbor \( \text{CN}^- \) ions with respect to the \( \text{Cu} \) 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-photon Raman process [37]. In this case, the quadrupole relaxation \( (T_1^{-1}) \) is described as \( T_1^{-1} = \frac{8}{5} \frac{1}{2} \frac{(2 \Omega \nu_0)^2}{|\Omega|^2} \frac{\nu_0^2}{m_0} k_B T (\epsilon_{\text{Cu}} / k_B T - 1)^{-2} \frac{\alpha}{\sqrt{\Omega^2 + \alpha^2 \nu_0^2}} \). Here, \( m_0, \nu_0, \Omega, \) and \( \alpha \) are the atomic mass of \( 63\text{Cu} \), sound velocity in the crystal, and cutoff frequency related to the Debye temperature (\( \Theta \)), respectively. \( F_2 \) is a parameter which can be approximated by \( 2\pi \nu_0 \) [37,38].

Assuming \( v = 10^3 \text{ m/s} \) [39], and a typical value \( \Theta = 0.023 \), we have calculated the \( T \) dependence of \( T_1^{-1} \). 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 \( T_1^{-1} \), \( 63T_1^{-1} \) is expected to decrease drastically at low \( T \) due to the suppression of thermal vibrations. However, \( 63T_1^{-1} \) gradually deviates from \( T_1^{-1} \) below \( \sim 60 \text{ K} \) and shows a \( T^{1/2} \) dependence between 10 and 40 K, which is the same as that of \( 13T_1^{-1} \) [27]. Since \( 13T_1^{-1} \) originates from the magnetic fluctuations from the \( \pi \) electrons of the ET layers [27,42], the similar \( T \) dependence of \( 63T_1^{-1} \) indicates that the magnetic fluctuations become dominant at the Cu site. In fact, this interpretation can be confirmed by looking at the ratio of \( 63T_1^{-1} \) to \( 13T_1^{-1} \).

The most striking feature in the \( T \) dependence of \( 63T_1^{-1} \) 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 \( 63T_1^{-1} \). 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 \( 63\text{Cu}-\text{NMR} \) 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 \( v_{\text{NQR}} \) and a finite value of \( \gamma \) as well as the superposition of four NMR lines \( (63\text{Cu} \text{Cu ions for the two Cu sites}) \). 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. \( 63T_1^{-1} \) 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].
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 \( \beta \) 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\(_1\) and \( T \). 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 \( \kappa\)-(ET)_2Cu_2(CN)_3 to investigate the charge dynamics. Two different Cu sites are observed in the \(^{63}\)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 \( \pi \) 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 \( \pi \) electrons in the ET layers. Our results require one to reconsider the current interpretation of the low-\( T \) electronic state of \( \kappa\)-(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.

The authors are grateful to Y. Saito, M. Dressel, and M. Lang for useful discussions. The research was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. Ames Laboratory is operated for the U.S. DOE by Iowa State University under Contract No. DE-AC02-07CH11358. This work was partially supported by the Japan Society for the Promotion of Science KAKENHI Grants No. 18H05843, No. 19K21033, and No. 16K05427. T.K. also thanks KAKENHI Grant No. JP15K21732: J-Physics for financial support to be a visiting scientist at Ames Laboratory.


[45] In κ-(ET)$_2$Cu[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-TTF)$_2$Cu[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 ($H_{\text{int}}^{(\text{Cu})}/H_{\text{int}}^{(\text{C})}$) in κ-(ET)$_2$Cu[N(CN)$_2$]Cl is considered to be scaled to the ratio of the hyperfine coupling constants ($A^{(\text{Cu})}/A^{(\text{C})}$).

[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)$_2$Cu[N(CN)$_2$]Cl [T. Kobayashi et al. (unpublished)]. From the magnitude of the splitting, we estimate an internal field of $\sim$70 G.


[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 $\nu_0$ determined by the NQR measurements and also $\eta = 0.5$ for each.

[50] $T_\text{c}$ was estimated from the fitting with $1 - M(t)/M(\infty) = 0.1 \exp\left[-(t/T_\text{c})^\beta\right] + 0.9 \exp\left[-(t/T_\beta)^\beta\right]$, where the $\beta$ value changes 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 $\sqrt{\kappa T/\kappa}$, where $\kappa$ is the force constant. $\kappa$ 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 0.7 kHz (corresponding to 70 ppm), respectively, which give a fractional charge ratio of ≈0.26.


