



Title	C-13 NMR study of the charge-ordered state near the superconducting transition in the organic superconductor $(\text{BEDT-TTF})_4[(\text{H}_3\text{O})\text{Ga}(\text{C}_2\text{O}_4)_3] \cdot \text{C}_6\text{H}_5\text{NO}_2$
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^{13}C NMR study of the charge-ordered state near the superconducting transition in the organic superconductor $\beta''\text{-(BEDT-TTF)}_4[(\text{H}_3\text{O})\text{Ga}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{NO}_2$

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The charge-ordered state in a quasi-two-dimensional organic superconductor $\beta''\text{-(BEDT-TTF)}_4[(\text{H}_3\text{O})\text{Ga}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{NO}_2$ has been investigated using ^{13}C NMR spectroscopy in a high magnetic field. Enhanced resolution of the high-field spectrum allows us to estimate the site charges in the low-temperature charge-ordered state below 8.5 K. The observed strong increase in the charge imbalance suggests that superconductivity appears on the electronic state with a strong charge modulation. From the NMR intensity ratio of signals from the charge-rich and charge-poor sites, we discuss a possible charge pattern with threefold modulation, which could be stabilized by the effects of electron-electron correlations.

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Unconventional superconductivity is frequently observed near the boundary of other ordered phases. In high- T_c pnictides and heavy fermion superconductors, superconductivity appears next to an antiferromagnetic phase, and its mechanism is related to the critical fluctuations of the second-order phase transition. By analogy with antiferromagnetism near superconductivity, the charge-ordering (CO) transition near the superconducting (SC) phase would also be related to the SC pairing mechanisms. In fact, it has been suggested theoretically that the charge fluctuations can contribute to form Cooper pairs both in the context of cuprates [1] and layered molecular crystals [2]. As in most of materials the SC and CO transitions appear at very different temperatures, particular attention should be paid to rare examples where these transitions (and related energy scales) are close [3], to reveal experimentally the complex relationship, perhaps not only competition, between the CO and SC phases.

Electronic charge localization is caused by a strong electron-electron interaction in half-filled or quarter-filled systems. The effects of on-site and off-site Coulomb interactions have been intensively investigated both from theoretical and experimental points of view [4–6]. In low-dimensional electronic systems, such as NbSe_3 [7] and organic conductor $(\text{TMTTF})_2X$ (tetramethyltetrathiafulvalene) salts [8], the charge-density-wave (CDW) state with fractional charge localization is driven by Fermi surface instability. Although these systems show superconductivity under pressure, the CDW state of NbSe_3 is completely suppressed when superconductivity sets in [9], and in $(\text{TMTTF})_2X$ a magnetic phase appears between the SC and CDW phases. Charge instability is also observed in quasi-two-dimensional organic conductors $(\text{BEDT-TTF})_2X$ [bis(ethylenedithio)-tetrathiafulvalene] salts. In some BEDT-TTF salts, superconductivity appears directly after the suppression of the CO transition by applying chemical or mechanical pressure [10–12]. However, the CO transition temperature is much higher than the SC transition temperature T_c [13,14], and the two phenomena thus appear

unrelated. In the BEDT-TTF salt with β'' -type molecular packing, $\beta''\text{-(BEDT-TTF)}_4[(\text{H}_3\text{O})\text{Ga}(\text{C}_2\text{O}_4)_3]\cdot\text{C}_6\text{H}_5\text{NO}_2$ ($\beta''\text{-Ga}$), a charge instability was observed below 8.5 K, very close to the SC transition temperature $T_c = 7$ K [15,16]. The $\beta''\text{-Ga}$ salt may therefore prove to be an exceptionally important model system for understanding the relationship between CO and SC states.

Besides the charge instability at 8.5 K, a CO with a small charge modulation was already observed in $\beta''\text{-Ga}$ salt at 100 K with Raman spectroscopy and resistivity measurements [17,18]. At 100 K, the deviation of site charge from the formal value ($0.5e$) was estimated as $\Delta\rho \sim 0.1e$. As in the case of other BEDT-TTF salts, this high-temperature CO may not be directly related to the SC pairing mechanism, because the temperature scale for a charge transition is one order of magnitude larger than that for superconductivity. Subsequent ^{13}C NMR spectroscopy detected another charge anomaly below 12 K [15]. This charge anomaly near T_c should be examined to understand the electronic state at low temperatures where superconductivity sets in. In a previous NMR experiment the character of the charge-ordered state could not be investigated because of limitations in the spectral resolution at low magnetic fields. In this Rapid Communication we explore the static properties of the charge-ordered state by analyzing the highly resolved NMR spectra taken at 15 T and precisely quantify the site-charge modulation that appears near the SC transition.

A single crystal of $\beta''\text{-Ga}$ salt was prepared with an electrochemical oxidation process [19]. The typical sample dimension was $2 \times 1 \times 0.2$ mm³. We utilized a single side ^{13}C enriched BEDT-TTF molecule, meaning that only one side of the central C=C bond was enriched with ^{13}C nuclei, so as to eliminate nuclear spin coupling between neighboring carbon nuclear spins [20]. The SC transition temperature of our sample was determined to be 7 K from the bulk susceptibility measurement at low magnetic fields. For the temperature sweep experiment, the magnetic field was applied along the b axis. We also measured the field direction dependence of NMR spectra at a lowest temperature of 1.6 K. The external field was rotated in the bc^* plane using a single axis rotator.

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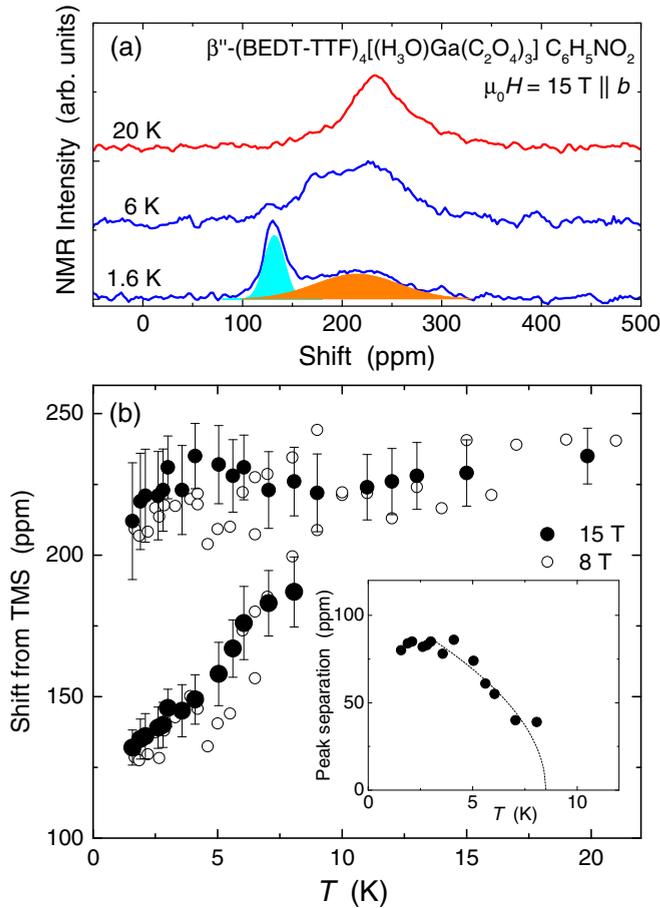


FIG. 1. (Color online) (a) ^{13}C NMR spectra at various temperatures. An external field of 15 T was applied parallel to the crystalline b axis. The peak splitting was observed below 8 K, and a clearly split two-peak structure was observed at 1.6 K. The ratio of the integrated area between the sharp and broad peaks was evaluated as 0.4 : 1. (b) Temperature dependence of the NMR shift at 15 T, shown together with the previous result at 8 T [15]. The vertical axis is the peak shift from tetramethylsilane (TMS). The field-independent peak separation at the lowest temperature indicates the absence of any fixed internal field, that could be associated with a magnetic transition. Inset: Peak separation between R and P sites. The dotted line represents a mean-field-type temperature dependence, $\propto \sqrt{8.5 - T}$.

When the external field was applied along the b axis, a single peak was observed at 20 K, as shown in Fig. 1(a). The single-peak spectrum was broadened at low temperatures and a clearly resolved two-peak structure was observed at 1.6 K. We determined the NMR shift δ from the peak positions and display the temperature dependence of the NMR shift for each peak in Fig. 1(b), together with the previous result at 8 T [15]. The peak splitting was observed below 8.5 K. This peak splitting cannot be explained by the effects of a SC transition, because T_c is suppressed to 3 K at 15 T [17]. Only a barely resolved kink in the NMR shift was observed at T_c . In our previous study at 8 T the spectral resolution was considerably lower and the onset of the anomaly was estimated to occur at 12 K. However, it is clear that the temperature variation of δ and the peak splitting in units of ppm at the lowest temperature are identical between 8 and 15 T. The field-independent splitting

confirms that conduction spins are in the paramagnetic state, and have polarization proportional to the field. This indicates the absence of any internal magnetic field, which could have been generated by some field-independent magnetic ordering. We suggest that the transition at 8.5 K is the order in the charge degrees of freedom, in which the molecular site charges deviate from the formal value of $0.5e$. A similar peak splitting was observed in other organic salts with a charge transition, such as $(\text{TMTTF})_2\text{AsF}_6$ [21]. We assigned the broad and the sharp peak as the NMR signal from the charge-rich (R) and charge-poor (P) sites, respectively. Details of the site assignment will be discussed later. The inset of Fig. 1(b) shows the temperature dependence of the peak separation, $s = \delta_R - \delta_P$, below 8 K. The peak separation gradually increased below the CO temperature and is compatible with the mean-field-type temperature dependence $s \propto \sqrt{8.5 - T}$, as represented by the dotted line. The peak separation is related to the charge imbalance between the R and P sites, and is proportional to the order parameter of the charge-ordered state. The mean-field-type behavior of the peak separation suggests the second-order nature of the CO transition.

The NMR intensity is proportional to the number of ^{13}C nuclei on the molecular sites. In the charge-ordered state, if the number of R sites were equal to that of P sites (PR pattern), the NMR intensity of the narrow peak would be comparable to that of the broad peak. However, as shown in Fig. 1(a), the intensity ratio between the peaks was 0.4 : 1, which indicates that there are at least twice as many R sites as P sites in the charge-ordered state (PRR pattern). The crystal structure of the β'' -Ga salt consists of two crystallographically independent BEDT-TTF molecules, each of which forms a pair with another molecule connected by inversion symmetry. The simplest PR CO pattern can be attributed to the inversion symmetry breaking between a pair of BEDT-TTF molecules. The experimentally suggested PRR pattern addresses a more complicated CO, possibly originating from the competition between the long and short range Coulomb interactions, which will be discussed later. We note here that the NMR spectrum at 1.6 K was recorded with a very long recovery time, more than four times longer than the nuclear spin-lattice relaxation time $T_1 \simeq 200$ s for the P site, in order to exclude the possibility that the NMR intensity is modified by an insufficient recovery of nuclear magnetization. We have also confirmed that the nuclear spin-spin relaxation time T_2 is much longer than the pulse-pulse separation time $\tau = 200$ μs , so that the nuclear spin-spin relaxation does not modify the NMR intensity.

The local site charge ρ_P and ρ_R in the charge-ordered state can be estimated from the peak positions at 1.6 K. The total NMR shift δ is the sum of the contribution from local valence electrons (Knight shift), which is proportional to the local charge, $K = A\rho$, and the chemical shift σ from the inner electronic shells:

$$\delta(\rho) = A\rho + \sigma(\rho). \quad (1)$$

Here, we assumed that the hyperfine coupling constant is independent of site charge. The chemical shift tensors for $\rho = 0.5e$ and $1e$ were determined in α -(BEDT-TTF) $_2\text{I}_3$ [22], and pure BEDT-TTF [23]. A linear relation was obtained from these values as $\sigma(\rho) = 108 - 46\rho/e$ ppm for β'' -Ga salt in $H \parallel b$. The intensity ratio of the lines suggests a PRR charge

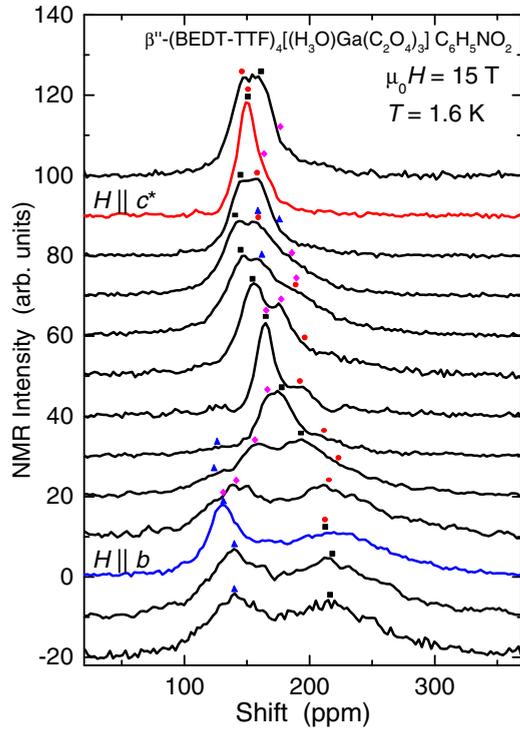


FIG. 2. (Color online) The angle dependence of NMR spectra for rotation of the field from the b to c^* axis at 1.6 K. The spectra are vertically offset proportionally to the rotation angle. Peak positions are marked by small symbols, which correspond to those shown in Fig. 3(a).

pattern, so that the corresponding charge conservation leads to $\rho_P + 2\rho_R = 3 \times 0.5e$. Using this constraint, and applying Eq. (1) to the two low-temperature (1.6 K) experimental values $\delta(\rho_R) = 212$ ppm and $\delta(\rho_P) = 132$ ppm, leads to the corresponding estimates of the site charges as $\rho_R = 0.67e$ and $\rho_P = 0.16e$. As σ is directly related to ρ , different σ values between R and P sites confirm the modulation in the site charges. We see that in the low-temperature charge-ordered state the deviation from the formal charge is much larger than that observed between 10 and 100 K by Raman spectroscopy ($\rho_R - \rho_P = 0.13e$ [18]). The NMR peak splitting due to this small charge disproportionation at high temperatures is probably concealed in the linewidth of our spectra (for the external field applied along the b axis).

The large charge modulation was confirmed by the field angle dependence of NMR spectra at the lowest temperature (Fig. 2). The two peaks observed for $H \parallel b$ split into four broad peaks when $\theta \sim 20^\circ$, and become a sharp peak in $H \parallel c^*$. We determined the peak positions from four-peak Lorentzian fitting and the results are shown in Fig. 3(a). The four independent branches are plotted with independent symbols. The angle dependence of the NMR shift originates from the anisotropic dipolar Knight shift from π electrons and from the anisotropy of the chemical shift. The Knight (chemical) shift becomes maximum (minimum) when the external field is along the long axis of the π orbital, which is perpendicular to the BEDT-TTF molecular plane, as represented by the small arrow in the inset of Fig. 3(b). The maxima of the two branches denoted by circles and squares are 24° and

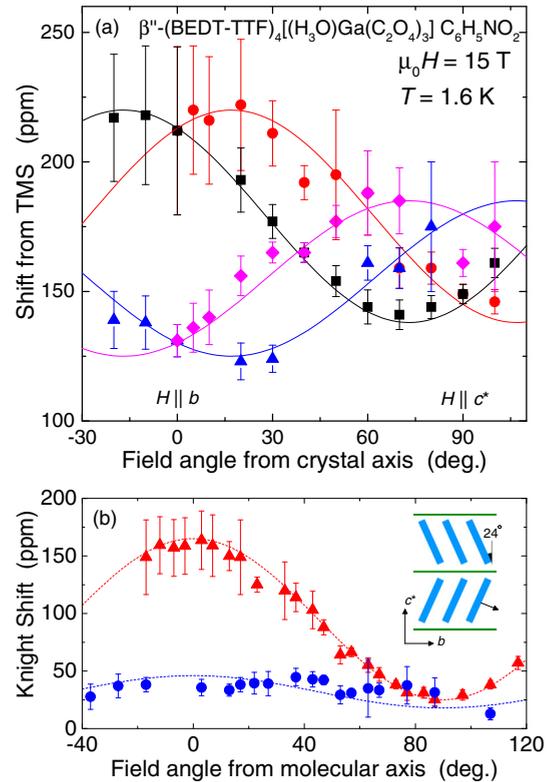


FIG. 3. (Color online) (a) Peak positions of the spectra shown in Fig. 2. Two pairs of branches were identified and plotted by different symbols. (b) For each pair, the angle dependence of the Knight shift only is plotted vs the angle relative to the normal to the molecular plane. This angle dependence for P sites is almost five times smaller than that for R sites. Inset: Schematic presentation of the crystal structure. The long axis of the BEDT-TTF molecule is tilted by 24° from the c^* axis. The small arrow denotes the long-axis direction of the π orbital.

-24° shifted from the $H \parallel b$ direction, which is explained by the molecular angle with respect to the crystalline b axis. Therefore, we assigned these branches to the NMR signal from the neighboring BEDT-TTF layers. For the branches denoted by triangles and diamonds, the NMR shift becomes minimum at 24° and -24° , for which the external field is close to the long axis of the π orbital. This result indicates that the Knight shift contribution is small for these branches.

To obtain the pure Knight shift contribution, the chemical shift contribution should be subtracted from the NMR shift. The angle dependence originating from the chemical shift can be calculated from the previously determined chemical shift tensor [22,23]. In Fig. 3(b), we show the Knight shift as a function of the angle between the field and the normal to the molecular plane. In this presentation, each pair of corresponding branches of Fig. 3(a) becomes superposed, because they possess the same site charges and demonstrate an identical angular dependence. The amplitude of this angle dependence is proportional to the spin density in the π orbital. The contrasting behavior for the two independent sites confirms that the site charge is strongly modified from the formal value ($0.5e$). In particular, a very weak angle dependence for the P sites indicates that they possess a small

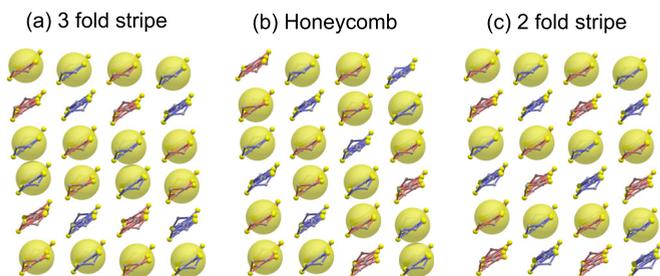


FIG. 4. (Color online) Schematic images of charge patterns in the conducting plane. The large balls indicate charge-rich (R) sites. Two out of three BEDT-TTF sites have a rich charge ($0.67e$) for the experimentally suggested PRR charge pattern. The vertical P-R-R pattern can be aligned horizontally to make stripes (a), or shifted by one site to form a honeycomb structure (b). The nearest-neighbor Coulomb potential can be further reduced by assuming a PR pattern (c), in which the P and R sites are alternatively stacked. Although the β'' -type packing structure has two crystallographically independent molecules, they appear almost identical in the figure, and also in the NMR spectrum, because the apparent difference can be seen only at the ethylene end groups.

site charge. From our estimate of local charges ($\rho_R = 0.67e$, $\rho_P = 0.16e$), the angle dependence of the P sites should be 4.2 times smaller than that for the R sites. The expected angle dependence corresponding to this ratio, shown as a dotted line in Fig. 3(b), fits to the experimental data, which reinforces the quantitative consistency of the charge estimate.

Now we discuss a possible charge pattern in the ordered state. The NMR intensity ratio between the R and P sites suggests a PRR structure ($0.16e$ - $0.67e$ - $0.67e$). In the two-dimensional conducting plane, we can assume PRR stripe and honeycomb structures, as shown in Figs. 4(a) and 4(b). The possibility of interlayer CO was excluded because of the large energy cost for a charge-rich plane. To get insight into the energetic stability of the structure, we calculated the average Coulomb potential (per site) between neighboring BEDT-TTF sites, by placing point charges on molecular sites,

$$E(q) = \frac{e^2}{4\pi\epsilon_0} \langle r^{-1} \rangle (1 - Cq^2), \quad (2)$$

where $\langle r^{-1} \rangle = 1/8 \sum 1/r_i$ is the average of the inverse intermolecular distance over eight neighboring BEDT-TTF sites, and qe is the charge deviation of the P site from the formal value $0.5e$. The coefficient C , which depends on the charge

pattern, is calculated to be 0.21 and 0.41 for the PRR stripe and honeycomb structures, respectively. The larger C value for the honeycomb structure suggests that the honeycomb structure is energetically more stable, and is thus expected to be realized.

However, we also considered the PR stripe structure [Fig. 4(c)], and estimated its C value to be 1.91. In terms of the nearest-neighbor Coulomb potential, the conventional PR stripe structure should thus be the most stable charge pattern, while this possibility is excluded by our NMR data. It is thus clear that other interactions should be taken into account. From theoretical studies on other BEDT-TTF salts with θ -type molecular packing we learn that the PRR charge pattern can be stabilized in a wide parameter range in the static limit of the extended Hubbard model [24]. Such a charge pattern was indeed experimentally observed as the diffuse rod of x-ray scattering [25]. The exotic charge pattern appears in a θ -type structure, because the in-plane structure is closer to the triangular than to the square lattice. Considering the in-plane structure of β'' -Ga salt to be a squeezed triangular lattice, the exotic charge pattern can be induced by the competition between the off-site and the on-site Coulomb interactions. As in β'' -Ga salt the CO transition occurs in a metallic state, the effect of the transfer integral should certainly be taken into account [26] to explain the charge pattern and understand the SC pairing mechanism inside the CO state.

In summary, we have performed a ^{13}C NMR experiment in a high magnetic field to investigate the electronic properties of β'' -Ga salt in the charge-ordered state. From the angle dependence of the NMR spectra in the charge-ordered state, we found that below 8.5 K the site charge deviates strongly from the formal average value. This deviation is much larger than that observed below 100 K from Raman spectroscopy [18]. The NMR intensity ratio of charge-rich to charge-poor sites leads us to suggest a threefold charge pattern, which can be stabilized by the competition between off-site and on-site Coulomb interactions. Superconductivity of β'' -Ga salt appears thus inside the charge-ordered state with a large charge modulation. Since the SC transition temperature is very close to the CO temperature, we suggest that the charge fluctuations near the second-order charge transition would be related to the SC pairing mechanisms. β'' -Ga salt should thus be considered to be representative of superconductivity with competing off-site and on-site Coulomb interactions.

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