Inhomogeneous site charges at the boundary between the insulating, superconducting, and metallic phases of β'' -type bis-ethylenedithio-tetrathiafulvalene molecular charge-transfer salts

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We have examined time-averaged charges of the molecular donors around the phase boundary between the insulating, superconducting, and metal phases for β'' -type ET [ET=bis-ethylenedithio-tetrathiafulvalene] salts with one (two) hole(s) per two (three) molecules by using vibrational spectroscopy. Around the phase boundary, the site charges are neither those expected for a well-developed charge-ordered (CO) state nor a homogeneous distribution. The molecular charges exhibit an inhomogeneous distribution just above the insulator-superconductor transition temperature. We have analyzed the distribution of the site charges from the viewpoint of the alternation of intersite Coulomb interactions along the stacking direction. The closeness in the energy of several CO patterns mostly contributes to the inhomogeneous distribution, whereas a large difference (no difference) in the energy levels contributes to the CO (homogeneous) state. Our observations indicate that the instability due to the closeness in the energy of several distributions correlates with the insulator-superconductor transition in nondimerized or weakly dimerized molecular conductors.

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I. INTRODUCTION

The charge-ordered (CO) state has attracted intense attention since inhomogeneous site charges are observed in low-dimensional and molecular conductors, which exhibit nonlinear conductivity, photoinduced phase transitions, etc.¹⁻³ The CO state is a localized state wherein molecular charges vary periodically in the two-dimensional organic layer or one-dimensional chain. Merino and McKenzie⁴ theoretically studied the insulator-superconductor (I-SC) transition for the 1/4-filled (with holes) square lattice system, where antiferromagnetism does not occur. They proposed a pairing mechanism mediated by the fluctuation of the CO state by using the slave-boson theory under the assumption of the extended Hubbard model.⁴ Their mechanism is striking since there has been no appropriate model for the I-SC transition of the 1/4-filled and 1/3-filled salts yet. The I-SC transition is observed for the molecular conductors based on the organic donor molecule bis-ethylenedithio-tetrathiafulvalene (ET), wherein one hole (or two holes) is (are) accommodated into two (three) molecules. Among the ET salts that exhibit the I-SC transition, however, most of the researchers have been investigating the κ -type ET salts, where the two-

dimensional layer consists of ET dimers. Owing to strong dimerization, an ET dimer can be regarded as one site so that one hole is accommodated into one site.⁵ Then, the formal band filling can be regarded as half-filling rather than 1/4-filling.⁵ Indeed, even in the insulating state, the ET molecule of the κ -type ET salts takes the formal charge.^{6,7} Therefore, one of the accepted stories for the κ -type ET salts is the half-filled picture: the conducting and magnetic properties of the κ -type ET salts is mapped with $U_{\text{intra}}/t_{\text{inter}}$, where U_{intra} and t_{inter} denote the magnitude of the intradimer on-site Coulomb integral and interdimer transfer integral, respectively.⁵ On the contrary, this picture is no longer applicable to the θ -type and β'' -type ET salts owing to the absence of strong dimerization.^{8,9} The CO transition of the 1/4-filled and 1/3-filled salts is evidenced for the insulating phase of several θ -type and β'' -type ET salts by using NMR, vibrational spectroscopy, and x-ray structural analysis.¹⁰⁻¹⁴ Therefore, the θ -type and β'' -type ET salts are candidates for the charge mediated SC transition. However, there is no evidence for the inhomogeneous site charges just above the I-SC transition temperature except for our preliminary study.¹⁵ Furthermore, it is necessary to understand the role of the intersite Coulomb interaction, V_{inter} , around the phase

boundary by using available materials. In this paper, we present the inhomogeneous molecular charges around the phase boundary among insulator, SC, and metal states of nondimerized or weakly dimerized molecular conductors and discuss what dictates the site charges.

As described above, there are two candidates for a model compound for studying the I-SC transition: θ -type ET salts and β'' -type ET salts. We have chosen the β'' -type ET salts rather than the θ -type ET salts because the electrical properties of θ -(ET)₂I₃, which is a unique superconductor among the θ -type ET salts, are sensitive to minor differences in the anion position.¹⁶ Since the ET molecules of the θ -type ET salt form nearly uniform but complex layers, such a minor structural change may contribute to the crucial effect on the intersite Coulomb interaction, transfer integral, electron-phonon interaction, etc.⁸ In contrast, most of the β'' -type ET salts have nonuniform columnar structures even at room temperature.⁹ The intermolecular distances show the alternation along the stacking direction. Since the alternation of the intermolecular distances induces the alternation of the magnitudes of the intersite Coulomb interactions, the amplitude and distribution of the site charges can be examined from the available distribution of the intermolecular distances.^{13,14} Moreover, a rich variety of superconductors is available among the β'' -type ET salts.^{17–21} Throughout the experiment, for several β'' -type ET salts, we can investigate what dictates the site charges around the phase boundary as well as in the insulating phase without a theoretical simulation.

We have applied the vibrational spectroscopy to the β'' -type ET salts around the phase boundary. Vibrational spectroscopy is one of the most powerful methods for studying the CO state because the pattern of the CO state as well as the molecular charge can be estimated from the frequency of the C=C stretching modes.²² The properties of the C=C stretching modes, described in Ref. 22, are briefly introduced as follows. Since there are three C=C bonds in the ET molecule, the number of the C=C stretching mode is 3: ν_2 , ν_{27} , and ν_3 modes. In the ν_2 (ν_{27}) mode, two C=C bonds in the two five-member rings vibrate in phase (out of phase). The frequencies of the ν_2 and ν_{27} modes have a linear relationship with the molecular charge.²² Since the frequency shifts between the neutral and radical cations are large, 120 and 140 cm⁻¹/hole for the ν_2 and ν_{27} modes, respectively, these modes are the charge-sensitive modes.²² Owing to the large frequency shift, the time resolution of the charge-sensitive modes is approximately 1 ps. Since the small time resolution allows us to investigate the time-averaged molecular charge, the delocalized, nearly localized, and fully localized states are distinguished from each other by using the line shape of the charge-sensitive modes. This property is advantageous in investigating the molecular charges around the phase boundary. The ν_3 mode, which is the stretching mode at the center C=C bond, is not always sensitive to the molecular charge owing to the large electron-molecular vibrational (e -mv) coupling constant (~ 0.1 eV).²³ The ν_3 mode of the crystalline materials exhibits a factor group splitting. The number of the ν_3 mode is at most the number of the ET molecule in the repeat unit of the organic layer. When the overlap integral between the ET molecules is non-negligible, the frequencies of the ν_3 modes are more or less

perturbed, the degree of which depends on the amount of charge transfer induced by each mode.^{11,13,14,22} This property allows us to conduct the factor group analysis. By applying the factor group analysis to the ν_3 modes, we can estimate the distribution of the site charges in the CO state and evaluate the development of the CO state.

The materials for which we have observed vibrational spectra are listed in Table I. Hereafter, we label the listed materials by the designations shown in Table I. The formal filling of the hole band is 1/4-filled (1/3-filled) since one hole (two holes) is (are) accommodated into two (three) molecules. As described in the next sections, however, the formal filling is not sufficient for discussing the distribution of the site charges. In this paper, we often use the ratio of the number of sites to holes in the repeat unit in the organic layer, e.g., 2:1 or 4:2 salts instead of the 1/4-filled salts, and 3:2 or 6:4 salts instead of the 1/3-filled salts. The 4:2 salts are classified into two groups depending on the counteranion: groups I and II. The electrical resistivity of group I exhibits an insulating behavior below 100 K.^{18,19} The M =Pt and Pd salts show the I-SC transition under hydrostatic pressure. The electrical resistivity for group II shows a weak increase with decreasing temperature below ~ 100 K, with the sol=PhNO₂ salt exhibiting an I-SC transition at ambient pressure.^{21,22,24} On the other hand, the SC transition is not observed for the sol=pyridine and CH₂Cl₂ salts at either ambient or hydrostatic pressure.^{21,24} Since Shubnikov-de Haas oscillations are observed for the sol=pyridine salt, the non-SC salts are inherently metal.^{15,25} Group III is the 2:1 salts. The temperature dependence of the electrical resistivity for group III exhibits a metallic behavior down to liquid helium temperature and no SC transition is observed under ambient or hydrostatic pressure.²⁶ Based on the experimental results for the 4:2 and 2:1 (=1/4-filled) salts, we discuss the distribution of the site charges from the viewpoint of the intermolecular distances. The I-SC transition is also observed in the temperature dependence of the electrical resistivity for one of the 1/3-filled salts, β'' -(ET)₃Cl₂·2H₂O, under hydrostatic pressure.¹⁷ Strictly, this material should be classified as the 6:4 salt since the repeat unit consists of six molecules with four holes. The pressure-temperature phase diagram for β'' -(ET)₃Cl₂·2H₂O has been reported in Ref. 27. The I-SC transition is observed under hydrostatic pressure between 1.0 and 1.6 GPa.²⁷ In this paper, we present the temperature dependence of the vibrational spectra under both ambient and hydrostatic pressures. We will discuss the distribution of the site charges for the superconductor β'' -(ET)₃Cl₂·2H₂O by comparison with the previous results for the non-SC material, particularly one of the 3:2 salts [β'' -(ET)₃(ClO₄)₂].¹⁴ As shown in Table I, the former is designated as group ii. The latter is denoted as group i.

The remainder of the paper is organized as follows: the experimental procedures are described in Sec. II. The results of vibrational spectra for the 4:2 and 2:1 (=1/4-filled) salts are shown in Sec. III A. In Sec. III B, we show that the properties of the electrical resistivity for the 4:2 and 2:1 salts are mapped with the time-averaged molecular charges and discuss what dictates time-averaged charges. The pressure dependence of the vibrational spectra for the 6:4

TABLE I. Intermolecular distances, distribution of the intermolecular distance, and difference in the molecular charges at the charge-rich and charge-poor sites, $\Delta\rho$, for the β'' -type ET salts. s and L denote the short and long distances, respectively. Averaged transfer integrals along the stacking and conducting directions, t_s and t_C , respectively, are shown in the right columns.

1/4-filled salts	N	Materials	Distribution of the intermolecular distances	Intermolecular distances ($\text{\AA}$)	Designations	$\Delta\rho$	t_s (meV)	t_C (meV)
Group I 4:2-salts	4	(ET) ₄ Ni(CN) ₄ ·H ₂ O	[sLsL']	4.100, 5.424, 4.100, 5.415 ^a	I-1 $M=N$	0.3	43 ^a	148 ^a
		(ET) ₄ Pd(CN) ₄ ·H ₂ O			I-2 $M=Pd$	0.3	42 ^b	146 ^b
		(ET) ₄ Pt(CN) ₄ ·H ₂ O		4.114, 5.462, 4.114, 5.427 ^a	I-3 $M=Pt$	0.15	40 ^a	146 ^a
Group II 4:2-salts	4	(ET) ₄ [(H ₃ O)Ga(C ₂ O ₄) ₃]PhNO ₂	[sL'LL']	4.026, 4.894, 5.068, 4.894 ^c	II-1 sol=PhNO ₂	0.13	84 ^d	185 ^d
		(ET) ₄ [(H ₃ O)Ga(C ₂ O ₄) ₃]CH ₂ Cl ₂			II-2 sol=CH ₂ Cl ₂	0.08		
		(ET) ₄ [(H ₃ O)Ga(C ₂ O ₄) ₃] pyridine		4.011, 4.864, 5.101, 4.861 ^c	II-3 sol=pyridine	0.05	97 ^d	197 ^d
Group III 2:1-salts	2	(ET) ₂ Br (diiodoacethylene)	[ss']	4.300, 4.363 ^e	III-1 Hal=Br	0.03	20 ^e	86 ^e
		(ET) ₂ Cl (diiodoacethylene)		4.321, 4.468 ^e	III-2 Hal=Cl	0.03	15 ^e	89 ^e
1/3-filled salts	N	Materials	Distribution of the intermolecular distances	Intermolecular distances ($\text{\AA}$)		$\Delta\rho$	t_s (meV)	t_C (meV)
Group ii 6:4-salt	3 × 2	(ET) ₃ Cl ₂ ·2H ₂ O	[LsL']	5.240, 4.049, 5.089 ^f		0.25	35 ^g	184 ^g

^aReference 18.

^bReference 19.

^cReference 21.

^dReference 34.

^eReference 26.

^fOur experimental data.

^gReference 35.

(=1/3-filled) salts is shown in Sec. III C. In Sec. III D, we will discuss the site charge for the 6:4 salts and indicate that, by analogy with the 4:2 and 2:1 salts, the pressure dependence is also correlated with time-averaged charges.

II. EXPERIMENT

Single crystals of groups I–III were prepared by using galvanostatic electrochemical oxidation at the Institute for Molecular Science, The Royal Institution of Great Britain, and RIKEN, respectively. The isotope analogs of β'' -(ET)₃Cl₂·2H₂O were prepared at Hokkaido University and at the Institute for Molecular Science.

Raman spectra were measured by using a Renishaw Ramascope with a backward scattering configuration. The incident light was polarized, and the unpolarized scattered light was collected. Among numerous vibrational modes, we have concentrated our attention on the C=C stretching modes: ν_2 , ν_3 , and ν_{27} . The properties of ν_2 , ν_3 , and ν_{27} modes have been described in Ref. 22 in detail. Figure 1 shows the organic and conducting layer of the β'' -type ET salts.^{9,18,19} The overlap integrals or intersite Coulomb interactions extend along the conducting, stacking, and diagonal directions, which are denoted as C, S, and D directions, respectively. We designate the direction perpendicular to the conducting plane

as the E direction because this direction contains the crystal edge. In most of the spectra, the incident light was irradiated onto the edge of the single crystal and was polarized along the E direction, which is approximately parallel to the molecular long axis. In this configuration, the intensity of the charge-sensitive mode ν_2 is strong. The intensity of the ν_3 mode, whose frequency is less perturbed by the e -mv interaction, is also strong. Some Raman spectra were measured with the incident light perpendicular to the conducting plane in order to observe the vibronic ν_3 mode whose frequency is strongly perturbed by the e -mv interaction. As for the $M=Pt$ salt and β'' -(ET)₃Cl₂·2H₂O, we obtained the

FIG. 1. Organic layer of group I, which is the prototype of the crystal structure of the β'' -type ET salts.

FIG. 2. Raman spectra of the 4:2 and 2:1 (=1/4-filled) salts (solid lines). *E*-polarized conductivity spectra of *M*=Pt salt (dotted line). The notations at the left and right sides of the spectra correspond to those in Table I.

E-polarized IR reflectance spectra in order to observe the ν_{27} mode. We have also obtained some reflectance spectra by using the incident light polarized along the *C* or *S* directions.

The pressure dependence of the Raman spectra for β'' -(ET)₃Cl₂·2H₂O was observed by using a sapphire anvil cell. The pressure medium was Fluorinert, which is manufactured at Sumitomo 3M Co. Ltd., and the gaskets were made from Inconel. The edge of the single crystal (perpendicular to the conducting plane) was placed on the surface of the sapphire. The incident light was polarized along the *E* direction. The samples under ambient and hydrostatic pressures were cooled by using a helium flow cryostat.

III. RESULTS AND DISCUSSION

A. Vibrational spectra of the 4:2 and 2:1 (=1/4-filled) salts

Figure 2 shows the Raman spectra of the 4:2 and 2:1 salts at low temperatures, which are obtained by using the *E*-polarized light. In the Raman spectra, some ν_2 and ν_3 modes are observed, while the ν_{27} mode is mostly observed

in the conductivity spectra obtained after a Kramers–Kronig transformation of the *E*-polarized IR reflectance spectra. In this paper, we have omitted the detailed procedures for assigning the C=C stretching modes since the criteria for the assignments were described in previous papers.^{13,14,22} Molecular charges are determined from the frequency of the ν_2 mode or the ν_{27} mode since these modes are weakly perturbed by or free from the *e*-mv interaction, respectively. The ν_2 mode splits into two for each group, except for the ν_2 mode of the *M*=Pt salt, which is denoted as I-3. The peak splitting of the charge-sensitive mode confirms the inhomogeneous site charges and that the organic layer consists of two kinds of ET molecules: a charge-rich site and a charge-poor site. Although the ν_2 mode of the *M*=Pt salt (I-3) does not show a clear peak splitting, the molecular charges in the *M*=Pt salt are also inhomogeneous since the linewidth is broad. As described in Ref. 22, the estimation of the site charges from the ν_{27} mode is often superior to that from the ν_2 mode. To examine the molecular charges of the *M*=Pt salt in detail, we have observed the ν_{27} mode of the *M*=Pt salt in the IR reflectance spectra. It exhibits a peak splitting in the low-temperature phase, which confirms that the organic layer consists of charge-rich and charge-poor sites. The ν_{27} mode is weakly observed in the Raman spectra of the *M*=Ni and Pd salts (I-1 and I-2, respectively). The differences in the frequency of the ν_2 or ν_{27} mode at the charge-rich and charge-poor sites are shown in Fig. 2. The difference in the fractional charges, $\Delta\rho$, is estimated from the difference in the frequency and the linear relationships: 120 cm⁻¹/hole for the ν_2 mode or 140 cm⁻¹/hole for the ν_{27} mode.²² The estimated $\Delta\rho$ is shown in Table I.

The differences in the fractional charges in the present compounds are significantly smaller compared to $\Delta\rho$ in the CO state for the θ -type ET salts and β'' -type (ET)₃X₂ salts [*X*=ReO₄, ClO₄, and HSO₄], whose electrical resistivities exponentially increase with decreasing temperature.^{11,13,14,28} On the other hand, the small $\Delta\rho$ values for the present compounds are almost identical to those in the highly conducting state for the β'' -type (ET)₃X₂ salts, wherein $\Delta\rho$ is attributed to the time-averaged site charges due to the nearly localized state.^{13,14} The nearly localized state is produced by the nearly degenerated state in several short-range ordering patterns.¹⁴ Interestingly, $\Delta\rho$ exhibits a decrease from the insulating material [*M*=Ni: I-1], the superconductor under hydrostatic pressure [*M*=Pd and Pt: I-2 and I-3, respectively], the ambient pressure superconductor [sol=PhNO₂: II-1], the materials where the electrical resistivity exhibits an insulating behavior below ~20 K but the Shubnikov–de Haas oscillation is observed [sol=pyridine: II-3], to the metallic compounds [Hal=Br and Cl: III-1 and 2]. This trend suggests that the insulating, SC, and metallic phases correlate with $\Delta\rho$.

The localization of the site charges due to the CO transition produces long-range ordering. A well-developed long-range order contributes to the development of the vibronic ν_3 mode, whose frequency is strongly or moderately perturbed by the *e*-mv interaction. On the other hand, the intensity of the less perturbed mode, whose frequency is the highest among the ν_3 modes, is insensitive to the development of the long-range order. Hereafter, we designate the less perturbed mode as the ν_{3H} band. The insensitivity to the long-range

FIG. 3. Vibronic ν_3 mode in the conductivity and Raman spectra for some 2:1 and 4:2 (=1/4-filled) salts. Dotted lines are a guide for the eyes.

ordering is due to the fact that the charge transfer is less induced by the ν_{3H} mode, where the ET molecules vibrate in phase.²⁹ Indeed, the intensity and frequency of the less perturbed band are almost unchanged with decreasing temperature and almost independent of the counteranion.^{11,13,14,28,29}

To examine the development of the long-range order, we have analyzed the vibronic ν_3 mode, whose frequency is strongly perturbed by the e -mv interaction. Figure 3 shows the Raman spectra obtained with the incident light polarized along the C direction. Analogous to the vibronic ν_3 mode in the CO state for the θ -type ET salts and the β'' -type (ET)₃X₂ salts [X=ReO₄, ClO₄, and HSO₄], the strongly perturbed band, which is denoted as ν_{3S} , is clearly observed in the Raman spectra for the M =Ni and Pd salts (I-1 and I-2, respectively). In contrast, this band is very weak in the spectra for the M =Pt salt (I-3) and is barely observed for groups II and III. Interestingly, the e -mv mode tends to be smeared with decreasing $\Delta\rho$. This trend indicates that the CO state is reduced with decreasing $\Delta\rho$, which supports our conjecture that groups I–III correlate with the time-averaged site charges.

In the spectra of the M =Ni and Pd salts (I-1 and I-2, respectively), the moderately perturbed band ν_{3M} is also observed in the Raman spectra. According to the x-ray structural analysis for group I, at room temperature, the organic

layer in the unit cell consists of two-dimensional tetramers in inversion symmetry, which is shown in Fig. 1.^{18,19} By assuming a tetramer in inversion symmetry in the low-temperature phase, four ν_3 modes are classified into two Raman-active bands and two IR-active bands. On the contrary, the number of ν_3 modes in the Raman spectra is at least 3. Our observation indicates that the insulating phase in the M =Ni and Pd salts is characterized as a well-developed CO state, where no inversion center is located in the two-dimensional tetramer. The asymmetric distribution is such that the charge-rich and charge-poor molecules are alternately aligned along the stacking direction. The charge-rich or charge-poor stripes are extended along either the C or D direction. Our conjecture is supported by comparing the IR and Raman spectra. Figure 3 shows the conductivity spectra obtained after a Kramers–Kronig transformation of the C - and S -polarized reflectance spectra of the M =Ni salt. The ν_{3M} band is observed in the C -polarized spectra, and the ν_{3S} band in the S -polarized spectra. This result confirms the absence of the inversion symmetry since the mutual exclusion rule is not applicable to both the IR and Raman spectra. It should be noted that the strongly perturbed band is observed in the S -polarized spectra. By assuming asymmetric distributions, a large charge transfer is allowed along the S direction when the charge-rich and charge-poor molecules undergo out-of-phase vibrations. Therefore, the polarization dependence of the vibronic ν_3 mode agrees with the distribution of the site charges deduced from the loss of the inversion center.

On the other hand, the strongly perturbed band is only weakly observed in the IR and Raman spectra of the M =Pt salt (I-3, Fig. 3). The weak intensity indicates that the charge ordering does not develop so strongly down to a low temperature as compared with the CO state for the M =Ni and Pd salts. Furthermore, this band is barely observed in the Raman spectra of groups II and III. This phenomenon suggests that the site charges for groups II and III are less localized as compared to the site charges in the M =Pt salt. Therefore, we conclude that the suppression of the vibronic ν_3 band is correlated with $\Delta\rho$, which strongly suggests that the CO state melts from group I to group III.

We summarize the experimental results for the 1/4-filled salts as follows: (1) the molecular charges largely deviate from the formal charge, 0.5, for the insulating materials, M =Ni salts, and Pd salts. The insulating phases of these materials are still the CO state with a development of long-range order. (2) The time-averaged charges in the insulating phase neighboring the superconductor phase are still inhomogeneous, but charges are not completely localized at sites; in fact, they are in a nearly localized state. (3) Time-averaged site charges in the metallic phase are almost homogeneous.

B. Distribution of the site charges in the 4:2 and 2:1 (=1/4-filled) salts

The site charges of the β'' -ET salts in the CO state are largely due to the intersite Coulomb interaction along the stacking direction (S direction), which is almost perpendicular to the conducting direction (C direction).^{13,14} The intermolecular distances along the S direction are useful param-

FIG. 4. Configuration of the ET molecules along the stacking direction for group I. L , L' , and s denote the intermolecular distances, $L > L' \gg s$. The distances are shown in Table I.

eters for analyzing the distribution of the site charges. As shown in Fig. 4, the intermolecular distance is defined from the distance between the center of the central C=C bond to that in the adjacent molecule. When the adjacent molecules lie face-to-face, the intermolecular distance is short. On the other hand, the intermolecular distance is long when adjacent molecules are slipped along the molecular long axis. Since the charge-rich pair does not favor a short intermolecular distance, the distribution of the site charges is obtained. This criterion applies quite well to the distribution of site charges in the nearly localized and highly conducting state above the CO transition temperature as well as the CO state for the β'' -(ET) $_3$ X $_2$ salts ($X = \text{ReO}_4$, HSO_4 , and ClO_4), (ET) $_5\text{Te}_2\text{I}_6$, and (BETS) $_5\text{Te}_2\text{I}_6$ (BETS = bis-ethelenedithio-tetraselenafulvalene).^{13,14,30} In the following, we examine the distribution of the site charges for the 1/4-filled salts from the viewpoint of the intermolecular distance.

Table I shows the number of ET molecules in the repeat unit along the S direction, N , the intermolecular distance, and the distribution of the intermolecular distance. The distribution of the intermolecular distances is represented by a short (long) intermolecular distance, denoted as s (L). The distribution of the site charges in the repeat unit is obtained after two holes (one hole) are (is) accommodated into four sites (two sites). Before discussing the distribution in the present compounds, we will comment on the distribution of the site charge for an exactly uniform columnar structure. A uniform columnar structure ($N=1$) can produce the homogeneous site charge as a time-averaged distribution since the energy level of the distribution, $[d\bullet d\circ]$, is identical to that of its counterpart, $[d\circ d\bullet]$, where d denotes the intermolecular distance between charge-rich “ $\bullet$ ” and charge-poor “ $\circ$ ” molecules. In other words, the distribution allowed in the organic layer is indefinite. Even though the intermolecular distance is short, $d=s$, the homogeneous distribution is expected to be robust unless additional interaction or structural changes driven by electron-phonon interaction, interaction with the counteranion, redistribution in the intersite Coulomb interaction, etc., participate in the distribution of the site charges. Indeed, homogeneous site charges are observed below ~ 100 K for β'' -(ET)(TCNQ) (TCNQ=tetracyanoquinodimethane), whose intermolecular distance is uniform and short ~ 4.106 Å.^{31,32}

Group III belongs to the 2:1 salt. The intermolecular distances for group III are almost but not exactly uniform

($N=2$; $[ss']$, $s' > s$).²⁶ Nevertheless, the energy level of $[s\bullet s'\circ]$ is identical to that of $[s\circ s'\bullet]$. Therefore, in this group, the almost homogeneous distribution is the result of a time averaging. This conclusion is supported by the observation of a single peak corresponding to the charge-sensitive mode in β'' -(ET) $_2\text{AuBr}_2$.²² Analogous to the intermolecular distances for group III, the intermolecular distance along the stacking direction of β'' -(ET) $_2\text{AuBr}_2$ is not uniform and two ET molecules form the repeat unit ($N=2$).^{9,33} Since the short ($s=4.146$ Å) and long ($L=5.636$ Å) distances occur alternately along the S direction, the energy of the $[s\bullet L\circ]$ distribution is identical to that of $[s\circ L\bullet]$.³³ Therefore, the homogeneous site charge is produced not only for $N=1$ but also for $N=2$. In other words, the localization of the site charges for the 2:1 salts with $N=2$ ($N=1$) requires some structural changes, for example, a doubling (tetramerization) of the repeat unit or broken inversion symmetry, anion ordering, etc. These structural changes then contribute to an alternation of the intersite Coulomb integral including the interlayer direction or the electron-phonon interaction.

Next, we examine the intermolecular distances for group I, where the repeat unit consists of four molecules ($N=4$). Strictly, the ratio of the number of sites to the number of holes should be represented as 4:2. As shown in Fig. 4 and Tables I and II, the number of short distances (s) is two and that of long distances also 2. However, one of the long distances is not exactly equal to the other ($L' < L$). Since the charge-rich pair does not favor the short distance, four patterns are allowed for group I, as shown in Table II. The most stable distribution is a pair of asymmetric distributions $[L\bullet s\circ L'\bullet s\circ L]$ and $[L\circ s\bullet L'\circ s\bullet L]$. When the energy levels between asymmetric distributions are identical to each other, a pair of the asymmetric distribution contributes (does not contribute) to the homogeneous (inhomogeneous) distribution. When either of the asymmetric distributions has the lowest energy, on the other hand, a localization of the site charges occurs. As shown in Fig. 3, at least three ν_3 modes are observed in the Raman spectra for the $M=\text{Ni}$ and Pd salts. Furthermore, the mutual exclusion rule cannot be applied to both IR and Raman spectra. This observation is clear evidence of a loss of inversion symmetry, which strongly supports that either of the asymmetric charge distributions contributes to the localization of the site charges. Throughout the discussion above, we have analyzed the distribution of the site charges along the one-dimensional direction. However, several structural properties are unresolved. The development of one of the asymmetric distributions requires a minor structural change, for example, $[L\ s\ L'\ s\ L] \rightarrow [L1\ s\ L'\ s\ L2]$. Such a minor change in the intermolecular distance is observed for the CO state of β'' (ET) $_3(\text{ReO}_4)_2$ salts, wherein $[L\ s\ L] \rightarrow [L1\ s\ L2]$. The development of the vibronic mode suggests the condensation of the CO state in the two-dimensional layer. As for the two-dimensional distribution in the low temperature phase of the $M=\text{Ni}$ and Pd salts, there are two candidates: charge-rich and charge-poor stripes could extend along either C or D direction. Both two-dimensional distributions satisfy the development of the asymmetric distribution and show a decrease in the magnetic susceptibility. To confirm the two-dimensional structure and a minor change in the

TABLE II. Distributions of the time-averaged site charges and energy diagrams for the possible distributions. L , L' , and s denote the intermolecular distances, $L > L' \gg s' > s$. The differences in the site charges at the charge-rich and charge-poor molecules, $\Delta\rho$, are shown in the right column. The time-averaged distribution corresponds to that under the ambient pressure, except for the distribution for group ii. A charge-rich pair with a short distance is omitted in this table.

1/4-filled salts		Time-averaged distribution Rich $\bullet > \circ > \diamond > \circ > \circ$ Poor	Distributions of the site charges and energy levels $\bullet$: Rich $\circ$: Poor		$\Delta\rho$
Group I 4:2-salts	$(\text{ET})_4\text{M}(\text{CN})_4 \cdot \text{H}_2\text{O}$ $\text{M}=\text{Ni, Pd}$	$L > L' > s$ 		non-degenerated	0.3
	$(\text{ET})_4\text{M}(\text{CN})_4 \cdot \text{H}_2\text{O}$ $\text{M}=\text{Pt}$	$L > L' > s$ 		nearly degenerated	0.15
Group II 4:2-salts	$(\text{ET})_4[(\text{H}_3\text{O})\text{Ga}(\text{C}_2\text{O}_4)_3]\text{sol}$ $\text{sol}=\text{PhNO}_2, \text{pyridine}, \text{CH}_2\text{Cl}_2$	$L > L' > s$ 		nearly degenerated	0.13 0.05
Group III 2:1-salts	$(\text{ET})_2\text{Hal}(\text{diiodoacetylene})$ $\text{Hal}=\text{Br, Cl}$	$s' > s$ 		degenerated	0.03
1/3-filled salts		Time-averaged distribution Rich $\bullet > \circ > \diamond > \circ > \circ$ Poor	Distributions of the site charges and energy levels $\bullet$: Rich $\circ$: Poor		$\Delta\rho$
Group i 3:2-salts	$(\text{ET})_3(\text{ClO}_4)_2$ ambient pressure	$L > s$ 		non-degenerated	0.8 ^{a)}
Group ii 6:4-salts	$(\text{ET})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ambient pressure	$L > L' > s$ 		non-degenerated	0.25 (ambient) ↓ 0.03 (2.0 GPa)
	$(\text{ET})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ $P < 1.6 \text{ GPa}$			nearly degenerated	
	$(\text{ET})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ high pressure			degenerated	

^aReference 14.

intermolecular distance, further experiment will be needed, for example, a structural analysis using synchrotron radiation.

On the other hand, $\Delta\rho$ in the $M=\text{Pt}$ salt is small and the intensity of the vibronic mode in the first run is very weak as

compared to those of the $M=\text{Ni}$ and Pd salts. The weak intensity of the ν_{3S} mode, which is inherently IR active, in the Raman spectra indicates that the asymmetric distributions are almost degenerated. The weak intensity of the ν_{3S} mode in the IR spectra of $M=\text{Pt}$ salt as compared with those of

$M=\text{Ni}$ and Pd salts suggests that the site charges of the former are more delocalized than the latter. An asymmetric pair contributes to the homogeneous site charges for the $M=\text{Pt}$ salt in the nearly degenerated state, which satisfies small $\Delta\rho$. Nevertheless, $\Delta\rho$ of the $M=\text{Pt}$ salt is finite, although small. As shown in Table II, one of two symmetric distributions [●○○●] is more stable than the other [○○●●], and between two symmetric distributions, the more stable one will contribute most to the time-averaged distribution, which results in a small but finite $\Delta\rho$ in that case.

As described above, the $M=\text{Ni}$ and Pd salts are characterized as the localized CO state, whereas the $M=\text{Pt}$ salt is characterized as the nearly localized CO state, whose $\Delta\rho$ is small as compared to those of the $M=\text{Ni}$ and Pd salts. Both the reduction in the intersite Coulomb integral along the S direction, V_S , and the increase in the transfer integral along the C direction, t_C , can contribute to the decrease in $\Delta\rho$. A minor contribution of the magnitudes of V_S and t_C is also supported by the similarity in the distributions of the site charges between $(\text{ET})_5\text{Te}_2\text{I}_6$ and $(\text{BETS})_5\text{Te}_2\text{I}_6$.³⁰ As for group I, the difference in $\Delta\rho$ is attributed to V_S rather than t_C . First, we examine the contribution of transfer integrals to $\Delta\rho$ in group I. Comparing the reflectance spectra for the $M=\text{Ni}$ salt with those for the $M=\text{Pt}$ salt does not necessarily give the difference in the transfer integrals since the reflectance spectra contain strong vibronic modes as well as the electronic transition. We have compared the transfer integrals obtained from the x-ray structural analysis.^{18,19} As shown in Table I, the transfer integral of the $M=\text{Pt}$ salt is slightly smaller than that of the $M=\text{Ni}$ salt.^{18,19} Therefore, the difference in the transfer integrals does not contribute to the difference in $\Delta\rho$ for group I. On the other hand, all intermolecular distances in the $M=\text{Pt}$ salt are longer than those of the $M=\text{Ni}$ salt.^{18,19} Since the long intermolecular distance reduces V_S , the decrease in $\Delta\rho$ for group I is ascribed to the decrease in V_S .

We now examine the time-averaged distribution in the group II salts. The absence of development in the e -mv mode indicates that there is no noticeable temperature dependence in the distribution of the intermolecular distances and time-averaged site charges. That no redistribution takes place in the intermolecular distances is supported by comparing the crystal structures at 295 and 30 K.²¹ These results allow us to regard the site charges over the whole temperature range as a result of the nearly localized picture. Group II belongs to the 4:2 salt. As shown in Table II, the repeat unit in the organic layer consists of four molecules ($N=4$).²¹ There is one short distance for group II, whereas there are two for group I. Since the charge-rich pair does not favor the short distance, five patterns are allowed for group II. Among the possible patterns, there are two pairs of asymmetric distributions and one symmetric one. Since there are no positive data suggesting a loss of inversion symmetry, an asymmetric distribution and its counterpart are degenerated, which contribute to homogeneous site charges. Only one kind of symmetric pattern can contribute to the inhomogeneous distributions. It should be noted that $\Delta\rho$ for group II is small compared with that for the $M=\text{Pt}$ salt. The difference between $\Delta\rho$ of group II and the $M=\text{Pt}$ salt is partly ascribed to the number of asymmetric

FIG. 5. Comparison of the conductivity spectra between sol = PhNO_2 and CH_2Cl_2 salts.

distributions, in the sense that group II contains two pairs, whereas the $M=\text{Pt}$ salt has one pair. Two pairs of asymmetric distribution favor a more homogeneous time-averaged distribution. The distance at the charge-rich pair in the symmetric distribution also contributes to a small $\Delta\rho$. The distance of the slipping configuration for group II is $L \sim 5.1$ Å, which is significantly shorter than the distances for the $M=\text{Pt}$ salt $L \sim 5.462$ and $L' \sim 5.427$ Å.^{18,21} Since the charge-rich pair favors a long intermolecular distance, the symmetric distribution for group II is unstable as compared to those for the $M=\text{Pt}$ salt. As a result, the most stable asymmetric distributions for group II have a large contribution to the time-averaged distribution as compared with those for the $M=\text{Pt}$ salts. Therefore, a small $\Delta\rho$ and the slight development of the long-range order for group II are ascribed to the distribution of the intermolecular distance.

A minor difference in $\Delta\rho$ is also observed among the materials in group II. A minor difference for group II is attributed to the transfer integral along the C direction, t_C , rather than the magnitude of the intersite Coulomb integral along the S direction, V_S . As shown in Fig. 5, an increase in the overlap integral is supported by the large optical conductivity of the $\text{sol}=\text{CH}_2\text{Cl}_2$ salt as compared with the $\text{sol}=\text{PhNO}_2$ salts. The transfer integrals obtained from the x-ray structural analysis have the same trend, which are shown in Table I.³⁴

In conclusion, we have shown that the degree of (de)localization, $\Delta\rho$, among groups I–III mostly depends on the energy levels in the possible distributions. The energy levels are attributed to the variation in the intermolecular distance along the stacking direction. The magnitude of the intersite Coulomb integral V_S and the transfer integral t_C make only a minor contribution to the time-averaged site charges.

Figure 6 shows a schematic phase diagram for groups I and II salts correlated with the time-averaged site charges, which are defined as the difference in the molecular charges at the charge-rich and charge-poor sites ($\Delta\rho$). In Ref. 18, the pressure-temperature phase diagram is presented for group I. As for group II, the temperature–chemical pressure (corresponding to the unit cell volume) phase diagram is shown in Ref. 25. In the former phase diagram, the insulating phase undergoes a transition to a superconducting phase with in-

FIG. 6. Schematic phase diagram of the β'' -type ET salts, where the nearly degenerated state is allowed. “SF” denotes β'' -(ET) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$, whose fractional charges are examined in Ref. 41.

creasing hydrostatic pressure.¹⁸ In the latter phase diagram, the superconducting phase reverts to metallic with decreasing unit cell volume.²⁵ Our phase diagram indicates that both phase diagrams are integrated by referring to the time-averaged site charges. The insulating phase is a ground state since the CO state contributes to reducing the intersite Coulomb interaction. In this phase diagram, the “metallic” phase is separated from the “metal” phase. The former corresponds to the highly conducting state, wherein a charge separation is survived without a long-range ordering. The temperature dependence of the electrical resistivity exhibits the so-called bad metal behavior. The latter is the normal metal, wherein Shubnikov–de Haas oscillation, Drude response, etc., are observed and the molecular charges are inherently homogeneous. The metal phase is also a ground state because of the energy reduction due to the kinetic term. The SC phase and CO state are separated from each other by the metallic (inhomogeneous) phase because the vibrational spectra of the M =Pt and sol=PhNO $_2$ salts indicate less development of the long-range ordering regardless of finite $\Delta\rho$. The M =Pt salt at low temperature, under ambient pressure, is the closest to the phase boundary between the CO and inhomogeneous (metallic) phases. As shown in the phase diagram, the superconducting material requires a small but finite $\Delta\rho$. The insulating state just above the I-SC transition temperature is characterized as the nearly localized state owing to the nearly degenerated distributions, which take neither a fully delocalized state nor a static CO state with long-range ordering. The nearly localized state cannot survive at the lowest temperature since the system is by no means stable. Our observation suggests the pairing mechanism, which dissolves the instability of the nonstatic but inhomogeneous site charges. By assuming that the nearly localized state plays an important role in the mechanism of the SC transition, a similar phenomenon should be looked for more closely in other organic superconductors, where the dimer-Mott model is not applicable owing to the absence of strong dimerization. To confirm our conjecture, we examine the molecular charge just above the I-SC transition temperature in the 1/3-filled salts, which is described in the next section.

FIG. 7. Temperature dependence of the E -polarized conductivity spectra for β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O.

C. Vibrational spectra of the 6:4 (=1/3-filled) salt: β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O

According to Ref. 27, the low-temperature electrical resistivity of β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O exhibits insulating, superconducting, and metallic behavior with increasing hydrostatic pressure. The temperature dependence from 1.0 to 1.6 GPa shows an I-SC transition.^{17,27} Prior to the measurement of the pressure dependence of the vibrational spectra, the assignment of the vibrational modes under ambient pressure must be confirmed. First, we measured the temperature dependence of the vibrational spectra under ambient pressure. Figure 7 shows the temperature dependence of conductivity spectra obtained after Kramers–Kronig transformation of the E polarized reflectance spectra. Since the intermolecular interaction along the E direction is negligibly small, the electronic transition is hardly observed in this spectral region. The E direction is almost parallel to the molecular long axis; hence, the ν_{27} mode is clearly observed in the E -polarized reflectance spectra, where its linewidth at 300 K is very broad. In analogy to the highly conducting phase of β'' -(ET) $_3$ X $_2$ salts (X =HSO $_4$, ClO $_4$, and ReO $_4$), the observation of such a broad line indicates a fluctuation or frustration of the site charges.^{13,14} With decreasing temperature, the broad band splits into two prominent peaks at $\sim$ 1450 and 1425 cm $^{-1}$, with the peak separation being clear below 100 K. The two prominent peaks at $\sim$ 1450 and 1425 cm $^{-1}$ are assigned to the ν_{27} mode at the charge-poor and charge-rich molecules, respectively. The weak peaks at $\sim$ 1410 and 1400 cm $^{-1}$ are assigned to the CH $_2$ bending mode, which is insensitive to the molecular charge. The clear peak separation of the charge-sensitive mode indicates the CO state in the low-temperature phase. In the spectra at 150 and 200 K, the ν_{27} mode at the charge-rich site has a shoulder at 1440 and 1430 cm $^{-1}$, respectively, which is assigned to the ν_{27} mode at the charge-poor site. This observation indicates that the charge separation continuously develops with decreasing temperature and the charges become localized below 100 K.

FIG. 8. Raman spectra of β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O at 13 K and the E -polarized conductivity spectra at 9 K. d_8 -C 12 , deuterium analog; h_8 -C 12 , natural abundant; h_8 -C 13 , isotope analog whose central C=C atoms are substituted for C 13 . The conductivity spectra are the same as those shown in Fig. 7. “cond.” and “edge” denote the experimental configurations, where the incident light is perpendicular to the conducting plane and the crystal edge.

The assignments of other C=C stretching modes, ν_2 and ν_3 modes, are confirmed by comparing the Raman spectra of isotopic analogs and the IR and Raman spectra of samples containing the naturally abundant isotopes. Figure 8 shows the 13 K Raman spectra of the deuterium analog (d_8 -C 12), the natural abundant (h_8 -C 12), and the isotopically substituted analog whose central C=C atoms are substituted by C 13 (h_8 -C 13), and the E -polarized conductivity spectra of the naturally abundant material at 9 K. By comparing the spectra of the d_8 -C 12 and h_8 -C 12 samples, the C=C stretching modes can be distinguished from the CH $_2$ bending modes because the frequency of the latter decreases to ~ 1000 cm $^{-1}$ in the deuterium analog. The assignment of the ν_3 mode is

confirmed by comparing the spectra of h_8 -C 12 and h_8 -C 13 compounds since the frequency of the stretching mode at the central C=C bond shows a redshift of approximately ~ 60 cm $^{-1}$, whereas the frequencies of the ν_2 and ν_{27} modes are almost unchanged. The ν_2 and ν_{27} modes are distinguished by comparing the IR and Raman spectra, of the natural abundant compounds since the ν_{27} mode is clearly observed in the IR spectra, whereas the ν_2 mode is observed in the Raman spectra. Based on these arguments, the assignments of the ν_2 , ν_3 , and ν_{27} modes are given in Fig. 8. In analogy to the ν_{27} mode, the ν_2 mode exhibits peak splitting in the low-temperature phase, which manifests the CO state at low temperature.

The observation of two peaks in the charge-sensitive modes suggests that the organic layer consists of two kinds of ET molecules whose molecular charges differ. The frequencies of the ν_2 modes in the CO state are ~ 1510 and 1480 cm $^{-1}$. By applying the linear relationship in Ref. 22, $1447 + 120(1 - \rho)$ cm $^{-1}$, to the frequency of the ν_2 modes, the molecular charges at the charge-rich and charge-poor molecules are estimated to be approximately 0.75 and 0.5, respectively. Therefore, the ratio of the charge-rich sites to the charge-poor site is 2:1. The assignment of the ν_2 modes allows us to examine the pressure dependence of the molecular charges by using the frequency of the ν_2 modes.

Gaultier *et al.* studied x-ray structural analysis in the low-temperature phase at ambient pressure and estimated the molecular charge and the distribution of the site charges.³⁵ They analyzed their structural data by assuming a hexameric repeat unit in the ET layer, based on inversion symmetry.³⁵ The three molecules were independent of each other. They analyzed molecular charges based on the temperature dependence of the bond lengths in the tetrathiafulvalene skeleton.³⁵ In the low-temperature phase, the charges at the three molecules are estimated to be ~ 0.96 , 0.88 , and 0.54 .³⁵ Since thermal contraction of the ET molecule is not taken into account, the summation of the site charges exceeds 2. If the summation is normalized to 2, the molecular charges are estimated to be ~ 0.80 , 0.74 , and 0.45 , respectively. As described in Ref. 35, the molecular charge obtained from the bond-length analysis has an accuracy of $\pm 10\%$. Therefore, the molecular charges estimated from our experiment are in agreement with those from the bond-length analysis. A hexameric repeat unit in inversion symmetry is also consistent with our experiment. Figure 9 shows the temperature dependence of the C -polarized conductivity spectra. Since the organic layer in the unit cell contains six ET molecules, the number of the ν_3 modes is at most 6, whose frequencies are usually perturbed by the e -mv interaction. In the IR and Raman spectra in the low-temperature phase, at least two ν_3 modes are observed. In the Raman spectra, the ν_{3H} mode is observed at ~ 1470 cm $^{-1}$ and is assigned to the highest frequency band, wherein the six molecules vibrate in phase. The other ν_3 mode, denoted as ν_{3S} , is observed in the IR spectra at very low frequency (~ 1300 cm $^{-1}$) and with a line-width exceeding ~ 100 cm $^{-1}$. This mode is assigned to one of the strongly perturbed bands due to the e -mv interaction. By comparing the IR and Raman spectra, we confirmed that the mutual exclusion rule holds for the vibronic ν_3 mode. Therefore, the distribution of the site charges deduced from

FIG. 9. Temperature dependence of the C-polarized conductivity spectra for β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O.

the x-ray structural analysis in Ref. 35 is consistent with the vibrational spectra. The distribution of site charges in the CO state is shown in Table II.

Next, we examine the pressure dependence of the charge-sensitive mode. Figure 10 shows the pressure dependence of the Raman spectra of β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O at 10 K along with the pressure dependence of the Raman spectra at 300 K.

FIG. 10. Pressure dependence of the Raman spectra for β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O at 300 and 10 K

With increasing pressure at 300 K, the frequency of the ν_2 and ν_3 modes monotonically increase, a phenomenon that is also observed in the pressure dependence of some ET salts.^{36,37} The monotonic blueshift in the pressure dependence is attributed to the contraction of the ET molecules. The broad linewidth of the ν_2 remains up to 2 GPa, which indicate that the nearly localized site charges remain in the high-temperature phase. As can be seen from the 10 K spectra, the frequencies of the ν_2 modes approach each other with increasing pressure. Nevertheless, the ν_2 mode does not become single even at 1.3 and 1.6 GPa. This observation indicates that the site charges under pressure should be interpreted as being time averaged in analogy with the charge-sensitive mode in the highly conducting phase of the β'' -(ET) $_3$ X $_2$ salts (X =HSO $_4$, ClO $_4$, and ReO $_4$).¹⁴ By curve fitting the Raman spectra, the frequencies of the ν_2 modes above 1.3 GPa can be estimated. Since the frequency of the ν_2 modes increases continuously owing to the contraction of the ET molecule, it is not possible to estimate the molecular charges under hydrostatic pressure from the linear relationship in Ref. 22, $1447 + 120(1 - \rho)$ cm $^{-1}$, at ambient pressure. Therefore, we estimate the difference in the molecular charges at the charge-rich and charge-poor sites by using the difference in the frequencies between the neutral and radical cation molecules (120 cm $^{-1}$ /hole).²² The difference in the site charges is shown in Fig. 10. We conclude that $\Delta\rho$ just above the SC transition temperature is small but finite for the 3:2 salts as well as the 2:1 salts. This experimental result indicates that the molecular charges should be ascribed a time-averaged distribution based on a nearly localized picture.

D. Distribution of the site charges in the 6:4 and 3:2 (=1/3-filled) salts

Before discussing the time-averaged distribution of β'' -(ET) $_3$ Cl $_2$ ·2H $_2$ O under hydrostatic pressure, we examine the distribution of the site charges of the 3:2 and 6:4 salts at ambient pressure from the viewpoint of the intermolecular distance. In analogy with the 4:2 and 2:1 salts, the intermolecular distance at the slipping configuration is long (~ 5 Å), whereas that at the nonslipping configuration is short (~ 4 Å).⁹ As for the 3:2 salts, the distributions of the intermolecular distances for the nonuniform columnar structure can be roughly classified into two categories. One is the distribution [sLs] with one long distance and two short distances, and the other is [LL's] with two long distances and one short distance.⁹ The former corresponds to that found in β'' -(ET) $_3$ (ClO $_4$) $_2$, where only one kind of distribution of the site charges, [s●L●sOs], is allowed in the CO state.¹⁴ The distributions of the intermolecular distances and site charges are shown in Table II. On the other hand, the second distribution, [LL's], leads to the frustration of the site charges in the case that $L=L'$.^{13,14} This case corresponds to the highly conducting state of β'' -(ET) $_3$ (ReO $_4$) $_2$, wherein the energy of [L●L'Os●L] is identical to that of [L●L'●sOsL].^{13,14} This frustration dissolves in the low-temperature phase since a structural change leading to $L>L'$ occurs.^{13,14} Since the distribution [L●L'Os●L] is more stable than

[L●L'●s○L], localization of the site charges takes place.^{13,14}

As shown in Tables I and II, the number of ET molecules in the unit cell for the 6:4 salt, $\beta''\text{-(ET)}_3\text{Cl}_2\cdot 2\text{H}_2\text{O}$, is 6 ($N=3\times 2$), which is different from $N=3$ found in $\beta''\text{-(ET)}_3(\text{ClO}_4)_2$ and $\beta''\text{-(ET)}_3(\text{ReO}_4)_2$.⁹ However, in common with the low-temperature phase of $\beta''\text{-(ET)}_3(\text{ReO}_4)_2$, the organic layer in the unit cell consists of asymmetric trimers, which include two long intermolecular distances, denoted as L' and L , and one short distance.^{9,35} When two holes are localized in the asymmetric trimer, the distribution [L●L'○s●L] is more stable than [L●L'●s○L]. Since a pair of asymmetric trimers forms a hexamer on the inversion center, the number of the distributions is 9. Among nine distributions, five distributions include a charge-rich pair with a short distance. After excluding five unstable distributions, there are four possible distributions of the site charges in the low-temperature phase. Among the four shown in Table II, the most stable one consists of a pair of the most stable distributions, [L●L'○s●L]. Indeed, this distribution agrees with the pattern of the CO state at ambient pressure.³⁵ Therefore, the distribution of the site charges at ambient pressure satisfies the requirement for reducing the intersite Coulomb interaction along the stacking direction.

The peak separation of the charge-sensitive mode is enhanced with decreasing temperature, consistent with that for the $X=\text{ClO}_4$ salt, and significantly different from that for $\beta''\text{-(ET)}_3(\text{ReO}_4)_2$, where the frequencies of the charge-sensitive modes approach each other down to the transition temperature.^{13,14} This difference in the temperature dependence is ascribed to a different distribution of the intermolecular distances in the high-temperature phase. The distribution of the intermolecular distances for the present compound is asymmetric over the whole temperature range, [LL's], while that for $\beta''\text{-(ET)}_3(\text{ReO}_4)_2$ is symmetric in the high-temperature phase, [LLs].^{13,14,38} Even though the thermal contraction enhances intersite Coulomb interaction, the site charges of $\beta''\text{-(ET)}_3(\text{ReO}_4)_2$ cannot be fully localized since the energy level of [L●L○s●L] is identical to that of [L●L●s○L].^{13,14} Thus, frustration of the site charges occurs in $\beta''\text{-(ET)}_3(\text{ReO}_4)_2$. The thermal contraction also enhances overlap integrals, particularly along the transverse direction. Therefore, time-averaged charges approach the molecular charges deduced from the chemical composition owing to the kinetic interaction.^{13,14} On the other hand, the most stable distribution is robust in the high-temperature phase for $\beta''\text{-(ET)}_3\text{Cl}_2\cdot 2\text{H}_2\text{O}$ and $\beta''\text{-(ET)}_3(\text{ClO}_4)_2$. The temperature dependence of the charge-sensitive modes for $\beta''\text{-(ET)}_3\text{Cl}_2\cdot 2\text{H}_2\text{O}$ and $\beta''\text{-(ET)}_3(\text{ClO}_4)_2$ is ascribed to the development of the most stable distribution; in other words, the fluctuation of the most stable distribution rather than a frustration between degenerated distributions.^{13,14}

Let us discuss time-averaged molecular charge under hydrostatic pressure. Since no significant change suggesting a discontinuous structural change or redistribution in the site charges is observed, the pressure dependence of molecular charges can be analyzed in terms of the intermolecular distance used for the ambient pressure. With increasing hydrostatic pressure, the difference in the fractional charges, $\Delta\rho$, decreases. It should be noted that inhomogeneous charges

are robust just above the SC transition temperature. In analogy with group II, the time-averaged distribution above the SC transition temperature is characterized as the nearly localized picture due to the nearly degenerated state among four distributions shown in Table II. The hydrostatic pressure reduces the area of the organic layer, which enhances the overlap integrals, particularly along the C and D directions. The enhancement of the overlap integral partly participates in the reduction in the difference of the energy levels among four possible distributions. It should be noted that hydrostatic pressure induces contraction not only within the organic layer but also in the interlayer direction. The contraction along the interlayer direction induces rotation of the ET molecules because the long axis of the ET molecule of the β'' -type ET salts is not exactly perpendicular to the organic layer, which is shown in Fig. 4. Then, hydrostatic pressure reduces the difference in the intermolecular distances. The similarity between the intermolecular distances, particularly between L and L' , also contributes to reducing the difference in the energy levels among four distributions. Therefore, a small but finite $\Delta\rho$ just above the SC transition temperature is attributed to the nearly degenerated state due to the similarity in the intermolecular distances along the stacking direction as well as the enhancement of the overlap integral along the C and D directions. With increasing pressure up to 1.7 and 2 GPa, $\Delta\rho$ is very small (~ 0.03). As shown in Ref. 27, the temperature dependence of the resistance in the high-pressure region exhibits metallic behavior. In analogy with group III, the metallic behavior with a very small $\Delta\rho$ is attributed to the almost identical intermolecular distances. We believe that high pressure induces almost homogeneous distances, wherein the distance at the nonslipping configuration is almost identical to that at the slipping configuration. The delocalized nature under the high-pressure region is attributed to the degeneration of the energy levels, including the charge-rich pair with a nonslipping configuration. In Table II, the distributions in one column are shown although the total number of the distributions in a unit cell is 9. The degeneration of the energy levels is supported by the pressure dependence of the electrical resistivity for $\beta''\text{-(ET)}_3(\text{ClO}_4)_2$, which is described in the next paragraph.

Based on the above discussion, we can surmise that a nearly degenerated state is required for the SC transition of the β'' -type ET salts. If this is the case, we can expect that there will be no SC transition in any material whose site charges are homogeneous or whose distribution of the site charges is uniquely determined. Indeed, the almost homogeneous site charge for group III agrees with the absence of a SC transition. The temperature dependence of the electrical resistivity of $\beta''\text{-(ET)}_3(\text{ClO}_4)_2$ under hydrostatic pressure also supports this conjecture.³⁹ The resistivity at ambient pressure exhibits a steep but continuous increase below about ~ 170 K.⁴⁰ This phenomenon is due to the development of the CO state.¹⁴ A steep increase in the temperature dependence disappears at around 9 kbar. Furthermore, neither I-SC nor metal-SC transitions were observed up to 15 kbar and down to ~ 1.5 K.³⁹ This observation indicates the absence of the SC transition or a very small area of the SC phase in the pressure-temperature phase diagram. As described above, the distribution of the site charges is uniquely

determined, $[s\bullet L\bullet s\circ s]$, for $\beta''\text{-(ET)}_3(\text{ClO}_4)_2$ at ambient pressure. Even when hydrostatic pressure is applied, the nearly degenerated state hardly occurs since the other distributions, $[s\bullet L\circ s\bullet s]$ and $[s\circ L\bullet s\bullet s]$, contain a charge-rich pair with a short distance. By increasing the pressure further, the long and short distances approach one another. When they are equal, the molecular charges become homogeneous because three distributions are completely degenerated. Hence, the site charges take either an ordered or a homogeneous state at low temperatures. Therefore, the abrupt change from insulating to metal phase and the absence of the SC transition are ascribed to the absence of the nearly localized state.

Throughout our analysis of the intermolecular distances and vibrational spectra, we have shown that the electrical resistivities among 4:2, 2:1, 3:2, and 6:4 salts are correlated with the time-averaged site charges ($\Delta\rho$). The universal phase diagram for the 4:2 salts, shown in Fig. 6, is also applicable to the 6:4 salts $[\beta''\text{-(ET)}_3\text{Cl}_2\cdot 2\text{H}_2\text{O}]$. The pressure-temperature phase diagram for $\beta''\text{-(ET)}_3\text{Cl}_2\cdot 2\text{H}_2\text{O}$ has been reported in Ref. 27, and if the CDW phase in Ref. 27 is replaced with the CO phase, our phase diagram is almost identical. The phase diagram shown in Fig. 6 is applicable to the materials where the distribution of the site charges takes a nearly localized state. On the other hand, group III materials and $\beta''\text{-(ET)}_3(\text{ClO}_4)_2$ are characterized by the other phase diagram, wherein the nearly localized state and the SC phase are absent or extremely small. On the basis of our universal phase diagram, we propose some conditions for observing the nearly localized state in organic superconductors: (a) the number of molecules in the repeat unit, N , is large and (b) the number of long intermolecular distances in a repeat unit is large, up to $N-1$.

We will give comments on the other β'' -type superconductors $[\beta''\text{-(ET)}_2\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3]$, where we have not measured vibrational spectra.⁴¹ Inhomogeneous site charges are also observed at ambient pressure.⁴¹ In this material, the number of independent ET molecules along the S direction is $N=2$.⁴¹ The organic layer contains two kinds of molecular columns. Then, the number of the repeat units in the unit cell is likewise 4.⁴¹ In both columns, the long distance and short distance alternately extend along the stacking direction, that is, $[sL]$ along the column A and $[s'L']$ along column B.⁴¹ As far as $N=2$ along the S direction, the molecular charges along the S direction are expected to be homogeneous. Since L and L' are comparable to the distance along the C direction, the intersite Coulomb interaction along the C direction together with that along the S direction can contribute to the distribution of the site charges. Therefore, we can expect that the time-averaged distribution takes a stripe structure along the S direction. Indeed, the stripe pattern is observed for $\beta''\text{-(ET)}_2\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3$, which is obtained from the bond-length analysis.⁴¹ Interestingly, $\Delta\rho$ is estimated to be 0.06.⁴¹ This value is smaller than those of I-SC materials. The small value of $\Delta\rho$ is in agreement with the more delocalized nature due to $N=2$ along the S direction and is consistent with our phase diagram because the temperature dependence of the electrical resistivity reveals a metal-SC rather than an I-SC transition.⁴¹ Therefore, the nearly localized picture is applied to the inhomogeneous site charges of $\beta''\text{-(ET)}_2\text{SF}_5\text{CH}_2\text{CF}_2\text{SO}_3$.

As described in the Introduction, the magnetic properties of the CO state for the $\beta''\text{-(ET)}_3\text{Cl}_2\cdot 2\text{H}_2\text{O}$ should be attributed not to the antiferromagnetic (AF) state but to a nonmagnetic state.⁴² Since the charge-rich stripe is not formed along the stacking direction in the present compounds, the charge-rich pair is formed along the C or D direction. Since the magnitude of the overlap integral along the C or D direction is large, it is reasonable to consider that the spin singlet is induced by the charge-rich pair. The absence of an AF fluctuation and the observation of the inhomogeneous site charges indicate the charge-fluctuation-mediated superconductivity proposed by Merino and McKenzie.⁴ Indeed, our observation indicates a pairing mechanism that dissolves the instability due to the nearly localized state. It is interesting to examine whether inhomogeneous site charges neighboring the SC phase are a general phenomenon for organic superconductors, where the dimer picture does not apply and explode the boundary between the dimer picture and nearly localized picture due to the CO state. The authors will now observe the molecular charges of some molecular conductors, whose organic layer has an intermediate nature between β'' -type and κ -type structures.

To summarize, we have studied the vibrational spectra around the phase boundary among the metal, superconducting, and insulating phases of the β'' -type ET salts, whose ratio of sites to holes are 2:1, 4:2, and 6:4. These phases are correlated with the time-averaged site charges ($\Delta\rho$). The inhomogeneous site charges are robust at temperatures just above the insulator-superconductor transition. The time-averaged site charges are ascribed to the number of permutations of the site charges and energy levels of the possible site-charge distributions. The number of permutations and energy levels mostly depend on the distribution of the intermolecular distance along the S direction. Our observation suggests that the energy levels of the site-charge distributions for a superconductor are neither nondegenerated nor degenerated, but nearly degenerated.

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- ¹K. Inagaki, I. Terasaki, H. Mori, and T. Mori, *J. Phys. Soc. Jpn.* **73**, 3364 (2004).
- ²M. Chollet, L. Guerin, N. Uchida, S. Fukaya, H. Shimoda, T. Ishikawa, K. Matsuda, T. Hasegawa, A. Ota, H. Yamochi, G. Saito, R. Tazaki, S. Adachi, and S. Koshihara, *Science* **7**, 86 (2005).
- ³N. Tajima, J.-I. Fujisawa, N. Naka, T. Ishihara, R. Kato, Y. Nishio, and K. Kajita, *J. Phys. Soc. Jpn.* **74**, 511 (2005).
- ⁴J. Merino and R. H. McKenzie, *Phys. Rev. Lett.* **87**, 237002 (2001).
- ⁵K. Kanoda, *Hyperfine Interact.* **104**, 235 (1997).
- ⁶M. Muksimuk, K. Yakushi, H. Taniguchi, K. Kanoda, and A. Kawamoto, *J. Phys. Soc. Jpn.* **70**, 3728 (2001).
- ⁷Although the charge-sensitive mode is observed at the frequency of the formal charge, the linewidth of the charge-sensitive mode is broad. This observation suggests inhomogeneous molecular charges.
- ⁸The structural properties of the θ -type ET slats are summarized in T. Mori, *Bull. Chem. Soc. Jpn.* **72**, 179 (1999).
- ⁹The structural properties of the β'' -type ET slats are summarized in T. Mori, *Bull. Chem. Soc. Jpn.* **71**, 2509 (1998).
- ¹⁰K. Miyagawa, A. Kawamoto, and K. Kanoda, *Phys. Rev. B* **62**, R7679 (2000).
- ¹¹K. Yamamoto, K. Yakushi, K. Miyagawa, K. Kanoda, and A. Kawamoto, *Phys. Rev. B* **65**, 085110 (2002).
- ¹²M. Watanabe, Y. Noda, Y. Nogami, and H. Mori, *J. Phys. Soc. Jpn.* **73**, 116 (2004).
- ¹³T. Yamamoto, M. Uruichi, K. Yakushi, J. I. Yamaura, and H. Tajima, *Phys. Rev. B* **70**, 125102 (2004).
- ¹⁴T. Yamamoto, M. Uruichi, K. Yakushi, and A. Kawamoto, *Phys. Rev. B* **73**, 125116 (2006).
- ¹⁵A. F. Bangura, A. I. Coldea, J. Singleton, A. Ardavan, A. Akutsu-Sato, H. Akutsu, S. S. Turner, P. Day, T. Yamamoto, and K. Yakushi, *Phys. Rev. B* **72**, 014543 (2005).
- ¹⁶B. Salameh, A. Nothardt, E. Baltes, W. Schmidt, D. Schweitzer, J. Stempfer, B. Hinrichsen, M. Jansen, and D. K. Maude, *Phys. Rev. B* **75**, 054509 (2007).
- ¹⁷T. Mori and H. Inokuchi, *Solid State Commun.* **64**, 335 (1987).
- ¹⁸H. Mori, I. Hirabayashi, S. Tanaka, T. Mori, Y. Maruyama, and H. Inokuchi, *Solid State Commun.* **80**, 411 (1991).
- ¹⁹T. Mori, Y. Maruyama, H. Inokuchi, H. Mori, I. Hirabayashi, and S. Tanaka, *Solid State Commun.* **82**, 177 (1992).
- ²⁰U. Geiser, J. A. Schlueter, H. H. Wang, A. N. Kini, J. M. Williams, P. P. She, H. I. Zakowicz, M. L. VanZile, J. D. Dudek, P. G. Nixon, R. W. Winter, G. L. Gard, J. Ren, and M.-H. Wangbo, *J. Am. Chem. Soc.* **118**, 9996 (1996).
- ²¹H. Akutsu, A. A-Sato, S. S. Turner, D. L. Pevelen, P. Day, V. Laukhin, A. K. Klehe, J. Singleton, D. A. Tocher, M. R. Probert, and J. A. Howard, *J. Am. Chem. Soc.* **124**, 12430 (2002).
- ²²T. Yamamoto, M. Uruichi, K. Yamamoto, K. Yakushi, A. Kawamoto, and H. Taniguchi, *J. Phys. Chem. B* **109**, 15226 (2005).
- ²³M. E. Kozlov, K. I. Pokhodnia, and A. A. Yurchenko, *Spectrochim. Acta, Part A* **45**, 437 (1989).
- ²⁴A. A-Sato, A. Kobayashi, T. Mori, H. Akutsu, J. Yamada, S. Nakatsuji, S. S. Turner, P. Day, D. A. Tocher, M. E. Light, and M. B. Hursthouse, *Synth. Met.* **152**, 373 (2005).
- ²⁵A. I. Coldea, A. F. Bangura, J. Singleton, A. Ardavan, A. Akutsu-Sato, H. Akutsu, S. S. Turner, and P. Day, *Phys. Rev. B* **69**, 085112 (2004).
- ²⁶H. M. Yamamoto, J. Yamaura, and R. Kato, *J. Mater. Chem.* **8**, 15 (1998).
- ²⁷W. Lubczynski, S. V. Demishev, J. Singleton, J. M. Caulfield, L. du Croo de Jongh, C. J. Kepert, S. J. Blundell, W. Hayes, M. Kurmoo, and P. Day, *J. Phys.: Condens. Matter* **8**, 6005 (1996).
- ²⁸K. Suzuki, K. Yamamoto, and K. Yakushi, *Phys. Rev. B* **69**, 085114 (2004).
- ²⁹T. Yamamoto, K. Yakushi, Y. Shimizu, and G. Saito, *J. Phys. Soc. Jpn.* **73**, 2326 (2004).
- ³⁰T. Yamamoto, J. Eda, A. Nakao, R. Kato, and K. Yakushi, *Phys. Rev. B* **75**, 205132 (2007).
- ³¹M. Uruichi, K. Yakushi, H. M. Yamamoto, and R. Kato, *J. Phys. Soc. Jpn.* **75**, 074720 (2006).
- ³²H. M. Yamamoto, M. Hagiwara, and R. Kato, *Synth. Met.* **133-134**, 449 (2003).
- ³³T. Mori, F. Sakai, G. Saito, and H. Inokuchi, *Chem. Lett.* 1986, 1037.
- ³⁴Transfer integrals were calculated by E. Canadell.
- ³⁵J. Gaultier, S. H. Bracchetti, P. Guionneau, C. J. Kepert, D. Chasseau, L. Ducasse, Y. Barrans, M. Kurmoo, and P. Day, *J. Solid State Chem.* **145**, 496 (1999).
- ³⁶R. Wojciechowski, K. Yamamoto, K. Yakushi, M. Inokuchi, and A. Kawamoto, *Phys. Rev. B* **67**, 224105 (2003).
- ³⁷K. Suzuki, K. Yamamoto, K. Yakushi, and A. Kawamoto, *J. Phys. Soc. Jpn.* **74**, 2631 (2005).
- ³⁸A. Miyazaki, T. Enoki, H. Uekusa, Y. Ohashi, and G. Saito, *Phys. Rev. B* **55**, 6847 (1997).
- ³⁹J. Eda, N. Tajima, and M. Tamura (private communication).
- ⁴⁰H. Kobayashi, R. Kato, T. Mori, A. Kobayashi, Y. Sasaki, G. Saito, T. Enoki, and H. Inokuchi, *Chem. Lett.* 1984, 179.
- ⁴¹J. A. Schlueter, B. H. Ward, U. Geiser, H. H. Wang, A. M. Kini, J. Parakka, E. Morales, H.-J. Koo, M.-H. Whangbo, R. H. Winter, J. Mohtasham, and G. L. Gard, *J. Mater. Chem.* **11**, 2008 (2001).
- ⁴²S. D. Obertelli, I. R. Marsden, R. H. Friend, M. Kurmoo, M. J. Rosseinsky, P. Day, F. L. Pratt, and W. Hayes, *The Physics and Chemistry of Organic Superconductors*, edited by G. Saito and S. Kagoshima (Springer-Verlag, Berlin, 1990), p. 181.