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Interplay of charge-density waves and superconductivity in the organic conductor β''-(BEDT-TTF)$_2$AuBr$_2$

Ryusuke Kondo,[*] Momoka Higa, and Seiichi Kagoshima
Department of Basic Science, University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan

Noriaki Hanasaki and Yoshio Nogami
Department of Physics, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan

Hiroyuki Nishikawa
Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan
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We studied the low-temperature electrical properties of the two-dimensional organic conductor β''-(BEDT-TTF)$_2$AuBr$_2$, whose electronic structure is similar to that of the pressure-induced superconductor β''-(DODHT)$_2$PF$_6$ having a charge-ordered transition at 255 K at ambient pressure. We found that the ground state of β''-(BEDT-TTF)$_2$AuBr$_2$ at ambient pressure has a charge-density-wave phase below 6.5 K accompanied by x-ray superlattice spots. We also discovered superconductivity in the vicinity of the charge-density-wave phase by applying uniaxial strain. Based on the obtained results, we propose a unified electronic phase diagram that suggests the relationships among the charge-ordered insulating state, the superconducting phase, and the charge-density-wave phase in β''-type organic conductors. The phase diagram shows that the superconducting phase is located near the charge-density-wave phase, which suggests that spin fluctuations play a minor role in the mechanism of the superconductivity and sheds light on the possibility of charge-fluctuation-mediated superconductivity in this type of organic conductor.

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I. INTRODUCTION

Since the discovery of high-T_c superconducting cuprates, superconductivity existing in the vicinity of insulating phases originating from strong electron-electron interactions has attracted avid interest in the field of condensed-matter physics.[1–4] This is because the exotic behavior originating from the electronic correlations and the low-dimensional electronic structures implies the possibility of a new mechanism for the superconductivity, which differs from the conventional one explained by the BCS theory.[5] One recent problem is the mechanism of superconductivity locating near a charge-ordered insulating state resulting from nearest-neighbor Coulomb repulsion. To study this, both inorganic and organic systems having charge-ordered insulating states and superconductivity are under intensive investigation.[6]

Layered organic conductors are an ideal system to study the existing problem because they have the following characteristics: (1) clean low-dimensional electronic structures of simple geometry in spite of the anisotropic and complicated structures of constituent molecules and (2) strong electronic correlations originating from the narrow bandwidth. Depending on the molecular arrangements in the layers, they are roughly classified into two groups: the half-filled band group and the 3/4-filled one.[7]

Many charge-ordered insulating states have been reported in organic conductors that have α-, θ-, and β''-type molecular arrangements and belong to the 3/4-filled band group. Some of the organic conductors show superconductivities when the charge-ordered insulating states are suppressed by hydrostatic pressure. As regards the mechanism of the superconductivity, McKenzie and Merino pointed out the possibility that both antiferromagnetism and charge fluctuations could lead to superconductivity in the vicinity of a charge-ordered insulating state and proposed that several organic superconductors are promising candidates for charge-fluctuation-mediated superconductivity.[8,9]

After careful consideration of their proposal, we focused on β''-type organic conductors that have only one crystallographically independent molecule, namely, two equivalent molecules, in a unit cell. We can easily confirm the existence of a charge-ordered state in this type of material by checking the crystallographic symmetry, as the charge-ordered transition from the normal metal is accompanied by the breaking of the crystallographic symmetry, such as the lowering of the space group or the breaking of the translational symmetry.

In some of the β''-type organic conductors proposed by Merino and McKenzie,[9] the molecules could have different valences from each other even in the normal metallic state due to the presence of multiple crystallographically independent sites in a unit cell. This presents a disadvantage in the study of the relationships among the charge-ordered insulating state, the normal metallic phase, and the superconducting phase because it is difficult to discriminate between charge disproportionation due to charge ordering and that due to the inequivalence of molecular sites.

One additional advantage of the β''-type organic conductors that we have focused on is the quasi-one-dimensional (1D) nature of their electronic structures. The tight-binding band-structure calculation suggests that such β''-type organic conductors have a pair of large 1D Fermi surfaces that possibly cause their nesting, leading to a charge-density wave (CDW) or a spin-density wave (SDW), in the normal metallic phase where Fermi surfaces are defined. The character of

TABLE I. Summary of electronic and structural properties of β''-type organic conductors having two equivalent molecules in a unit cell. COI: charge-ordered insulating state. SC: superconductivity. NM: normal metal.

		β''-(DODHT)$_2$PF$_6$		β''-(BEDT-TTF)$_2$AuBr$_2$	β''-(BEDT-TTF)$_2$CsCd(SCN)$_4$
	atm	7.5 kbar (Hydrostatic)	19 kbar (Hydrostatic)	atm	atm
Electronic property	COI at 255 K	COI at around 150 K	SC at 2.5 K	CDW at 6.5 K (SC under uniaxial strain) Present work	CDW at 32 K (NM under uniaxial strain)
DOS(E_F) (states/eV/molecule)	1.12	1.07	0.83	0.92	0.83
$\bar{V}$ (eV)	2.48	2.53	2.59	2.38	2.33
$\bar{t}/\bar{V}$ ([DOS(E_F)$\bar{V}$]$^{-1}$)	0.36	0.37	0.46(5)	0.45(7)	0.52

the density wave gives a clue to determine whether spin fluctuations or charge fluctuations are stronger in the vicinity of the superconducting phase. Some theoretical studies have proposed that a CDW exists near a charge-fluctuation-mediated superconducting phase while an SDW exists near a spin-fluctuation-mediated one.[10,11]

Another organic system, the α-type organic conductor, has been also studied intensively from this viewpoint; α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ (Ref. 12) has a superconducting phase, α-(BEDT-TTF)$_2$KHg(SCN)$_4$ (Ref. 13) shows a CDW phase, and α-(BEDT-TTF)$_2$I$_3$ exhibits a charge-ordered transition accompanied by the lowering of the space group,[14–16] where BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene. However, α-type materials cannot be free from the site-equivalence problem discussed above as they have three crystallographically independent molecules in a unit cell. The molecular valences are different among molecules on different sites as pointed out by a theoretical study even without taking into account Coulomb interactions between conduction electrons.[17]

In order to investigate the general relationships among a charge-ordered insulating state, a superconducting phase, and a density wave phase, we examined β''-type organic conductors in previous studies and clarified the following: β''-(DODHT)$_2$PF$_6$ [where DODHT denotes (1,4-dioxane-2,3-diyldithio)dihydrotetrathiafulvalene, abbreviated as DODHT salt] has a charge-ordered transition accompanied by the breaking of the translational symmetry along the a axis at ambient pressure at 255 K, and exhibits superconductivity at the critical temperature of approximately 2 K at pressures above 1.5 GPa.[18] The crystal structure analyses suggested that the electronic structure of DODHT salt under hydrostatic pressure for the superconductivity is similar to those of β''-(BEDT-TTF)$_2$AuBr$_2$ (abbreviated as AuBr$_2$ salt) and β''-(BEDT-TTF)$_2$CsCd(SCN)$_4$ (abbreviated as CsCd salt).[19] We have found that the ground state of CsCd salt has an incommensurate CDW below 32 K.[20] These results suggest that the CDW caused by nesting of the 1D Fermi surface is realized in the normal metallic phase as a result of suppression of the charge-ordered insulating state by applying hydrostatic pressure to such β''-type organic conductors, although the relationships between the superconducting phase and the CDW phase are unclear.

Our previous study of the structural properties of these organic conductors is summarized in Table I. We have estimated the average of the nearest-neighbor Coulomb interactions and transfer integrals, $\bar{V}$ and $\bar{t}$, as a charge-ordered insulating state arises when $\bar{V}$ overcomes $\bar{t}$.[21] $\bar{V}$ is estimated from the average of the Coulomb interactions between nearest-neighbor constituent molecules calculated by the point-charge approximation.[22] $\bar{t}$ is estimated as the reciprocal of the density of states at the Fermi level [abbreviated as DOS(E_F)], which was obtained by the tight-binding band-structure calculation with transfer integrals based on the overlap integrals between constituent molecules.[23]

We note two important points from Table I: (I) a large $\bar{t}/\bar{V}$ suppresses the charge-ordered insulating state and stabilizes the superconducting phase and the CDW phase in the low-temperature region, consistent with theoretical studies.[8–11] (II) DODHT salt under the hydrostatic pressure of 19 kbar and exhibiting the superconductivity at around 2.5 K is located at almost the same position as AuBr$_2$ salt at ambient pressure on the $\bar{t}/\bar{V}$ axis. These results suggest the possibility of proposing a unified electronic phase diagram constructed from a charge-ordered insulating state, a superconducting phase, and a CDW phase for β''-type organic conductors.

Previous studies of AuBr$_2$ salt reported appreciable hysteretic behavior of the resistivity and a large decrease in the spin susceptibility at around 20 K.[24,25] The magnetoresistance measurements of AuBr$_2$ salt suggested ascribing the anomaly to an SDW transition by nesting of the 1D Fermi surfaces, although no confirmation has been made by x-ray scattering measurements or NMR studies.[26,27] No superconductivity has been observed down to the millikelvin order. The small quantity of β''-type AuBr$_2$ salt produced in the process of the crystal growth has prevented further studies.

The objectives of the present study were (1) to conduct electrical and x-ray scattering measurements of AuBr$_2$ salt to clarify whether the ground state of AuBr$_2$ salt has a CDW phase or not, and (2) to propose a unified electronic phase diagram showing the temperature and $\bar{t}/\bar{V}$ relationship for the possible phases of a charge-ordered insulating state, a superconducting phase, and a CDW phase in this type of β''-type organic conductor. Specifically, we paid attention to the nature of the CDW phase and the problem of whether the

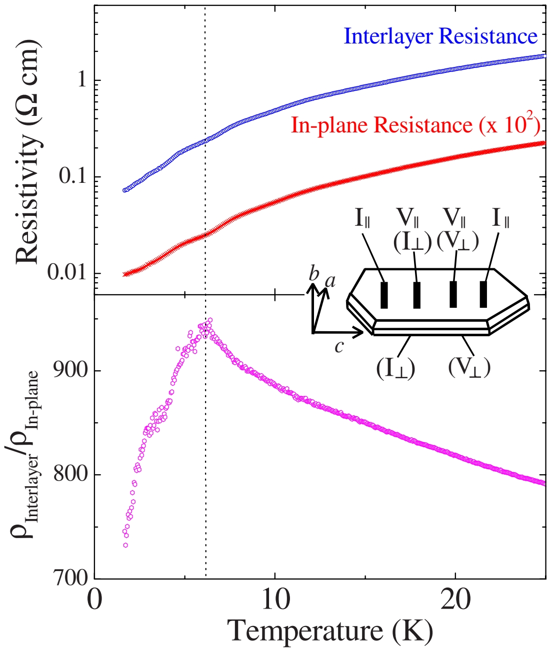

FIG. 1. (Color online) (Upper figure) Temperature dependence of interlayer and in-plane resistances of β''-(BEDT-TTF)$_2$AuBr$_2$. Inset shows the arrangement of electrical terminals for the resistance measurements. ∥ and ⊥ denote directions parallel and perpendicular to the 2D plane. (Lower figure) Temperature dependence of the ratio of interlayer resistance to in-plane resistance.

superconducting phase contacts the CDW phase or not.

We found that the ground state of AuBr$_2$ salt at ambient pressure also has a CDW phase below 6.5 K. We also discovered superconductivity under uniaxial strain in the vicinity of the CDW phase. We considered that the observed superconductivity in AuBr$_2$ salt is similar to that in DODHT salt under hydrostatic pressure, as they have almost the same value of $\bar{t}/\bar{V}$. Based on the experimental results, we propose a unified electronic phase diagram that is characteristic of the superconducting phase located near the CDW phase, for this class of material. Our findings suggest the minor role of spin fluctuations in the mechanism of the superconductivity. They also shed light on the possibility of charge-fluctuation-mediated superconductivity in β''-type organic conductors.

II. EXPERIMENTAL PROCEDURES

Single crystals were prepared by electrooxidation of BEDT-TTF in the presence of tetra-*n*-butylammonium dibromoaurate (n-Bu$_4$NAuBr$_2$) as the electrolyte. The solvent was 1,1,2-trichloroethane. β''-type crystals were selected visually and separated manually.

Interlayer and in-plane dc resistance measurements were performed with the conventional four-probe method in the temperature range of 0.6–300 K employing an ^{3}He refrigerator. The electrical terminals were formed on the crystals with typical dimensions of approximately $(0.4-0.3\times0.15-0.05\times0.7-0.5)$ mm^3 using gold wires (25 μm) and carbon paste. The configuration of the electrical leads is shown in the inset of Fig. 1. Uniaxial strain was applied by means of the epoxy method,[28] and its magnitude was estimated from the pressure applied to the cross section of an epoxy-sample composite. Magnetic fields were applied with a solenoid-type magnet.

X-ray scattering measurements were performed with a low-temperature vacuum camera (LTVAC) using the synchrotron radiation facility SPring-8 BL02B1 and applying the oscillation photograph method. The used wavelength was 1.08755 Å. The sample was set in the vacuum on the cold head of a refrigerator. The angle for the sample oscillation was 3°. Each x-ray photograph was exposed for 180 s.

III. EXPERIMENTAL RESULTS

A. CDW ground state at ambient pressure

First, we measured the transition temperature of the possible density wave transition to determine the ground state of AuBr$_2$ salt. This was accomplished by measuring the anisotropic resistance of single crystals between interlayer and in-plane directions. The upper figure in Fig. 1 shows the temperature dependence of the in-plane and interlayer resistances of AuBr$_2$ salt. Both lines basically show similar metallic behavior having multiple small anomalies, dips and peaks, at almost the same temperatures. We could not find any appreciable changes at around 20 K where a rapid decrease in the magnetic susceptibility was found in the preceding study.[21]

The in-plane resistance measured by such a method was much less reliable: some components of the interlayer resistance got mixed in the measured in-plane resistance in the measurements of highly anisotropic materials.[29] Adopting Buravov's calibration method,[30,31] we obtained similar curves to those in Fig. 1, although the absolute value of the in-plane resistance was smaller than those shown in Fig. 1 by a factor of approximately 1/500. They had multiple similar anomalies at almost the same temperatures and also the similar resistance ratio, $\rho_{in,25\ \mathrm{K}}/\rho_{in,1.5\ \mathrm{K}}(\simeq 23)$.

The lower figure shows the temperature dependence of the ratio of the interlayer resistance to the in-plane resistance appearing in the upper figure. We can see a clear change at approximately 6.5 K although there is no anomaly at approximately 20 K where the rapid decrease in the magnetic susceptibility was reported. We also obtained a similar result employing Buravov's calibration method in spite of the difference in the absolute value. We observed such a peak near this temperature in another sample although it was slightly broadened due to spurious and inhomogeneous pressure caused by the grease for gluing the sample onto the sample stage.

We infer that the peak in the resistance ratio is a result of a change in the electronic structure. This is because density wave transitions are generally accompanied by changes in the electronic structures. We tried to find changes in the electronic structure of AuBr$_2$ salt using a method that employs Kohler's rule as reported in Ref. 20 but were unsuccessful because the curves measured under different magnetic fields perpendicular to the two-dimensional (2D) plane gradually deviated from a universal curve as the temperature decreased. This problem remains to be solved in future studies.

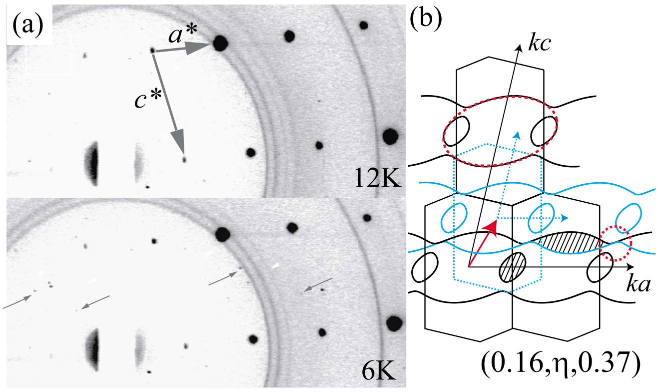

FIG. 2. (Color online) (a) Oscillation photographs of β''-(BEDT-TTF)$_2$AuBr$_2$ at 12 K (upper) and 6 K (lower). Arrows indicate superlattice spots. (b) Possible nesting vector determined from the x-ray study (a red arrow). Vanishing part of Fermi surfaces is shown by a red dashed circle. Shaded regions indicate Fermi pockets resulting from the transition. Original elliptic Fermi surface is marked by a red broken line.

We performed x-ray scattering studies at two temperatures across 6.5 K to determine whether the anomaly in the resistance ratio at 6.5 K could be ascribed to a CDW or an SDW. We found several superlattice spots below 6.5 K, suggesting that the ground state of AuBr$_2$ salt has a CDW phase. Figure 2(a) shows x-ray photographs of AuBr$_2$ salt at 12 and 6 K (upper and lower figures, respectively).[32] The incident x-ray beam was almost perpendicular to the 2D plane. One can see sharp spots indicated by gray arrows in the lower figures, which are absent at 12 K, suggesting that the spots are superlattice spots. The wave number is approximately $(0.14,\eta,0.38)$. Here, the component parallel to the incident beam gives the uncertain result, η. The average intensity of the spots is approximately 10^3-10^4 times lower than that of genuine Bragg spots.

We found that the observed wave number of the superlattice spots is consistent with the CDW caused by nesting of planar Fermi surfaces, although it is rather different from that in CsCd salt, $(0.18,\eta,0.56)$. Figure 2(b) shows a possible nesting vector, $(0.16,\eta,0.37)$, near the observed one, and the resulting Fermi surface after the nesting. The Fermi surface was obtained with transfer integrals reported in Ref. 27, which were suggested to be suitable for describing the Fermi surfaces of AuBr$_2$ salt.[26] The original elliptic Fermi surface is drawn by a red broken line. The red dashed circle in Fig. 2(b) shows part of the Fermi surface vanishing below the transition temperature, indicating that a very small part of the 1D Fermi surface vanishes in the present CDW transition. As a result, two shaded Fermi pockets remain: one is from the original Fermi pocket and the other, whose area is almost twice as large as the former, is composed of the remaining 1D Fermi surfaces.

We consider that the CDW phase of β''-type organic conductors is unstable because it is accompanied by a vanishing small part of the 1D Fermi surfaces. The large difference in the nesting vector between AuBr$_2$ salt and CsCd salt is ascribed to the difference in the type of nesting: two sheets of large warped 1D Fermi surfaces nest inside or outside. Only a small part of the 1D Fermi surfaces also vanishes in the transition of CsCd salt. This is because the Fermi surfaces of β''-type organic conductors keep their original elliptic shape. These results suggest that the CDW phase of β''-type organic conductors is rather unstable from the viewpoint of a gain of free energy in the electronic system compared to other CDW transitions accompanied by the vanishing of almost the entire 1D Fermi surfaces, such as α-(BEDT-TTF)$_2$KHg(SCN)$_4$ or tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).[13,33]

A preceding study of Shubnikov-de Haas oscillations of AuBr$_2$ salt suggested the existence of three kinds of Fermi pockets and their configurations in the unit cell: one is from an original Fermi pocket and the other two are composed of remaining 1D Fermi surfaces. The areas are 180, 40, and 220 T, respectively.[26] We can roughly reproduce these results if a small k_c^* component is added to our nesting vector to produce the smallest Fermi pocket observed in the magnetotransport studies. To check their areas quantitatively, one needs the three-dimensional (3D) electronic structure of AuBr$_2$ salt at low temperature. This will be studied in the future.

B. Superconductivity under uniaxial strain

We discovered superconductivity in AuBr$_2$ salt when we applied uniaxial strain along in-plane *a* and *c* axes to examine the electronic phases surrounding the CDW phase. Figures 3(a) and 3(b) show the results under *c*-axial strain and *a*-axial strain, respectively. As a guide, the inset of Fig. 3(c) shows the molecular arrangement and the Fermi surfaces at ambient pressure and room temperature. The fact that we could not observe superconductivity under hydrostatic pressures down to 0.6 K suggests that anisotropic compression is necessary to induce superconductivity.

The upper figure of Fig. 3(a) shows the temperature dependence of the interlayer resistance under *c*-axial strain of up to 20 kbar below 12.5 K. The reason for measuring the interlayer resistance is that the in-plane resistance is small in the low-temperature region and it is difficult to discover a decrease in resistivity originating from the superconductivity. One can clearly find decreases in the resistance below 1.1 K under *c*-axial strain in the range of 10–15 kbar. We conclude that the resistance decrease originated from the superconductivity, as the resistance was recovered by magnetic field application and non-Ohmic resistances could be clearly observed, as shown in the inset.

The upper figure of Fig. 3(b) shows the temperature dependence of the interlayer resistance under *a*-axial strain of up to 10 kbar below 12.5 K. With an increase in *a*-axial strain, the resistance first increases and then decreases. The inset shows the temperature dependence of non-Ohmic resistivity under *a*-axial strain of 1.5 kbar and a magnetic field of 1 T applied parallel to the *a* axis. The reason for applying the magnetic field is that the resistivity itself in the absence of a magnetic field is rather small and it is difficult to observe a decrease in resistivity originating from the superconductivity. We conclude that the decrease in the resistivity also originated from the superconductivity as the decrease was suppressed by the magnetic field of 2 T [inset of the lower panel

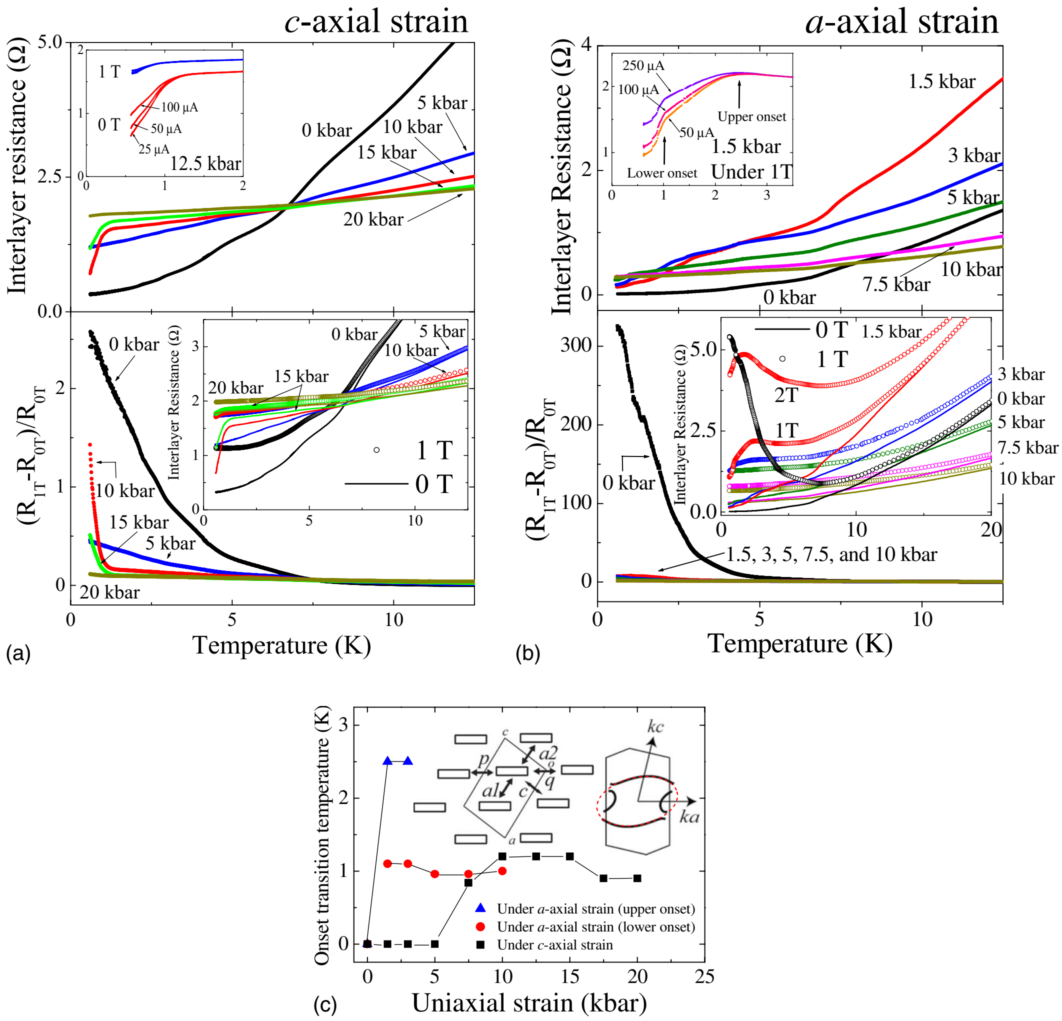

FIG. 3. (Color online) (a) (Upper figure) Temperature dependence of interlayer resistance of β''-(BEDT-TTF)$_2$AuBr$_2$ under c-axial strain of 0, 5, 10, 15, or 20 kbar. Inset shows temperature dependence of the interlayer resistance under c-axial strain of 12.5 kbar and magnetic fields of 0 and 1 T. (Lower figure) Temperature dependence of magnetoresistance under a magnetic field of 1 T. Inset shows temperature dependence of the interlayer resistance under 0 T (lines) and 1 T (empty circles). (b) (Upper figure) Temperature dependence of interlayer resistance of β''-(BEDT-TTF)$_2$AuBr$_2$ under a-axial strain of 0, 1.5, 3, 5, 7.5, or 10 kbar. Inset shows temperature dependence of the interlayer resistance under a-axial strain of 1.5 kbar and magnetic field of 1 T. (Lower figure) Temperature dependence of magnetoresistance under a magnetic field of 1 T. Inset shows temperature dependence of the interlayer resistance under 0 T (lines) and 1 T (empty circles). (c) Uniaxial strain dependence of superconducting transition temperature (onset). Insets show the molecular arrangement (left) and calculated Fermi surfaces (right) of β''-(BEDT-TTF)$_2$AuBr$_2$. The original Fermi surface is marked by a red broken line.

of Fig. 3(b)] and non-Ohmic resistances could be clearly observed under 1 T. The transition has two steps at around 2.5 and 1 K, as shown in the inset of Fig. 3(b). With an increase in a-axial strain above 1.5 kbar, the higher-temperature step was gradually suppressed up to 5 kbar while the lower-temperature step around 1 K remained observable up to 10 kbar. The reason for the two-step superconducting transition remains an open question.

We examined the electronic state that exhibits the superconductivity. The large magnetoresistance that was observed below the determined CDW transition temperature at ambient pressure was found to be almost suppressed when the superconductivity emerged under both a- and c-axial strains. This suggests that the most probable scenario is that the superconductivity emerges in a normal metal phase as a result of the suppression of the CDW phase by applying uniaxial strain. We conjecture that the application of both a- and c-axial strains can suppress the CDW phase because of the unstable nature of the CDW phase in β''-type organic conductors, as discussed above.

The lower figures of Figs. 3(a) and 3(b) show the temperature dependence of the magnetoresistance, $(R_{1T} - R_{0T})/R_{0T}$, under c- and a-axial strains, respectively. The magnetic fields were applied parallel to the direction of the uniaxial strain, i.e., the c axis in Fig. 3(a) and the a axis in Fig. 3(b). The insets of the lower figures of Figs. 3(a) and 3(b) show the original data, the temperature dependence of the resistance under 1 T (empty circle) and 0 T (thin line). In the inset of the lower figure of Fig. 3(b), the resistance curve under 1.5 kbar and 2 T is added, as mentioned above.

In the lower figure of Fig. 3(a), at 0 kbar where the CDW is present, a positive magnetoresistance appears below 7 K, namely, near the CDW transition temperature determined in this work. As the magnetic field is applied to this class of layered material along the in-plane direction, no large magnetoresistance should be observed in a typical normal metal, suggesting that the positive magnetoresistance comes from small pockets resulting from the CDW phase. Above 10 kbar, the positive magnetoresistances are almost suppressed down to the onset of the superconducting transition. In the lower figure of Fig. 3(b), at 0 kbar where the CDW is present, a rather large positive magnetoresistance is also observed below the CDW transition temperature, as is the case of the *c*-axial strain. The difference in the size of the positive magnetoresistances between the applied magnetic fields parallel to the *c* and *a* axes is considered to be due to the angular-dependent magnetoresistance effect.[34] Above 1.5 kbar where the superconductivity is observed, remarkable suppression of the magnetoresistance is noted. Under both *c*- and *a*-axial strains, the superconductivities emerge after the suppression of the magnetoresistance. This suggests the most probable scenario that the superconductivity emerges in the normal metal after completely suppressing the CDW, although it is possible that the superconductivity emerges in the remaining Fermi surface of another CDW phase having a different nesting vector.

Figure 3(c) shows the uniaxial strain dependence of the superconducting transition temperature. The maximum transition temperature under *a*-axial strain is higher than that under *c*-axial strain. The reason can be ascribed to the direction dependence of the uniaxial strain to decrease DOS(E_F), which is an important factor affecting the transition temperature.

We performed preliminary crystal structure analyses under the hydrostatic pressure of 5 kbar, the *c*-axial strain of 5 kbar, and the *a*-axial strain of 3 kbar, and found that all overlap integrals between constituent molecules increased evenly under the hydrostatic pressure while those almost parallel to the direction of uniaxial strain mainly increased under the uniaxial strain. These changes in the overlap integrals under uniaxial strain can account for the uniaxial strain direction dependence of the superconducting transition temperature with the change in DOS(E_F). The application of *c*-axial strain mainly increases the bandwidth of 1D Fermi surfaces, almost normal to the *c* axis and occupying most of the original elliptic Fermi surface (red broken line in the right inset), leading to a large decrease in DOS(E_F), while the application of *a*-axial strain mainly increases the bandwidth of the small 2D pocket occupying a small part of the original Fermi surface, leading to a small decrease in DOS(E_F). The obtained DOS(E_F) values were 0.843 under the *c*-axial strain and 0.882 under the *a*-axial strain, qualitatively supporting the above examination.

The rapid suppression of the onset of superconductivity under large *a*-axial strain should be due to possible damage to the sample caused by the extremely large uniaxial strain along the incompressible crystal axis, since we could not perform the crystal structure analyses under uniaxial strain that exceeded the above values due to the rapid deterioration of Bragg spots, and Bragg spots under *a*-axial strain deteriorated at a lower pressure than those under *c*-axial strain. The variation in the lattice parameters also suggests that the *a* axis is less compressible than the *c* axis, and the sample under uniaxial strain is compressed not only parallel to the external force but also perpendicular to it.[35] The difference in Poisson's effect between the sample and epoxy as the pressure medium must cause such an incomplete uniaxial strain and failure in the crystal structure analyses under larger uniaxial strain.

IV. DISCUSSION

We discuss the relationships among the charge-ordered insulating state, the superconducting phase, and the CDW phase in β''-type organic conductors having two equivalent molecules in a unit cell. We present the experimental results as follows: the ground state of AuBr$_2$ salt has the CDW phase whose transition temperature is 6.5 K. The superconductivity emerges in the possible normal metal as a result of suppression of the CDW phase by applying in-plane uniaxial strain. We conclude that the CDW phase of AuBr$_2$ salt emerges when the Fermi surfaces have good nesting condition while the superconductivity of AuBr$_2$ salt emerges at low temperature in the normal metallic state as a result of the poor nesting condition under uniaxial strain.

In addition to our results, we use the experimental results of CsCd salt under uniaxial strain. CsCd salt is also a β''-type organic conductor whose electronic structure is similar to that of DODHT salt.[19] It exhibits a CDW transition accompanied by a humplike structure at 32 K in the graph of the temperature dependence of the resistivity.[20] Although we tried to unravel the superconducting behavior in CsCd salt by applying uniaxial strain, we observed only the disappearance of the humplike anomaly, indicating suppression of the CDW phase and stabilization of the normal metallic state. No superconductivity was observed down to 0.6 K.

Figure 4 shows our proposed electronic phase diagram for β''-type organic conductors having two equivalent molecules in a unit cell. We determined the positions of DODHT salt, AuBr$_2$ salt, and CsCd salt from the values of $\bar{t}/\bar{V}$ in Table I. We consider that the superconductivity of AuBr$_2$ salt, which emerges in the possible normal metal as a result of suppression of the CDW phase, is substantially the same as that of DODHT salt, because they have almost the same $\bar{t}/\bar{V}$ value in Table I.

The left half essentially corresponds to the pressure-temperature phase diagram of DODHT salt reported in Ref. 17. It should be noted that the key experimental parameter is hydrostatic pressure. From the $\bar{t}/\bar{V}$ values in Table I, we find that the superconductivity and the CDW are realized by an increase in $\bar{t}$ to overcome the increase in $\bar{V}$. One should also take into account $\bar{V}$ because a decrease in intermolecular distances under compression enhances not only the bandwidth but also $\bar{V}$.

The onset temperature line of the CDW phase is drawn on the basis of the experimental results for the transition temperatures, 6.5 K for AuBr$_2$ salt and 32 K for CsCd salt. We speculate that when Fermi surfaces have good nesting condition, a CDW transition occurs on this line while under poor nesting condition, the normal metallic state above the tem-

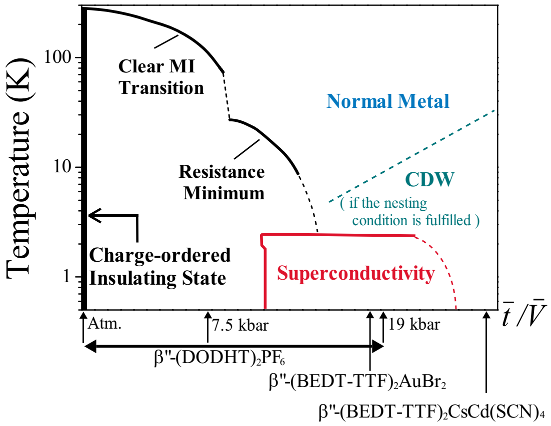

FIG. 4. (Color online) Proposed electronic phase diagram of β''-type organic conductors having two equivalent molecules in a unit cell. The relationships between CDW and superconductivity are as follows: the CDW emerges when Fermi surfaces have good nesting condition while the superconductivity emerges at low temperature in a normal metallic state as a result of poor nesting condition.

perature line of the CDW transition is preserved down to low temperature, leading to the emergence of superconductivity. The red dashed curve between the superconducting phase and the CDW phase shows our expectation that the decrease in DOS(E_F) generally suppresses the superconductivity.

Our phase diagram suggests close relationships among the three electronic phases: the charge-ordered insulating state, the superconducting phase, and the CDW phase. The suppression of the charge-ordered insulating state with increasing $\bar{t}/\bar{V}$ first induces the superconducting transition. This superconducting phase is partially covered with a nonmetallic insulating phase without clear transition behavior but with a slow increase in the resistance below the temperature line of the resistance minimum, which was realized in DODHT salt under the hydrostatic pressure of 13.7–15.1 kbar.

We conjecture that a large increase in $\bar{t}/\bar{V}$ stabilizes a normal metallic state having Fermi surfaces. If the Fermi surfaces are stable and suitable for nesting, a CDW transition should occur and superconductivity does not emerge, as observed in the present study of $AuBr_2$ salt at ambient pressure. If the Fermi surfaces are unsuitable for nesting, the CDW transition is suppressed and the normal metallic state is preserved down to low temperature, leading to the emergence of the superconductivity, as observed in the present study of $AuBr_2$ salt under uniaxial strain. The right part of the electronic phase diagram in Fig. 4, where the superconducting phase overlaps with the CDW phase, shows such circumstances.

The reason for the absence of a CDW transition in DODHT salt should be ascribed to the poor nesting condition of the Fermi surfaces. Actually, angular-dependent magnetoresistance measurements of the salt under 19 kbar showed a peak structure when the direction of the constant magnetic field was varied around perpendicular to the warped planar 1D Fermi surfaces, the so-called small closed orbit effect.[36,37] This suggests that the Fermi surface under 19 kbar has a 3D nature that is unfavorable for nesting.

An increase in $\bar{t}/\bar{V}$ should lead to the decrease in both DOS(E_F) and transition temperatures of the CDW and the superconductivity. This is consistent with the absence of the superconductivity in CsCd salt but contradicts the high transition temperature of the CDW phase in CsCd salt. The electron-phonon interaction of the two salts, $AuBr_2$ salt and CsCd salt, may be markedly different, as inferred from the difference in their nesting vectors. This point should be explored in the future.

The preliminary structural studies mentioned above also gave qualitatively consistent results of $\bar{t}/\bar{V}$. The corresponding $\bar{t}/\bar{V}\{=[\mathrm{DOS}(E_F)\bar{V}]^{-1}\}$ values are as follows: $0.531(0)\{=[0.792\times 2.38(3)]^{-1}\}$ under the hydrostatic pressure of 5 kbar, $0.497(7)\{=[0.843\times 2.38(2)]^{-1}\}$ under the c-axial strain of 5 kbar, and $0.480(0)\{=[0.882\times 2.38(2)]^{-1}\}$ under the a-axial strain of 3 kbar. We noticed that (I) $\bar{t}/\bar{V}$ under the hydrostatic pressure is larger than that of CsCd salt showing no superconductivity under the uniaxial strain, and (II) $\bar{t}/\bar{V}$ values under both uniaxial strains are smaller than that of CsCd salt. The results are qualitatively consistent with our experimental results from the viewpoint of $\bar{t}/\bar{V}$, the observation of the superconductivity under uniaxial strain, and no observation of superconductivity under hydrostatic pressure in $AuBr_2$ salt.

We suggest two important conclusions for this system: the emergence of the CDW, but not the SDW, in the normal metallic state as a result of suppression of the charge-ordered insulating state suggests a minor role played by the spin degree of freedom in the normal metallic phase adjacent to the charge-ordered insulating state. The emergence of the superconductivity from the normal metal that has the possibility to induce the CDW phase suggests that the spin degree of freedom plays a minor role in the mechanism of the superconductivity, i.e., superconductivity in such β''-type organic conductors is a promising candidate for charge-fluctuation-mediated superconductivity although one has to keep in mind the possibility of the conventional phonon mechanism.

We compared our phase diagram with those of other β''-type organic superconductors, β''-(BEDT-TTF)$_3$Cl$_2\cdot$2H$_2$O,[38,39] β''-(BEDT-TTF)SF$_5$CH$_2$CF$_2$SO$_3$,[40] and β''-(BEDT-TTF)$_4$[(H$_3$O)M(C$_2$O$_4$)$_3$]$\cdot$Y,[41] which are suggested to be the typical materials for superconductivity induced by charge fluctuations by Merino and McKenzie.[9] Although they all have insulating phases in the vicinity of the superconducting phases,[42–44] their insulating behavior is similar not to that in the clear metal-insulator transition region but to that in the resistance minimum one, the intermediate phase between the superconducting phase and the charge-ordered one, in our phase diagram. For example, the temperature-dependent resistivity of β''-(BEDT-TTF)$_3$Cl$_2\cdot$2H$_2$O presents a broad minimum centered at around 150 K and a gradual increase below 100 K in the low-pressure side near the superconducting phase in the pressure-temperature phase diagram, and even at ambient pressure. This is in sharp contrast to the temperature dependence of the resistivity of DODHT salt having a clear bend followed by a rapid increase at the metal-insulator transition at ambient pressure, and our phase diagram having a clear metal-insulator transition region.

The crystal structure analysis of β''-(BEDT-TTF)$_3$Cl$_2 \cdot$ 2H$_2$O at low temperature at ambient pressure demonstrated that the degree of charge disproportionation only increases without the breaking of the crystallographic symmetry when the metallic behavior changes into the insulating one with decreasing temperature.[45] This suggests that the metal-insulator transitionlike behavior is not a phase transition but a crossover. The difference in the resistance behavior at ambient pressure between DODHT salt and β''-(BEDT-TTF)$_3$Cl$_2 \cdot$2H$_2$O might be ascribed to the existence of crystallographic symmetry breaking. In the metal-insulator transitionlike behavior of β''-(BEDT-TTF)SF$_5$CH$_2$CF$_2$SO$_3$ and β''-(BEDT-TTF)$_4$[(H$_3$O)M(C$_2$O$_4$)$_3$]$\cdot$Y, not only their changes in the degree of charge disproportionation but also the presence or absence of crystallographic symmetry breaking should be investigated due to the existence of multiple crystallographically independent molecules in their unit cells.

The existence of a charge-ordered insulating state, a superconducting phase, and a CDW phase is also observed in the α-type organic conductor family. Dressel *et al.* discussed in detail the relationships among the charge-ordered insulating state, the superconducting phase, and the CDW phase;[46–48] the superconducting phase and the CDW phase contact each other and the CDW phase exists between the superconducting phase and the charge-ordered insulating state in their phase diagrams, although the electronic state between the CDW phase and the charge-ordered insulating state could not be experimentally proven due to the lack of materials existing between them from a structural viewpoint. The development of new α-type organic conductors suitable for investigating the intermediate electronic state is needed, and uniaxial strain may provide a more effective way to tune existing α-type materials.[49]

Charge-modulated states, including the CDW states produced by the nesting of Fermi surfaces, near/in superconducting phases are present in many superconducting systems, such as charge stripes in high-T_c superconducting cuprates[50] or charge-fluctuated states in heavy-fermion superconductors,[51,52] and the contributions of charge degree of freedom to superconductivity have been extensively discussed. The existence of the charge-ordered insulating state, the superconducting phase and the CDW phase in one phase diagram of α- and β''-type organic conductors strongly suggests the importance of the contribution of charge degree of freedom to superconductivity in organic systems. The relationships among them should be discussed together in the future, although those between superconductivity and a CDW, or superconductivity and the charge-ordered insulating state, have been separately discussed as a contributor to the mechanism of superconductivity.[53–55]

In a theoretical study of DODHT salt, two possibilities for the intermediate electronic phase between the charge-ordered insulating state and the superconducting phase (the normal metallic state) were proposed:[56] (I) a charge-ordered metal (weakened charge-ordered state), and (II) a mixture of the charge-ordered metal with and its separation from other surrounding phases, the charge-ordered insulating state and the normal metallic state, as the free energy of the charge-ordered metal is almost the same as those of the others. The emergence of superconductivity from the charge-ordered metal was suggested to be due to the mechanism of spin fluctuation, which seems to contradict the existence of the CDW in this study. Studies of the electronic properties of the intermediate phase will be performed in the future.

V. SUMMARY

We investigated the low-temperature electrical properties of the two-dimensional organic conductor β''-(BEDT-TTF)$_2$AuBr$_2$, whose electronic structure is similar to that of the pressure-induced superconductor β''-(DODHT)$_2$PF$_6$ having a charge-ordered transition at 255 K at ambient pressure. We found that the ground state of β''-(BEDT-TTF)$_2$AuBr$_2$ at ambient pressure has a CDW phase below 6.5 K, and also discovered superconductivity in a possible normal metallic state as a result of suppression of the CDW phase by applying uniaxial strain. On the basis of the obtained experimental results, we propose a unified electronic phase diagram of β''-type organic conductors having two equivalent molecules in a unit cell. It is useful to examine the general relationships among the charge-ordered insulating state, the superconducting phase, and the CDW phase. The presence of the CDW phase near the superconducting phase suggests a minor role played by spin fluctuations in the mechanism of the superconductivity, and the present material is a promising candidate for charge-fluctuation-mediated superconductivity.

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*crkondo@mail.ecc.u-tokyo.ac.jp

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