

**Determination of Band-filling Change  
in the Two-dimensional Organic Conductor,  
 $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ )  
by the Quantum Oscillation of Magnetoresistance**

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The effect of thermal treatment on the transport properties is studied for a two-dimensional organic conductor  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ ). The temperature dependence of the electric resistivity below room temperature was found to be changed from metallic down to low temperature to semiconducting by heating up to 420 K. One of the two frequencies of Shubnikov-de Haas oscillations are found to be different between the non-heated and heated parts from a single crystal, while no evidence of structural change in X-ray photograph was observed. The present result clearly shows that nominal valence or band filling can be controlled by simple thermal treatment for the quasi-two-dimensional organic metal. The mechanism of the change in the band filling is discussed in terms of anion decomposition.

KEYWORDS: organic conductor, quasi-two-dimensional system, thermal treatment, magnetoresistance, quantum oscillations, band-filling control

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## 1. Introduction

$\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ ), which is abbreviated as OO-SS-AuBr<sub>2</sub> below, is a two-dimensional (2D) organic conductor that shows many interesting phenomena including weak ferromagnetic behavior,<sup>1–3</sup> large negative magnetoresistance,<sup>4,5</sup> giant Shubnikov-de Haas (SdH) oscillations<sup>6–8</sup> and a plateau of Hall resistance reminiscent of quantum Hall effect.<sup>9,10</sup> EDO-*S,S*-DMEDT-TTF is an abbreviation of the organic donor ethylenedioxy-*S,S*-dimethylethylenedithio-tetrathiafulvalene, where *S,S* denotes the absolute configuration of asymmetric carbon atoms. Although temperature dependence of the electric resistivity of OO-SS-AuBr<sub>2</sub> turns from metallic to semiconducting at about 50 K on cooling, the observed SdH oscillations at 0.5 K shows the existence of two small 2D Fermi surfaces. Fast-Fourier-transform (FFT) analysis of the SdH oscillations gives the area of the Fermi surfaces as 6.1 and 0.66% of the first Brillouin zone, respectively.<sup>6–8</sup>

Recently sample dependence of the electric resistivity and the heat capacity was reported for OO-SS-AuBr<sub>2</sub>.<sup>11</sup> The sample dependence is larger at lower temperatures and some samples remain metallic. On the other hand, another  $\tau$ -type conductor  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(I<sub>3</sub>)<sub>1+y</sub> (OO-SS-I<sub>3</sub>) has been known to show aging effect on the temperature dependence of the electric resistivity. Murata *et al.*<sup>4</sup> reported that a semiconducting sample of OO-SS-I<sub>3</sub> became slightly metallic after about one year and pointed out the possibility of escape of iodine from the sample. In fact,  $\tau$ -type organic conductors are non-stoichiometric compounds with the composition of D<sub>2</sub>A<sub>1+y</sub>, where D is a donor, A is an anion

and  $y$  is estimated as 0.75 from the elemental analysis<sup>12</sup>) and as 0.875 from the recent X-ray study,<sup>13</sup>) respectively. The non-stoichiometric composition suggests the stability of the crystal over a certain range of  $y$ . If it is the case, the concentration  $y$  and, therefore, the filling of donor band can be controlled by accelerating the anion escape from the crystal at higher temperatures. The present study is aimed to prove this assumption by utilizing the SdH oscillations as the direct tool to observe the band-filling change for the thermally treated sample.

## 2. Experimental

Single crystals of OO-SS-AuBr<sub>2</sub> were grown by a standard electrochemical oxidation method reported elsewhere.<sup>12</sup> Recently it was found that an amount (a few to 25%) of bromine atoms in AuBr<sub>2</sub><sup>−</sup> are replaced by chlorine ones when dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) is used as solvent during the electrochemical crystallization. This does not, however, give any serious problems in the present study focusing the change in the physical properties of *each* crystal by the thermal treatment. Furthermore, we checked that the sample dependence of the electric resistivity reproduces for the samples newly obtained by using tetrahydrofuran (THF) as solvent to avoid the chlorine impurity.

To investigate the effect of thermal treatment on the temperature dependence of the electric resistivity, three single crystals (#0214, #0215, #0216) whose resistivity was metallic down to 4.2 K were selected. The electric resistivity along the most resistive *c*-axis was measured by the usual DC four-probe method. Two pairs of annealed Au wires (10  $\mu$ m in diameter) were attached with carbon paste (XC-12, Furuuchi Kagaku Co.) on the opposing crystal surfaces parallel to the *ab* plane, where *b* is equivalent to *a* (see the

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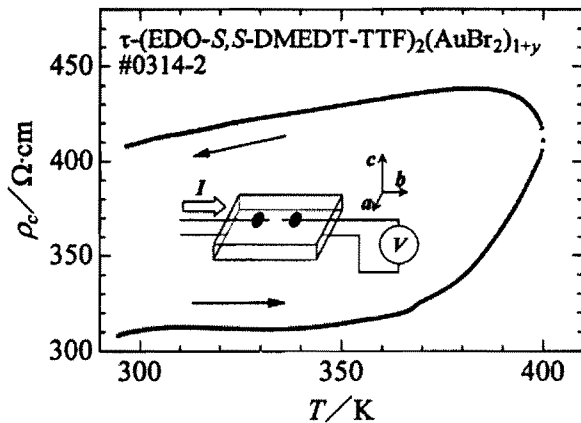


Fig. 1. Temperature dependence of the *c*-axis resistivity of  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ ) during the thermal treatment on the sample #0314-2 up to 400 K. The inset shows a schematic image of the terminal configuration.

insets in Figs. 1 and 2). It is known that the carbon paste itself is stable at least up to 500 K.<sup>14,15</sup> Temperature dependence of the electric resistivity between 4.2 and 300 K was repeatedly measured after each thermal treatment. The thermal treatment was carried out by heating the samples in vacuum with a rate of 20 K·h<sup>-1</sup> up to a target temperature. The heater power was immediately turned off after the target temperature was achieved. The target temperature was increased from 320 up to 440 K by steps of 20 K after each measurement below 300 K.

The effect of the thermal treatment on the band filling was examined by measuring magnetoresistance for the electric current and the magnetic field along the *c*-axis ( $I \parallel c$  and  $B \parallel c$ , the inset in Fig. 3). Another single crystal (#0314) was cut into two pieces and one of them was heated up to 400 K. This prevents the ambiguity due to the sample dependence noted above. The measurement in the magnetic field was carried out by using the 45-T hybrid magnet at National High Magnetic Field Laboratory in U.S.A. The virgin (#0314-1) and heated (#0314-2) samples were mounted on a sample holder and their electric resistivity

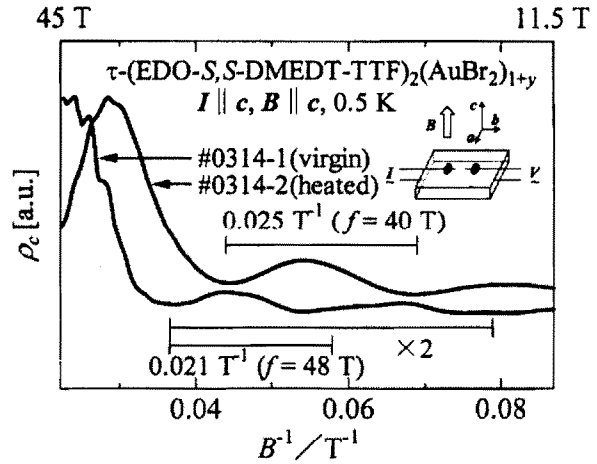


Fig. 3. Magnetic field dependence of the electric resistivity of the virgin (#0314-1) and heated (#0314-2) samples of OO-SS-AuBr<sub>2</sub> at 0.5 K for the electric current and the magnetic field along the *c*-axis. The unit of the *y*-axis is arbitrary. Roughly estimated frequency *f* of the magnetoresistance oscillations against the inverse magnetic field is about 48 and 40 T for the virgin and heated samples, respectively. The inset shows a schematic image of the terminal configuration and the direction of the magnetic field.

was measured simultaneously by two lock-in amplifiers. The frequency of the excitation voltage was 23.78 and 17.75 Hz for #0314-1 and #0314-2, respectively, and the time constant was kept 1 s. The lowest temperature was achieved by pumping <sup>3</sup>He and magnetoresistance was measured at 0.5 K. The magnetic field was swept between 11 and 44 T with the speed of 3.0 T·min<sup>-1</sup>. The magnitude of the magnetic field was corrected by considering the position of the samples relative to the magnetic center of the magnet.

To check the effect of the thermal treatment on the crystal structure, X-ray diffraction pattern was also examined at Okayama University for the virgin (#0302-1) and the heated (#0302-2) samples from another single crystal. The sample #0302-2 was heated up to 420 K by the same manner noted above. The diffraction pattern was obtained by the oscillating crystal method at 90 K and room temperature, respectively.

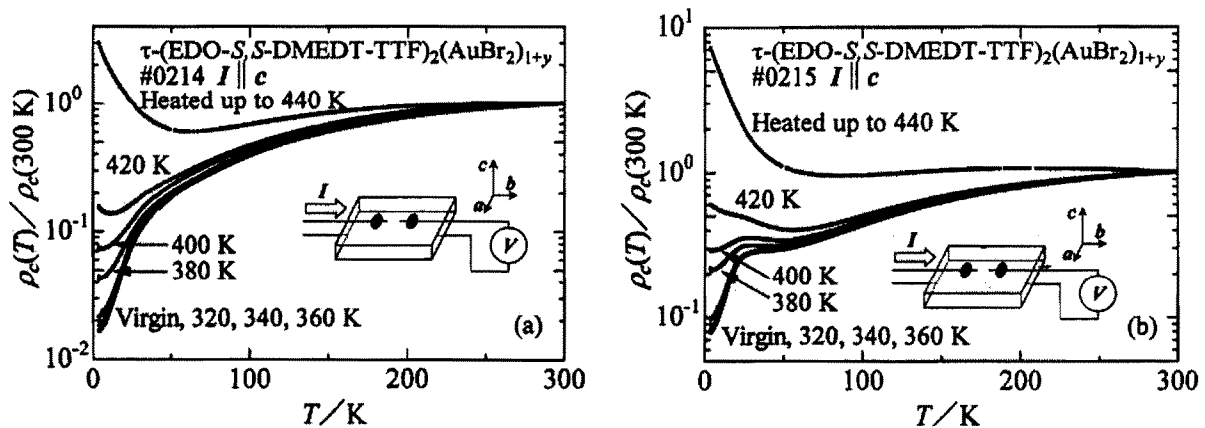


Fig. 2. Temperature dependence of the *c*-axis resistivity of  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ ) normalized at 300 K. Each data curve except for the beginning (virgin) was obtained after the thermal treatment up to a target temperature from 320 to 440 K. The sample #0214 (a) was metallic down to 4.2 K without any anomalies before the thermal treatment, while #0215 (b) showed a hump around 40 K. Each inset shows a schematic image of the terminal configuration (same for #0214 and #0215).

### 3. Results and Discussion

#### 3.1 Thermal treatment and $\rho_c(T)$

Figure 1 shows the temperature dependence of the electric resistivity of #0314-2 during the thermal treatment between room temperature and 400 K. Rapid increase in the resistivity occurred above 360 K and continued until the temperature came back to 380 K after reaching 400 K. The resistivity curve on cooling did not trace that on heating, namely, irreversible change occurred for #0314-2. The appearance of #0314-2 was little changed and remained being a shiny black plate. Both #0314-1 and #0314-2 were used for the magnetoresistance measurement described in the next subsection.

The variation of the temperature dependence of the electric resistivity,  $\rho_c(T)$ , was studied by changing the target temperature of the thermal treatment systematically for other samples (Fig. 2). Among the samples which show various kinds of  $\rho_c(T)$ , the samples metallic down to 4.2 K were selected and heated up to a target temperature from 320 to 440 K. Before the thermal treatment the sample #0215 showed the anomaly of  $\rho_c(T)$  around 40 K as in Fig. 2(b), while no anomaly was observed for #0214 [Fig. 2(a)]. This is the sample dependence noted in §1. After each thermal treatment  $\rho_c(T)$  below 300 K was measured repeatedly. It was found that the effect of the thermal treatment on  $\rho_c(T)$  is distinct for heating above 380 K and -larger at lower temperatures. The resistivity of #0215 shows a broad minimum around 50 K after heating up to 420 K and this is very similar to that reported previously<sup>1,2)</sup> and the spectrum of the present data curves from metallic to semiconducting at low temperatures is very similar to that seen in the sample dependence.<sup>16)</sup> It is, therefore, probable that an important factor responsible for the sample dependence can be continuously controlled by the thermal treatment on each single crystal.

As shown below the thermal treatment increases the band filling through the possible anion decomposition. It is, however, the band-filling increase cannot explain the change from metallic to semiconducting behavior within the single-electron band picture. Thus it will be needed to consider, for example, the effect of randomness that should be introduced by the decomposition of the anions.

#### 3.2 Magnetoresistance

The magnetic field dependence of the resistivity between 11 and 44 T at 0.5 K is plotted against inverse of the magnetic field in Fig. 3. The slower and faster oscillations due to the Shubnikov–de Haas effect were observed for the both samples as was previously reported. Surprisingly large difference of phase and frequency is, however, recognized between the slow oscillations of #0314-1 and #0314-2 as seen in Fig. 3. The frequency estimated by the eye is 48 T for the virgin sample (#0314-1) and 40 T for the heated one (#0314-2), respectively. Since the amplitude of the faster oscillations observed at higher magnetic field is much smaller than that of the slower ones, the numerical derivative  $d\rho_c/dB^{-1}$  was calculated to see the oscillations clearly. No distinct difference in the frequency of the fundamental oscillations was found in the faster oscillations between #0314-1 and #0314-2 as in Fig. 4.

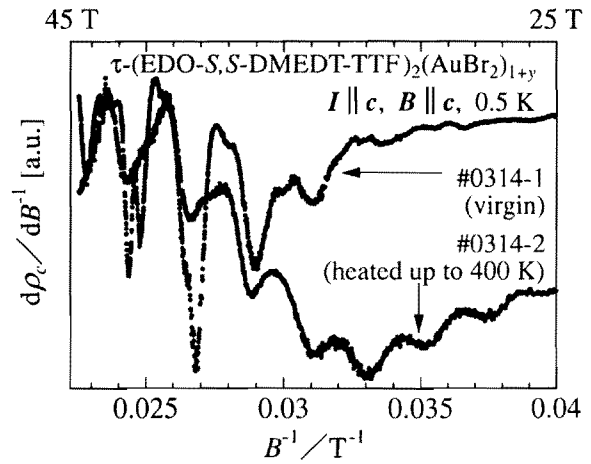


Fig. 4. Numerical derivative of the electric resistivity with respect to the inverse of the magnetic field  $d\rho_c/dB^{-1}$  for the virgin (#0314-1) and heated (#0314-2) samples of OO-SS-AuBr<sub>2</sub> from the data between 25 and 44 T in Fig. 3.

#### 3.3 FFT and MEM analyses

The features observed by the eye are also seen in the result of the FFT and the maximum-entropy-method (MEM)<sup>17)</sup> analyses (Figs. 5 and 6).

The FFT spectra were calculated after subtracting the background quadratic curves from the data in Figs. 3 and 4, respectively. The data below and above 30 T were used for the analysis of the slower and faster oscillations, respectively. The resolution of the FFT spectra of the slower oscillations is rather poor ( $\Delta f = 18.7$  T) due to the small number of waves included in the used range of the magnetic field, while the frequency resolution is improved in the MEM spectra in Fig. 6(a). Irrespective of the different frequency resolution, both the FFT and MEM analyses demonstrate the large shift of the frequency (20–30%) for the slower oscillations as a result of the heat treatment. As well as the observation by the eye, no distinct change in the fundamental frequency by heating is seen in the spectra for the faster oscillations [Figs. 5(b) and 6(b)]. One can also see its higher harmonics especially for #0314-1 in Fig. 5(b). A low frequency peak at 97 T in Fig. 5(b) and at 105 T in Fig. 6(b) for #0314-2 is probably artificial and extrinsic because its period [ $\sim 1/(100$  T)] corresponds to the data window on the  $B^{-1}$ -axis. The fundamental SdH frequencies determined by the MEM analysis are listed in Table I with corresponding Fermi surface area for #0314-1 and #0314-2, respectively.

Table I. Fundamental frequencies of the SdH oscillations of  $\tau$ -(EDO-S,S-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ ) determined by the MEM analysis ( $F_1$  and  $F_2$ ) and corresponding Fermi surface area relative to the first Brillouin zone ( $S_1/S_{\text{FBZ}}$  and  $S_2/S_{\text{FBZ}}$ ).

Sample	#0314-1 (virgin)	#0314-2 (heated)
$F_1/T$ ( $S_1/S_{\text{FBZ}}$ )	52.4 (0.670%)	42.3 (0.541%)
$F_2/T$ ( $S_2/S_{\text{FBZ}}$ )	505 (6.45%)	492 (6.29%)

$$S_{\text{FBZ}} = 0.7467 \text{ \AA}^{-2} = (2\pi/a)^2$$

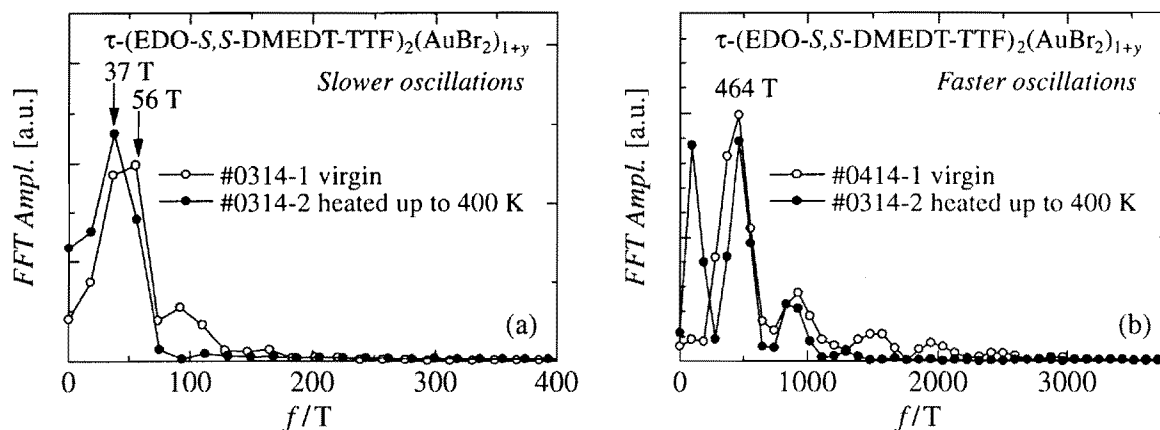


Fig. 5. The fast-Fourier-transform (FFT) spectra of the slower (a) and faster (b) SdH oscillations of  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub> ( $y \leq 0.875$ ). The data below and above 30 T in Figs. 3 and 4 were used after subtracting background as quadratic functions for the calculation of (a) and (b), respectively.

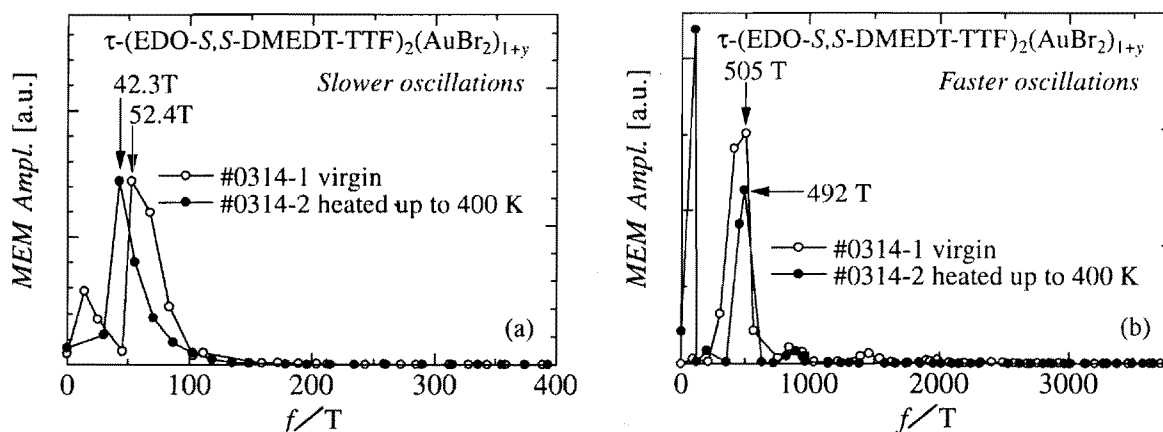


Fig. 6. The frequency spectra of the slower (a) and faster (b) SdH oscillations of  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub> ( $y \leq 0.875$ ) by the maximum-entropy-method (MEM).<sup>17)</sup> The data below and above 30 T in Figs. 3 and 4 were used after subtracting background as quadratic functions for the calculation of (a) and (b), respectively.

There are three possible factors that affect the SdH frequency, namely, the orientation of the crystal to the magnetic field, the crystal structure (or the band-structure) and the band filling. By assuming the crystal structure is not affected by the thermal treatment, only the band-filling change can explain the fact that the frequency of the slower oscillations decreased after heating, though that for the faster ones remained unchanged. This is because the two kinds of Fermi surfaces are expected to be highly two-dimensional from the anisotropy of the electric conductivity ( $\sim 10^4$ ).<sup>12)</sup> When the magnetic field is tilted from the *c*-axis, the SdH frequencies for the slower and faster oscillations will increase by the same factor of  $1/\cos\theta$ . Possible difference between the relative orientation of the samples to the magnetic field, therefore, should affect the faster oscillations as well as the slower ones. But this is not the case.

### 3.4 Crystal and band structures

To check whether the thermal treatment affects the crystal structure or not, we compared X-ray diffraction patterns between the virgin (#0302-1) and heated (#0302-2) samples

from another single crystal. Temperature of the thermal treatment was 420 K for #0302-2 and this is 20 K higher than that for the SdH sample #0314-2. The X-ray diffraction patterns were obtained by the oscillating crystal method at 90 K (Fig. 7) and room temperature (not shown). Diffuse streaks (arrows in the figure), which were reported previously<sup>13)</sup> and originate from a superstructure of, probably, the insulating anion layers, were observed at room temperature. Diffuse spots of  $2a \times 2b$  are also known to appear below 230 K and reproduced as in the inset of Fig. 7 (circles). There is no detectable difference in the diffraction patterns between the virgin and heated samples. Thus it is concluded that the band-filling change is responsible for the shift of the SdH frequency.

Although the early study of the band structure of OO-SS-AuBr<sub>2</sub><sup>12)</sup> does not take account of the superstructure, we attempted to explain the two series of SdH oscillations by this band structure. Figure 8 shows the dispersion relation (a) and the density of states (b) calculated for one conducting layer of OO-SS-AuBr<sub>2</sub> by the tight-binding approximation with the transfer integrals<sup>18)</sup> between the donor molecules as

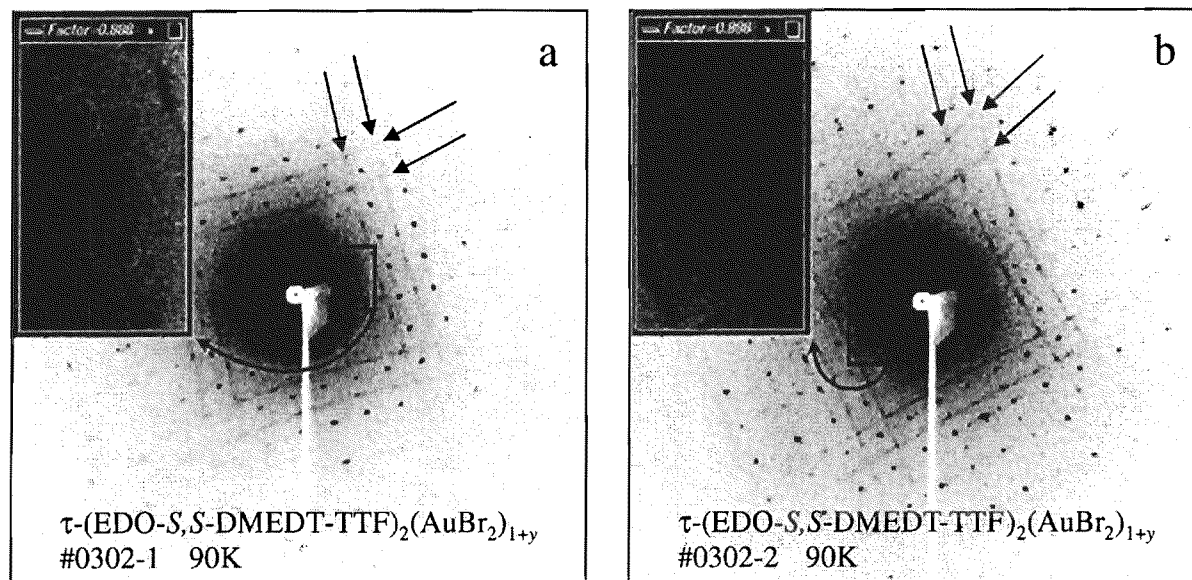


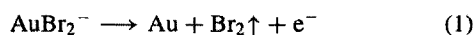
Fig. 7. Diffraction patterns of the virgin (#0302-1) and heated (#0302-2) samples from a single crystal of  $\tau$ -(EDO-*S,S*-DMEDT-TTF) $_2$ (AuBr $_2$ ) $_{1+y}$ , ( $y \leq 0.875$ ) for X-ray along the *c*-axis at 90 K. The arrows and circles indicate the diffuse streaks and diffuse spots, respectively.

in the inset. Since the intermolecular interaction has the four-fold symmetry in the conducting layer, the band structure is two-dimensional. The Fermi energy  $E_F$  is uncertain due to the ambiguity of the anion concentration  $1 + y$ , where  $y$  is 0.75 from the early elemental analysis<sup>12)</sup> and 0.875 from the recent X-ray study.<sup>13)</sup> Fermi surfaces are illustrated in Fig. 8(c) for typical values of  $y$ . It is interesting that the present band structure is semimetallic and two small Fermi pockets are expected for a certain range of  $y$ . As in Fig. 8(c),  $y \sim 1$  gives an elliptic Fermi pocket around X (Y) and an star-shape larger one around M are obtained from the lower and upper bands, respectively.

The area of the closed Fermi surfaces is shown as a function of a normalized band-filling in Fig. 9 (solid curves). The discontinuities at the band-filling of 0.48 and 0.57 is due to contacting/detaching of the Fermi surface to/from the zone boundary [see the Fermi surfaces for  $y = 0.5$  and 0.75 in Fig. 8(c)]. The present band parameters give two Fermi pockets between 0.485 and 0.505. This semimetallic nature originates from the small positive value of  $t_3$ . It is difficult to estimate the magnitude of  $t_3$  due to the AuBr $_2^-$  between the donors within the conducting layer. It is possible that the real  $\tau$ -type conductors have much wider region of band filling where two Fermi pockets coexists as is calculated for larger  $t_3$  in Fig. 9 (dashed and dotted curves).

### 3.5 Band-filling control

The semimetallic band also explains the decrease in the area of the smaller Fermi pocket by heating. Since the crystal is enough clean to show the SdH effect, the donor molecules are probably not deteriorated by heating. The change is, therefore, considered to occur at the anions. A possible chemical reaction at high temperature is as follows.



This is probable because metallic luster of gold is always

observed after heating of the gold-containing organic conductors above their decomposition temperature.<sup>15)</sup> At a moderate temperature some of the anions decompose into neutral gold atoms and gaseous bromine molecules, the latter of which escape from the crystal. Then electrons will be left and fill the conduction band. A slight increase in the band filling results in the rapid decrease in the hole-like Fermi pocket area from the lower band, while the area of the electron-like larger Fermi pocket is not changed so much for the band filling larger than 0.5 as in Fig. 9. If it is the case, the slower SdH oscillations with giant amplitude originate from the hole-like Fermi pocket from the lower band, and the faster oscillations from the upper one, respectively. The FFT and MEM analyses noted in §3.3 show the thermal treatment decreases area of the smaller Fermi pocket 20–30%. Since the area is about 0.6% of the first Brillouin zone, this corresponds to the change in  $y$ ,  $\Delta y = (3-4) \times 10^{-3} = 3000-4000$  ppm.

The series of change in the temperature dependence of the resistivity from metallic to semiconducting in Fig. 2 strongly suggests that the band filling can be continuously controlled by the simple thermal treatment for OO-SS-AuBr $_2$ . The band-filling control (or the carrier doping) is a usual way to investigate and to control the physical properties of electric conductors. It has been, however, seldom applied for organic conductors of charge-transfer complexes and radical cation/anion salts. The present study is, as far as we know, the first example of the band-filling control of the organic conductor whose variation of the filling has been determined precisely by utilizing the quantum oscillations.

Considerable number of examples have been reported for the band-filling control of the organic conductors. Many of them are based on the substitution of molecules of different valences or, in other words, alloying. Tracing back to the literature, the earliest study on the band-filling control of the organic conductor was reported by Miller and Epstein<sup>19-22)</sup> for a series of quasi-one-dimensional charge transfer com-

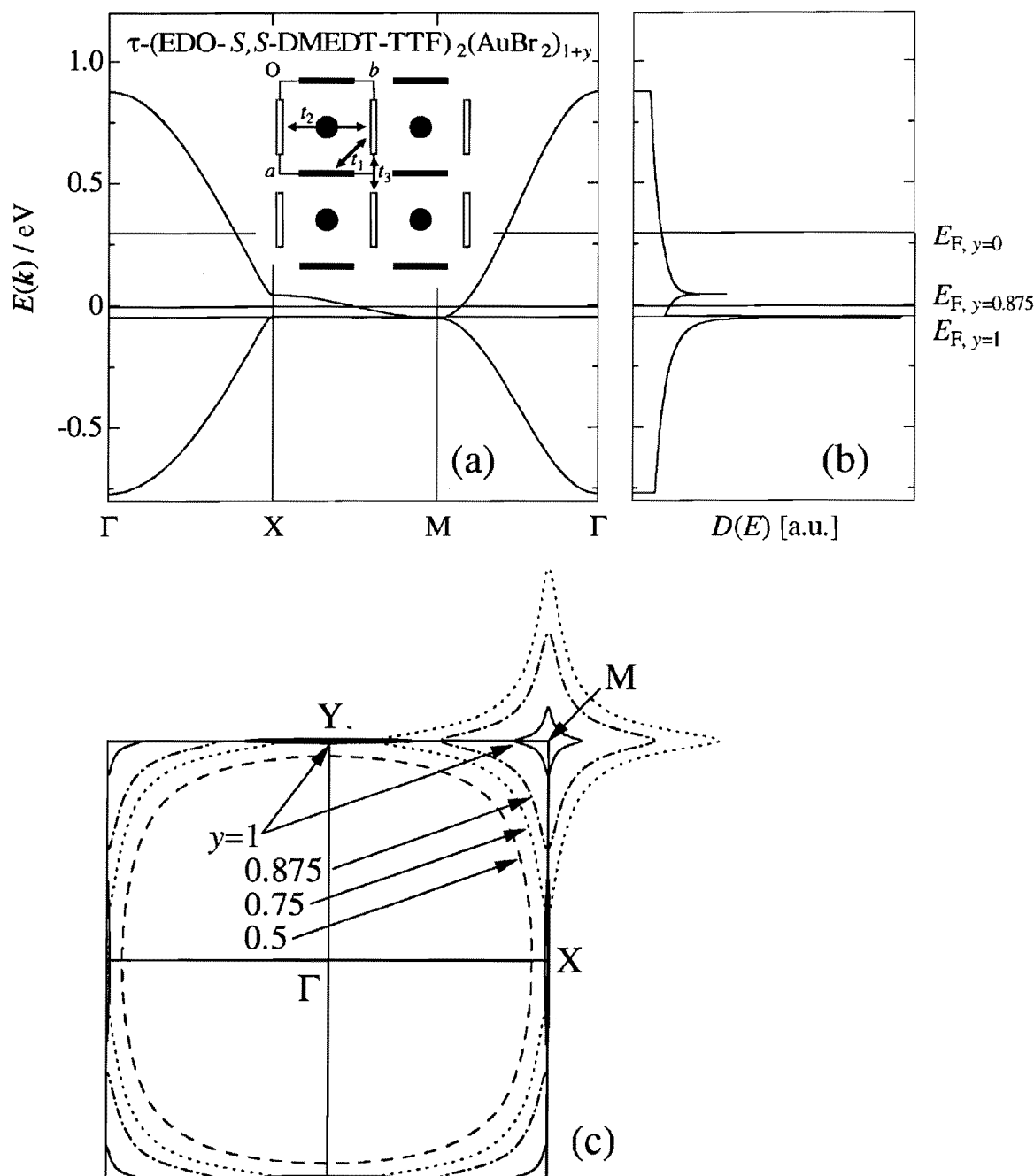


Fig. 8. Dispersion relation (a) and density of states (b) calculated for one conducting layer of  $\tau$ -(EDO-*S,S*-DMEDT-TTF) $_2$ (AuBr $_2$ ) $_{1+y}$ , ( $y \leq 0.875$ ) by the tight-binding method. The inset in (a) shows the notation of the transfer integrals between the donor molecules used for the calculation. The open and solid rectangles represent the donors in the opposite directions and solid circles are anions in the conducting layer. Ducasse<sup>18)</sup> reported that  $t_1 = 206$  meV,  $t_2 = 24$  meV and  $t_3 = 2$  meV, respectively. (c) Fermi surfaces calculated from the dispersion relation for  $y = 1$  (solid curve), 0.875 (broken curve), 0.75 (dotted curve) and 0.5 (chain curve), respectively. The two Fermi pockets are obtained for  $y = 1$ . Those around Y (X) and M points are from the lower and upper bands, respectively, and ratio of their areas is 1 : 10. Note that the definition of the first Brillouin zone is different from that in the previous report.<sup>12)</sup>

plexes (NMP $^+$ ) $_x$ (Phen $^0$ ) $_{1-x}$ (TCNQ $^-$ ) $_x$ (TCNQ $^0$ ) $_{1-x}$  ( $0.5 < x \leq 1$ ), where NMP = *N*-methylphenazine, Phen = phenazine and TCNQ = 7,7,8-tetracyano-*p*-quinodimethane, respectively. Structural<sup>22)</sup> and transport<sup>19-22)</sup> properties were systematically investigated for single crystals as well as other physical and chemical properties for polycrystalline and solution samples. Several groups<sup>23-27)</sup> reported the effect of the band-filling control on physical properties of (DMe-DCNQI) $_2$ Cu $_{1-x}$ Li $_x$ , where DMe-DCNQI = dimethyl-*N,N'*-

dicyanoquinodimine, by alloying Cu $^{2+}$  and Li $^+$ . The alloying of monovalent and divalent anions was applied for several BEDT-TTF salts.<sup>28-32)</sup> H. Mori *et al.* reported, for example, decrease in electric resistivity and activation energy of semiconducting  $\lambda$ -(BEDT-TTF) $_2$ (GaCl $_4^+$ ) $_{1-x}$ (CoCl $_4^{2+}$ ) $_x$  ( $0 \leq x \leq 0.06$ ) and  $\delta'$ -(BEDT-TTF) $_2$ (GaCl $_4^+$ ) $_{1-x}$ (CoCl $_4^{2+}$ ) $_x$  ( $0 \leq x \leq 0.14$ ) on increasing  $x$ .<sup>31,32)</sup>

As for the band-filling control by methods other than alloying, T. Mori and Ashizawa *et al.*<sup>33,34)</sup> reported direct

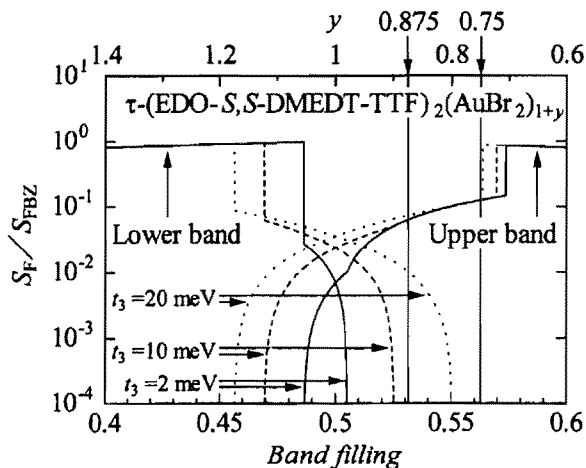


Fig. 9. Area of the two closed Fermi surfaces of  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ ) as a function of the normalized band-filling or  $y$  that is 0.75 from the early elemental analysis<sup>12)</sup> and 0.875 from the recent X-ray study.<sup>13)</sup> Solid curves were obtained from the dispersion relation in Fig. 8. The dashed and dotted curves were calculated for  $t_3 = 10$  and 20 meV, respectively, while  $t_3 = 2$  meV for the solid curves.

doping of iodine to neutral crystals of TTC<sub>*n*</sub>-TTP (= 2,2'-bis[4,5-alkylthio-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrahydropentalenylidene] with four alkylthio chains of  $n$  carbon atoms). They measured time dependence of the electric resistivity in the iodine atmosphere and found that (TTC<sub>3</sub>-TTPY)<sub>3</sub> shows metallic resistivity, while the other doped TTC<sub>*n*</sub>-TTPY and its analogs are semiconducting. Naito *et al.*<sup>35-37)</sup> reported very recently the success of the p-n junction on a single crystal of (DCNQI)<sub>2</sub>Ag by light emission to a part of crystal. They claimed that the white light induces the charge transfer reaction from DCNQI<sup>-</sup> to Ag<sup>+</sup> and hole-doping is realized.

On the other hand, changes in physical properties by the thermal treatment have been reported for organic conductors. For example, it is well known that the thermal treatment above 340 K converts the crystal structure of  $\alpha$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> to  $\alpha'$ -type that is almost identical to  $\beta$ -type crystal structure.<sup>38,39)</sup> In this case the result of the thermal treatment is remarkable because  $\alpha'$ -crystal shows the superconductivity below 8 K, though  $\alpha$ -crystal undergoes a metal-to-insulator transition at 135 K. In many cases, especially in the radical salts of BEDT-TTF showing polymorphism, the thermal treatment results in the change in crystal structures.<sup>40-46)</sup>

The present study is the first report of the continuous band-filling control of the organic conductor by the thermal treatment, where no change in the crystal structure occurs and the relative variation of the band filling has been determined precisely. We owe this success to two factors. One is that OO-SS-AuBr<sub>2</sub> has the small Fermi pockets observed by the quantum oscillation of the magnetoresistance. The other is the very high static magnetic field up to 44 T as a powerful tool to see the quantum oscillation clearly. Other methods such as elemental and X-ray analyses will not give a precise estimate of the band-filling change. It will also be difficult to determine the variation of the band filling for other organic conductors with much larger Fermi surface than that of OO-SS-AuBr<sub>2</sub>.

The band-filling control is considered to be difficult for the organic conductors in general. This is due to their stability of stoichiometric composition such as 1 : 1 and 2 : 1. Except for the DCNQI salts noted above, to sweep the composition (or band filling) continuously as a tunable parameter, rather large molecules must be partially replaced by other ones with different valence or by vacancies in organic materials, while the replacement is atomic level in inorganic ones. In this sense,  $\tau$ -type conductors are very remarkable because all the family compounds have non-stoichiometric composition of 2 : (1 +  $y$ ).<sup>4,12,47-53)</sup>

#### 4. Conclusion

The present study has clearly shown that the thermal treatment is a simple way of the band-filling control of the organic conductors. We detected slight change in the the band-filling by exploiting the non-stoichiometry and the small Fermi surfaces of  $\tau$ -(EDO-*S,S*-DMEDT-TTF)<sub>2</sub>(AuBr<sub>2</sub>)<sub>1+y</sub>, ( $y \leq 0.875$ ). This is the first report of the continuous band-filling control of the organic conductors, where the relative band-filling change has been determined precisely from the frequency shift of the SdH oscillations. Non-stoichiometric organic superconductors such as  $\kappa$ -(BEDT-TTF)<sub>4</sub>Hg<sub>2.89</sub>Br<sub>8</sub> ( $T_c = 4.3$  K),<sup>55)</sup> (MDT-TSF)(AuI<sub>2</sub>)<sub>0.436</sub> ( $T_c = 4.5$  K, MDT-TSF = methylenedithio-tetra-selenafulvalene),<sup>56-58)</sup> are also candidates to study the relation between the band filling and physical properties by the thermal treatment.

Finally we propose that the thermal treatment can be applied for not only the non-stoichiometric but also the stoichiometric organic conductors. Some of the present authors reported that the SDW transition temperature of the 2 : 1 salt of (DIMET)<sub>2</sub>I<sub>3</sub> [DIMET = dimethyl(ethylenedithio)tetrathiafulvalene] decreased from 41 to 20 K by the thermal treatment.<sup>14)</sup> This strongly suggests the possibility of the band-filling control on the known halogen-containing stoichiometric organic conductors/superconductors. Although the absolute change in the band filling may be small as in the present case ( $\sim 1000$  ppm), one can expect fruitful results once he remembers  $\kappa'$ -(BEDT-TTF)<sub>2</sub>Cu<sub>2</sub>(CN)<sub>3</sub> where substitution of Cu<sup>2+</sup> of 100–1000 ppm with Cu<sup>+</sup> changes the ground state from insulating to superconducting.<sup>59,60)</sup>

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- 1) H. Yoshino, K. Murata, T. Sasaki, K. Iimura, A. Oda and G. C. Papavassiliou: *Synth. Met.* **103** (1999) 2010.
- 2) H. Yoshino, K. Iimura, T. Sasaki, A. Oda, G. C. Papavassiliou and K. Murata: *J. Phys. Soc. Jpn.* **68** (1999) 177.
- 3) T. Konoike, A. Oda, K. Iwashita, T. Yamamoto, H. Tajima, H. Yoshino, K. Ueda, T. Sugimoto, K. Hiraki, T. Takahashi, T. Sasaki, Y. Nishio, K. Kajita, G. C. Papavassiliou, G. A. Mousdis and K. Murata: *Synth. Met.* **120** (2001) 801.
- 4) K. Murata, N. Shirakawa, H. Yoshino, Y. Tsubaki, G. C. Papavassiliou, A. Terzis and J. S. Zambounis: *Synth. Met.* **86** (1997) 2021.
- 5) G. C. Papavassiliou, D. J. Lagouvardos, I. Koutselas, K. Murata, A. Graja, I. Olejniczak, J. S. Zambounis, L. Ducasse and J. P. Ulmet: *Synth. Met.* **86** (1997) 2043.
- 6) T. Konoike, K. Iwashita, H. Yoshino, K. Murata, T. Sasaki and G. C. Papavassiliou: *Phys. Rev. B* **66** (2002) 245308.
- 7) T. Konoike, K. Murata, K. Iwashita, H. Yoshino, T. Sasaki, K. Hiraki, T. Takahashi, Y. Nishio, K. Kajita, H. Tajima and G. Papavassiliou: *J. Phys. Chem. Solids* **63** (2002) 1245.
- 8) T. Konoike, K. Iwashita, T. Sasaki, K. Hiraki, T. Takahashi, G. C. Papavassiliou, H. Yoshino and K. Murata: *Synth. Met.* **133–134** (2003) 157.
- 9) K. Murata, T. Nakanishi, H. Yoshino, T. Konoike, J. Brooks, D. Graf and G. C. Papavassiliou: *J. Phys. IV (Paris)* **114** (2004) 343.
- 10) K. Murata, H. Yoshino, T. Nakanishi, T. Konoike, J. Brooks, D. Graf, C. Mielke and G. C. Papavassiliou: *Curr. Appl. Phys.* **4** (2004) 488.
- 11) Y. Nishio, K. Nara, K. Kajita, H. Yoshino, K. Murata and G. C. Papavassiliou: *Synth. Met.* **135–136** (2003) 667.
- 12) G. C. Papavassiliou, D. J. Lagouvardos, J. S. Zambounis, A. Terzis, C. P. Raptopoulou, K. Murata, N. Shirakawa, L. Ducasse and P. Delhaes: *Mol. Cryst. Liq. Cryst.* **285** (1996) 83.
- 13) T. Konoike, K. Iwashita, I. Nakano, H. Yoshino, T. Sasaki, Y. Nogami, J. S. Brooks, D. Graf, C. H. Mielke, G. C. Papavassiliou and K. Murata: *Physica E* **18** (2003) 188. The period of the diffuse streaks reported in this paper suggests the existence of the superstructure of  $2a \times (8/7)b$  at room temperature and gives  $y = 0.875$ .
- 14) H. Yoshino, K. Murata, Y. Yamamura, T. Tsuji, H. Nishikawa, K. Kikuchi and I. Ikemoto: *J. Therm. Anal. Cal.* **69** (2002) 865.
- 15) H. Yoshino, K. Murata, Y. Yamamura, T. Tsuji, J. Yamada, S. Nakatsuji, H. Anzai, H. Nishikawa, K. Kikuchi, I. Ikemoto and K. Saito: *Mol. Cryst. Liq. Cryst.* **380** (2002) 239.
- 16) T. Nakanishi, L. Li, H. Yoshino, S. Yasuzuka, D. Graf, E. S. Choi, J. S. Brooks, G. C. Papavassiliou and K. Murata: submitted to *Synth. Met. as Proc. Int. Conf. Synthetic Metals (ICSM)* 2004.
- 17) K. Tokiwano, N. Ohtomo and Y. Tanaka: *Saidai-entropy-houni yoru Jikeiretsu Kaiseki* (Time Series Analysis by Maximum Entropy Method) (Hokkaido University Press, Sapporo, 2002) [in Japanese].
- 18) L. Ducasse: private communication.
- 19) A. J. Epstein and J. S. Miller: *Solid State Commun.* **27** (1978) 325.
- 20) J. S. Miller and A. J. Epstein: *J. Am. Chem. Soc.* **100** (1978) 1639.
- 21) A. J. Epstein, J. S. Miller and P. M. Chaikin: *Phys. Rev. B* **43** (1979) 1178.
- 22) J. S. Miller and A. J. Epstein: *Solid State Chemistry: A Contemporary Overview* (Oxford University Press, New York, 1980) *Advances in Chemistry Series*, No. 186, pp. 195–205.
- 23) H. Sawa, M. Tamura, S. Aonuma, M. Kinoshita and R. Kato: *J. Phys. Soc. Jpn.* **63** (1994) 4302.
- 24) T. Hiraki and K. Kanoda: *Mol. Cryst. Liq. Cryst.* **285** (1996) 157.
- 25) N. Maruyama, T. Nakamura, T. Takahashi, S. Aonuma, H. Sawa and R. Kato: *Synth. Met.* **86** (1997) 2093.
- 26) K. Hiraki and K. Kanoda: *Synth. Met.* **86** (1997) 2111.
- 27) T. Yamamoto, H. Tajima, J. Yamaura, S. Aonuma and R. Kato: *J. Phys. Soc. Jpn.* **68** (1999) 1384.
- 28) R. Kumai, A. Asamitsu and Y. Tokura: *J. Am. Chem. Soc.* **120** (1998) 8263.
- 29) H. Mori, T. Okano, M. Kamiya, M. Haemori, H. Suzuki, S. Tanaka, M. Tamura, Y. Nishio, K. Kajita, K. Takimiya, T. Otsubo and H. Moriyama: *Synth. Met.* **120** (2001) 979.
- 30) H. Mori, M. Kamiya, M. Haemori, H. Suzuki, S. Tanaka, Y. Nishio, K. Kajita and H. Moriyama: *J. Am. Chem. Soc.* **124** (2002) 1251.
- 31) H. Mori, M. Kamiya, S. Suzuki, M. Suto, S. Tanaka, Y. Nishio, K. Kajita and H. Moriyama: *J. Phys. Chem. Solids* **63** (2002) 1239.
- 32) H. Mori, M. Kamiya, H. Suzuki, M. Suto, S. Tanaka, Y. Nishio, K. Kajita and H. Moriyama: *Synth. Met.* **133–134** (2003) 161.
- 33) T. Mori, M. Ashizawa, S. Kimura, A. Akutsu-Sato, B. Noda, Y. Misaki and K. Tanaka: *J. Phys. IV (Paris)* **114** (2004) 549.
- 34) M. Ashizawa, S. Kimura, T. Mori, Y. Misaki and K. Tanaka: *Synth. Met.* **141** (2004) 307.
- 35) T. Naito and T. Inabe: *J. Phys. IV (Paris)* **114** (2004) 553.
- 36) T. Naito, T. Inabe, H. Niimi and K. Asakura: *Adv. Mater.* **16** (2004) 1786.
- 37) T. Naito, H. Niimi and K. Asakura: submitted to *Synth. Met. as Proc. Int. Conf. Synthetic Metals (ICSM)* 2004.
- 38) G. O. Baram, L. I. Buravov, L. C. Degtariev, M. E. Kozlov, V. N. Laukhin, E. E. Laukhina, V. G. Orischenko, K. I. Pokhodnia, M. K. Scheinkman, R. P. Shibaeva and E. B. Yagubskii: *JETP Lett.* **44** (1986) 239 [*Pis'ma Zh. Eksp. Teor. Fiz.* **44** (1986) 239].
- 39) D. Schweitzer, P. Bele, H. Brunner, E. Gogu, U. Haeblerlen, I. Hennig, I. Klutz, R. Swietlik and H. J. Keller: *Z. Phys. B* **67** (1987) 67.
- 40) V. A. Merzhanov, E. E. Kostyuchenko, V. N. Laukhin, R. M. Lobkovskaya, M. K. Makova, R. P. Shibaeva, I. F. Shchegolev and E. B. Yagubskii: *JETP Lett.* **44** (1986) 376 [*Pis'ma Zh. Eksp. Teor. Fiz.* **44** (1986) 376].
- 41) H. H. Wang, D. Carlson, L. K. Montgomery, J. A. Schlueter, C. S. Cariss, W. K. Kwok, U. Geiser, G. W. Crabtree and J. M. Williams: *Solid State Commun.* **66** (1988) 1113.
- 42) H. Yamochi, H. Urayama, G. Saito and K. Oshima: *Synth. Met.* **27** (1988) A485.
- 43) H. Yamochi, H. Urayama, G. Saito, K. Oshima, A. Kawamoto and J. Tanaka: *Chem. Lett.* (1988) 1211.
- 44) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M.-H. Whangbo: *Organic Superconductors (Including Fullerenes)* (Prentice Hall, NJ, 1992) pp. 203–205.
- 45) S. Sekizaki, H. Yamochi and G. Saito: *Synth. Met.* **120** (2001) 961.
- 46) E. Laukhina, J. Vidal-Gancedo, V. Laukhin, J. Veciana, I. Chuev, V. Tkacheva, K. Wurst and C. Rovira: *J. Am. Chem. Soc.* **125** (2003) 3948.
- 47) G. C. Papavassiliou, D. Lagouvardos, V. Kakoussis, G. Mousdis, A. Terzis, A. Hountas, B. Hilti, C. Mayer, J. Zambounis, J. Pfeiffer and P. Delhaes: in *Organic Superconductivity*, ed. V. Z. Kresin and W. A. Little (Plenum, New York, 1990) pp. 367–373.
- 48) A. Terzis, A. Hountas, B. Hilti, G. Mayer, J. S. Zambounis, D. Lagouvardos, V. Kakoussis, G. Mousdis and G. C. Papavassiliou: *Synth. Met.* **41–43** (1991) 1715.
- 49) G. C. Papavassiliou, D. J. Lagouvardos, V. C. Kakoussis, A. Terzis, M.-H. Whangbo, J. Ren and D. B. Kang: *Mater. Res. Soc. Symp. Proc.* **247** (1992) 535.
- 50) J. S. Zambounis, J. Pfeiffer, G. C. Papavassiliou, D. J. Lagouvardos, A. Terzis, C. P. Raptopoulou, P. Delhaes, L. Ducasse, N. A. Fortune and K. Murata: *Solid State Commun.* **95** (1995) 211.
- 51) G. C. Papavassiliou, K. Murata, J. P. Ulmet, A. Terzis, G. A. Mousdis, H. Yoshino, A. Oda and D. Vignolles: *Synth. Met.* **103** (1999) 1921.
- 52) G. C. Papavassiliou, G. A. Mousdis, A. Terzis, C. Raptopoulou, K. Murata, T. Konoike and H. Yoshino: *Synth. Met.* **120** (2001) 743.
- 53) G. C. Papavassiliou, G. A. Mousdis, A. Terzis, C. Raptopoulou, K. Murata, T. Konoike, H. Yoshino, A. Graja and A. Łapiński: *Synth. Met.* **135–136** (2003) 651.
- 54) L. Li, H. Yoshino, T. Nakanishi, G. C. Papavassiliou, G. A. Mousdis, T. Sasaki and K. Murata: submitted to *Synth. Met. as Proc. Int. Conf. Synthetic Metals (ICSM)* 2004.
- 55) R. N. Lyubovskaya, E. I. Zhilyaeva, S. I. Pesotskii, R. B. Lyubovskii, L. O. Atovmyan, O. A. Dyachenko and T. J. Takhirov: *JETP Lett.* **46** (1987) 188 [*Pis'ma Zh. Eksp. Teor. Fiz.* **46** (1987) 188].
- 56) K. Takimiya, Y. Kataoka, Y. Aso, T. Otsubo, H. Fukuoka and S. Yamanaka: *Angew. Chem., Int. Ed.* **40** (2001) 1122.
- 57) T. Kawamoto, T. Mori, K. Takimiya, Y. Kataoka, Y. Aso and T. Otsubo: *Phys. Rev. B* **65** (2002) 140508(R).
- 58) T. Kawamoto, T. Mori, C. Terakura, T. Terashima, S. Uji, H. Tajima, K. Takimiya, Y. Aso and T. Otsubo: *Eur. Phys. J. B* **36** (2003) 161.
- 59) T. Komatsu, N. Matsukawa, T. Inoue and G. Saito: *J. Phys. Soc. Jpn.* **65** (1996) 1340.
- 60) T. Komatsu, N. Kojima and G. Saito: *Synth. Met.* **85** (1997) 1519.