Pressure-Induced Superconductivity of the Quasi-One-Dimensional Organic Conductor (TMTTF)$_2$TaF$_6$

Miho Itoi $^{1, *}$, Toshikazu Nakamura $^{2}$ and Yoshiya Uwatoko $^{3}$

$^{1}$ Physics Section, Division of Natural Sciences, Nihon University School of Medicine, Itabashi 173-8610, Japan
$^{2}$ Institute for Molecular Science, Okazaki 444-8585, Japan; t-nk@ims.ac.jp
$^{3}$ Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan; uwatoko@issp.u-tokyo.ac.jp
* Correspondence: itoi.miho@nihon-u.ac.jp

Abstract: We investigated the superconductivity of (TMTTF)$_2$TaF$_6$ (TMTTF: tetramethyl-tetrathiafulvalene) by conducting resistivity measurements under high pressure up to 8 GPa. A cubic anvil cell (CAC) pressure generator, which can produce hydrostatic high-pressure, was used for this study. Since the generalized temperature-pressure $(T-P)$ diagram of (TMTCF)$_2$X $(C = Se, S; X: monovalent anion) based on (TMTTF)$_2$PF$_6$ ($T_{CO} = 70$ K and spin-Peierls: $SP$, $T_{SP} = 15$ K) was proposed by Jérôme, exploring superconductivity states using high-pressure measurement beyond 4 GPa has been required to confirm the universality of the electron-correlation variation under pressure in (TMTTF)$_2$X (TMTTF)$_2$TaF$_6$, which has the largest octahedral-symmetry counter anion TaF$_6$ in the (TMTTF)$_2$X series, possesses the highest charge-ordering (CO) transition temperature ($T_{CO} = 175$ K) in (TMTTF)$_2$X and demonstrates an anti-ferromagnetic transition ($T_{AF} = 9$ K) at ambient pressure. A superconducting state in (TMTTF)$_2$TaF$_6$ emerged after a metal-insulator transition was suppressed with increasing external pressure. We discovered a superconducting state in 5 $\leq P \leq$ 6 GPa from $T_c = 2.1$ K to 2.8 K, whose pressure range is one-third narrower than that of $X = SbF_6$ (5.4 $\leq P \leq$ 9 GPa). In addition, when the pressures with maximum SC temperatures are compared between the $PF_6$ and the $TaF_6$ salts, we found that (TMTTF)$_2$TaF$_6$ has a 0.75 GPa on the negative pressure side in the $T-P$ phase diagram of (TMTTF)$_2$PF$_6$.

Keywords: one-dimensional organic conductor; superconductivity; high-pressure measurement

1. Introduction

Since the discovery of the first organic superconductivity in (TMTSF)$_2$PF$_6$ (tetramethyl-tetraselenafulvalene-hexafluorophosphate), quasi-one-dimensional (Q1D) organic conductors (TMTCF)$_2$X $(C = Se and S; X: monovalent anion) have been extensively investigated because electronic-correlations related to spin, charge, and dimensionality generate various types of ground states [1–5]. In the (TMTCF)$_2$X crystal, face-to-face TMTCF molecules align perpendicularly along the $c$-axis. The hybridization of $p$-electrons on Se or S atoms in the TMTCF molecules leads to strong one-dimensional conductivity, and the 1D-TMTCF chain is well-separated by the monovalent anion $X$ layer. The (TMTCF)$_2$X system has a 3/4 filling band structure [6]. Their flexible-molecular packing consequently produces multihued ground states, which change from AFM (anti-ferromagnetism) I-SP (spin-Peierls), AFM II (commensurate SDW), and incommensurate SDW (spin density wave) to an SC (superconductivity) phase at low temperatures, by controlling the superposed electron density in both inter-and intra-chains using chemical and the applied pressures [1]. For more than three decades, the generalized phase diagram has been extended by efforts in synthesizing TMTTF salts with centrosymmetric (cs) $(X = Br, I, PF_6, AsF_6, SbF_6, NbF_6$, and TaF$_6$) and non-centrosymmetric (necs) anions $(X = BF_4, ClO_4$ and $ReO_4$). Simultaneously, many scientists have attempted to clarify the ground state changes of (TMTTF)$_2$X by conducting pressure measurements, and the validity of the temperature-pressure $(T-P)$ diagram corresponding...
between the chemical pressure and the external pressure has been confirmed. In particular, the high-pressure investigation exceeding 4 GPa has revealed the existence of the superconductivity phase in the (TMTTF)$_2$X series [2,3,7–10].

The emergence of the superconducting phase in the (TMTTF)$_2$X series is understood as a crossing over anti-ferromagnetic fluctuation. (TMTTF)$_2$Br is the first superconductor in TMTTF series ($T_C = 0.8$ K@ 2.6 GPa) [11], whose ground state shifts from AFM II ($T_{AF} = 15$ K, C-SDW: commensurate) to SDW (I-SDW: incommensurate) by external pressure [12–14]. The SDW transition temperature decreases due to the imperfect nesting of Fermi surfaces by applying external pressure. The SDW phases observed in (TMTSF)$_2$MF$_6$ ($M = P, As, Sb$) were explained by the electron correlation and two-dimensionality with mean-field theory [15]. As it stands that the SC phase in (TMTCF)$_2$X always neighbors the SDW, there are many reports about the exotic superconductivity properties of (TMTCF)$_2$X, for instance, the anisotropic SC revealed by high magnetic field measurements [16,17] and by muon spin rotation [18].

The charge-ordering (CO) state was observed in the (TMTTF)$_2$X series, except for (TMTTF)$_2$ClO$_4$, (TMTTF)$_2$SCN, and (TMTTF)$_2$I [19–21]. The CO transition of (TMTTF)$_2$X is called a structureless transition since only a small change in the dimer position was observed by X-ray diffraction measurement [22]. The spatial charge disproportion on TMTTF molecules affects the spin state at low temperatures. In the case of (TMTTF)$_2$X, which has an octahedron symmetry counter anion, the $X = PF_6$ and AsF$_6$ salts go into the SP phase from the CO phase, while the $X = SbF_6$, NbF$_6$ [23], and TaF$_6$ salts change to AFM I phase by cooling, depending on the CO pattern, dimensionality, and spin fluctuation [24,25]. Below 3 GPa pressure region, $^{13}$C NMR studies in $X = SbF_6$ have revealed that the ground states vary from AFM I $\rightarrow$ spin gap $\rightarrow$ AFM II (C-SDW) (Figure 1) [26,27]. The ground state change from SDW to SC became decisive through the high-pressure resistivity measurement up to 10 GPa using a cubic anvil cell (CAC); the superconducting phase of (TMTTF)$_2$SbF$_6$ was observed as an anomalously wide pressure range (5.4 $<$ $P < 9$ GPa) under limited temperature above 1.8 K [9].

(TMTTF)$_2$TaF$_6$ has the largest cell volume in the (TMTCF)$_2$X series, with a $cs$ anion. The one-dimensional character was confirmed by the result of the single-crystal X-ray diffraction analysis [28]. To understand the electron correlation, confirmations of the existence of the SC state and the pressure-dependent ground-state change toward the SC state in (TMTTF)$_2$TaF$_6$ are necessary. In this paper, we investigated the resistivity behaviors of (TMTTF)$_2$TaF$_6$ under high pressures up to 8 GPa and compared it to those for other TMTTF compounds ($X = PF_6$, AsF$_6$, and SbF$_6$).

![Figure 1. Electronic temperature-pressure ($T$-$P$) diagram for quasi-one-dimensional (Q1D) organic conductors (TMTCF)$_2$X ($C = S$ and Se), which start from the ground state of the (TMTTF)$_2$TaF$_6$ salt](image-url)

Figure 1. Electronic temperature-pressure ($T$-$P$) diagram for quasi-one-dimensional (Q1D) organic conductors (TMTCF)$_2$X ($C = S$ and Se), which start from the ground state of the (TMTTF)$_2$TaF$_6$ salt.
(CO state $T_{CO} = 175$ K and AFM $T_{AF} = 9$ K), suggested by Dressel et al. and Oka et al. This $T$-$P$ diagram is depicted from the references [5,23,26,27,29–32]. The generalized $T$-$P$ diagram (i.e., generalized electron correlation diagram) of (TMTTF)$_2$X was first established by D. Jérome and coworkers in 1991 [1]. The abbreviations for described states in the diagram are CO (charge-ordering state), CL (charge-localized state), SP (spin-Peierls state), AFM (anti-ferromagnet, I: commensurate state, II: commensurate SDW), SDW (spin density wave), and SC (superconducting state).

2. Experimental Section

The sample preparation of (TMTTF)$_2$TaF$_6$ was detailed in Ref. [28]. The single crystal (TMTTF)$_2$TaF$_6$ is a black needle type; the sample size used for resistivity measurement was $800 \mu m \times 15 \mu m \times 10 \mu m$. The high-pressure resistivity measurement was performed by using a CAC apparatus at the Institute for Solid State Physics (ISSP), The University of Tokyo. The resistivity of (TMTTF)$_2$TaF$_6$ was measured along the $a$-axis (crystal growing direction) by a conventional four-probe method. The four Au electric terminals ($\phi \ 10 \mu m$ Au wire) were in contact with carbon paste on the sample surface and the ends of Au wires were relayed to $\phi \ 15 \mu m$ Pt wires with Au paste to avoid wire cutting during the application of high pressures. The four relayed Pt wires are fixed with a small piece of paper by using epoxide resin adhesives to prevent sample breaking by the shock when the high pressure was applied. The sample with electrodes was sealed in a small Teflon cell ($\phi \ 2.0 \ mm$) with the pressure medium Fluorinert 70:77 (1:1) mixture and then wrapped with a cubic MgO gasket (6 mm squares), which also served as the second pressure medium. The four Pt electric leads outside of the Teflon cell were wired with thin Au ribbons on the MgO gasket. The MgO gasket was isotopically compressed up to 250 tons by Tungsten carbide anvils, which also play a role in four-wire electronic contact materials. The CAC can generate a high-quality steady hydrostatic pressure by controlling a constant load system up to 12 GPa. The temperature range for this measurement was from 1.8 K to 295 K and the resistance value of (TMTTF)$_2$TaF$_6$ was recorded upon heating. External pressure was applied on (TMTTF)$_2$TaF$_6$ between 0 GPa and 1.4 GPa; the resistance varied due to unsteady attachment between the gasket and CAC anvils. At 1.5 GPa, the MgO gasket was compressed enough to achieve steady resistance of the TaF$_6$ salt. Therefore, we did not measure the resistivity at 0 GPa; the measurement starts from 1.5 GPa. The resistivity along the $a$-axis was normalized by using the length and the surface values at room temperature.

3. Results and Discussion

At ambient pressure, the CO phase transition temperature ($T_{CO} = 175$ K) of $X = TaF_6$ is the highest in the TMTTF series with octahedron monovalent anion. The CO transition temperature increases with increasing the octahedron anion size, PF$_6$ (70 K), AsF$_6$ (102 K) SbF$_6$ (154 K), and NbF$_6$ (165 K) [23]. The stoichiometry-controlled salt (TMTTF)$_2$[AsF$_6$]$_{1-x}$[SbF$_6$]$_x$ (x~0.3) has a higher $T_{CO}$ of 120 K, which is between the temperatures of the AsF$_6$ and SbF$_6$ salts, and the characteristic SP magnetic susceptibility behavior is suppressed at a low temperature [33]. It was reported that the transition between SP and AFM I states occurs at $x \sim 0.5$ chemical pressure [34], while the pressure experiment on (TMTTF)$_2$SbF$_6$ revealed that the AFM I state changes to a spin gap state due to the external pressure of 0.5 GPa, and the CO state becomes unclear above 0.5 GPa. [26]. (More details for the pressure effect on the CO state in $X = AsF_6$ and SbF$_6$ are in Ref [35]). The CO state in the TaF$_6$ salt has a -O-o-O-o- pattern (O: charge-rich site, o: charge-poor site) as in the SbF$_6$ salt, which coexists in the AFM I phase at ambient pressure [27,32]. The temperature-dependent magnetic susceptibility shows a characteristic one-dimensional decrease from 300 K to 50 K, and a rapid decrease was observed around 30 K. (TMTTF)$_2$TaF$_6$ undergoes an anti-ferromagnetic transition at 9 K [27].

Figure 2a shows the temperature-dependent resistivity of (TMTTF)$_2$TaF$_6$ in the $a$-axis direction under pressures from 1.5 GPa to 8 GPa. For the measurement, the initial temperature was set to around 1.8 K by cooling from room temperature, and then the temperature was gradually heated. Generally, the metallic conductivity of the TMTTF
Materials 2022, 15, 4638

4 of 10

series becomes unstable due to the charge localization at \( T_\rho \) in the high-temperature region. For the TaF\(_6\) salt, \( T_\rho \) is reported as \( \sim 200 \) K, which is quite close to \( T_{CO} = 175 \) K. The resistivity at room temperature is 0.1 \( \Omega \cdot \text{cm} \) [32]. In the case of our pressure measurement, the resistivity at 1.5 GPa was 0.35 \( \Omega \cdot \text{cm} \) at room temperature, whose value was two orders higher than that of (TMTTF)\(_2\)SbF\(_6\) (Figure 2b). A possible cause of the high resistivity value at 1.5 GPa is considered as a partial remnant charge localization caused by interfering with smooth volume compression and/or exceeding the anisotropic crystal deformation by a large TaF\(_6\) anion under low pressures.

Figure 3a shows the resistivity value at 290 K under several pressures for (TMTTF)\(_2\)X (\( X = \text{PF}_6, \text{AsF}_6, \text{SbF}_6 \), and TaF\(_6\)) by using the CAC pressure generator. The pressure-dependent resistivities of \( X = \text{PF}_6, \text{AsF}_6, \text{SbF}_6 \) were plotted with the data in Refs. [7–9]. The resistivity rapidly decreases up to 5 GPa and the value becomes almost unchanged beyond 6 GPa, although the resistivities for (TMTTF)\(_2\)X (\( \text{PF}_6, \text{AsF}_6, \text{SbF}_6 \)) are almost suppressed below 2 GPa (Figure 3a inset). It should be noted that the resistivity of the SbF\(_6\) salt is the lowest in the (TMTTF)\(_2\)X series from 1.5 GPa to 10 GPa.

For the resistivity of the TaF\(_6\) salt at 1.5 GPa, we observed the drastic resistivity drop up to 100 K upon heating. After the temperature reached 100 K, the resistivity has a gradual incline (Figure 2b). The activation energies of \( \Delta_\rho \) and \( \Delta_\delta \) were obtained from a simple formula, \( \log \rho(T) = \frac{\Delta}{T} + \log \rho_0 \). The inclination changes at a higher temperature and a second inclination change at a lower temperature correspond to \( T_\rho \) and \( T_S \) in Figure 2c, in \( \log (\rho(T)) \) plot. Here, the sample size reduction caused by thermal expansion and pressure effects is not taken into account for the \( \log (\rho(T)) \) calculation. Figure 3b,c show the pressure-dependent activation energies (\( \Delta_\rho \) and \( \Delta_\delta \)) for (TMTTF)\(_2\)X (\( X = \text{PF}_6, \text{AsF}_6, \text{SbF}_6 \), and TaF\(_6\)). It should be noted that the \( \Delta_\rho \) value in Figure 3b includes both activation energies coming from CO and Mott localization. The CO gap \( \Delta_{CO} \) has been discussed in several reports by resistivity measurements [20,32,33], using the formula \( \Delta_{CO} = \sqrt{\Delta(T)^2 - \Delta^2(T_{CO})} \) (here \( \Delta(T) = T \ln \rho \) in the CO state and \( \Delta^2(T_{CO}) \) is the value above \( T_{CO} \)). Each \( \Delta_{CO} \) gap at ambient pressure is \( \sim 560 \) K for TaF\(_6\), \( \sim 500 \) K for SbF\(_6\), \( 430 \) K for [AsF\(_6\)\(_{1-x}\)SbF\(_6\)\(_x\)] (\( x \sim 0.3 \)), \( \sim 315 \) K for AsF\(_6\), and \( \sim 217 \) K for PF\(_6\), which increases proportionally to \( T_{CO} \) [32,33]. \( \Delta_{CO} \) values are less than half of the obtained \( \Delta_\rho \) values at 0 GPa and the order of magnitude of (TMTTF)\(_2\)X is \( \Delta_\rho (\text{SbF}_6) > \Delta_\rho (\text{AsF}_6) > \Delta_\rho (\text{PF}_6) \), which is different from \( \Delta_{CO} \) (TaF\(_6\) > \( \Delta_{CO} \) (SbF\(_6\)) > \( \Delta_{CO} \) (AsF\(_6\)) > \( \Delta_{CO} \) (PF\(_6\))). For the obtained data of high-pressure measurements for the TaF\(_6\) salt, the extraction of the \( \Delta_{CO} \) value at around 1.5 GPa is already unresolved due to an unclear transition at \( T_{CO} \).

The \( \Delta_\rho \) and \( \Delta_\delta \) at 1.5 GPa for (TMTTF)\(_2\)TaF\(_6\) are 117 K (\( T_\rho \sim 90 \) K) and 116 K (\( T_S \sim 20 \) K), respectively, which correspond to the values at about 2.1 GPa and 1.5 GPa for those of (TMTTF)\(_2\)SbF\(_6\), respectively. The \( \Delta_\rho \) becomes comparable to those of other (TMTTF)\(_2\)X salts near 2.0 GPa since the CO state of the TaF\(_6\) salt already vanishes, then \( \Delta_\rho \) values coincide with almost constant values in (TMTTF)\(_2\)X salts above 3 GPa. Meanwhile, activation energy \( \Delta_\delta \) corresponds to a spin-related transition (SP, AFM II, and SDW), according to the similar analysis of (TMTTF)\(_2\)X [2,3,7–9]. With increasing applied pressures, high resistivity at low temperatures dramatically drops and the metallic behavior becomes dominant above 40 K upon heating (see Figure 2b). At 3 GPa, the resistivity at room temperature still shows a high value of 0.3565 \( \Omega \cdot \text{cm} \); the minimum drop in the resistivity curve appears at around 20 K in the resistivity-temperature curve, written in both logarithmic axes. The respective activation energies \( \Delta_\delta \) at 3 GPa and 4 GPa are 22 K (\( T_S = 13 \) K) and 10 K (\( T_S = 8 \) K), respectively, which correspond to the activation energies observed in the X = SbF\(_6\) salt at \( \sim 4.6 \) GPa and 5.3 GPa, respectively (see Figure 3c). It should be noted that the AFM II (C-SDW) and SDW (I-SDW) transition temperatures are \( \sim 15 \) K (at \( 0 \leq P \leq 0.3 \) GPa) and \( \sim 23 \) K (at \( 0.3 < P \leq 0.75 \) GPa) in (TMTTF)\(_2\)Br [12]. Here, the resistivity of the TaF\(_6\) salt between 200 K and 300 K at 4 GPa becomes almost equal to that of X = SbF\(_6\) at room temperature (see Figure 2b).
Figure 2. (a) Temperature dependence of the resistivity of (TMTTF)$_2$TaF$_6$ under several pressures (from 1.5 GPa to 8 GPa). The external pressure was applied by using the CAC pressure generator, which can compress the sample with liquid pressure-transmitted medium in a Teflon cell-surrounded MgO gasket from six directions simultaneously, using an external automatic 250-ton load piston. The temperature range for the measurement was from 1.8 K to room temperature. The resistivity along the $a$-axis direction was measured by the four-probe method; the resistivity data were recorded on heating procedure by slow temperature control. (b) Resistivity versus temperature for (TMTTF)$_2$TaF$_6$ (black lines) and (TMTTF)$_2$SbF$_6$ (dash-dot lines). The resistivity of (TMTTF)$_2$SbF$_6$ is reproduced by Ref. [9]. The ground states for both samples are CO ($T_{\text{CO}} = 175$ K for $X = \text{TaF}_6$ and 154 K for $X = \text{SbF}_6$) and AFM (anti-ferromagnetism, $T_{\text{AF}} = 9$ K for $X = \text{TaF}_6$ and 8 K for $X = \text{SbF}_6$). (TMTTF)$_2$TaF$_6$ shows higher resistivity than (TMTTF)$_2$SbF$_6$. (c) log $\rho(T)$ versus $1/T$ plot. $T_\rho$ and $T_S$ are defined as points of the first slope change and the second change in log $\rho(T)$ - $1/T$ plot.

At 5 GPa, the zero-resistivity is observed due to an occurrence of a pressure-induced superconductivity transition at 2.83 K. It should be noted that the value of resistivity (0.047 Ω·cm) at 300 K is one order higher than that of the SbF$_6$ salt and the zero-resistivity was observed using the CAC apparatus in (TMTTF)$_2$X series except for the $X = \text{SbF}_6$ salt [7–9]. Figure 4 displays the temperature-dependent resistivity from 5 GPa to 8 GPa at low temperatures (between 1.8 K and 10 K). The superconductivity phase exists in a quite short pressure region of $5 \leq P \leq 6$ GPa; the shape of the SC phase is completely different from the (TMTTF)$_2$SbF$_6$ salt ($5.4 \leq P \leq 9$ GPa). The maximum $T_C$ is 2.8 K at 5 GPa, the superconducting temperature shifts to a slightly lower temperature with increasing pressure, and then the SC state almost disappears at 6 GPa. Above 7 GPa, only metallic behavior is observed. By estimating the power of temperature ($T$) with $\rho(T) \sim T^\alpha$ between 6 GPa and 8 GPa, the $\alpha$ increases linearly as pressure increases and reaches $\sim$1.5 at 8 GPa.
Figure 3. (a) Resistivity at 290 K versus pressure plots for \((\text{TMTTF})_2X\) \((X = \text{PF}_6, \text{AsF}_6, \text{SbF}_6, \text{and TaF}_6)\) obtained using the CAC pressure generator (single logarithmic plot). (Inset) Enlarged resistivity-pressure graphs below 6 GPa. Pressure-dependent activation energy (b) \(\Delta\rho\) and (c) \(\Delta S\) for \((\text{TMTTF})_2X\) \((X = \text{PF}_6, \text{AsF}_6, \text{SbF}_6, \text{and TaF}_6)\) obtained by fitting of \(\log \rho(T)\) vs \(1/T\) plots. Dot lines are a guide for the eyes. The resistivities \(\rho(T)\) along \(a\)-axis are regulated by the sample size at ambient pressure of 300 K. To compare with the data for \((\text{TMTTF})_2\text{TaF}_6\), we reproduced the resistivity-pressure plot \(\Delta\rho\) and \(\Delta S\) for \(X = \text{PF}_6, \text{AsF}_6, \text{and SbF}_6\) using references [7–9].

Figure 4. Temperature-dependent resistivity from 1.8 K to 10 K for \((\text{TMTTF})_2\text{TaF}_6\) under various pressures. The lowest-achieving temperature is 1.8 K for the resistivity measurement using the CAC pressure generator. Superconducting behavior is observed around 2 K in the narrow pressure region, between 5 GPa and 6 GPa. Above 7 GPa, the superconducting state is not observed in the measured temperature range; the resistivity linearly increases as temperature increases.
The main physical parameters, maximum superconducting transition temperature $T_C$ and the pressure $P_C$, activation energy $\Delta_S$ at 3 GPa, lattice parameters along the a-axis, volumes, and ground states at ambient pressure for $\text{(TMTTF)}_2X$ ($\text{PF}_6$, $\text{AsF}_6$, $\text{SbF}_6$, and $\text{TaF}_6$) are listed in Table 1. The $T$-$P$ diagram of $\text{(TMTTF)}_2\text{TaF}_6$ based on the result of this resistivity measurement is described in Figure 5, in which the electron-correlation change is referred to in the data of $\text{(TMTTF)}_2\text{PF}_6$. This phase diagram is obtained by adjusting both pressure points of $\text{TaF}_6$ and the $\text{PF}_6$, where the maximum SC transition temperatures ($T_C$ ($\text{PF}_6$) and $T_C$ ($\text{TaF}_6$)) were recorded. The ground states of the $\text{TaF}_6$ salt vary in CO/AFM I -(SP)-SDW (C-SDW: commensurate spin density wave and I-SDW: incommensurate spin density wave) and SC as referred to in reports [1,2] and the previous studies [7–9]. In this case, the chemical pressure between the $\text{PF}_6$ and $\text{TaF}_6$ salts is roughly estimated as 0.75 GPa. Due to the fact that the ground state change at a lower pressure in the $\text{TaF}_6$ salt has not yet been proven, the pressure range on the lower pressure side of Figure 1 differs from that of this $T$-$P$ phase diagram.

Table 1. Physical properties of $\text{(TMTTF)}_2X$ ($X = \text{PF}_6$, $\text{AsF}_6$, $\text{SbF}_6$, and $\text{TaF}_6$). $T_{\text{CO}}$, activation energies for $\Delta_S$ at 3 GPa, lattice parameters and volumes at ambient temperature, superconducting (SC) temperature $T_C$ and the observed pressure, and ground states at low temperature (0 GPa). $\Delta_S$, $T_C$, and pressure region for SC were obtained using resistivity measurements with the CAC pressure generator.

| $\text{(TMTTF)}_2X$ | $T_{\text{CO}}$ [K] | Activation Energy 3 GPa [kcal/mol] | Lattice Parameter a* [Å] | V [Å³] at Room Temperature | Superconducting Temperature $T_C$ [K] | Pressure at Maximum $T_C$ [K] (Pressure Region for SC Phase) ** | $T_{\text{AP}}$ [K] | $T_{\text{AP}}$ [K] |
|---------------------|---------------------|----------------------------------|--------------------------|-----------------------------|----------------------------------|----------------------------------------------------------|-----------------|------------------|
| $\text{PF}_6$       | 70                  | 16                               | 7.17(21)                  | 426.6                       | 2.5                              | $4.3 \leq P \leq 5.0$ GPa                                    | 14              |                  |
| $\text{AsF}_6$      | 102                 | 17                               | 7.16(26)                  | 466.15                      | 2.6                              | $5.0 \leq P \leq 6.0$ GPa                                    | 14              |                  |
| $\text{SbF}_6$      | 134                 | 17                               | 7.17(31)                  | 502.95                      | 2.6                              | $6.0 \leq P \leq 9.0$ GPa                                    | 8               |                  |
| $\text{TaF}_6$      | 175                 | 22                               | 7.16(26)                  | 595.55                      | 2.8                              | $5.0 \leq P \leq 6.0$ GPa                                    | 9               |                  |

* Lattice parameters and volumes refer to Ref. [28]. ** The temperature region for the resistivity measurement by the CAC was from 1.8 K to 300 K.

The emergence of the SC phase in the narrow pressure region for the $\text{TaF}_6$ salt is similar to those observed in the $\text{PF}_6$ and $\text{AsF}_6$ salts; however, the SC phase of the $\text{SbF}_6$ salt is observed over a wide pressure range (see Figure 5b). The reason is probably attributed to the difference in structural compression sensitivity corresponding to the dimensionality by applied pressure and thermal expansion upon cooling. The structural investigation and the DFT calculations indicated that pressure (~2.7 GPa) and a lower temperature increase two-dimensionality in $X = \text{PF}_6$ and $\text{SbF}_6$ [36,37]. It was reported that, in the structure of $\text{(TMTTF)}_2\text{PF}_6$ under high pressure, the space group $P\overline{1}$ remains up to 8 GPa and a pressure-induced structural transition (triclinic → monoclinic phase transition) occurs above 8.5 GPa [38]. The lattice $a$ is dramatically compressed to approximately 12.5% and then the total unit cell volume shrinks by about 27.5% by external pressure up to 8 GPa. At the SC-appearing pressure (~4.3 GPa), the compressed lattice and volume where the SC can be observed are $a(\text{PF}_6) \approx 6.44$ Å and $V(\text{PF}_6) \approx 540$ Å³, which are approximately 90% and 80% of the values at ambient pressure, respectively (see Table 1). Considering a simple estimation, since the actual pressure of the $\text{TaF}_6$ salt shifts by 1 GPa to the negative pressure side of that of the $\text{PF}_6$ salt, the volume of $\text{TaF}_6$ would be compressed to approximately 22.5% by $V(\text{TaF}_6) \approx 547$ Å³ to appear in the SC phase. Unfortunately, the bulk modulus and thermal expansion of $X = \text{SbF}_6$ and $\text{TaF}_6$ under high pressure are unknown. High pressure structural investigations in $X = \text{SbF}_6$ and $\text{TaF}_6$ are necessary to understand not only the origin of the high resistivity of $\text{TaF}_6$ but also the narrower SC phase compared to that of the $\text{SbF}_6$ salt.
Figure 5. (a) Temperature-pressure (T-P) diagram of (TMTTF)$_2$TaF$_6$. The denoted ground states were obtained by referring to the electronic correlation of the PF$_6$ salt. The offset pressure between the SC (superconducting) phases of PF$_6$ and TaF$_6$ is estimated at 0.75 GPa by adjusting the pressures, at which the highest temperatures of the SC were observed in TaF$_6$ and PF$_6$ salts. (b) Superconducting transition temperature versus applied pressures in (TMTTF)$_2$X for indicating the pressure region of superconducting phases observed by the resistivity measurements using the CAC pressure generator (X = PF$_6$ [7], AsF$_6$ [8], SbF$_6$ [9], and TaF$_6$ (this work)). A horizontal dot line indicates the lowest temperature limit of 1.8 K when high-pressure resistivity measurements were carried out by the CAC.

4. Conclusions

We measured resistivity for (TMTTF)$_2$TaF$_6$ under high pressure (up to 8 GPa) using a CAC pressure apparatus that can generate hydrostatic pressure. (TMTTF)$_2$TaF$_6$ has charge-ordering ($T_{CO} = 175$ K) and anti-ferromagnetic ($T_{AF} = 9$ K) states at ambient pressure. At 3 and 4 GPa, the growth of resistivity was observed at low temperatures due to spin-related transition; SDW (C-SDW and/or I-SDW) is predicted from our T-P phase diagram, as observed in (TMTTF)$_2$X (X = PF$_6$, AsF$_6$, and SbF$_6$). With increasing applied pressure, a superconducting (SC) state appears at 5 GPa. The $T_C$ of (TMTTF)$_2$TaF$_6$ records the highest SC temperature of 2.8 K (at 5 GPa) in the (TMTTF)$_2$X series. However, the SC phase is observed in the short pressure region between 5 GPa and 6 GPa above ~2 K. From the results of high-pressure resistivity measurements with the CAC pressure generator for the Q1D organic conductor (TMTTF)$_2$X (X = PF$_6$, AsF$_6$, SbF$_6$, and TaF$_6$), the generalized TMTCF T-P diagram could be extended by confirming the SC phase in TaF$_6$ salt with a negative offset pressure of $\Delta P \sim 0.75$ GPa when the pressures at maximum SC temperature were compared between the PF$_6$ and the TaF$_6$ salts. High-pressure X-ray structural measurement is future work required to reveal the different appearances of SC phase shapes between TaF$_6$ and SbF$_6$ salts under high pressure.
References

1. Jérôme, D. The Physics of Organic Superconductors. Science 1991, 252, 1509–1514. [CrossRef] [PubMed]
2. Adachi, T.; Ojima, E.; Kato, K.; Kobayashi, H.; Miyazaki, T.; Tokumoto, M.; Kobayashi, A. Superconducting Transition of (TMTTF)$_2$PF$_6$ above 50 kbar [TMTTF = Tetramethyltetraethylvalene]. J. Am. Chem. Soc. 2000, 122, 3238–3239. [CrossRef]
3. Jaccard, D.; Wilhelm, H.; Jérôme, D.; Moser, I.; Carcel, C.; Fabre, J.M. From spin-Peierls to superconductivity: (TMTTF)$_2$PF$_6$ under high pressure. J. Phys. Condens. Matter 2001, 13, L89–L95. [CrossRef]
4. Dressel, M. Spin-charge separation in quasi one-dimensional organic conductors. Naturwissenschaften 2003, 90, 337–344. [CrossRef]
5. Balicas, L.; Behnia, K.; Kang, W.; Auban-Senzier, P.; Canadell, E.; Jerome, D. Anomalous In-Plane Anisotropy Revealed by Synchrotron X-ray Diffraction. J. Phys. Soc. Jpn. 2006, 75, 051011. [CrossRef]
6. Ishiguro, T.; Yamaji, K.; Saito, G. The Physics of Organic Superconductors. 2nd ed.; Fulde, P., Ed.; Springer Series in Solid-State Sciences 88; Springer: Berlin, Germany, 1998.
7. Hirose, S.; Liu, Y.; Kawamoto, A. $^{13}$C NMR study of commensurate antiferromagnetism in (TMTTF)$_2$Br: (TMTTF)$_2$Br. Adv. Mater. 1994, 6, 762–765. [CrossRef]
8. Lee, I.J.; Brown, S.E.; Naughton, M.J. Unconventional Superconductivity in a Quasi-One-Dimensional Organic System, (TMTSF)$_2$PF$_6$. Phys. Rev. Lett. 2003, 91, 051003. [CrossRef]
9. Yonezawa, S.; Kusaba, S.; Maeno, Y.; Auban-Senzier, P.; Pasquier, C.; Bechgaard, K.; Jérôme, D. Anomalous In-Plane Anisotropy of the Onset of Superconductivity in (TMTSF)$_2$ClO$_4$. Phys. Rev. Lett. 2008, 100, 117002. [CrossRef]
10. Pratt, F.L.; Lancaster, T.; Blundell, S.J.; Baines, C. Low-Field Superconducting Phase of (TMTSF)$_2$ClO$_4$. Phys. Rev. Lett. 2013, 110, 107005. [CrossRef]
11. Adachi, T.; Ojima, E.; Kato, K.; Kobayashi, H.; Miyazaki, T.; Tokumoto, M.; Kobayashi, A. Superconducting Transition of (TMTTF)$_2$PF$_6$ above 50 kbar [TMTTF = Tetramethyltetraethylvalene]. J. Am. Chem. Soc. 2000, 122, 3238–3239. [CrossRef]
12. Hisano, M.; Nakamura, T.; Takahashi, T.; Saito, G. SDW wave number and charge localization in (TMTTF)$_2$AsF$_6$. Phys. Rev. B 2007, 76, 053703. [CrossRef]
13. Kitou, S.; Fujii, T.; Kawamoto, T.; Katayama, N.; Maki, S.; Nishibori, E.; Sugimoto, K.; Takata, M.; Nakamura, T.; Sawa, H. Superconducting Transition in (TMTTF)$_2$PF$_6$ Revealed by Synchrotron X-ray Diffraction. Phys. Rev. Lett. 2017, 119, 065701. [CrossRef] [PubMed]
14. Hirose, S.; Liu, Y.; Kawamoto, A. $^{13}$C NMR study of commensurate antiferromagnetism in (TMTTF)$_2$Br: (TMTTF)$_2$Br. Adv. Mater. 1994, 6, 762–765. [CrossRef]
15. Lee, I.J.; Brown, S.E.; Naughton, M.J. Unconventional Superconductivity in a Quasi-One-Dimensional Organic System, (TMTSF)$_2$PF$_6$. Phys. Rev. Lett. 2008, 100, 117002. [CrossRef]
16. Pratt, F.L.; Lancaster, T.; Blundell, S.J.; Baines, C. Low-Field Superconducting Phase of (TMTSF)$_2$ClO$_4$. Phys. Rev. Lett. 2013, 110, 107005. [CrossRef]
17. Wood, R.; Morris, D.; Moser, J.; Carcel, C.; Fabre, J.M. From spin-Peierls to superconductivity: (TMTTF)$_2$PF$_6$ under high pressure. J. Phys. Condens. Matter 2001, 13, L89–L95. [CrossRef]
18. Ishiguro, T.; Yamaji, K.; Saito, G. Organic Superconductors. 2nd ed.; Fulde, P., Ed.; Springer Series in Solid-State Sciences 88; Springer: Berlin, Germany, 1998.
19. Itoi, M.; Araki, C.; Hedo, M.; Uwatoko, Y.; Nakamura, T. Anomalously Wide Superconducting Phase of One-Dimensional Organic Conductor (TMTTF)$_2$SBF$_6$. J. Phys. Soc. Jpn. 2008, 77, 23701. [CrossRef]
20. Kano, M.; Mori, H.; Matsubayashi, K.; Itoi, M.; Hedo, M.; Murphy, T.P.; Tozer, S.W.; Uwatoko, Y.; Nakamura, T. Anisotropy of the Onset of Superconductivity in (TMTSF)$_2$PF$_6$. Phys. Rev. B 2003, 67, 212404. [CrossRef]
23. Kitou, S.; Zhang, L.; Nakamura, T.; Sawa, H. Complex changes in structural parameters hidden in the universal phase diagram of the quasi-one-dimensional organic conductors (TMTTF)$_2$X (X = NbF$_6$, AsF$_6$, PF$_6$, and Br). Phys. Rev. B 2021, 103, 184112. [CrossRef]

24. Nakamura, T. Possible Charge Ordering Patterns of the Paramagnetic Insulating States in (TMTTF)$_2$X. J. Phys. Soc. Jpn. 2003, 72, 213–216. [CrossRef]

25. Yoshimi, K.; Seo, H.; Ishibashi, S.; Brown, S.E. Tuning the Magnetic Dimensionality by Charge Ordering in the Molecular TMTTF Salts. Phys. Rev. B 2011, 84, 115140. [CrossRef]

26. Yu, W.; Zhang, F.; Zamborszky, F.; Alavi, B.; Baur, A.; Merlic, C.A.; Brown, S.E. Electron-lattice coupling and broken symmetries of the molecular salt (TMTTF)$_2$SbF$_6$. Phys. Rev. B 2004, 70, 121101. [CrossRef]

27. Iwase, F.; Sugiura, K.; Furukawa, K.; Nakamura, T. $^{13}$C NMR study of the magnetic properties of the quasi-one-dimensional conductor (TMTTF)$_2$SbF. Phys. Rev. B 2011, 84, 115140. [CrossRef]

28. Iwase, F.; Sugiura, K.; Furukawa, K.; Nakamura, T. Electronic Properties of a TMTTF-Family Salt, (TMTTF)$_2$TaF$_6$: New Member Located on the Modified Generalized Phase-Diagram. J. Phys. Soc. Jpn. 2009, 78, 104717. [CrossRef]

29. Dressel, M.; Dumm, M.; Knoblauch, T.; Masino, M. Comprehensive Optical Investigations of Charge Order in Organic Chain Compounds (TMTTF)$_2$X. Crystals 2012, 2, 528–578. [CrossRef]

31. Jacko, A.C.; Feldner, H.; Rose, E.; Lissner, F.; Dressel, M.; Valentí, R.; Jeschke, H.O. Electronic properties of Fabre charge-transfer salts under various temperature and pressure conditions. Phys. Rev. B 2013, 87, 155139. [CrossRef]

32. Pashkin, A.; Dressel, M.; Ebbinghaus, S.G.; Hanfland, M.; Lissner, F.; Schleid, T.; Dressel, M. Pressure-dependent structural and electronic properties of quasi-one-dimensional (TMTTF)$_2$PF$_6$. J. Phys. Condens. Matter. 2013, 25, 014006. [CrossRef] [PubMed]

33. Rose, E.; Loose, C.; Kortus, J.; Pashkin, A.; Kuntscher, C.A.; Ebbinghaus, S.G.; Hanfland, M.; Lissner, F.; Schleid, T.; Dressel, M. Pressure-dependent optical investigations of Fabre salts in the charge-ordered state. J. Phys. Condens. Matter. 2017, 29, 115601. [CrossRef] [PubMed]