Uniaxial Compression on the Superconductivity of β-BDA-TTP Salts

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Abstract. The β-type BDA-TTP superconductors attract attention due to the high transition temperature $T_C$ at ambient pressure for organic superconductors. In order to get insight into the superconductivity in terms of the dimerized anisotropic triangular lattice model, $T_C$ of β-(BDA-TTP)$_2$X [X=SbF$_6$, X=AsF$_6$] is studied under uniaxial compression by resistivity measurements. Under compression parallel to the donor stack, $T_C$ increases gradually up to 3 (X=SbF$_6$), 5 (X=AsF$_6$) kbar, and decreases under further piston pressure. Under compression perpendicular to the donor stack, $T_C$ decreases gradually up to 2.5 (X=SbF$_6$), 4 (X=AsF$_6$) kbar and then decreases rapidly under further pressure. Only for X=AsF$_6$, a $T_C$ minimum at 3 kbar is found for both direction. These trends in $T_C$ are understood as an interplay between the enhancement of antiferromagnetic spin fluctuation and frustration on the triangular lattice. By the interplane compression, $T_C$ increased by 0.5 K up to 2 kbar for both salts, demonstrating the importance of the interlayer interaction.

1. Introduction
The superconductivity of the two-dimensional BEDT-TTF salts attracts attention from experimental and theoretical viewpoints [1]. Recently, the theoretical framework based on the Hubbard model on the anisotropic triangular lattice has been developed to clarify the mechanism and the phase diagram of the superconductivity of κ-type BEDT-TTF salts [2, 3, 4, 5]. In κ-type donor arrangements, the molecules form dimers since the transfer integral between the dimer is much larger than the others. The HOMO band splits into two bands letting the upper band be half-filled. Considering the upper band, the effective on-site Coulomb energy $U_{\text{eff}}$ evaluated by the transfer integral between the dimer is close to the bandwidth ($W$). It is a strongly correlated electronic system with antiferromagnetic spin fluctuation evaluated by $U_{\text{eff}}/W$. The superconductivity is caused by the short-range spin fluctuation close to the boundary of the metal-insulator transition [6, 7]. The phase diagram comprised of superconducting, metallic, antiferromagnetic, and spin liquid phases has been proposed as a function of the ratio of the transfer integrals between the dimer units forming anisotropic triangular lattice, $t'/t$ [5, 8]. In case $t'/t$ is close to unity, the superconductivity is suppressed owing to a frustration effect between spins on the triangular lattice and a spin liquid phase appears instead. The superconducting phase is stabilized at an intermediate range of $t'/t$ and $U_{\text{eff}}/W$. 
Figure 1. (a) The arrangement of molecules and the transfer integrals between the molecules within the conduction layer of $\beta$-(BDA-TTP)$_2$X. The ellipses represent BDA-TTP molecules. The dotted ellipses indicate dimers. (b) The triangular-lattice structure taking the dimer as a unit.

In the meantime, a new series of charge transfer salts composed of BDA-TTP molecules, $\beta$-(BDA-TTP)$_2$X, attracts attention because they possess the high transition temperature of 7 K for organic superconductors [9]. BDA-TTP molecules are packed in layers in $\beta$-type arrangement with donor stacks along $a+c$ axis, as shown in Fig. 1(a). Like the $\kappa$-type, molecules form dimers, although the dimerization of the molecules is not so strong as the $\kappa$-type salts [10]. Taking the dimer as a unit, the electronic structure can also be understood on the anisotropic triangular lattice shown in Fig. 1(b). The superconducting transition under magnetic field behaves as a two-dimensional superconductor like the $\kappa$-BEDT-TTF salts [11]. The BDA-TTP salts are good counterpart materials to the BEDT-TTF salts to get insight into the mechanism of the superconductivity of the two-dimensional organic superconductors.

Uniaxial strain method is a unique technique to get insight into the phase diagram of the low-dimensional conductors since we can access each transfer integral selectively [12]. The $\kappa$-type BEDT-TTF salts has been studied by several groups [13, 14, 15, 16]. The uniaxial compression controls the anisotropy $t'/t$ of the triangular lattice. Maesato et al. summarized the results on the $\kappa$-type BEDT-TTF salts in terms of the anisotropic triangular-lattice model [17, 18]. The experimental results on three different salts align so that the $T_C$ peaks at $t'/t \sim 0.8$. This result is consistent with the theoretical calculations [?, 4].

Here we report the uniaxial compression effect on the $T_C$ of $\beta$-(BDA-TTP)$_2$X [X=SbF$_6$, AsF$_6$] and discuss the results in terms of the strength of spin fluctuation and the frustration effect on the triangular-lattice phase diagram.

2. Experimental
Samples were prepared by an electrochemical method [9]. The single crystal was aligned with respect to the compression direction with help of stripe-like patterns visible on the $ac$ plane. The direction of the stripe is found to be perpendicular to $a+c$ by Xray and ESR measurements. In Fig. 2, the angle dependences of the ESR g-values is shown when a single crystal of X=SbF$_6$ is rotated with an axis parallel to the stripe. The g-value takes a minimum of 2.003 at the angle $\theta = +30^\circ$ from the $ac$ plane and takes a maximum of 2.011 at the angle $\theta = -60^\circ$. Since the molecular plane of BDA-TTP molecules is tilted by 30° from the interplane direction, the magnetic field is perpendicular to the molecular plane at $\theta = +30^\circ$, as shown in the inset of Fig. 2. When the sample rotated with an axis perpendicular to the stripe, the magnetic field is
never perpendicular to the molecular plane and the angle dependence is much weaker than that of the parallel axis rotation. Thus, the direction of the stripe is found to be perpendicular to the donor stacks. The same result is obtained for X=AsF$_6$.

For the resistivity measurements, current and voltage electrodes were attached to a single crystal using graphite paste for four-probes resistivity measurements along the interplane direction. Applied current was of the order of 0.1 to 0.01 mA. The uniaxial compression was applied with the epoxy-encapsulation method developed by Maesato and Kagoshima et al. [12], in which the sample and electrodes were embedded into epoxy resin (stycast 1266) and clamped within a Be-Cu clamp cell. Unidirectionality of the applied pressure was checked by setting a strain gauge at sample position. Before epoxy encapsulation, the sample was coated with enamel in order to prevent reaction with the epoxy. In the present study, we denote the pressure values by the piston pressure applied at room temperature. The pressure inside the cell decreases to c.a. 80% of that applied at room temperature. The resistivity measurements were performed during heating from liquid helium temperature. Typical heating rate was 0.3 K/min. Temperature was monitored with a calibrated Cernox resistor. Two or three samples from different batch were measured for each compression direction to ensure the reproducibility of the data. For the hydrostatic pressure measurement, the sample was set in a teflon cap filled with Daphne 7373 oil.

3. Results
In Fig. 3, we show the piston pressure dependence of $T_C$ of X=SbF$_6$ defined as onset, mid point, offset of the resistive transition under in-plane compressions parallel (a) and perpendicular (b) to $a+c$ and under interplane compression (c), respectively. The over-all behaviors of $T_C$ described below are common to the all definitions of $T_C$. Under in-plane compression parallel to $a+c$ (parallel compression), $T_C$ increases gradually by 0.5 K up to 3 kbar, and decreases under further piston pressure. Under in-plane compression perpendicular to $a+c$ (perpendicular compression), $T_C$ decreases gradually up to 2.5 kbar and then decreases rapidly under further pressure. Under interplane compression, $T_C$ rapidly increases up to a piston pressure of 0.5 kbar and remains high up to $\sim$ 3 kbar, and decreases under further piston pressure. The overall behaviors of $T_C$ under uniaxial compression agree qualitatively with magnetization measurements [19].
Because $T_C$ increases under interplane compression but remains almost unchanged under in-plane compression up to 1 kbar, it is expected that $T_C$ will increase under weak hydrostatic pressure. In fact, a 0.4 K increase in $T_C$ is observed under a hydrostatic pressure of 0.5 kbar, as shown in Fig. 5.

In Fig. 4, we show the piston pressure dependence of $T_C$ of X=AsF$_6$ defined as onset, mid point, offset of the resistive transition under in-plane compressions parallel (a) and perpendicular (b) to $a+c$ and under interplane compression (c), respectively. The temperature width of the superconducting transition is wider than that for X=SbF$_6$, owing to the inferior quality of the sample crystal. $T_C$ increases under parallel compression and decreases under perpendicular compression up to 1.5–2 kbar. However, for both compressions, $T_C$ exhibits a minimum at $\sim 3$ kbar, above which it increases again by 0.2–0.6 K. $T_C$ decreases above 5 kbar gradually for parallel compression and rapidly for perpendicular compression. The tendency that the $T_C$ under perpendicular compression decreases more rapidly than that under parallel compression is the same as the case for X=SbF$_6$. Under interplane compression, $T_C$ increases up to the piston pressure of 2 kbar and remain high up to $\sim 6$ kbar, and decreased under further piston pressure.
4. Discussion

In order to understand the results in terms of the dimerized triangular-lattice phase diagram, we calculate the changes in the transfer integrals expected under uniaxial compression assuming uniform displacements of molecules. The compressibility is assumed to be 0.3 %/kbar according the results for \( \beta\)-(BEDT-TTF)\(_2\)I\(_3\) [20]. For the calculation, we assume that the shape of the BDA-TTP molecule, that is, the HOMO of the molecule is not deformed and only the separations between molecules are reduced under compression. We assume that 1 kbar of hydrostatic pressure is already applied by the epoxy encapsulation before the application of the uniaxial compression. Then we map the calculated transfer integrals onto the dimerized triangular-lattice with parameters of \( t_0 = -t q_1/2 \), \( t_1 = -t q_2/2 + t_c \) and \( t_2 = -t q_2/2 \) with effective on-site Coulomb interaction of \( U_{\text{eff}} = 2t_{p1} \) [21]. We adopt the ratio between the longitudinal transfer integrals \( t'/t \) and the average of the two transverse transfer integrals \( t = (t_0 + t_1)/2 \) as a parameter representing the strength of spin frustration.

The variations in \( T_C \) (defined as mid points of the transition) as functions of \( t'/t \) and \( U_{\text{eff}}/W \) are illustrated in Fig. 6 for X=SbF\(_6\) and X=AsF\(_6\). In the figure, \( T_C \)'s under parallel compression \((//a + c)\) are plotted at right hand side (closed symbols) and \( T_C \)'s under perpendicular compression \((\perp a + c)\) are plotted at left hand side (open symbols). Under parallel compression, \( t'/t \) increases leading to the enhancement of the spin frustration, which lowers \( T_C \). However, at the same time, \( U_{\text{eff}}/W \) increases enhancing the antiferromagnetic spin fluctuation which raises \( T_C \). \( T_C \) peaks at \( t'/t = 0.76 \) for X=SbF\(_6\) and \( t'/t = 0.90 \) for X=AsF\(_6\) are understood as results of the competition between the two effects. Under perpendicular compression, \( t'/t \) decreases. The spin frustration is released favorable for superconductivity, however, \( U_{\text{eff}}/W \) also decreases due to the increase in \( W \), which suppresses the superconductivity. In this case the latter effect is effective to reduce \( T_C \). In this way, \( T_C \) variations of the two salts under uniaxial compression are understood as the interplay between the enhancement of spin fluctuation and the frustration effect on the phase diagram. This behavior of \( T_C \) is consistent with the phase diagram postulated for \( \kappa \)-BEDT-TTF salts by Maesato et al [17, 18]. In the phase diagram, \( \kappa \)-type BEDT-TTF salts lie at the higher side of \( U/W \) giving a higher maximum in \( T_C \) than the present salts [18].

The minimum in \( T_C \) at 3 kbar observed only for X=AsF\(_6\) cannot be understood by the present model. This may be a result of nonuniform displacements of molecules under uniaxial compression. For further study to understand the \( T_C \) behaviors in detail, structural studies under uniaxial compression is needed.

The interplane compression effects on the superconductivity demonstrate the importance of
Figure 6. The variation of $T_C$ defined by the mid point of the transition as a function of $U_{\text{eff}}/W$ and $t'/t$ for $X=$SbF$_6$ and $X=$AsF$_6$.

the three dimensionality of the superconductivity of $\beta$-(BDA-TTP)$_2$SbF$_6$, which is not taken into account by theoretical models. The presence of a broad magnetoresistance peak under magnetic field almost parallel to $ac$ plane tells that the interplane transfer integral is approximately one order of magnitude larger than those of BEDT-TTF salts [22]. The interplane effects may be caused by the presence of the trimethylene bases at both ends of the BDA-TTP molecule, which enhance the interlayer interaction in comparison with the BEDT-TTF salts.

Change in $T_C$ close to ambient pressure under uniaxial compression indicates the presence of a jump in the thermal expansion coefficient. Since the superconducting transition is a kind of the second-order phase transition, the Ehrenfest relation must hold between the jump in the thermal expansion $\Delta \alpha$ and the pressure $\sigma$ dependence of the $T_C$,

$$\left(\frac{dT_C}{d\sigma}\right)_{\sigma \to 0} = \frac{V_{\text{mol}} \times T_C \times \Delta \alpha}{\Delta C}$$

where $V_{\text{mol}}$ is the molar volume and $\Delta C$ is the jump in the specific heat at the superconducting transition. For $X=$SbF$_6$, the molar volume is $V_{\text{mol}} = 919.6 \text{Å}^3$ and the $\Delta C$ is $2.29 \times 10^2 \text{mJ/K/mol}$ [11]. Since we find a positive derivative of $dT_C/d\sigma \sim 1 \text{K/kbar}$ for $X=$SbF$_6$ under interplane compression near the ambient pressure, a positive jump in thermal expansion coefficient of $\sim 6 \times 10^{-7} \text{K}^{-1}$ along interplane direction must be relevant at the superconductivity transition. For $X=$AsF$_6$, a smaller jump in the thermal expansion coefficient of $\sim 2 \times 10^{-7} \text{K}^{-1}$ is expected assuming the same value for $\Delta C$. The positive jump in thermal expansion coefficient along interplane direction is opposite to the results of the BEDT-TTF salts [23, 24]. For the in-plane compression, $T_C$ is not sensitive at low pressure region up to 1 kbar. Then we have almost no jump in the thermal expansion coefficient along in-plane directions.

5. Summary
The uniaxial compression dependence of $T_C$ was measured resistively for the two-dimensional organic superconductor $\beta$-(BDA-TTP)$_2X$ [$X=$SbF$_6$, $X=$AsF$_6$]. Under parallel compression, $T_C$
increases gradually up to 3 (X=SbF$_6^-$), 5 (X=AsF$_6^-$) kbar, and decreases under further piston pressure. Under compression perpendicular to the donor stack, $T_C$ decreases gradually up to 2.5 (X=SbF$_6^-$), 4 (X=AsF$_6^-$) kbar and then decreases rapidly under further pressure. Only for X=AsF$_6^-$, a $T_C$ minimum at 3 kbar is found for both directions. The in-plane uniaxial compression dependence on $T_C$ is understood in terms of the dimerized anisotropic triangular-lattice phase diagram. It is found that the $T_C$ peaks a maximum as a function of the $U/W$ and $t'/t$, as a result of the interplay between the enhancement of spin fluctuation and the frustration effect, in the similar way as for the $\kappa$-type BEDT-TTF salts.

$T_C$ increase under interplane compression demonstrates the importance of the interlayer interaction. In view of the Ehrenfest relation, a positive jump in the thermal expansion coefficient is relevant along the interplane direction at the superconducting transition.

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