Charge ordered insulating phases of DODHT salts with octahedral anions and a new radical salt, $\beta''$-(DODHT)$_2$TaF$_6$

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Abstract. Physical properties of isostructural $\beta''$-(DODHT)$_2$X [DODHT = (1,4-dioxane-2,3-diyl)dihydrotetrathiafulvalene; X = PF$_6$, AsF$_6$, and SbF$_6$] at ambient pressure have been compared. The insulating phase of $\beta''$-(DODHT)$_2$PF$_6$ salt has already been revealed to be a charge ordering (CO) state by X-ray diffraction study and magnetic behavior. CO in this salt was also confirmed by the observation of satellite reflections in oscillation photograph using synchrotron radiation. Transport property of $\beta''$-(DODHT)$_2$SbF$_6$ salt was reinvestigated up to the pressure of 3.7 GPa applied by a cubic anvil apparatus. Although the SbF$_6$ salt turned to be metallic above 2.0 GPa, no superconductivity was observed. In order to examine the anion size dependence of DODHT salts with octahedral anions, we prepared a new DODHT salt, $\beta''$-(DODHT)$_2$TaF$_6$, which has the larger counter anion compared with the previous salts. Crystal structure of this salt was isosctructural to the other DODHT salts. The electrical and magnetic properties of this salt were similar to those of $\beta''$-(DODHT)$_2$SbF$_6$ salt.

1. Introduction

Reduced $\pi$-electron donor, DODHT (figure 1(a)), provided pressure-induced superconductors with PF$_6^-$, AsF$_6^-$, and BF$_4^-$ as a counter anion [1, 2]. Crystal structure of all the pressure-induced superconducting salts is $\beta''$-type. Among them, physical properties and electrical state of $\beta''$-(DODHT)$_2$PF$_6$ have been investigated in detail: observation of satellite reflection corresponding to 2-fold superlattice along $a$-axis and magnetic behavior interpreted by 1-dimensional (1-D) alternating Heisenberg model revealed the insulating phase at ambient pressure below 255 K, where a clear transition was observed, to be a stripe-type charge ordering (CO) state along $p$-$q$ direction as shown in figure 1(b) [3]. By applying hydrostatic pressure, the charge ordered insulating phase was suppressed to be metallic at the pressure above 1.14 GPa, and superconductivity emerged above 1.32 GPa at ca. 3

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K. Crystal structure analyses at hydrostatic pressure of 0.75 and 1.9 GPa suggested that one of the ratios between intermolecular nearest neighbor Coulomb interaction energy and the transfer integral, \( V / |t| \), perpendicular to CO stripes plays an important role in suppressing the CO phase [4]. Recently, theoretical calculation for \( \beta''-(\text{DODHT})_2\text{PF}_6 \) using the random phase approximation based on the mean field theory by Kobayashi et al. suggested that, with applying pressure, the insulating state with the CO changes into a metallic state with the weakened CO at an intermediate pressure, and the normal metallic state without CO emerges at higher pressures [5].

Transport and magnetic properties of the other DODHT salts with octahedral anions were quite different from those of \( \beta''-(\text{DODHT})_2\text{PF}_6 \). The \( \text{AsF}_6 \) salt showed superconducting transition under hydrostatic pressure similarly to \( \beta''-(\text{DODHT})_2\text{PF}_6 \), but no superconductivity was observed at the pressure of up to 1.75 GPa for the \( \text{SbF}_6 \) salt [6]. In this paper, we compare the difference of the physical properties among \( \beta''-(\text{DODHT})_2X \) (\( X = \text{PF}_6, \text{AsF}_6, \) and \( \text{SbF}_6 \)). For the charge ordered insulating phase of \( \beta''-(\text{DODHT})_2\text{PF}_6 \), we disclosed the result of X-ray diffraction study using synchrotron radiation. We reexamined the transport property under pressure up to the pressure of 3.7 GPa by a cubic anvil apparatus for \( \beta''-(\text{DODHT})_2\text{SbF}_6 \). We also reexamined the magnetic property for this salt, because there was a problem in purity of the sample and an inadequate treatment for the diamagnetic term in the data reported previously [6]. In order to investigate the anion size dependence on the physical properties and electronic states of DODHT salts with octahedral anions, we newly prepared \( \beta''-(\text{DODHT})_2\text{TaF}_6 \), which has the largest anion size among the DODHT salts with octahedral anions obtained so far.

![Figure 1](image-url)

Figure 1. (a) Molecular structure of DODHT. (b) Schematic representation of the donor arrangement in \( \beta''-(\text{DODHT})_2\text{PF}_6 \) and charge pattern of CO with stripes along p-q direction. Molecules indicated by gray color represent the charge rich sites.

2. Experiment

The \( \beta''-(\text{DODHT})_2X \) (\( X = \text{PF}_6, \text{AsF}_6, \) and \( \text{SbF}_6 \)) salts were prepared according to our reported method [1]. The \( \text{TaF}_6 \) salt was prepared by electrochemical oxidation at a constant current of 0.5 \( \mu \text{A} \) at 25 \( ^\circ \text{C} \) in PhCl containing \( n-\text{Bu}_4\text{NTaF}_6 \). Oscillation photographs were taken with oscillation range of 5\(^\circ\) and exposure time of 10 min using synchrotron radiation of 18 keV at the beam line BL-1B of KEK-PF (High Energy Accelerator Research Organization, Photon Factory). Electrical resistivity was measured using standard dc four-probe method for a single crystal. High pressure measurements were carried out with a cubic anvil apparatus and the Daphne 7373 oil was used as a pressure medium. Magnetic susceptibility was measured for a powder sample using a superconducting quantum interference device (SQUID) magnetometer with 10000 Oe field application. The diamagnetic contribution of the DODHT molecule was experimentally determined to be \( 1.52 \times 10^{-4} \) emu mol\(^{-1} \) and those of anions were calculated using Pascal’s law.
3. Results and Discussion

3.1. Comparison of physical properties of $\beta''$-(DODHT)$_2X$ ($X = PF_6$, AsF$_6$, and SbF$_6$)

All the salts crystallize isostructurally and have the $\beta''$-type donor arrangement. Among the DODHT salts with octahedral anions, $\beta''$-(DODHT)$_2X$ ($X = PF_6$ and AsF$_6$) exhibited superconducting transition under hydrostatic pressure. However, conducting behaviors at ambient pressure were quite different between the PF$_6$ and AsF$_6$ salts: $\beta''$-(DODHT)$_2PF_6$ showed a clear transition to CO insulating phase at 255 K, but that of the AsF$_6$ salt was not clear. On the other hand, the conducting behavior of the SbF$_6$ salt was semiconductive described by the activation-type conduction without any anomaly as shown in figure 2.

Figure 3 shows temperature dependence of magnetic susceptibility of $\beta''$-(DODHT)$_2X$ ($X = PF_6$ and AsF$_6$). The magnetic susceptibility of the PF$_6$ salt showed a broad maximum around 200 K with a small jump at 255 K where the clear insulator transition was observed in the resistivity measurement. Temperature dependence of the magnetic susceptibility was well reproduced by the 1-D $S = 1/2$ alternating Heisenberg chain model, which is reasonably explained by the CO with a stripe-type charge pattern along p-q direction; localized electron spins on the charge rich molecular sites make a 1-D alternating antiferromagnetic chain as shown in figure 1(b). In contrast, a clear inflection point at 240 K and an abrupt drop to nonmagnetic state at 90 K were observed in the magnetic susceptibility of the AsF$_6$ salt. Furthermore, the magnetic susceptibility of the AsF$_6$ salt could not be fitted by the 1-D alternating Heisenberg chain model.

![Figure 2](image1.png)  
Figure 2. Temperature dependence of resistivity of $\beta''$-(DODHT)$_2X$ ($X = PF_6$, AsF$_6$, SbF$_6$, and TaF$_6$) at ambient pressure.

![Figure 3](image2.png)  
Figure 3. Temperature dependence of magnetic susceptibility of $\beta''$-(DODHT)$_2X$ ($X = PF_6$ and AsF$_6$). The solid line is a fit by 1-D alternating Heisenberg model.

3.2. Observation of satellite reflections in CO state of $\beta''$-(DODHT)$_2PF_6$

We have already found that the insulating state of $\beta''$-(DODHT)$_2PF_6$ is the CO phase with a stripe-type charge pattern along p-q direction as shown in figure 1(b). In this CO case, the unit cell becomes double along $a$-axis as indicated by broken lines in figure 1(b). The 2-fold superstructure along $a$-axis was confirmed by the observation satellite reflections at (0.5, 0, 3), (1.5, -1, 1), and (1.5, -1, 2) below the insulator transition temperature by using monochromatized Mo K$\alpha$ X-rays of 30 kV, 40 mA. However, we could not observe superlattice reflections for the AsF$_6$ and SbF$_6$ salts with the same experimental conditions. Thus, we carried out the diffraction experiments by using synchrotron radiation at KEK-PF to clarify the difference of the physical properties of isostructural DODHT salts.
with octahedral anions from the structural point of view. First of all, we measured oscillation photographs for the PF$_6$ salt whose properties and superstructure have already been investigated in detail. The 2a superlattice structure was also confirmed by the X-ray diffraction study using synchrotron radiation. Figure 4 shows the X-ray oscillation photograph of $\beta''$-(DODHT)$_2$PF$_6$ taken at 40 K. Satellite reflections of $q = a^*/2$, indicated by white arrow in figure 4, appeared below the transition temperature to the insulating state accompanied by the CO.

![Figure 4](imageurl)

Figure 4. X-ray oscillation photograph taken at 40 K by using synchrotron radiation at a beam line BL-1B of KEK-PF. Reflections indicated by white arrows are satellite spots of $q = a^*/2$ corresponding to the 2-fold superlattice structure along a-axis.

3.3. **Transport properties under high pressure and magnetic susceptibility of $\beta''$-(DODHT)$_2$SbF$_6$**

As mentioned in section 3.1, conductive behavior of $\beta''$-(DODHT)$_2$SbF$_6$ at ambient pressure is quite different from those of $\beta''$-(DODHT)$_2$X (X = PF$_6$ and AsF$_6$); temperature dependence of resistivity of the SbF$_6$ salt is semiconductive without any distinct anomaly. In contrast, the PF$_6$ salt shows a clear transition to insulator accompanied by CO, and the AsF$_6$ salt is not an activation-type semiconductor and the transition is unclear (figure 2). The PF$_6$ and AsF$_6$ salts undergo superconducting transition

![Figure 5](imageurl)

Figure 5. Temperature dependence of resistivity of $\beta''$-(DODHT)$_2$SbF$_6$ under various pressures from 1.5 to 3.7 GPa.

![Figure 6](imageurl)

Figure 6. Temperature dependence of magnetic susceptibility of $\beta''$-(DODHT)$_2$X (X = SbF$_6$, and TaF$_6$). The solid line is a fit by 1-D alternating Heisenberg model.
under pressure, but no superconductivity was observed at the hydrostatic pressure of up to 1.76 GPa for the SbF6 salt [5]. We examined the transport property of β"-(DODHT)2SbF6 at much higher pressure in the range of 1.5 to 3.7 GPa using a cubic anvil technique. Figure 5 shows the resistivity of β"-(DODHT)2SbF6 as a function of temperature down to 4.2 K under various pressures. At 1.5 GPa, the temperature dependence of resistivity was very weak down to 50 K. Above 1.8 GPa, the SbF6 salt became metallic. A small upturn of resistivity below ca. 10 K was not suppressed even at the pressure of up to 3.7 GPa.

Figure 6 shows temperature dependence of the magnetic susceptibility of β"-(DODHT)2SbF6, which was obtained by subtracting the value of Curie-like impurity and the diamagnetic contributions. The magnetic susceptibility at 300 K was 8.12×10⁻⁴ emu mol⁻¹, which is comparable with the values of the PF6 and AsF6 salts (PF6; 7.68×10⁻⁴ emu mol⁻¹, AsF6; 8.16×10⁻⁴ emu mol⁻¹). Similarly to the PF6 salt, the magnetic susceptibility data are reproduced by 1-D S = 1/2 alternating Heisenberg chain model as shown by the solid line in figure 6. The least-square fit is found for the intrachain exchange interaction parameter J = −204 K and the alternation parameter α = 0.16. Although the similar magnetic behavior to β"-(DODHT)2PF6, interpreted by 1-D alternating Heisenberg chain model, suggests the charge ordered insulating phase for the SbF6 salt, no clear insulator transition was observed in the transport properties. So more detailed study is necessary to clarify the insulating state of β"-(DODHT)2SbF6.

3.4. Crystal structure and physical properties of a new DODHT salt, β"-(DODHT)2TaF6
The transport and magnetic properties of β"-(DODHT)2X (X = PF6, AsF6, and SbF6) are different depending on the size of anions. Preparation of a new DODHT salt with other octahedral anion is important to investigate the anion size effect on the difference of physical properties and electronic state of a series of the DODHT salts with octahedral anions. Thus, we synthesized a new salt, β"-(DODHT)2TaF6, the counter anion of which is the largest size compared with the other salts.

![Crystal structure of β"-(DODHT)2TaF6](image)

Figure 7. Crystal structure of β"-(DODHT)2TaF6. (a) Stacking column of DODHT molecules. Intermolecular distances: d₁ = 3.7249 and d₂ = 4.1247 Å. (b) Donor arrangement viewed from molecular long axis. Dotted lines indicate S···S contacts shorter than the sum of the van der Waals radii (3.70 Å).
Crystal structure of $\beta''$-(DODHT)$_2$TaF$_6$ is shown in Figure 7, indicating this salt is isostructural to the other DODHT salt; the donor arrangement is $\beta''$-type. CrystaL data for $\beta''$-(DODHT)$_2$TaF$_6$ are as follows: C$_{20}$H$_{20}$O$_4$S$_{12}$TaF$_6$. F. W. = 1004.1; triclinic, space group P$ar{1}$, a = 5.6567(10), b = 9.5686(17), c = 15.928(3) Å, $\alpha$ = 72.829(2), $\beta$ = 82.052(2), $\gamma$ = 72.982(2)$^\circ$, V = 786.3 Å$^3$, Z = 1, $R$ = 0.032, $R_w$ = 0.089. Although the anion size of TaF$_6$ is slightly larger than that of SbF$_6$, the cell volume of $\beta''$-(DODHT)$_2$TaF$_6$ is almost comparable to that of the SbF$_6$ salt; CrystaL data for $\beta''$-(DODHT)$_2$SbF$_6$ are as follows: C$_{20}$H$_{20}$O$_4$S$_{12}$SbF$_6$, F. W. = 944.83; triclinic, space group P$ar{1}$, a = 5.6729(5), b = 9.5620(8), c = 15.9023(13) Å, $\alpha$ = 72.9030(10), $\beta$ = 82.011(2), $\gamma$ = 72.8400(10)$^\circ$, V = 786.64 Å$^3$, Z = 1, $R$ = 0.087, $R_w$ = 0.278.

As shown in figure 7(a), donor molecules are stacked in a head-to-tail manner and dimerized with intermolecular distances of $d_1 = 3.7249$ and $d_2 = 4.1247$ Å. Due to the largest anion size of TaF$_6$, intermolecular distances are longest among $\beta''$-(DODHT)$_2$X (X = octahedral anion): X = PF$_6$; $d_1 = 3.5922$ and $d_2 = 3.9104$ Å, AsF$_6$; $d_1 = 3.6213$ and $d_2 = 3.9801$ Å, SbF$_6$; $d_1 = 3.6244$ and $d_2 = 4.0279$ Å. There are several intermolecular S···S contacts shorter than the sum of the van der Waals radii (3.70 Å) between stacks, but no short S···S contact is observed within a stack, which is similar to the other DODHT salts.

Electrical resistivity of $\beta''$-(DODHT)$_2$TaF$_6$ was measured for a single crystal sample. Temperature dependence of the resistivity is displayed in figure 2 together with those of the other DODHT salts. The TaF$_6$ salt exhibited semiconductive behavior without any anomaly. Electrical conductivity at 300 K was 3.94 Scm$^{-1}$ and the activation energy was 97 meV. Conducting behavior of the TaF$_6$ salt is quite similar to that of $\beta''$-(DODHT)$_2$SbF$_6$; the electrical conductivity and activation energy are comparable with those for the SbF$_6$ salt ($\sigma$(300 K) = 2.82 Scm$^{-1}$, $E_a$ = 155 meV). Preliminary measurement of resistivity under pressures of up to 1.58 GPa revealed that no superconductivity exists for $\beta''$-(DODHT)$_2$TaF$_6$ under hydrostatic pressure.

Temperature dependence of the magnetic susceptibility of $\beta''$-(DODHT)$_2$TaF$_6$ is shown in figure 6 together with that for $\beta''$-(DODHT)$_2$SbF$_6$. The magnetic susceptibility at 300 K was 8.28×10$^{-4}$ emu mol$^{-1}$, which is comparable with the values of the SbF$_6$ salt (see section 3.3). The magnetic susceptibility data are also reproduced by 1-D $S = 1/2$ alternating Heisenberg chain model as shown by the solid line in figure 6 to give the intrachain exchange interaction parameter $J = -198$ K and the alternation parameter $\alpha = 0.36$. The transport and magnetic properties of $\beta''$-(DODHT)$_2$TaF$_6$ were very similar to those of the SbF$_6$ salt.

4. Conclusion

We summarized the differences of the transport properties and magnetic behavior among $\beta''$-(DODHT)$_2$X (X = PF$_6$, AsF$_6$, and SbF$_6$) and newly prepared $\beta''$-(DODHT)$_2$TaF$_6$. Among them, the PF$_6$ and AsF$_6$ salts are the pressure-induced superconductors. The charge ordered insulating state with a stripe-type CO pattern along p-q direction of $\beta''$-(DODHT)$_2$PF$_6$ was also confirmed by the X-ray diffraction using synchrotron radiation. Transport properties of $\beta''$-(DODHT)$_2$SbF$_6$ was reexamined at the pressure of up to 3.7 GPa with a cubic anvil apparatus. The SbF$_6$ salt became metallic at 1.8 GPa but no superconductivity was detected up to 3.7 GPa. Magnetic susceptibility of the SbF$_6$ salt was also interpreted by 1-D alternating Heisenberg chain model similarly to the PF$_6$ salt. From the viewpoint of the pressure-induced superconductivity, the PF$_6$ salt is analogous to the AsF$_6$ salt. The magnetic behavior, however, was quite different between these two salts: magnetic susceptibility data of the PF$_6$ salt was well interpreted by 1-D alternating Heisenberg chain model, but the same model could not reproduce the susceptibility data of the AsF$_6$ salt. In contrast, although the magnetic behaviors of the PF$_6$ and SbF$_6$ salts are resemble, applying pressure did not induce superconductivity for the SbF$_6$ salt.

Crystal structure of a newly synthesized $\beta''$-(DODHT)$_2$TaF$_6$ was isoostructural to the other DODHT salts. The conducting and magnetic properties of the TaF$_6$ salt are quite similar to those of $\beta''$-(DODHT)$_2$SbF$_6$. A distinct difference among $\beta''$-(DODHT)$_2$X (X = PF$_6$, AsF$_6$, SbF$_6$, and TaF$_6$) can be
seen in the values of calculated transfer integrals; Transfer integrals are almost comparable among all the salt except for the value of q. The transfer integral q decreases with increasing the anion size (the q value of $\beta''$-(DODHT)$_2$X ($\times 10^{-3}$ eV): X = PF$_6$: –8.14, AsF$_6$: –6.40, SbF$_6$: –4.92, TaF$_6$: –4.83). It is an important subject of continued interest to reveal the insulating state of $\beta''$-(DODHT)$_2$X (X = AsF$_6$, and SbF$_6$) and the effect of the change of intermolecular interaction at q to the insulating phase, in connection with the relationship between CO and superconductivity. Further work using synchrotron radiation and a spectroscopic measurement such as Raman spectroscopy is ongoing.

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