Transport properties of HMTSF-TCNQ up to 8 GPa and a novel hysteresis and quantum oscillatory behavior in magnetoresistance in magnetic field up to 31 Tesla

K Murata, K Yokogawa, JS Brooks, A Kismarahardja, E Steven, M Kano, Y Seno, NR Tamilselvan, H Yoshino, T Sasaki, D Jérome, P Senzier, K Bechgaard, M Uruichi and K Yakushi

1 Graduate School of Science, Osaka City University Sumiyoshi-ku, Osaka, 558-8585, Japan
2 Department of Physics, FSU/NHMFL, Tallahassee FL 32306-4005, USA
3 Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
4 Laboratoire de Physique des Solides, Université Paris–Sud, 91405 Orsay, France
5 H. C. Oersted Institute, Universitetsparken 5, DK 2100 Copenhagen, Denmark
6 Institute for Molecular Science, Okazaki, Aichi, 444-8585, Japan

E-mail: muratak@sci.osaka-cu.ac.jp

Abstract. With the interest of ground state near CDW at low temperature, the electronic properties under high pressure, at low temperature and in high magnetic field of HMTSF-TCNQ are examined. Up to 8 GPa, the overall resistivity-temperature behaviour are unchanged, i.e. broad resistance minimum around 100-150 K and subtle resistance decrease below around 30 K. The pressure insensitive nature is not consistent with previous data. At 1.5 -1.6 GPa, but not at P = 0, a novel hysteretic behaviour and probable quantum oscillations in magnetoresistance are found in a clear form.

1. Introduction

In 1970’s, a quasi-1D (one-dimensional) organic conductor, TTF-TCNQ, i.e. tetrathiafulvalene-tetracyanoquinodimethane, was examined deeply. It is a good metal at 300 K, and on cooling it undergoes metal-insulator transition around 50 K due to the occurrence of CDW (charge density wave). Pressure once enhances CDW up to 19 GPa, and then suppresses CDW. It was recently found by the present authors with using cubic anvil that pressure eventually stabilizes metallic state beyond 9-10 GPa [1]. However, up to now, superconductivity has not been found, although it is proposed.

In 1980, superconductivity was firstly found in an organic material, (TMTSF)_{2}PF_{6}, where TMTSF is a tetramethyltetraselenafulvalene. This material is also a good metal at 300 K, and undergoes metal-insulator transition around 12 K but due to SDW (spin density wave) in contrast to CDW in TTF-TCNQ. By a small pressure of 0.6 GPa, the insulating SDW state is suppressed and the superconductivity appears [2].
Between the two families of TTF-TCNQ and (TMTSF)$_2$PF$_6$, number of materials were examined to find superconductivity by utilizing pressure. However, in the late 1970’s, refined hydrostatic high pressure technique reaching 8 GPa has not been well-developed. We are very much interested in revisiting those succeeding materials of TTF-TCNQ, which were once studied, just before reaching (TMTSF)$_2$X-salts, since new electronic phases including superconductivity are expected in the non-explored pressure region beyond around 3 GPa. The present material, HMTSF-TCNQ is one of those salts thought to be bridging between the two families, where HMTSF is hexamethyltetraselenafulvalene. X-ray diffuse streaks are already seen at 300 K indicating the precursor of CDW like TTF-TCNQ [3]. This material shows the highest conductivity at least at that time at 300 K, 1379-2178 S/cm [4]. However, no clear metal-insulator transition temperature is observed in the temperature dependence of resistivity because of the broad resistance minimum around $T_{\text{min}} \sim 50 – 100$ K depending on samples. Specific heat and magnetic susceptibility indicate the existence of phase transition at 32 K[5,6]. Compared with TTF-TCNQ, at least two structural differences are pointed out. One is that both TTF and TCNQ donors are planar, while HMTSF is not and structural disorder is present. And the other is that HMTSF- and TCNQ-columns are not separated in a way of sheet. One HMTSF-column is surrounded by four TCNQ-columns, and one TCNQ-column is surrounded by four HMTSF-columns, i.e. alternate stacking is realized in HMTSF-TCNQ.

By these backgrounds, we are motivated to revisit the properties of HMTSF-TCNQ to see the ground state in the higher pressure region above 3 GPa. We are also interested in the Fermi surface pocket, if present around 1.5 GPa, since the discussion of the pocket is given the previous works experimentally [6] and theoretically[7]. The purpose of the present paper is to show 1) the properties up to 8 GPa in the temperature region down to 2 K and 2) the properties in high magnetic field up to 31 T at 1.5-1.6 GPa.

2. Temperature dependence of resistance and its pressure dependence

Figure 1 shows the temperature dependence of resistance under various pressures, studied with cubic anvil with the pressure medium, Daphne 7373 [8,9,10]. Resistance is measured along the 1D( $b$-) axis. At ambient pressure, it exhibits a resistance minimum around 100 K (now shown) and is not much different from other higher pressure in the overall behaviour. This data is not consistent with the previous report by Cooper et al. of resistivity vs temperature under pressure up to 1.9 GPa [11,12]. According to Cooper, the resistance upturn at low temperature vanishes already at 1.4 GPa. However, our measurement always showed resistance upturn up to 8 GPa, which is the maximum pressure we studied. We note another discrepancy with the previous report, which is the charge transfer ratio, $\rho$. Weyl et al. reported that $\rho$ is 0.74 based on the X-ray diffuse streak at 300 K [3]. We checked the charge transfer ratio by Raman method at the Institute for Molecular Science, and found that it is $\rho = 0.64 \pm 0.06$ (5 K) for HMTSF-TCNQ, but the value for 300 K was not obtained successfully. In the same measurement, $\rho = 0.63 \pm 0.06$ (300 K) and $\rho = 0.59 \pm 0.06$ (5 K) for TTF-TCNQ is obtained, which reproduce the commonly accepted values at least for 5 K, which confirms the validity of this Raman measurement. We also checked lattice
constants and confirmed no essential difference from the old data of Phillips [13], claiming monoclinic, though nearly orthorhombic.

Possible origin of discrepancies in \( \rho \) and the temperature dependence of resistivity is that the crystals are aged. We used the crystals of almost 30 years old kept at the shelf in Orsay, France. However, rather benefited by the comparison in data, we are favored to discuss the nature of resistance upturn at low temperature. If it is totally governed by the partial lost of Fermi surface due to nesting by CDW stabilization, resistance upturn at low temperature may be suppressed by pressure as high as 8 GPa as TTF-TCNQ [1]. Therefore even at ambient pressure, resistance upturn may not be due to Fermi surface nesting, rather due to some disorder arising from the bending disorder of non-planar HMTSF or other reason. The transition takes place at 30 K seen by magnetic and specific heat measurements [5,6], where resistance anomalies in \( d\rho/dT \) or \( d\log\rho/dT \) are not obvious, but from where very subtle resistance decrease starts by lowering temperature.

In the case of TTF-TCNQ, the M-I (metal-insulator) transition temperature is well-defined by the clear divergence of \( d\rho/dT \) or \( d\log\rho/dT \) even up to 8 GPa[1], while in the present material, HMTSF-TCNQ, it is quite dull even at \( P = 0 \). The broad minima of resistivity against temperature sweep reminds us of the charge ordered states, which is commonly observed in (TMTTF):X family. However, charge disproportionation requires a quarter-filled band, in the present case of HMTSF-TCNQ, charge transfer ratio in 0.64, which may vary with pressure. The present results show the \( R \) vs \( T \) behavior is rather unchanged with pressure. So, charge ordering is not likely.

3. The properties in magnetic field under pressure of 1.5 - 1.6 GPa

By a careful reading the \( R \) vs \( T \) behavior, the resistivity slightly decreases by lowering temperature below the broad resistivity peak, implying the existence of Fermi surface at low temperature, which is also mentioned in the previous report, where the values of 7.2 x 10^{12} \text{ cm}^{-2} (0.9 GPa), and 1.5 x 10^{13} \text{ cm}^{-2} (1 GPa) for the Fermi surface pocket[6]. We were motivated to examine the electronic properties under pressure of 1.5 – 1.6 GPa. We started to study at Tokoku University and then in Tallahassee in Florida in magnetic field up to 31 T and temperature down to 0.5 K.

Three samples are placed in a piston cylinder with the pressure medium Daphne 7373, so that reproducibility check is very easy by comparing the data from different samples in the same cell. The samples’ shape is rectangular and fixing the orientation of the sample is easy. In Tohoku university, we put samples’ plate perpendicular to the axis of the piston-cylinder, i.e. magnetic field is perpendicular to the plate-like surface of the sample. This direction is parallel to the crystallographical \( a \)-axis. No quantum oscillations are observed, instead we observed a positive magnetoresistance with some kink at 14 Tesla.

Further examination towards higher field and lower temperature was strongly motivated. Actually, experiment to the field of 31 Tesla and to a temperature of 0.5 K was performed at Tallahassee. One day experiment was devoted to \( H // \) plane (\( H // c \)-axis) configurations, other day with \( H \perp \) plane (\( H // a \)-axis) with multiple samples at the same time.

As expected, or more than expected, the experiment carried out in Tallahassee made some symptom of phenomena to a highly clarified ones. Eventually, oscillations were observed as shown in Fig. 2, not with \( H \perp \) plane but with the \( H // \) plane (\( H // c \)-axis) configurations. Observing quantum oscillation by \( H // \) plane (i.e. plane of the outside-shape of the crystal) configuration is very exceptional but is
consistent with the orientation of sample axis which Weger proposed, who calculated cylindrical Fermi-surfaces of hole and electron.

What happens with $H \perp \text{plane}$ (i.e. $H//a$-axis) configuration? Clear kink in magnetoresistance was observed, i.e. positive magnetoresistance becomes more steeper passing through 14 Tesla, which became more pronounced below 1.5 K (not shown). Therefore oscillatory ($H//\text{plane}$, i.e. $H//c$-axis) or just a kink ($H\perp\text{plane}$, i.e. $H//a$-axis) behavior is of orbital origin.

What is remarkable is that hysteretic behavior against field sweep is observed in both configurations of field orientation relative to sample axes. This hysteresis, which becomes obvious below 2-1.5 K and above 14 Tesla, is not like that based on the high-field and low-field states. In Fig. 1, two oscillating curves are shown, corresponding to upward (top curve) and downward (bottom curve) sweeps. The hysteresis loop apparently looks against the usual hysteresis. (Imagine the $M-H$ curve in magnetization!) When the field is reduced on the way below 31 Tesla, resistance takes a new path without tracing the path of upward sweep, instead it crosses in between the top and bottom curves. When the down sweep of the field is wide enough, the resistance passes reversibly along the traversing straight line. It is the same for the sweep of traverse from bottom curve and top curve. So long as the upward sweep of traverse does not well touch the top curve, downward sweep on the way of crossing traces back the traversing line. These phenomena are common to both $H//\text{plane}$ and $H\perp\text{plane}$ configurations. Therefore the hysteresis-like phenomena are not of orbital origin, which reminds me of one example reported in the two-dimensional $\tau$-organic conductor [14], but whose hysteresis-loop direction is conventional.

Finally we note that although $R-T$ curves looks similar between $P = 0$ and 1.5-1.6 GPa, the oscillatory behavior as well as hysteretic behavior are not observed at $P = 0$. The origin of these phenomena is open.

4. Summary
We presented the electronic properties under high pressure, in low temperature and at high magnetic field of HMTSF-TCNQ. Up to 8 GPa, the overall resistivity-temperature behaviour are unchanged, i.e. broad resistance minimum around 100-150 K and subtle resistance decrease below around 30 K. Comparing the present and previous reports on the $R$ vs $T$ behaviour, it is implied that the origin of low temperature resistance upturn might not be due to CDW stabilization. A novel hysteretic behaviour and probable quantum oscillations in magnetoresistance are found at 1.5 -1.6 GPa, but not at $P = 0$. Detailed analysis is under way.

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