High-pressure transport study of a charge-transfer salt based on Cytosine and TCNQ using a diamond anvil cell

Masafumi Sakata1, Mitsuhiko Maesato1*, Takafumi Miyazaki2, Kazukuni Nishimura1, Tsuyoshi Murata1, Hideki Yamochi3,4, Gunzi Saito1,3

1Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto, 606-8502, Japan.
2Graduate School of Science, Graduate School of Science and Engineering, Ehime University, Matsuyama, 790-8577, Japan.
3Research Center for Low Temperature and Materials Sciences, Kyoto University, Kyoto, 606-8501, Japan.
4ERATO “Non-equilibrium Dynamics Project”, JST.

*E-mail: maesato@kuchem.kyoto-u.ac.jp

Abstract. Transport properties of a strongly correlated organic conductor (CHC+)TCNQ− were examined under high pressures up to about 7 GPa using a diamond anvil cell, where CHC+ denotes hemiprotonated cytosine pair and TCNQ represents 7,7,8,8-tetracyanoquinodimethane. This salt is a highly conductive semiconductor as a fully ionic TCNQ salt with the activation energy \( E_a \) of 0.14 eV at ambient pressure. Application of high pressure gradually increased the conductivity. The \( E_a \) decreased monotonically by a rate of 0.013 eV/GPa.

1. Introduction

High pressure application is one of the powerful methods for the study of electronic states and search for novel electronic states in solid. In the field of organic conductors, most of the high pressure studies have been performed using clamp-type piston cylinder cell, which is convenient and can generate up about few GPa [1]. However, much more pressures are needed for the study of strongly correlated systems. For example, the highest superconducting transition temperature for the organic superconductors was reported in a Mott insulator \( \beta'-(ET)_2ICl_2 \) under very high pressure of 8 GPa using cubic anvil cell [2]. The cubic anvil cell can generate hydrostatic pressures up to around 10 GPa, however it costs and requires rather big apparatus. The diamond anvil cell (DAC) can generate extremely high pressure of the order of 100 GPa rather easily. However, there are many difficulties in measuring conductivity of fragile organic conductors using DAC: The sample space and, therefore, the sample should be small and electrical leads should be isolated from metal gasket and connected to the tiny sample. The deformation of gasket is necessary to generate pressure, but it may cause a trouble to the electrical isolation of electrical leads and sample, and also may cause damage to electrical contacts or sample itself. In spite of these difficulties, the use of DAC is attractive because DAC is compact and generate ultra high pressures. Therefore, it is suitable for the experiments under multi extreme conditions, such as the combination with very low temperatures and high magnetic field. Utilizing the DAC, we have investigated transport properties of a strongly correlated organic conductor (CHC+)TCNQ−.
Recently, charge transfer salts based on cytosine (C) and TCNQ derivatives are developed [3,4]. The (CHC⁺)TCNQ⁻ is obtained by the reaction of TCNQ and C in the presence of methanol (MeOH). Despite the weak electron-donating ability of C, it can form complex with TCNQ, since C is a good proton accepter. A mechanism is proposed to explain the generation of radical anion of TCNQ and the complex formation [4].

Fig. 1(a) and (b) shows the molecular structure of CHC⁺ and crystal structure of (CHC⁺)TCNQ⁻, respectively. The most characteristic feature of this compound is multiple hydrogen bonds (HBs): There are triple self-complementary HBs in CHC⁺, double complementary HBs between neighboring CHC⁺s forming one-dimensional ribbon structure, and HBs between the cytosine and TCNQ. These HBs enable TCNQ to stack regularly with a short interplanar distance (d = 3.14 Å at 200 K) and prevent the lattice distortion inherent to one-dimensional electronic structure down to 10 K. Magnetic properties are, however, inconsistent with the uniform structure and the ground state is not fully understood. The details are discussed in the chapter 3. To the best of our knowledge, this compound is the most conductive one based fully ionic TCNQ (3×10⁻² Scm⁻¹ at room temperature with the activation energy Eₐ of 0.14 eV) [3,4]. The conducting property motivated us to study the high pressure effects on this compound and search for novel electronic states such as superconductivity.

2. Experimental
Black plate single crystals of (CHC⁺)TCNQ⁻ was prepared by slow diffusion of C and TCNQ in the MeOH-acetonitrile mixed solvent. Our DAC method is essentially the same as the one reported by Adachi et al.[5] The upper diamond anvil was doubly beveled, while the lower one was not beveled. The culet size of the anvil was 1 mm. The tension-annealed stainless steel SUS304TA with the thickness of 0.4 mm was used as a metal gasket. It was pre-pressed prior to use by applying about 60% of the expected maximum pressure of the experiments. The size of crystal used in this study was 0.24 × 0.1 × 0.03 mm³. The annealed gold wire of 10 µm in diameter was used as electrode. Four gold wires were attached to the single crystal using carbon paste. After attaching the electrodes, the sample surface was coated with thin layer of enamel to prevent wires from being removed while handling. The sample was inserted in the hole of metal gasket (φ = 0.5 mm) together with a small piece of Ruby as a pressure gauge. It is necessary to isolate electrodes from metal gasket. Therefore, four grooves were made on the metal gasket, and top surface of which was covered with insulating layer prepared using a mixture of alumina powder and epoxy adhesive. Then, electrodes were put into the grooves.
We used Daphne oil 7373 as the pressure medium. Pressure was applied at room temperature and determined by monitoring the shift of Ruby fluorescence lines using the relation of $d\lambda/dP = 0.364$ nm/GPa for R1 lines, where $\lambda$ is wavelength and $P$ is pressure [6]. The pressure calibration at low temperature was no performed.

3. Results and discussion

Fig. 2 shows the temperature dependence of resistivity of (CHC$^+$)TCNQ$^-$ under the pressures of 2.10, 4.08, and 6.95 GPa. The resistivity was monotonically suppressed by applying high pressure.

![Fig. 2. Temperature dependence of resistivity of (CHC$^+$)TCNQ$^-$ under the pressures of 2.10 GPa (black), 4.08 GPa (red), and 6.95 GPa (green). The inset shows a picture of the measured single crystal in the diamond anvil cell under pressure.](image)

Fig. 3. Arrhenius plot of resistivity under pressures (a). The pressure dependence of activation energy (b).
Fig. 3 (a) shows the Arrhenius plot of the resistivity. The temperature dependences are well described by the Arrhenius model in the whole temperature range. The activation energy $E_a$ at each pressure was evaluated by the Arrhenius plot, and plotted as a function of pressure in Fig. 3 (b). It clearly indicates that $E_a$ is monotonically decreased with increasing pressure by a rate of 0.013 eV/GPa. Therefore, the energy gap of electrons is monotonically reduced by pressure, and no distinct phase transitions appear up to 7 GPa. Such behavior is reasonably explained by the increase of bandwidth by the pressure.

Based on the structural and transport properties, the salt is considered to be a Mott insulator, since the Coulomb repulsion between two electrons on the same TCNQ molecule U is considerably larger than the transfer energy of t, and TCNQ forms uniform columns. Therefore, it is expected to show one-dimensional Heisenberg antiferromagnetic behavior. However, the magnetic properties cannot be explained by this scenario. The temperature dependence of spin susceptibility showed an activated behavior above 200K, which is explained by the singlet-triplet excitation model [3,4]. At low temperatures below about 150 K, paramagnetic behavior due to minority spins was observed, and the EPR parameters reminded us a random-exchange Heisenberg antiferromagnetic chain model [4]. These results suggest the spin-singlet state of majority spins, although the lattice dimerization is hardly seen in the X-ray structural investigation down to 10 K.

The $a_g$ vibration modes of TCNQ are known to be sensitive to lattice distortion [7,8]. They appear in the reflectance spectra of (CHC+)$\text{TCNQ}^-$ and develop with decreasing temperature as seen in the supporting information of Ref. 4. These results suggest that local dimeric displacements exist but are fluctuated or randomly distributed in the TCNQ columns. It is considered that the robust and multiple HBS play a key role to suppress long range ordering of dimerization, in other words, spin-Peierls transition. In the present study, we found no anomaly in the temperature dependence of resistance under pressures as well as at ambient pressure, indicating that no magnetic transition occurs at least up to 7 GPa in the whole temperature range investigated.

By extrapolating the value of $E_a$ to the horizontal axis in Fig. 3 (b), the gap is expected to vanish at around 10 GPa or above. Thus, a half-filled band metal will be realized under extreme pressures above about 10 GPa in this salt.

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