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Highly Conducting 1:1 Radical Cation Salts: (DMTSA)X With X = NO_3 and BF_4

Kazushige Kawabata [a] , Motoki Yanai [a] , Takashi Sambongi [a] , Yoshio Aso [b] , Kazuo Takimiya [b] & Tetsuo Otsubo [b]
[a] Dept. of Physics, Hokkaido Univ., Sapporo, 060, JAPAN
[b] Dept. of Applied Chemistry, Hiroshima Univ., Higashi-Hiroshima, 724, JAPAN

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HIGHLY CONDUCTING 1:1 RADICAL CATION SALTS: (DMTSA)X WITH X = NO_3 AND BF_4

KAZUSHIGE KAWABATA, MOTOKI YANAI and TAKASHI SAMBONGI
Dept. of Physics, Hokkaido Univ., Sapporo 060, JAPAN

YOSHIO ASO, KAZUO TAKIMIYA and TETSUO OTSUBO
Dept. of Applied Chemistry, Hiroshima Univ., Higashi-Hiroshima 724, JAPAN

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Abstract (DMTSA)NO_3 and -BF_4 show high conductivity at room temperature, in spite of fully ionic salt of 1:1 stoichiometry with uniform segregated stack column structure. DMTSA denotes 2,3-dimethyltetraselenoanthracene. The NO_3 salt is semiconducting below room temperature, and the BF_4 salt is metallic above 220 K and semiconducting at lower temperatures. We found that their magnetic susceptibility is paramagnetic and independent of temperature from 300 K down to 10 K in common. The obtained magnetic property can not be attributed to conduction electrons but discussed in terms of Mott insulating state. Furthermore, high pressure experiment reveals that the NO_3 salt is not semiconducting but rather semi-metallic, and more that the BF_4 salt shows a small conductive anomaly around 70 K and maintains metallic at low temperatures under the pressure of 0.5 GPa.

Keywords: organic metal, Mott insulator, DMTSA, magnetic property, electron correlation

INTRODUCTION

Coulomb interaction between electrons plays an important role to conducting and magnetic property of low dimensional systems such as organic conductors or high Tc oxide superconductors. Especially it is expected to induce a strong effect to electronic properties, in the case that a system has one conducting carrier per a site. Such a system has a half filled conduction band and is a metal as electron correlation is weak. However, when the interaction energy is larger than electron transfer energy, carriers will be localized on each site, that is, a Mott-Hubbard insulating state is stabilized according to the Hubbard model.[1] Fully ionic organic complexes of donor : acceptor = 1:1 with uniform segregated column are considered in this case.

There are many fully ionic organic complexes of 1:1 stoichiometry, but most of them do not have uniform segregated stack columns in crystal structure and mixed stack ones or segregated stack ones with isolated dimers. In these cases, there is no electronic

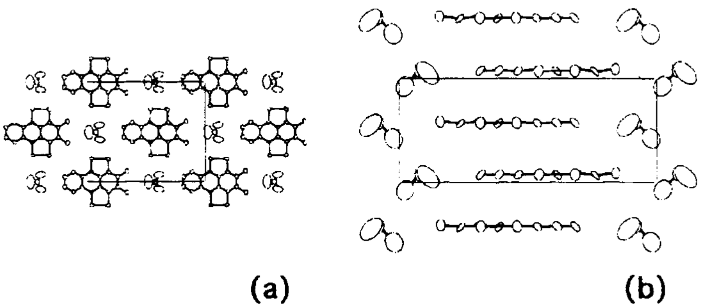

FIG. 1. Crystal structure of (DMTSA)X projected along the c-axis (a) and along the a-axis(b).

TABLE 1 Crystal data of (DMTSA)NO3 and -BF4

	(DMTSA)NO3	(DMTSA)BF4
Crystal system	Orthorhombic	Orthorhombic
Space group	*Cmc21*	*Cmcm*
a/nm	1.3787(1)	1.3922(1)
b/nm	1.6331(1)	1.6454(1)
c/nm	0.6677(1)	0.67087(6)
Z	4	4

band structure and they are insulating.[2] Some complexes have uniform segregated stack columns with electronic band structure and is a Mott-Hubbard insulator as expected theoretically[3] Recently, there are several reports on existence of highly conducting complexes of 1:1 stoichometory with uniform segregated stack columns; δ-(BEDT-TTF)I_3(TCE)$_{1/3}$,[4] (TTM-TTP)I_3[5] and the present DMTSA system[6]. These complexes are expected that charge transfer is complete from cation to anion molecule because of fully ionic anion molecules. It is still not clear why these exhibit such a high conductivity, and then they have been examined in detail.

Radical cation salts of anthra [1,9-cd:4,10-c'd'] bis [1,2] dichalcogenoles were introduced as a new family of conducting charge transfer complexes.[7] DMTSA and DMTTA are promising donor molecules to synthesize high conducting materials, where DMTSA and DMTTA denote 2,3-dimethyl-tetraselenoanthracene and -tetrathio-anthracene, respectively. Especially, (DMTSA)NO_3 and -BF_4 show conductivity as high as 7 and 90 S/cm at room temperature, respectively.[6] These crystal structures are isostructure; orthorhombic and uniform segregated stack column, as shown in Fig. 1.[7] The system is considered as quasi-one dimensional band structure, because of highly anisotropic intermolecular distances between DMTSA molecules. The present 1:1 radical cation salts of (DMTSA)NO_3 and -BF_4 are considered as completely charge transfer complexes because of full ionization of anion molecules of

NO_3^- and BF_4^-. On the other hand, the on-site Coulomb energy of DMTSA molecule is expected to be comparable with that of other organic conductors from redox potential.[6] Then it is considered naturally that the present system will be a Mott insulator. However, this is highly conducting and then we consider that the present system is a good candidate for investigate conducting property with strong electron correlation.

In this work, we report that electric and magnetic properties of (DMTSA)X (X = BF_4 and NO_3) in detail. High pressure experiments reveal that the BF_4 salt is a new organic metal under 0.5 GPa.

EXPERIMENTAL

Single crystals of (DMTSA)NO_3 and -BF_4 were grown by the standard electrochemical growth method. Tetrabutylanmonium-NO_3 for the NO_3 salt and -BF_4 for the BF_4 salt and $C_2H_3Cl_3$ were used as electrolytes and solvent, respectively. The single crystals show a similar morphology and are black needle in shape and a typical dimension of the examined crystals is 3 x 0.05 x 0.05 mm^3. The needle axis of both salts is the c-axis. The crystal symmetry and the lattice parameters were assigned by using X-ray oscillation and Weissenberg methods. Its stoichiometry and no contamination of solvent molecule were confirmed by compositional analysis within experimental accuracy of 5 at%, where chemical compositional analysis was carried out for C and H atoms and electron probe microanalysis for Se and Cl atoms.

Electrical conductivity of a single crystal was measured by four-probe dc method. Magnetic susceptibility was obtained by using a superconducting quantum interference device. On the magnetic measurement, 20 mg of the crystals for the NO_3 salt and 15 mg for the BF_4 salt were used and their orientations were random in a basket. Constant magnetic field of 5 T was applied for measuring temperature dependence of magnetic susceptibility. Field dependence of magnetization was measured at 5 K. The basket was made of Stycast 1266 and its magnetization was measured separately just before each measurement for the crystals in order to avoid impurity contamination and to examine a small magnetization of the crystals precisely.

Pressure was generated by a 30 ton press with a piston-cylinder apparatus in which the sample was enclosed in a Teflon cell. The pressure was applied at room temperature and the apparatus was cooled down to liquid He temperature. The pressure load was automatically controlled constant during both cooling and heating processes in order to perform experiments under constant pressure.

RESULTS AND DISCUSSION

(DMTSA)NO3

Figure 2 shows the temperature dependence of conductivity along the needle axis at ambient pressure and under several pressures. At ambient pressure, the salt has high conductivity of 7 S/cm at room temperature and is semiconducting with an small activation energy of 0.08 eV. When the pressure is applied, the temperature dependence tends to be gradual at low temperatures. This suggests that the electronic

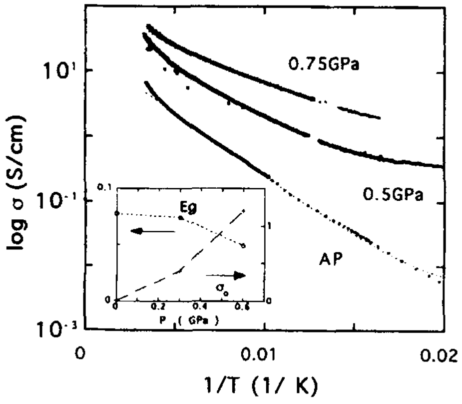

FIG. 2 Temperature dependence of the conductivity of (DMTSA)NO3 at ambient pressure and under several constant pressures. The broken line is the best fit to the eq.1 for the result at ambient pressure. Inset shows pressure dependence of Δ and σo obtained by the fitting.

structure of the NO3 salt is not semiconducting but rather semi-metallic. The temperature dependence curves both at ambient pressure and under the high pressures are reproduced well by a following expression.

$$\sigma(T) = a \exp(-\Delta/kT) + \sigma_0 \qquad (1)$$

where a, Δ, k and σ_0 are a constant, an activation energy, Boltzmann constant and temperature independent conductivity, respectively. The fitting parameters of Δ is lowered and σ_0 increased steeply with increasing pressure. Such a pressure dependence is also understood in terms of semi-metallic characteristic feature, that is, overlapping between conduction and valence bands is very small at ambient pressure and sensitive to pressure, and then increases steeply with increasing the pressure.

Figure 3 shows the temperature dependence of magnetic susceptibility, $\chi(T)$, after subtraction of core diamagnetic ones of the donor and the acceptor molecules. Core diamagnetic susceptibility of DMTSA was measured separately at room temperature and estimated at -1.9×10^{-4} emu/mol. The tabulated value of -2.0×10^{-5} emu/mol was used as that of NO_3^-.[8] The $\chi(T)$ of the sample is 1.2×10^{-4} emu/mol around room temperature and shows a Curie-like increase at lower temperatures. On the other hand, the magnetization was measured at 5 K in order to clarify an origin of Curie-like behavior. It depends linearly on the magnetic field and tends to saturate at higher field. This magnetization curve can be reproduced well by Brillouin function, and then content and total angular momentum of localized spins in the crystals can be estimated at 7×10^{19} /mol and 2.5, respectively. Since the content of localized spins corresponds to about 0.01 at.% in the crystals, Curie-like behavior is attributed to impurity. In Fig. 3, $\chi(T)$ after subtracting the estimated Curie paramagnetic one is replotted against temperature. It is found that (DMTSA)NO3 shows paramagnetic susceptibility of 1.0×10^{-4} emu/mol which is almost independent of temperature.

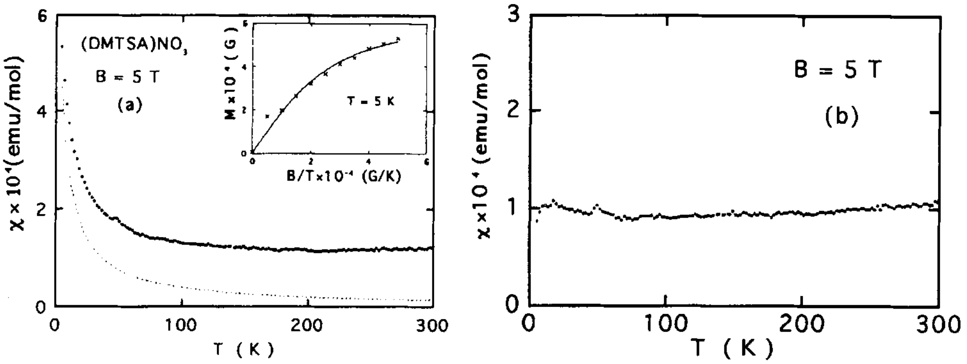

FIG.3. Temperature dependence of the susceptibility of the NO_3 salt. The broken line is impurity contribution estimated from field dependence of magnetization. Inset shows field dependent magnetization at 5K. The solid line is the best fit to Brillouin function.(a) Resultant susceptibility of the NO_3 salt after subtracting Curie paramagnetic one.(b)

Since zero value on magnetization measurements is generally sensitive to instrumental error or subtracting procedure of core diamagnetic one, we confirm that the observed $\chi(T)$ is intrinsic of the crystals by means of same magnetic measurement for other crystal (DMTSA)$_2$Cl, which is carried out by using the same instrument and subtracting procedure. (DMTSA)$_2$Cl consists of the same donor molecule DMTSA but undergoes a metal-insulator transition at 240 K.[9] In this crystal, $\chi(T)$ corresponding to carrier density was observed at room temperature and decreases steeply below 240 K and goes to zero value within experimental accuracy of 1×10^{-6} emu/mol at lowest temperature. Then, we conclude that $\chi(T)$ of (DMTSA)NO_3 is almost temperature-independent over the examined temperature range.

This crystal is expected to have quasi-one dimensional electronic band from the anisotropic crystal structure, as mentioned above. Assuming that the present system is Mott insulator, magnetic property can be considered as one dimensional Heisenberg magnets. In this case, $\chi(T)$ was calculated by Bonner and Fisher.[10] They suggest that $\chi(T)$ shows a small monotonous decrease below room temperature when exchange interaction is very strong. The obtained temperature independent $\chi(T)$ and semiconducting behavior can be explained qualitatively by this model.

(DMTSA)BF4

Figure 4 shows temperature dependence of conductivity along the needle axis at ambient pressure and under several pressures. The conductivity is as high as 90 S/cm at room temperature even at ambient pressure. Its temperature dependence is metallic above 220 K and becomes semiconducting at lower temperatures. Some jumps are observed in this curve but these often occur on cooling or heating crystals. Since such a conducting jump are frequently observed in low dimensional organic conductors, these are not related to conducting change around 220 K in the present system. When the pressure of 0.5 GPa is applied, a small conductive anomaly appears at about 50 K and the crystal maintains metallic down to 10 K which is the present experimental limit.

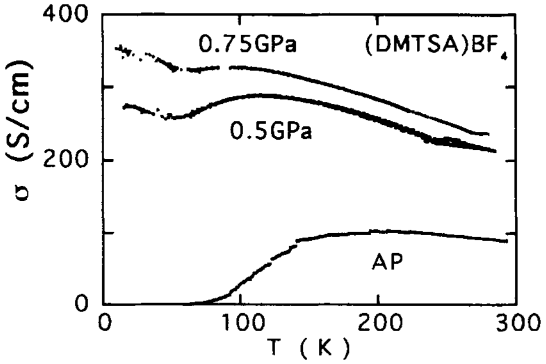

FIG.4. Temperature dependence of the conductivity of (DMTSA)BF4 at ambient pressure(AP) and under the constant pressures of 0.5 GPa and 0.75 GPa.

Magnitude of the anomaly is suppressed to some extent with increasing pressure. Although its origin for the small anomaly is not still clear, the crystal achieves metallic conduction at low temperatures. Thus (DMTSA)BF_4 is a new organic metal.

Magnetic susceptibility is plotted against temperature under constant magnetic field of 5 T in Fig. 5, where the data are subtracted by the core diamagnetic ones of -1.9 x 10^{-4} emu/mol for DMTSA and -3.9 x 10^{-5} emu/mol for BF_4^-. The $\chi(T)$ is 4.1 x 10^{-4} emu/mol around room temperature and shows Curie-like behavior at lower temperatures. The observed $\chi(T)$ can be separated to Curie-like behavior and temperature-independent ones as in the case of (DMTSA)NO_3. The content of localized spins in the crystals can be estimated at 7 x 10^{19} /mol from the obtained Curie constant, assuming its total angular momentum is 1/2. Since the content corresponds to about 0.05 at.% in the crystals, the observed Curie-like behavior is attributed to impurity. In Fig. 5, the resultant $\chi(T)$ after subtracting core diamagnetic and Curie-like ones is replotted as a function of temperature. The BF_4 salt shows almost temperature independent paramagnetic $\chi(T)$ of 4.0 x 10^{-4} emu/mol down to 10 K and more there is no break around 220 K at which the temperature dependence of conductivity changes from metallic to semiconducting. This value of 4.0 x 10^{-4} emu/mol is enough large, in comparison with experimental accuracy of 1 x 10^{-6} emu/mol.

The magnitude of the observed $\chi(T)$ is comparable with ones of organic metals such as $(TMTSF)_2AsF_6$,[11] which is originated to conduction electrons. Then the observed $\chi(T)$ may be explain by Pauli paramagnetism. However, it is ruled out because there is no break of $\chi(T)$ around 220 K where the conductivity changes drastically from metallic to semiconducting. On the other hand, it should be noted that the magnetic behavior of the BF_4 salt is quite similar to that of the NO_3 salt, except for the magnitude of $\chi(T)$. Then the magnetic property of the BF_4 salt may be ascribed to Mott insulating state. Magnetic behavior calculated by Bonner-Fisher model for 1-D Heisenberg magnet is in qualitative agreement with the present results, although the system is treated as a completely localized state in this model. Recently, electron spin

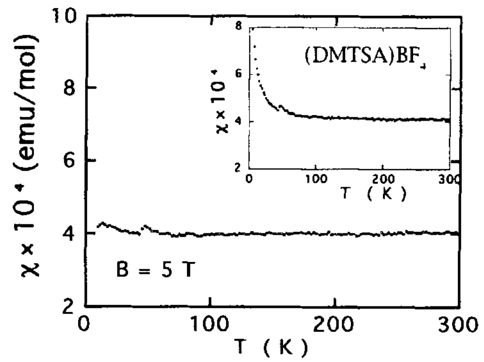

FIG. 5 The resultant susceptibility of the BF_4 salt after subtracting the Curie paramagnetic one. Inset shows temperature dependence of the susceptibility of the BF_4 salt before subtraction.

resonance experiment for κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$ shows that a small number of carriers arising from defects gives so large effect to conducting property of Mott insulators but does not to its magnetic property.[12] In the present system, there is no anomaly in $\chi(T)$ around 220 K, that is, the observed $\chi(T)$ in metallic state coincides to that in semiconducting one around 220 K. The present salt may be the above Mott insulator, if it should be possible that both temperature dependence and magnitude of $\chi(T)$ of a Mott insulator coincide those with a small amount of carriers. If it is in this case, difference of magnitude of $\chi(T)$ between the NO_3 and the BF_4 salts may be ascribed to that of exchange interaction between localized spins. However, we can not conclude whether the present system is in this case or not, since there is a possibility that the BF_4 salt is a metal with strong correlation around room temperature. In the case, we should, furthermore, compare magnetic properties between a Mott insulator and a metal with strong correlation at 220 K. In order to clarify origin for the observed magnetism and high conductivity of the present system, further experimental and theoretical investigations are needed.

CONCLUSION

The conductivity of $(DMTSA)NO_3$ is semiconducting and the BF_4 salt is metallic above 220 K and semiconducting at low temperatures at ambient pressure. We found that both crystals exhibit a similar temperature-independent paramagnetic susceptibility down to 10 K while their conducting properties are quite different. The observed paramagnetic susceptibility may be attributed not to Pauli paramagnetism but to Mott insulating state. High pressure experiments reveal that the NO_3 salt is semi-metallic and the BF_4 salt is metallic with a small conductive anomaly around 70 K under the pressure of 0.5 GPa. These results support that DMTSA family is a very promising material to synthesize highly conducting complexes and to investigate electron correlation effect in conducting system.

Dedication- It is a great pleasure to dedicate this paper to Professor Fumio Ogura and Professor Yusei Maruyama. The author (K.K) would like to express great thanks Prof. F. Ogura and Prof. Y. Maruyama for many valuable personal communications over many years.

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