IV-N Systematic Study of Organic Conductors

Thanks to the systematic view to structure-property relationship studied particularly in BEDT-TTF-based conductors, recently our understanding of organic conductors has made a great progress. From the concept of "universal phase diagram" in the θ-phase, we can predict metal-insulator transition temperatures of a large number of organic conductors. This kind of concept is generalized to δ-phase salts, that have twisted overlaps. Examining symmetry-property relationship in organic conductors, we can extract a general rule that magnetism of insulator phases is paramagnetic for uniform and dimerized structures, whereas non magnetic for tetramerized or lower-symmetry structures. We have attempted to apply this rule to TTM-TTP compounds, which have metallic one-dimensional half-filled bands. Contrary to the above rule, these compounds, which have been expected to be paramagnetic in view of the uniform columns, show non magnetic ground states owing to their extreme one-dimensionality and the lattice modulation.

IV-N-1 Structural Genealogy of BEDT–TTF–Based Organic Conductors III. Twisted Molecules: δ and α' Phases

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[*Bull. Chem. Soc. Jpn.* **72**, 2011 (1999)]

δ-phase (β-PF_6 type) BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene)-based organic conductors are characterized by the twisted overlap mode in the stack. Since the twisted mode has large intermolecular orbital overlap, the δ-phase is regarded as a twisted dimer structure. This type of overlap is, however, insensitive to small changes of the structure. On the contrary, an oblique interaction alters the warping of the open Fermi surface, to control the metal-insulator transition temperature, T_{MI}. Through the change of this oblique interaction, T_{MI} is scaled by the axis ratio for a family of salts with the same stacking pattern. As a general summary of BEDT-TTF salts, an empirical rule is proposed to predict, from the number of crystallographically independent molecules, whether an insulating state of BEDT-TTF salts will be paramagnetic or nonmagnetic. This rule is based on hypothetical pair formation of spins located on each dimer, and universally applies to all BEDT-TTF salts. This rule is extended to metallic salts, and among the potentially nonmagnetic salts, a dimerized dimer structure is the necessary condition of superconductivity. The potentially paramagnetic superconductors have strongly dimerized structures like β and κ phases (Table 1). From this we can make a reasonable prediction as to superconducting phases.

Table 1. Classification of Organic Superconductors.

ET-Based	Other Donors
Potentially paramagnetic	
β-Phase	$(TMTSF)_2X$
κ-Phase	$(DMET)_2X$
	$(DTEDT)_3Au(CN)_2$
Potentially nonmagnetic	
$\beta_{21\times2}$-$(ET)_2ReO_4$	$\beta''_{20\times2}$-$(BO)_2ReO_4H_2O$
$\beta''_{211\times2}$-$(ET)_2SF_5CF_2SO_3$	
β''_{421}-$(ET)_2Pt(CN)_4H_2O$	
β''_{421}-$(ET)_2Pd(CN)_4H_2O$	
$\beta''_{321\times2}$-$(ET)_3Cl_2(H_2O)_2$	
β''_{431}-$(ET)_4H_2O[Fe(ox)_3]PhCN$	
α-$(ET)_2NH_4Hg(SCN)_4$	
θ-$(ET)_2I_3$	

IV-N-2 Raman and Optical Investigations on Charge Localization in the One-Dimensional Organic Conductors (TTM–TTP)$(I_3)_{5/3}$ and (TSM–TTP)$(I_3)_{5/3}$

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[*Phys. Rev. B* **60**, 4635 (1999)]

The title compounds, which have polyiodide chains along the donor stacking direction and show characteristic copper luster, exhibit metallic behavior above T_{MI} = 20 K. High pressure resistivity, the Raman spectra, and optical reflectance of these salts have been measured to investigate the origin of the low-temperature insulating state and the iodine species. For (TSM-TTP)$(I_3)_{5/3}$ two kinds of conducting behavior have been observed (Figure 1); below 20 K some low-conducting samples have shown an increase of the resistivity of more than 10^3 times, but other high-conducting samples have shown an increase of less than ten times. The increase of resistivity is almost suppressed under a pressure of 11.5 kbar in the high-conducting phase of (TSM-TTP)$(I_3)_{5/3}$. The Raman spectra provide clear evidence that the polyiodide chain is composed of I_3^- in these compounds. The Raman spectra and the X-ray photographs indicate that the increase of resistivity originates in the disorder. The chain axis optical reflectance spectra show plasma edges appearing in the infrared region and three peaks from the infrared to the visible range; the latter originate from the intramolecular transition and polyiodide ions. Temperature dependence of optical conductivity is metallic even below T_{MI}. From these results, the origin of the low-temperature insulating state is attributed to disorder driven localization.

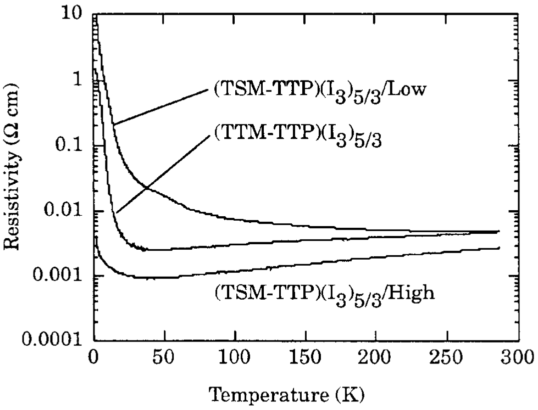

Figure 1. Temperature dependence of electrical resistivity of (TTM-TTP)$(I_3)_{5/3}$ and (TSM-TTP)$(I_3)_{5/3}$.

IV-N-3 Raman Investigation of the One-Dimensional Organic Conductor with a Half-Filled Band, (TTM-TTP)I_3

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[*J. Phys. Soc. Jpn.* **68**, 3748 (1999)]

Raman spectra of the title compound, which shows metallic conduction in spite of the 1:1 composition, have been investigated. The Raman line at 112 cm^{-1}, originating from the symmetric stretching of the discrete I_3^- anions, splits in two below 150 K. This corresponds to the lattice modulation coming from the triiodide anions.

IV-N-4 ESR Investigation of Organic Conductors (DTM-TTP)(TCNQ)(TCE) and (TMET-TTP)(TCNQ)

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[*J. Phys. Soc. Jpn.* **69**, 1845 (2000)]

Magnetic properties of the title compounds are investigated by ESR measurements, and from the temperature dependence of the *g*-values, the spin susceptibility is separated into donor and TCNQ contributions. For (DTM-TTP)(TCNQ)(TCE), the overall spin susceptibility decreases gradually from room temperature to 200 K, and more rapidly below 200 K, indicating a gradual crossover from a metallic to nonmagnetic insulating state. For (TMET-TTP)$_2$-(TCNQ), the spin susceptibility exhibits a gradual increase from room temperature to 50 K, followed by a rapid Curie-like increase that is attributed to the isolated TCNQ molecules (Figure 1). The donors remain paramagnetic even in the insulating state in accordance with the two-dimensional θ-type arrangement of the donor conducting sheet.

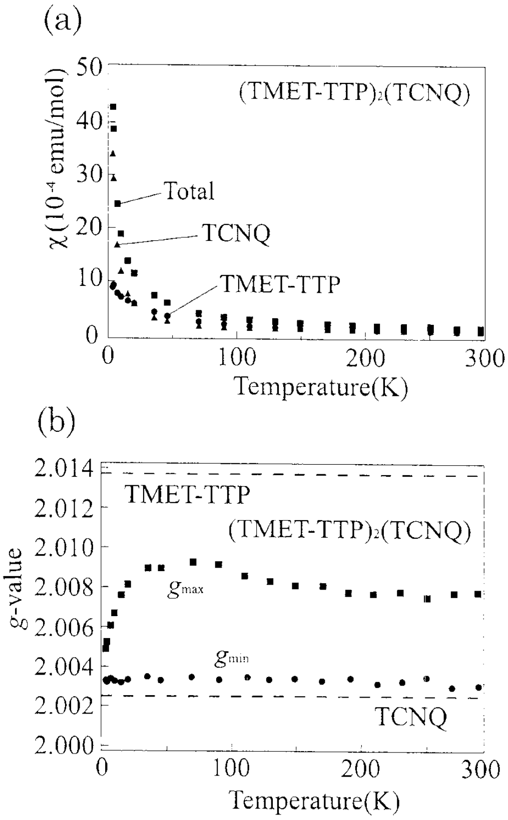

Figure 1. (a) Spin susceptibility and (b) *g*-value of (TMET–TTP)$_2$(TCNQ). The *g*-value are measured in the directions of g_{max} and g_{min} in the ac plane. The broken lines in (b) are *g*-values of TMET–TTP and TCNQ.

IV-N-5 Structural and Magnetic Properties of Cu$[C(CN)_3]_2$ and Mn$[C(CN)_3]_2$

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[*Inorg. Chem.* **38**, 4229 (1999)]

Single crystal X-ray structure analyses and the measurements of static magnetic susceptibility and ESR have been performed for the title compounds. Crystal data for Cu$[C(CN)_3]_2$: space group P_{mna}, a = 7.212(5), b = 5.452(7), c = 10.696(7) Å, and Z = 2, Mn$[C(CN)_3]_2$: space group P_{mna}, a = 7.742(5), b = 5.411(6), c = 10.561(6) Å, and Z = 2. Both salts are essentially isostructural (Figure 1). The Cu atoms are bridged by two $[C(CN)_3]^-$ anions to form an infinite double chain structure, in which Cu has a square planar coordination (d_{Cu-N} = 1.986(6) Å). The third CN end of the anion is weakly coordinated to the adjacent Cu chain (d_{Cu-N} = 2.47(1) Å), making a three-dimensional network. The crystal is composed of two such interwoven networks. In the Mn complex, the third Mn-N distance (2.256(6) Å) is as short as the equatorial coordinations (2.236(4) Å), so that Mn is coordinated octahedrally. These compounds exhibit paramagnetic behavior following the Curie-Weiss law with Weiss temperatures, –1.4 K and –9 K, respectively, and the Mn complex undergoes an antiferromagnetic transition at T_N = 5 K.

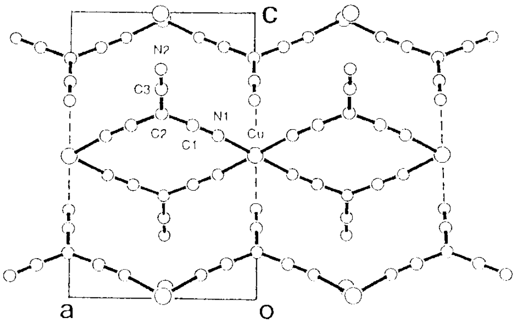

Figure 1. Double chain structure of $Cu[C(CN)_3]_2$.