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Temperature Dependence of Magnetic Susceptibilities of (TTT)(TCNQ) and (TTT)(TCNQ)$_2$

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Static magnetic susceptibility and ESR studies of 1:1 and 1:2 charge-transfer complexes of naphthaceno-[5,6-*cd*:11,12-*c′d′*]bis[1,2]dithiole and 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile) [(TTT)-(TCNQ) and (TTT)(TCNQ)$_2$] in the temperature region of 2—310 K are described. (TTT)(TCNQ)$_2$ exhibits a temperature dependent spin susceptibility, while the spin susceptibility of (TTT)(TCNQ) is almost independent of temperature. Spin susceptibilities of the TTT and TCNQ chains, which are evaluated with a *g*-value decomposition technique, are interpreted in terms of a one-dimensional Hubbard model. In both complexes, the on-site Coulomb repulsion is comparable with or larger than the band width on the TCNQ chains and is smaller on the TTT chains. Two magnetic phase transitions are observed in (TTT)(TCNQ)$_2$. The transition is driven in each chain independently by the Peierls instability. The amount of charge transfer in (TTT)-(TCNQ) is determined to be 0.73±0.05 from an X-ray photoelectron spectroscopic study.

Naphthaceno[5,6-*cd*: 11,12-*c′d′*]bis[1,2]dithiole [tetrathiotetracene; abbreviated as TTT hereafter] is known to be a powerful donor and forms many highly conductive low dimensional organic solids with some organic acceptors and inorganic anions.[1-7] TTT forms two distinct charge-transfer complexes with 2,2′-(2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile) [tetracyanoquinodimethan; abbreviated as TCNQ]. One is (TTT)(TCNQ)[3,4] and the other is (TTT)(TCNQ)$_2$.[2,4] Electrical conductivity of a single crystal of (TTT)-(TCNQ)$_2$ has been found to be about 100 Ω^{-1} cm^{-1} at room temperature and shows metallic temperature dependence down to about 90 K, but becomes semiconductive below 90 K.[2] Room temperature conductivity of a powdered sample of (TTT)(TCNQ) has been found to be 0.1—1 Ω^{-1} cm^{-1}.[2,4] and is comparable with that of (TTT)(TCNQ)$_2$. Therefore (TTT)(TCNQ) is also regarded as a highly conductive compound, though its single crystal conductivity has not yet been reported.

The temperature dependence of magnetic susceptibility is an important physical property for an organic conductor because it provides information on the band width and the on-site Coulomb correlation effects. The temperature dependences of magnetic susceptibilities of (TTT)(TCNQ) and (TTT)(TCNQ)$_2$ have been reported previously by two groups.[2,3] In these reports, a large contribution ((2—8)$\times10^{-2}$ spins per molecule) of paramagnetism described by Curie law inhibits an accurate evaluation of intrinsic paramagnetism. Furthermore, it is necessary to decompose total spin susceptibilities into individual contributions from the two chains in order to discuss quantitatively the band width and the Coulomb correlation effects. For this purpose, a decomposition technique has been developed which uses the g-value observed in electron spin resonance.[8] Therefore, we have reexamined the temperature dependence of the magnetic susceptibilities and, for the first time, measured ESR of (TTT)(TCNQ) and (TTT)-(TCNQ)$_2$ in the temperature range of 2—310 K.

In this report we describe the relation between the band width and the on-site Coulomb correlation in detail using the results of magnetic susceptibility and ESR measurements. Insight into magnetic phase transition is also provided. Moreover to evaluate the band width, the amount of charge transfer in (TTT)-(TCNQ) is estimated from the results of X-ray photoelectron spectroscopy.

Experimental

Materials. TTT was synthesized by using the procedures described in the literature[5,9] with a slight modification and purified by repeated vacuum sublimation.

TCNQ (Aldrich) was purified twice by recrystallization from an acetonitrile solution and for several times by sublimation under reduced pressure.

(TTT)(TCNQ) was obtained by the following procedures. A 50 cm^3 of hot toluene solution containing 20 mg (0.1 mmol) of TCNQ was added to a boiling solution of 35 mg (0.1 mmol) of TTT in 350 cm^3 of toluene and refluxed for 30 min. The solution stood for overnight and the precipitated crystals were collected, washed with ethanol, and dried in atmosphere. Yield; 48 mg. Found: C, 65.70; H, 2.09; N, 10.16; S, 20.92%. Calcd for $C_{30}H_{12}N_4S_4$: C, 64.72; H, 2.18; N, 10.67; S, 23.04%. Room temperature resistivity on a compressed powder sample was 1.8 Ω cm.

(TTT)(TCNQ)$_2$ was obtained in the same manner as (TTT)(TCNQ) except for using twice amount of TCNQ. Yield; 71 mg. Found: C, 65.98; H, 2.11; N, 13.54; S, 16.14%. Calcd for $C_{42}H_{16}N_8S_4$: C, 66.29; H, 2.12; N, 14.73; S, 16.85%. Resistivity at room temperature on a compressed powder sample was 4.5 Ω cm.

M(TCNQ) (M=Na, K, Rb) and (tetraethylammonium)-(TCNQ)$_2$ were prepared by the method in the literature.[10] The complex of 2,2′-bi(1,3-dithiolylidene), [tetrathiafulvalene; abbreviated as TTF], and TCNQ was prepared by direct reaction of equimolar amounts of TTF and TCNQ in purified hot acetonitrile solutions.

Magnetic Susceptibility. Static magnetic susceptibility of powder samples was measured with a Faraday susceptometer described below. The construction of the susceptometer system is schematically illustrated in Fig. 1. The susceptometer is composed of three main parts; a cryostat in combination with superconducting magnets (Oxford Instruments Limited), an electric microbalance (Cahn model 2000), and a temperature control unit.

The superconducting magnets consist of a main solenoid coil which produces homogeneous field up to 50 kOe[11] and a couple of quadrupole-type gradient coils which produces

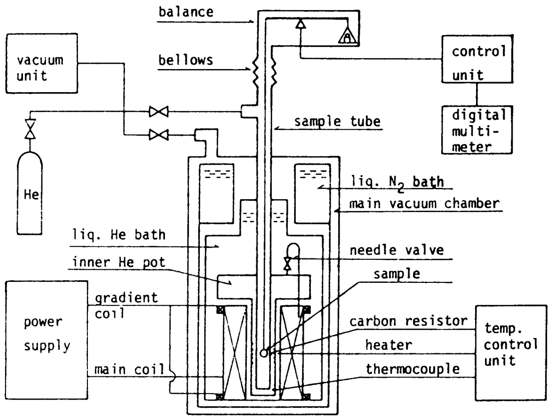

Fig. 1. Construction of the Faraday magnetosusceptometer system.

field gradient up to 1 kOe cm^{-1}. The solenoid and gradient coils are wound from NbTi filamentary wire. The magnets allow the field and field gradient to be set at desired values independently. The two magnets are used in superconducting state; in paticular, the main coil is used in a persistent current state for susceptibility measurements, and consequently fluctuation of the field strength is almost completely suppressed. The relation between a loading current and generated field was calibrated by measuring the susceptibility of sodium chloride.

The maximum loading capacity of the balance is 1 g and the magnetic force is reproducible within 1 μg, giving a maximum precision of the present system of 1×10^{-8} erg Oe^{-1} g^{-1} 11) for magnetization and 2×10^{-11} emu g^{-1} 11) for magnetic susceptibility.

A compressed powder sample of about 50 mg was contained in a quartz bucket and suspended from the balance beam with tungsten wire 30 μm in diameter. The output from the balance was read with a digital multimeter (Takeda Riken TR 6840). The sample and balance were pumped to less than 2×10^{-3} Pa to remove adsorbed oxygen and water. Typically evacuation for 90 h was necessary for (TTT)(TCNQ) to be free from paramagnetism of adsorbed oxygen. During the measurement, the sample tube was filled with purified helium gas at about 3 Pa to keep thermal contact between the sample and a copper heat sink.

Temperature below 20 K was measured with a carbon resistor and from 20 to 300 K with a 0.03% Fe-Au/chromel thermocouple. Temperature was controlled with an Oxford DTC2 temperature controller and calibrated by measuring the magnetic susceptibility of *N,N,N′,N′*-tetramethyl-1,2-ethanediammonium tetrachlorocuprate(II).12) The accuracy of temperature was to ±0.2 and ±0.5 K at 10 and 100 K, respectively.

Electron Spin Resonance. Temperature dependence of X-band electron spin resonance (ESR) spectra from 120 to 310 K were recorded on a JES-FX-1 equipped with a cryostat of cold gas nitrogen flow type. Spectra in the temperature region of 7—260 K were measured using a JES-FX-3AX with an Oxford ESR 900 continuous flow cryostat. In every measurement the modulation width was kept to be within 0.05 Oe in order to prevent a distortion of lineshape due to overmodulation.

X-Ray Photoelectron Spectroscopy (XPS). X-Ray photoelectron spectra of (TTT)(TCNQ) were measured by means of a McPherson ESCA 36 electron spectrometer on powder samples pressed onto aluminum plates employing Mg *Kα* (1253.6 eV) as the stimulating radiation. The binding energy was calibrated against the Au4f$_{7/2}$ peak (83.8 eV) of a thin film deposited on the sample surface in the spectrometer. Data for neutral TTT and (TTT)ClO$_4$ measured under the same conditions were kindly supplied by Professor Ikemoto.

Infrared Spectra. Infrared (IR) spectra were recorded using KBr disks of powdered samples with a Perkin-Elmer PE684 spectrometer.

Evaluation of the Amount of Charge Transfer

The amount of charge transfer, *ρ*, is one of the important quantities to consider physical properties of organic conductors, because it is related to the filling of electrons in an electron energy band. Several methods are proposed for estimation of *ρ*; X-ray13,14) and neutron15) scattering techniques, Raman16) and IR17) spectroscopies and XPS18–21) method. Ikemoto *et al.*20) have already evaluated *ρ* of (TTT)(TCNQ)$_2$ to be 0.93±0.05 with XPS. However, since *ρ* of (TTT)(TCNQ) has been left unknown, we have estimated it by means of XPS method.

The N1s core level peak of (TTT)(TCNQ) observed in this measurement has a broadened and asymmetric shape which is evidence for the presence of two kinds of TCNQ (*i.e.*, TCNQ^0 and TCNQ$^-$) in this solid as observed in (TTF)(TCNQ) and related compounds.18–21) Since (TTT)(TCNQ) has the stoichiometry of 1 : 1, this observaton suggests that an incomplete charge transfer from TTT to TCNQ occurs in this complex.

Ikemoto *et al.* have suggested that the S2p peak is suitable for estimation of *ρ* for sulfur containing charge transfer complexes, because this peak is not accompanied with any strong satellite and is free from radiation damage in contrast to the N1s peak.19,20) Our analysis is carried out by following the method proposed by them. We use the S2p peak profiles of TTT and (TTT)ClO$_4$ as standards for TTT^0 and TTT$^+$, respectively. *ρ* is estimated by trying to reproduce the observed (TTT)(TCNQ) peak as a sum of the TTT$^+$ and TTT^0 peaks by varying the relative intensities and separation of the two component peaks. The best fit profile is shown in Fig. 2. From the ratio of the cation peak area to the total one, *ρ* is estimated to be 0.73±0.05.

Chappell *et al.* have proposed an alternative method for estimation of *ρ* from IR spectra.17) According to their result, wavenumber, *ω*, of the highest frequency vibration among those of the nitrile stretching bands has a linear relation to *ρ*.

We have measured the IR spectra of neutral TCNQ, alkali metal(Na, K, and Rb)-TCNQ, (TTF)(TCNQ) and tetraethylammonium(TCNQ)$_2$. The observed spectra for Na-, K-, and Rb(TCNQ) are in good agreement with the reported ones.22–24) However, agreement with those of Chappell *et al.* is not satisfactory: For example, our results for the nitrile stretching mode are 2202 cm^{-1} for Na(TCNQ) and 2196 cm^{-1} for K-(TCNQ), while the values reported by Chappell *et al.* are 2185 and 2183 cm^{-1}, respectively. Our plot of *ρ versus ω* in several TCNQ salts shows a poor linearlity so that the evaluation of *ρ* from this plot would include larger error.

The value of $\omega=2183$ cm^{-1} for K(TCNQ), which has been used as the standard for TCNQ$^-$ by them, seems to

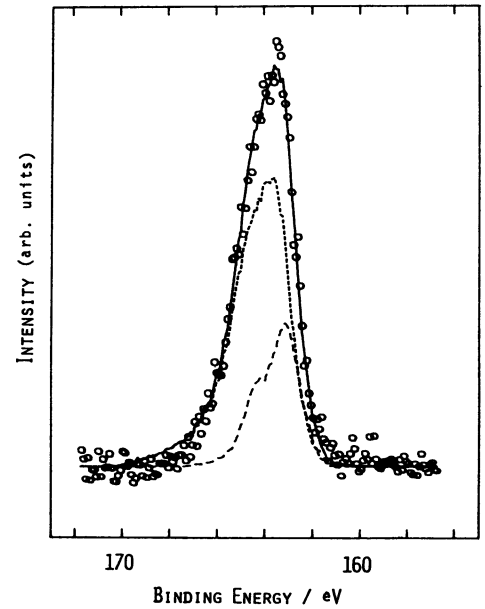

Fig. 2. Observed and calculated S2p peak profiles of X-ray photoelectron spectrum of (TTT)(TCNQ). ○: Observed data; ----: TTT$^+$ component; — — —: TTT^0 component; ——: superimposed peak.

correspond to the middle band among the three observed bands in the nitrile stretching band region. This band becomes allowed by vibronic coupling on the TCNQ chain[25,26] and the frequency is influenced by the strength of the coupling. Thus this band seems to be unsuitable for a reference.

For the reasons mentioned above, we employ the values of 0.73±0.05 derived from the XPS measurement as the amount of charge transfer. It has been shown that careful applicaton of the XPS method provides the ρ values in good agreement with those derived from other methods.[19-21]

Magnetic Susceptibilities

Temperature dependences of the total paramagnetic susceptibilities (χ_p) of (TTT)(TCNQ) and (TTT)(TCNQ)$_2$ obtained by subtracting the diamagnetic contribution are shown in Fig. 3. The contribution of core diamagnetism to the observed susceptibility is estimated from the reported values of 2.15×10^{-4} emu mol^{-1} [11] for TTT[7] and 1.21×10^{-4} emu mol^{-1} for TCNQ.[27]

The temperature dependences of the susceptibilities of both complexes are different above 20 K and similar below there. To clarify the behavior in the low temperature region, log(χ_p/emu mol^{-1}) is plotted against log(T/K) in Fig. 4. Below 20 K, the susceptibilities increase steadily with decreasing temperature according to the equation,

$$\chi_p = AT^{-\alpha}, \qquad (1)$$

where A and α are constants. The values of α= 0.64 and A=1.37×10^{-2} emu K mol^{-1} for (TTT)(TCNQ) and α=0.82 and A=4.35×10^{-3} emu K mol^{-1} for (TTT)(TCNQ)$_2$ are obtained from the plots of Fig. 4. Either value of α is unexpectedly less than unity, indicating that neither of the complexes obeys the Curie law in the low temperature region.

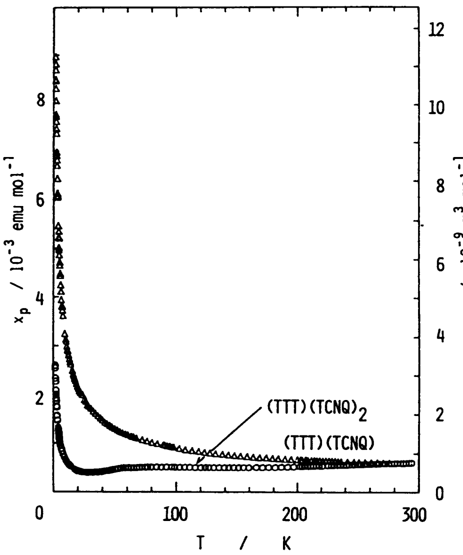

Fig. 3. Temperature dependence of total paramagnetic susceptibility. △: (TTT)(TCNQ); ○: (TTT)(TCNQ)$_2$.

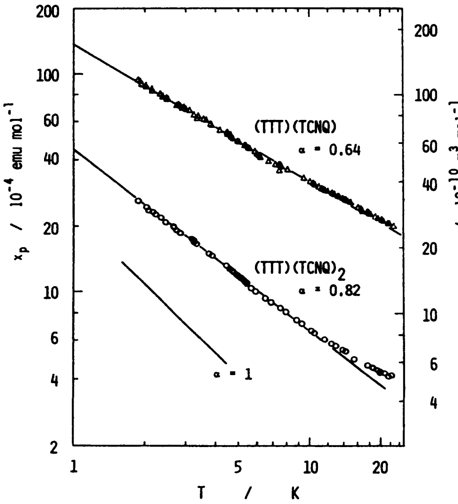

Fig. 4. Total paramagnetic susceptibility at low temperature. △: (TTT)(TCNQ); ○: (TTT)(TCNQ)$_2$; solid lines represent the least squares fit susceptibilities with T-power law.

Some groups of organic conductors have been shown recently to exhibit the susceptibility obeying the power law expressed by Eq. 1 at low temperatures. This behavior has been interpreted in terms of a random exchange Heisenberg antiferromagnetic chain with S= 1/2 spins.[28-32] One of the groups is represented by TCNQ complexes with asymmetric donors such as N-methylphenazinium(TCNQ),[29,33] acridinium (TCNQ)$_2$,[29] and quinolinium(TCNQ)$_2$.[29,33-36] The other group is comprised of complexes involving disorders additionally introduced by chemical doping or X-ray or neutron irradiation. Typical examples are (HMTTF)$_x$-

(HMTSF)$_{1-x}$(TCNQ), $x<1$,[35] and irradiated (TTF)-(TCNQ),[34,35] where HMTTF and HMTSF stand for 2,2′-bi(5,6-dihydro-4*H*-cyclopenta[1,3]dithiolylidene) and its selenium derivative.

Our samples seem to belong to the latter group because of the symmetric shape of TTT and TCNQ molecules. Disorder may be introduced by solvent molecules randomly included or by deviation from ideal stoichiometry. Our mass spectroscopic measurements have shown that (TTT)(TCNQ) and (TTT)(TCNQ)$_2$ include toluene, used as the solvent, in the crystals. The molar ratios of TCNQ to TTT are 1.1 for (TTT)-(TCNQ) and 1.9 for (TTT)(TCNQ)$_2$ with slight deviations among batches. This nonstoichiometry makes up kinks and missfits of the array of molecules in the molecular stacks to violate the periodic potential of the lattice and thus spins are trapped near the kinks or defects. In a similar way randomly included solvent molecules would also create the randomly trapped spins.

The reproducibility of α is good and the values of 0.63 ± 0.05 for (TTT)(TCNQ) and 0.82 ± 0.05 for (TTT)(TCNQ)$_2$ are obtained from the several measurements for each complex, while the magnitude of A, which corresponds to the Curie constant when $\alpha=1$, varies from sample to sample.

Regarding A as the Curie constant, though $\alpha\neq1$, we may estimate the spin concentration contributing to the susceptibility at low temperature. In spite of careful preparations of the samples, the spin concentrations estimated range from 1×10^{-2} to 4×10^{-2} spins per molecule for several batches of the both complexes. These values are comparable with or slightly less than those reported previously (about $(2-8)\times10^{-2}$ spins per molecule[4,5]). Therefore, we believe that the low temperature paramagnetism is inherent nature to the two complexes and is ascribed to the disorder mentioned above.

The spin susceptibilities (χ_s) of the two complexes in the higher temperature region are obtained by subtracting the low-temperature disorder paramagnetism discribed by Eq. 1 from the total paramagnetism. They are shown in Fig. 5. It will be shown later from the results of ESR study on powdered samples that this separation of susceptibility is appropriate for these complexes.

The χ_s values of the two complexes are quite different in temperature dependence and magnitude from each other. In (TTT)(TCNQ), χ_s is almost independent of temperature above 30 K, suggesting that no magnetic phase transition occurs in this temperature range. The value of about 2×10^{-4} emu mol^{-1} is rather smaller than that of various TCNQ complexes.

On the other hand, χ_s of (TTT)(TCNQ)$_2$ is similar to that of (TTF)(TCNQ) in temperature dependence and magnitude. The feature of temperature dependence of the observed spin susceptibility is in good agreement with the reported one in the whole temperature range, though the magnitude of our result is larger by about 30% than that.[2] The spin susceptibility increases rapidly with increase of temperature in the semiconducting region ($T\leq55$ K). Two sudden changes in χ_s are observed at about 55 and 85 K, implying occurrence of magnetic phase transitions like those found in (TTF)-(TCNQ).[27,37] In the metallic region above 90 K, χ_s increases rather slowly with increasing temperature as observed with other organic conductors in their metallic region. We would be able to regard (TTT)(TCNQ)$_2$ as a characteristic organic conductor which is subject to a phase transition into semiconducting state at low temperature.

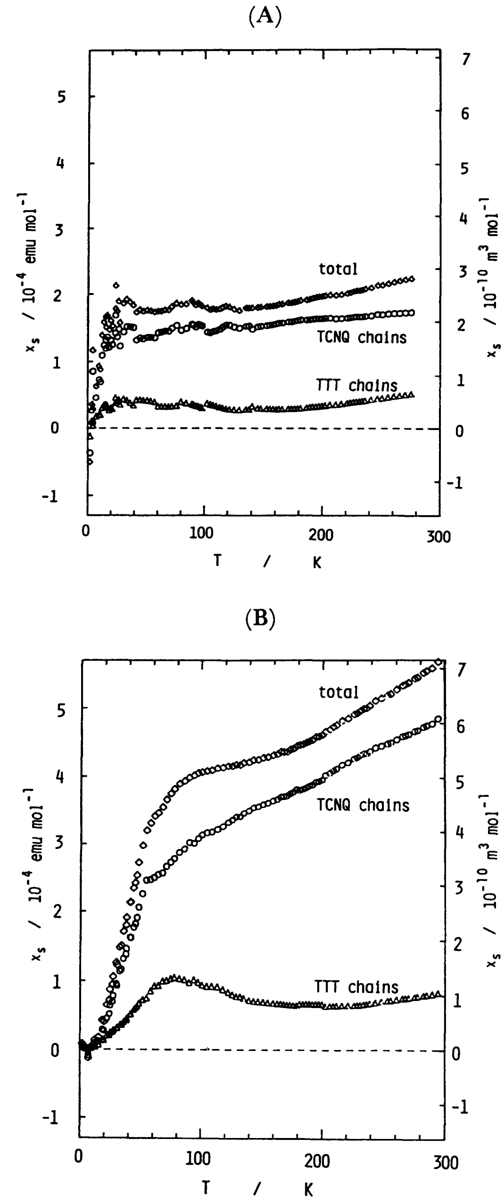

Fig. 5. Temperature dependence of total and individual spin susceptibilities. (A): (TTT)(TCNQ); (B): (TTT)(TCNQ)$_2$. ◇: Total susceptibilities; △: TTT chains; ○: TCNQ chains.

Decomposition of Total Spin Susceptibility into Contributions from Individual Chains

The observed spin susceptibilities of (TTT)(TCNQ) and (TTT)(TCNQ)$_2$ are total ones, namely the sums of spin susceptibilities of the TTT and TCNQ chains.

Both of the TTT and TCNQ chains are expected to exhibit finite magnetic susceptibilities almost independently. Thus separation of total susceptibilities into the individual components becomes important for further discussion. Two techniques for such separation have been proposed. One is the technique to use the g-values of ESR spectra.[8] The other is the method to make use of Knight-shift in ^{13}C-NMR spectra[38] The former technique is readily available to us and is employed here.

The observed ESR spectra at various temperatures are shown in Fig. 6. The structure appearing in the spectrum at high temperature is attributed to a g-value anisotropy for both complexes, because the lineshape cannot be reproduced by a superposition of absorption lines of TTT$^+$ and TCNQ$^-$ radicals. Indeed, a preliminary ESR measurement on a single crystal of (TTT)(TCNQ)$_2$ shows a single narrow absorption.

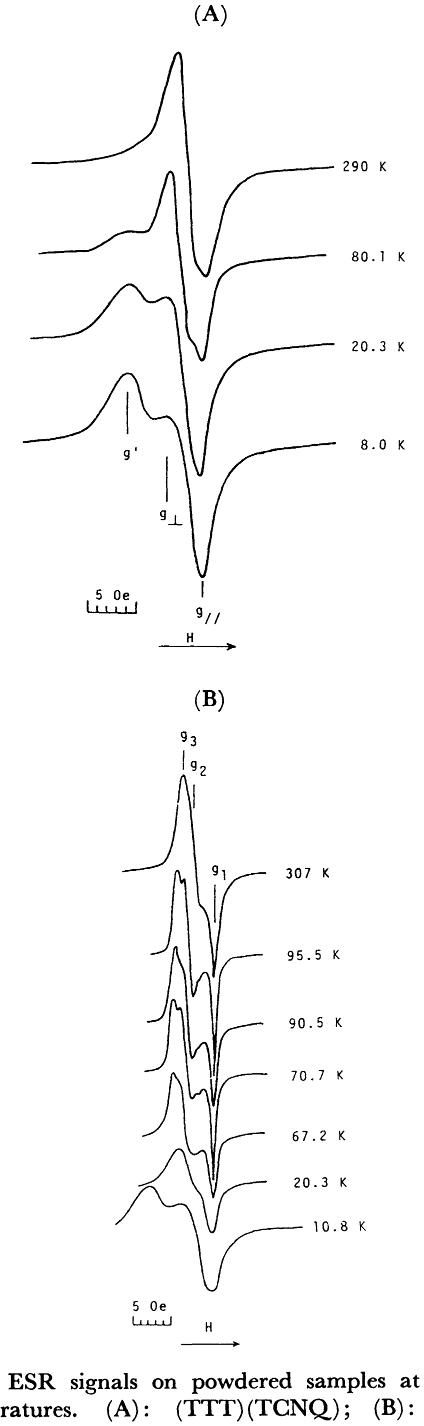

Fig. 6. ESR signals on powdered samples at various temperatures. (A): (TTT)(TCNQ); (B): (TTT)(TCNQ)$_2$. Assignment of anisotorpic g-values is tentative.

Lineshapes of the spectra of the two complexes are clearly different and their temperature dependence reflects the presence or absence of magnetic phase transition. In (TTT)(TCNQ), the lineshape varies continuously from 300 K down to 7.8 K. There is no indication of magnetic phase transition in this temperature range. This behavior is consistent with the result of magnetic susceptibility in the preceding section. The low field line additionally appears below 200 K with $g'=2.0073$ and seems to be arising from the spins mainly localized on TTT, because the observed value of g' is close to the g-value of the TTT cation radical.[39] Since the intensity of this line increases rapidly on cooling, this line is likely caused by the localized paramagnetic centers introduced by disordered nature of the solid observed in the static susceptibility.

In (TTT)(TCNQ)$_2$, the lineshape varies suddenly at some temperatures. On cooling, the depth of the dip near g_1 increases and the width narrows gradually. Sud-

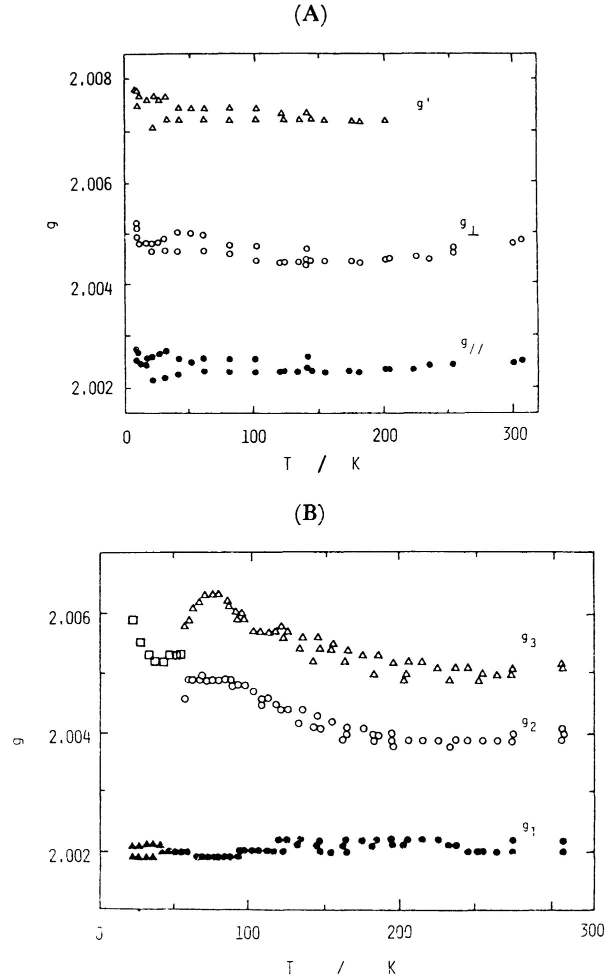

Fig. 7. Temperature dependence of g-values. (A): (TTT)(TCNQ); (B): (TTT)(TCNQ)$_2$.

den decrease in depth and increase in width are observed near 90 and 67 K, indicating the presence of phase transitions. The variation below 55 K is rather continuous, though the linewidth becomes broadened with decreasing temperature. A new line appearing below 15 K at the lower magnetic field would also be attributed to the signal due to the spin on disordered TTT site as discussed for (TTT)(TCNQ).

The temperature dependences of g-values shown in Fig. 7 support the results of the measurements of the temperature dependences of lineshape and magnetic susceptibility. Variation is continuous in (TTT)(TCNQ), while two irreguralities are found at 65 and 90 K in the temperature dependence of g_2 and g_3 in (TTT)(TCNQ)$_2$.

Since the main structures of the ESR spectra of (TTT)(TCNQ) and (TTT)(TCNQ)$_2$ are only due to the g-value anisotropy, the magnetic exchange interaction between TTT and TCNQ chains is expected to exceed the difference in the Larmor frequency, and averages out the g-values of the component radicals. Tomkiewicz *et al.* have shown that the observed g-value of such a complex is determined by a weighted average of the g-values of the component radicals,[8] where weight is proportional to χ_s of the donor and acceptor chains. Thus we may expect the following relationship to our complexes.

$$\bar{g} = \frac{\chi_{s,T}\bar{g}_T + \chi_{s,Q}\bar{g}_Q}{(\chi_{s,T} + \chi_{s,Q})}, \tag{2}$$

where $\bar{g}$, $\bar{g}_T$, and $\bar{g}_Q$ are the averaged g-values of the complex, the TTT$^+$ radical, and the TCNQ$^-$ radical, respectively, and $\chi_{s,T}$ and $\chi_{s,Q}$ are the spin susceptibility of the TTT and TCNQ chains. The value of 2.0029 is known as the average g-value of tetraethylammonium (TCNQ)$_2$.[40] The value of $\bar{g}_T$ is presently determined to be 2.0083 for (TTT$^+$)(CH$_3$CO$_2^-$).[39] Using the relation of Eq. 2, we may estimate $\chi_{s,T}$ and $\chi_{s,Q}$ from these g-values. In this estimation, we have assumed that the $\bar{g}_T$ and $\bar{g}_Q$ are independent of temperature. The results are shown in Fig. 5 together with total χ_s.

In both complexes, $\chi_{s,Q}$ is larger than $\chi_{s,T}$. In particular the temperature dependence of χ_s of (TTT)(TCNQ)$_2$ is primarily dominated by the susceptibility of the TCNQ chains. It is clearly seen from Fig. 5 that the phase transition near 90 K is related to the TTT chains and that near 60 K is to the TCNQ chains, and moreover each phase transition does not seem to influence the other.

Estimation of Band Width and On-site Coulomb Repulsive Energy

Spin susceptibilities of organic conductors have often been explained in terms of a one-dimensional Hubbard model,[41] which takes into account of transfer of electron between neighboring sites and on-site Coulomb repulsion between two electrons on the same site. The magnetic properties on this model are known for the following three limiting cases which are characterized by the relation between the band width ($4t$) and the on-site Coulomb repulsive energy (U), where t is the transfer integral between neighboring sites; (a) non-interacting case (U=0), (b) small U limit ($U \ll 4t$), and (c) large U limit ($U \gg 4t$).

In the non-interacting case, the system is in metallic state and the magnetic susceptibility would be given by the Pauli paramagnetism. Assuming a tight-binding approximation, the Pauli susceptibility at T=0 K is given by[42]

$$\chi_{\mathrm{Pauli}}(0) = \frac{N_A \mu_B^2}{t\pi \sin(\pi\rho/2)}, \tag{3}$$

where N_A is the Avogadro constant, μ_B is the Bohr magneton and ρ is the electron-to-site ratio. The temperature dependence of Pauli paramagnetism, $\chi_{\mathrm{Pauli}}(T)$, has been calculatd only for ρ=1 by Shiba.[43] Therefore we have to assume that the temperature dependence of Pauli susceptibility for arbitrary ρ is given by dividing $\chi_{\mathrm{Pauli}}(T)$ by filling factor, $\sin(\pi\rho/2)$.

In the small U limit ($U \ll 4t$), the spin susceptibility due to the Pauli paramagnetism would be enhanced by the on-site Coulomb repulsion and is given by[44]

$$\chi_s = \frac{\chi_{\mathrm{Pauli}}(T)}{(1 - U/4\pi t)\sin(\pi\rho/2)}. \tag{4}$$

As the on-site Coulomb repulsion increases, electrons tend to be scattered with each other and localized character of them gradually increases. In the large U limit ($U \gg 4t$), electrons are strongly localized on each site and this situation just coincides with the one-dimensional Heisenberg antiferromagnetic chain. In this case, the exchange coupling constant, J, is related to U, $4t$, and ρ by the equation,[45]

$$J = \frac{2t^2}{U + (4t/\pi)\sin\pi\rho}\left(1 - \frac{\sin 2\pi\rho}{2\pi\rho}\right). \tag{5}$$

The band width and the Coulomb repulsion energy may be estimated from these equations by examining the susceptibilities at various temperatures. Representative results of such fittings are shown in Fig. 8 for the spin susceptibilities of TTT and TCNQ chains in (TTT)(TCNQ) and (TTT)(TCNQ)$_2$, performed by using the values of ρ derived from the XPS study. Unfortunately, however, the agreement between the calculated and observed susceptibilities are not satisfactory in the whole temperature region in either case. In (TTF)(TCNQ), Torrance *et al.*[44] have also found lack of agreement in the temperature dependence of calculated susceptibilities with those observed. We concentrate then our attention on getting agreement in the magnitude of χ_s only at room temperature in order to see what is the most reasonable case as discussed by Torrance *et al.*

We examine the TCNQ chains at first. For the non-interacting case, agreements are obtained when we choose $4t$ to be 0.3 eV for (TTT)(TCNQ) and 0.15 eV for (TTT)(TCNQ)$_2$. Since most of the band widths of organic conductors have been estimated to be 0.4—1.5 eV from different experiments and calculations,[46,47] these obtained values seem to be too small. If we intend to apply the reasonable band width, we have to take into account of enhancement of χ_s by introducing a finite on-site Coulomb repulsive interaction.

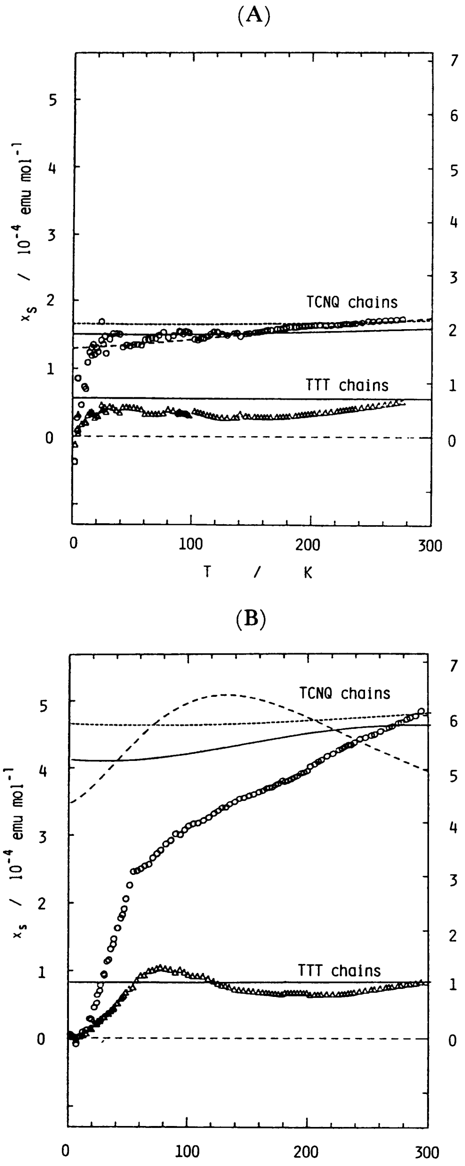

Fig. 8. Estimated spin susceptibilities with the one-dimensional Hubbard model for three limits. (A): (TTT)(TCNQ): △; $\chi_{s,T}$ observed, ——; non-interacting case ($U=0$, $4t=0.8$ eV), ○; $\chi_{s,Q}$ observed, ——; non-interacting case ($U=0$, $4t=0.3$ eV), ----; small U limit ($4t=0.4$ eV, $U/4t=1.0$), — — —; large U limit ($J=420$ K, $U/4t=1.2$), (B) (TTT)(TCNQ)$_2$: △; $\chi_{s,T}$ observed, ——; non-interacting case ($U=0$, $4t=0.5$ eV), ○; $\chi_{s,Q}$ observed, ——; non-interacting case ($U=0$, $4t=0.15$ eV), ----; small U limit ($4t=0.4$ eV, $U/4t=2.1$), — — —; large U limit ($J=100$ K, $U/4t=2.1$).

TABLE 1. TOTAL ($\chi_{s,t}$), DONOR ($\chi_{s,d}$), AND ACCEPTOR ($\chi_{s,a}$) SPIN SUSCEPTIBILITIES OF TWO-CHAINS ORGANIC CONDUCTORS AT 300 K. SUSSCEPTIBILITIES ARE GIVEN IN 10^{-4} emu mol^{-1}

	$\chi_{s,t}$	$\chi_{s,d}$	$\chi_{s,a}$	Reference
(TTF)(TCNQ)	6.0	3.2	2.8	27), 51)
(TSF)(TCNQ)	3.3	0.7	2.6	51), 56)
(TMTTF)(TCNQ)$^{a)}$	4.8	2.6	2.2	27), 53)
(HMTTF)(TCNQ)	2.4	0.7	1.7	51), 54)
(TMTSF)(DMTCNQ)$^{b,c)}$	5.5	1.65	3.85	55)
(TTT)(TCNQ)$_2$	5.8	0.9	4.9	This work
(TTT)(TCNQ)	2.3	0.5	4.9	This work

a) TMTTF=2,2′-Bi(4,5-dimethyl-1,3-dithiolylidene). b) TMTSF=2,2′-Bi(4,5-dimethyl-1,3-diselenolylidene). c) DMTCNQ=2,2′-(2,5-Dimethyl-2,5-cyclohexadiene-1,4-diylidene)bis(propanedinitrile).

Berlinsky *et al.*[47] have estimated $4t$ of TCNQ chains in (TTF)(TCNQ) to be 0.44 eV based on extended Hückel MO calculation. The X-ray analysis of (TTT)(TCNQ)$_2$[2,48] shows that the manner of overlap of the TCNQ molecules is similar to that of (TTF)(TCNQ),[49] *i.e.*, so called ring-external bond type. The interplanar spacing between TCNQ molecules (318 pm) is nearly the same as that of (TTF)(TCNQ)(317 pm). By expecting that a value of $4t$ is not much influenced by the change in the manner of stacking, the band width of the TCNQ chains of the two complexes may be assumed to be 0.4 eV. On this assumption, the best fit is obtained when $U/4t$ is 1.0 for (TTT)(TCNQ) and 2.1 for (TTT)(TCNQ)$_2$ in the small U limit.

For the large U limit, fitting with Bonner-Fisher susceptibility[50] gives the J value of 420 K for (TTT)(TCNQ) and 100 K for (TTT)(TCNQ)$_2$. From these J, the values of $U/4t$ is estimated to be 1.2 for (TTT)(TCNQ) and 2.5 for (TTT)(TCNQ)$_2$.

In each limit, the estimated $U/4t$ falls into the range of 1—2.5 and contradicts the initially assumed condition, that is, small or large U. This fact suggests that the magnitude of U is comparable with that of $4t$; *i.e.*, the relation between U and $4t$ is in an intermediate case, since the behavior of susceptibility for intermediate U is simply intermediate between the behavior calculated for small U and that for large U. Torrance *et al.* have suggested that the intermediate U can be expected for (TTF)(TCNQ) and the role of the on-site Coulomb repulsion is important in magnetic properties of one-dimensional organic conductors.[44] Similar findings on χ_s have also been reported for organic conductors such as (TSF)(TCNQ) and (HMTTF)(TCNQ).[51]

For the TTT chains, the situation seems to be different. In the non-interacting limit, $4t$ of the TTT chains are evaluated to be 0.8 eV for (TTT)(TCNQ) and 0.5 eV for (TTT)(TCNQ)$_2$. These values seem to be in agreement with the reported values of 0.6—1.5 eV for (TTT)$_2$I$_3$.[5,6,52] Therefore, the on-site Coulomb repulsion seems to be very small on the TTT chains in both complexes.

It is of interest to compare the evaluated spin susceptibilities with those of other two-chains organic conductors. The spin susceptibilities of donor ($\chi_{s,d}$) and acceptor chains ($\chi_{s,a}$) of some two-chains conductors at 300 K are listed in Table 1 together with those of (TTT)(TCNQ) and (TTT)(TCNQ)$_2$. Table 1 indicates that the variation of $\chi_{s,d}$ among these complexes is larger than that of $\chi_{s,a}$. Since the TCNQ molecules in these complexes make stacking in the similar manner,[49,57-60] it is reasonably expected that $\chi_{s,Q}$ does not differ too much, though the interplanar spacings are varied from 317 to 331 pm. For the donor stacks, on the other hand, the large variation of $\chi_{s,d}$ may be ascribed to the large difference in molecular structure and chemical properties of the donors.

Among these compounds, the susceptibility of donor chains in (HMTTF)(TCNQ) exhibits behavior similar to that in (TTT)(TCNQ) and (TTT)(TCNQ)$_2$ in temperature dependence and magnitude. The spin susceptibility of HMTTF chains in (HMTTF)(TCNQ) is almost independent of temperature above the transition temperature of 50 K and its magnitude is 0.75×10^{-4} emu mol^{-1}, which corresponds to the Pauli paramagnetism with $4t = 0.57$ eV. Tomkiewicz *et al.* have explained this finding in terms of reduction of U arising from the following two possible ways;[51] (1) reduction of bare U, caused by chemical modification of donor molecule and (2) effective reduction of U, arising from a screening effect of counter ions which has been first proposed by LeBlanc.[61]

Since the interplanar distance of the donor in (TTT)(TCNQ)$_2$ (352 pm) is larger to a small extent than that in (TTF)(TCNQ) (347 pm), the band width of TTT is expected to be comparable with or slightly narrower than that of TTF. Therefore the flat temperature dependence of the small magnitude of susceptibility would have to be attributed to the reduction of the on-site Coulomb repulsion as discussed in the case of (HMTTF)(TCNQ). It is plausible to assume that the reduction of U arises from the chemical modification of donor molecule, because it is rather difficult to see that the screening effect of TCNQ as a counter ion contributes markedly to reduction of U from its molecular and crystal structure.

Spin density distribution calculations[62] on sulfur containing organic cation radicals would support this idea. The calculation on the TTT$^+$ radical has revealed that more than 70% of unpaired electron spins are distributed on the 5-, 6-, 11-, and 12-carbon atoms and the four sulfur atoms of the TTT molecule. In the TTF$^+$ radical, most of the spins are located on the 2- and 2′-carbon atoms and the four sulfur atoms. A comparison of the spin distributions allows us to regard TTT as a molecule similar to TTF, but the four sulfur atoms in TTF are pulled apart from 1,1′,3,3′-positions to 4,4′,5,5′-positions. Since the sulfur-sulfur distance between different five-membered rings is prolonged in TTT in comparison with that of TTF, U is expected to be reduced. At the same time, the four benzene rings in TTT also contribute to reduction of U as a result of the delocalization of electrons

Phase Transitions and Low-temperature Spin Susceptibility

As discussed in previous sections, the presence of the magnetic phase transition becomes apparent in (TTT)(TCNQ)$_2$ by the measurements of magnetic susceptibility and ESR. In (TTT)(TCNQ), however, no evidence for a phase transition has been found at least above 20 K. Thus our discussion about the phase transition is limited only to (TTT)(TCNQ)$_2$.

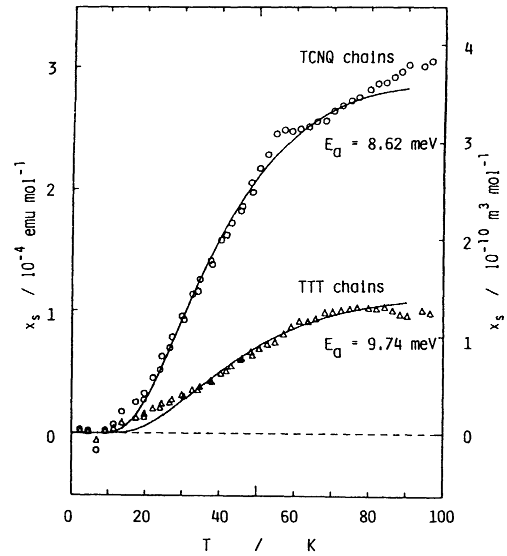

Fig. 9. Spin susceptibilities of TTT and TCNQ chains in (TTT)(TCNQ)$_2$ below the transition temperature. Solid lines are calculated susceptibilities with $\chi_s = (C/T) \exp(-E_a/k_B T)$, $E_a = 9.74$ meV for TTT chains and 8.62 meV for TCNQ chains.

The temperature-dependent $\chi_{s,T}$ and $\chi_{s,Q}$ are shown in Fig. 9. On lowering the temperature below the transition temperature, the spin susceptibilities of both chains decrease monotonously with the activation-type equation,

$$\chi_s = (C/T) \exp(-E_a/k_B T) , \tag{6}$$

where C is a constant and E_a is an activation energy. The values of C and E_a are found to be 0.034 emu K mol^{-1} and 9.74 meV for the TTT chains and 0.077 emu K mol^{-1} and 8.62 meV for the TCNQ chains. The temperature dependence of the susceptibilities arises from the spins which are thermally excited across a gap that is formed by a phase transition. This type of temperature dependence of susceptibility has often been found in the low temperature region of organic conductors which become semiconductive by the Peierls transition.[53,63] Indeed, the conductivity measurement carried out by Buravov *et al.* has shown that (TTT)(TCNQ)$_2$ is semiconductive below the transition temperature of about 90 K.[2] Thus the phase transition may be attributed to a metal-semiconductor transition driven by the Peierls instability.

The activation energies of paramagnetism of the TCNQ chains for (TTF)(TCNQ)[63] and (HMTTF)(TCNQ)[53] are known to be 36 and 21.5 meV, respectively, in the semiconductive region. The observed E_a of 8.62 meV for the TCNQ chains of (TTT)(TCNQ)$_2$ is smaller than these values. Since a magnetic activation energy is related to the strength of electron-phonon coupling,[64] the small value for (TTT)(TCNQ)$_2$ suggests a weaker electron-phonon coupling on the TCNQ chains in (TTT)(TCNQ)$_2$. The activation energies of the donor chains for (TTF)(TCNQ) and (TMTTF)(TCNQ) have been estimated to be 10.8 and 13.8 meV, respectively, and are slightly larger than those for the TTT chains of (TTT)(TCNQ)$_2$ (9.74 meV). Thus the magnitude of electron-phonon coupling on the TTT chains in(TTT)(TCNQ)$_2$ seems to be close to that on TTF in (TTF)(TCNQ), whose donor chains are distorted at 49 K.[38,63]

The transition temperature of the TTT chains in (TTT)(TCNQ)$_2$ is rather high compared with that of the donor chains in other two-chains complexes, while that of the TCNQ chains is not so different from that of (TTF)(TCNQ). A transition temperature driven by the Peierls instability is associated with the strength of the electron-phonon coupling and the dimensionality, namely the strength of interchain interactions. The stronger the electron-phonon coupling and the weaker the interchain interaction, the higher phase transition temperature is expected. The crystal structure analysis suggests that the interchain interaction is weak in (TTT)(TCNQ)$_2$. The shortest interchain distances are 344 and 348 pm, and are considerably longer than those of (TTF)(TCNQ) (320 and 325 pm)[49] and (HMTTF)(TCNQ) (325 pm).[55] The weak interchain interaction is also suggested by our preliminary ESR measurements on a single crystal of this complex. The peak-to-peak linewidth of ESR signal at room temperature is quite narrow (1.1 Oe) among the sulfur containing organic conductors.[53,55] This finding indicates that the spin relaxation is suppressed, because if interchain interaction is too weak to transfer effectively the magnetic energy three-dimensionally, the correlation among spins is generally kept for rather long time.

Therefore high transition temperature of TTT chains reflects the low-dimensional character of this complex. For the TCNQ chains, the observed weak electron-phonon coupling would lower the transition temperature, whereas weak interchain interaction would raise the transition temperature. The two effects on the TCNQ chains counteract each other and consequently, the transition temperature of the TCNQ chains would not change much from that of (TTF)-(TCNQ).

Summary

The susceptibilities of both of the donor and acceptor chains extracted by the manipulation of the data indicate that, in the metallic region, the susceptibility of the TCNQ chains is considerably enhanced by the on-site Coulomb repulsion and dominates the magnitude of the total susceptibility, while the susceptibility of the TTT chains is explained by the Pauli paramagnetism.

The discontinuities in the temperature dependence of the spin susceptibility in (TTT)(TCNQ)$_2$ are driven by the Peierls instability, resulting in the thermally activated paramagnetism below the transition temperature. The susceptibility of (TTT)(TCNQ) is almost temperature independent above 20 K. Although some insight into electronic state is given in the latter complex, further experiments such as conductivity measurement on a single crystal and structure analysis are indispensable for detailed discussion.

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References

1) For reviews see a) L. C. Isett and E. A. Perez-Albuerne, *Ann. N. Y. Acad. Sci.*, **313**, 395 (1978); b) I. F. Shchegolev and E. B. Yagubskii, "Extended Linear Chain Conductors," ed by J. S. Miller, Plenum Press, New York (1982), Vol. 2, p. 385.

2) L. I. Buravov, O. N. Eremenko, R. B. Lyubovskii, L. P. Rozenberg, M. L. Khidekel', R. P. Shibaeva, I. F. Shchegolev, and E. B. Yagubskii, *Pis'ma Zh. Eksp. Teor. Fiz.*, **20**, 457 (1974). (*JETP Lett.*, **20**, 208 (1974).)

3) P. Delhaès, S. Flandrois, G. Keryer, and P. Dupuis, *Mater. Res. Bull.*, **10**, 825 (1975).

4) R. C. Wheland and J. L. Gillson, *J. Am. Chem. Soc.*, **98**, 3916 (1976).

5) L. C. Isett and E. A. Perez-Albuerne, *Solid State Commun.*, **21**, 433 (1977).

6) G Mihály, A. Jánossy, and G. Grüner, *Solid State Commun.*, **22**, 771 (1977).

7) L. C. Isett, *Phys. Rev. B*, **18**, 439 (1978).

8) a) Y. Tomkiewicz, A. R. Taranko, and J. B. Torrance, *Phys. Rev. Lett.*, **36**, 751 (1976); b) *Phys. Rev. B*, **22**, 3113 (1980).

9) C. Marschalk and C. Stumm, *Bull. Soc. Chim. Fr.*, **1948**, 418; E. P. Goodings, D. A. Mitchard, and G. Owen, *J. Chem. Soc., Perkin Trans. 1*, **1972**, 1310.

10) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

11) We employed in this report the c.g.s. electromagnetic units, in the interest of comparison with values in references. To convert into the SI unit, the following relations should be used; $1\ \mathrm{A\ m^{-1}}=4\pi\times10^{-3}$ Oe, $1\ \mathrm{A\ m^2\ kg^{-1}}=1$ erg $\mathrm{Oe^{-1}\ g^{-1}}$, $1\ \mathrm{m^3\ kg^{-1}}=10^3/4\pi$ emu $\mathrm{g^{-1}}$, and $1\ \mathrm{m^3\ mol^{-1}}=10^6/4\pi$ emu $\mathrm{mol^{-1}}$.

12) D. B. Brown, V. H. Crawford, J. W. Hall, and W. E. Hatfield, *J. Phys. Chem.*, **81**, 1303 (1977).

13) F. Denoyer, R. Comès, A. F. Garito, and A. J. Heeger, *Phys. Rev. Lett.*, **35**, 445 (1975).

14) S. Kagoshima, H. Anzai, K. Kajimura, and T. Ishiguro, *J. Phys. Soc. Jpn.*, **39**, 1143 (1975).

15) G. Shirane, S. M. Shapiro, R. Comès, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **14**, 2325 (1976).

16) S. Matsuzaki, R. Kuwata, and K. Toyoda, *Solid State Commun.*, **33**, 403 (1980); S. Matsuzaki, T. Moriyama, and K. Toyoda, *ibid.*, **34**, 857 (1980).

17) J. S. Chappell, A. N. Bloch, W. A. Bryden, M. Maxfield, T. O. Poehler, and D. O. Cowan, *J. Am. Chem. Soc.*, **103**, 2442 (1981).

18) W. D. Grobman and B. D. Silverman, *Solid State Commun.*, **19**, 319 (1976).

19) I. Ikemoto, T. Sugano, and H. Kuroda, *Chem. Phys. Lett.*, **49**, 45 (1977).

20) I. Ikemoto, M. Yamada, T. Sugano, and H. Kuroda, *Bull.Chem. Soc. Jpn.*, **53**, 1871 (1980).

21) M. Tokumoto, N. Koshizuka, H. Anzai, and T.

Ishiguro, *J. Phys. Soc. Jpn.*, **51**, 332 (1982).

22) M. S. Khantkale and J. P. Devlin, *J. Chem. Phys.*, **70**, 1851 (1979).

23) Z. Iqbal, C. W. Christoe, and D. K. Dawson, *J. Chem. Phys.*, **63**, 4485 (1975).

24) R. Bozio, A. Girlando, and C. Pecile, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1237 (1972).

25) R. Bozio, I. Zanon, A. Girlando, and C. Pecile, *J. Chem. Soc., Faraday Trans. 2*, **74**, 235 (1978).

26) G. R. Anderson and J. P. Devlin, *J. Phys. Chem.*, **79**, 1100 (1978).

27) J. C. Scott, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **10**, 3131 (1974).

28) For review articles; W. G. Clark, J. Jamann, J. Sanny, and L. C. Tippie, "Lecture Notes in Physics," ed by S. Barišić, A. Bjeliš, J. R. Cooper, and B. Leontić, Springer-Verlag, Berlin (1979), Vol. 96, p. 255; W. G. Clark, "Physics in One Dimension," ed by Bernasconi and T. Schneider, Springer-Verlag, Berlin (1981), p. 289.

29) L. N. Bulaevskii, A. V. Zvarykina, Yu. S. Karimov, R. B. Lybovskii, and I. F. Shchegolev, *Zh. Eksp. Tero. Fiz.*, **62**, 725 (1972). (*Sov. Phys. JETP*, **35**, 384 (1972).)

30) W. G. Clark and L. C. Tippie, *Phys. Rev. B*, **20**, 2914 (1979).

31) G. Theodorou, *Phys. Rev. B*, **16**, 2254, 2264 (1977).

32) L. P. Gor'kov, O. N. Dorokhov, and F. V. Prigara, *Solid State Commun.*, **37**, 869 (1981); C. Dasgupta and S. Ma, *Phys. Rev. B*, **22**, 1305 (1980); Z. G. Soos and S. R. Bondeson, *Mol. Cryst. Liq. Cryst.*, **85**, 1409 (1982); J. E. Hirsch and J. V. José, *J. Phys. C*, **13**, L53 (1980).

33) G. Theodorou, *Phys. Rev. B*, **16**, 2273 (1977).

34) M. Miljak, B. Korin, J. R. Cooper, K. Holczer, G. Grüner and A. Jánossy, *J. Mag. Mag. Mater.*, **15-18**, 219 (1980).

35) M. Miljak, B. Korin, J. R. Cooper, K. Holczer, and A. Jánossy, *J. Phys. (Paris)*, **41**, 639 (1980).

36) L. C. Tippie and W. G. Clark, *Phys. Rev. B*, **23**, 5846 (1981).

37) Y. Tomkiewicz, B. A. Scott, L. J. Tao, and R. S. Title, *Phys. Rev. Lett.*, **32**, 1363 (1974).

38) E. F. Rybaczewski, L. S. Smith, A. F. Garito, A. J. Heeger, and B. G. Silbernagel, *Phys. Rev. B*, **14**, 2746 (1976); E. F. Rybaczewski, A. F. Garito, A. J. Heeger, and E. Ehrenfreund, *Phys. Rev. Lett.*, **34**, 524 (1975).

39) Measured values on $(\mathrm{TTT}^+)(\mathrm{CH_3CO_2}^-)$; $g_{/\!/}=2.0034(1)$, $g_{\perp}=2.0107(1)$, and $\bar{g}=2.0083(1)$.

40) J. Kurti and G. Menczel, *Phys. Status Solidi B*, **102**, 639 (1980); $g_1=2.00236$ $g_2=2.00276$, $g_3=2.00355$, and $\bar{g}=2.00289$.

41) J. Hubbard, *Proc. R. Soc. London, Ser. A*, **276**, 238 (1963); *ibid.*, **281**, 401 (1964).

42) H. Shiba, *Phys. Rev. B*, **6**, 930 (1972).

43) H. Shiba, *Prog. Theor. Phys.*, **48**, 2171 (1972).

44) J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman, *Phys. Rev. B*, **15**, 4738 (1977).

45) D. J. Klein and W. A. Seitz, *Phys. Rev. B*, **10**, 3217 (1974).

46) For example, proposed $4t$ for (TTF)(TCNQ) is in the range of 0.2—0.7 eV; A. A. Bright, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **10**, 1328 (1974); P. M. Grant, R. L. Greene, G. C. Wrighton, and G. Castro, *Phys. Rev. Lett.*, **31**, 1311 (1973); D. R. Salahub, P. R. Messmer, and F. Herman, *Phys. Rev. B*, **13**, 4252 (1976); A. Karpfen, J. Ladik, G. Stollhoff, and P. Fulde, *Chem. Phys.*, **8**, 215 (1975).

47) A. J. Berlinsky, J. F. Carolan, and L. Weiler, *Solid State Commun.*, **15**, 795 (1974).

48) R. P. Shibaeva and L. P. Rozenberg, *Kristallografiya*, **20**, 943 (1975). (*Sov. Phys. Cryst.*, **20**, 581 (1976).)

49) T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **30**, 763 (1974).

50) J. C. Bonner and M. E. Fisher, *Phys. Rev.*, **135**, A640 (1964).

51) Y. Tomkiewicz, B. Welber, P. E. Seiden, and R. Schumaker, *Solid State Commun.*, **23**, 471 (1977).

52) R. B. Somoano, S. P. S. Yen, V. Hadek, S. K. Khanna, M. Novotny, T. Datta, A. M. Hermann, and J. A. Woollam, *Phys. Rev. B*, **17**, 2853 (1978).

53) Y. Tomkiewicz, A. R. Taranko, and D. C. Green, *Solid State Commun.*, **20**, 767 (1976).

54) Y. Tomkiewicz, A. R. Taranko, and R. Schumaker, *Phys. Rev. B*, **16**, 1380 (1977).

55) Y. Tomkiewicz, J. R. Andersen, and A. R. Taranko, *Phys. Rev. B*, **17**, 1579 (1978).

56) R. L. Greene, J. J. Mayerle, R. Schmaker, G. Castro, P. M. Chaikin, S. Etemad, and S. J. LaPlaca, *Solid State Commun.*, **20**, 943 (1977).

57) L. I. Buravov, R. N. Lybovskaya, R. B. Lybovskii, and M. L. Khidekel', *Zh. Eksp. Teor. Fiz.*, **70**, 1982 (1976). (*Sov. Phys. JETP*, **43**, 1033 (1977).)

58) K. Bechgaard, T. J. Kistenmacher, A. N. Bloch, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **33**, 417 (1977).

59) T. E. Phillips, T. J. Kistenmacher, A. N. Bloch, J. P. Ferraris, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **33**, 422 (1977).

60) J. R. Andersen, K. Bechgaard, C. S. Jacobsen, G. Rindorf, H. Soling, and N. Thorup, *Acta Crystallogr., Sect. B*, **34**, 1901 (1978).

61) O. H. LeBlanc, Jr., *J. Chem. Phys.*, **42**, 4307 (1965).

62) F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, *J. Am. Chem. Soc.*, **100**, 4612 (1978); W. E. Geiger, Jr., *J. Phys. Chem.*, **77**. 1862 (1973).

63) Y. Tomkiewicz, A. R. Taranko, and J. B. Torrance, *Phys. Rev. Lett.*, **36**, 751 (1976).

64) Ref. 55 and the references cited therein.