Metal-Insulator Transition in the Organic Metal $(\mathrm{TTM\text{-}TTP})\mathrm{I}_3$ with a One-Dimensional Half-Filled Band

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The title 1:1 composition organic conductor, with a highly one-dimensional half-filled energy band, exhibits metallic conductivity down to $T_{\mathrm{MI}} \approx 160$ K, but the spin susceptibility follows the one-dimensional Heisenberg model from room temperature to 2 K, without any anomaly at T_{MI}. The insulating state is regarded as a Mott insulator. The small U, related to the extended molecular structure, gives rise to the small charge gap and the high-temperature metallic conduction. [S0031-9007(97)03940-9]

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It has been widely believed that organic conductors with half-filled energy band will not show metallic conduction because the Coulomb interaction in these conductors is of essential importance in making the conduction electrons localized. In the present paper we will report the first exception of this general rule; the title compound $(\mathrm{TTM\text{-}TTP})\mathrm{I}_3$, where TTM-TTP is 2,5-bis(4,5-bis(methylthio)-1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (Fig. 1), exhibits metallic conduction above $T_{\mathrm{MI}} \approx 160$ K, although it has a highly one-dimensional half-filled energy band.

X-ray crystal structure analysis has shown that the donor to the anion ratio is 1:1 [1]. A unit cell contains only one donor molecule, which makes face-to-face stacks along the crystallographic c axis. Since the transfer integral along this stacking direction, $t_c = 0.26$ eV, estimated from the overlap of the highest occupied molecular orbital (HOMO) calculated on the basis of the extended Hückel molecular orbital calculation, is much larger than the interchain interactions, $t_a, t_b < 0.01$ eV, the electronic structure is recognized as highly one dimensional along the stacking direction. Figure 1 shows the energy band structure and the Fermi surface calculated by using the transfer integrals given in Ref. [1]. Because a unit cell contains only one donor molecule, there is only one energy band, which has large dispersion along the c axis with the bandwidth of about 1 eV, yet having very little dispersion along the other directions. Since one electron has been transferred from one donor to I_3^-, namely, $\mathrm{TTM\text{-}TTP}^+$ is generated, this one-dimensional band is half filled. Therefore the energy band structure is extremely simple: a single one-dimensional half-filled band.

Nevertheless, this compound exhibits a very high conductivity, 700 $\mathrm{S\,cm}^{-1}$, at room temperature, and weakly metallic temperature dependence down to about 160 K, below which it undergoes a transition to an insulating state [1]. It is surprising that an organic conductor with a half-filled band, or in other words with 1:1 composition, shows such a high conductivity and moreover even metallic conductivity. The thermoelectric power is exactly and constantly zero from room temperature to T_{MI}; this is a straightforward consequence of the half-filled band and in addition its experimental evidence [1].

The on-site Coulomb repulsion U and the transfer integral t_c have been estimated from the polarized reflection

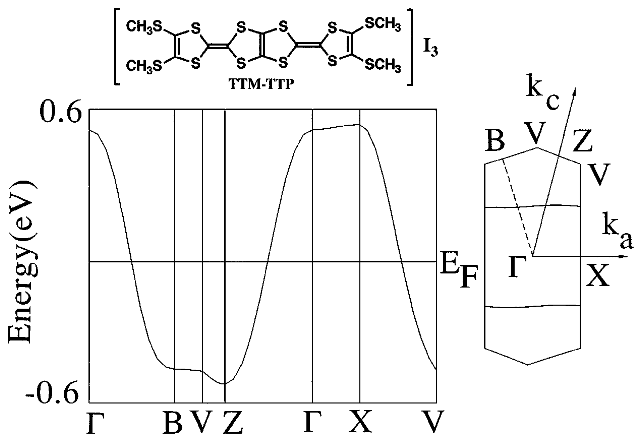

FIG. 1. Tight-binding energy band structure and Fermi surface (right), calculated from the overlap of the highest occupied molecular orbital (HOMO) obtained on the basis of the extended Hückel molecular orbital calculation [1].

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spectra by assuming the half-filled one-dimensional Hubbard model; the results are $U = 0.57$ eV and $t_c = 0.16$ eV [2]. The Coulomb repulsion U is smaller than the usual values of organic conductors, typically about 1.0 eV; this is related to the extended π electrons of the donor molecule (Fig. 1). The same conclusion has been obtained from the measurement of the oxidation potentials; the difference of the oxidation potentials between D^0/D^+ and D^+/D^{2+} is about one third of the usual TTF donors (TTF: tetrathiafulvalene) [3]. It is worth noting that U is smaller than the bandwidth $4t = 0.64$ eV. Small U is probably the key to the realization of the half-filled metallic organic conductor.

In the present paper we report (1) conductivity at high pressures, (2) static magnetic susceptibility, (3) ESR, and (4) temperature dependence of the lattice constants.

In order to obtain the T-P phase diagram, we have measured the electrical conductivity under high pressure. The measurements were carried out by the conventional clamp cell technique. Because the pressure is released by about 3 kbar between room temperature and 200 K, this value was subtracted from the room-temperature values.

Figure 2 shows the electrical resistivity under high pressure. The metal-insulator (MI) transition temperature shifts to lower temperatures with an increase of the pressure. The shift is, however, very gradual, and the insulator phase is not completely suppressed even at 11.5 kbar. The MI transition temperature T_{MI}, defined by the steep rise of the resistance, is plotted in Fig. 3. The principal effect of pressure is the enhancement of t, whereas U is expected to remain basically unchanged because it is a property of a molecule. If we assume that charge localization associated with U is responsible for the MI transition, the obtained phase diagram is convincing.

Figure 4 shows the temperature dependence of the static magnetic susceptibility under $H = 10$ kOe, measured by a SQUID magnetometer. The crystals were aligned so as to make their crystallographic c axis parallel to the field direction. The Pascal diamagnetic contribution (-4.13×10^{-4} emu/mol) has been subtracted from the observed susceptibility. The magnetization curve showed no anomaly at low temperatures.

The spin susceptibility is, at a first approximation, almost constant from room temperature to helium temperatures, and can be regarded as Pauli-like. The magnitude of the spin susceptibility is not particularly enhanced. The most remarkable point is the absence of any anomaly around T_{MI}. If the MI transition is associated with the charge-density wave or spin-density wave transitions, decrease of the spin susceptibility is expected. Therefore we can definitely exclude the possibilities of the density-wave transitions as the origin of the MI transition. At T_{MI} the freedom of the charge dynamics is lost, yet the spin degree of freedom seems to be unchanged and remains finite down to helium temperatures. The present system exhibits a complete separation of spin and charge degrees of freedom.

Although roughly speaking the spin susceptibility can be regarded as Pauli-like, its gradual decrease is reminiscent of the low-temperature part of the Bonner-Fisher-like susceptibility. The solid curve in Fig. 4 is a fitting to the $S = 1/2$ one-dimensional Heisenberg model [4]. Although such a fitting is a quite rough estimation, the solid curve in Fig. 4 gives a value of $J/k_{\mathrm{B}} = 640$ K. By using the results of the optical measurements the same value is estimated as $J/k_{\mathrm{B}} = 2t^2/U = 1040$ K. Anyway, we can regard the spin system of the present compound as an antiferromagnetic chain with comparatively large J. This is obviously associated with the comparatively small U. Nevertheless, we should not take this picture too literally, because the existence of well-defined localized spins is not certain, particularly in the metallic phase.

Figure 5 shows intensity and linewidth of the X-band ESR. The g values are $g_b = 2.013$ and $g_c = 2.009$ at 29 K, which are reasonable values as free spins on the organic molecules. The intensity is, except the low-temperature

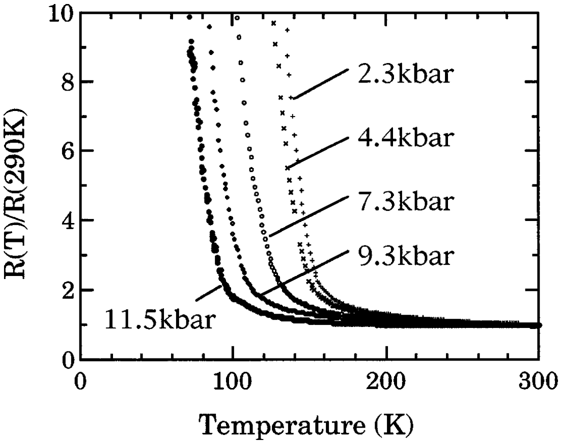

FIG. 2. Temperature dependence of electrical resistance (|| c) under high pressure; each measurement is normalized at room temperature.

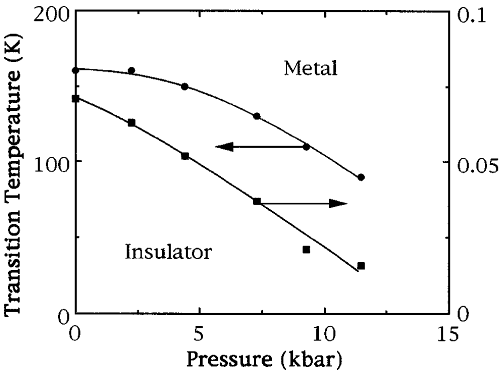

FIG. 3. Metal-insulator transition temperature extracted from the steep rise of the resistance, and activation energy estimated from the $\log R$ vs $1/T$ plot in the insulating region.

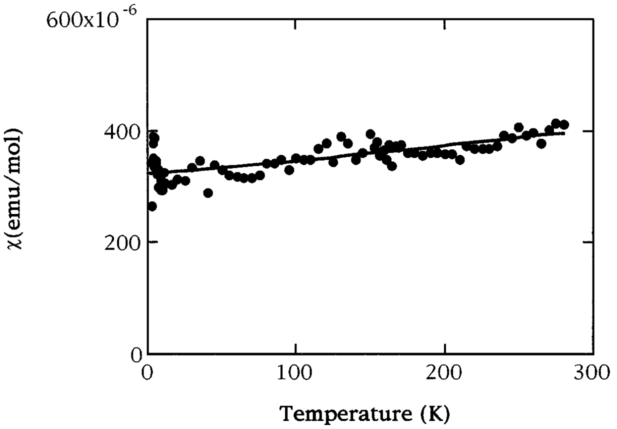

FIG. 4. Static magnetic susceptibility under $H = 10$ kOe. The solid curve represents the one-dimensional Heisenberg model.

Curie-like part, which may come from the impurities, almost constant from 40 to 120 K. This agrees with the Pauli-like spin susceptibility in the static measurement. In this temperature region the linewidth changes linearly to the temperature. The linewidth at low temperatures, 6 G, is comparatively sharp as a sulfur-containing donor, and may be associated with the one dimensionality of the system.

Above 120 K the linewidth suddenly broadens by at least several times, and practically we could not observe the signal above this temperature. The broadening is probably associated with the MI transition; above T_{MI} the scattering mechanism of the electrons changes because they become itinerant. By judging from the almost constant static susceptibility, when the linewidth broadens by several times the peak height is expected to decrease more than 1 order, and it is not unlikely that the signal apparently disappears. Similar behavior has been observed in another organic conductor, $(\mathrm{BEDT\text{-}TTF})_2\mathrm{RbZn(SCN)}_4$ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) [5].

In order to investigate the possibility of the charge-density wave transition, we have carried out a preliminary x-ray diffraction measurement. At 130 K a carefully taken oscillation photograph along the c direction showed no diffuse lines or satellite spots. Therefore together with the results of the magnetic measurements we can eliminate the possibility of the charge-density wave transition as an origin of the MI transition.

Figure 6 shows the temperature dependence of the lattice constants and lattice volume. Because no clear anomaly of the lattice constants has been observed, we can conclude that the MI transition is not associated with any structural transition. The lowest-measured temperature in Fig. 6 is, however, not sufficiently lower than T_{MI}. It may be desirable to carry out the diffraction measurement down to helium temperatures in order to confirm this point.

Crystal structure and energy band calculation have unambiguously indicated that the present system is not only highly one dimensional but also half-filled. It is therefore quite reasonable that one-dimensional Hubbard model is applicable to this system. The magnetic measurements together with the x-ray diffraction definitely eliminate the possibilities of the charge-density or spin-density wave transitions as an origin of the MI transition. From this perspective the low-temperature insulating state is reasonably regarded as a Mott insulator. One may expect a Curie-like behavior as the magnetic susceptibility of a Mott insulator. We have, however, shown that the magnetic susceptibility can be regarded as a Bonner-Fisher-like. Because the one dimensionality of the present system is extremely high, the fluctuation is so important that the susceptibility becomes Bonner-Fisher-like instead of Curie-like.

The most remarkable feature of the present system is the perfect separation of the spin and charge degrees of freedom. Theoretically the spin-charge separation in a one-dimensional system has been demonstrated starting from the Luttinger model [6]. Although the applicability of this theory to the actual systems such as some organic conductors has been discussed for a long time, the present system is by far the simplest with respect to its electronic structure and its half-filled band as well as its experimental properties.

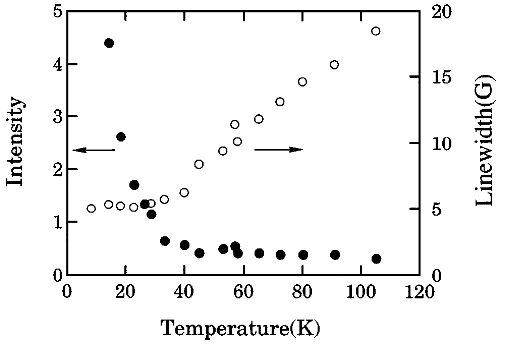

FIG. 5. ESR intensity (arbitrary unit) and linewidth, measured along $H \parallel c$.

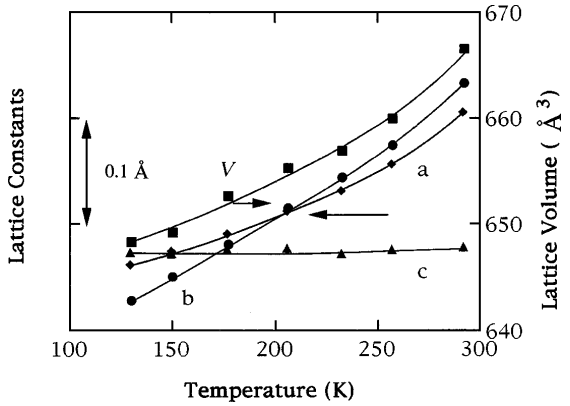

FIG. 6. Temperature dependence of the lattice constants and lattice volume.

The metallic conduction of the present system can be attributed to the thermal excitation across the charge gap. Since U is comparatively small, the charge gap is comparatively small, resulting in apparently metallic conduction at high temperatures. If this explanation is valid, the population of the doubly occupied sites must be of fundamental significance at least in the metallic temperature region. Nevertheless, it has been theoretically predicted that no matter how small is U, the ground state is the Mott insulator, because the system is half filled. In addition, the spin-charge separation takes place as far as U is finite [6].

It is also surprising that the present system shows finite, neither zero nor infinite, magnetic susceptibility in the limit of 0 K. Such a paramagnetic state is probably not the true ground state. We have carried out the magnetic measurements down to 2 K, below which a transition to either an antiferromagnetic state or a spin-Peierls state is expected. Because the system is highly one dimensional, the spin-Peierls state seems to be more plausible. In any case it is still surprising that the transition temperature is very low. As for the antiferromagnetic transition, it can be understood by considering the high one-dimensionality, because the interchain J is also very small, resulting in very low three-dimensional antiferromagnetic transition temperature. In case of the spin-Peierls transition the one-dimensional fluctuation is also regarded as very important. Anyway on account of the high one dimensionality the fluctuation of the spin system is so large that the transition temperature becomes very low.

It is noteworthy that in the present system electron-phonon coupling does not play any important role. In the conventional highly one-dimensional organic conductors the charge-density wave state is the most likely ground state. Since the softening of the lattice does not occur, the present system maintains a Mott-like paramagnetic state.

In this context a comparison with the universal phase diagram of $(\mathrm{TMTSF})_2X$ analogs is instructive (TMTSF: tetramethyltetraselenafulvalene) [7]. Although these compounds are formally quarter filled, their energy band can be regarded as half filled if the weak dimerization along the stacking direction is taken into account. This picture states that as an increase of the interchain coupling the system transforms from (1) a charge localized state with a low-temperature spin-Peierls state to (2) a spin-density wave state, (3) a metallic to low-temperature superconducting state, and finally (4) a simple metal state. Because the present system is highly one-dimensional, it must fall into the category (1). A typical example of category (1), $(\mathrm{TMTTF})_2\mathrm{PF}_6$ (TMTTF: tetramethyltetrathiafulvalene) undergoes a metal-insulator transition at 160 K, which is attributed to a charge localization, whereas its magnetic susceptibility gradually decreases below about 20 K, where a spin-Peierls transition takes place. This behavior is quite similar to that of the present compound except the existence of the spin-Peierls transition and the difference of the formal composition.

In summary, $(\mathrm{TTM\text{-}TTP})\mathrm{I}_3$ is regarded as a small-U case of a one-dimensional conductor with a *not* effectively but *inherently* half-filled energy band. Since U is small, this compound shows metallic conductivity at high temperatures, although the low-temperature state is a Mott insulator, because no matter how small is U, it gives rise to charge localization in a half-filled band. Nonetheless the magnetic susceptibility exhibits no anomaly and remains paramagnetic down to low temperatures. Since the one-dimensional fluctuation is of essential importance, the susceptibility is Bonner-Fisher-like rather than Curie-like, and the system does not undergo either spin-Peierls or antiferromagnetic transitions down to 2 K.

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[1] T. Mori, H. Inokuchi, Y. Misaki, T. Yamabe, H. Mori, and S. Tanaka, Bull. Chem. Soc. Jpn. **67**, 661 (1994).

[2] H. Tajima, M. Arifuku, T. Ohta, T. Mori, H. Inokuchi, Y. Misaki, T. Yamabe, H. Mori, and S. Tanaka, Synth. Met. **71**, 1951 (1995).

[3] Y. Misaki, H. Nishikawa, T. Yamabe, K. Kawakami, S. Koyanagi, T. Yamabe, and M. Shiro, Chem. Lett. **1993**, 2321 (1992).

[4] W.E. Hartfield, W.E. Estes, W.E. Marsh, M.W. Pickens, L.W. Haar, and R.R. Weller, in *Extended Linear Chain Compounds*, edited by J.S. Miller (Plenum, New York, 1983), Vol. 3, p. 43.

[5] H. Mori, S. Tanaka, and T. Mori, Synth. Met. **284**, 15 (1996).

[6] H.J. Schulz, Int. J. Mod. Phys. B **5**, 57 (1991), and references therein.

[7] D. Jérome, Science **252**, 1509 (1994); D. Jérome, P. Auban-Senzier, L. Balicas, K. Behnia, W. Kang, P. Wzietek, C. Berthier, P. Caretta, M. Horvatic, P. Segransan, L. Hibert, and C. Bourbonnais, Synth. Met. **70**, 719 (1995); R. Laversanne, C. Coulon, B. Gallois, J.P. Pouget, and R. Moret, J. Phys. (Paris) **45**, L393 (1984).