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Current-Induced Metallic State in an Organic (EDT-TSF)$_2$GaCl$_4$ Conductor

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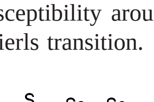
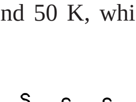
Organic metals are susceptible to various metal−insulator (MI) transitions, such as the Peierls transition and charge order, and a considerable number of organic metals become insulating at low temperatures.[1] To suppress the MI transitions, application of pressure has been widely used.[2] Recently, giant nonlinear conductance has been found in θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene),[3] in which the resistance exhibits a several-order drop by the application of a moderate voltage (1 V) or a current (1 mA). The resulting negative resistance has been used to make a new type of organic device, an organic thyristor.[4] At high voltages, the insulating behavior below 20 K is suppressed, and a metallic state is restored. Nonlinear conductance in one-dimensional systems has been investigated for a long time,[5] but excess conductance in one-dimensional organic conductors, such as (TMTSF)$_2$X (TMTSF = tetramethyltetraselenafulvalene), is at most 50% of the normal conductance, and a metallic state has never been restored.[6] Here we report restoration of a metallic state in a different material, (EDT-TSF)$_2$GaCl$_4$ (EDT-TSF = ethylenedithiotetraselenafulvalene). Since this is a new material, we report the crystal structure, conducting and magnetic properties, and low-temperature X-ray investigation together with those of the isostructural salt with a magnetic anion, (EDT-TSF)$_2$FeCl$_4$. For the all-sulfur analogue, EDT-TTF (ethylenedithiotetrathiafulvalene), many radial cation salts have been reported.[7] The crystal structures of all these compounds consist of quasi-one-dimensional stacks similar to (TMTSF)$_2$X. Although (EDT-TTF)[Ni(dmit)$_2$] and (EDT-TTF)$_4$Hg$_{3-\delta}$I$_8$ are ambient-pressure superconductors,[8] many of the EDT-TTF salts exhibit MI transitions at low temperatures. The GaCl$_4^-$ and FeCl$_4^-$ salts are insulating below room temperature,[9] but those of the selenium analogues, EDST and EDTS, undergo MI transitions around 40 K.[9] The GaCl$_4^-$ salt of not only these selenium-substituted donors but also EDT-TTF exhibits a drop of magnetic susceptibility around 50 K, which has been attributed to a spin-Peierls transition.


EDT-TSF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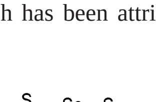
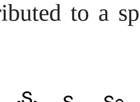

EDST


EDTS

EDT-TSF was prepared similarly to the methylenedithio analogue (MDT-TSF), which forms incommensurate superconductors.[10] Crystals of the GaCl$_4^-$ salt were grown by electrochemical oxidation of EDT-TSF in PhCl + 5% EtOH using Bu$_4$N·GaCl$_4$ as a supporting electrolyte under a constant current of 0.2 μA at 0 °C. Crystals of the FeCl$_4^-$ salt were similarly grown using Bu$_4$N·FeCl$_4$ at 20 °C. The crystal structure analyses of these GaCl$_4^-$ and FeCl$_4^-$ salts were performed using a Rigaku AFC-7R diffractometer (Figure 1).[11] There is one crystallographically independent donor molecule and a half unit of the anion located on a mirror plane. The donor molecules are stacked along the *a* axis, and construct an *ac*-conducting plane. There are many Se···Se contacts shorter than the sum of the van der Waals radii not only in the stacking direction but also in the interchain directions. The FeCl$_4^-$ ions have short Cl···Cl contacts, 4.11 (‖*c*) and 4.57 Å (‖*a*), and a short Cl···S contact (3.54 Å) with the ethylenedithio ring of the donor molecule.

The overlap integrals, band dispersion, and Fermi surface were calculated by the tight-binding method based on the extended Hückel approximation (Figures 1b and 2). There is open Fermi surface, and the energy band is essentially one-dimensional along the *a* axis. The difference of *a*1 and *a*2 is small, so that the dimerization is weak. The interchain overlap integrals are about 0.15 of the intrachain interaction. Although the electronic structure is still quasi-one-dimensional, the interchain interactions are considerably enhanced in comparison with the sulfur analogues.

The electrical conductivity at room temperature is 12 S cm^{-1}. The resistivity is metallic (Figure 3a), but makes a minimum at 30 K (35 K) and becomes insulating below 20 K (18 K) for the GaCl$_4^-$ (FeCl$_4^-$) salt. The thermoelectric power does not show a *T*-linear behavior typical of metals, but takes a nearly constant value around zero in the metallic temperature region.

Figure 3b shows temperature dependence of resistivity at various applied currents. To avoid the heating effect, the measurement is carried out with a short pulse, 0.2 ms, and a pulse interval, 1 s. Since the sample resistance is small, the measurement is performed by the four-probe method, and the applied current is regulated. The observed nonlinearity is obviously not a simple heating effect because the low-temperature resistance under 5 mA is smaller than the resistance minimum under 50 μA at high temperatures. The behavior at large currents does not show any MI transition, and a metallic state is restored.

To explore the origin of the MI transition, low-temperature X-ray investigation is performed at BL-1B in the Photon Factory at KEK. The oscillation photograph does not show any diffuse scattering or extra spots even at 9 K (Figure 4a), and the lattice constants are continuous down to this temperature. This suggests that the insulating state is associated with charge order rather than the spin-Peierls transition.

Magnetic susceptibility of the GaCl$_4^-$ salt is almost constant except for the low-temperature small Curie-like term (Figure 4b). ESR is observed only below 140 K (g_c = 2.016 and g_b = 2.032),

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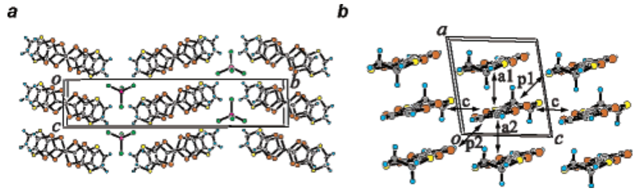

Figure 1. Crystal structure of (EDT-TSF)$_2$GaCl$_4$ (a) projected down to the *bc*-plane, and (b) the donor array in the *ac*-conduction plane and overlap integrals between the neighboring donor molecules: $a1 = 19.6$, $a2 = 21.8$, $c = 1.2$, $p1 = 2.4$, and $p2 = 3.2 \times 10^{-3}$ for the GaCl$_4^-$ salt, and $a1 = 19.4$, $a2 = 21.7$, $c = 1.2$, $p1 = 2.5$, and $p2 = 3.2 \times 10^{-3}$ for the FeCl$_4^-$ salt.

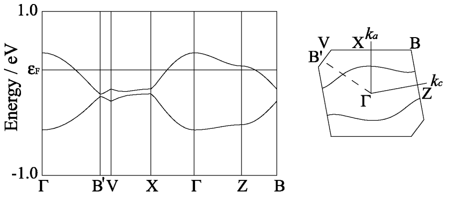

Figure 2. Band dispersion and Fermi surface of (EDT-TSF)$_2$GaCl$_4$.

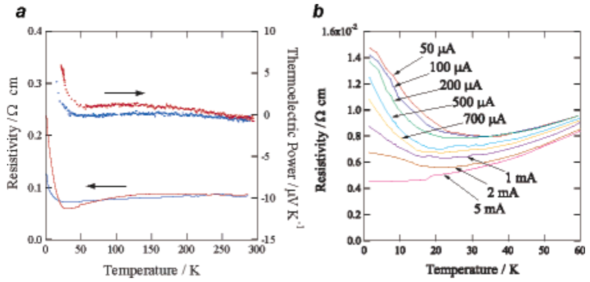

Figure 3. (a) Electrical resistivity and thermoelectric power of (EDT-TSF)$_2$GaCl$_4$ (red) and (EDT-TSF)$_2$FeCl$_4$ (blue). (b) Temperature dependence of the electrical resistivity of (EDT-TSF)$_2$GaCl$_4$ at various applied currents.

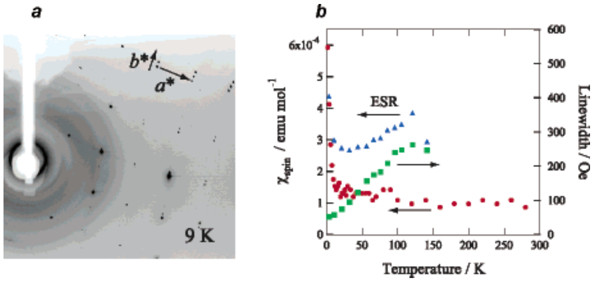

Figure 4. (a) X-ray oscillation photograph at 9 K in (EDT-TSF)$_2$GaCl$_4$. (b) Spin susceptibility of (EDT-TSF)$_2$GaCl$_4$ measured on several pieces of aligned crystals (red, $H \| a$, $H = 10$ kOe) using a SQUID magnetometer, together with ESR intensity (blue, $H \| c$, plotted in arbitrary units) and line width (green, $H \| c$).

but the intensity remains paramagnetic down to low temperatures. The line width does not show any anomaly around 20 K, indicating that the MI transition at 20 K is not a magnetic transition. The static susceptibility of the FeCl$_4^-$ salt obeys the Curie–Weiss law originating in the Fe $S = {}^5/_2$ spin with practically zero Weiss temperature. This indicates very small magnetic interactions, consistent with the molecular orbital calculations, $J_{dd} = 0.012$ K and $J_{\pi d} = 2.26$ K.[12]

The absence of anomaly in the low-temperature X-ray and magnetic measurements indicates that the 20 K MI transition is not a true thermodynamical phase transition. Nonetheless, the observed increase of the resistance implies partial transformation to such insulating states as observed in the EDST and EDTS salts. These insulating states are nearly suppressed by the selenium substitution, but the low-temperature state contains a glassy mixture of frozen clusters of charge-ordered states. This reminds us of the low-temperature state of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$, which has been ascribed to an inhomogeneous mixture of two competing charge-order patterns.[3,4,13] A considerable number of organic conductors show similar gradual crossover to low-temperature insulating states. The present investigation demonstrates that the measurement of nonlinear conductance is a versatile tool to suppress this kind of insulating state.

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Supporting Information Available: An X-ray crystallographic file for the crystals of (EDT-TSF)$_2$GaCl$_4$ and (EDT-TSF)$_2$FeCl$_4$ in CIF format, a table of intermolecular short contacts, Arrhenius plots of the resistivity, spin susceptibility of the FeCl$_4^-$ salt, temperature dependence of the lattice constants, and current dependence of the nonlinear conductance. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Crystal data for (EDT-TSF)$_2$GaCl$_4$: C$_{16}$H$_{12}$Cl$_4$GaS$_4$Se$_8$, $M = 1175.72$, monoclinic, $a = 7.290(4)$, $b = 30.690(6)$, $c = 6.700(3)$ Å, $\beta = 100.38(4)°$, $V = 1474(1)$ Å^3, $T = 293$ K, space group $P2_1/m$, $Z = 2$, μ(Mo Kα) $= 114.65$ cm^{-1}, 5202 reflections measured ($R_{int} = 0.020$), 4367 unique. The final R and Rw were 0.037 and 0.116, respectively. Crystal data for (EDT-TSF)$_2$FeCl$_4$: C$_{16}$H$_{12}$Cl$_4$FeS$_4$Se$_8$, $M = 1161.85$, monoclinic, $a = 7.290(5)$, $b = 30.655(4)$, $c = 6.696(2)$ Å, $\beta = 100.42(4)°$, $V = 1471(1)$ Å^3, $T = 293$ K, space group $P2_1/m$, $Z = 2$, μ(Mo Kα) $= 110.63$ cm^{-1}, 5223 reflections measured ($R_{int} = 0.030$), 4369 unique. The final R and Rw were 0.038 and 0.119, respectively.
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