A new ambient-pressure organic superconductor $(TMET\text{-}STF)_2BF_4$ [TMET-STF = trimethylene(ethylenedithio)diselenadithiafulvalene]

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Under ambient pressure, the cation radical salt $(TMET\text{-}STF)_2BF_4$, where the tight-binding band calculation suggests coexistence of one- and two-dimensional Fermi surfaces associated with two different conduction layers within the crystal, shows two types of resistivity anomalies around 115 and 13 K, followed by a superconducting transition at 4.1 K (onset).

Extensive studies on organic superconductors have revealed that they display various electronic structures ranging from the quasi-one-dimensional type (*e.g.* TMTSF salts) to the two-dimensional type (*e.g.* BEDT-TTF salts) (TMTSF = tetramethyltetraselenafulvalene, BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene].[1] The dimensionality of the electronic structure is one of the essential factors which determine the physical properties of the system. The organic donor TMET-STF [trimethylene(ethylenedithio)diselenadithiafulvalene] is a hybrid between BEDT-TTF and HMTSF (hexamethylenetetraselenafulvalene) and was first reported in 1986.[2] We found an improved synthetic route to this molecule *via* a titanocene complex and pointed out the possibility of coexistence of one- and two-dimensional Fermi surfaces in its ClO_4 salt, $(TMET\text{-}STF)_2ClO_4$.[3] We report here that the isostructural BF_4 salt is an ambient-pressure superconductor with T_c (onset) = 4.1 K.

Plate-like single crystals used for the resistivity and magnetization measurements were grown by galvanostatic electrolysis (1 μA) of TMET-STF (9.8 mg) in the presence of $NBu^n_4BF_4$ (50.2 mg) in thf (20 ml) at 20 °C under Ar. An H-tube and platinum electrodes (1 mm diameter) were used. The electrical resistivity in the crystallographic *ac* plane was measured by the standard four-probe method. Gold leads (15 μm diameter) were attached to the sample with carbon paste. The contacts remained ohmic through the measurement. Resistivity measurements under pressure were performed in a clamp cell with a 1 : 1 mixture of Fluorinert No. FC70 and FC77 as the pressure transmitting medium. The pressure was calibrated with the superconducting transition temperature of Sn. The dc magnetization was measured with a Quantum Design MPMS SQUID magnetometer. Four crystals with a total mass of 0.06 mg were glued onto a sample holder (polypropylene, 1.17 mg) with a small amount of grease (Apiezon N).

Fig. 1 shows the temperature dependence of the resistivity under ambient pressure. The room-temperature resistivity was *ca.* 2×10^{-2} Ω cm. With lowering temperature, the resistivity decreased monotonously and displayed a first upturn around 115 K. The resistivity, however, formed a small peak around 100 K and decreased again. The second upturn appeared around 13 K. The ratio of ρ(4.1 K)/ρ(13 K) was sample dependent and ranged between 2 and 9. We did not observe hysteresis at either resistivity anomaly. An abrupt drop of the resistivity occurred at 4.1 K (onset) and we observed this behaviour in all seven samples. An application of pressure effectively suppressed the first upturn of the resistivity, while the second one remained up to *ca.* 7 kbar. The pressure effect on the transition temperature for the abrupt resistivity drop was rather moderate ($dT_c/dP \approx -0.2$ K $kbar^{-1}$).

Fig. 2 shows the zero-field-cooled (ZFC) and field-cooled (FC) temperature dependence of the dc magnetization, uncorrected for demagnetization, at a fixed field of 10 Oe perpendicular (approximately) to the crystallographic *ac* plane. The protocol was as follows: after cooling to 1.8 K in zero field, a magnetic field of 10 Oe was applied and the dc magnetization was measured while warming to 6.0 K (ZFC). The sample was then cooled to 2.0 K under the same field, 10 Oe (FC). The onset of a diamagnetic transition was observed at 3.8 K. This value is consistent with the result of the resistivity measurement. From the ZFC curve, we can roughly estimate that a volume fraction is *ca.* 50% of perfect diamagnetism; accuracy, however, is not high as the amount of the sample was very small. Such a large diamagnetism and the abrupt resistivity drop can be explained only by the appearance of a superconducting phase. Hysteresis

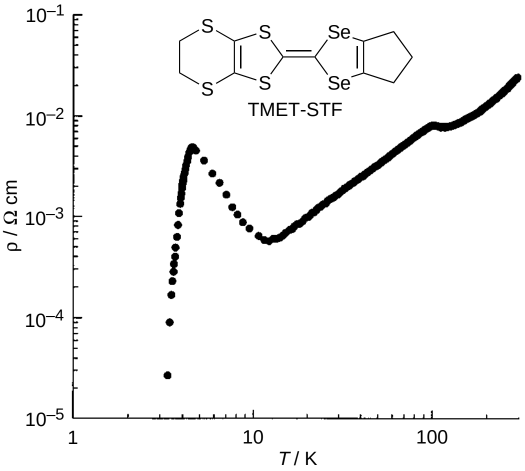

Fig. 1 Temperature dependence of the resistivity at ambient pressure

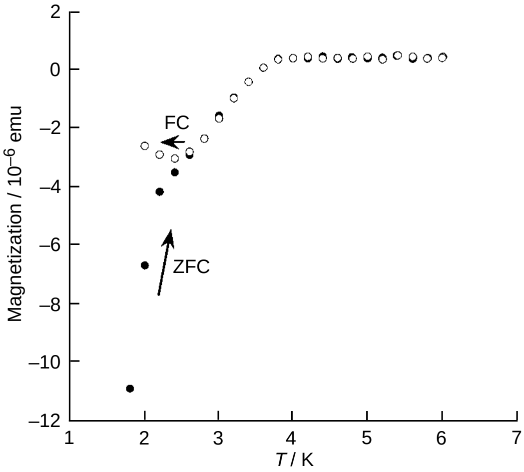

Fig. 2 Temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) dc magnetization with a fixed applied field of 10 Oe

between the FC and ZFC curves indicates that flux is trapped in the sample as it is cooled below the transition temperature.

This BF_4 salt is isostructural with the ClO_4 salt.[3]† The unit cell contains two crystallographically independent donor molecules (A, B) which are associated with conduction layers A and B, respectively (Fig. 3). In both layers, unsymmetrical donor molecules are stacked alternately in a slightly dimerized fashion. The molecular packing in layer B is very similar to that in TMTSF salts. On the other hand, in layer A, donor molecules are packed more loosely. This can be seen by enlarged interplanar distances and seems to be related to a positional disorder of the terminal ethylene group as reflected by the largely elongated thermal ellipsoids (Fig. 3). By comparison, it should be noted that the ethylene group is completely ordered in layer B. Comparison of the bond lengths in these two donor units (A, B) suggests that the difference in the formal charge is rather small and therefore the formal charge is close to +0.5 for each molecule. Layers A and B are separated from each other by an anion layer.

A very unique feature is that these two donor layers differ in anisotropy of the intermolecular interaction, which has been examined by overlap integrals among the HOMOs obtained by the extended Hückel method.[4] As is the case of the ClO_4 salt,[3] the intracolumn interactions in the layer A are largely reduced, which results in a reduction of the anisotropy. The interaction between layers A and B is very small. The conduction band (3/4 filled) is constructed by the HOMO and is composed of two branches associated with the layers A and B, respectively. The tight-binding band calculations, where the interlayer interaction is neglected, indicate that layer A provides a two-dimensional Fermi surface, while layer B provides a quasi-one-dimensional one (Fig. 3).‡ Therefore, the electronic structure of this compound can be described as a hybrid between the TMTSF and BEDT-TTF systems. Almost all superconducting cation radical salts have a single type of conducting layer (column) within the crystal and thus a single type of Fermi surface in the Brillouin zone. In $(TMET\text{-}STF)_2BF_4$, however, there exist two crystallographically independent conduction layers composed of the 'same' molecule, within the 'same' crystal providing different types of Fermi surfaces. Although we neglected the interlayer interaction in the band calculation, there should be small but significant interactions between layers A and B which would affect the physical properties.

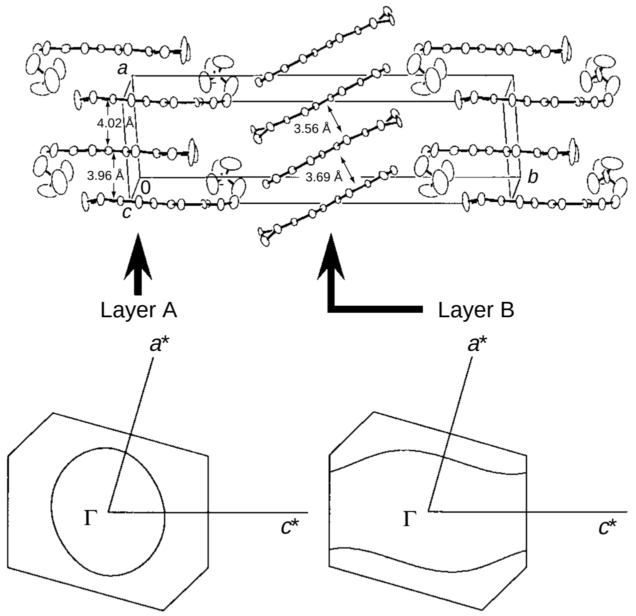

Fig. 3 Crystal structure and calculated Fermi surfaces of $(TMET\text{-}STF)_2BF_4$

The resistivity measurement clearly suggests two types of anomalies in the metallic state which have never previously been observed in conventional organic superconductors. Although they are suggestive of a special electronic state mechanistic details await clarification.

The resistivity behaviour of the isostructural ClO_4 salt was similar to that of the BF_4 salt, except that a superconducting transition was not observed down to 1.5 K under pressures from 1 bar to 16.8 kbar.

In summary, the ambient-pressure superconductivity in the cation radical salt $(TMET\text{-}STF)_2BF_4$ has been established by resistivity and magnetization measurements. This system is a 'two-band' system associated with (quasi) one- and two-dimensional conduction layers within the crystal and is of special interest in view of an interplay among one-dimensional charge localization, higher dimensionality, and superconductivity. TMET-STF is known to provide a variety of cation radical salts.[5–7] Detailed studies on structural and physical properties of these salts are in progress.

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Footnotes

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† *Crystal data* for $(TMET\text{-}STF)_2BF_4$: $C_{22}H_{20}BF_4S_8Se_4$, $M_w = 943.50$, triclinic, space group $P\bar{1}$, $a = 8.030(1)$, $b = 29.646(5)$, $c = 6.546(1)$ Å, $\alpha = 92.48(1)$, $\beta = 105.65(1)$, $\gamma = 93.86(1)°$, $U = 1494.1(4)$ Å^3, $Z = 2$, $D_c = 2.10\ \mathrm{g\ cm^{-3}}$, $F(000) = 914.00$, $R = 0.079$, $R_w = 0.077$, GOF = 3.77. X-Ray diffraction data were collected on a MAC Science automatic four-circle diffractometer with monochromated Mo-Kα ($\lambda = 0.71069$ Å; 50 kV, 300 mA) radiation up to $2\theta = 60°$. The intensities were corrected for Lorentz and polarization effects. The analytical absorption correction was carried out. The structure was solved by the direct method and refined with full-matrix least-squares using 5022 reflections with $I \geqslant 3\sigma(I)$. Anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were included but not refined. All calculations were performed with use of the 'teXsan' crystallographic software package of Molecular Structure Corporation. Two carbon atoms of the ethylene group in molecule A exhibit very large thermal parameters due to positional disorder. It was impossible to refine this ethylene group as a superposition of two possible conformations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/439.

‡ It has been assumed that the transfer integral (t) is proportional to the overlap integral (S), $t = \varepsilon S$ (ε is a constant of the same order as the orbital energies of the HOMO). Based on the filling of each band, we estimated the formal charge of the molecule A to be +0.4 and that of the molecule B to be +0.6. This is consistent with the result of the bond length analysis; each molecule has a formal charge close to +0.5.

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