Superconducting Transition of $(TMTTF)_2PF_6$ above 50 kbar [TMTTF = Tetramethyltetrathiafulvalene]

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Since the discovery of the first organic superconductor $(TMTSF)_2PF_6$ in 1980 (TMTSF = tetramethyltetraselenafulvalene),[1] much progress has been achieved in the field of organic conductors. Two-dimensional organic superconductors such as β- and κ-$(BEDT\text{-}TTF)_2I_3$ were discovered at 1984 and 1987, respectively (BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene),[2,3] which were followed by the discoveries of so-called "10 K-class" κ-type BEDT-TTF superconductors.[4−7] Furthermore, exotic magnetic organic superconductors such as paramagnetic and antiferromagnetic organic superconductors and organic superconductor with Fe^{3+} ions exhibiting the superconductor-to-insulator transition have been also developed recently.[8,9] Despite the vast number of organic conductors developed so far, there are many physicists and chemists who still regard the TMTSF superconductor to be the most attractive organic conductor. Besides superconductivity, this system exhibits novel transport phenomena related to the spin density wave (SDW) instability originating from the one-dimensional nature of the electronic structure. From the chemical viewpoint, the crystal and electronic band structures of $(TMTSF)_2PF_6$ gave us a very useful guiding principle to develop two-dimensional organic conductors.[10,11] That is, the simple extended Hückel tight-binding band calculation based on the frontier molecular orbitals of the constituent π molecules enabled us to analyze the molecular conductors from the viewpoint of molecular design.[12]

Soon after the discovery of the superconductivity in $(TMTSF)_2PF_6$, a series of organic superconductors, the so-called Bechgaard salts $(TMTSF)_2X$ ($X = PF_6$, ClO_4, AsF_6, ...), were discovered.[13] Almost a decade ago, the generalized pressure−temperature ($P-T$) phase diagram was proposed, where all the Bechgaard salts including isostructural sulfur analogues ($(TMTTF)_2X$) were located:[13] TMTTF is tetramethyltetrathiafulvalene and $(TMTSF)_2X$ and $(TMTTF)_2X$ systems are frequently collectively referred to as TM_2X systems. This diagram predicts that $(TMTTF)_2Br$ and $(TMTTF)_2PF_6$ become superconductors by applying 25 and 35 kbar of pressure, respectively. In fact, the superconductivity of $(TMTTF)_2Br$ was discovered in 1994 ($T_c = 0.8$ K at 26 kbar).[14] However, there have been no TM_2X systems whose superconductivities were confirmed in both Se- and S-analogues. Therefore, the discovery of the superconductivity in $(TMTTF)_2PF_6$ has been highly desired. Recently, Moser et al. have reported the detailed phase diagrams of $(TMTSF)_2PF_6$ and $(TMTTF)_2PF_6$ up to 30 kbar.[15] Combining these phase diagrams, $(TMTTF)_2PF_6$ is expected to become a superconductor around 38 kbar. However, this expected critical pressure is too high to be realized by the usual clamp-type high-pressure cell currently used in the high-pressure experiments on organic conductors. We have recently succeeded in improving the technique of diamond anvil four-probe resistivity measurements and obtained the resistivity of an organic single crystal up to 150 kbar.[16] In the course of these studies, we have examined the possibility of superconducting transition in $(TMTTF)_2PF_6$.[17]

The black needle crystals were prepared electrochemically from acetonitrile solution containing TMTTF and $[Bu_4N][PF_6]$. Fresh crystals with typical dimension of $0.30 \times 0.08 \times 0.08$ mm^3 were used. Four gold wires (5 or 10 μm ϕ) bonded to the crystal with gold paint were used as leads, which were set in the four ditches engraved in the surface of a metal gasket by stiff needles. Powdered alumina and epoxy resin were used to keep the insulation between the leads and gasket. Mixed silicone oil was used as a pressure medium. The pressure was determined by the standard ruby fluorescence method. The detailed procedure will be reported elsewhere.[16] The resistivities were measured along the needle axes of the crystals ($\parallel a$) down to 1.7 or 0.5 K.

The results of the resistivity measurements are shown in Figures 1 and 2. Despite of the difficulty in obtaining high-quality resistivity data by the diamond anvil technique, sufficiently accurate resistivity data comparable to those obtained by the usual clamp-type high-pressure cell were obtained by virtue of the

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[1] Jérome, D.; Mazaud, M.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *L95*, 1416.

[2] Yagubskii, E. B.; Shchegolev, I. F.; Laukihin, V. N.; Buravov, L. I. *Pis'ma Zh. Eksp. Teor. Fiz.* **1984**, *39*, 12.

[3] Kobayashi, A.; Kato, R.; Kobayashi, H.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 459−462. Kato, R.; Kobayashi, H.; Kobayashi, A.; Moriyama, S.; Nishio, Y.; Kajita, K.; Sasaki, W. *Chem. Lett.* **1987**, 507−510.

[4] Urayama, H.; Yamochi, H.; Saito, G.; Kawamoto, A.; Tanaka, J.; Mori, T.; Maruyama, Y.; Inokuchi, H. *Chem. Lett.* **1988**, 463.

[5] Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoort, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 2555.

[6] Williams, J. M.; Kini, A. M.; Wang, H. H.; Carlson, K. D.; Geiser, U.; Montgomery, L. K.; Pyrka, G. J.; Watkins, D. M.; Kommers, J. M.; Boryschuk, S. J.; Strieby Crouch, A. V.; Kwok, W. K.; Schirber, J. E.; Overmyer, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 3262.

[7] Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes)*; Prentice Hall, Englewood Cliffs, NJ, 1992.

[8] Kurmoo, M.; Graham, A. W.; Day, P.; Coles, S. J.; Hursthouse, M. B.; Caulfield, J. L.; Singleton, J.; Pratt, F. L.; Hayes, W.; Ducasse, L.; Guionneau, P. *J. Am. Chem. Soc.* **1995**, *117*, 12209−12217.

[9] Kobayashi, H.; Sato, A.; Arai, E.; Akutsu, H.; Kobayashi, A.; Cassoux, P. *J. Am. Chem. Soc.* **1997**, *119*, 12392−12393. Tanaka, H.; Adachi, T.; Ojima, E.; Fujiwara, H.; Kato, K.; Kobayashi, H.; Kobayashi, A.; Cassoux, P. *J. Am. Chem. Soc.* **1999**. *121*, 11243−11244. Ojima, E.; Fujiwara, H.; Kato, K.; Kobayashi, K.; Tanaka, H.; Kobayashi, A.; Cassoux, P. *J. Am. Chem. Soc.* **1999**, *121*, 5581−5582.

[10] Thorup, N.; Rindorf, G.; Soling, H.; Bechgaard, K. *Acta Crystallogr.* **1981**, *B37*, 1236−1240.

[11] For example: Mori, T.; Kobayashi, A.; Sasaki, Y.; Kobayashi, H. *Chem. Lett.* **1982**, 1923−26.

[12] For example: Kobayashi, H.; Kato, R.; Kobayashi, A. *Synth. Met.* **1987**, *19*, 623−628. Kobayashi, A.; Kim, H.; Sasaki, Y.; Kato, R.; Kobayashi, H. *Solid State Commun.* **1987**, *62*, 57−64.

[13] Jérome, D. *Science* **1991**, *252*, 1509−1514.

[14] Balicas, L.; Behnia, K.; Kang, W.; Auban-Senzier, P.; Canadell, E.; Jérome, D. *Adv. Mater.* **1994**, *6*, 762−765.

[15] Moser, J.; Gabay, M.; Auban-Senzier, P.; Jérome, D.; Bechgaard, K.; Fabre, J. M. *Eur. Phys. J.* **1998**, *B1*, 39−46.

[16] Adachi, T.; Miyazaki, T.; Kobayashi, H. To be submitted for publication.

[17] Adachi, T. Annual Meeting on the Molecular Structures, Sept. 27−30, 1999, Osaka, Japan. Kobayashi, H. International Workshop on Control of Conduction Mechanism in Organic Conductors (ConCOM'99), Nov. 22−24, 1999, Tokyo, Japan.

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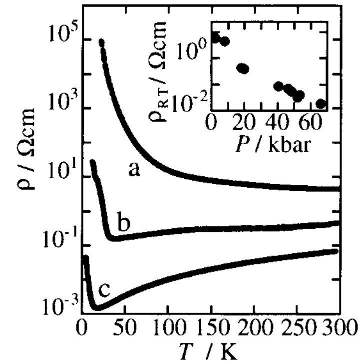

Figure 1. The resistivity of (TMTTF)$_2$PF$_6$ along the molecular stacking direction (∥*a*): (a) 8, (b) 18, and (c) 47 kbar. The inset shows the pressure dependence of the room temperature resistivity.

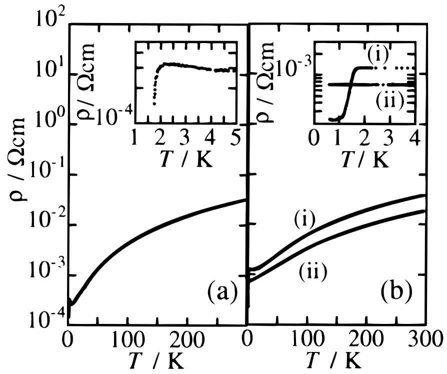

Figure 2. (a) The resistivity of (TMTTF)$_2$PF$_6$ at 52 kbar. (b) The resistivity of (TMTTF)$_2$PF$_6$ at (i) 54 and (ii) 66 kbar.

improved diamond-anvil four-probe technique. Below 10 kbar, the resistivity showed a sluggish increase with decreasing temperature, indicating the localization of conduction electrons. It has been reported that the system has a spin-Peierls (SP) ground state in this low-pressure region.[13,15] The resistivity around 18 kbar showed a metallic behavior down to ca. 30 K and increased very sharply below 25 K. This resistivity behavior is essentially the same as that reported by Moser et al.[15] The ground state in this pressure region has been reported to be the SDW state.[13,15] The resistivity increase due to the SDW transition was suppressed with increasing pressure. Unexpectedly, however, the crystal showed a metal−insulator (MI) transition even at 47 kbar. The room temperature resistivity (ρ_{RT}) was decreased with increasing pressure (see the inset of Figure 1): the ratio of ρ_{RT}(1bar)/ρ_{RT}(50 kbar) was about 100.

As shown in Figure 2a, the small resistivity increase in the low-temperature region, which is the trace of the SDW transition, was observed even around 52 kbar. Thus the critical pressure was revealed to be much higher than the expected one (35 kbar).[13,15] The resistivity measurements at 52 kbar showed a peak around 2.3 K and a sharp drop around 1.8 K, indicating the superconducting transition. The resistivity drop was observed in all the crystals (three samples) examined up to 52 kbar and down to 1.7 K. At 54 kbar the low-temperature resistivity increase was suppressed and a sharp resistivity drop was observed at 1.4 K (Figure 2b). At 66 kbar no trace of any resistivity drop was observed down to 0.5 K, showing the suppression of the superconducting phase by higher pressure. These results are in good agreement with the generalized $P-T$ phase diagram except for the pressure scale (Figure 3). However, it should be noted that the maximum T_{c} of (TMTTF)$_2$PF$_6$ (=1.4−1.8 K at 52−54 kbar) is much higher than the T_{c} of the (TMTSF)$_2$PF$_6$ system: the maximum T_{c} of (TMTSF)$_2$PF$_6$ estimated from the reported $P-T$ phase diagram is about 1.2 K.[15] Roughly speaking, the important parameters to characterize the electronic structure of the TM$_2$X system are the transfer integral (t) and on-site Coulomb interaction (U). It may be imagined that t can be enhanced by pressure but U is considered to be almost pressure independent. It is well-known that the difference between the first and second oxidation potentials of the donor molecule ($\Delta E_{1/2} = E_{1/2}(1) - E_{1/2}(2)$) can be regarded as a rough measure of U: $\Delta E_{1/2}$(TMTTF) = 480 meV and $\Delta E_{1/2}$(TMTSF) 390 meV.[18] The generalized $P-T$ phase diagram suggests the value of t/U of (TMTSF)$_2$PF$_6$ at 9 kbar is approximately equal to that of (TMTTF)$_2$PF$_6$ around 50 kbar, which requires the large t for large U. The larger t and U in (TMTTF)$_2$PF$_6$ will be consistent with the higher T_{c}. This allows us to have a new understanding of a very simple way to elevate T_{c} of the organic superconductor. That is, the simultaneous enhancement of both U and t will elevate T_{c}. In the present (TMTTF)$_2$PF$_6$ system, large U is realized by the replacement of Se atoms into S atoms and large t is realized by pressure. The enhancement of T_{c} by the strong electron correlation has been found in κ-type BEDT-TTF and λ-type BETS superconductors with correlated semiconducting properties around room temperature: maximum T_{c} is 13 K for κ-type BEDT-TTF superconductors[7] and 10 K for λ-type BETS superconductors (BETS = bis(ethylenedithio)tetraselenafulvalene).[19] In general, strong electron correlation (or large U) and metallic properties are contradictive to each other but the present work supports the very simple idea that the design of organic conductor with large U and large t will be a shortcut to obtain an organic superconductor with enhanced T_{c}.

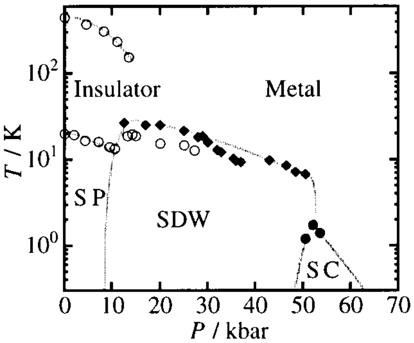

Figure 3. The $P-T$ phase diagram of the (TMTTF)$_2$PF$_6$ system. The data points indicated by closed squares and circles were obtained in this work and the open circles are taken form ref 15. SP, spin-Peierls phase; SDW, spin density wave phase; and SC, superconducting phase.

In summary, we have observed a superconducting transition of (TMTTF)$_2$PF$_6$: T_{c} is 1.4−1.8 K at 52−54 kbar. The present work shows not only the validity of the reported generalized $P-T$ phase diagram of Bechgaard salts but also the applicability of the convenient diamond anvil four-probe resistivity measurements to the soft organic single crystals.

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(18) Papavassiliou, G. C.; Terzis, A.; Delhaes, P. In *Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, New York 1997.

(19) Tanaka, H.; Kobayashi, A.; Sato, A.; Akutsu, H.; Kobayashi, H. *J. Am. Chem. Soc.* **1999**, *121*, 760−768. Kobayashi, H.; Akutsu, H.; Arai, E.; Tanaka, H.; Kobayashi, A. *Phys. Rev.* **1997**, *B56*, R8526−R8529.