Two-dimensional electrons realized in a quasi-one-dimensional conductor with anions having finite electric dipole moments

W. Kang,[1,3,*] O. H. Chung,[2,4] Y. J. Jo,[1] Haeyong Kang,[1] and I. S. Seo[2]
[1]*Department of Physics, Ewha University, Seoul 120-750, South Korea*
[2]*Department of Physics, Sunchon University, Sunchon 540-742, South Korea*
[3]*National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA*
[4]*Material Science Laboratory, Korea Basic Science Institute, Taejeon 305-333, South Korea*
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Genuine two-dimensional electrons have been realized in the Bechgaard salt, the representative quasi-one-dimensional electron system. Two-dimensional characteristics such as Yamaji resonance, conventional magnetic quantum oscillations, a coherent interlayer magnetoresistance peak effect, and so on were clearly observed in tetramethyltetraselenafulvalene fluorosulfonate $(TMTSF)_2FSO_3$, a unique example that has anions with finite electric dipole moments. The introduction of additional periodic potential due to electric dipole moments drastically changes the electronic structure.

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Although a variety of physical phenomena such as metal-insulator transition superconductivity, spin-density waves, field-induced spin-density waves, etc., have been observed in the Bechgaard salts $(TMTSF)_2X$ (TMTSF =tetramethyltetraselenafulvalene, X=monovalent anions) when temperature, pressure, magnetic field, or anions were varied, all of them could be explained in the context of quasi-one-dimensional electron physics[1] with the Fermi surface consisting of a pair of simple weakly warped sheets at $k_x \sim \pm k_F$. $X = FSO_3$ anions are unique in that they carry permanent electric dipole moments.[2] The first studies showed only a simple pressure-temperature phase diagram in which the physical ground states were often not well defined.[3,4] However, our recent reinvestigation showed that $(TMTSF)_2FSO_3$ has a very reproducible and very complex phase diagram,[5] which is presumably related to the additional degree of freedom given by the electric dipole moments. [See Fig. 1(a).]

Physical properties of low-dimensional metal are very sensitive to the Fermi surface morphology. Angle-dependent resistance under a constant magnetic field, or angular magnetoresistance, is particularly sensitive to the details of the Fermi surface such as amplitude and direction of warping, electronic dimension, etc. For example, Lebed resonance[6–11] or Danner-Kang-Chaikin[12] resonance occur in a quasi-one-dimensional electron system like the Bechgaard salts when a magnetic field rotates in the *b*-*c* or *a*-*c* plane, respectively. On the other hand, Yamaji resonance[13] occurs for the quasi-two-dimensional weakly corrugated cylindrical Fermi surface such as those of numerous $(BEDT\text{-}TTF)_2X$ (BEDT-TTF =bisethylenedithiotetrathiofulvalene) compounds.[14–17] A similar effect has also been found in inorganic two-dimensional compounds such as Sr_2RuO_4 (Ref. 18) and stage two $SbCl_5$ intercalated graphite.[19]

In this paper we report on the field-dependent and angle-dependent magnetoresistance study of $(TMTSF)_2FSO_3$ along the least conducting c direction under the pressure around 6.2 kbar. Although Lebed resonance has been found in at least three sister compounds, $X = ClO_4$,[8,9] PF_6,[10] and ReO_4,[11] strikingly different behavior was found in the angular magnetoresistance of $(TMTSF)_2FSO_3$. We interpret it in terms of Yamaji resonance, rendering $(TMTSF)_2FSO_3$ the first Bechgaard salt showing a genuine two-dimensional electron behavior. We also present a series of additional evidence supporting the presence of genuinely two-dimensional electrons. Finally, a possible mechanism for the formation of two-dimensional electrons is discussed.

The samples were grown using typical electrocrystallization techniques. Four 20-μm annealed gold wires were attached to each sample with silver paste to measure the interlayer resistance (R_{zz}). A conventional low-frequency ac lock-in method was used. The soundness of the present data is confirmed through three independent experiments at two different places involving three samples each using three different pressure cells. Pressure was generated in a self-clamped pressure cell using the 1:1 mixture of the Daphne 7373 and kerosen oils as a pressure medium.[20] Throughout the paper pressure values calibrated at low temperature are used.

Figure 1(a) shows $R_{zz}(T)$ on cooling under 6.2 kbar. An approximate cooling path is indicated on the phase diagram in Fig. 1(b).[5] Transition I is known to be an (1/2,1/2,1/2)

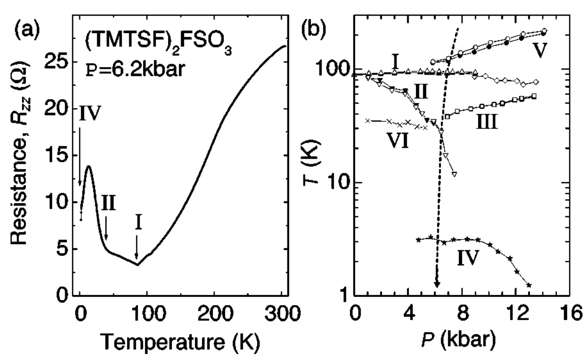

FIG. 1. (a) R_{zz} versus temperature at 6.2 kbar. (b) Approximate cooling path on the phase diagram. Some of transitions are indicated on the cooling curve. For details of the phase diagram refer to Ref. 5.

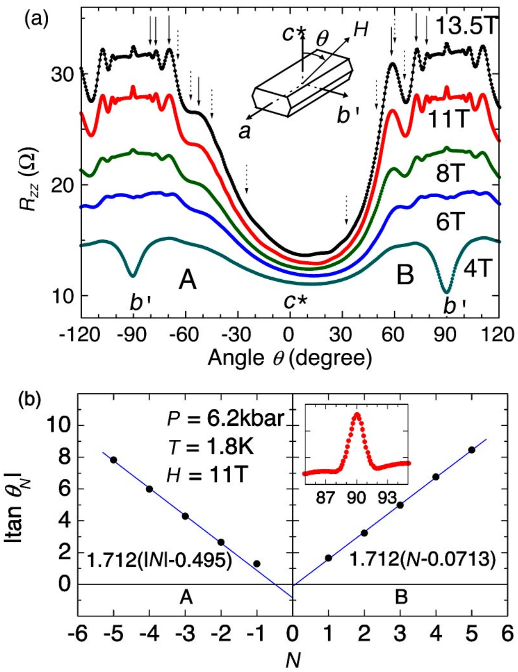

FIG. 2. (a) Angular magnetoresistance of $(TMTSF)_2FSO_3$ under 6.2 kbar and at 1.8 K. The angles predicted by Eq. (1) are indicated with broken arrows. The peak of the 11-T curve around the b' direction is enlarged in (b). (b) Plot of $|\tan\theta_N|$ versus N where θ_N are angles for the peaks in angular magnetoresistance [solid arrows in (a)]. Parts A and B correspond to the sides for negative and positive N, respectively. Lines are the least-square fittings. The point for $N=-1$ is excluded because its angular position is difficult to determine precisely.

anion ordering transition.[21,22] Across transition II, resistance increases abruptly, but the metallic state is soon recovered under intermediate pressure and an incomplete superconducting transition is observed (IV) around 3 K. For the moment, the detailed nature of transition II is unknown.

Angular magnetoresistance of $(TMTSF)_2FSO_3$ under 6.2 kbar and at 1.8 K for five different magnetic fields is shown in Fig. 2(a). Oscillations are clearly seen superposed on a slowly varying background. Strikingly, their overall feature is quite different from the Lebed oscillations observed in other Bechgaard salts.[8–11] Neither the angular positions of dips nor those of peaks correspond to the angles predicted for the Lebed resonance (indicated with broken arrows on the 13.5-T curve).

At this point we need to review briefly the two resonance phenomena of the low-dimensional electrons. Lebed and Bak predicted that quasi-one-dimensional metals would exhibit magnetoresistance peaks at special orientations of the magnetic field in the bc plane, where the periods of electron motions along the k_b and k_c directions on an open Fermi-surface sheet are commensurate.[6,7] The so-called magic angles are given for the triclinic lattice by

$$\tan\theta=\frac{p}{q}\,\frac{b\sin\gamma}{c\sin\beta\sin\alpha^*}-\cot\alpha^*, \qquad (1)$$

in which θ denotes the angle that the magnetic field makes from the c^* direction; p and q are small integers; and b, c, β, γ, and α^* are lattice parameters.[8,9] From its nature, Lebed resonance is present only in quasi-one-dimensional electron systems such as $(TMTSF)_2X$.

On the other hand in case of the cylindrical Fermi surface with weak modulation along the k_c direction, there are special angles at which the distribution of the Fermi-surface cross section disappears completely. The electron eigenenergies near the Fermi surface are then fully quantized into Landau levels and the magnetoresistance is very much enhanced.[13] More realistic analysis with a consideration of the general triclinic structure was developed by Kartsovnik *et al.*[14] The angles are given in the simplest form when a magnetic field rotates in a plane containing one of major axes, as[13,14]

$$ck_F|\tan\theta_N|=\pi\left(|N|-\frac{1}{4}\right)\pm C(\phi), \qquad (2)$$

where c is the distance between adjacent conducting planes, k_F is the average Fermi wave vector parallel to the major axis, N is the index of resonance, and θ_N is the angle for the Nth peak measured from the axis of the cylindrical Fermi surface. $C(\phi)$ is a function of azimuthal angle ϕ and disappears for the tetragonal system. The Fermi wave vector k_F can be readily determined quantitatively from the $\tan\theta_N$ versus N plot in Eq. (2).

Surprisingly the angular positions of resistance peaks in Fig. 2(a) are well fitted by Eq. (2), as shown in Fig. 2(b). In fact, the overall angular magnetoresistance is very similar to those observed in the textbook examples of quasi-two-dimensional electron systems such as β-$(BEDT\text{-}TTF)_2X$, $X=IBr_2$,[14] and I_3.[16] Figure 2(b) reveals some interesting facts. First, the left side can be fitted with $\tan\theta_N=1.712(N-0.0713)$ and the right side with $|\tan\theta_N|=1.712(|N|-0.495)$. The slopes of two sides agree with each other remarkably well and give 0.139 $Å^{-1}$ for the Fermi wave vector. Second, the phases or the intercepts with the x axis of the linear fittings are very different from the standard Yamaji formula and are strongly asymmetric. This reflects the triclinic structure of this compound for which the corrugation is not symmetric.

Another important result suggesting the quasi-two-dimensional Fermi surface in $(TMTSF)_2FSO_3$ is the narrow peak of width 4.0°, observed when the magnetic field is nearly parallel to the b' axis, is shown enlarged in the inset of Fig. 2(b). The existence of the small belly due to the third directional warping of the otherwise two-dimensional cylindrical Fermi surface, that is, the coherent interlayer transport, is the origin of this peak.[15–17] The half width of the peak is related with the transfer integral along the third direction such as

$$\frac{\pi}{2}-\theta_c=\frac{2m^*t_cc}{\hbar^2k_F}, \qquad (3)$$

where θ_c is the critical angle above which the resistance increases rapidly.[15] Using the values of m^* and k_F obtained by the temperature dependence of amplitudes of Shubnikov–de Haas oscillations (see below) and the fitting to Eq. (2), respectively, we have $t_c \simeq 1.01\times 10^{-3}$ eV, which can be compared with values reported by Danner *et al.*[12] from the fitting of ρ_{zz} of $(TMTSF)_2ClO_4$ in the *ac* rotation.

The third argument that supports the idea of a two-dimensional Fermi surface in $(TMTSF)_2FSO_3$ is the temperature and field dependence of Shubnikov–de Haas oscillations. Oscillations arising from conventional closed orbits are in general well interpreted with the Lifshitz-Kosevich formula.[23] In a simplified form in which only the first harmonic is considered and the spin-splitting effect is ignored, the Lifshitz-Kosevich formula states that the oscillation amplitude $\Delta R/R$ can be represented as

$$\Delta R/R \propto T \exp(-\lambda \mu T_{\mathrm{D}}/H)/\sqrt{H}\sinh(\lambda \mu T/H), \qquad (4)$$

where $\lambda = 2\pi^2 k_{\mathrm{B}} m_0/e\hbar = 14.7$ T/K, μ is the effective cyclotron mass in relative units of the free-electron mass m_0, and T_{D} the Dingle temperature. Although Shubnikov–de Haas-like oscillations are frequently observed in magnetoresistance of other $(TMTSF)_2X$, they do not arise from closed electron orbits but from a complex interplay between magnetic breakdown and Bragg reflection between the warped open Fermi surfaces.[24] While they are also periodic in $1/H$ such as the conventional Shubnikov–de Haas oscillations, the temperature dependence of oscillation amplitude has one or two maxima and the oscillation eventually vanishes at very low temperature. Application of the Lifshitz-Kosevich formula has never worked for them.

Magnetoresistance of $(TMTSF)_2FSO_3$ at several temperatures is shown in Fig. 3(a). The fast Fourier-transform (FFT) spectrum of the data between 6.25 and 18 T at 0.2 K is also shown in Fig. 3(b). The fundamental frequency of oscillations is 130.3 T. The amplitude of the second harmonic is as large as 20% of the fundamental. We present the oscillation amplitude $\Delta R/R$ as a function of temperature and magnetic field in Figs. 3(c) and 3(d). Lines in the figures are fittings to Eq. (4) which reveals $\mu = 1.39$ and $T_{\mathrm{D}} = 2.5$ K. Angular variation of oscillation frequency, showing the $1/\cos\theta$ behavior of the oscillation frequency up to $\pm 70°$ from the c^* axis [inset of Fig. 3(b)], is another typical characteristic of the Shubnikov–de Haas oscillations arising from the cylindrical Fermi surface.

Determined from the frequency of Shubnikov–de Haas oscillations, the cross-sectional area of the cylindrical Fermi surface is 1.24×10^{14} cm^{-2} corresponding to about 1.6% of the first Brillouin zone. To conciliate k_{F} previously determined in Fig. 2, we consider a Fermi surface section that is strongly elongated along the k_b direction.

The fourth argument favoring the two-dimensional electrons is absence of the field-induced spin-density waves up to a magnetic field as high as 33 T [inset of Fig. 3(a)]. It was suggested that the presence of superconductivity at zero field is prerequisite to the field-induced spin-density waves under magnetic field.[25] While this argument has been supported by $(TMTSF)_2NO_3$ it fails for $(TMTSF)_2FSO_3$ where the superconducting transition (transition IV in Fig. 1, inset) is readily observed, whereas the field-induced spin-density waves are

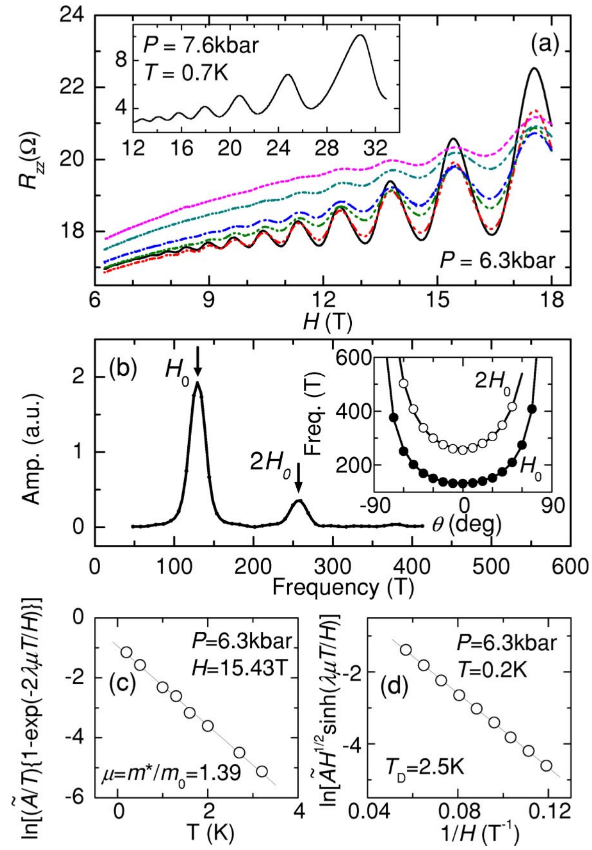

FIG. 3. (a) Magnetoresistance $R_{zz}(H)$ at temperatures 0.2, 1.0, 1.6, 2.0, 2.7, and 3.5 K from below. Inset shows the high-field data up to 33 T. (b) FFT spectrum of the data at 0.2 K, and the plot of the two lowest harmonic frequencies versus the angle between the magnetic field and the c^* axis in the inset. Solid lines are fittings to $nH_0/\cos\theta$. (c) Fitting to the Lifshitz-Kosevich formula with $\mu = 1.39$ as a function of temperature. $\tilde{A} = \Delta R/R$ is the oscillating amplitude of resistance normalized by background resistance at 15.43 T. (d) Fitting to the Lifshitz-Kosevich formula as a function of $1/H$ at 0.2 K.

absent.[5] But the absence of field-induced spin-density waves is natural if $(TMTSF)_2FSO_3$ has two-dimensional electrons instead of quasi-one-dimensional electrons. In addition, an unusually high superconducting critical temperature T_c of $(TMTSF)_2FSO_3$, about 3 K rather than 1 K typical in other Bechgaard salts, may also be due to the two dimensionality since the T_c in two-dimensional organic superconductors is usually higher than that in quasi-one-dimensional superconductors.

Now let's consider the mechanism that induces two-dimensional electrons in the Bechgaard salts. Figure 4(a) shows that the normalized magnetoresistance, $\Delta R/R$, is very similar between 5.6 and 6.2 kbar, suggesting that the electronic structure is almost the same while the number of carriers changes substantially between two pressures. To the contrary, the characteristics of two dimensionality deteriorate quickly on increasing pressure further [Fig. 4(b)]. These observations rule out the simple argument that the two-dimensional Fermi surface results from the optimized nesting between open Fermi surfaces by pressure. It seems that struc-

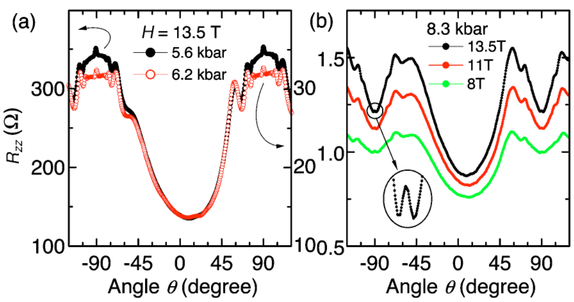

FIG. 4. (a) Comparison of angular magnetoresistance under 5.6 and 6.2 kbar. In spite of the tenfold increase of resistance the overall structure is the same. (b) Only remnants of the resonances and the 90° peak are present under 8.3 kbar.

tural ordering of anions around 90 K is not important either. A preliminary x-ray analysis confirmed that the almost temperature-independent transition line I is due to the (1/2, 1/2,1/2) anion ordering, and showed that (1/2,1/2,1/2) and anion ordering is present at 20 K both at the ambient pressure and under 7.2 kbar.[22] Then, it is probable that transition II in the phase diagram is responsible for the formation of the two-dimensional Fermi surface, possibly by the ordering of the electric dipole moment. At low pressure, the large anion ordering gap at high temperature limits the number of carriers on the two-dimensional Fermi surface. Then, the overall resistance increases while keeping the whole structure of Yamaji resonance. Nondiverging and then metallic thermopower below transition II at low pressure support this hypothesis.[5]

In summary we report that genuine two-dimensional electrons can be realized in the Bechgaard salts which have been regarded as a representative of quasi-one-dimensional electron systems. $(TMTSF)_2FSO_3$ showed the characteristics of typical quasi-two-dimensional Fermi surface such as the Yamaji resonance in the angular magnetoresistance, the conventional Shubnikov–de Haas effect following the Lifshitz-Kosevich formula rigorously, the magnetoresistance peak due to the presence of belly orbits, and the absence of field-induced spin-density waves, while all other Bechgaard salts exhibit typical quasi-one-dimensional characteristics. From the pressure dependence of the two-dimensional nature, we attribute the two dimensionalization to a new phase transition (possibly, the line II) and suggest that it is closely related to the existence of finite electric dipole moments on anions.

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*Electronic address: wkang@ewha.ac.kr

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