# Interlayer Charge Disproportionation in the Layered Organic Superconductor $\kappa_H$-(DMEDO-TSeF)$_2$[Au(CN)$_4$](THF) with Polar Dielectric Insulating Layers

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We report the molecular dipole effect on conduction electrons in the title superconductor. The angular-
dependent magnetoresistance has a peak for fields nearly parallel to the conducting layer, and the peak
width scales as the field component perpendicular to the layer, indicating incoherent interlayer transport.
However, two closed Fermi surfaces are observed in quantum oscillation. Accordingly, crystallograph-
ically independent layers have different charge densities in a bulk single crystal. The electric dipole of
tetrahydrofuran gives rise to interlayer charge disproportionation.

Typical layered organic superconductors are composed
of organic donor and inorganic anion molecules, and
donors (anions) form conducting (insulating) layers. How-
ever, some organic superconductors contain another
chemical component, a neutral solvent molecule, in their
anion insulating layer [1]. When polar solvent molecules
are involved, a permanent electric-dipole moment poten-
tially affords a profound effect on conduction electrons in
conducting layers. However, the effect of a molecular
dipole on conduction electrons in layered superconductors
has not been clarified yet.

Layered conductors have another interesting problem,
interlayer coherency. The interlayer coherency of layered
conductors has been investigated by many research groups
[2–9]. If interlayer coupling is strong, namely, the inter-
layer hopping rate $t_\perp/\hbar$, where $t_\perp$ is the interlayer transfer
integral and $\hbar$ is the Planck constant, is sufficiently larger
than the intralayer scattering rate $\tau^{-1}$, interlayer electronic
transport is coherent and described by the warped cylin-
drical Fermi surface (FS) [Fig. 1(a)]. In another limit,
$\hbar/\tau \gg t_\perp$, incoherent interlayer transport is expected. In
this case, interlayer conductivity is proportional to the rate
of tunneling between two adjacent layers, and the FS is
defined only in the plane of the layers [Fig. 1(b)]. Since
most of the layered conductors investigated so far show
coherent transport, a study of an incoherent system is of
fundamental interest.

We can naively expect that an organic conductor
with thick anion layers potentially has a small inter-
layer interaction. Two organic superconductors with
the same chemical composition, i.e., $\kappa_L$- and
$\kappa_H$-(DMEDO-TSeF)$_2$[Au(CN)$_4$](THF) [where DMEDO-
TSeF is dimethyl(ethylenedioxy)tetraselenafulvalene and

THF is tetrahydrofuran] as shown in Figs. 1(c) and 1(d),
have been developed [10]. The $\kappa_L$ phase (onset
$T_c = 3.0$ K) has a disordered solvent molecule THF, and
shows an orthorhombic-monoclinic distortion phase tran-
sition at $T_d = 209$ K [11–13]. The low temperature struc-
ture consists of two monoclinic domains. By contrast, THF
in the $\kappa_H$ phase (onset $T_c = 4.8$ K) is ordered. THF is a
polar molecule and exhibits ferroelectric-like ordering
in the insulating layer of the $\kappa_H$ phase, even at room
temperature [Fig. 1(d)]; the relationship between the insu-
lating layers is antiferroelectric-like. Moreover, there are
two crystallographically independent conducting layers (*A*
and *B*) and both layers have a $\kappa$-type structure [Figs. 1(c)
and 1(d)]. The $\kappa_H$ phase is expected to have a strong
interaction between the permanent electric-dipole moment
of THF and conduction electrons. This is reminiscent of
Ginzburg's mechanism of superconductivity because its
conducting layer is sandwiched by dielectric insulating
layers [14]. The $\kappa_H$ phase is a two-dimensional super-
conductor confirmed from the angular dependence of the
upper critical fields and the small interlayer coherence
length, $\xi_\perp = 3.1(3)$ Å [15]. This indicates a possibility
of an incoherent interlayer transport system for the $\kappa_H$
phase. In the present Letter, we report the angular-
dependent magnetoresistance and the Shubnikov–de Haas
(SdH) oscillations of the $\kappa_H$ phase. The results reveal that
the $\kappa_H$ phase is an incoherent system and that the charge
transfer degrees of the donor layer *A* differs from that of
*B* in a bulk single crystal.

Single crystals were prepared by electrocrystallization
[10]. The energy band structure was calculated by the
extended Hückel method and tight binding approximation
[16]. Interlayer resistance ($I \parallel a^*$) was measured by the
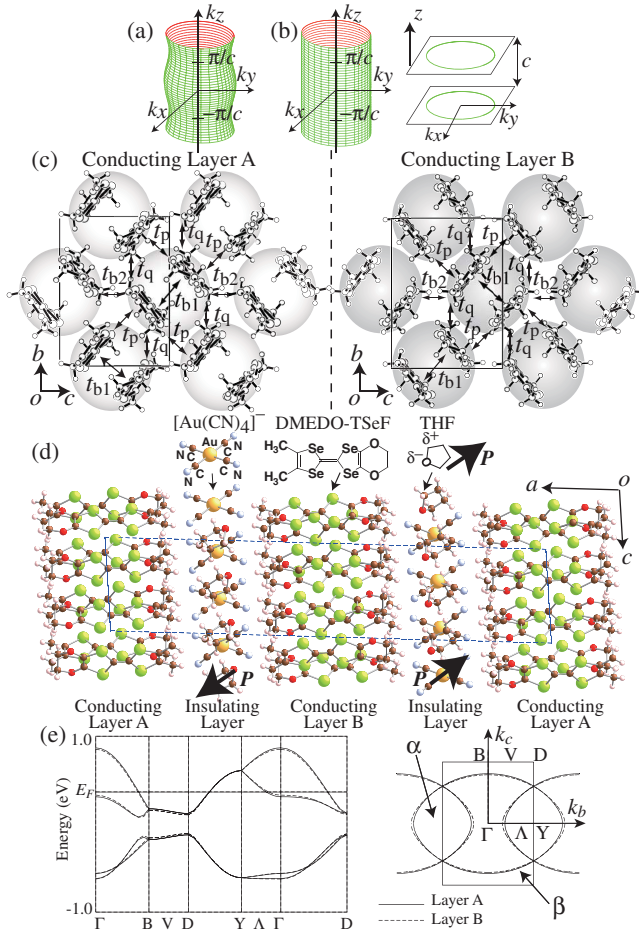
FIG. 1 (color).   Fermi surfaces of (a) coherent and (b) incoherent layered systems. For the incoherent layered system, the cylindrical FS with no dispersion along the $k_z$ direction is independently defined within each layer. The stack structure of independent cylindrical FSs is schematically depicted in the right panel of (b), where $c$ is the layer distance in real space. (c) Crystal structure projected along molecular long axis and (d) projection onto $ac$ plane of $\kappa_H$-(DMEDO-TSeF)$_2$[Au(CN)$_4$](THF). The shaded circles in (c) represent dimers, and the bold arrows in (d) denote the polarization vector $\boldsymbol{P}$ of THF molecules. (e) Band structure and FSs. The transfer integrals calculated are $t_{b1} = -355.9$, $t_{b2} = -234.0$, $t_p = -76.7$, and $t_q = 62.3$ meV for the layer $A$, and $t_{b1} = -348.8$, $t_{b2} = -242.1$, $t_p = -73.3$, and $t_q = 57.1$ meV for the layer $B$.

four probe method with ac current (0.01–0.3 $\mu$A). A bridge circuit was used to accurately measure the peak structure of angular-dependent magnetoresistance. The angular-dependent magnetoresistance measurement was performed using a 35 T resistive magnet at NHMFL in Tallahassee. The SdH measurement was performed using a 20 T superconducting magnet at NIMS.

The calculated band structure and FSs are shown in Fig. 1(e), where we assume that the charge transfer degree from the donor to anion is 0.5 per molecule for both $A$ and $B$. The FS consists of overlapping cylinders, which

generate the fundamental $\alpha$ and $\beta$ orbits. The FSs obtained are similar to that of the $\kappa_L$ phase. The energy bands are degenerate on both BD and DY lines of the first Brillouin zone (BZ), owing to the crystallographic symmetries. When a dimer has one hole for both layers, the cross-sectional area of the $\alpha$-orbit is about 25% of the first Brillouin zone $S_{BZ}$, and that of the $\beta$-orbit, $S_\beta$, is exactly the same as $S_{BZ}$ for both layers.

Figure 2(a) shows the angular-dependent magnetoresistance at 1.2 K for various magnetic fields. The field orientation is defined by a tilt angle $\theta$ between the field direction and the $a^*$-axis. Although a common shape of the angular-dependent interlayer magnetoresistance has a minimum at $\theta = 0°$ and a maximum at $\theta = 90°$ in a quasi-two-dimensional system [7,9], the present results show an opposite behavior at 12.5 T. This unusual behavior suggests that the present compound is not a coherent system [8].

The magnetoresistance of a conductor with a cylindrical FS for magnetic fields nearly parallel to the conducting plane, i.e., $\theta = 90°$, has a peak structure. Hanasaki *et al.* have demonstrated that the magnetoresistance peak
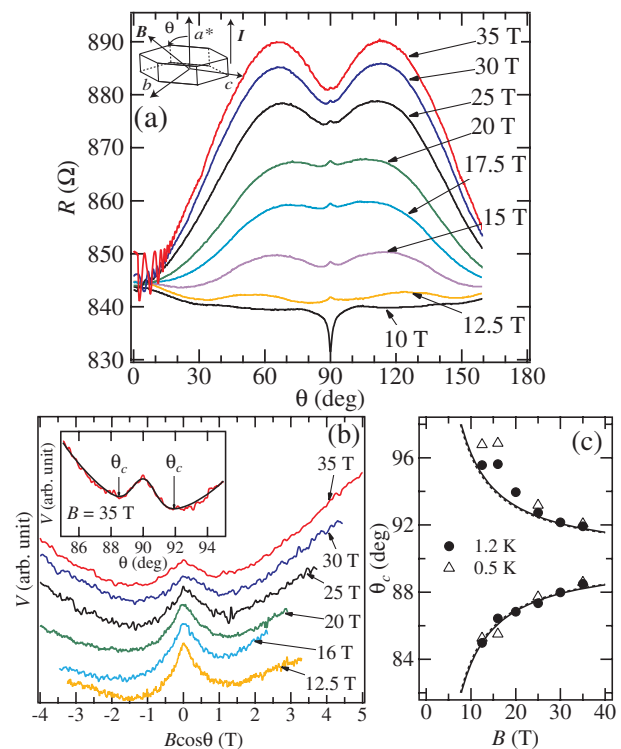


FIG. 2 (color).   (a) Angular-dependent magnetoresistance at 1.2 K for various magnetic fields. The fast oscillating behavior at approximately $\theta \lesssim 20°$ under high fields is the SdH oscillation. The resistance dip at $\theta = 90°$ at 10 T shows superconductivity surviving owing to the anisotropic upper critical fields. (b) The peak structure at approximately $\theta = 90°$ scaled by $B\cos\theta$. The inset shows the definition of the critical angle $\theta_c$. (c) Magnetic field dependence of the critical angle. Solid and dotted lines are fitted to the $\cos^{-1}(B_0/B)$ dependence.

structure, which we call the 90° peak, is ascribed to the closed orbits formed on the side of the corrugated cylindrical FS [17]. McKenzie and Moses have shown that the 90° peak is one indication for the coherency of interlayer transport [3,4]. In the model of Hanasaki *et al.*, this peak width is related to the interlayer transfer integral $t_\perp$ as $[(\pi/2) - \theta_c] = (2m^* t_\perp d)/(\hbar^2 k_F)$, where $\theta_c$ is the critical angle defined in Fig. 2(b), $m^*$ is the effective cyclotron mass, $d$ is the interlayer spacing, and $k_F$ is the Fermi wave number. This means that the critical angle is independent of magnetic field. The present compound shows that the peak width clearly decreases with increasing magnetic field, and that the magnetoresistance at approximately $\theta = 90°$ is scaled by $B\cos\theta$ [Fig. 2(b)]. The critical angle exhibits $\theta_c = \cos^{-1}(B_0/B)$, where $B_0$ is a characteristic magnetic field and the only fitting parameter [Fig. 2(c)]. The obtained $B_0$ is independent of temperature; $B_0$ is 1.09(4) T at 1.2 K; it is 1.07(9) T at 0.5 K.

Kennett and McKenzie have proposed a new model for the 90° peak in the angular-dependent magnetoresistance [18]. They have considered quantum correction to the semiclassical conductivity in the incoherent layered system, and found that the 90° peak appears owing to the weak localization effect. If the 90° peak comes from the localization effect for the two-dimensional electron system, magnetoresistance is scaled by $B\cos\theta$. This means that a negative magnetoresistance appears under a magnetic field perpendicular to conducting layers below $B_0$; this is a type of Anderson localization. Unfortunately, we cannot observe such a phenomenon because the present compound is a superconductor.

Figure 3(a) shows the magnetic field dependence of interlayer resistance at 0.04 K ($B \parallel a^*$). Above 11 T, magnetoresistance shows an oscillating behavior. The oscillatory part (SdH signal) of resistance represented by $[R(B) - R_0(B)]/R_0(B)$, rescaled by the nonoscillatory background $R_0(B)$, is shown in the inset. The fast Fourier transformation (FFT) spectrum based on the SdH signal shows three peaks: $\beta_1$, $\beta_2$, and $2\beta_1$ [Fig. 3(b)]. The obtained frequencies are summarized in Table I, and the uncertainty of the SdH frequencies in Table I is given by the full width at half maximum of the peak in the FFT spectrum. The observed $S_{\beta_1}$ is 98.0(7)% of $S_{BZ}$, and that of the $\beta_2$ orbit is 108.2(7)%, where $S_{BZ}$ is calculated using the lattice constants at room temperature. Both $S_{\beta_1}$ and $S_{\beta_2}$ are assigned to the large cross section estimated from the band calculation [Fig. 1(e)]. The second-harmonic orbit of the $\beta_1$ orbit, $2\beta_1$, is also observed. The degeneracy of the bands on the DY line of the first Brillouin zone in Fig. 1(e) is consistent with absence of the $\alpha$-orbit, $F_\alpha \sim 1100$ T.

The SdH signals are analyzed using the two-dimensional Lifshitz–Kosevich formula for FFT amplitude [19]. SdH frequencies show a $1/\cos\theta$ dependence and have no tendency to cross each other [Fig. 3(c)]. This indicates that the both $\beta_1$ and $\beta_2$ orbits are two-dimensional FSs and that the
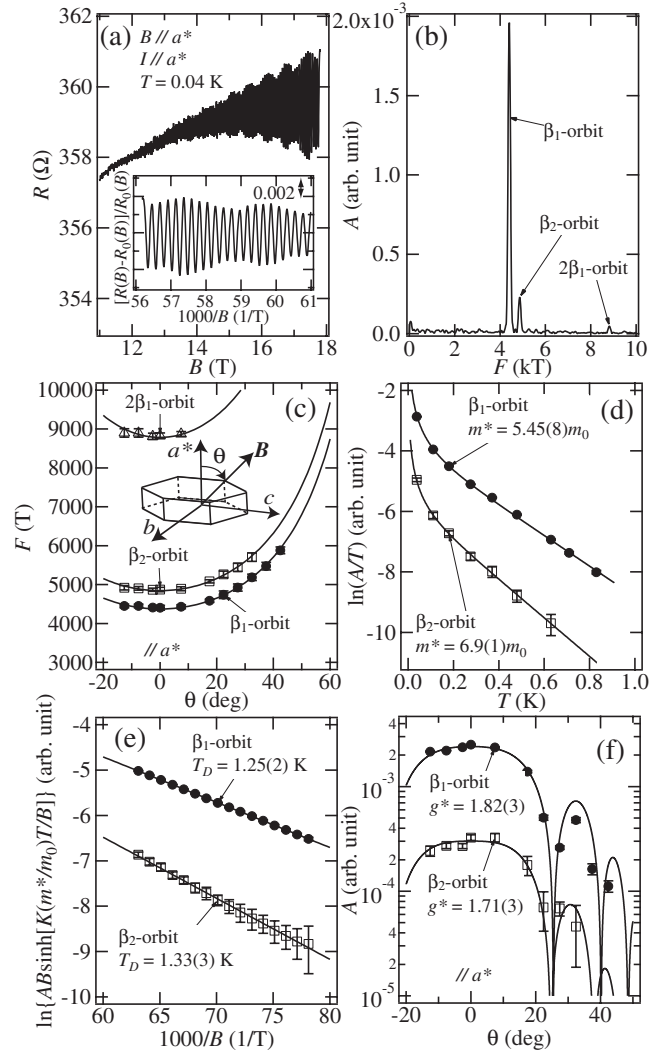


FIG. 3. (a) Magnetoresistance at 0.04 K ($B \parallel a^*$). The inset shows the SdH signal. (b) FFT spectrum of SdH oscillation. (c) Angle dependence of SdH frequency. Solid lines show the $1/\cos\theta$ dependence. (d) Mass plots. (e) Dingle plots. (f) Angle dependence of SdH amplitude. Solid lines in (d), (e), and (f) are fits to the data.

energy band of the $\beta_1$ orbit differs from that of the $\beta_2$ orbit. The temperature dependencies of oscillation amplitude divided by temperature, i.e., mass plots, are presented in Fig. 3(d). The determined effective cyclotron mass ratios $m^*/m_0$ ($m_0$ is the free electron mass) are listed in Table I, which are large for $\kappa$-type organic superconductors [20]. The Dingle temperatures $T_D$, simply determined from the field dependence of oscillation amplitude [Fig 3(e)], are

TABLE I. Parameters obtained by SdH oscillation.

| Orbit | $F$ (T) | $S/S_{BZ}$ (%) | $m^*/m_0$ | $T_D$ (K) | $g^*$ |
|---|---|---|---|---|---|
| $\beta_1$ | 4405(32) | 98.0(7) | 5.45(8) | 1.25(2) | 1.82(3) |
| $\beta_2$ | 4866(33) | 108.2(7) | 6.9(1) | 1.33(3) | 1.71(3) |

also shown in Table I. We can estimate the average mean free path from $T_D$ as $l_{\beta_1} = 758(16)$ Å for the $\beta_1$-orbit and as $l_{\beta_2} = 591(14)$ Å for the $\beta_2$-orbit. The in-plane coherence length $\xi_\parallel = 530(20)$ Å [15] is smaller than the mean free path ($l/\xi_\parallel > 1$); this indicates that the present compound is a clean superconductor. Finally, the angular dependence of oscillation amplitude shows a spin-splitting zero state at approximately $\theta = 25°$ [Fig. 3(f)]; this gives the effective electron $g$-factors (Table I). The values obtained are smaller than the free electron $g$-factor, which indicates a large renormalization induced by many-body effects [19].

The present SdH oscillations indicate that two fundamental closed orbits exist. If the FS is a warping cylinder in a coherent layered system, there are two extreme areas, corresponding to the neck and belly orbits [Fig. 1(a)]. We cannot use this picture, because the present compound is an incoherent layered system. Two closed FSs observed are explained by two crystallographically independent conducting layers, $A$ and $B$ [Figs. 1(c) and 1(d)]. If the charge transfer degree from the donor molecule of $A$ to the anion differs from that of $B$, the cross-sectional area of the FS of $A$ differs from that of $B$. This is a type of charge disproportionation, i.e., an interlayer charge disproportionation. This originates from polar THF molecules in insulating layers. A polarized THF makes the anion $[\mathrm{Au(CN)_4}]^-$ a polarized anion. The anion with four crystallographically nonequivalent CN units is in agreement with the polarization. As a result, the degree of charge transfer from the donor molecule in $A$ to the anion differs from that in $B$. The total charge transfer degree does not change, because the anion is $[\mathrm{Au(CN)_4}]^-$. Therefore, we can estimate that the differential charge transfer degrees between $A$ and $B$ is $\Delta\rho = 0.051(5)e$ per donor molecule, where $e$ is the elementary electric charge, from the difference between the SdH frequencies. The charge transfer degree of $A$ should be larger than that of $B$, because the electron-rich CN units of the anion are opposite the layer $A$. The charge transfer degree of $A$ is $\rho_A = (1 + \Delta\rho)/2$ per donor molecule and that of $B$ is $\rho_B = (1 - \Delta\rho)/2$. This indicates that energy band filling deviates from the effective half filling for both layers. Thus, we obtain FSs on the basis of magnetoresistance, as shown in Fig. 4(a). Although the band dispersion does not change from Fig. 1(e), the Fermi level $E_F$ of $A$ decreases but that of $B$ increases. For the present compound, two nonequivalent FSs alternately stack [Fig. 4(b)], where the cross-sectional area of $B$ is smaller than that of $A$.

The temperature dependence of the resistance $R(T)$ in $\kappa$-type organic superconductors has a broad peak at approximately 100 K; this is considered to reflect the profile of the Mott phase boundary [21]. Moreover, the $\kappa_L$ phase also has a broad peak [10]. By contrast, the resistance of the $\kappa_H$ phase decreases monotonically with decreasing temperature despite its $\kappa$-type structure [10,15]. This is further evidence of interlayer charge disproportionation
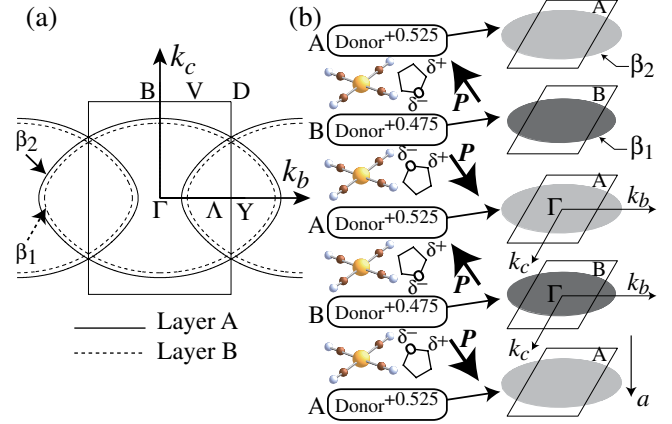


FIG. 4 (color online).   (a) FSs calculated on the basis of magnetoresistance. (b) Alternate stack structures of $A$ and $B$ (left panel), and of corresponding FSs with different cross sections (right panel).

in the $\kappa_H$ phase. In semiconductor superlattices, two-dimensional conducting layers with different charge densities, where both layers are well separated by a barrier, have been built using molecular beam epitaxy [22]. Our results show that such an interesting electronic structure can be realized in a bulk single crystal.

In summary, our observation of a clear angular-dependent magnetoresistance of $\kappa_H$-(DMEDO-TSeF)$_2$ $[\mathrm{Au(CN)_4}]$(THF) proves the incoherent interlayer transport properties. We have found a clear field dependence of the critical angle of the magnetoresistance peak at approximately $\theta = 90°$ as $\cos^{-1}(B_0/B)$, which indicates that the origin of the peak is a weak localization effect. SdH oscillation showing two closed orbits indicates that crystallographically independent donor layers have different charges; interlayer charge disproportionation occurs in a bulk single crystal. Interlayer charge disproportionation is realized for an incoherent layered system including antiferroelectric-like insulating layers with polarization vectors perpendicular to conducting layers.

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