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Interlayer Charge Disproportionation in the Layered Organic Superconductor $\kappa_{\text{H}}\text{-(DMEDO-TSeF)}_2[\text{Au(CN)}_4](\text{THF})$ with Polar Dielectric Insulating Layers

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Abstract

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, crystallographically independent layers have different charge densities in a bulk single crystal. The electric dipole of THF gives rise to interlayer charge disproportionation.

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Typical layered organic superconductors are composed of organic donor and inorganic anion molecules, and donors (anions) form conducting (insulating) layers. However, 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 potentially 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 interlayer hopping rate t_{\perp}/\hbar , where t_{\perp} is the interlayer transfer integral and \hbar is the Plank constant, is sufficiently larger than the intralayer scattering rate τ^{-1} , interlayer electronic transport is coherent and described by the warped cylindrical 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 interlayer interaction. Two organic superconductors with the same chemical composition, i.e., κ_L - and κ_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 κ_L phase (onset $T_c = 3.0$ K) has a disordered solvent molecule THF, and shows an orthorhombic-monoclinic distortion phase transition at $T_d = 209$ K [11–13]. The low-temperature structure consists of two monoclinic domains. By contrast, THF in the κ_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 κ_H phase, even at room temperature [Fig. 1(d)]; the relationship between the insulating layers is antiferroelectric-like. Moreover, there are two crystallographically independent conducting layers (A and B) and both layers have a κ -type structure [Figs. 1(c) and 1(d)]. The κ_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

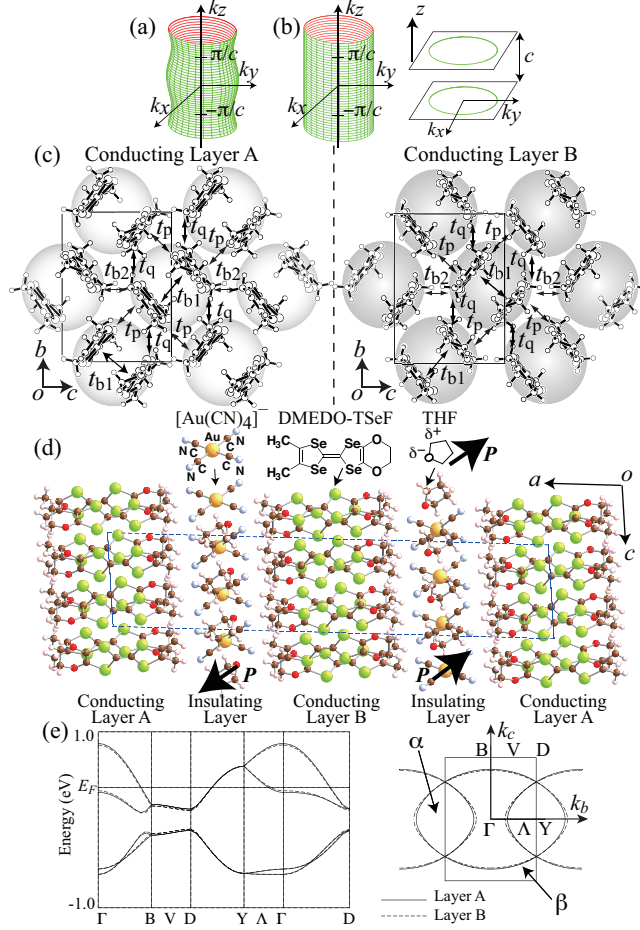


FIG. 1. Fermi surfaces of (a) coherent and (b) incoherent layered systems. For the incoherent layered system, the cylindrical FS with no dispersion along the k_z direction is independently defined within each layer. The stack structure of independent cylindrical FSs is schematically depicted in the right 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 κ_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 \mathbf{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.

κ_H phase is a two-dimensional superconductor 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 κ_H phase. In the present paper, we report the angular-dependent magnetoresistance and the Shubnikov-de

Haas (SdH) oscillations of the κ_H phase. The results reveal that the κ_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 four-probe method with ac current ($0.01 - 0.3 \mu\text{A}$). A bridge circuit was used to accurately measure the peak structure of angular-dependent magnetoresistance. Angular-dependent magnetoresistance measurement was performed using a 35 T resistive magnet at NHMFL in Tallahassee. 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 α and β orbits. The FSs obtained are similar to that of the κ_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 α -orbit is about 25% of the first Brillouin zone S_{BZ} , and that of the β -orbit, S_β , 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 θ between the field direction and the a^* -axis. Although a common shape of the angular-dependent interlayer magnetoresistance has a minimum at $\theta = 0^\circ$ and a maximum at $\theta = 90^\circ$ 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., $\theta = 90^\circ$, has a peak structure. Hanasaki *et al.* have demonstrated that the magnetoresistance peak 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 Hanasaki *et al.*'s model, 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 θ_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

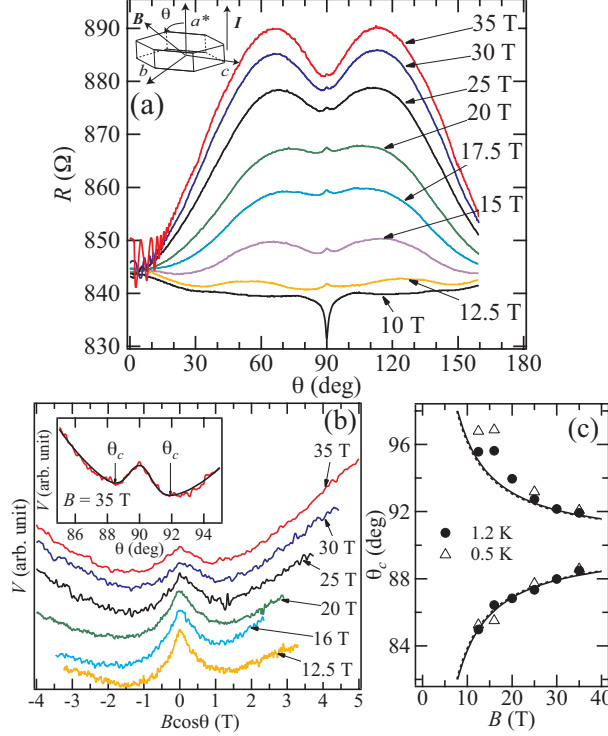


FIG. 2. (a) Angular-dependent magnetoresistance at 1.2 K for various magnetic fields. The fast oscillating behavior at approximately $\theta \leq 20^\circ$ under high fields is the SdH oscillation. The resistance dip at $\theta = 90^\circ$ at 10 T shows superconductivity surviving owing to the anisotropic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

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 $\theta = 90^\circ$ 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 semi-classical 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

TABLE I. Parameters obtained by SdH oscillation.

Orbit	F (T)	S/S_{BZ} (%)	m^*/m_0	T_D (K)	g^*
β_1	4405(32)	98.0(7)	5.45(8)	1.25(2)	1.82(3)
β_2	4866(33)	108.2(7)	6.9(1)	1.33(3)	1.71(3)

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: β_1 , β_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_{β_1} is 98.0(7)% of S_{BZ} , and that of the β_2 orbit is 108.2(7)%, where S_{BZ} is calculated using the lattice constants at room temperature. Both S_{β_1} and S_{β_2} are assigned to the large cross section estimated from the band calculation [Fig. 1(e)]. The second-harmonic orbit of the β_1 orbit, $2\beta_1$, is also observed. The degeneracy of the bands on the DY line of the first BZ in Fig. 1(e) is consistent with absence of the α -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 β_1 and β_2 orbits are two-dimensional FSs and that the energy band of the β_1 orbit differs from that of the β_2 orbit. The temperature dependences 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 κ -type organic superconductors [20]. The Dingle temperatures T_D , simply determined from the field dependence of oscillation amplitude [Fig 3(e)], are 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 β_1 -orbit and as $l_{\beta_2} = 591(14)$ Å for the β_2 -orbit. The in-plane coherence length $\xi_{\parallel} = 530(20)$ Å [15] is smaller than the mean free

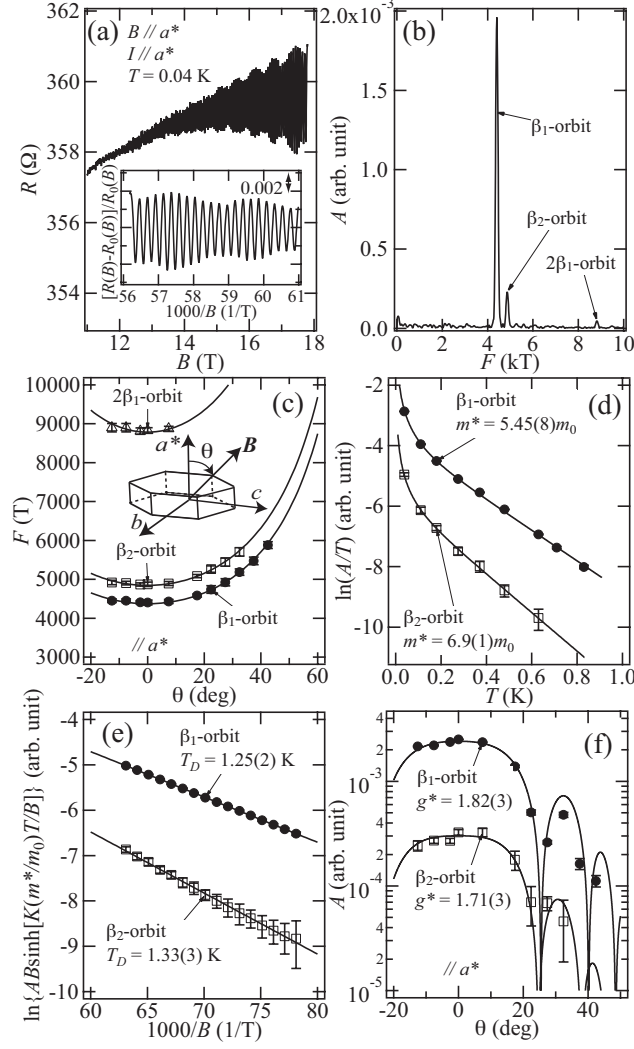


FIG. 3. (a) Magnetoresistance at 0.04 K ($B \parallel a^*$). The inset shows the SdH signal. (b) FFT spectrum of SdH oscillation. (c) Angle dependence of SdH frequency. Solid lines show the $1/\cos \theta$ dependence. (d) Mass plots. (e) Dingle plots. (f) Angle dependence of SdH amplitude. Solid lines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

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 $\theta = 25^\circ$ [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 $[\text{Au}(\text{CN})_4]^-$ 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 $[\text{Au}(\text{CN})_4]^-$. 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 κ -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 κ_L phase also has a broad peak [10]. By contrast, the resistance of the κ_H phase decreases monotonically with decreasing temperature despite its κ -type structure [10, 15]. This is further evidence of interlayer charge disproportionation in the κ_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 κ_H -(DMEDO-TSeF) $_2$ [Au(CN) $_4$](THF) proves the incoherent interlayer transport properties.

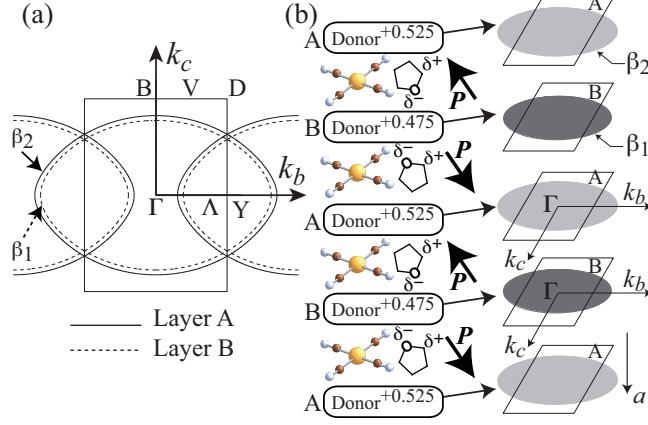


FIG. 4. (a) FSs calculated on the basis of magnetoresistance. (b) Alternate stack structures of A and B (left panel), and of corresponding FSs with different cross sections (right panel).

We have found a clear field dependence of the critical angle of the magnetoresistance peak at approximately $\theta = 90^\circ$ 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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