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1. Introduction and summary

Organic conductors have attracted great interest because of the variety of possible electronic states, such as Mott insulating, superconducting, metallic, and charge ordering states. The electronic states in most organic conductors are highly two-dimensional (2D) because such conductors are layered structures composed of organic molecules and anions. In these layered organic conductors, spin, charge, and orbital degrees of freedom lead to intriguing physical properties at low temperatures. For such properties, strong electron correlations in these 2D electronic structures play an essential role. Hence, along with transition metal oxides and rare-earth metal complexes, organic conductors are being recognized as important targets for studying strong correlation effects in the electronic states.

In layered 2D organic conductors, the interlayer charge transport properties are well-known to show characteristic features in temperature and magnetic field dependent phenomena. Such phenomena are strongly affected by scattering caused by (1) local magnetic moments in the anion layers and (2) impurities (or defects) in the conducting layers. Despite the extensive experiments performed so far, detailed mechanisms of the characteristic phenomena in the interlayer charge transport remain unsolved problems.

As high-quality single crystals can be produced, 2D organic conductors are good candidates to study the interlayer charge transport. For this thesis, two material systems with layered structures were chosen and systematic measurements of their electric and magnetic properties were obtained.

1. Conductivity and magnetism in \( \pi-d \) systems \( \kappa-(BDH-TTP)_2\text{FeX}_4 \) (\( X = \text{Br, Cl} \))

In \( \pi-d \) organic conductors, the \( \pi \) conduction electrons within the organic molecular layers, where transport behavior is strongly affected by electron correlations, are expected to interact with the localized \( d \) electrons in the anion layers. To investigate the correlation between the conductivity and magnetism, the magnetic and magnetotransport properties of the \( \pi-d \) systems \( \kappa-(BDH-TTP)_2\text{FeBr}_4 \) (FeBr\(_4\) salt) and \( \kappa-(BDH-TTP)_2\text{FeCl}_4 \) (FeCl\(_4\) salt) have been investigated. The \( \pi \) electrons in the BDH-TTP sheets exhibit simple metallic behavior down to 30 mK for both salts. The magnetic susceptibility of the FeBr\(_4\) salt, which is mainly associated with the Fe\(^{3+}\) \( d \) spins (\( S = 5/2 \)), obeys the Curie-Weiss law, indicating the presence of an antiferromagnetic (AF) transition at \( T_N = 3.9 \) K. In the AF state, a steep S-shaped increase in the magnetization at 1.5 T (\( H_{SF} \)) in the field parallel to the \( a \)-axis is found, which is ascribed to a spin-flop transition. Additionally, the magnetization curves for fields perpendicular to the easy axis show an inflection point at \( H_c = 3.1 \) T, suggesting a spin canting configuration in the \( bc \)-plane. A possible AF spin structure based on the magnetization data and molecular orbital calculations features a triangular lattice consisting of the Fe \( d \) and the donor \( \pi \) electron spins. A steep decrease of the magnetoresistance (MR) for the AF state is...
observed at $H_{SF}$ for $H//a$, proving that the strong $\pi$-$d$ interaction affects the electron transport in the donor system. An anomalous broadening of the electron spin resonance (ESR) linewidth in the critical region above $T_N$ is suggestive of a developing magnetic short-range order, for which the low-dimensionality in the spin system is responsible. For the FeCl$_4$ salt, a rapid change in the magnetic torque at low magnetic fields is associated with a change in sign at low temperatures below 0.4 K. The systematic measurements reveal that the 3$d$ spins have an AF order at about 0.4 K and that the torque sign change is caused by a metamagnetic transition. A rapid decrease in the MR at the metamagnetic transition field provides clear evidence of a finite $\pi$-$d$ interaction. Characteristic temperature dependences of the magnetic susceptibility and the ESR $g$-value are found in the paramagnetic phase, which are explained in terms of a single-ion anisotropy effect. These physical properties of the FeCl$_4$ salt indicate that both the $\pi$-$d$ and $d$-$d$ interactions in this salt are much weaker than those in the FeBr$_4$ salt.

(2) Incoherent interlayer charge transport in $\alpha$-(BEDT-TTF)$_2$NH$_2$Hg(SCN)$_4$

To investigate the incoherent interlayer transport in a 2D organic superconductor, $\alpha$-(BEDT-TTF)$_2$NH$_2$Hg(SCN)$_4$, the interlayer MR measurements have been performed for many samples with different qualities. The temperature dependence of the interlayer resistivity is found to be strongly sample-dependent. For some samples, the Shubnikov-de Hass (SDH) oscillations are measured to determine the Dingle temperature ($T_D$), characterizing the sample quality. When $T_D$ is relatively low, the incoherent interlayer transport becomes evident only in high magnetic fields parallel to the layers. This incoherent behavior is due to the confinement effect of the electrons by the parallel field.

When $T_D$ is sufficiently high, the interlayer transport is incoherent in the whole angle and field region. From the systematic measurements, we obtained the crossover field from the coherent to incoherent interlayer transport as a function of $T_D$. The crossover field is constant in the low $T_D$ region below 1.2 K but decreases with $T_D$ above it. This behavior is explained in terms of two conducting channels, the band coherent and impurity-assisted incoherent channels.

This thesis is composed of four main sections; the introduction, experimental methods, $\kappa$-(BDH-TTP)$_2$FeX$_4$ ($X = \text{Br, Cl}$), and $\alpha$-(BEDT-TTF)$_2$NH$_2$Hg(SCN)$_4$. In the introduction, a detailed background is presented and purposes of the study are explained. Next, experimental methods are explained and followed by a discussion on the magnetotransport properties and other magnetic properties arising from the $\pi$-$d$ interaction for $\kappa$-(BDH-TTP)$_2$FeX$_4$ ($X = \text{Br, Cl}$). The incoherence in the interlayer charge transport is then discussed for $\alpha$-(BEDT-TTF)$_2$NH$_2$Hg(SCN)$_4$.

The experimental results are shown below.

2. Results

2.1 $\pi$-$d$ system $\kappa$-(BDH-TTP)$_2$FeX$_4$ ($X = \text{Br, Cl}$)

In $\pi$-$d$ systems, some interesting phenomena have been found, where the cooperation of strong $\pi$-$d$ interaction (exchange interaction between the conducting $\pi$ spins and localized 3$d$ spins) and strong correlation among the $\pi$ electrons play an essential role. So far, a lot of $\pi$-$d$ systems, which have been newly designed, have been under investigation, although most of them are insulators or semiconductors at low temperatures due to the electronic instability. These points require us to make effort for finding typical examples of metallic $\pi$-$d$ systems since the insulating or semiconducting states sweep away intriguing phenomena arising from the interplay of the electron transport and magnetism.
The isostructural π-d organic conductors \( \kappa-(\text{BDH-TTP})_2\text{FeBr}_4 \) (FeBr\(_4\) salt) and \( \kappa-(\text{BDH-TTP})_2\text{FeCl}_4 \) (FeCl\(_4\) salt)\(^3\) form sandwiched layered structures, in which the BDH-TTP donor layers and the anion layers are alternately arranged along the \( b \)-axis. These salts show simple metallic conductivity down to 30 mK. Owing to the large 3\(d\) moment of the Fe spins (\( S = 5/2 \)), the AF order of the Fe spins at low temperatures are expected. In order to elucidate the effect of the \( \pi-d \) interaction on the interlayer charge transport of the itinerant \( \pi \) spins, the magnetization, magnetic torque, ESR, interlayer resistance, and interlayer MR of both salts were investigated.

The magnetic susceptibility \( \chi \) obeys the Curie-Weiss law for the FeBr\(_4\) salt. The sharp peaks of \( \chi \) correspond to an AF transition of the 3\(d\) spins (\( T_N = 3.9 \) K). The magnetization (\( M \)) vs. \( H \) plots at 2 K is presented in Fig. 1. For \( H//a \), a steep increase at 1.5 T is evident, which can be ascribed to a spin-flop transition of the Fe 3\(d\) spins (\( H_{SF} = 1.5 \) T) with the magnetic easy axis along the \( a \)-axis. For \( H//b \) and \( H//c \), the magnetization curves increase more gradually with \( H \), but we note that the curvatures slightly change (inflection points) at 3.1 T (\( H_c \)). They are likely due to a weak ferromagnetic (WF) transitions (spin canting) along these axes. An ESR signal with a single Lorentzian lineshape is observed down to about 20 K. The

![Fig. 1. Magnetization vs. field plot of \( \kappa-(\text{BDH-TTP})_2\text{FeBr}_4 \) measured at 2 K for three different field directions. The derivative curves, \( dM/dH \) are also shown in (a).](image1)

![Fig. 2. Temperature dependences of (a) the ESR linewidth \( \Delta H_{pp} \), (b) \( g \)-value of \( \kappa-(\text{BDH-TTP})_2\text{FeBr}_4 \) for three different field directions. Inset: ESR signal at 31 K.](image2)

![Fig. 3. Field dependences of the magnetic torque of \( \kappa-(\text{BDH-TTP})_2\text{FeCl}_4 \) (a) at 30 mK and (b) at different temperatures for \( \theta = 83^\circ \).](image3)
observation of the Lorentzian-shaped single ESR signal proves the exchange narrowing effect, evidencing that the $d$ electron spins are coupled by the exchange interaction. The temperature dependence of the linewidth ($\Delta H_{pp}$) and the $g$-value are shown in Figs. 2(a) and 2(b), respectively. For all the field directions, $\Delta H_{pp}$ gradually decreases with decreasing temperature, and then it increases divergently with further decrease in the temperature below 100 K. As the temperature approaches $T_N$, the spin fluctuations related to the $q$-vector defining the AF ordered state grows. This process takes place as the development of the short-range magnetic order in a wide temperature range especially for low dimensional antiferromagnets. It should be noted that the divergent behavior is more pronounced in the field direction parallel to the $b$- and $c$-axes, which are the direction of spin canting. Therefore, it is concluded that the fluctuations related to the spin canting are importantly pronounced in the critical region.

For the FeCl$_4$ salt, no magnetic transition is found above 2 K. However, the magnetic toque ($\tau$) shows a rapid change with increasing field when the field is nearly parallel to the $a$-axis at 30 mK as shown in Fig. 3(a). Similar sign changes are already observed in the other $\pi$-$d$ systems, and they are ascribed to the spin-flop transitions. Therefore, it is concluded that the easy axis of the 3$d$ spins is the $a$-axis and a metamagnetic (or spin-flop) transition takes place at 0.15 T. The torque curves for $\theta = 83^\circ$ at various temperatures are shown in Fig. 3(b). The steep sign change induced by the metamagnetic transition occurs at

![Figure 4](image_url)

Fig. 4. Interlayer magnetoresistance ratio $\Delta R(H)/R(0) = (R(H) - R(0))/R(0)$ at 30 mK for fields in (a) the $ab$- and (b) $bc$-planes for $\kappa$-(BDH-TTP)$_2$FeBr$_4$.

![Figure 5](image_url)

Fig. 5. Interlayer magnetoresistance ratio $\Delta R(H)/R(0)$ at 30 mK for fields in (a) the $ab$- and (b) $bc$-planes for $\kappa$-(BDH-TTP)$_2$FeCl$_4$. 

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0.15 T in a low temperature range. As temperature increases, the change at 0.15 T is smeared and is completely suppressed above 0.5 K. The results show that $T_N$ of the AF order is around 0.4 K.

Figure 4 shows the interlayer MR ratio of the FeBr$_4$ salt at 30 mK. The resistance for $H//a$ ($\theta=90^\circ$) suddenly drops at 2.0 T, corresponding to $H_{SF}$. This steep change provides direct evidence of the strong $\pi$-$d$ interaction. When the $\pi$ spins pass through the layers in the AF state, the magnetic potential alternately changes the sign, depending on the direction of the Fe 3$d$ spin polarization. It will effectively reduce the interlayer transfer integral; the interlayer resistance of the $\pi$ spins will increase. When all the Fe 3$d$ spins are aligned by fields, on the other hand, the $\pi$ spins see the homogeneous magnetic potential, which will decrease the resistance. Above $H_{SF}$, the resistance increases quadratically and then linearly with field, which is explained by the Boltzmann transport theory of 2D systems. As the field is tilted from the $a$- to $b$-axis, the sharp drop at $H_{SF}$ is smeared out. For $H//b$, the resistance gradually decreases up to 5 T. Figure 4(b) presents MR for the fields in the $bc$-plane. All the curves show the gradual decreases up to 5 T, corresponds to the gradual increase of the magnetization.

The MR behavior of the FeCl$_4$ salt is similar to that of the FeBr$_4$ salt [Fig. 5(a)]. MR for $H//a$ exhibits an abrupt drop at 0.2 T and then increases with increasing field. Even for the FeCl$_4$ salt, clear evidence of the strong $\pi$-$d$ interaction is obtained.

2.2 $\alpha$-(BEDT-TTF)$_2$NH$_2$Hg(SCN)$_4$

The incoherent behavior of the interlayer charge transport in the highly anisotropic conductors has been one of the long-standing issues in the solid state physics.\textsuperscript{4,9} The coherence of the interlayer charge transport will be determined by the relation between two factors, the interlayer transfer integral $t_z$ and the scattering time $\tau$. For $t_z >> h/\tau$, a cylindrical 2D Fermi surface with a corrugation given by $t_z$ is well defined and the electrons can easily move in the interlayer direction without scattering: the interlayer transport is then coherent. The angular dependence of the MR is well described by the Boltzmann transport theory. In the opposite limit ($t_z << h/\tau$), the electrons cannot tunnel between the layers without scattering in the layers. The interlayer transport becomes incoherent since the interlayer transport must be associated with scattering in the layers. In the incoherent interlayer transport, therefore, the in-plane momentum and energy of the electrons are no longer conserved. A reversal of the angular dependence of the MR, similar to the 1D system, is observed. In this limit, it is expected that each layer has an independent 2D Fermi surface. In the intermediate condition, $t_z \approx h/\tau$, the interlayer transport between the adjacent layers is dominated by a tunneling process. However, the successive tunneling rarely occurs because the scattering probability is relatively large.\textsuperscript{5,10} Some studies revealed that the crossover from the incoherent to coherent interlayer transport can take place when $t_z$ or $\tau$ changes.\textsuperscript{6,7} However, no systematic investigations have been performed, and it remains unclear how the crossover from the coherent to incoherent transport is induced.

In this thesis, the systematic measurements are reported for many crystals with different qualities for a 2D organic superconductor $\alpha$-(BEDT-TTF)$_2$NH$_2$Hg(SCN)$_4$. This organic superconductor has anisotropic Fermi surfaces, one of which is a pair of 1D Fermi surface and the other is a 2D Fermi surface as shown in Fig. 8(a). The quality of each sample is quantitatively checked by the quantum oscillation measurements. The angular dependence of the MR and the temperature dependence of the resistance for various single crystals can provide much information on coherence of the interlayer charge transport.
The SdH oscillations are observed for all samples at 0.3 K. The Dingle temperature, which is a measure of the sample quality, is given by $T_D = \frac{\hbar}{2\pi k_B \tau}$, and is experimentally estimated from the fitting of the oscillation amplitude. $T_D$ is determined for six samples, which ranges from 0.93 to 1.73 K. For samples #7-#9, we cannot estimate $T_D$ because the oscillations are too small, probably $T_D > 2$ K. The angular dependences of the MR for some samples at 0.3 K are shown in Fig. 6. At low fields under 3 T, the resistances decrease to zero around $\theta = 90^\circ$, due to the superconducting transition. The MR above 3 T shows large sample dependence. For sample #1 with $T_D = 0.93$ K, the MR at high field shows large AMROs, where the small and rapid SdH oscillation is superimposed, as shown in Fig. 6(a). The background MR has a maximum around $90^\circ$ and a minimum around $0^\circ$. For samples #5 ($T_D = 1.40$ K) and #6 ($T_D = 1.73$ K), V-shaped dips around $\theta = 90^\circ$ appear at high fields and the AMRO amplitudes are suppressed [Figs. 6(b) and 6(c)]. We note that the angle region of the V-shaped dip is wider for the larger $T_D$ sample. In the other angle region, the MR is similar to that for sample #1. For sample #9 ($T_D$ is unknown), the angular dependence of the MR has no AMRO and the MR is completely reversed in the whole angle region at high fields [Fig. 6(d)].

Fig. 6. Angular dependences of the interlayer resistance at various fields at 0.3 K for $\alpha$-(BEDT-TTF)$_2$NH$_2$Hg(SCN)$_4$.

Fig. 7. Angular dependences of the resistance at 14.5 T and 1.6 K for (a) sample #2 ($T_D = 1.16$ K) and (b) sample #7. The curves are shifted for clarity.
The reversed MR at high fields is scaled by the perpendicular field component to the \( ac \)-plane \((\mu_b H \cos \theta)\). For sample \#9, the field-dependent resistance is fitted by equation \( \Delta R = (\mu_b H \cos \theta)^p \), where \( p \) is a scaling factor about 1.3.

The horizontal angular dependences of the MR at various azimuthal angles from the \( a \)-axis (\( \varphi \)) are presented in Fig. 7. For samples \#1-\#3, the AMRO strongly depends on \( \varphi \), reflecting the anisotropy of the Fermi surface structure. The V-shaped MR reversal around \( \theta = \pm 90^\circ \) is evident around \( \varphi = 45^\circ \) and 225\(^\circ\) but not clearly observed at the other angles. For sample \#7 (\( T_D \) is unknown), it is surprising that the MR is almost independent of \( \varphi \) and the V-shaped feature appears around \( \theta = \pm 90^\circ \) at all the \( \varphi \) values [Fig. 7(b)].

The similar scaling behavior has already been observed in the angular dependent MR of the 1D systems (TMTSF)\(_2\)X (X = ClO\(_4\), PF\(_6\)) with \( p = 1.25 \) \(^8\) and a 2D system \( \alpha\)-(BEDT-TTF)\(_2\)KHg(SCN)\(_4\) (\( p \) is unknown). \(^6\) The scaling for the 1D systems has been explained in terms of the confinement of the electron motion within the layer at high parallel fields. For the 1D system, when the high magnetic field is applied along the second conducting direction (\( b \)-axis), the electrons are driven in the \( k_z \) direction on the Fermi surface by the Lorentz force. In real space, the electrons run at constant velocity in the most conducting direction (\( a \)-axis) but move sinusoidally in the least conducting direction (\( c \)-axis). As the field increases, the amplitude of the sinusoidal motion shrinks, and the electrons are confined in each layer; the electronic states are decoupled between the adjacent layers. Therefore, the interlayer transport becomes incoherent in high fields. \(^8\) For the 2D Fermi surface, in the field along the long axis of the elliptic cross-section, the electrons on the most (flat) part of the Fermi surface will be confined in each layer by the Lorentz forces more easily that in field along the short axis. \(^9\) Thus, the interlayer transport is prohibited without scattering. For sample \#2, the V-shaped MR background reversal around \( \theta = \pm 90^\circ \) is observed at the directions indicated by red arrows in Fig. 8(b). These azimuthal angles correspond to the directions parallel to the flat parts of the 1D and 2D Fermi surfaces as shown by the dashed lines in Fig 8(a). This is evidence that the V-shaped MR background reversal around \( \theta = \pm 90^\circ \) is caused by the confinement effect for samples with \( T_D < 1.2 \) K.

Here, we can see the crossover from the coherent to incoherent interlayer transport, characterized by the crossover parallel field \( H_{ij}^{CO} \). For the relatively high \( T_D \) samples, \( H_{ij}^{CO} \) should be quite low since the incoherent behavior is observed even for \( \theta = 0^\circ \). For simplicity, we define \( H_{ij}^{CO} \) at \( \varphi \approx 45^\circ \), where the

![Fig. 8](image1.png)

**Fig. 8.** (a) Calculated Fermi surface of \( \alpha\)-(BEDT-TTF)\(_2\)NH\(_3\)Hg(SCN)\(_4\)\(^{10}\). Dashed lines denote the flat parts of the 1D and 2D Fermi surfaces. (b) Cross section of the 2D Fermi surface obtained by the AMRO for sample \#2. The MR background reversal is clearly observed at the angles denoted by red arrows.

![Fig. 9](image2.png)

**Fig. 9.** Crossover in-plane field vs. Dingle temperature plot for \( \alpha\)-(BEDT-TTF)\(_2\)NH\(_3\)Hg(SCN)\(_4\). Dashed (red) and dot-dashed (blue) lines are guides for the eye.
incoherent behavior is the most evident. For instance, $\Delta R$ for sample #2 follows the power law $\Delta R \propto (\mu_0 H_{B})^{p}$ up to $\theta = 80.4^\circ$, but deviates from the law above it at 14.5 T. Therefore, the crossover field is estimated as $\mu_0 H_{B}^{CO} = 14.5 \cos(80.4^\circ) = 14.3$ T. Similarly, we can define $H_{B}^{CO}$ for samples #1-#6 ($T_D \leq 1.73$ K), which is plotted as a function of $T_D$ as shown in Fig. 9. In the low $H_{B}^{CO}$ region, the interlayer transport is in the coherent regime. In Fig. 9, we note $\mu_0 H_{B}^{CO} \approx 14$ T, independent of $T_D$ in the low $T_D$ region. When $T_D$ is sufficiently low, it is reasonable that the confinement condition is determined only by the parameters of the electronic structure $t_z$ and the Fermi velocity. As $T_D$ increases above ~1.2 K, $H_{B}^{CO}$ decreases almost linearly.

The above results can be interpreted according to the two-conducting-channel model, the band coherent and impurity-assisted incoherent channels in the interlayer transport. The band coherent channel $\sigma_{\perp}^B$ gives the conventional MR behavior, but the electrons undergo the confinement effect by the parallel field. The impurity-assisted incoherent channel $\sigma_{\perp}^{imp}$ gives the V-shaped MR, characterized by the power law behavior $\Delta R \propto (\mu_0 H_{B})^{p}$. When $T_D > 1.2$ K (the impurity concentration is sufficiently large), the $\sigma_{\perp}^{imp}$ term becomes relatively large especially in the field parallel to the layer, which leads to the V-shaped MR. In the high $T_D$ limit, the $\sigma_{\perp}^{imp}$ term is dominant; the power law MR is observed in the whole angle and field region.

References